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IN THEIR MOLTEN CHLORIDES.

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ACTIVITIES OF ALKALINE EARTH METALS

IN THEIR MOLTEN CHLORIDES

by

John Adrian Van Westenburg

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Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University  
Of Science and Technology  
Ames, Iowa

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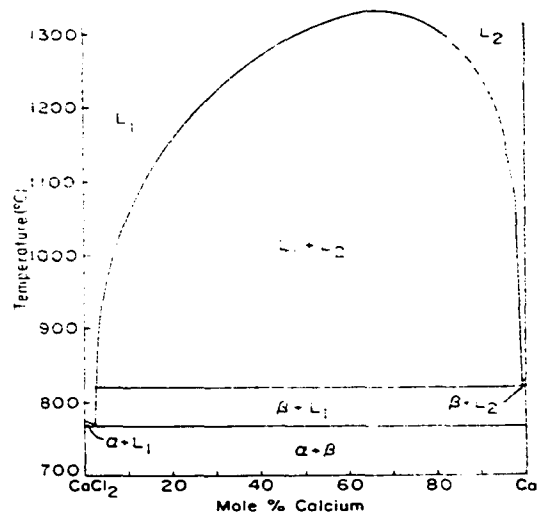
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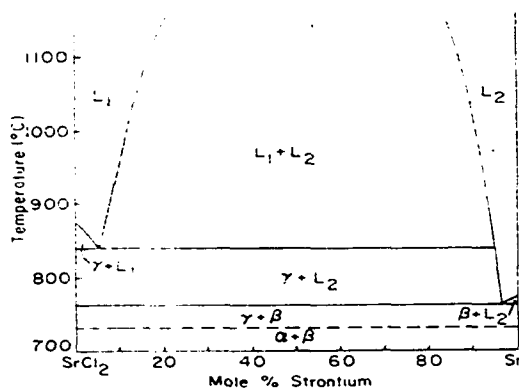
## INTRODUCTION

The solubility of various metals in fused chlorides, a phenomenon not widely recognized, has been summarized by Corbett (1) and Eastman et al. (2). For alkaline earth metals the available information on these solubilities ranges from data at one or two temperatures for magnesium-magnesium chloride as reported by Rogers et al. (3) to complete phase diagrams for barium-barium chloride, calcium-calcium chloride, and strontium-strontium chloride. The phase diagrams compiled from the literature are shown in Figure 1. The diagrams of most investigators show general similarity, but there are discrepancies in locations and types of reactions and solubility limits. A summary of the critical points reported by various investigators is presented in Table 1. The investigation by Staffanson (4) has drawn attention to the difficulties encountered using quenching and sampling techniques. This work indicated the data of Cubicciotti (5) and others were at least partially in error due to segregation on cooling. In view of the reactivity of the components in these systems some of the discrepancies may be traceable to impurity effects.

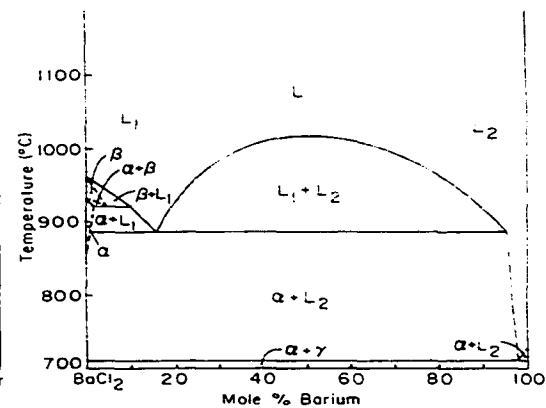
Figure 1. Metal-metal chloride phase diagrams



CALCIUM - CALCIUM CHLORIDE  
SYSTEM



STRONTIUM - STRONTIUM CHLORIDE  
SYSTEM



BARIUM - BARIUM CHLORIDE  
SYSTEM



Table 1. Summary of phase diagram critical points

System	Monotectic or Eutectic			Consolute temp. °C	Investigator
	Region on diagram	Mole % metal	Temp. °C		
Barium-barium chloride	Salt-rich	39	840	----	Cubieciotti (5)
	"	15	880	1010	Schäfer & Niklas (6)
	"	15	890	1017	Peterson and Hinkebein (7)
	"	16	880	----	Emons <u>et al.</u> (8)
	Metal-rich	96	688		(5)
	"	--	710		(6)
	"	98	710		(7)
	"	--	708		(8)
	Phase transformation in solid BaCl <sub>2</sub> at 920°C				
Calcium-calcium chloride	Salt-rich	1.6	767	----	Cubieciotti (5)
	"	2.0	768	----	Peterson and Hinkebein (7)
	"	---	763	1335	Staffanson (4)
	"	8.0	753	----	Emons <u>et al.</u> (9)
	"	2.2*	785*	----	Dworkin <u>et al.</u> (10)
	"	2.95*	855*	----	(10)
	Metal-rich	99	825	----	(5)
	"	99.5	820	----	(7)
	"	98.5	829	----	(9)
Strontium-strontium chloride	Salt-rich	18	736	----	Emons and Hellmond (11)
	"	5.5	839	----	Staffanson (4)
	"	8.5*	910*	----	Dworkin <u>et al.</u> (10)
	Metal-rich	96.5	762	----	(11)
	Phase transformation in solid SrCl <sub>2</sub> at 730°C				Dworkin and Bredig (12)

\*Not eutectic composition.

In an early investigation Borchers (13) electrolyzed calcium chloride and, upon finding no metal, hypothesized the formation of a subhalide. Following this, Guntz (14), Wöhler and Rodewald (15), and Borchers and Stochem (16) reported preparing alkaline earth monochlorides or mixtures of the monochloride and the dichloride. As was common to all these early investigators, the formula of the new compound or the proportions of this compound and the normal compound was frequently arrived upon solely on the basis of elemental analyses and ratios. Guntz and Benoit (17) attempted to prepare pure subhalides of calcium, strontium, and barium. They computed the enthalpy of formation of the supposed compound, calcium monochloride, by measuring its heat of solution in hydrochloric acid. Bichowsky and Rossini (18) calculated the heat of solution in hydrochloric acid of a mixture of calcium and calcium dichloride stoichiometrically equivalent to calcium monochloride, found it identical to that reported, and concluded that monochloride formation was improbable. The search for stable subhalides was in no little part prompted by the calculations of Grimm and Herzfeld (19), Emons (20), and Rabinowitsche and Thiele (21). These investigators used Born-Haber cycles and concluded that lower halides of the alkaline earth metals with the exception of magnesium

and beryllium are stable. In 1954 Ehrlich and Gentsch (22, 23) reported a solid compound,  $\text{CaCl}$ , and gave x-ray data in support of their claim. They reported unique diffraction patterns and determined the crystal structure and space groupings. Later investigation by Ehrlich et al. (24) showed this earlier work to be in error and the compound was shown to be  $\text{CaHCl}$ . Wehner (25) also reported a  $\text{CaCl}$  compound, but the amount of hydrogen liberated upon dissolving this compound in water was much too low to correspond to calcium monochloride. Emons et al. (8) concludes on the basis of x-ray analyses and phase diagram studies there is no valid experimental evidence for the formation of solid alkaline earth subchlorides, though the species are reported to exist in the gaseous state by Blue (26) and Walters and Barrat (27).

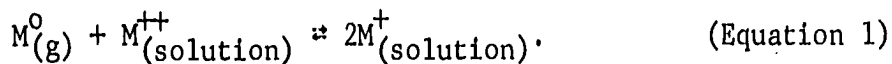
The observation of colloidal metal particles in the solid metal-salt mixtures obtained on cooling melts led Lorenz (28) to hypothesize the colloid theory of metal solution. He called these solutions "Pyrosole" or "Metallnebel". Lorenz and Eitel (29) marshalled considerable evidence in support of this theory but the arguments were based chiefly on the results of optical and x-ray studies of solid crystallized systems. Eitel and Lange (30) using a hot stage ultra-

microscope concluded the colloidal particles would have to be less than 35 microns in diameter. Belozerskii(31) on the basis of surface tension values for the pyrosole showed the particle size of the dissolved metal was about  $3 \cdot 10^{-8}$  centimeters in diameter, a value on the order of atomic dimensions. Aten (32) showed a true depression of the freezing point in the cadmium-cadmium chloride system and demonstrated the absence of any Tyndall effect in these molten salt-metal solutions. The metal colloid hypothesis has been discarded by all modern investigators.

The general lack of physico-chemical data and the contradictory nature of some reported data are probably due to experimental difficulties encountered when working with these reactive metals at elevated temperatures. Tantalum or stainless steels must be employed for reaction vessels and containers as the commonly used quartz and Vycor as well as most other refractory oxides will react with these alkaline earth metals and salts. All handling, storage, and experimentation must be done in an atmosphere of the noble gases or in a vacuum. These metal-metal salt mixtures react rapidly even at room temperature with many gases such as water, oxygen, nitrogen and hydrogen.

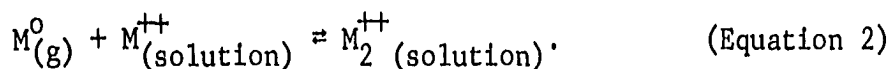
There have been four principle models hypothesized to describe the true solution of a metal in its salts. Many subtle variations or combinations of these models have also been described but are not different in concept. Most models are proposed on the basis of meager data and are based more on speculation than on confirming facts. It is generally accepted that molten chloride solutions are ionic in nature and hence all the proposed models invariably include ionic species. An excellent discussion of these models is presented by Corbett (1).

The reaction between a metal and its salt to form a monovalent ion in solution may be written



In this description an electron transfer from the metal atom to the solvent ion occurs and the electron is tightly held by the monovalent ion.

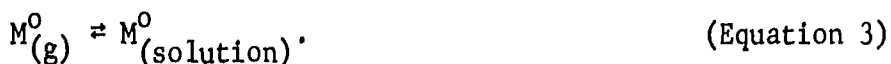
Dimeric species of monovalent ions could be formed by the following reaction



In this case there would be covalent bonding between the two metal atoms with a localization of the electrons in the vicinity of the dimeric ion.

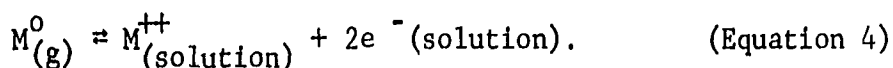
A model in which solution of metal occurred as a neutral

entity would be written as



This would likely be accompanied by solvation effects from the ions present in the molten salt solution.

A fourth solution model involves the complete separation of the electrons from the solute atom as follows:



This model proposes the liquid to be quasi-crystalline in nature with the electrons occupying anion vacancies in the melt in a manner similar to the color centers or "F" centers in solid alkali halide salts.

Several authors have attempted to utilize freezing point depression data to provide evidence for the nature of the solute in solutions of molten halides. One calculation is based on the approach of Grjotheim et al. (33) which uses the expression

$$\ln N_M(\text{solution}) = -\Delta H_f/T (1/T - 1/T_f), \text{ where}$$

$N_M(\text{solution})$  = mole fraction of the species in solution,

$\Delta H_f$  = molar enthalpy of fusion of the pure salt,

$T_f$  = solidification temperature of the pure salt  
in  $^{\circ}\text{K}$ , and

$T$  = liquidus temperature for the solution in  $^{\circ}\text{K}$ .

Since the expression for  $N_M$  (solution) is different for the various models postulated, a choice of models is made to best fit measured enthalpy data. Fechotte-Ostertag (34) and Emons et al. (8), using Blanc's (35) enthalpy data, state that solution of the metal in the alkaline earth metal-metal chloride systems proceeds by the formation of polymer ions of the type  $M_n^{++}$  where  $n$  is a number from two to four. Dworkin et al.

(10) uses a similar approach based on the equation:

$$\Delta T = n N_{M^0} \frac{RT_E}{\Delta S_f}, \text{ where}$$

$\Delta T$  = freezing point depression,

$n$  = the number of particles formed in solution for each dissolving metal atom,

$T_E$  = eutectic or monotectic temperature, and

$\Delta S_f$  = molar entropy of fusion of the pure salt.

Dworkin using his own data with that from Peterson and Hinkebein (7, 36) finds a eutectic composition of 2.0 mole per cent metal for the salt rich side in the calcium-calcium chloride system and concludes that " $n$ " must be approximately two to correspond to Moore's (37) calorimetrically measured  $\Delta S_f$  of 6.5 entropy units. Staffanson (4) by extrapolating his own data estimates an " $n$ " of about one for the solution of both calcium in calcium chloride and strontium in stron-

tium chloride. Dworkin et al. (10) used his own strontium-strontium chloride data along with Staffanson's (4) data and an estimated entropy of fusion of 7.0 entropy units instead of Kelley's (38) value of 3.6 and arrived at a cryoscopic number of two. A later paper by Dworkin and Bredig (12) reported a calorimetrically measured entropy of fusion of 3.39 entropy units for strontium chloride. The earlier data by Cubicciotti (5) would give still different results.

The validity of the freezing point depression equations assumes no solid solubility of metal in the chloride and the metal chloride behaves as an ideal solution i.e. there is no heat of solution upon dissolving metal in the molten salt. The first of these assumptions is questionable, while the second is simply not known. These approaches to this problem all attempt to infer properties of the minor component from measurements made on the major component. Considering the difficulties with container materials, available reagent purity and general chemical reactivity encountered in working in these systems, the discrepancies found are not surprising and the results to date are far from conclusive.

Direct thermodynamic measurements on the fugacity of the solute species could provide information helpful in interpret-



ing this problem. If the solute is in the same state of aggregation in solution as in the reference state, Henry's Law would predict for dilute solutions

$$f(\text{solute}) = K N(\text{solute}), \text{ where}$$

$f(\text{solute})$  = fugacity of the solute,

$N(\text{solute})$  = mole fraction of solute, and

$K$  = a constant.

Darken and Gurry (39) point out it is necessary to realize that the validity of Henry's Law depends on the proper choice of solute species. The state of aggregation of a solute in solution with respect to its reference state determines the form of the equation giving the variation of solute activity with solute concentration. In quite dilute solutions for a two particle state of aggregation in the solvent this takes the form

$$f(\text{solute}) = K N^2(\text{solute}),$$

or in general

$$f(\text{solute}) = K N^x(\text{solute})$$

where  $x$  represents the number of individually distinguishable particles of the solute in solution relative to its reference state.

Examination of the four models previously postulated

shows the model for the monovalent ion,  $M^+$ , and the model for the divalent ion plus electrons each form two distinguishable particles in solution for each atom in the reference state. The model postulating dimeric species,  $M_2^{++}$ , and the model postulating unionized metal atoms both show only one distinguishable particle in solution for each atom in the reference state. If the solution mechanism were some combination of these models or still some other mechanism, non-integer values of  $x$  would be expected. At higher concentrations of dissolved metal a further distinction between these models can be made. However, it is always well to remember that thermodynamic data can tell in principle only if a suggested model is possible and will frequently be unable to decide which one of several models is correct or if a particular model is the only one possible.

At low pressures the fugacity of a component is given by its vapor pressure. Isothermal measurements of the variation of vapor pressure of the solute species with concentration should provide data to calculate the state of aggregation of the solute in solution relative to its reference state. On the basis of vapor pressure measurements using a carrier gas

technique, Johnson (40) reported the solution of calcium in calcium chloride to be a two particle process. Rigney's (41) work using a Knudsen Effusion technique also supported this observation, though neither of these investigators had sufficiently precise results to rule out alternate interpretations.

This investigation was undertaken to measure the vapor pressure of the solute metal on the salt rich side of the alkaline earth metal-metal chloride systems as a function of metal concentration. These measurements were made by the Knudsen Effusion method. From the relationships between solute vapor pressure and composition possible solution reactions will be inferred.

## EXPERIMENTAL

## A. Materials

1. Barium chloride

Anhydrous barium chloride was prepared by dehydration of Baker's Analyzed barium chloride. The hydrated chloride was heated in air to 150°C for three days. This partially dehydrated chloride was placed in a platinum boat inside a Vycor tube and heated to 950°C for 8-10 hours in a flowing stream (50 cc per minute) of anhydrous hydrogen chloride. Prior to cooling the tube was evacuated to less than ten microns pressure to remove dissolved and adsorbed hydrogen chloride. The salt was cooled under vacuum and transferred in an argon filled dry box into screw top Mason jars for storage.

The hydrogen chloride was generated by dehydrating concentrated hydrochloric acid with concentrated sulfuric acid. The gas was dried by bubbling through concentrated sulfuric acid. Cylinder anhydrous hydrogen chloride had a carbon containing contaminant which decomposed and discolored the salt during dehydration.

The hydrated salt was reported to be 99.80 per cent barium chloride hydrate and contained 0.03 per cent strontium and 0.007 per cent calcium. The final product was neutral to

phenolphthalein.

## 2. Calcium chloride

Anhydrous calcium chloride was prepared by dehydrating Baker's Analyzed reagent calcium chloride by heating it for three days at 150°C. This material was placed in a platinum boat, inserted into a Vycor tube, and heated to 750°C for 8-10 hours in a flowing stream (50 cc per min) of anhydrous hydrogen chloride. Before cooling, the tube was evacuated to less than 10 microns pressure to remove dissolved and adsorbed hydrogen chloride. The salt was cooled under vacuum and transferred in an argon filled dry box into screw top Mason jars for storage. The hydrated calcium chloride was reported to be 99.92 per cent pure and contained 0.002 per cent barium and 0.05 per cent magnesium and alkali salts. After dehydration the salt contained from 0 to 0.005 per cent calcium oxide as determined by titration to the methyl red end point with standard hydrochloric acid.

## 3. Strontium chloride

Anhydrous strontium chloride was prepared by dehydration of Baker's Analyzed reagent strontium chloride. The dehydration was carried out by first heating the salt to 150°C in air for a period of three days. The partially dehydrated

salt was transferred to a platinum boat, inserted into a Vycor tube, and heated to  $850^{\circ}\text{C}$  for 8-10 hours in a flowing stream (50 cc per min) of dry hydrogen chloride. Prior to cooling the dissolved hydrogen chloride was removed by evacuating the tube to less than 10 microns pressure. The salt was cooled under vacuum and transferred in an argon filled dry box into air tight screw top jars for future use. The hydrated strontium chloride was reported to be 99.8 per cent pure and to contain 0.14 per cent magnesium and alkali salts as sulphate. The barium content was reported as 0.006 per cent. Strontium chloride dehydrated in this manner was neutral to phenolphthalein.

#### 4. Barium metal

Impure cast barium sticks were purified by distillation under reduced pressure as described by Hinkebein (42) and Peterson and Indig (43). After distillation the sealed retort was placed into a helium filled drybox and disassembled. The distilled barium was obtained as needle-like crystals about 0.1 inch in diameter and from 1/4 to 3/4 inch long. This metal was removed from the condenser with a chisel and placed into screw top Mason jars for storage. An analysis of a typical batch of this metal is given in Table 2.

Table 2. Analysis of barium metal

	Nitrogen PPM	Carbon PPM	Iron PPM	Manganese PPM
Crude barium	430	500-800	53	50
Distilled barium	70	40	<11	80

From qualitative spectrographic analyses it was estimated the aluminum, copper, calcium, magnesium, silicon, and strontium were each less than 50 parts per million. No oxygen or hydrogen analyses were available. Exclusive of oxygen and hydrogen the metal would be about 99.9 per cent pure barium.

#### 5. Calcium metal

Calcium metal prepared by the aluminothermic reduction of calcium oxide was obtained from the New England Lime Co., Canaan, Connecticut. The metal was distilled under vacuum using the method described by Smith et al. (44). The condensed metal was obtained in the form of angular crystals about four to six millimeters on all sides. All handling of the distilled metal was done in a dry box under a helium atmosphere. An analysis of a typical batch of this metal is given in Table 3. Hydrogen analysis of this metal using the method of Peterson and Fattore (45) showed 190-200 ppm of hydrogen. Smith et al. (44) estimated the oxygen content of

this type calcium to be less than 0.01 per cent on the basis of the nitrogen analysis.

Table 3. Analysis of calcium metal

Element	Spectroscopic (ppm)	Chemical (ppm)
Al	20	--
Ba	50	--
C	---	200-300
Cr	5	--
Fe	<50	40
N	---	33
Ni	---	20
Mg	500	--
Mn	<20	--
Si	20	--

#### 6. Strontium metal

Strontium metal obtained from King Laboratories, Syracuse, New York was purified by distillation at  $825^{\circ}\text{C}$  under an argon atmosphere at a pressure of 8.0 millimeters of mercury. The apparatus used was that described by Hinkebein (42). After distillation the sealed retort was placed into a helium filled dry box and disassembled. The metal was removed from the condenser and placed into screw top Mason jars for storage. The distilled strontium was obtained as angular platelets with faces from three to six millimeters on a side. An analysis of a typical batch of this metal is



given in Table 4.

