[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

An Ion-exchange Study of Possible Hybridized 5f Bonding in the Actinides[1]

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A study has been made of the elution behavior of curium(III), americium(III), plutonium(III), actinium(III), plutonium(IV), neptunium(IV), uranium(IV), thorium(IV), neptunium(V), plutonium(VI), uranium(VI), lanthanum(III), cerium(III), europium(III), ytterbium(III), yttrium(III), strontium(II), barium(II), radium(II), cesium(I) with 3.2, 6.2, 9.3 and 12.2 M HCl solutions from Dowex-50 cation-exchange resin columns. These elutions indicate that in high concentrations of hydrochloric acid the actinides may form complex ions with chloride ion to a greater extent than the lanthanides. In order to explain these results, a partial covalent character may be ascribed to the bonding in the transuranium complex ions. It is shown that a reasonable structure for such covalent bonding involves hybridization of the 5f-orbitals in the actinide elements.

Study of the physical and chemical properties of the transuranium elements has revealed similarities and regularities in their behavior analogous to those in the properties of the rare earth elements. Much evidence, such as chemical, crystallographic, spectroscopic and magnetic susceptibility measurements, now leads to the view that the 5f-electron shell is being filled in the transuranium elements, similarly to the filling of the 4f-shell in the rare earths.[3]

The ion-exchange resin elution of the tripositive ions furnishes a very interesting and striking piece of chemical evidence for the similarity of the lanthanides and actinides. The two series on elution with 0.25 M ammonium citrate solution, pH 3.5 at 87°, are very similar, even to the spacings between the ions, for the elements with 6, 7, 8 and 9f-electrons: europium, gadolinium, terbium, dysprosium and the corresponding heavy elements americium, curium, berkelium and californium[4] (Fig. 1).

However, some previous work[5] in this Laboratory brought to light certain important differences in the behavior of the actinide and lanthanide elements on elution from Dowex-50 cation-exchange resin columns with hydrochloric acid solutions of

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) Based on the Ph.D. Thesis submitted to University of California, Berkeley, September, 1951, by R. M. D.

(3) G. T. Seaborg, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 21.1, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(4) K. Street, Jr., S. G. Thompson and G. T. Seaborg, THIS JOURNAL, 72, 4832 (1950).

(5) K. Street, Jr., and G. T. Seaborg, ibid., 72, 2790 (1950).

various concentrations. For example, it was observed that in varying the concentration of the hydrochloric acid solutions from 3 to 6 M HCl, the actinides and lanthanides moved up in their positions of elution, but that in going from 6 to 9 to 12 M HCl solutions, the lanthanides lutetium, promethium and cerium gradually moved back, that is, they showed slower and slower elution rates. However, the elution rates of the actinides americium and curium continued to increase as a monotonic function of the hydrochloric acid concentration. Also, although lutetium, promethium and cerium kept the same relative order at the various hydrochloric acid concentrations, and while curium came off ahead of americium with 3 and 6 M HCl, as was also observed in the citrate elutions (and as would be expected from a comparison of their ionic radii), in 12 M HCl the order of elution of americium and curium was reversed, with americium moving up just ahead of curium. An explanation was suggested involving complex ion formation of the actinides with chloride ion in the higher concentrations of hydrochloric acid.

In order to confirm these results and to obtain additional evidence on the nature of the complex ion formation in the transuranium elements, the present study of the properties of the actinides and lanthanides on elution with various concentrations of hydrochloric acid was undertaken.

Experimental

First, in order to confirm that the previously observed[5] maximum in the elution rates of the lanthanide ions cerium(III), promethium(III) and lutetium(III) from Dowex-50 cation columns with hydrochloric acid solutions of varying
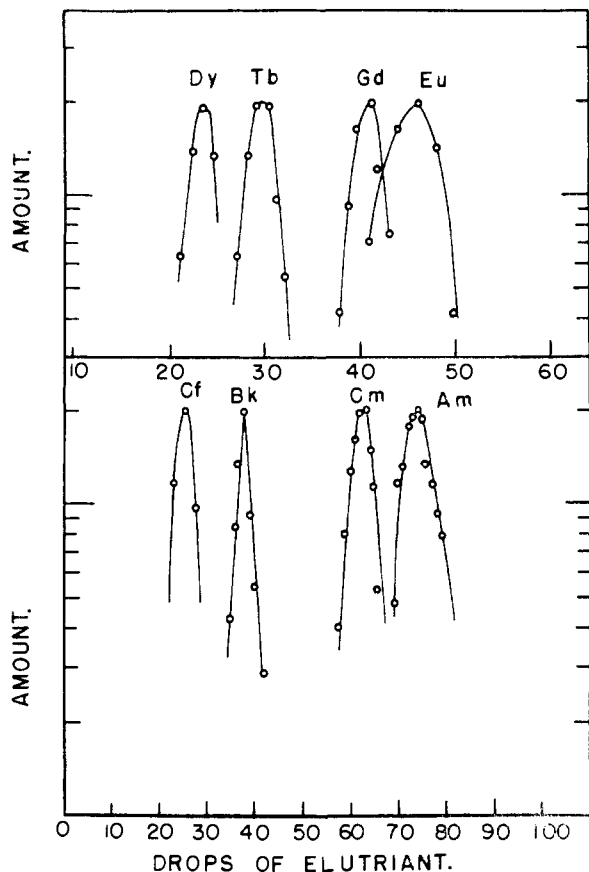
Fig. 1.—Comparison of the elution rates of californium, berkelium, curium and americium with those of their homologs dysprosium, terbium, gadolinium and europium.

concentrations is due to an actual minimum in the equilibrium distribution coefficients of the ions and not to some unknown column effect, and similarly, that in the same range of concentration of hydrochloric acid the apparent nonexistence of such a maximum in the column elution rates of the actinide ions americium(III) and curium(III) is a real equilibrium effect, a series of equilibrium distribution experiments was performed at room temperature on tracer amounts of alpha particle emitting Am^{241} and β-particle emitting Pm^{147}. The resin used was colloidal Dowex-50, hydrogen form, wet graded to settle at *ca.* 0.5 cm./min., and then oven dried at 95–105° overnight. Known amounts of the radioactive ions in 5.00-ml. samples of solutions of hydrochloric acid varying in concentration from 1.12 to 13.1 *M* were shaken for about 30 minutes with small amounts (0.0076 to 1.8013 g.) of resin. The 5-ml. volumetric flasks containing the resin and solution were then centrifuged, and 0.50-ml. aliquots of the supernatant solutions were withdrawn for counting of the tracers and for titration to determine the acid concentration.

