to bond orbitals of neutral titanium and neutral vanadium, respectively.

In Table II there are given the final calculated values for the boron single-bond radius for each of the compounds, as well as the assumed valences of each atom and the calculated bond numbers. The average value for the single-bond radius of boron is 0.767 Å., with an average deviation of 0.011 Å.

ADDED IN PROOF.—Russell, *et al.*,[11] have just published a short report of their investigations on the magnesium–boron system. Their results are in essentially exact agreement with ours. The values which they report for lattice parameters of MgB_2 are $a_0 = 3.084 \pm 0.001$ Å., $c_0 = 3.522 \pm 0.002$ Å.; in addition, they find evidence for three other crystalline phases, one apparently being MgB_4. These other phases doubtless correspond to the unidentified impurity in our preparations.

The single-bond radius of boron might be expected to vary inversely with the valence of boron, as is observed for other atoms. Indeed, if a least-squares line is passed through the nine points representing a plot of single-bond radius of boron against v_B, this line may be expressed in the form $R_1(B) = A + C(3 - v_B)$; best values of A and C are 0.767 and 0.004, with the coefficient C being positive as predicted. However, the calculated standard deviation in C, 0.016, is so large as to make even the sign of C unreliable.

It should be pointed out that the calculated single-bond radius for boron in each compound is dependent upon the single-bond radius chosen for the other atom, which in turn is very sensitive to the amount of p- or d-character assigned to the bond orbitals. Furthermore, there is little valid reason to suppose that the d-character of bond orbitals of charged atoms can be accurately determined by simple interpolation. Thus, the compounds NbB_2 and TaB_2, which give evidence of little electron transfer, yield single-bond radii for boron very close to the average value 0.77 Å.; the compounds with an appreciable amount of electron transfer, which necessitates an interpolation of p- or d-character, show larger discrepancies.

The observed pattern of electron transfer is in agreement with Pauling's theory[12] in that boron, although a hypoelectronic atom, tends to transfer electrons to the less electronegative and likewise hypoelectronic atoms magnesium and aluminum. The tendency for boron to donate electrons decreases as the hypoelectronic character of the other atom decreases (and its electronegativity increases), until the buffer atom chromium, with an electronegativity approximately equal to that of boron, is able to transfer a relatively large amount of charge to boron.

The derived value for the single-bond radius of boron, 0.77 Å., is somewhat smaller than the value 0.80 Å. reported by Hedberg[9] for boron hydrides and related compounds. This discrepancy is probably to be expected in view of the great dissimilarity in the types of structures involved. In particular, the AlB_2 structure, with well-defined layers and consequent anisotropy of bonding, would be open to strain and deformation of bonds; perhaps more important is the high coördination of boron (9-fold) compared to that in the more co-valent type structures. A complete study on other metal–boron type compounds would throw some light on the bonding characteristics of boron.

The authors are indebted to the Office of Naval Research for financial help in this investigation and to Professor Linus Pauling for valuable discussions and critical comments.

PASADENA, CALIFORNIA

(11) J. Russell, R. Hirst, F. A. Kanda and A. J. King, *Acta Cryst.*, **6**, 870 (1953).

(12) L. Pauling, *Proc. Natl. Acad. Sci.*, **36**, 533 (1950).

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

Determination of Activity Coefficients by Ultracentrifugation. Ultracentrifugation of Uranyl Fluoride Solutions[1a,b]

BY JAMES S. JOHNSON, KURT A. KRAUS AND T. FRASER YOUNG[1c]

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Equilibrium ultracentrifugation of two-component systems is discussed from the point of view of determination of stoichiometric activity coefficients. Ultracentrifugation of cadmium iodide solutions was found to yield activity coefficients which were in satisfactory agreement with those in the literature. By ultracentrifugation, activity coefficients of UO_2F_2 in aqueous solution were obtained which were similar to those found by freezing point depressions, thus supporting the earlier hypothesis of a monomer–dimer equilibrium. The dimerization constant appears to increase slightly with temperature, indicating a small and positive heat of dimerization. Ultracentrifugation of UO_2F_2 in KF solutions indicates that excess fluoride ions increase the stability of the dimer considerably.

It has been pointed out, particularly by Pedersen[2] and Drucker,[3] that ultracentrifugation to equilibrium can be used for the determination of activity coefficients of solutes, since at equilibrium there is essentially a balance between the chemical and centrifugal potentials. Pedersen used activity coefficients of various solutes in the literature to calculate the (known) molecular weights;

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(1) (a) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory. (b) Table I has been deposited as Document number 4146 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm by check or money order payable to: Chief, Photoduplication Service, Library of Congress. (c) George Herbert Jones Chemical Laboratory, University of Chicago. Consultant to the Chemistry Division, Oak Ridge National Laboratory.

(2) (a) K. O. Pedersen, *Z. physik. Chem.*, **A170**, 41 (1934); (b) T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," The Clarendon Press, Oxford, England, 1940, p. 53.

(3) C. Drucker, *Z. physik. Chem.*, **A180**, 359 (1937).

Drucker computed activity coefficients and compared them either with those in the literature or with those determined by him with various "standard" techniques. For computation, both authors used the usual[2b,4] (approximate) integrated equation for centrifuge equilibrium

$$\ln a_\beta/a_\alpha = \frac{M(1-\bar{v}\rho)\omega^2}{2RT}(x_\beta^2 - x_\alpha^2) \qquad (1)$$

