BASIC CHEMISTRY OF

HIGH TEMPERATURE INORGANIC SYSTEMS

SEMIANNUAL PROGRESS REPORT

JULY — DECEMBER, 1956

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.

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ABSTRACT

HIGH TEMPERATURE THORIUM CHEMISTRY

The vapor pressure determination of solid ThF_4 has been completed. The corrected vapor pressure of solid ThF_4 from 1055 to 1297° K is:

$$Log\ P_{(atm)} = \frac{-16,860}{T°K} + 9.107$$

Experiments to determine the heat of formation of ThF_4 by studying the reaction of ThF_4 with SiO_2 are described. A kinetic study of the thermal decomposition of $Th(NO_3)_4$ has been initiated.

CHEMISTRY OF METAL — METAL SALT SYSTEMS AT HIGH TEMPERATURES

The results of the $Bi-BiCl_3$ solubility experiments indicate the possibility that the consolute temperature exists at about 775° C. The solubility of Cd in $CdCl_2$ increases with increasing temperature to a value of 24 mole per cent at 963° C. The solubility studies of $Hg-Hg_2Cl_2$ are also under way. Vapor pressure experiments on bismuth trichloride dissolved in bismuth indicated large positive deviations from Raoult's law. Two series of cryoscopic experiments are described: one in which $HgCl_2$ is the solvent, and one in which molten Bi is the solvent. In order to gain information on the species in molten salts, a study of the transport number in fused salts has begun.

HIGH TEMPERATURE CHEMISTRY OF CERAMICS

A new program has been initiated to examine the nature of ceramics at high temperatures. Knudsen and Langmuir vaporization studies are under way on La_2O_3, BeO, and ZrC. The electron density distribution of BeO is being determined by three-dimensional X-ray diffraction measurements. Also, an experimental program is under way to seek principles to guide the search for new and superior refractories.

I. HIGH TEMPERATURE THORIUM CHEMISTRY

Experiments have continued on the determination of the vapor pressure of thorium by the Knudsen technique. The Knudsen vapor pressure meaurements on ThF_4 have been completed. Two new studies have been initiated: 1) a kinetic study of the thermal decomposition of $Th(NO_3)_4$ and 2) a study of the reaction of SiO_2 with ThF_4 to yield the heat of formation of ThF_4.

A. THE VAPOR PRESSURE OF THORIUM METAL (T. A. Milne)

Several changes have been made in the apparatus, described earlier,[1] for a Knudsen effusion study of the vapor pressure of thorium metal. The waxed-on brass end plate was replaced by a Vycor standard taper joint which can be immersed in liquid nitrogen if necessary. The pumping speed of the system was increased by relocating the trap and diffusion pump. Quartz was substituted for Vycor in the area near the heated effusion cell. With these improvements, vacua of 2×10^{-7} mm Hg are readily attained without cold traps while the system is at room temperature. During effusion experiments, it has been possible to maintain vacua as low as 8×10^{-7} mm Hg. This system appears to be adequate for a study of the effect of small partial pressures of oxygen on the rate of vaporization of thorium.

Two series of runs have been made on thorium metal held in tungsten crucibles. In the first series, carried out in an auxilliary vacuum system, the vapor effusing from a partially sintered tungsten Knudsen cell was collected simultaneously on a quartz sleeve and a tantalum disk. The system was opened after each run to permit changing of the collectors.

Seven runs were made at temperatures ranging from about 1650° C to 1760° C and vacua of 5×10^{-5} to 2×10^{-6} mm Hg. Six of these runs were carried out with solid thorium which exhibited no apparent interaction with the tungsten cell. However, when the thorium was melted it soaked completely into the partially sintered crucible. In the second series of runs, carried out in the improved apparatus, a fully sintered, drilled tungsten crucible was used. Five runs were carried out on solid thorium, without breaking the vacuum, at temperatures from 1550° C to 1650° C and vacua of 2×10^{-5} to 8×10^{-7} mm Hg. This series, which

was to be extended to permit measurements at higher temperatures and lower vacua, was interrupted due to an accidental break in the vacuum system after the fifth exposure.

Chemical analyses of these two series of runs are currently being carried out. Additional runs on solid and liquid thorium in tantalum and tungsten containers are under way. Experiments employing the Langmuir technique are also planned using an apparatus and thorium wires available from the Solid State Physics Group.

B. VAPOR PRESSURE OF THORIUM TETRAFLUORIDE (A. J. Darnell)

The work for the current period consisted in completing the study of the vapor pressure of solid ThF_4. Additional experimental results were obtained and corrections applied to these and previously reported data in order to obtain more accurate vapor pressure information. The quantity of effused ThF_4 in these experiments was determined by the weight loss from the effusion cell. In order to check that thorium tetrafluoride is the effusing material, a chemical analysis of the sublimate will be made. A mass balance experiment was carried out. The weight collected checked satisfactorily with the weight loss of the crucible. A melting point determination was made on thorium tetrafluoride contained in a nickel cell under an atmosphere of argon. A calibrated Pt-Pt, 10%Rh thermocouple was used for temperature measurements. Three determinations yielded a melting point of 1110° ± 2° C. Asker, Segnit, and Wylie[2] report a melting point of 1111° ± 2° C while Bergman and Dergunov[3] obtained 1114° C. The vapor pressure data are shown in Table I and include three new experimental points which extend the lower limit of the measurements by 50° C. Three experiments, previously reported,[1] were rejected because the experimental conditions under which they were performed were different from those of the later measurements. The incorporation of these results would require temperature and time calibrations on the original apparatus which was abandoned in favor of the improved apparatus.

The Pt-Pt, 10%Rh thermocouple, used to measure the temperature, was calibrated against the melting point of sodium chloride. Temperature and effective effusion time calibrations were made on the apparatus under conditions similar to those during the actual vapor pressure measurements. These corrections

were applied to obtain the data given in Table I. A least squares analysis of the data given in Table I gives the following relationship for the vapor pressure of solid ThF_4.

$$\log P_{(atm)} = \frac{-16,861}{T°K} + 9.107 \qquad \ldots (1)$$

The straight line shown in Fig. 1 represents this equation. The value of $\Delta H_{sublimation}$ calculated from the above equation is 77.1 kcal/mole.

TABLE I

VAPOR PRESSURE OF THORIUM TETRAFLUORIDE
BY KNUDSEN EFFUSION METHOD

Temp. (°K)	Wt. Loss (gm)	Time (sec)	Orifice Area (cm^2)	Clausing Factor (K)	Pressure (atm)
1054.6	0.0150	3.32×10^5	0.0164	0.86	1.21×10^{-7}
1065.8	0.0259	3.38×10^5	0.0164	0.86	2.06×10^{-7}
1077.3	0.0295	2.42×10^4	0.0164	0.86	3.31×10^{-7}
1112.8	0.0066	2.35×10^5	0.00196	0.65	8.55×10^{-7}
1112.8	0.0724	2.38×10^5	0.0164	0.86	8.36×10^{-7}
1166.0	0.0212	1.52×10^5	0.00196	0.65	4.33×10^{-6}
1184.0	0.0256	1.20×10^4	0.0164	0.86	6.08×10^{-6}
1185.5	0.1651	6.35×10^4	0.0164	0.86	7.41×10^{-6}
1212.1	0.0386	1.30×10^5	0.00196	0.65	1.39×10^{-5}
1214.1	0.0354	6.02×10^4	0.00196	0.65	1.87×10^{-5}
1218.1	0.0480	6.22×10^4	0.00196	0.65	2.47×10^{-5}
1225.2	0.0515	1.35×10^4	0.00815	0.82	2.38×10^{-5}
1277.3	0.0393	1.70×10^4	0.00196	0.65	7.54×10^{-5}
1297.1	0.0552	1.47×10^4	0.00196	0.65	1.23×10^{-4}

Emphasis is now being placed on the completion of the vapor pressure determination of liquid ThF_4 by the "quasi-static" Rodebush[4] method. The apparatus has been re-built to operate at higher temperatures and has been checked by repeating the measurement on sodium chloride.

MELTING POINT
OF Th F₄
(1110°C)

$$LOG\ P\ (atm) = \frac{-16,861}{T(°K)} + 9.1074$$

$$\Delta H°_{sublimation} = 77.1\ k\,cal/mole$$
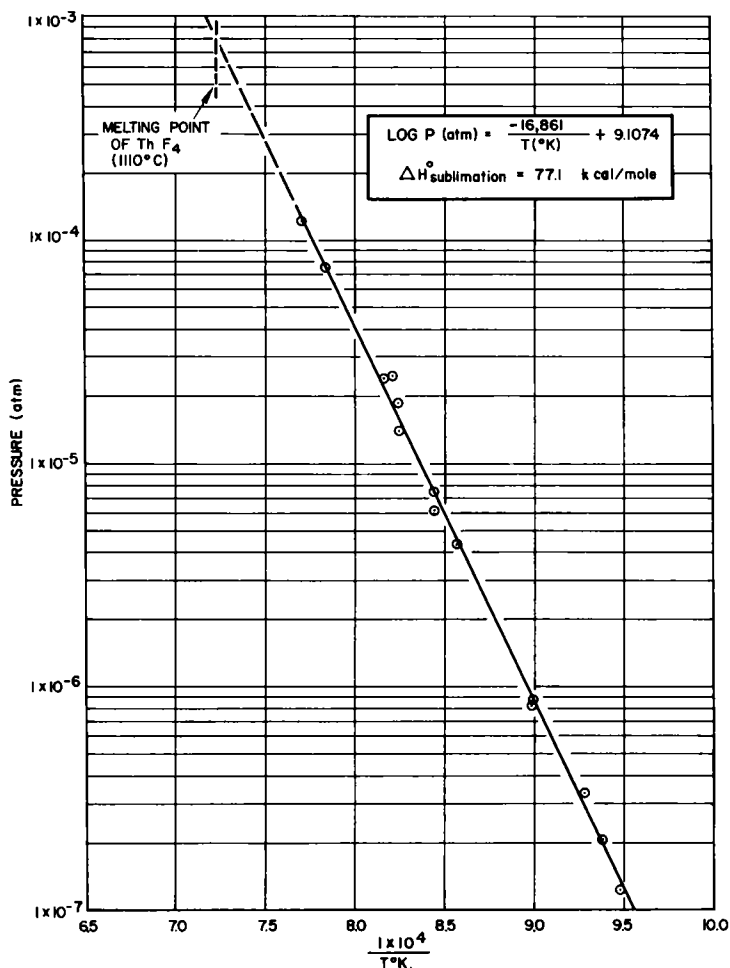
Fig. 1. Vapor Pressure of Solid
Thorium Tetrafluoride

C. THERMAL STABILITY OF THORIUM TETRAFLUORIDE (A. J. Darnell)

During this period experiments were carried out to determine the thermochemical properties for formation of thorium tetrafluoride. Only estimated values are available for this compound, based upon measurements on thorium tetrachloride and analogy with the tetrahalides of uranium.[5] It was felt that these data could be most conveniently obtained by studying the reaction of ThF_4 with SiO_2 to yield the volatile SiF_4. By measuring the pressure of SiF_4, one can calculate

thermochemical values, assuming that the following reaction occurs:

$$ThF_{4(s)} + SiO_{2(s)} \rightleftharpoons SiF_{4(g)} + ThO_{2(s)} \qquad \dots (2)$$
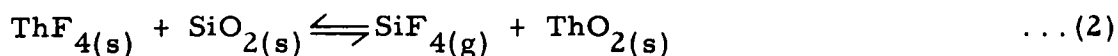
Four preliminary experiments have been carried out in the temperature range of 549° to 813° C with an equimolar mixture of thorium tetrafluoride and silicon dioxide. The pressure of the silicon tetrafluoride produced from this reaction was measured and thermochemical values calculated. The values obtained are in fair agreement with the estimate given by Brewer.[5] A recheck of the data will be necessary because in these experiments the sample was contaminated by air. An analysis of the solid products from Reaction (2) will be made to determine if the reaction proposed is the one that occurs.

