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BASIC CHEMISTRY OF HIGH TEMPERATURE INORGANIC SYSTEMS
SEMIANNUAL PROGRESS REPORT
JANUARY - JUNE, 1956

ATOMICS INTERNATIONAL
A DIVISION OF NORTH AMERICAN AVIATION, INC.

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CHEMISTRY

BASIC CHEMISTRY OF HIGH TEMPERATURE INORGANIC SYSTEMS
SEMIANNUAL PROGRESS REPORT
JANUARY - JUNE, 1956

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ABSTRACT

The programs to study the "High Temperature Chemistry of Thorium" and the "Chemistry of Metal-Salt Systems" are well under way. Experiments dealing with the vapor pressure of thorium and thorium tetrafluoride are described. The vapor pressure of thorium tetrafluoride from 1128 to 1311° K is:

$$\log P_{(atm)} = \frac{-18{,}740}{T(^{\circ}K)} + 10.51$$

A study of the thermal stability of thorium tetraiodide has begun.

Solubility studies of the Bi-$BiCl_3$ and U-UCl_3 systems are being carried out. Methods for determining solubilities are described. Experiments to determine the thermodynamic activities of these solutions are also described.

I. INTRODUCTION

During the past six month, Atomics International, a Division of North American Aviation has moved from Downey, California to Canoga Park, California. Work on the two programs, High Temperature Thorium Chemistry and Chemistry of Metal-Metal Salt Systems, has continued although experimental progress was seriously impeded by the necessity of dismantling and reassembling all equipment.

The experimental program described in the first semiannual report[1] is now well under way. In the High Temperature Thorium Chemistry studies, the experimental work consists of vapor pressure determinations of thorium and of thorium fluoride, and the initiation of the study of the thermal stability of thorium tetraiodide.

Emphasis in the studies dealing with the Chemistry of Metal-Metal Salt Systems at High Temperatures is being placed on obtaining the phase diagram of Bi-$BiCl_3$ and U-UCl_3 in order to determine the consolute temperature of these systems. Experiments to determine the activities of these solutions by measuring the partial vapor pressures are described.

II. HIGH TEMPERATURE THORIUM CHEMISTRY

The apparatus for the study of the vapor pressure of thorium metal is complete and initial measurements have been made. The vapor pressure of thorium tetrafluoride has been measured in the range 10^{-7} to 10^{-4} mm Hg by the Knudsen effusion method. A study of the thermal stability of thorium tetraiodide has been initiated.

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

During the current period the apparatus shown schematically in Fig. 1 was set up in the new laboratory. This apparatus is constructed of vycor and pyrex, and contains only one removable joint which is a brass end plate, waxed on to facilitate loading and unloading of crucible assemblies. The all-tantalum crucible assembly is inductively heated with a six-kw Ajax spark gap converter. The system is evacuated via a cold trap by means of a three stage fractionating oil diffusion pump. The entire system can be baked out at 300° C by the use of glass-woven heater tapes. Vapor, effusing from the crucible, is condensed on platinum collectors supported in a movable aluminum holder. This holder can be magnetically moved along an aluminum track to permit up to 24 exposures without opening the system. The system is equipped with a magnetically operated shutter to protect the optical window from effusing vapor.

Experiments to date have been concerned mainly with testing the above apparatus. Difficulty has been experienced in maintaining a sufficiently good vacuum during heating. One series of vapor pressure determinations has been made in which pure thorium, received from the Ames Laboratory, was held in a tantalum crucible for two hours at a temperature of about 1900° C. The thorium vapor which effused from a 1/16-in. diameter orifice was collected on three platinum discs. During this two hour run the crucible attack by the thorium was so severe that the thorium leaked through the bottom of the crucible and froze to the lower shields and support. Chemical and metallurgical analyses of the

