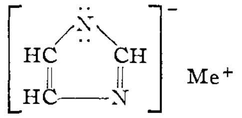
methyl groups would weaken complex formation.

Hoffmann[9] mentions that imidazole forms salts with metals of the general structure shown below



The complexes discussed in this paper with cadmium and copper ions, on the basis of what has been presented, cannot be expected to have this structure.

Acknowledgment.—The authors wish to express their appreciation to the National Science Foundation for support of this work. and to Dr. R. W. Cowgill for a gift of 1-methylimidazole.

Pittsburgh, Pa.

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[9] K. Hoffmann, "Imidazole," Interscience Publishers, Inc., New York, N. Y., 1953, p. 15.

[Contribution from the Department of Chemistry, The University of Wisconsin]

The Ion Exchange of Zirconium and Hafnium in Perchloric Acid with Amberlite IR-120[1]

By Edwin M. Larsen and Pei Wang

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Batch experiments with zirconium–hafnium perchlorate solutions and Amberlite IR-120 were made over total metal ion concentrations of 1×10^{-2} to 1×10^{-5} molar, and at 2, 1 and 0.5 M perchloric acid at constant ionic strength of 2. The data show that the metal ions are hydrolyzed in the resin phase. The data can be interpreted in terms of unhydrolyzed metal species M^{+4} in the aqueous phase at 1 and 2 M hydrogen ion. The distribution data show that zirconium is favored over hafnium in the resin phase, with the ratio of the distribution coefficients, D_{Zr}/D_{Hf}, increasing in favor of zirconium at the lower aqueous hydrogen ion concentration. At high total metal ion concentration, the hafnium appears to enter into mixed zirconium–hafnium polymers at hafnium concentrations considerably below that at which the hafnium polymer formation alone would be significant.

Nearly all previous studies on the ion exchange behavior of zirconium and hafnium have been limited to investigations of the separation of these two elements.[2–7] Only a few attempts have been made to use ion-exchange resins to study the nature of zirconium species in solution. Kressman and Kitchner[8] concluded that multivalent cations in general obeyed the mass action law. However, their experiments with zirconium were very limited and apparently at very high metal ion concentrations in which case most of the metal ions in the aqueous phase must have been polymerized. Lister[9] interpreted his data as indicating the presence of polynuclear hydrolysis products in solution at low acidities, and at higher acidities, zirconium–anion complexes. He concluded that, contrary to the data of Connick, *et al.*,[10–12] there was no evidence for the existence of unhydrolyzed M^{+4} ion. We hoped that this investigation would provide an independent check on the nature of the tetravalent ions in solution and on the resin, and that any differences in behavior of zirconium and hafnium would be demonstrated.

In this research, exchange experiments were carried out using Amberlite IR-120, a sulfonic acid type cation exchanger, and zirconium–hafnium solutions 2, 1 and 0.5 M in perchloric acid. The ionic strength was maintained constant at two with sodium perchlorate. The concentration range of the total ion concentration was varied from 0.01 M to 2.5×10^{-5} M so that the exchange behavior of solutions containing both polymers and monomers[10–12] might be observed. The starting metal salt contained only a few per cent. of hafnium, so the total hafnium concentration in solution was never more than 2×10^{-4} M.

Conditions were chosen such that the hydrogen ion concentration of the solution remained essentially constant during the course of the experiment. When the aqueous solutions contained sodium ion, a mixed sodium–hydrogen resin was used which contained the equilibrium concentrations of the sodium and hydrogen ions.

The ratio of the solution volume to the resin weight was kept large, no less than 100/1, to minimize the change in solution concentrations produced by losses in solvent volume due to resin swelling.

We have chosen to express the metal concentrations in the resin phase in terms of moles of metal ion per equivalent weight of resin. For the sodium–hydrogen resin this concentration term is the same as mole fraction since these ions are univalent. The equivalent weight of the resin is that weight which contains one mole of exchangeable hydrogen or its equivalent. For the hydrogen form of Amberlite IR-120 used here, the exchange capacity was 3.73 meq./g. of air-dried resin, or 4.84 meq./g. of dry resin. The moisture content of the air-dried resin varied with composition and with the humidity, so it had to be determined with each preparation.

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[1] Based on a thesis submitted by Pei Wang in partial fulfillment of the requirements for the degree of Doctor of Philosophy, and carried out under Task Order 4 of Contract N7 onr-28504 between the Office of Naval Research and the University of Wisconsin.

[2] G. T. Seaborg and K. J. Street, This Journal, **70**, 4268 (1948).

[3] K. A. Kraus and G. E. Moore, *ibid.*, **71**, 3263 (1949).

[4] I. E. Newnham, *ibid.*, **73**, 5899 (1951).

[5] E. H. Huffman and R. C. Lilly, *ibid.*, **73**, 2902 (1951).

[6] J. T. Benedict, W. C. Schumb and C. D. Coryell, *ibid.*, **76**, 2036 (1954).

[7] B. A. J. Lister and J. M. Hutcheon, *Research* (*London*), **5**, 291 (1951).

[8] T. R. E. Kressman and J. A. Kitchner, *J. Chem. Soc.*, 1201 (1949).

[9] B. A. J. Lister and L. A. McDonald, *ibid.*, 4315 (1952).

