AN INVESTIGATION OF CERTAIN PHYSICAL PROPERTIES OF AMMONIUM AMALGAM

Thesis for the Degree of Ph. D.
MICHIGAN STATE COLLEGE
Mary Jo Boehm
1955

THESIS

AN INVESTIGATION OF CERTAIN PHYSICAL PROPERTIES
OF AMMONIUM AMALGAM

By

Mary Jo Boehm

A THESIS

Submitted to the School of Graduate Studies of Michigan
State College of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1955

ACKNOWLEDGMENT

The author wishes to express her sincere appreciation to Professor M. T. Rogers for his guidance and assistance throughout the course of this work, and to the Office of Naval Research for a grant which partially subsidized this research.

* * *

VITA

Mary Jo Boehm

candidate for the degree of

Doctor of Philosophy

Oral Examination, September 20, 1954, 2:00 P.M., Room 200, Kedzie Chemical Laboratory

Dissertation: An Investigation of Certain Physical Properties of Ammonium Amalgam

Outline of Graduate Studies:

Major subject: Physical Chemistry
Minor subjects: Inorganic Chemistry, Mathematics

Biographical Items:

Born, June 10, 1927, Columbus, Ohio
Undergraduate Studies, Bowling Green State University, 1945-49
Graduate Studies, Michigan State College, 1949-54

Experience: Teaching assistant, Bowling Green State University, 1948-49; Graduate Teaching Assistant, Michigan State College, 1949-52; continued 1954; Graduate Research Assistant, Michigan State College, 1952-1953.

Member of American Chemical Society, Pi Mu Epsilon, Sigma Pi Sigma, Society of the Sigma Xi.

ABSTRACT

Many of the physical and chemical properties of ammonium amalgam have been reported to be comparable to the properties of the alkali metal amalgams; although the exact manner in which nitrogen, hydrogen, and mercury are combined in ammonium amalgam is unknown. It has been suggested that ammonium amalgam, analogous to the alkali metal amalgams, is either a compound of the "ammonium" radical with mercury, or a solution of such a compound in mercury. Other evidence indicates that the amalgam may be a stable froth which floats on mercury. To gain further information about the nature of the substance the magnetic properties, the solid-liquid equilibria, the behavior of an electrode, and the compressibility of ammonium amalgam were studied.

Following an investigation of several methods for preparing and handling ammonium amalgam, an electrolytic preparation was adopted, and a means for purifying and manipulating the amalgam at temperatures in the vicinity of -30°C was devised. Acid extraction of the ammonia from the decomposing amalgam provided a means for analyzing samples of the amalgam. In most cases the amalgams on which measurements were made contained less than 0.50 mole per cent of ammonium.

Magnetic susceptibility measurements by the Gouy method at -30°C gave evidence that ammonia and hydrogen were combined with mercury in a way which decreased the freedom of electrons in mercury. Values as large as -0.270×10^{-6} c.g.s.units/gm. were observed for the specific susceptibility of the amalgam as compared to -0.167×10^{-6} c.g.s.units/gm. for

the specific susceptibility of mercury. The large increase in the diamagnetism of mercury to which only a small amount of ammonium had been added established that uncombined $NH_4 \cdot$ radicals comparable to alkali metal atoms were not present in the amalgam. Apparently the amalgam is an entity of the type $NH_4^+Hg_x^-$ in which the few electrons furnished by ammonium to mercury suffice to remove the temperature independent paramagnetism of mercury. Failure to find a relationship between the composition and the density of the amalgam suggests that the amalgam is partially decomposed at -30°C and contains ammonia and hydrogen gases entrapped in the mercury as well as some ammonium in solution in, or in combination with mercury. The amalgam ordinarily studied thus appears to be a mixture containing gaseous decomposition products.

A study of the solid-liquid equilibria in the system ammonium-mercury showed that about 60% of the ammonia and hydrogen present in the mercury were released during a single freezing and that the decomposition produced by additional freezings was insignificant, although an appreciable quantity of ammonium remained in the mercury. This indicated that some ammonia and hydrogen are very loosely bound to mercury in the amalgam perhaps as entrapped gas and that the remainder is present as ammonium or a compound of mercury with ammonium. The amalgam or possibly a stable froth containing the amalgam floats on top of mercury as indicated from cooling curves obtained simultaneously for each phase of the amalgam in which the cooling curve of the lower phase was not significantly different from that of pure mercury. From the cooling curves it was observed that during the solidification process the temperature of

the system increased slightly perhaps as a result of the breaking of some type of bond between the components of the system. Definite freezing temperatures were not obvious from the cooling curves for the amalgam, although the shape of the curves was reminiscent of solid solution formation. If the "true" amalgam exists as a colloidal dispersion or a froth of colloidal particles in mercury then the freezing curves would be reasonable since only the mercury would freeze at -40°C; the fusion point of the amalgam would be higher than -40°C.

Ammonium amalgam electrodes were found to be largely irreversible in aqueous ethanol solution at -30°C, although a value of 1.57 volts for the potential of an amalgam electrode in solution with ammonium ions was computed. Only in very dilute solutions immediately after connecting the potentiometer does one observe e.m.f. values approximating those for the alkali metal amalgams.

Compressibility measurements were made on samples of the amalgam. These indicated that the amalgam contained ammonia, which was liquefied during compression, as well as ammonium, in solution with mercury or in combination with mercury.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES - Continued

Page

LIST OF FIGURES

FIGURE Page

I. INTRODUCTION

The exact manner in which ammonium is combined with mercury in ammonium amalgam has not been characterized, although many investigations of the physical and chemical properties of the amalgam have been undertaken in the past 150 years. The true nature of the amalgam has been somewhat masked by its tendency to decompose into ammonia, hydrogen, and mercury at all temperatures above its freezing point, which is approximately -40°C; however, temperatures below -20°C inhibit the decomposition of dilute amalgams appreciably.

A comparison of the properties of ammonium amalgam with those of the alkali metal amalgams suggests that the ammonium radical is bound in some way with mercury. Magnetic susceptibility studies of the dilute alkali metal amalgams show that small quantities of solute vary the diamagnetism of mercury and that compound formation takes place at relatively low concentrations of alkali metal. An analogous study was expected to clarify the nature of ammonium amalgam, so that the purpose of this investigation was to study the magnetic properties of ammonium amalgam at temperatures sufficiently low to minimize decomposition. If ammonium dissolves in mercury as a neutral species the amalgam should be strongly paramagnetic due to the uncompensated spin of the unpaired electron, but if ammonium is ionized in mercury the diamagnetism will be increased by the contribution of an additional atomic core.

Supplementary investigations of the freezing process, the decomposition on freezing, the behavior of ammonium amalgam electrodes, and the compressibility were carried out in order to gain further information about the state of ammonium in the amalgam.

II. HISTORICAL SUMMARY

Ammonium Amalgam

Ammonium amalgam has been the subject of many unusual experiments from the time that Seebeck[1] reported the formation of the substance during electrolysis of moistened ammonium carbonate in contact with mercury. Seebeck's finding in 1808 in Jena was simultaneous with the announcement of Berzelius and Pontin in Stockholm that a soft solid less dense than mercury was produced in the electrolysis of ammonia solution with a mercury cathode. Berzelius and Pontin communicated their discovery to Sir Humphrey Davy[2] explaining that ammonia like potash and soda was an oxide, the metallic part of which combined with mercury to form an amalgam. Only a short time previously Davy had isolated sodium and potassium and learned of their vigorous exothermic reaction with mercury; therefore, he immediately began experimenting with ammonium amalgam. He prepared hollowed-out blocks of ammonium chloride and ammonium carbonate which he moistened and filled with mercury. The block of salt rested on a platinum strip joined to the positive electrode of a battery while the mercury pool was joined to the negative pole through a platinum wire. During electrolysis an amalgam of very low density formed and a black deposit was observed on the surface which Davy thought to be a residue of carbonaceous matter from the decomposition of carbonate. He prepared somewhat less pure amalgams by the reaction of ammonium salts with mercury solutions of alkali and alkaline-earth metals. He attempted

unsuccessfully to preserve samples of the amalgam but was able to determine the specific gravity as being less than three. Davy was puzzled that upon decomposition of the amalgam he was unable to form the oxide of ammonia comparable to potash and soda, the "oxydes" of potassium and sodium. He proposed that "deoxygenated" ammonium was present in mercury "in the nascent state, or at least in that condensed form in which it exists in ammoniacal salts, or solutions." Later Davy[3] concluded that ammonium and mercury form a compound.

Gay-Lussac and Thénard[4] regarded ammonium amalgam as a compound of hydrogen, nitrogen, and mercury on the basis of their experiments which indicated that the ratio of ammonia to hydrogen in the amalgam was 2.5:1 by volume. That ammonium is a radical which behaves like a metallic substance was first proposed in 1816 by Ampere[5] whose theory was elaborated by Berzelius and was generally accepted as explaining the composition of ammonium salts, but various theories arose concerning the amalgam. Daniell[6] believed that mercury absorbed ammonia and hydrogen in the way that silver absorbed oxygen. Grove[7] electrolyzed ammonium chloride solution with cathodes of zinc, cadmium, copper, silver, and gold in an attempt to find a reaction of ammonium chloride with other metals comparable to the reaction with mercury. During the electrolyses dark-colored and sometimes spongy deposits formed from which ammonia was never observed to be released, although possibly nitrogen and hydrogen were, according to Grove. He interpreted the results to mean that ammonium also reacted with mercury to form a nitrogen-mercury compound

interspersed with hydrogen which was responsible for the swelling apparent in ammonium amalgam.

The volume ratio of ammonia to hydrogen in an amalgam sample as determined by Landolt[8] was 2.15-2.4 to 1, a result considered inconclusive by Routledge,[9] who devised an apparatus similar to a gas burette that provided a means for measuring the total volume of gas released from a decomposing amalgam. The ammonia was absorbed in acid dropped into the apparatus and the volume which remained represented the volume of hydrogen. The results of four experiments gave values between 1.98 and 1.93 for the volume of ammonia per volume of hydrogen. Seeley[10] reported in 1870 that the volume of ammonium amalgam varied according to Boyle's law when pressure was applied to an amalgam sample by means of a plunger in a glass tube. Routledge, in a more thorough compressibility study, subjected a sample in a glass tube to various pressures through the use of a syringe. The pressure was measured with a manometer and the volume was determined from the change in level of the sample as pressure was applied. Routledge studied the compressibility of electrolytically prepared amalgams and found that at room temperature the amalgam was slightly less compressible than expected for a mixture of ammonia and hydrogen under the same conditions. Routledge concluded that the amalgam was a compound of ammonium and mercury which decomposed readily into ammonia, hydrogen and mercury. His publication contained a complete historical review on ammonium amalgam up to 1872.

LeBlanc[11] measured the polarization, relative to an amalgamated zinc electrode, of a series of alkali and alkaline earth amalgams prepared

electrolytically from their salt solutions. The polarization of these amalgams was about one volt greater than that observed in the electrolysis of hydrochloric acid solution with the amalgamated zinc electrode, and was the same as the value measured for ammonium amalgam. LeBlanc concluded that in ammonium amalgam a metallic substance comparable to sodium and potassium was combined with the mercury. If in the electrolysis of ammonium amalgam the polarization had corresponded with that of hydrochloric acid then the polarization could have been attributed to the discharge of hydrogen ions, since ammonia was not an ion.

Coehn and Dannenberg[12] measured the depolarization in electrolyses of alkali metal and ammonium salt solutions with a mercury cathode. The decomposition potential for hydrogen at the mercury cathode is 1.52 volts, but as a result of the formation of amalgams the decomposition potential in the presence of alkali metal ions is lowered by an amount dependent upon the particular metal ion. In the presence of ammonium ion hydrogen is evolved continuously from the mercury cathode at 1.24 volts which is entirely comparable to the value for potassium and gives further indication that ammonium amalgam is similar to alkali metal amalgams. Coehn[13] repeated part of Landolt's work on the displacement of ions from solution by ammonium amalgam. If the temperature was as low as 0°C, copper, cadmium, and zinc were displaced from sulfate solutions by the amalgam; otherwise, the radical decomposed before reaction took place. Coehn's results suggested that ammonium amalgam is a good reducing agent, and we know now that even the alkali metal ions can be displaced from solution in the presence of mercury.

In 1902 Henri Moissan[14] published the results of his experiments on ammonium amalgam. He treated a solution of ammonium iodide in liquid ammonia with sodium amalgam to make an ammonium amalgam which was more fluid than sodium amalgam and which did not evolve gas. Purification consisted of rinsing with ammonia and decanting the iodide solution. Moissan cooled the amalgam to -80°C washed it with ether at -80°C and placed it under reduced pressure under which conditions no gas was evolved. As the temperature rose above -80°C the amalgam decomposed slowly with a noticeable volume increase appearing at -30°C and a volume increase of 25 to 30 times the original at +15°C. In all the experiments the temperature of the amalgam during decomposition was 5 to 6 degrees above the temperature of the surroundings. The decomposition proceeded for 12 to 15 hours in some cases but could be enhanced by warming. If the amalgam was washed with an acid instead of ether at -80°C some decomposition took place at the lower temperature, but the ratio of ammonia to hydrogen evolved was always 1.99 to 1. For analyzing the decomposing amalgam, ammonia was collected in water and the hydrogen volume measured in a eudiometer. Moissan did not feel that his results showed that the ammonium radical existed in mercury but that actually the amalgam was an "ammoniacal metallic hydride." He based his decision on an analogy with sodium amalgam which if placed in liquid ammonia slowly released hydrogen with no change in volume, but addition of sodium hydride to the solution expanded the volume of the sodium amalgam for two or three days.

Rich and Travers[15] utilized Moissan's method to prepare ammonium amalgams for a series of freezing point determinations in an attempt to learn whether the amalgam was a true solution or an emulsion of ammonia, hydrogen and mercury. A conventional type of apparatus used in freezing point measurements for molecular weight determinations was employed, along with a platinum resistance thermometer. The ammonium amalgams were examined for sodium content but no mention was made of the analytical method used. The ammonium concentration was determined by titration with standard acid following the freezing process. Amalgams with concentrations of ammonium between 0.1 and 5 atom per cent were frozen by means of an alcohol bath maintained at temperatures 5 or 10 degrees below the freezing point of mercury. The freezing point depression per mole of ammonia was calculated to be about 42 degrees for four of seven solutions and approximately half that value for the more concentrated solutions. Rich and Travers decided that ammonium amalgam was a solution of NH_4 in mercury, but Smith[16] in 1907 showed that their conclusion was not the only one which suited the data. Smith demonstrated that if the solute were assumed to be a compound, e.g., NH_4Hg_{12}, in which one ammonium is combined with many atoms of mercury the same freezing point depression would apply. Smith prepared ammonium amalgam by electrolysis at 0°C and washed the amalgam several times in ice water. He poured samples of the amalgam into potassium chloride, potassium hydroxide, barium chloride, and barium hydroxide solutions and washed the amalgam by decantation until negative tests for potassium and barium were obtained. Upon extraction of the resulting amalgams with hydrochloric

acid an analysis showed that ammonium ions had displaced barium and potassium ions from solution. Smith felt that this interchange of ions proved the amalgam to be a true compound of NH_4 and mercury in solution with mercury. Smith's disagreement with Rich and Travers' work and the similarity of his experiments and conclusions with those of Coehn[17] brought criticism from both sources and produced two publications by Smith[18,19] in his own defense, but no additional experimental results.

Perhaps it was to be expected that following the turn of the century when the phenomenon of radioactivity was not completely understood, that an unstable substance such as ammonium amalgam should be examined for radioactive content. In 1906 Baborovsky and Vojtech[20] prepared amalgam by electrolysis and also by displacement of sodium from sodium amalgam. They placed silver bromide gelatine plates 3 cm. from decomposing amalgams for several hours, but the photographic emulsion remained unexposed; therefore, any "rays" emitted from the substance were apparently not of radioactive origin. In another experiment Coehn[21] found that ammonium amalgam discharged a negatively charged electroscope. About this time organic derivatives of ammonium chloride were found to yield the corresponding amalgams by electrolysis,[22] and the properties of certain of these, e.g. methylammonium amalgam and tetramethylammonium amalgam, were being investigated. McCoy and West[23] reported that tetramethylammonium amalgam, which can be isolated from mercury in the form of crystals, rapidly discharged a positively charged electroscope, while ammonium and monomethylammonium amalgam discharged the electroscope

regardless of whether the charge was positive or negative. However, ammonium amalgam discharged a negatively charged leaf 20 to 50 times more rapidly than a positively charged leaf. Radioactivity was ruled out as the cause of the ionization effect of amalgams because the rate of discharge was not constant and varied with the sign of the charge on the gold leaf. Following a series of investigations as to the effect of temperature and exposure to ultraviolet light on the decomposition of tetramethylammonium amalgam, McCoy and West concluded that the gas particles become electrified upon bubbling through the surface of mercury. Lennard[24] had shown in 1892 that bubbles of gas passing through mercury actually gain a potential which may be either positive or negative depending on the particular gas. Aronheim[25] made a more exhaustive study of the ionization properties of decomposing ammonium amalgam in which he plotted many time-versus-electroscope deflection curves at various temperatures. These plots approximated straight lines up to a maximum potential which was dependent on the temperature of the amalgam. The data were those anticipated if the ionization was a result of the "Lennard effect."

In 1928 Sander and Nitchsche[26] exposed ammonium, sodium, and potassium amalgams to light of various wave-lengths and measured the photoelectric emission produced by each amalgam. The electrometer in the photosensitive circuit registered deflections when light of wave-lengths between 4000 and 4500 A°. irradiated an ammonium amalgam sample. The long wave-length limit for sodium amalgam was 4950 A°. and for potassium was

somewhat higher although the exact value was not obtained. From these data it can be concluded that the ammonium radical has a higher electron affinity than sodium or potassium.

Alden Deyrup[27] studied the rate of decomposition of ammonium amalgam at -20°C and -30°C. He prepared amalgams by electrolysis of aqueous ammonium acetate saturated with ammonia gas at -38°C. The mercury cathode was kept partially frozen and was stirred. Following their preparation the amalgams were stored at -78°C. A frozen amalgam was placed in a hydrogen-nitrogen atmosphere and warmed to the temperature of the decomposition study. An amalgam sample was removed periodically for analysis. Although Deyrup observed that freezing partially decomposed the amalgam, he froze the samples taken from the reaction vessel to preserve them before analyzing the ammonium content by reduction of iodate ion. The velocity constants for the decomposition of several amalgams at -20°C and -30°C agreed very precisely, and the kinetics appeared to be representative of an autocatalytic reaction. The decomposition became a second order reaction following the addition of lithium metal to the amalgam. Deyrup proposed that two decomposition reactions took place, a heterogeneous reaction at the surface between the amalgam and bubbles of reaction products, and a homogeneous reaction as a result of collision between two ammonium ions and two electrons. The molal freezing point depression constant was determined to be 51°, but no experimental data were listed.

At pressures between 30 and 600 atmospheres the potential of ammonium amalgam was measured with respect to a reference electrode of

$Hg(l)/HgBr_2(s),NH_4Br(aq)$ at 0°C by Náray-Szábo and Szlatinay.[28] The amalgam was prepared by electrolysis of ammonium bromide solution in a cell enclosed in a pressure chamber. The electrolysis was discontinued every forty seconds for an e.m.f. measurement. High pressure decreased the rate of decomposition and stabilized the cell potential to some extent; however, the e.m.f. dropped by 1.316 v. after 40 minutes at 30 atmospheres, and by 0.746 v. after 40 minutes at 600 atmospheres. The potential varied with the concentration of ammonium bromide, but not with pH, and became less negative with pressure. A plot of E_H, the cell potential with respect to the hydrogen electrode, against the logarithm of the current density of the electrolysis was a straight line for each series of measurements at a constant pressure, but no value for E_0 was computed, since the concentration of ammonium was unknown. The initial values observed for E_H varied between 1.60 and 1.83 volts.

The behavior of ammonium amalgam as a reducing agent for organic compounds was widely investigated by Takaki and Ueda,[29] who prepared amines and β-hydroxylamines from nitro compounds with the amalgam. They treated ammonium amalgam with many different ketones and aldehydes and characterized a variety of products from each reaction; for example, benzaldehyde reacted with the amalgam to form benzyl alcohol, hydrobenzoin, benzylamine, isohydrobenzoin, dibenzylamine, and mesostilbenediamine.

The polarographic reduction of ammonium ion to the amalgam at the dropping mercury cathode was studied in a saturated solution of tetrabutylammonium iodide in liquid ammonia by Laitenen and Shoemaker,[30] who

found the half-wave potential of ammonium ion to lie between the values for lithium and sodium.

In 1951 Johnston and Ubbelohde[31] studied amalgams prepared at room temperature by electrolysis of ammonium sulfate solution between 10 and 20 milliamperes. They analyzed the electrolyte for ammonium released as ammonia and the amalgam for "latent ammonium" retained in the amalgam. The formation of "latent ammonium" was suppressed when the electrolysis was carried out at temperatures above 50°C, or in the presence of ammonium sulfide which poisoned the mercury cathode. Optimum conditions for preparing ammonium amalgam corresponded well with those for preparing potassium amalgam from electrolysis of potassium sulfate. At the voltage corresponding to formation of ammonium amalgam the surface tension of the mercury decreased appreciably. The surface viscosity at the cathode as measured with an oscillating-disc viscometer increased much more rapidly during amalgam formation with ammonium sulfate then with potassium sulfate. A phenomenon, called the "wedge effect", is evident during electrolysis in a glass column with electrolytes of alkali or alkaline earth salt solutions over a mercury cathode. The electrolyte forces itself between the glass and mercury in a wedge with the apex downward. The length of the "wedge" was dependent upon the cation, and the largest "wedge" ever obtained by Ubbelohde and Johnston was 16 cm. long when ammonium sulfate was electrolyzed under optimum conditions for amalgam formation. The experiments show that potassium and ammonium amalgam behave similarly. The authors believe that ammonium amalgam is a froth which is stabilized by low surface tension and high surface viscosity and that

the rate of decomposition is less than predicted by Deyrup.