where M is the molecular weight, ω the angular velocity, x the distance from the center of rotation, $\bar{v}$ the partial specific volume of the solute, ρ the density of the solution, R the gas constant, T the absolute temperature, and where a is the activity of the solute. Subscripts α and β refer to positions in the centrifuge cell. For non-electrolytes $\mathrm{d}\ln a = \mathrm{d}\ln cy = \mathrm{d}\ln m\gamma$ where c is the molarity, m the molality and y and γ the corresponding stoichiometric activity coefficients. For electrolytes $\mathrm{d}\ln a = \mathrm{d}\ln c_\pm^\nu y_\pm^\nu = \mathrm{d}\ln m_\pm^\nu \gamma_\pm^\nu = \mathrm{d}\ln m_+^{\nu_+} m_-^{\nu_-} \gamma_\pm^\nu$ where ν_+ and ν_- are the assigned numbers of moles of positive and negative ions per mole of solute consistent with the computation of $\gamma_\pm$ and where $\nu = \nu_+ + \nu_-$. In the derivation of equation 1 $\bar{v}$ and ρ are assumed independent of concentration and pressure. When $\bar{v}$ and ρ depend on concentration and pressure integration of the partial differential equation for the centrifuge equilibrium yields[5]

$$\ln a_\beta/a_\alpha = \nu \ln (m_\pm)_\beta/(m_\pm)_\alpha + \nu \ln (\gamma_\pm)_\beta/(\gamma_\pm)_\alpha = \frac{M\omega^2}{2RT}(x_\beta^2 - x_\alpha^2) - \frac{M}{RT}\int_{P_\alpha}^{P_\beta} \bar{v}_\beta \mathrm{d}P \qquad (2)$$

where

$$\mathrm{d}P = \omega^2 \rho x \, \mathrm{d}x \qquad (2a)$$

If the position x_α is taken to be the meniscus of the solution in the centrifuge cell, $P_\alpha \backsimeq 1$ atmosphere and the activity coefficients calculated by equation 2 are for one atmosphere, *i.e.*, comparable with others determined under "bench top" conditions. In equation 2, $\bar{v}_\beta$ is the partial specific volume of the solute at the concentration m_β occurring at position x_β in the cell. The pressure limits of the integral in Equation (2) are determined from integration of Equation (2a) in which ρ must be known as a function of x. On the other hand, $\bar{v}_\beta$ refers only to the composition m_β, but must be known as a function of P.

The determination of ratios of activity coefficients of a solute of known molecular weight M involves, according to equation 2, the determination of concentrations as a function of x. The optical system of the centrifuge used yields only refractive index gradients, as discussed below. From these and separately determined refractive index–concentration data, concentration gradients as a function of x are computed. Actual concentrations as a function of x can then be determined, since the total amount of solute in the cell is given by the initial concentration of the solution and the known geometry of the cell.[6]

Since both Pedersen and Drucker had some reservations concerning the precision which can be obtained in the determination of activity coefficients by ultracentrifugation, and since it was desirable to test the equipment used here, experiments were carried out with cadmium iodide solutions. The results were compared with data in the literature and indicated satisfactory precision of the method. The method was then applied to the determination of activity coefficients of uranyl fluoride and the results compared with those calculated from freezing point depressions.[7] Experiments were also carried out in the presence of potassium fluoride as "supporting electrolyte."

Experimental

The solutions were centrifuged in a Specialized Instrument Corporation ("Spinco") Model E Ultracentrifuge[8] operated at speeds around 30,000 r.p.m. Average speeds can be determined in this machine with a counter. These averages, each measured over a period of several hours, were constant to better than ±20 r.p.m. during an experiment.

The centrifuge cells were equipped with the standard quartz windows which apparently were not appreciably attacked by either the uranyl fluoride or potassium fluoride solutions. The (sector shaped) center pieces of the cells, however, were made of Kel-F plastic to avoid corrosion. The plastic was molded into an aluminum retaining ring to minimize deformation. For the dilute solutions cells with a column of solution h = 12 mm. were used, while for the more concentrated solutions cells with h = 3 mm. The distance h, perpendicular to the plane of rotation, was determined (to 0.01 mm.) after the cells were assembled, by subtracting the thickness of the quartz windows from the over-all thickness of the cell. The center pieces were found to be compressed about 1% on assembly. It was assumed that distortion of the cell was the same in the experiments and in "background runs." The midpoint of the cells was 64.96 ± 0.05 mm. from the center of rotation.

The machine is equipped with a Philpot-Svensson[9] optical system, which gives, on a photographic plate, a curve whose abscissa is proportional to x, and whose ordinate (Z) is proportional to the gradient of the refractive index (n) with respect to radius of rotation, x, or $\mathrm{d}n/\mathrm{d}x$. This distance Z is the displacement, by the refractive index gradients in the cell, of the shadow of an inclined bar (or wire).

The photographic plates (Kodak Spectroscopic I-D) on which the results are recorded were examined with a comparator, which permitted measurements of distances to ±0.002 mm. in directions perpendicular to each other. This is considerably better than the accuracy warranted by the definition of the bar shadows in the photographs.

According to the manufacturer, the sensitivity of the photographic plates, combined with the standard filter of the instrument (Wratten No. 16), makes the instrument sensitive essentially only to the 546 and 579 mμ lines of the mercury arc light source. This system was used in the experiments with cadmium iodide. Most uranyl fluoride experiments were carried out with a Corning orange filter. In this way, only the 579 mμ mercury line was used. For solutes of normal dispersion, the use of this line should cause negligible error when the supplementary refractive index data for the solutions are determined with the sodium D lines.

The optical constants of this centrifuge were: radial magnification of the cell at the photographic plate 2.04, magnification (ϕ) by the cylindrical lens 4.47, and distance from the upper collimating lens to the bar (optical lever arm) L = 58.26 cm. Bar settings (θ) of 35–70° (angles complementary to the inclination of the bar to the axis of the cylindrical lens) were used. The 90° position of the bar was calibrated to ±5′ of arc by determining the setting which gave zero displacement (Z) of the bar shadow with a strongly sedimenting substance. The consistency of other settings were found to be within 5′. The optical constants allow[9] conversion of Z to $\mathrm{d}n/\mathrm{d}x$ by the equation

$$\mathrm{d}n/\mathrm{d}x = Z \tan \theta / L\phi h \qquad (3)$$

The temperature of the solutions during equilibration

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(4) (a) The Svedberg, *Kolloid-Z.*, **36**, 53 (1925), (*Zsigmondy-Festschrift*); (b) *Z. physik. Chem.*, **121**, 65 (1926).