[10] R. E. Connick and Wm. McVey, This Journal, **71**, 3182 (1949).

[11] R. E. Connick and W. H. Reas, *ibid.*, **73**, 1171 (1951).

[12] A. J. Zielen, United States Atomic Energy Commission UCRL-2268, 81 pp., July, 1953.

The distribution coefficient was defined as

$$D = \frac{\text{moles } MO_2/\text{eq. wt. resin}}{\text{moles } MO_2/\text{liter}}$$

When D was plotted as log D against the log of the equilibrium metal ion concentration (Fig. 1), a series of curves were obtained for the different hydrogen ion concentrations which resembled the extraction data plots obtained with β-diketones in the two phase distribution system.[10] The D values plotted were not distribution coefficients corrected to unit hydrogen resin activity, $D°$, as the $D°$ values could be calculated only if we had a method of determining the HR activity and the charge of the metal ion species in the resin phase.

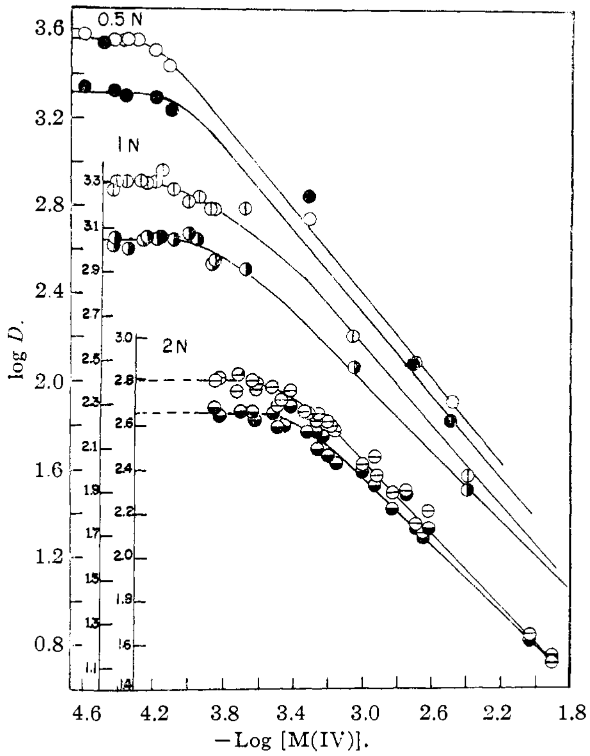

Fig. 1.—○⦶⊖, Zr; ●◑◒, Hf

Contrary to the experience of Lister,[9] we have been unable to determine the hydrogen resin concentration in the presence of the zirconium resin. An attempt was made to determine the hydrogen resin concentration by equilibrating the resin with successive portions of 2 M sodium chloride, separating the solution from the resin and titrating the liberated hydrogen ions with standard sodium hydroxide. No zirconium was removed from the resin under these conditions, but upon repeated equilibration with sodium chloride, small amounts of titratable hydrogen were found even after the seventh equilibration. This is clearly shown in Table I in which is also given the behavior of an air-dried hydrogen resin for comparison.

It would appear from this that the metal ion in the resin phase was hydrolyzing during the equilibration with the salt solution, thus releasing hydrogen ion. Although the meq. of base used in the later equilibrations was small, there is no assurance that an appreciable fraction of the total meq. found was not due to the hydrolysis of the metal in the resin phase. It was concluded, therefore, that an accurate determination of the HR concentration could not be made in the presence of the zirconium and hafnium.

TABLE I

MEQ. H ION RELEASED PER GRAM OF AIR-DRIED RESIN

	HR		HR-ZrR	
	a	*b*	*a*	*b*
1	3.39	3.39	2.29	2.30
2	0.34	0.34	0.30	0.30
3	.03	.03	.12	.12
4	.007	.007	.06	.06
5	...	...	.05	.05
6	...	...	.03	.03
7	...	...	.03	.03

The average charge of the metal ion species in the resin phase must also be known if these data are to be treated quantitatively. At constant hydrogen ion concentration, the average charge of the metal species on the resin should be a constant. If polymer formation occurred in the resin phase, however, the average charge per metal atom would be different from that of the monomer if the polymerization process were hydrogen ion dependent. If no polymers formed in the resin phase then the average charge for the monomeric metal species at a given hydrogen ion concentration could be found by saturating the resin with metal ion. This assumes of course that the equilibrium can be shifted so that the reaction goes to completion for all practical purposes, that is, all the exchange sites are occupied by tetravalent metal ions. Since the metallic ions had such a large charge this seemed reasonable. Experiments were carried out at high aqueous metal ion concentrations to determine the saturation capacity of the resin for the metal.

From the data in Table II we see that in 2 M perchloric acid, the resin has become saturated with metal ion at a capacity of about 40.8×10^{-2} mole MO_2/eq. wt. of resin. Now if the M^{+4} ions had gone on the resin as such, the maximum capacity should have been only 25×10^{-2} mole MO_2/eq. wt. resin. How can this be accounted for? The experimentally determined capacity, assuming all exchange sites occupied, gives an average charge per metal in the resin species of about 2.45, which must mean that the metal in the resin is associated with some anion.[13] This then introduces the following possibilities, the ions are already hydrolyzed in the aqueous solution, the ions hydrolyze in the resin phase, polymers are formed or exchanged in the resin phase, zirconium perchlorate complexes are formed in the resin, or a combination of these effects. For all these possibilities, except perhaps the perchlorate complex formation, the *average* charge per metal atom in the resin should go down with decreasing aqueous hydrogen ion concentration. What actually does happen?

