The measurement of ΔW of this sample yielded

$$\Delta W_{\text{NaTMB soln.-solvent}}.$$

$\Delta W_{\text{TMB soln.-solvent}}$ was obtained by repeating the measurement on a TMB solution containing the same amount of TMB as that used in the preparation of NaTMB.

For solutions of NaTMB in benzene–tetrahydrofuran mixtures, a measured amount of tetrahydrofuran was used for the reaction between TMB and sodium amalgam. Following completion of the reaction, an appropriate amount of benzene was introduced and the solution filtered into the calibrated sample tube. $\Delta W_{\text{TMB soln.-solvent}}$ was measured as described for using only benzene as solvent.

Molecular Weight Determination.—The apparatus used in the molecular weight determination by the freezing point depression method was as follows. Two dumpers, A and C, were connected in series and the latter attached by means of a T-joint to a reaction vessel E, with a constriction D. The dumper A was provided with a sidearm B, and dumper C with a fritted glass disk. A freezing point tube F (30 mm. diameter and 20 cm. length) containing a Beckmann thermometer G, and a stirrer H, was connected to reaction vessel E at a position slightly below the constriction D. The stirrer was made of a thin Pyrex rod, the upper portion of which was attached to a piece of Pyrex tubing containing a small iron bar. Stirring was effected by applying an intermittent magnetic field outside the tube F. In a typical run, about 2 g. of mercury was placed in dumper A and 2 g. of freshly cut sodium above the constriction in the sidearm B. About 0.5 g. of TMB was introduced into dumper C and the apparatus assembled and attached to the vacuum line. After thorough evacuation, the sodium in sidearm B was melted and allowed to pass through the constriction into dumper A where it combined with mercury to form the amalgam. Predried tetrahydrofuran was distilled into dumper C and the amalgam introduced from A. After shaking for about one hour, the solvent was evaporated and the residue dried by pumping for several hours. A measured amount of benzene or cyclohexane was introduced by distillation from a 25-ml. graduated pipet to dissolve the residue. The red solution was filtered through the sintered glass into the vessel E and the latter sealed off at D. The solvent in E was next distilled into F, which was placed into the Beckmann molecular weight apparatus and the freezing point of the solvent determined. The solid in E was put into solution by transferring the solvent to the vessel E and the freezing point of the solution determined in F.

The molal freezing point constants of benzene and cyclohexane were also determined using purified triphenylmethane. Values of 5.11 and 20.0, respectively, in agreement with the generally accepted values, were obtained.

Oxygen Absorption Measurements on NaTMB.—The apparatus used to determine the oxygen uptake of NaTMB in tetrahydrofuran solution was similar to that described under "Molecular Weight Determination" with the following modification. The freezing point apparatus F was replaced by an open-end mercury manometer equipped with a reservoir of approximately 100 ml. and a stopcock which was attached to the sidearm of E by means of a ball joint.

In performing the experiment, the system was evacuated and dry oxygen introduced through the vacuum line. The manometer stopcock was then closed, and the pressure of oxygen in the manometer and reservoir recorded. The volume occupied by the oxygen was later determined by calibration of the manometer and reservoir with water. The rest of the system, comprised of units A, B, C and E, was thoroughly evacuated and NaTMB in tetrahydrofuran prepared in C using sodium amalgam, by the method previously described. The blue NaTMB solution was transferred quantitatively to E and the latter sealed off at D. E was immersed in a constant temperature bath at 25° for 0.5 hour, the stopcock leading to the reservoir of oxygen opened, and the solution in E gently agitated. After one minute the solution had lost its blue color, turning yellow. The final pressure of the system, which was constant over a period of several hours, was recorded. The volume of the reaction vessel E was determined by calibration with water. In order to account for the amount of oxygen absorbed by the tetrahydrofuran and the contribution of tetrahydrofuran vapor to the final pressure, a second run was made using tetrahydrofuran alone, the volume of which corresponded to that of the solution used in the previous run. The initial and final pressures and volumes of oxygen obtained from these two runs, permitted calculation of the amount of oxygen absorbed by NaTMB.

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Pittsburgh, Pa.

[Contribution from the Oak Ridge National Laboratory, Chemistry Division]

Hydrolytic Behavior of Metal Ions. V. Ultracentrifugation of Hafnium(IV)[1,2]

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By equilibrium ultracentrifugation hafnium(IV) was found to form a low molecular weight hydrolytic polymer (or polymers) in *ca.* one molar acid solutions with an approximate degree of polymerization N of 3 or 4 (trimer or tetramer). Studies were carried out as a function of initial Hf(IV) concentration (0.008 to 0.1 M), of supporting electrolyte concentration (1 to 2 M), of type of supporting electrolyte (HCl, and HCl with LiCl, NaCl and CsCl), of acidity (0.5 to 2 M H_3O^+) and of temperature (*ca.* 1 to 30°). By combination of these experiments simultaneous evaluation of N and of the charge z of the polymeric ion was attempted.

The hydrolytic behavior of Hf(IV) has received very little attention although generally the assumption is made that the hydrolysis of Hf(IV), as well as its chemistry in general, is very similar to that of Zr(IV), which has been studied rather extensively.[3] Since Zr(IV) was found to polymerize in acidic solutions, polymerization of Hf(IV) was also expected. Although the results regarding polymerization of Zr(IV) have been somewhat contradictory,[3] there appears now to be considerable evidence that low molecular weight polymers are formed in solutions of acidity approximately 1 M. The present centrifugation results indicate that Hf(IV) also forms low molecular weight polymers under these conditions; further, Hf(IV) is either predominantly monodisperse (only one principal polymeric aggregate), or

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous paper, K. A. Kraus and F. Nelson, This Journal, **77**, 3721 (1955).

[3] See for example the following papers, where further references are given: (a) G. Jander and K. F. Jahr, *Kolloid-Beih.*, **43**, 295 (1935); (b) R. E. Connick and W. H. Reas, This Journal, **73**, 1171 (1951); (c) B. A. Lister and L. A. McDonald, *J. Chem. Soc.*, 4315 (1952); (d) K. A. Kraus and J. S. Johnson, This Journal, **75**, 5769 (1953); (e) W. B. Blumenthal, *Ind. Eng. Chem.*, **46**, 528 (1954); (f) in a recent paper E. M. Larsen and A. M. Gammill (This Journal, **72**, 3615 (1950)) point out that Hf(IV) precipitates less readily than Zr(IV). However, the work reported here was carried out in strongly acidic solutions where the observations of Larsen and Gammill do not necessarily apply.

occurs only in a narrow range of molecular weights. The procedure recently outlined[4] for calculating the degree of polymerization of charged solutes from equilibrium ultracentrifugations in the presence of excess supporting electrolytes appears applicable. Although this procedure implies certain idealized conditions, it is felt that these conditions are sufficiently met here to permit meaningful estimation of the degree of polymerization.

