

ions the greater the tendency to form colloidal precipitates and the longer the time available for expulsion of strontium ions before crystallization. Accordingly, when all other conditions are the same, an increase in concentration tends to favor calcite formation rather than aragonite, as was found when 1 molar solutions were mixed.

Thus far only the first two stages have been discussed—the formation of aggregates and the orientation or first crystallization. The work of de Keyser and Dugeldre⁴ was concerned only with these first two steps, but extensive changes from aragonite to calcite can take place by further contact with the solution from which the precipitates were formed. The transformation of the solid aragonite to solid calcite all in the same crystal is an exceedingly slow process at room temperature, but if these crystals are in contact with water, the more soluble aragonite goes into solution and recrystallizes as the less soluble calcite. Moreover, the redissolved calcium carbonate produced by the solution of the aragonite brings its strontium into solution where it is diluted so that it is less likely to produce aragonite.

Spectrographic analyses showed a higher per cent. of strontium (80 p.p.m.) in the 70% aragonite precipitated at 45° (Fig. 1) than in the recrystallized calcite (25 p.p.m. strontium) after 10 hours of standing in the solution.

The removal of strontium ions from aragonite which is undergoing recrystallization is believed responsible for the formation of calcite. This hypothesis was confirmed with additional experiments. Pure aragonite precipitated at 50° and its surrounding solution was divided equally and placed in two separate flasks and maintained at 50°. To one of these was added 100 ml. of 0.1

M $Sr(NO_3)_2$. In this flask there was no trace of calcite formation after 20 hours, whereas in the flask to which strontium nitrate had not been added, about 50% of the aragonite had changed to calcite in the same period of time.

The fact that similar results were obtained with calcium nitrate of two different manufacturers probably indicates that after a certain minimum concentration of strontium and other critical impurities are reached, higher concentrations have but little further effect.

At first sight, it would be expected that the recrystallization from aragonite to calcite would go faster at high temperatures, but an examination of Fig. 1 shows that at 40° the 95% calcite changes to 100% calcite in half an hour, at 45° it changes from 30 to 100% in about 10 hours, and at 50° it changes only from zero to about 35% in 18 hours. The number of calcite crystals to act as nuclei for further growth is much less in the precipitates formed at the higher temperatures. The slowness to go from aragonite to calcite at the higher temperatures is thus explained as due to the relative absence of calcite seed crystals. This hypothesis was checked by taking out a precipitate of 50% aragonite and 50% calcite slowly changing at 45°. When this precipitate in its solution was heated to 70° the change to calcite was complete in two hours, whereas at 45° it required ten hours. If sufficient seed crystals are present, the higher temperature does give a faster rate of transformation to the stable calcite, as would be expected.

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

Equilibrium Ultracentrifugations of Acidic Hg(I), Hg(II), In(III), and Au(III) Solutions¹

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Equilibrium ultracentrifugations confirm that In(III) in HBr and Au(III) in HCl exist as mononuclear complexes. The results contradict recent suggestions based on solvent extraction data that dimers of In(III) and Au(III) exist in the aqueous phase. The method was checked by comparing apparent molecular weights of Hg(I) and Hg(II) in nitrate solutions.

In recent years the extractability of several metal ions from aqueous into organic phases has been reported to increase with decreasing concentration of the metal. For example, from 3.7 M HCl, the extraction coefficient of Ga(III) into bis-2-chloroethyl ether increases manyfold as the aqueous Ga(III) concentration is decreased from 10^{-2} M to 10^{-8} M .² Similar changes in extractability have been observed for Au(III) in HCl, In(III) in HBr and Tl(III) in HCl.³ It has been

suggested² that such results could be explained by the formation of unextractable dimers of the metal ion species in the aqueous phase at the higher metal concentrations, but alternate explanations have also been advanced.⁴⁻⁶ Recently Irving and Rossotti have attributed this change in extractability for In(III) from HBr solutions to dimerization.⁷

We have attempted to decide between alternate explanations by molecular weight measurements with the equilibrium ultracentrifuge.

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

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(3) J. W. Irvine, Jr., R. J. Dietz, L. C. Bogar, G. S. Golden and R. H. Herber, in Progress Report, Laboratory for Nuclear Science, Massachusetts Institute of Technology, May, 1954, AECU 2943, p. 18.