(5) T. F. Young, K. A. Kraus and J. S. Johnson, *J. Chem. Phys.*, in press.

(6) See reference 2b, p. 312.

(7) J. S. Johnson and K. A. Kraus, THIS JOURNAL, **74**, 4436 (1952).

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

(9) (a) H. Svensson, *Kolloid-Z.*, **87**, 181 (1939); (b) **90**, 141 (1940).

could be controlled only by the regulation of the room temperature. The temperature of the rotor at the end of the experiment was taken to be the equilibrium temperature.

The time necessary to reach equilibrium varied from about three to ten days. Equilibrium was considered attained when photographs taken at least 15 hours apart indicated no significant change in Z.

Eimer and Amend C.P. CdI_2 was used, which, by iodide titration, gave within 0.1% the theoretical percentage of iodine. The uranyl fluoride preparations were the same as in previous freezing point measurements.[7]

Results and Discussion

(1) CdI_2 in **Water.**—Cadmium iodide solutions with initial concentrations 0.3504 and 0.5234 *M* were centrifuged to equilibrium at 33,450 r.p.m. in 3- and 12-mm. cells, respectively. Temperature at equilibrium was 27.5 ± 0.5° for both solutions.

The observed displacements Z of the bar shadow were converted to refractive index gradients with the optical constants of the centrifuge (equation 3). These refractive index gradients can be considered to be the sum of three terms, as shown in equation 4

$$dn/dx = (\partial n/\partial m)_P\, dm/dx + (\partial n/\partial P)_m\, dP/dx + \epsilon \quad (4)$$

where ϵ is an extraneous gradient due to distortion of the cell and windows. In the computations it was assumed that $(\partial n/\partial m)_P$ is equal to its value at $P = 1$, and that $(\partial n/\partial P)_m$ is equal to the value for pure water at $P = 1$ (1.4×10^{-5}/kg. cm.$^{-2}$).[10,11] If it is assumed that the extraneous gradient ϵ is the same in a "background run" with pure water and in experiments with the solutions, ($\epsilon + (\partial n/\partial P)_m\, dP/dx$) and hence dm/dx can be evaluated from the observed values of Z in the two experiments and the differences in pressure gradients dP/dx. The latter result from differences in the densities of water and the solutions. The differences in the pressure correction term ($(\partial n/\partial P)_m\, dP/dx$) for water and the solutions were usually small (0.5 to 1%) but reached values as large as 5% in the more concentrated uranyl fluoride solutions whose densities were of the order of 2.

The concentration gradients (dc/dx) were computed from the (corrected) refractive index gradients with the value $dn/dc = 0.0486$ (sodium D light, 27.5°), which was obtained from the refractive index measurements of Getman and Gilroy[12] and Spacu and Popper,[13] supplemented by a few measurements of our own. This value of dn/dx is probably correct to within 0.5% in the concentration range of interest, and was assumed to be directly applicable to the centrifuge measurements although the latter involve mainly the mercury lines 546 and 579 mμ.

From the density data of Gibson,[14] $\bar{v}$ (0.182 to 0.188) and ρ were obtained. According to Gibson, the effect of pressure on $\bar{v}_{CdI_2}$ appears negligible for the present purposes.

The ratios of the mean ionic activity coefficients for $\nu = 3$ were calculated with equation 2. To permit ready comparison of these activity coefficients with the data in the literature, the assignment $y_\pm = 0.70$ at $c = 0.5329$ was made for both solutions. This value was obtained from the data of Bates[15] by conversion of his values of $\gamma_\pm$ to $y_\pm$ and by interpolation to 27.5°.

As shown in Fig. 1, the activity coefficients calculated from the two experiments are in satisfactory agreement with each other in the considerable region of overlap. In addition, they are in good agreement with the activity coefficients obtained from data of Bates throughout the concentration range studied. At the highest concentrations, the centrifuge data appeared to be 0.5% lower than those of Bates. Actually, the agreement is considerably better than could have been expected from the known errors in the centrifugation experiments.

(2) UO_2F_2 **in Water.** (a) **Activity Coefficients of UO_2F_2.**—Uranyl fluoride solutions of initial concentrations *ca.* 0.25, 0.69, 1.33, 2.20 and 3.35 *M* UO_2F_2 were centrifuged to equilibrium to obtain activity coefficients of UO_2F_2 in the concentration range *ca.* 0.15 to 5 molal; 12-mm. cells were used for the two most dilute solutions and 3-mm. cells for the others. All experiments were carried out at 27,700 r.p.m. except for the 0.25 *M* solution, which was run at 31,410 r.p.m. All experiments were carried out in duplicate except in one case when poor agreement between the two runs (probably due to an erroneous value of initial concentration) necessitated a third experiment.

Agreement between duplicate experiments was satisfactory, as illustrated in Table I (see footnote 1B), for one case (0.7 *M*). Except for this concentration, this table contains the results of only the second set of duplicate experiments since in this set some minor improvements in technique had been made. In Table I are recorded, at 1-mm. intervals of x, values of the bar shadow displacement Z^* (obtained by subtraction of Z of water background experiments from Z of uranyl fluoride experiments), and values of dn/dx for uranyl fluoride, which were computed from Z^* after application of the pressure correction discussed in Section 1. Concentration gradients were calculated from dn/dx and refractive index–concentration data,[16] and from these by integration the concentrations c listed in the table. Activity coefficients y were obtained through equation 2 and the values of ρ and $\bar{v}_{UO_2F_2}$ reported earlier.[16] The computations of y were carried out for $\nu = 1$ (*i.e.*, for undissociated UO_2F_2) to permit ready comparison with the freezing point measurements.[7]

In Table II ratios of the activity coefficients (γ^*) of UO_2F_2 to that at $m = 0.15$ are reported at round concentrations. These activity coefficient ratios are given only to two significant figures, since in their evaluation several uncertainties occur which could easily affect the results, particularly at higher concentration, by several per cent. At these higher concentrations, where the density is high, distortion of the cell windows could introduce

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(10) V. Raman and K. S. Venkataraman, *Proc. Roy. Soc.* (*London*), **A171**, 137 (1939).