From the experimental data given in Table I, values of K_d, the equilibrium distribution coefficient, were calculated for promethium and americium at various hydrochloric acid concentrations

$$K_d = \frac{1 - F_s}{F_s} \times \frac{V_s}{W_R} = \frac{(counts/g. \; of \; resin)}{(counts/ml. \; soln.)}$$

where F_s is the fraction of activity in the solution phase, W_R is the weight of resin taken and V_s is the volume of solution.

The values of K_d are plotted against the corresponding hydrochloric acid concentration in Fig. 2, and the results confirm the previous observations on column elutions. The plot of K_d *vs.* hydrochloric acid concentration for americium(III) shows a steady decrease, while that for promethium(III), after decreasing at first, passes through a minimum around 7 *M* HCl, and then increases.

Next, a series of column elutions of various actinide and

TABLE I

EQUILIBRIUM DISTRIBUTION DATA FOR AMERICIUM AND PROMETHIUM

| Expt.	Resin wt., g.	Soln. vol., ml.	Soln. normality	α-counts/min./ml. $\times 10^{-2}$	K_d of Am	β-counts/min./ml. $\times 10^{-2}$	K_d of Pm
1	0.000	7.0	1.12	44.7	....	40.6	....
2	.0076	4.0	1.12	10.0	1.8×10^3	10.3	1.6×10^3
8	.0061	10.0	1.12	20.4	1.9×10^3	20.2	1.7×10^3
3	.0468	5.0	3.02	28.9	58.5	28.0	48.3
4	.0825	4.5	3.02	22.2	60.0	21.4	52.8
5	.4771	5.0	5.30	20.4	12.5	19.15	11.7
6	.6697	5.0	7.61	21.1	8.36	16.8	10.6
9	.6863	5.0	9.04	25.8	5.33	15.5	11.4
7	1.1800	5.0	10.44	2.8	4.06	9.02	14.6
10	1.8013	5.0	13.06	24.1	2.37	4.25	23.7
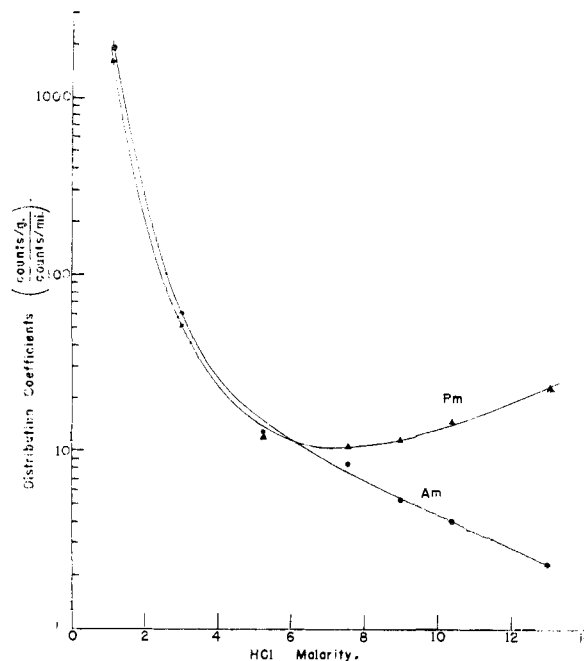
Fig. 2.—Plot of the equilibrium distribution coefficients of promethium and americium *vs.* hydrochloric acid molarity.

lanthanide ions using 3.2, 6.2, 9.3 and 12.2 *M* HCl solutions as eluting agents were performed. The elution behavior of tracer amounts of tripositive Cm^{242}, Am^{241}, Pu^{239}, $Eu^{152,154}$, Ce^{144}, Y^{90}, La^{140}, Yb^{159}, of tetrapositive Pu^{239}, Np^{237}, Th^{230}, U^{233}, of pentapositive Np^{237}, of hexapositive U^{233}, Np^{237}, Pu^{239}, of dipositive Sr^{90}, Ba^{140}, Ra^{226} and of monopositive Cs^{134} was studied.

The resin used was again Dowex-50, hydrogen form, 250–500 mesh, wet graded to settle at *ca.* 0.5 cm./min. Two columns were used, one 10 cm. long by 1 mm. in diameter, and the other 10 cm. long by 1.5 mm. in diameter. The linear flow rate was *ca.* 0.1 cm./min. Before an elution the resin column was rinsed overnight with the hydrochloric acid solution to be used as the eluting agent. To preserve reducing conditions in the 10 cm. by 1 mm. column, a drop of hydriodic acid was also added to this rinse solution, and a drop or two of nitric acid was added in the case of the 10 cm. by 1.5 mm. column to maintain oxidizing conditions. In this manner different oxidation states of the transuranium elements could be studied, and the low concentration of hydriodic or nitric acid used apparently did not affect the relative elution rates of other ions. Whenever the concentration of the eluting solution was changed, going from one experiment to another, the resin bed was backwashed with water, and then allowed to repack in the new hydrochloric acid solution.