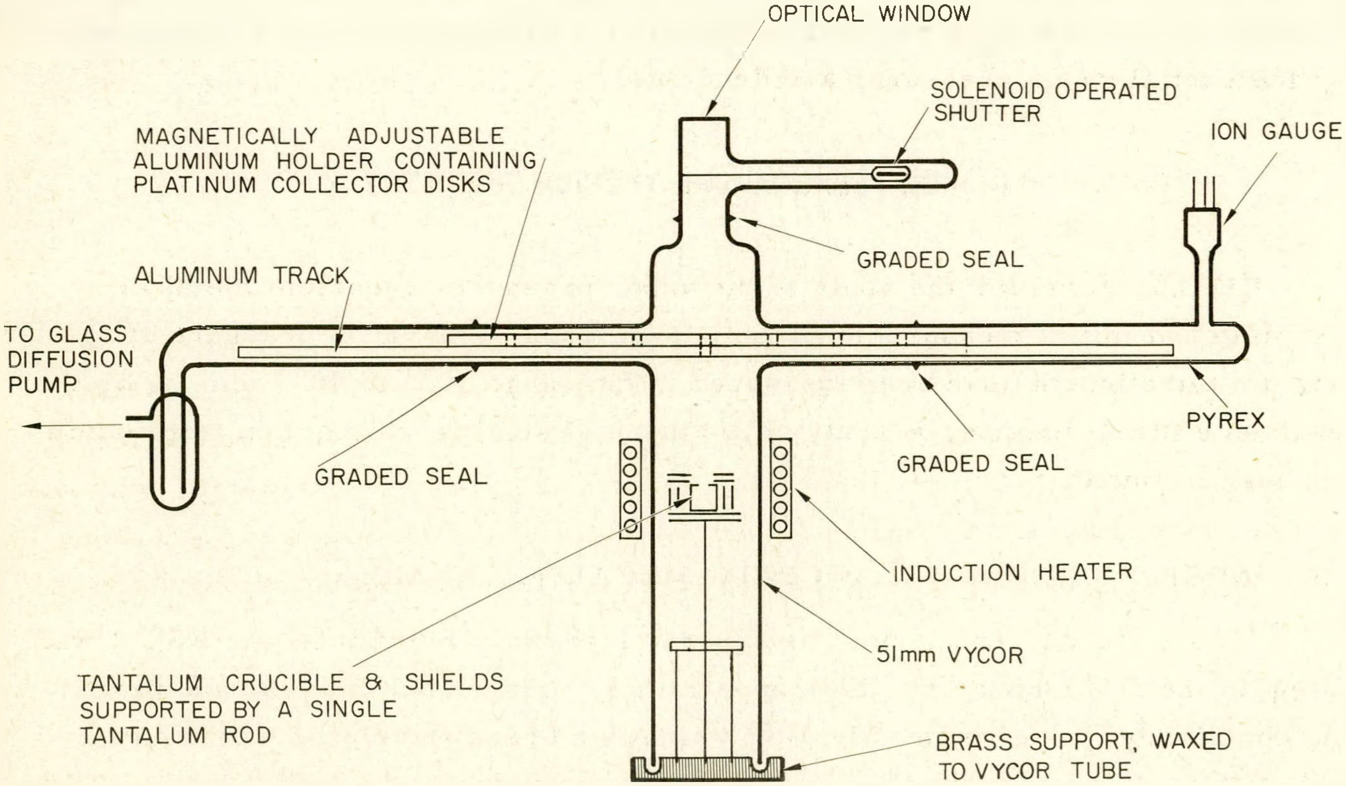

Fig. 1. High Vacuum Vapor Pressure Apparatus

thorium remaining in the crucible will soon be available. The pressure in the system during this run was quite high, about 8 x 10^{-5} mm Hg, so that vaporization of the thorium metal might well have been suppressed. The solution of tantalum in the thorium should also have lowered the activity of the thorium and hence the rate of vaporization. It is believed that during the first disc exposure, which lasted one hour, the thorium had not yet corroded through the crucible and hence the results from this first run may be used to fix a probable lower limit to the vapor pressure of pure thorium metal.

In this Knudsen effusion experiment the equilibrium vapor pressure of thorium is related to the weight of thorium deposited on the collector disc by the following equation:

$$P_{atm} = \frac{0{\cdot}0226\,g}{Kat}\sqrt{\frac{T}{M}}\left(\frac{l^2 + r^2}{r^2}\right) \qquad \ldots(1)$$

where;

g = thorium deposited on disc (gms)
l = distance from orifice to collector (cm)
K = Clausing correction factor for effusion from a non-knife edged orifice
a = area of the orifice (cm^2)
t = time of exposure (sec)
T = temperature (°K)
M = molecular weight of the effusing species

In the above run it is assumed that K is unity and that all of the vapor which struck the collector was deposited. The corrected temperature of the run was 1900° C ± 20° C, the time was 3600 seconds, and the fraction of vapor collected was about 1/64. The orifice area was 0.02 cm^2 and the collector weight gain was 24.0 micrograms. The resulting calculated value of the pressure of thorium at 1900° C is: $P_{atm} = 1.5 \times 10^{-6}$ atms. Brewer's[2] estimated vapor pressure at this temperature is 4 x 10^{-7} atm. The results of this single experiment indicate that Brewer's estimated vapor pressures may be low. In the future, determinations of the vapor pressure of thorium will be made under conditions in which vacua of less than 10^{-6} mm Hg will be maintained during effusion. If possible, vapor pressure determinations will be extended to temperatures below the melting point of thorium to decrease corrosion and to permit study on the volatility from the solid

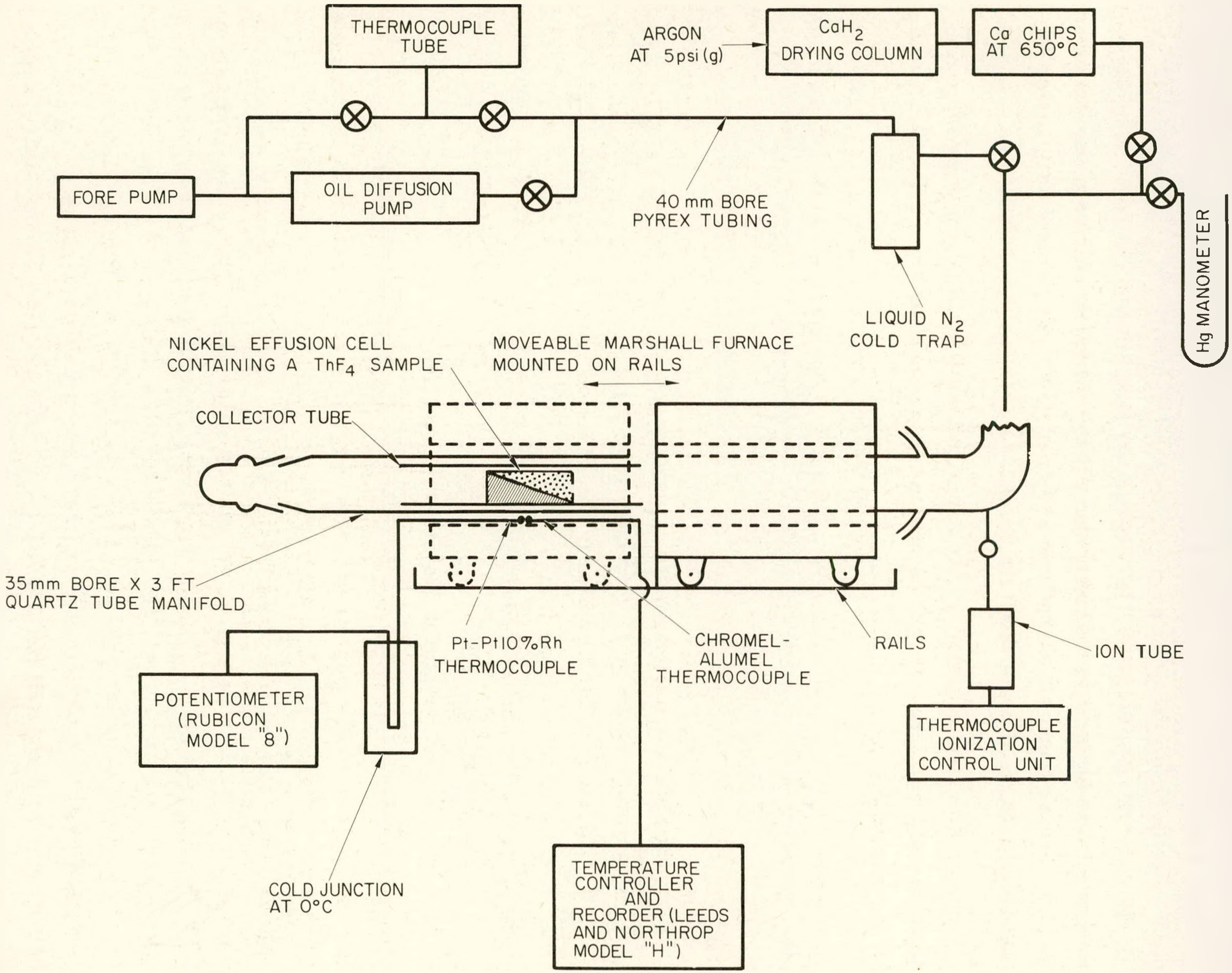

Fig. 2. Thorium Tetrafluoride Vapor Pressure Apparatus

as well as the liquid state. In addition, tungsten crucibles will be used in an effort to reduce the corrosion by thorium.