(11) F. F. Poindexter and J. S. Rosen, *Phys. Rev.*, [2] **45**, 760 (1934).

(12) "International Critical Tables," Vol. VII, McGraw-Hill Book Co., New York, N. Y., 1930, p. 70.

(13) "Landolt-Börnstein," 5th Ed., Egbd. 3, 185 (p. 1705) Julius Springer, Berlin, 1935.

(14) R. E. Gibson, This Journal, **59**, 1521 (1937).

(15) R. G. Bates, *ibid.*, **63**, 399 (1941). The (e.m.f.) data of Bates were used since they were given as a function of temperature. These data at 25° agree with the isopiestic data of Robinson and Wilson (*Trans. Faraday Soc.*, **36**, 738 (1940)) to better than 1% in the region of interest.

(16) J. S. Johnson and K. A. Kraus, This Journal, **75**, 4594 (1953).

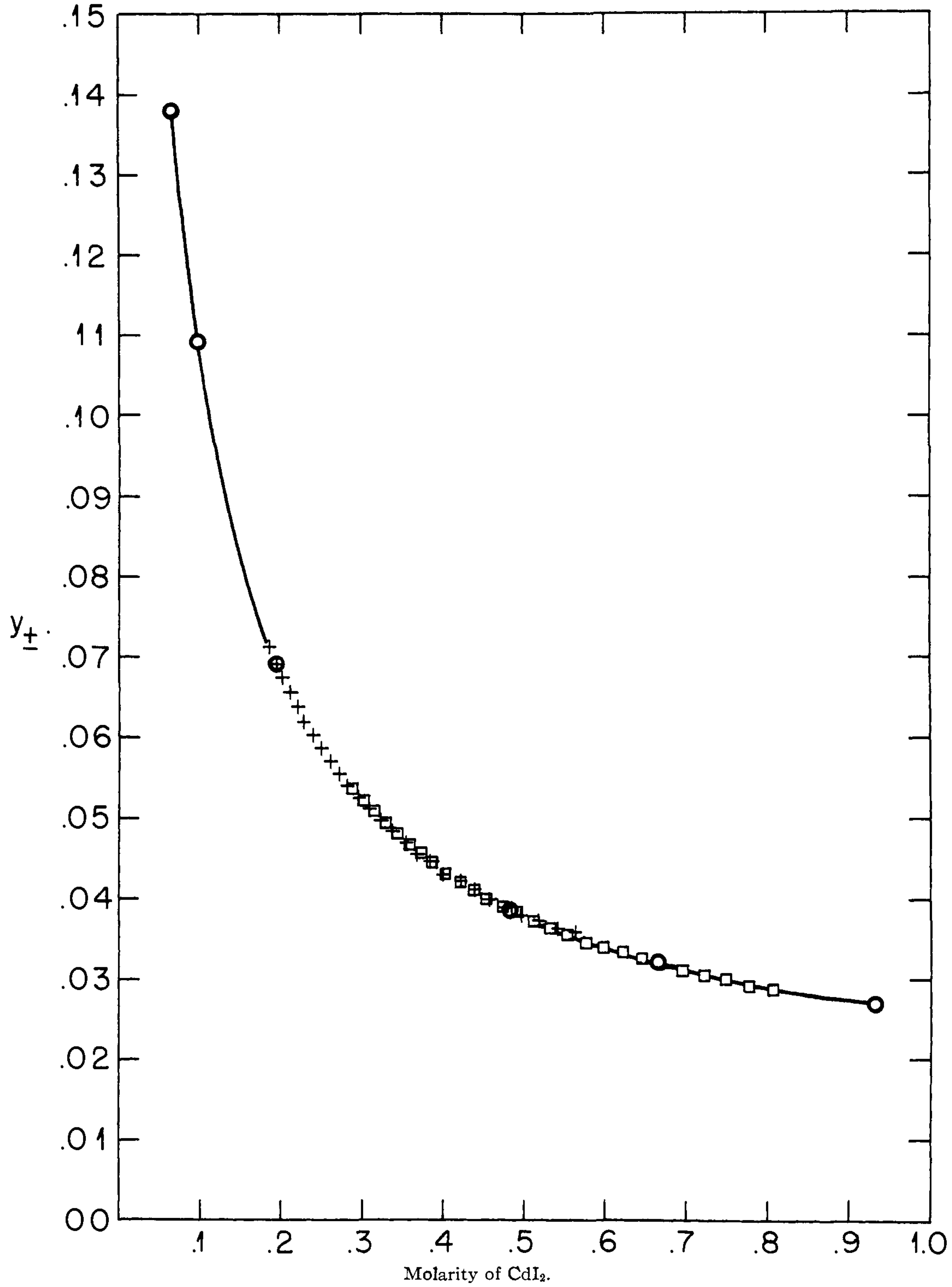

Fig. 1.—Activity coefficients of CdI_2: -O-, e.m.f. (Bates); +, centrifuge c_0 = 0.3504 *M*; □, centrifuge c_0 = 0.5234 *M*

an error of unknown magnitude. The assumption that $\bar{v}$ is independent of pressure would not introduce a serious error if $\partial\bar{v}/\partial P$ is similar to that of CdI_2 but is of more moment if it is similar to that of NaCl.[17] Since $\bar{v}_{UO_2F_2}$ changes considerably with concentration, variations with pressure might be anticipated. This error again would be more serious for the more concentrated solutions. In addition it might be pointed out that the change of the activity coefficients with concentration in the regions of overlap was not as close for two adjacent experiments with UO_2F_2 as for the CdI_2 experi-

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(17) R. F. Gibson and O. H. Loeffler, *Anal. N. Y. Acad. Sci.*, **51**, 727 (1949).

ments. This difference, though small, is suggestive of a small systematic error, such as would arise from a significant variation of $\bar{v}$ with P.