D. THERMAL DECOMPOSITION OF THORIUM NITRATE (A. Lipschitz)

The object of this research is to study the decomposition of pure thorium salts at elevated temperatures. The salt chosen for this study was thorium nitrate. It is hoped that the rate and mechanism of thermal decomposition of this salt can be studied by a determination of the volume of gases evolved as a function of time. From the data it may be possible to obtain rate constants and to determine the energy of activation and related quantities for the thermal decomposition of $Th(NO_3)_4$.

This technique was applied with considerable success by Freeman[6] to the thermal decomposition of sodium nitrate. Exploratory experiments indicated that the rate of decomposition of thorium nitrate was markedly influenced by water of hydration. Therefore, it was necessary to prepare anhydrous thorium nitrate. Attempts to prepare the anhydrous salt by thermal dehydration of commercially available thorium nitrate tetrahydrate were unsuccessful due to decomposition of the nitrate. A second approach was based on the phase diagram of the ternary system: thorium nitrate-water-nitric acid.[7]

According to this diagram, thorium nitrate should be precipitated by the vacuum distillation of nitric acid from a dilute solution of $Th(NO_3)_4 \cdot 4H_2O$ in anhydrous nitric acid. Using this method a solid product was obtained which melted with decomposition at 202° C (melting point of $Th(NO_3)_4 \cdot 4H_2O$, 175° C). However, an analysis by the conventional Karl Fischer Reagent showed that the salt contained

water corresponding to a tri-hydrate. The technique of Katzin et al ,[8] is now being examined for the preparation of anhydrous thorium nitrate. The method utilizes the reaction of $Th(NO_3)_4 \cdot 4H_2O$ with N_2O_5 in anhydrous nitric acid. The resulting compound, $Th(NO_3)_4 \cdot 2N_2O_5$, is then decomposed in vacuum at 150° to 160° C to give anhydrous thorium nitrate.

To study the thermal decomposition of thorium nitrate, an apparatus similar to that used by Freeman[6] was constructed. The apparatus, illustrated in Fig. 2, is made of pyrex glass except for the Vycor reaction chamber which is heated in the Marshall furnace.
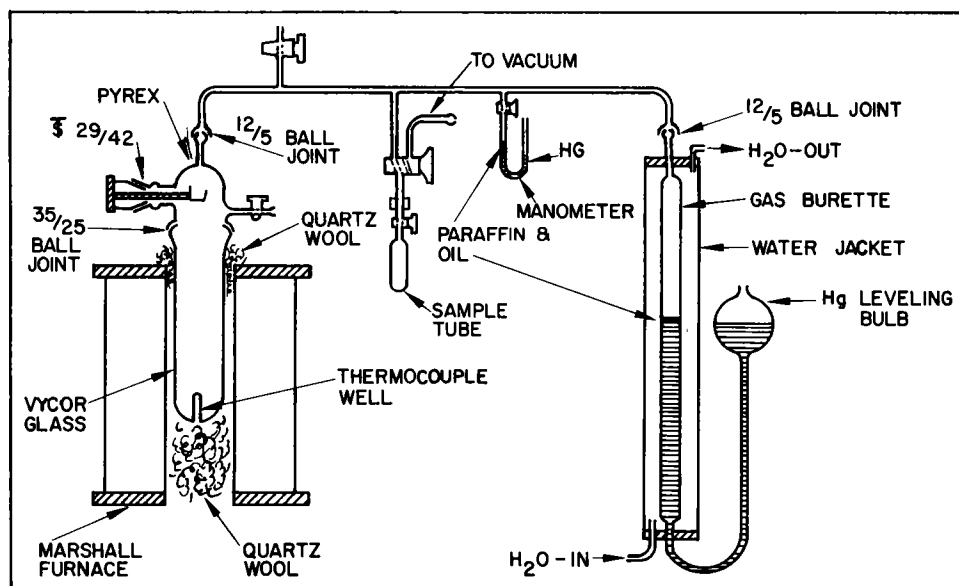
Fig. 2. Apparatus for Determination of the Thermal
Decomposition of Thorium Nitrate

For an experiment, the reaction chamber is brought to the desired temperature by means of the thermostatically regulated Marshall furnace. Any foreign gas in the apparatus is removed by flushing with purified helium gas for several hours. The source of helium is then shut off and the thorium nitrate dropped into the chamber. The system is then maintained at constant pressure by frequent adjustment of the mercury leveling bulb attached to the gas burette. Gaseous samples for analyses can be removed by means of the gas sampling attachment. This apparatus was tested with a sample of partially dehydrated thorium nitrate. As soon as an anhydrous sample of thorium nitrate is prepared, a study will be made of the composition of gaseous products as a function of time.

II. CHEMISTRY OF METAL-METAL SALT SYSTEMS AT HIGH TEMPERATURES

Experiments on the solubilities of metals in molten salts containing a common cation are continuing, emphasis being placed on nonquenched type experiments. One of the objectives of this study is the attainment of the consolute temperature. Once this temperature is known, it may be possible to study the continuous change in properties of the system as a function of composition.

The results of the Bi-BiCl$_3$ solubility experiments indicate the possibility that the consolute temperature exists at about 775° C. In the case of the Cd-CdCl$_2$ system, a solubility of 24 mole per cent Cd in CdCl$_2$ at 963° C was noted. Studies of the Hg-HgCl$_2$ and the Hg-Hg$_2$Cl$_2$ systems have been initiated. Vapor pressure studies of BiCl$_3$ dissolved in Bi indicate marked positive deviations from Raoult's law. Two series of cryoscopic measurements are described, one in which HgCl$_2$ is the solvent and the other in which Bi is the solvent. The results in the former case indicate that HgCl$_2$ is sufficiently ionized to exhibit the common ion effect. The cryoscopic effect of NaBr is equivalent to two particles while the effects of NaCl, Hg$_2$Cl$_2$, and Hg are equivalent to one particle. BiCl$_3$ dissolves in molten Bi giving a cryoscopic effect of three particles.

In order to learn something of the species in molten salts a study of the transport numbers in fused salts has been initiated.

A. Bi-BiCl$_3$ SOLUBILITY STUDIES (A. J. Darnell, S. J. Yosim)

During this period, work on the Bi-BiCl$_3$ phase diagram continued, emphasis being placed on non-quenched type experiments. The techniques consisted mainly of decantation and visual observations. The decantation experiments, by methods similar to those of Bredig's,[9, 10] consisted of equilibrating the two phases at the desired temperature and pouring some of the salt phase into a side arm by tilting the entire system. The principle is schematically shown in Fig. 3. The quartz tube containing the sample was mounted in a tilt furnace in a position that prevented entrapment of any part of the sample in the side arm. The entire sample was held in a uniform temperature zone for a minimum period of twenty hours. The furnace containing the sample was then tilted to a predetermined angle such that part of the salt rich phase was decanted into the side arm. The sample tube was then placed in a vertical position, taken from the furnace and allowed to cool

in air. By this method sampling of the salt-rich phase was effected at temperature.

The solubility measurements on the metal rich side of the phase diagram were carried out by a visual method. This consisted of sealing a mixture of Bi and $BiCl_3$ in a Vycor tube, heating the system in a Marshall furnace equipped with a window, and observing the interface with a cathetometer. The disappearance of the interface signified the temperature at which a given mixture of metal and salt formed one phase.
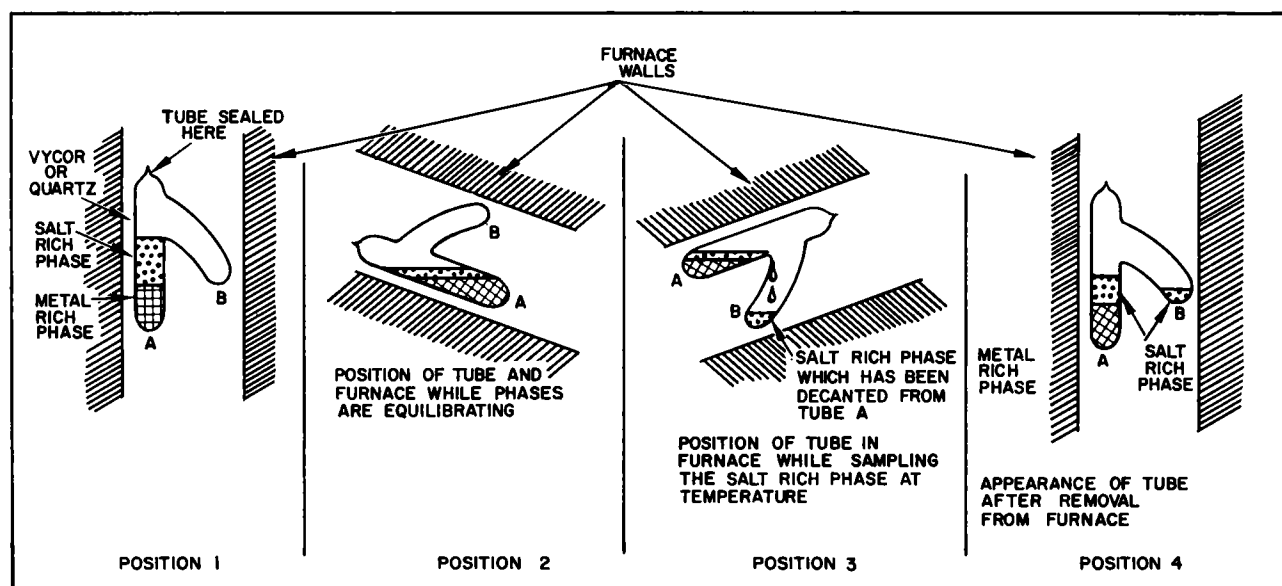
Fig. 3. Furnace Positions for Sampling Salt Phase at Temperature

The results of these experiments are shown in Fig. 4. While the data are only tentative, certain conclusions may be drawn. It appears that the solubility of the metal in the salt first decreases with increasing temperature and then begins to increase, while the solubility of the salt in the metal continues to increase as the temperature is increased. If the trends of the two legs of the immiscibility curve are correct, one might expect a consolute temperature at about 775° C. Visual experiments on the metal rich side will continue. Heavier walled quartz tubes will be used, since, at about 735° C the mechanical limit of the tubes used to date is reached. In the case of the salt rich side, the visual experiments have not been very successful. Very often at any given temperature a two phase system would appear to become one phase when the system was cooled about 30° C. When heated, two phases would reappear. However, this temperature was not a phase