Experimental

Equilibrium ultracentrifugations were carried out in a Specialized Instrument Corporation Model E Ultracentrifuge.[5] The analytical rotor and cells (12 and 30 mm.) standard with this machine were used, except that the cell centerpieces were specially fabricated (by the manufacturer) of Kel-F plastic to avoid corrosion in the strongly acidic media. Details of the experimental procedure were described earlier.[6]

Concentration distribution in this centrifuge is determined from the refractive index gradient ($\mathrm{d}n/\mathrm{d}x$) as a function of radius x. For this purpose the machine is equipped with a Philpot-Svenssan[7] optical system in which refractive index gradients (arising from concentration gradients, compression effects, etc.) cause a displacement of the shadow of an inclined wire. This displacement Z is proportional to $\mathrm{d}n/\mathrm{d}x$ and is recorded on a photographic plate. It will be expressed in cm.

All experiments required two centrifugations, one in the presence of Hf(IV) ("polymer experiment") and one for which all conditions were the same as far as possible except that Hf(IV) was absent ("background experiment"). The values of Z for the background experiment were subtracted from those obtained in the polymer experiment to yield the quantity Z^*, which was used for interpretation. No correction was attempted for possible differences in $\mathrm{d}n/\mathrm{d}x$ induced by pressure differences in these two parallel experiments since the densities of the solutions were nearly the same. Equilibrium was considered attained when no significant change in Z could be observed over a period of at least 16 hours. This occurred after *ca.* 4 days in the Hf(IV) experiments and in 2 to 3 days in the background experiments.

The experiments were performed near 30°, except for a few carried out near 0°. In the latter case cooling was achieved with the refrigeration system which is standard with the machine, and the rotor was darkened with "Rubalt" to increase the rate of radiative heat exchange. The temperature of the rotor was determined after centrifugation, since the built-in "fixed" thermocouple was found to give readings several degrees too high during low temperature experiments.

Hafnium(IV) containing only negligible amounts ($<0.1\%$) of zirconium[8] was obtained from the ORNL Materials Chemistry Division. For most experiments solutions of hafnium oxychloride were used, though one was carried out with a solution of anhydrous $\mathrm{HfCl_4}$. No significant difference was found. The oxychloride (as octahydrate) was purified by recrystallization from 9 M HCl and no appreciable impurities could be detected spectrographically.[8] The composition of the compound was checked by analysis for hafnium and chloride. Samples of anhydrous $\mathrm{HfCl_4}$ were prepared by Dr. S. Y. Tyree, Jr., of the Chemistry Department, University of North Carolina.

Mackay C.P. cesium chloride was used after recrystallization from water. Spectrographic analysis[8] indicated no significant impurities except for a few per cent. of rubidium. Lithium chloride was either recrystallized from water or prepared from recrystallized reagent grade lithium carbonate[9] with no difference in results. All other chemicals were reagent grade and used without further purification.

Densities of the hafnium solutions ($\mathrm{HfCl_4}$ in 1 M HCl–1 M NaCl solutions) which were needed for the determination of the partial specific volumes, were measured by the gradient tube method.[10]

Results and Discussion

1. Computational Procedure.—The procedure reported earlier[4] for estimation of the degree of polymerization involves carrying out a series of equilibrium ultracentrifugations under different conditions of concentration of polymeric solute, of concentration of supporting electrolyte, of type of supporting electrolyte and perhaps of speed of rotation. From the results of each centrifugation, computed degrees of polymerization, $N_{z'}$, are obtained as a function of the assumed charge z' per monomer unit. From a comparison of the plots of $N_{z'}$ *vs.* z' for all experiments, the actual degree of polymerization, N, is then estimated. This value of N is selected at that z' for which the values of $N_{z'}$ for the various experiments are the same, or differ least.

In the derivation of equations for three-component systems the polymeric component (component 2) was defined as $\mathrm{PX_z} - (z/2)\,\mathrm{BX}$, where BX is the supporting electrolyte (component 3). $\mathrm{PX_z}$ is composed of the polymer ion $\mathrm{P^{+z}}$ and the counter ions $\mathrm{X^-}$ and $z = z'N$ is the charge on the polymer ion. The equations were derived for an idealized monodisperse polymer system with constant solution density ρ, constant species activity coefficients $g_\pm$, constant charge z', constant refractive index gradients ($\partial n/\partial c_i$) and constant partial specific volumes $\bar{v}_i$. It has been shown (equation 28, ref. 4) that, except for an approximation which is usually minor, the degree of polymerization N in a three-component system is given by the equation

$$N = \frac{S/A_2'}{1 - z'\eta(S - \sigma)/A_2'} \tag{1}$$

The following equations define the symbols

$$S = \mathrm{d}\ln c_2'/\mathrm{d}(x^2) \tag{2}$$

$$\sigma = \mathrm{d}\ln c_3/\mathrm{d}(x^2) \tag{3}$$

$$A' = \frac{M_2'(1 - \bar{v}_2\rho)\omega^2}{2RT} = L_2'\omega^2/2RT \tag{4}$$

$$M_2' = M'_{\mathrm{PX_z}} - (z'/2)M_{\mathrm{BX}} = \frac{1}{N}\left(M_{\mathrm{PX_z}} - \frac{z}{2}\,M_{\mathrm{BX}}\right) \tag{5}$$

$$\bar{v}_2 = \bar{v}'_2 = \frac{\left(\bar{V}'_{\mathrm{PX_z}} - \frac{z'}{2}\,\bar{V}_{\mathrm{BX}}\right)}{M'} \tag{6}$$

$$\eta = z'c_2'/2c_3 \tag{7}$$

where ω is the angular velocity, R the gas constant, T the absolute temperature, M the molecular weight, and $\bar{V}$ the partial molal volume. Concentration is expressed as molarity c.[11] The primes refer to the monomer unit. Note that in a three-component system A_2' is a constant.

From the experimental data, the derivative

$$\mathrm{S_e} = \frac{\mathrm{d}\ln Z^*/x}{\mathrm{d}(x^2)} \tag{8}$$

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(4) J. S. Johnson, K. A. Kraus and G. Scatchard, *J. Phys. Chem.*, **58**, 1034 (1954).