Table 4. Analysis of strontium metal

Element	Spectroscopic (ppm)	Chemical (ppm)
Ba	<1000	--
Ca	<1000	--
Mg	<500	--
N	---	60
C	---	200
Fe	---	15
Mn	---	20
Ni	20	--
Cr	10	--

The hydrogen content of this metal is about 350 parts per million. This is equivalent to 1.5 mole per cent  $\text{SrH}_2$ .

No oxygen analyses were available.

## B. Methods

### 1. Apparatus

All vapor pressure measurements were made using the Knudsen effusion method (46). In this method of measurement, a small amount of the vapor in equilibrium with a solid or liquid is allowed to escape through a small orifice into a vacuum. The rate of escape is determined by measuring the rate of weight loss of the vessel. The rate of weight loss is related to the vapor pressure within the cell by an

expression presented in a later section.

The weight loss of the effusion vessel was measured using a modified Ainsworth Keyboard microbalance mounted in an evacuated bell jar. The addition and removal of weights was accomplished by actuating a lever-rod mechanism through a bellows seal. Magnetic damping was employed to minimize oscillations set up during changing of weights. The balance could be used to measure weight change of up to 621 milligrams in one milligram increments. For each weight loss determination, a mark on the pointer scale was chosen and the time required to return to the same mark was noted.

The sensitivity of this balance was found to be about 30 micrograms per scale division. Using optical magnification an estimation of one-tenth of a scale division was possible. This placed the error in determining each position of the pointer on the scale at about three micrograms. The weights employed were class M weights. These were checked against National Bureau of Standards weights and found to be within  $\pm 0.005$  milligram of their nominal values, well within the prescribed tolerance for this class of weights.

The time interval for a given weight loss was measured using a Precision Scientific Company electric timer with a

least scale reading of 0.01 minute.

Effusion cells for the vapor pressure determinations on the individual components were made of Type 304 stainless steel. For the binary mixtures and solutions tantalum cells were also employed since some evidence of attack by the metal-metal chloride liquid was noted on the stainless vessels. The stainless effusion cells were about 17 millimeters outside diameter, from 30 to 50 millimeters long, and of 0.38 millimeter in wall thickness. The lids varied in thickness from 0.127 to 3.630 millimeters in the region of the orifice. The effusion orifices were made by drilling a hole in the center of the effusion lid using a jeweler's micro drill press. The entrance and exit sides of the hole were deburred by hand polishing with #600 silicon carbide abrasive paper and the hole was burnished with a piano wire of approximately the same diameter as the hole. These orifices were examined and photographed on both sides using a Baush and Lomb metallograph. From these photographs and a reference photo of a stage micrometer, the orifice area was determined with a planimeter. The lids containing the orifice were then arc welded onto the tube body using a non-consumable tungsten electrode within an argon filled dry box. After use in

several vapor pressure determinations, the orifices were rephotographed and the area compared to the original area. Figure 2 shows photographs of a typical orifice before and after use. For all but the knife-edged orifices, no change in area was detected upon remeasurement. To support the effusion cells in the furnace a loop of 0.127 millimeter diameter tantalum wire was spot welded to the top of the cell.

The pumping equipment consisted of a three stage mercury diffusion pump backed by a Welch Duo-Seal mechanical pump and a liquid nitrogen trap. During operation the vacuum was measured using a NRC Type 507 ionization gauge. The pumping system, with the exception of the cold trap and furnace tube, was constructed of 50 millimeter Pyrex pipe sealed with neoprene O-rings and held together with standard Pyrex pipe clamps. Ground glass joints were sealed with Apiezon W wax.

The effusion cell was heated in the furnace arrangement shown in Figure 3. The stainless steel liner was used to reduce thermal gradients. The effusion vessel was suspended from the balance pan using 0.127 millimeter diameter tantalum wire. The three independent furnace windings were connected to individual auto transformers and voltage stabilizers. During vapor pressure determinations the temperature was

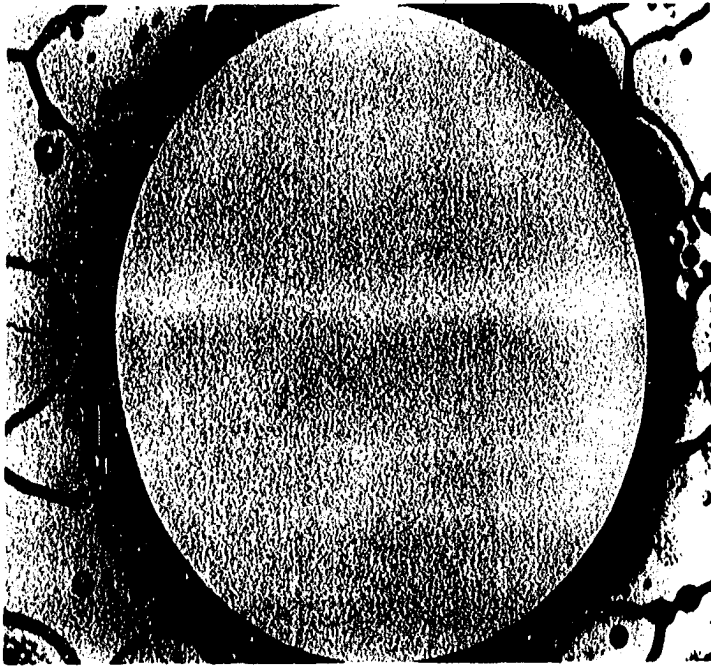


Figure 2a. Orifice photograph, orifice before use, 250X

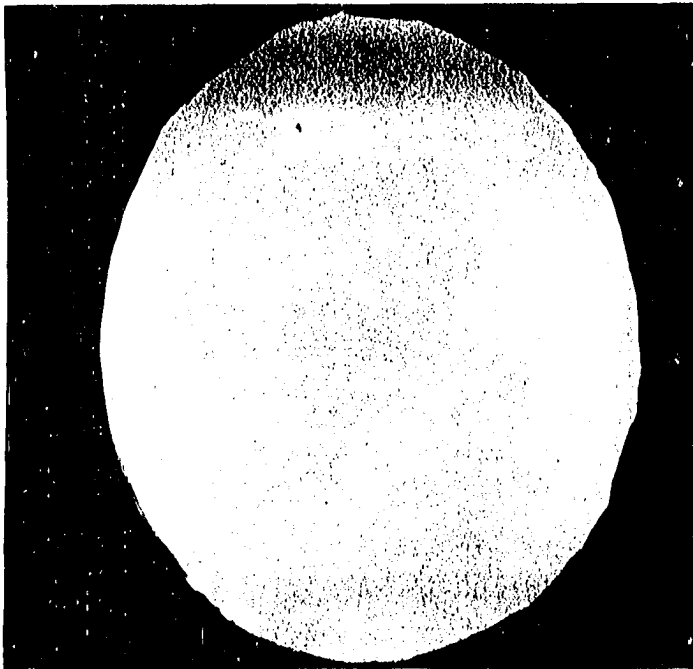
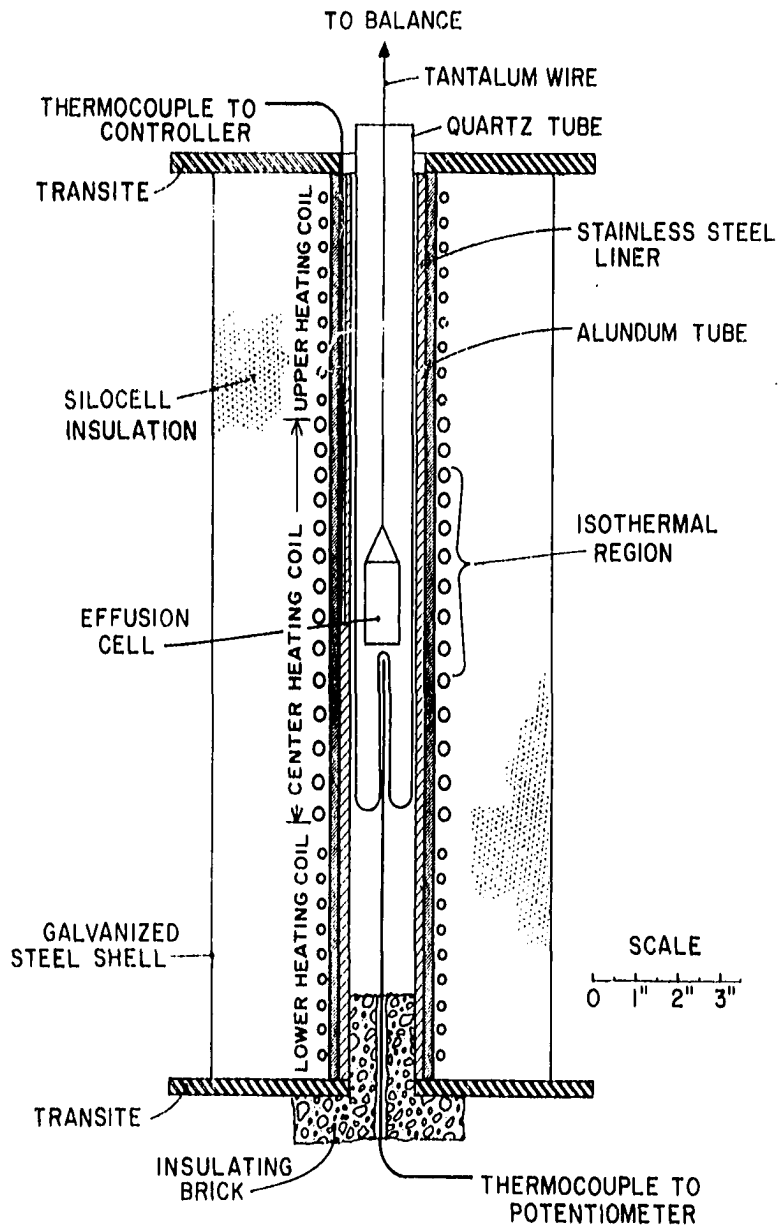


Figure 2b. Orifice photograph, orifice after use, 250X

Figure 3. Schematic drawing of furnace



controlled by manual regulation of the auto transformer supplying the center winding.

The sample temperature was measured with an 18 gauge chromel-alumel thermocouple, which had been calibrated against a U. S. Bureau of Standards standard melting point aluminum sample and a coulombmeter grade silver sample. For the calibration of the thermocouples, graphite crucibles of the design recommended by the Bureau of Standards and reported by Roeser and Wensel (47) were used. The thermocouples agreed at both temperatures to within  $\pm 0.25^{\circ}\text{C}$  with the temperature-EMF table for chromel-alumel couples listed in the National Bureau of Standards Circular 561. The reference junction of thermocouple was maintained at the ice point.

The potential of the thermocouple was measured with a Rubicon model 2745 potentiometer having a sensitivity of 0.01 millivolts. With the chromel-alumel couple this represents  $0.25^{\circ}\text{C}$ . This potentiometer was checked against a Leeds and Northrup model K-3 potentiometer using a National Bureau of Standards cell. The Rubicon potentiometer was found to be accurate within the sensitivity of the instrument.

The three individually controlled furnace windings permitted control of the temperature profile within the furnace.



The temperature profile inside the furnace tube was determined by using ten thermocouples placed at known locations within the evacuated quartz tube. By proper adjustment of the individual windings it was possible to obtain a region four inches long in which the temperature was constant to within  $\pm 0.25^{\circ}\text{C}$  at all temperatures from  $600^{\circ}\text{C}$  to  $1000^{\circ}\text{C}$ . To complete the calibration, a dummy effusion capsule with thermocouples welded to both top and bottom was placed in the position normally occupied by the effusion cell during vapor pressure determinations. The relationship between the temperature in this cell and the indicated temperature in the quartz finger was obtained over the temperature range from  $600^{\circ}$  to  $1000^{\circ}\text{C}$ . It was found that the temperature of the bottom of the effusion cell was within  $\pm 0.5^{\circ}\text{C}$  of the indicated temperature over the entire range, even when operating the top furnace winding at a power level that increased the temperature of the top of the effusion cell by two degrees. No changes in temperature characteristics were noted when the dummy effusion cell was loaded with about three grams of salt.

## 2. Operating procedure

a) Unary systems      For the determinations of the vapor pressure of the pure components, an appropriate effusion cell complete with attached lid and supporting wire was loaded within an argon filled dry box with from 0.5 to 1.0 gram of material. The bottom was then inserted into the inverted effusion cell and sealed by tungsten arc welding. This filled cell was then stored in an argon atmosphere in a screw top Mason jar. Transfer of the effusion cell from the container into the vacuum system was the only exposure of the sample to air. The effusion cell and a radiation baffle were hung on the support wire and lowered into the furnace tube. This transfer took from 20 to 30 seconds. The entire vacuum system was continuously filled and flushed with argon during the transfer and all subsequent operations prior to re-evacuating the system. Following the taring of the balance, the bell jar was placed in position, but not sealed, and helium allowed to displace the air from within the bell jar. The time for the entire operation was four to five minutes. When the mechanical pump had pumped the system down to 10 microns or less, the cold trap was filled with liquid nitrogen and the mercury diffusion pump started. When the

pressure was below  $10^{-5}$  mm of Hg the furnace was brought to temperature and the experiment initiated.

It was possible to measure the rate of weight loss at three to six different temperatures with one effusion cell before the limit of the balance range was reached. After each change of temperature, sufficient time was allowed to attain thermal equilibrium before taking further readings. This time for equilibrium varied from over one hour at low temperatures to as little as fifteen minutes at high temperatures. When dealing with the metals in the liquid range, it was found necessary to increase the power input to the top furnace winding to insure that the orifice region at the top of the effusion cell remained one to two degrees hotter than the bottom. This effectively prevented the vapor from condensing on the top of the cell, wetting it, and plugging the orifice through flow of the liquid metal promoted by its surface tension.

b) Binary systems      The salt phase used for the binary mixtures was prepared by pre-alloying the anhydrous metal chloride with the appropriate metal. The approximate amounts of salt and metal were individually weighed in the dry box to the nearest 0.1 gram in proportions to make a total charge of

twenty grams. These two components were sealed into a tantalum crucible by welding and this crucible enclosed in an Inconel retort by welding. The charged crucible was placed into a furnace at 1000-1100°C and held at temperature for 12 to 24 hours. The crucibles were inverted several times during this interval and were immediately water quenched on removal from the furnace. The Inconel container was removed and the tantalum crucible placed in the dry box. On opening the tantalum crucible the phases were separated and stored in argon filled screw top jars. The salt phase, which was always on the bottom of the crucible, ranged in color from light grey to violet. The brittle salt phase was readily separated from the malleable metal phase, which usually adhered to the tantalum container.

The effusion cells were loaded with a weighed amount of this prealloyed salt and enough excess metal to insure that the resulting sample would be a two phase mixture at the temperature of the investigation. The details of the crucible loading and subsequent transfer into the apparatus were the same as described for the pure components.

All binary system vapor pressure determinations were carried out isothermally with the composition of the alloy

being the only intended variable. Since the relative amounts of the components of the starting alloy were known only approximately, it was necessary to observe weight losses on each cell until all the metal had escaped. The amount of non-volatile salt remaining in the effusion cell was determined by analysing for the total chloride in the cell. It was then possible to calculate the alloy compositions at which the individual pressure determinations had been made.

Upon completing measurements on a given effusion cell as evidenced by near or complete depletion of the volatile metal component, the apparatus was cooled and the effusion cell removed. A hole was drilled through the bottom of the cell and the entire cell, contents, and all drillings placed into distilled water. The alkalinity of the resulting solution was titrated with a standard nitric acid solution to the phenolphthalein end point. This titration measured the residual metal or oxide which had reacted with the distilled water. It is not possible to distinguish between oxide or metal by this titration. The neutral or slightly acid solution was then titrated for chloride ion by Fajan's method which uses a standard silver nitrate solution and dichlorofluorescein as an adsorption indicator.

### C. Error Analysis

The vapor pressures of the metals and metal chlorides were calculated from the following equation, which will be discussed more fully in the next section;

$$P = \frac{w}{t} \cdot \frac{1}{aQ} \left[ \frac{2\pi kT}{m} \right]^{\frac{1}{2}}, \text{ where}$$

P is the pressure,

w is the weight loss,

t is the time interval for the weight loss,

a is the orifice area,

m is the mass of the vapor species,

k is the Boltzman Constant, and

Q is the Clausing Factor.

The values chosen for the Boltzman constant and the mass of the effusing species were taken as being correct as any errors in these values were considered to be small compared to other errors.

The orifice area was determined by measuring the area of a photomicrograph of the hole taken at room temperature. This area was measured by using a planimeter calibrated on a photograph of a stage micrometer taken under the same conditions as the orifice photograph. An absolute error in the

accuracy of this measurement cannot be assigned since the accuracy of the calibrating stage micrometer was not known. Repeated measurements on the same photograph show deviations in the measured area of 0.2 to 0.7 per cent. The linear coefficients of expansion for Type 304 stainless steel and tantalum as given in the Metals Handbook (48) are respectively 11.2 and 3.6 microinches per inch per  $^{\circ}\text{F}$ . The increase in orifice area upon heating to  $850^{\circ}\text{C}$  amounts to 3.0 per cent for the stainless steel and about 1.0 per cent for the tantalum. The areas as measured at room temperature were corrected to  $800^{\circ}\text{C}$ . The change in area with temperature over the range from 650 to  $950^{\circ}\text{C}$  would amount to 0.10 to 0.50 per cent. It is estimated that the error in the measured pressure introduced by the orifice should be set at about 1.5 per cent. This is an error in accuracy only and should not effect the precision of measurements using the same orifice.

The time interval for loss of a given weight was measured with an electric timer with a least scale reading of 0.01 minutes. The major contribution to the time error was considered to be in reading the timer. This error was assumed to be 0.01 minute. For the shortest time interval,

2.00 minutes, this error would contribute a 0.5 per cent error in the measured pressure; for most of the measurements the error in time was less than 1 part in 500.

The error in measuring the weight loss was considered only for the weights involved in the actual weighing operation. The error in each weight was estimated to be  $\pm 0.005$  milligrams and the uncertainty in reading scale divisions was  $\pm 0.003$  milligram. Since these errors were random ones they were weighted and combined according to the relationships presented in Beers (49).

$$\sigma_w = [\sigma_{wc}^2 + \sigma_{NP}^2]^{\frac{1}{2}}, \text{ where}$$

$\sigma_w$  = the error in weight loss,

$\sigma_{wc}$  = the error in the total of the weights changed, and

$\sigma_{NP}$  = the error in the scale reading of the null point.

For this investigation the error was 0.6 per cent for a one milligram weight loss and 0.06 per cent for a ten milligram weight loss.

The error in the measured temperature was taken as the square root of the sum of the squares of the individual contributions according to the equation



$$\sigma_T = [\sigma_{\text{cal.}}^2 + \sigma_R^2 + \sigma_I^2]^{\frac{1}{2}}, \text{ where}$$

$\sigma_T$  is the error in measured temperature,

$\sigma_{\text{cal.}}$  is the error in indicated temperature due to thermocouple location,

$\sigma_R$  is the range of temperature during an experiment, and

$\sigma_I$  is the instrument error.

The variation of indicated temperature in the finger compared to the actual sample temperature was estimated to be  $\pm 0.5^\circ\text{C}$ . The error in reading the potentiometer was  $\pm 0.25^\circ\text{C}$ . The temperature was not entirely constant during the course of a vapor pressure measurement. The mean temperature was taken as the temperature of the measurement and the maximum observed variation as the error in that temperature. The exponential dependence of vapor pressure on temperature magnifies the error in pressure caused by an error in temperature. For the metals used in this investigation, at  $1000^\circ\text{C}$  a  $1^\circ\text{C}$  error in temperature results in about a 2.4 per cent error in the measured pressure.

The Clausius Factor,  $Q$ , was determined by interpolation of the values given by Demarcus (50). These are considered slightly more precise than the values originally calculated

by Clausing (51). The contributions to the error in the Clausing Factor consist of an interpolation error in reading the graph, an error in estimation of the orifice length to radius, and an error due to the departure of the orifice shape from the supposed right circular cylinder. The magnitude of this latter source of error could not be exactly determined, but was considered to be negligible. The orifices were very close to the supposed geometry as evidenced by the circularity seen in the photographs of the entrance and exit ends. When the other Clausing Factor errors are summed in the manner used previously, the error in  $Q$  is estimated to be  $\pm 0.5$  per cent.

