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.

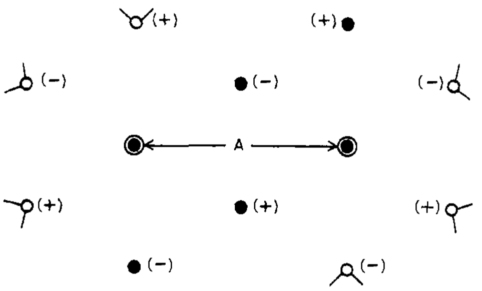

Fig. 4.—Suggested structure of $(UO_2F_2)_2$ (based on uranyl fluoride structure of Zachariasen): ⊙, uranyl groups, oxygen perpendicular to plane of paper (±1.91 Å.); ●, fluoride ions; (+) and (−) indicate positions above and below plane of paper (±*ca.* 0.61 Å.); ⊃o, water molecules of hydration; A,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

OAK RIDGE, TENN.

[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

RECEIVED DECEMBER 1, 1953

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).

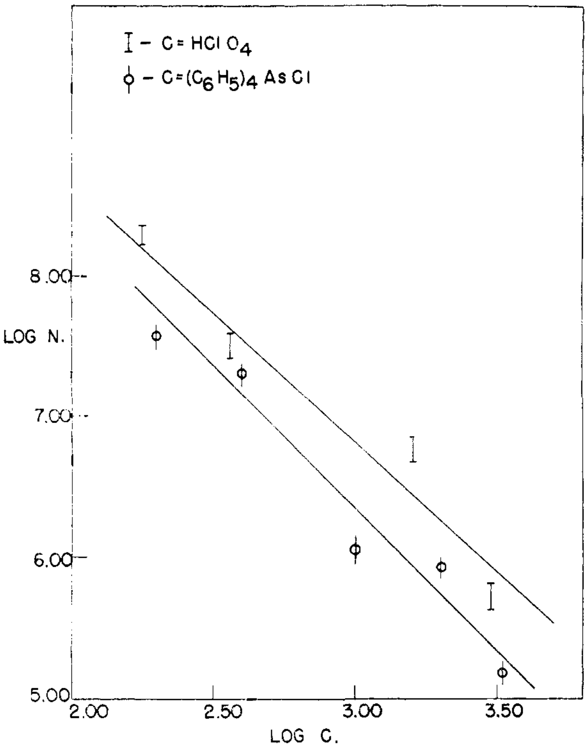

Fig. 1.—Variation of number of crystals with concentration.

cleus is thus considered to be no less than a unit cell of the crystal. When a slow reaction is followed by a rapid one, the steady state approximation holds and dx/dt = 0. Thus

$$\mathrm{d}N/\mathrm{d}t = k_2(A_nB_m)A^pB^q = k_1A^nB^m \qquad (1)$$

where N is the number of crystals.

The equation for nucleus growth is

$$\mathrm{d}P/\mathrm{d}t = k_2SA^{n'}B^{m'} \qquad (2)$$

where P is the amount of precipitate formed, S the surface or number of sites available to ions on the growing crystal; t the time; k_2 the rate constant; and n' and m' the order of the growth reaction in each of the ions indicated. Combining the two equations yields

$$\mathrm{d}N/\mathrm{d}P = k_1A^{n-n'}B^{m-m'}/k_2S \qquad (3)$$

S may be expressed in terms of N and P as follows: the volume of the precipitate PM/ρ, where M is the molecular weight and ρ the density, divided by V_P, the volume of a particle, gives the number of particles, N. The surface per particle is $V_P{}^{2/3}$ providing the particles are all the same size, and the total surface is then

$$S = \frac{P^{2/3}M^{2/3}N^{1/3}}{\rho^{2/3}}$$

Substituting in equation 3 above yields

$$\frac{\mathrm{d}N}{\mathrm{d}P} = \frac{k_1A^{n-n'}B^{m-m'}\rho^{2/3}}{k_2P^{2/3}M^{2/3}N^{1/3}} \qquad (4)$$

Integration yields

$$N^{4/3} = \frac{4k_1A_0{}^{n-n'}B_0{}^{m-m'}\rho^{2/3}P^{1/3}}{k_2M^{2/3}} \qquad (5)$$

in the region where an insignificant fraction of the total A and B have been precipitated, that is, before significant changes in the original concentrations of A and B, A_0 and B_0, have occurred. It is assumed that the number of particles is fixed in this region and the formation of nuclei cannot compete with the nucleus growth even while the nuclei are very small.