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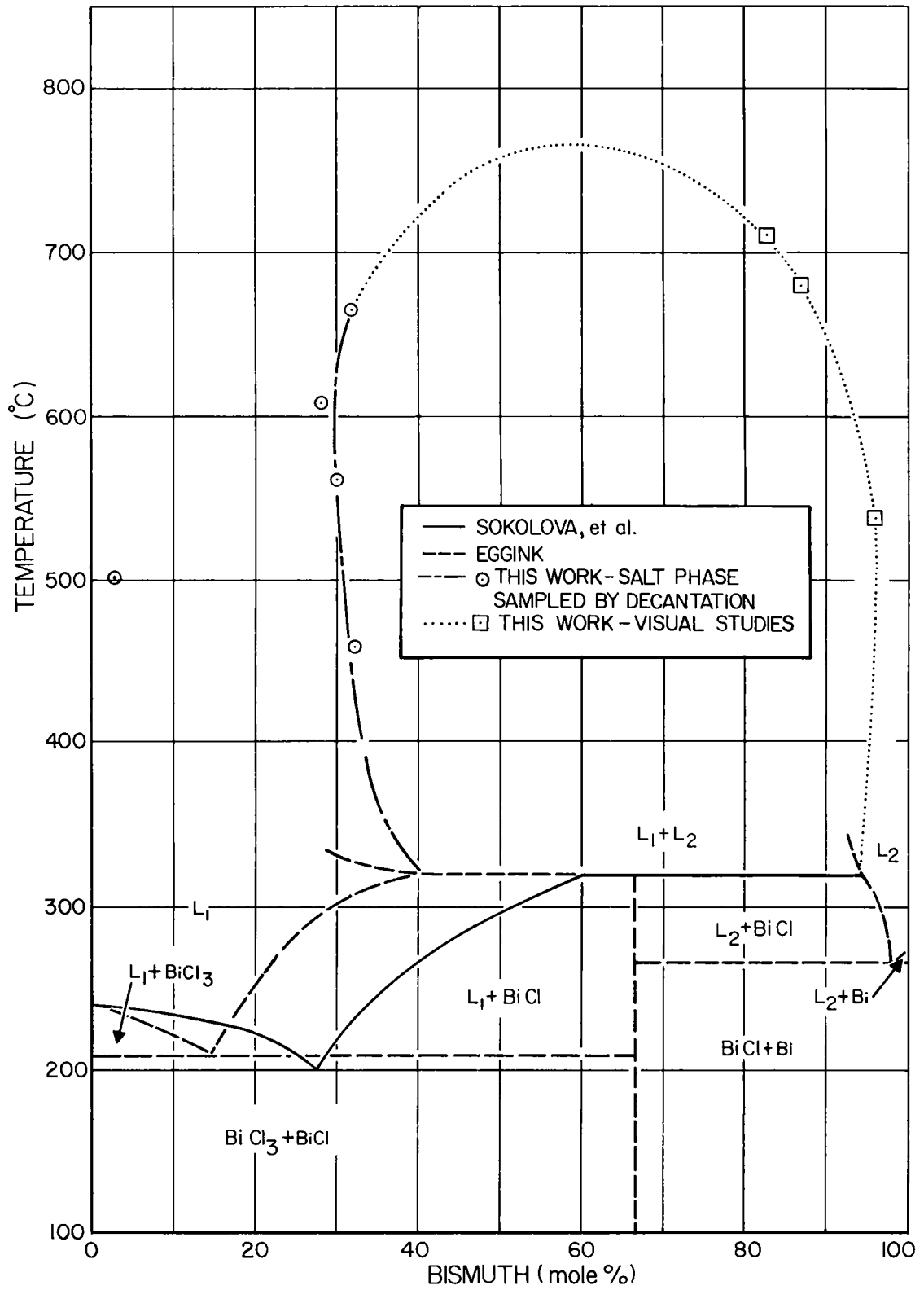
Fig. 4. Temperature-Composition Diagram for Bismuth-Bismuth
Trichloride System
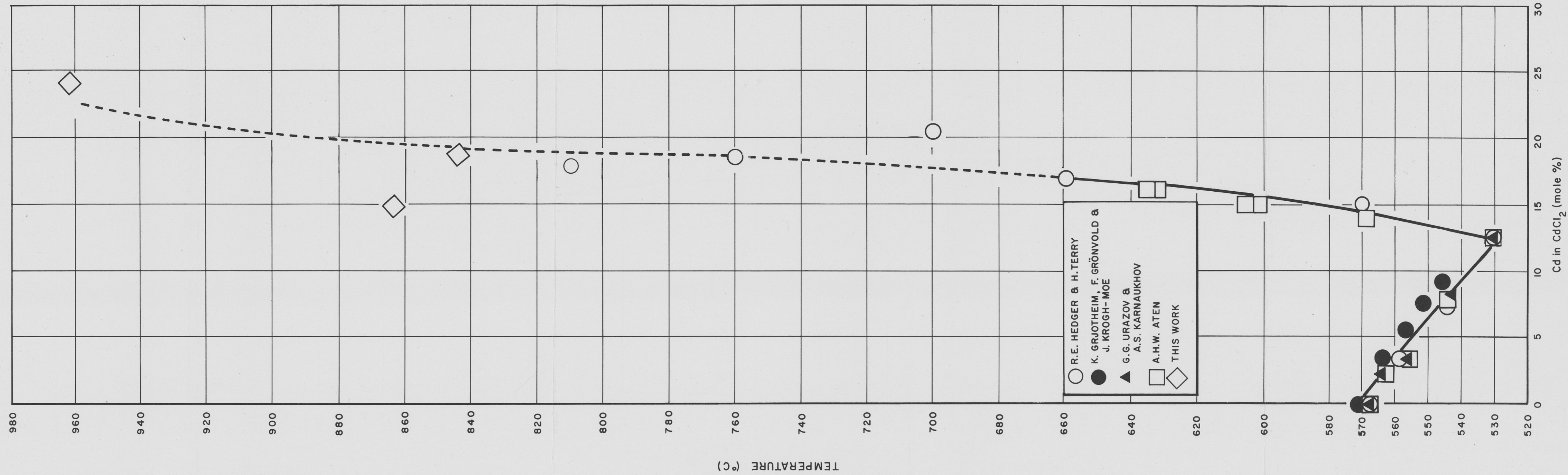
Fig. 5. Temperature-Composition
Diagram for Cadmium-
Cadmium Chloride System

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transition temperature since at any given composition, this "transition" temperature varied as much as 100° C. One explanation, which appears likely, is that there is a thin opaque film of salt between the metal and glass wall which disappears upon heating and reappears upon cooling. This will be studied in greater detail.

Thermal analysis has also proved useful for examining metal-salt systems.[11] A differential thermal analysis system is now being assembled. The temperature at which two liquid phases appear during cooling will be measured. The temperatures at which the solid phase appears will also be measured since these points are in dispute.[12, 13]

B. THE CADMIUM - CADMIUM CHLORIDE SYSTEM (A. Lipschitz)

Although the $Cd-CdCl_2$ system has been studied by various workers,[14-19] the knowledge of the behavior of this system is far from complete. The techniques which were used include quenching and mechanical separation of phases, pipetting the salt rich phase at temperature, and thermal analysis. The chief disadvantage of the quenching technique is that during solidification the phases may change composition. The pipetting technique, although it allows sampling at temperature, is limited to temperatures at which the system does not have an appreciable vapor pressure.

In order to eliminate some of the disadvantages described above, the decantation method of sampling the salt rich phase at temperature was used. The cadmium used in this work was cp reagent grade and was filtered under vacuum through quartz wool. The cadmium chloride was cp reagent grade previously treated with anhydrous hydrogen chloride gas at 150° C.

The results obtained in this preliminary investigation are compared with those of other workers in Fig. 5. The lower values obtained in this study may be due to non-equilibrium conditions. In future experiments, mechanical agitation will be employed during heating. The value of 24.1 mole per cent of cadmium in the salt rich phase at 963° C is the highest obtained thus far for the system. Additional solubility experiments will be carried out at higher temperatures.

C. Hg-HgCl$_2$ SYSTEM (S. J. Yosim)

Mercurous chloride may be considered as an example of a stable solid sub-halide. A study of this compound should lead to a greater understanding of metal-metal salt solutions, since the formation of a subhalide is a suggested mechanism for solution of a metal in a salt. While there is no doubt as to the stability of this subhalide in the solid phase, the stability of molten Hg$_2$Cl$_2$ is uncertain; especially since the vapor phase above 300° C is known to consist of Hg and HgCl$_2$ only.[20,21] Thus, a study of molten mercurous chloride seems appropriate. Further, solubility measurements of Hg in Hg$_2$Cl$_2$ should be interesting since the justification of appreciable solubility by a subhalide mechanism would then require the formation of a subhalide richer in mercury than Hg$_2$Cl$_2$, i.e., ionic species containing more mercury than Hg$_2{}^{++}$. To obtain some information as to the stability of molten Hg$_2$Cl$_2$, a sample of reagent grade powdered Hg$_2$Cl$_2$ was heated in an evacuated, sealed quartz tube. At about 500° C, the volume of the salt decreased sharply and a dark liquid was observed. This liquid still con-tained some solid matter which persisted to over 600° C. Upon cooling to room temperature the sample was white with small black areas. This experiment will be repeated with carefully purified Hg$_2$Cl$_2$. Further experiments, employing bomb techniques, are planned to study the solubility of molten Hg in Hg$_2$Cl$_2$.

Some exploratory experiments were also carried out in which mercury and mercuric chloride were sealed in a pyrex tube which had been evacuated. No reaction was noted until the melting point of the HgCl$_2$ was reached. A black ring appeared at the interface and began to increase in size. After several min-utes, it was noted that the salt was a grey solid mass. Heating a mixture of Hg and Hg$_2$Cl$_2$ to the same temperature resulted in no reaction, the Hg$_2$Cl$_2$ remain-ing white. These reactions will be studied in further detail.

D. CRYOSCOPIC MEASUREMENTS IN MOLTEN MERCURIC CHLORIDE SOLUTION (S. Mayer)

The cryoscopic technique has been employed for research studies with several molten salt solutions,[22] including solvents such as: AgNO$_3$, KSCN, KNO$_3$, KCl, NaCl, SrCl$_2$, and CaCl$_2$. With these solvents, and with dilute solutions of NaCl, KBr, Na$_2$SO$_4$, and HgBr$_2$, the observed freezing point depressions are readily interpretable on the basis of the classical Raoult-van't Hoff freezing point

depression law which gives the expected number of solute ions in the melt. As anticipated on theoretical grounds,[22] the freezing point is not depressed by those solute ions which are common to the ions formed by the solvent.

In view of the systematic and informative results obtained by the cryoscopic technique in molten salt solutions, a series of cryoscopic studies has been initiated to apply this technique to fused metal-metal salt solutions. Molten mercuric chloride was selected as an initial solvent for cryoscopic study for the following reasons. Mercurous chloride can be considered to be a stable subhalide, as was pointed out in the preceding section, and consequently it was of interest to study the behavior of solutions of Hg_2Cl_2 and of Hg in $HgCl_2$. In addition, it was desirable to measure the cryoscopic effect of well understood salts such as NaCl and NaBr in molten $HgCl_2$. The question also arose as to whether chloride ion will exhibit a common ion effect in molten $HgCl_2$ in view of mercuric chloride's non-ionic characteristics, e.g., low equivalent conductance.

The experimental procedure was designed to obtain a precision of 0.02° C in the cryoscopic measurements. Reagent grade salts were employed throughout, and the mercury was the triple-distilled grade. Chemicals were dried in a vacuum system at room temperature for at least three days. The temperature of the container was then slowly raised to 110° C while still pumping, and this temperature was maintained for at least 24 hours, before cooling.

The salts were then precisely weighed into a Pyrex cryoscopy tube (18 mm diameter) having a thin-walled Pyrex thermcouple well (20 mm long) sealed into the bottom of the tube. The tube was then sealed about 90 mm above the base, with the contents still under vacuum. The measurements were carried out with sealed tubes because of the high toxicity and volatility of $HgCl_2$. A chromel-alumel thermocouple, electrically insulated with woven glass, was inserted into the thermocouple well and fastened firmly to the cryoscopy tube. The tube was then suspended in a Marshall furnace which was packed with Pyrex wool above and below the tube.

The thermocouple cold junctions were maintained in oil-filled tubes in a distilled water-ice equilibrium mixture. Leads from the cold junction were connected to a large rotary multiple switch which led to a Rubicon B precision potentiometer sensitive to one-tenth micro-volt. The potential of the thermocouple

in the cryoscopy tube could be measured directly in this way, or the temperature could be recorded automatically by switching the thermocouple to the input of a Leeds and Northrup microvolt amplifier which fed into a Brown Elektronik automatic recording potentiometer. Sensitivity in the latter arrangement was one-tenth microvolt, and the range was twenty-five microvolts. By suitable switches on the amplifier and recorder the range could be increased by factors of 2, 4, 10, 20, 40, 100, and 400, with a corresponding decrease in sensitivity. The zero-point could be adjusted to a convenient arbitrary value by bucking out excess voltage with the Rubicon B potentiometer.