The overall error in the pressure determinations was computed by summing the contributions made by the individual errors in the following manner:

$$\sigma_P = [\sigma_w^2 + \sigma_A^2 + \sigma_T^2 + \sigma_t^2 + \sigma_Q^2]^{\frac{1}{2}}, \text{ where}$$

$\sigma_P$  = the per cent error in pressure,

$\sigma_w$  = the per cent contribution by the error in weight loss determination,

$\sigma_A$  = the per cent error due to orifice area measurement,

$\sigma_T$  = the per cent contribution by the error in temperature,

$\sigma_t$  = the per cent contribution by the error in time,

and

$\sigma_Q$  = the per cent contribution by the error in the

Clausing Factor.

The overall error in the measured pressure as computed by the preceding expression varied from about two per cent to five per cent with the average being about 2.4 per cent. It is to be emphasized that this error analysis is primarily concerned with accuracy. The precision obtained using the same effusion cell was considerably better.

For the binary systems, the composition of the salt phase was determined on the basis of analyses of the contents of the effusion cell upon completion of the vapor pressure determinations. The error in the volumetric chloride determination of the quantity of salt was estimated to be  $\pm 1.0$  milligram. The error in determining the metal content of the effusion cell was due primarily to the error in determining the weight at which the metal had been completely volatilized from the effusion cells. This zero point error was estimated to be  $\pm 0.5$  milligrams which resulted in a  $\pm 0.2$  to  $0.5$  mole per cent error in metal composition, depending on the sample size used in the effusion cell.

## RESULTS AND DISCUSSION

## A. Knudsen Effusion Conditions

In the classical Knudsen method (46) of vapor pressure measurement, a small portion of the vapor within an isothermal enclosure is allowed to escape through a small orifice into a high vacuum. The rate of escape of the vapor is determined and pressure is computed from the following relation;

$$P = \frac{w}{t} \frac{1}{aQ} \left[ \frac{2\pi kT}{m} \right]^{\frac{1}{2}} \quad (\text{Equation 5})$$

where  $P$  = the vapor pressure in dynes-cm<sup>-2</sup>,

$w$  = weight loss through the orifice in grams,

$t$  = time for the weight loss in seconds,

$a$  = orifice area in cm<sup>2</sup>,

$k$  = Boltzman's Constant in ergs °K<sup>-1</sup> molecule<sup>-1</sup>,

$Q$  = Clausing Factor, and

$m$  = weight in grams of the species effusing through the orifice.

This equation represents an idealized situation which assumes equilibrium conditions prevail within the isothermal enclosure containing the vapor. Furthermore, the flow through the orifice is assumed to be random molecular flow, sometimes

called Knudsen Flow, rather than lamillar or turbulent fluid flow.

Carlson et al. (52) treats the problem of equilibrium within the cell by considering the interior of the effusion vessel as composed of three regions; the interior of the cell exclusive of orifice and evaporating areas, the evaporation surface, and the orifice area. The introduction of an orifice is treated as a perturbation on the equilibrium conditions which would prevail in the absence of this orifice. This perturbation arises from several considerations. The escape of molecules from the cell would cause the velocity distribution of the confined gas to become non-Maxwellian. At equilibrium the net rate of evaporation from the surface of the substance being investigated would be zero. In the presence of the orifice at steady state flow conditions, the net rate of escape of molecules through the orifice must be equal to the net rate of evaporation from the surface of the material being investigated. If the maximum net rate of evaporation was low, the measured pressure could be considerably lower than the equilibrium pressure. In the treatment by Carlson et al. (52) the cell parameters considered for circular effusion cells are as follows:

$H \equiv L/R_1$  and  $D \equiv \frac{R_0}{R_1}$ , where

$L$  = height of cell,

$R_1$  = radius of the cell body, and

$R_0$  = radius of the orifice.

These authors, assuming an evaporation coefficient of 0.1 or greater, tabulate deviations from true pressures for various values of  $H$  and  $D$ . As  $D$  and  $H$  increase, the deviations from equilibrium pressure become larger. For the cells used in those experiments the maximum value of  $D$  was 0.037 and the maximum value of  $H$  was 8.0. For these values the measured pressure would be 0.2 per cent lower than the equilibrium vapor pressure.

In the preceding discussion, the inclusion of a numerical value for the evaporation coefficient might be open to question, since it is usually not measured. Rossman and Yarwood (53) present an estimate of the maximum error introduced by a variation in the evaporation coefficient as follows:

$$P_m/P_E = 1/[1 + f/\alpha] \quad (\text{Equation 6})$$

where  $P_m$  = apparent pressure as computed from Equation 5,

$P_E$  = true equilibrium pressure,

$f$  = ratio of effective orifice area to evaporation area, and

$\alpha$  = evaporation coefficient.

For the cells utilized in these experiments, the surface area of the liquid, assuming no meniscus, was from 500 to 3000 times larger than the effective orifice area. This represents "f" values of from 0.002 to 0.0003. By utilizing Equation 6, it is estimated that only for an  $\alpha$  of 0.1 or less would a pressure variation be detected in these experiments. No variation of measured pressure with variation in "f" was detected. Knacke and Stranski (54) report  $\alpha$  values of about unity for most liquid surfaces and feel that, in general, liquids should exhibit evaporation coefficients close to unity.

The problem as to the nature of the flow through the orifice is not easily answered. Knudsen (46) originally stated that when the mean free path of the gas was at least ten times larger than the diameter of the orifice random molecular flow would occur. In theory, Knudsen flow conditions could be obtained even at quite high pressures provided sufficiently small orifices could be made. In practicality, mechanical details of construction of the orifices set upper limits on the applicability of pressure measurements by Knudsen effusion. Dushman (55) presents graphs and equations

showing the departure from Knudsen flow as the ratio of mean free path to orifice diameter decreases. These equations are not experimentally determined and hence the validity of Knudsen flow conditions must be verified by direct experimentation for the higher pressure regions.

Preliminary experiments indicated the vapor pressure of liquid strontium to be in the range of uncertainty as to type of flow occurring through the available orifices. A series of vapor pressure determinations were carried out on liquid strontium over the temperature range from 775 to 950°C with orifices varying in diameter from 0.150 to 0.686 millimeters. These results are tabulated in Appendix A. From plots of  $\log_{10} P$  versus  $1/T$  for each orifice used, interpolated values of pressure were obtained at twenty-five degree intervals over the range from 775°C to 900°C. These values are listed in Table 5. The measured pressures at each of these temperatures were plotted against orifice diameter as shown in Figure 4. At a given temperature, the pressure was found to be independent of orifice diameter up to a point and then show an increase in pressure for increasing orifice diameters. The observed breaks in the curves were termed "critical diameters" and were interpreted to signify the breakdown of



Table 5. Interpolated vapor pressures of strontium for different orifice diameters

Orifice diameter (inches)	Pressure mm Hg	Temperature °K	Clausing factor
0.006	2.4	1048	0.447
"	3.7	1073	"
"	5.8	1098	"
"	8.9	1123	"
"	13.3	1148	"
"	19.6	1173	"
"	28.7	1198	"
0.0086	2.4	1048	0.566
"	3.8	1073	"
"	5.9	1098	"
"	9.0	1123	"
"	13.5	1148	"
"	19.3	1173	"
0.0142	2.3	1048	0.423
"	3.7	1073	"
"	5.7	1098	"
"	9.0	1123	"
"	15.8	1148	"
0.0274	8.36*	1047.5	0.786
0.0236	3.12*	1049	.737
0.0192	2.4	1048	1.000
"	3.5	1073	"
"	12.6	1098	"
0.021	2.36*	1045	"
"	5.41*	1073	"
0.168	2.3	1048	0.656
"	3.5	1073	"
"	6.8	1098	"
0.0112	2.35	1048	0.465
"	3.7	1073	"
"	5.7	1098	"
"	8.7	1123	"
"	12.8	1148	"
"	20.8	1173	"

\*Denoted a measured pressure.

Table 5. (Continued)

Orifice diameter (inches)	Pressure mm Hg	Temperature °K	Clausing factor
0.0140	3.8	1073	0.455
0.0146	2.4	1048	0.2081
"	3.7	1073	"
"	5.8	1098	"
"	10.3	1123	"
"	34.0	1148	"
0.0136	3.6	1073	0.452
"	5.9	1098	"
"	8.9	1123	"
"	14.2	1148	"
"	26.8	1173	"

Knudsen flow conditions. The "critical diameter" as a function of temperature was plotted in Figure 5 and compared to the mean free path of the atoms in the gas. The mean free path was calculated from the equation presented by Dushman (55) as follows:

$$L = \frac{2.331 \cdot 10^{-2} T}{P_{\text{mm Hg}} D^2} \quad (\text{Equation 7})$$

where  $L$  = mean free path in centimeters,

$T$  = absolute temperature °K,

$P_{\text{mm Hg}}$  = equilibrium vapor pressure in mm of Hg, and

$D$  = molecular diameter in centimeters.

Figure 4. Pressure variation with orifice diameter for various temperatures

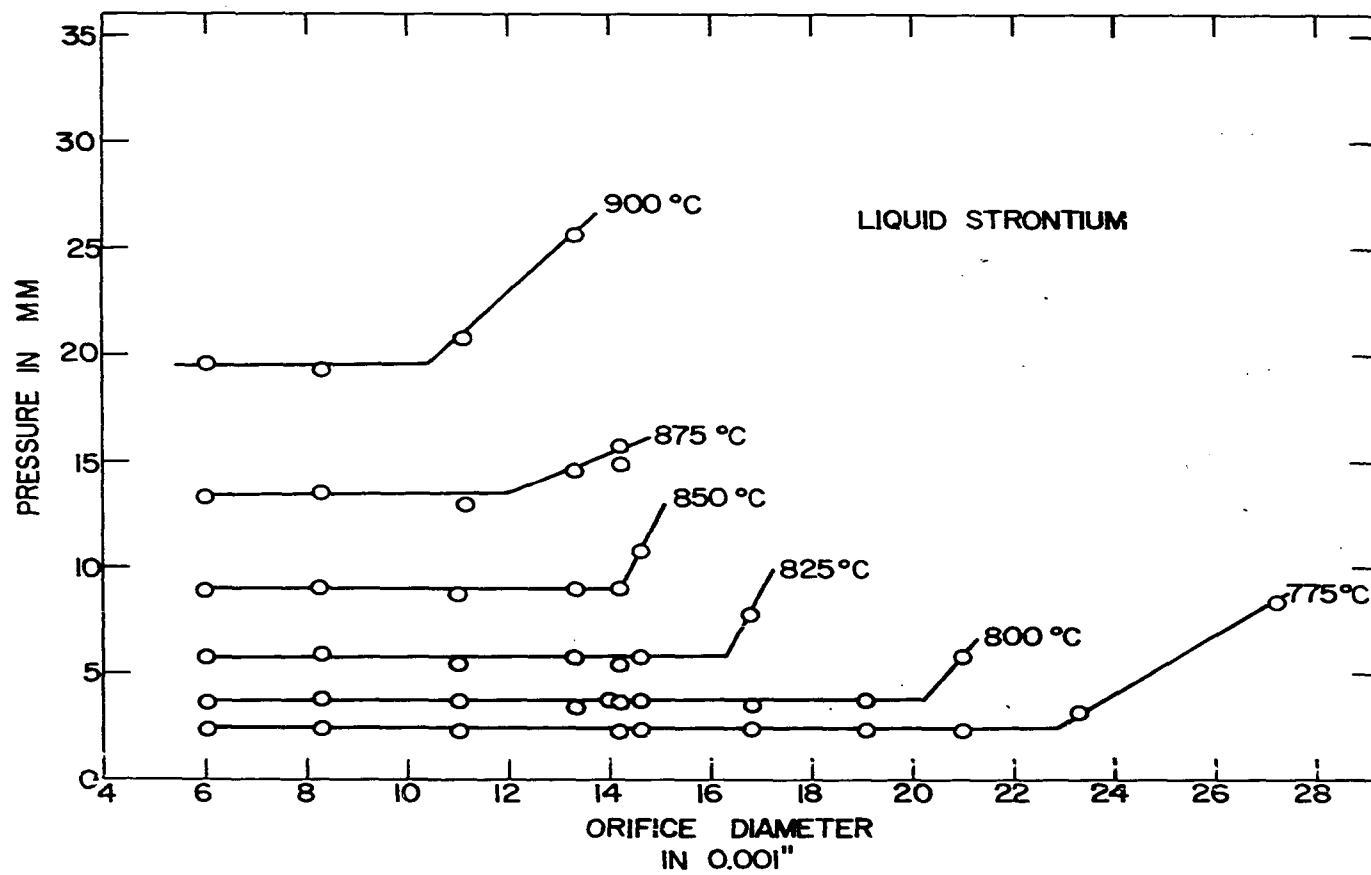
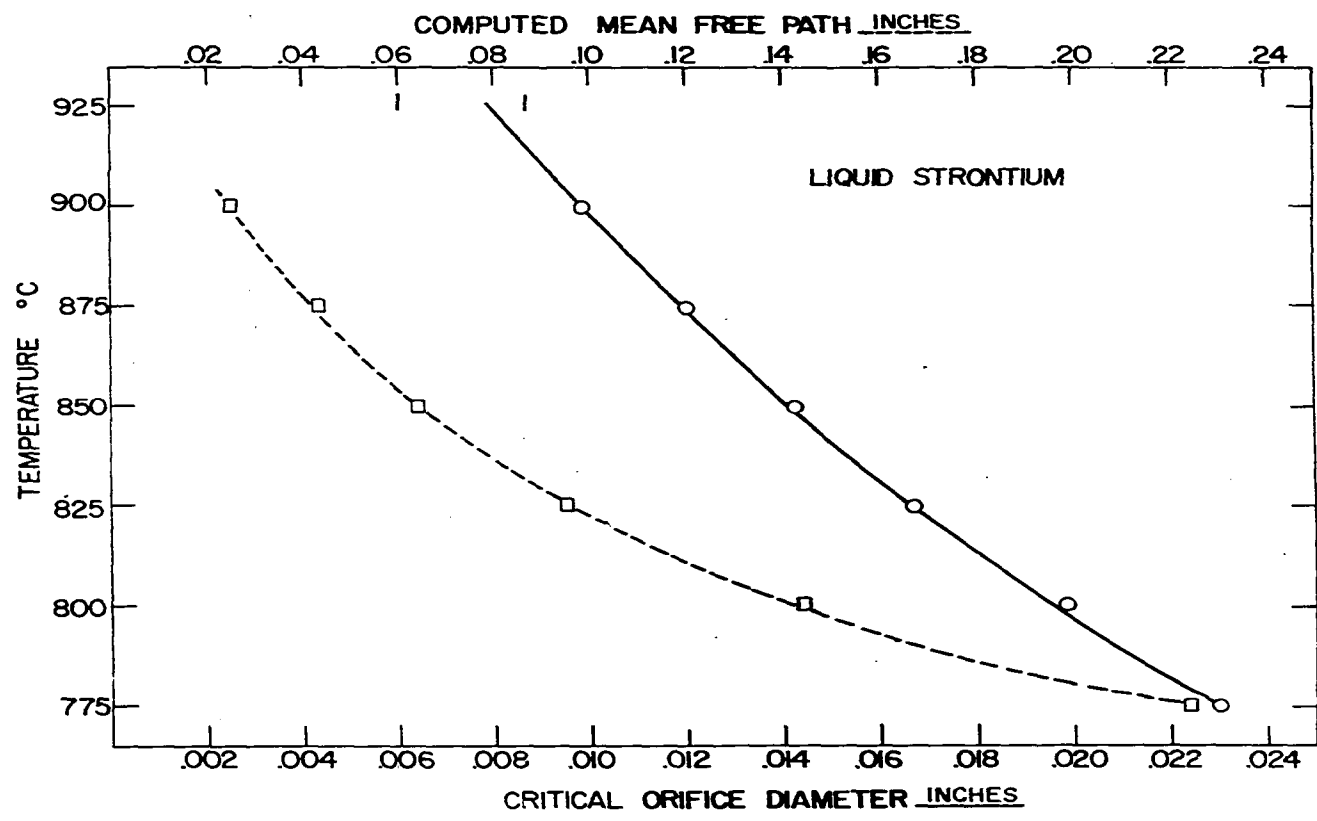


Figure 5. Critical orifice diameter and mean free path variation with temperature



The molecular diameter was computed from the x-ray density for the solid given by Hanawalt (56) by using a hard sphere approximation and assuming no change in diameter upon volatilization. From Figure 5 it may be seen that a simple ratio of mean free path to orifice diameter does not represent a valid criterion for determining the onset of hydrodynamic flow. Though the value of ten for this ratio, as quoted by Knudsen (46) would certainly be satisfactory at all temperatures and pressures used in this experiment, it does not represent the lower limit for the onset of hydrodynamic flow. Values of the ratio of mean free path to orifice diameter as low as two were found to give valid Knudsen Flow conditions through the orifice at 900°C.

The vapor pressure of calcium and barium was considerably lower than that for strontium and no detectable effect of orifice diameter on the measured pressure was observed. The orifices used for barium and calcium were 0.356 mm in diameter or less.

The Clausing factor,  $Q$ , (51) represents a correction necessitated by the use of an orifice of finite length. For orifices of finite length, some of the vapor passing through the orifice is reflected by the orifice walls back into the

vapor chamber, with the result that less vapor is transmitted to the outside vacuum. The calculation of this factor assumes that when an atom or molecule collides with the wall there is no persistence of velocity and the particle leaves the surface in a direction which is totally independent of the direction of incidence. The distribution of directions of an infinitely large number of particles after reflection from a surface follows Lambert's cosine law. The results of this calculation for cylindrical and rectangular orifices are tabulated in Demarcus (50). Balson (57) shows results of a similar calculation for a conical orifice.

The term  $m$  in Equation 5, the weight of the effusing particle can present difficulties when the vapor species are unknown. The alkaline earth metals, calcium, barium, and strontium, have been reported by Bacher and Goudsmit (58) and Ditchburn and Gilmour (59) to be monatomic in the vapor state. Herzberg (60) presents data which indicate the only gaseous species expected for the alkaline earth chlorides will be the dichlorides.



## B. Vapor Pressure of Pure Components

### 1. Barium

The vapor pressure of liquid barium was measured from 1029° to 1280°K. A least squares treatment of the data gave the following equation:

$$\text{Log}_{10}P_{(\text{mm Hg})} = -(9938 \pm 272)T^{-1} + (8.154 \pm 0.198).$$

(Equation 8)

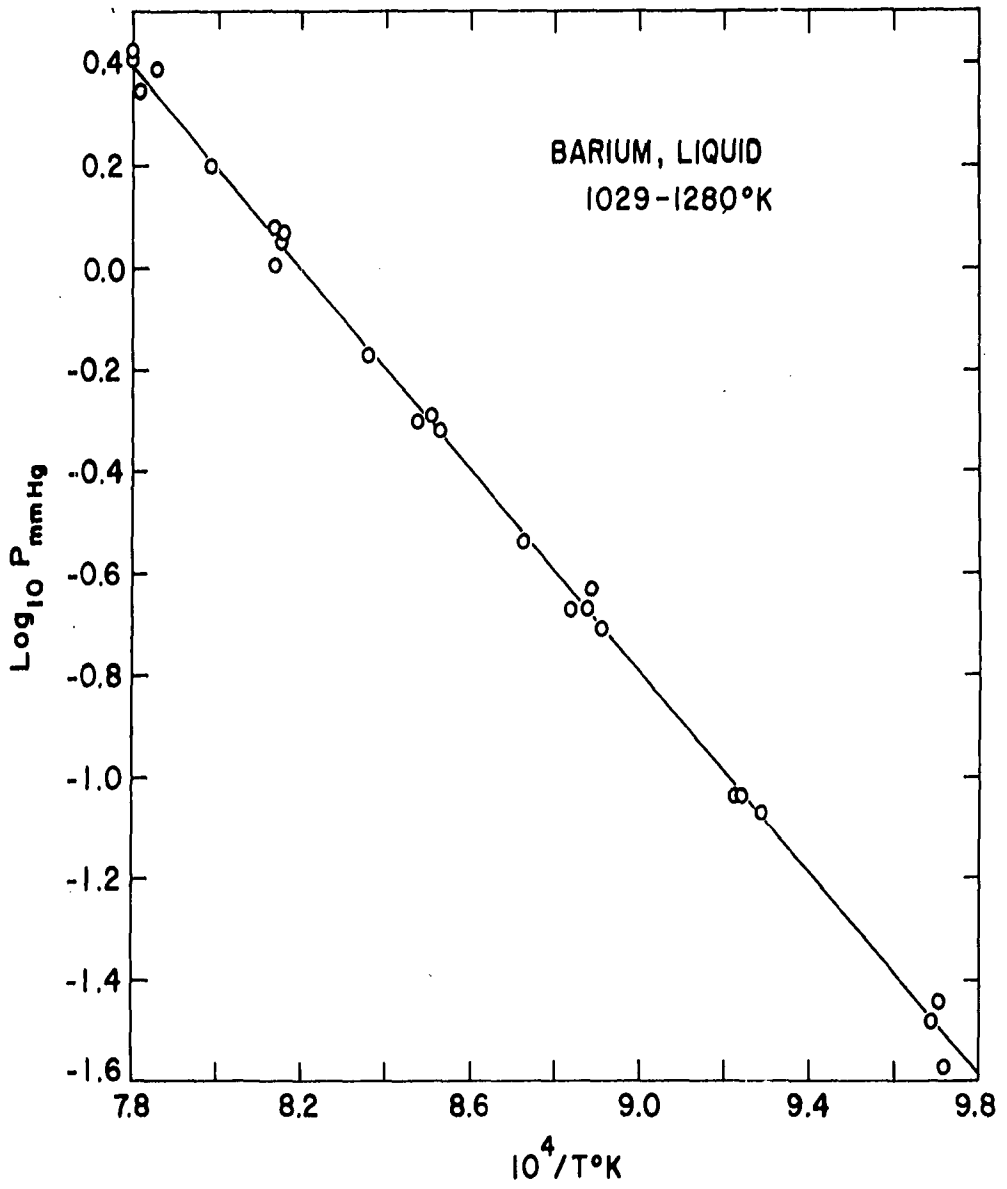
In this and all subsequent least squares representation of data the uncertainties listed represent 95 per cent confidence limits calculated from the deviations from the mean. Though they are greater than the average deviations, they do not account for systematic errors and are only measures of precision, not estimated accuracy. This equation gave an enthalpy of vaporization of  $45.48 \pm 1.24$  Kcal per mole. The results of the vapor pressure measurements are given in Table 6 and shown graphically in Figure 6.