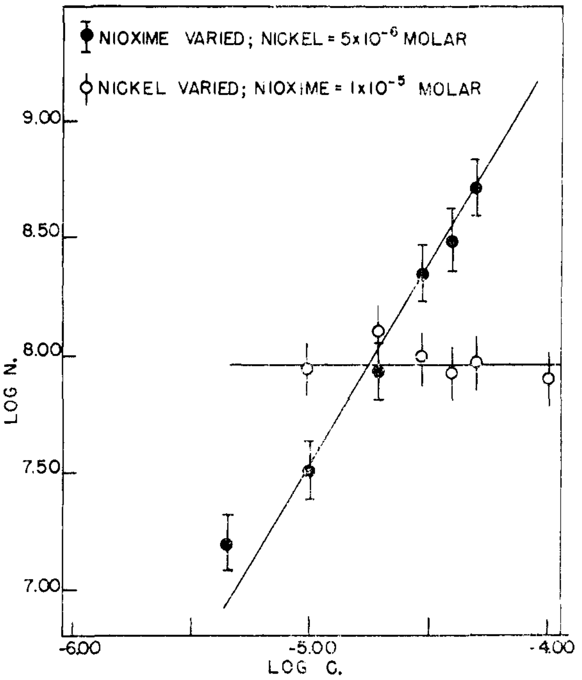

Fig. 2.—Variation of the number of nickel nioxime crystals with concentration of the reagent present in excess.

The equation describing the point where nucleation ceases to compete effectively with nucleus growth is

$$\frac{\mathrm{d}N}{\mathrm{d}P} = C = \frac{k_1A_0{}^{n-n'}B_0{}^{m-m'}\rho^{2/3}}{k_2P^{2/3}N^{1/3}M^{2/3}} \qquad (6)$$

C is the value approached by dN/dP after which nucleus formation becomes insignificant. The justification for assuming that this happens before A_0 and B_0 have changed significantly is that k_2 experimentally appears to be much larger than k_1. The long induction periods observed in crystallization from dilute solution and the small ratio of number of crystals to number of molecules, $<10^{-12}$, indicate that for most highly insoluble substances, the assumption is justified. Since C contains both the surface available and also the concentrations of ions in solution, C for any given substance should be a constant. Solving 6 for $P^{1/3}$ and substituting in equation 5, we obtain

$$N = \frac{2^{4/3}k_1\rho^{2/3}}{k_2M^{2/3}C^{1/3}}A_0{}^{n-n'}B_0{}^{m-m'}$$

Thus, a plot of log N *vs.* log A_0, B_0 held constant, should yield a straight line of slope $n - n'$. Similarly, the value of $m - m'$ may be determined.

Experimental

Tetraphenylarsonium chloride hydrochloride obtained from the Hach Chemical Company, Ames, Iowa, C.P. $HClO_4$ and $NaClO_4$ prepared by neutralization of $HClO_4$ with C.P. NaOH were the reagents used in the tetraphenylarsonium perchlorate study (T.P.A.). Pure crystalline nioxime prepared in this Laboratory and C.P. $NiCl_2{\cdot}6H_2O$

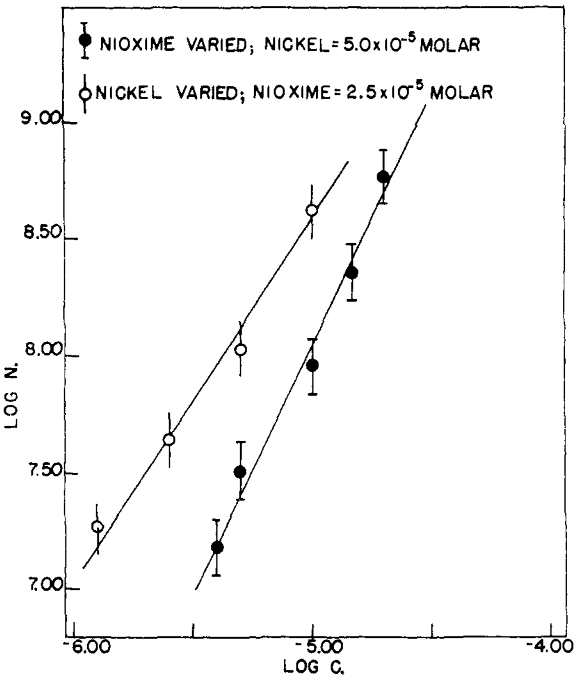

Fig. 3.—Variation of the number of nickel nioxime crystals with concentration of the more dilute reagent.

were used in the nickel nioxime study. Solutions were prepared by weight and the standardization checked gravimetrically.

The T.P.A. work was done with one ion held at 2×10^{-4} M while the other was varied from 4×10^{-4} to 1×10^{-2} M. The appropriate amounts of each reagent, each dissolved in 25 ml. of conductivity water, were mixed at constant temperature (25 ± 0.1°, water-bath) with good stirring for five seconds. Then the stirring was discontinued, and the precipitate allowed to form. The concentrations chosen ensure slow precipitation, making improbable local effects upon mixing.