The temperature of the Marshall furnace was automatically controlled by a Wheelco regulator-pyrometer operating through a Variac. The furnace was maintained at a temperature fifteen degrees above the melting point of mercuric chloride until the salt mixture melted completely. Then the sealed cryoscopic tube was withdrawn from the furnace, and the melt was shaken vigorously to dissolve and mix the solute. The tube was then returned to the furnace, and the $HgCl_2$ solution heated until it reached the furnace temperature. The heating of the furnace was then discontinued, and the temperature was followed as the molten solution cooled slowly. In general, supercooling of less than one degree was obtained, followed by a rapid rise to a steady temperature which remained constant within 0.02° C (about 0.8 microvolt) for about one minute. Because of the favorable characteristics of the cooling curve, it was found that freezing-point measurements could be reproduced to one microvolt in the duplicate runs, which were always carried out, and it was not necessary to extrapolate to correct for the supercooling effect. The thermocouples were standardized against the freezing point of pure tin by measurements carried out following the above procedure.

Tables II and III summarize the data on the freezing point depressions in mercuric chloride and mercuric bromide, respectively. Figure 6 presents the data obtained for molten mercuric chloride. The freezing points were 279.52° and 236.38° C for pure, dry, mercuric chloride and mercuric bromide, respectively; compared to 277° and 237° C, respectively, as listed in the International Critical Tables.

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TABLE II

CRYOSCOPIC DATA FOR NaBr, NaCl, Hg_2Cl_2, Hg AND K_2SO_4 IN MOLTEN MERCURIC CHLORIDE

Solute	Mole Per Cent of Solute	ΔT_f (°C)	Cryoscopic n*
NaBr	0.51	1.41	1.91
NaBr	0.89	2.56	2.00
NaBr	1.35	3.63	1.86
NaBr	1.92	5.12	1.84
NaBr	2.77	6.97	1.75
NaBr	3.65	8.07	1.52
NaCl	0.81	1.19	1.03
NaCl	1.22	1.78	1.00
NaCl	2.46	3.31	0.94
NaCl	3.35	4.73	0.97
NaCl	4.10	5.58	0.94
NaCl	6.97	7.06	0.70
Hg_2Cl_2	0.87	1.32	1.04
Hg_2Cl_2	1.37	2.14	1.08
Hg_2Cl_2	2.50	3.90	1.08
Hg_2Cl_2	3.41	4.99	1.02
Hg_2Cl_2	4.76	6.78	0.99
Hg_2Cl_2	7.02	7.14	0.70
Hg	0.69	1.05	1.05
Hg	1.10	1.73	1.08
Hg	2.19	3.31	1.05
Hg	3.26	5.04	1.07
Hg	5.12	7.04	0.95
Hg	7.55	7.58	0.69
K_2SO_4	0.50	1.22	1.69
K_2SO_4	0.95	2.19	1.59
K_2SO_4	1.48	3.19	1.50

* The cryoscopic "n" is the apparent number of particles of solute, in molten $HgCl_2$, per molecule of solute.
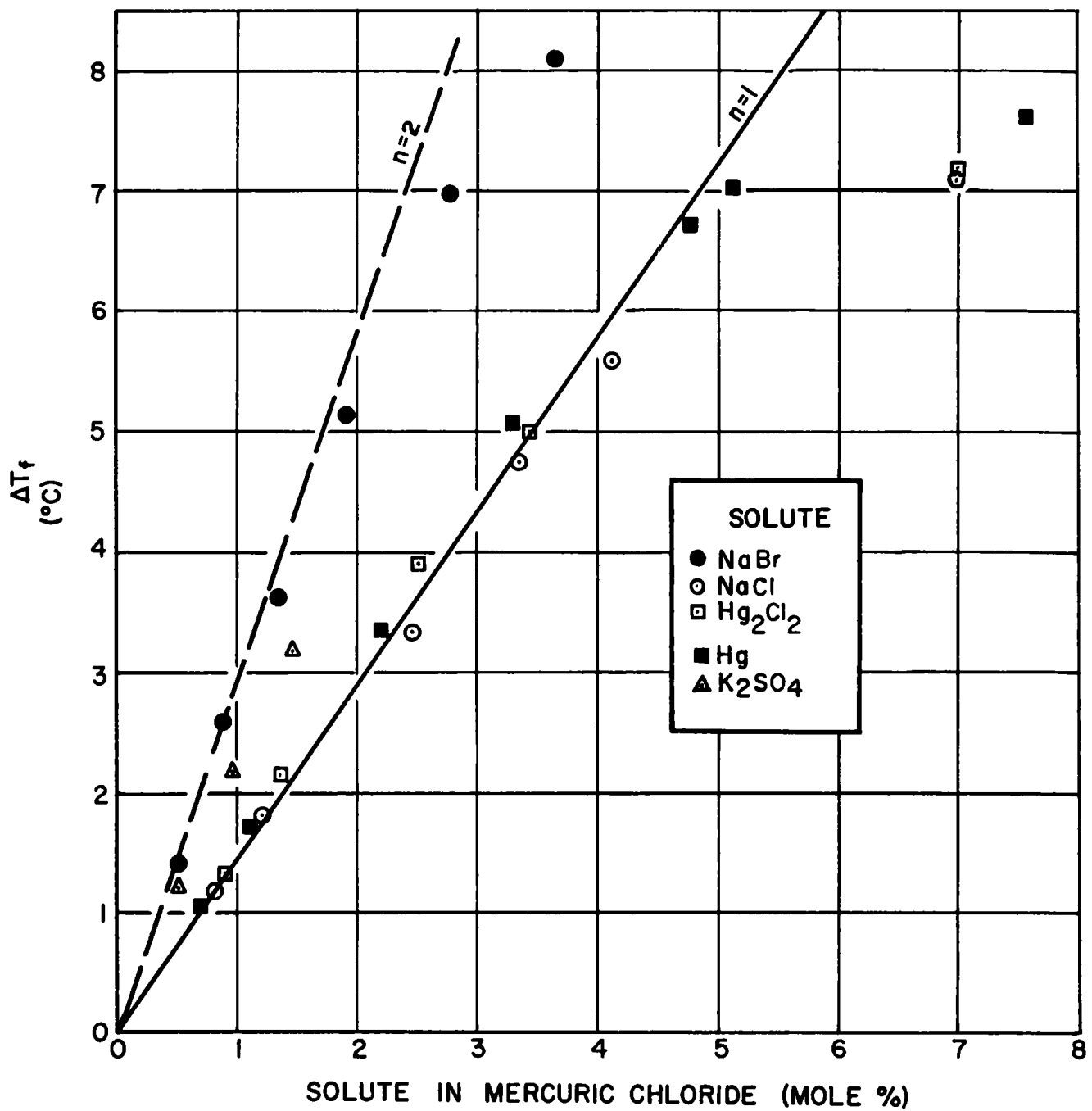
Fig. 6. Cryoscopic Data for Molten Mercuric Chloride Solvent

TABLE III

CRYOSCOPIC DATA FOR NaCl
IN MOLTEN MERCURIC BROMIDE

NaCl (Mole %)	ΔT_f of $HgBr_2$ (°C)	Cryoscopic n*
0.54	1.06	1.49
1.05	2.15	1.54
1.48	2.81	1.44

*The cryoscopic "n" is the apparent number
of particles of solute, in molten $HgBr_2$, per
molecule of NaCl

The freezing-point depressions were calculated from the usual Raoult-van't
Hoff equation:

$$\Delta T_f = \frac{RT^2 N_2}{\Delta H_f} \qquad \ldots (3)$$

The heats of fusion employed for $HgCl_2$ and $HgBr_2$ were 4,150 cal/mole and
3,960 cal/mole, respectively.[25] The absolute temperatures used were those of
the observed freezing points.

It can be seen from the data in Table II that sodium bromide has a cryoscopic
effect equal to that of two particles, when dissolved in molten mercuric chloride.
At NaBr concentrations below two mole percent, the average negative deviation
from ideality of the cryoscopic effect was 5 per cent. The reproducibility of the
freezing-point measurement leads to a probable error of 0.02° C in this experi-
mental measurement. This experimental error corresponds to approximately
2 per cent in the concentration range below 2 per cent. Accordingly, it is pos-
sible that the somewhat low values observed for the cryoscopic effect of NaBr
represent a real effect. Results deviating from Eq. (3) are not unexpected, of
course, in cryoscopic studies. They can be attributed to:

1) Formation of solid solutions at the freezing point;

2) Association of ions in the melt;

3) Dissociation of molecules to yield larger cryoscopic effects;

4) Reactions in the melt;

5) Failure of Eq. (3) at higher concentrations because of its omission of higher terms of the MacLaurin series expansion used in its derivation.

The cryoscopic effect of NaBr does, in fact, deviate more markedly from ideality at higher concentrations in fused $HgCl_2$, but the deviation cannot be attributed to the MacLaurin series termination error inasmuch as that effect produces only an error of 0.2 per cent at 10 mole per cent concentration of the solute. The increased association of ions at higher concentrations would appear to be the major probable cause of the greater deviation from ideality since the other factors listed in the previous paragraph would not be expected to have so rapid an effect in this direction.

The question of whether chloride exhibits a common ion effect in molten $HgCl_2$, despite the latter's apparently low degree of dissociation, appears to be answered by the data for NaCl shown in Fig. 6. The cryoscopic effect of NaCl is equal to that which would be expected from one particle, at concentrations of four mole per cent or less. Consequently, the low electrical conductivity of fused $HgCl_2$ cannot be considered to bring it into the non-ionic class of organic halides, with respect to its cryoscopic properties at least. Of course, if NaCl existed in molten $HgCl_2$ as an associated pair to form one molecule, its cryoscopic effect would also be equal to that of one particle. However, it is unreasonable to expect NaCl to exist as an un-ionized molecule under such circumstances particularly in view of the fact that experimental measurements with the similar salt, NaBr, show dissociation into two particles. Calculations are being carried out to investigate the relationship between the degree of ionization and the appearance of the common ion effect in weakly ionized solvents.

Mercurous chloride also has the cryoscopic effect of one particle, at concentrations below four mole per cent. This observation is in agreement with the occurrence of the common ion effect deduced from the NaCl data, although the basis for expecting dissociation of Hg_2Cl_2 into chloride ions when dissolved in melts is not as sound as for NaCl. The behavior of Hg_2^{++} ion as one particle in molten $HgCl_2$ is not unexpected in view of the reported stability of this entity in aqueous solutions even at high dilutions. However, the possibility of the formation of Hg_2Cl^+ cation cannot be excluded. The average of the observed cryoscopic

effects of Hg_2Cl_2 to 2.50 mole per cent is 1.07, significantly higher than unity, and higher than the average of NaCl and NaBr per particle. This could possibly represent some dissociation of Hg_2^{++}, but such a conclusion does not appear sound in view of the other possible reasons for deviations from Eq. (3) mentioned earlier.

In addition, the possibility exists that the value used for the heat of fusion of $HgCl_2$ might be in error to some extent. Dissociation of Cl^- from Hg_2Cl^+ would not affect the cryoscopic number, because of the common ion effect. In any event, dissociation of Hg_2^{++} in molten $HgCl_2$ is not very pronounced, if it occurs at all.

The cryoscopic effect of mercury metal was very similar to that of Hg_2Cl_2, per molecule. This observation may support the view that mercury dissolves in fused $HgCl_2$ according to the reaction:

$$Hg + HgCl_2 = Hg_2Cl_2 \qquad \qquad ...(4)$$

However, this does not rule out the possibility that solution is not dependent on this reaction. Solution by this reaction would not increase the total number of moles in the melt since the gain of a molecule of Hg_2Cl_2 is counter-balanced by the loss of a molecule of $HgCl_2$. Solution of mercury as a neutral atom would increase the total number of moles in the melt and this would change the magnitude of the cryoscopic effect, which is dependent on the mole fraction. The mole fractions of mercury in Table II were calculated on the tentative assumption that Reaction (4) occurs. Solution of mercury as a neutral atom would lead to a cryoscopic number larger by a percentage equal to the mole per cent of mercury. It appears unwarranted to believe that the reliability of the freezing-point measurements is good enough to distinguish between the above two mechanisms of solution. The results do demonstrate that mercury does not dissolve as associated atoms.

