

relationship.⁸ It is seen from Table II that these force constants have large values beyond expectation. The frequencies calculated on the basis of these force constants are shown in Table I. For Li_4UO_5 , the addition of the interaction force constant f to the modified force field gives the best agreement between the observed and calculated frequencies. Furthermore, the band broadening at near 590 cm^{-1} can be well explained by the appearance of the A_{2u} (624 cm^{-1}) vibration mode (Figure 3) caused by the $\text{Li}\cdots\text{O}$ interaction. On the other hand, for Na_4UO_5 , the agreement between observed and calculated frequencies is exact except for one (260 cm^{-1}) of the A_{2u} lattice vibrations. As in the case of Li_4UO_5 , the band broadening at near 410 cm^{-1} can also be well ex-

plained by the appearance of the A_{2u} (465 cm^{-1}) vibration mode (Figure 3) caused by the $\text{Na}\cdots\text{O}$ interaction.

The correlation between the U-O stretching force constants and the bond distances is satisfactory in comparison with other available data^{9,10} and with the results derived from Badger's relationship modified by Jones⁵ and other investigators.^{11,12}

It is concluded from the above treatments that the two models used here are useful not only for the interpretation of the absorption spectra of the Li_4UO_5 and Na_4UO_5 crystals but also for obtaining information on the approximate crystalline force field of such crystals.

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Mercury Species in Chloroaluminate Melts. Characterization of the New Ion Hg_3^{2+} 1a

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A new ion, Hg_3^{2+} , has been obtained in acidic chloroaluminate melts (mole ratio $\text{AlCl}_3:\text{MCl} > 1$, where M is an alkali metal) by the oxidation of mercury metal, present in excess, or by the partial reduction of Hg_2^{2+} . Hg_3^{2+} has been characterized by absorption spectra, stoichiometric measurements in AlCl_3 , and electrochemistry. The Raman spectrum of the yellow polycrystalline compound $\text{Hg}_3(\text{AlCl}_4)_2$ has been obtained and explained on the basis of the slightly bent Cl-Hg-Hg-Hg-Cl chain joined to two AlCl_3 groups. Equilibrium constants for the reactions $\text{Hg}_2^{2+} + \text{Hg}_3^{2+} = 2\text{Hg}_2^{2+}$ and $\text{Hg}_2^{2+} + \text{Hg} = \text{Hg}_3^{2+}$ are reported for several melt compositions and temperatures.

Introduction

We have previously reported² evidence for the existence of a new ion Hg_3^{2+} in acidic chloroaluminate melts (mole ratio $\text{AlCl}_3:\text{MCl} > 1$ where M is an alkali metal).³ In this paper, the characterization of Hg_3^{2+} by spectral and thermodynamic data is reported.

The electrochemistry of mercury in a ternary eutectic $\text{AlCl}_3\text{-NaCl-KCl}$ (66:20:14 mol %) has been previously investigated.⁴⁻⁶ Gut⁵ showed a polarogram indicative of an intermediate oxidation state between Hg_2^{2+} and Hg; however, no attempt was made to explain this result. Hames and Plambeck⁶ concluded from polarographic and potentiometric measurements that Hg_2^{2+} is reduced in a conventional manner to Hg_2^{2+} and Hg. Although no electrochemical work on mercury in the melts employed in this study ($\text{AlCl}_3\text{-NaCl}$, AlCl_3 varied from approximately 50 to approximately 70 mol %) has been previously reported, there is no significant difference in the nature of the binary melts used in this study and the ternary melts employed previously.⁴⁻⁶

The absorption spectra of soluble mercury species in

chloroaluminates have not been reported by other workers. Colored solutions were observed by Yosim and Mayer⁷ in their studies of the $\text{HgCl}_2\text{-Hg}$ system; the formation of colors was not attributed to a new species.

Experimental Section

The $\text{AlCl}_3\text{-NaCl}$ melt was prepared from optical grade NaCl (Harshaw Chemical Co.) and AlCl_3 ("anhydrous and free from iron," from Fluka AG). NaCl was heated at approximately 400° under vacuum for several hours prior to use. The desired quantities of NaCl and AlCl_3 were weighed, placed in a quartz tube with pieces of aluminum wire (m5N grade from Alfa Inorganics), sealed under vacuum, and digested for several days at approximately 300° . After the impurities had settled, the water-clear melt was cooled slowly, frozen, and stored in a drybox (typical moisture level < 2 ppm). In experiments requiring the use of AlCl_3 only, AlCl_3 , prepared in the laboratory of G. P. Smith at the Oak Ridge National Laboratory using the materials and the procedure previously described,⁸ was employed.