Since high precision was not required the elutions were performed at room temperature without any thermostatting
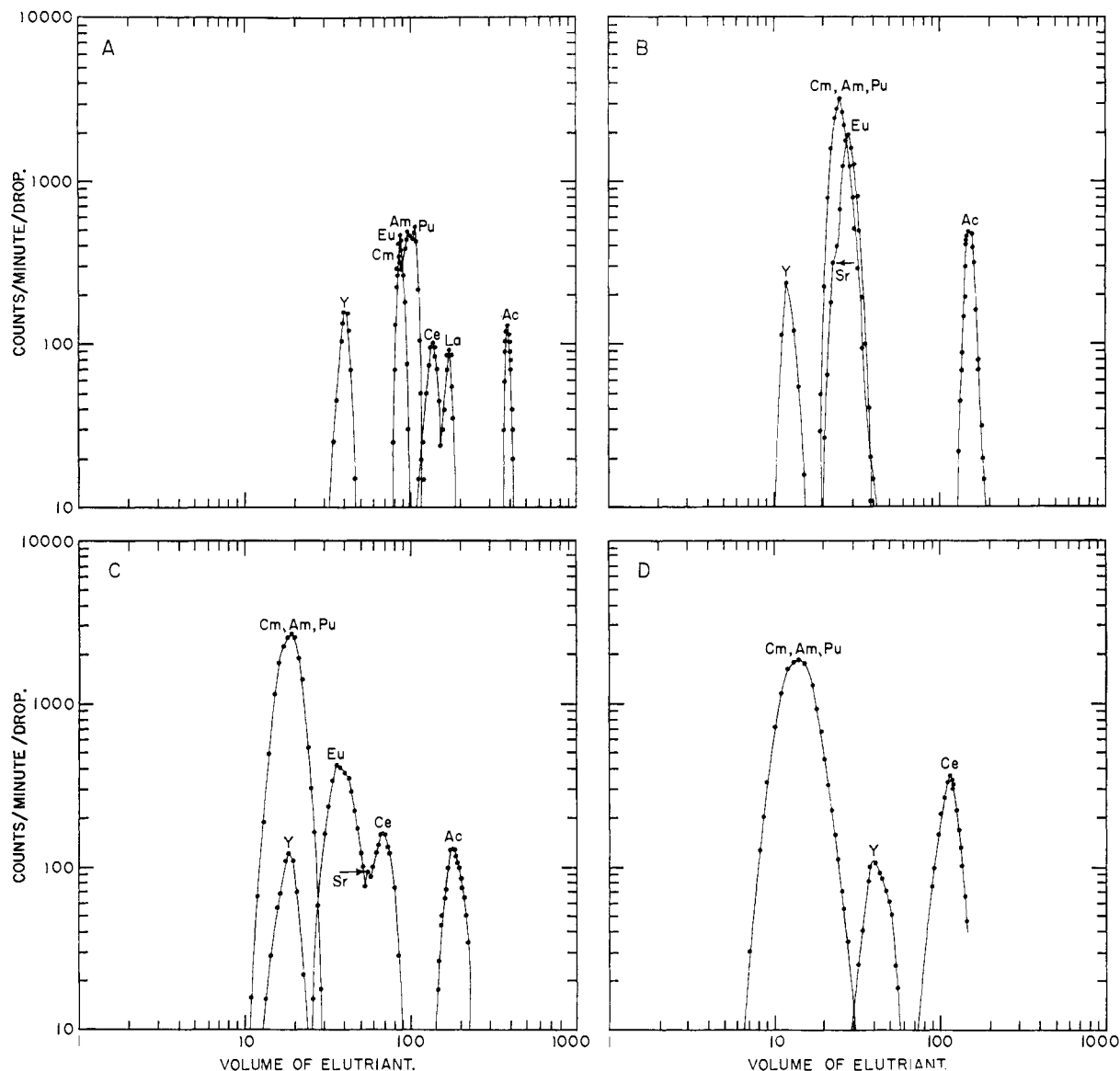
Fig. 3.—Typical elution curves in: A, 3 M HCl; B, 6 M HCl; C, 9 M HCl; D, 12 M HCl.

of the system. Preliminary equilibrium distribution coefficient determinations over a range of temperature from 15 to 80° showed only as mall temperature coefficient for hydrochloric acid elutions in contrast, for example, to the situation with citrate solutions. Nevertheless, due to the slow flow rate used, and the fact that times up to many days were required for some of the elutions, variations in the temperature up to 15–20° during a long elution were possible and probably contribute to the scattering of the results. Another possible contributing factor to such scattering of the experimental data is the gradual decrease in concentration of the 9.3 and 12.2 M HCl solutions by volatilization loss of HCl during a long elution.

The elution of the tracer ions was assayed by counting aliquots of evaporated solutions on plates on standard α-particle and end-window G.M. counters. Whenever necessary, the various nuclides were identified by their radiation characteristics and half-lives. Typical runs are illustrated in Fig. 3. In the case of the close curium, americium, plutonium triad, resolution of the total α-particle peak was made using the 48-channel pulse analyzer[6] with the results

(6) A. Ghiorso, A. H. Jaffey, H. P. Robinson and B. B. Weissbourd, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 16.8, McGraw–Hill Book Co., Inc., New York, N. Y., 1949.

shown in Fig. 4. The ordinate is given as counts/minute/drop since in this type of experiment the actual number of atoms is unimportant. The abscissa, given in drops, is an arbitrary unit, as the volume of solution necessary to elute a given element, even under the near equilibrium conditions employed in this work, will vary somewhat with the particular "batch" of resin used and with the packing and previous history of the resin in the column.

Sodium dichromate was used to oxidize neptunium and plutonium to the hexapositive state, but in the 9 and 12 M HCl elutions the dichromate was reduced during the experiment and eluted in the first few drops as the green chromic chloride complex. However, enough plutonium remained in the (VI) state to give results in agreement with predictions based on the behavior of uranium(VI). The results for neptunium(VI) in 9 and 12 M HCl are very ambiguous, as the (V) and (VI) states should elute in about the same place, namely in the first column volume, and furthermore, it has been observed[7] that neptunium(VI) is unstable in strong hydrochloric acid solutions. Evidently no neptunium(VI) remained in these elutions at 9 and 12 M HCl, although the presence of neptunium(VI) is quite definite at 3 M HCl.