Table I

Activity Coefficients of UO_2F_2

m	c (30°)	$y/y_{0.1485}$ (30°)	$\gamma/\gamma_{0.15}$ (30°)	$\gamma/\gamma_{0.15}$ (0°)
0.15	0.1485	1.00	1.00	1.00
.3	.2961	0.88	0.88	0.90
.5	.4904	.78	.78	.80
.7	.6820	.72	.71	.74
1.0	.9646	.66	.64	.68
1.5	1.422	.60	.58	.63
2.0	1.862	.57	.54	.60
2.5	2.285	.56	.52	.59
3.0	2.692	.56	.50	.59
3.5	3.083	.56	.50	.60
4.0	3.459	.57	.50	.61
4.5	3.822	.59	.50	.63
5.0	4.171	.61	.51	.65

Comparison of the activity coefficients determined by ultracentrifugation at 30° with those determined by freezing point depressions indicated that the latter were consistently higher. It thus appeared that the implicit neglect of the relative heat content of water ($\bar{L}_1$) in the earlier freezing point work could introduce a significant error. These activity coefficients, therefore, have been recalculated. The ratio of the activity of water to that at $m = 0.15$ $((a_1)/(a_1)_{0.15})$ at 0° was estimated through linear interpolation of the logarithms of these ratios between the freezing points and 30°. This procedure corresponds to the assumption that $(\bar{L}_1)_{0.15}$ is negligible and that $\bar{L}_1/T^2$ is temperature independent. It does not greatly differ from the equally bold assumption that $\bar{L}_1$ is constant.[18] Activity ratios $(a_1)/(a_1)_{0.15}$ of water at 30° were obtained from the activity coefficients by means of the Gibbs–Duhem equation. The activities of water at the freezing points were directly obtained from the freezing point depressions.[19] By integration of the Gibbs–Duhem equation at 0° the activity coefficient ratios $\gamma^* = \gamma/\gamma_{0.15}$ listed in Table I were then obtained.

(2) **(b) Dimerization of UO_2F_2.**—The freezing point data had previously been interpreted on the assumption that the solutions contained primarily undissociated uranyl fluoride and that dimerization according to the reaction

$$2UO_2F_2 \rightleftarrows (UO_2F_2)_2 \tag{5}$$

occurs. The dimerization constant K, is given by

$$K = a_{(2)}/a^2_{(1)} = m_{(2)}g_{(2)}/m^2_{(1)}g^2_{(1)} \tag{6}$$

where a, m and g stand for the activities, molalities and activity coefficients of the species indicated as subscripts, *i.e.*, $g_{(2)}$ being the activity coefficients of the dimeric species and $g_{(1)}$ that of the monomeric species. It was further assumed that the activity coefficients of the species follow the equations

$$\log g_{(1)} = b_{(1)}m \tag{7a}$$

$$\log g_{(2)} = b_{(2)}m \tag{7b}$$

and

$$2b_{(1)} = b_{(2)} \tag{7c}$$

where m is the stoichiometric molality of UO_2F_2. The dimerization constant K and the parameter $b_{(1)}$ could then be estimated from the stoichiometric activity coefficient ratios γ^* through the equation

$$a_{(1)} = m_{(1)}g_{(1)} = a = m\beta\gamma^* \tag{8}$$

which applies if the standard molal free energy of the solute is taken to be equal to the standard molal free energy of the monomeric species. Note that a constant β appears in equation 8 since only activity coefficient ratios γ^* of UO_2F_2 (Table I) have been determined.

Numerical estimation of K through use of equations 6, 7 and 8 is subject to considerable uncertainties because of the limited precision of the data and the possibility that some "dissociation reaction" may occur at low concentrations.[20] With these limitations, values of K and $b_{(1)}$ were selected by the following criteria[21]: (1) Significant deviations of experimental data from calculated values were permitted only in the direction indicating dissociation; (2) the smallest dimerization constant consistent with (1) was selected. The method of computation becomes apparent by rearrangement of equation 8

$$\log \gamma^* - \log \frac{m_{(1)}}{m} = \log \frac{1}{\beta} + b_{(1)}m \tag{9}$$

A plot of the left hand side of equation 9 *vs.* m should yield a straight line with slope $b_{(1)}$. Ratios $m_{(1)}/m$ were calculated by equations 6 and 7 for various values of K and the corresponding values of $b_{(1)}$ were evaluated. In Fig. 2, $m\gamma^*/m_{(1)}g_{(1)}$ *vs.* m is plotted. Satisfactory fit of the data is indicated by constant ordinate and is obtained by using $K = 3$, $b_{(1)} = 0.069$ at 0° and $K = 7$, $b_{(1)} = 0.053$ at 30°. The deviations at low concentrations indicate that the calculated values of $m_{(1)}$ are too large, *i.e.*, that a dissociation reaction or hydrolysis reaction of the type discussed in footnote 20 occurs.[22] If these reactions occur to a greater extent

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[18] T. F. Young, *Chem. Revs.*, **13**, 103 (1933).

[19] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, Sec. Ed., p. 285.

(20) One might be tempted, at first glance, to postulate that dissociation to $UO_2F^+ + F^-$ occurs and that the extent of this reaction could be roughly estimated from the extremely low values of the conductivity of these solutions (G. R. Dean, Report CC-2092 (September 1944), R. D. Brown, private communication). However, this procedure is not safe since uranyl fluoride solutions are considerably acidic (W. L. Marshall, J. S. Gill and C. H. Secoy, Report ORNL 795, June, 1950, p. 22), making it unlikely that large concentrations of F^- occur in the solutions. Of the many other possible reactions, which might occur at low concentrations, the following may be mentioned: (a) $UO_2F_2 + H_2O \rightarrow UO_2OHF + HF$; (b) $2UO_2F_2 + H_2O \rightarrow UO_2OHF + H^+ + UO_2F_2^-$. Although reaction (a) would contribute some acidity and conductance to the solutions because of a small amount of dissociation to H^+ and F^-, a rough evaluation indicates that this reaction could not contribute a sufficiently high concentration of ions to explain the data. Reaction (b) appears a more likely source of such ions.