HgCl_2 and Hg_2Cl_2 were prepared by sublimation of AR grade materials at approximately 10^{-2} Torr. Sealed, evacuated Pyrex cells were employed for electrochemical measurements. The electrode connections were made with tungsten wire sealed in uranium glass to Pyrex. The reference electrode was an aluminum wire⁹ immersed in the melt separated from the main compartment by a thin Pyrex membrane. The melt in the reference electrode compartment was either of the same composition as that in the main compartment or the melt in the reference electrode compartment was saturated with NaCl. The latter composition was employed for work at higher temperatures. Be-

(1) (a) Research sponsored by the U. S. Atomic Energy Commission under Contract AT-(40-1)-3518 and under contract with the Union Carbide Corporation. (b) University of Tennessee. (c) On leave, University of Bari, Bari, Italy. (d) Oak Ridge National Laboratory.

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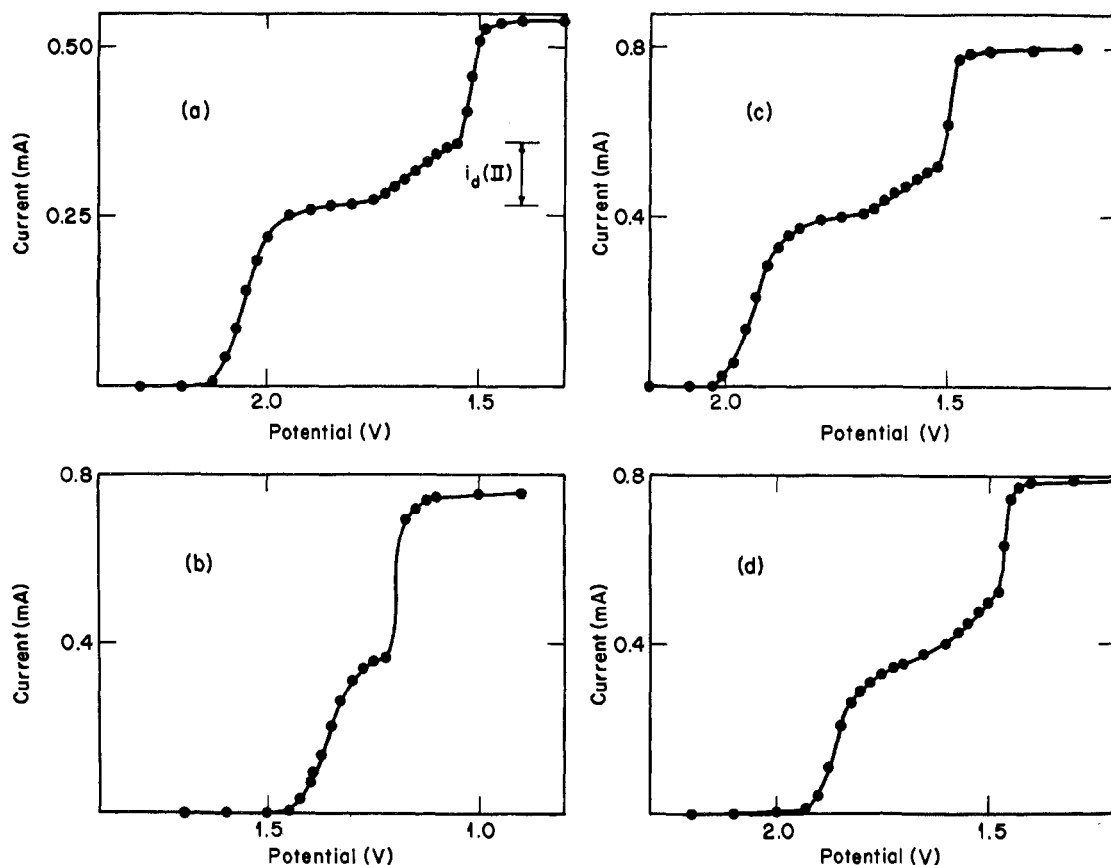


Figure 1.—Polarograms for the reduction of Hg^{2+} in molten $\text{AlCl}_3\text{-NaCl}$, constructed from current-time curves at a platinum electrode; temperature 175° ; current measured at 5 sec; electrode area $\sim 0.1 \text{ cm}^2$; Al(III)-Al reference electrode (NaCl -saturated melt): (a) melt saturated with AlCl_3 , $2.3 \times 10^{-2} M \text{ HgCl}_2$; (b) melt saturated with NaCl , $3.0 \times 10^{-2} M \text{ HgCl}_2$; (c) $\text{AlCl}_3\text{-NaCl}$ (65:35 mol %), $3.4 \times 10^{-2} M \text{ HgCl}_2$; (d) $\text{AlCl}_3\text{-NaCl}$ (52:48 mol %), $3.0 \times 10^{-2} M \text{ HgCl}_2$.

cause of the relatively high resistance of the Pyrex membrane, a platinum quasireference electrode⁹ was used in measurements involving the controlled-potential, controlled-current cyclic voltammeter.¹⁰ The potential of the quasireference electrode was checked before and after each run; this potential was constant to $\pm 0.01 \text{ V}$. The use of this arrangement is advantageous in a long experiment to avoid mixing of the solutions in the two compartments. The indicator electrodes were platinum and gold wires, 0.5 mm in diameter, and a pyrolytic graphite rod, 1 mm in diameter, immersed directly in the melt. A large-area platinum electrode was used as the counter electrode.

