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# A radioactive tracer dew point method for measuring vapor pressures of binary alloys

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FOR MEASURING VAPOR PRESSURES OF BINARY  
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A RADIOACTIVE TRACER DEW POINT METHOD  
FOR MEASURING VAPOR PRESSURES OF BINARY ALLOYS

by

George John Lutz

A Dissertation Submitted to the  
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1962

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## I. INTRODUCTION

The dew point method of determining a vapor pressure uses the equilibrium between a condensed phase and its vapor in an unique manner. When the vapor in equilibrium with a multicomponent system is cooled, condensation starts at the "dew point" i. e., the temperature at which the vapor pressure of the pure condensable component is equal to its partial pressure over the multicomponent system. The dew point method is a relative method. If the temperature at which condensation occurs is determined, the vapor pressure over the system can be determined from the vapor pressure-temperature relationship of the pure (condensable) component.

A static system is used and negligibly small depletion of the volatile component in the condensed phase occurs. The accuracy depends on the sensitivity of detection of the formation of the condensate.

The method was proposed for aqueous solutions by H. Lescoeur in 1889. The procedure was first applied to metals by R. J. Hargreaves (1) in 1939 in his classical work on the vapor pressure of zinc over brasses. Hargreaves placed an evacuated quartz tube containing the brass sample at one end in a resistance wound tubular furnace with two independently heated sections. Both ends of the quartz cell were provided with re-entrant tubes which carried thermocouples. The temperature of the whole furnace was raised to a desired value,

and the end away from the sample was cooled. The coolest portion of the quartz tube was observed through a hole through the furnace. At the dew point temperature, condensation of zinc was observed.

Refinements of the method were made by Frost and Maskrey (2) who employed a photoelectric cell and determined the dew point temperature by a decrease in the light transmittancy in the region of condensation. Burgan, Hall and Hehemann (3) sealed tungsten probes into the cooled area, and assumed that the dew point was reached when the condensing metal closed an electrical circuit.

The main objective of the present investigation was to develop a method of determining the dew point based on the detection of the gamma radiation from a radioisotope of the condensing metal. Radiotracer techniques have served well in the determination of vapor pressures. Nesmeyanov (4) has surveyed these methods which include the transpiration method, the Knudsen effusion method, the boiling point method and the method of Langmuir as well as the techniques which can only be used with radiotracers; namely, the method of isotope exchange and direct measurement of radioactivity in the vapor by counting.

Schadel and Birchenall (5) have measured the vapor pressure of silver by the Knudsen effusion method in the temperature range  $750^{\circ}$  to  $1050^{\circ}$  C using radioactive  $\text{Ag}^{110}$  as a tracer. Rauh and Thorn (6) measured the vapor pressure

of uranium by this technique. The quantity of uranium collected was determined from fission product activity obtained by irradiation of the uranium in a nuclear reactor.

Nesmeyanov (7) has determined the vapor pressure of cadmium and zinc solids containing  $\text{Cd}^{113}$  or  $\text{Zn}^{65}$  by the Langmuir method.

In these methods radioactivity is used as an analytical tool. A dew point method based on detection of radiation will differ from these techniques in that counting rates obtained will serve only to indicate that condensation has occurred.

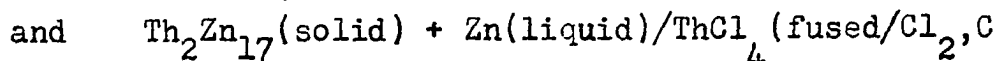
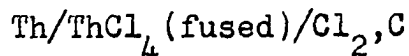
The second objective of this investigation was to determine some of the thermodynamic properties of the intermetallic phases in the aluminum-zinc, thorium-zinc and yttrium-zinc systems based on the measurement of the zinc vapor pressure over varying compositions of these alloys as a function of temperature.

Anderson (8) has reviewed previous work on the thermodynamic properties of liquid alloys in the aluminum-zinc system. Kawakami (9) in 1930 measured heats of formation by direct reaction of liquid alloys at  $800^{\circ}\text{C}$ , finding  $\Delta H = 4500 X_{\text{Al}} X_{\text{Zn}}$ . Schneider and Stoll (10) in 1941 measured vapor pressures of zinc over liquid alloys by the dew point method in the temperature range  $700\text{-}800^{\circ}\text{C}$ , finding  $\overline{\Delta F}_{\text{Zn}}^{xs} \sim 2300 X_{\text{Al}}^2$ . Their temperature coefficients give slightly negative values for  $\overline{\Delta S}_{\text{Zn}}^{xs}$ . Leitgeb (11) has determined boiling points over the composition range  $X_{\text{Zn}} = 0.026 - 0.788$ .

Chiotti and his co-workers (12) (13) have studied the phase diagram and thermodynamic properties of the thorium-zinc and yttrium-zinc systems by means of thermal, metallographic and vapor pressure measurements.

They observed four compounds in the thorium-zinc system corresponding to the stoichiometric formulas  $\text{Th}_2\text{Zn}$ ,  $\text{ThZn}_2$ ,  $\text{ThZn}_4$  and  $\text{Th}_2\text{Zn}_{17}$ . Seven compounds in the yttrium-zinc system were identified:  $\text{YZn}$ ,  $\text{YZn}_2$ ,  $\text{YZn}_3$ ,  $\text{YZn}_4$ ,  $\text{YZn}_5$ ,  $\text{Y}_2\text{Zn}_{17}$  and  $\text{YZn}_{11}$ . Utilizing the dew point method with visual detection of the condensation, they made zinc vapor pressure measurements in two-phase regions of interest and evaluated the standard free energy, enthalpy and entropy of formation of the compounds from these data and from previously determined values for the free energy and enthalpy of vaporization of pure zinc.

Smirnov et. al., (14) investigated the two-phase region between  $\text{Th}_2\text{Zn}_{17}$  and zinc. Based on their emf measurements on the cells



they obtained the relation for the free energy of formation of  $\text{Th}_2\text{Zn}_{17}$   $\Delta F^\circ = -45200 + 11.26T$ . This is in substantial disagreement with the results of Chiotti and Gill who obtained the relationship  $\Delta F^\circ = -106879 - 263.319 T + 99.042 T \log T$ . Chiotti and Gill have suggested the possibility that the  $\text{ThCl}_4$



in the cell

$\text{Th}_2\text{Zn}_{17}(\text{solid}) + \text{Zn}(\text{liquid})/\text{ThCl}_4(\text{fused})/\text{Cl}_2$ 
  
 was reduced to  $\text{ThCl}_3$  upon equilibration of the cell. On the basis of this assumption they have combined the emf data with Glasner's (15) value for the free energy of formation of  $\text{ThCl}_3$  to calculate the free energy of formation of  $\text{Th}_2\text{Zn}_{17}$ . The calculated values for  $\Delta F^\circ$  and  $\Delta H^\circ$  ( $\text{Th}_2\text{Zn}_{17}$ ) at  $973^\circ \text{K}$  are  $-71.4$  kcal per mole and  $-85.0$  kcal per mole respectively. Vapor pressure measurements gave corresponding values at  $973^\circ \text{K}$  of  $-75.2$  kcal and  $-148.7$  kcal. The free energy values are in reasonable agreement but the enthalpy values are in poor agreement.

## II. EXPERIMENTAL

### A. The Dew Point Apparatus

The experimental set-up used to measure the zinc pressure is shown schematically in Figure 1. The sample, in a tantalum crucible, was placed in a quartz cell approximately one inch in diameter and eleven inches long. The top of the cell was welded on and the assembly was evacuated to  $5-10$  microns through a quartz tube sealed into the cell. The system was then flushed with helium. This procedure was repeated two or three times and followed by a final evacuation after which the tube was sealed off.

The top of the cell was provided with two small re-entrant tubes. One extended to the bottom of the cell and contained a thermocouple for measuring the sample temperature. The other terminated in a  $3/8$  inch diameter condensation bubble at the top of the cell and served as an inlet for cooling gas as well as a thermocouple well for continuous monitoring of the bubble temperature.

The furnace had three separate sets of windings to insure good temperature control in all parts of the furnace. In addition, it was fitted with a stainless steel sleeve which surrounded most of the dew point cell. The purpose of this was to level out temperature gradients. It was necessary to provide a "window" in the furnace casement for positioning the dew point cell prior to taking data. In some experiments

this opening was stopped with a firebrick or quartz plug or a metal radiation shield or fitted with a set of furnace windings. These precautions appeared to have no effect on the data obtained.

Temperatures were measured with chromel-alumel thermocouples calibrated against pure copper, silver and aluminum. They were usually discarded after 200 - 300 hours of use.

The furnace assembly was placed in a well constructed of lead bricks and the experiments were conducted in a "hot cell" provided with a lead glass and lead ports so that all operations could be conducted from outside the cell.

The counting apparatus consisted of a Nuclear Chicago DS-5 standard scintillation detector probe with a one inch NaI (Tl) crystal connected to a Nuclear Chicago M186P scaling unit. The crystal was fitted with a water cooled lead jacket and collimator and the detector probe was positioned co-axially with the opening in the furnace casement and placed so that the crystal was about 14 inches away from the condensation bubble. The crystal was shielded from radiation from the alloy by its jacket and the lead furnace well. The jacket was water cooled to keep the crystal at room temperature.

The sensitivity of any counting experiment depends in part on the background radiation. In this work the major portion of the background came from the alloy and could be reduced by use of lead shielding. A smaller portion came

from gamma radiation from various sources in the vicinity of the experiment including degraded radiation from the sample. This radiation would generally be of lower energy than the 1.11 Mev gamma radiation associated with the  $Zn^{65}$  used. Since the amplitude of the input pulse from detector to counter is proportional to the energy of the gamma radiation giving rise to the pulse, radiation below a certain level can be "discriminated against" by allowing the apparatus to count only pulses of a certain minimum height. This was accomplished in the present work by adjustment of the sensitivity MV switch on the scaling unit. This control was adjusted empirically by counting a standard  $Zn^{65}$  sample and background at various settings. A block diagram of the counting apparatus used is shown in Figure 2.

#### B. Preparation of Alloys

The zinc metal used in these experiments was Bunker Hill slab zinc, 99.99 percent pure. The metal was cleaned with dilute hydrochloric acid and rinsed in water and then acetone prior to using. The zinc was neutron irradiated to a specific activity of about 30 mc of  $Zn^{65}$  per gram at the CP-5 reactor at the Argonne National Laboratory.

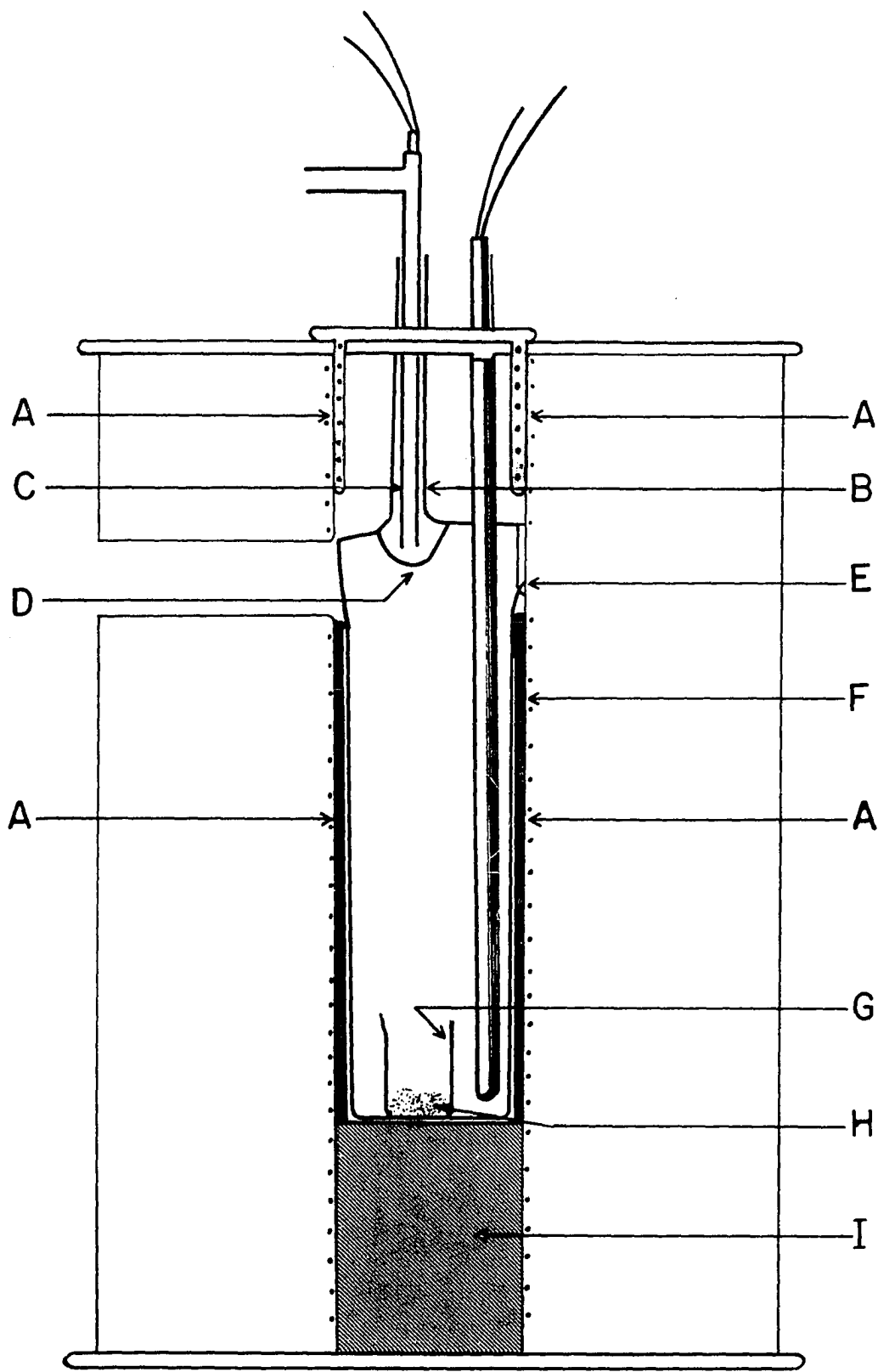
##### Aluminum-zinc alloys

The aluminum metal used in these experiments was notch-bar ingot obtained from the Aluminum Company of America. It was specified by the manufacturer to be 99.99+% aluminum. The

Figure 1. Dew-point apparatus

- A. Furnace windings
- B. Thermocouples
- C. Cooling gas inlet
- D. Condensation bubble
- E. Quartz dew point cell
- F. Stainless steel sleeve
- G. Tantalum crucible
- H. Alloy sample
- I. Refractory block