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

During the previous period, the vapor pressure of thorium tetrafluoride was measured from 9.6×10^{-4} atm at 1421° K to 9.34×10^{-3} atm at 1549° K by a quasi-static method[3]. The results are represented by the following equation:

$$\log P_{atm} = -16,260/T + 8.48 \qquad \ldots(2)$$

The work during the current period consisted of extending the range of vapor pressure measurements down to 9×10^{-7} atm at 1128° K. These determinations were carried out by the Knudsen effusion method in the apparatus shown in Fig. 2. The effusion cell, shown in Fig. 3, was made of commercially pure nickel and was fitted with a screw cap so that discs with orifices of different areas could be used.

The discs were made from 0.010-in. nickel sheet stock. Care was taken to select discs with orifices which had square edges and which were of uniform diameter. Several diameters of each orifice were determined and mean diameters were used to calculate the cross-sectional area of each orifice.

The effusion cell containing the thorium tetrafluoride sample was heated with a Marshall furnace which had been adjusted to produce a temperature zone

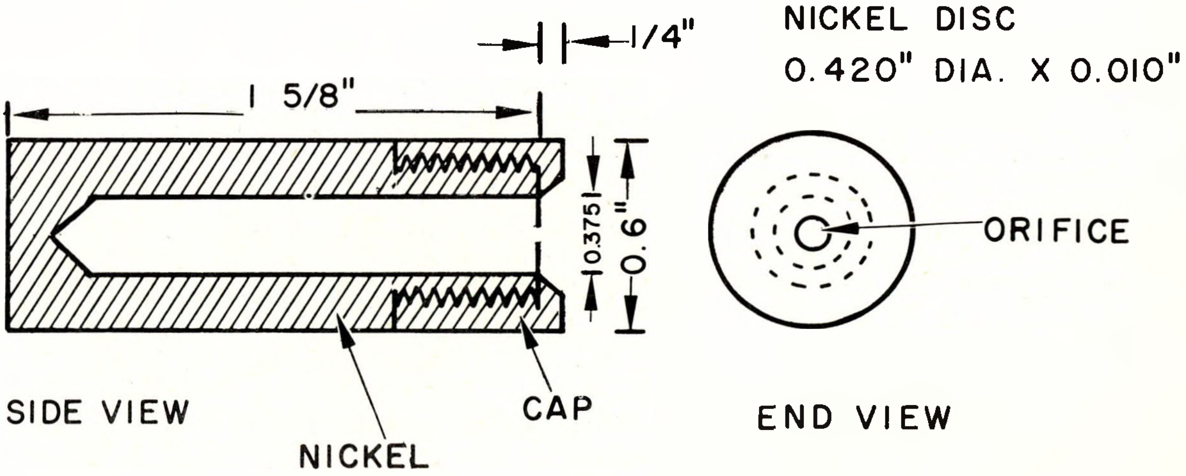

Fig. 3. Knudsen Type Effusion Cell

uniform to ± 2 ° C over a 3-inch length along its axis. The temperature of the Marshall furnace was held constant to within ± 1 ° C by a Leeds and Northrup temperature controller-recorder Model H. The temperature of the cell was measured with a calibrated Pt-Pt, 10%Rh thermocouple and a Rubicon type B potentiometer. In each experiment the temperature was measured at each end and at the center of the cell and a mean value was taken as the temperature of the run. The pressure in the vacuum system was kept below 5×10^{-5} mm Hg during each experiment.

In a typical experiment, the thorium tetrafluoride contained in the nickel cell was placed inside a quartz collector tube and this in turn was placed inside a quartz tube which is part of the high vacuum system. The manifold portion of the apparatus which contained the cell was then exhausted to a high vacuum before heat was applied. After the furnace was at operating temperature, it was moved along the manifold and centered over the cell. The amount of material effused was determined from the weight loss of the cell which had occured during an experiment.

The thorium tetrafluoride used in these experiments was obtained from the A. D. Mackay Company. X-ray analysis showed only thorium tetrafluoride lines in its pattern. Chemical analysis showed less than 0.2 weight per cent oxygen or water in the material. An analysis of this material yielded a value of 74.8 per cent thorium compared to 75.3 per cent for thorium tetrafluoride. The thorium tetrafluoride was heated for three hours under high vacuum to remove any volatile impurities before the sample was used for an effusion experiment. The results of the vapor pressure measurement, calculated by Eq. (1), are given in Table 1 and Fig. 4. In these experiments the orifice disc thickness was 0.0254 cm and the diameters of the orifices used were 0.050, 0.102, and 0.144 cm. The Clausing factor K, the ratio of the number of molecules that pass through the orifice to the number that enter the orifice, was calculated and the vapor pressure obtained with Eq. (1). A correction to the effusion time interval for an experiment was also made to account for the time required for the cell to attain operating temperature. An inspection of Table 1 and Fig. 4 shows clearly that the measured vapor pressures are unaffected by a variation in orifice area by a factor of eight. This constitutes an excellent check that equilibrium conditions existed inside the cell. The vapor pressure, determined from 1128 to 1311 ° K, can be expressed by:

TABLE I

VAPOR PRESSURE OF SOLID ThF_4

Temperature (°K)	Reciprocal Temperature $\left(\frac{1}{°K}10^4\right)$	Wt. Loss (gms)	Time Interval (Hrs.)	Orifice Area (cm^2)	Correction Factor (K)	P of ThF_4 (atmospheres)
1128	8.87	0.0066	65.0	0.00196	0.65	8.9×10^{-7}
1128	8.87	0.0724	65.75	0.0164	0.86	8.5×10^{-7}
1181	8.46	0.0212	41.9	0.00196	0.65	4.4×10^{-6}
1198	8.35	0.0517	16.5	0.00815	0.802	5.4×10^{-6}
1199	8.34	0.1651	17.28	0.0164	0.86	7.6×10^{-6}
1199	8.34	0.0256	3.7	0.0164	0.86	5.6×10^{-6}
1226	8.16	0.0386	24.3	0.00196	0.65	1.41×10^{-5}
1229	8.15	0.0354	17.3	0.00196	0.65	1.83×10^{-5}
1233	8.11	0.0480	17.0	0.00196	0.65	2.5×10^{-5}
1241	8.06	0.0515	3.3	0.00815	0.802	2.7×10^{-5}
1242	8.05	0.1274	15.1	0.00815	0.802	1.45×10^{-5}
1286	7.77	0.2319	3.0	0.00815	0.802	1.35×10^{-4}
1291	7.74	0.0393	4.38	0.00196	0.65	8.2×10^{-5}
1311	7.63	0.0552	3.9	0.00196	0.65	1.3×10^{-4}

$$\log P_{(atm)} = \frac{-18{,}740}{T\ °K} + 10.51 \qquad \ldots(3)$$

These data must be viewed as tentative pending final corrections for temperatures and effusion times. Further experiments are in progress to complete this phase of the study.