The data in Table II show that the cryoscopic effect of K_2SO_4 is considerably less than would be expected ideally for the formation of three ions. This negative deviation could be caused by solid solution formation, although limited dissociation of K_2SO_4 to K^+ and KSO_4^- is also a possible explanation.

Inspection of Fig. 6 shows that for Hg, Hg_2Cl_2, and NaCl a decrease from the maximum cryoscopic effect per molecule becomes evident at solute concentrations above four mole per cent. For NaBr, the decrease becomes evident at two mole per cent; this concentration is equivalent to four mole per cent of non-common ions. This relatively ideal cryoscopic effect in molten salts, up to a non-common ion (or particle) concentration of four mole per cent, may be characteristic for colligative effects in molten salts for those solutes which do not form solid solutions or which do not react with the solvent. Generally, activity coefficients in aqueous solutions deviate markedly from unity at much lower concentrations than four mole per cent.

In contrast with the relatively close approach to ideality found with molten $HgCl_2$ solvent in this investigation previous measurements[24] with molten $HgBr_2$ showed large deviation from ideality. Inasmuch as the $HgBr_2$ work[24] involved melting-point measurements with a micro melting-point capillary tube, and these observations with $HgCl_2$ involved macro-scale measurements of the cooling curve with more than 20 grams of $HgCl_2$, a brief series of measurements with $HgBr_2$ was carried out using our macro-scale cooling curve techniques to determine whether or not the difference in experimental techniques was the basis for the observations indicating low activity coefficients in $HgBr_2$.

The data in Table III show that sodium chloride in fused mercuric bromide solvent deviated from the ideality shown by sodium bromide in fused mercuric chloride. This agrees with Jander and Brodersen's[24] observations, and indicates that the experimental procedures used in their study and in this work were reliable. Jander and Brodersen do not purport to show why solutions in molten $HgBr_2$ are not ideal; solid solution and compound formation would be possible causes of the observed negative deviations.

E. CRYOSCOPIC STUDIES OF $BiCl_3$ SOLUTE IN MOLTEN BISMUTH SOLVENT (S. Mayer)

In this investigation, the cryoscopic technique is being applied to help characterize the behavior of dilute solutions of salts in molten metals since there appears to be a scarcity of information concerning the metal-rich side of the phase diagram. Molten bismuth was chosen as the solvent for this initial study because of our interest in the $Bi-BiCl_3$ system.

The experimental apparatus and procedure were, in general, similar to those employed for the cryoscopic investigation with molten $HgCl_2$ solvent. Six replicate measurements were made of the freezing point of bismuth. The mean freezing point was found to be 271.01° C, with a standard deviation of 0.06° C (compared to the reported[25] value 271.0° C). In general, the reproducibility of the freezing point measurements with molten bismuth solvent was not as good as that obtained with molten $HgCl_2$. The rise from the lowest temperature of supercooling was relatively slow, and the extent of supercooling was greater, although it was possible to reduce supercooling by vigorously shaking the cryoscopy tube with an attached wire while the tube was still in the furnace.

The results summarized in Table IV give the freezing point depression and the calculated number of particles formed per molecule of $BiCl_3$ in molten bismuth solvent. The molar heat of fusion[26] for bismuth employed in the latter calculation was 2,630 cal. Figure 7 also summarizes the data and includes the lines for cryoscopic numbers of 4.0 and 3.1. The average cryoscopic number was found to be 3.1 in the concentration range from 0.09 to 0.5 mole per cent. There was no strong trend towards lower cryoscopic numbers, up to the solubility limit of about 0.53 mole per cent $BiCl_3$. Cryoscopic numbers were not calculated for concentrations higher than the solubility of $BiCl_3$ in bismuth.

It was anticipated at the time of the initiation of this study that the cryoscopic number given by $BiCl_3$ could be four since studies with diatomic gases dissolved in molten metals had indicated essentially complete dissociation of the gases to atoms in the melt[27] and freezing point depressions produced by dilute solutions of metals in molten salts had indicated that the metal had a cryoscopic effect,[28, 9, 10] rather than the behavior of a common ion. The observed cryoscopic number of three could be explained if, on the average, one $BiCl^{+2}$ ion existed in the molten bismuth, in addition to two Cl^- ions. (The charge on such ions dissolved in a metal is uncertain.) On the other hand, subhalide formation would produce three particles if BiCl were not dissociated:

$$BiCl_3 + 2Bi = 3BiCl \ . \hspace{4cm} \ldots (5)$$

It is expected that additional experiments will shed light on these questions.

Eggink[12] indicated a solubility of more than 1.6 per cent $BiCl_3$ in Bi at the eutectic temperature; however, he did not give any experimental points between 95 a/o Bi and 100 a/o Bi, so that the liquidus line drawn from 100 per cent Bi may be only an approximation. The maximum solubility of $BiCl_3$ in Bi at the eutectic temperature based on our data is 0.53 mole per cent $BiCl_3$. Sokolova et al.,[11] drew a phase diagram indicating a maximum solubility of 0.7 per cent.

The maximum freezing point depression observed by Eggink was 4° C, with a probable error of at least 0.5° C. The corresponding mean maximum depression from our data was 3.67° C, essentially in agreement with Eggink's data and with Sokolova's work.

TABLE IV

CRYOSCOPIC DATA FOR $BiCl_3$ SOLUTIONS
IN MOLTEN BISMUTH

$BiCl_3$ (mole %)	Freezing Point Depression (°C)	Cryoscopic Number
0.089	0.63	3.2
0.092	0.61	3.0
0.161	1.12	3.1
0.177	1.18	3.0
0.187	1.39	3.3
0.226	1.51	3.0
0.236	1.58	3.0
0.334	2.42	3.1
0.391	2.53	2.9
0.410	2.76	3.2
0.521	3.62	3.1
0.549	3.67	3.0
0.739	3.62	-
0.962	3.59	-
1.372	3.81	-
2.188	3.70	-
2.698	3.67	-

Further experimental work is planned to apply the cryoscopic approach to examine the behavior of $BiBr_3$, BiI_3, Bi_2S_3, Bi_2O_3, NaCl, UCl_3, $ThCl_4$, etc. in molten bismuth. Studies with zinc, cadmium, and other metals as the molten solvents are also anticipated.
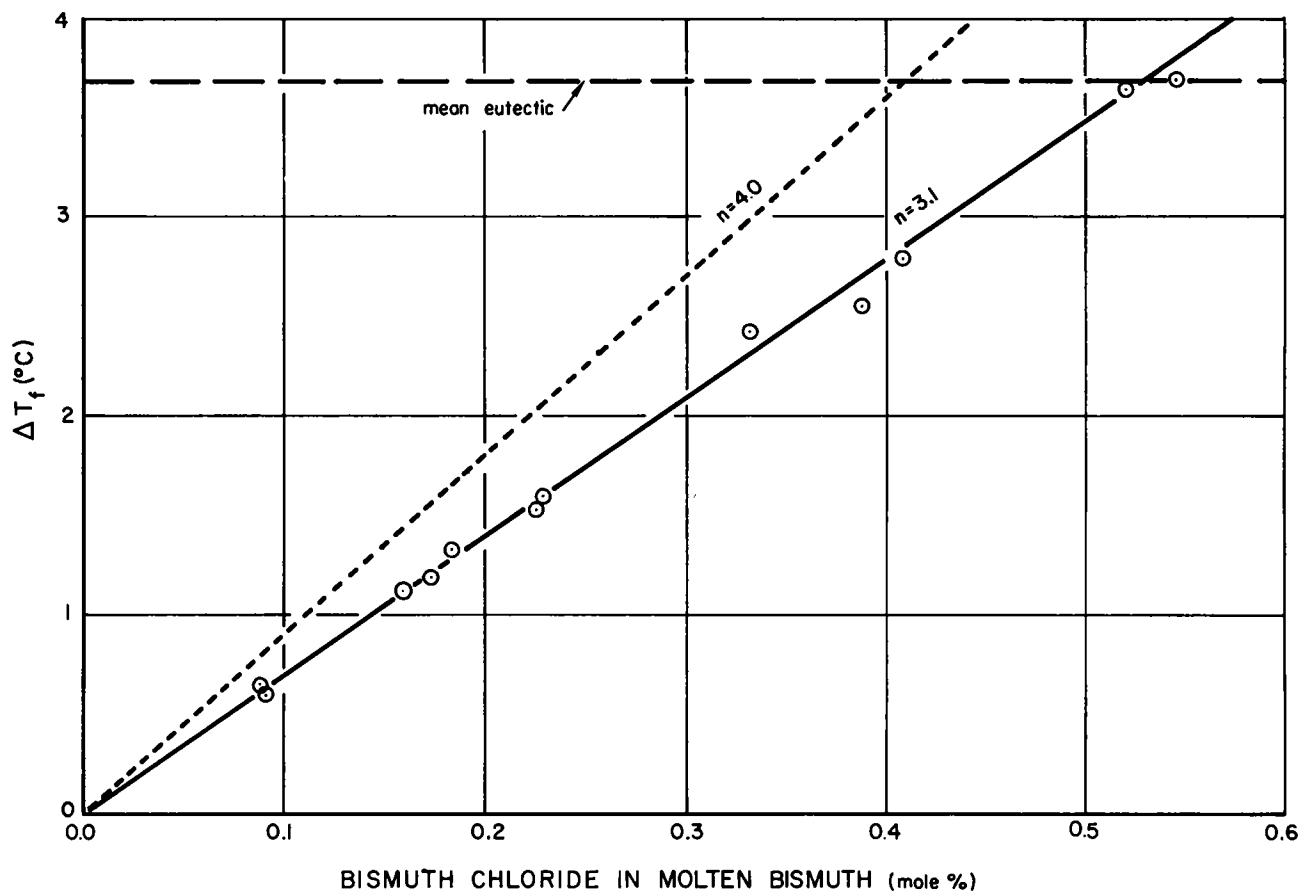
Fig. 7. Cryoscopic Data for Bismuth Trichloride Solute
in Molten Bismuth Solvent

F. VAPOR PRESSURE OF METAL-SALT SOLUTIONS

(A. J. Darnell and S. J. Yosim)

Due to the emphasis on the phase equilibrium studies, relatively little progress on the vapor pressure studies took place. As mentioned in the latest progress report,[1] it was desired to observe the null point non-visually by the static method. A self balancing relay was therefore incorporated into the system.