(21) It must be emphasized that if reaction with solvent occurs, as discussed in footnote 20, the ultracentrifuge does not measure activity coefficients of UO_2F_2 with the refractive index techniques used here.[5] Even if the concentrations of all species as functions of radius were determined, as would be necessary for a complete thermodynamic treatment, ultracentrifugation differs from determination of freezing points, osmotic pressures, etc., since the reaction products will distribute differently in the centrifugal field and will not be in the same ratio to each other at all points in the cell.

(22) In a previous paper,[7] it was stated erroneously that the concavity of the type shown at low concentrations in Fig. 2 is inconsistent with dissociation. Hence, in that paper the lower limit estimated for the dimerization constant was too low.

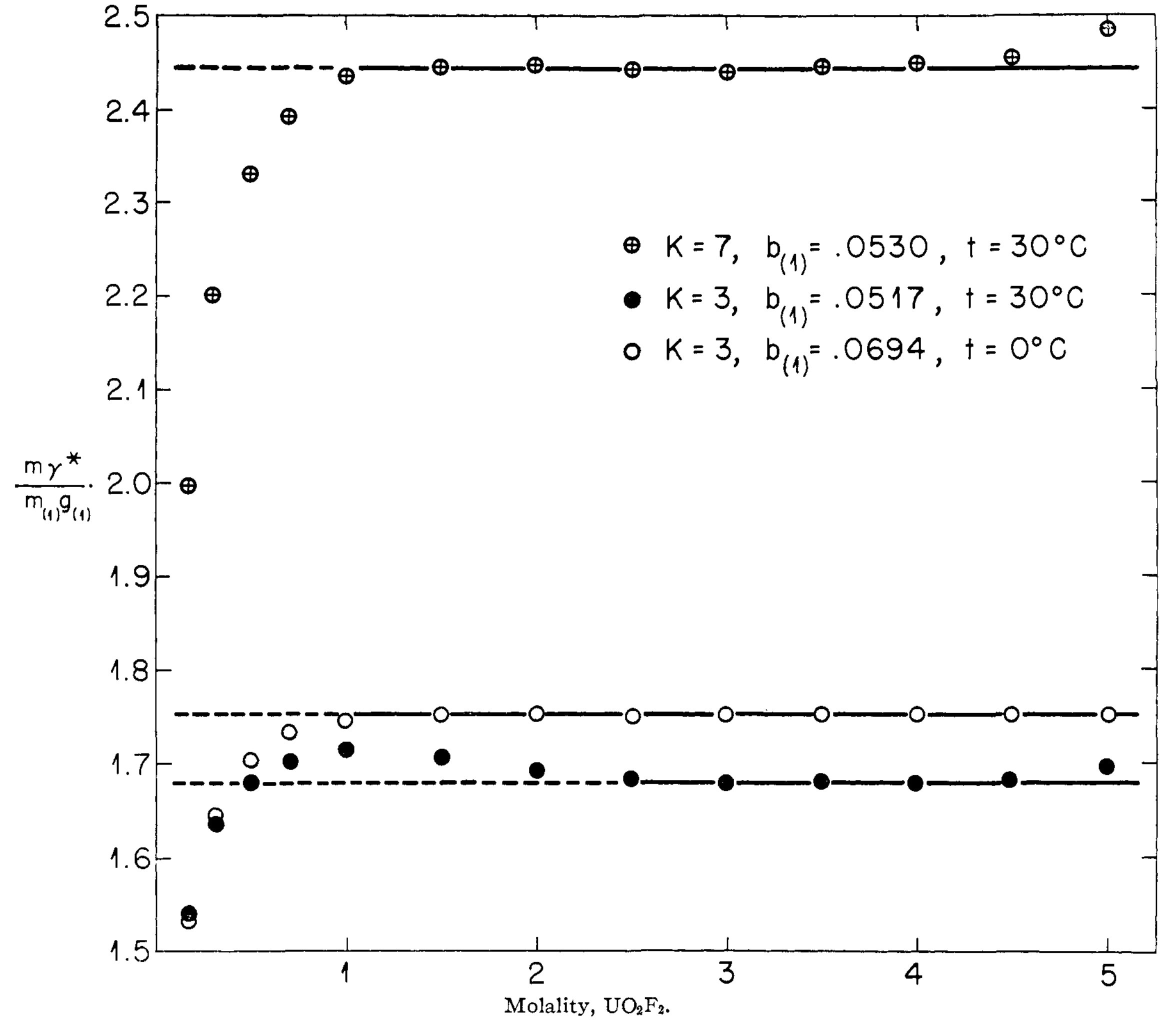

Fig. 2.—Estimation of dimerization constant.

than indicated in Fig. 2, the dimerization constant selected will be too small. An example of the elimination of a value of K by criterion (1) is illustrated in Fig. 2 for $K = 3$ at 30° (note the positive deviation at concentrations near 1 molal).

These data thus suggest that the dimerization constant increases somewhat with temperature and that the interaction constant $b_{(1)}$ decreases with temperature. From these values of K a positive heat of dimerization ΔH = *ca.* 5 kcal. was calculated, as well as an entropy change of ΔS = *ca.* 19 e.u. In view of the uncertainties in this interpretation, this heat and entropy of dimerization should be taken with caution, and should be considered only a rough first approximation even if the assumptions are basically correct.

(3) **UO_2F_2 in KF Solutions.**—In order to determine the effect of addition of excess fluoride ions on the degree of polymerization of uranyl fluoride, two ultracentrifugations in potassium fluoride solutions were carried out (0.04 M UO_2F_2 in 0.73 M KF, 0.15 M UO_2F_2 in 1 M KF). In these systems the stoichiometric activity coefficients (computed on the basis $\nu = 1$) decrease more rapidly with concentration than in the UO_2F_2 water system. It appeared that polymerization of UO_2F_2 occurs to a greater extent in the presence of KF than in water solutions. Actually, as shown below, the assumption that dimerization has gone to completion ($\nu = 0.5$) is consistent with the data.