Only two investigators have reported vapor pressures of liquid barium. Ruff and Hartmann (61) made measurements over the temperature range from 1203-1403°K using an evaporation technique. The data of this early investigation have been considered incorrect by Hultgren et al. (62) due to an improbably low boiling point and high entropy of vaporization.

Table 6. Vapor pressure of liquid barium

Temp. °K	P <sub>mm Hg</sub>
1029.2	0.02705 ± 0.00060
1076.0	0.0843 ± 0.0160
1121.8	0.193 ± 0.0042
1145.3	0.2895 ± 0.0061
1172.9	0.4835 ± 0.0103
1195.7	0.671 ± 0.015
1228.0	1.0216 ± 0.022
1250.4	1.587 ± 0.031
1031.7	0.0332 ± 0.0008
1082.8	0.0909 ± 0.002
1130.5	0.213 ± 0.006
1179.4	0.500 ± 0.011
1228.0	1.199 ± 0.028
1279.5	2.659 ± 0.054
1124.3	0.235 ± 0.006
1173.9	0.602 ± 0.014
1224.8	1.182 ± 0.024
1280.3	2.599 ± 0.058
1029.3	0.0358 ± 0.001
1081.7	0.0920 ± 0.002
1126.3	0.213 ± 0.005
1174.9	0.510 ± 0.010
1225.0	1.149 ± 0.022
1271.9	2.459 ± 0.051

Figure 6. Vapor pressure of liquid barium



Hartmann and Schneider (63) measured the vapor pressure of liquid barium over the temperature range from 1345 to 1409°K. This data gives an extrapolated pressure at 1273°K of about 6.7 mm Hg compared to 2.6 mm of Hg as found in this investigation. From the data of Hartmann and Schneider (63), Hultgren et al. (62) estimate an enthalpy of vaporization of 36.7 Kcal per mole. From a description of the starting materials used for the above investigation it may be possible the starting barium contained some magnesium which is known to have a much higher vapor pressure than barium.

Van Liempt (64) used the data of Rudberg and Lempert (65) for solid barium in the temperature range from 798°-1023°K to estimate the vapor pressure of liquid barium. By assuming an enthalpy of fusion of 2.4 Kcal per mole for barium Van Liempt estimated,

$$\log_{10} P_{\text{mm Hg}} = (-9727)T^{-1} + 7.83.$$

This expression gives a vapor pressure at 1273°K of 1.75 mm and an enthalpy of vaporization of 44.75 Kcal per mole, very close to the values found in this investigation.

## 2. Calcium

The vapor pressure of liquid calcium was measured from 1118° - 1227°K. A least squares analysis of the data gave

the following equation:

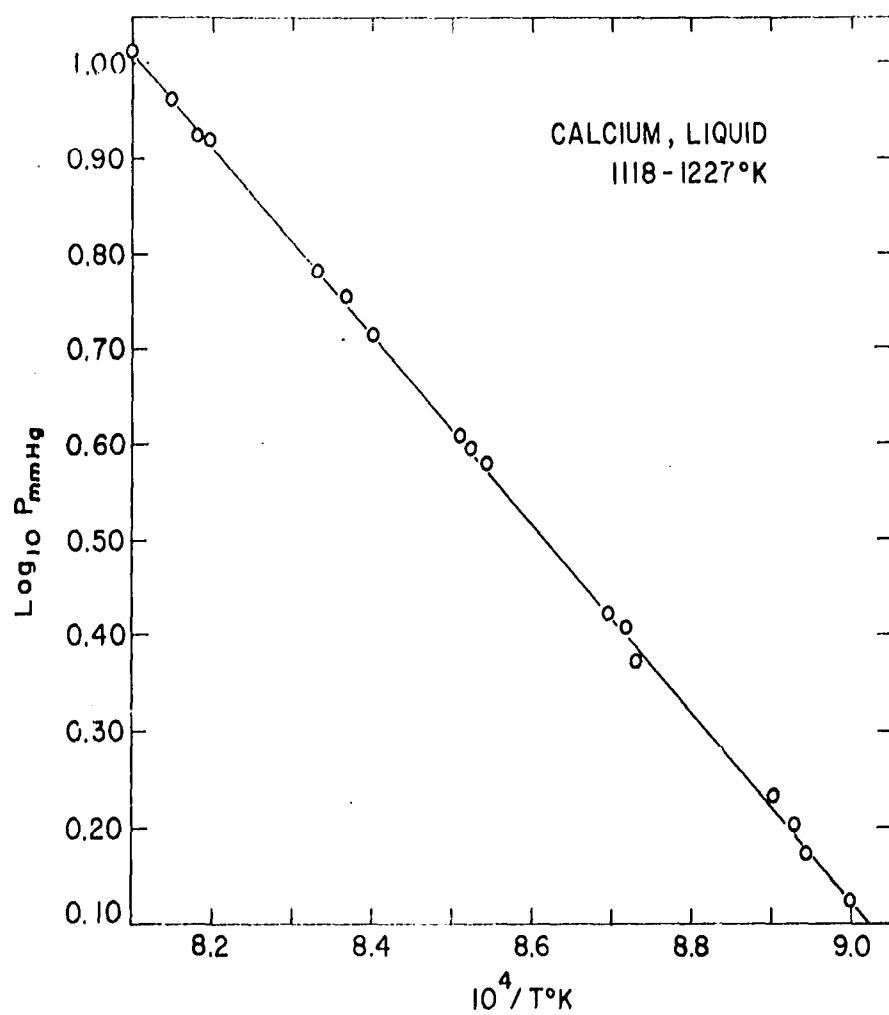
$$\log_{10} P_{\text{mm Hg}} = -(9767 \pm 190)T^{-1} + (8.920 \pm 0.160). \quad (\text{Equation 9})$$

The enthalpy of vaporization obtained from this expression is  $44.69 \pm 0.87$  Kcal per mole. The results of the vapor pressure measurements are given in Table 7 and shown graphically in Figure 7.

Table 7. Vapor pressure of liquid calcium

Temp. °K	P <sub>mm Hg</sub>
1118.0	1.49 $\pm$ 0.04
1147.2	2.57 $\pm$ 0.05
1173.0	3.95 $\pm$ 0.08
1194.7	5.69 $\pm$ 0.12
1222.0	8.41 $\pm$ 0.18
1123.2	1.72 $\pm$ 0.04
1145.0	2.54 $\pm$ 0.06
1174.7	4.06 $\pm$ 0.08
1190.0	5.19 $\pm$ 0.11
1227.2	9.20 $\pm$ 0.19
1120.0	1.59 $\pm$ 0.04
1150.0	2.66 $\pm$ 0.06
1170.0	3.80 $\pm$ 0.09
1200.0	6.05 $\pm$ 0.14
1220.0	8.32 $\pm$ 0.18

Figure 7. Vapor pressure of liquid calcium





The vapor pressure of liquid calcium has been previously measured by Hartmann and Schneider (63) and Johnson (40) by the carrier gas method. Rigney (41) measured the vapor pressure of liquid calcium by the Knudsen effusion method. These results and others based on measurements made on the solid are given in Table 8. From this table it can be seen the results of this investigation agree quite well with other published values.

Table 8. Comparison of vapor pressure data

Investigator	Vapor pressure at melting point 1114°K (mm Hg)	Enthalpy of vaporization
Smith & Smythe (66)	1.67	41.0*
Johnson (40)	1.29	41.0
Rigney (41)	1.41	44.91
Hartmann & Schneider (63)	1.35	40.30
This investigation	1.43	44.69
Tomlin (67)	3.16	43.0*
Douglas (68)	3.39	44.1*
Pilling (69)	3.98	44.4*
Rudberg (70)	0.22	42.1*
Priselkov & Nesmayanev (71)	1.37	36.9*

\*Estimated from enthalpy of sublimation by using Kubaschewski's (72) enthalpy of fusion of 2.1 Kcal/mole.

### 3. Strontium

The vapor pressure of solid strontium was measured from 877° - 1041°K. A least squares treatment of the data gave

the following equation:

$$\begin{aligned} \text{Log}_{10} P_{\text{mm Hg}} = & -(9531 \pm 106)T^{-1} + \\ & (9.474 \pm 0.093). \end{aligned} \quad (\text{Equation 10})$$

The enthalpy of sublimation calculated from this expression is  $43.61 \pm 0.49$  Kcal per mole. The vapor pressure of liquid strontium was measured from  $1050^{\circ}$  to  $1197^{\circ}\text{K}$ . A least squares analysis of the data gave the expression:

$$\begin{aligned} \text{Log}_{10} P_{\text{mm Hg}} = & -(9045 \pm 145)T^{-1} + \\ & (9.004 \pm 0.130). \end{aligned} \quad (\text{Equation 11})$$

From this equation the enthalpy of vaporization was calculated as  $41.39 \pm 0.66$  Kcal per mole. The results of the vapor pressure measurements are given in Table 9 and shown graphically in Figures 8 and 9. A simultaneous solution of Equations 10 and 11 for temperature shows a melting point of  $760^{\circ}\text{C}$ . This is considered an excellent comparison with the melting point of  $768^{\circ}\text{C}$  as reported by Rinck (73) and Hirst et al. (74). The vapor pressure of strontium in the vicinity of the melting point is not reported in the literature.

There are only two generally accepted investigations on the vapor pressure of strontium. Hartmann and Schneider (63) measured the vapor pressure of liquid strontium in the temperature range  $1199^{\circ}$  to  $1379^{\circ}\text{K}$  using a carrier gas technique.

Priselkov and Nesmeyanov (71) measured the vapor pressure of solid strontium over the temperature range from 673° to 873°K using an effusion method in conjunction with a radioactive strontium 90 tracer and a condensation target. Table 10 lists a comparison of the data for the various investigations.

Table 9. Vapor pressure of strontium

Solid		Liquid	
T°K	P <sub>mm Hg</sub>	T°K	P <sub>mm Hg</sub>
982.0	0.621 ± 0.014	1051.7	2.478 ± 0.051
1020.0	1.300 ± 0.027	1079.7	4.088 ± 0.088
936.2	0.199 ± 0.005	1101.7	5.986 ± 0.131
977.7	0.512 ± 0.013	1125.0	9.042 ± 0.181
869.7	0.033 ± 0.001	1150.2	13.570 ± 0.281
869.2	0.038 ± 0.001	1174.2	19.296 ± 0.401
926.2	0.154 ± 0.004	1050.2	2.496 ± 0.051
973.2	0.486 ± 0.011	1071.4	3.713 ± 0.072
1003.0	1.000 ± 0.021	1096.0	5.804 ± 0.141
1041.0	2.221 ± 0.045	1120.7	8.809 ± 0.179
877.6	0.037 ± 0.001	1150.0	14.027 ± 0.282
922.6	0.146 ± 0.003	1172.4	19.841 ± 0.400
970.0	0.462 ± 0.012	1197.4	28.531 ± 0.610
1023.0	1.499 ± 0.031	1087.0	4.787 ± 0.099
		1131.6	10.700 ± 0.213

Figure 8. Vapor pressure of solid strontium

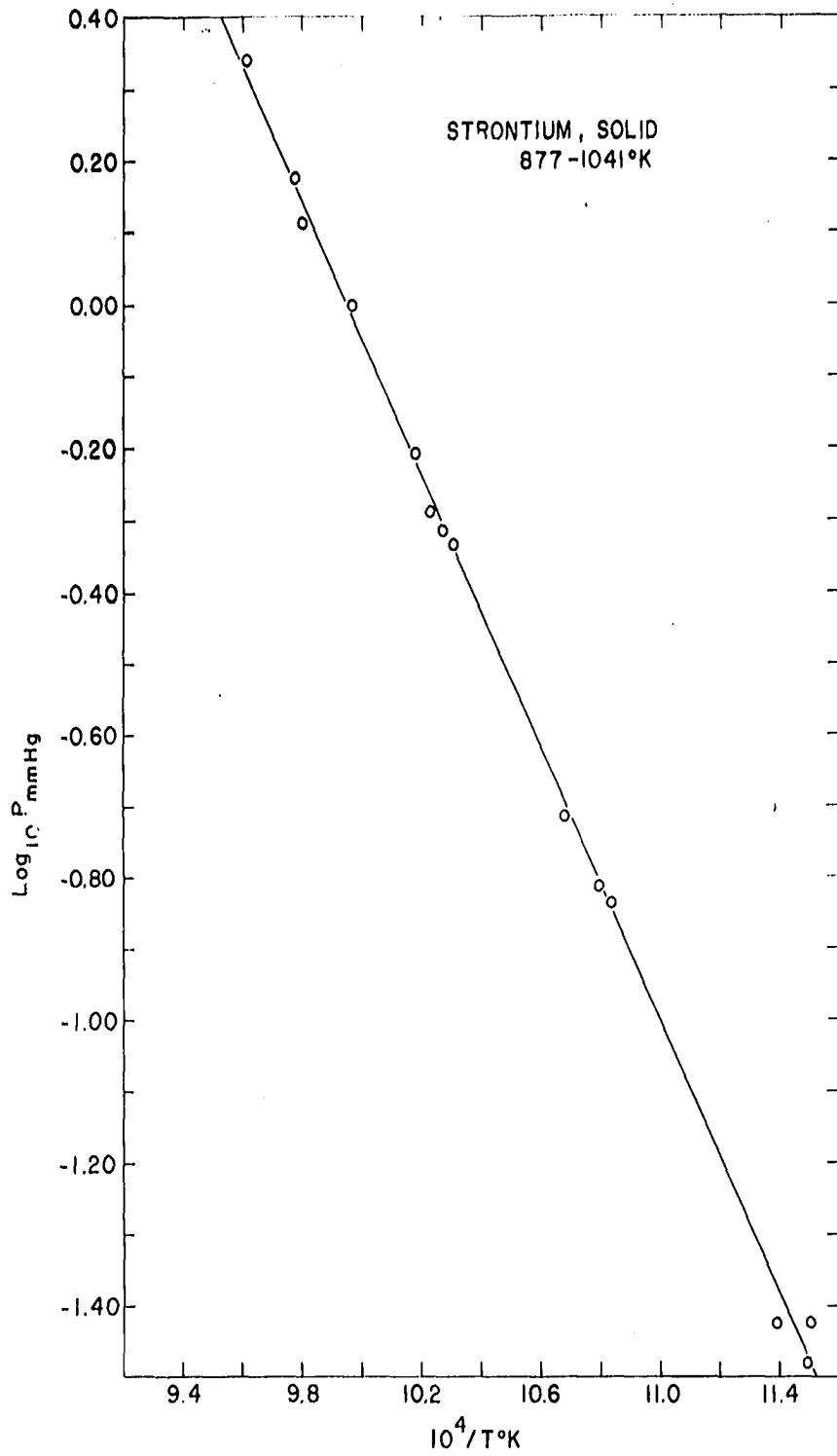


Figure 9. Vapor pressure of liquid strontium



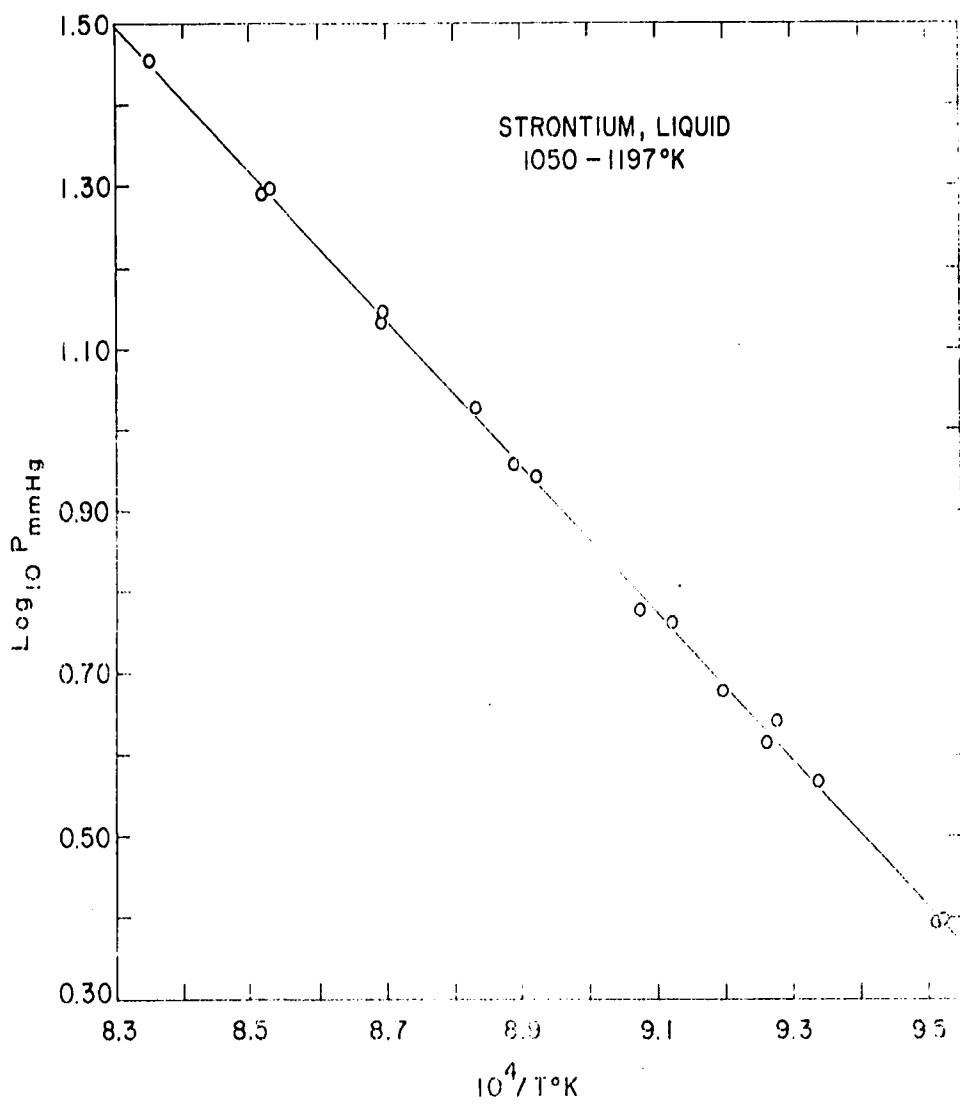




Table 10. Comparison of vapor pressure data for strontium

Investigator	Pressure mm Hg	Temp. °K	Enthalpy of vaporization or sublimation
Hartmann and Schneider (63)	13.5	1199( $\lambda$ )	40.0
This investigation	30.0	1199( $\lambda$ )	41.4
Priselkov and Nesmeyanov (71)	0.061	873 (s)	34.5
"	1.53*	1041(M.P.)	----
This investigation	0.037	873(s)	43.6
"	2.22	1041(M.P.)	----

\*Extrapolated value.