The most recently published work on ammonium amalgam is an x-ray diffraction study of amalgams prepared by reaction of ammonium iodide with $NaHg_4$ in liquid ammonia at -40°C, and stored at -78°C.[32] Following their preparation the amalgams were washed with liquid ammonia and frozen by stirring with liquid air to form powders. In three x-ray powder diagrams of ammonium amalgam made at -190°C several intense lines appeared which were not explainable on the basis of any known impurities. Lines characteristic of $NaHg_4$ were absent because of excessive strains in the compound at -190°C. Several amalgams were carefully analyzed by passing the hydrogen evolved in decomposition over heated copper oxide and observing the weight change. The analyses indicated that the amalgams contained some unreacted $NaHg_4$ and less ammonium amalgam than should have been present had no decomposition taken place at -78°C as predicted by Deyrup. Baenziger and Nielsen believed that certain lines characteristic of the amalgam were present in the powder diagram; however, no obvious relationship existed between the lines which would have enabled them to predict a crystal structure for ammonium amalgam.

Ammonium Radicals in Liquid Ammonia

In addition to the many experiments concerning the nature of ammonium in amalgams, three investigations of the possible existence of free ammonium in liquid ammonia have been made. Otto Ruff[33] in 1901 attempted to prepare free ammonium at -95°C in a solution of potassium and ammonium iodide in liquid ammonia subjected to a pressure of 60 atmospheres.

He predicted that if free ammonium formed according to the reaction

$$K + NH_4I \longrightarrow KI + NH_4$$

the blue color characteristic of potassium in solution with liquid ammonia would disappear. Ruff was unsuccessful in this attempt, as was Moissan,[34] who in the same year reported that he was unable to prepare free ammonium by the same reaction as Ruff, under the pressure of the atmosphere.

In 1921 Schlubach and Ballauf[35] repeated the experiments of Ruff and Moissan only to obtain the same negative results. Using much more dilute solutions than in previous experiments they found that when ammonium chloride was added to a solution of potassium in liquid ammonia and the solution was kept at -70°C for three hours the blue color disappeared and an amount of hydrogen, much less than that calculated if all the ammonium had decomposed, was evolved. After the potassium chloride was filtered off, iodine, which does not react with liquid ammonia at -70°C, was discolored by the filtrate. When the solution was warmed the remaining hydrogen was released at -40°C. Hydrogen was found to be much less soluble in liquid ammonia than would have been necessary for all the hydrogen to be retained uncombined in solution. Ammonium salts form colorless solutions during electrolysis in liquid ammonia at -70°C as do methyl salts which evolve ethane as a product when their solutions are decomposed at higher temperatures. Tetraethylammonium salts under similar conditions acquire a deep blue color analogous to the alkali metals and form a series of decomposition products including triethylamine and ethane.

Alkyl-Substituted Ammonium Amalgams

Two organic amalgams, monomethylammonium amalgam and tetramethylammonium amalgam, have been prepared by electrolysis of the respective chlorides in alcohol solution at -10°C. McCoy and Moore, who have investigated the properties of these amalgams, found that both are unstable above 0°C and that the monomethylammonium amalgam was soft and had the appearance of ammonium amalgam, while the tetramethylammonium amalgam contained almost crystalline lumps and was relatively stable at temperatures around 0°C. Trimethylamine is a product in the decomposition of tetramethylammonium amalgam which might follow the reaction:

$$\cdot NMe_4 \longrightarrow NMe_3 + Me\cdot$$

In 1954 Porter[36] detected methyl radicals in the decomposition products of tetramethylammonium amalgam through the use of tellurium mirrors, using the method of Paneth.

III. THE PREPARATION OF AMMONIUM AMALGAM

Introduction

Ammonium amalgam has been commonly prepared by two different methods--by electrolysis of an ammonium salt solution with a mercury cathode and by displacement of an alkali metal amalgam with ammonium ion. The choice of ammonium salt for either preparation depends on the choice of solvent. Sodium amalgam has been almost exclusively employed for the displacement reaction.

In this investigation ammonium amalgam was first prepared in order to make magnetic susceptibility measurements. An amalgam free from impurities which might interfere with interpretation of the measurements or with the analysis of the amalgam was desired. The amalgam had to be reasonably concentrated and in a physical state that would permit its transfer to a tube of 6.5 mm. inside diameter. An apparently straightforward method employed by several investigators is that of Moissan[14] in which ammonium ion is reacted with sodium amalgam in liquid ammonia. For Moissan's preparation to be satisfactory in the present work the sodium amalgam would have to be reacted completely and all sodium ions removed in the purification process.

Preparation from Sodium Amalgam

The first step in the preparation of ammonium amalgam by Moissan's method was the synthesis of a 3 per cent sodium amalgam prepared directly

from weighed quantities of mercury and sodium.[37] An introductory experiment was attempted in which a piece of sodium amalgam was dropped into an aqueous solution of ammonium chloride in a beaker at room temperature. The sodium amalgam immediately expanded into a sponge-like material and within five minutes occupied a volume more than twenty times the original. The amalgam was quite black in color and sufficiently less dense than water that at one stage it floated on the solution. Decomposition of the amalgam was rapid at room temperature and appeared to be complete in an hour. The solution that remained above the mercury was strongly alkaline as a result of the displaced sodium. When ice water was used for making the ammonium chloride solution the rate of decomposition of the amalgam decreased, but not enough to make this an acceptable method of preparation.

In a second attempt to prepare ammonium amalgam by Moissan's method liquid ammonia was poured from a gas cylinder into a Dewar flask and sufficient ammonium chloride was added to make a one molar solution. About 50 g. of coarsely ground sodium amalgam was added to the solution with stirring. No reaction was immediately apparent, but as ammonium amalgam formed the consistency of the sodium amalgam became paste-like. From the first this reaction did not appear to be rapid and even after five hours pieces of unreacted sodium amalgam remained. This procedure was followed several times but the reaction was never found to go to completion. This was shown by removing the ammonium amalgam prepared in this way from the liquid ammonia and decomposing it by warming to room temperature. When the evolution of gas from the amalgam was complete an aqueous ammonium chloride solution was poured over the amalgam, resulting

in the typical reaction of ammonium ion and sodium amalgam. Later Baenziger and Nielsen[32] reported that in their investigation ammonium ion failed to displace sodium from sodium amalgam completely.

Electrolytic Preparation

Apparatus

An electrolytic method was then adopted for the preparation of ammonium amalgam. A series of different electrolytes, reaction vessels, and refrigerants were investigated before a wholly satisfactory method was devised. Initially a low-voltage power supply was used for the electrolyses; however, the current varied with the resistance of the electrolyte and the resistance changed appreciably as electrolysis proceeded. Heat generated in the cell at electrolysis currents of two or three amperes enhanced decomposition of the amalgam. A more satisfactory power supply was constructed according to the circuit diagram in Figure 1.[38] This power supply was a constant current device with a variable output between 0 and 420 milliamperes at a maximum potential of 250 volts. The current during an electrolysis with this power supply was constant to within 1.5 per cent as determined by measuring the voltage drop across a one ohm resistance with a Brown-Honeywell Electronic Potentiometer. The composition of amalgams prepared by electrolysis with the constant current power supply could be readily adjusted by variation of the current or electrolysis time.

If the amalgam was to be preserved in a relatively concentrated form for more than a few minutes the temperature had to be lower than -10°C

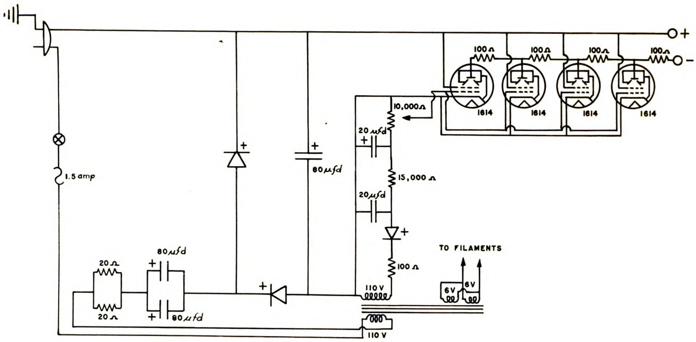


Figure 1. Schematic diagram for constant current power supply: the output is variable between 0 and 420 milliamperes at a maximum voltage of 250 volts D. C.

during all manipulations of the amalgam. According to Deyrup's[27] investigation of the rate of decomposition of ammonium amalgam, dilute amalgams are quite stable at -30°C. A cold atmosphere suitable for the preparation and handling of the amalgam was provided by blocks of Dry Ice placed in the bottom of a wooden box converted from a discarded "dry box." The box had been constructed from 0.5 inch plywood which served as good insulation. About three hours were required to cool the box to between -25° and -30°C using about 50 pounds of Dry Ice. The positive pressure of carbon dioxide created by vaporization of the Dry Ice reduced the quantity of moist air which entered the cold atmosphere.

The electrolysis cell was constructed from a six-inch Pyrex funnel and an 8 mm. stopcock. A tungsten wire sealed above the stopcock made electrical connection between the mercury cathode and the negative pole of the power supply as illustrated in Figure 2. The anode consisted of a piece of platinum foil 2 inches by 0.5 inch which had been fused to a platinum wire and was connected to the positive junction of the power supply.

Procedure

In the preparation of an amalgam about 30 ml. of mercury* and approximately 100 ml. of a stock solution of electrolyte were introduced into the cell. The electrolyte was a one molar solution of ammonium chloride** in 50 per cent aqueous ethanol; the solvent was prepared from equal

---

*Metal Salts Corporation High Purity.
**Mallinckrodt Analytical Reagent Grade.

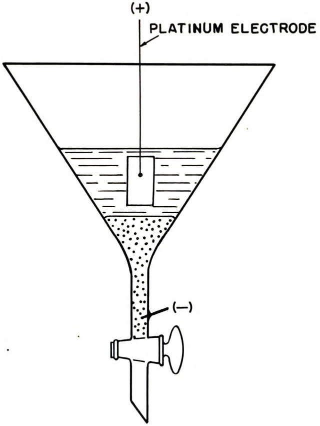


Figure 2. Cell for the electrolytic preparation of ammonium amalgam.

volumes of absolute ethanol and conductivity water. The electrolyte could be cooled below -30°C without freezing. An air stirrer was mounted above the cell for stirring the mercury cathode. All wash solutions, and equipment which needed to be cooled before filling with amalgam, were placed in a small box kept in the cold atmosphere. Cakes of Dry Ice were then arranged inside the cold box which was closed but not sealed tightly. The fan and stirrer were turned on and after three hours, or whenever the temperature was between -25° and -30°C, the electrolysis was begun. During most electrolyses the power supply was operated at 400 milliamperes and 250 volts which was nearly the maximum output. The time of electrolysis as well as the volume of mercury electrolyzed depended on the concentration and quantity of amalgam that was desired. The cathode was stirred only intermittently during electrolysis to aid the evolution of gaseous ammonia and hydrogen produced by decomposition of the amalgam. Presumably the cell reaction for the electrolysis may be represented by the equation

$$nHg + mNH_4Cl \longrightarrow (NH_4)_mHg_n + m/2\ Cl_2.$$

The amalgam floated on top of the mercury cathode during the electrolysis and occasionally a black deposit appeared on the surface of the cathode in the vicinity of the anode. This deposit has been reported by many investigators in the past and was found by McCoy and Moore[22] to be at least 95 per cent mercury.

At the completion of electrolysis the amalgam was purified inside the cold box. The mercury-rich solution was first drawn off through the

stopcock of the cell and then the amalgam was drained into a 1:1 aqueous alcohol wash solution, while the electrolyte was retained in the cell. The amalgam was washed two times with aqueous alcohol by decantation and finally a third time in a separatory funnel from which it was introduced into the appropriate experimental apparatus. The surface of the amalgam was then touched with absorbent tissue to remove the alcohol-water wash solution more completely. The composition of the amalgam depended greatly on the temperature in the cold box during the electrolysis and purification procedure, as well as on the amount of handling necessary to fill a sample tube for a particular measurement.

IV. ANALYSIS OF AMMONIUM AMALGAM

Introduction

Four different analytical techniques have been employed for determining the concentration of ammonium in the amalgam. The method of gas analysis is dependent on the decomposition of ammonium into hydrogen and ammonia in the volume ratio of 1 to 2, a ratio which has been well established.[9,14] Measurement of the combined volumes of ammonia and hydrogen or absorption of the ammonia and measurement of the volume of hydrogen alone is sufficient for the analysis. Analyses dependent upon the amount of ammonia or hydrogen released during decomposition have the disadvantage of providing a value which may include the quantity of ammonia or hydrogen entangled as gas in the amalgam in addition to that present as the ammonium radical. Amalgams which are to be analyzed should be kept at low temperatures to inhibit decomposition. The most common analytical method for the determination of metals dissolved in mercury consists of extraction of the metal with an excess of standard acid followed by titration of excess acid with standard base. Baenziger and Nielsen[32] analyzed the amalgam by reduction of hot copper oxide with the hydrogen released from a decomposing amalgam. The method appeared to have the disadvantage of determining a small change in weight of a relatively heavy absorption tube. Deyrup[27] used the reducing property of ammonium to determine the composition by reduction of iodate according to the reaction

$$6H_2O + IO_3^- + 6NH_4 \longrightarrow 6NH_4^+ + I^- + 3H_2O + 6OH^-.$$

Following reduction and acidification the iodine formed was distilled into potassium iodide solution and titrated with standard thiosulfate.

Experimental Procedure

Several amalgams were analyzed by measurement of the volume of hydrogen released through decomposition into a gas burette. A sample tube of amalgam at a low temperature was joined by means of a ground glass connection to a 10 ml. gas burette. As the amalgam warmed to room temperature the evolved ammonia was dissolved by the water in the burette and the volume of gas observed was that of the hydrogen alone. Complete decomposition of the amalgam required at least an hour during which time the possibility existed that hydrogen might diffuse from the system. Frequently the volume of hydrogen released from an amalgam was as little as 2 ml., so that errors introduced by diffusion would be appreciable, and the method was abandoned.

The analytical method adopted for the determination of ammonium was the acid extraction technique. An amalgam sample at the temperature of the physical measurement, usually -30°C, was quickly run into an iodine flask containing an aliquot of standard sulfuric acid. The amalgam was set aside for several hours to allow complete decomposition, after which the acid was titrated with standard sodium hydroxide using methyl-red indicator. On occasion the transfer of amalgam to the standard acid was made inside the cold box. Since this contained an essentially carbon

dioxide atmosphere, particular precaution was taken to remove carbon dioxide from the acid solution. Slightly before the end point was reached in the titration with sodium hydroxide a stream of compressed air, which had been passed in succession over Ascarite and Drierite, was run into the titration flask for five minutes to remove carbon dioxide. Without this precaution the endpoint was not sharp. Following the titration the water solution was decanted from the mercury remaining in the bottom of the iodine flask and the mercury was washed several times with distilled water, dried with acetone, and weighed.

An approximately 0.25N stock solution of sodium hydroxide was prepared from sodium hydroxide pellets[*] and conductivity water. Barium chloride solution was added to precipitate carbonate. The sodium hydroxide was standardized against potassium hydrogen phthalate with phenolphthalein indicator.[39]

A 0.3N sulfuric acid solution made with boiled air-free water was standardized against the standard base using methyl-red indicator. Two liters of each of the stock solutions sufficed for all the analyses. More dilute standard solutions were made from each of these stock solutions whenever necessary.

---

[*] Baker's Analyzed Reagent C.P. sodium hydroxide.

V. AN INVESTIGATION OF THE MAGNETIC PROPERTIES OF AMMONIUM AMALGAM AND OF MERCURY

Introduction

The Nature of the Alkali Metal Amalgams

That the alkali metals are soluble in mercury was first observed by Kerp[40] in 1898, who determined the composition of certain of the solid phases and advanced the idea that definite compounds exist between mercury and the alkali metals. Smith and Bennett[41] reported that the alkali metals form compounds with mercury which are in solution in mercury. Most investigations of the physical properties of the alkali amalgams have been directed toward learning whether the alkali metals exist as ions, atoms, or compounds in mercury. The conductivities of the amalgams have been widely investigated since Bornemann and Muller[42] established that the conductivity of mercury is lowered by the addition of sodium rather than increased, which would be the case if the metal were in mercury in an ionized state. Hine[43] studied the conductivity of very dilute sodium, potassium, and lithium amalgams and found that each exhibited a somewhat different behavior in mercury, but that all decreased the conductivity. Vanstone[44] measured the electrical conductivity of 20 different sodium amalgams from 0 to 45 atom per cent mercury and reported that changes in conductivity occur at compositions corresponding to breaks in the thermal diagram for the sodium-mercury system. Vanstone[45] determined the specific volume of sodium-mercury

alloys and reported that mercury contracts on the addition of sodium up to concentrations of 48 per cent sodium. Vapor pressure measurements of the alkali metal amalgams show that compound formation takes place even in very dilute solutions.[46] Thallium and the elements of Groups I and II actually form compounds with mercury, since the melting points of the amalgams are higher than the melting points of either of the components; while other metals, except those of group VIII, form solutions or isomorphous mixtures with mercury.[47]

The Magnetic Properties of Amalgams

The ionic state of a particular metal in solution with mercury can be predicted from magnetic susceptibility studies which provide a means for determining the difference in the number of free electrons in the pure metal and in mercury solutions of the metal. If a Group I or Group Ia element goes into solution with mercury as a neutral atom the diamagnetic susceptibility of the solution should be less than that of mercury as a result of the uncompensated spin of the electron of the element; but if the element is present in mercury in the ionic state the diamagnetism should be greater than that of mercury. Compound formation between elements and mercury may be detected by magnetic studies since systems with odd numbers of electrons should be less diamagnetic than mercury and systems with even numbers of electrons should be more diamagnetic.[48]

The magnetic properties of the amalgams of gallium, gold, indium, and tin were studied by Davies and Keeping;[49] those of zinc, cadmium,

bismuth, copper, chromium, manganese, and silver, by Bates and his co-workers.[48,50,51,52,53]

The magnetic properties of the sodium-mercury system were studied by Franke and Katz[54] who investigated amalgams of compositions between 21 per cent and 95 per cent sodium by weight. Their investigations show that sodium is in a state comparable to that in which it exists in concentrated liquid ammonia solutions, rather than in the form of atoms. They were unable to show definite breaks in the magnetic susceptibility-composition diagrams at compositions predicted from thermal analysis of the sodium-mercury system.

Aravamuthachari[55] measured the magnetic susceptibility of dilute sodium amalgams containing up to 10 atom per cent sodium and found that the diamagnetic susceptibility decreases below the value for mercury slowly at first, then more rapidly, finally leveling off and again increasing. He found that as little as 0.02 atom per cent of lithium increased the diamagnetism of mercury but that greater concentrations reduced the diamagnetism to slightly less than that of mercury. Mercury became less diamagnetic when very small quantities of potassium or rubidium were dissolved in it, but more diamagnetic, when greater than 0.05 atom per cent was added. Klemm and Hauschulz[56] made a thorough investigation of the magnetic susceptibility of the alkali amalgams at compositions between 0 and 100 atom per cent of the alkali metals at 20°C and at -183°C. In most cases the maxima, minima, and direction changes in their composition-susceptibility diagrams correspond to compound formation

predicted by thermoanalysis, although a few points should be further investigated. Dilute solutions of potassium and rubidium in mercury exhibit much greater diamagnetism at -183°C than at 20°C, while the susceptibility of lithium and sodium amalgams were relatively unchanged at the lower temperature.

The Magnetic Properties of Mercury

Magnetic susceptibility studies for amalgams have led to several detailed investigations of the magnetic properties of mercury. The experimental value reported by Shur[57] for the atomic susceptibility of mercury vapor is -78×10^{-6} which compares well with the theoretical value of -84.6×10^{-6} calculated for mercury as a monatomic gas. Liquid mercury is probably polyatomic since the atomic susceptibility at room temperature is -33.8×10^{-6}. Mercury has a rhombohedral structure in the solid state and a close-packed structure in the liquid state.[58] Apparently electrons move much more freely in the solid mercury than in liquid mercury because the electrical resistance of the solid is only one-fourth that of the liquid. Moreover, mercury is less diamagnetic in the solid state than in the liquid.

The magnetic susceptibility of solid mercury has been reported at several temperatures. Vogt[59] determined the atomic susceptibility parallel and perpendicular to the trigonal axis in single crystals of mercury at liquid nitrogen temperatures and reported an average value for the gram susceptibility of -0.118×10^{-6}. Owen[60] reported the value -0.15×10^{-6} for the gram susceptibility of mercury at -80°C and Oxley[61] reported -0.155×10^{-6} at -130°C.

Theoretical Discussion

Conductivity and magnetic susceptibility studies have supplied the most information about the nature of the metallic solute in various amalgams and should supply similar information for ammonium amalgam. The measurement of the conductivity of ammonium amalgam was contemplated but found infeasible, as a result of the tendency for the amalgam to decompose into gaseous materials with the formation of bubbles which would increase the electrical resistance and invalidate any conductance data. The Gouy method for determining magnetic susceptibility appeared to be acceptable for studying the properties of the ammonium-mercury system. Bates[62] has designed an improved apparatus for measuring magnetic susceptibility in non-homogeneous systems such as amalgams. Actually the Gouy method should be suitable for determining whether ammonium amalgam is diamagnetic or paramagnetic and should give some information on the variation of magnetic properties with composition.