From the data in Tables II, III and IV, one would conclude that although in 2 M perchloric acid the resin was saturated with metal ion at a capacity of 40.8×10^{-2} mole MO_2/eq. wt. resin, in 0.5 M perchloric acid, the saturation capacity was only

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(13) Benedict[6] reported a capacity of zirconium on Dowex-50 such that ZrR_4 was assumed to be the species in the resin phase.

TABLE II

EQUILIBRIUM CONCENTRATIONS

2 *M* HClC$_4$ Run	Aqueous phase, (moles MO$_2$/1.) × 10^5 ZrO$_2$	HfO$_2$	Total	Resin phase, (moles MO$_2$/eq. wt. for resin) × 10^2 ZrO$_2$	HfO$_2$	Distribution coefficients × 10^{-3} Zr	Hf
A	1220	19.5	1240	40.3	0.699	0.033	0.0358
A	916	15.9	932	40.7	.662	.0444	.0416
A	242	4.68	247	39.5	.639	.163	.136
C	226	2.95	229	29.4	.356	.130	.121
B	203	2.57	206	28.5	.349	.140	.136
A	182	3.12	185	36.9	.610	.201	.195
B	150	2.09	152	29.5	.346	.197	.165
B	121	1.59	123	28.4	.346	.235	.218
A	119	2.58	122	34.4	.550	.289	.213
C	102	1.40	103	27.1	.346	.268	.247
B	71	1.19	72	26.9	.319	.38	.268
A	66	1.17	67	26.5	.437	.40	.374
B	63	1.06	64	26.3	.304	.42	.286
E[a]	61	0.72	62	26.7	.321	.44	.45
B	60	.82	61	24.1	.294	.40	.36
B	56	.96	57	25.6	.302	.46	.32
C	54	.73	55	23	.28	.43	.38
A	49	.81	50	22.2	.372	.45	.46
D	49	.73	50	22.4	.273	.46	.37
C	45	.64	46	21	.25	.47	.39
E[a]	38	.52	39	22	.26	.58	.50
D	34	.55	35	18	.22	.53	.40
C	32	.48	33	16	.19	.50	.40
A	30	.65	31	18	.30	.60	.46
E[a]	30	.44	30	19	.23	.64	.52
D	24	.46	25	15	.19	.63	.41
E[a]	24	.34	24	15	.18	.63	.53
A	24	.53	25	14	.22	.58	.41
D	23	.39	23	15	.18	.65	.46
A	19	.40	19	11	.19	.58	.48
D	19	.34	19	13	.16	.69	.47
D	15	.27	15	10	.12	.67	.45
A	14	.31	14	9.1	.15	.65	.48

Run	Volume ml. exchange soln.	Wt. air-dried resin, g.	Temp., °C.	Initial mole Zr/Hf ratio
A	50	0.40	25 ± 0.05	60
B	100	.60	Rm. temp.	81
C	100	.60	Rm. temp.	81
D	100	1.00	Rm. temp.	81
E[a]	100	0.60	Rm. temp.	..

[a] Sample E resin was the Zr–Hf resin from experiment C; initial resin composition, HR; moisture content air-dried, 23.0%.

about 26 × 10^{-5} mole MO$_2$/eq. wt. resin. In the 1 *M* case, the saturation value apparently had not quite been reached, although the ultimate value would appear to fall between the other two. This hydrogen dependence was contrary to that required by the equilibrium expression, for it resulted in a higher average charge per metal atom at lower aqueous hydrogen ion concentrations.

The explanation appears to lie in the fact that saturation is not reached, since the actual change in monomer concentration with changes in the total metal ion concentration is small at the higher total metal concentration. From the paper of Zielen,[12] the fraction of monomer present as a function of the total metal ion concentration was calculated at 2 and 1 *M* hydrogen ion concentration. From these data one can conclude that although the monomer

TABLE III

EQUILIBRIUM CONCENTRATIONS

1 *M* HCl-O$_4$ Run	ZrO$_2$	Aqueous phase, (moles MO$_2$/1. × 10^5) HfO$_2$	Total	Resin phase (moles MO$_2$/eq. wt. of resin) × 10^2 ZrO$_2$	HfO$_2$	Distribution coefficients × 10^{-3} Zr	Hf
G	392	12.2	404	36.9	0.998	0.0941	0.0819
G	83.3	3.20	86.5	34.9	.945	0.418	.295
G	19.8	1.02	20.8	30.8	.847	1.56	.830
F	14.0	0.283	14.3	21.9	.254	1.56	.897
F	13.3	.281	13.3	20.7	.240	1.56	.854
F	11.4	.203	11.6	19.7	.231	1.73	1.14
F	9.7	.162	9.9	16.4	.193	1.7	1.19
F	7.9	.158	8.1	15.0	.175	1.9	1.11
G	6.5	.357	6.9	15	.41	2.3	1.15
F	6.4	.133	6.5	13	.15	2.0	1.13
G	5.4	.269	5.7	11	.31	2.0	1.15
F	5.3	.117	5.4	11	.13	2.1	1.11
F	4.3	.098	4.4	8.8	.10	2.1	1.0
F	3.6	.075	3.7	6.8	.079	1.9	1.1
G	3.6	.176	3.8	7.4	.20	2.1	1.13

Run	Volume, ml. exchange soln.	Wt. air-dried[a] resin, g.	Temp., °C.	Initial mole Zr/Hf ratio
F	100	0.80	Rm. temp.	85
G	50	.40	25 ± 0.05°	36

[a] Moisture content air-dried, 21.5%. Resin composition: HR mole fraction 0.434, NaR mole fraction 0.566 at zero zirconium concentration.