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(5) J. Saldick, *J. Phys. Chem.*, **60**, 500 (1956).

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(7) H. Irving and F. J. C. Rossotti, *J. Chem. Soc.*, 1938 (1955).

Experimental

Centrifugation techniques have been described earlier.^{8,9} All centrifugations were carried out in an excess of supporting electrolyte to diminish the effect of charge. Equilibrium temperatures were $30 \pm 2^\circ$ in all cases. Density measurements were made with a pycnometer. Bromide analysis of InBr_3 , kindly supplied us by Dr. J. W. Irvine, Jr., indicated 67.2% Br (theoretical 67.6%). Merck reagent grade $\text{AuCl}_3 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ was used; chloride and gold analysis indicated an empirical formula $\text{HAuCl}_4 \cdot 3.3\text{H}_2\text{O}$. Reagent grades of Hg(I) and Hg(II) nitrates were employed, and the compositions established by mercury and nitrate analyses. All other chemicals were also reagent grade.

Results and Discussion

The optical system of the centrifuge measures the refractive index gradients (dn/dx) as a function of the radius, x . The gradients displace the shadow of an inclined bar, and the results are in terms of a displacement, Z^* (corrected for background) assumed proportional to the concentration gradient dc/dx for the solute of interest.⁹ For all experiments, the values of $\ln(Z^*/x)$ at equilibrium were plotted against x^2 , and the slopes, S_e , of the curves at the average radius of the cell obtained. These values of S_e and the experimental conditions are summarized in Table I.

TABLE I
ULTRACENTRIFUGATION OF HgNO_3 , $\text{Hg}(\text{NO}_3)_2$, HAuCl_4 , AND InBr_3 SOLUTIONS NEAR 30°

Solute and formula wt.	Concn. (M)	Supporting electrolyte	S_e	M_e	Conditions ^a
HgNO_3 (262.6)	0.035	0.1 M HNO_3	0.0705	505	D-2
$\text{Hg}(\text{NO}_3)_2$ (324.6)	.116	1.9 M NaNO_3	.0689	495	G-2
	.042	2 M HNO_3	.0435	315	C-2
	.103		.0403	295	F-2
InBr_3 (354.5)	.023		.0313	300	B-1
	.049	2 M HBr	.0269	260	A-1
	.093		.0256	245	E-1
HAuCl_4 (340.0)	.056	3 M HCl	.0394	330	A-2

^a Bar angle: A, 35° ; B, 40° ; C, 45° ; D, 50° ; E, 55° ; F, 60° ; G, 65° . Approximate speed of rotation (r.p.m.): (1) 24,600; (2) 27,670.

For an ideal solution of an uncharged, mono-disperse solute, a straight line should be obtained, *i.e.*, S_e constant. Further, $S_e = d \ln(Z^*/x) / d(x^2)$ would also equal $d \ln c_2 / d(x^2)$, where c_2 is the concentration of the solute of interest. For all experiments reported here, S_e was essentially constant. (See Fig. 1, a deviation plot of $\log(Z^*/x) - (S_e/2.303)x^2$ vs. x^2 .) From the values of S_e , apparent molecular weights, M_e , defined by the equation

$$M_e = \frac{2RT}{(1 - \bar{v}_2\rho)\omega^2} S_e \quad (1)$$

were computed (Table I). In this expression, R is the gas constant; T , the absolute temperature; \bar{v}_2 , the partial specific volume of the solute of interest; ρ , the solution density; and ω , the angular velocity. The term "apparent molecular weight" is used because zero charge (*i.e.*, the solute is not dissociated into ions) is assumed in the derivation of equation 1. Ignoring charge leads to values of M_e which are lower limits of the actual molecu-

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

(9) J. S. Johnson, K. A. Kraus and R. W. Holmberg, *ibid.*, **78**, 26 (1956).