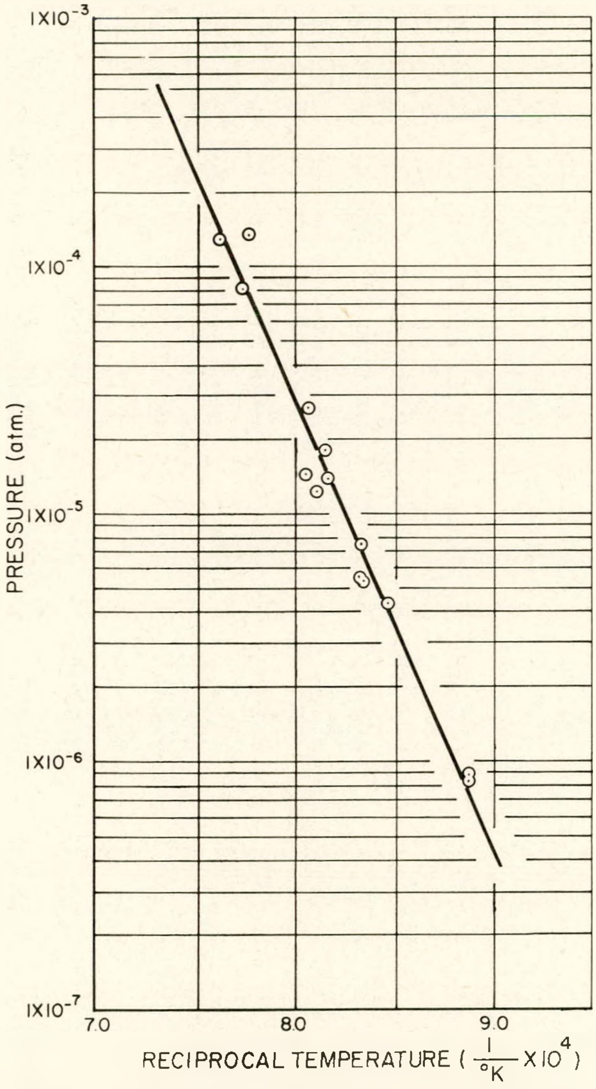

Fig. 4. Vapor Pressure of Solid Thorium Tetrafluoride

C. THERMAL STABILITY OF THORIUM TETRAIODIDE (T. A. Milne)

The equilibrium, $ThI_{4(g)} = Th_{(s)} + 4I_{(g)}$, has been studied by Allen and Yost[4] in 1954. Their experiments were of a transpiration type in which iodine, in a helium stream, was passed over thorium strips contained in an inductively heated molybdenum tube. Only the partial pressure of iodine was measured, the partial pressure of thorium tetraiodide being computed by difference. The iodine partial pressure was measured by means of an optical absorption method.

The temperature range studied by Allen and Yost was from 1394 to 1706° K. At 1395° K the partial pressure of thorium tetraiodide was too small to be calculated accurately; while at 1706° K, in two experiments, the partial pressure of iodine leaving the reaction chamber was about 1.5 times greater than the initial partial pressure. This was explained in terms of desorption of previously adsorbed iodine in some part of the flow system.

In view of the short temperature range over which data could be interpreted, 1447 to 1602° K and of the uncertainty connected with the influence of adsorbed iodine at these temperatures, it seems useful to repeat a study of this equilibrium. The need for this study is strengthened by the fact that the enthalpy and entropy of formation of thorium tetraiodide obtained from Allen and Yost's experiments, are in pronounced disagreement with Brewer's[5] estimated values, although the free energy values are in rough agreement. Their experimental heat was 95 kcal more negative and the entropy 72 e.u. more negative than Brewer's values.

It is planned to make a more extensive transpiration study of the equilibrium $ThI_{4(g)} = Th_{(s)} + 4I_{(g)}$ with the following features:

1. The partial pressures of both iodine and thorium tetraiodide will be measured.
2. The temperature range will be extended.
3. A pure thorium tube will be used as a reaction vessel to minimize possible alloying effects.
4. The equilibrium will be approached from each side by starting alternately with pure iodine gas or with pure thorium tetraiodide gas.

A conventional transpiration apparatus with these features incorporated is being assembled to initiate studies on this problem.

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

Exploratory experiments on the solubilities of metals in molten salts containing common cations have been carried out. The systems being studied thus far are U-UCl_3 and Bi-$BiCl_3$. The vapor pressure of the Bi-$BiCl_3$ system is being studied in order to obtain the thermodynamic activities of these solutions.

A. URANIUM-URANIUM TRICHLORIDE SOLUBILITY STUDIES (N. D. Potter)

Earlier experiments, in which molten uranium and fused uranium trichloride were equilibrated and quenched, revealed a limited solubility of about six per cent uranium in uranium trichloride at 1140° C[6]. Nevertheless there is a question as to whether samples which are quenched are equivalent to those at the higher temperatures.

In the case of alkali metals in their halide salts, it has been shown that much higher solubility results are obtained by sampling "at temperature" than by sampling mixtures subsequent to quenching[7,8]. Thus, it was felt that further investigation of the system U-UCl_3 by sampling "at temperature" was in order.

A system shown in Fig. 5 was built in which a graphite dipstick and sampler could be lowered into the melt. The arrangement was such that when the sampler touched the bottom of the crucible, samples of both the metal and the salt could be taken.

A run has been made in which uranium trichloride was prepared in situ by partially reacting uranium hydride with hydrogen chloride at 400° C thus forming a mixture of uranium trichloride and uranium. The mixture was heated to above the melting point of uranium trichloride by means of a resistance furnace and the graphite sampler was then lowered into the melt. It was found, however, that the melt was so viscous that the sampler would hardly penetrate it. The high viscosity is tentatively attributed to impurities in the melt. Samples have been submitted to the Analytical Group for a check on the purity of the salt and metal.

Equipment is being set up to purify the uranium trichloride by use of a method described by Gregory,[9] which is briefly, to pass iodine gas over the impure uranium trichloride to form UCl_3I. The mixed halide volatilizes and decomposes upon striking a hot surface to form uranium trichloride. Further equilibration studies will be made as soon as pure uranium trichloride is obtained.