The concentrations in the nickel nioxime experiments varied from 5×10^{-6} M to 1×10^{-4} M. In this study not only the reagent in excess but also the reagent not in excess was varied.

The method for determining N differed in the two cases, because of the difference in size and shape of the two types of crystal. The T.P.A. perchlorate crystals observed to be uniform in size in a given run were photomicrographed and the average size of 25–100 of the crystals determined by measurement on the photomicrograph. The density of T.P.A. perchlorate, 1.55 g./cc., was found by suspending the crystals in mixtures of carbon tetrachloride and toluene of known density. Then N, the number of crystals per mole, could be calculated.

The nickel nioxime crystals, small and needle shaped, were better handled by taking an aliquot of the precipitating solution with a blood pipet, and counting under the microscope all of the crystals in the aliquot. Tests showed that 0.01 ml. could be measured ±10% with a good pipet of 0.1-ml. total capacity. A Veeder hand tally counter was used to record counts.

Results and Discussion

Plots of log N *vs.* log of concentration are shown in Fig. 1 for T.P.A. perchlorate. From these plots, $n - n'$ and $m - m'$ are both estimated as being 2. Thus, the nucleus is $(\text{T.P.A.})_{2+n'}(\text{ClO}_4^-)_{2+m'}$. Since n' and m' are the kinetic orders for crystal growth for T.P.A. and ClO_4^-, respectively, it is likely that the nucleus contains three, four or five of each kind of ion. That is, it is probable that the kinetic growth order is not greater than third for each ion.

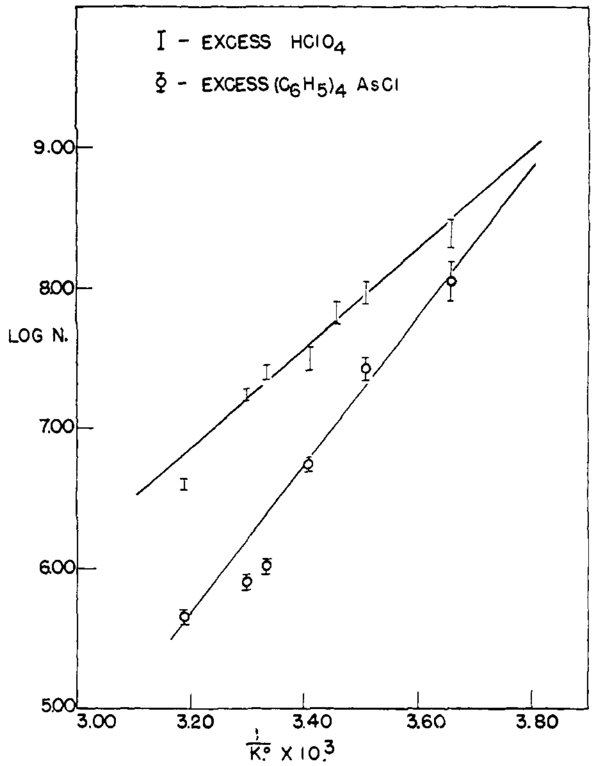

Fig. 4.—Variation of number of crystals with temperature.

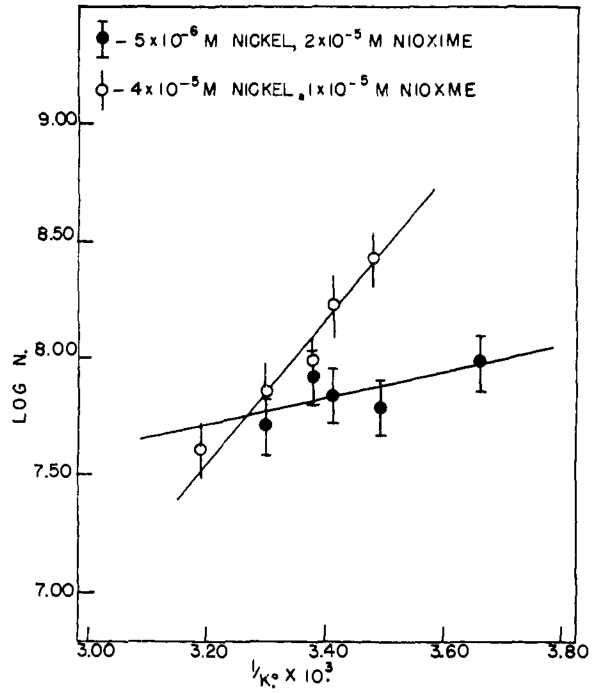

Fig. 5.—Variation of the number of nickel nioxime crystals with temperature.