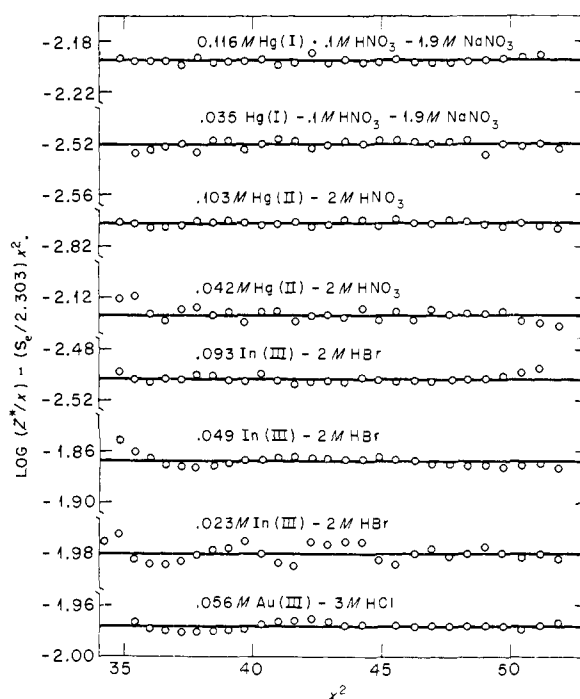


Fig. 1.—Test of constancy of S_e .

lar weights.¹⁰ In principle, it is possible to estimate the charge or, conversely, the average degree of complexing by anions, from the decrease of S_e with concentration in one or more equilibrium centrifugations. We do not feel that the present data are accurate enough for such a detailed analysis, even if other necessary assumptions could be made. For the experiments reported here, however, estimates of the charge indicate that in no cases is it large enough to lead to confusion between monomeric and dimeric species.

Equation 1 requires the partial specific volume of the solute in question. Density values for solutions of all these compounds are in the literature.¹¹ Extreme accuracy is not required for present purposes, since the quantity $(1 - \bar{v}_2\rho)$ does not differ greatly from unity. However, the literature values are rather old, and, in the case of the mercury compounds, the density measurements indicate the rather surprising result that the molar volume of HgNO_3 is greater than that of $\text{Hg}(\text{NO}_3)_2$. We have, therefore, made a few measurements of apparent molal volumes, ϕ_v , of these salts (Table II). Our results agree fairly well with those computed from literature values of solution densities for InBr_3 (*ca.* 60 cc./mole in water^{11c}), and HgNO_3 (*ca.* 39 cc./mole^{11b}), but disagree rather strongly with those for HAuCl_4 (*ca.* 126 cc./mole^{11a}), and $\text{Hg}(\text{NO}_3)_2$ (*ca.* 35 cc./mole^{11b}).

In the computation of molecular weights we have used for \bar{v}_2 the apparent specific volumes measured under conditions closest to those of the centrifugations (Table II). Differences between

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

(11) (a) $\text{Au}(\text{III})$: J. Traube, *Z. anorg. Chem.*, **8**, 12 (1895); (b) $\text{Hg}(\text{I})$ and $\text{Hg}(\text{II})$: P.-Th. Muller and E. Carrière, *Compt. rend.*, **154**, 695 (1912); (c) $\text{In}(\text{III})$: A. Heydweiller, *Z. anorg. Chem.*, **88**, 103 (1914).

TABLE II
 APPARENT MOLAL VOLUMES

Solute	Concn. (% by wt.)	Medium	ϕ_v	Apparent specific vol.
HgNO ₃	4.87	1 M HNO ₃	35.5	0.135
	4.35	2 M HNO ₃	36.5	.14 ^a
Hg(NO ₃) ₂	4.57	0.1 M HNO ₃	46	.14
	4.51	1 M HNO ₃	50	.155
	4.62	2 M HNO ₃	53	.165 ^a
InBr ₃	1.54	2 M HBr	63	.18 ^a
HAuCl ₄	7.90	H ₂ O	91	.27
	3.46	3 M HCl	91	.27 ^a

^a These values were used for \bar{v}_2 in computation of M_e .

the measured apparent volumes and the partial volumes required by equation 1, as well as errors stemming from uncertainties in the analyses of the salts (about 3 cc. in ϕ_v), are not expected to be important for present purposes. In cases where the salt used in preparing solutions for density measurements was a hydrate, the measured values of ϕ_v were corrected to the formula listed in Table II by subtracting 18 cc. per mole water of hydration.