TABLE IV

EQUILIBRIUM CONCENTRATIONS

0.5 *M* HCl-O$_4$ Run	ZrO$_2$	Aqueous phase (moles MO$_2$/1. × 10^5) HfO$_2$	Total	Resin phase (moles MO$_2$/eq. wt. of resin) × 10^2 ZrO$_2$	HfO$_2$	Distribution coefficient × 10^{-3} Zr	Hf
H	314	4.20	318	25.6	0.283	0.0817	0.0674
H	196	2.35	198	23.6	.287	.120	.122
H	48.6	0.47	49	27.3	.333	.562	.71
H	8.9	.17	9.0	24.6	.295	.561	1.7
H	6.3	.13	6.4	20.5	.256	2.07	2.0
I	5.0	.11	5.1	18.4	.221	3.7	2.0
I	4.2	.091	4.3	15.5	.188	3.7	2.1
H	4.1	.089	4.2	14.5	.174	3.5	2.0
I	3.6	.073	3.7	12.8	.155	3.6	2.1
I	2.4	.051	2.5	9.3	.110	3.9	2.2

Run	Vol. (ml.) exchange soln.	Wt. air-dried[a] resin (g.)	Temp., °C.	Initial mole Zr/Hf ratio
H	100	0.50	Rm. temp.	83
I	100	.80	Rm. temp.	83

[a] Moisture content air-dried, 16.9%, resin composition: HR mole fraction 0.217, NaR mole fraction 0.783 at zero zirconium concentration.

TABLE V

FRACTION OF ZIRCONIUM PRESENT AS MONOMER AS CALCULATED FROM THE DATA OF ZIELEN[12]

Equilibrium concentrations, mole × 10^3/l.

Total Zr 2 *M* H	1 *M* H	Monomer Zr 2 *M* H	1 *M* H	Fraction monomer 2 *M* H	1 *M* H
	0.32		0.30		94
3.9		2.9		71	
	1.0		0.64		64
6.3		4.5		58	
	3.2		1.1		34
12.4		5.0		41	
	5.2		1.3		25
	7.8		1.5		19
	13		1.8		14

concentration varied appreciably with the total metal ion concentration over the range used at 2 *M* hydrogen ion concentration, this was less true at the 1 *M* perchloric acid concentration. From our data at 1 *M* perchloric acid, it does not appear that we have reached saturation of the resin with metal ion but, from the data of Zielen, it does not seem possible to significantly raise the monomer concentration by further increasing the total metal ion concentration (Table V). It would appear, therefore, that the data at 2 *M* perchloric acid probably represent the true saturation value for the metal ion capacity, and therefore the average charge per metal atom on the resin can be calculated from these data. It does not seem that the saturation value at 1 *M* perchloric acid can be determined, and certainly not at the 0.5 *M* perchloric acid. Therefore, the low saturation value at 0.5 *M* perchloric acid is not a true value, and the average charge per metal atom in the resin cannot be calculated from these data.

It also should be pointed out that at the 1 *M* and the 0.5 *M* acid concentrations the ionic strength was maintained constant by adding sodium perchlorate. Although the sodium–hydrogen resin equilibrium constant is not far from one, the sodium ion is favored slightly over the hydrogen ion by the resin. This factor will also work against the attainment of saturation of the resin with zirconium at the same aqueous metal ion concentrations used at 2 *M* perchloric acid.

Our experiments also showed that the high capacity for the metal ion was not due to absorbed metal salt solution, for when the resin was separated from the liquid by filtration, blotted with absorbent paper to remove the excess liquid, and then washed with distilled water, no zirconium was found in the washings.

It would be interesting to test our data to see whether or not the ideas of the unhydrolyzed tetravalent ion in 2 *M* perchloric acid, and the hydrolyzed metal species in the resin phase are reasonable. To do this we will consider a generalized expression and see how the data fit under different assumptions, without making use of the zirconium capacity of the resin which may be subject to a variety of interpretations. The calculations made are based on the fact that at low metal ion concentrations in the aqueous and resin phases, the *D* values are independent of the metal ion concentration (Fig. 1). This was taken to mean, (1) that in this region the activity of the NaR–HR resin was essentially constant, and therefore at infinitely dilute metal ion concentrations, the HR concentration of the resin phase could be taken as that of the pure resin; (2) that the metal species in the aqueous and the resin phases over this region contained the same number of metal atoms per ion, probably being monomeric, since the metal ion concentration of these solutions is well below the limit established for polymer formation.[10–12] We also had to assume that at 2 and 1 *M* H the composition of the species in the resin phase was the same; this is considered again in more detail later. It was felt that this was not a safe assumption to make for the 0.5 *M* H solutions, and since there was no way to get at the formula of the species on the resin at this hydrogen ion concentration, no calculations involving these data were made. The data were included however, to show the general trend of *D* with hydrogen ion.