(5) E. G. Pickels, *Machine Design*, **22**, 102 (Sept., 1950).

(6) J. S. Johnson, K. A. Kraus and T. F. Young, THIS JOURNAL, **76**, 1436 (1954).

(7) (a) J. St. L. Philpot, *Nature*, **141**, 283 (1938); (b) H. Svensson, *Kolloid-Z.*, **87**, 181 (1939); **90**, 141 (1940).

(8) We are indebted to Messrs. M. Murray, J. Gillespie and C. Feldman of the ORNL Analytical Division for the spectroscopic analyses.

(9) E. R. Caley and P. J. Elving, *Inorganic Syntheses*, Vol. 1, McGraw-Hill Book Co., New York, N. Y., 1939, p. 1.

(10) K. Linderstrøm-Lang and H. Lantz, *Compt. rend. trav. lab. Carlsberg*, **21**, 315 (1938).

(11) In ref. 4 the equations were written in terms of molality m rather than molarity c. The substitution c for m is made here to simplify normalization to the total quantity of solute in the cell whenever this is desirable. This substitution is equivalent to assuming $\mathrm{d}\ln a/c = 0$ and $\partial n/\partial c = $ const. rather than $\mathrm{d}\ln a/m = 0$ and $\partial n/\partial m = $ const. (a is the activity of the solute).

is obtained. Under certain idealized conditions, assumed to hold here, the approximation

$$\mathbf{S}_e = \frac{\mathrm{d}\ln Z^*/x}{\mathrm{d}(x^2)} \approx \frac{\mathrm{d}\ln \dfrac{\mathrm{d}c_2'}{x\mathrm{d}x}}{\mathrm{d}(x^2)} = S_e \qquad (9)$$

may be made.[12] The relationship between S and S_e is given by the equation

$$S_e - S = \frac{\mathrm{d}\ln S}{\mathrm{d}(x^2)} \qquad (10)$$

which follows directly from the definition of S and S_e. The term d ln $S/\mathrm{d}(x^2)$ can be evaluated by differentiation of equation 1 to give

$$S_e - S = -\frac{(z'\eta/A_2')(S-\sigma)^2}{1+(z'\eta/A_2')\sigma} \qquad (11)$$

with the additional approximation that $\mathrm{d}\sigma/\mathrm{d}(x^2)$ is small in comparison with $\mathrm{d}S/\mathrm{d}(x^2)$.

For any centrifugation, a series of values $N_{z'}$ as a function of z' can be computed from equations 1, 9 and 11. If $\mathbf{S}_e$ does not change greatly with x^2, the slope at the center of the cell may be used in equation 11 in conjunction with the values of η computed from the original concentrations, since these concentrations will be found near the center of the cell. With equation 9 and the assumption that σ is the same in the presence and absence of polymer,[12] S may be obtained from $\mathbf{S}_e$ by equation 11. Values of $N_{z'}$ are then computed with equation 1.

If the solution contains two supporting electrolytes, 3 and 5, *e.g.*, HX and BX (four-component system), the polymeric component is defined as $PX_z - \{zm_3/2(m_3+m_5)\}$ HX $- \{zm_5/2(m_3+m_5)\}$ BX. The analog of equation 1 is

$$N_{z'} = \frac{S/A_2'}{1 - \dfrac{z'\eta^*}{A_2'}(S-\sigma^*) + \dfrac{z'}{2A_2'}\ln\dfrac{c_3}{c_5}\dfrac{\mathrm{d}\theta}{\mathrm{d}(x^2)}} \qquad (12)$$

where $\eta^* = z'c_2'/2(c_3+c_5)$, $\sigma^* = \mathrm{d}\ln(c_3+c_5)/\mathrm{d}(x^2)$, $\theta = c_3/(c_3+c_5)$. The equation for $S_e - S$ is obtained in the same way as equation 11, but since components 3 and 5 do not in general sediment to the same extent, A_2' here is not constant but a function of radius.[13] If the initial concentrations of components 3 and 5 are the same and evaluation of $N_{z'}$ is carried out at the center of the cell, the terms including $\ln(c_3/c_5)$ can usually be neglected. The equation then becomes

$$S_e - S = \frac{\dfrac{\mathrm{d}\ln A_2'}{\mathrm{d}(x)^2} - \dfrac{z'\eta^*}{A_2'}(S-\sigma^*)^2 + \dfrac{z'}{2A_2'}\theta(\sigma_3-\sigma^*)(\sigma_3-\sigma_5)}{1+(z'\eta^*/A_2')\sigma^*}$$

$$= \frac{-z'\eta^*(S-\sigma^*)^2/A_2'}{1+(z'\eta^*/A_2')\sigma^*} \qquad (13)$$

where $\sigma_3 = \mathrm{d}\ln c_3/\mathrm{d}(x^2)$ and $\sigma_5 = \mathrm{d}\ln c_5/\mathrm{d}(x^2)$.

Values of $N_{z'}$ and z' which are improbable can be eliminated immediately by comparison of the different experiments, and the uncertainty of the admissible values caused by experimental inaccuracy and breakdown of assumptions is apparent. An alternate interpretive procedure which is quicker and may be obtained in the following way. By differentiation of equation 1 with respect to $y = c_2'/c_3$ one obtains

$$\frac{\mathrm{d}S}{\mathrm{d}y} = -Nk\frac{\mathrm{d}(yS)}{\mathrm{d}y} + Nk\frac{\mathrm{d}(y\sigma)}{\mathrm{d}y} \qquad (14)$$

after the substitution $(z')^2/2 = k$ and with the assumption that N, k and A_2' are independent of y. These assumptions imply that the degree of polymerization is independent of y, although N does not have to be an integral value, and that the charge on the polymer is independent of the supporting electrolyte concentration. Equation 14, with neglect of $\mathrm{d}\sigma/\mathrm{d}y$, simplifies to

$$\frac{\mathrm{d}\ln S}{\mathrm{d}y} = -\frac{Nk}{1+Nky}\left(1-\frac{\sigma}{S}\right) \qquad (15)$$

When σ/S is small, integration of equation 15 yields

$$\frac{1}{S} = \frac{1}{S_0} + \frac{Nk}{S_0}y \qquad (16)$$

where S_0 is the extrapolated value of S at $y = 0$. The same equation may be obtained directly from (1) if σ is neglected, since $NA_2' = S_0$. With similar approximations, combination of equations 10 and 15 yields

$$S_e = S + \left(\frac{\mathrm{d}\ln S}{\mathrm{d}y}\right)\frac{\mathrm{d}y}{\mathrm{d}(x^2)} = S + \frac{\mathrm{d}\ln S}{\mathrm{d}y}(yS) = \frac{S}{1+Nky}$$