In order to determine the elution peak positions of ura-

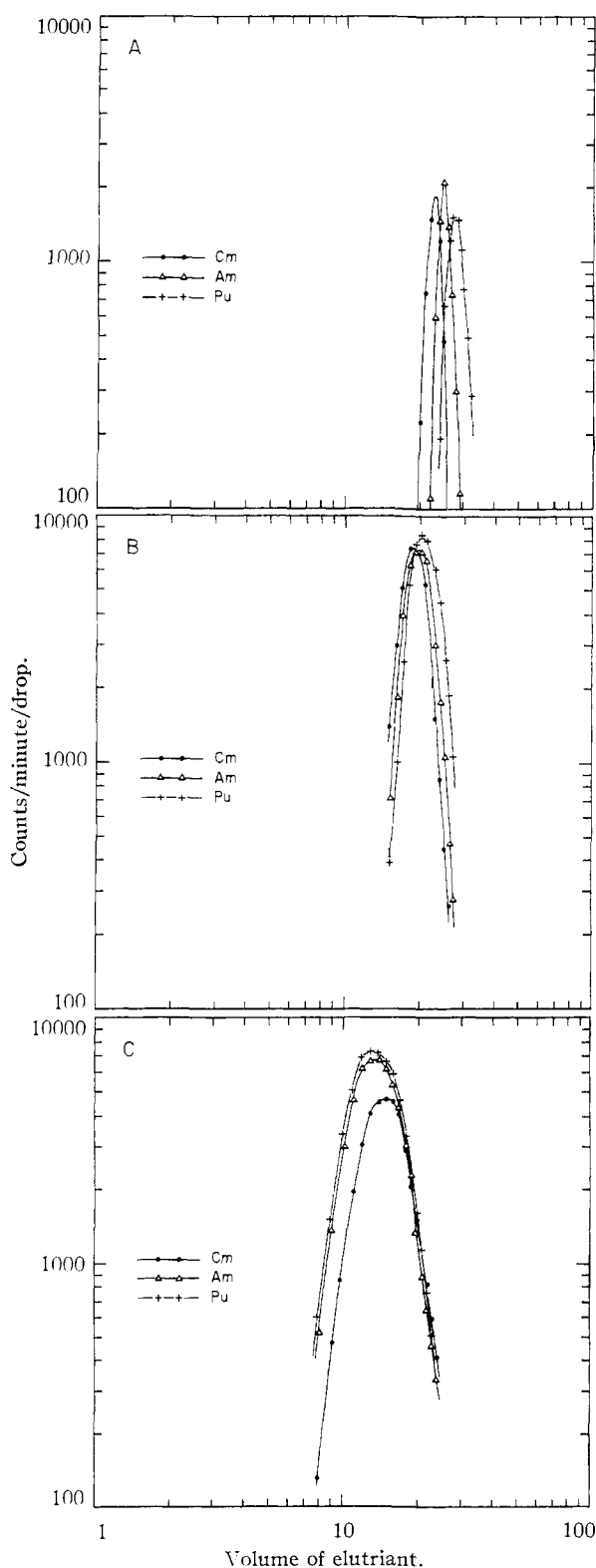(7) J. C. Hindman, L. B. Magnusson and T. J. LaChapelle, ibid., Papers 15.2 and 15.11.

Fig. 4.—α-Particle pulse analyses of elution peaks: A, 6 M HCl; B, 9 M HCl; C, 12 M HCl.

nium(IV), a tracer solution was prepared by reducing a solution of U^{233} in 0.5 M HCl or $HClO_4$ by stirring for 15–60 minutes with a small piece of metallic U^{238}. At the hydrogen ion concentration employed, the metallic uranium apparently does not react rapidly with hydrogen ion but does

reduce the uranium(VI) ions, providing a solution of tetrapositive U^{233} which does not contain too much U^{238} to load the column seriously.
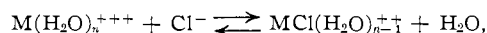
A summary of what were considered successful elutions, i.e., those that were not disturbed mechanically by factors beyond control, bubbles in the resin bed, overly great temperature fluctuations, etc., is given in Fig. 5 in which the average values of the elution peak positions from various runs have been plotted. The drop is again used as the elution unit volume. Although two columns of different diameter were used, the relative positions of the ions on elution should be the same, so the results have been normalized to the 10 cm. by 1 mm. column by adjusting the relative positions of the ions to that of one of the ions chosen as a standard.

Results and Discussion

The results of the equilibrium distribution experiments on americium and promethium in hydrochloric acid solutions of various concentrations, Fig. 2, illustrate very well the minimum in the K_d for the lanthanides around 7 M HCl, and the continuous decrease in K_d with increasing hydrochloric acid concentration for the actinide ions. There are at least four main factors involved in such equilibria. These are: (1) the mass action effect of hydrogen ion in the exchange reaction

$$M(H_2O)_n^{+++} (aq.) + 3H(H_2O)_m^+(resin) \rightleftarrows$$
$$M(H_2O)_n^{++}(resin) + 3H(H_2O)_m^+ (aq.)$$
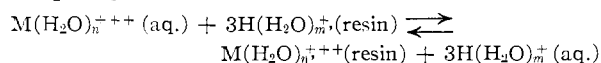
(2) complex ion formation of the metal ion with chloride ion

$$M(H_2O)_n^{+++} + Cl^- \rightleftarrows MCl(H_2O)_{n-1}^{++} + H_2O,$$
$$MCl(H_2O)_{n-1}^{++} + Cl^- \rightleftarrows MCl_2(H_2O)_{n-2}^{+} + H_2O, \text{ etc.}$$

(3) changes in the solvation shell of each metal ion other than those due to complex ion formation, i.e., dehydration

$$M(H_2O)_n^{+++} \rightleftarrows M(H_2O)_{n-1}^{+++} + H_2O$$

(4) shrinkage of the resin.

The first factor should cause the equilibrium distribution constants of both americium and promethium to decrease continuously with increasing hydrogen ion concentration, but would not allow for any differentiation in the behavior of the two classes of ions, or for an increase in K_d with hydrochloric acid concentration as is observed with the lanthanide promethium. This latter behavior, i.e., the increased attraction of the resin for a rare earth ion at high hydrochloric acid concentrations, is very likely due to factors 3 and 4. Increasing the hydrochloric acid concentration in the contacting solution causes the resin to shrink, and this shrinkage of the resin causes an increase in the concentration of the functional groups inside the resin, hence shifting the ion equilibrium toward the resin and increasing the time required for elution. Also, the environment of an ion in hydrochloric acid of 12 M concentration is quite different from that which it is in 3 or 6 M; there are fewer water molecules to solvate the ion so that its hydration shell is smaller, giving the ion a smaller *effective* radius. Since it is this *effective* radius which is of importance in determining a resin's affinity for the ion,[8] a smaller effective radius should also cause the K_d to increase with increasing hydrochloric acid concentration.

(8) F. C. Nachod and W. Wood, THIS JOURNAL, 67, 629 (1945); O. E. Boyd, J. Schubert and A. W. Adamson, ibid., 69, 2818 (1947).

In dilute solutions the predominating factor in the exchange process is the first one mentioned above so that in this concentration region all the ions studied showed a decrease in K_d with increasing hydrochloric acid concentration. Above about 1 M, however, the shrinkage of the resin begins to become appreciable and so tends to slow down the elution rate. Above 6 M HCl the result of this phenomenon and the smaller effective radius of the ion, due to partial dehydration, may overcome the mass-action effect of increasing hydrogen ion concentration and result in an increase in K_d with increasing hydrochloric acid concentration. It is proposed that the behavior of promethium is the "normal" type of elution, the americium being unusual, since the latter does not show this minimum in the value of K_d around 7 M HCl.

However, the second factor mentioned above, association and complex ion formation with chloride ion, must also be considered for these tri-positive ions. Data in the literature indicate that the rare earth and transuranium cations associate to a varying degree with chloride ion in hydrochloric acid solutions of the concentrations used in this work.[9] The differentiation of americium from promethium in hydrochloric acid solutions greater than 7 M could then be due to a greater tendency toward complex ion formation of the former, or toward desolvation of the latter.