10



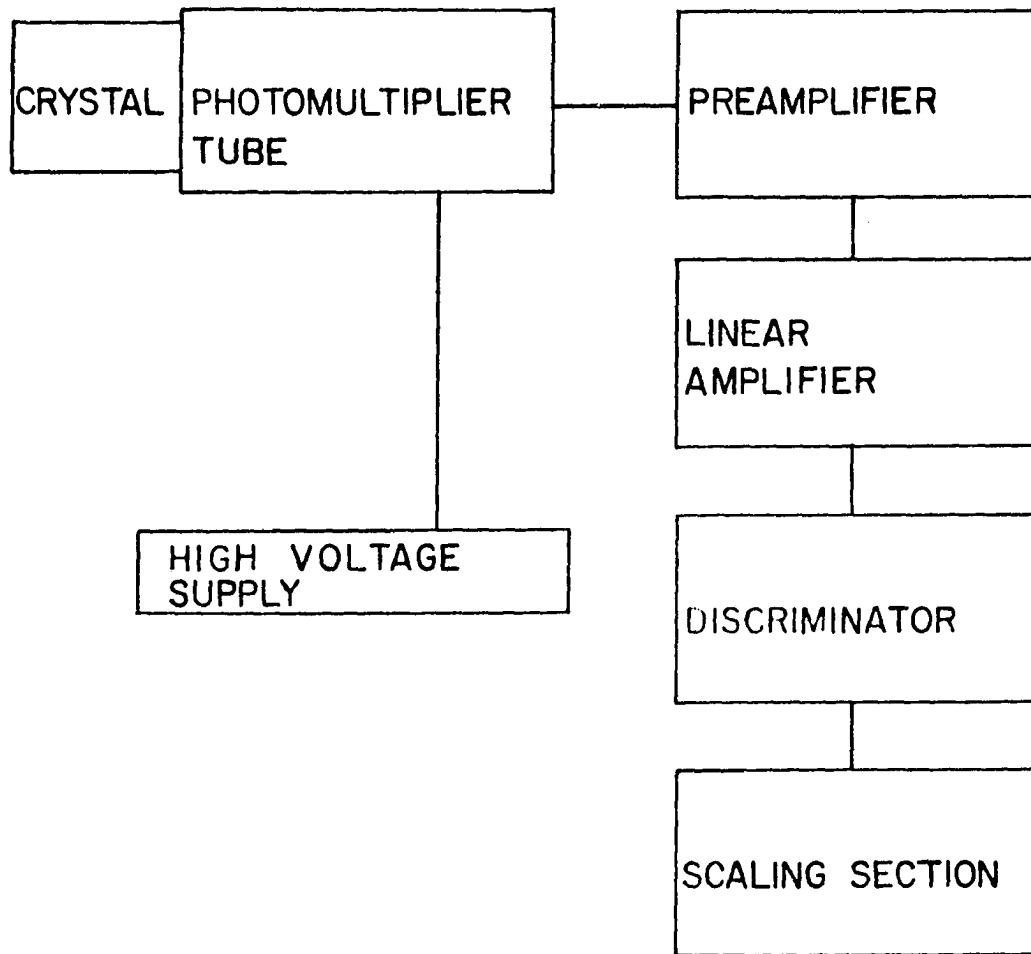


Figure 2. Block diagram of counting apparatus

major impurity was iron estimated to be present in the amount of 200-500 ppm. Qualitative spectrographic analysis detected Ag, Ca, Cu, Mg, Ni, Si, and Zr but these were estimated to be present in amounts of less than 100 ppm.

The aluminum and irradiated zinc metals were placed in a tantalum crucible which was sealed into a dew point cell. The cell was placed in the dew point furnace. The temperature of the furnace was raised to just above the melting point of aluminum and held there for several hours to insure homogeneity. The furnace was then cooled to a suitable temperature for vapor pressure measurements.

#### Yttrium-zinc alloys

The yttrium-zinc alloys were prepared by Mr. John Mason of the Ames Laboratory. Arc melted yttrium sponge from the Ames Laboratory was used. Major impurities included C-129 ppm, Fe-209 ppm, Ni-126 ppm and  $O_2$ -307 ppm. The yttrium and zinc metals were placed in a tantalum crucible and a preformed lid sealed on under an argon atmosphere. This was then placed in a steel bomb and a lid welded on under protective atmosphere. The assembly was heated well into the liquid region for the composition to be prepared. After equilibration, the alloy was cooled. Portions of the alloy were pulverized with a porcelain mortar and pestle. Small flat pieces of the pulverized alloy of 1/16 inch diameter or less were sealed into a quartz ampoule for irradiation. Sample weights were selected so as to contain



1-1.5 grams of zinc. After a seven day irradiation in a neutron flux of about  $2.5 \times 10^{13}$  n/cm<sup>2</sup>-sec the samples were allowed to cool for three weeks at the reactor site to allow the attendant 64 hour Y<sup>90</sup> activity to decay. After the irradiated alloys had been returned from the reactor, they were removed from the quartz ampoule, placed in a tantalum crucible and sealed into a dew point cell without further treatment.

#### Thorium-zinc alloys

Irradiation of inactive alloys is a very desirable method of preparing samples suitable for dew point measurements. This is not feasible, however, in the case of thorium-zinc alloys. Calculations show that at the end of a typical irradiation, there would be several curies of Pa<sup>233</sup> activity associated with each gram of thorium in the alloy. Although this would probably not interfere seriously with vapor pressure measurements, it was considered an intolerable amount of activity from a radiological health point of view. It would be possible to allow the 28 day protoactinium activity to decay to a level that could be handled, but in view of the long cooling time (8-10 months) and the toxicity of Pa<sup>233</sup>, direct alloying of tracer zinc metal with thorium was selected as the method of preparation.

Battelle Memorial Institute crystal-bar thorium was used to prepare the alloys. A piece of irradiated zinc

weighing between 1.2 and 1.8 grams and a quantity of thorium to yield the desired composition of alloy were charged to a tantalum crucible  $3/8$  inch in diameter and about  $2\ 1/2$  inches long. A prefit tantalum cap was arc welded on the crucible under an argon atmosphere. The sealed crucible was placed in another tantalum crucible  $1/2$  inch in diameter and about three inches long. A cap was welded on this crucible under a protective atmosphere and the whole assembly finally sealed in a  $3/4$  inch inside diameter iron bomb. The reason for using a dual tantalum crucible was that in the event of failure of the inner crucible, the outer container would serve to keep the zinc activity contained and prevent contamination of the furnace and the surrounding area.

The stainless steel bomb was fitted with a thermocouple and placed in an oscillating furnace. The temperature was slowly brought to  $1150^{\circ}$  C. Alloys in the composition range 0-90 weight percent thorium are completely molten at this temperature. The alloy was held at this temperature for about 30 minutes with occasional rocking. The furnace was allowed to cool and the bomb assembly removed. The iron jacket and outer tantalum crucible were removed by a remote operation. The sealed inner tantalum crucible containing the alloy was placed in a vise and the alloy crushed to fine particles. A hole was punched in the lid of the crucible with

a sharp steel spike and the crucible containing the alloy was immediately sealed into a dew point cell.

### C. Technique of Operation

Samples were heated to a desired temperature in the apparatus and allowed to come to equilibrium. A controlled stream of air was allowed to pass into the gas inlet tube. This was adjusted so that, as the dew point temperature was approached, the condensation bubble was being cooled at the rate of 1-2 degrees per minute or less. Simultaneously the counting rate was recorded in 30 second intervals. When the dew point was reached, an increase in counting rate of 30% or more was observed. Inclusion of a rate meter or recorder in the counting system did not increase the precision or sensitivity of the method.

The apparatus was first tested with pure zinc. The dew point was observed to randomly occur 0.5-1.75 degrees below the sample temperature. The temperature of the sample and the initial difference between the sample and bubble temperatures had no apparent effect on the temperature difference when condensation occurred.

Zinc vapor pressure measurements on alloys ranged from less than 1 mm to above 100 mm. One generally starts making measurements at a low sample temperature and works toward the highest temperature desired. As a check on the attainment of equilibrium, measurements were made on a

number of alloys both upon increasing and decreasing the sample temperature from the previous measurement. The determinations were in agreement with each other.

In the visual method of determining dew points, several heating and cooling cycles across the dew point temperature are made at each sample temperature and the temperature range in which condensation occurs can be narrowed to  $0.5^{\circ}\text{C}$ . This could not be done with the apparatus used in the present investigation. Upon warming above the dew point temperature, the increased counting rate usually persisted for several degrees. Therefore, as a check on each sample temperature, the dew point temperature was determined twice. The two determinations almost always agreed within one or two degrees.

The vapor pressure of zinc over the alloys was calculated at a given composition and sample temperature from the dew point temperature and the equation

$$\log P_{(\text{atm})} = 9.843 - \frac{6754.5}{T} - 1.318 \log T - 6.011 \times 10^{-3}T \quad (1)$$

which is Kelley's<sup>f</sup> (16) equation representing the vapor pressure of pure zinc. Chiotti and Gill (12) have compared this expression with the following expression derived from Kelley's revised heat capacity data (17) and the data given by Stull and Sinke (18) for the enthalpy and free energy of vaporization and sublimation of zinc.

$$\log P_{(\text{atm})} = \frac{-6678}{T} - 1.274 \log T + 9.568 \quad (2)$$

This expression is valid in the temperature range  $693^{\circ} - 1181^{\circ}\text{K}$ .

Equations (1) and (2) are in very close agreement. The maximum difference in  $\log P$  calculated from these two equations, (1) minus (2), in the temperature range indicated is 0.008 at about  $950^{\circ}$  K. The staff of the Minerals Research Laboratory of the University of California (19) have summarized the thermodynamic properties of a large number of metals and alloys. They have examined the zinc vapor pressure measurements of nine different investigators in the temperature range of interest, and have commented on the remarkable concordance of the values obtained. The  $\log P$  values that they have tabulated are within 2% of those obtained from Kelley's equation. Equation (2) was used in this work for an evaluation of the free energy and enthalpy of vaporization of zinc.

## III. PRESENTATION OF DATA

In the dew point method, one makes only two sets of measurements - the temperature of the sample and the dew point temperature. These, together with the composition of the sample studied, an analytical representation of the vapor pressure-temperature relationship of the condensable component, and a knowledge of the intermetallic phases in the system are sufficient in many cases to calculate some of the more useful thermodynamic properties of the system of interest.

In the systems studied in this investigation, the dew point temperature data were converted to  $\log P$  by use of Kelley's equation

$$\log P_{(\text{atm})} = 9.843 - \frac{6754.5}{T} - 1.318 \log T - 6.011 \times 10^{-5} T \quad (1)$$

These vapor pressure data were then expressed as empirical equations relating the logarithm of the pressure to sample temperature. Two-constant equations of the form

$$\log P = \frac{A}{T} + B$$

were utilized since the accuracy of the data did not warrant a more complex treatment.

Using standard statistical methods, the slope and intercept of each run and their standard deviations were calculated.

## A. The Aluminum-Zinc System

The constitutional diagram for the aluminum-zinc system according to Hansen (20) is shown in Figure 3. Alloys of ten different compositions varying from 9.3 to 70.0 atom percent zinc were measured. All measurements were made in the liquid region. Samples of sufficient size were utilized and a suitable temperature range for measurements selected so that there was generally no concern over depletion of zinc in the condensed phase. A summary of the results obtained is shown in Table 1 and plots of logarithm of pressure versus  $10^3/T$  are shown in Figures 4 - 13.

Table 1. Zinc vapor pressure as a function of temperature for various compositions in the aluminum-zinc system

Mole percent Zinc	$\log P = A/T + B$		Temperature range (°K)
	Log pressure in atmospheres		
	Temperature in °K		
	A	B	
9.3	-7889 ± 95	6.146 ± .094	960 - 1065
21.1	-6667 ± 64	5.239 ± .067	782 - 1079
33.5	-6571 ± 100	5.271 ± .106	896 - 1051
33.8	-6167 ± 161	4.907 ± .165	929 - 1055
44.2	-6533 ± 63	5.317 ± .068	853 - 995
49.1	-6308 ± 60	5.141 ± .062	894 - 1071
56.0	-6000 ± 312	4.881 ± .349	867 - 952
56.7	-6188 ± 92	5.063 ± .116	823 - 1000
61.7	-6394 ± 34	5.289 ± .036	824 - 1043
70.0	-6089 ± 49	5.026 ± .052	855 - 1036

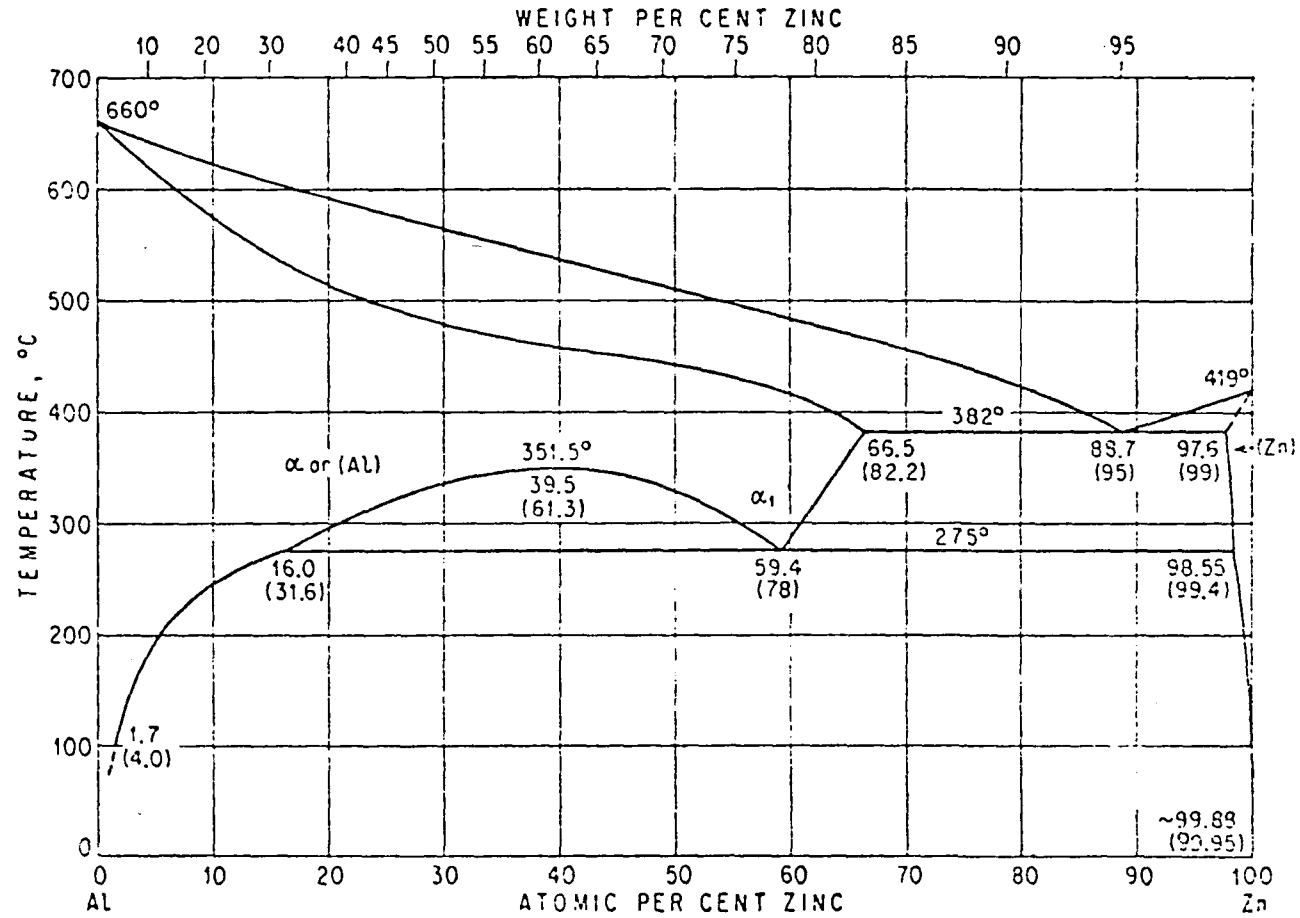


Figure 3. The aluminum-zinc system (20)



Figures 4 - 7. Plots of logarithm of zinc vapor pressure versus reciprocal temperature for aluminum-zinc alloys of various compositions.