In the Gouy method the magnetic susceptibility of a sample is determined by weighing the sample in an inhomogeneous magnetic field. The apparatus illustrated in Figure 3 had been constructed for earlier investigations in this laboratory.[63] The magnetic field exerts a force along the length of a cylindrical sample proportional to the field strength according to the following expression:[64]

$$F = 1/2(k_1^{*} - k_2)\ H^2A = g\ \Delta w,$$

---

[*] The letter k is substituted for the Greek letter kappa, which by convention represents volume susceptibility.

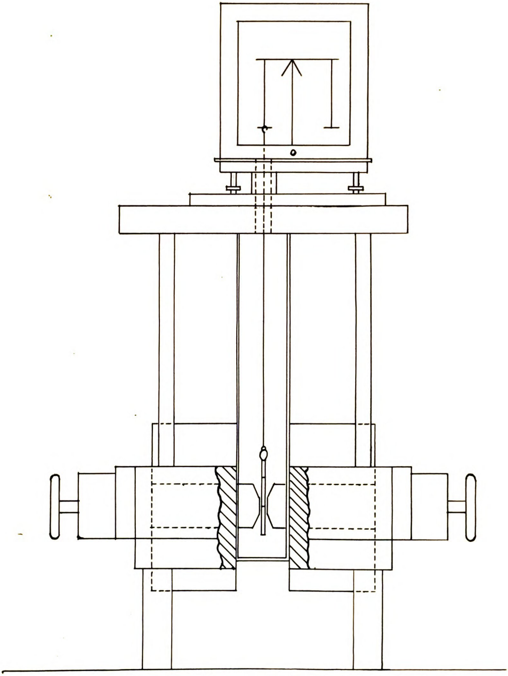


Figure 3. The Gouy magnetic balance

where

k_1 = the volume susceptibility of the sample,

k_2 = the volume susceptibility of air (or medium in which the tube is suspended),

H = the magnetic field strength in Oersteds at one end of the sample (assuming the other end to be in zero field),

A = the cross-sectional area of the sample tube at the position of the septum and was 0.369 cm.^{2} for these measurements,

g = gravitational acceleration,

and

Δw = the change in weight of the sample produced by weighing in the magnetic field.

Rather than determining the field strength at each applied current it is simpler to calibrate the apparatus with a substance of known volume susceptibility and compute the susceptibility in c.g.s. units/gm. directly by the relation

$$X_1^{*} = \frac{k_{air}}{\rho_1} - \frac{k_2 \Delta w_1}{\rho_1 \Delta w_2}$$

where k_2 and Δw_2 are the volume susceptibility and the corresponding weight change at a given field strength for the calibrant, while ρ_1 and Δw_1 are the density and weight change at the same field strength for the sample. Traces of ferromagnetic impurities in a sample can completely conceal the true magnetic properties. Ferromagnetism varies with field strength while paramagnetism and diamagnetism do not vary, so that in

---

*The letter X will be used to designate the Greek letter chi, the usual symbol for gram susceptibility.

the Gouy method all samples are weighed at a series of different field strengths to detect errors produced by impurities.

The Magnetic Susceptibility Measurements

Apparatus

The magnetic susceptibility of ammonium amalgam had to be measured at temperatures at which the amalgam was stable, so that an apparatus which provided a means for cooling the sample tube was constructed as shown in Figure 4. The magnetic susceptibility tube C was made from 8 mm. o.d. Pyrex tubing with a septum 10 cm. from the reference mark and 3.25 inches from the bottom of the tube. At the top of the tube was a ₸ 7/25 joint. The corresponding male joint was sealed at the top and contained a loop for connection to a gold chain with which the tube was suspended from the left pan of the balance. The tube was enclosed by the jacket A which extended some distance above the Dewar flask to prevent movement of the chain to the sample tube by air currents. The jacket A was surrounded by refrigerant in a Dewar flask.

The Dewar flask was constructed in the glass shop from Pyrex tubing. Prior to silvering, the inner walls of the flask were cleaned with chromic acid solution, rinsed, cleaned with 50 per cent hydrofluoric acid solution, and finally rinsed with distilled water. A reducing solution of dextrose and water was added to alkaline silver nitrate and the mixture was poured between the walls of the flask. The flask was strip-silvered to permit viewing of the interior. After the silvering solution was removed the coated surface was rinsed with distilled water and the flask

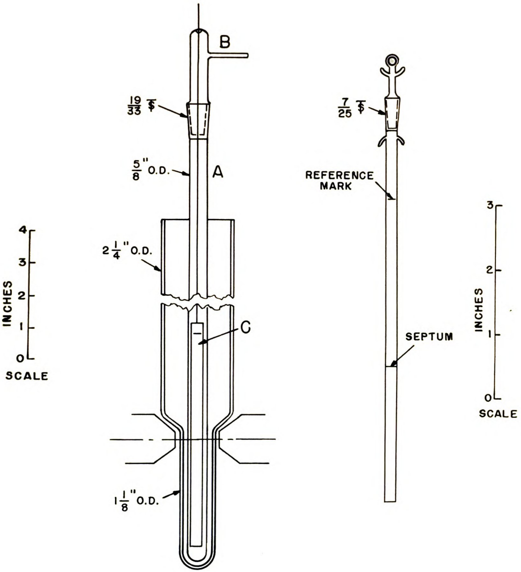


Figure 4. Left: Apparatus for low temperature measurement of magnetic susceptibility: A, jacket enclosing sample tube; B, sidearm for nitrogen inlet; C, magnetic susceptibility tube. Right: Detailed drawing of tube C.

dried in an oven at 200°C. The flask was sealed to a vacuum line and evacuated while being heated with a bushy flame at about 400°C. In order to remove adsorbed gases more completely a charcoal-liquid air trap at reduced pressure was opened to the evacuated flask for about thirty minutes before the flask was sealed off.[65]

Experimental Procedure

The refrigerant employed for these measurements was boiling Freon-12* which was liquefied as it passed from the cylinder through a copper coil immersed in isopropyl alcohol and Dry Ice. Pressure from the tank forced the liquid through a Teflon tube into the Dewar flask. With the Dewar flask filled with boiling Freon-12 the temperature at various levels inside jacket A was measured with a thermocouple and was found to differ with the height of the tube; however, in the vicinity between the pole pieces the temperature became constant after 20 minutes within 0.5° of -29.8°C, the boiling temperature of Freon-12. Before each series of measurements at low temperatures, where condensation of moisture on the sample tube might interfere with the weighings, the air in jacket A was displaced by nitrogen dried over Drierite. Air was displaced from the jacket A by passing nitrogen** into a length of 3 mm. i.d. rubber tubing which entered at the top and extended to the bottom of A. After about 20 minutes the tubing was removed from the jacket and connection was made to the nitrogen supply through the side-arm B. A slow stream of

---

*Mathieson dichlorodifluoromethane.

**Ohio Chemical Company water-pumped nitrogen, dried over Drierite.

dry nitrogen was passed into this side-arm and out through the top to prevent moist air from entering the apparatus while weighings were being made.

The field strength of the magnet at currents of 0, 4, 8, 12, and 16 amperes was determined by calibration with Mohr's* salt at -30°C and also with air-free conductivity water at room temperature. The gram susceptibility of Mohr's salt is

$$\chi = \frac{9500 \times 10^{-6}}{(T + 1)}$$

and the gram susceptibility of water is -0.720×10^{-6} at 20°C.[64] The Mohr's salt was freshly ground before it was packed into the tube, since it was observed to become less paramagnetic on standing in air. The data for these calibrations appear in Table I.

The Magnetic Susceptibility of Mercury at Low Temperature

As a preliminary to making a magnetic study of ammonium amalgam the magnetic susceptibility of mercury** was measured at room temperature to compare the gram susceptibility with the values obtained by other investigators. Bates[66] found that the gram susceptibility of mercury varied with the purification process and that it decreased slightly upon standing in air. Apparently no particular precautions were necessary to purify the mercury for the present investigation since a value of -0.156×10^{-6} was obtained for the gram susceptibility at 25°C as compared

---

*Merck Reagent Grade hydrated ferrous ammonium sulfate.

**Metal Salts Corporation High Purity mercury.

with Bates' value of -0.168×10^{-6}. Prior to weighing, the mercury was carefully poured into the sample tube which was then connected to an aspirator to draw off bubbles of entrapped air. The weight of the sample and the mercury was about 70 grams, which was large for making weighings on a semi-micro balance. The change in weight upon application of the field was sufficiently large that weighings were only made to within 0.1 mg.

The magnetic susceptibility of mercury has never been determined in a single series of measurements at several low temperatures by the Gouy method. It was decided to obtain magnetic susceptibility data for mercury at -29.8°C, the temperature of boiling Freon-12; at -75°C, a temperature readily obtained with Dry Ice-isopropyl alcohol; and at -190°C, the boiling temperature of liquid nitrogen. Prior to these measurements the magnetic properties of the susceptibility tube when filled with dry nitrogen and weighed in nitrogen were studied at the temperatures at which mercury was to be investigated. The tube was increasingly paramagnetic at low temperatures necessitating an appreciable correction for the change in weight of the tube at each field strength as shown in Table II. The samples of mercury were weighed in a nitrogen atmosphere during measurements at low temperature and in air for measurements at room temperature. The data for these measurements are listed in Table III. The temperatures were measured with a copper-constantan thermocouple in conjunction with a Leeds and Northrup Electronic Potentiometer. The values at -30°C are not different from those at room temperature by amounts larger than experimental error. The value at

TABLE I

CALIBRATION OF THE FIELD STRENGTH OF THE ELECTROMAGNET

Mohr's Salt (-29.8°) Δ w	Field Strength (Oersteds)	Conductivity Water (25°) Δ w	Field Strength (Oersteds)
0.144	3880	-0.0020	3780
0.524	7380	-0.0077	7420
0.866	9500	-0.0127	9520
1.097	10680	-0.0158	10630

TABLE II

MAGNETIC SUSCEPTIBILITY TUBE CORRECTIONS AT VARIOUS TEMPERATURES

Field Strength (Oersteds)	Δ w (gms.)			
	25°C	-29.8°C	-75°C	-194°C
3880	0.0000	0.0001	0.0002	0.0002
7380	0.0000	0.0002	0.0004	0.0004
9500	0.0000	0.0002	0.0006	0.0006
10600	0.0000	0.0002	0.0007	0.0007

TABLE III

THE MAGNETIC SUSCEPTIBILITY OF MERCURY AT VARIOUS TEMPERATURES

Field Strength (Oersteds)	Δ w (gms.) 1	2	3	4	Δ wave (gms.)	$-X_{Hg} \times 10^6$	$-X_{Hg} \times 10^6$ (Avg.)
				t = 25 ± 1°C			
3880	0.0063	0.0068	0.0062	0.0067	0.0065	0.168	0.166
7380	0.0225	0.0236	0.0226	0.0237	0.0231	0.165	
9500	0.0379	0.0386	0.0387	0.0388	0.0385	0.166	
10680	0.0479	0.0495	0.0485	0.0495	0.0488	0.166	
				t = -29.3 ± 0.5°C			
3880	0.0068	0.0061			0.0064	0.165	0.167
7380	0.0234	0.0238			0.0236	0.167	
9500	0.0389	0.0388			0.0388	0.168	
10680	0.0500	0.0493			0.0496	0.169	
				t = -75 ± 1°C			
3880	0.0051	0.0051	0.0049		0.0050	0.131	0.135
7380	0.0187	0.0191	0.0187		0.0180	0.136	
9500	0.0311	0.0315	0.0309		0.0311	0.136	
10680	0.0396	0.0406	0.0396		0.0399	0.137	
				t = -194 ± 2°C			
3880	0.0042	0.0042	0.0044		0.0043	0.113	0.118
7380	0.0164	0.0161	0.0164		0.0163	0.118	
9500	0.0278	0.0266	0.0267		0.0270	0.118	
10680	0.0351	0.0338	0.0344		0.0344	0.118	

-190°C is identical with the average of Vogt's[59] results at -183°C obtained from single crystal studies. However, the only other measurement reported in the vicinity of -75°C was that of Oxley[61] who reported a gram susceptibility of -0.15×10^{-6} which differs significantly from the value obtained in these experiments. The results of the measurements at room temperature and at the temperature of liquid nitrogen agree well with those of other investigators; therefore, it can be concluded that the values obtained at -30°C and -75°C are also acceptable.

The Magnetic Susceptibility of Ammonium Amalgam at -30°C

While the amalgam was being prepared the air in jacket A was displaced with dry nitrogen and the Dewar flask was filled with Freon-12. The magnetic susceptibility tube was kept stoppered at both ends in the "cold box". At the completion of electrolysis the tube was carefully filled with purified amalgam, particular care being taken to remove bubbles from the sample. The amalgam was "pushed" into the tube by pressure from a stream of dry nitrogen. When the tube was filled to the mark the top was secured with a ground glass joint and the filled sample tube was placed in a jacket made from 12 mm. o.d. Pyrex tubing. The jacket containing the susceptibility tube was placed in a Dewar flask of boiling Freon-12 inside the cold box, while the Dewar flask containing jacket A in a Freon-12 bath was moved from its position between the pole pieces of the magnet into the cold box. With the Dewar flask containing jacket A clamped inside the cold box the filled magnetic susceptibility tube was quickly wiped with absorbent tissue and the stopper was removed

from the bottom opening of the tube. The top was removed from jacket A and the magnetic susceptibility tube placed in position with the chain passing up through the opening in the top. A cork placed in this opening along with the chain held the sample tube in place while the apparatus was removed from the cold box to its position between the pole pieces of the magnet. The chain from the sample tube was joined to the balance chain and as soon as possible a stream of nitrogen was passed over the tube. After 20 minutes weighings were made at the various calibrated field strengths. Immediately following a series of weighings the sample was poured out into standard sulfuric acid. After decomposition of the amalgam the excess acid was back-titrated with standard base. The gram susceptibilities X, measured at various field strengths, the densities ρ, and the compositions of the amalgams are shown in Tables IV and V. The relation between the density of the amalgam and its composition was not known, so that several additional density-composition measurements were made to obtain data for the more dilute and the very concentrated amalgams. The results of this study appear in Table VI. A tube other than the magnetic susceptibility tube was used as a pycnometer in this particular case.

Discussion of Results

In the investigation of 19 ammonium amalgams, all but two were more diamagnetic than mercury. No obvious relationship exists between the composition and the diamagnetism of the amalgams. When the density is

TABLE IV

THE SPECIFIC MAGNETIC SUSCEPTIBILITIES AND DENSITIES OF AMMONIUM AMALGAMS AT -30°C

ρ (gms./cm.³)	3880 Oersteds		7380 Oersteds		9500 Oersteds		10700 Oersteds	
	Δw	$-X \times 10^6$	Δw	$-X \times 10^6$	Δw	$-X \times 10^6$	Δw	$-X \times 10^6$
13.8	0.0065	0.167	0.0233	0.165	0.0387	0.165	0.0497	0.167
12.0	0.0062	0.183	0.0226	0.183	0.0376	0.185	0.0484	0.186
11.3	0.0060	0.188	0.0225	0.194	0.0373	0.194	0.0478	0.196
10.3	0.0027	0.096	0.0275	0.260	0.042	0.243	0.050	0.223
10.1	0.0052	0.18	0.0239	0.231	0.0384	0.224	0.0499	0.230
9.40	0.0058	0.219	0.0220	0.228	0.0362	0.227	0.0467	0.231
9.23	0.0057	0.27	0.0217	0.229	0.0363	0.232	0.0460	0.232
9.16	0.0047	0.186	0.0213	0.226	0.0364	0.234	0.0464	0.236
9.03	0.0073	0.29	0.0211	0.227	0.0354	0.231	0.0444	0.229
8.56	0.0059	0.244	0.0211	0.240	0.0350	0.241	0.0448	0.242
8.05	0.0055	0.242	0.0199	0.241	0.0336	0.245	0.0429	0.247
7.70	0.0070	0.32	0.0219	0.277	0.0350	0.268	0.0477	0.270
7.27	0.0047	0.229	0.0178	0.238	0.0301	0.244	0.0401	0.256
7.05	0.0048	0.241	0.0186	0.257	0.0306	0.256	0.0394	0.259
6.51	0.0049	0.267	0.0173	0.259	0.0292	0.264	0.0373	0.265
5.95	0.0036	0.219	0.0144	0.235	0.0234	0.232	0.0305	0.239
5.27	0.0027	0.18	0.0101	0.186	0.0170	0.189	0.0217	0.191
4.10	0.0018	0.16	0.0067	0.159	0.0116	0.167	0.0146	0.165
3.93	0.0014	0.14	0.0054	0.134	0.0092	0.138	0.0118	0.139

TABLE V

COMPOSITIONS OF AMALGAMS

ρ (gms./cm.^{3})	$-X \times 10^6$	Moles Hg	Millimoles NH_4	Mole Per Cent NH_4
13.8	0.167	0.254	0.044	0.0173
12.0	0.186	0.221	0.69	0.312
11.3	0.196	0.208	1.35	0.649
10.3	0.233	0.190	0.698	0.367
10.1	0.230	0.182	0.218	0.120
9.40	0.231	0.174		
9.23	0.232	0.170	0.474	0.279
9.16	0.236	0.169	0.456	0.270
9.03	0.229	0.166	0.640	0.385
8.56	0.242	0.158	0.560	0.355
8.05	0.247	0.148	0.353	0.239
7.70	0.270	0.142	0.206	0.145
7.27	0.255	0.134	1.43	1.07
7.05	0.259	0.130	0.66	0.507
6.51	0.265	0.120	1.64	1.37
5.95	0.239	0.110	0.434	0.395
5.27	0.191	0.0973	1.85	1.90
4.10	0.165	0.0752	0.472	0.219
3.93	0.139	0.0727	1.37	1.89

TABLE VI

THE RELATIONSHIP BETWEEN DENSITY-COMPOSITION DATA OF AMMONIUM AMALGAM

ρ (gm./ml.)	Mole Per Cent NH_4
13.61	0.0
13.61	0.059
13.51	0.001
13.43	0.002
13.33	0.002
13.03	0.021
10.11	1.45
9.770	0.172
9.231	0.240
8.672	0.272
8.201	0.595
5.798	0.122
3.469	1.10

plotted versus diamagnetism as shown in Figure 5 the points fall on two intersecting curves. The maximum specific susceptibility -0.270×10^{-6} c.g.s. units/gm. was observed for a sample with density 7.70 gm./ml. The relationship between magnetic susceptibility and density would be more understandable if the density were a function of the composition. The composition-density data suggest that the amalgam contained some gaseous ammonia and hydrogen produced from the partial decomposition of the amalgam under which circumstances the concentration of ammonium as determined by titration would include a concentration of ammonia gas and would not represent the exact composition of the amalgam.

Other impurities in the amalgam consisted of small quantities of ammonium chloride, water and alcohol all of which should have remained largely at the upper surface of the amalgam where the magnetic field was weak and their effect on the magnetic properties of the amalgam were small. Following decomposition amalgams contracted so that a volume of mercury less than sufficient to cover the reference mark remained in the tube, a situation which made weighing of the residue in the magnetic field meaningless. However, the magnetic susceptibility for dilute amalgams which did not contract appreciably following decomposition was essentially the same as mercury. A similar result was obtained if before weighing enough mercury was added to a decomposed concentrated amalgam to increase the volume to the calibration mark of the tube.

Five amalgams had ammonium concentrations between 0.270 and 0.395 mole per cent and specific magnetic susceptibilities between -0.229×10^{-6}

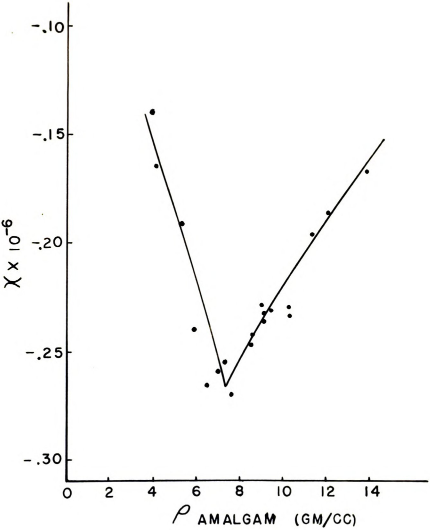


Figure 5. Gram susceptibility-density relationship for ammonium amalgam at -30°C.

and -0.239×10^{-6}. The specific susceptibility of ammonium in each of these amalgams was calculated from the relationship

$$X_{amalgam} = P_{Hg}X_{Hg} + P_{NH_4}X_{NH_4}$$

where P_{Hg} and P_{NH_4} represent the respective weight fractions of mercury and ammonium. The data necessary for these calculations and for the calculation of the corresponding molar susceptibilities appear in Table VII.

The average value -4100×10^{-6} for the molar susceptibility of ammonium seems impossibly high. This must mean that the Brillouin zone in mercury is nearly full and that the few electrons supplied by as little as 0.3 mole per cent of ammonium suffice to complete it. The small concentration of ammonium apparently removed the paramagnetism of the metallic electrons in mercury. If this explanation is correct then the specific susceptibility of ammonium amalgam represents approximately the specific susceptibility of mercury minus its temperature independent paramagnetism. Under these circumstances the diamagnetic susceptibility of mercury is about -0.23×10^{-6} per gram and -46×10^{-6} per mole which is not unreasonable. If the amalgam consists of a mercury solution of a compound such as NH_4Hg_{12}, which is comparable to certain sodium and potassium compounds with mercury, then the molar susceptibility of NH_4Hg_{12} when calculated on the basis of the present measurements would be about -5000×10^{-6} which is an unlikely value for such an entity. Indeed, the fact that ammonium, unlike all the alkali metals except lithium, has no vacant orbitals with which to form intermetallic

TABLE VII

THE MOLAR SUSCEPTIBILITY OF AMMONIUM IN AMMONIUM AMALGAM

$-X_{\text{amal.}} \times 10^6$ (c.g.s. units/gm.)	Mole Per Cent NH_4	$-X_{NH_4} \times 10^6$ (c.g.s. units/gm.)	$-X_M \times 10^6$ (c.g.s. units/mole)
0.229	0.385	180	3200
0.232	0.279	260	4700
0.233	0.367	210	3800
0.236	0.270	290	5200
0.239	0.395	200	3600
		Avg. 230	Avg. 4100

compounds strongly suggests that an ionic compound of the type $NH_4^+Hg_x^-$ must exist. Such a compound may be analgous to the "polyanionic" compounds which sodium forms with lead and tin in liquid ammonia. The compound Na_4Pb_7 imparts the properties of an electrolytic conductor rather than of a metallic conductor to its solution in liquid ammonia; during electrolysis of such solutions sodium ions go to the cathode and Pb_7^{-4} ions go to the anode. A conductivity study of ammonium amalgam should give further evidence as to the similarity of its structure with that of the "polyanionic" compounds described by Huckel[66]; however, the gaseous decomposition products of the amalgam make such a study impractical.