Since as a group the actinides have ionic radii comparable to the lanthanides (Table II), in fact,

Fig. 5.—Summary of the elution peak positions of the ions studied with 3.2, 6.2, 9.3 and 12.2 M HCl.

TABLE II

IONIC RADII OF ACTINIDE AND LANTHANIDE ELEMENTS[10]

	Lanthanide series Element	Radius, Å.	Actinide series Element	Radius, Å.
1	La(III)	1.04	Ac(III)	1.11
2	Ce(III)	1.02	.....	..
3	Pr(III)	1.00	.....	..
4	Nd(III)	0.99	U(III)	1.03
5	Pm(III)	(0.98)	Np(III)	1.01
6	Sm(III)	0.97	Pu(III)	1.00
7	Eu(III)	0.96	Am(III)	0.99

slightly larger values, differences in solvation of the ions are not likely. While all of the factors affecting complex ion formation are not clearly understood, *ionic* complex ion formation does not seem likely to be the answer to the differences in behavior for such similar elements of nearly the same radii. Therefore, chloride complex ion formation of a *covalent* nature must be considered for the transuranium ions. Such a concept does explain

(9) R. E. Connick and S. W. Mayer, THIS JOURNAL, **73**, 1176 (1951); S. W. Mayer and S. D. Schwartz, *ibid.*, **73**, 222 (1951).

(10) W. H. Zachariasen, Chapter 18, National Nuclear Energy Series, Plutonium Project Record, Vol. 14A, "The Actinide Elements," G. T. Seaborg and J. J. Katz, Editors, McGraw–Hill Book Co., Inc., New York, N. Y., 1954.
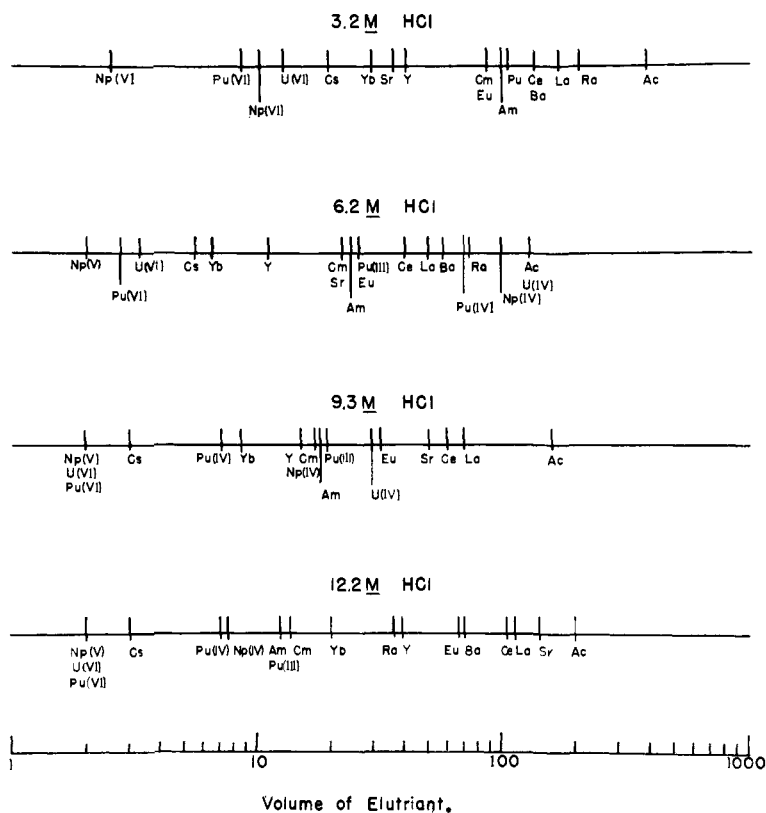
the results, and is, in fact, suggested by the differences in stability and size of the 5f-eigenfunctions in the actinides and the 4f-functions in the lanthanides. M. G. Mayer has shown on theoretical grounds that the f-eigenfunctions have a unique behavior compared to the s-, p-, or d-functions,[11] that is, they undergo a sudden change in spatial extent and energy at certain atomic numbers. The effective potential energy of an f-electron in the field of the residual atom has two negative regions after a minimum Z (about 47) and at first the outer potential minimum is dominating so the 4f-eigenfunctions have a maximum there and are "outside" functions, that is, they extend out spatially as far as, or beyond, the 5d- and 6s-orbitals. The 4f-orbitals, however, are at a higher energy level than the 5d or 6s, so these latter fill in first. With increasing atomic number, the inner potential minimum gets deeper very rapidly so that it comes to dominate the nature of the 4f-functions and in a small range of Z the shape of the function changes abruptly to that of an "inner" orbit. The rapidly decreasing potential also brings the energy down so that the 4f-level begins to fill at cerium, $Z = 58$, and at this point the 4f-functions are already "inside" the 5s- and 5p-electron shells. This can be seen by the negligible effect of the 4f-electrons on the valence properties of the atoms, the rare earths all having a common oxidation state, and by the very sharp absorption lines shown by the lanthanides. These lines are due to (forbidden)

(11) M. Goeppert-Mayer, *Phys. Rev.*, **60**, 184 (1941).

f- to f transitions, and so are shielded from external influences.

Because the 4f-eigenfunctions have already shrunk at cerium, they are not very useful for covalent bonding in the lanthanide elements, since, for bonding, orbitals must not only be energetically favorable, but also must be available spatially at normal bond distances, i.e., they must extend out far enough to have sufficient overlap with the bonding orbitals of the other atom or atoms. However, at a lower atomic number than that of cerium, the 4f-eigenfunctions, although at a higher energy, are appreciable beyond the 5s- and 5p-shell maxima, and so, if more energy can be gained by using them in hybridized covalent bonding than is lost in promoting or placing electrons in these higher levels, the 4f-orbitals may become bonding orbitals. It has been noted that TeF_6 hydrolyzes readily in water in contrast to the inert behavior of SeF_6 and SF_6, and the explanation offered involves such a use of 4f-orbitals.[12] Such 4f-hybridization has also been given as the explanation for the enhanced stability of the higher oxidation states of antimony, tellurium and iodine over those of arsenic, selenium and bromine, and of the ability of the former to bond a larger number of atoms.[13]

The 5f-eigenfunctions go through a transformation similar to that of the 4f after the completion of the rare earth series. At first they are "outside" functions, but again, as the atomic number increases, a critical region of Z is reached at which the eigenfunctions shrink and become "inner" functions and their energy level falls so that the 5f-shell starts to fill. In this actinide series, however, the 5f-orbitals either do not shrink as rapidly as in the 4f-series, or they have a greater spatial extension relative to the 6s- and 6p-orbitals than the 4f-orbitals have relative to the 5s- and the 5p-functions. In either case the result is a lower shielding of the 5f-electrons.