The second method, also described earlier,[1] employs an apparatus shown schematically in Fig. 8. The $BiCl_3$ gas dissolves in the liquid bismuth to form a solution that continues to change in composition until the partial pressure of the $BiCl_3$ over the solution is equal to the vapor pressure over the pure $BiCl_3$ phase. Every

part of the system above the salt is kept at a temperature higher than that of the salt.
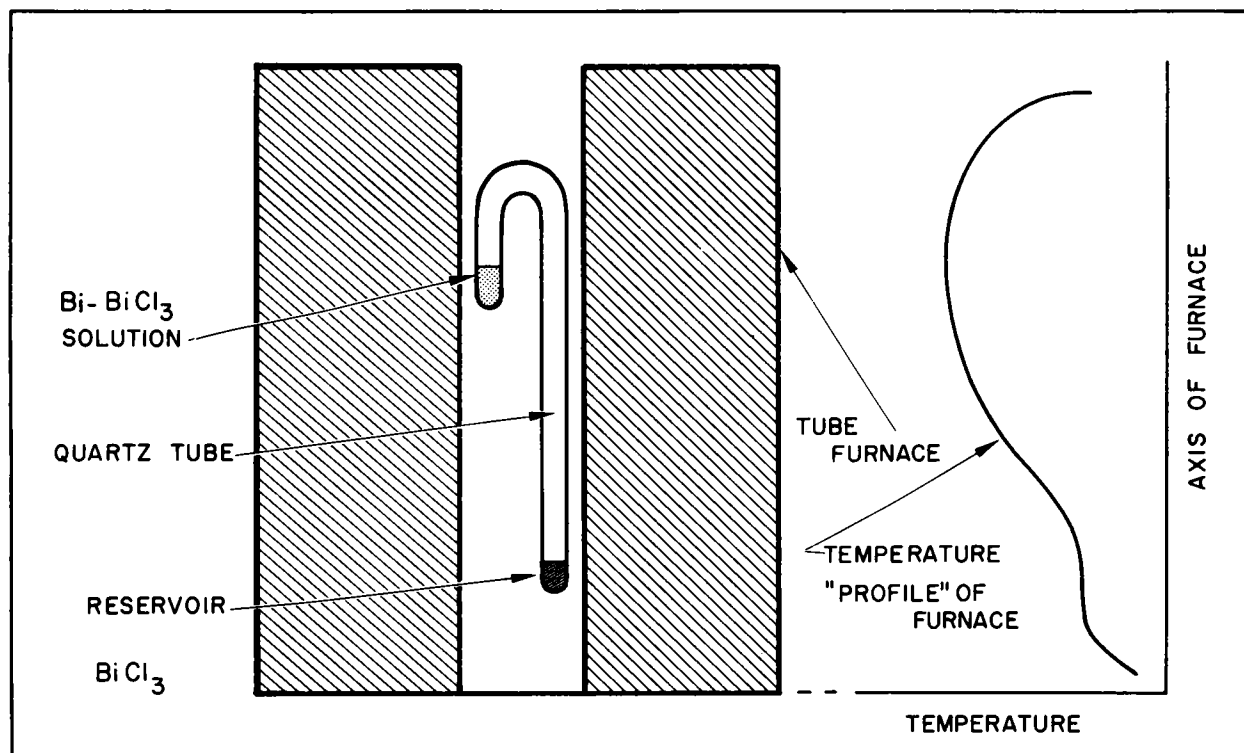
Fig. 8. Vapor Pressure Apparatus for Bismuth-Bismuth
Trichloride Solutions

Two experiments were carried out in which the metal phase was at 351° C and at 397° C. The results are shown in Table V. To illustrate the interpretation of the data, the calculations are explained in detail for run No. 3. In this run, the phase which was originally pure bismuth, was held at a temperature of 351° C while the temperature of the $BiCl_3$ reservoir was 328° C. The analysis of the metal after the run showed that it contained 1.44 mole per cent $BiCl_3$. Since the pressure over the two phases is equal, one can conclude that the vapor pressure of the metal solution at 351° C is equal to that of the pure $BiCl_3$ at 328° C (0.087 atmospheres).[29] A comparison of the value of 0.087 atmosphere for the metal solution containing 1.44 mole per cent $BiCl_3$ with 0.158 atmosphere,[29] the vapor pressure of pure $BiCl_3$ at 351° C, indicates marked positive deviation from Raoult's law. The positive deviation from ideality is not surprising since the solubility of $BiCl_3$ in bismuth is quite low. Taking pure $BiCl_3$ as the standard state, one can calculate the activity of $BiCl_3$ in the solution by:

$$a_{BiCl_3} = \frac{P_{(BiCl_3 \text{ in solution})}}{P_2^\circ \text{ (pure BiCl}_3)}$$

Thus $a_{BiCl_3} = \frac{0.087}{0.158} = 0.55$ while the activity coefficient $\gamma = \frac{a_{BiCl_3}}{N_{BiCl_3}} = 38.2$.

In the case of experiment No. 4, a = 0.57 while γ = 22.1. The above treatment is based on the assumption that $BiCl_3$ is the major gaseous species. If another bismuth containing species is important, this may affect the results in two ways:

1) Bismuth may be transferred to the pure $BiCl_3$ reservoir. This can be checked by analysis of the $BiCl_3$ for bismuth metal.

2) The total pressure can not be equated to the partial pressure of $BiCl_3$. Thus, the final interpretation of these results will depend upon analysis of the gas phase.

TABLE V

ACTIVITY COEFFICIENT OF BiCl$_3$
DISSOLVED IN BISMUTH

	t	T_1	T_2	N_{BiCl_3}	P_1°	P_2°	a_{BiCl_3}	γ_{BiCl_3}
Exp. No.	Time at Temp. (hr)	Temp. of BiCl$_3$ Phase (°C)	Temp. of Soln. (°C)	In Soln. at T_2	Vapor Pressure of Pure BiCl$_3$ at T_1 (atm)	Vapor Pressure of Pure BiCl$_3$ at T_2 (atm)	$\frac{P_1^\circ}{P_2^\circ}$	$\frac{a_{BiCl_3}}{N_{BiCl_3}}$
3	65	328	351	0.0144	0.087	0.158	0.55	38.2
4	22	372	397	0.0258	0.257	0.448	0.57	22.1

G. TRANSFERENCE NUMBERS IN MOLTEN SALTS (G. Wolten)

Since transport number experiments in aqueous solutions have often yielded valuable data on the presence and nature of complex ions, it appears that the study of transport numbers in molten salts which contain dissolved metal might be similarly revealing. Experimentally, this involves a determination of the transport numbers in the pure molten salts and then a determination of the changes in these numbers when the metal is dissolved in the salt.

The phenomenon of ion transport or transference under the influence of a DC potential has the net effect of transporting some material from one part of the liquid to another part. In solutions, this enables one to measure concentration changes in the vicinity of the electrodes, and this forms the basis for the historical Hittorf method of determining transport numbers in aqueous solutions. However, in pure molten salts, there can be no concentration changes. The transfer of material from one part of the liquid to another would result in a difference in level if gravitation did not immediately and continuously operate to equalize the levels.

Karpachev and Pal'guev[30] thought that a porous plug, dividing the apparatus into a cathode and an anode compartment, might permit the passage of ions under the influence of an electric field but would restrain bulk flow sufficiently to permit a difference in level on the two sides of the plug. Using this technique, an anionic transport number, t^-, of 0.78 was obtained for molten lead chloride at temperatures ranging from 520° to 680° C.

Duke and Laity[31] performed similar experiments, in which the porous plug was replaced by a fritted membrane. In principle, their technique is similar to that of Karpachev and Pal'guev. However, the difference in level was not measured directly but was indicated by the motion of an air bubble in a capillary. Duke and Laity's result for the anionic transport number of $PbCl_2$ was 0.76, both at 565° and 635° C; in excellent agreement with the earlier work.

In the solid state, the conduction of lead chloride is purely anionic[32], i.e., t^- = 1.0; hence, a value of t^- between 0.7 and 0.8 for the fused salt appears quite reasonable by comparison with that for the solid. It is interesting to note that Holtan,[33] using the thermodynamics of irreversible processes, has derived an expression which relates transport numbers to entropies and to the experimentally determinable temperature coefficient of the EMF of a thermocell. The thermocell in the above case would consist of two lead electrodes at different temperatures, and immersed in molten lead chloride. Lorenz and Velde[34] have measured the temperature coefficient of the EMF of this cell between 560° and 800° C and found a substantially constant value of -6.5×10^{-4} v/deg.

According to Holtan, this is related to entropies and transference numbers in the following manner:

$$F\left(\frac{\Delta E}{\Delta T}\right) = \frac{1}{2} S_{Pb} - t^- \times \frac{1}{2} S_{PbCl_2} . \qquad \ldots (6)$$

where F is the value of the faraday constant, i.e., 96,500 coulombs/equivalent, S_{Pb} and S_{PbCl_2} are the absolute entropies of these substances at the chosen temperature, and t^- is the anionic transport number. This expression arises from the fact that the passage of one faraday through the melt would transfer one equivalent of lead from one side of the melt to the other and t^- equivalents of the salt in the opposite direction. The half values, of course, convert molar entropies into equivalent entropies.

This expression neglects the entropy of transfer of the electrons as well as other terms involving entropies of transfer. It will be assumed that this is valid for the calculation below. In order to compare the transport number calculated from Eq. (6) with that obtained by Duke and Laity, the absolute entropies of lead and $PbCl_2$ at 908° K were computed[33, 35] to be 25.4 and 64.6 cal/mole-deg. respectively. According to the values already given,

$$F\frac{\Delta E}{\Delta T} \text{ is } -96500 \times 6.5 \times 10^{-4} \frac{\text{amp volt sec}}{\text{equiv.-deg.}}, \text{ or } -14.95 \frac{\text{cal}}{\text{equiv.-deg.}}$$

Substitution of these values in Eq. (6) gives a transport number t^-, of 0.86 at 908° K. The good agreement of this value with those discussed above is perhaps surprising in view of the approximations made in deriving the relationship and in view of the calculation, which involves first the difference and then the ratio of numbers which are not known to a high degree of accuracy.

Recently, Bloom and Doull[36] reported a further investigation of the transport number in pure molten lead chloride. The result of this determination, $t^- = 0.38$ to 0.39, is grossly at variance with the values so far considered. This work was performed in a cell which was entirely horizontal so that all gravitational flow was thought to be eliminated. The boundary between the salt and the molten lead anode was observed and the increase in the amount of lead chloride in the anode compartment was calculated from the advancing boundary of the salt. Their cell was made of quartz to avoid the deformation which pyrex may undergo at these temperatures. Also careful temperature control of the cell was

maintained but this seems an unimportant factor since transport numbers in mol-
ten salts have small temperature coefficients. Bloom and Doull criticize the work
of Duke and Laity, but it seems worthwhile to point out that their objections, if
valid, would result in Duke and Laity's obtaining an apparent anionic transport
number which is too low; these objections do not explain the discrepancy since
Bloom and Doull's own result is even lower. Nevertheless, it seems desirable
to have an independent method of measuring transport numbers in pure molten
salts. In aqueous systems, the so-called moving boundary method is considered
to be one of the most reliable for transport number measurements.[37] It appears
on preliminary analysis, that this method may be applicable to molten salt sys-
tems; therefore, a cell has been designed to test this method.

This cell is similar to that used by Whetham[38] in some of the early work on
the moving boundary method (aqueous). It is constructed of Vycor (96 per cent
silica) and is shown in Fig. 9. The electrodes are carbon or tungsten rods pro-
tected by Vycor sleeves except for the last 1/4 inch which dip into pools of molten
lead. The long side tube contains molten $PbBr_2$, the short one $PbCl_2$, and a
junction is produced in the narrow (about 4 mm I.D.) central tube. Under the in-
fluence of an applied potential, both anions, Cl^- and Br^- move toward the anode
causing a motion of the boundary. In effect, one observes the migration of Cl^-
through liquid $PbCl_2$. By measuring the distance travelled as a function of the
number of coulombs passed, the transport number can be calculated if gravita-
tional back-flow is hindered. The motion of the boundary can be observed by
means of a cathetometer while the cell is in a controlled temperature furnace.