It may be assumed that the density of an amalgam corresponds approximately to the concentration of ammonium in such a way that the density is least for the more concentrated amalgams. The relationship between density and specific susceptibility as diagrammed in Figure 5 then might be interpretable. In the system ammonium-mercury two opposing effects appear to be in operation with regard to the magnetic properties. On the one hand an increase in concentration of ammonium decreases the density and reduces the paramagnetism of mercury as described previously, while on the other hand the decrease in density alone tends to increase the paramagnetic susceptibility component of the free electrons as shown by Stoner[55] and verified by Bates and Baker[67] for mercury. When the increase in paramagnetism produced by the decrease in density overcomes the effect of additional ammonium on the temperature independent paramagnetism a slope change appears in the plot of density versus susceptibility.

VI. SOLID-LIQUID EQUILIBRIA IN THE SYSTEM AMMONIUM-MERCURY

Theoretical Introduction

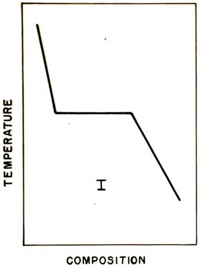
A useful method for establishing the relationship between two substances in solution consists of determining the freezing points of different solutions of the two components. The two substances form a true solution in which there is no interaction between the components if the freezing point of the solvent is decreased by the amount predicted from Raoult's law and the Clausius-Clapeyron equation,

$$\Delta T = \frac{-RT_0^2}{\Delta H}\ln N_a,$$

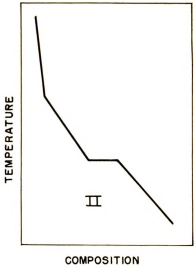
in which ΔT is the freezing point lowering, T_0 is the freezing point of the pure solvent, ΔH is the molar heat of fusion of the solvent, and N_a is the mole fraction of the solute. The freezing point depression of the solvent will be less than that predicted by Raoult's law if the solute forms polymers or if the solute and solvent form compounds; it will be greater than predicted if the solute dissociates to form additional species,[68] and it may be greater, or less, if the components form solid solutions.[69] Different solutions of two substances frequently exhibit a different behavior; for example, the components may form an ideal solution at one concentration of the solute, and a compound at some other concentration. Generally when two substances form a compound, and no solid solutions form, a eutectic composition exists at which one pure

component and the compound freeze out of solution simultaneously. For a two component system the freezing temperatures at various concentrations may be plotted to form a phase diagram from which the composition of compounds and eutectics is established as shown in Figure 6. The method of thermal analysis, in which one plots time-temperature curves during the cooling of a particular solution, provides a useful means for obtaining data for making a phase diagram. Whenever a phase change or transition in structure takes place during the cooling process, the rate at which heat is evolved from the system changes, and thus the slope of the cooling curve is altered.

In Figure 6, curve I represents the time-temperature plot as a pure substance is cooled below its freezing temperature. The temperature remains constant at the freezing point until all the liquid has solidified and then the temperature falls uniformly again. Curve II is a typical cooling curve for a two component system which shows only a simple eutectic point. The first break appears in the curve when solid begins separating out with evolution of heat and a corresponding change in the cooling rate. As the solid phase forms the composition of the solution varies continuously so that at no time does the temperature remain constant until the eutectic composition is attained. The length of time during which the temperature remains constant at the eutectic point varies with the original composition of the solution and is a maximum for the pure eutectic solution.



Cooling curve for a pure substance.



Cooling curve with eutectic halt in a two-component system.

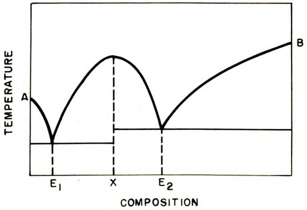


Figure 6. Phase diagram for a two-component system with a compound of composition x, and eutectics with compositions E_1 and E_2.

Historical Summary

Amalgams are two component systems for which rather complete phase diagrams are available. In the phase diagrams for lithium, sodium, and potassium amalgams several maxima appear as a result of compound formation with mercury.[70] A freezing point-composition study of ammonium amalgam should provide information concerning the nature of the substance, and particularly as to whether compounds form between ammonium and mercury. Rich and Travers[15] reported in 1906 the freezing points of several ammonium amalgams prepared from sodium amalgam and ammonium iodide in liquid ammonia. In Table VIII appear the results of their investigation which are not entirely consistent, but do suggest that the freezing point lowering constant of mercury decreases as the concentration of ammonium increases. Bent[71] calculated the freezing point lowering of mercury to be 1.9°C per atom percent of solute for dilute solutions obeying Raoult's law. Using Vanstone's[45] phase diagrams of sodium amalgams, Bent verified the calculated value. For the more dilute amalgams in Rich and Travers' investigation, the freezing point lowering evaluated with Bent's value agrees favorably with the experimental results, but for the concentrated amalgams the behavior is non-ideal.

Introduction to Experimental Procedure

A phase diagram obtained by determining the freezing points of ammonium amalgams of various compositions should show whether compounds of the type NH_4Hg_x do, or do not, exist. However, certain observations during this present investigation suggest that the freezing process in ammonium amalgam is not a simple one. Ammonium amalgams appear not to

TABLE VIII

DEPRESSION OF THE FREEZING POINT OF MERCURY BY AMMONIUM

(Freezing point of mercury = -39.40°C)

$\frac{\text{Gms. } NH_4}{\text{100 gms. Hg}}$*	Mole Per Cent NH_4	**Freezing* Point (°C)**	Δt (°C)	Δt Predicted by Theory (°C)	**K_m* for Mercury**
0.0094	0.104	-39.62	0.22	0.20	420
0.0117	0.13	-39.67	0.27	0.25	420
0.027	0.30	-40.01	0.61	0.57	410
0.079	0.88	-40.81	1.19	1.7	320
0.084	0.93	-41.605	1.99	1.8	470
0.415	4.7	-44.82	5.20	8.9	230
0.507	5.6	-45.61	5.99	10	220

*From observations by Rich and Travers.[15]

be of the same consistency after freezing and melting as they were before freezing. When a tube of amalgam prepared by electrolysis is immersed in a Dewar flask containing liquid nitrogen, gas is rapidly evolved and the odor of ammonia is very apparent. The upper surface of the amalgam attains a sponge-like appearance with large bubbles being interspersed in the mercury. Upon warming a frozen amalgam additional ammonia appears to be evolved, but a second freezing is usually not accompanied by so vigorous a release of gaseous material as a first freezing.

A qualitative measurement of the volume of gas released by an amalgam during freezing was made. Inside the cold box the magnetic susceptibility tube was filled with amalgam and immersed in a bath of boiling Freon-12. The tube was attached to the gas burette previously used in the analysis of some amalgams. With the amalgam at the temperature of boiling Freon a slight increase of about 0.2 ml. in volume was noted after five minutes. When a liquid nitrogen bath was substituted for the Freon bath bubbles were evolved from the amalgam but the gas burette showed a decrease in volume due to the contraction of the amalgam and gas at the liquid nitrogen temperature. Upon warming the frozen amalgam in Freon-12 the volume of gas in the system had increased to about two milliliters. An additional freezing and melting produced no observable volume change.

Apparatus for Recording Cooling and Warming Curves

The freezing process of ammonium amalgam was investigated by obtaining a series of cooling curves for several amalgams in three types of

experiment. In each case the apparatus consisted of a freezing tube for the amalgam, an air jacket to keep the cooling rate uniform, and a Dewar flask for immersing the sample tube and jacket in a suitable refrigerant. The temperature in each of the three different experiments was measured with copper-constantan thermocouples connected to a Leeds and Northrup Type K-2 Potentiometer. In addition, complete cooling and heating curves were produced on a Brown-Honeywell Electronic Recorder operated in conjunction with a Leeds and Northrup D.C. Indicating Amplifier and a bucking voltage produced by three 1.5 volt dry cells and regulated with the slide wire of a Leeds and Northrup Student Potentiometer. The circuit diagram appears in Figure 7. Without additional modification a maximum potential of 2.4 millivolts could be measured with the amplifier and recorder with a sensitivity of only 0.2 millivolts (about six degrees) per inch of recorder tape. For the proposed study of the freezing process in ammonium amalgam both the range and the sensitivity of the recording potentiometer were increased through use of the bucking voltage which, as seen from Figure 7, was a variable e.m.f. opposed to the e.m.f. produced by the thermocouple junctions. By opposing the potential difference between the thermocouples with a sufficiently large known voltage the total potential difference was reduced to any suitable small value which could be amplified to satisfy the requirements of the experiment. At any time the e.m.f. which represented the difference in temperature between the two junctions was the sum of the absolute value of the bucking voltage and

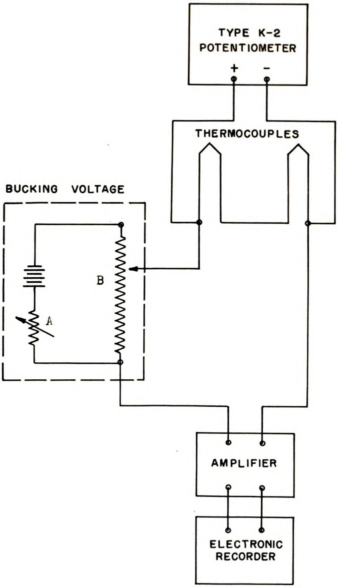


Figure 7. Schematic diagram for recording cooling curves: A, Heathkit Resistance Decade for coarse adjustment of bucking voltage; B, slidewire of L. & N. student potentiometer for fine adjustment.

the voltage read from the recording potentiometer. A scale sensitive enough to allow detection of small arrests in the cooling curves was necessary, so that sufficiently large bucking voltages were introduced to make the scale factor either 0.02 or 0.05 millivolts per inch in all the recorded cooling curves. A maximum e.m.f. of 1.6 volts could be measured in this way without the introduction of a voltage multiplying device on the potentiometer. The exact e.m.f. produced by the thermocouple at any time was read from the Type K-2 potentiometer and simultaneously marked on the recorder tape. From the Type K-2 potentiometer reading and the scale sensitivity of the recorder, the voltages could be accurately calculated for each setting of the bucking voltage without actually knowing the bucking voltage.

Cooling and Warming Curves for Each of the Two Phases of an Amalgam

Experimental Procedure

The first type of experiment performed in the investigation of the freezing process of ammonium amalgam was the simultaneous procurement of cooling curves for each of the two phases of an amalgam in an attempt to distinguish differences between the phases. If the upper phase contains a higher concentration of ammonium, combined in some way with mercury, than the lower phase contains, then the cooling curves of the two phases should be dissimilar. The effect on the freezing point of successively freezing and melting the same amalgam was also investigated.

The freezing temperature of an amalgam should differ after freezing and melting if the composition changes during freezing.

Two thermocouples were used for measuring the temperature of each of the two phases independently. To keep the phases separate stirring was eliminated in this particular experiment. In most freezing point determinations stirring is necessary to keep the temperature of the sample uniform throughout, but stirring is not so essential when a good thermal conductor such as mercury is a large constituent of the material under observation. At the same time the good conducting properties of mercury may have been a hindrance in this study because the two phases of the amalgams were in no way insulated from one another, so that some of the heat produced by changes in one phase was probably transferred to the other and may have altered the appearance of the cooling curve for the second phase.

For accurate comparison of the temperature in two phases with two different thermocouples the thermocouples had to be well matched. A longer segment of the thermocouple used in studying the lower phase must necessarily be immersed in the sample than of the thermocouple used in the upper phase. Such difference in immersion depths could introduce a slight temperature deviation between the two thermocouples as a result of variations in the amounts of heat conducted down the wires from the different surroundings of the two thermocouples. To minimize the effect of heat conductance the smallest diameter thermocouple wires available were used, namely, number 40 copper wire and number 30 constantan wire.

Each thermocouple was constructed with two silver-soldered junctions, one junction for an ice bath at 0°C and the other junction for the sample. To further lessen the differences in heat conducted down the thermocouple wires the length of the wire actually exposed to the cold area was made larger by coiling the wires. A six inch piece of 3 mm. Teflon tubing was sealed at one end by warming in a small flame. About fifteen inches of insulation were removed from each wire just above one junction and the wires then coiled around the Teflon tubing with the junction at the sealed end. Along three inches of the Teflon the wires were coiled as tightly and as closely as possible without shorting. The tube was warmed very gently to embed the wires partially in the Teflon, after which the tube and wires were covered with a thin coat of polystyrene to protect the thermocouple wires from reaction with mercury in the amalgams. In the same manner one junction of the other thermocouple was mounted on the outside of a four inch piece of 7 mm. Teflon tubing which had not been sealed at one end. After the coating had hardened on each thermocouple the larger diameter Teflon tube was slipped over the smaller diameter tube in a sleeve-like arrangement which permitted adjustment of the relative positions of the two junctions. The sample tube was made from 25 mm. i.d. Pyrex tubing and was supported with a rubber stopper inside a jacket made from 45 mm. i.d. Pyrex tubing. The thermocouples were centered in the sample tube by a one-hole rubber stopper as shown in Figure 8. The two thermocouples were checked against one another by measuring their respective temperatures when both junctions of each were immersed in an ice-water bath at 0°C, and when one junction

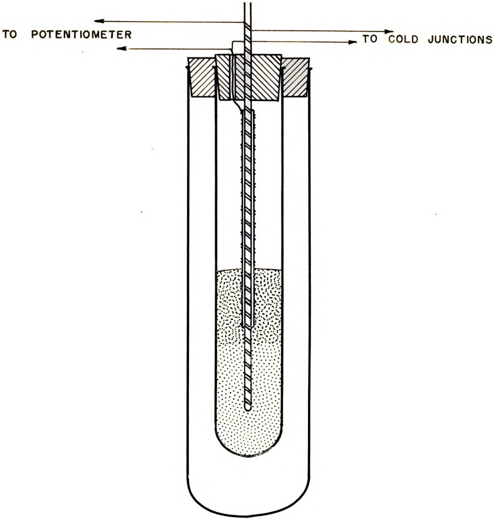


Figure 8. Pyrex freezing tube and jacket for studying the freezing process in a two-phase system. The thermocouples are mounted on concentric fluorethene tubes.

of each was in powdered Dry Ice and the other junction was at 0°C. Three pairs of mounted thermocouples were made before a sufficiently well matched pair was obtained. The difficulty in matching was largely a result of differences in the amount of heat conducted from the surroundings down through the wires because of the difference in level of the two thermocouple junctions in the sample. The problem was overcome by coiling the upper thermocouple up and down the Teflon tube several times and by using a thinner coat of polystyrene on the two thermocouples. The two thermocouples were calibrated, and simultaneously the purity of the mercury used for preparing the amalgams established, by comparing the freezing point of mercury measured by the matched thermocouples with the freezing point measured by a calibrated thermocouple. The calibrated thermocouple made from copper-constantan was checked at several temperatures with a platinum resistance thermometer and found to compare well with the values listed in tables. The freezing point of mercury was determined from the cooling curve obtained using the calibrated thermocouple and the electronic recorder, and was found to be -38.87°, or -1.423 millivolts, which agrees exactly with the best reported freezing point of mercury.[72] The freezing point of mercury determined from the matched thermocouples was -1.409 millivolts. A suitable correction was made for all measurements with these thermocouples.

Ammonium amalgam was prepared by electrolysis, washed in alcohol and water, and dried as well as possible with absorbent tissue. Inside the cold box the freezing tube and jacket, which had been kept in the cold during the electrolysis, were placed inside a Dewar flask containing

a Dry Ice-acetone bath. About 30 ml. of the amalgam was poured into the sample tube, and the thermocouples were fixed into place with the lower couple about 1/2 inch from the bottom of the tube and the upper couple centered in the less dense phase. The Dewar flask containing the sample was left inside the cold box during cooling. During warming the jacket and tube were removed from the Dewar flask, but kept inside the cold box. The cooling curve produced by either phase of the amalgam was plotted by switching the proper thermocouple into the circuit of the recorder. As the temperature decreased the indicator would move to the far end of the recorder scale, but upon introduction of the proper bucking voltage the indicator returned to the zero point and was permitted to scan the width of the scale once again. For each adjustment of the bucking voltage a Type K Potentiometer reading was made and marked on the recorder chart.

Results and Discussion

Cooling curves extending down to -74°C for two amalgams were obtained by means of the described procedure. Warming curves were likewise plotted. For two amalgams the successive cooling and warming curves appear in Figures 9, 10, 11, and 12, which were plotted from the data on the recorder chart. During freezing gas bubbles were evolved from the surface of the amalgams and the volume of the samples was observed to decrease after the first freezing and melting. The amalgams were not analyzed for ammonium content as it was felt that appreciable decomposition took place during the freezing process and that an analysis after freezing would be of little significance.

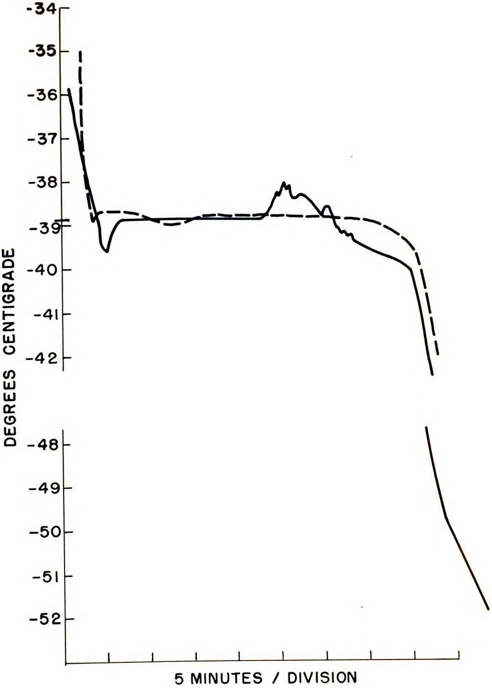


Figure 9. Cooling curves procured simultaneously for two phases of amalgam I: extension shows solid state transition; --- cooling curve for lower phase; ——— cooling curve for upper phase; f.p. of Hg is -38.9°C.

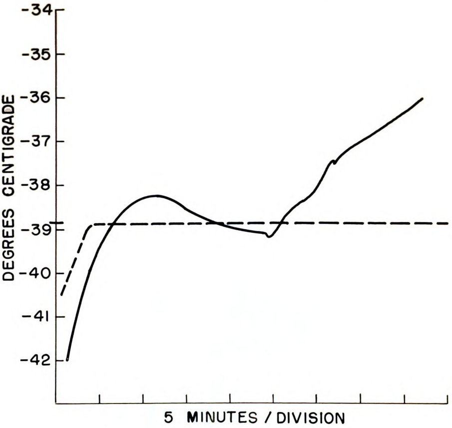


Figure 10. Warming curves procured simultaneously for two phases of amalgam I: --- warming curve for lower phase; ___ warming curve for upper phase; f. p. of Hg is -38.9°C.

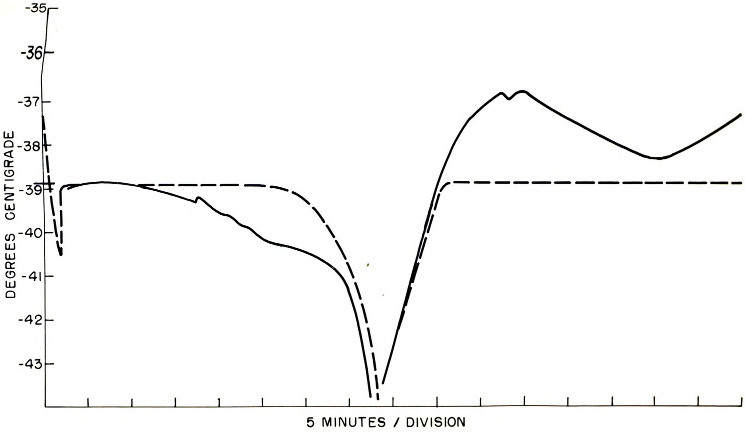


Figure 11. First successive cooling and warming curves for the two phases of amalgam II: --- lower phase; —— upper phase; f. p. of Hg is -38.9°C.

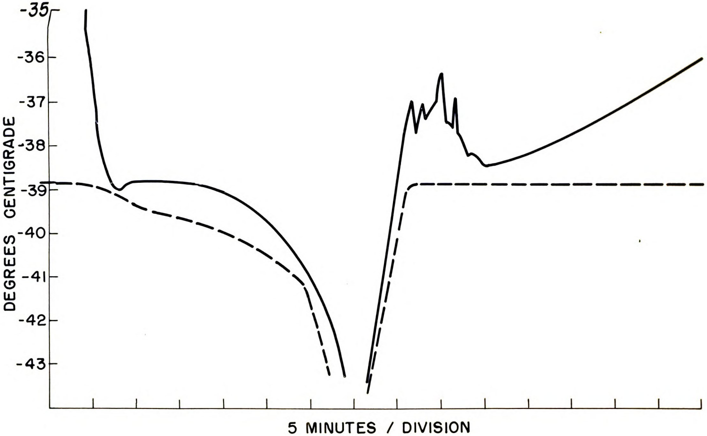


Figure 12. Second successive cooling and warming curves for the two phases of amalgam II: --- lower phase; —— upper phase; f. p. of Hg is -38.9°C.