Differentiation of this equation gives

$$\frac{\mathrm{d}\ln S_e}{\mathrm{d}y} = -\frac{2Nk}{1+Nky} \qquad (17)$$

After integration or by direct combination of (10) (15) and (16) one obtains

$$\frac{1}{\sqrt{S_e}} = \frac{1}{\sqrt{S_{eo}}} + \frac{Nky}{\sqrt{S_{eo}}} \qquad (18)$$

where S_{eo} is the extrapolated value of S_e to $y = 0$ and hence $S_{eo} = S_o$. According to equation 9 and 18 a plot of $1/\sqrt{\mathbf{S}_e}$ *vs.* y should be a straight line with slope $Nk/\sqrt{S_{eo}}$ and intercept $1/\sqrt{S_{eo}}$ from which both N and k (or z') may be evaluated, since by equation 1, $S_{eo} = NA_2'$. Equations 16 and 18, though derived for a single experiment, may also be applied for comparison of the results from a series of experiments which are carried out in the same supporting electrolyte and at the same speed of rotation and temperature, since S is independently a function of y only, *i.e.*, $(\partial S/\partial(x^2))_y = 0$.

It is often desirable to compare experiments which are carried out in the same supporting electrolyte but at different temperatures and speeds of rotation. For these A_2' is not constant, and equations 16 and 18 no longer apply. After substitution of the variables $\alpha_e = 10^6 S_eT/\omega^2$ and $\alpha = 10^6 ST/\omega^2$ and with the assumption that L_2' (equation 4) is constant, the equations

$$\frac{1}{\alpha} = \frac{1}{\alpha_0} + \frac{Nky}{\alpha_0} \qquad (16a)$$

and

$$\frac{1}{\sqrt{\alpha_e}} = \frac{1}{\sqrt{\alpha_{eo}}} + \frac{Nky}{\sqrt{\alpha_{eo}}} \qquad (18a)$$

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(12) Equation 9 is approximate since d ln $(1-\eta^2)$ is neglected (ref. 4, equation 18) and since the same concentration (c_{BX}) of supporting electrolyte is used in the background and polymer experiments, though in the presence of the polymeric component $c_3 \neq (c_{BX})_{b.g.}$. The ratio of the sum of these errors to $(\partial n/\partial c_2)\,\mathrm{d}c_2/\mathrm{d}x$ was shown to be reasonably independent of x^2 for a simulated, less favorable system (row 8, Table II, ref. 4) than those treated here and hence the approximation introduces only a small error.

(13) An approximation is introduced in equation 9 for the four-component system in addition to those discussed in footnote 12. Because of the variation of the ratio c_3/c_5 with radius, $(\partial n/\partial c'_2,)$ is not constant. This variation has been neglected here.

can be derived in a manner analogous to the derivations of equations 16 and 18. In equations 16a and 18a, $\alpha_{e0} = \alpha_0$ is the extrapolated value of α (or α_e) to $y = 0$.

2. Monomer Unit and Partial Specific Volumes.—For the computation of $N_{z'}$, evaluation of M_2' and $\bar{v}_2$ is necessary. This in turn requires estimation of the degree of hydrolysis of Hf(IV) in these acidic solutions. Though the hydroxyl number **n**[14] is not known exactly, probable limits can be set. From potentiometric studies (glass electrode) of the hydrolysis of Zr(IV) and Hf(IV) at acidities 0.2 *M* and less in chloride solutions it can be concluded[15] that $\mathbf{n} \leqslant 2.33$ at acidities above 0.2 *M*. The fact that $HfOCl_2$ (as well as $ZrOCl_2$) crystallizes (as hydrate) from concentrated HCl solutions with a minimum solubility near *ca.* 9 *M* HCl[16] indicates that $n \geqslant 2$ is probable for the acid range studied here. Hence, the monomer unit was assumed to have the stoichiometric composition $HfOCl_2$, *i.e.*, n = 2. Actually, for aqueous chloride systems the computation of $N_{z'}$ is not very sensitive to the assumed degree of hydrolysis. If, to cite an extreme example, the formula of the monomer unit were taken to be $Hf(OH)_3Cl$ or $Hf(OH)Cl_3$, then for $\rho = 1.05$ and $z' = 0$, N_z' would differ by less than $\pm 10\%$.

The partial molal volume $\bar{V}_{HfOCl_2}$ was obtained from the experimental value of $\bar{V}_{HfCl_4}$ in 1 *M* HCl–1 *M* NaCl solutions by the equation

$$\bar{V}_{HfOCl_2} = \bar{V}_{HfCl_4} - 2\bar{V}_{HCl} + \bar{V}_{H_2O} \qquad (19)$$

In the concentration range of interest $\bar{V}_{HfCl_4} = ca.$ 38 cc. was found. From this value and $\bar{V}_{HCl} = 19.9$ cc. (2 *M* HCl[17]) and the assumed $\bar{V}_{H_2O} = 18.0$ cc., $\bar{V}_{HfOCl_2} = 16.2$ cc. was computed. This corresponds to $\bar{v}_{HfOCl_2} = 0.06$ cc./g. which was used for all conditions of temperature, pressure and composition. The error which this simplification causes should be small, since $(1 - \bar{v}\rho)$ here is insensitive to $\bar{v}$. The partial specific volume of component $2(\bar{v}_2)$ was computed from $\bar{V}_{HfOCl_2}$ with equation 6 (or its analog for four-component systems) and the values of $\bar{V}_{BX}$ given in the literature.[17]

3. Centrifugation Conditions.—Equilibrium ultracentrifugations were carried out as a function of Hf(IV) concentration (0.008 to 0.12 *M* initial concentration), as a function of concentration of supporting electrolyte (1 *M* HCl in comparison with 1 *M* HCl–1 *M* LiCl and 1 *M* HCl–1 *M* NaCl), and as a function of molecular weight of supporting electrolyte (1 *M* HCl–1 *M* CsCl in comparison with the other experiments). In addition, the acidity was varied from 0.5 to 2 *M* HCl, and the temperature from approximately 0 to 30°. The experimental conditions and results are summarized in Table I.

