TABLE VII

SUMMARY OF RESULTS FOR SODIUM VANADATE WITH SODIUM PHOSPHATE PRESENT

$\dfrac{H_2PO_4^-}{NaVO_3}$	$\dfrac{H^+}{NaVO_3} = 0.5$		$\dfrac{H^+}{NaVO_3} = 0.6$		$\dfrac{H^+}{NaVO_3} = 0.7$	
	$(\Delta T/C)_{exptl}$	$(\Delta T/C)_{apparent}$	$(\Delta T/C)_{exptl}$	$(\Delta T/C)_{apparent}$	$(\Delta T/C)_{exptl}$	$(\Delta T/C)_{apparent}$
0	0.34	0.34	0.50	0.50	0.75	0.75
0.1	0.64	0.32	0.72	0.40	0.72	0.40
0.2	0.96	0.32	1.07	0.43	0.88	0.24
0.3	1.30	0.34	1.23	0.27	1.06	0.10

summarized in Table VII. Presented are the experimental $(\Delta T/C)$ values, *i.e.*, the change in transition temperature with vanadium ions, and the $(\Delta T/C)_{apparent}$ values due to the vanadium and acid after the contribution to be expected for $H_2PO_4^-$ (*i.e.*, $H_2PO_4^-/NaVO_3 \times 3.20$) was subtracted. This is, of course, only a convenient way of looking at deviations from a simple additivity of $(\Delta T/C)$ values.

At an $H^+/NaVO_3$ ratio of 0.5, $(\Delta T/C)_{apparent}$ was the same with and without $H_2PO_4^-$. At an $H^+/NaVO_3$ of 0.6, although there was some inconsistency, $(\Delta T/C)_{apparent}$ was less when $H_2PO_4^-$ was present than when it was not. Again, at $0.7H^+/NaVO_3$, $(\Delta T/C)_{apparent}$ was lowered by the presence of phosphate, and this time the lowering progressed in a regular manner with phosphate concentration. The two

important trends which can be seen from this behavior are: (1) At an $H^+/NaVO_3$ of 0.7, $(\Delta T/C)_{apparent}$ decreased as $H_2PO_4^-/NaVO_3$ increased, and this general trend occurred at $0.6H^+/NaVO_3$ also. The $(\Delta T/C)_{apparent}$ values were too low to be accounted for on the basis of a protonation of $H_2PO_4^-$. The results can best be explained by the formation of a heteropolyanion between vanadium and phosphate. (2) At an $H^+/NaVO_3$ of 0.5, the vanadium and phosphate simply act additively on transition temperature depression, therefore no interaction takes place between the polyvanadate and phosphate. It seems reasonable to propose, therefore, that only the polyvanadate species that predominates at the higher $H^+/NaVO_3$ ratios, $H_2V_{10}O_{28}^{-4}$, forms the complex with $H_2PO_4^-$.

A Computer Analysis of Static and Dynamic Models of the Hafnium Fluoride Complexes Extracted by Tri-*n*-octylphosphine Oxide

BY LOUIS P. VARGA AND DAVID N. HUME

Distribution measurements at 25° between fluoride-containing trace hafnium solutions in 3 M perchloric acid and 0.01 and 0.05 M tri-*n*-octylphosphine oxide (TOPO) in cyclohexane were interpreted in terms of both static and dynamic models of the hafnium-containing TOPO adducts extracted into the organic phase. The static model which best fits the experimental data assumed the extraction of four species: $Hf(ClO_4)_4 \cdot TOPO$, $Hf(ClO_4)_4 \cdot 2TOPO$, $HfF_2(ClO_4)_2 \cdot TOPO$, and $HfF_2(ClO_4)_2 \cdot 2TOPO$. The dynamic model assumed a labile solvate equilibrium between the hafnium species and TOPO to give average compositions for two extracting species of $Hf(ClO_4)_4 \cdot 1.5TOPO$ and $HfF_2(ClO_4)_2 \cdot 1.5TOPO$. This model concedes the inability and lack of necessity of the equilibrium measurements to distinguish between labile solvate species and treats data in a practical fashion by assuming only the two extractable species. This was the most satisfactory model both from the standpoint of the number of parameters required to explain the data and the goodness of fit. The distribution coefficients for all assumed species were determined and these were used to calculate the over-all formation constants of the hafnium fluoride system.