The moving boundary experiment using pure molten salts has its own associ-
ated difficulties. In particular, it is not clear whether there can be a mechanism
in molten salts which will substitute for the automatic concentration adjustment
which takes place in the indicator solution at the boundary in aqueous moving
boundary experiments. It is conceivable that this point will cause the experiment
either to fail or to lack precision. In that event, the course of action indicated
would be a repetition of the work by the techniques previously described, in order
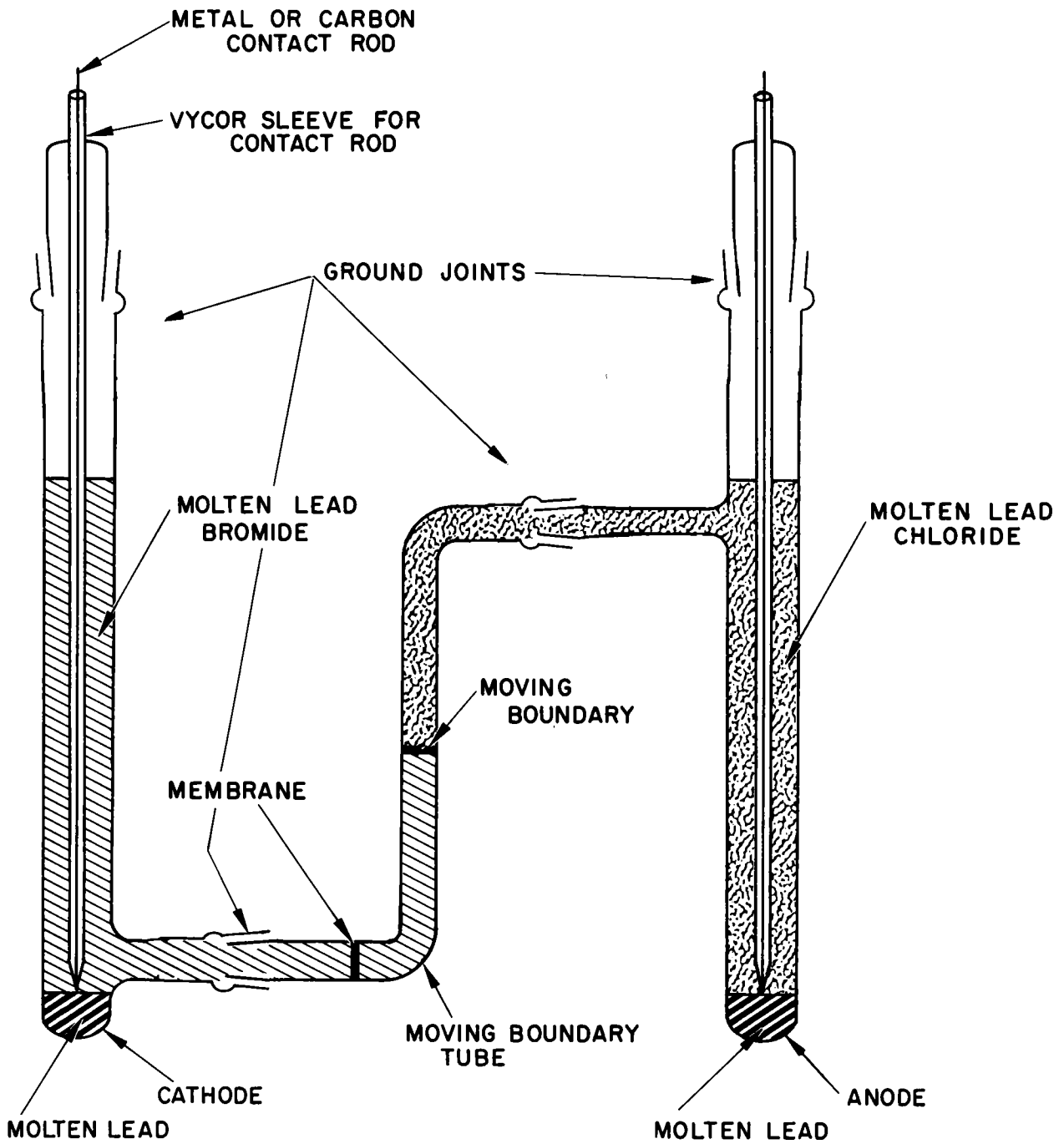to reconcile the divergent results obtained.

Fig. 9. Equipment for Determining Transference Numbers in Molten Salts
by the Moving Boundary Method

III. HIGH TEMPERATURE CHEMISTRY OF CERAMICS

In order to understand and to predict the behavior of ceramics in high temperature environments, a variety of basic thermodynamic information is needed. A program has been initiated to obtain such information for a number of ceramic compounds and mixtures. Knudsen and Langmuir vaporization studies are underway on La_2O_3, BeO, and ZrC.

This project is also concerned with the establishment of a set of principles to guide the search for new and superior refractories. The first principles to be tested will involve the study of compounds of elements from Groups III, IV, and V of the Periodic Table. Lack of experimental knowledge of the actual charge distribution in solids is one of the key problems involved in establishing such a set of guiding principles. To aid in shedding light on this problem, the electron density distribution in solid BeO is being determined by three-dimensional X-ray diffraction techniques.

A. THE VAPORIZATION OF La_2O_3 (T. A. Milne)

The past work on the vaporization of this oxide is very meager. Mott[39] has estimated the boiling point to be about 4470° K. Brewer[40] discusses the possible vaporization processes, pointing out that the·spectroscopic data necessary to calculate the dissociation energy, D_o, of gaseous LaO are too uncertain to establish the importance of $LaO_{(g)}$ in the equilibrium vapor. Recently, Chupka, Inghram, and Porter[41] have studied the system $La-La_2O_3$ by a mass spectrographic analysis of the vapor effusing from Knudsen cells. From measurements on $La-La_2O_3$ mixtures held in ThO_2 crucibles with tantalum covers, they observed the species La^+ and LaO^+. From temperature dependence and absolute intensities of these species they calculated the heat of sublimation of lanthanum and $D_o(LaO)_g$. They also made one measurement on pure La_2O_3 held in an Al_2O_3 Knudsen cell, which showed that LaO is much more important than lanthanum in the equilibrium vapor. However, the pressure of $LaO_{(g)}$ over pure La_2O_3, calculated from their experimental determination of $D_o(LaO)_g$, is about 100 times lower than the pressure of $LaO_{(g)}$ which they measured directly over La_2O_3. In addition, a number of stable oxides have been reported to be significantly reduced by tantalum at high tempera-

Thus, it is possible that the use of tantalum lids in work with $La_2O_{3(s)}$ could cause significant error.

To better understand the vaporization of La_2O_3 and the possible interaction with tantalum and tungsten metal, conventional Knudsen experiments are being carried out on $La_2O_{3(s)}$ held in tantalum and tungsten crucibles. So far, one exploratory series of heatings has been made in a tantalum crucible. All of the La_2O_3 was vaporized from the crucible with the resultant loss of a considerable amount of tantalum.

Further experiments will be necessary to establish the reaction taking place since it is not yet known how much of the La_2O_3 was lost by straight vaporization or how important the blank losses from the tantalum were. For this information, a series of runs in a tantalum Knudsen cell is planned with analysis of the tantalum and lanthanum effusing. In addition, runs in tungsten Knudsen cells will be carried out with the hope that tungsten will not reduce the La_2O_3. From the results of these experiments it should be possible to establish the vapor pressure of La_2O_3, $D_o(LaO)_g$ and the extent of interaction of La_2O_3 with tantalum and tungsten.

B. THE VAPORIZATION OF BeO (T. A. Milne)

The only previous comprehensive study of the vaporization of BeO is that in 1950, by Erway and Seifert[42] who measured the vapor pressure of solid BeO by the Knudsen effusion method, utilizing radio-active $_4Be^7$ as a tracer. It was assumed by them that BeO vaporized primarily as BeO. Drummond and Barrow,[43] following Erway and Seifert's assumption that BeO was the predominant species, made thermochemical calculations establishing the dissociation energy of $BeO_{(g)}$. Livey and Murray[44] have made calculations on the vaporization behavior of BeO and have obtained experimental data in rough qualitative agreement with their predictions that BeO vaporizes as BeO.

In a recent review by Brewer,[40] arguments are presented which indicate that BeO vaporizes primarily by decomposition to $Be_{(g)}$ + $1/2 O_{2(g)}$ or $O_{(g)}$. These arguments are based on calculations involving the heat of formation of solid BeO and the dissociation energy of gaseous BeO as determined by spectroscopic means.

In view of the uncertainty as to whether BeO vaporized predominantly as $BeO_{(g)}$ or as $Be_{(g)} + O_{(g)}$ and the consequent uncertainty in $D_O(BeO)$, it appears useful to study in detail the vaporization behavior of this oxide. The planned experimental program will consist of three studies:

1) Conventional Knudsen experiments on BeO contained in a tungsten cell with chemical analysis of collected Be (deposited either as $Be_{(g)}$ or as $BeO_{(g)}$). This study will check the data of Erway and Seifert and will furnish the beryllium mass-loss data for use with the results of the second and third studies.

2) Mass spectrometric analysis of the species vaporizing from BeO in both the Knudsen and Langmuir types of experiments. From these data and the results of the first study, the partial pressures of beryllium and BeO over solid BeO and the value of $D_O(BeO)$ may be calculated. If gaseous BeO cannot be detected, only an upper limit to $D_O(BeO)$ may be obtained. The simultaneous Knudsen and Langmuir experiments may give interesting information on the mechanism of vaporization.

3) A study of the possible interaction between tungsten and BeO. The reliability of the work of Erway and Seifert as well as of our planned work depends on the extent of this interaction. It is planned to study this interaction by chemical and mass spectrographic means.

The apparatus for the first study mentioned above consists simply of a high vacuum system in a glove box. The system is equipped with a quartz tube for induction heating of the tungsten Knudsen cells. This system is now complete and experiments will begin as soon as the glove box is assembled.

C. VAPORIZATION OF ZIRCONIUM CARBIDE (B. D. Pollock)

Refractory metal carbides are of interest because their strength, electrical and thermal conductivities, and high melting points render them of potential value in high temperature applications. In these applications however, one must consider their vaporization behavior. as well as their reactions with the environment. Further, quantitative rate-of-evaporation or effusion data may be used in conjunction with knowledge of vaporizing species to calculate high temperature thermodynamic properties.

Zirconium carbide was chosen to begin a study of vaporization processes of carbides because of the simplicity of the Zr-C system in which only one solid compound, ZrC, exists. This compound melts at about 3530° C and shows no solid-solid transitions.[45] The study may also be simplified because ZrC is expected to volatilize congruently. This prediction is based on estimated high temperature stability, published vapor pressure data for zirconium and carbon, and on reasonable estimates of the nature of the vaporizing species.[46,47] It can be shown by consideration of the equilibrium constants for the processes, 1) ZrC→Zr(g) + C(g) and 2) ZrC→Zr(g) + C(s), that Reaction 2) cannot occur if the stability of $ZrC_{(s)}$ at temperatures in the range 2100° to 2300° K is greater than about 15 kcalories. It appears also from the low volatility of refractory carbides that the process 3) ZrC→ZrC(g) is not very probable. Thus, one would expect that if an excess of carbon were present in ZrC, the composition of the mixture would shift toward a value at which the composition of the vapor would be the same as that of the solid, i.e., eventually, congruent vaporization would occur.

A vacuum induction furance to heat specimens of ZrC to temperatures up to 2500° C at residual gas pressures below 10^{-5} mm Hg has been constructed and put into operation. Figure 10 shows the general features of the system and
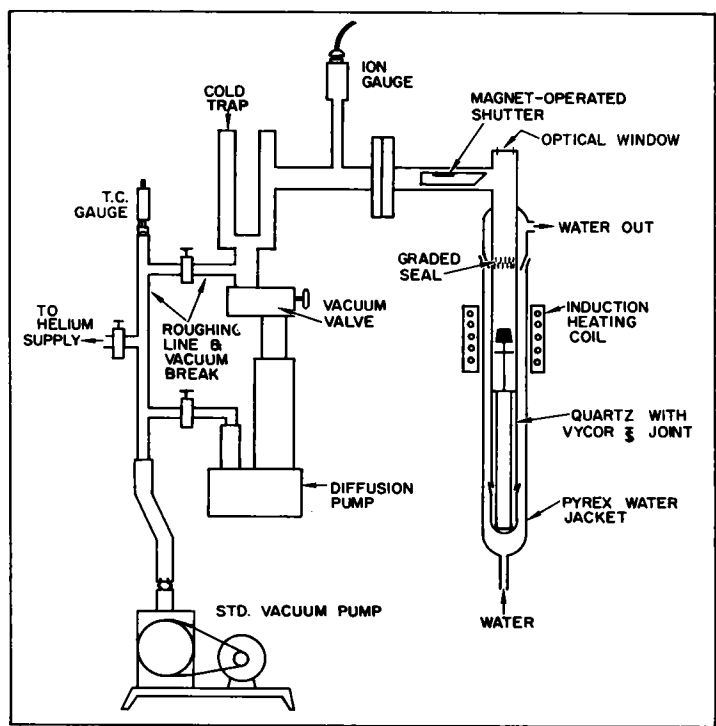

Fig. 10. Vacuum Induction Furnace

Fig. 11 shows one typical heating arrangement that has been used. The sample consists of an annular ring of ZrC, 0.9 in. OD by 0.5 in. ID by 0.8 in. high. A "black body" hole 1/16 in. ID by 3/8 in. deep is used to measure temperature with a Leeds and Northrup disappearing-filament type optical pyrometer. The ring was prepared from a crucible of technical grade ZrC supplied by the Norton Co., and was known to contain impurities since the material was ferro magnetic. An X-ray diffraction pattern showed the presence of free graphite. Test heatings at temperatures up to about 2200° C were made. The sample lost about 0.6 per cent of its initial weight and a depletion of free carbon from the surface layer was observed.