TABLE I

ULTRACENTRIFUGATION OF HAFNIUM(IV)

Expt.[a]	Medium	Initial molarity Hf(IV)	HCl	MCl	$\mathbf{S}_e'$	α_e'	Temp. (°C.)
1	HCl	0.050	2.0		0.0357	1.82	25.9
2	HCl–LiCl	.008	1.0	1.0	.0375	1.94	29.7
3	HCl–LiCl	.020	1.0	1.0	.0404	2.07	28.2
4a	HCl–LiCl	.020	1.0	1.0	.0395	2.02	26.4
4b					.0375	1.78	5.2
5a	HCl	.049	1.0		.0382	1.96	26.8
5b					.0391	1.83	1.4
6a	HCl	.050	1.0		.0383	1.96	26.4
6b					.0394	1.87	5.2
7[b]	HCl–NaCl	.048	1.0	1.0	.0517	1.88	32.2
8	HCl–CsCl	.050	1.0	1.0	.0328	1.71	32.8
9	HCl–LiCl	.119	1.0	1.0	.0335	1.73	29.7
10	HCl	.103	1.0		.0316	1.61	26.5
11	HCl–LiCl	.050	0.5	1.5	.0384	1.96	26.7

[a] Cell size 12 mm. for experiments 1, 3, 5, 7, 8, 10, 11 and 30 mm. for all others. Bar angles: 35° (experiments 2, 3), 45° (experiments 1, 5, 8, 10, 11), 55° (experiment 7), 60° (experiments 4, 6), 70° (experiment 9). [b] Hf(IV) introduced as $HfCl_4$. In all other experiments solutions of $HfOCl_2 \cdot 8H_2O$ were used. This experiment at *ca.* 27,700 r.p.m. All others at *ca.* 23,100 r.p.m.

To a first approximation, graphs of log Z^*/x *vs.* x^2 were linear (*i.e.*, $\mathbf{S}_e$ was essentially constant) for all experiments. This is shown in Fig. 1, a deviation plot of $(\log Z^*/x - \mathbf{S}_e' x^2)$ *vs.* x^2 where $\mathbf{S}_e' = \mathbf{S}_e/2.303$. The average value of the slope S_e' is given in the table, and, to permit comparison of experiments at different ω and T, values of $\alpha_e' = \alpha_e/2.303$ are also listed.

4. Applicability of Computational Procedure.—The procedure discussed in section 1 is based on an idealized system. It is necessary to consider whether or not the assumptions are expected to be adequate for the systems studied. With one exception, the experiments were carried out (see Table I) in light supporting electrolytes (HCl, HCl–LiCl and HCl–NaCl) for which at equilibrium the ionic strength changes relatively little across the cell. Neglect of variations of $\bar{v}$, $g_\pm$, ρ and $(\partial n/\partial c)$ thus seems reasonable. The assumption that z' is constant may be questioned, since experiments were carried out at different total chloride concentrations, in which differences in degree of complexing or in degree of binding of counter ions might be anticipated. However, it will appear (section 5) that such differences in z' are not supported by the results.

The computational procedure was derived for a monodisperse system. Considerable evidence will be presented that Hf(IV) may be essentially a monodisperse polymer under most of the conditions studied. However, the present technique, though making monodispersity probable, cannot establish this unambiguously and therefore it is desirable to see what modifications are necessary to apply the procedure to polydisperse systems. For such systems, equation 17, reference 4, may be written for the ith species

$$\mathrm{d}\ln(c_2)_\mathrm{i} = \frac{\mathrm{d}(c_2)_\mathrm{i}}{(c_2)_\mathrm{i}} = \frac{\mathrm{d}(w_2)_\mathrm{i}}{(w_2)_\mathrm{i}} = (M_2)_\mathrm{i}\, C_2\, \mathrm{d}(x^2) - z_\mathrm{i}\mathrm{d}\eta^\ddagger \qquad (20)$$

if $(\eta^\ddagger)^2$ is neglected in comparison with unity. In equation 20 $(w_2)_\mathrm{i}$ is the weight of species i in a

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[14] The hydroxyl number **n** has been defined as the average number of moles of hydroxide ions per mole of metal ion.

[15] K. A. Kraus, S. Y. Tyree, Jr., and R. W. Holmberg, Report ORNL-499 (1949), page 26.

[16] G. v. Hevesy, *Kgl. Danske Vidensk. Selsk. Math.fys. Medd.*, **6**, No. 7, 1 (1925).

[17] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, Ch. 8. When two supporting electrolytes are present, $\bar{V}$ of each electrolyte was computed as though it were present alone at the ionic strength of the solution.