Figure 4. 9.3 atomic percent zinc

Figure 5. 21.1 atomic percent zinc

Figure 6. 33.5 atomic percent zinc

Figure 7. 33.8 atomic percent zinc

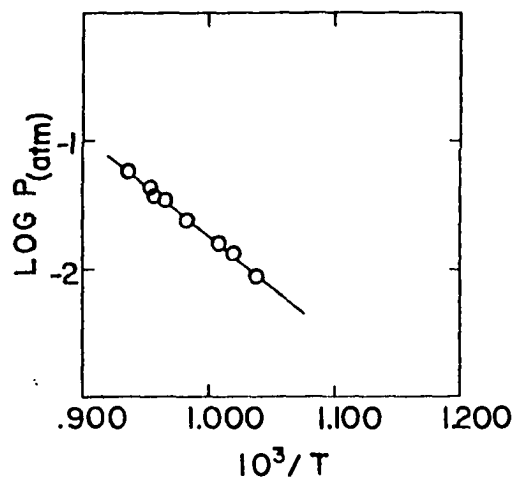


FIGURE 4

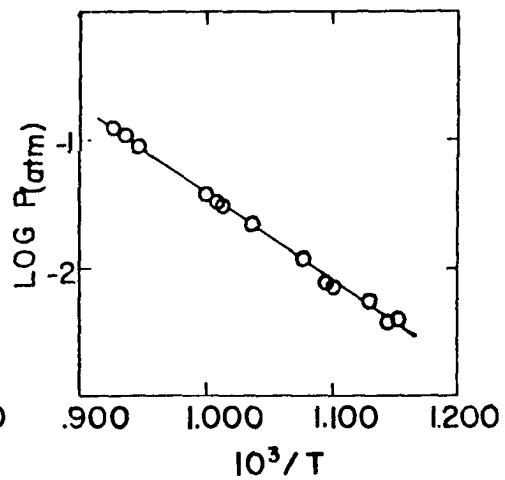


FIGURE 5

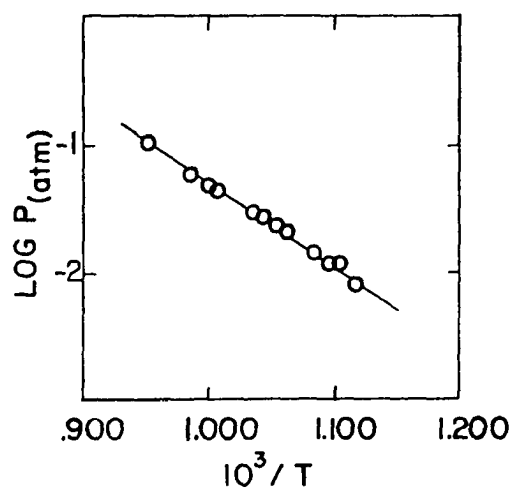


FIGURE 6

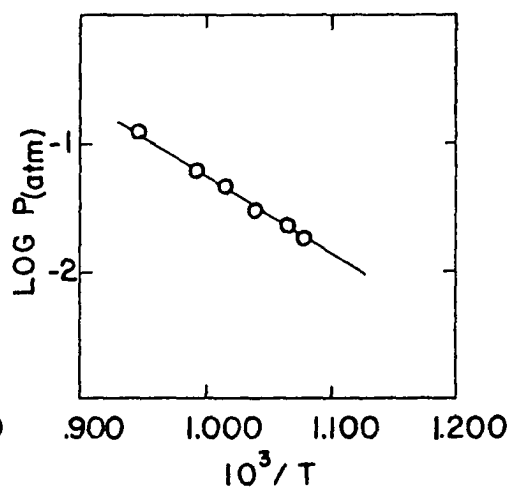


FIGURE 7

Figures 8 - 11. Plots of logarithm of zinc vapor pressure versus reciprocal temperature for aluminum-zinc alloys of various compositions.

Figure 8. 44.2 atomic percent zinc

Figure 9. 49.1 atomic percent zinc

Figure 10. 56.0 atomic percent zinc

Figure 11. 56.7 atomic percent zinc

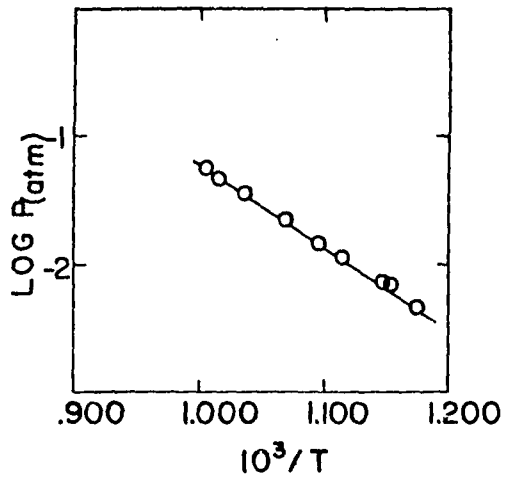


FIGURE 8

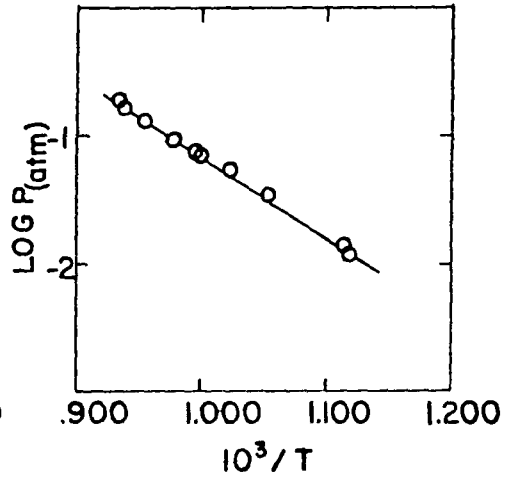


FIGURE 9

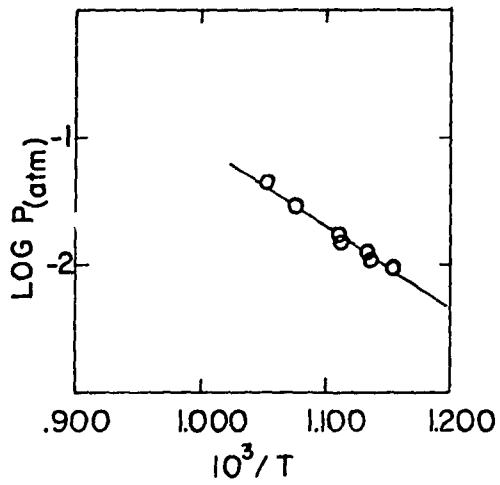


FIGURE 10

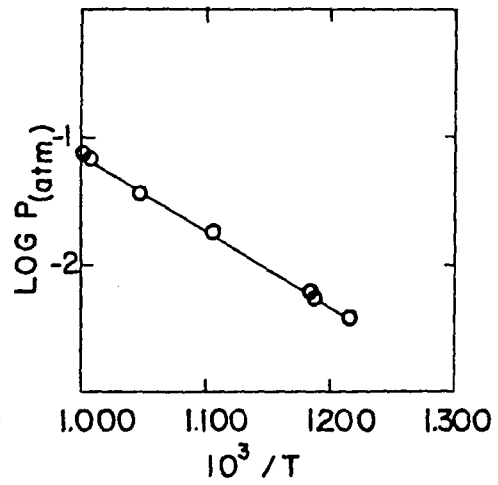


FIGURE 11

Figures 12 - 13. Plots of logarithm of zinc vapor pressure versus reciprocal temperature for aluminum-zinc alloys of various compositions.

Figure 12. 61.7 atomic percent zinc

Figure 13. 70.0 atomic percent zinc

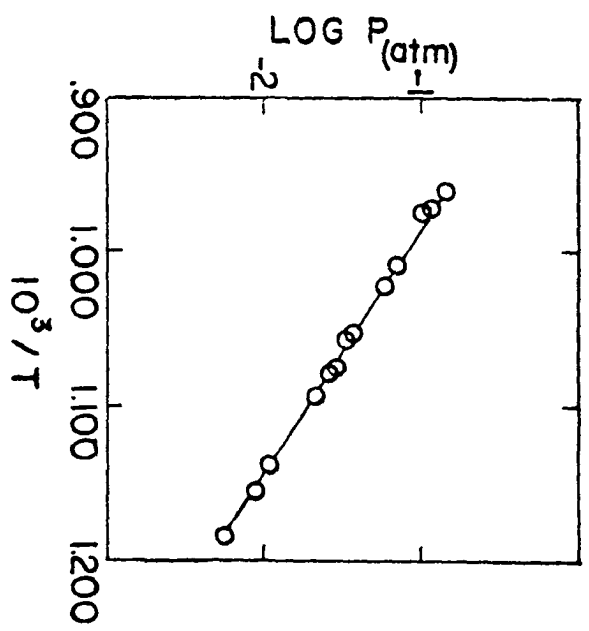


FIGURE 12

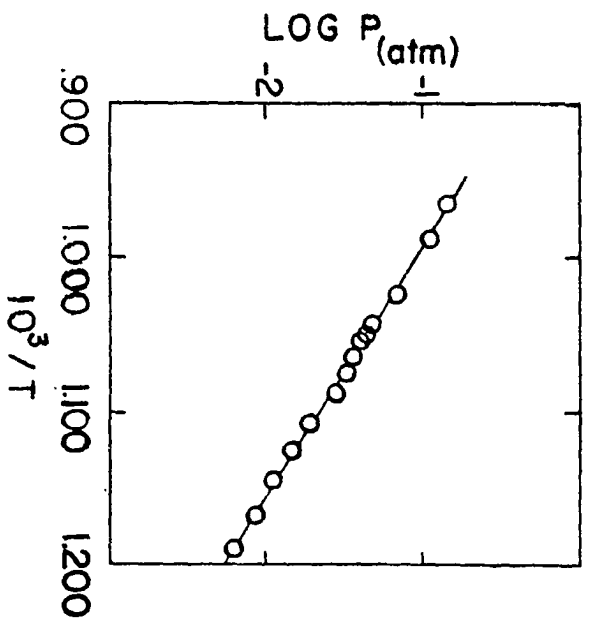


FIGURE 13

## B. The Yttrium-Zinc System

The phase diagram constructed for the yttrium-zinc system by Chiotti *et. al.* (13) is shown in Figure 14. Vapor pressure measurements were made in each two phase region of interest. The temperature range over which measurements were made was limited at the lower end by the fact that with the present experimental arrangement, vapor pressures of less than one millimeter were difficult to measure and at the upper end by concern over the integrity of the quartz cell. In narrow two-phase regions and at high pressures, there was also the danger that with these small samples, the composition of the condensed phase would shift to the next region due to depletion of zinc.

A summary of the results obtained on this system is shown in Table 2 and plots of logarithm of pressure versus  $10^3/T$  ( $K^0$ ) are shown in Figures 15 - 17.