There is an allotropic transformation reported by Rinck (73) and Peterson and Colburn (75) around  $933^{\circ}$  to  $963^{\circ}$ K. This might help account for some of the discrepancy in the low temperature data. There cannot be considered any accord in the vapor pressure data for strontium to date. The enthalpy of fusion of  $2.22 \pm 1.15$  Kcal per mole calculated from the data of this investigation is quite consistent with the values of 2.1 Kcal per mole estimated by Kubaschewski (72) and 2.4 Kcal per mole estimated by Hultgren et al. (62).

#### 4. Barium chloride

The vapor pressure of liquid barium chloride was measured over the temperature range from  $1243^{\circ}$  to  $1277^{\circ}$ K. This data is listed in Table 11 and shown graphically in Figure

10. The analytical expression for these data are as follows:

$$\log_{10} P_{\text{mm Hg}} = -(14,100)T^{-1} + 8.98. \quad (\text{Equation 12})$$

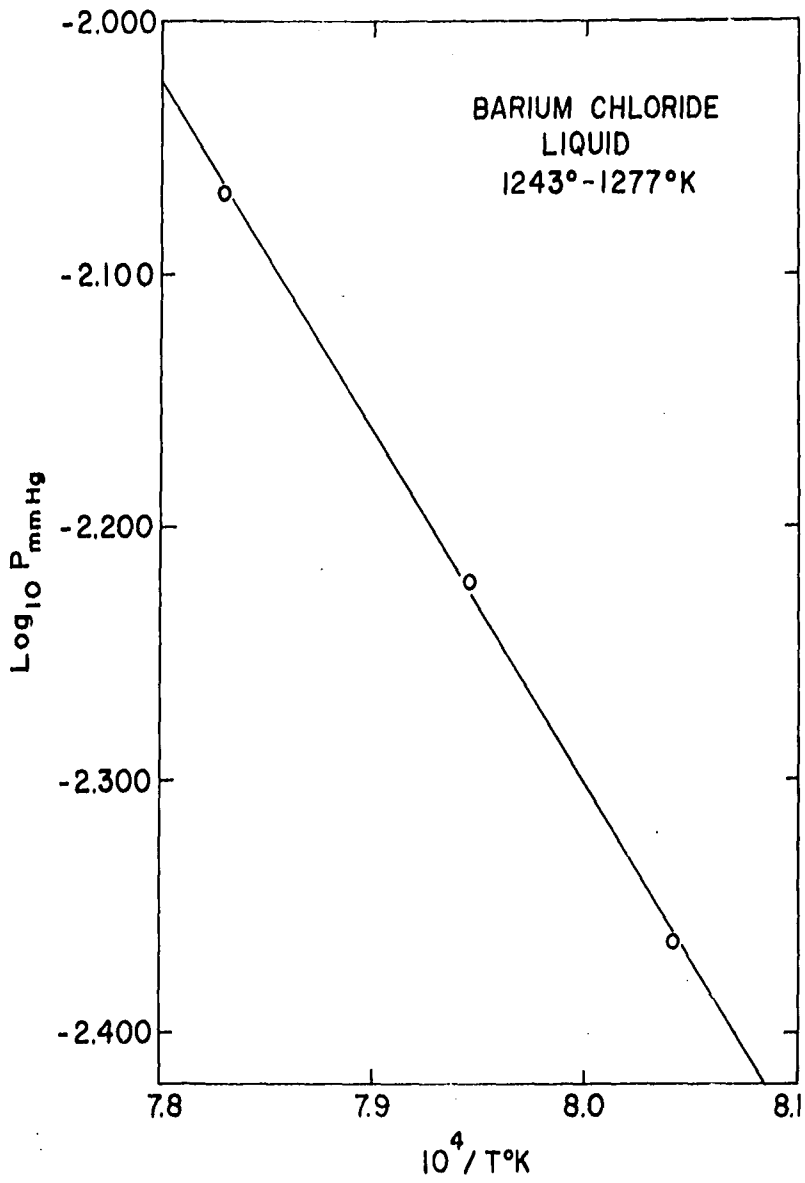
Since only three points were measured and the temperature interval was small, no confidence limits are given. From Equation 12 the enthalpy of vaporization was estimated to be  $63 \pm 4$  Kcal per mole and the normal boiling point to be  $2300 \pm 100^\circ\text{K}$ .

Table 11. Vapor pressure of liquid barium chloride

Temperature $^\circ\text{K}$	Pressure mm Hg
1243.5	$(4.33 \pm 0.10)10^{-3}$
1258.5	$(6.00 \pm 0.13)10^{-3}$
1277.0	$(8.56 \pm 0.18)10^{-3}$

Maier (76) measured the vapor pressure of barium chloride in the temperature range  $1343^\circ$  to  $1487^\circ\text{K}$  using a static pressure method. By the author's own admission (76, p. 26) this method is not suited for pressures below 1 mm of Hg and the results are not dependable. Nevertheless, Maier (76) estimated a normal boiling temperature of  $1835^\circ\text{K}$  and an enthalpy of vaporization of 59.9 Kcal per mole. Brewer (77) estimated a boiling temperature of  $2100^\circ\text{K}$  and an enthalpy of

Figure 10. Vapor pressure of liquid barium chloride



vaporization of 50.0 Kcal per mole.

### 5. Calcium chloride

The vapor pressure of liquid calcium chloride was measured over the temperature range from 1064° to 1232°K. These data are listed in Table 12 and plotted in Figure 11. The analytical expression obtained from a least squares analysis of the data is as follows:

$$\log_{10} P_{\text{mm Hg}} = -(10,656 \pm 290)T^{-1} + (7.225 \pm 0.248). \quad (\text{Equation 13})$$

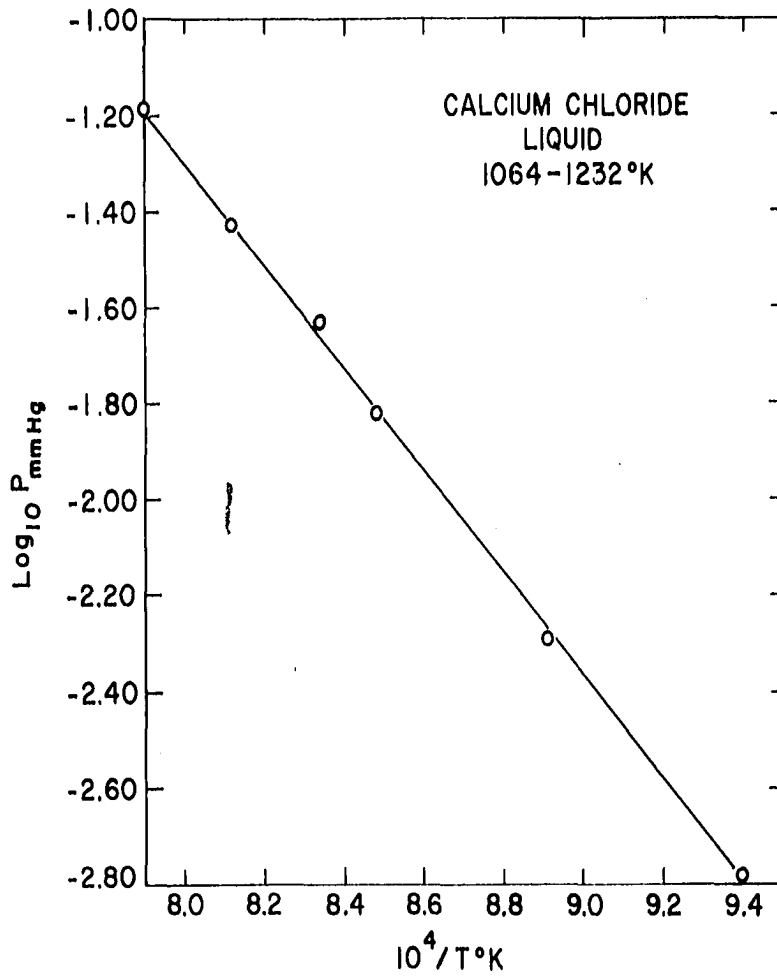
The enthalpy of vaporization calculated from Equation 13 was found to be  $48.8 \pm 1.3$  Kcal per mole and the normal boiling point was 2460°K.

Table 12. Vapor pressure of liquid calcium chloride

Temperature °K	$P_{\text{mm Hg}} \times 10^3$
1063.7	$1.660 \pm 0.033$
1122.2	$5.051 \pm 0.114$
1179.2	$15.15 \pm 0.321$
1199.0	$23.39 \pm 0.478$
1231.5	$37.21 \pm 0.743$
1265.7	$63.10 \pm 1.250$

Johnson (40) found the vapor pressure of calcium chloride at 1255°K to be 0.056 mm Hg as compared to the value of

Figure 11. Vapor pressure of liquid calcium chloride



0.054 mm calculated from Equation 13 of this investigation. Rigney (41) found a vapor pressure of calcium chloride at 1255°K to be 0.045 mm Hg and the enthalpy of vaporization to be  $49.8 \pm 1.3$  Kcal per mole. Brewer (77) estimated an enthalpy of vaporization of 55.0 Kcal per mole and a normal boiling point of 2300°K.

#### 6. Strontium chloride

The vapor pressure of liquid strontium chloride was measured from 1174° to 1286°K. A least squares treatment of the data gave the following equation:

$$\text{Log}_{10} P_{\text{mm Hg}} = -(14,688 \pm 168)T^{-1} + (9.618 \pm 0.139). \quad (\text{Equation 14})$$

This equation gave an enthalpy of vaporization of  $67.2 \pm 0.77$  Kcal per mole. The results of the vapor pressure measurements are given in Table 13 and shown graphically in Figure 12. The literature contains no reports of measurements of the vapor pressure of strontium chloride. Brewer (77) estimated an enthalpy of vaporization of 55 Kcal per mole and a normal boiling point of 2300°K. The boiling point found by extrapolation of Equation 14 from this investigation was 2190°K.



Figure 12. Vapor pressure of liquid strontium chloride

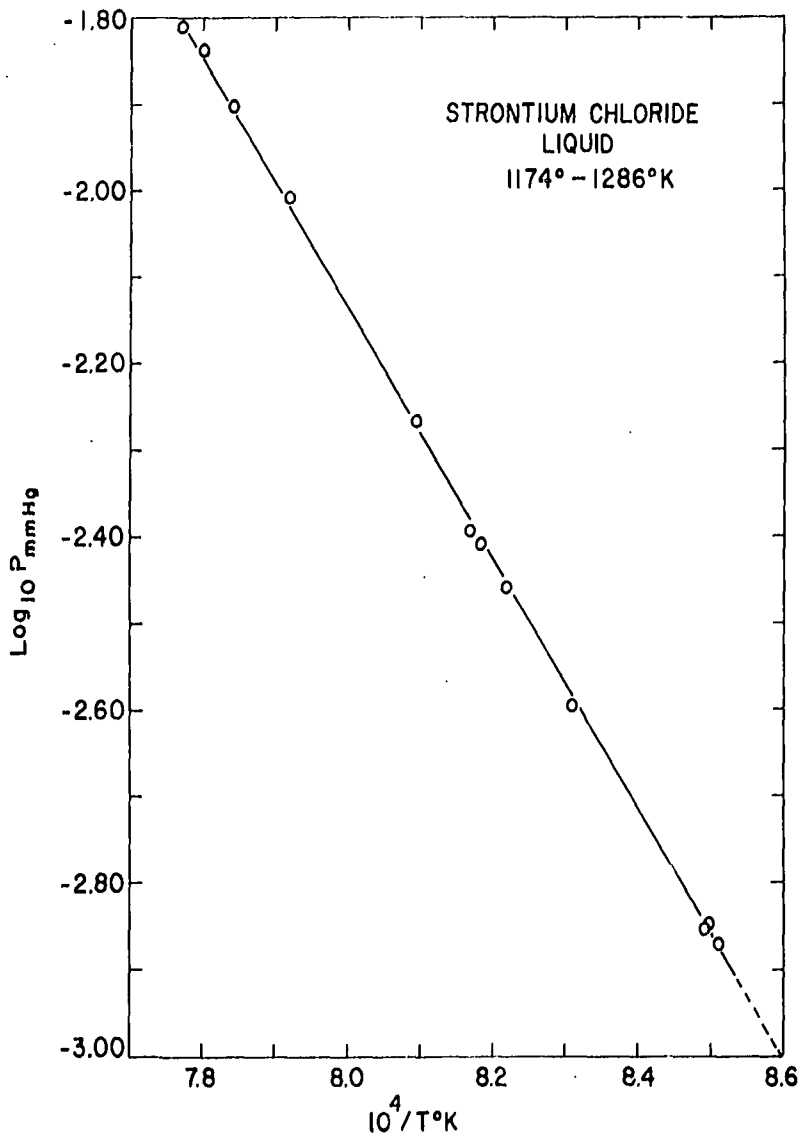


Table 13. Vapor pressure of liquid strontium chloride

Temperature °K	P <sub>mm Hg</sub> × 10 <sup>3</sup>
1178.0	1.402 ± 0.029
1217.2	3.481 ± 0.071
1264.2	9.831 ± 0.198
1281.0	14.520 ± 0.300
1177.2	1.401 ± 0.029
1203.2	2.556 ± 0.057
1224.0	4.005 ± 0.090
1174.7	1.325 ± 0.028
1221.7	3.899 ± 0.080
1275.0	1.250 ± 0.252
1235.0	5.399 ± 0.110
1286.7	15.411 ± 0.302

### C. Partial Pressures in Binary Systems

#### 1. Calcium-calcium chloride system

The vapor pressure of calcium dissolved in calcium chloride was found to obey Henry's law for a solute forming two distinguishable particles in solution for each molecule in the vapor phase. This is shown by the slope of approximately two for the plot of the isothermal variation of  $\log P_{Ca}$  vs  $\log N_{Ca}$  as shown in Figure 13. This confirms the observations made by Johnson(40) and Rigney (41) on the concentration dependence of the vapor pressure. Figure 14 shows

Figure 13: Variation of  $\log_{10}P_{Ca}$  with  $\log_{10}N_{Ca}$  for  
calcium dissolved in calcium chloride at  
860.5°C

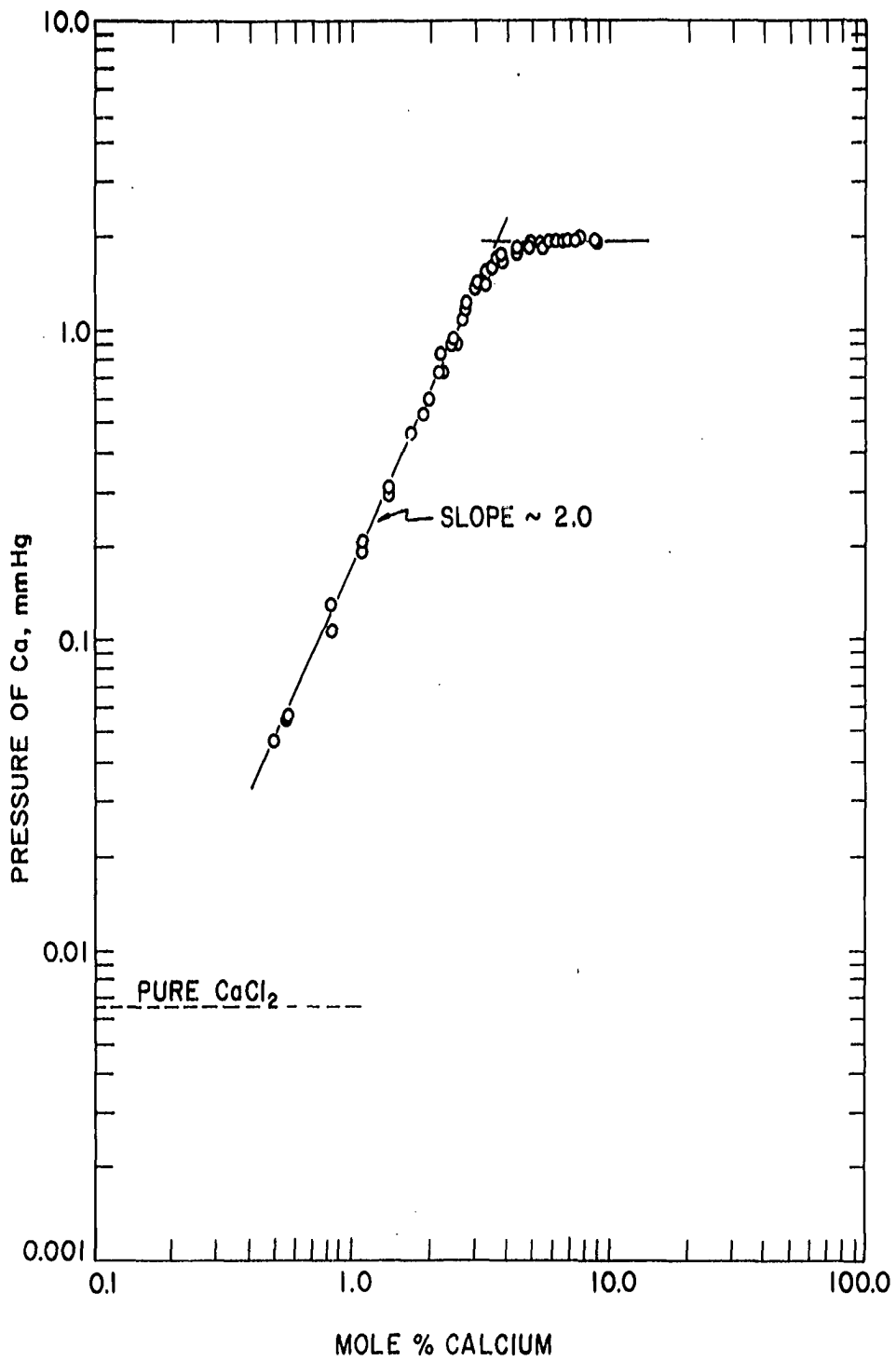
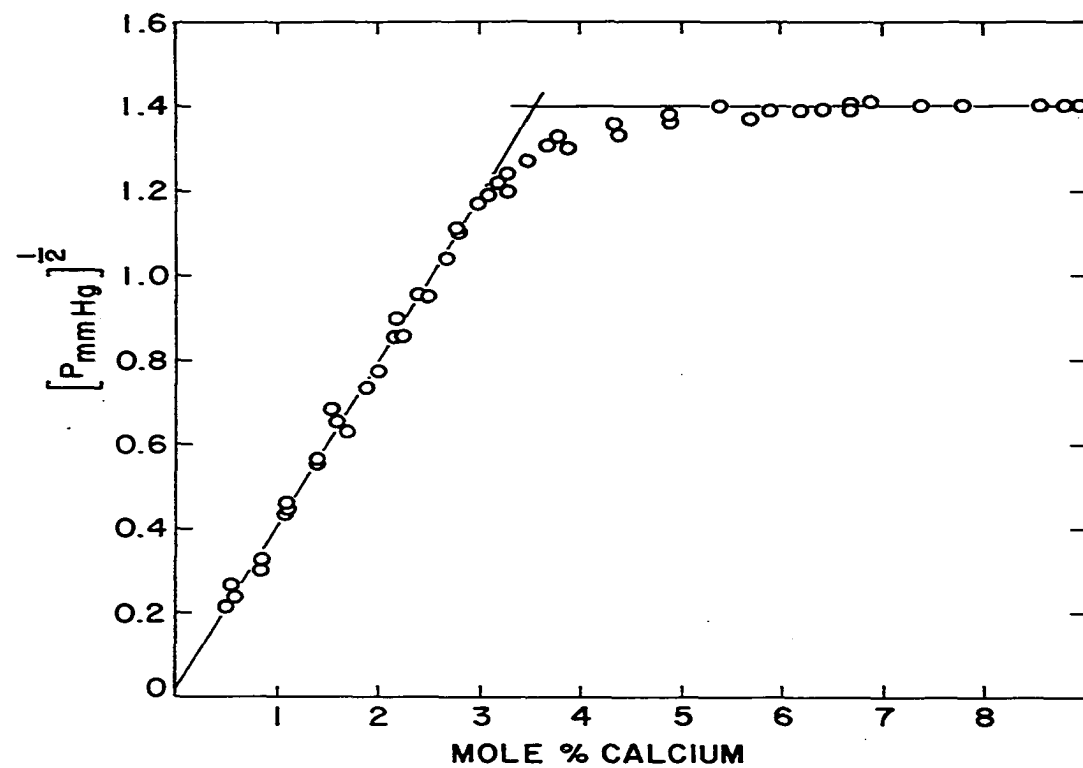


Figure 14. Variation of the square root of the vapor pressure of calcium with concentration of calcium dissolved in calcium chloride at 860.5°C



the variation of the square root of the calcium partial pressure with calcium concentration for the calcium-calcium system at 860.5°C. These data are given in Table 14. All compositions are considered to be accurate to  $\pm 0.2$  mole per cent and all pressures are considered to be accurate to  $\pm 2.8$  per cent.