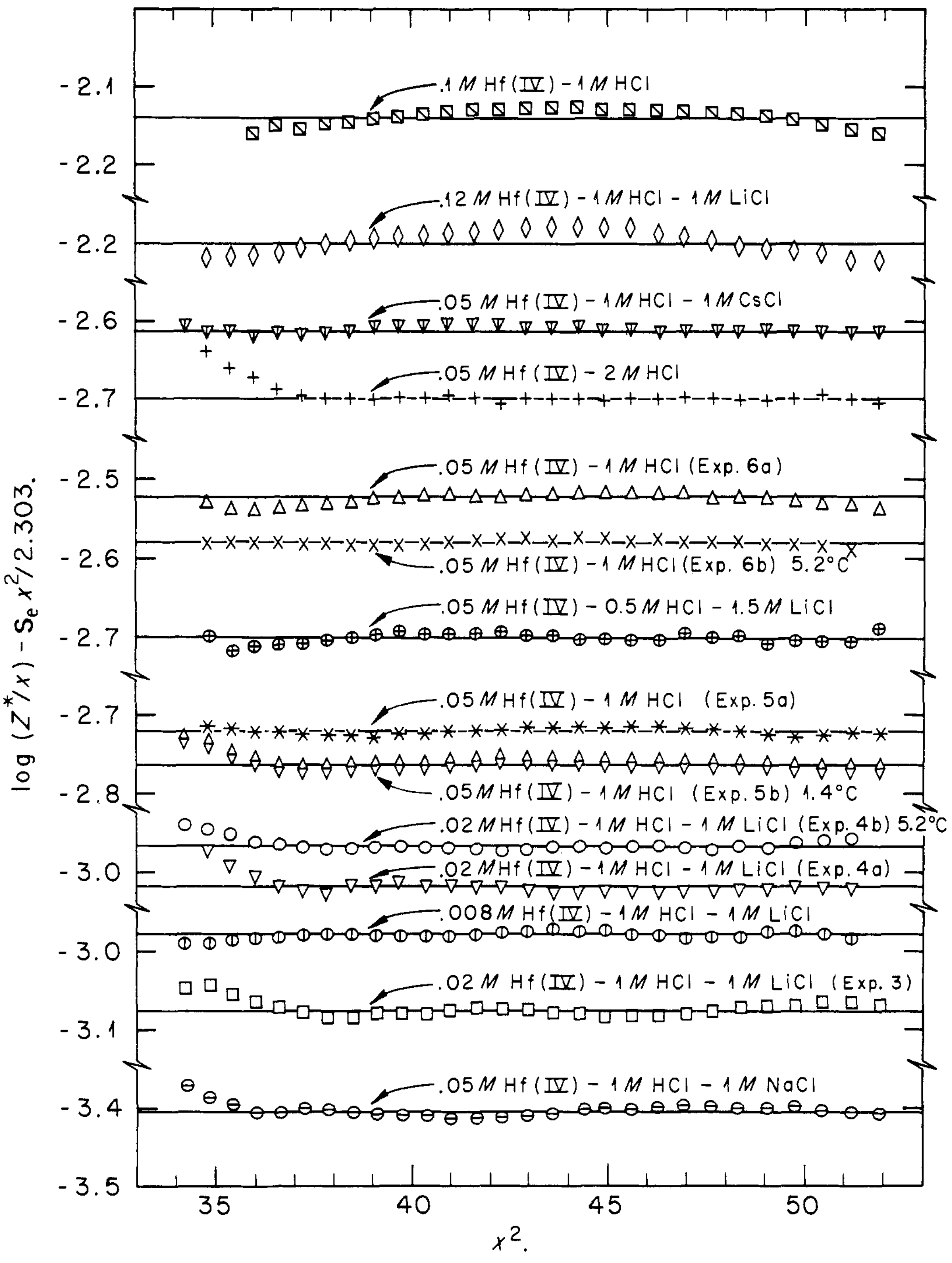

Fig. 1.—Test of constancy of S_e (all centrifugations near 30° unless otherwise noted).

given volume of solution, $C_2 = (A_2'/M_2')$, $\eta^{\ddagger} = \sum_i[(z)_i(c_2)_i]/2c_3$. It is assumed that the partial specific volumes, $(\bar{v}_2)_i$, and the gradients of refractive index, $(\partial n/\partial(w_2)_i)$, are independent of the degree of polymerization. Furthermore, if the charge per monomer unit is assumed independent of the degree of polymerization, $\sum_i(z)_i(c_2)_i$ becomes equal to $z'c_2'$ and $\eta^{\ddagger}$ reduces to $\eta = z'c_2'/2c_3$, where c_2' is the total polymer concentration expressed in terms of monomer; *i.e.*, η has the same meaning as in the monodisperse system. By summation of equations 20 for all species and division by $\sum_i(w_2)_i = w_2$, the equation

$$\frac{\sum_i d(w_2)_i}{\sum_i (w_2)_i} = \frac{d\sum_i (w_2)_i}{\sum_i (w_2)_i} = d \ln w_2 = d \ln c_2' =$$
$$\frac{\sum_i (M_2)_i(w_2)_i}{\sum_i (w_2)_i} C_2 d\,(x^2) - \left[\frac{z'c_2'}{2c_3}(d \ln c_2' - d \ln c_3)\right]\frac{\sum_i (z)_i(w_2)_i}{\sum_i (w_2)_i} \quad (21)$$

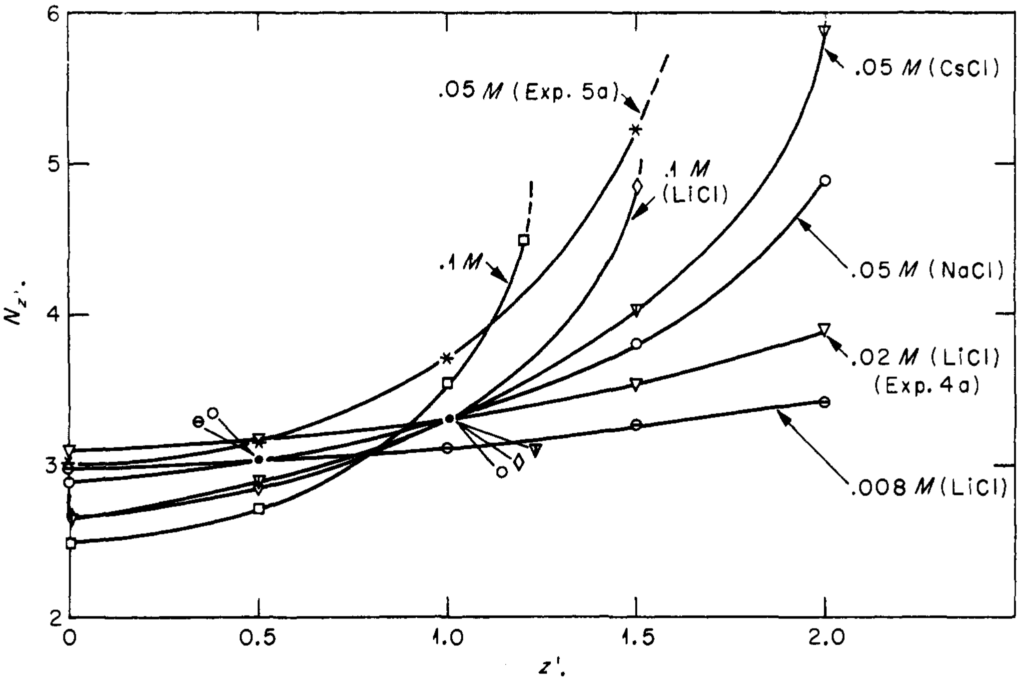

Fig. 2.—Effect of charge on computed degree of polymerization of Hf(IV); all solutions 1 *M* in HCl and at molarity of Hf(IV) indicated; additional supporting electrolyte, when present, at 1 *M*.

is obtained. Since $(z)_i/(M_2)_i = (z'/M_2')$ and since the weight average molecular weight is defined as $M_w = \dfrac{\sum_i (w_2)_i (M_2)_i}{\sum_i (w_2)_i}$, equation 21 becomes

$$S = (M_2)_w C_2 - \frac{(M_2)_w}{(M_2')} z' [\eta(S - \sigma)] \qquad (22)$$

The weight average degree of polymerization, $N_w = (M_2)_w/M_2'$, is given by the equation[18]

$$N_w = \frac{S/A_2'}{1 - z'\eta(S - \sigma)/A_2'} \qquad (23)$$

Equation 23 indicates that for a polydisperse solute, obeying the restrictions stated, solution of equation 1 at any value of x gives the weight average degree of polymerization at this value of x. If the molecular weight distribution of the solute is narrow, N_w may be essentially constant over the concentration range of a single experiment, *i.e.*, $\mathrm{d}\,N_w/\mathrm{d}(x^2) \cong 0$. In this case, equation 11 is essentially valid and the procedure of section 1, though derived for a monodisperse system, is applicable. Since the various observed values of $\mathbf{S}_e$ are as a first approximation independent of x^2 (Fig. 1), it appears that for most of the centrifugations reported here, N_w is essentially independent of x^2, and the results were therefore treated as described in section 1.