The cells were cleaned with chromic acid cleaning solution, washed with distilled water, flamed under reduced pressure, loaded in a drybox, closed with vacuum-tight fittings, evacuated to 10^{-2} Torr for about 1 hr using a liquid nitrogen trap between the pump and the rest of the system, gently heated (carefully preventing sublimation of AlCl_3), and then sealed. Additions were made in the drybox. After each addition the cell was evacuated and resealed. This procedure was checked and shown not to introduce impurities in measurable quantities.

Voltammograms, chronopotentiograms, and current-time curves were obtained with a controlled-potential, controlled-current cyclic voltammeter.¹⁰ The potentials were measured with a Model 895A dc differential voltmeter (John Fluke Mfg. Co., Inc.). The curves were recorded with a Moseley 2D-2A X-Y recorder or a Type 549 Tektronix storage oscilloscope with a Polaroid camera. The polarograms were constructed from current-time curves obtained by stepping the potential from a value at which no electrochemical reaction was taking place to some chosen value. This procedure has been employed previously.¹¹ The temperature was controlled to $\pm 2^\circ$ using an air thermostat.

The chemical analyses of $\text{Hg}_2(\text{AlCl}_4)_2$ (see below) were per-

formed as follows. Aluminum was determined by emission spectroscopy (Stewart Laboratories, Knoxville, Tenn.) after dissolving the compound in concentrated nitric acid. For the determination of mercury and chlorine, the compound was fused with sodium carbonate, and the resulting solid was extracted with water. Chlorine was determined gravimetrically as silver chloride after acidifying the solution with nitric acid.¹² The water-insoluble residue was boiled with concentrated nitric acid, and mercury in the solution was determined by the Volhard method.^{12,13}

The spectrophotometric measurements were made in 1-cm quartz cells, using spacers wherever convenient. These measurements were done at Oak Ridge National Laboratory using the high-temperature spectrophotometric apparatus of Smith and coworkers.¹⁴

A Cary Model 81 monochromator, coupled with a cooled 9558 EMI photon multiplier tube and a photon-counting system, was used to record the Raman spectrum of the yellow polycrystalline solid (see Results and Discussion). Observations were made using both the 514.5-nm laser line from a Spectra-Physics Model 141 argon ion laser and the 632.8-nm line from a Spectra-Physics Model 125 helium-neon laser. The samples were illuminated by placing them in their original Pyrex glass containers in the laser beam. The Raman light was collected at right angles to the laser beam. Appropriate spike filters were employed to eliminate the background plasma lines from the Raman spectrum. Several attempts were made to obtain the spectrum of the molten compound or of the compound dissolved in $\text{AlCl}_3\text{-NaCl}$ melts. Melting of the yellow compound, however, gave a reddish brown liquid (see below) which did not give a satisfactory Raman spectrum.

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Results and Discussion

Stoichiometry in AlCl_3 .—Additions of mercury, HgCl_2 , or Hg_2Cl_2 to pure AlCl_3 at 200–250° do not result in colored solutions. However, either Hg_2Cl_2 or HgCl_2 in AlCl_3 at 200–250° reacts with mercury to produce a reddish brown liquid. The ratio of the reactants was obtained by mixing excess amounts of AlCl_3 and mercury with a known weight of HgCl_2 . The mixture was sealed under vacuum and heated at 240°. After the reaction (36 hr) the excess AlCl_3 and mercury were distilled off and condensed in one end of the tube which was at 100°. A yellow solid was obtained by cooling the liquid slowly. The excess AlCl_3 and mercury were weighed. The resulting mole ratio of HgCl_2 : Hg : AlCl_3 was 1:1.98:2.08 (two experiments). The mole ratio of Hg : Hg_2Cl_2 , determined similarly, was 1.07 (three experiments). A more accurate stoichiometry was obtained by the chemical analysis of the yellow crystals that were obtained as described below. Exact amounts of HgCl_2 , Hg , and AlCl_3 (1:2:2) were mixed and heated at 240° for about 6 days (for complete reaction). The temperature was then decreased gradually below the melting point (203–205°), usually to 150° for complete solidification (apparently supercooling occurs). The temperature was then raised, and a thermal gradient was set up in the tube. One end of the tube was kept at $\sim 210^\circ$ (above the melting point); the other, at $\sim 195^\circ$. After 3–4 days, long yellow needles were obtained in the cool zone. The chemical analysis of yellow needles corresponds to $\text{Hg}_3(\text{AlCl}_4)_2$. Calcd: Hg, 64.07; Al, 5.73; Cl, 30.20. Found: Hg, 63.7; Al, 5.9; Cl, 30.1. The compound is very sensitive to moisture and decomposes in water to give mercury metal and Hg_2Cl_2 .