The freezing point observed from cooling curves with the upper and lower thermocouples in pure mercury are essentially the same. The length of the break at the freezing point depends on the quantity of material in the region of the thermocouple and for this reason is shorter for the upper thermocouple, which occupied a more shallow position in the mercury, than for the lower thermocouple. The effect of the amalgam on the freezing point of mercury is not entirely clear. In the series of cooling curves for amalgam I the freezing point at the lower thermocouple is essentially that of pure mercury. The break produced by the upper thermocouple is not completely linear, but in some cases crosses the freezing point break of the lower couple. During warming the temperature tends to rise near the completion of the break of the upper phase, and during cooling, at the initiation of the break. A slight change of slope appeared during the first cooling of amalgam I in the vicinity of -69°C to -70°C and was not present in the successive warming and cooling curves.

During the first cooling of amalgam II the freezing point in the vicinity of both thermocouples was essentially the same as the freezing point of mercury, although a second break appeared at -40°C in the cooling curve of the upper phase. The second break approximates that of a eutectic break, but does not appear in any of the other cooling curves from this experiment and cannot be regarded as particularly significant. On the same cooling curve a third small break occurred at -61°C. The warming curves produced by the lower thermocouple in amalgam II are comparable to that of mercury, although the freezing temperature during the

second freezing and melting is lower than that of mercury. Both warming curves show that the temperature of the material near the upper thermocouple rises at the beginning of melting, falls for a time, and then rises again at the completion of melting.

Cooling and Warming Curves Obtained During Agitation of Amalgams

Experimental Procedure

A second type of experiment for investigating the freezing process in ammonium amalgam consisted of freezing an amalgam in a fluorethene tube attached to the shaft of a reciprocating stirrer.[73] The shaking motion of the stirrer provided a means for making the amalgam sample relatively homogeneous with respect to composition and temperature. In the apparatus for this experiment a single copper-constantan thermocouple was coiled around a fluorethene rod attached to the top of the tube as shown in Figure 13. To decrease the rate of cooling the freezing tube was enclosed in a jacket made from sheets of fluorethene and sealed together with fluorethene wax. Inside the cold box the sample tube with the jacket attached was filled with about 30 ml. of amalgam, quickly placed outside the cold box in a Dewar flask filled with Dry Ice-acetone, and connected to the stirrer by fitting the tube over the machined fluorethene top. The reciprocating stirrer was turned on and the amalgam sample moved up and down through the cooling bath as the time-temperature curve was plotted on the electronic recorder in the same manner as in the previous experiment. During warming the Dry Ice-acetone bath was removed and the tube shaken in air. Three successive cooling and warming curves obtained by this method for one amalgam sample appear in Figures 14 and 15.

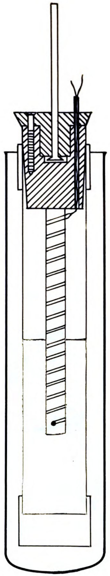


Figure 13. Fluorethene freezing tube and jacket: the shaft was attached to the chuck of a reciprocating stirrer.

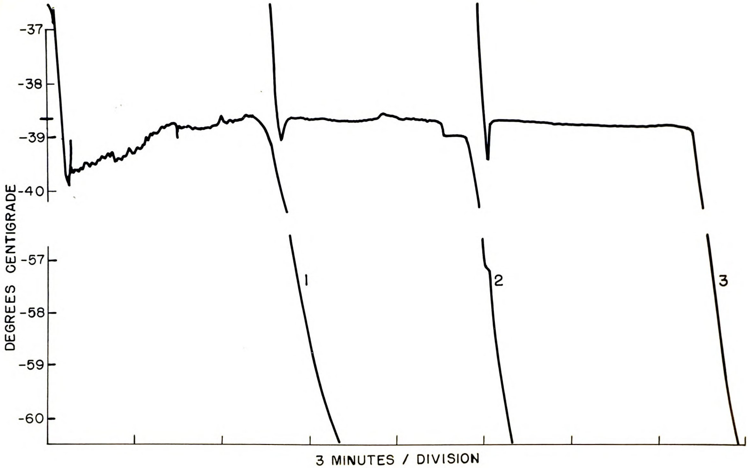


Figure 14. Successive cooling curves for amalgam III obtained while shaking the amalgam: extensions show possible solid state transitions; f. p. of Hg is -38.9°C.

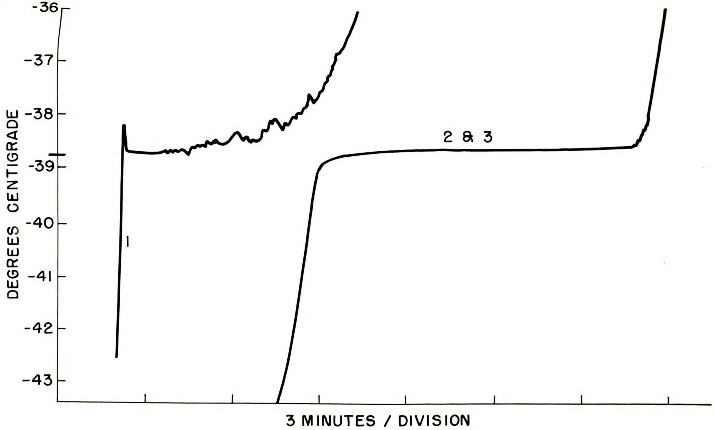


Figure 15. Warming curves for amalgam III obtained while shaking the amalgam. The curves for the second and third warming of amalgam III were essentially identical; f. p. of Hg is -38.9°C.

Results and Discussion

During the first freezing the initial break in the cooling curve occurred below the freezing point of pure mercury but the temperature rose above the freezing point of mercury before the amalgam solidified. The first warming curve, although slightly erratic above the freezing point of mercury, contained a definite break at the freezing point of mercury, while in the last two cooling and warming curves the freezing temperature of the amalgam was slightly above that of mercury. Between -56°C and -59°C the slope of each of the cooling curves changed. The break occurred at a higher temperature and became less pronounced after each consecutive freezing.

The time-temperature curves produced in this experiment suggest that some decomposition of the amalgam takes place either during freezing or as a result of the agitation of the stirrer.

A transition in the solid phase which occurs at different temperatures depending on the original composition of the amalgam would explain the breaks in the cooling curves at low temperatures. However, since no relationship can be established between the temperatures at which the slope changes occurred and the compositions of the amalgams, it seems possible that the breaks resulted from failure to attain thermal equilibrium during the cooling process.

Cooling and Warming Curves Obtained While Ammonium Amalgam Was Decomposing in a Closed System

Experimental Procedure

To investigate further the nature of ammonium amalgam a system was devised in which an amalgam could be frozen and the volume of hydrogen and ammonia released during the freezing could be measured. If ammonium amalgam contains gaseous material only loosely combined with mercury some separation of gas from the mercury could be expected when an amalgam was placed in an evacuated vessel. Measurements of the volume of hydrogen, which diffuses readily, are better made under reduced pressure than under positive pressure in a gas burette.

The apparatus, as illustrated in Figure 16, consisted of a pump for evacuating the system, a manometer for measuring pressures between 0.1 cm. and 76 cm., a freezing tube for the amalgam samples, a trap for complete removal of water and alcohol from the amalgams, and a flask of known volume for calibration purposes. The freezing tube shown in Figure 17 was made from 14 mm. o.d. Pyrex tubing attached to a $ 19/38 ground joint and the jacket surrounding the tube was made from 25 mm. o.d. Pyrex tubing. The trap D in Figure 16 was used for condensing alcohol or water vapor which remained in the sample--under the assumption that most of the alcohol and water would vaporize as soon as the amalgam was under reduced pressure and that the vapors would condense rapidly in the trap surrounded by liquid air. The apparatus would have been improved if a means for stirring the amalgam had been provided, but no space was

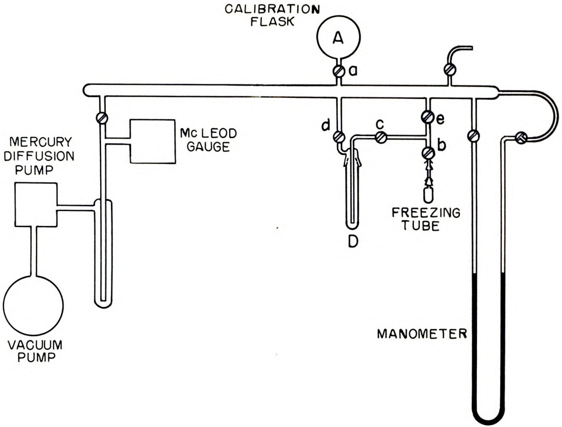


Figure 16. Vacuum system for measuring the volume of gas evolved by an amalgam during freezing.

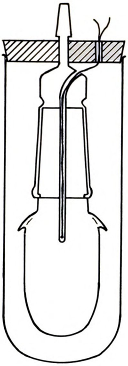


Figure 17. Pyrex freezing tube and jacket for studying the rate of decomposition of an amalgam during freezing: a 10/30 standard taper joint connects to vacuum line.

available for putting a stirrer through the top of the tube and the necessity of surrounding the sample with a cooling bath prevented the use of a magnetic stirrer. Liquid nitrogen was used as a refrigerant to provide rapid cooling of the amalgam to a temperature below that attainable with a Dry Ice-acetone bath. Liquid nitrogen provided too rapid cooling in the previous experiments.

Before flask A was sealed to the manifold the volume was calculated from the weight and density of the distilled, air-free water which just filled the flask to the stopcock. The volume of flask A was found to be 514.2 ml. With the flask attached to the manifold the volume V of the vacuum system was determined through the use of the perfect gas relation,

$$PV = P'V'.$$

A volume of V ml. of helium was introduced into the system at P cm. pressure and the flask A of volume V' ml. was closed to the manifold. The remainder of the system was evacuated and the helium from flask A was released into the system at pressure P'. The pressures P and P' were measured by observing the level of the mercury in each arm of the manometer with a cathetometer; the volume V' of the flask had previously been determined, so that only V was unknown and was computed from the above equation.

In the measurement of pressure with a mercury-filled manometer convention requires that the height of the mercury column at the temperature of measurement be corrected to the height at $0^{o}C$. Mercury expands

on heating; therefore, the height of the column is greater at room temperature than at 0°C and a correction is subtracted according to the equation

$$h_o = h_t(1 - \alpha t)$$

where h_o and h_t are respectively the height of mercury at 0°C and at t°C. The coefficient of expansion of mercury is represented by α and has the value 182×10^{-6} ml./ml.°C. The stainless steel scale of the cathetometer expands as the temperature increases, which makes the measured height of the mercury column less than the true value and necessitates the addition of a correction to the height of the column at 0°C:

$$h_o = h_t(1 - \alpha t)(1 - \gamma t)$$

where γ is the coefficient of expansion of No. 18-8 stainless steel and has the value 10×10^{-6} ml./ml.°C. The term which contains the product of α by γ was negligible, so that the corrected value for the pressure readings in this investigation was

$$h_o = h_t(1 - \alpha t - \gamma t) = h_t(1 - .000172t).$$

The data for the calibration of the volume of the closed system appear in Table IX. The volume V measured in the calibration with helium is represented by the expression

V = V' + volume of amalgam + volume of mercury
displaced in left arm of the manometer
+ volume of flask A,

TABLE IX

CALIBRATION OF THE VOLUME OF THE CLOSED SYSTEM

	Pressure of Helium (cm.)	Volume V' (ml.)	ΔV_L (ml.)	Volume of Flask (ml.)	Volume of Freezing Tube (ml.)	Volume of System (ml.)
Including trap	28.56	1302	10.2	514.2	27.43	750
Including trap	27.33	1303	9.8	514.2	27.43	752
Without trap	31.08	1204	11.1	514.2	27.8	650
Without trap	29.81	1202	10.6	514.2	27.8	649

where V' is the actual volume occupied by the gas evolved from an amalgam. The volume of mercury (in ml.) displaced in the left arm of the manometer was calculated from the equation

$$\Delta v_L = \pi r^2 \Delta h_L$$

where r was the radius of the manometer tubing in centimeters and Δh_L was the difference in the levels of the mercury at zero pressure and at the measured pressure in centimeters.

Before a sample of the amalgam was placed on the line the system was pumped out and then closed to the pumps. A Dewar flask of liquid nitrogen was placed around the trap D and all stopcocks were closed except the one to the left arm of the manometer. Inside the cold box the freezing tube was filled with amalgam, particular care being taken to remove the alcohol and water from the surface of the amalgam. The freezing tube and jacket were assembled as illustrated in Figure 17 and immediately put into place as shown in Figure 16. An unsilvered Dewar flask with liquid nitrogen was placed around the jacket and the thermocouple wires were connected to the potentiometer. Stopcocks b, c, and d to the liquid nitrogen trap were opened for two or three minutes and then the trap was closed while stopcock e was opened. Under decreased pressure gas was vigorously released from the amalgam. The pressure in the system increased rapidly soon after the amalgam was placed on the system and during the initial stages of freezing. Whenever possible several cooling and warming curves were plotted on the electronic recorder for a given

amalgam sample. The pressure in the closed system was recorded at the minimum and maximum temperatures. During warming, the Dewar flask containing liquid nitrogen was replaced by a Dewar flask containing isopropyl alcohol at room temperature. At the completion of a series of measurements the amalgam was warmed to room temperature while it decomposed slowly on the vacuum line. On several occasions after the amalgam had remained at room temperature for a time the residue was frozen and the pressure at the low temperature recorded. In each case the pressure and volume of the enclosed gas decreased noticeably probably as a result of contraction of mercury in the sample tube and of gas in the vicinity of the cold area. In addition small quantities of alcohol and water vapors which had not been removed earlier may have condensed. That the pressure change after cooling a decomposed sample was not unreasonably large suggests that most of the alcohol and water impurities had been removed. Droplets of liquid always were present in trap D after a series of measurements. After four to eight hours the decomposed amalgam was removed from the apparatus and the mercury was dried and weighed.

Results and Discussion

The observations made on five amalgams appear in Tables X and XI and Figures 18 through 21. A sample of pure mercury was also frozen on the vacuum line and a cooling curve plotted down to about -150°C to show that none of the breaks in the curves were produced from solid state transitions in pure mercury. The pressure remained constant while

TABLE X

MEASUREMENT OF THE DECOMPOSITION OF AMALGAMS DURING FREEZING AND MELTING

	Pressure of NH_3 and H_2 (cms.)	Δh_L (cms.)	ΔV_L (ml.)	Total Volume NH_3 and H_2 S.T.P.
		Amalgam IV		
	Volume of gas in trap = 6.5 ml.		t = 26°	
At -74°	5.32	2.70	1.9	49.9
At -35°	6.39	3.26	2.3	58.6
At room temp. (after 7 hrs.)	10.55	5.32	3.8	92.7
		Amalgam V		
	Volume of gas in trap = 8.6 ml.		t = 29°	
At -160°	7.15	2.73	2.0	65.9
After melting*	6.79	3.43	2.5	63.7
At -100°	6.72	3.43	2.5	63.2
After melting	8.11	4.12	2.9	74.2
At -74°	8.06	4.11	2.9	73.8
After melting	8.64	4.45	3.2	78.6
At -160°	8.24	4.20	3.0	75.3
After melting	8.60	4.40	3.1	78.2
Final (after 4 hrs.)	14.23	7.23	5.0	123.7
		Amalgam VI		
	Volume of gas in trap = 4.8 ml.		t = 26°	
At -160°	3.99	2.00	1.4	37.6
After melting*	4.11	2.06	1.5	38.5
At -160°	3.74	1.88	1.4	35.6
After melting	3.80	1.91	1.4	35.9
At -160°	3.39	1.72	1.2	32.6
After melting	3.41	1.73	1.2	32.7
At -160°	3.22	1.62	1.1	31.1
After melting	3.31	1.67	1.2	31.9
At room temp. (after 4 1/2 hours)	7.33	3.67	2.6	64.7
After freezing residue	6.78	3.42	2.4	60.1

*Between -35°C and -40°C.

Continued next page

TABLE X - Continued

	Pressure of NH_3 and H_2 (cms.)	Δh_L (cms.)	ΔV_L (ml.)	Total Volume NH_3 and H_2 S.T.P.
		Amalgam VII		
	Volume of gas in trap = 1.2		t = 32°	
At -160°	0.98	0.49	0.35	9.00
Melting) Freezing) Melting)	No data			
At -160°	1.01	0.52	0.37	9.24
After melting* (1 hr. later)	4.68	2.40	1.70	38.8
After freezing (1 hr. later)	4.32	2.18	1.55	35.9
Final	6.10	3.10	2.20	50.2
		Amalgam VIII		
	Volume of gas in trap = 5.3 ml.		t = 30°	
At -160°	4.40	2.20	1.6	40.8
After melting*	3.93	1.96	1.4	37.0
Freezing) Melting)	No data			
At -160°	4.57	2.30	1.6	42.1
Final	5.78	2.90	2.1	52.1
After freezing residue (-160°)	5.71	2.86	2.0	51.2

*Between -35°C and -40°C.

TABLE XI

THE CHANGE IN COMPOSITION OF AMMONIUM AMALGAMS ON FREEZING

Amalgam	Wt. of Hg	Moles of Hg	Sample Volume	Sample Density	Moles NH_4 Released by First Freezing	Total Moles NH_4	Mole Per Cent NH_4 in Amalgam Originally	Per Cent Decomposition During First Freezing and Melting
IV	320.2	1.60	27.8	11.5	0.00174	0.00276	0.173	63.0
V	298.0	1.49	27.8	10.7	0.00189	0.00368	0.254	51.6
VI	261.1	1.31	23.6	11.1	0.00115	0.00192	0.147	59.9
VII	277.4	1.38	23.6	11.7	0.00268	0.00149	0.108	18.0
VIII	234.0	1.17	23.6	9.90	0.00110	0.00152	0.132	72.5

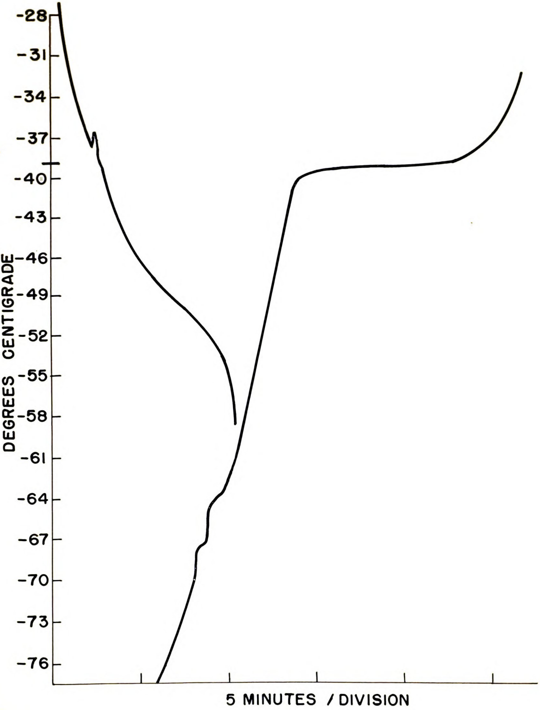


Figure 18. First successive cooling and warming curves for amalgam V obtained with the freezing tube joined to an evacuated apparatus; f. p. of Hg is -38.9°C.

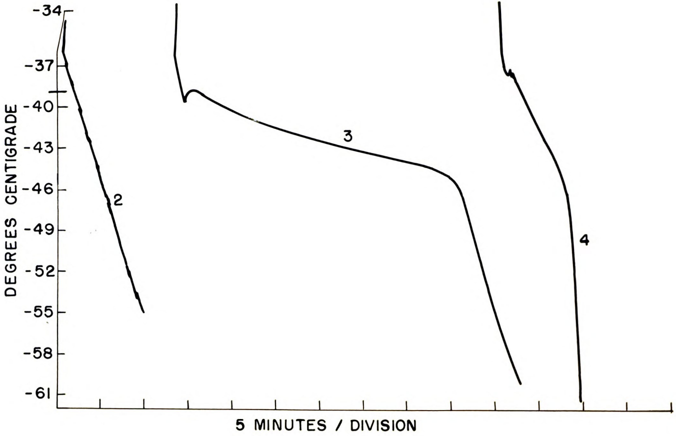


Figure 19. Second, third, and fourth cooling curves for amalgam V obtained with the freezing tube joined to an evacuated apparatus; f. p. of Hg is -38.9°C.

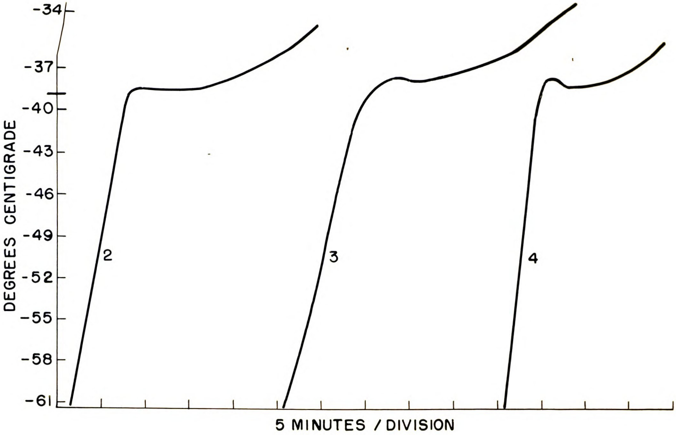


Figure 20. Second, third, and fourth warming curves for amalgam V obtained with the freezing tube joined to an evacuated apparatus; f.p. of Hg is -38.9°C.