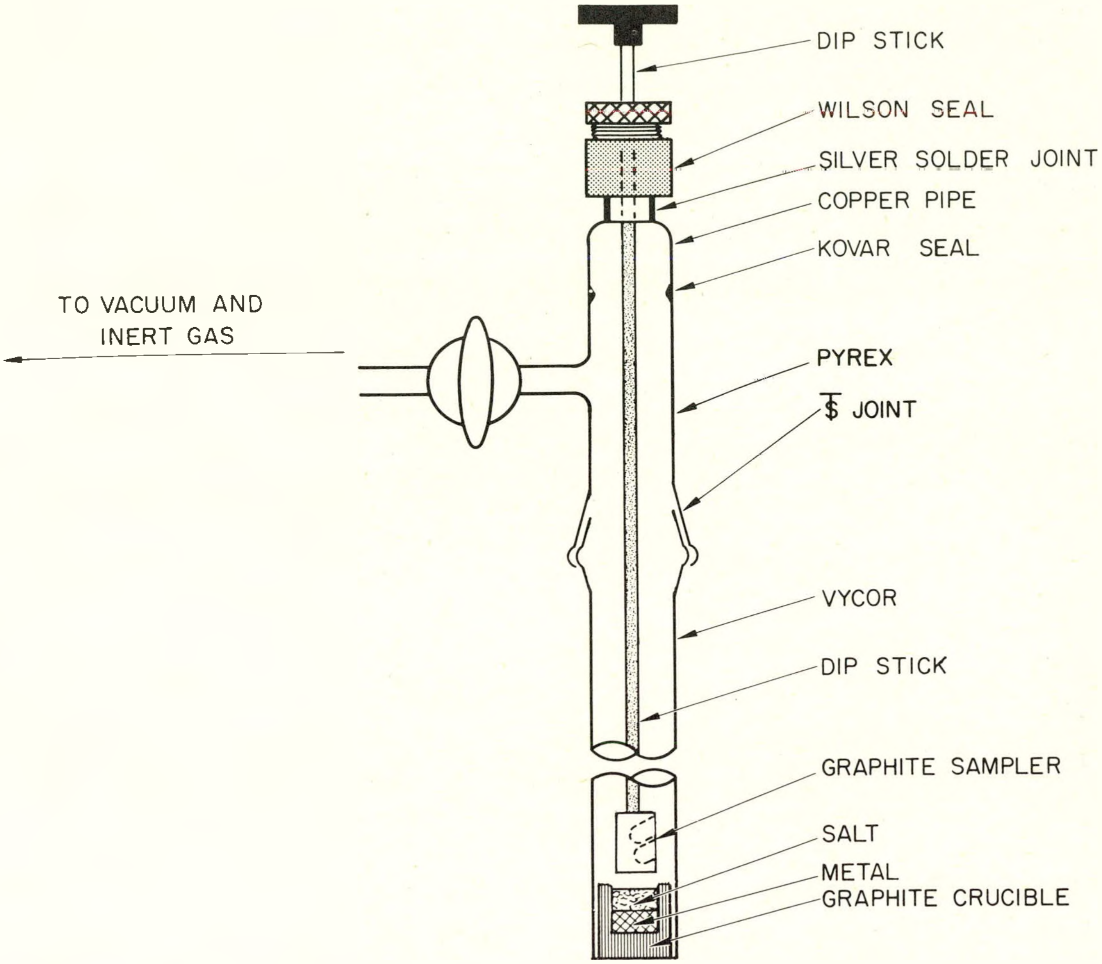

Fig. 5. System for Sampling Uranium and Uranium Trichloride

B. BISMUTH-BISMUTH-TRICHLORIDE SOLUBILITY STUDIES (A. J. Darnell)

During the period covered by this report experiments have been devised, apparatus built, and highly purified materials have been obtained or prepared in order to study the solubility of the Bi-$BiCl_3$ system at high temperatures. The solubilities of this system are being determined by four different methods:

1. Quenching the heated sample and analyzing the quenched phases.
2. Sampling the salt phase at temperature by tilting the system.
3. Pipetting the salt and metal phase while under relatively high pressure.
4. Observing the phases visually.

Six exploratory solubility experiments were made by the quench method in the temperature range of 280 to 490° C. In these runs the bismuth and bismuth trichloride were sealed in a pyrex or Vycor tube, equilibrated at the desired temperature, and finally quenched. The analytical results from these runs yielded widely scattered data which indicated less solubility than those of Eggink[10] who sampled "at temperature". The lack of reproducibility and of lower solubility results are probably caused by composition changes occurring in the sample before it was "frozen".

In view of Bredig's interesting results obtained when sampling "at temperature"[7,8], emphasis is being placed on nonquenching types of experiments. With this thought in mind, a tilt furnace apparatus is being constructed so that samples may be decanted "at temperature" from the molten salt-rich phase. The decanted sample will then be cooled and analyzed for bismuth metal and bismuth trichloride.

Since it is difficult to decant samples from the metal-rich phase by the tilt method, a pipetting method to remove a sample "at temperature" from a closed bomb as shown in Fig. 6 has been devised. In this apparatus the vapor pressure of the material in the bomb is utilized to force the liquid sample up the pipette tube to the collection bulb. This is accomplished by puncturing the sealed tip of the pipette tube with a nickel rod attached to a magnetic striker. A sample of the molten metal-salt solution is removed from the bomb at operating temperature and allowed to cool in the bulb.

The disadvantage of this method is that there might be phase separation with resultant composition changes along the length of the pipette.

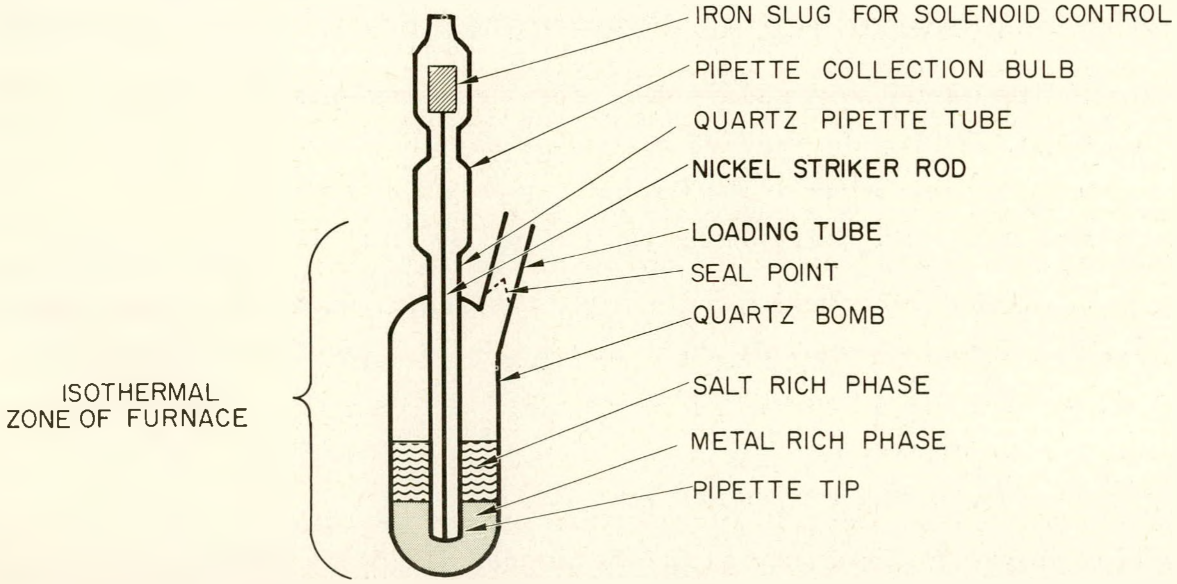

Fig. 6. Closed Bomb Apparatus for Sampling With a Pipette

However, since this tube has a small cross-section and has a considerable length, diffusion of material from the bulb back into the bomb would be expected to be small.