The net equation for the general reaction is given by

$$\mathrm{M(OH)}_n^{4-n} + 4 - (n+x)\mathrm{H_2O} + x\mathrm{HR} \longleftrightarrow \mathrm{M(OH)}_{(4-x)}R_x + (4-n)\mathrm{H}^+$$

Our data cannot be treated rigorously because of the lack of information concerning activity coefficients, but we believe that for the conditions cited above, certain simplifications and assumptions can be made which will permit us to arrive at some valid conclusions from the data.

Among these assumptions are the following: (1) at constant ionic strength the activity of the water in the resin phase will be constant with changes in the hydrogen ion concentration. (2) At constant ionic strength the activity coefficients of the zirconium–hafnium species both in the resin and aqueous phase will be constant with changes in hydrogen ion concentration. (3) The activity of pure HR is 1, and the activity coefficient for HR in mixed NaR–HR resin is so close to 1 even down to a mole fraction of HR as low as 0.4, that activity coefficients will not be considered. This simplification is based on the data of Bonner[14] for activity coefficients of a mixed NaR–HR resin with Dowex-50, which like Amberlite IR-120 is a strong acid cation-exchange resin. (4) For the activity coefficient of hydrogen ion in the aqueous phase, the mean activity coefficients of 2 *M* perchloric acid, and for perchloric acid in the presence of sodium perchlorate were used. The latter values were calculated from the equation of Glueckauf,[15] and then corrected from the molal to the molar scale.

On the basis of these assumptions and simplifications, the equilibrium constant expression is reduced to

$$\begin{aligned} K' &= \frac{D(a_\mathrm{H})^{4-n}}{(\mathrm{HR})^x} \\ &= D^\circ(a_\mathrm{H})^{4-n} \qquad (1) \end{aligned}$$

where D° is the distribution coefficient corrected to unit HR activity.

The data can be tested in a general way by determining the hydrogen dependence of D°. To do this, a set of values of x was taken, and D° values calculated for each value of x (Table VI). The value for each D was taken from the curves in Fig. 1, for zirconium 2.80 and 3.30, for hafnium 2.66 and 3.05, at 2 and 1 *M* perchloric acid, respectively.

TABLE VI

H ion concn., *M* molarity	H ion activity coef.	HR, mole fraction	x =	log D°			
				1	2	3	4
2	0.88	1	Zr	2.80	2.80	2.80	2.80
			Hf	2.66	2.66	2.66	2.66
1	0.80	0.434	Zr	3.66	4.03	4.39	4.76
			Hf	3.41	3.78	4.14	4.50

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[14] O. D. Bonner, W. J. Argersinger, Jr., and A. W. Davidson, THIS JOURNAL, **74**, 1044 (1952).

[15] E. Glueckauf, *Nature*, **163**, 414 (1949).

The hydrogen dependence of D° can be found by examining the expression

$$D_2^0(a_{H_2})^{4-n} = D_1^0(a_{H_1})^{4-n} \qquad (2)$$

which is arrived at from the equilibrium constant expression. This also requires the assumption that x is the same at both the 2 and 1 M perchloric acid concentrations. This is not exactly true, but the estimate can be made that if the average charge were 2.5 for the experiments run in 2 M perchloric acid, then it would be about 2.3 for the experiments run in 1 M perchloric acid. This is partly based on the fact that the acid concentration within the resin is substantially smaller than the acid concentration outside the resin. For instance, Baumann and Eichhorn[16] have shown that for Dowex-50 with an HCl concentration of 2 M outside of the resin, the concentration inside was about 0.2 M. Similarly for 1 M HCl outside, the concentration was 0.09 inside. Using these hydrogen ion concentrations and the value of 2.5 for the average charge on the tetravalent metal ion in the resin phase, the equilibrium constant for the reaction

$$M(OH)^{+3} + H_2O = M(OH)_2^{+2} + H^+$$

can be estimated, since for an average charge of 2.5, the concentration of both tetravalent metal species must be equal. This requires the assumption that these two species are predominant. Using the calculated K, and 0.09 for the hydrogen ion concentration, the concentrations of the two species for the 1 M aqueous perchloric acid solutions experiments must be such that the average charge is about 2.3. As one can estimate from Table VI, the value of D° wouldn't change appreciably with this change in x. In a similar fashion, the assumption that n is essentially constant in 1 and 2 M aqueous perchloric acid may be justified. The hydrogen dependence of D° can be calculated from equation 2 by making the proper substitutions for the hydrogen ion activity, and using logarithms to solve for $4 - n$. This results in the expression

$$(4 - n) = -\frac{\log D_2^0 - \log D_1^0}{0.342} \qquad (3)$$

For the different assumed values of x, the corresponding D° values were substituted, and $4 - n$ values calculated. A plot of the $4 - n$ values against the assumed x values permitted one to easily interpolate for values of $4 - n$ at other x's. A representative set of data is given in the following Table VII.