Table 2. Zinc vapor pressure as a function of temperature for seven of the two-phase regions of the yttrium-zinc system

Weight percent zinc and equilibrium phases	$\log P = A/T + B$		Temperature range ( $^0K$ )
	Log pressure in atmospheres	Temperature in $^0K$	
	A	B	
22.0 - 30.2 Y-YZn	-11125 $\pm$ 291	6.796 $\pm$ .264	1040 - 1140
55.1 YZn-YZn <sub>2</sub>	- 8892 $\pm$ 80	6.051 $\pm$ .072	1022 - 1180

Table 2. (Continued)

Weight percent zinc and equilibrium phases	log P = A/T + B		Temperature range (°K)
	Log pressure in atmospheres Temperature in °K A	B	
67.7 YZn <sub>2</sub> -YZn <sub>3</sub>	-7966 ± 106	6.249 ± .105	909 - 1102
72.7 YZn <sub>3</sub> -YZn <sub>4</sub>	-7912 ± 55	6.310 ± .059	845 - 1127
77.9 YZn <sub>4</sub> -YZn <sub>5</sub>	-7519 ± 45	6.104 ± .047	985 - 1159
82.1 YZn-Y <sub>2</sub> Zn <sub>17</sub>	-7886 ± 60	6.501 ± .054	851 - 1065
87.2 Y <sub>2</sub> Zn <sub>17</sub> -YZn <sub>11</sub>	-6500 ± 80	5.478 ± .088	843 - 950

### C. The Thorium-Zinc System

The phase diagram of the thorium-zinc system (12) is shown in Figure 18. Vapor pressure measurements were made in all two-phase regions of interest. The difficulty in obtaining measurements at low zinc vapor pressures was present in this system as in the yttrium-zinc system. There was the added consideration that pulverized alloys were not inspected for particle size or oxide impurity. The radiological hazard associated with these fine particles required that the crucible containing the crushed alloy be sealed into a dew point cell as soon as its lid had been pierced. An



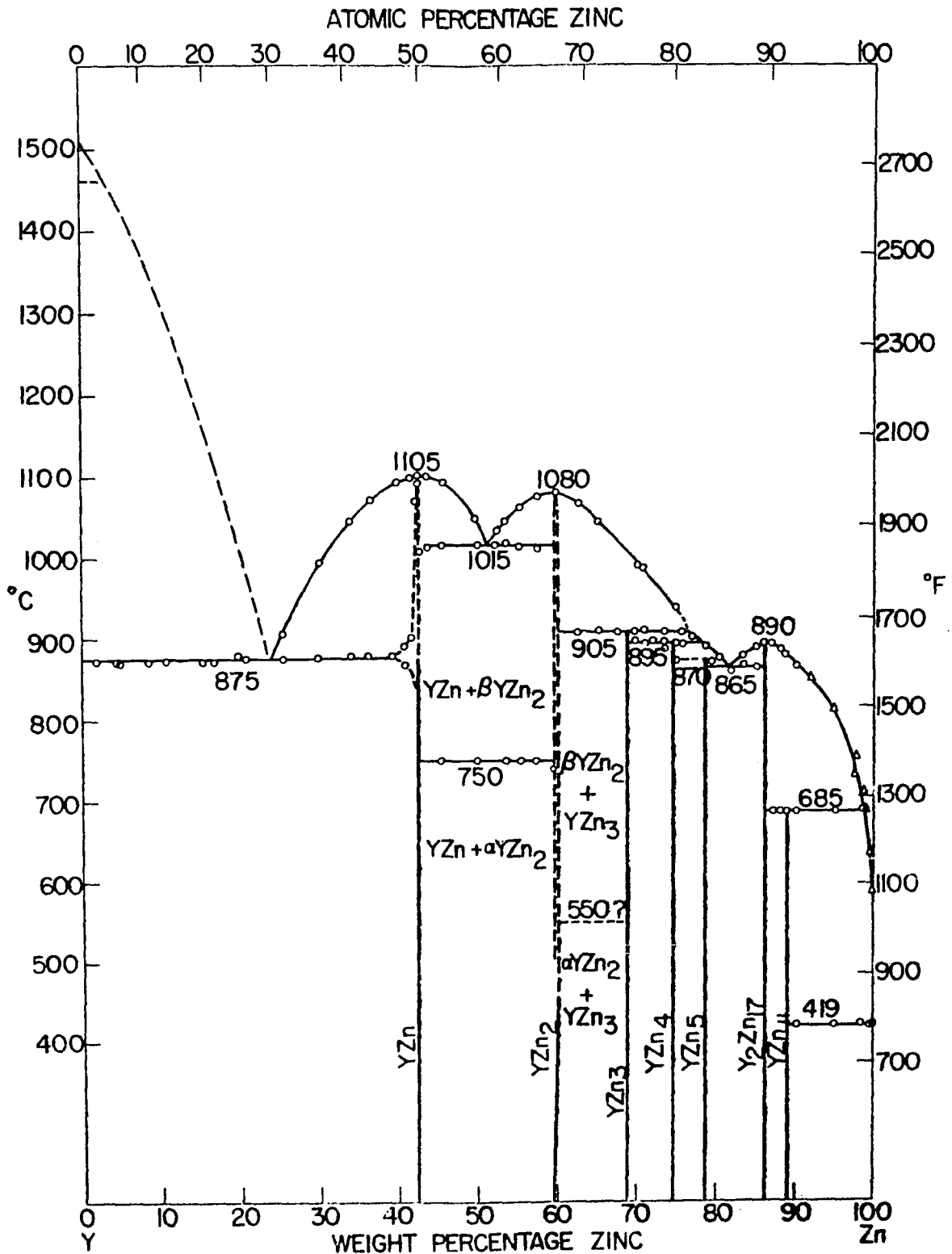


Figure 14. The yttrium-zinc system (13)

Figure 15. Plot of logarithm of zinc vapor pressure over yttrium-zinc alloys of 22.0, 30.2, 55.1 and 67.7 weight percent zinc versus reciprocal of temperature.

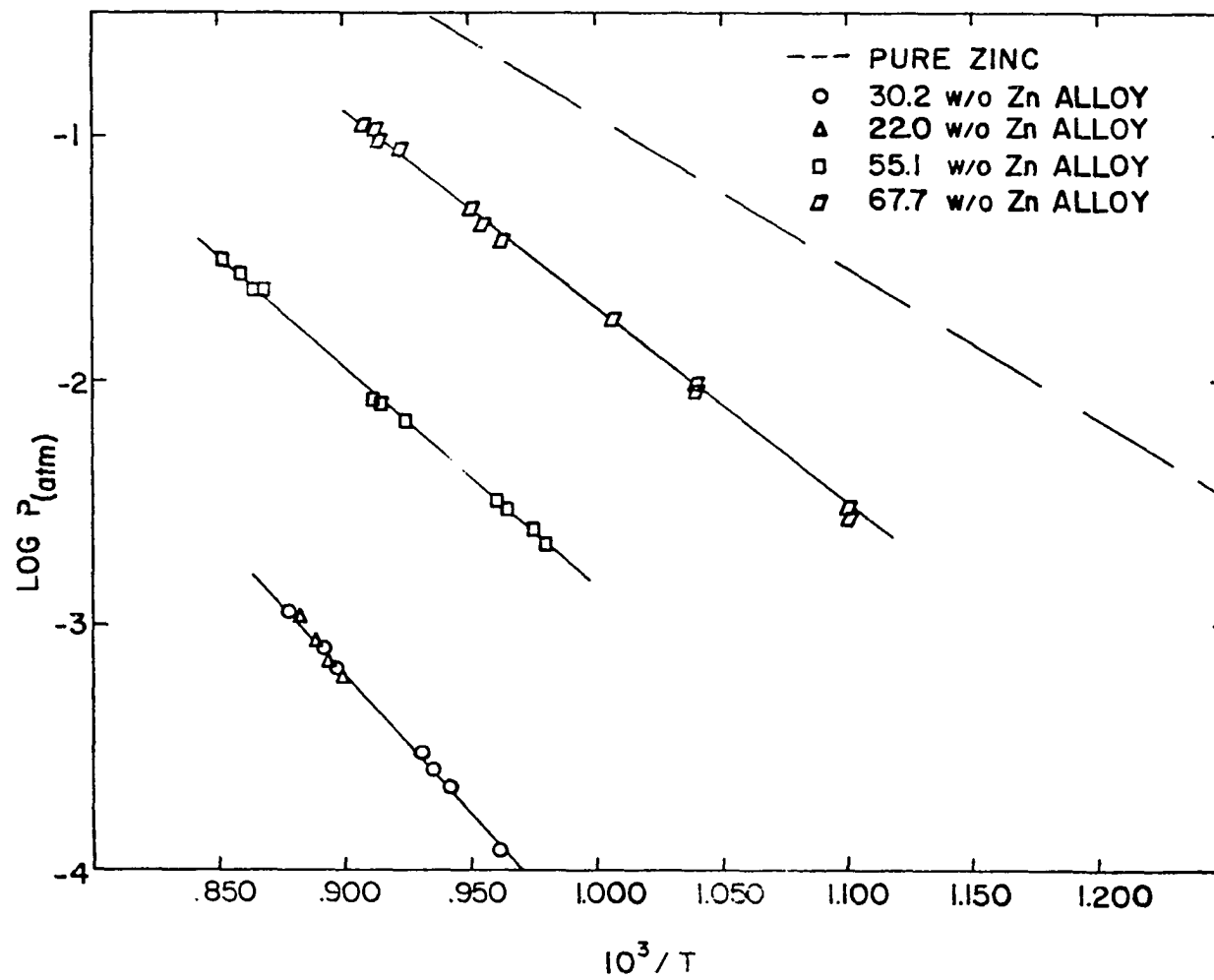


Figure 16. Plots of log vapor pressure over alloys of 72.7 and 77.9 weight percent zinc versus reciprocal of temperature.

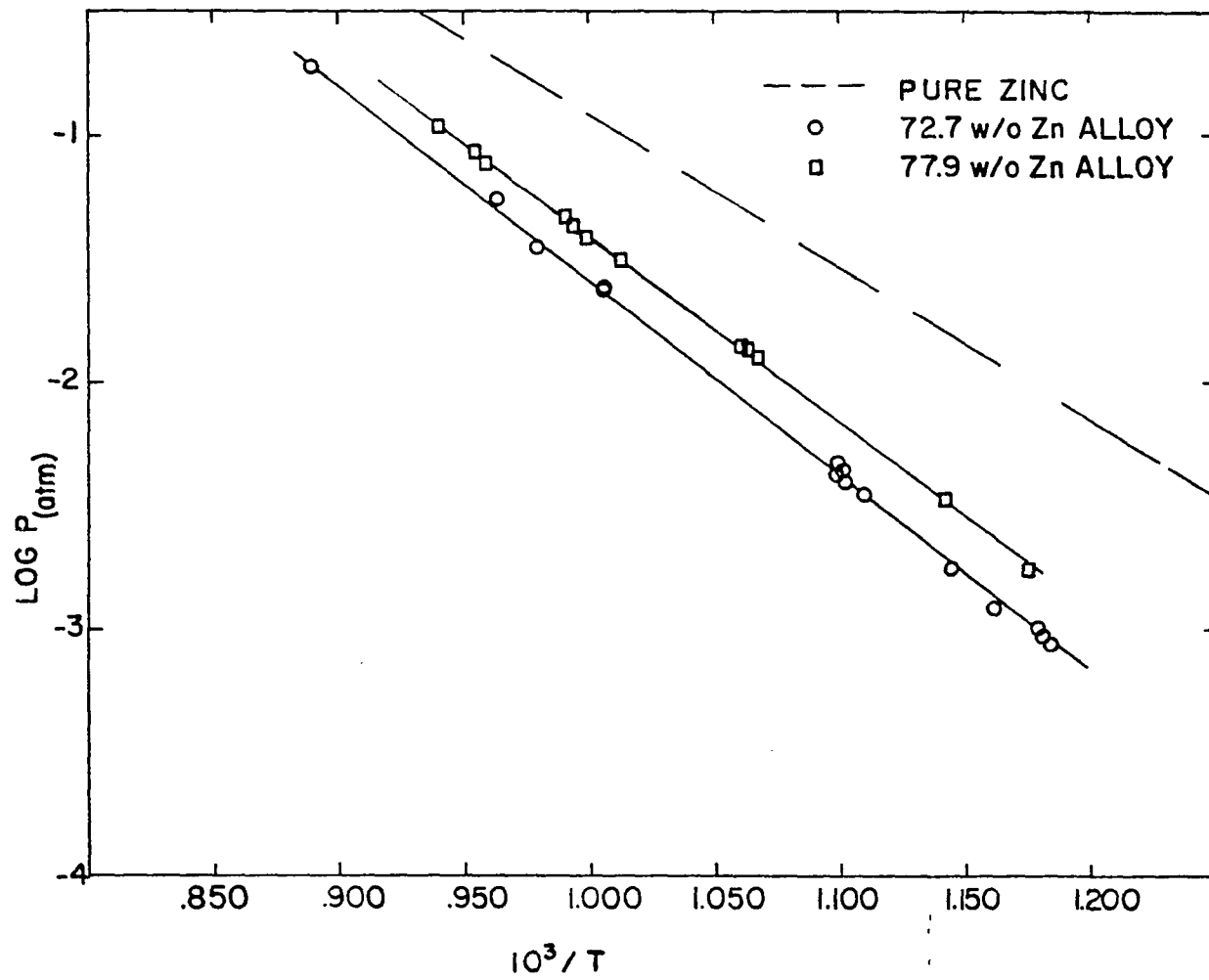
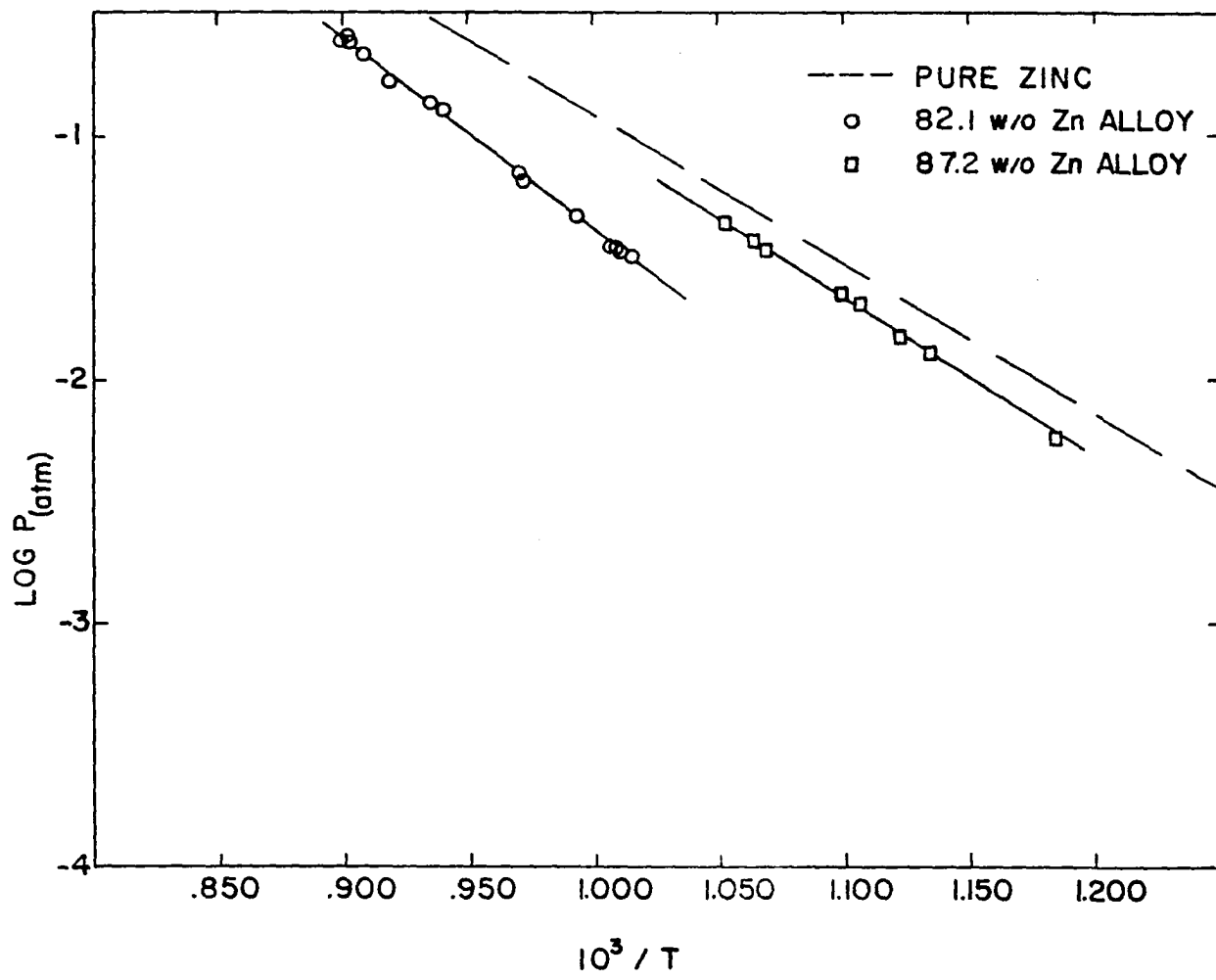