The solvent extraction behavior of organophosphorus compounds toward a variety of metal species has been described by several workers[1] and in a recent solvent extraction symposium[2] several studies on extrac-

tion mechanisms and the extractable metal species were reported. In the case of the monoacidic phosphates and phosphonates nonintegral extractant dependencies have been noted[3] in the extraction of Ca(II) but discrete extracting species were nevertheless postulated. Burger[4] described the mechanism of extraction for metals using neutral organophosphorus compounds, such as the phosphine oxides, as solvation for metal salts, and this mechanism was assumed in this paper.

(1) (a) C. A. Blake, K. B. Brown, and C. F. Coleman, U. S. Atomic Energy Commission ORNL-1964, Nov. 17, 1955; (b) L. L. Burger, *J. Phys. Chem.*, **62**, 590 (1958); (c) J. P. Young and J. C. White, *Anal. Chem.*, **31**, 393 (1959); (d) W. J. Ross and J. C. White, *ibid.*, **31**, 1847 (1959); (e) W. J. Maeck, G. L. Booman, M. C. Elliott, and J. E. Rein, *ibid.*, **32**, 922 (1960); (f) J. C. White and W. J. Ross, "Separations by Solvent Extraction with Tri-*n*-octylphosphine Oxide," U. S. Atomic Energy Commission, NAS-NS 3102, February 8, 1961.

(2) Solvent Extraction Chemistry Symposium, U. S. Atomic Energy Commission, Gatlinburg, Tenn., Oct. 23–26, 1962.

(3) D. F. Peppard and G. W. Mason, ref. 2, paper No. 1.

(4) L. L. Burger, ref. 2, paper No. 8.

$-\log$ (HF)	$-\log$ (F$^-$)	ϕ (TOPO = 0.01 M)	ϕ (TOPO = 0.05 M)
∞	∞	8.00	82.4
5.25	9.00	8.15	68.6, 74.8, 86.8
4.95	8.70	7.96	83.4
4.55	8.30	. . .	49.5
4.25	8.00	3.03	40.8
3.95	7.70	4.36	31.9
3.55	7.30	2.55	38.0
3.25	7.00	2.34	32.2
2.95	6.70	2.40	32.6
2.55	6.30	1.88	25.3, 27.7
2.25	6.00	1.13	15.8, 19.0
1.95	5.70	0.594	9.61
1.55	5.30	. . .	2.17, 2.47
1.25	5.00	. . .	0.626, 0.629, 0.623
0.086	3.95	. . .	9.5×10^{-4}, 1.12×10^{-3}, 1.08×10^{-3}

It is shown in this paper that thermodynamic equilibrium studies can be interpreted equally well on the basis of nonintegral solvate numbers and on the basis of discrete species with fixed numbers of coordinated solvent.
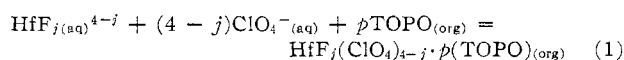
Experimental

The hafnium-181 perchlorate solution was the same as that used in earlier extraction studies[5] with thenoyltrifluoroacetone. Solutions of hydrofluoric acid in 3 M perchloric acid were prepared from stock solutions of reagent grade acids standardized against sodium hydroxide. The relation between fluoride ion concentration and hydrofluoric acid concentration in 3 M perchloric acid was as described previously.[5] The various fluoride concentrations are listed in Table I. Eastman Kodak White Label tri-n-octylphosphine oxide (TOPO) was weighed directly to make solutions 0.05 and 0.01 M in Baker reagent grade cyclohexane.

Five-ml. portions of the various fluoride solutions in 3 M perchloric acid were pipetted into 50-ml. Lusteroid test tubes which were fitted with polyethylene stoppers, 5 or 10 μl. of Hf-181 solution and 5 ml. of the organic phase were added, and the mixtures were equilibrated in a water bath shaker at 25 ± 0.2° for a minimum of 4 hr. After equilibration the tubes were centrifuged and samples ranging from 0.01 to 3 ml. were pipetted into plastic vials containing volumes of solvent such that the final volumes of the counting samples were equal for both phases. γ-Scintillation counting was accomplished with the equipment described previously.[5] The observed distribution ratios, ϕ, the ratio of the specific activities of hafnium in the organic and aqueous phases at the various fluoride and TOPO concentrations, are listed in Table I.