Similar plots for the nickel nioxime crystals are shown in Fig. 2, where the reagent in excess is varied. Here, $n - n'$ is zero, while $m - m'$ is 2. Thus, the kinetic nucleation and growth orders are identical for Ni^{++}, but the growth order is two less than the nucleation order in nioxime. Figure 3 contains plots where the reagent not in excess is varied, and a different nucleus is indicated, since the values of $n - n'$ and $m - m'$ are both 2. The indication is that the reagent in excess predominates in the nucleus.

The effect of temperature is shown in Figs. 4 and 5. The activation energy difference between growth and nucleation is the slope of the line. The difference is small when comparing the T.P.A. excess to the perchlorate excess. The implication is that the nuclei are probably the same in the two cases. In the case of the nickel nioxime precipitate, however, the large difference in activation energy differences upon going from excess nickel to excess nioxime definitely indicates, as do the results above, that the two nuclei are different.

Experiments not detailed here show that $n - n'$ and $m - m'$ are independent of the temperature between 0 and 40°. The effect of stirring also was tested and found to be critical only when the growing crystals were of a certain size, regardless of the ultimate size of the crystals. Thus, when stirred during the period of critical size, the crystals appeared to be mechanically broken up. Stirring before or after this period had no noticeable effect. The effect of ionic strength with a neutral salt was also studied and the number of crystals was found to decrease as the ionic strength was increased.

AMES, IOWA

NOTES

The AlI_3–HCl–$AlCl_3$–HI System. The Free Energy of Formation of Aluminum Iodide

BY J. D. CORBETT AND N. W. GREGORY

RECEIVED NOVEMBER 23, 1953

A brief study has been made of the equilibrium resulting from the reaction of hydrogen chloride and anhydrous aluminum iodide at 25°. A separate mixed halide phase (intermediate between AlI_3 and $AlCl_3$), analogous to that observed in the hydrogen chloride–aluminum bromide system,[1] was not formed. The equilibrium ratio P_{HI}/P_{HCl} remained essentially constant as the composition of the solid was changed from AlI_3 to nearly pure $AlCl_3$ by successive additions of HCl.

TABLE I

EQUILIBRIUM DATA FOR REACTION OF HCl AND AlI_3 AT 25°

Days equilibration	Mole fraction HI (gas phase)	Mole % AlI_3 (solid phase)
6	0.992	85.5
5	.994	70.8
8	.995	56.9
4	.994	43.1
5	.990	28.9
7	.989	4.5
	0.9925 (average)	

X-Ray powder patterns of aluminum iodide and of three annealed mixtures of aluminum chloride and aluminum iodide (mole per cent. AlI_3, 98.1, 86.6, 5.8) were made to investigate solid solution effects. The spacings of AlI_3 (Table II) changed only slightly in the annealed mixtures, the small shift indicating the presence of less than 1% chloride. The spacings of the chloride phase (annealed mixtures) were not appreciably different from those of pure $AlCl_3$.[1,2]

TABLE II

POWDER PATTERN SPACINGS FOR ALUMINUM IODIDE[3]

d (obs.)	Intensity	d (obs.)	Intensity
3.48	vs	1.402	f
3.05	s	1.390	mf
2.99	m	1.365	vf
2.232	mf	1.343	vf
2.160	mf	1.246	mf
2.134	ms	1.234	mf
1.841	ms	1.177	f
1.811	f	1.170	f
1.753	mf	1.125	mf
1.528	vf	1.073	vf

In view of these results it has been assumed that solid solutions of significant concentrations are not formed in the equilibrium system. The gas composition may then be used to calculate the equilibrium constant and the standard free energy change for the reaction $AlI_3(s) + 3HCl(g) = AlCl_3(s) + 3HI(g)$, $\Delta F° = -8.7 \pm 0.2$ kcal., and, using tabulated values for aluminum chloride and the hydrogen halides,[4] the standard free energy of formation of $AlI_3(s)$ (−74.4 kcal.). The NBS tables give $\Delta F° = -75.0$ kcal. for the latter, apparently based on a heat of formation reported by Klemm and Tanke[5] and an estimated entropy of 48 e.u. Our value, together with heats of formation and other entropies from the NBS tables, leads to an entropy of 46.0.

Previous work on the dissociation of aluminum halide dimers indicates that the bridge in Al_2I_6 is appreciably less stable than that in Al_2Br_6.[6,7]

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[1] J. D. Corbett and N. W. Gregory, THIS JOURNAL, **75**, 5238 (1953).

[2] J. A. A. Ketelaar, C. H. MacGillavry and P. A. Renes, *Rec. trav. chim.*, **66**, 501 (1947).

[3] Spacings previously reported for AlI_3 are less complete, with some disagreement between the two references at d's > 1.5; see J. E. Hanawalt, H. W. Rinn and L. K. Frevel, *Ind. Eng. Chem.*, **10**, 457 (1938); and W. C. Schumb and H. H. Rogers, THIS JOURNAL, **73**, 5806 (1951).

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