The fact that the first members of the actinide series have higher oxidation states than the characteristic tripositive state, i.e., protactinium(V), uranium(IV), uranium(VI), neptunium(IV), neptunium(V), neptunium(VI), plutonium(IV), plutonium(V), plutonium(VI), in contrast to the beginning of the lanthanide series, shows that the first 5f-electrons are not bound as tightly as the 4f-electrons and that they are more easily affected by external influences, although the gradual uniform stabilization of the tripositive state indicates the presence of a regular f series, analogous to the rare earths.

The nearness of the 5f- and 6d-levels over a region of several atomic numbers makes it difficult to determine where they cross, i.e., at which value of Z the first 5f-electron enters, and the lower shielding of the 5f-orbitals compared to the 4f, makes it possible that, at the beginning of the 5f-series, the levels change positions depending on the chemical binding of the element or on its degree of ionization. Thus, the gaseous atom may have a different electronic configuration than the metallic atom, and the electronic configuration of the ion may differ from compound to compound in solids and in solution. These small energy differences are evident also in the spectroscopic data; for example, spectroscopic evidence seems to show that the ground state of the neutral thorium atom has a $7s^26d^2$-configuration[14] (although X-ray data indicate the presence of a 5f-electron)[15] but the ground state of the triply ionized atom has a single 5f electron.[16]

The comparable binding energy, at the beginning of the actinide series, of the 5f-, 6d- and 7s-levels for a range of several atomic numbers, is a favorable condition for their use in hybridized bonds. Furthermore the greater spatial extension of the 5f-orbitals relative to the 4f and their slower shrinkage, might make them more available for such hybridization closer to the atomic number where the levels start to fill, rather than several numbers earlier as is probably the case with the 4f-orbitals. Thus such hybridization involving 5f-orbitals seems reasonable to account for the results reported in the present paper, i.e., the greater tendency for covalent complex ion formation of the transuranium elements as compared to the rare earth elements.

The use of 5f-orbitals in complexes formed by uranyl nitrate has been postulated by Glueckauf and McKay[17] to explain a series of facts about its chemistry, including its unusual solubility in oxygenated organic solvents, although Katzin[18] does not believe that such coördination is unique or different in kind from that found lower in the periodic table. Still another view is presented by Connick and Hugus, who, from consideration of the X-ray diffraction evidence on the crystal structure and a thorough analysis of the hydrolytic behavior of the uranyl ion, come to the conclusion that f orbitals participate in the metal–oxygen bonding in the uranyl, neptunyl and plutonyl ions.[19]

With these considerations in mind, the experimental results of the ion-exchange studies may be interpreted. The elutions with the tripositive ions of lanthanum, cerium, europium, ytterbium, actinium, plutonium, americium, curium are summarized in Fig. 6. Yttrium(III) is also included because it acts as a pseudolanthanide, with no possibility of f-orbital bonding.

The molarity of the eluting hydrochloric acid solution is plotted as abscissa, and the elution peak position in drops, normalized to the 10 cm. by 1 mm. column, is plotted as ordinate. The elution peak position is directly related to the equilibrium distribution coefficient of the ion and is directly comparable to Fig. 2, although the curves are distorted toward too high values at high hydrochloric acid concentration, since somewhat larger amounts of resin were used to maintain the column constant to a 10 cm. length.

Certain features in Fig. 6 are of interest. The difference in behavior of curium, americium and

(12) G. E. Kimball, J. Chem. Phys., 8, 188 (1940).

(13) Z. Z. Hugus, Jr., THIS JOURNAL, 74, 1076 (1952).

(14) P. Schuurmans, Thesis, Amsterdam, 1946.

(15) H. Russell, Jr., Los Alamos Scientific Laboratory Report LA-145 (Sept. 24, 1944); Manhattan District Declassified Document MDDC-406 (Oct. 22, 1946).

(16) P. F. A. Klinkenberg and R. J. Lang, Physica, 15, 774 (1949).

(17) E. Glueckauf and H. A. C. McKay, Nature, 165, 594 (1950).

(18) L. I. Katzin, ibid., 166, 605 (1950).

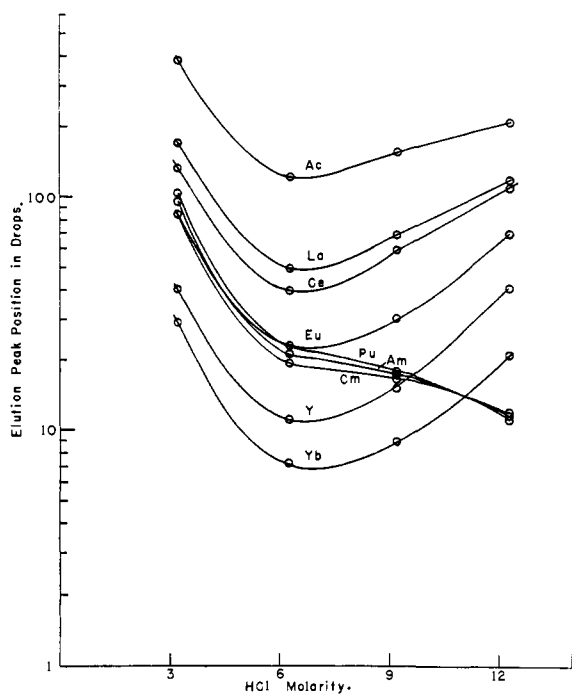(19) R. E. Connick and Z. Z. Hugus, Jr., THIS JOURNAL, 74, 6012 (1952).