Future work will include a series of runs to check the prediction made above. For this purpose, the material used will first be heated to high temperatures to drive out volatile impurities which might obscure the main reaction. This sample will then be heated for a sufficient time and at sufficiently high temperatures to vaporize an appreciable amount of the compound. If the prediction is correct, there should be no change in surface composition as shown by X-ray diffraction patterns and analysis of the sublimate. The next step will then be to obtain accurate rate-of-evaporation or rate-of-effusion data. When the mass spectrograph becomes available, a search will be made for the existence of $ZrC_{(g)}$.
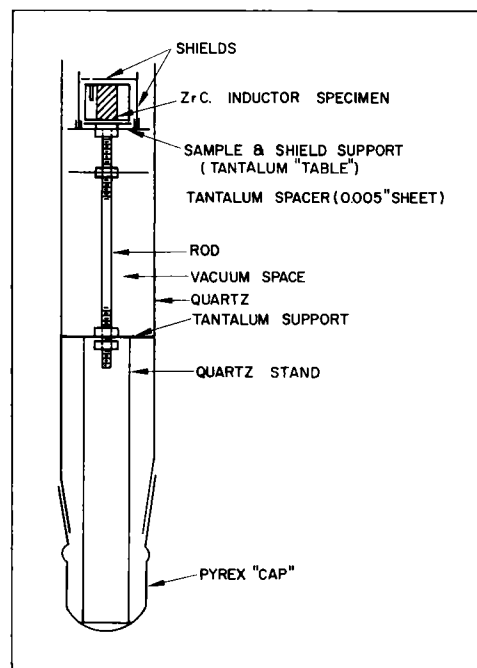
Fig. 11. Typical Heating Assembly

D. THREE-DIMENSIONAL X-RAY ELECTRON DENSITY DISTRIBUTION OF BeO (S. W. Mayer)

Although a great volume of fundamental and applied information on the properties of solids and molecules has been obtained in the last forty years by means of two-dimensional X-ray diffraction techniques, there has been recognition among the scientists active in the field of X-ray diffraction research that a three-dimensional technique is intrinsically more powerful and informative. The extremely lengthy computations required had been the major problem preventing widespread

use of the three-dimensional technique, but the increasing availability of high-speed electronic computing machines has solved that problem.

At the time of the inception of three-dimensional X-ray computation, it was anticipated that complex electronic density distribution in solids which could not be resolved by two-dimensional techniques would be amenable to the three-dimensional method, and that the accuracy of the measured electron densities could be much greater. These expectations have been confirmed.[48,49] An additional dividend from results obtained by computing machines is the calculation of magnitudes and directions of vibration of the individual atoms in the solid.[49]

These newer, more powerful techniques have heretofore been applied virtually exclusively to organic compounds and large molecules. It is our intent to utilize the three-dimensional technique and electronic computing machine to expand our knowledge of the inorganic compounds and elements.

Beryllium oxide has been selected for the initial study. A novel feature of this investigation, which will improve the precision of the three-dimensional Fourier representation of the electron distribution in BeO, will be the inclusion of unobserved (but calculated) structure factors in the Fourier summation. Measurements obtained in this investigation of BeO should provide information on:

1) Polarization of the electron "atmosphere" about the nucleus;

2) Directions and electron densities of chemical bonds;

3) Degree of covalent and ionic character in bonds; and,

4) The magnitude and direction of the vibration of the atoms in the crystal lattice.

These properties are, in turn, related to thermodynamic quantities and transport phenomena (diffusion, thermal and electrical conductivity) in BeO and similar refractories.

BeO, like most oxides, has a close-packed type of structure and, consequently, the three-dimensional techniques employed in this study will also provide precise measurement of atomic parameters, bond distances, and bond angles, which could not be obtained by the older, two-dimensional techniques.

Two samples of BeO crystals were received from E. M. Levin of the National Bureau of Standards. One sample contained crystals grown by high temperature water vapor transport, and the other sample contained smaller crystals grown from molten KOH solutions of BeO. The X-ray diffraction examination was initially directed to the water-vapor transport crystals because several were of almost ideal size for single crystal techniques. Several rotation and Weissenberg X-ray diffraction films of a vapor transport crystal have been prepared. The locations of the diffraction lines obtained with this sample are shown in Table VI and are compared with those for authentic BeO and $Be(OH)_2$. The data for the BeO sample grown from molten KOH are also included. Evidently, the vapor transport sample is different from known crystal forms of BeO or $Be(OH)_2$. Furthermore, the X-ray diffraction films prepared by Weissenberg and rotation techniques show that its space group is different from that reported by Zachariasen[50] for BeO, and that the unit cell is larger.

Powder and rotation films of BeO specimens grown from molten KOH, demonstrate that this material has a crystal structure identical to that determined by Zachariasen (see Table VI). Additional work on the X-ray and chemical characterization of the two preparations is planned. The BeO crystals grown from molten KOH will be used for the precise three-dimensional X-ray diffraction measurements.

In cooperation with Mr. Donald Criley of I. B. M.'s Applied Science Division, coding has been prepared for carrying out the computation of three-dimensional structure factors on the I. B. M. 704 high-speed electronic computing machine. The structure factor coding comprises 40 per cent of the total coding required, including the three-dimensional Fourier summation. Mr. Criley applied the new "Fortran" method, which is a rapid semi-automatic coding procedure.

E. NEW CERAMIC COMPOUNDS (W. Gehman)

The aim of this project is the establishment of a set of principles to guide the search for new and superior refractories. The first principle to be tested arose from an idea of D. B. Bowen of the Solid State Physics Group. Bowen suggested that the refractory properties of the Group IV elements which possess the diamond structure, e. g. carbon and silicon, might be improved by combination with pairs

TABLE VI

DIFFRACTION LINE DISTANCES FOR SAMPLES
OF BeO AND Be(OH)$_2$, IN Å, AS OBSERVED
ON POWDER X-RAY FILMS

Water-Vapor Transport Sample*	Sample Grown from Molten KOH	A. S. T. M. BeO[†]	A. S. T. M. Be(OH)$_2$[**]
6.1	2.33	2.34	4.27
3.6	2.19	2.19	3.85
3.1	2.06	2.06	2.91
2.33	1.60	1.60	2.79
2.08	1.34	1.35	2.64
1.80	1.24	1.24	2.39
1.72	-	1.17	2.19
1.43	1.15	1.15	1.98
1.36	1.13	1.13	1.91
1.20	-	1.10	1.78
1.12	-	1.03	1.65
1.04	-	0.99	1.56
1.02	0.91	0.91	1.41
0.95	0.88	0.88	1.34
0.89	0.86	0.87	1.28
0.86	-	0.85	1.25
0.83	0.82	0.82	1.19
0.80	-	-	0.88
0.79	-	-	0.87
0.78	-	-	0.83
-	-	-	0.82
-	-	-	0.80

* These distances were measured along the zero layer-line of the rotation film.

† A. S. T. M. powder diffraction card index (from Swanson and Tatge, NBS Reports, 1951).

** A. S. T. M. powder diffraction card index (from Fricke and Humme, Z. anorg. Chem., 178, 404, 1929).

of elements from groups symmetrically displaced from the fourth group in the Periodic Table.

The diamond lattice possesses cubic symmetry with each atom having four nearest neighbors arranged tetrahedrally. It appears that its stability is due to the covalent, tetrahedral bonding of the atoms. It is apparent that compounds of elements symmetrically arranged relative to the fourth group would have the right number of electrons to form covalent, tetrahedral bonds and, with appropriate restrictions on lattice dimensions, would fit into the diamond lattice. It may be anticipated that the resulting products would have either the sphalerite or wurtzite structures, since these consist of infinite three-dimensional arrays of covalent tetrahedrally bonded atoms. In order to avoid the complications that arise from large difference in the electronegativity of the elements, the initial study will consider compounds of elements from Groups III, IV, and V of the Periodic Table. Equal numbers of Group III and Group V elements will be used in order to retain the conditions for the formation of covalent, tetrahedral bonds.

The restriction to a diamond-like lattice plus a strict adherance to the "iso-electronic principle" leads to a very small number of compounds, the most promising of which is AlSiP. Extending this approach and considering elements from different periods of the Periodic Table, leads to new possibilities; however, a new restriction on atomic dimensions arises. By comparing all the covalent bond-lengths of a variety of possible compounds and by arbitrarily restricting our interest to combinations in which all the bond-lengths agree within 10 per cent, the following compounds were selected in addition to AlSiP: AlC_2As, AlSiAs, and AlSiCN. The same approach as that above leads to a further group of compounds which might be made by the combination of materials not all of which possess a diamond-like structure, but for which it seems likely that the final product would possess either the sphalerite or the wurtzite structure: BCN, BSi_2N, BSiCP, AlSiTiP, AlSiTiAs, $AlTi_2P$, AlTiAs, and AlTiSb.

A second principle arises as an offshoot of Bowen's original idea. Some binary compounds of Group III, IV, and V elements form interstitial compounds which are among the highest melting substance known. It is suggested that combinations of these interstitial compounds, containing equal numbers of Group III and Group V elements, might have high refractory properties. Using appropriate

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restrictions with respect to atomic dimensions, the following possibilities have been derived: B_2TiCTa_2, B_2ZrCTa_2, and B_2HfCTa_2, which would be expected to have a hexagonal structure; and BZr_2N, $BZrCNb$, $BZrCTa$, $ScTiCN$, $ScZrCN$, and $ScHfCN$, which would be expected to have a face-centered cubic structure.

Preliminary study of two of the predicted compounds, BSi_2N and B_2TiCTa_2, has already been made and a full-scale experimental program is now being started.

In an attempt to synthesize BSi_2N, a compact of BN and Si, in a 1:2 mole ratio, was heated to approximately 1675° C in a pressurized carbon resistor furnace. The product contained silicon (m.p. 1420° C) intermixed throughout the BN, but no evidence of a significant amount of reaction was found. Since BN is reported to sublime at 3000° C and might not have been sufficiently activated at 1675° C to react with the liquid silicon, this reaction will be repeated at a higher temperature.

To test the synthesis of B_2TiCTa_2, a compact of TiB_2 and supposed Ta_2C was sintered at 1825° C in an induction furnace. However, control X-ray analyses of the starting materials have shown the supposed Ta_2C to be TaC; it will be of interest to compare the product of this test with that obtained when known Ta_2C is used. The sample heated at 1825° C was essentially a simple mixture of TiB_2 and TaC. When the sample was heated to 2800° C, without melting, a considerable change in the X-ray pattern resulted. The lattice constant of the cubic TaC had decreased slightly from 4.46 to 4.43 Å, and the strong TiB_2 lines present in the X-ray pattern of the 1825° C run had weakened, indicating, some possible solution of the TiB_2 in the TaC. Finally, the appearance of several new weak lines indicates the possible formation of a new phase. Further work, including a melting point determination, will be done on this material since its properties appear promising.

Materials are on hand or have been ordered which will permit a more complete study of eighteen of the originally suggested twenty-one initial compounds. Some difficulty is being found in locating a source of ScN which is a component of three of the compounds.

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