Electrochemical Measurements.—Polarograms for the reduction of Hg^{2+} as a function of melt composition at 175° and as a function of temperature for the AlCl_3 – NaCl (65:35 mol %) melt are shown in Figures 1 and 2, respectively. The presence of three waves, particularly in more acidic melts and at lower temperatures (Figures 1a and c, Figure 2a) should be noted. In the melt saturated with NaCl only two waves of equal height were obtained (Figure 1b). Similar results were obtained with gold and pyrolytic graphite working electrodes. The diffusion currents for the three waves are in the ratio 3:1:2 for all concentrations studied (see Table I). The measurement of the diffusion current

TABLE I^a
DEPENDENCE OF THE DIFFUSION CURRENTS
ON THE CONCENTRATION OF Hg^{2+}

$10^2[\text{Hg}^{2+}]$, <i>M</i>	$i_d(\text{I})$, mA	$i_d(\text{II})$, mA	$i_d(\text{III})$, mA
0.4	0.05	0.015	0.035
2.3	0.27	0.09	0.18
3.17	0.43	0.14	0.29

^a Platinum electrode area ~ 0.1 cm²; current measured at 5 sec; temperature 175°; melt saturated with AlCl_3 .

for the second wave is illustrated in Figure 1a. The simplest reaction scheme that is in agreement with the diffusion data is

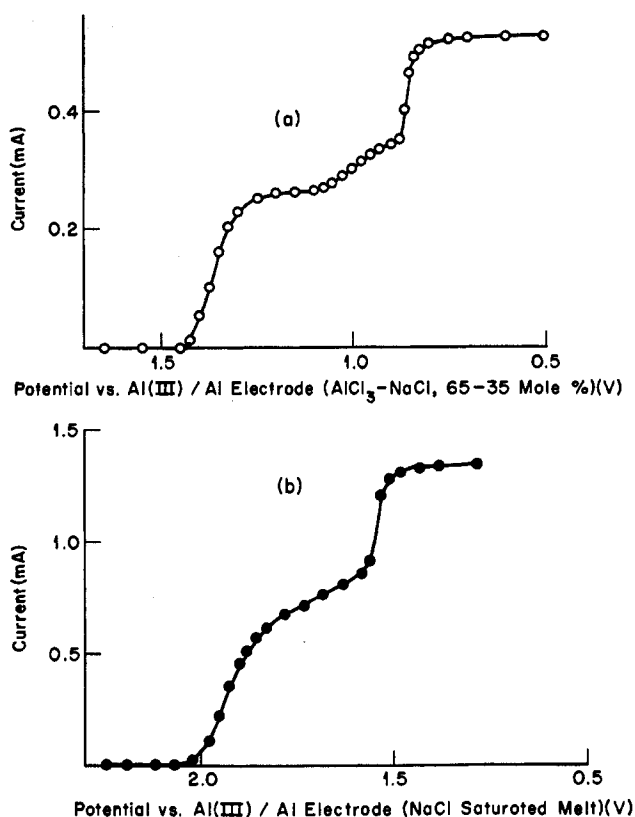
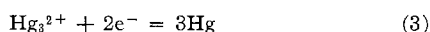
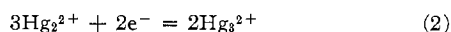
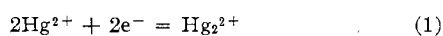


Figure 2.—Polarograms for the reduction of Hg^{2+} in molten AlCl_3 – NaCl , constructed from current–time curves at a platinum electrode; AlCl_3 – NaCl (65:35 mol %); current measured at 5 sec; electrode area ~ 0.1 cm²: (a) 125°, 3.5×10^{-2} M HgCl_2 ; (b) 250°, 3.3×10^{-2} M HgCl_2 .

The formation of Hg_3^{2+} is in agreement with the stoichiometry of the yellow compound $\text{Hg}_3(\text{AlCl}_4)_2$. Logarithmic plots [for reaction 1, $\log(i/(i_d - i)^2)$ vs. E ; for reaction 2, $\log(i^2/(i_d - i)^3)$ vs. E]¹⁵ yield straight lines (Figure 3) with the slopes predicted for $n = 2$.

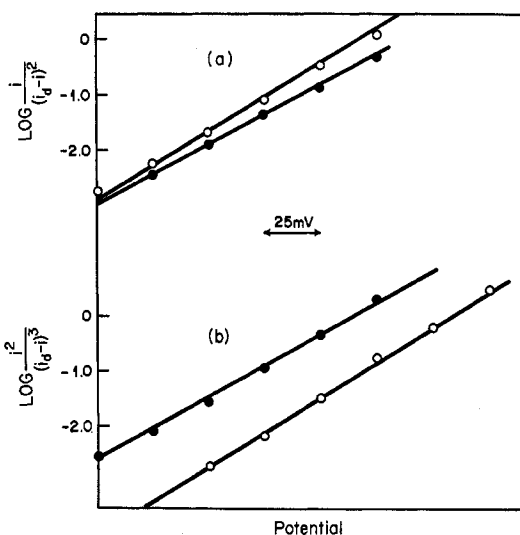


Figure 3.—Logarithmic plots: (a) first wave; (b) second wave. Open circles are points from the polarogram of Figure 2a. Black circles are points from the polarogram of Figure 1a. The lines were drawn with the theoretical slopes.