TABLE VII

x		0.50	1.00	1.50	2.00	2.39	2.65
Hydrogen dependence $(4 - n)$	Zr	1.98	2.51	3.07	3.59	4.00	
	Hf	1.64	2.19	2.74	3.28	3.70	4.00
n	Zr	2.02	1.49	0.93	0.41	0.00	
	Hf	2.36	1.81	1.26	0.72	0.30	0.00

Now consider the three conditions possible.

1. The metal ion is unhydrolyzed in aqueous solution but hydrolyzed in the resin phase. In this case, n is zero, and the D° should show a fourth power dependence on the hydrogen ion concentration. This condition is met when x, the charge on the zirconium species in the resin phase, is 2.39 and for the hafnium species 2.65. This is very close to the average charge of the combined metals 2.45 found by saturating the resin with metal ion at the 2 M perchloric concentration, although this may not be significant, since these data are for very dilute aqueous and resin metal concentrations, whereas the saturation data are for concentrated metal ion solutions. Under these circumstances the possibility of polymers in the resin phase should not be discounted.[17]

2. No hydrolysis in the resin phase, but with values of n and x other than zero, and their sum equal to four. In this case the calculated hydrogen ion dependence $(4 - n)$ would have to be the same as the value of x chosen for the calculated of D°, since $n + x = 4$ and $x = 4 - n$. One can see from the data in Table VII, that this condition cannot be met, and therefore one must conclude that the condition of no hydrolysis occurring in the resin phase is eliminated.

3. The intermediate case where $n + x$ is less than four and n is other than zero. In this situation hydrolysis would be occurring in both the aqueous and resin phases, and the hydrogen dependence of D° would be less than four. From the data in Table VII one can see that these conditions can be met for zirconium at values of x less than 2.39, in which case n would be slightly greater than zero; to values of x approaching zero where n approaches two. Therefore the possibility of a hydrolyzed species occurring in the aqueous phase which is further hydrolyzed in the resin phase cannot be eliminated on the basis of these data. However, if this is the case, then the experimentally determined average charge for the metal species on the resin would be much too high, so this possibility does not completely fit the experimental facts. All things considered, the facts seem to fit best for the condition in which an unhydrolyzed species exists in the aqueous phase, but which is hydrolyzed in the resin phase. The failure to consider this resin phase hydrolysis seems to invalidate Lister's interpretation of his data for the non-existence of unhydrolyzed Zr^{+4} at high acid concentrations.

The data at the higher metal ion concentrations were not quantitatively evaluated, because many of the assumptions made would be invalid at the higher metal ion concentrations. Thus the possibility of polymer formation in the resin phase at the higher metal ion concentrations, and the activity coefficients of zirconium (hafnium), sodium and hydrogen in the resin phase, and the effect of one upon the other with changing concentrations would

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(16) W. C. Baumann and J. Eichhorn, THIS JOURNAL, **69**, 2831 (1947).

(17) It was pointed out by R. E. Connick that a plot of log (Zr) resin *vs.* log (Zr) aqueous has a slope of about unity right up to saturation and then breaks over abruptly to a slope of zero, whereas theoretical curves show a much more gradual approach to saturation. He suggested that such a phenomenon could occur if the species in the resin are changing from a monomer (or low polymer) at low zirconium concentrations to higher polymers at high zirconium concentrations, although the predominant species in solution is the monomer over the whole range. The polymers would be held more tightly by the resin than is the monomer, both because of larger net charge and larger size of the polymers. The high concentration of zirconium in the resin phase would favor polymer formation.

have to be known. Some preliminary calculations showed that even in the simplest case in 2 *M* H these complications became important.

In addition to information on the nature of the metal species several other conclusions can be drawn from these data. The distribution coefficient for hafnium appears to be a function of the total metal ion concentration, rather than the hafnium concentration. This effect can plainly be seen in the curves in Fig. 1, for *D* falls with increasing metal ion concentration although at no time does the hafnium concentration approach that at which polymers are considered to form. This would mean that in solution zirconium and hafnium form mixed polymers. This statement is made assuming that the log $D°$ plot if it could have been made would show the same general form, except with a little longer plateau. This conclusion is important, for in any practical separation process the *total* metal ion concentration must be kept below 10^{-4} molar.

Like the distribution coefficients in the extraction systems, the zirconium distribution coefficients are larger than the hafnium distribution coefficients at each hydrogen ion concentration. There is also a slight change in the ratio of the distribution coefficients in favor of the zirconium as the aqueous acid concentration is reduced. At the high metal ion concentrations the distribution coefficients become more alike.

Table VIII

	2 *M H*		1 *M H*		0.5 *M H*	
	log D_{Zr}	log D_{Hf}	log D_{Zr}	log D_{Hf}	log D_{Zr}	log D_{Hf}
	2.81	2.66	3.31	3.05	3.56	3.12
$\frac{D_{Zr}}{D_{Hf}}$	1.41		1.82		2.76	

Experimental

Materials Used.—The mixed hafnium–zirconium perchlorate solutions were prepared from a crystalline salt made from purified oxychloride 8-hydrate by fuming off the hydrochloric acid and then crystallizing from the concentrated perchloric acid.[11]

The sodium perchlorate used to maintain a constant ionic strength was crystallized from a solution of anhydrous sodium carbonate in perchloric acid.