5. Degree of Polymerization.—The results of those experiments which had as their primary objective estimation of N (or of N_w), *i.e.*, those which were carried out in 1 *M* HCl solutions near 30°, are summarized in Fig. 2 as a plot of $N_{z'}$ *vs.* z'.[19] The computations were carried out with the values of α_e' $(= \alpha_e/2.303)$ listed in Table I, which are for the average radii, and with values of η computed from the initial concentrations c_2', c_3 and c_5.[20] The HCl–LiCl and HCl–NaCl systems were treated by the three-component equations (1 and 11), since in these cases A_3 and A_5 were small enough and close enough together so that use of an average of these values introduces little error. The sum of c_3 and c_5 was used in place of c_3. However, comparable accuracy in the HCl–CsCl case requires use of four-component equations and estimates of the terms involving c_3 and c_5. Arguments similar to those used for three-component systems[4,12] indicate that the distribution of components 3 and 5 is but little affected by the presence of the polymer and values of these distributions computed from A_3 and A_5 were therefore used to evaluate σ_3, σ_5, σ^* and $\mathrm{d}\ln A_2'/\mathrm{d}(x^2)$.

The curves of N_z' *vs.* z' of Fig. 2 approach close to each other near $z' = 1$, and the value of N indicated is *ca.* 3.2. Although the scatter of the experiments prevents exact assignment, particularly of z', the sharp divergence at large values of z' makes it improbable that the polymer is highly charged.

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[18] For ideal uncharged polydisperse systems, the slope of a plot of log Z^*/x *vs.* x^2 divided by A' gives the Z average degree of polymerization, N_Z, of the solution in the cell at the radius for which the slope is determined (W. D. Lansing and E. O. Kraemer, THIS JOURNAL, **57**, 1369 (1935)). The quantity N_Z is the Z average molecular weight $M_Z = \Sigma w_i M_i^2/\Sigma w_i M_i$ divided by the weight of the monomer. An expression for N_Z for charged polydisperse systems can be derived in a manner similar to equation 23, with the same assumptions. The equation is

$$N_Z = \frac{\dfrac{\mathbf{S}_e}{A'} - \dfrac{\mathrm{d}\ln[1 - z'\eta(S - \sigma)/A_2']}{A_2'\,\mathrm{d}(x^2)}}{1 - \dfrac{z'\eta(S - \sigma)}{A_2'}}$$

[19] Of the duplicate experiments, 3 and 4a, only the latter is given in Fig. 2, since it was carried out in a 30 mm. cell and is therefore presumably more accurate. The duplicates 5a and 6a gave essentially the same result.

[20] The uncertainty in the assignment of the average value S_e to the initial concentrations introduces a small error, which may become significant at large values of y.

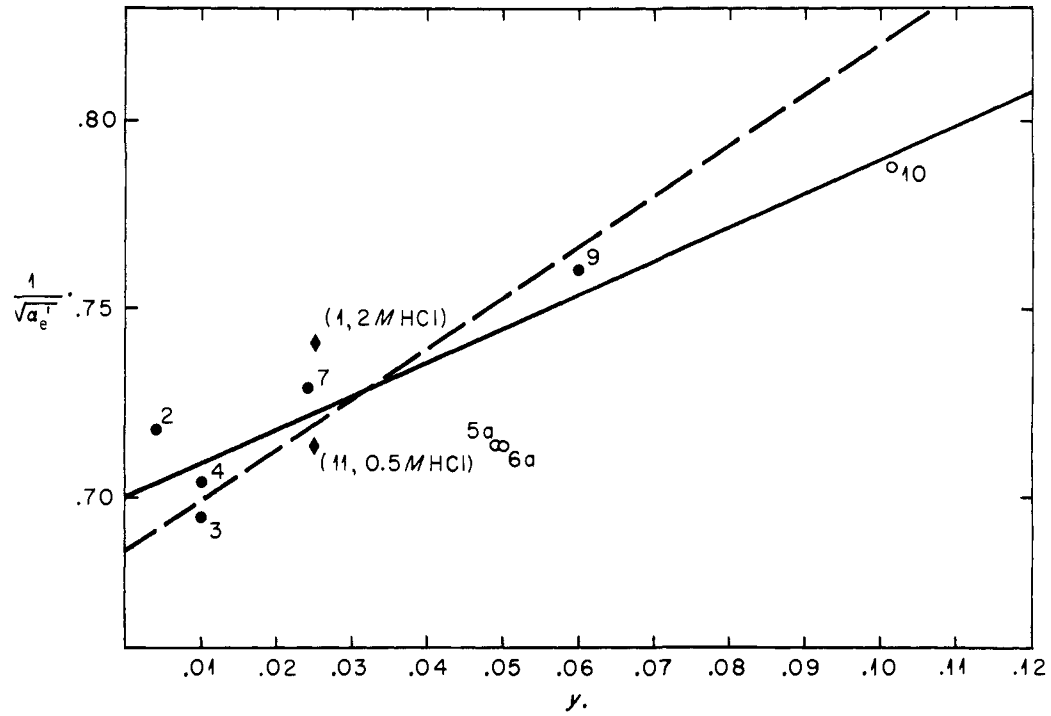

Fig. 3.—Test of coherence of experiments (eq. 18a): circles = 1 *M* in HCl, numbers refer to Table I; ●, 2 *M* chloride; ○, 1 *M* chloride.