Table 14. Partial pressures of calcium over calcium-calcium chloride solutions at 860.5°C

Mole % Ca	P <sub>mm Hg</sub>	Mole % Ca	P <sub>mm Hg</sub>
6.7	1.94	2.4	0.915
6.2	1.94	2.2	0.730
5.7	1.87	1.9	0.544
4.9	1.84	1.6	0.428
4.4	1.76	1.4	0.306
3.9	1.70	1.1	0.194
3.3	1.55	0.88	0.092
3.1	1.41	0.50	0.048
2.8	1.20	6.9	1.98
2.5	0.940	6.4	1.95
2.3	0.737	5.9	1.94
2.0	0.66	5.4	1.96
1.7	0.396	4.9	1.92
1.4	0.315	4.4	1.85
1.1	0.201	3.8	1.76
0.85	0.109	3.3	1.42
0.57	0.058	2.8	1.22
8.8	1.98	2.2	0.820
3.7	1.72	1.7	0.470
3.5	1.61	1.1	0.219
3.2	1.49	0.56	0.0487
3.0	1.38	8.9	1.97
2.7	1.09	7.4	1.97
		7.8	1.96



Application of the Gibbs phase rule to a two component system at constant temperature and constant phase composition shows the vapor pressure must be invariant in a two phase region. However, there was a slight but definite decrease in the partial pressure of calcium as the calcium depleted from the two phase alloy. This effect might be attributed to several causes. A first consideration was the possibility of the occurrence of some kinetic effect such as a diffusion limited surface depletion of calcium from the less dense metal-rich phase. Several different effusion cells were used with cross sectional areas varying by a factor of ten and with orifices having effusion rates varying by a factor of two. No significant differences in the variation of the partial pressure with composition were detected with these effusion cells having different evaporation area to orifice area ratios. This ruled out the possibility that kinetic effects were causing the pressure variation over the two phase region. As an alternate explanation, the effect of an impurity was considered. If some non-volatile impurity were present in the metal-rich phase, even in initially minute amounts, as the calcium was continually depleted by effusion, the amount of metal-rich phase decreases and the

concentration of this impurity would increase. If the solubility of this impurity in the metal-rich phase were substantial, a point would be reached where the impurity would be a major constituent of this phase. The system would be a ternary system and the phase rule predicts that the partial pressure of calcium would not have to remain constant. The calcium would be present at a reduced activity from that expected for the binary system and a decrease in partial pressure would be expected. This conjecture concerning the influence of impurities cannot be proved conclusively, but it was noted that even for the one vapor pressure determination which was continued until the vapor pressure of the pure salt was reached, a small but significant titration for basicity was obtained. This basicity indicates the presence of residual oxide or hydride in the salt phase.

The vapor pressure of calcium over the chloride saturated metal-rich phase was found to be 1.96 mm Hg at the higher metal concentrations where the extent of the metal-rich phase was considerable. At this same temperature of 860.5°C the vapor pressure of pure calcium was 2.02 mm Hg. Peterson and Hinkebein (36) found that calcium dissolved 1.02 mole per cent of calcium chloride at 900° C and 1.56

mole per cent of salt at 950°C. If Raoult's law is obeyed by the calcium in the saturated metal-rich phase, the presence of the salt dissolved in the metal should result in about a one per cent lowering of the vapor pressure of the calcium at the temperature of this investigation. This investigation noted about a 1.5 per cent decrease in the vapor pressure of the calcium in the two phase region.

A least squares analysis of the data below 3.5 mole per cent calcium gave the following equation:

$$[P_{\text{mm Hg}}]^{\frac{1}{2}} = 0.392 N, \quad (\text{Equation 15})$$

where P is the partial pressure of the calcium and

N is the mole per cent calcium in solution.

The solubility limit obtained by extrapolation of Equation 15 to the vapor pressure of the saturated metal-rich phase was found to be  $3.57 \pm 0.20$  mole per cent calcium at 860.5°C. This value compares very well with the measurements by Dworkin et al. (10), Peterson and Hinkebein (36), and Rigney (41).

In a later section a more complete discussion of the various solute models will be undertaken in an attempt to distinguish between the two models in which the solute was considered to form two distinguishable particles in solution

with respect to the reference state.

## 2. Strontium-strontium chloride system

The partial pressure of strontium dissolved in strontium chloride was found to obey Henry's law for a solute forming two distinguishable particles in solution for each molecule in the vapor phase. This is shown in Figure 15 by the slope of approximately two obtained from the plot of  $\log P_{Sr}$  versus  $\log N_{Sr}$ . Figure 16 shows the isothermal variation of the square root of the strontium partial pressure with strontium concentration for the strontium-strontium chloride system at 883°C. These data are given in Table 15. All compositions are considered accurate to  $\pm 0.2$  mole per cent and all pressures are considered accurate to  $\pm 2.6$  mole per cent.

The slight decrease in measured partial pressure over the two phase region was attributed to an impurity effect, since even when the vapor pressure of the pure salt was reached at the end of a run, the salt remaining in the cell gave small titration for basicity which indicated the presence of residual oxide or hydride in the specimen. The vapor pressure of strontium over the chloride saturated, metal-rich phase was found to be  $12.9 \pm 0.3$  mm of Hg at the higher metal concentrations where the extent of the metal

Figure 15. Variation of  $\log_{10}P_{\text{Sr}}$  with  $\log_{10}N_{\text{Sr}}$  for strontium dissolved in strontium chloride at  $883^{\circ}\text{C}$

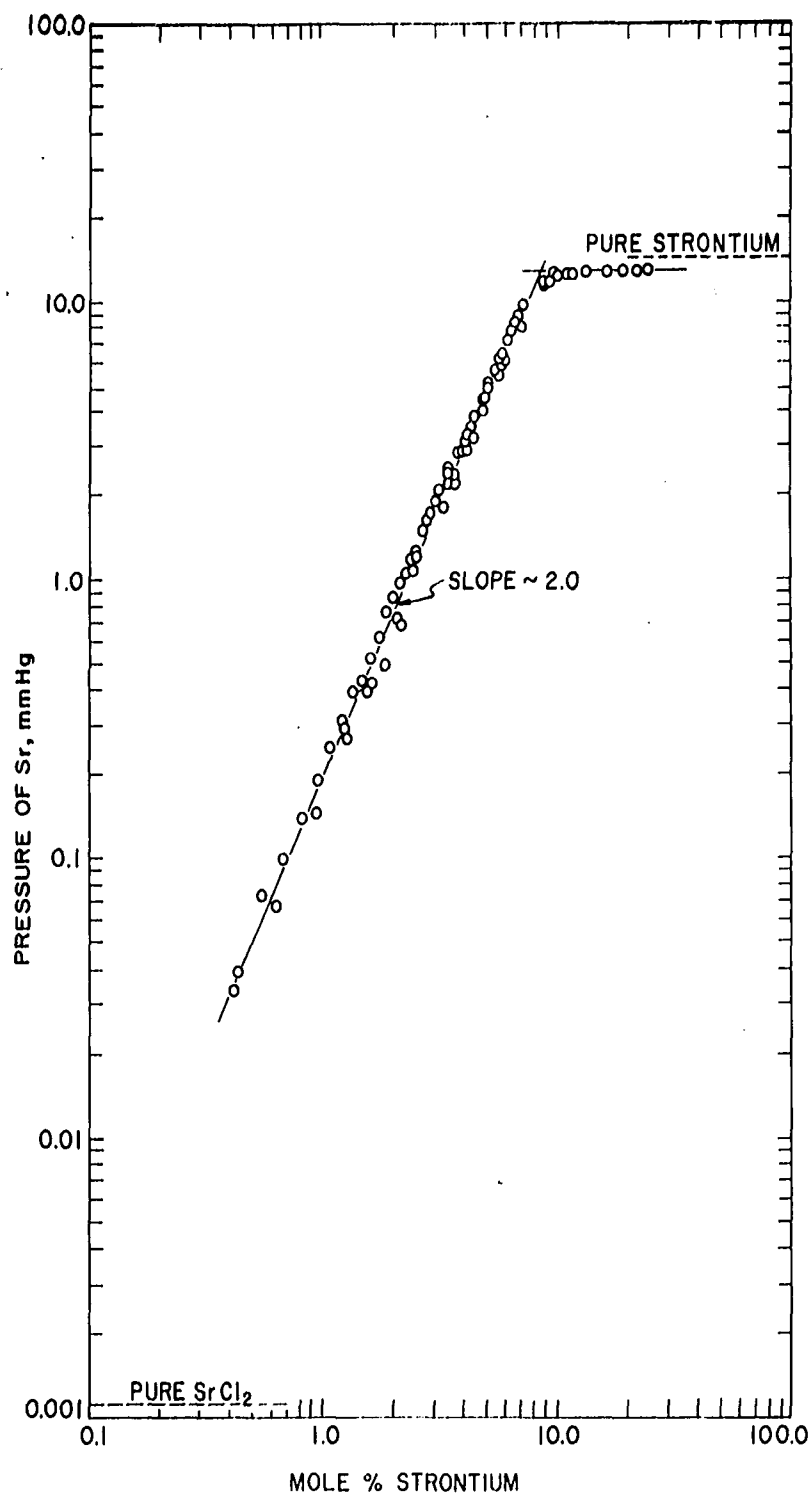


Figure 16. Variation of the square root of the vapor pressure of strontium with concentration of strontium dissolved in strontium chloride at 883°C

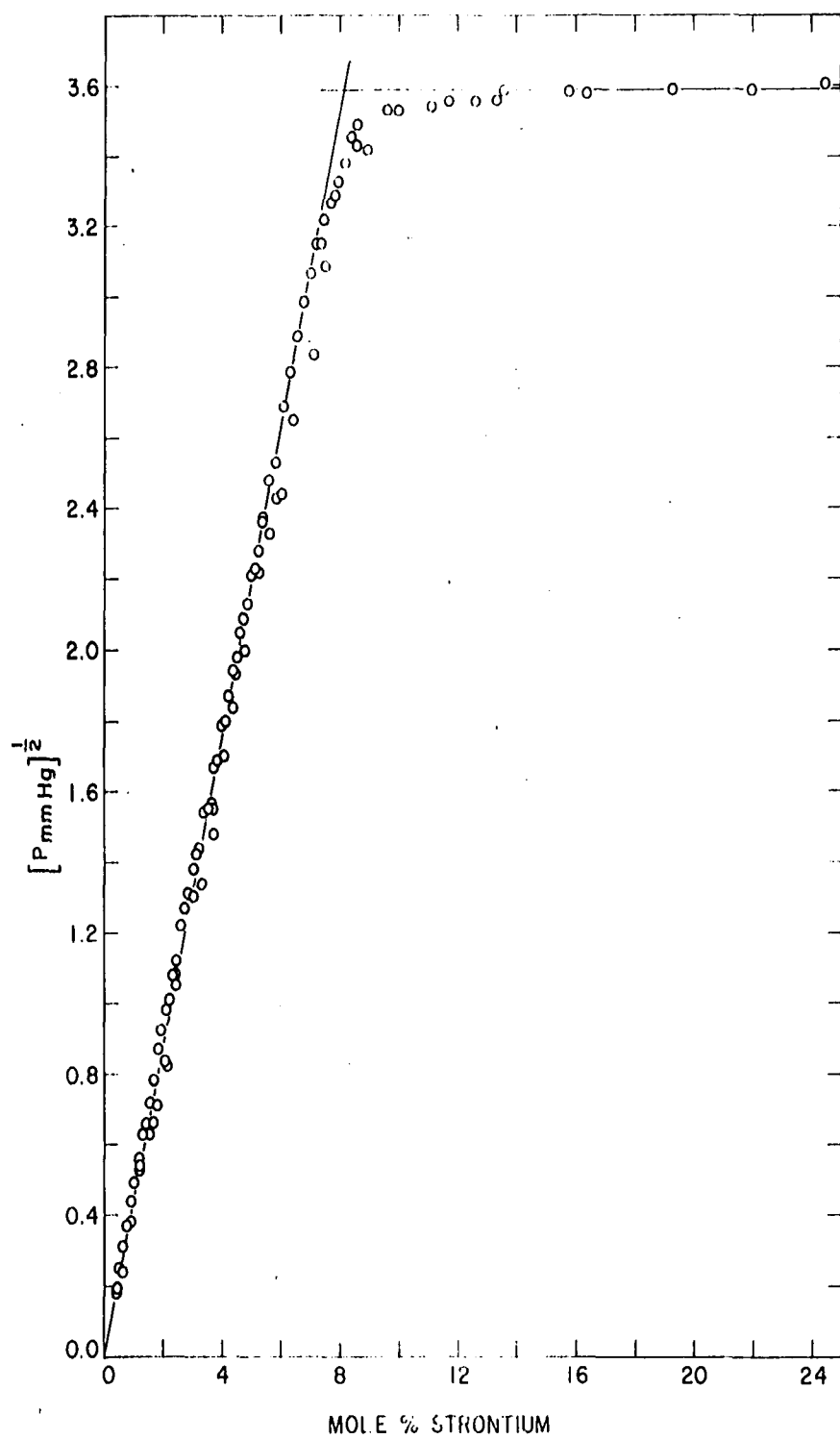




Table 15. Partial pressures of strontium over strontium-strontium chloride solutions at 883°C

Mole % Sr	P <sub>mm Hg</sub>	Mole % Sr	P <sub>mm Hg</sub>
24.54	13.02	2.50	1.20
22.02	12.94	2.09	0.71
19.33	12.90	1.68	0.44
16.44	12.86	1.27	0.28
13.35	12.70	0.43	0.04
11.71	12.62	8.63	12.18
10.01	12.47	8.40	11.80
9.66	12.47	8.20	11.36
9.31	11.75	7.95	11.08
8.96	11.85	7.72	10.71
8.24	11.43	7.49	10.40
7.88	10.82	7.26	9.91
7.52	9.57	7.03	9.41
7.15	8.07	6.79	8.91
6.03	5.96	6.31	7.81
5.65	5.41	6.08	7.22
5.27	5.02	5.84	6.39
4.49	3.71	5.60	6.15
4.10	2.90	5.36	5.58
3.71	2.20	5.24	5.20
3.31	1.80	5.12	5.00
5.00	4.90	1.98	0.860
4.87	4.52	1.85	0.761
4.75	4.40	1.72	0.619
4.63	4.21	1.59	0.515
4.51	3.87	1.46	0.436
4.39	3.77	1.33	0.396
4.26	3.51	1.20	0.321
4.14	3.26	1.07	0.246
4.01	3.21	0.94	0.192
3.95	2.78	0.94	0.150
3.89	2.86	0.81	0.138
3.77	2.78	0.67	0.100
3.65	2.47	0.54	0.0637
3.52	2.42	0.41	0.034
3.39	2.40	13.68	12.90
3.26	2.21	11.25	12.50
3.14	2.08	8.68	11.82

Table 15. (Continued)

Mole % Sr	P <sub>mm</sub> Hg	Mole % Sr	P <sub>mm</sub> Hg
3.01	1.90	7.34	9.91
2.88	1.72	5.96	5.89
2.75	1.61	5.40	5.61
2.62	1.49	4.82	4.00
		4.49	3.42
2.49	1.26	3.66	2.40
		3.07	1.70
2.37	1.18	2.47	1.10
		2.17	0.70
2.24	1.03	1.86	0.50
		1.56	0.40
2.11	0.968	1.25	0.30

phase was appreciable. At this temperature of 883°C, the vapor pressure of pure strontium would be  $14.8 \pm 0.3$  mm Hg. Emons and Hellmond(11) report the metal-rich phase to contain 3.5 mole per cent strontium chloride at 768°C. From the phase diagram presented by these authors (11) it was estimated that the solubility of strontium chloride in strontium would be about 3.6 mole per cent at 883°C. If Raoult's law were obeyed by the strontium in the saturated metal-rich phase, a lowering of the strontium partial pressure of about 3.6 per cent of that of the pure metal would be expected. In this investigation the partial pressure of strontium over the salt saturated phase was about 13 per cent lower than the vapor pressure of the pure strontium. No explanation

for this larger decrease in partial pressure is offered, but the results were reproducible using different effusion cells with widely different evaporation areas and effusion rates. It may be conjectured that the solubility limits reported by Emons and Hellmond (11) are in error, perhaps due to water contamination of the salt used in their alloy preparation.

A least squares analysis of the data for alloy compositions with less than 8.5 mole per cent strontium gave the following equation:

$$[P_{\text{mm Hg}}]^{\frac{1}{2}} = 0.441 N, \quad (\text{Equation 16})$$

where P is the partial pressure of the strontium and

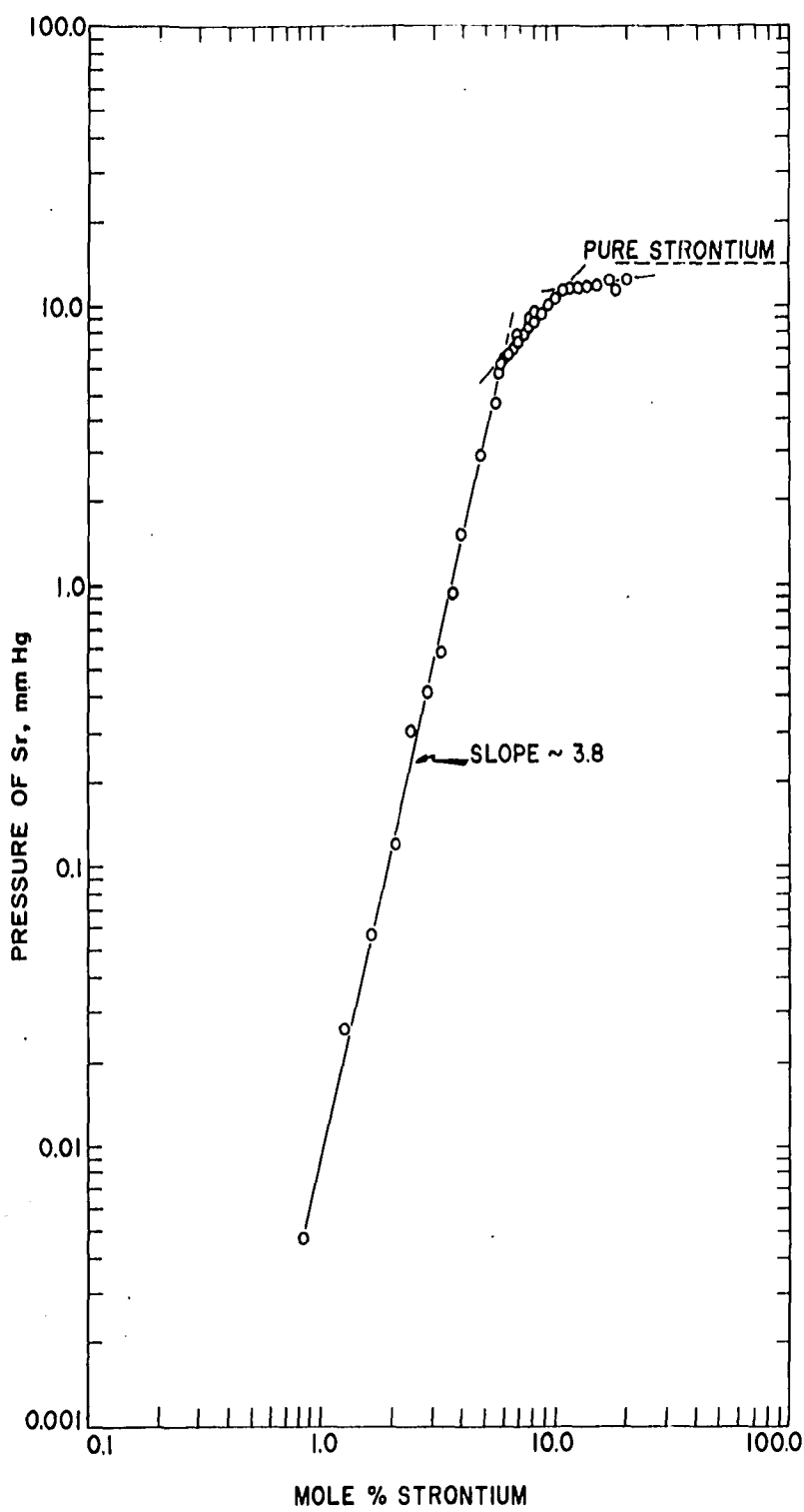
N is the mole per cent strontium in solution.