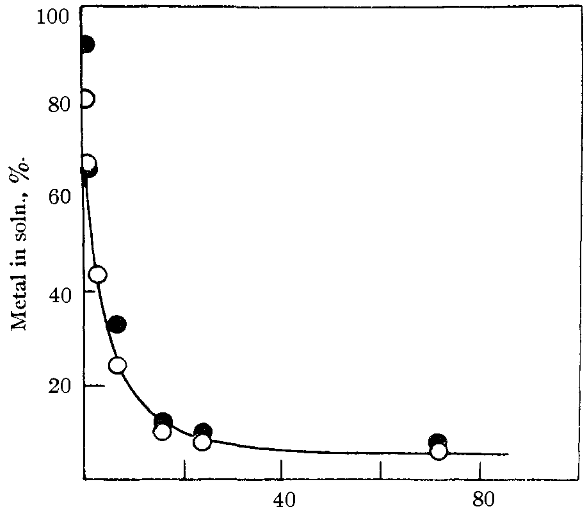

Fig. 2.—○, Zr; ●, Hf.

The hydrogen form of the resin was prepared from the stock sodium form by successive treatments with 6 *M* hydrochloric acid until no further exchange between hydrogen and sodium ions was observed. It was rinsed with distilled water until the wash water was free from any chloride ion, then air-dried and screened. The portion in the range of 20–40 mesh was used.

The sodium resin was prepared by treating the purified hydrogen resin with successive portions of 3 *M* sodium hydroxide until there was no further exchange. It was then washed free of excess alkali with distilled water and air-dried.

The proper composition of the sodium-hydrogen resin mixture to be used in the exchange studies at solution compositions other than 2 *M* perchloric acid was determined by successive equilibrations with aqueous solutions of the desired composition, until the acid concentration of the equilibrium solutions remained constant.

Studies on Amberlite IR-120.—The hydrogen capacity of the prepared hydrogen resin was investigated by several methods, including repeated equilibration of a weighed sample of the air-dried resin with a 2 *M* sodium chloride solution and subsequent titration of the liberated hydrogen ions with standard sodium hydroxide, direct titration of resin suspended in 1 *M* sodium chloride solution with sodium hydroxide, treatment with excess sodium hydroxide and titrating the excess with known hydrochloric acid and the method proposed by Topp and Pepper.[18]

The values found varied between 3.6 to 3.73 milliequivalents per gram air-dried hydrogen resin. The latter value, obtained by the repeated titration method, was adopted in the calculation.

The moisture content of the air-dried Amberlite IR-120 was determined by oven-drying at 107–110° from 2 hours to overnight. The loss in weight, denoted as moisture content, was then checked by letting the dried sample stand in air at room temperature for a long time and determining the regain in weight.

The ash content of the air-dried hydrogen resin, determined by igniting a weighed sample to constant weight, was found to be 0.8%.

Methods of Analysis.—For equilibrium studies, it is highly desirable to make analysis of the compositions of both phases; however, in most cases only the changes in concentrations of zirconium and hafnium aqueous species were determined. The hafnium was followed by using the β-emission of the radioactive hafnium tracer, Hf^{181}.[19] Aliquots of the perchlorate solution before and after exchange were transformed to chloride solution, and samples of suitable size were taken with a micro-pipet, mounted on either stainless steel dishes or 20 mm. watch glasses, dried under an infrared lamp and counted, using a Geiger counter with a Nancy Wood mica thin window tube. The activity and counting time were such as to give a counting error of approximately 2%.

For the determination of the total MO_2, a gravimetric or colorimetric method was used depending upon the concentration range of the metal ion. The MO_2 was determined gravimetrically as the ignited oxide, and colorimetrically as the alizarin lake. Zirconium and hafnium are known to form a lake with sodium alizarin sulfonate[20,21] which has been used for analytical purposes. A standard curve was established from a series of zirconium perchlorate solutions of known concentration in which the lake color was developed with 3 ml. of 0.05% sodium alizarin sulfonate solution per 100 ml. of final solution. The solution was about 0.3 *M* in hydrogen ion. After standing for 24 hours the optical density was determined at 520 mμ, using a Beckman model DU quartz spectrophotometer. The standard curve followed Beer's law over the concentration range of 0.05 to about 0.50 mg. MO_2 per 100 ml. of solution. The aliquot of the aqueous equilibrium phase was treated in the same manner. From the hafnium distribution, the original zirconium-hafnium composition, and the total MO_2 in the aqueous phase, the zirconium distribution was calculated. The

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[18] N. E. Topp and K. W. Pepper, *J. Chem. Soc.*, 3299 (1949).

[19] Isotope Branch, United States Atomic Energy Commission, Oak Ridge, Tenn.

[20] H. A. Liebhafsky and E. H. Winslow, This Journal, **60**, 1776 (1938).

[21] J. E. Flagg, H. A. Liebhafsky and E. H. Winslow, *ibid.*, **71**, 3630 (1949).

original HfO_2 content of the MO_2 was 2.06%. This was modified in some case owing to the addition of the active hafnium sample.

To check our analytical methods a material balance study (Table IX) was made on the metal distribution, by gravimetric determination of the MO_2 in the resin phase, and gravimetric or colorimetric determination in the aqueous phase. The total metal in the resin phase was determined by igniting a portion of the resin after exchange, weighing the residue as the mixed oxides and deducting from this the corresponding weight of ash. The results of this study were excellent, and it was concluded that our analytical methods and separation methods were satisfactory.