It has been demonstrated[2a] that if the activity coefficients of a species which exists in the solutions are essentially constant in the concentration range covered by an experiment and if $\bar{v}$ and ρ are constant, then

$$c_\beta/c_\alpha = (Z^*/x)_\beta/(Z^*/x)_\alpha \qquad (10)$$

Hence, by combining equations 1 and 10, a plot of log (Z^*/x) *vs.* x^2 should give a straight line, the slope of which multiplied by $2RT(2.303)/(1 - \bar{v}\rho)\omega^2$ gives the apparent molecular weight of the solute species. Z^* here is obtained by subtracting a background Z for a KF–water experiment from the Z for UO_2F_2–KF–water experiment. The term "apparent molecular weight" is used because this statement is not exactly true for a charged species, though it is approached if the heavy ion carries a low charge and is in an excess of slightly sedimenting electrolyte.[23]

As shown in Fig. 3, such plots of log Z^*/x *vs.* x^2 for the UO_2F_2–KF systems are indeed straight lines.

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[23] O. Lamm, *Arkiv Kemi, Mineral. Geol.*, **17A**, Paper 25 (1944).

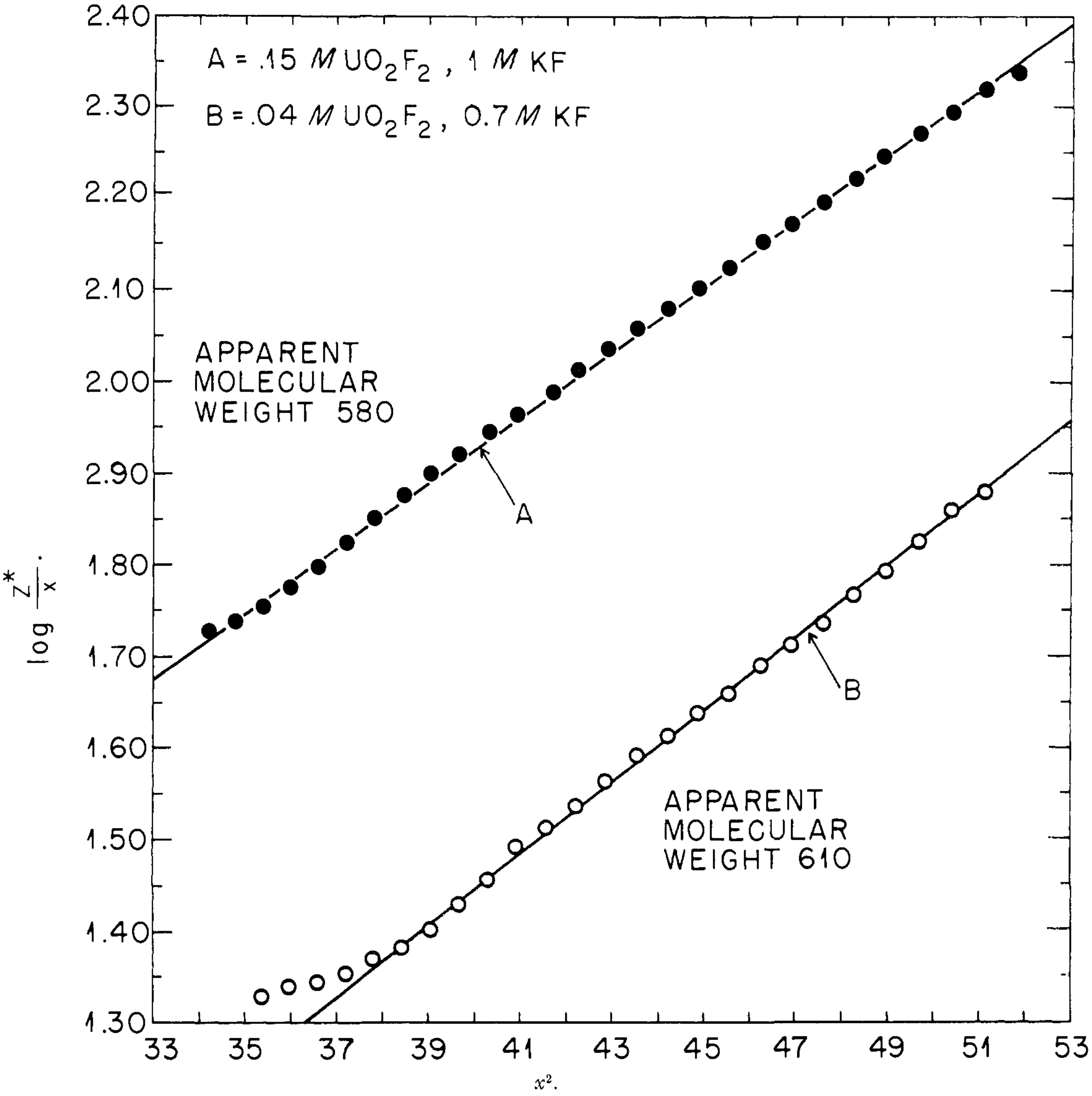

Fig. 3.—Aqueous UO_2F_2–KF solutions at equilibrium in a centrifugal field.

Their slopes yield apparent molecular weights of 610 and 580 for the experiments with 0.04 and 0.15 *M* UO_2F_2, respectively. These may be compared with the (theoretical) molecular weight 308.1 of UO_2F_2. In these computations the estimate $(1 - \bar{v}\rho) = 0.85$ was used, which implies that the partial specific volume of the uranium species in this medium is about the same as that of UO_2F_2 in water. The error introduced by this assumption should be small, and it thus appears that uranyl fluoride exists predominantly as a dimeric species in KF solutions at concentrations at which it could be only moderately dimerized in water alone.

Since the dimer in potassium fluoride solution probably contains more than 4 fluoride ions and hence carries a (negative) charge, the apparent molecular weights should be less than the actual molecular weights of the pertinent species.[23] An estimate of the magnitude of this effect indicates that the observed apparent molecular weights are consistent with the assumption of a dimer of low negative charge, although the data are not sufficiently accurate to establish the magnitude of this charge conclusively.