Fig. 6.—Elution peak positions of the tripositive ions *vs.* hydrochloric acid molarity.

plutonium, on one hand, and ytterbium, yttrium, europium, cerium, lanthanum and actinium on the other, is clearly evident. In hydrochloric acid above 6 M in concentration the actinide ions show a much larger elution rate than the rare earth ions. The latter are delayed due to the resin shrinkage and consequent increase in concentration of exchange groups, and also to the decrease of the effective radii caused by the increasing disruption of their hydration shells. While the actinides also experience a greater attraction by the resin at higher hydrochloric acid concentration, the greater extent of their complex ion formation with chloride apparently more than offsets this and is responsible for their earlier elution. This complex formation with chloride ion is borne out by other types of data. For example, absorption spectra measurements on plutonium(III) show that changes in the spectrum indicative of complex ion formation occur in hydrochloric acid solutions above 6 M in concentration.[20] Further, transference experiments on plutonium(III) in hydrochloric acid solutions indicate that a small but appreciable fraction of the plutonium migrates to the anode in 1 M HCl, and that a somewhat larger amount[21] does so in 10 M HCl. These facts are compatible with the actinides forming negative complex ions with chloride ion, and more detailed anion-exchange work with europium and americium in 12 M HCl does indeed show a small delay in the elution peak position of americium(III) compared to europium(III).[22] Similar experiments in 5 M

(20) J. C. Hindman and D. P. Ames, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 4.2, McGraw-Hill Book Co., Inc., New York, N. Y., 1949; J. C. Hindman, *ibid.*, Paper No. 4.4.

(21) C. R. McLane, J. S. Dixon and J. C. Hindman, *ibid.*, Paper No. 4.3.

(22) D. A. Orth, unpublished data, this Laboratory (1949).

HCl show no such differentiation indicating that the tendency of americium to form complex anions with chloride, although pronounced relative to the rare earths, is still quite weak requiring concentrated hydrochloric acid to become observable.

Examination of Fig. 6 shows that yttrium(III) which has a comparable radius to the actinides and lanthanides (and has d-orbitals available) but which also has such a low atomic number that the 4f-orbitals are still at too high an energy to be useful for bonding, elutes with the lanthanides, and, in fact, shows a curve rising more steeply from 6 to 12 M HCl than that of any of the lanthanide ions. This behavior is indicative of even less complex ion formation in this range of hydrochloric acid concentration than that displayed by the lanthanide ions. Examination of Fig. 6 also shows that actinium(III) resembles the lanthanides more closely in its elution behavior than it does plutonium(III), americium(III) and curium(III), *i.e.*, its tendency toward complex ion formation is smaller than in the case of the latter ions, though greater than that of any of the lanthanides. This may indicate that the 5f-orbitals in actinium are still at too high an energy to be readily available for bonding.

In order to illustrate further the point that the actinides complex more chloride ions than do the lanthanides, the data of Table I are shown in Fig. 7,
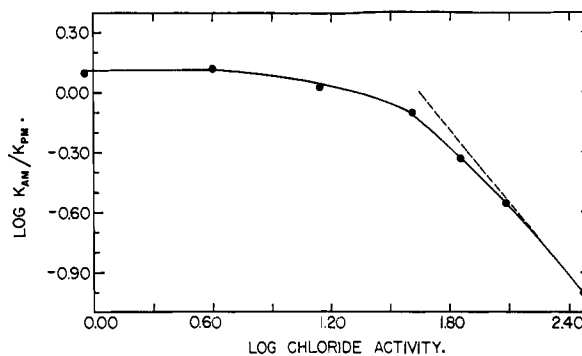

Fig. 7.—Plot of the logarithm of the ratio of the equilibrium distribution coefficient of americium to that of promethium *vs.* the logarithm of the mean activity of chloride ion.

where the logarithm of the ratio of the equilibrium distribution coefficient of americium to that of promethium is plotted against the logarithm of the chloride activity. The latter is the mean activity as tabulated by Robinson and Stokes.[23] With certain assumptions, the negative of the slope of this curve gives a measure of the number of excess chloride ions bound up with americium over those tied up with promethium. Actually, the assumptions make the slope a lower limit, so that the observed slope of about -1.2 at 12 M HCl may well indicate that there are, on the average, two more chlorides bound to an americium ion than to a promethium ion in strong hydrochloric acid solutions. For the reasons already discussed, this difference in complex ion formation ability is very likely due to a greater contribution to hybridization by the

(23) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

5f-orbitals in the actinides than by the 4f-orbitals in the rare earths.

A smaller effect, but a very striking one, is the reversal of the elution order of the ions plutonium-(III), americium(III) and curium(III) in 12 M HCl, from that in the less concentrated hydrochloric acid solutions, where the elution sequence is curium, americium and plutonium, as might be expected from their hydrated radii. This anomaly may be due to the already mentioned spatial contraction of the f-orbitals with increasing atomic number. For the 4f-orbitals this shrinkage has occurred already at cerium, where they commence to fill, but for the 5f-orbitals it may occur most prominently around neptunium or plutonium. (It is interesting to note that a maximum value for the force constant, as determined by infrared absorption, occurs for NpO_2^{++} in the sequence UO_2^{++}—NpO_2^{++}—PuO_2^{++}—AmO_2^{++} which might also be due to the changing availability of 5f-orbitals in this region.)[24] The 5f-orbitals in curium would then be smaller than those in americium, which would in turn be smaller than those in plutonium, and so their ability to overlap the orbitals of the chloride ions would consequently be less and the resulting bonding would be weaker. This would cause the strength of the complex ions to vary in the order plutonium > americium > curium and would give the observed reversal of the elution order. However, this explanation must be reconciled with the fact that even in 12 M HCl berkelium and californium elute ahead of plutonium and that they have even stronger tendencies to form complex ions with chloride ion.[25] Actually, this latter behavior is not incompatible with the idea of the spatial contraction of the 5f-orbitals, since, by analogy with the rare earths, the berkelium(III) ion is

probably considerably smaller than the plutonium-(III), americium(III) and curium(III) ions, and the californium(III) ion is probably even smaller. This decrease in size of the ion, that is, of the filled 6s- and 6p-orbitals, may be comparable to the shrinkage of the 5f-orbitals and thus allow the latter to be of greater effective use again in hybridized bonding. It should be mentioned that a study of the elution behavior of europium and of gadolinium, the homologs of americium and curium, showed no reversal of their relative elution peak positions in 12 M HCl.

Another possibility, which is perhaps not separate or incompatible with the foregoing discussion, is that the tendency of plutonium(III), americium-(III) and curium(III) to form positively charged chloride complex ions is about the same, but in the process the hydration shells of the ions are necessarily disrupted. In 12 M HCl these complex ions are then partially desolvated so that their effective radii go in the order plutonium > americium > curium, so that their elution peak positions are reversed. The behavior of berkelium and californium, eluting even faster than plutonium in 12 M HCl, is again explainable as caused by a much stronger complex ion forming tendency, due to their smaller size.