Least Squares Curve-Fitting of Various Models.
—The hafnium fluoride–TOPO partition reaction in perchlorate solutions may be written

$$HfF_{j(aq)}{}^{4-j} + (4 - j)ClO_4{}^-{}_{(aq)} + pTOPO_{(org)} = HfF_j(ClO_4)_{4-j} \cdot p(TOPO)_{(org)} \quad (1)$$

with

$$K'_{jp} = \frac{(HfF_j(ClO_4)_{4-j} \cdot p(TOPO))_{org}}{(HfF_j)(ClO_4{}^-)^{4-i}(TOPO)^p} \quad (2)$$

(5) L. P. Varga and D. N. Hume, *Inorg. Chem.*, **2**, 201 (1963).

where j may be assumed to have one or more integral values from 0 to 4. Possible values of p ranged from ≥ 1 to some maximum solvation number, but, as shall be shown, need not be integral. The distribution ratio, ϕ, becomes then

$$\phi = \frac{\displaystyle\sum_0^J \sum_1^P (HfF_j(ClO_4)_{4-j} \cdot p(TOPO)_{org}}{\displaystyle\sum_0^N (HfF_n)_{(aq)}} \quad (3)$$

or

$$\phi = \frac{\displaystyle\sum_0^J \sum_1^P K'_{ip}\beta_j(HF)^j(ClO_4)^{4-i}(TOPO)^p}{\displaystyle\sum_0^N \frac{\beta_n}{(H^+)^n}(HF)^n} \quad (4)$$

in terms of the equilibrium constants for extraction and the over-all aqueous formation constants of the hafnium fluoride system. At the trace hafnium concentrations and high acidity, hydrolytic and polynuclear species were presumed to be absent.

Fluoride Ligand Numbers of the Extractable Species.—To determine the fluoride ligand numbers of the extractable hafnium complexes, the simplifying assumption was tentatively made that p would have the same average value for all values of j. Equation 4 may be written

$$\frac{\phi}{(TOPO)^p} = \frac{\displaystyle\sum_0^J K_{jp}(HF)^j}{\displaystyle\sum_0^N \frac{\beta_n}{(H^+)^n}(HF)^n} \quad (5)$$

where $K_{jp} = K'_{jp}\beta_j(ClO_4{}^-)^{4-j}$ at the high constant perchlorate concentration. Equation 5 shows that at constant acidity $\phi/(TOPO)^p$ is a function of (HF) only. The dependence of the distribution ratio on the concentration of TOPO in the organic phase was determined by plotting log $[\phi/(TOPO)^p]$ *vs.* log (HF) at various values of p between 1 and 4 for all corresponding experimental values of ϕ and (TOPO). When p was assigned the value $^3/_2$, the best smooth curve could be drawn through the data points. The data in Table I have been normalized and plotted in Fig. 1.

Having a usable value of p, eq. 5 could be solved directly by cumbersome nonlinear regression machine calculations, but in the case of the hafnium fluoride system in 3 M perchlorate the over-all formation constants, β_n, have been determined from potentiometric and TTA solvent extraction data[5] so that

$$\sum_{n=0}^6 \frac{\beta_n}{(H^+)^n}(HF)^n = FN$$

was evaluated independently and the model for the determination of the extractable hafnium fluoride species became