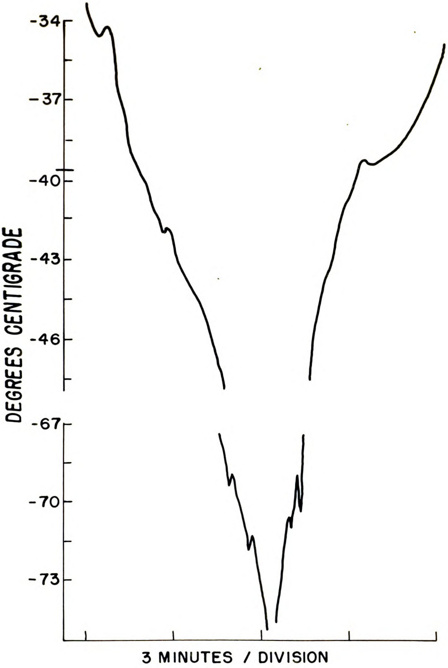


Figure 21. Cooling and warming curve for amalgam VIII obtained with the freezing tube attached to an evacuated apparatus; f. p. of Hg is -38.9°C.

the sample was cooled and warmed on the vacuum line and no changes in slope were apparent in the time-temperature plots.

The volume of gas present in the system at any time under standard conditions was represented by the equation

$$V = V'P'T/PT' = (\text{volume of system})(273^{\circ}C)P'/76\text{cm}.T'.$$

A small correction was added for the volume of mercury displaced in the arm of the manometer by the gas in the system:

$$\Delta v_L = \pi r^2 \Delta h_L.$$

The initial pressure was measured after the liquid nitrogen trap had been opened to the system. For this reason the pressure as first measured was the pressure of a volume which included the volume of the trap. The volume of the gas in the trap at standard conditions was also computed with the above equation and that volume was added to each of the volumes measured after the trap was closed. In Table X the volume of ammonia and hydrogen which was released from the amalgams up to the time at which the second freezing was begun is listed in the second line of the data for each amalgam in column 5. The per cent of decomposition during the initial exposure to reduced pressure and during the first freezing was calculated, but there is no obvious correlation between this decomposition and the original density or composition of the amalgam. Perhaps the amount of loosely held gas which is present in an amalgam depends on the past history of the sample.

The accuracy with which the temperature of the amalgam and the pressure in the closed system could be measured doubtlessly surpass the fundamental errors in the procedure. The temperature of the ammonia and hydrogen in the vicinity of the freezing tube was probably lower than room temperature and the measured volume of the gases accordingly less than if the system were entirely at the temperature of the room. The means for trapping out alcohol and water may not have been entirely effective although the largest decrease in volume observed on cooling a decomposed amalgam to -160°C was about three milliliters as is shown in the data for amalgam VII. Although about 0.5 ml. of this change can be attributed to the contraction of mercury the decrease is appreciable, but should have been much larger if vapors of impurities were present before cooling the tube with liquid nitrogen. A correction was made for volume of ammonia and hydrogen which remained in trap D, but the possibility exists that this correction may have been too small because more ammonia and hydrogen may have been entrapped at the low temperature than if the trap were at room temperature where its volume was calibrated. Since some of these errors would have opposite effects on the measurements the maximum inaccuracy of the volumes should not be more than about five per cent.

The results from this series of observations on freezing amalgams in a closed system indicate that in certain cases ammonia and hydrogen are so loosely held in the amalgam that reduced pressure and freezing remove about half of the gaseous material. Nevertheless, the remaining

ammonia and hydrogen form a stable combination with mercury that decomposes only at higher temperatures and after several hours. No correlation between the composition of the amalgam and the halts in the cooling curves could be established. It is difficult to assign an actual freezing temperature to a given amalgam from the appearance of the corresponding cooling curve.

The rate of cooling in most cases was much more rapid in this experiment than in the previous experiments, and the appearance of the curves varies somewhat depending on whether liquid nitrogen or Dry Ice-isopropyl alcohol was used as a refrigerant. In general arrests appear in the cooling curves at higher temperatures on successive freezing and warming, and at times occur even above the freezing point of mercury. The shape of the cooling curves is perhaps more characteristic of a two component system in which solid solutions form than of a system in which a eutectic composition exists. A eutectic halt produces a horizontal portion in the curve, but when two substances form a continuous series of solid solutions only breaks appear at the beginning and at the completion of freezing. Slope changes at temperatures between -60°C and -75°C were observed in several of the cooling curves from this particular series of observations. However, the rate of cooling was much too rapid for equilibrium to be attained so the arrests in the cooling curves cannot be easily interpreted.

Conclusions

The cooling and warming curves for the system ammonium-mercury show that the system is more complex than that expected if ammonium forms an ideal solution in mercury. If the freezing point of mercury was actually lowered by ammonium the depression was masked by the rise in temperature as a result of decomposition at the freezing temperature. The first freezing decomposes the upper phase of the amalgam extensively as observed by the volume of gas released during freezing, the contraction of the volume of the amalgam after freezing, and the tendency of the upper phase to disappear after the amalgam has been frozen and melted several times. Nevertheless, an appreciable concentration of ammonium was retained in the amalgam after a succession of freezings and meltings. The fact that many of the cooling curves exhibit definite changes in slope without a horizontal break in the vicinity of -41.5°C suggests that a solid solution may form. Such a solution might well be a solution of some compound between ammonium and mercury in mercury. The concentration of ammonium in the amalgams was so small that the possibility of the solutions exhibiting anything but ideal behavior might be thought unlikely; however, in the thermal analysis diagrams for sodium and potassium amalgams eutectics appear at concentrations of less than two atom per cent. The corresponding eutectic halt for sodium occurs at -50°C and for potassium at -45°C.

On seven cooling curves definite slope changes appeared between -50°C and -68°C while similar breaks appeared on six warming curves between -54°C and -73°C; no correlation was found between the appearance

of these breaks and the freezing temperature of the amalgams. These slope changes were not necessarily exhibited by successive warming and cooling curves. The rate of warming and cooling may have been such that a solid state transition did not always occur, so that one form of the solid was in a metastable state part of the time. The possibility that these breaks appeared because thermal equilibrium was not attained during cooling of the solid mixture must be considered. Equilibrium may not have been reached particularly in the experiments in which liquid nitrogen was employed as a refrigerant and the rate of cooling was accordingly very rapid. On the other hand under circumstances where equilibrium should have been reached; e.g., when the rate of cooling was very slow as shown in Figures 9 through 12 and when an amalgam was stirred during cooling, similar breaks appeared in the cooling curves. Comparable breaks were never observed when pure mercury was cooled down to the same low temperatures.

No experiments have been performed which show whether or not ammonium amalgam is a colloidal dispersion or whether it contains a colloidally dispersed solid. If "ordinary" ammonium amalgam were a colloidal dispersion or a froth of solid colloidal $NH_4^+Hg_x^-$ particles in mercury then the cooling curves might be reasonable since the "true" amalgam or compound phase would already be solid at higher temperatures and only the mercury phase would freeze at -30°C. Johnston and Ubbelohde[31] found that the (already very high) surface tension of mercury is greatly lowered by the amalgam which would then tend to concentrate in the interface to form a stable froth.

VII. CERTAIN OBSERVATIONS OF THE BEHAVIOR OF AMMONIUM AMALGAM ELECTRODES

Historical Introduction

Amalgam electrodes have been the source of many interesting investigations. The standard electrode potentials of the alkali metals in aqueous solution were determined by a series of ingenious experiments by G. N. Lewis and his co-workers using alkali metal electrodes.[74,75,76,77] The reactivity of the alkali metals with water prevented direct measurement of the electrode potentials but Lewis determined the potential between the alkali metal and its amalgam in ethylamine or propylamine solution of the metal ion, and subsequently determined the potential of the amalgam with respect to a standard electrode in an aqueous solution of the metal ion. The sum of the two potentials was the standard oxidation potential of the alkali metal in aqueous solution.

Data procured by Richards and Daniels[78] from e.m.f. measurements of thallium amalgam concentration cells were used by Lewis and Randall[79] for computation of the activity of thallium in the amalgams. The electromotive force produced by the concentration cell was

$$E = - \frac{RT}{NF} \log \frac{a_2}{a_2'} ,$$

where a_2 and a_2' represented the activities of the metal solute in each amalgam electrode. Lewis and Randall demonstrated that for a concentration cell in which one electrode was an amalgam of fixed mole fraction

N_2' and the other was an amalgam of any mole fraction N_2 the following expression related the electromotive force E to the concentration terms:

$$\log \frac{a_2}{N_2} = [-E (\frac{NF}{RT}) - \log N_2] + \log a_2'.$$

From a plot of the term in brackets versus N_2 the value of log a_2' was calculated. At infinite dilution when $N_2 = 0$ and by definition log $\frac{a_2}{N_2} = 0$, log a_2' is the intercept on the y-axis. Knowing a_2', the activity of thallium in the reference amalgam, Lewis and Randall calculated the activities of thallium and mercury in the amalgam of variable composition, and from this information the partial molal thermodynamic functions for each component. Richards and Conant[80] made similar experiments and calculations for sodium amalgam concentration cells in aqueous solution, while Bent and Swift[81] studied sodium amalgam concentration cells in dimethylamine solutions.

Bent and Forziatti[82] measured the e.m.f. of a concentration cell in which one electrode was a very dilute sodium amalgam and the other electrode was a sodium amalgam of composition varying between 0 and 100 per cent sodium. In their plot of e.m.f. against concentration, plateaus appeared at the e.m.f. values corresponding to the compositions of the mercury-sodium compounds predicted from Vanstone's[45] phase diagram for the solid-liquid equilibria.

The investigations of LeBlanc,[11] Coehn,[13] and Smith[16] on the reducing properties of ammonium in the amalgam suggest that the oxidation potential of ammonium in aqueous solution is comparable to the alkali [illegible] H_0' and the other

[illegible]

metals. LeBlanc and Coehn also reported that the polarization properties of ammonium amalgam electrodes were characteristic of the alkali metal amalgams. Náray-Szabó and Szlatinay[28] measured the electrode potential of ammonium amalgam at pressures up to 600 atmospheres in order to minimize decomposition. Their observations were made in aqueous solution at 0° with a reference electrode of $Hg(l)/HgBr_2(s),NH_4Br(aq)$. The potentials with respect to the hydrogen electrode calculated from observations made as soon as the cell was in operation were 1.80 ± 0.10 v., but the electrode potential was not entirely stable even under high pressure and decreased to values as low as -1.75 volts within forty minutes. In Table XII appear the potentials of the alkali metal amalgams in aqueous solution which were reported by Lewis and his collaborators. The values for E^0 would differ slightly from the values for E_H since the concentrations are not those for the standard state.

Instability of the potential of the ammonium amalgam electrode may be attributed to polarization by gaseous products from two different reactions:

$$NH_4 + H_2O \longrightarrow NH_4OH + 1/2\ H_2$$

$$NH_4 \longrightarrow NH_3 + 1/2\ H_2 .$$

The decomposition reaction should be suppressed at sufficiently low temperatures, as well as at high pressures, but the reaction of the amalgam with water is comparable to that of the alkali metal amalgams which was observed by Lewis and Kraus[74] and which interfered with their

TABLE XII

POTENTIALS OF THE ALKALI METAL AMALGAMS IN AQUEOUS SOLUTION[*]

Electrode	E (With Respect to Hydrogen Electrode)
Li amalgam[**] (0.0350%)/Li^+(1 N)	+2.0720 v.
K amalgam (0.2216%)/K^+ (1 N)	+1.8781 v.
Na amalgam (0.206%)/Na^+ (1 N)	+1.8673 v.
Rb amalgam (Unknown Concentration)/ Rb^+(1 N)	+1.8486 v.

[*] Reported by Lewis[74,75,76,77] and his collaborators.

[**] The composition of each amalgam is given in atom per cent.

e.m.f. measurements. The alkali metal amalgams were not attacked immediately by water but once hydrogen evolution had begun the reaction proceeded rapidly. Lewis and Kraus overcame the problem by the use of a device comparable to a dropping electrode which continuously supplied a fresh surface of amalgam to the electrolyte. The viscosity of ammonium amalgam made its passage through the capillary of such an electrode infeasible, so that in the present investigation stirring was relied upon to decrease polarization effects.

Two types of experiments involving ammonium amalgam as an electrode were attempted. One experiment was an investigation of the relation between the concentration of ammonium in an amalgam and the potential of the amalgam with respect to a standard electrode; the other experiment was an unsuccessful attempt to measure the e.m.f. of a concentration cell consisting of two amalgam electrodes.

The Effect of Ammonium Concentration on Electrode Potential

All measurements were made at -30°C in a 1 N solution of ammonium chloride in 50% aqueous ethanol. Electromotive force was measured with a Leeds and Northrup Type K-2 Potentiometer. In order to record the e.m.f. a high impedance, which served as a filter to overcome the impedance of the cell, was placed in parallel with the recording potentiometer. A silver-silver chloride reference electrode was prepared by electrolyzing a silver wire anode in 1 normal potassium chloride solution for two hours at one milliampere. An approximate value of -0.195 volt for the

electrode potential of the silver chloride electrode with respect to the hydrogen electrode at -30°C in a 50% ethanol-water mixture was obtained by extrapolation of data reported by Patterson and Felsing.[83]

The potential between pure mercury and the silver chloride electrode was +0.0285 ± 0.0005 volts. Two different reactions might explain the behavior of the mercury electrode. In the chloride solution sufficient mercury may have dissolved to form a calomel electrode. The potential difference between such an electrode and the silver chloride electrode in an ethanol-water solution not saturated with calomel would not be the same as the potential difference between a normal calomel electrode in water and a normal silver chloride electrode which is +0.06 volts. In addition the potential between mercury and the silver-silver chloride electrode could be attributed to the deposition of ammonium ions to form ammonium amalgam with the mercury. The potential of the mercury electrode when compared to the silver-silver chloride electrode did not change when ammonium amalgam was placed in the electrolyte. The potential of the amalgam was negative with respect to both the silver chloride and the mercury electrodes.

The effect of varying the ammonium concentration in the amalgams on the e.m.f. of the cell shown in Figure 22 was studied. The potential-time curves for amalgams which were warming from -30°C to room temperature were recorded on the electronic potentiometer, and similar data were recorded for amalgams maintained at constant temperature. Curves 1 and 2 in Figure 23 show that the e.m.f. varied irregularly with time for

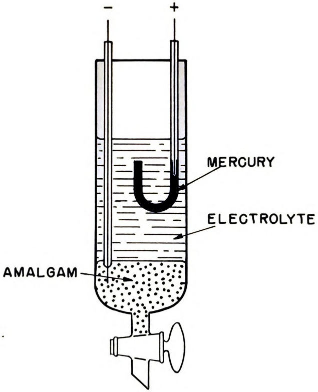


Figure 22. Cell for obtaining e.m.f.-concentration data for ammonium amalgam: electrolyte was 1 N ammonium chloride in 50% aqueous ethanol.

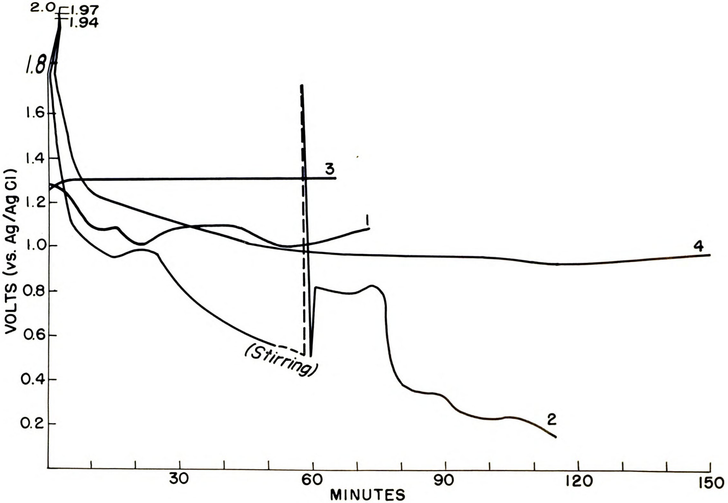


Figure 23. Time - e.m.f. plots for ammonium amalgams: 1 and 2, temperature was slowly rising; 3 and 4, temperature remained constant at -17°C. and -30°C., respectively.

two amalgams which were slowly warmed to room temperature while curves 3 and 4 show that the e.m.f. of the amalgam attained a constant value when the temperature was not varied. The initial reading in each case was that observed as soon as electrical connection was made between the cell and the potentiometer circuit, and does not necessarily represent the maximum potential of the cell. Apparently concentration polarization was partially responsible for the decrease in e.m.f. with time as indicated by the large increase in potential immediately following stirring.

The potential of a number of amalgams of different concentrations was measured at -30°C with the Type K-2 potentiometer. For each amalgam a series of potentiometer readings was made until the potential remained constant, after which time the amalgam was immediately withdrawn from the bottom of the cell into 0.3027 normal sulfuric acid and following decomposition was titrated with 0.2246 normal sodium hydroxide. The data for these observations appear in Table XIII and suggest that the cell potential decreased as the ammonium concentration increased. The potential difference observed for many amalgams was approximately 1.30 volts with respect to the silver-silver chloride electrode and no values lower than 1.26 volts were observed.

The experiment may be considered to be a study of the effect of ammonium concentration on the irreversibility of the amalgam electrode. High negative potentials approaching the value of the alkali metal amalgam electrodes were observed for extremely dilute amalgams, and in certain cases where the initial potential of the cell was recorded

TABLE XIII

ELECTROMOTIVE FORCE-CONCENTRATION DATA FOR AMMONIUM AMALGAMS AT -30°C

Electrolysis time (Minutes)	E.M.F. Amalgam vs. Ag/AgCl	Millimoles NH_4	Weight Hg (gms.)	Moles Hg	Mole Per Cent NH_4
5	-1.82	0.00	321	1.60	0
5	-1.80	0.03	337	1.68	0.0018
10	-1.77	0.55	410	2.05	0.0268
10	-1.77	1.32	409	2.05	0.0645
15	-1.70	0.84	301	1.50	0.0560
30	-1.67	0.76	346	1.73	0.0440
15	-1.60	1.56	427	2.14	0.0729
60	-1.33	1.59	327	1.63	0.0975
3000	-1.32	1.61	384	1.92	0.0839
60	-1.31	1.14	322	1.61	0.0707
25	-1.30	2.75	353	1.76	0.156
20	-1.27	1.64	330	1.65	0.0994
61	-1.27	2.01	343	1.71	0.118
120	-1.26	2.80	277	1.38	0.203

electronically. The ammonium amalgam electrode was apparently most irreversible when the ammonium concentration was high, under which conditions a correspondingly large amount of gaseous decomposition products would accumulate at the electrode surface.

A Concentration Cell with Ammonium Amalgam Electrodes

An attempt was made to procure data for ammonium amalgam comparable to that obtained by Richards and Daniels[78] for thallium amalgam concentration cells. The problem was not pursued to completion because the electrode appeared to be irreversible and the potentials fluctuated too widely.

A cell was designed with compartments for two amalgam samples as shown in Figure 24. In the cold box an amalgam was divided into two portions of as nearly equal concentrations as possible and each portion was poured through a funnel into a compartment of the cell and covered with ammonium chloride electrolyte which had been cooled to about -30°C. The cell was then immersed in a Dewar flask containing boiling Freon-12 at -30°C. The platinum electrodes were placed in the two amalgams and the silver chloride electrode was suspended in the electrolyte which was stirred with a motor driven stirrer. Measurements of the e.m.f. between each amalgam and the silver-silver chloride electrode, as well as between the two amalgams were made with the Leeds and Northrup Type K-2 Potentiometer. The potential between the two amalgams was never zero and was usually about 0.020 volts while the potentials with respect to

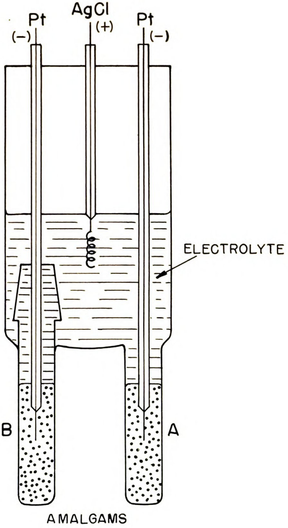


Figure 24. Concentration cell with ammonium amalgam electrodes: electrolyte was 1 N ammonium chloride in 50% aqueous ethanol; the diluted amalgam was placed in compartment A.

the silver chloride electrode varied within ± 0.05 volts of 1.27, the same potential as was observed with many amalgams in the previous experiment. Potentials above this value were never observed even when readings were made immediately after stirring the amalgams with the platinum electrodes. After several hours the potential of the cell was not constant and did not drift in a particular direction but merely varied about the value-1.27 volts. One hundred grams of mercury which had been cooled to -30°C was added in 10 gram increments to the amalgam in compartment A of the cell. The potential of the diluted amalgam was never observed to differ appreciably from that of the original amalgam. As a result of the unsteadiness of the potential a much greater dilution would have been necessary to produce significant e.m.f. changes, and moreover, polarization and decomposition might completely obscure the effect. The compositions of the amalgams were determined by the usual procedure. The data procured from two series of measurements appear in Table XIV.

From these experiments it can be concluded that an ammonium amalgam electrode rapidly becomes irreversible at -30°C in a 1 normal solution of ammonium chloride in aqueous ethanol.