Figure 17. Plot of log vapor pressure over alloys of 82.1 and 87.1 weight percent zinc versus reciprocal of temperature



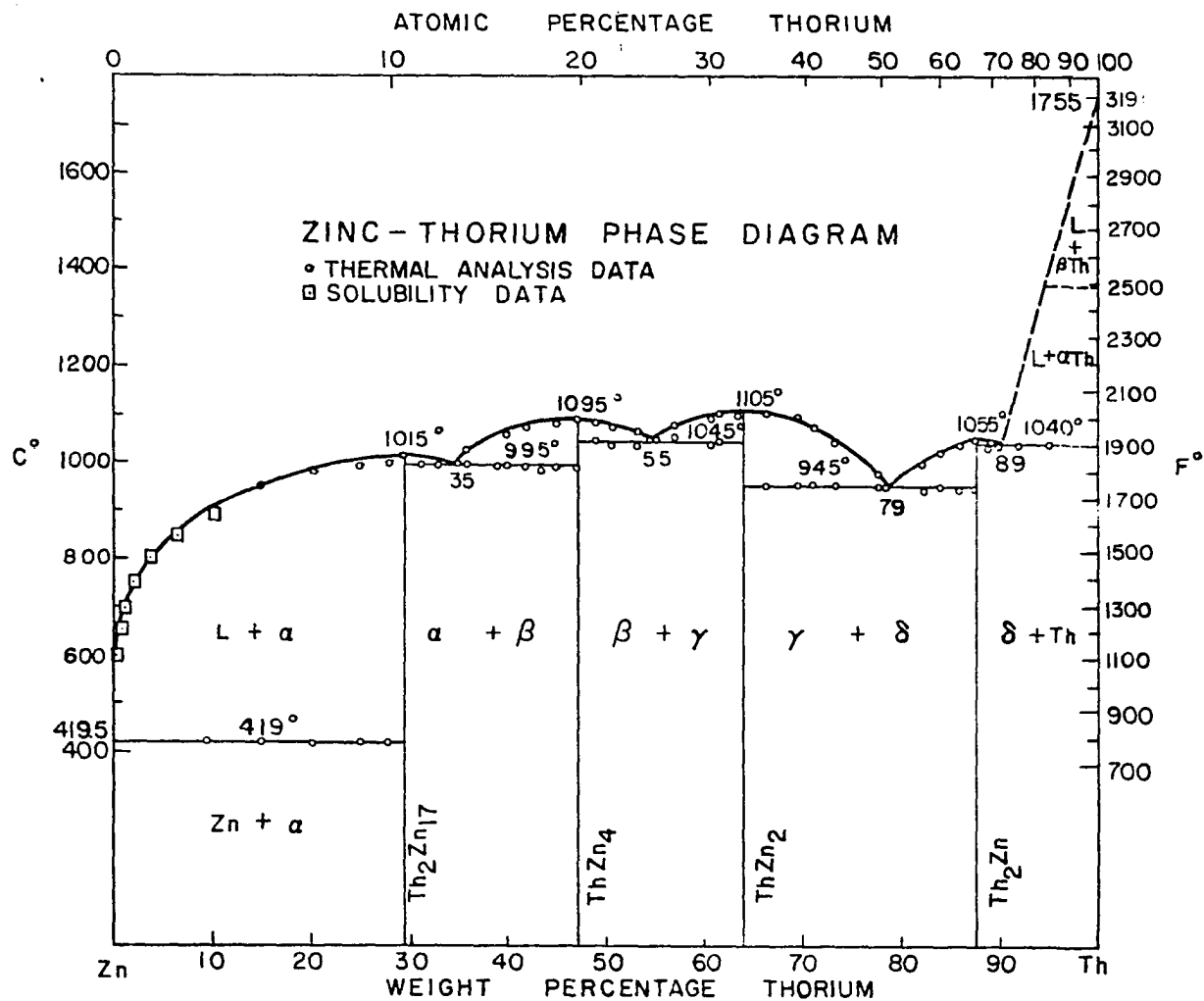


Figure 18. The thorium-zinc system (12)



examination of inactive alloys of various compositions indicated, however, that crushing in a vise yielded shiny particles of a desirable size.

A summary of the vapor pressure measurements is shown in Table 3, and plots of logarithm of pressure versus  $10^3/T$  ( $^{\circ}\text{K}$ ) are shown in Figure 19.

Table 3. Zinc vapor pressure as a function of temperature for four of the two-phase regions of the thorium-zinc system.

Weight percent zinc and equilibrium phases	$\log P = A/T + B$		Temperature range ( $^{\circ}\text{K}$ )
	Log pressure in atmospheres	Temperature in $^{\circ}\text{K}$	
	A	B	
10.0 Th-Th <sub>2</sub> Zn	-10130 $\pm$ 177	6.711 $\pm$ .158	1023 - 1166
24.8 Th <sub>2</sub> Zn-ThZn <sub>2</sub>	- 9000 $\pm$ 560	6.324 $\pm$ .603	1000 - 1098
44.9 ThZn <sub>2</sub> -ThZn <sub>4</sub>	- 8824 $\pm$ 199	6.835 $\pm$ .207	876 - 1057
61.8 ThZn <sub>4</sub> -Th <sub>2</sub> Zn <sub>17</sub>	- 7142 $\pm$ 88	5.753 $\pm$ .099	829 - 966

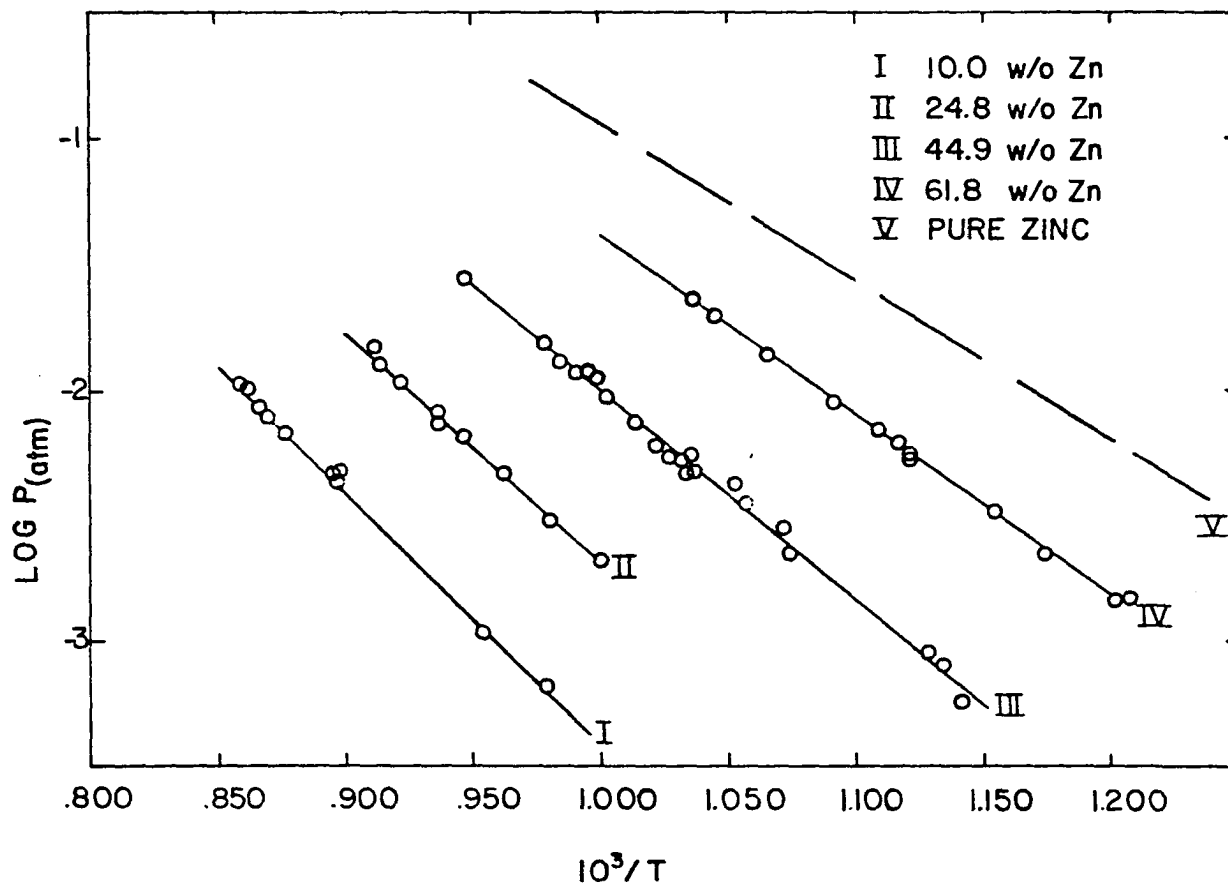


Figure 19. Plot of log zinc vapor pressure over thorium-zinc alloys of 10.0, 24.8, 44.9 and 61.8 weight percent zinc versus reciprocal of temperature

## IV. THERMODYNAMIC CALCULATIONS

The purpose of the vapor pressure measurements in this investigation is to permit a calculation of various thermodynamic properties of the systems studied. Measurements and calculations of this type are used on metal systems for a variety of applications ranging from blast furnace technology to processing of nuclear reactor fuels.

The thermodynamic standard reference state for a substance is commonly chosen as the pure liquid or solid at one atmosphere pressure and a given temperature or as the gas at unit fugacity and the temperature under consideration. The fugacity may be considered a corrected pressure and is defined to approach the pressure as the pressure approaches zero. In most work dealing with metal vapors, the ideal gas approximation is made and is generally valid since pressures are low.

The thermodynamic activity is related to the vapor pressure of component  $i$  in a condensed system by the relation

$$a_i = \frac{f_i}{f_i^0} \sim \frac{p_i}{p_i^0}$$

where

- $f_i$  = fugacity of pure  $i$
- $f_i^0$  = fugacity of  $i$  in the condensed phase
- $p_i$  = vapor pressure of pure  $i$
- $p_i^0$  = vapor pressure of  $i$  over the condensed phase

The thermodynamic activity coefficient, a measure of the departure from ideality is defined as

$$\gamma_i = \frac{a_i}{X_i} \quad (4)$$

The partial molal free energy of component  $i$ ,  $\overline{\Delta F}_i$ , is expressed by the relationship

$$\overline{\Delta F}_i = RT \ln a_i = RT \ln \frac{p_i}{p_i^0} \quad (5)$$

where  $R$  is the gas constant and  $T$  is the absolute temperature.

The enthalpy for a reaction in general is given by

$$\Delta H = \frac{d \frac{\Delta F}{T}}{d \frac{1}{T}} \quad (6)$$

and the entropy

$$\Delta S = \frac{\Delta H - \Delta F}{T} \quad (7)$$

In a binary system, the activity of the second component can be evaluated by integration of the Gibbs-Duhem equation

$$X_1 d \ln a_1 + X_2 d \ln a_2 = 0 \quad (8)$$

and the corresponding partial molal thermodynamic quantities can be calculated.

The integral quantities per mole of solution for the free energy, enthalpy and entropy of mixing are

$$\Delta F = X_1 \overline{\Delta F}_1 + X_2 \overline{\Delta F}_2 \quad (9)$$

$$\Delta H = X_1 \overline{\Delta H}_1 + X_2 \overline{\Delta H}_2 \quad (10)$$

$$\Delta S = X_1 \overline{\Delta S}_1 + X_2 \overline{\Delta S}_2 \quad (11)$$

## A. The Aluminum-Zinc System

Thermodynamic activities of zinc in solutions of various compositions were calculated at various temperatures from the vapor pressure data in Table 1 and Kelley's equation for the vapor pressure of pure zinc. It is difficult to evaluate accurately the errors in the activities calculated. Because of this and the fact that the partial molal quantities of the aluminum component would normally have to be evaluated by a graphical integration of the Gibbs-Duhem equation, it would be desirable to fit the data to an analytical expression relating activity and mole fraction.

In view of the fact that the molar volumes of zinc and aluminum differ by less than 9%, it was decided to fit the data to the so-called regular solution (21) (22) for equal size molecules.

By this definition, a regular solution is one in which

$$\ln \gamma_1 = \alpha X_2^2 \quad (12)$$

where  $\alpha$  is a characteristic parameter reflecting the deviation from Raoult's law.

The activity coefficient of the other component can be evaluated from the Gibbs-Duhem equation

$$X_1 d \ln a_1 + X_2 d \ln a_2 = 0 \quad (8)$$

$$X_1 + X_2 = 1 \quad (13)$$

$$dX_1 + dX_2 = 0 \quad (14)$$

$$X_1 \frac{dX_1}{X_1} + X_2 \frac{dX_2}{X_2} = 0 \quad (15)$$

$$X_1 d \ln X_1 + X_2 d \ln X_2 = 0 \quad (16)$$

adding (8) and (16)

$$X_1 d \ln \gamma_1 + X_2 d \ln \gamma_2 = 0 \quad (17)$$

$$d \ln \gamma_2 = \frac{-X_1}{X_2} d \ln \gamma_1 \quad (18)$$

from the definition of the regular solution

$$d \ln \gamma_1 = 2 \alpha X_2 dX_2 \quad (19)$$

$$d \ln \gamma_1 = \frac{-X_1}{X_2} 2 \alpha X_2 dX_2 \quad (20)$$

and since

$$dX_1 = -dX_2 \quad (14)$$

$$d \ln \gamma_2 = 2 \alpha X_1 dX_1 \quad (21)$$

$$\ln \gamma_2 = \alpha X_1^2 + \text{const.} \quad (22)$$

$$\text{At } X_1 = 0, \gamma_2 = 1 \text{ and } \ln \gamma_2 = 0 \text{ so const.} = 0 \quad (23)$$

$$\text{and } \ln \gamma_2 = \alpha X_1^2$$

The integral molal thermodynamic properties of a regular solution are readily derived

$$\Delta F_{\text{mix}} = RT (X_1 \ln a_1 + X_2 \ln a_2) \quad (24)$$

$$= RT (X_1 \ln \gamma_1 X_1 + X_2 \ln \gamma_2 X_2) \quad (25)$$

$$= RT (X_1 \ln X_1 + X_2 \ln X_2) + (X_1 \ln \gamma_1 + X_2 \ln \gamma_2) \quad (26)$$

$$= RT \left\{ (X_1 \ln X_1 + X_2 \ln X_2) + (\alpha X_1 X_2^2 + \alpha X_2 X_1^2) \right\} \quad (27)$$

$$= RT \left\{ (X_1 \ln X_1 + X_2 \ln X_2) + \alpha (X_1 X_2) \right\} \quad (28)$$

The expression in the first set of parenthesis in equation (28) reflects the free energy of mixing of an ideal solution and the  $\alpha (X_1 X_2)$  term is a correction term.