$$Y = \frac{\phi FN}{(TOPO)^{3/2}} = \sum_0^J K_{jp}(HF)^j \quad (6)$$

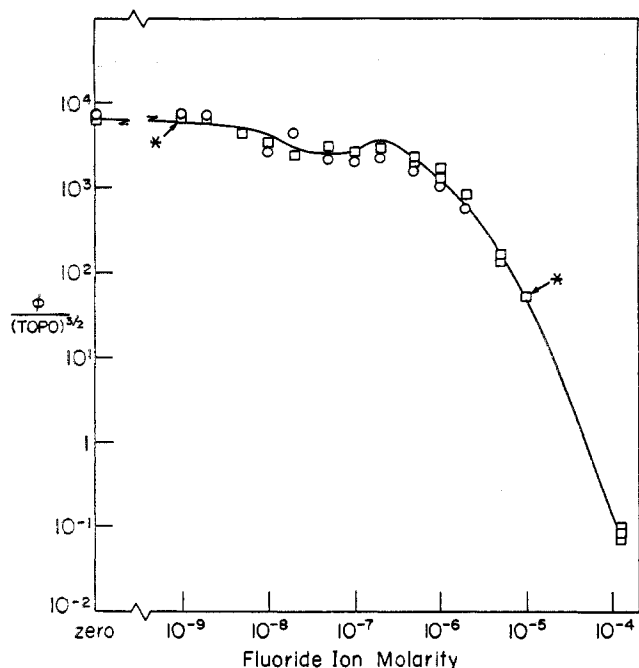Equation 6 is a polynomial linear in the coefficients, and 27 data points ((HF), Y) with variable TOPO

Fig. 1.—Normalized distribution ratio, $\phi/(\text{TOPO})_0^{3/2}$, of hafnium between $3.0\ M$ HClO$_4$ and tri-*n*-octylphosphine oxide in cyclohexane as a function of fluoride ion concentration at 25°. The curve was calculated from the constants of Table II. Starred values represent three superimposed points: $\odot$, 0.01 M TOPO in cyclohexane; $\square$, 0.05 M TOPO in cyclohexane.

concentrations were tested by least-squares curve fitting methods using an IBM 650. The machine program written by Pulley[6] and similar to the one described by Sullivan and associates[7] allowed the use of weighted data, $W_y = 1/\sigma_y{}^2$, where $\sigma_y{}^2$ is the variance of Y estimated from experimental considerations. The quantity minimized was

$$S = \Sigma_i W_i (Y_i - \bar{Y}_i)^2 \qquad (7)$$

where $\bar{Y}_i$ was the machine calculated Y for the ith data point. Since an internal estimate of the over-all variance is $\Sigma(Y - \bar{Y})^2/(k - 1)$, where k is the number of degrees of freedom of the system, the quantity $S_{\min}/(k - 1)$ has a value near unity when the mathematical model and external estimates of weights are consistent with the data. It is used throughout this paper as a measure of the over-all goodness of fit. An estimate of the variances of the calculated parameters was obtained from the product of $S_{\min}/(k - 1)$ and the corresponding main diagonal element of the inverse matrix.[7]

Inspection of the slope of the normalized distribution curve, Fig. 1, showed that hafnium species containing zero fluoride and at least one fluoride-containing species were extracted by TOPO in the fluoride concentration range studied. On the first iteration, all values of J were assumed from 0 to 4. The weights, $W_y = 1/\sigma_y{}^2$, were calculated from error propagation theory, assuming a 15% error in ϕ and using directly the calculated variances of the β_n from ref. 5. No

(6) G. Pulley, Computer Center, Oklahoma State University, Stillwater, Okla.

(7) J. C. Sullivan, J. Rydberg, and W. F. Miller, *Acta Chem. Scand.*, **13**, 2023 (1959).

error was assumed in the stoichiometric concentrations of TOPO and HF. Thus from

$$\sigma_y{}^2 = \left(\frac{\partial Y}{\partial \phi}\right)^2 \sigma_\phi{}^2 + \sum_{n=1}^{6} \left(\frac{\partial Y}{\partial \beta_n}\right)^2 \sigma_{\beta_n}{}^2 \qquad (8)$$

$$\sigma_y{}^2 = (0.15 Y)^2 + \left(\frac{\phi}{(\text{TOPO})^{3/2}}\right)^2 \sum_{n=1}^{6} \sigma_{\beta_n}{}^2 (\text{HF})^{2n} \qquad (9)$$

the corresponding weights were calculated and used in the machine program.