(15) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience, New York, N. Y., 1952, p 233.

Alternative reaction schemes for the second wave, such as $2\text{Hg}_2^{2+} + 2e^- = \text{Hg}_4^{2+}$ or $3\text{Hg}_2^{2+} + 2e^- = \text{Hg}_6^{4+}$, resulted in poor linearity of logarithmic plots or a value of n quite different from what would be expected from the electrode reactions. In addition, for the reaction $2\text{Hg}_2^{2+} + 2e^- = \text{Hg}_4^{2+}$ the diffusion current for the second wave would be expected to be half that of the first wave, instead of the experimentally found one-third value. For the third wave, the experimental points for the logarithmic plot of $\log(i_d - i)$ vs. E ¹⁵ were somewhat scattered from the line corresponding to the slope for $n = 2$. These results are probably due to the varying activity of mercury on the electrode surface.¹⁶

The reduction of Hg_2^{2+} was also investigated by linear-sweep voltammetry and chronopotentiometry. A linear-sweep voltammogram for reactions 1 and 2 is shown in Figure 4. Similar results are obtained with gold

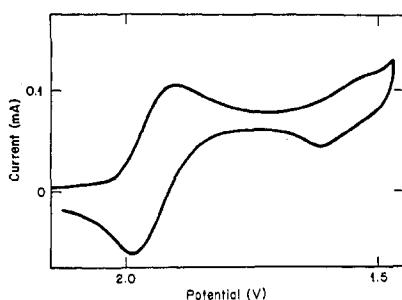


Figure 4.—Linear-sweep voltammogram for the reduction of Hg_2^{2+} in molten $\text{AlCl}_3\text{-NaCl}$ (65:35 mol %); $[\text{HgCl}_2] = 1.5 \times 10^{-2} M$; temperature 175° ; Pt working electrode, area $\sim 0.1 \text{ cm}^2$; Al(III)-Al reference electrode (NaCl-saturated melt); scan rate 0.02 V/sec .

and pyrolytic graphite electrodes. For the first wave the difference between cathodic and anodic peak potentials, as well as the difference between peak and half-peak potentials, is in agreement with theoretical predictions for a second-order reversible electrode reaction.¹⁷ The theory has not been worked out for the case corresponding to reaction 2 for linear-sweep voltammetry. The chronopotentiometric transition times for reaction 2 were too poorly defined (because of close proximity of reduction potentials for reactions 2 and 3) to apply the criteria developed by Reinmuth.¹⁸

The Nernst expressions corresponding to electrode reactions 1-3 are

$$E = E_1^\circ + \frac{RT}{2F} \ln \{[\text{Hg}^{2+}]^2/[\text{Hg}_2^{2+}]\}$$

$$E = E_2^\circ + \frac{RT}{2F} \ln \{[\text{Hg}_2^{2+}]^3/[\text{Hg}_3^{2+}]^2\}$$

$$E = E_3^\circ + \frac{RT}{2F} \ln [\text{Hg}_3^{2+}]$$

where the concentrations are expressed as molarities. The densities were taken from ref 19. Using polarographic half-wave potentials and known initial concentrations and assuming that the diffusion coefficients of the soluble mercury species are the same, one may estimate the standard potentials for reactions 1-3. These potentials are shown in Table II for the melt composi-

TABLE II
Standard Potentials for Electrode Reactions 1-3 at Different Temperatures vs. Al(III)-Al Reference Electrode^a

Temp, °C	E_1° , V	E_2° , V	E_3° , V
125	1.42	1.06	0.96
175	2.02	1.69	1.60
250	2.01	1.72	1.67

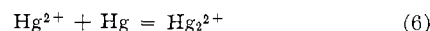
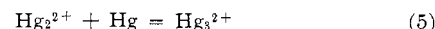
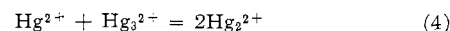
Standard Potentials for Different Melt Compositions at 175° vs. Al(III)-Al Reference Electrode (Melt Saturated with NaCl)

Melt compn	E_1° , V	E_2° , V	E_3° , V
Satd with NaCl	1.43		1.30 ^b
$\text{AlCl}_3\text{-NaCl}$, 52:48 mol %	1.91	1.65	1.55
$\text{AlCl}_3\text{-NaCl}$, 65:35 mol %	2.02	1.69	1.60
Satd with AlCl_3	2.12	1.73	1.62

^a Reference electrode composition: at 125° , $\text{AlCl}_3\text{-NaCl}$, 65:35 mol %; at 175 and 250° , melt saturated with NaCl. Solvent melt composition: $\text{AlCl}_3\text{-NaCl}$, 65:35 mol %. ^b For the reaction $\text{Hg}_2^{2+} + 2e^- = 2\text{Hg}$.

tion $\text{AlCl}_3\text{-NaCl}$ (65:35 mol %) at three temperatures as well as for different melt compositions at 175° . The standard potentials at 175° for reactions 1 and 2 were confirmed by a potentiometric titration (platinum and gold indicator electrodes and the same reference electrode as employed in polarographic measurements) of $0.08 M \text{Hg}_2^{2+}$ with mercury metal.