Since

$$\begin{aligned} \Delta H_{\text{mix}} &= \frac{d \frac{\Delta F_{\text{mix}}}{T}}{d \frac{1}{T}} \\ \Delta H_{\text{mix}} &= \frac{d}{d \frac{1}{T}} R \left\{ (X_1 \ln X_1 + X_2 \ln X_2 + \alpha (X_1 X_2)) \right\} \\ &= R (X_1 X_2) \frac{d \alpha}{d \frac{1}{T}} \end{aligned} \quad (29)$$

Values of  $\alpha$  were calculated at 950, 975, 1000, 1025 and 1050°K for each alloy. The average value at each temperature was computed as was its standard deviation. (23) The standard deviation for a series of measurements is given as

$$\sigma_m = \sqrt{\frac{\sum (X_i - \bar{X})^2}{N_o (N_o - 1)}} \quad (30)$$

where  $N_o$  is the number of determinations,  $\bar{X}$  is the average value of the series and  $X_i$  is the value of the  $i$ th determination. Values of  $\alpha$  and their standard deviations are tabulated for each temperature in Table 4.

Table 4. Values of  $\alpha$  at 950, 975, 1000, 1025 and 1050 °K.

Temperature (°K)	$\alpha$	$\sigma_\alpha$
950	0.500	0.051
975	0.548	0.037
1000	0.592	0.036
1025	0.626	0.026
1050	0.666	0.033

A plot was made of  $\alpha$  versus reciprocal temperature and is shown in Figure 20. The slope of this line,  $\frac{d\alpha}{d\frac{1}{T}}$ , was calculated to be  $-1428 \pm 108$  °K.

Equations (28) and (30), the data in Table 4 and the value of  $\frac{d\alpha}{d\frac{1}{T}}$  were utilized to calculate the integral free energy, enthalpy and entropy of mixing of various compositions at 950 and 1050 °K. These values are shown in Table 5 along with the thermodynamic activities for the two components.

The standard deviations of the various thermodynamic quantities are also given in Table 5. The standard deviations of the free energy and enthalpy of mixing are  $\sigma \Delta F_{\text{mix}} = RT X_1 X_2 \sigma_\alpha$  and  $\sigma \Delta H_{\text{mix}} = R X_1 X_2 \sigma \frac{d\alpha}{d\frac{1}{T}}$ .  $\sigma \Delta S_{\text{mix}}$  was calculated from  $T \sigma \Delta S_{\text{mix}} = \sqrt{\sigma \Delta F_{\text{mix}}^2 + \sigma \Delta H_{\text{mix}}^2}$ . The standard deviations of the



Figure 20. Plot of  $\alpha$  versus reciprocal temperature for the aluminum-zinc system.

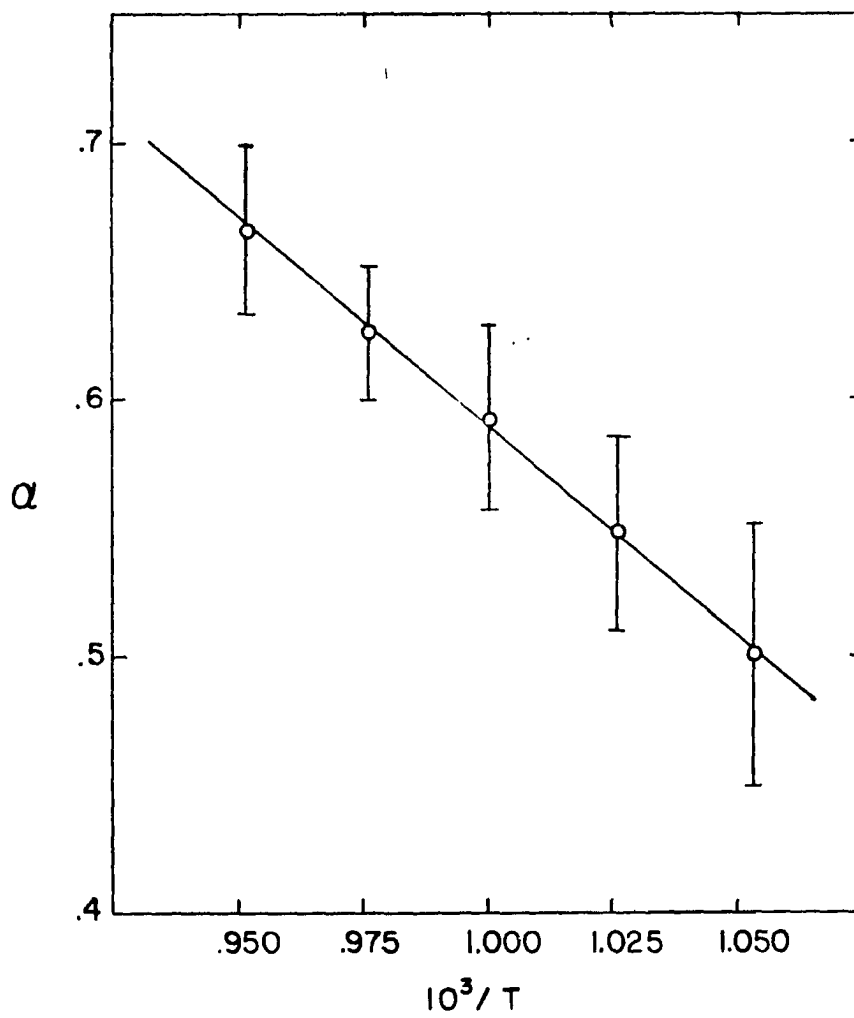


Table 5. Thermodynamic activities and free energy, enthalpy and entropy of mixing in the aluminum-zinc system.

950 °K						
$X_{Zn}$	$a_{Zn}$	$a_{Al}$	$\Delta F_{mix}$	$\Delta H_{mix}$	$\Delta S_{mix}$	
			(cal/mole)	(cal/mole)	(cal/deg - mole)	
.1	$\pm .150$ $\pm .006$	$\pm .904$ $\pm .001$	- 529 $\pm 9$	- 255 $\pm 19$	$\pm .29$ $\pm .02$	
.2	$\pm .276$ $\pm .011$	$\pm .816$ $\pm .002$	- 793 $\pm 16$	- 454 $\pm 34$	$\pm .36$ $\pm .04$	
.3	$\pm .383$ $\pm .009$	$\pm .732$ $\pm .003$	- 955 $\pm 20$	- 596 $\pm 45$	$\pm .38$ $\pm .05$	
.4	$\pm .479$ $\pm .008$	$\pm .650$ $\pm .005$	- 1043 $\pm 23$	- 681 $\pm 52$	$\pm .38$ $\pm .06$	
.5	$\pm .567$ $\pm .007$	$\pm .567$ $\pm .007$	- 1073 $\pm 24$	- 709 $\pm 54$	$\pm .38$ $\pm .06$	
.6	$\pm .650$ $\pm .005$	$\pm .479$ $\pm .008$	- 1043 $\pm 23$	- 681 $\pm 52$	$\pm .38$ $\pm .06$	
.7	$\pm .732$ $\pm .003$	$\pm .383$ $\pm .009$	- 955 $\pm 20$	- 596 $\pm 45$	$\pm .38$ $\pm .05$	
.8	$\pm .816$ $\pm .002$	$\pm .276$ $\pm .011$	- 793 $\pm 16$	- 454 $\pm 34$	$\pm .36$ $\pm .04$	
.9	$\pm .904$ $\pm .001$	$\pm .150$ $\pm .006$	- 529 $\pm 9$	- 255 $\pm 19$	$\pm .29$ $\pm .02$	
1050 °K						
.1	$\pm .171$ $\pm .004$	$\pm .907$ $\pm .001$	- 553 $\pm 6$	- 255 $\pm 19$	$\pm .28$ $\pm .02$	
.2	$\pm .306$ $\pm .006$	$\pm .822$ $\pm .001$	- 822 $\pm 11$	- 454 $\pm 34$	$\pm .35$ $\pm .03$	
.3	$\pm .416$ $\pm .007$	$\pm .743$ $\pm .002$	- 983 $\pm 14$	- 596 $\pm 45$	$\pm .37$ $\pm .04$	

Table 5. (Continued)

1050 °K					
$X_{Zn}$	$a_{Zn}$	$a_{Al}$	$\Delta F_{mix}$ (cal/mole)	$\Delta H_{mix}$ (cal/mole)	$\Delta S_{mix}$ (cal/deg - mole)
.4	.509 ± .006	.668 ± .004	- 1071 ± 17	- 681 ± 52	.37 ± .05
.5	.591 ± .005	.591 ± .005	- 1099 ± 17	- 709 ± 54	.37 ± .05
.6	.668 ± .004	.509 ± .006	- 1071 ± 17	- 681 ± 52	.37 ± .05
.7	.743 ± .002	.416 ± .007	- 983 ± 14	- 596 ± 45	.37 ± .04
.8	.822 ± .001	.306 ± .006	- 822 ± 11	- 454 ± 34	.35 ± .03
.9	.907 ± .001	.171 ± .004	- 533 ± 6	- 255 ± 19	.28 ± .02

thermodynamic activities were calculated from the expressions

$$\sigma \ln \gamma_1 = X_2^2 \sigma_\alpha \quad \text{and} \quad \ln a_1 = \ln \gamma_1 + \ln X_1$$

so that

$$\sigma \ln a_1 = X_2^2 \sigma_\alpha$$

#### B. The Yttrium-Zinc System

The yttrium-zinc system shown in Figure 14 contains seven intermetallic phases which have been treated as line compounds separated by heterogeneous fields. In the first field, below 858 °C, we have yttrium, YZn and zinc vapor in equilibrium.

Since the number of components in the system is two, the variance is one -- indicating that at a fixed temperature in the region, the pressure of zinc and all other intensive variables become determinate. This equilibrium pressure is related to the  $\Delta F^\circ$  of the reaction



by the relationship

$$\Delta F^\circ = RT \ln p_{Zn} \quad (32)$$

This is combined with the reaction



for which the standard free energy is

$$\Delta F^\circ = -RT \ln p_{Zn}^\circ \quad (34)$$

Combining equations (31) and (33), giving the expression for the formation of YZn from the elements in their standard states,



for which the  $\Delta F^\circ$  is the sum of (32) and (34)

$$\Delta F^\circ = RT \ln \frac{p}{p^\circ} \quad (36)$$

The enthalpy,  $\Delta H^\circ$ , =

$$\frac{d \frac{\Delta F^\circ}{T}}{d \frac{1}{T}} = R \frac{d \ln \frac{p}{p^\circ}}{d \frac{1}{T}} \quad (37)$$

Equivalent calculations can be accomplished for each succeeding compound in the system, utilizing the thermodynamic values computed for the preceding compound. Thus the accuracy of the calculated value of the enthalpy or free energy of formation will depend in part on the error involved in the determination of the corresponding value of the preceding compounds. A summary of the data required to evaluate the standard free energy and enthalpy of the compounds in the yttrium-zinc system is given in Tables 6 and 7.

These calculations assume that the solid solubility of zinc in yttrium is negligible. The linear form used for relating  $\log P$  and  $1/T$  assumes that  $\Delta C_p$  for the reaction of a compound plus zinc vapor going to the next higher compound is zero. This appears to be valid within the accuracy of the data. The best fit straight line of logarithm of zinc pressure versus reciprocal temperature for each run was examined and residuals of individual data are randomly scattered with respect to sign and magnitude. Any appreciable change in  $\Delta C_p$  with temperature for the reaction should be reflected in a gradual change in the value of these residuals as the temperature changes.

The equations outlined in Tables 6 and 7 and the vapor pressure equations for this system were combined with the expressions relating the vapor pressure of pure zinc to its enthalpy and free energy of vaporization to give analytical

Table 6. Relationship between free energy and vapor pressure for compounds on the yttrium-zinc system.