The solubility limit calculated from this equation was found to be  $8.14 \pm 0.20$  mole per cent strontium at  $883^{\circ}\text{C}$ . This value is in excellent agreement with the solubilities reported by Staffanson (4) and Dworkin et al. (10).

During the course of this investigation a number of anomalous results were obtained when utilizing one particular batch of pre-alloyed strontium chloride. These results were consistent and reproducible but vastly different from the data obtained utilizing other batches of strontium chloride. The possibility of contamination or incomplete dehydration

of the salt utilized in preparation of the master alloy was suspected. In an attempt to determine the cause of the anomalies, an effusion cell was loaded with the usual charge of freshly prepared master alloy and placed into an argon filled screw top Mason jar along with a piece of blotting paper moistened with 10 to 20 milligrams of water. After allowing the effusion cell to remain in this jar for about ten hours, the vapor pressure determinations were carried out. These results duplicated the anomalous data noted earlier. Figure 17 shows a plot of these results at  $883^{\circ}\text{C}$ . These compositions were determined by continuing the effusion until the vapor pressure of pure strontium chloride was realized. Analysis of the contents of the effusion cell gave a large basicity titration indicating the presence of about 10 mole per cent oxide or hydride in the salt phase. Comparing Figure 17 to Figure 15 reveals several important differences. The slope of the plot of  $\log P_{\text{Sr}}$  versus  $\log N_{\text{Sr}}$  is much different for the water contaminated specimen and indicated a different solution reaction. For this contaminated run, the vapor pressure of strontium over the two phase region was lower and showed a greater decrease with decrease in amount of metal-rich phase than did the anhydrous

Figure 17. Variation of  $\log_{10}P_{\text{Sr}}$  with  $\log_{10}N_{\text{Sr}}$  for strontium dissolved in water contaminated strontium chloride at 883°C



materials. The apparent solubility limit of strontium in strontium chloride was about 11 mole per cent for the water contaminated material. This is a possible explanation for the high metal solubilities reported by Emons and Hellmond (11).

### 3. Barium-barium chloride system

The vapor pressure of barium dissolved in barium chloride was found to obey Henry's law, in dilute solutions, for a solute forming two distinguishable particles in solution for each molecule in the vapor phase. This is shown by the slope of two for the initial portion of the plot of the variation of  $\log P_{Ba}$  versus  $\log N_{Ba}$  in Figure 18. Figure 19 shows the variation of the square root of the barium vapor pressure with barium concentration for the barium-barium chloride system at  $975^{\circ}\text{C}$ . These data are presented in Table 16. All compositions are considered accurate to  $\pm 0.20$  mole per cent and all pressures are considered accurate to  $\pm 2.8$  per cent.

In the calcium and the strontium systems the vapor pressure of the salt was thirty to fifty times less than the vapor pressure of metal at the lowest concentrations measured and no corrections for the vapor pressure of the salt were

Figure 18. Variation of  $\log_{10}P_{Ba}$  with  $\log_{10}N_{Ba}$  for  
barium dissolved in barium chloride at  
975°C



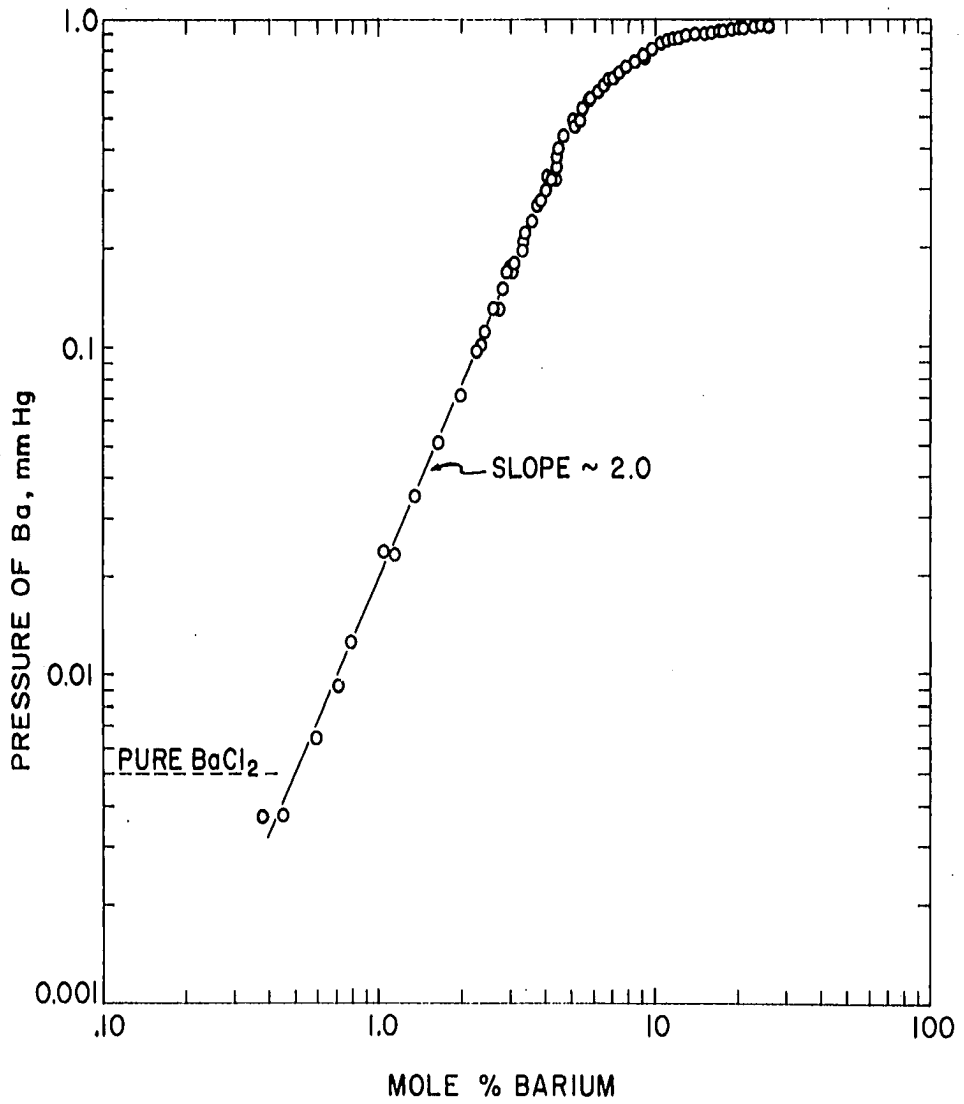


Figure 19. Variation of the square root of the vapor pressure of barium with concentration of barium dissolved in barium chloride at 975°C

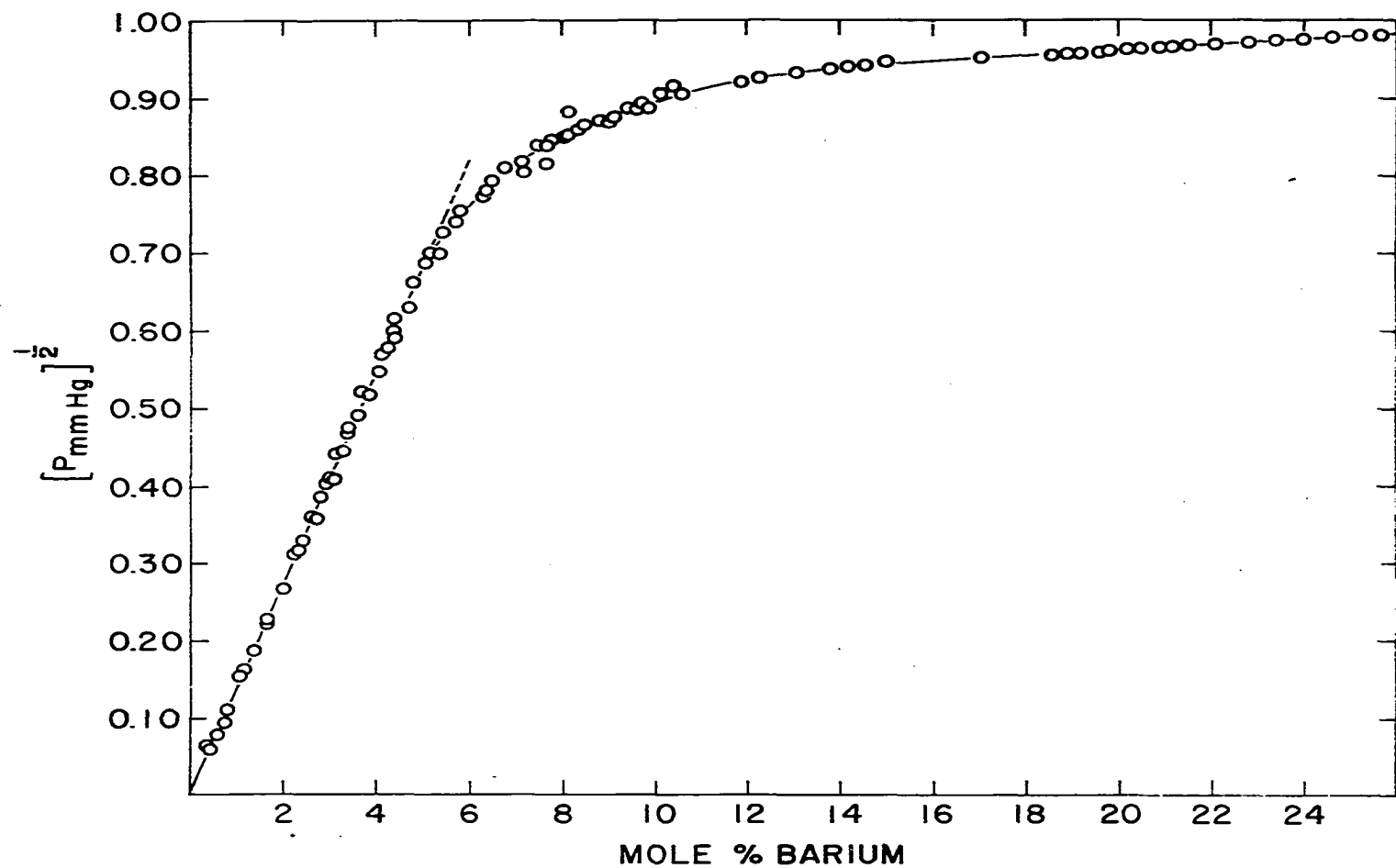


Table 16. Partial pressures of barium over barium-barium chloride solutions at 975°C

Mole % Ba	P <sub>mm Hg</sub>	Mole % Ba	P <sub>mm Hg</sub>
9.62	0.78	1.66	0.051
9.00	0.76	2.00	0.071
8.36	0.73	1.35	0.034
7.72	0.70	1.05	0.023
7.07	0.65	0.79	0.012
6.41	0.60	0.60	0.0064
5.74	0.55	0.46	0.0037
5.06	0.46	25.73	0.97
4.37	0.34	25.21	0.96
3.61	0.24	24.58	0.96
2.95	0.17	23.99	0.95
2.29	0.097	23.39	0.95
1.66	0.048	22.16	0.94
1.11	0.023	21.51	0.94
0.72	0.0091	21.22	0.94
0.38	0.0037	20.89	0.93
10.38	0.84	20.24	0.93
10.09	0.82	19.86	0.92
9.75	0.80	19.57	0.92
9.44	0.78	19.25	0.92
9.12	0.77	18.90	0.91
8.80	0.76	18.56	0.91
8.48	0.75	17.17	0.91
8.15	0.73	16.82	0.91
7.83	0.72	15.00	0.90
7.50	0.70	14.61	0.89
7.17	0.67	14.24	0.88
6.83	0.66	13.86	0.88
6.50	0.63	13.09	0.87
6.16	0.59	12.30	0.86
5.82	0.57	11.90	0.85
5.47	0.53	10.66	0.82
5.13	0.49	9.86	0.79
4.78	0.44	8.15	0.78
4.43	0.38	7.71	0.67
4.07	0.33	7.18	0.66
3.72	0.27	6.37	0.60

Table 16. (Continued)

Mole % Ba	P <sub>mm</sub> Hg	Mole % Ba	P <sub>mm</sub> Hg
3.38	0.22	5.37	0.49
3.03	0.17	4.72	0.40
2.68	0.13	4.37	0.35
2.33	0.10	4.25	0.34
		4.06	0.30
		3.87	0.27
		3.39	0.22
		3.29	0.20
		3.10	0.18
		3.00	0.17
		2.81	0.15
		2.61	0.13
		2.41	0.11

necessary. In the barium-barium chloride system for compositions less than about three mole per cent barium, it was necessary to correct the effusion data to take into account the barium chloride which effused during the time for the observed weight loss. This correction was made by assuming Raoult's Law behavior for the vapor pressure of the barium chloride, the major constituent of the salt phase. Since Knudsen flow conditions through the orifices are known to prevail at these low pressures, it was further assumed that the two vapor species would effuse independently through the orifice. The total time for a given weight loss was measured. The weight of the barium chloride which would effuse during

this same time interval could be calculated from the known vapor pressure of the pure salt. The weight loss due to the barium alone was then obtained by difference. From this weight loss of barium and the known time for this loss, the vapor pressure of barium was calculated.

The zero point of metal concentration could not be obtained by depletion of the barium from the salt solution. An alkalinity titration of the salt phase at the completion of the effusion measurements gave the total amount of the residual barium plus any other base forming constituents such as oxide or hydride. The choice as to how much of this basicity titration to credit as residual metal was made in such a manner as to give a smooth extension of the data at the higher metal concentration portions of the  $\log P_{Ba}$  versus  $\log N_{Ba}$  curve.

The solubility limit of barium in barium chloride could not be determined by these vapor pressure observations. Attempts to measure the vapor pressure over mixtures containing in excess of 26 mole per cent barium invariably failed due to partial or complete plugging of the orifice. The white, acid soluble substance obstructing the orifice could not be identified because of the small quantity avail-

able. If any evidence of orifice restriction was noted, none of the data of that run were used because there was no way of ascertaining when the obstruction of the orifice occurred. Extrapolation techniques would not be very accurate in determining the solubility limit in this system as the vapor pressure of barium changes slowly at high metal contents as seen in Figure 19. From Figure 19 it is estimated the solubility limit of barium in barium chloride is in excess of 25 mole per cent. This estimate is compatible with the phase diagrams by Hinkebein (42) and Schäfer and Niklas (6) which show solubility limits of about 27 and 26 mole per cent barium respectively.

A least squares analysis of the data below 5.5 mole barium gave the following equation:

$$[P_{\text{mm Hg}}]^{1/2} = 0.137 N, \quad (\text{Equation 17})$$

where P is the partial pressure of barium and

N is the mole per cent barium in solution.

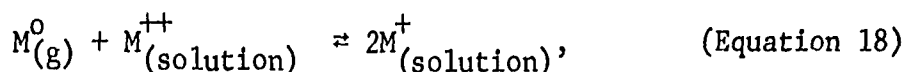
From Figure 19 it is apparent that an extrapolation of this equation would not yield a valid solubility limit.

#### D. Solution Models

The results of these experiments on the binary metal-metal chloride systems of barium, calcium, and strontium can

only be interpreted by assuming that the solute metal formed two distinguishable particles in solution for each atom of metal in solution. This measurement is the most unambiguous evidence on the solution reaction which has been reported to date. Of the four solution mechanisms previously considered, two were in accord with the observation of two distinguishable particles in solution, namely, the model in which the solute was considered to form monovalent ions in solution and the model in which the solute ionized to form divalent ions and electrons. By a closer examination of the partial pressure-composition relationships predicted for these two models, a further distinction between the two may be conjectured.

In these experiments on the binary systems the observable composition variables were the weights of the salt and metal in each sample, from which the corresponding mole fractions were calculated. In the following discussion " $N_x$ " will be used to designate the mole fraction of the subscripted species  $x$ . Considering the monovalent ion formation reactions as follows:



the equilibrium constant,  $K$ , may be written as



$$K = \frac{a_{M^+}^2}{a_{MO} \cdot a_{M^{++}}} , \quad (\text{Equation 19})$$

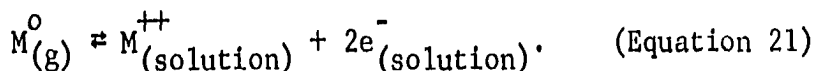
where "a" denotes the activity of the species subscripted. Considering Raoult's and Henry's laws to be valid for this solution, the following equation was derived (see Appendix B):

$$P_{MO} = \frac{K_1 N_{MO}^2}{1 - 2N_{MO}} \quad (\text{Equation 20})$$

where  $P_{MO}$  represents the vapor pressure of the dissolved metal over the solution and

$N_{MO}$  is the mole fraction of metal dissolved.

The quasi crystalline solution model with electrons occupying anion vacancies is expressed by the equation



The equilibrium constant for this reaction is

$$K = \frac{a_{M^{++}} \cdot a_{e^-}^2}{a_{MO}} . \quad (\text{Equation 22})$$

In the solution reaction represented by Equation 21, it is postulated that additional dipositive ions are created, but this would not change their activity since the effect would be only to increase the extent of the phase containing these ions. If Henry's law behavior is assumed for the activity of the electrons, expressing this in terms of observables in

the system,

$$a_{e^-} = K_2 N_{e^-} = 2K_2 N_{Mo}. \quad (\text{Equation 23})$$

The activity of the metal in the gas phase can be represented by its partial pressure  $P_{Mo}$  as follows

$$a_{Mo} = P_{Mo}. \quad (\text{Equation 24})$$

Substitution of Equations 23 and 24 into Equation 22, rearrangement of terms, and grouping the constants gives

$$P_{Mo} = K_3 N_{Mo}^2. \quad (\text{Equation 25})$$

At low metal concentrations attempts to compare the fit of experimental data to Equations 20 and 25 would not distinguish between these two models due to the similarity of the equations and the normal scatter in the data. Above about two mole per cent metal the differences in the functional relationships of the two equations are significantly greater than the experimental scatter in the data and permit a distinction between the two models. The best correlation of experimental data was obtained utilizing Equation 25. This may be seen by examination of Figures 14, 16 and 19, in which the initial linear region of these curves exactly corresponds to the prediction of Equation 25.

In the derivation of Equation 25, it was tacitly assumed the electrons did not interact with one another. Conceptu-

ally the molten salt solutions may be considered as an approximately close packed but irregular lattice of anion sites with the smaller cations occupying some of the interstitial positions. Each anion site would thus be within a shell of eleven or twelve other anion sites. In the pure molten salt, some of these anion sites would probably be unoccupied similar to vacancies in solids. If electrons were substituted randomly into some of the vacant anion sites or into newly created anion sites, the supposition of no interaction of individual electrons would surely be expected to begin to break down when more than one electron was placed into each anion shell. This corresponds to an anion to electron ratio of about eleven or twelve to one. The upper limit of this non-interaction of electrons postulate would thus be at about eight to nine mole per cent metal. Referring to Figures 16 and 19 it is noted that departures from linearity occur at about seven mole per cent metal in the Sr-SrCl<sub>2</sub> system and at about 5 mole per cent metal in the Ba-BaCl<sub>2</sub> system. The low solubility limit of calcium in calcium chloride prevents any similar comparison in this system. These correlations would appear to favor the model in which the electrons from the solute metal occupied anion

positions.

This model, postulating electrons in anion vacancies, is conceptually attractive for still other reasons. In these metal-salt systems there is complete miscibility in the liquid state at reasonable temperatures. This implies the transition from pure metal to pure salt must occur continuously. A commonly used model for a metal considers the atoms in the metallic state to exist as ion cores surrounded by "free" or conduction electrons. Gradual replacement of these free electrons by anions would result in the structure postulated for the molten salt. Some reservations may exist as to whether such a model can satisfactorily account for the wide variations in solubility encountered in the various systems at lower temperatures or is at all amenable to quantitative interpretation. In the case of the alkali metal-metal halide systems where more data are available, Bronstein and Bredig (78) have shown the observed properties of these melts and the concept of substitution of electrons for anions and vice versa are compatible.

Pitzer (79) considered these alkali metal-metal halide systems from the view of intermixing of electrons and anions in the melt using regular solution theory. Salt rich

solutions were regarded as a random mixture of anions and electrons within the irregular cation lattice. These electrons were considered to be in normal anion positions like those of "F" centers in the solid and considered to exhibit wave functions similar to those of the electrons in "F" centers in solids. The energy change in the formation of a solution was then considered as the change in energy in converting the metal to an ionic lattice of cations and electrons plus an energy of mixing this with the salt. The results of this treatment predict the observed increase in metal solubility from lithium to cesium and the parallel decrease of the heat of solution of the metals in the halides. A similar treatment of the solution of halide in metal was less satisfactory. No similar treatment has been attempted for the alkaline earth metal-metal halide solutions though Pitzer (79) mentions the possibility of extension of his treatment to include these systems.