The standard potentials in Table II were used to calculate the constants for the reactions



where the constants are given by

$$K_4 = \frac{[\text{Hg}_2^{2+}]^2}{[\text{Hg}^{2+}][\text{Hg}_3^{2+}]}$$

$$K_5 = \frac{[\text{Hg}_3^{2+}]}{[\text{Hg}_2^{2+}]}$$

$$K_6 = \frac{[\text{Hg}_2^{2+}]}{[\text{Hg}^{2+}]} = K_4 K_5$$

These constants at different temperatures and melt compositions are given in Table III. It may be noted

TABLE III
Dependence of the Equilibrium Constants on Melt Composition at 175°

Melt compn	K_4	K_5	K_6
Satd with NaCl	30
$\text{AlCl}_3\text{-NaCl}$, 52:48 mol %	8×10^2	5	4×10^3
$\text{AlCl}_3\text{-NaCl}$, 65:35 mol %	4.5×10^3	5	2.2×10^4
Satd with AlCl_3	2×10^4	7	1.4×10^5

Dependence of the Equilibrium Constants on Temperature (Melt Composition $\text{AlCl}_3\text{-NaCl}$, 65:35 mol %)

Temp, °C	K_4	K_5	K_6
125	3×10^4	7	2.1×10^5
175	4.5×10^3	5	2.2×10^4
250	5×10^2	3	1.5×10^3

that the species Hg_3^{2+} becomes more stable at lower temperatures and AlCl_3 -rich melts.

Spectrophotometric Measurements.—The $\text{AlCl}_3\text{-NaCl}$ (65:35 mol %) melt has a spectral cutoff (absorbance >1 for a 1-cm cell) at approximately 230 nm. The spectrum of mercury metal (present in excess) in

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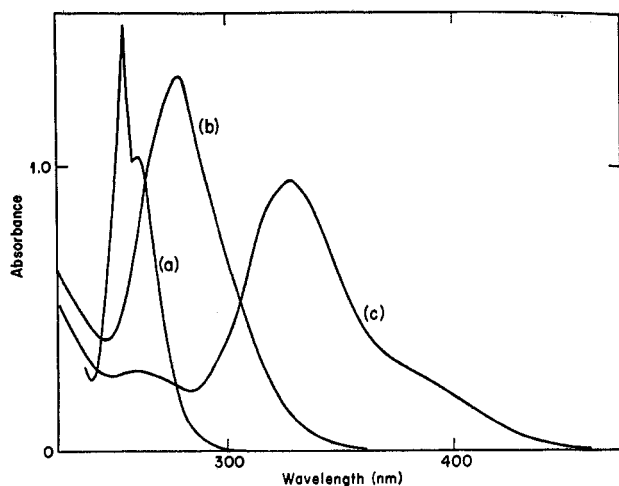


Figure 5.—Absorption spectra of Hg, Hg_2^{2+} , and Hg_3^{2+} in molten AlCl_3 - NaCl (65:35 mol %) at 175° : (a) melt saturated with Hg metal; cell thickness 1 cm; (b) $[\text{Hg}_2\text{Cl}_2] \approx 2 \times 10^{-2} M$; cell thickness $\sim 10^{-2}$ cm; (c) $[\text{Hg}_3\text{Cl}_2] \approx 10^{-2} M$; melt saturated with mercury; cell thickness $\sim 10^{-2}$ cm.

this solvent is shown in Figure 5a. This spectrum is similar to the spectra of dissolved mercury in other solvents,^{20,21} although the intensity of the narrow 254-nm line is much greater than that of the broader 262-nm line. The intensities of both lines double in going from 125 to 250° . In the presence of oxidizing impurities, such as a trace of H^+ , a small band due to Hg_3^{2+} (the characterization of the new ion as Hg_3^{2+} was done by methods other than absorption spectroscopy) was observed at ~ 325 nm; this band could be eliminated by the addition of a very small amount of aluminum metal. The addition of aluminum metal did not change the spectrum of the dissolved mercury metal (mercury was present in excess). Addition of HgCl_2 to the melt did not result in absorption bands in the region studied (600–230 nm). Addition of Hg_2Cl_2 produced the spectrum shown in Figure 5b. In aqueous solution at room temperature Hg_2^{2+} absorbs at 237 nm.²² Since melts prepared by the method described above usually contain traces of reducing materials (possibly aluminum metal), the spectrum of Hg_2^{2+} was frequently accompanied by a weak band due to Hg_3^{2+} . The latter band could be eliminated by adding a small amount of Hg^{2+} .