Region	Reactions	$\Delta F$
Y-YZn	$Y + Zn_{(v)} \rightleftharpoons YZn$	$\Delta F_1 = RT \ln p_1$
	$Zn_{(l)} \rightleftharpoons Zn_{(v)}$	$\Delta F^\circ = -RT \ln p^\circ$
	<hr/> $Y + Zn_{(l)} \rightleftharpoons YZn$	<hr/> $\Delta F_I^\circ = RT \ln \frac{p_1}{p^\circ}$
YZn-YZn <sub>2</sub>	$YZn + Zn_{(v)} \rightleftharpoons YZn_2$	$\Delta F_2 = RT \ln p_2$
	$Zn_{(l)} \rightleftharpoons Zn_{(v)}$	$\Delta F^\circ = -RT \ln p^\circ$
	$Y + Zn_{(l)} \rightleftharpoons YZn$	$\Delta F_I^\circ$
	<hr/> $Y + 2Zn_{(l)} \rightleftharpoons YZn_2$	<hr/> $\Delta F_{II}^\circ = \Delta F_I^\circ + RT \ln \frac{p_2}{p^\circ}$
YZn <sub>2</sub> -YZn <sub>3</sub>	$YZn_2 + Zn_{(v)} \rightleftharpoons YZn_3$	$\Delta F_3 = RT \ln p_3$
	$Zn_{(l)} \rightleftharpoons Zn_{(v)}$	$\Delta F^\circ = -RT \ln p^\circ$
	$Y + 2Zn_{(l)} \rightleftharpoons YZn_2$	$\Delta F_{II}^\circ$
	<hr/> $Y + 3Zn_{(l)} \rightleftharpoons YZn_3$	<hr/> $\Delta F_{III}^\circ = \Delta F_{II}^\circ + RT \ln \frac{p_3}{p^\circ}$

Table 6. (Continued)

Region	Reactions	$\Delta F$
$YZn_4 - YZn_3$	$YZn_3 + Zn_{(v)} \rightleftharpoons YZn_4$	$\Delta F_4 = RT \ln p_4$
	$Zn_{(l)} \rightleftharpoons Zn_{(v)}$	$\Delta F^{\circ} = RT \ln p^{\circ}$
	$Y + 3Zn_{(l)} \rightleftharpoons YZn_3$	$\Delta F^{\circ}_{III}$
	<hr/>	<hr/>
	$Y + 4Zn_{(l)} \rightleftharpoons YZn_4$	$\Delta F^{\circ}_{IV} = \Delta F^{\circ}_{III} + RT \ln \frac{p_4}{p^{\circ}}$
$YZn_5 - YZn_4$	$YZn_4 + Zn_{(v)} \rightleftharpoons YZn_5$	$\Delta F_5 = RT \ln p_5$
	$Zn_{(l)} \rightleftharpoons Zn_{(v)}$	$\Delta F^{\circ} = -RT \ln p^{\circ}$
	$Y + 4Zn_{(l)} \rightleftharpoons YZn_4$	$\Delta F^{\circ}_{IV}$
	<hr/>	<hr/>
	$Y + 5Zn_{(l)} \rightleftharpoons YZn_5$	$\Delta F^{\circ}_V = \Delta F^{\circ}_{IV} + RT \ln \frac{p_5}{p}$
$Y_2Zn_{17} - YZn_5$	$2YZn_5 + 7Zn_{(v)} \rightleftharpoons Y_2Zn_{17}$	$7\Delta F_6 = 7RT \ln p_6$
	$7Zn_{(l)} \rightleftharpoons 7Zn_{(v)}$	$7\Delta F^{\circ} = -7RT \ln p^{\circ}$
	$2Y + 10Zn_{(l)} \rightleftharpoons 2YZn_5$	$2\Delta F^{\circ}_V$
	<hr/>	<hr/>
	$2Y + 17Zn_{(l)} \rightleftharpoons Y_2Zn_{17}$	$\Delta F^{\circ}_{VI} = 2\Delta F^{\circ}_V + 7RT \ln \frac{p_6}{p^{\circ}}$



Table 6. (Continued)

Region	Reactions	$\Delta F$
YZn <sub>11</sub> -Y <sub>2</sub> Zn <sub>17</sub>	$1/2Y_2Zn_{17} + 5/2Zn_{(v)} \rightleftharpoons YZn_{11}$	$5/2\Delta F_7 = 5/2RT \ln p_7$
	$5/2Zn_{(1)} \rightleftharpoons 5/2Zn_{(v)}$	$5/2\Delta F^\circ = -5/2RT \ln p_0$
	$Y + 17/2Zn_{(1)} \rightleftharpoons 1/2Y_2Zn_{17}$	$1/2\Delta F_{VI}^\circ$
	$Y + 11Zn_{(1)} \rightleftharpoons YZn_{11}$	$\Delta F_{VII}^\circ = 1/2\Delta F_{VI}^\circ + 5/2RT \ln \frac{p_7}{p_0}$

Table 7. Relationship between the enthalpy and vapor pressure for compounds in the yttrium-zinc system.

Region	Reactions	$\Delta H$
Y-YZn	$Y + Zn_{(v)} \rightleftharpoons YZn$	$\Delta H_1 = R \frac{d \ln p_1}{d \frac{1}{T}}$
	$Zn_{(l)} \rightleftharpoons YZn_{(v)}$	$\Delta H^\circ = -R \frac{d \ln p^\circ}{d \frac{1}{T}}$
	<hr/>	<hr/>
	$Y + Zn_{(l)} \rightleftharpoons YZn$	$\Delta H_I^\circ = \Delta H_1 + \Delta H^\circ$
YZn-YZn <sub>2</sub>	$YZn + Zn_{(v)} \rightleftharpoons YZn_2$	$\Delta H_2 = -R \frac{d \ln p_2}{d \frac{1}{T}}$
	$Zn_{(l)} \rightleftharpoons Zn_{(v)}$	$\Delta H^\circ = R \frac{d \ln p^\circ}{d \frac{1}{T}}$
	$Y + Zn_{(l)} \rightleftharpoons YZn$	$\Delta H_I^\circ$
	<hr/>	<hr/>
	$Y + 2Zn_{(l)} \rightleftharpoons YZn_2$	$\Delta H_{II}^\circ = \Delta H_2 + \Delta H^\circ + \Delta H_I^\circ$

Table 7. (Continued)

Region	Reactions	$\Delta H$
YZn <sub>2</sub> -YZn <sub>3</sub>	$YZn_2 + Zn_{(v)} \rightleftharpoons YZn_3$	$\Delta H_3 = R \frac{d \ln p_3}{d \frac{1}{T}}$
	$Zn_{(l)} \rightleftharpoons Zn_{(v)}$	$\Delta H^\circ = -R \frac{d \ln p_o}{d \frac{1}{T}}$
	$Y + 2Zn_{(l)} \rightleftharpoons YZn_2$	$\Delta H_{II}^\circ$
	$Y + 3Zn_{(l)} \rightleftharpoons YZn_3$	$\Delta H_{III}^\circ = \Delta H_3 + \Delta H^\circ + \Delta H_{II}^\circ$
YZn <sub>4</sub> -YZn <sub>3</sub>	$YZn_3 + Zn_{(v)} \rightleftharpoons YZn_4$	$\Delta H_4 = R \frac{d \ln p_4}{d \frac{1}{T}}$
	$Zn_{(l)} \rightleftharpoons Zn_{(v)}$	$\Delta H^\circ = -R \frac{d \ln p^\circ}{d \frac{1}{T}}$
	$Y + 3Zn_{(l)} \rightleftharpoons YZn_3$	$\Delta H_{III}^\circ$
	$Y + 4Zn_{(l)} \rightleftharpoons YZn_4$	$\Delta H_{IV}^\circ = \Delta H_4 + \Delta H^\circ + \Delta H_{III}^\circ$

Table 7. (Continued)

Region	Reactions	$\Delta H$
$YZn_5 - YZn_4$	$YZn_4 + Zn_{(v)} \rightleftharpoons YZn_5$	$\Delta H_5 = R \frac{d \ln p_5}{d \frac{1}{T}}$
	$Zn_{(l)} \rightleftharpoons Zn_{(v)}$	$\Delta H^\circ = -R \frac{d \ln p^\circ}{d \frac{1}{T}}$
	$Y + 4Zn_{(l)} \rightleftharpoons YZn_4$	$\frac{\Delta H^\circ_{IV}}{\quad}$
	$Y + 5Zn_{(l)} \rightleftharpoons YZn_5$	$\Delta H^\circ_V = \Delta H_5 + \Delta H^\circ + \Delta H^\circ_{IV}$
$Y_2Zn_{17} - YZn_5$	$2YZn_5 + 7Zn_{(v)} \rightleftharpoons Y_2Zn_{17}$	$7\Delta H_6 = 7R \frac{d \ln p_6}{d \frac{1}{T}}$
	$7Zn_{(l)} \rightleftharpoons 7Zn_{(v)}$	$7\Delta H^\circ = -7R \frac{d \ln p^\circ}{d \frac{1}{T}}$
	$2Y + 10Zn_{(l)} \rightleftharpoons 2YZn_5$	$\frac{2\Delta H^\circ_V}{\quad}$
	$2Y + 17Zn_{(l)} \rightleftharpoons Y_2Zn_{17}$	$\Delta H^\circ_{VI} = 7\Delta H_6 + 7\Delta H^\circ + 2\Delta H^\circ_V$

Table 7. (Continued)

Region	Reactions	$\Delta H$
$YZn_{11} - Y_2Zn_{17}$	$1/2Y_2Zn_{17} + 5/2Zn_{(v)} \rightleftharpoons YZn_{11}$	$5/2\Delta H_7 = 5/2R \frac{d \ln p_7}{d \frac{1}{T}}$
	$5/2Zn_{(l)} \rightleftharpoons 5/2Zn_{(v)}$	$5/2\Delta H^\circ = -5/2R \frac{d \ln p^\circ}{d \frac{1}{T}}$
	$Y + 17/2Zn_{(l)} \rightleftharpoons 1/2Y_2Zn_{17}$	$1/2\Delta H_{VI}^\circ$
	$Y + 11Zn_{(l)} \rightleftharpoons YZn_{11}$	$\Delta H_{VII}^\circ = 5/2\Delta H_7 + 5/2\Delta H^\circ + 1/2\Delta H_{VI}^\circ$

relationships for the integral free energy, enthalpy and entropy of formation of the seven compounds in the system. The expressions obtained are listed in Table 8. From these equations values of the thermodynamic quantities were calculated at 750 and 1000 °K. These are given in Table 9.

Also given in Table 8 are standard deviations for the calculated values. These have been derived solely from the data obtained in this investigation and are based on the standard deviations calculated for the slope and intercept of the vapor pressure equations. No estimation was made of the errors in  $\Delta H_{\text{vap}}^{\circ}$  and  $\Delta F_{\text{vap}}^{\circ}$  of pure zinc. Since the vapor pressure-temperature relationship of zinc has been quite accurately characterized, they are undoubtedly quite small compared to the errors in the present work.

The standard deviations of the constants in the vapor pressure equations were obtained from the equations

$$\sigma_{\text{intercept}} = \sigma_y \sqrt{\frac{\sum X^2}{k \sum X^2 - (\sum X)^2}} \quad (24)$$

$$\sigma_{\text{slope}} = \sigma_y \sqrt{\frac{k}{k \sum X^2 - (\sum X)^2}}$$

where  $k$  equals the number of determinations,  $\sum X$  is the sum of all reciprocal temperature values and  $\sigma_y$  is given by

Table 8. Analytical expressions for the standard thermodynamic properties of formation of compounds in the yttrium-zinc system in the temperature range studied.

YZn	$\Delta F_{\text{form}}^{\circ}$	=	-20361	+	5.826 TlogT	-12.667T
	$\Delta H_{\text{form}}^{\circ}$	=	-20361	-2.53T		
	$\Delta S_{\text{form}}^{\circ}$	=	10.14	-5.826 logT		
YZn <sub>2</sub>	$\Delta F_{\text{form}}^{\circ}$	=	-30484	+11.652 TlogT	-28.744T	
	$\Delta H_{\text{form}}^{\circ}$	=	-30484	-5.06T		
	$\Delta S_{\text{form}}^{\circ}$	=	23.68	-11.652 logT		
YZn <sub>3</sub>	$\Delta F_{\text{form}}^{\circ}$	=	-36389	+17.478 TlogT	-43.915T	
	$\Delta H_{\text{form}}^{\circ}$	=	-36389	-7.59T		
	$\Delta S_{\text{form}}^{\circ}$	=	36.33	-17.478 logT		
YZn <sub>4</sub>	$\Delta F_{\text{form}}^{\circ}$	=	-42047	+23.304 TlogT	-58.806T	
	$\Delta H_{\text{form}}^{\circ}$	=	-42047	-10.12T		
	$\Delta S_{\text{form}}^{\circ}$	=	48.69	-23.304 logT		
YZn <sub>5</sub>	$\Delta F_{\text{form}}^{\circ}$	=	-45907	+29.130 TlogT	-74.640T	
	$\Delta H_{\text{form}}^{\circ}$	=	-45907	-12.65T		
	$\Delta S_{\text{form}}^{\circ}$	=	61.99	-29.130 logT		

Table 8. (Continued)

$Y_2Zn_{17}$	$\Delta F^\circ_{\text{form}}$	=	-130479	+99.042 TlogT	-247.493T
	$\Delta H^\circ_{\text{form}}$	=	-130479	-43.01T	
	$\Delta S^\circ_{\text{form}}$	=	244.48	-99.042 logT	
$YZn_{11}$	$\Delta F^\circ_{\text{form}}$	=	-63232	+64.086 TlogT	-170.494T
	$\Delta H^\circ_{\text{form}}$	=	-63232	-27.83T	
	$\Delta S^\circ_{\text{form}}$	=	142.66	-64.086 logT	

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Table 9. Calculated values for  $\Delta F_{\text{form}}^{\circ}$ ,  $\Delta H_{\text{form}}^{\circ}$  and  $\Delta S_{\text{form}}^{\circ}$  at 750 and 1000 °K.

Compound	750 °K			1000 °K		
	$-\Delta F_{\text{form}}^{\circ}$ (k cal/mole)	$-\Delta H_{\text{form}}^{\circ}$ (k cal/mole)	$-\Delta S_{\text{form}}^{\circ}$ (cal/deg- mole)	$-\Delta F_{\text{form}}^{\circ}$ (k cal/mole)	$-\Delta H_{\text{form}}^{\circ}$ (k cal/mole)	$-\Delta S_{\text{form}}^{\circ}$ (cal/deg- mole)
YZn	17.29±0.43	22.24±1.33	6.60±1.21	15.54±0.11	22.87±1.33	7.33±1.21
YZn <sub>2</sub>	26.92±0.44	34.26±1.38	9.80±1.25	24.28±0.12	35.52±1.38	11.26±1.25
YZn <sub>3</sub>	31.63±0.46	42.04±1.46	13.89±1.34	27.87±0.13	43.94±1.46	16.07±1.34
YZn <sub>4</sub>	35.89±0.46	49.59±1.49	18.26±1.37	30.95±0.14	52.12±1.49	21.17±1.37
YZn <sub>5</sub>	39.07±0.47	55.40±1.50	21.77±1.38	36.76±0.14	58.56±1.50	21.80±1.38
Y <sub>2</sub> Zn <sub>17</sub>	102.54±1.09	162.74±3.46	80.27±3.26	80.85±0.42	173.49±3.46	92.64±3.26
YZn <sub>11</sub>	52.91±0.56	84.11±4.16	41.60±1.92	41.47±0.21	91.06±1.96	49.59±1.92

The relationship

$$\sigma_y = \sqrt{\frac{\sum (\delta y)^2}{k - 2}}$$

$\delta y$  is the difference between the measured logarithm of pressure and the value calculated from the least squares line at the experimental temperature.