1. Hg(I) and Hg(II) in Nitrate Solution.—From our previous results^{8,9} there seemed no reason to doubt that a clear distinction could be made between monomeric and dimeric species of the ions in question by equilibrium ultracentrifugation. Nevertheless, it appeared advisable to test this on a known system of a similar type. Nitrate solutions of Hg(I) and Hg(II) were selected. Hg(I) is known to form dimers in solution, and Hg(II) is generally considered to be monomeric. The experiments were carried out in 2 M nitrate, and acidities selected to preclude interference from hydrolysis.¹² For 0.116 M Hg(I) in 0.1 M HNO₃–1.9 M NaNO₃ the apparent molecular weight computed by equation 1 is 495; for an initial concentration of 0.035 M Hg(I) in the same supporting electrolyte, 505 is obtained. These may be compared with 525, the formula weight for (HgNO₃)₂. The experimental values are not much different from each other, nor much lower than the theoretical value for the dimer; *i.e.*, there is little interference from a charge effect.

For 0.103 M Hg(II) in 2 M HNO₃ we find $M_e = 295$; for 0.042 M Hg(II) the value is 315. The formula weight of Hg(NO₃)₂ is 325. The method thus definitely distinguishes between a monomeric Hg(II) and a dimeric Hg(I) species of mercury.

2. In(III) in HBr.—The solvent extraction measurements of Irving and Rossotti,⁷ which indicated dimerization of In(III) in aqueous bromide solutions, were carried out with 1M HBr solutions. For the centrifugations, 2M HBr solutions were used. With the stability constants reported for In(III) bromide complexes¹³ and with constants for dimerization given by Irving and

Rossotti,⁷ one concludes that most of the In(III) should be dimerized even at the lowest In(III) concentrations encountered in the centrifugations.

Centrifugations were carried out at initial In(III) concentrations 0.023, 0.049 and 0.093 M. The values of M_e obtained were 300, 260 and 245, respectively. Comparison with the formula weight of InBr₃, 355, indicates that no appreciable fraction of the indium is dimeric under these conditions. The substantial decrease of M_e with increasing In(III) concentration, and the lowness of all values with relation to the formula weight suggest that the average number of bromide ions complexed by In(III) is not as great as estimated by Irving and Rossotti.^{13b} More accurate results are required, however, before the charge of such complexes can be determined with confidence.

3. Au(III) in HCl.—A single centrifugation of Au(III) in 3M HCl was carried out at an initial gold concentration of 0.056M. The observed value of M_e was 330; the formula weight of HAuCl₄ is 340, *i.e.*, Au(III) is not dimerized in these solutions.

4. General Discussion.—The results of the equilibrium ultracentrifugations leave little doubt that both the In(III) bromide and Au(III) chloride complexes are monomeric (mononuclear) under conditions where anomalies in solvent extraction data have been interpreted in terms of formation of dimeric complexes in the aqueous phase. The explanation for the non-constancy of the extraction coefficients (increase with decreasing metal concentration) for these and similar complex salts must, therefore, be sought in the properties of the organic phase, *i.e.*, in a decrease of the stoichiometric activity coefficients γ_0 of the distributing components (*e.g.*, HAuCl₄ or HInBr₄) in the organic phase. This could result from various dissociation reactions as, for example, proposed by Saldick.⁵

The low concentration extraction anomaly which gave rise to this study limits the region where solvent extraction substantially follows Nernst's law (concentration independence of extraction coefficients) in much the same way that a similar anomaly limits it, at least for some systems, at high metal concentrations.¹⁴ In these cases, extractability increases with metal concentration. There is apparently now general agreement that the deviations from Nernst's law at high concentrations also stem from a decrease of the stoichiometric activity coefficients γ_0 in the organic phase¹⁵ (polymerization in the organic phase), though for a short time variations of the activity coefficients in the aqueous phase had been held responsible.¹⁶

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(14) See, *e.g.*, R. W. Dodson, G. J. Forney and E. H. Swift, *THIS JOURNAL*, **58**, 2573 (1936).

(15) See, *e.g.*, R. J. Meyers, D. E. Metzler and E. H. Swift, *ibid.*, **72**, 3767 (1950); N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **74**, 897 (1952).

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