(4) **General Considerations.**—If one uses the crystallographic data on solid uranyl fluoride as a guide,[24] one may assume that the postulated dimer of uranyl fluoride is held together by one or two fluoride bridges since the solid consists of a layer structure in which the uranyl groups are held together by fluoride ions. Using a section of such a layer, the proposed structure of the dimer of uranyl fluoride can be described by Fig. 4. In this figure, the uranyl groups would stand perpendicular to the plane of the paper with one of the oxygens above and one below the plane of the paper. One of the fluoride ions of the bridge would probably also be above and one below the plane of the paper. Since the uranyl groups in the solid have a coördination number of 6, one might preserve this in the dimer by placing the remaining 2 fluoride ions and 6 water molecules in the remaining coördination positions.

One might attempt to explain the apparent posi-

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[24] W. H. Zachariasen, *Acta Cryst.*, **1**, 277 (1948).

tive entropy change of dimerization by considering the oriented water molecules which surround the uranyl group and the fluoride ions of the monomer. On dimerization some of these water molecules of hydration in the space between two monomers are removed, lose their orientation and give rise to a positive entropy change. This change in the entropy of hydration apparently is considerably larger than the negative entropy change which one might expect on producing a dimeric molecule from two monomeric species.

The increased stability of the dimer on addition of excess fluoride ions at first glance is very surprising since one might have expected that addition of fluoride ions would cause dissociation. Since increased association was observed, one may conclude that the uranyl group is not a sufficiently strong complexing agent with respect to fluoride ions to form $UO_2F_6^{-4}$ under these conditions and that the repulsion between fluoride ions must be less than the added attraction gained by having the fluoride ions as fluoride bridges in the field of both uranium(VI) ions.

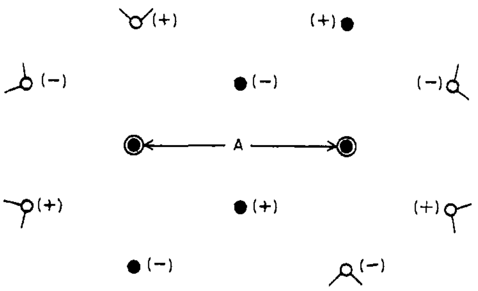

Fig. 4.—Suggested structure of $(UO_2F_2)_2$ (based on uranyl fluoride structure of Zachariasen): ⊙, uranyl groups, oxygen perpendicular to plane of paper (±1.91 Å.); ●, fluoride ions; (+) and (−) indicate positions above and below plane of paper (±*ca.* 0.61 Å.); ꝏ, water molecules of hydration; A, distance between uranyl groups (*ca.* 4.20 Å.).

Acknowledgment.—We are indebted to Mrs. Rooney Weaver of the ORNL Mathematics Panel and to Miss Zella Bonner for their assistance with the computations.

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[CONTRIBUTION NO. 290 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

Crystal Nucleation from Supersaturated Aqueous Solution. Tetraphenylarsonium Perchlorate and Nickel Nioxime

BY FREDERICK R. DUKE AND LOUIS M. BROWN

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The number of crystals obtained in the crystallization of a self-nucleating substance from supersaturated solution depends upon the relative rates of the nucleation and the growth processes. The rapidity of crystallization of most of the precipitates of the type used for analytical purposes, as well as the variation in number of crystals with conditions indicate that such solutions are self-nucleating. The relatively long induction periods before precipitate appears in dilute supersaturated solutions, when compared with the time for crystal growth, indicate that generally the growth process is very much faster than the nucleation process. The treatment below of two precipitates is a study of the variation in number of crystals per mole with variation in degree of supersaturation, the data being interpreted in terms of the kinetics of the nucleation and growth processes. The effect of temperature also is studied.

Volmer[2] considered the crystal nucleus to be the agglomerate of ions or molecules of just sufficient size to be stable in a separate phase in contact with a solution of given degree of supersaturation. For a reasonable range of values of the interfacial tension, one calculates that even the smallest nuclei consist of several tens of molecules.

Recent work has led to the conclusion that a very small number of ions is involved in the nucleation of silver chromate[3a] or barium sulfate[3b] crystals. LaMer also has discussed this matter.[4,5]

The question immediately apparent concerns the forces holding a small nucleus together, particularly one composed of large ions in aqueous solution.[6,7] It seems probable that the sort of forces which cause the crystals to be insoluble are involved in nucleus formation. Thus, the nucleus should be considered to be a complex of ions or molecules held together by short range forces in addition to any coulombic forces present; and this complex has the geometric properties of the crystal.

Since a large number of crystals are formed when a sparingly soluble salt is precipitated from solution, one should be able to treat the nucleation process statistically; thus, ordinary rate laws are assumed to hold. The rate equation for nucleation is

$$dx/dt = k_1A^nB^m - k_2(A_nB_m)A^pB^q$$

where x is the number of nuclei; A and B, the concentrations of the ions of which the crystal is composed; t the time; n and m, the number of ions of the kind indicated comprising the nucleus; and p and q the order in A and B, respectively, of the next addition to the cluster after the nucleus is formed. The rate of formation of the nucleus involves setting up the geometry of the crystal and this rate assumed to be small compared with the rate of addition of ions or molecules to those already possessing the proper geometry. The nu-

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] M. Volmer, "Kinetik der Phasenbildung," Steinkopff, Leipzig, 1939.

[3] (a) J. A. Christiansen and A. Nielsen, *Acta Chem. Scand.*, **5**, 674 (1951); (b) F. R. Duke, R. J. Bever and H. Diehl, *Iowa State Coll. J. Sci.*, **23**, 297 (1949).

[4] V. K. LaMer, *Ind. Eng. Chem.*, **44**, 1270 (1952).

[5] V. K. LaMer and R. H. Dinegar, THIS JOURNAL, **72**, 4847 (1950).

[6] N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

[7] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1919 (1933).