In order to test this method two experiments have been performed at 500° C; one in which the salt-rich phase was sampled and one in which the metal-rich phase was sampled. These two pipetted samples were markedly different in appearance, which would indicate that the consolute temperature for this system is above 500° C. The pipetted portion from each experiment was separated into four parts and submitted for analysis to determine if the sample was homogeneous after it was removed and cooled.

The final method being tested is the visual one which consists of heating a mixture of Bi-$BiCl_3$ in a Vycor bomb and visually observing the movement of the interface. Two exploratory experiments were done in which the mixtures were heated in a fused KCl-LiCl bath. No consolute temperature was noted at temperatures as high as 600° C. These experiments will be repeated with purified bismuth trichloride at higher temperatures.

Because of the hygroscopic nature of bismuth trichloride, special precautions will be taken to handle this material at all times in an inert atmosphere. Fig. 7 shows a schematic diagram of the vacuum system, inert gas purification train, and "dry box" apparatus to be used to introduce purified bismuth trichloride into the experimental apparatus. The dry box apparatus consists of a lucite box 10 in. x 10 in. x 10 in. with an air lock chamber for introducing samples and a connection to the high vacuum system. The dry box is prepared for use by inflating a polyethylene bag inside the box, thereby displacing 95% of its volume, and subsequently refilling it with purified argon. This procedure is repeated three times to insure thorough purging of water vapor from the box. Entrance of air from the exit flushing line is prevented by a collapsible bag, drying column, and a Bunsen valve. This prevents air from being "pumped" back into the box by movement of the gloves and by back diffusion. The "dry box" is flushed with argon that has been purified by passing it through the gas purification train which is also shown in Fig. 7.

Bismuth trichloride has been purified by the following procedures: Baker's analytical reagent bismuth trichloride is dried with anhydrous hydrogen chloride in the apparatus shown in Fig. 8.

This anhydrous bismuth trichloride is then transferred to the fractionation apparatus shown in Fig. 9 and distilled three successive times using an inert gas stream as a carrier. The first one-tenth and the last one-tenth of the sample are discarded. The remainder of the sample is then transferred to an apparatus where it is vacuum sublimed and collected for use in the experiments.

During the next six months emphasis will be placed on experiments done at elevated temperatures in order to determine if complete miscibility of bismuth and bismuth trichloride exists under attainable experimental conditions.