Similar conclusions can be drawn from the plot (Fig. 3) of $1/\sqrt{\alpha_e'}$ *vs.* y (equation 18a). For this plot minor variations of L_2' between centrifugations in the presence of HCl, HCl–LiCl and HCl–NaCl are neglected. Experiment 8 (HCl–CsCl) is not included in Fig. 3, since variation in L_2' is too great to be disregarded here. The best straight line which can be drawn through the points of Fig. 3 (solid line) has a slope $Nk/\sqrt{\alpha_{e0}'} = 0.89$ and intercept $1/\sqrt{\alpha_{e0}'} = 0.70$. From these the values $N = 3.2$ and $z' = 0.9$ are computed. The scatter of the points around this straight line is large, and the values of $1/\sqrt{\alpha_e'}$ for experiments 3 and 5 are especially far off the line. These experiments were repeated (experiments 4 and 6). The reproducibility suggests that the scatter of the data does not stem entirely from lack of experimental precision. In particular, experiments 5a and 6a in 1 *M* HCl appear to have significantly low values of $1/\sqrt{\alpha_e'}$. This suggests that experiment 10, also in one molar chloride, should fall below the line defined by the experiments in 2 *M* chloride. The dotted line of Fig. 3 is drawn on this basis, and $N = 3.4$ and $z' = 1.1$ are computed from its slope and intercept. The value of $1/\sqrt{\alpha_e'}$ for experiment 2 appears significantly above the dotted line, or, in this most dilute solution (0.008 *M* Hf(IV)), some depolymerization may have occurred. In any case, these values of N and z' do not differ greatly from those obtained from the solid line of this figure, and both are in reasonable agreement with the estimates made from Fig. 2.

The coherence of the experimental results over the 25-fold variation of y is striking. There appears to be no significant variation of α_e' in a direction suggesting concentration dependence of the degree of polymerization (decrease of $1/\sqrt{\alpha_e'}$ with increase of concentration). Instead, the slope of the plot $1/\sqrt{\alpha_e'}$ *vs.* y is positive as it should be when charge effects are predominant, and N (or N_w) is essentially independent of concentration.

From this coherence of the results one can conclude that Hf(IV) in the concentration range studied is probably predominantly monodisperse. The scatter of the points in Fig. 3, or the corresponding spread of the intersections of the curves in Fig. 2, and the non-integral values estimated for N, preclude an unambiguous conclusion. On the other hand, even in absence of experimental error, the observed scatter would not necessarily indicate polydispersity, since it is unlikely that the system under study adheres in detail to the rather stringent idealizations made in the derivation of the equations. Thus the assumption of constancy of z' between experiments at different chloride concentrations is questionable. However, a comparison of the values of α_e' between experiments 5a and 7 shows that a change in complexing cannot be an overriding effect. The higher value of α_e' in 5a is in the direction opposite to that expected if the polymer were less complexed at the lower concentration of chloride. Changes of the activity coefficients of the species are difficult to predict, but obviously variations could cause intersections at non-integral values of N and at different values of N between pairs of experiments. In the present state of knowledge of such factors as the effect of pressure on partial volumes and refractive indices of polymeric species, further speculation on sources of discrepancy is probably fruitless.

Additional evidence for the existence of preferred polymeric species of Hf(IV) comes from the experiments on the effects of acidity and temperature on α_e'. In 2 M total chloride and at 0.05 M Hf(IV), values of 1.96, 1.88 and 1.82 were obtained for α_e' in 0.5, 1.0 and 2.0 M HCl solutions (experiments 11, 7 and 1). The downward trend of α_e' probably indicates some decrease in the degree of polymerization with increasing acidity, but no strong acid dependence is evident. In contrast, outside of this range of acidity, solutions become obviously polydisperse, and the α_e' values change rapidly with acidity.[21]

Unless the heat of polymerization is near zero, a change of temperature should give a pronounced change in degree of polymerization for a polydisperse system. No major change is observed (experiments 4, 5 and 6, Table I), though α_e' is apparently significantly lower in all cases at the lower temperatures. Much sharper changes are noted at lower acidities where the system is obviously polydisperse.[21]

To summarize, the conclusion is drawn from the equilibrium ultracentrifugations that Hf(IV) under the conditions studied forms small polymers with a degree of polymerization approximately 3. Further, complexing of this polymer by chloride ions occurs. The polymeric species of Hf(IV) are probably held together by hydroxide or oxide bridges which have been postulated earlier for similar hydrolytic polymers of other elements on the basis of structural data of basic salts.[22] Existence of preferred species suggests a special structure for these species, *e.g.*, a closed ring structure.

Recently, data on the hydrolytic polymerization of certain inorganic solutes have been interpreted by Sillén and others with a hypothesis of continuous polymerization.[3b,22–24] Briefly, this hypothesis implies that, at least after the earliest stage of polymerization, the free energy change of adding another monomer to the polymer is independent of N or changes in a regular manner with N. There would therefore be no preferred species of special stability after the beginning of hydrolytic polymerization. Such an interpretation frequently gives a highly polydisperse system, with degree of polymerization strongly concentration and acid dependent. It can be concluded that continuous polymerization does not occur in the Hf(IV) system at the acidities studied and that species of special stability occur. Similar preferred species were found by ultracentrifugation for Zr(IV)[3d] and recently also for Bi(III).[25] In the latter case, equilibrium ultracentrifugations suggest predominance of a low molecular weight polymer (N = *ca.* 5 or 6) under conditions where computations based on a continuous polymerization hypothesis indicate a highly polydisperse system with N_w considerably larger than 40.[22a,23c] On the other hand, equilibrium ultracentrifugations of Th(IV)[25] did not indicate preferred stability for any one species, and the degrees of polymerization found by ultracentrifugation are in reasonable agreement with those computed from *p*H data by a continuous polymerization hypothesis.[23d] However, the possible occurrence of preferred polymeric species in solution makes interpretation based on an otherwise unsupported hypothesis of continuous polymerization a doubtful procedure.

Acknowledgment.—The authors are greatly indebted to Professor George Scatchard for a number of valuable discussions and suggestions.

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[21] J. S. Johnson and K. A. Kraus, Abstracts 126th ACS Meeting, New York, September, 1954, page 60R.

[22] See *e.g.*, (a) F. Granér and L. G. Sillén, *Acta Chem. Scand.*, **1**, 631 (1947); (b) G. Lundgren and L. G. Sillén, *Arkiv. Kemi.*, **1**, 277 (1950); (c) G. Lundgren, *ibid.*, **2**, 535 (1951); **4**, 421 (1953); (d) K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).

[23] (a) L. G. Sillén, *Acta Chem. Scand.*, **8**, 299 (1954); (b) **8**, 318 (1954); (c) S. Hietanen and L. G. Sillén, *ibid.*, **8**, 1607 (1954); (d) S. Hietanen, *ibid.*, **8**, 1626 (1954); (e) S. Ahrland, S. Hietanen and L. G. Sillén, *ibid.*, **8**, 1907 (1954).

[24] R. Ginell, *Trans. N. Y. Acad. Sci.*, [II], **16**, 142 (1954).

[25] K. A. Kraus, R. W. Holmberg and J. S. Johnson (unpublished results).