If polarization decreased the potential of the ammonium amalgam electrode below the potential of the alkali metal amalgam electrodes one seems justified in selecting the highest observed potential for ammonium amalgam for comparison with the alkali metal amalgams. The single electrode potential for ammonium amalgam was computed using 0.20 volts

TABLE XIV

DATA FOR TWO CONCENTRATION CELLS WITH AMMONIUM AMALGAM ELECTRODES AT -30°C

	E.M.F. vs. Ag/AgCl (volts)				Moles NH_4	Moles Hg	Molality
	Initial	After 1 Hr.	After 2 Hrs.	After 5 Hrs.			
Cell I							
a)	-1.263	-1.286	-1.283	-1.284	0.290×10^{-3}	0.714	0.00204
b)	-1.274	-1.277	-1.256	-1.271*	0.259×10^{-3}	0.884	0.00146*
Cell II							
a)	-1.261	-1.307	-1.255		0.131×10^{-3}	1.174	0.00056
b)	-1.265	-1.296	-1.259		0.174×10^{-3}	0.570	0.00153

* After the addition of 100 grams of mercury.

for the silver chloride electrode potential and an estimated value of 0.2 for the activity of chloride ion in aqueous-ethanol at -30°C. For an amalgam electrode of concentration 0.0018 mole per cent ammonium the single electrode potential was calculated:

$$\mathrm{NH_4\ amal.\ (0.0018\%)} \longrightarrow \mathrm{NH_4^+(1\ N\ NH_4Cl)} + e^-.$$

$$\text{At } -30^\circ,\ E(\mathrm{NH_4\ amal.}) = E^\circ(\mathrm{NH_4\ amal.}) - 0.048 \log \frac{(\mathrm{NH_4^+})}{(\mathrm{NH_4\ amal.})}$$

$$\mathrm{AgCl(s)} + e^- \longrightarrow \mathrm{Ag(s)} + \mathrm{Cl^-(1\ N\ NH_4Cl)}.$$

$$\text{At } -30^\circ,\ E\,(\mathrm{AgCl}) = 0.20 - 0.048 \log (\mathrm{Cl^-}).$$

$$E_{\mathrm{cell}} = E(\mathrm{NH_4\ amal.}) + E\,(\mathrm{AgCl}) = 1.80 \text{ volts}.$$

$$E(\mathrm{NH_4\ amal.}) = 1.80 - 0.20 + 0.048 \log 0.2 = 1.57 \text{ volts}.$$

The potential, 1.57 volts, represents the potential of a 0.0018 mole per cent, or 9×10^{-5} molal, solution of ammonium in mercury in a 1 N ammonium chloride solution in aqueous ethanol at -30°C. The potential of a sodium amalgam of comparable concentration in a 1 N sodium chloride solution in aqueous ethanol at -30°C was calculated from Lewis and Randall's data which appears in Table XII. The assumption was made that a 1 molal solution of metal dissolved in mercury represents the standard state for an amalgam. The activity of a 1 N sodium chloride solution at 25°C is 0.657,[84] and an activity of 0.3 was assumed for sodium ion in aqueous ethanol at -30°C.

$$\begin{aligned} \text{At } 25^\circ,\ E^\circ(\mathrm{Na\ amal.\ 0.206\%}) &= E(\mathrm{Na\ amal.,\ 1\ N\ NH_4Cl}) \\ &\quad + 0.059 \log \frac{(\mathrm{Na^+})}{(\mathrm{Na\ amal.})} \\ &= 1.867 + 0.059 \log \frac{(0.657)}{(0.0103)}; \end{aligned}$$

$$\text{at } -30^{\circ},\ E(\text{Na amal.},\ 9 \times 10^{-5}\text{m}) = E^{\circ}(\text{Na amal.}) - 0.048 \log \frac{(\text{Na}^{+})}{(\text{Na amal.})}\ ;$$

$$\text{therefore, at } -30^{\circ},\ E(\text{Na amal.},\ 9 \times 10^{-5}\text{m}) = 1.867 + 0.107 - 0.167 = 1.80 \text{ volts.}$$

The value 1.80 volts for the electrode potential of the sodium amalgam is significantly higher than the value 1.57 volts for the ammonium amalgam under the same conditions, and suggests that even in the cell in which the potential was highest for an amalgam of known concentration the ammonium amalgam electrode was irreversible. Possibly this value is not greatly in error since sodium amalgam reduces ammonium ion to give ammonium amalgam in a conventional method of preparing the amalgam. It has been reported that this reaction goes essentially to completion.[14]

VIII. COMPRESSIBILITY OF AMMONIUM AMALGAM AT -30°C

Theoretical Introduction

In 1807 Seeley reported that ammonium amalgam was more compressible than mercury. In 1872 Routledge[9] made some quantitative measurements of the volume of the amalgam at various pressures up to about three atmospheres. The results of Routledge's investigation indicate that the compressibility is slightly less than that expected for a mixture of ammonia, hydrogen, and mercury. His experiments were carried out at room temperature, under which conditions the amalgam may have been largely a combination of gas and mercury as a result of decomposition. It was decided that a study of the compressibility of the liquid amalgam at a temperature low enough to minimize decomposition, and up to pressures at which the volume change per atmosphere is negligible, would give more information as to the composition of the amalgam. The compressibility of an amalgam which has been frozen and subsequently melted might differ from one which has never been frozen if some decomposition occurs on solidification. For this reason compressibility measurements on liquid amalgams which had previously been frozen were also planned.

Isothermal compressibility is the change in volume per unit volume for a unit change in pressure at constant temperature, and is defined by the equation

$$\beta = \frac{1}{V_0}\left(-\frac{\partial V}{\partial t}\right)$$

where V_0 is the initial volume, and V is the volume measured at pressure P. Compressibility is determined with an apparatus, called a piezometer, by measuring the volume as increasingly large pressures are exerted on a sample of the material under study. At room temperature and relatively low pressures gases have measurable compressibilities, but most liquids and solids require several hundred atmospheres' pressure to produce a significant volume change. A piezometer frequently employed for compressibility measurements on fluids consists of a large bulb for the sample to which is attached a capillary containing mercury. The change in the height of the mercury column as pressure is applied provides a measure of the volume change of the fluid. The apparatus containing a sample may be placed inside a pressure chamber and subjected to the pressure of an hydraulic press. The external and internal pressures on the glass apparatus are equal so that the danger of breaking the glass apparatus is eliminated. For investigations in which the pressure is low enough for the piezometer to withstand, the pressure may be applied by an air pump to the mercury in the capillary. Suitable variations of these methods were used in determining the compressibilities of many liquids and solutions, particularly by T. W. Richards and his collaborators.[85] The most recent measurements of compressibility on systems comparable to ammonium amalgam were made on liquid metals by an ultrasonics method. The velocity of sound in a substance is related to isothermal compressibility according to the following expression

$$\beta = \frac{1}{\rho u^2} \frac{C_p}{C_v}$$

where V_0 is the initial volume, and V is the volume measured at pressure P. Compressibility is determined with an apparatus, called a piezometer, by measuring the volume as increasingly large pressures are exerted on a sample of the material under study. At room temperature and relatively low pressures gases have measurable compressibilities, but most liquids and solids require several hundred atmospheres' pressure to produce a significant volume change. A piezometer frequently employed for compressibility measurements on fluids consists of a large bulb for the sample to which is attached a capillary containing mercury. The change in the height of the mercury column as pressure is applied provides a measure of the volume change of the fluid. The apparatus containing a sample may be placed inside a pressure chamber and subjected to the pressure of an hydraulic press. The external and internal pressures on the glass apparatus are equal so that the danger of breaking the glass apparatus is eliminated. For investigations in which the pressure is low enough for the piezometer to withstand, the pressure may be applied by an air pump to the mercury in the capillary. Suitable variations of these methods were used in determining the compressibilities of many liquids and solutions, particularly by T. W. Richards and his collaborators.[85] The most recent measurements of compressibility on systems comparable to ammonium amalgam were made on liquid metals by an ultrasonics method. The velocity of sound in a substance is related to isothermal compressibility according to the following expression

$$\beta = \frac{1}{\rho u^2} \frac{C_p}{C_v}$$

where ρ is the density of the substance, u is the velocity of sound in the substance, and C_p/C_v is the ratio of the heat capacities.[86]

Apparatus

Neither ultrasonics equipment nor an hydraulic press were readily available; therefore, a simpler device was devised for the investigation of the compressibility of ammonium amalgam. If an amalgam sample contains entrapped gas the volume should change significantly when subjected to pressures of a few atmospheres; otherwise it should be relatively incompressible at such low pressures. In order to determine the presence or absence of entrapped gas the apparatus illustrated in Figure 25 was designed for exerting low pressures on an amalgam sample at -30°C, the temperature of boiling Freon-12.

Pressure is force per unit area and may be represented by the expression

$$p = \frac{F}{A} = \frac{mg}{A}$$

in which p is pressure, F is force, A is the cross-sectional area over which the force is applied, and mg is the weight of mass m under the influence of gravitational acceleration g. In the piezometer designed for measuring the compressibility of ammonium amalgam pressures above one atmosphere were produced by the weight of a column of mercury acting on an amalgam sample of uniform cross-section area. The height of the mercury column was the same as the lower level of the sample when the applied pressure was the pressure of the atmosphere, and higher pressures

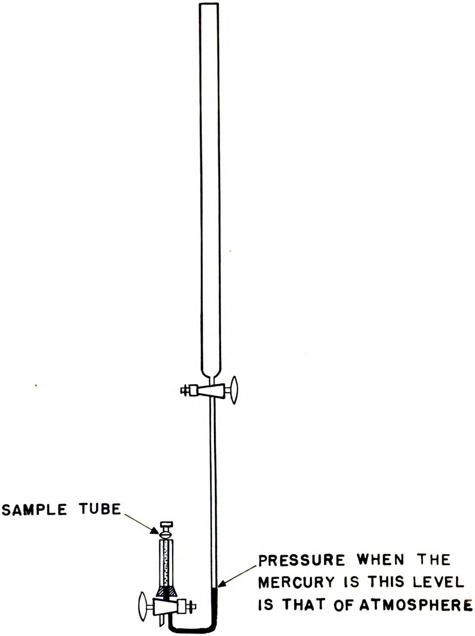


Figure 25. Apparatus for studying the compressibility of ammonium amalgam.

were obtained by the addition of weighed quantities of mercury of the column.

The weight of mercury which exerted one atmosphere of pressure on the sample was the weight in grams of a column of mercury which had a cross-sectional area in square centimeters equal to that of the sample tube, and was 76.0 cm. high under standard conditions of temperature and pressure. The pressure in atmospheres exerted on the amalgam in the apparatus was $1 + P_{Hg}$ where P_{Hg} is the pressure exerted by the mercury column above the one atmosphere level.

With the application of pressure to the sample a volume of mercury equal to the decrease in volume of the amalgam entered the sample tube from the reservoir. The volume of the amalgam sample was calculated at each pressure by measurement of the height of the mercury in the column before and after a given increment of pressure was applied to the sample. A cathetometer was used to determine the level of the mercury within ± 0.005 cm. The volume of mercury entering the sample tube was

$$\Delta V = \pi r_2^2 \Delta h = 8.1 \Delta h,$$

where r_2 is 1.55 cm., the radius of the reservoir column, and Δh is the change in the height of the mercury in this column. The original volume of the amalgam V_0 is calculated from the volume of the sample tube, so that the volume at any pressure is $V_0 - V_p$.

The piezometer, Figure 25, was constructed in the glass shop from heavy walled Pyrex tubing. As protection against leakage stopcock retainers were employed and a rubber stopper was wedged tightly into the

ball and socket joint clamp to prevent it from opening readily. A piece of 34 mm. o.d. tubing was fitted over a rubber stopper just above the two-way stopcock to provide a means for keeping the sample at -30°C with a Freon-12 cooling bath. Melted paraffin was poured around the stopper inside the jacket to prevent leaking of the refrigerant. The piezometer was secured firmly by means of clamps to a vacuum rack.

That part of the apparatus from the spherical joint to the two-way stopcock was the sample tube. A glass seal was made just above the stopcock, which means that the crosssectional area of the tube was not uniform throughout. For this reason a weighed amount of mercury, on the order of 35 grams, was poured in the tube before the amalgam was introduced. The weight of mercury added to the tube varied somewhat with each series of measurements and likewise the initial volume of amalgam varied, as well as the initial height of the mercury column. The volume of the sample tube was calculated from the weight and density of the amount of mercury required to fill it. The mean value of four weighings of the mercury contained in the tube is 153.2 grams.

$$\text{Volume of tube} = \frac{\text{weight of mercury}}{\text{density of mercury}} = \frac{153.2 \text{ gm.}}{13.54 \text{ gms./ml.}}$$

$$\text{Volume of sample} = \text{volume of tube} - \text{volume of mercury necessary to cover seal.}$$

Experimental Procedure

Before each series of measurements mercury was poured through the sample tube into the pressure column until the level was that of the top

of the sample tube. That level in the pressure column corresponds to about one atmosphere of pressure, the exact value of which was obtained from a barometer reading. The mercury was drained from the sample tube by the proper change of the stopcock which was then closed to both chambers and never moved again until a measurement was made on some amalgam. Air was removed from the mercury in the pressure column by carefully heating the area containing mercury with a Bunsen burner and simultaneously pumping on the column. A weighed quantity of mercury sufficient to cover the non-uniform area was poured into the sample tube and the level was measured with the cathetometer. The mercury to be added to the column in portions corresponding to the desired pressures was weighed. The first weighed portion of mercury was carefully poured into the column and the air bubbles removed by pumping. The cooling jacket was filled with Freon-12 about ten minutes before the amalgam was introduced into the apparatus.

Amalgam which had been prepared and washed in the usual way was put into a Pyrex tube in a Dewar flask containing Freon-12 for five minutes and then transferred to the sample tube of the apparatus. With the two-way stopcock still closed and the one-way stopcock open the height of the mercury in the column was measured with the cathetometer. Pressure was applied to the amalgam by opening the two-way stopcock to the mercury column and again the level of the mercury was determined with the cathetometer. With the stopcock closed to the pressure column another weighed portion of mercury was added and the effect of this additional pressure on the volume likewise measured. In this manner about three

atmospheres of pressure could be applied to the sample. Even at the higher pressures the more concentrated amalgams retained a frothy appearance as if gas were entrapped. When a pressure was reached at which the sample volume did not change upon two successive additions of mercury to the column, observations were discontinued. The sample was removed from the tube into a solution of 0.0517 N sulfuric acid by first opening the two-way stopcock and then removing the cap from the tube. A definite odor of ammonia was apparent when the cap was removed. The excess acid was titrated with 0.0379 N sodium hydroxide in the usual way. The mercury from the decomposed amalgam was rinsed, dried, and weighed. To remove the mercury from the apparatus a glass tube with a sperical connection was clamped to the top of the sample container. This attachment was bent so that mercury would run from the pressure column into the sample container and out of the apparatus into a bottle. Some mercury always remained in the apparatus but no more than that supported by the weight of the atmosphere.

By the method described compressibility data were obtained for two samples of pure mercury at room temperature and for five different amalgam samples which were never at temperatures below -30°C. In addition samples of two of the five amalgams were placed in a Pyrex tube, immersed in liquid air for an hour, and melted in a Freon-12 bath at -30°C. Volume-pressure data were then taken for these two samples. No changes appeared in the volume of the pure mercury samples as pressure was applied.

Calculations and Results

Data for the volume-pressure measurements of mercury and the amalgams appear in Table XV and Figure 26. Detailed calculations for amalgam V are as follows:

Uncorrected barometer reading at 27°C = 73.80 cm.

Correction to 0°C for expansion of the brass scale and of the mercury = -0.32 cm.[71]

Correction of sea level from altitude 860 ft. and latitude 42° = -0.02 cm.[71]

Corrected barometer reading = 73.80 - 0.32 - 0.02 = 73.46 cm.

Pressure in atmospheres = $\frac{73.46}{76.00}$ atm. = 0.967 atm.

The pressure exerted on the sample when the volume is V_0 is 0.967 atm.

V_0 = volume of tube - weight of mercury covering seal/ density of mercury at 25°C.

$V_0 = 11.31 \text{ ml.} - \frac{43.2 \text{ gm.}}{13.5 \text{ gm./ml.}} = 8.15 \text{ ml.}$

The pressure on the sample at any time = P
= $P_a + P_{Hg}$, where P_a is atmospheric pressure and
P_{Hg} is the pressure due to the mercury in the column.

P_1 = 73.46 + 66.38 mm. = 139.84 cm. = 1.84 atm.

P_2 = P_1 + 12.93 = 152.77 cm. = 2.0 atm.

Δh_1 = difference in cathetometer readings = 0.26 cm.

$\Delta v_1 = \pi r_2^2 \Delta h_1 = 8.1 \times 0.26 = 2.1$ ml.

$V_1 = V_0 - \Delta v_1$ = 8.2 ml. - 2.1 ml. = 6.1 ml.

$V_2 = V_1 - \Delta v_2$ = 6.1 - 0.3 = 5.8 ml.

By this same procedure all other volumes and pressures for this series of observations were computed. V_0 was calculated from the weight and

TABLE XV

PRESSURE-VOLUME DATA FOR A COMPRESSIBILITY STUDY OF AMMONIUM AMALGAM

Sample	P (cm.Hg)	P (atm.)	Ht. of Mercury		Δ h (cm.)	Δ V (ml.)	Vol. of Amalgam (ml.)
			Closed (cm.)	Open (cm.)			
I	74.38	0.978					8.4
	134.8	1.78	2.57	2.25	0.32	2.6	5.8
	141.1	1.85	8.91	8.82	0.08	0.6	5.2
	147.1	1.95	15.45	15.40	0.05	0.4	4.8
	154.3	2.03	22.11	22.06	0.05	0.4	4.4
	161.0	2.12	28.78	28.74	0.04	0.3	4.1
	167.7	2.21	35.40	35.35	0.05	0.4	3.7
	180.9	2.38	48.55	48.53	0.02	0.2	3.5
	187.4	2.46	55.10	55.10	0.00	0.0	3.5
II	74.4	0.978					8.7
	135.1	1.78	2.42	2.39	0.03	0.2	8.5
	141.8	1.87	9.06	9.05	0.01	0.1	8.4
	148.3	1.95	15.64	15.64	0.00	0.0	8.4
	154.9	2.04	22.22	22.22	0.00	0.0	8.4
III	74.4	0.978					8.4
	141.2	1.85	8.95	8.86	0.07	0.6	7.8
	167.5	2.20	35.19	35.16	0.03	0.2	7.6
	180.4	2.37	48.13	48.10	0.03	0.2	7.4
	193.5	2.55	61.26	61.26	0.00	0.0	7.4
IV	74.4	0.978					8.0
	140.6	1.85	8.37	8.37	0.00	0.0	8.0
	153.9	2.02	21.67	21.62	0.05	0.4	7.6
	167.1	2.20	34.87	34.87	0.02	0.2	7.4
	180.2	2.37	47.93	47.93	0.00	0.0	7.4
V	73.5	0.967					8.2
	139.8	1.84	8.31	8.05	0.26	2.1	6.1
	152.8	2.01	21.24	21.20	0.04	0.3	5.8
	166.0	2.18	34.49	34.44	0.05	0.4	5.4
	179.1	2.36	47.57	47.57	0.00	0.0	5.4
	192.3	2.52	60.80	60.80	0.00	0.0	5.4
VI	73.8	0.972					8.3
	134.1	1.76	1.75	1.61	0.14	1.1	7.2
	140.5	1.85	8.20	8.13	0.07	0.6	6.6
	153.8	2.02	21.52	21.48	0.04	0.3	6.3
	167.1	2.20	34.75	34.73	0.02	0.2	6.1
	180.0	2.37	47.71	47.71	0.00	0.0	6.1
	193.2	2.54	60.88	60.88	0.00	0.0	6.1
VII	73.8	0.972					9.0
	135.0	1.78	1.52	1.48	0.04	0.3	8.7
	141.6	1.87	8.05	8.03	0.02	0.2	8.5
	154.8	2.04	21.27	21.26	0.01	0.1	8.4
	168.1	2.21	34.58	34.58	0.00	0.1	8.4
	181.3	2.38	47.76	47.76	0.00	0.0	8.4

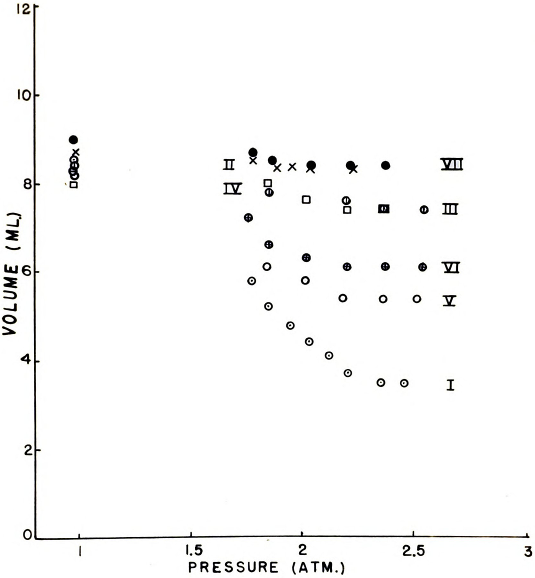


Figure 26. Volume-pressure data at -30° for six ammonium amalgams of varying composition; Sample I, ⊙; Sample II, X; Sample III, ⦶; Sample IV, □; Sample V, ⊖; Sample VI, ⊕; Sample VII, ● .

density of mercury which are known to four significant figures; therefore, in these measurements the inaccuracy of V_0 depends only on Δv which in turn depends on the accuracy with which Δh was measured. The difference Δh between two cathetometer readings is accurate to ± 0.01 cm. which makes the error in Δv

$$\Delta (\Delta v) = 0.01 \pi r_2^2 = 0.1 \text{ ml.}$$

The volumes are listed with only two significant figures and are accurate to ± 0.1 ml. which introduces a maximum error of three per cent for volumes at higher pressures for amalgam sample I. In most cases the volume is in error by only one and one-half per cent.