In the first iteration the values of $K_{3,3/2}$ and $K_{4,3/2}$ were within one standard deviation of zero, and these parameters were therefore omitted on the next iteration. $K_{1,3/2}$ was similarly eliminated on the second iteration, and a third iteration gave the values $K_{0,3/2} = (8.24 \pm 0.39) \times 10^3$ and $K_{2,3/2} = (2.49 \pm 0.18) \times 10^{11}$ with $S_{\min}/(k - 1) = 1.08$. These results were sufficient statistical evidence that hafnium species containing 0 and 2 fluoride ligands per hafnium and only those species were simultaneously extracted into the cyclohexane phase by the TOPO extractant under the conditions used here. Furthermore, the excellent fit of the curve to the experimental data as shown by the value of 1.08 for $S_{\min}/(k - 1)$ justified the assumption that the average TOPO solvate number was $^3/_2$ for both extractable hafnium species. The average composition of the extractable species may be written Hf(ClO$_4$)$_4 \cdot 1.5$ (TOPO) and HfF$_2$(ClO$_4$)$_2 \cdot 1.5$(TOPO).

Integral (TOPO) Dependence.—The question as to whether integral values of the TOPO solvate number would explain the data as well as the nonintegral values was investigated for the most reasonable models. The assumption was made that the fluoride ligand numbers of the hafnium species extractable by TOPO remained fixed, and for each postulated set of extractable species, the corresponding expressions for ϕ and Y were derived and tested for correspondence to the experimental data. On the basis of the resulting $S_{\min}/(k - 1)$ values of 10.3 for the model assuming Hf(ClO$_4$)$_4 \cdot$ TOPO and HfF$_2$(ClO$_4$)$_2 \cdot$ 2TOPO extractable, 3.16 for the model assuming Hf(ClO$_4$)$_4 \cdot$ TOPO, Hf(ClO$_4$)$_4 \cdot$ 2TOPO, and HfF$_2$(ClO$_4$)$_2 \cdot$ TOPO extractable, and 1.47 for the model assuming Hf(ClO$_4$)$_4 \cdot$ TOPO, Hf(ClO$_4$)$_4 \cdot$ 2TOPO, and HfF$_2$(ClO$_4$)$_2 \cdot$ 2TOPO extractable, all of the above models were eliminated. The best fit was given by the model assuming four extractable species: Hf(ClO$_4$)$_4 \cdot$ TOPO, Hf(ClO$_4$)$_4 \cdot$ 2TOPO, HfF$_2$(ClO$_4$)$_2 \cdot$ TOPO, and HfF$_2$(ClO$_4$)$_2 \cdot$ 2TOPO. Here

$$\phi = \frac{K_{0,1}(\text{TOPO}) + K_{0,2}(\text{TOPO})^2 + K_{2,1}(\text{HF})^2 (\text{TOPO}) + K_{2,2}(\text{HF})^2(\text{TOPO})^2}{FN} \qquad (10)$$

and

$$Y = \frac{\dfrac{\phi FN}{(\text{TOPO})} - K_{0,1} - K_{0,2}(\text{TOPO})}{(\text{HF})^2} = K_{2,1} + K_{2,2}(\text{TOPO}) \qquad (11)$$

From Table I, two values of ϕ at (HF) equal to zero and (TOPO) equal to 0.01 and 0.05 M allowed calculation of $K_{0,1} = 5.88 \times 10^2$ and $K_{0,2} = 2.12 \times 10^4$.

In this model Y was a function of (TOPO) only and

Table II
The Effect of the Model on the Over-All Formation Constants and Goodness of Fit

	$\beta_n/(H^+)^n$		
n	$K_{0,1}, K_{0,2}, K_{2,2}$	$K_{0,1}, K_{0,2}, K_{2,1}, K_{2,2}$	$K_{0,3/2}, K_{2,3/2}$
0 (fixed)	1.0	1.0	1.0
1	$(1.35 \pm 0.38) \times 10^4$	$(1.29 \pm 0.27) \times 10^4$	$(1.45 \pm 0.28) \times 10^4$
2	$(5.27 \pm 1.34) \times 10^7$	$(6.59 \pm 1.16) \times 10^7$	$(6.17 \pm 1.10) \times 10^7$
3	$(7.83 \pm 4.92) \times 10^9$	$(1.29 \pm 0.42) \times 10^{10}$	$(1.26 \pm 0.38) \times 10^{10}$
4	$(1.57 \pm 0.26) \times 10^{12}$	$(1.28 \pm 0.18) \times 10^{12}$	$(1.10 \pm 0.16) \times 10^{12}$
6	$(5.23 \pm 1.07) \times 10^{12}$	$(4.73 \pm 0.73) \times 10^{12}$	$(4.21 \pm 0.62) \times 10^{12}$
$S_{min}/(k-1)$	1.73	0.73	1.03