TABLE IX

MATERIAL BALANCE STUDY

Metal ions, 2 *M* $HClO_4$

Sample no.	MO_2 initial, mg.	MO_2 resin, mg.	MO_2 soln., mg.	Total mg. MO_2 found
1	153.0	74.5	77.1	151.6
2	135.0	73.2	58.1	131.3
3	117.0	72.2	45.6	117.8
4	90.0	71.8	15.40	87.2
5	72.0	64.6	7.60	72.2
6	36.0	35.0	1.92	36.9
7	22.5	21.6	1.21	22.8

Equilibration Procedure.—In the study of exchange phenomena of the system under investigation, carefully weighed samples of air-dried cation exchanger were equilibrated in glass vessels fitted on a mechanical shaker with measured volume of zirconium–hafnium perchlorate solutions of known compositions. For accurate results, the vessels were thermostated at 25 ± 0.05° during equilibration. However, as the temperature effect on ion-exchange equilibria was in general small, many of the experiments were made at room temperature, usually varying between 22 and 26°.

From the data (Fig. 2) it was concluded that three days of moderate shaking were needed to reach equilibrium at room temperature. Also, the equilibrium conditions were tested by starting with a zirconium–hafnium resin and equilibrating it with 2 *M* perchloric acid solution. These runs are marked with *a* and are included in Table II. The results agree quite well with the other experiments except that the hafnium distribution coefficient is a little higher in these cases.

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Chemical Properties of Elements 99 and 100

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A description of some of the chemical properties and of the methods used in the separations of elements 99 and 100 is given. The new elements exhibit the properties expected for the tenth and eleventh actinide elements. Attempts to produce an oxidation state greater than III of element 99 have been unsuccessful. In normal aqueous media only the III state of element 100 appears to exist. The relative spacings of the elution peaks of the new elements in some separations with ion-exchange resin columns are the same as the relative spacings of the homologous lanthanide elements. The results of experiments involving cation-exchange resins with very concentrated hydrochloric acid eluant show that the new elements, like the earlier actinides, are more strongly complexed than the lanthanides. The new elements also exist partially as anions in concentrated hydrochloric acid, as do earlier actinide elements, and they may be partially separated from each other by means of ion-exchange resins. With some eluants interesting reversals of elution positions are observed in the region Bk-Cf-99-100, indicating complex ion formation involving unusual factors.

Isotopes of elements 99 and 100 have been produced by neutron irradiation of Pu^{239}; the final steps in their production are indicated by the following reaction sequence[1–5]

$$\ldots\ldots\ldots Cf^{252}(n,\gamma)Cf^{253} \xrightarrow[20\text{ d}]{\beta^-} 99^{253}(n,\gamma)99^{254} \xrightarrow[36\text{ h}]{\beta^-} 100^{254}$$

The properties of some of the isotopes thus produced are listed in Table I. These were the isotopes used for the present tracer studies of the chemical properties of the new elements.

TABLE I

Isotope	Radiations	Half-life
99^{253}	6.68 Mev. α	~20 days
99^{254}	1.1 Mev. β^-	36 hours
100^{254}	7.22 Mev. α	3.2 hours

The first separation and identification of the new elements proved that prior expectations[6] concerning the stability of their tripositive states, their precipitation properties and exchange column elution sequences were correct; in short, that they are chemically very similar to their actinide predecessors,[7,8] differing in the manner to be expected for ions of somewhat smaller radius.

The results reported here were obtained in several instances in experiments which were primarily intended to separate and identify isotopes of the new elements rather than to obtain the maximum information concerning chemical properties. Since most of the experiments were essentially independent of each other, a separate introduction and discussion of each experiment is given in the section describing the experiment.

In the experiments to be described, the radioactivity of the isotopes of the new elements was normally measured by α-particle pulse analysis of thin

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(1) S. G. Thompson, A. Ghiorso, B. G. Harvey and G. R. Choppin, *Phys. Rev.*, **93**, 908 (1954).

(2) B. G. Harvey, S. G. Thompson, A. Ghiorso and G. R. Choppin, *ibid.*, **93**, 1129 (1954).

(3) M. H. Studier, P. R. Fields, H. Diamond, J. F. Mech, A. M. Friedman, P. A. Sellers, G. Pyle, C. M. Stevens, L. B. Magnusson and J. R. Huizenga, *ibid.*, **93**, 1428 (1954).

(4) P. R. Fields, M. H. Studier, J. F. Mech, H. Diamond, A. M. Friedman, L. B. Magnusson and J. R. Huizenga, *ibid.*, **94**, 209 (1954).

(5) G. R. Choppin, S. G. Thompson, A. Ghiorso and B. G. Harvey, *ibid.*, **94**, 1079 (1954).

(6) G. T. Seaborg, "The Actinide Elements," McGraw-Hill Book Co., Inc., New York, 1954, National Nuclear Energy Series, Plutonium Project Record, Vol. 14A, p. 733.

(7) S. G. Thompson, B. B. Cunningham and G. T. Seaborg, THIS JOURNAL, **72**, 2798 (1950).

(8) K. Street, Jr., S. G. Thompson and G. T. Seaborg, *ibid.*, **72**, 4832 (1950).