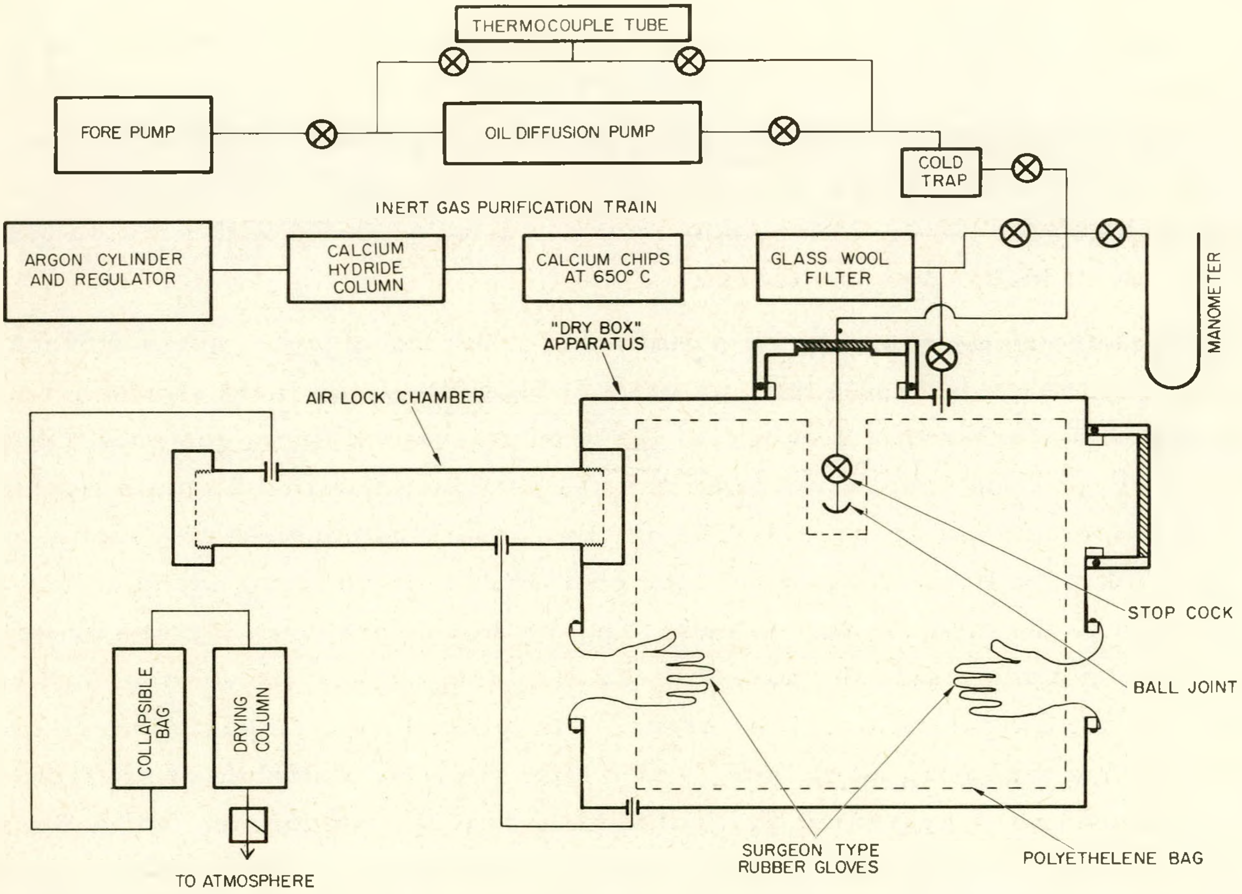

Fig. 7 Dry Box Apparatus

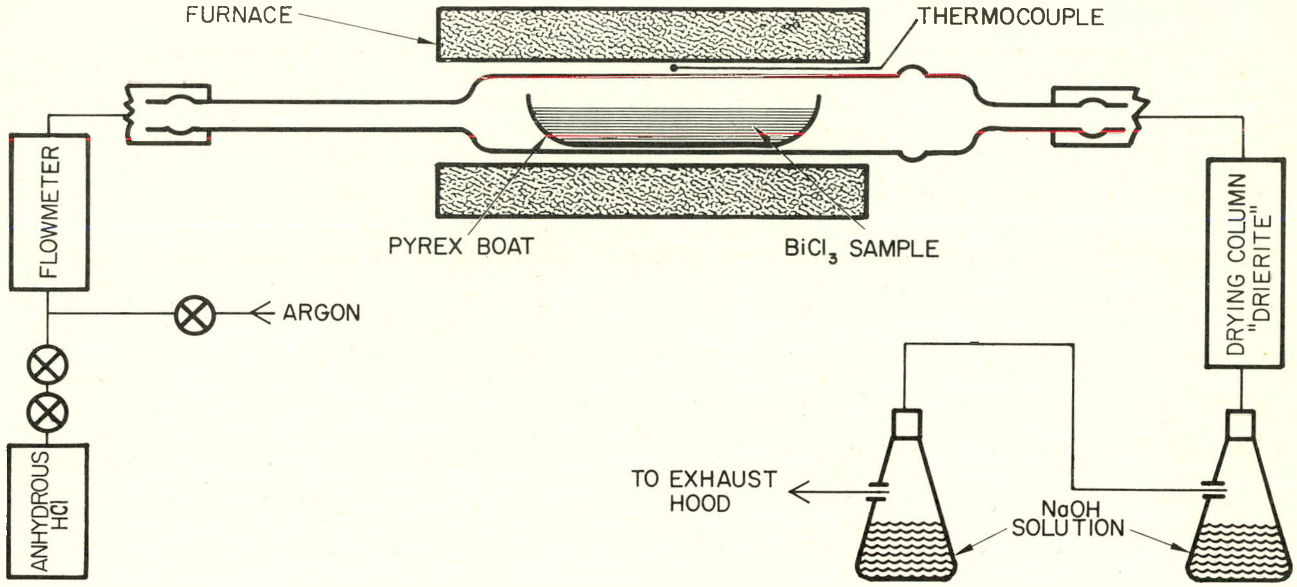

Fig. 8. Dehydration Apparatus for Bismuth Trichloride

C. VAPOR PRESSURE OF METAL-SALT SOLUTIONS

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

In cases where at least one of the components is volatile, one can determine the activities of the components by vapor pressure measurements. From these activities one can then obtain partial molal free energy, enthalpy, and entropy of solution.

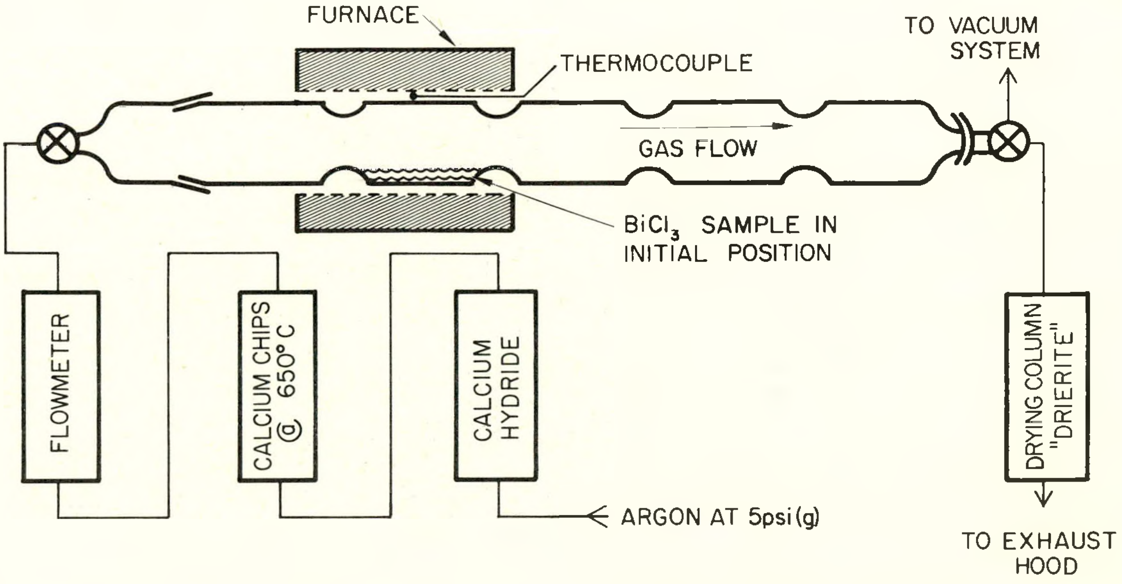

Fig. 9. Fractionation Apparatus for Purification of Bismuth Trichloride

The vapor pressure of the K-KF system has been measured[8] and a considerable deviation from Raoult's law has been observed. Emphasis in this laboratory is being placed on vapor pressure determinations in the Cd-$CdCl_2$ and Bi-$BiCl_3$ system as a function of composition and temperature. Two approaches are being carried out simultaneously at present.

The first method is a static one in which the pressure is continuously measured while the temperature is varied. The apparatus for measuring the vapor pressure of metal-salt solutions is shown in Fig. 10. It consists of a sealed bulb containing the solution and a known volume of inert gas which is used to reduce the extent of refluxing. As the system is heated, the increased pressure due to the expanding inert gas and the increasing vapor pressure of the solution, forces the solution to rise up the open tube. Purified inert gas is then admitted until the level of the solution in the tube is equal to that of the remaining solution. The vapor pressure P of the solution **at** temperature "T" can then be calculated from the observed reading on the manometer by:

$$P = P'' - \frac{P' T}{T'}$$

where; P' = the pressure of the inert atmosphere (mm Hg), at room temperature

P'' = the pressure reading from the manometer (mm Hg)

T' = room temperature (°K)