the data points at (HF) = 0 were omitted. Also Y was negative at two points and these were also omitted, leaving 23 data points for the calculation. As in the calculation of $K_{0,3/2}$, the error in ϕ (and in $K_{0,1}$ and $K_{0,2}$) was taken as 15% and the weights were calculated from the theory of propagation of errors as before, with the result that $K_{0,1} = (5.88 \pm 0.88) \times 10^2$; $K_{0,2} = (2.12 \pm 0.32) \times 10^4$; $K_{2,1} = (1.23 \pm 0.34) \times 10^{10}$; $K_{2,2} = (1.02 \pm 0.16) \times 10^{12}$; $S_{min}/(k-1) = 1.11$.

The choice between the two-parameter dynamic model with nonintegral TOPO dependence and the four-parameter static model with integral TOPO dependence could not be made on comparison of their respective values of $S_{min}/(k-1)$, 1.08 and 1.11 calculated above. Both fits must be considered good. There is, of course, only one physical phenomenon, although there are two mathematical models which give good fits. Based on the explicitly stated rule in statistical inference that that model which explains the experimental data with the fewest number of parameters is the best model, the two-parameter conception of the extraction process is considered preferable. This suggests a labile equilibrium between TOPO solvate molecules and free TOPO in the organic phase, in which the average solvate numbers are not necessarily integral. A similar situation has appeared in the tantalum fluoride–TOPO system, where the TOPO dependence was found to increase gradually from 1 to 1.75 over a portion of the fluoride concentration range studied.[8]

Calculation of Over-all Formation Constants.—A further test of the two models was made by using the parameters above to recalculate the over-all aqueous formation constants of the hafnium fluoride system. Only 27 data points at variable (TOPO) were used to evaluate the K values while 35 points were observed; the other eight points at high fluoride concentrations used 0.05 M TOPO only in the cyclohexane phase. This test was useful since the quantity

$$\sum_{n=0}^{6} \frac{\beta_n}{(H^+)^n} (HF)^n$$

used to calculate the K values was evaluated only at the lower 27 fluoride concentrations using the β values from ref. 5 while a recalculation of the β values would test the fit over the entire fluoride concentration range studied in the TOPO experiments. The mathematical

model is obtained on rearranging the general eq. 5, which in the case of the dynamic model was

$$Y = \frac{(TOPO)^{3/2}[K_{0,3/2} + K_{2,3/2}(HF)^2]}{\phi} = \sum_{0}^{N} \frac{\beta_n}{(H^+)^n}(HF)^n \quad (12)$$

For estimates of the weights, the error in ϕ was taken as 15% while the errors in the K values were those calculated above. The results of the three most promising calculations are given in Table II. The values are for 3.0 M perchloric acid medium at 25°.

Inspection of the $S_{min}/(k-1)$ values indicated a considerably better fit in the case of the nonintegral model than the best two other models tried. These results suggested, further, a preference for the two-parameter dynamic model since by several criteria this model best interpreted the experimental data. The TOPO extraction data could not be forced to yield all six formation constants. A fit to the first five constants could be made but this was not consistent with the previous results.[5] As Table II shows, omitting β_5 gave a very satisfactory fit, which meant that if the species HfF_5^- existed, these experiments simply were not sensitive to its presence. Comparison of the formation constants with those calculated from previous potentiometric and TTA extraction data[5] indicated satisfactory agreement except in the case of β_6. This was not surprising considering that data points from ref. 5 sensitive to the presence of HfF_6^{-2} were entirely from potentiometric measurements. Inspection of the normalized TOPO data points in Fig. 1 at (F$^-$) = 10^{-4} M suggests the extreme sensitivity of the calculated results on the slope in this rapidly changing portion of the curve from which the calculation of β_6 in this paper was highly dependent. The satisfactory over-all agreement of the β values calculated on the assumption of nonintegral TOPO solvation coefficients with the β values derived from the TTA data is further evidence for the validity of using nonintegral solvation number models.

(8) L. S. Nicolson and L. P. Varga, Southwest Regional Meeting, American Chemical Society, Dallas, Texas, Dec. 6-8, 1962.