Results of the data for computing the density and composition of the amalgams appear in Table XVI. The weight of an amalgam is essentially the weight of the mercury in the amalgam. The weight of mercury added to the sample tube to cover the glass seal and the weight of the mercury which entered the sample from the reservoir during compression were subtracted from the weight of mercury remaining after decomposition of the amalgam. Following are exemplary calculations necessary to complete the data for amalgam V in Table XVI:

Weight of mercury which entered the sample tube during compression is $(V_0 - V_{final})_{Hg}$ = 2.8 ml. x 13.6 gm./ml. = 38 gm.

Weight of mercury added to cover glass seal = 43.2 gm.

Weight of amalgam = 116 - 43 - 38 = 35 gm.

Density of amalgam = weight of mercury/sample volume = 35.1/8.15 = 4.31 gm./ml.

TABLE XVI

COMPOSITION OF AMALGAMS FOR WHICH COMPRESSIBILITY DATA WERE OBTAINED

Amalgam	Wt. of Hg in Sample Tube (gm.)	Wt. of Hg Over Seal (gm.)	$V_o - V_f$ (ml.)	Wt. of Hg in $V_o - V_f$ (gm.)	Wt. of Hg in Amalgam (gm.)	Sample Volume (ml.)	Amalgam Density (gm./ml.)	Moles of Hg	Milli-moles NH_4	Mole Per Cent NH_4
I	107.7	39.9	4.9	66	2	8.4	0.24	0.01	0.96	9.0
II	154.4	36.1	0.3	4	114	8.67	13.2	0.570	0.076	0.0134
III	151.7	39.7	1.0	13	99	8.4	12	0.50	0.0340	0.068
IV	154.1	46.0	0.6	8	100	7.95	12.6	0.500	0.016	0.032
V	116.3	43.2	2.8	38	35	8.2	4.3	0.18	0.63	0.35
VI	145.4	40.6	2.2	30	75	8.3	9.0	0.38	0.30	0.079
VII	153.9	31.5	0.6	6	116	9.01	12.9	0.580	0.0177	0.0311

Mole per cent of ammonia in the amalgam = (moles NH_3/moles Hg) · (100%) = 0.35 mole per cent.

From Figure 26 it appears that the very concentrated amalgams are somewhat more compressible than the dilute amalgams. Amalgams II and IV, which are samples I and III after freezing, retain slight compressibility and only a small concentration of ammonium.

The weight and density of the mercury recovered from each decomposed amalgam were used to calculate the volume occupied by the mercury alone. See Table XVII. If the difference between the volume of the amalgam and the volume of the mercury represents a volume of ammonia and hydrogen gas entrapped in the amalgam, then the compressibility of this volume should be the same as that of a combination of ammonia and hydrogen gas in a 2:1 mole ratio. The volume increase over that of pure mercury for amalgam VI was considered to be V_0. Employing the same Δ v's as in Table XV the volume was computed at each pressure for amalgam VI, and these data plotted as points on Figure 27. Actually the points plotted in Figure 27 are identical to those for amalgam VI in Figure 26 except for their positions with respect to the volume axis.

The molar volumes of ammonia and hydrogen at -30°C and at each half atmosphere of pressure between one and three atmospheres were computed. For calculation of the molar volume of ammonia two terms of the Beattie-Bridgmann equation were employed in conjunction with the re-evaluated Beattie-Bridgmann constants of Maron and Turnbull.[87] The part of the Beattie-Bridgmann equation used here was

$$P = \frac{RT}{V} + \frac{\beta}{V^2}$$

TABLE XVII

A COMPARISON OF THE VOLUMES OF AMMONIA, HYDROGEN, AND MERCURY WITH THE VOLUME OF AMMONIUM AMALGAM

Sample	Wt. of Hg in Sample (gm.)	Volume Occupied By Pure Hg (ml.)	Volume of Amalgam At 1 atm. (ml.)	Volume Expanded (ml.)	Vol. Occupied by NH_3 and H_2 At 1 atm. (ml.)	Volume of NH_3 and H_2 As Ammonium In Amalgam (ml.)
I	2	0.15	8.4	8.2	29	+21
II	114	8.45	8.7	0.3	2.4	+ 2.1
III	99	7.3	8.4	1.1	1.0	-0.1
IV	100	7.5	8.0	0.5	0.47	-0.3
V	35.1	2.60	8.2	5.6	19	+13
VI	74.8	3.32	8.3	5.0	8.9	+ 3.9
VII	116	8.59	9.0	0.4	0.53	+ 0.1

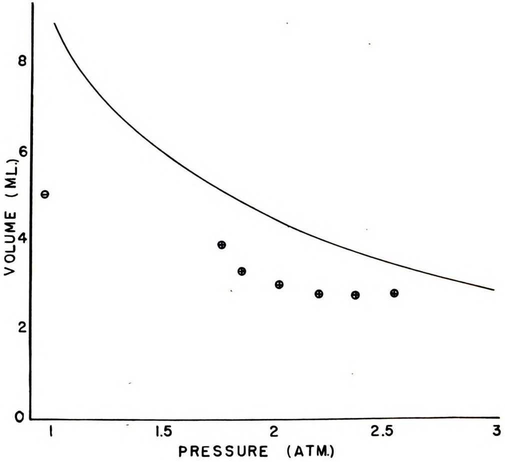


Figure 27. Volume-pressure relationship at -30°C. for a volume of ammonia and hydrogen equal to the difference between the volume of amalgam VI and the volume of mercury in amalgam VI: the points represent experimental values; the curve represents ideal gas behavior.

where β for ammonia has the value of -3.291. The molar volume of ammonia at 1 atmosphere and at -30°C is

$$V_1 = \frac{-RT \pm \sqrt{R^2T^2 - (4 \times 3.291 \times P)}}{2P} = 19.8 \text{ liters}$$

The Beattie-Bridgman equation could not be expected to apply to ammonia at pressures above 1 atmosphere and at -30°C, which is only 3° above its boiling point, but no better corrections were available in the literature. Molar volumes for hydrogen were calculated from the ideal gas law. The combined volume occupied by one-half mole of hydrogen and one mole of ammonia was evaluated for each pressure. In Table XVIII are listed the volumes in milliliters which would be occupied at each pressure by the ammonia and hydrogen in each amalgam if all the ammonia and hydrogen were in the gaseous state. The pressure-volume curve for amalgam VI in Figure 27 was plotted from the data in Table XVIII. A comparison of the curves for the gaseous mixture with the pressure-volume data shows that the initial volume of some of the amalgams is not as large as the volume would be if all the ammonia and hydrogen contained by them were in the gaseous state, but that the change in volume with pressure is greater than for the gaseous mixture.

Discussion

If all the ammonia and hydrogen were combined with mercury in the amalgam, the amalgam should have been much less compressible than a perfect gas. The data show that the amalgams at the pressures for which

TABLE XVIII

VOLUME OCCUPIED BY GASEOUS AMMONIA AND HYDROGEN IN EACH AMALGAM AT -30°

P (atm.)	Molar Volume $NH_3 + 1/2H_2$ (liters)	Volume of NH_3 and H_2 (ml.)						
		I	II	III	IV	V	VI	VII
1.0	29.7	29	2.4	1.0	0.47	19	8.9	0.53
1.5	18.9		1.45	0.7	0.30	12	5.9	0.40
2.0	14.8	14.2	1.1	0.5	0.24	9.3	4.4	0.26
2.5	11.7	11.1	0.9	0.4	0.20	7.4	3.4	0.20
3.0	9.8	9.4	0.75	0.33	0.16	6.2	2.9	0.17
(Concentration NH_4 in millimoles)		0.96	0.764	0.0340	0.016	0.63	0.30	0.0177

measurements were obtained were more compressible than an essentially perfect gas. Only an imperfect gas is more compressible than a perfect one, which means that ammonia was doubtlessly being liquified during the compression at -30°C. The assumption was made that all the ammonia present in an amalgam was compressed by the exertion of 1.5 atmospheres on a sample and that hydrogen behaved as a perfect gas, so that 1.5 atmospheres' pressure reduced its volume to one-third of the original volume. If this assumption was true then the following expression in which $V_{o(NH_3)}$ and $V_{o(H_2)}$ represent initial volumes applies:

$$V_{o(NH_3)} + 2/3\ V_{o(H_2)} = V_{2.5\ atm.} - V_{1\ atm.}$$

If each ammonium radical dissociates into one molecule of ammonia and one atom of hydrogen then

$$V_{o(NH_3)} = 2V_{o(H_2)},$$

and

$$2V_{o(H_2)} + 2/3\ V_{o(H_2)} = V_{2.5\ atm.} - V_{1\ atm.}\ .$$

The preceding relation was used to calculate the initial volume of hydrogen from which the total initial volume of gaseous material present was computed. The difference between the volume of amalgam in the tube and the original volume of gas was then the actual volume occupied by an amalgam in which no gas was entrapped.

Data from these calculations appear in Table XIX. Using the corrected initial volume and the weight of mercury in the sample as the weight of the amalgam the density of each amalgam at one atmosphere containing no gas entrapped was computed and listed in the last column of the table. The density of pure mercury is 13.56 gm./ml. at -30°C. For all the dilute amalgams the corrected density corresponded to mercury, but for the concentrated amalgams was less than that of mercury. The large difference in the actual volume of the amalgam and the volume that would be occupied if all the ammonia and hydrogen were in the gaseous state establishes that ammonium, hydrogen, and mercury are combined in some way in common amalgam. Only a few compressibility measurements were made and those were in a narrow range of pressures, but the information gained was sufficient to show that at -30°C the amalgam contains ammonia which can be liquefied, and must also contain ammonium in combination with mercury.

TABLE XIX

THE DENSITY OF AMMONIUM AMALGAMS CORRECTED FOR THE PRESENCE OF GASEOUS DECOMPOSITION PRODUCTS

Amalgam	$V_o(NH_3)$ + 2/3 $V_o(H_2)$	$V_o(H_2)$	$V_o(NH_3)$	Initial Volume of Gas	Initial Volume of Amalgam (ml.)	Corrected Volume of Amalgam (ml.)	Weight of Hg (gm.)	Corrected Density (gm./ml.)
I	4.9	1.84	3.68	5.5	8.4	2.9	1.7	0.57
II	0.3	0.11	0.22	0.33	8.7	8.4	114	13.6
III	1.0	0.38	0.76	1.14	8.4	7.3	99	13.6
IV	2.6	0.22	0.44	0.66	8.0	7.3	100	13.7
V	2.8	1.1	2.2	3.3	8.2	4.9	35	7.14
VI	2.2	0.83	1.66	2.5	8.3	5.8	75	12.9
VII	0.6	0.22	0.44	0.66	9.0	8.3	116	14.0

SUMMARY

Following an investigation of several methods for preparing and handling ammonium amalgam, an electrolytic preparation was adopted, and a means for purifying and manipulating the amalgam at temperatures in the vicinity of -30°C was devised. Acid extraction of the ammonia from the decomposing amalgam provided a means for analyzing samples of the amalgam. In most cases the amalgams on which measurements were made contained less than 0.50 mole per cent of ammonium.

Magnetic susceptibility measurements by the Gouy method at -30°C gave evidence that ammonia and hydrogen were combined with mercury in a way which decreased the freedom of electrons in mercury. Values as large as -0.270×10^{-6} c.g.s.units/gm. were observed for the specific susceptibility of the amalgam as compared to -0.167×10^{-6} c.g.s. units/gm. for the specific susceptibility of mercury. The large increase in the diamagnetism of mercury to which only a small amount of ammonium had been added established that uncombined $NH_4\cdot$ radicals comparable to alkali metal atoms were not present in the amalgam. Apparently the amalgam is an entity of the type $NH_4^+Hg_x^-$ in which the few electrons furnished by ammonium to mercury suffice to remove the temperature independent paramagnetism of mercury. Failure to find a relationship between the composition and the density of the amalgam suggests that the amalgam is partially decomposed at -30°C and contains ammonia and hydrogen gases entrapped in the mercury as well as some ammonium in solution in, or in

combination with mercury. The amalgam ordinarily studied thus appears to be a mixture containing gaseous decomposition products.

A study of the solid-liquid equilibria in the system ammonium-mercury showed that about 60% of the ammonia and hydrogen present in the mercury were released during a single freezing and that the decomposition produced by additional freezings was insignificant, although an appreciable quantity of ammonium remained in the mercury. This indicated that some ammonia and hydrogen are very loosely bound to mercury in the amalgam perhaps as entrapped gas and that the remainder is present as ammonium or a compound of mercury with ammonium. The amalgam or possibly a stable froth containing the amalgam floats on top of mercury as indicated from cooling curves obtained simultaneously for each phase of the amalgam in which the cooling curve of the lower phase was not significantly different from that of pure mercury. From the cooling curves it was observed that during the solidification process the temperature of the system increased slightly perhaps as a result of the breaking of some type of bond between the components of the system. Definite freezing temperatures were not obvious from the cooling curves for the amalgam, although the shape of the curves was reminiscent of solid solution formation. If the "true" amalgam exists as a colloidal dispersion or a froth of colloidal particles in mercury then the freezing curves would be reasonable since only the mercury would freeze at -40°C; the fusion point of the amalgam would be higher than -40°C.

Ammonium amalgam electrodes were found to be largely irreversible in aqueous ethanol solution at -30°C, although a value of 1.57 volts

for the potential of an amalgam electrode in solution with ammonium ions was computed. Only in very dilute solutions immediately after connecting the potentiometer does one observe e.m.f. values approximating those for the alkali metal amalgams.

Compressibility measurements were made on samples of the amalgam. These indicated that the amalgam contained ammonia, which was liquefied during compression, as well as ammonium, in solution with mercury or in combination with mercury.

LITERATURE CITED

1. Seebeck, Ann., 66, 191 (1808).
2. H. Davy, Phil. Trans., 1808, 353.
3. H. Davy, Phil. Trans., 100, 37 (1810).
4. J. Gay-Lussac and L. Thenard, Reserches Physico-Chimiques, i, 52 (1809); R. Routledge, Chem. News, 26, 210 (1872).
5. P. Ampere, Ann. chim. phys., 2, 16 (1816).
6. Daniell, Chemical Philosophy, p. 420; R. Routledge, Chem. News, 26, 210 (1872).
7. W. Grove, Phil. Mag., 19, 97 (1841).
8. H. Landolt, Annalen der Chemie du Pharmacie, 6, 346 (1868).
9. R. Routledge, Chem. News, 26, 210 (1872).
10. C. A. Seeley, Chem. News, 24, (1870); R. Routledge, op. cit.
11. M. LeBlanc, Z. physik. Chem., 5, 467 (1890).
12. A. Coehn and K. Dannenberg, Z. physik. Chem., 8, 628 (1901).
13. A. Coehn, Z. anorg. Chem., 25, 430 (1900).
14. H. Moissan, Chem. News, 86, 76 (1902).
15. E. Rich and M. Travers, J. Chem. Soc., 89, 872 (1906).
16. G. Smith, J. Am. Chem. Soc., 29, 844 (1907).
17. A. Coehn, Z. Elektrochem., 8, 591 (1902).
18. G. McP. Smith, Ber., 40, 4298 (1907).
19. G. McP. Smith, Ber., 40, 4893 (1907).
20. C. Baborovsky and V. Vojtech, Physik Z., 7, 846 (1906).
21. A. Coehn, Zeit. Elektrochem., 12, 609 (1906).

22. H. McCoy and W. C. Moore, J. Am. Chem. Soc., 33, 273 (1911).

23. H. McCoy and F. West, J. Phys. Chem., 16, 261 (1912).

24. P. Lennard, Wiedemann's Annalen, 46, 584 (1892); H. McCoy and F. West, op. cit.

25. G. Aronheim, Z. physik. Chem., 97, 95 (1921).

26. Sander and Nitchsche, Z. Elektrochem., 34, 244 (1928).

27. A. Deyrup, J. Am. Chem. Soc., 56, 2594 (1934).

28. St. v. Náray-Szábo and L. Szlatinay, Z. physik. Chem., A173, 89 (1935).

29. S. Takaki and T. Ueda, J. Pharm. Soc. Japan, 58, 797-805 (1938); C. A., 33, 2508 (1939).

30. H. A. Laitenen and C. E. Shoemaker, J. Am. Chem. Soc., 72, 4975 (1950).

31. R. Johnston and A. Ubbelohde, J. Chem. Soc., 1951, 1731.

32. N. Baenziger and J. Nielsen, University Microfilm, Pub. No. 5488, June, 1953, 88 pp.

33. O. Ruff, Ber., 34, 2604 (1901).

34. H. Moissan, Compt. rend., 133, 713 (1901).

35. H. Schlubach and F. Ballauf, Ber., 54B, 2825 (1921).

36. G. Porter, J. Chem. Soc., 1954, 760.

37. A. H. Blatt, Organic Syntheses, Collective Volume II, Revised Edition, John Wiley and Sons, New York, 1943, p. 609.

38. H. B. Thompson, Private Communication.

39. E. H. Swift, Introductory Quantitative Analysis, Prentice-Hall Inc., New York, 1950, pp. 249-250.

40. W. Kerp, Z. anorg. Chem., 17, 284 (1898).

41. G. M. Smith and H. C. Bennett, J. Am. Chem. Soc., 32, 622 (1910).

42. K. Bornemann and P. Muller, Chem. Zentr., 2, 434 (1910).

43. T. B. Hine, J. Am. Chem. Soc., 39, 882 (1917).

44. E. Vanstone, Trans. Faraday Soc., 9, 291 (1914).

45. E. Vanstone, Trans. Faraday Soc., 7, 42 (1911).

46. H. E. Bent and J. H. Hildebrande, J. Am. Chem. Soc., 49, 3011 (1927).

47. G. M. Smith, Am. Chem. J. 38, 671 (1907).

48. L. F. Bates and E. M. Somekh, Proc. Phys. Soc. London, 56, 182 (1944).

49. W. G. Davies and E. S. Keeping, Phil. Mag., 7, (7th Series), 145 (1929).

50. L. F. Bates and L. C. Tai, Proc. Phys. Soc. London, 48, 795 (1936).

51. L. F. Bates and P. F. Illsley, Proc. Phys. Soc. London, 49, 611 (1937).

52. L. F. Bates and A. W. Ireland, Proc. Phys. Soc. London, 49, 642 (1937).

53. L. F. Bates and C. J. Baker, Proc. Phys. Soc. London, 52, 436 (1940).

54. W. Franke and H. Katz, Z. anorg. allgem. Chem., 231, 63 (1937).

55. S. Aravamauthachari, Current Sci., 7, 179 (1938).

56. W. Klemm and B. Hauschulz, Z. Elektrochem., 45, 346 (1939).

57. Y. S. Shur, Nature, 139, 804 (1937).

58. R. W. Wyckoff, Crystal Structures, Interscience Publishers, New York, 1948, Volume 1, p. 7.

59. E. Vogt, Ann Physik, 21, 791 (1935).

60. M. Owen, Ann. Physik (4) 37, 657 (1912).

61. A. E. Oxley, Trans. Roy. Soc. London, 214A, 109 (1914).

62. L. F. Bates, C. J. Baker, R. Meakin, Proc. Phys. Soc. London, 52, 425 (1940).

63. R. E. VanderVennen, Unpublished Ph. D. Thesis, Michigan State College, 1954.

64. P. W. Selwood, Magnetochemistry, Interscience Publishers, Inc., New York, 1943.

65. J. Strong, Procedures in Experimental Physics, Prentice-Hall, New York, 1942, pp. 152-7.

66. L. F. Bates and C. J. W. Baker, Proc. Phys. Soc. London, 50, 409 (1938).

67. W. Hückel, Structural Chemistry of Inorganic Compounds, Elsevier Publishing Co., Houston, 1951.

68. A. Weissberger, Physical Methods of Organic Chemistry, 2nd Edition, Interscience Publishers, Inc., 1949, p. 52.

69. A. Findlay and A. N. Campbell, The Phase Rule and Its Applications, 9th Edition, Dover Publishers, New York, 1951.

70. M. Hansen, Aufbau der Zweistofflegierungen, Verlag von Julius Springer, Berlin, 1936, pp. 779-797.

71. H. E. Bent, J. Phys. Chem., 37, 431 (1933).

72. N. A. Lange, Handbook of Chemistry, 8th Edition, Handbook Publishers, Inc., Sandusky, Ohio, 1952.

73. M. T. Rogers, M. B. Panish, and J. L. Speirs, Unpublished work.

74. G. N. Lewis and C. A. Kraus, J. Am. Chem. Soc., 32, 1459 (1910).

75. G. N. Lewis and F. G. Keyes, J. Am. Chem. Soc., 34, 119 (1912).

76. G. N. Lewis and F. G. Keyes, J. Am. Chem. Soc., 35, 340 (1913).

77. G. N. Lewis and W. L. Argo, J. Am. Chem. Soc., 37, 1983 (1915).

78. T. W. Richards and F. Daniels, J. Am. Chem. Soc., 41, 1732 (1919).

79. G. N. Lewis and M. Randall, J. Am. Chem. Soc., 43, 233 (1921).

80. T. W. Richards and J. B. Conant, J. Am. Chem. Soc., 44, 601 (1922).

81. H. E. Bent and E. Swift, Jr., J. Am. Chem. Soc., 58, 2216 (1936).

82. H. E. Bent and A. F. Forziatti, J. Am. Chem. Soc., 58, 2220 (1936).

83. A. Patterson and W. A. Felsing, J. Am. Chem. Soc., 64, 1478 (1942).

84. B. E. Conway, Electrochemical Data, Elsevier Publishing Co., New York, 1952.

85. P. W. Bridgman, The Physics of High Pressures, G. Bell and Sons, Ltd., London, 1931.

86. O. J. Kleppa, J. Chem. Phys. 17, 668 (1949).

87. S. H. Maron and D. Turnbull, Ind. Eng. Chem., 33, 408 (1941).