Upon closer consideration the models representing the reduced or monovalent metal ion and the free electron-anion vacancy are not radically dissimilar and perhaps only amount to a difference in the degree of electron localization. The distinction between these two models may be thought of as

the question of the location of the electron. The answer to a question of this nature is rightfully not inferred from thermodynamic measurements. The assumption of the presence of free electrons should be supported by other observations by which it might be possible to distinguish between the unpaired electrons in  $M^+$  ions and mobile or free electrons. Emons et al. (8) qualitatively report these metal-metal chloride solutions to be diamagnetic which, if true would indicate neither of these models are correct, since this observation would necessitate few unpaired electrons. No experimental details of the measurements are given and it may be questioned if the observations were made on the liquid salt solutions and if the measurements were precise enough to warrant this conclusion. Other experiments that might elucidate this problem would look at some transport property in which the solute species participated such as diffusivity, Hall coefficients, transport number, or electrical conductivity of the metal-metal halide solutions. Other experiments such as Ramon Spectra or molar volume measurements might infer some aspect of the electron localization. With the exception of a few incomplete resistivity measurements by Dworkin et al. (10) none of the above mentioned techniques

have been applied to any alkaline earth metal-metal halide systems.

## SUMMARY

The Knudsen effusion method was used to measure the vapor pressures of the individual components and the vapor pressures of the metals in solution in the calcium-calcium chloride systems. The vapor pressures were measured by observation of the weight loss of the effusion vessels with a keyboard microbalance. The pure metallic components of the above systems had vapor pressures high enough to warrant concern as to whether Knudsen flow occurred within the orifices of the effusion cells. A series of experiments were conducted with strontium, the metal with the highest vapor pressure, to determine the orifice dimensions necessary to insure Knudsen flow conditions. It was found for strontium that orifices less than 0.25 mm in diameter gave valid vapor pressure measurements up to 900°C. For barium up to 1000°C and for calcium up to 950°C no detectable effect of orifice diameter on measured pressure was observed for orifices up to 0.356 mm in diameter. The equation expressing the vapor pressure as a function of temperature for the six pure components is summarized in Table 17. The measured vapor pressures of calcium were in reasonable agreement with those



of other investigators. For the other substances, vapor pressures in the temperature ranges of this investigation have not been reported.

Table 17. Vapor pressure of pure components

$$\text{Log}_{10} P_{\text{mm Hg}} = \frac{A}{T(^{\circ}\text{K})} + B$$

Substance	Temp. Range $^{\circ}\text{K}$	-A	B
Barium, liquid	1029-1280	$9938 \pm 272$	$8.154 \pm 0.198$
Calcium, liquid	1118-1227	$9767 \pm 190$	$8.920 \pm 0.160$
Strontium, solid	877-1014	$9531 \pm 106$	$9.474 \pm 0.093$
Strontium, liquid	1050-1197	$9045 \pm 145$	$9.004 \pm 0.130$
Barium chloride, liquid	1243-1277	14,100	8.98
Calcium chloride, liquid	1064-1232	$10,656 \pm 290$	$7.225 \pm 0.248$
Strontium chloride	1174-1286	$14,688 \pm 168$	$9,618 \pm 0.138$

The variation of the vapor pressure of calcium dissolved in calcium chloride with changing calcium composition was measured at  $860.5^{\circ}\text{C}$ . Below the solubility limit, the vapor pressure obeyed Henry's law for a solute forming two distinguishable particles from each atom in the vapor state. The solubility limit of calcium in calcium chloride was found to be 3.57 mole per cent metal at  $860.5^{\circ}\text{C}$ , a value

in excellent agreement with values from other investigators.

For strontium dissolved in strontium chloride, the variation of the vapor partial pressure with composition was measured at 883°C. The solute was again found to form two distinguishable particles in solution relative to the reference state and a solubility limit of 8.14 mole per cent strontium in strontium chloride was observed. For this system, the effects on the equilibria of small quantities of water were found to be drastic. In the water contaminated alloys, vastly different vapor pressure-composition relationships were observed and the apparent solubility limit of strontium in strontium chloride was increased to about 11 mole per cent metal.

The variation of the vapor pressure of barium dissolved in barium chloride with changing barium composition was measured at 975°C. The data indicated that the solution process involved the formation of two distinguishable particles in solution from each atom in the vapor phase. The solubility limit of barium in barium chloride could not be determined but was estimated to be about 25 mole per cent metal, a value quite in accord with published phase diagrams.

Four models for the solution of these metals in their

fused salts were considered. In these four models the solute metal atom was postulated to form; (1) monovalent monomer ions, (2) a dimeric monovalent ion, (3) a neutral metal atom, and (4) a divalent positive ion plus two electrons. The observed variation of solute partial pressure with composition in the three binary systems investigated was shown to eliminate models 2 and 3 from further consideration. The remaining choice between models 1 and 4 cannot be positively resolved on the basis of thermodynamic measurements, though the data of this investigation favors model 4. This model has been reported to give good quantitative agreement with observed experimental results in the alkali metal-metal halide systems and is capable of qualitative application to explain existing data for the alkaline earth metal-metal halide systems. Considerably more experimentation, particularly of a non-thermodynamic nature, is necessary to permit a more exact description of the solution reaction in these alkaline earth metal-metal chloride systems.

## BIBLIOGRAPHY

1. Corbett, J. The solution of metals in their molten salts. In Sundheim, B., ed. Molten Salts. New York, New York, McGraw Hill Book Co., Inc. To be published ca. 1964.
2. Eastman, E., Cubicciotti, D., and Thurmond, C. Temperature composition diagrams of metal-metal halide systems. In Quill, L., ed. The chemistry and metallurgy of miscellaneous materials. pp. 6-12. New York, New York, McGraw Hill Book Co., Inc. 1950.
3. Rogers, P., Tomlinson, J., and Richardson, F. Physical chemistry of process metallurgy, part 2. In Metallurgical Society Conferences. 8: 909. New York, New York, Interscience Publishers, Inc. 1961.
4. Staffanson, L. Phase relationships in some alkaline earth metal-metal halide systems. Unpublished Ph.D. thesis. London, England, Library, Imperial College. 1960.
5. Cubicciotti, D. High temperature equilibria in metal-metal halide systems. United States Atomic Energy Commission Report MDDC-1058 Manhattan District, Oak Ridge, Tennessee. 1946.
6. Schäfer, H. and Niklas, A. Angewandte Chemie 64: 611. 1952.
7. Peterson, D. and Hinkebein, J. Equilibria in the reaction of barium with calcium chloride. U. S. Atomic Energy Commission Contribution No. 685 Iowa State University of Science and Technology, Ames. Institute for Atomic Research. 1959.
8. Emons, H., Grothe, W., Hellmond, P., and Richter, D. Zeitschrift für anorganische und allgemeine Chemie 323: 114. 1963.

9. Emons, H., Richter, D., Grothe, W., and Reckzeh, U. Zeitschrift für Chemie, Leipzig, Deutscher Verlag für Grundstoffindustrie 2: 313. 1962.
10. Dworkin, A., Bronstein, H., and Bredig, M. Discussions of The Faraday Society 32: 188. 1962.
11. Emons, H. and Hellmond, P. Zeitschrift für Chemie, Leipzig, Deutscher Verlag für Grundstoffindustrie 2: 377. 1962.
12. Dworkin, A. and Bredig, M. Journal of Physical Chemistry 67: 697. 1963.
13. Borchers, W. Zeitschrift für Elektrochemie 8: 938. 1902.
14. Guntz, A. Comptes rendus hebdomadaires des séances de l'académie des sciences 117: 732. 1903.
15. Wöhler, L. and Rodewald, G. Zeitschrift für anorganische und allgemeine Chemie 61: 54. 1909.
16. Borchers, W. and Stochem, L. Zeitschrift für Elektrochemie 8: 757. 1902.
17. Guntz, A. and Benoit, F. Bulletin de la société chimique de France 35: 709. 1924.
18. Bichowsky, F. and Rossini, F. The thermochemistry of chemical substances. New York, New York, Reinhold Publishing Co., Inc. 1936.
19. Grimm, H. and Herzfeld, K. Zeitschrift für Physik 19: 141. 1923.
20. Emons, H. Zeitschrift für Physikalische Chemie, Leipzig 222: 65. 1963.
21. Rabinowitsche, E. and Thiele, E. Zeitschrift für Physikalische Chemie, Frankfurter 6B: 284. 1930.
22. Ehrlich, P. and Gentsch, L. Naturwissenschaften 40: 460. 1953.

23. Ehrlich, P. and Gentsch, L. *Naturwissenschaften* 41: 211. 1954.
24. Ehrlich, P., Alt, B., and Gentsch, L. *Zeitschrift für anorganische und allgemeine Chemie* 283: 58. 1956.
25. Wehner, G. *Zeitschrift für anorganische und allgemeine Chemie* 276: 72. 1954.
26. Blue, G. D. Mass spectrometric studies of the stabilities of gaseous alkaline earth mono fluorides. Unpublished Ph.D. thesis. Madison, Wisconsin, Library, University of Wisconsin. 1962.
27. Walters, O. and Barrat, S. *Proceedings of the Royal Society, London* 118A: 120. 1928.
28. Lorenz, R. *Zeitschrift für anorganische und allgemeine Chemie* 10: 78. 1895.
29. Lorenz, R. and Eitel, W. *Pyrosole*. Leipzig, Akademische Verlagsgesellschaft. 1926.
30. Eitel, W. and Lange, B. *Zeitschrift für anorganische und allgemeine Chemie* 171: 168. 1928.
31. Belozerskii, N. *Stalin Institute of Applied Chemistry* 25: 40. 1940. Original not available; cited in Delimarskii, U. and Markov, B. *Electrochemistry of Fused Salts*. Translation by Peiperl, A. p. 208. Washington 7, D. C., The Sigma Press. 1961.
32. Aten, A. *Zeitschrift für Physikalische Chemie* 73: 578. 1910.
33. Grjotheim, K., Grønvold, F., and Kroghe-Moe, J. *Journal of American Chemical Society* 77: 5824. 1955.
34. Fehotte-Ostertag, H. *Annales de Chimie, Paris* 6: 791. 1961.
35. Blanc, M. *Annalen der Physik* 40: 615. 1960.

36. Peterson, D. and Hinkebein, J. *Journal of Physical Chemistry* 63: 1360. 1959.
37. Moore, J. *Journal of American Chemical Society* 65: 1700. 1943.
38. Kelley, K. *U. S. Bureau of Mines Bulletin* #393. 1936.
39. Darken, L. and Gurry, R. *Physical chemistry of metals*. New York, New York, McGraw Hill Book Co., Inc. 1953.
40. Johnson, E. Vapor pressure of calcium over solutions of calcium in calcium chloride. Unpublished M. S. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.
41. Rigney, D. Activity of calcium dissolved in calcium chloride. Unpublished M. S. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1962.
42. Hinkebein, J. Equilibrium in the reaction of barium with calcium chloride. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1958.
43. Peterson, D. and Indig, M. *Journal of the American Chemical Society* 82: 5645. 1960.
44. Smith, J., Carlson, O., and Vest, R. *Journal of the Electrochemical Society* 103: 409. 1956.
45. Peterson, D. and Fattore, V. *Analytical Chemistry* 34: 579. 1962.
46. Knudsen, M. *Annalen der Physik* 28: 999. 1909.
47. Roeser, W. and Wensel, H. *Journal of Research of National Bureau of Standards* 14: 247. 1935.
48. *Metals Handbook*. Properties and selection of metals. 8th ed. Volume 1. Novelty, Ohio, American Society for Metals. 1961.

49. Beers, Y. Introduction to the theory of error. 2nd ed. Reading, Massachusetts, Addison-Wesley Publishing Co., Inc. 1957.
50. Demarcus, W. U. S. Atomic Energy Commission Report K-1302, Part 3. Oak Ridge Gaseous Diffusion Plant Oak Ridge, Tennessee. 1956.
51. Clausning, P. Annalen der Physik 86: 471. 1930.
52. Carlson, J., Gilles, P., and Thorn, R. Journal of Chemical Physics 38: 2064. 1963.
53. Rossman, M. and Yarwood, J. Journal of Chemical Physics 21: 1406. 1953.
54. Knacke, O. and Stranski, I. Progress in Metal Physics 6: 181. 1956.
55. Dushman, S. Scientific foundations of vacuum technique. 1st ed. New York, New York, John Wiley and Sons, Inc. 1959.
56. Hanawalt, H. Analytical Chemistry 10: 475. 1938.
57. Balson, E. Journal of Physical Chemistry 65: 1151. 1961.
58. Bacher, R. and Goudsmit, S. Atomic Energy States. New York, New York, McGraw Hill Book Co., Inc. 1932.
59. Ditchburn, R. and Gilmour, J. Reviews of Modern Physics 13: 310. 1941.
60. Herzberg, G. Molecular spectra and molecular structure. New York, New York, Prentice-Hall, Inc. 1939.
61. Ruff, O. and Hartmann, H. Zeitschrift für anorganische und allgemeine Chemie 133: 29. 1924.
62. Hultgren, R., Orr, R., Anderson, P., and Kelley, K. Selected values of thermodynamic properties of metals and alloys. New York, New York, John Wiley and Sons, Inc. 1963.



63. Hartmann, H. and Schneider, R. Zeitschrift für anorganische and allgemeine Chemie 180: 275. 1929.
64. Van Liempt, J. Recueil des travaux chimiques des Pays Bas 55: 468. 1936.
65. Rudberg, E. and Lempert, J. Journal of Chemical Physics 3: 627. 1935.
66. Smith, J. and Smythe, R. Acta Metallurgica 7: 261. 1959.
67. Tomlin, D. Proceedings of the Physical Society, London 67B: 787. 1954.
68. Douglas, C. Proceedings of the Physical Society, London 67B: 783. 1954.
69. Pilling, N. The Physical Review 18: 362. 1921.
70. Rudberg, E. The Physical Review 46: 763. 1934.
71. Priselkov, Y. and Nesmayanov, A. Doklady Akademii Nauk S.S.S.R. 95: 1207. 1954.
72. Kubaschewski, O. and Evans, E. Metallurgical thermochemistry 3rd ed. New York, New York, Pergamon Press. 1958.
73. Rinck, E. Annales de Chimie, Paris, Series 10, 18: 395. 1932.
74. Hirst, R., King, A., and Kanda, F. Journal of Physical Chemistry 60: 302. 1956.
75. Peterson, D. and Colburn, R. The strontium-strontium hydride phase system. U. S. Atomic Energy Commission Contribution No. 1282. Iowa State Univ. of Science and Technology, Ames. Inst. for Atomic Research. 1962.
76. Maier, C. U. S. Bureau of Mines Technical Paper No. 360. 1925.

77. Brewer, L. The fusion and evaporation data of the halides. In Quill, L. ed. The chemistry and metallurgy of miscellaneous materials. pp. 193-275. New York, New York, McGraw Hill Book Co., Inc. 1950.
78. Bronstein, H. and Bredig, M. Journal of American Chemical Society 80: 2077. 1958.
79. Pitzer, K. Journal of American Chemical Society 84: 2025. 1962.

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## APPENDIX A. STRONTIUM VAPOR PRESSURE DATA FOR VARYING

## ORIFICE DIMENSIONS

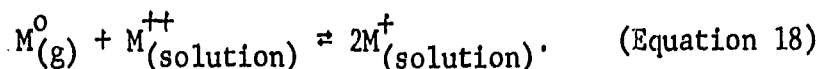
Orifice diameter inches	Pressure mm Hg	Temperature °K	Clausing factor
0.006	2.50 ± 0.05	1050.2	0.447
"	3.71 ± 0.07	1071.4	"
"	5.08 ± 0.14	1096.0	"
"	8.81 ± 0.18	1120.7	"
"	14.03 ± 0.28	1150.0	"
"	19.84 ± 0.40	1172.4	"
"	28.53 ± 0.61	1197.4	"
"	40.40 ± 0.92	1223.0	"
0.086	2.48 ± 0.05	1051.7	0.566
"	4.09 ± 0.09	1079.7	"
"	5.99 ± 0.13	1101.7	"
"	9.04 ± 0.18	1125.0	"
"	13.57 ± 0.28	1150.2	"
"	19.30 ± 0.40	1174.2	"
0.0142	1.50 ± 0.04	1023.0	0.423
"	4.79 ± 0.12	1087.0	"
"	10.70 ± 0.22	1131.6	"
"	17.08 ± 0.38	1151.2	"
0.0274	8.36 ± 0.18	1047.5	0.786
0.0236	3.12 ± 0.07	1049.0	0.737
0.0168	2.28 ± 0.05	1046.0	0.656
"	3.77 ± 0.08	1064.7	"
"	5.95 ± 0.13	1094.2	"
"	9.00 ± 0.19	1103.5	"
0.021	2.36 ± 0.01	1045.5	None
"	5.40 ± 0.19	1073.0	"
0.0192	2.23 ± 0.06	1039.7	None
"	3.09 ± 0.08	1067.7	"
"	5.09 ± 0.12	1084.0	"
"	13.87 ± 0.28	1097.7	"
0.0112	2.51 ± 0.06	1050.2	0.465
"	4.21 ± 0.09	1079.7	"
"	6.94 ± 0.15	1108.7	"
"	10.05 ± 0.22	1135.0	"
"	16.76 ± 0.34	1162.7	"

## Appendix A. (Continued)

Orifice diameter inches	Pressure mm Hg	Temperature °K	Clausing factor
0.0112	23.01 $\pm$ 0.48	1174.5	0.465
0.014	2.22 $\pm$ 0.05	1041.0	0.455
"	4.41 $\pm$ 0.09	1078.7	"
0.0136	3.87 $\pm$ 0.08	1075.5	0.452
"	6.70 $\pm$ 0.14	1101.2	"
"	10.86 $\pm$ 0.23	1134.0	"
"	16.87 $\pm$ 0.34	1155.0	"
"	28.47 $\pm$ 0.601	1175.2	"
0.0146	2.50 $\pm$ 0.05	1050.3	0.2081
"	3.86 $\pm$ 0.08	1076.8	"
"	9.54 $\pm$ 0.20	1115.8	"
"	16.23 $\pm$ 0.34	1127.3	"

## APPENDIX B. DERIVATION OF EQUATION 20

Consider the monovalent ion formation reaction as follows:



The equilibrium constant for the reaction above may be written as

$$K = \frac{a_{M^+}^2}{a_{M^0} \cdot a_{M^{++}}} \quad (\text{Equation 19})$$

where  $a$  denotes the activity of the species subscripted.

Considering Henry's and Raoult's laws to be valid for this solution, the activity terms in Equation 18 can be rewritten as follows,

$$a_{M^+} = K_2 N_{M^+},$$

$$a_{M^{++}} = N_{M^{++}}, \text{ and}$$

$$a_{M^0} = P_{M^0},$$

where  $P_{M^0}$  is the partial pressure of the metal  $M^0$  in the gas phase. The mole fractions  $N_{M^+}$  and  $N_{M^{++}}$  are defined as

$$N_{M^{++}} = \frac{n_{M^{++}}}{n_{M^+} + n_{M^{++}}}, \text{ and}$$

$$N_{M^+} = \frac{n_{M^+}}{n_{M^+} + n_{M^{++}}},$$

where "n" represents the number of moles of the species subscripted. The quantities  $n_{M^+}$  and  $n_{M^{++}}$  are not direct composi-

tion observables in these systems, but are related to the observables through Equation 17 as follows:

$$n_{M^+} = 2n_{MO}, \text{ and}$$

$$n_{M^{++}} = n_{MCl_2} - n_{MO} ,$$

where  $n_{MO}$  is the number of moles of metal in solution, and

$n_{MCl_2}$  is the number of moles of metal chloride in solution.

Substituting the above results into the expressions for the mole fractions yields:

$$N_{M^+} = \frac{2n_{MO}}{n_{MCl_2} + n_{MO}} = 2N_{MO}, \text{ and}$$

$$N_{M^{++}} = N_{MCl_2} - N_{MO} .$$

Substituting into Equation 18, rearranging and collecting constants gives

$$P_{MO} = \frac{K_1 N_{MO}^2}{N_{MCl_2} - N_{MO}} ,$$

but for the observable composition variables,

$$N_{MCl_2} + N_{MO} = 1.$$

Substituting this into the previous equation gives the desired equation:

$$P_{MO} = \frac{K_1 N_{MO}^2}{1 - 2N_{MO}} . \quad (\text{Equation 20})$$