As noted above, the spectrum of Hg_3^{2+} (Figure 5c) could be produced by adding a substance capable of oxidizing mercury metal, present in excess, or by a partial reduction of Hg_2^{2+} . The molar absorptivity of Hg_3^{2+} at 325 nm was estimated to be $2 \times 10^4 M^{-1} \text{cm}^{-1}$. The narrow cell thickness (10^{-2} cm) was used to keep the concentration of strongly absorbing mercury ions much higher than the concentration of impurities. The use of high concentrations in turn enabled one to weigh significant amounts (approximately 10 mg) of solute species.

Raman Spectrum of $\text{Hg}_3(\text{AlCl}_4)_2$.—Figure 6 reproduces the Raman spectrum of the yellow polycrystalline compound. Very strong Raman peaks were observed at 93 and 123 cm^{-1} and weaker peaks at 178, 225, 242, and 350 cm^{-1} . The spectrum shows no evi-

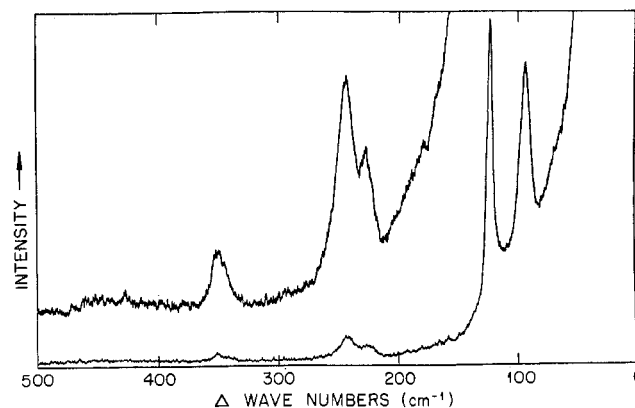


Figure 6.—Raman spectrum of polycrystalline $\text{Hg}_3(\text{AlCl}_4)_2$; 514.5-nm laser excitation.

dence of Al_2Cl_6 , or of Al_2Cl_7^- ,²³ while the absence of the strong stretching vibration of Hg_2Cl_2 reported²⁴ at 167 cm^{-1} indicates that no or very little Hg_2Cl_2 is present. AlCl_4^- has its strongest band²³ at 351 cm^{-1} and weaker bands at 121, 186, and 490 cm^{-1} . We would not expect to see the 490-cm^{-1} band because of its weakness, and the 121-cm^{-1} band would be hidden by the strong line at 123 cm^{-1} . A weak peak can be seen near 180 cm^{-1} in the spectrum. Therefore we assign the 350-cm^{-1} band to the AlCl_4^- group.

The crystalline compound Hg_2Cl_2 has its symmetric Raman-active Hg-Cl stretching frequency²⁴ at 270 cm^{-1} and its infrared-active antisymmetric stretching frequency at 261 cm^{-1} . We observe bands at 225 and 242 cm^{-1} . We believe these bands to be the result of Hg-Cl stretching vibrations. Since the vibrational frequencies of HgCl_2 are much higher²⁵ (ν_1 314 cm^{-1}), we must conclude that the Hg to which the Cl is bonded is probably also linked to another Hg atom.

The two strong Raman peaks at 93 and 123 cm^{-1} are thought to be symmetric and antisymmetric vibrations of the Hg_3 group. The vibrational frequency observed previously²⁶ for Hg-Hg bonds varies from 108 to 193 cm^{-1} . Either a nonlinear Hg-Hg-Hg or a triangular, three-membered ring would produce two Raman-active bands in the observed region. The sharpness of the 123-cm^{-1} band and the strength of the two bands originally led us to postulate a triangular (Hg)₃ ring and assign the higher frequency to the A_1' and the lower to the E' vibrational mode. This assignment was supported by comparison with the Raman spectra of $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$.^{26,27} Preliminary single-crystal X-ray crystallographic data,²⁸ however, show that the molecule contains a nearly linear Cl-Hg-Hg-Hg-Cl group with a Hg-Hg-Hg angle of $\sim 174^\circ$ and Cl-Hg-Hg angle of $\sim 175^\circ$. The two remaining AlCl_3 groups have approximately tetrahedral angles and are attached to the Cl groups with Al-Cl-Hg angles of $\sim 105^\circ$. The complete X-ray analysis will be published shortly. Therefore, we must assign the mercury-mercury stretching frequencies as A_1 , 93 cm^{-1} (symmetric stretch), and B_1 , 123 cm^{-1} (antisymmetric stretch), in accord-

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ance with expectations for a nearly linear model.²⁹ The Raman activity of the antisymmetric stretch apparently results from the nonlinearity of the Cl-Hg-Hg-Hg-Cl chain.

In summary, we assign the bands of the Raman spectrum to vibrations of the AlCl_4^- group and to the sym-

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metric and antisymmetric Hg-Cl and Hg-Hg stretching vibrations of the slightly bent Cl-Hg-Hg-Hg-Cl entity.