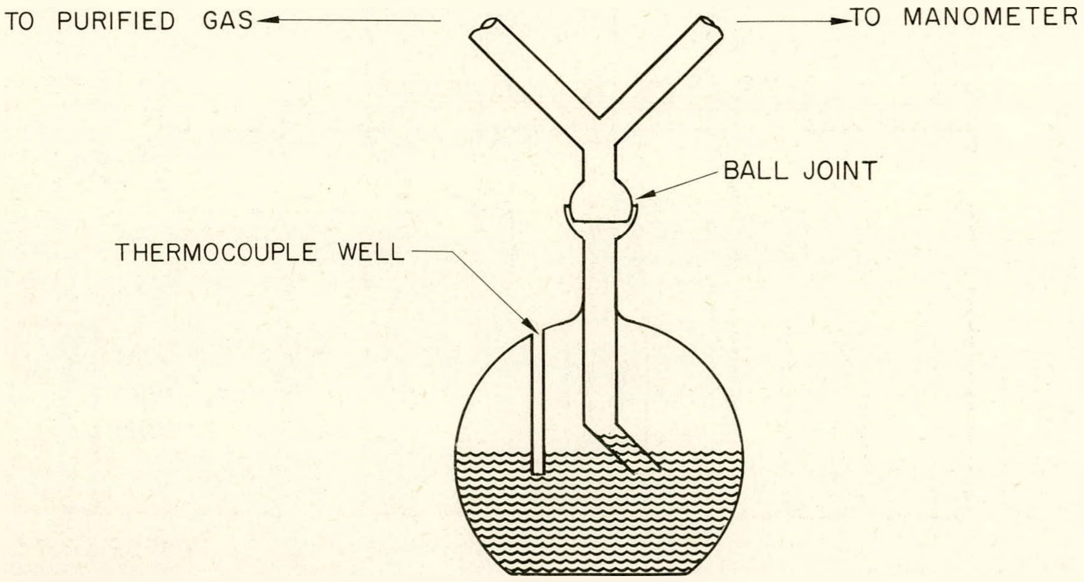

Fig. 10. Vapor Pressure Apparatus

To check this method, it was desirable to observe the nulling visually. The method has been successfully checked using water and mercury, and a fused nitrate bath. At higher temperatures it will be necessary to detect the null point nonvisually; therefore, a self balancing relay is being incorporated into the system.

One disadvantage of this method is the possibility of changing composition during the measurements as a result of refluxing or freezing out of the higher melting component; therefore, a second method similar to the one used by Herasymenko[11] on solid solutions is being used. In this method, schematically shown in Fig. 11, the vapor pressure of the volatile component is fixed and the composition of the two phases adjusts itself until the partial pressure of the solution is equal to that of the fixed vapor pressure.

In this case bismuth trichloride gas dissolves in the liquid bismuth to form a solution that continues to change in composition until the partial pressure of the bismuth trichloride in this solution is equal to the vapor pressure of the pure bismuth trichloride phase. Every part of the system above the salt is kept at a

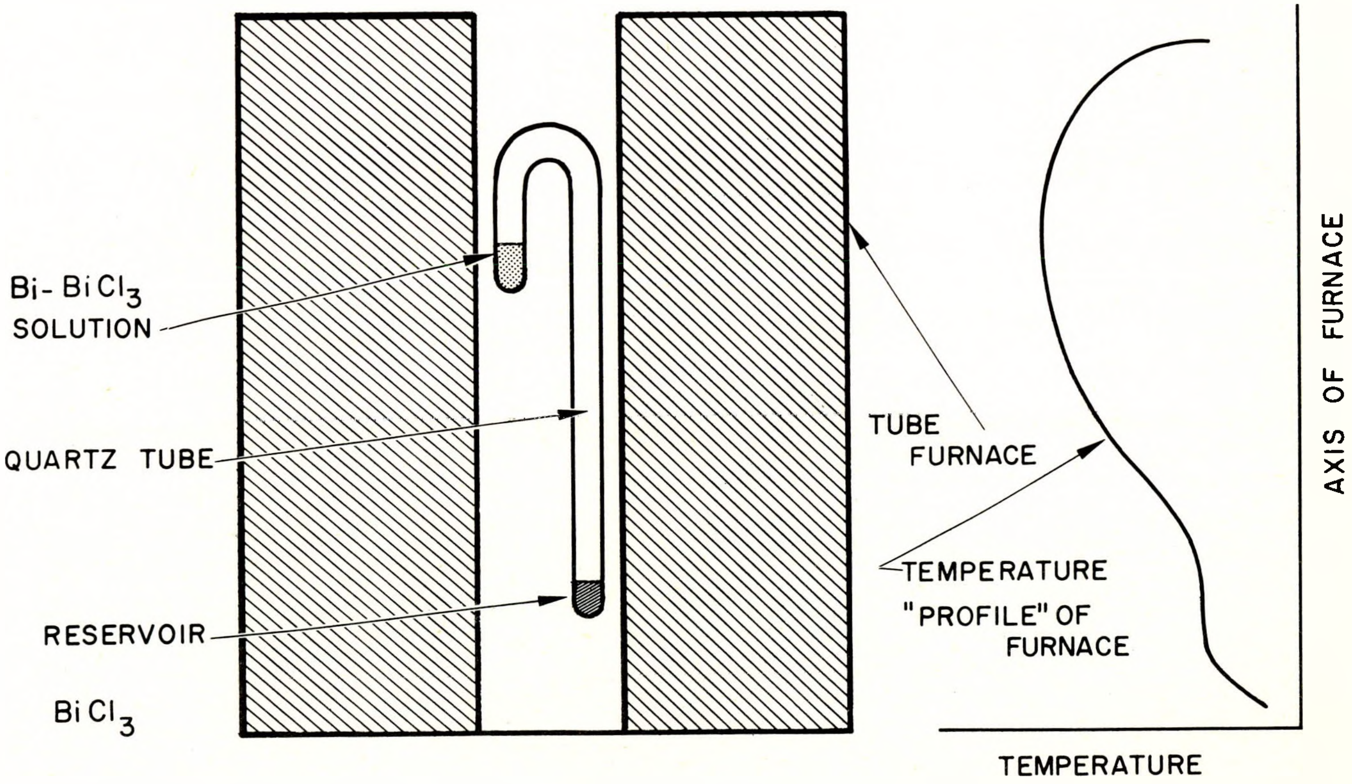

Fig. 11. Vapor Pressure Apparatus for Bismuth-Bismuth Trichloride Solutions

temperature hotter than that of the salt, thus preventing transfer by condensation of bismuth trichloride. The experiment showed that the rate of transfer of metallic bismuth is negligible due to the very low volatility of the metal.

Two exploratory experiments were performed at 500° C to check the technique. In the two runs, the metal phase was 12 to 17° C hotter than the salt reservoir. In each case bismuth trichloride dissolved in the bismuth in what appeared to be a single phase at high temperatures. During cooling, this phase appeared to separate into two phases, one metal rich and the other salt rich. Equilibrium solubility appeared to have been reached within the twelve hours that these experiments were carried out. Analyses of these runs are being carried out. In future runs the amount of dissolved bismuth trichloride will be determined by determining the increase in weight of the metal phase.

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