The standard deviation for a value of  $\log P$  was derived from the following expression in Beers (24), which is the general relation for the standard deviation of a  $y_0$  corresponding to a specific  $x_0$

$$\sigma_{y_0} = \sigma_y \sqrt{\frac{\sum x^2 - 2x_0 \sum x + kx_0^2}{k \sum x^2 - (\sum x)^2}}$$

This yields upon appropriate substitution

$$\sigma_{\log P} = \sqrt{\sigma_I^2 + \sigma_s^2 \left[ \frac{1}{T} - \left( \frac{2}{T} \right) \text{Average} \right]}$$

and the corresponding  $\Delta F$  is given by the relationship

$$\sigma_{\Delta F} = 2.303 R T \sigma_{\log P}$$

The standard deviations of the enthalpy and entropy were calculated from the standard deviations of the slope and intercept respectively and are given by the relationships

$$\sigma_{\Delta H} = 2.303 R \sigma_s$$

$$\sigma_{\Delta S} = 2.303 R \sigma_I$$

Since the value of the thermodynamic properties of a compound are calculated in part from the value of a preceding compound, the precision of a given value of a property will reflect the precision in the value of the corresponding

property of preceding compounds. The precision indices for the value of a property were propagated by the root mean square relation.

### C. The Thorium-Zinc System

The thorium-zinc system was treated in a manner analogous to the yttrium-zinc system. The information required to calculate the free energy, enthalpy and entropy of formation of the compounds in the system is outlined in Tables 10 and 11. The vapor pressure data in Table 3 was combined with values for the enthalpy and free energy of vaporization of zinc to yield empirical relationships for the integral free energy, enthalpy and entropy of formation of the four compounds in the system. These are given in Table 12 and calculated values of the quantities and their standard deviations at 750 and 1000 °K are given in Table 13.

The results obtained at 1000 °K are compared in Table 14 with those of Chiotti and Gill (12) who made vapor pressure measurements of the system using a visual dew point method. The values obtained are in good agreement with the exception of the enthalpy values of  $\text{ThZn}_4$ .

Table 10. Relationship between free energy and vapor pressure for compounds in the thorium-zinc system.

Region	Reactions	$\Delta F$
Th-Th <sub>2</sub> Zn	$2\text{Th} + \text{Zn}_{(v)} \rightleftharpoons \text{Th}_2\text{Zn}$	$\Delta F_1 = RT \ln p_1$
	$\text{Zn}_{(l)} \rightleftharpoons \text{Zn}_{(v)}$	$\Delta F^0 = -RT \ln p^0$
	<hr/> $2\text{Th} + \text{Zn}_{(l)} \rightleftharpoons \text{Th}_2\text{Zn}$	<hr/> $\Delta F_I^0 = RT \ln \frac{p_1}{p^0}$
Th <sub>2</sub> Zn-ThZn <sub>2</sub>	$1/2\text{Th}_2\text{Zn} + 3/2\text{Zn}_{(v)} \rightleftharpoons \text{ThZn}_2$	$3/2\Delta F_2 = 3/2RT \ln p_2$
	$3/2\text{Zn}_{(l)} \rightleftharpoons 3/2\text{Zn}_{(v)}$	$3/2\Delta F^0 = -3/2RT \ln p^0$
	$\text{Th} + 1/2\text{Zn}_{(l)} \rightleftharpoons 1/2\text{Th}_2\text{Zn}$	$1/2\Delta F_I^0$
	<hr/> $\text{Th} + 2\text{Zn}_{(l)} \rightleftharpoons \text{ThZn}_2$	<hr/> $\Delta F_{II}^0 = 1/2\Delta F_I^0 + 3/2RT \ln \frac{p_2}{p^0}$

Table 10. (Continued)

Region	Reactions	$\Delta F$
ThZn <sub>2</sub> -ThZn <sub>4</sub>	$\text{ThZn}_2 + 2\text{Zn}_{(v)} \rightleftharpoons \text{ThZn}_4$	$2\Delta F_4 = 2RT \ln p_3$
	$2\text{Zn}_{(l)} \rightleftharpoons 2\text{Zn}_{(v)}$	$2\Delta F^\circ = 2RT \ln p_0$
	$\text{Th} + 2\text{Zn}_{(l)} \rightleftharpoons \text{ThZn}_2$	$\Delta F_{\text{II}}^\circ$
	<hr/>	<hr/>
	$\text{Th} + 4\text{Zn}_{(l)} \rightleftharpoons \text{ThZn}_4$	$\Delta F_{\text{III}}^\circ = \Delta F_{\text{II}}^\circ + 2RT \ln \frac{p_3}{p_0}$
ThZn <sub>4</sub> -Th <sub>2</sub> Zn <sub>17</sub>	$2\text{ThZn}_4 + 9\text{Zn}_{(v)} \rightleftharpoons \text{Th}_2\text{Zn}_{17}$	$9\Delta F_4 = 9RT \ln p_4$
	$9\text{Zn}_{(l)} \rightleftharpoons 9\text{Zn}_{(v)}$	$9\Delta F^\circ = -9RT \ln p_0$
	$2\text{Th} + 8\text{Zn}_{(l)} \rightleftharpoons 2\text{ThZn}_4$	$2\Delta F_{\text{IV}}^\circ$
	<hr/>	<hr/>
	$2\text{Th} + 17\text{Zn}_{(l)} \rightleftharpoons \text{Th}_2\text{Zn}_{17}$	$\Delta F_{\text{IV}}^\circ = 2\Delta F_{\text{III}}^\circ + 9RT \ln \frac{p_4}{p_0}$

Table 11. Relationship between the enthalpy and vapor pressure for compounds in the thorium-zinc system.

Region	Reactions	$\Delta H$
Th-Th <sub>2</sub> Zn	$2\text{Th} + \text{Zn}_{(v)} \rightleftharpoons \text{Th}_2\text{Zn}$	$\Delta H_1 = R \frac{d \ln p_1}{d \frac{1}{T}}$
	$\text{Zn}_{(l)} \rightleftharpoons \text{Zn}_{(v)}$	$\Delta H^\circ = -R \frac{d \ln p^\circ}{d \frac{1}{T}}$
	<hr/>	<hr/>
	$2\text{Th} + \text{Zn}_{(l)} \rightleftharpoons \text{Th}_2\text{Zn}$	$\Delta H_I^\circ = \Delta H_1 + \Delta H^\circ$
Th <sub>2</sub> Zn-ThZn <sub>2</sub>	$1/2\text{Th}_2\text{Zn} + 3/2\text{Zn}_{(v)} \rightleftharpoons \text{ThZn}_2$	$3/2\Delta H_2 = 3/2R \frac{d \ln p_2}{d \frac{1}{T}}$
	$3/2\text{Zn}_{(l)} \rightleftharpoons 3/2\text{Zn}_{(v)}$	$3/2\Delta H^\circ = -3/2R \frac{d \ln p^\circ}{d \frac{1}{T}}$
	<hr/>	<hr/>
	$\text{Th} + 1/2\text{Zn}_{(l)} \rightleftharpoons 1/2\text{Th}_2\text{Zn}$	$1/2\Delta H_I^\circ$
	<hr/>	<hr/>
	$\text{Th} + 2\text{Zn}_{(l)} \rightleftharpoons \text{ThZn}_2$	$\Delta H_{II}^\circ = 1/2\Delta H_I^\circ + 3/2\Delta H_2 + 3/2\Delta H^\circ$

Table 11. (Continued)

Region	Reactions	$\Delta H$
ThZn <sub>2</sub> -ThZn <sub>4</sub>	$\text{ThZn}_2 + 2\text{Zn}_{(v)} \rightleftharpoons \text{ThZn}_4$	$2\Delta H_3 = 2R \frac{d \ln p_3}{d \frac{1}{T}}$
	$2\text{Zn}_{(l)} \rightleftharpoons 2\text{Zn}_{(v)}$	$2\Delta H^\circ = -2R \frac{d \ln p^\circ}{d \frac{1}{T}}$
	$\text{Th} + 2\text{Zn}_{(l)} \rightleftharpoons \text{ThZn}_2$	$\Delta H_{II}^\circ$
	$\text{Th} + 4\text{Zn}_{(l)} \rightleftharpoons \text{ThZn}_4$	$\Delta H_{III}^\circ = \Delta H_{II}^\circ + 2\Delta H_2 + 2\Delta H^\circ$
ThZn <sub>4</sub> -Th <sub>2</sub> Zn <sub>17</sub>	$2\text{ThZn}_4 + 9\text{Zn}_{(v)} \rightleftharpoons \text{Th}_2\text{Zn}_{17}$	$9\Delta H_4 = 9R \frac{d \ln p_4}{d \frac{1}{T}}$
	$9\text{Zn}_{(l)} \rightleftharpoons 9\text{Zn}_{(v)}$	$9\Delta H^\circ = -9R \frac{d \ln p^\circ}{d \frac{1}{T}}$
	$2\text{Th} + 8\text{Zn}_{(l)} \rightleftharpoons 2\text{ThZn}_{17}$	$2\Delta H_{III}^\circ$
	$2\text{Th} + 17\text{Zn}_{(l)} \rightleftharpoons \text{Th}_2\text{Zn}_{17}$	$\Delta H_{IV}^\circ = 2\Delta H_{III}^\circ + 9\Delta H_4 + 9\Delta H^\circ$

Table 12. Analytical expressions for the standard thermodynamic properties of formation of compounds in the thorium-zinc system in the temperature range studied.

$\text{Th}_2\text{Zn}$	$\Delta F^\circ_{\text{form}}$	=	-15788	+5.826 TlogT	-13.070T
	$\Delta H^\circ_{\text{form}}$	=	-15788	-2.53T	
	$\Delta S^\circ_{\text{form}}$	=	10.54	-5.826 logT	
$\text{ThZn}_2$	$\Delta F^\circ_{\text{form}}$	=	-23822	+11.652 TlogT	-28.795T
	$\Delta H^\circ_{\text{form}}$	=	-23822	-5.05T	
	$\Delta S^\circ_{\text{form}}$	=	23.75	-11.652 logT	
$\text{ThZn}_4$	$\Delta F^\circ_{\text{form}}$	=	-43450	+23.304 TlogT	-53.800T
	$\Delta H^\circ_{\text{form}}$	=	-43450	-10.11T	
	$\Delta S^\circ_{\text{form}}$	=	43.69	-23.304 logT	
$\text{Th}_2\text{Zn}_{17}$	$\Delta F^\circ_{\text{form}}$	=	-105985	+99.042 TlogT	-264.666T
	$\Delta H^\circ_{\text{form}}$	=	-105985	-42.99T	
	$\Delta S^\circ_{\text{form}}$	=	221.68	-99.042 logT	

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Table 13. Calculated values of the standard free energy, enthalpy and entropy of formation of compounds in the thorium-zinc system.

Compound	Temp. °K	$-\Delta F^\circ$ kcal/mole	$-\Delta H^\circ$ kcal/mole	$-\Delta S^\circ$ cal/mole-degrees
Th <sub>2</sub> Zn	750	13.03±0.27	17.69±0.81	6.21±0.72
	1000	11.38±0.09	18.32±0.81	6.94±0.72
ThZn <sub>2</sub>	750	20.29±1.28	27.62±3.86	9.75±4.85
	1000	17.66±0.34	28.87±3.86	11.21±4.85
ThZn <sub>4</sub>	750	33.55±1.34	51.04±4.27	23.31±5.21
	1000	27.34±0.39	53.56±4.27	26.62±5.21
Th <sub>2</sub> Zn <sub>17</sub>	750	90.93±2.76	138.24±9.28	63.07±6.61
	1000	73.53±0.98	148.98±9.28	75.45±6.61

Table 14. Comparison of values obtained for the  $\Delta F^{\circ}_{\text{form}}$ ,  $\Delta H^{\circ}_{\text{form}}$  and  $\Delta S^{\circ}_{\text{form}}$  of  $\text{Th}_2\text{Zn}$ ,  $\text{ThZn}_2$ ,  $\text{ThZn}_4$  and  $\text{Th}_2\text{Zn}_{17}$  at 1000 °K with those of Chiotti and Gill.

Compound	Present Investigation		Chiotti and Gill	
	$\Delta F^{\circ}_{\text{form}}$	$\Delta H^{\circ}_{\text{form}}$	$\Delta F^{\circ}_{\text{form}}$	$\Delta H^{\circ}_{\text{form}}$
$\text{Th}_2\text{Zn}$	-11.4	- 18.3	-10.9	-16.5
$\text{ThZn}_2$	-17.7	- 28.9	-18.0	-28.8
$\text{ThZn}_4$	-27.3	- 53.6	-27.0	-46.4
$\text{Th}_2\text{Zn}_{17}$	-73.5	-149.0	-73.0	-149.9

This rather large variance can be traced directly to a 10% discrepancy in both the slope and intercept of the vapor pressure equation in the region  $\text{ThZn}_2$ - $\text{ThZn}_4$  alloy. The discrepancy cancels in the free energy expression which reflects both slope and intercept. In the enthalpy, however, this disagreement in slope reflects a 7 k cal/mole difference in the calculated values. Another alloy of this composition was run and the slopes and intercepts of the two determinations made in this investigation agreed within 2-3 percent.

## V. SUMMARY

A dew point method based on detection of the gamma radiation from a radioisotope of the condensing metal has been described. The zinc vapor pressure was measured over a number of alloys in the aluminum-zinc, yttrium-zinc and thorium-zinc systems. Thermodynamic properties of intermetallic phases in these systems were calculated for the temperature range of measurements.

The disadvantages of the method over a visual method are generally those inherent in the use of radioactivity. Shielding and special handling procedures are necessary to prevent contamination or exposure of personnel. Melts may not be examined for complete alloying and sample sizes are limited. All procedures must be practiced "cold" before tracer work is attempted.

Perhaps the main advantage of the method is the more objective and less eye-straining method of ascertaining the dew point. The author has attempted on occasions to make dew point measurements visually and feels that the radioactive counting method is immeasurably easier and probably as accurate.

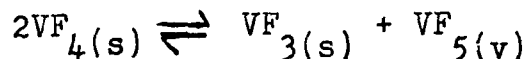
The sensitivity of the method - that is, the minimum amount of condensate that can be observed, is probably about the same as a visual method. This is, of course,

dependent on the specific activity of the material used as well as the propinquity of the detector to the region of condensation and the background of the counter. It is estimated that a condensate of about 10 micrograms of zinc is the minimum that can be observed with the apparatus described.

Kubachewski and Evans (25) have stated that the dew point method is applicable down to  $10^{-2}$  mm, but the author agrees with Kilp (26) that it is very difficult to get data below one mm of pressure.

The method has obvious extensions to ternary systems. Two components would be radioactively tagged and their individual dew points determined. A gamma ray analyzer would be included in the counting circuit to assure no interference between the radioisotopes of the two volatile components.

The method could be applied to other than metal vapors, for example the vanadium pentafluoride pressure in the reaction,



Of course, the vapor pressure of pure  $\text{VF}_5$  must be well known as a function of temperature.

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