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.

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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

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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).

[4] Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, Circ. 500, Series I, Tables 10-2, 59-3, U. S. Gov't Printing Office, Washington, D. C. (1950).

[5] W. Klemm and E. Tanke, *Z. anorg. allgem. Chem.*, **200**, 343 (1931).

[6] W. Fischer and O. Ralphs, *ibid.*, **205**, 1 (1932).

[7] K. K. Kelley, U. S. Bur. Mines Tech. Paper 383, 17 (1935).

This offers a reasonable explanation for the lack of formation of a mixed halide phase of composition $Al_2I_2Cl_4$, corresponding to the $Al_2Br_2Cl_4$ phase found in the bromide–chloride system. The latter appears to have some thermodynamic stability (relative to $AlBr_3$ and $AlCl_3$) but owes most of its inertness toward HCl at 25° to the low reactivity of the bridge halogens.[1]

Experimental Part

The method used to study the exchange equilibrium has been described in an earlier paper.[1] Aluminum iodide (23 g.) (prepared by reaction of resublimed iodine and excess, iron-free aluminum in an evacuated thick-walled glass tube at 300°) was sublimed into the reaction vessel (painted black to minimize photodecomposition of HI), measured volumes of anhydrous HCl added, and the system allowed to equilibrate after each addition for from four to eight days. Only a small amount of hydrogen and iodine was formed during the equilibration. The HCl–HI mixture was purified by fractionation prior to analysis which was effected by measuring the vapor pressure of the liquefied mixture at −45.3°, the melting point of chlorobenzene. The vapor pressures of the pure components at −45.3° were calculated to be 498 mm. (HI)[8] and 4664 mm. (HCl).[9] As the mixtures were nearly pure HI, Raoult's law was used to relate the total vapor pressure to the composition of the mixture.

The composition of the solid at each equilibrium point was determined from the amount of hydrogen halide reacting, and checked at the end of the series of measurements by direct analysis (total halide, Mohr titration; iodine, oxidation of iodide to iodate with hypochlorite solution[1,10]). The AlI_3 was of good quality (>99% AlI_3) and remained white in powder samples of both AlI_3 and the annealed mixtures. The latter were prepared as described for mixtures of $AlBr_3$ and $AlCl_3$.[1]

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(8) J. R. Bates, J. O. Halford and L. C. Anderson, *J. Chem. Phys.*, **3**, 415 (1935).

(9) F. Henning and A. Stock, *Z. Physik*, **4**, 226 (1921).

(10) I. M. Kolthoff and H. Yutzy, *Anal. Chem.*, **9**, 75 (1937).

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Evidence for the Presence of Hydroxylamine as an Intermediate in the Decomposition of Chloramine by Hydroxide

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It has long been known that the reaction of hydroxide with chloramine solutions yields no hydroxylamine but evolves nitrogen in accordance with the equation

$$3NH_2Cl + 3OH^- \longrightarrow NH_3 + N_2 + 3H_2O + 3Cl^-$$

The present author postulated that the initial step in this reaction might indeed be

$$NH_2Cl + OH^- \longrightarrow NH_2OH + Cl^- \qquad (1)$$

but that this step is slow compared to the oxidation of hydroxylamine by chloramine

$$NH_2Cl + 2NH_2OH + OH^- \longrightarrow NH_3 + N_2 + 3H_2O + Cl^- \qquad (2)$$

Addition of these steps gives the previously reported reaction.

The rate of disappearance of chloramine in alkaline solutions was investigated iodometrically. With OH^- concentrations less than 1 *N* the decomposition was somewhat too slow to be conveniently studied. A thorough kinetic study was not attempted, since several trials with concentrated OH^- solutions showed only qualitative reproducibility, and the author was interested primarily in testing the tenability of the hypothesis previously stated. In concentrated sodium hydroxide solution the disappearance of chloramine is at first fairly rapid, but soon slows appreciably. For example, a solution initially $6^2/_3$ *M* in NaOH and 0.0515 *M* in NH_2Cl lost 32% of its oxidizing power in 5 minutes, but in 41 minutes, only 38%. It was suspected that product inhibition might account, at least in part, for this behavior. This explanation was supported by the observation that the addition of ammonia, one of the reaction products, to chloramine solutions markedly depressed the rate of decomposition by hydroxide.

The oxidation of hydroxylamine by chloramine proved much more rapid than the destruction of chloramine by hydroxide, as required by the postulated reaction route. Evolution of gas (assumed to be nitrogen) was observed on mixing 0.1 *M* solutions of hydroxylamine and chloramine, and the odor of ammonia could be detected shortly after mixing. Consumption of reactants agreed with the equation

$$NH_2Cl + 2NH_2OH + OH^- \longrightarrow NH_3 + N_2 + 3H_2O + Cl^-$$

Chloramine concentration was determined iodometrically after the complete destruction of hydroxylamine, as indicated by a very sensitive color test.[1] The reaction went to completion in about ten minutes at 0° in approximately neutral solution. The reaction is accelerated by addition of hydroxide and by increase in temperature. In a mixture 30% saturated with NaOH at 0° the reaction was complete within one half minute. In saturated NaOH solution at 50° the reaction was complete before any measurement could be made.

In an attempt to identify hydroxylamine before it could be oxidized, cold chloramine solution was added dropwise to a mixture of concentrated NaOH solution and cyclohexanone, stirred vigorously and maintained at a temperature in the range 50–90°. Cyclohexanone was chosen as the simplest carbonyl compound not attacked by sodium hydroxide or chloramine. The conditions were chosen in an attempt to increase the rate of formation of hydroxylamine and the rate of oxime formation, while keeping the chloramine concentration low to try to minimize the oxidation of hydroxylamine by chloramine. (Unfortunately the high OH^- concentration and higher temperature both favor the oxidation; however, no oxime was obtained at room temperature or low hydroxide concentration.) The precipitate obtained on cooling the reaction mixture contained the sodium salt of cyclohexanone oxime. On neutralization the oxime was obtained in poor over-all yield and somewhat impure condition (m.p. 86° compared to 89° for carefully purified oxime). Positive identification was obtained by X-ray diffraction analysis; similar results were obtained in several trials.

It was shown that chloramine solution attacks cyclohexanone oxime appreciably at 60° even when present as the solid sodium salt. The oxime may

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(1) A. Angeli, *Ber.*, **29**, 1884 (1896).