Although a definite answer as to why plutonium, americium and curium show a reversal in their elution order in hydrochloric acid solutions of greater than 9 M concentration requires further study, a similar, but much more pronounced reversal of elution order with the alkaline earth ions, strontium(II), barium(II), radium(II), Fig. 8, indicates the importance of considering the effect of ion dehydration in concentrated hydrochloric acid solutions. With dilute hydrochloric acid these ions elute in the order to be expected from their effective (hydrated) radii, namely, in the sequence strontium, barium and radium, but at 12 M HCl they have reversed this order to radium, barium, strontium, and with considerable spacing between the elution peak positions. Chloride complex ion formation with these alkaline earth ions is probably not very important, certainly less so than in the case of the rare earth and transuranium ions. The larger Ra(II) ion is probably only partially hydrated even in 3 M HCl so it shows a continuous decrease in K_d with increase in hydrochloric acid concentration due mainly to the mass-action effect of increasing the hydrogen ion concentration. In contrast, the smaller strontium ion is certainly more hydrated in dilute hydrochloric acid solutions, but with increasing concentration of hydrochloric acid the free water left available for this purpose decreases and so the ion's effective radius becomes smaller. This, plus the effect of resin shrinkage, appears more than sufficient to overcome the mass action effect of the hydrogen ion in solutions above a concentration of 6 M HCl, and so Sr(II) goes back on the resin, i.e., it elutes slower and slower. The behavior of the barium ion is intermediate between that of the strontium and radium ions, as would be expected.

The results for the hexapositive states of uranium, neptunium and plutonium are given in Fig. 5.
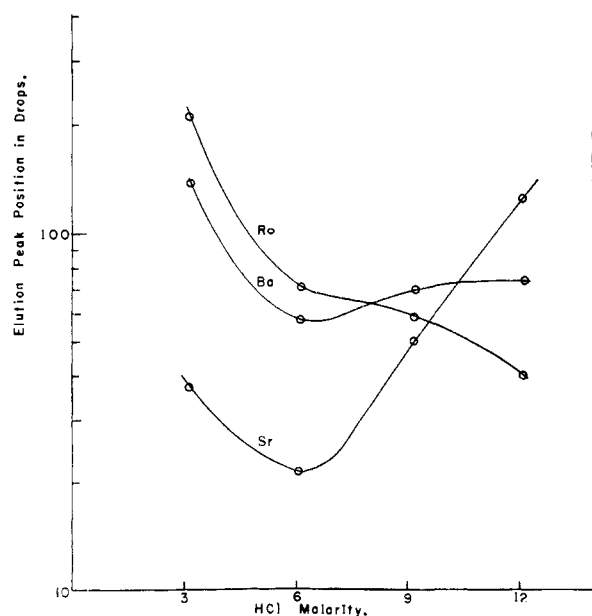

Fig. 8.—Elution peak positions of the dipositive alkaline earth ions vs. hydrochloric acid molarity.

(24) L. H. Jones and R. A. Penneman, J. Chem. Phys., 21, 542 (1953).

(25) S. G. Thompson and K. Street, Jr., unpublished work (1951).

These are oxygenated to form the UO_2^{++}, NpO_2^{++} and PuO_2^{++} ions, which are often considered as large dipositive cations. At concentrations as low as 6 M HCl these ions come off in the first column volume, indicating strong complex ion formation with chloride ion, with little attraction by the resin. Evidence for the formation of such complex ions with chloride ion for this oxidation state can be found in the literature from transference experiments[21] and spectroscopic studies.[20] Also similar to these ions is neptunium(V) which exists in the form NpO_2^+, and washes right through the resin column even in 3 M HCl. Since cesium(I), a typical monopositive ion, is held up somewhat on the resin column in hydrochloric acid solutions of such concentration, the rapid elution of NpO_2^+ indicates that appreciable complex ion formation occurs with the neptunium(V) in 3 M HCl.

Still another series of ions can be considered in the actinides: the tetrapositive states of thorium, uranium, neptunium and plutonium. The results for these are summarized in Fig. 9 where again elution peak position is the ordinate and hydrochloric acid molarity is the abscissa. All these ions are presumably "bare" ions, $i.e.$, are not oxygenated, and so due to their high charge should be strongly adsorbed on the resin in the absence of complexing agents. However, the same high charges should also cause these ions to be strongly bound in complex ions. No data are given for 3 M HCl solutions, as the ions are all bound so tightly to the resin at this hydrochloric acid concentration that the elution could not be conveniently observed. With the 6, 9 and 12 M HCl solutions, however, the tetrapositive ions elute in the sequence plutonium, neptunium, uranium and then thorium, which is the order expected from their radii if there was no complex ion formation. As the hydrochloric acid concentration is increased, these ions elute more rapidly, showing a large variation in the
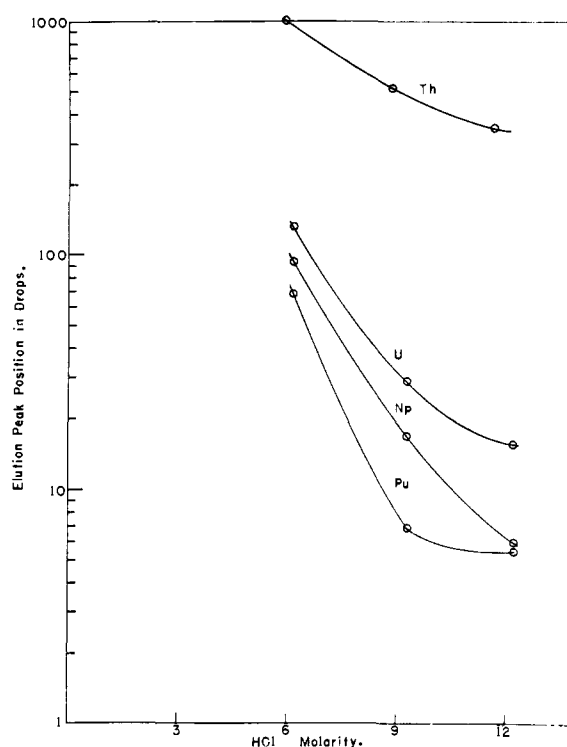

Fig. 9.—Elution peak positions of the tetrapositive ions $vs.$ hydrochloric acid molarity.

value of K_d, and indicating strong complex ion formation, particularly for plutonium, neptunium and uranium.

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