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Acidity Measurements at Elevated Temperatures.

V. Aluminum Ion Hydrolysis¹

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The hydrolysis of aluminum ion, which is kinetically slow at ordinary temperatures, was studied between 62.5 and 149.8° in 1 *m* KCl to establish better the hydrolysis reactions which occur and their temperature coefficients. Potentiometric measurements were made with hydrogen electrodes in a concentration cell previously described which permits precise acidity measurements at elevated temperatures. The results at low \bar{n} (ligand number) in acidic media and with varying aluminum concentration have led to the choice of two schemes of initial hydrolysis products each containing pairs of species: $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$; $\text{Al}_2(\text{OH})_3^{3+}$, $\text{Al}_3(\text{OH})_5^{4+}$. The authors prefer the first choice because of the apparent absence of 2,3 species in other known hydrolysis schemes. The species AlOH^{2+} , detected by other workers at relatively low aluminum concentration, was not present in detectable amounts under the conditions of these measurements. The identification of the major additional species formed at high \bar{n} values has been narrowed to a polymer with 14 ± 1 Al atoms by least-squares analysis of a large array of alternative species with 11–15 aluminum atoms. The following values of $-\log Q_{x,y}$ have been determined for the most probable scheme (where $Q_{x,y} = [\text{Al}_x(\text{OH})_y]^{(3x-y)+} [\text{H}^+]^y / [\text{Al}^{3+}]^x$ and the numbers in parentheses denote *x* and *y*): 25°: (2,2) 7.45, (3,4) 13.36, (14,34) 110.45 (literature data); 62.5°: (2,2) 5.90, (3,4) 10.74; 99.6°: (2,2) 4.81, (3,4) 8.20, (14,34) 67.89; 124.8°: (2,2) 3.95, (3,4) 7.01, (14,34) 55.68. The stabilities of $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, and $\text{Al}_4(\text{OH})_6^{4+}$ as a function of temperature have been used to estimate their thermodynamic parameters at 25°. Results in basic media at 149.8° indicate the presence of one species with a hydroxide-to-aluminum ratio of 4.0. This result combined with literature data indicates this species to be $\text{Al}(\text{OH})_4^-$ or AlO_2^- .

Introduction

The hydrolysis of aluminum ion, the most abundant of the metal ions in the earth's crust, has been studied extensively;² however, the important hydrolysis products produced in aqueous solution have not been well established. It is likely that the principal reasons for this are the slow rate of hydrolysis, first investigated in some detail by Brosset,³ and the severe demands placed on the accuracy of the data by the occurrence of at least one relatively large polymeric ion.

Those species which appear to be the best supported by previous studies are listed in Table I along with selected values for their formation quotients

$$Q_{x,y} = [\text{Al}_x(\text{OH})_y]^{(3x-y)+} [\text{H}^+]^y / [\text{Al}^{3+}]^x \quad (1)$$

Of these, AlOH^{2+} has been reported by numerous investigators, many of whom^{4–9} have found reasonably

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

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concordant values for the equilibrium quotient $Q_{1,1}$. In most of these studies, however, the extent of hydrolysis was measured in a series of dilutions of stoichiometric aluminum salt solutions. Unfortunately such measurements alone cannot uniquely identify a hydrolysis product since the concentration of aluminum and the extent of hydrolysis vary simultaneously. In particular, when such dilution data yield nearly constant values of $Q_{1,1}$, as in the case of aluminum, the same data can yield reasonably constant formation quotients for any species of the general formula $\text{M}_x(\text{OH})_{2x-1}$.¹⁰

The results of Kubota⁶ are therefore noteworthy since, in addition to dilution measurements, a set of

(10) If only one such hydrolysis product is formed in a stoichiometric salt solution, its concentration is given by (charges on complexes omitted)

$$[\text{M}_x(\text{OH})_{2x-1}] = \frac{1}{2x-1} [\text{H}^+]$$

and its formation quotient by

$$Q_{x,2x-1} = \frac{[\text{M}_x(\text{OH})_{2x-1}] [\text{H}^+]^{2x-1}}{[\text{M}]^x} = \left(\frac{1}{2x-1} \right) \left(\frac{[\text{H}^+]^{2x}}{m_{\text{M}} - \frac{x}{2x-1} [\text{H}^+]} \right)^x$$

For small degrees of hydrolysis we therefore obtain the approximation

$$Q_{x,2x-1} = \left(\frac{1}{2x-1} \right) \left(\frac{[\text{H}^+]^{2x}}{m_{\text{M}}} \right)^x$$

Hence, data for slightly hydrolyzed stoichiometric solutions which yield a constant value for $Q_{1,1}$ (*i.e.*, a constant quotient $[\text{H}^+]^2/m_{\text{M}}$) will yield approximately constant values for other quotients, $Q_{x,2x-1}$, as well, and hence be consistent with values of *x* greater than unity.