VAPORIZATION THERMODYNAMICS OF $YbBr_2$

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ABSTRACT

VAPORIZATION THERMODYNAMICS OF $YbBr_2$

By

Michael Daniel Gebler

The vaporization thermodynamics of the reaction

$$YbBr_2(\ell) \rightarrow YbBr_2(g)$$

were described over the 1190-1514 K temperature range by the use of a target collection Knudsen effusion technique. The microgram quantities of effusate which plated onto targets were analysed with X-ray fluorescence by the use of an external calibration procedure.

From a plot of the natural logarithm of partial pressures due to $YbBr_2$ versus reciprocal temperature the second law enthalpy and entropy at the median temperature were obtained as: $\Delta H^{o}_{1360} = (66._{9} \pm 3._{5})$ kcal/mole, $\Delta S^{o}_{1360} = (30._{0} \pm 2._{6})$ eu. Choice of a $HgBr_2$ model system permitted thermodynamic parameters of $YbBr_2(g)$ to be described thus leading to reduction of median temperature values to a reference temperature (298 K).

The estimation of free energy functions by the use of the $HgBr_2$ model system and an estimated absolute entropy allowed third law analysis of the vapor pressure data. The second and third law values obtained were:

ΔH^{o}_{298} (2nd law) $= (79._{8} \pm 4._{4})$ kcal/mole,

$\Delta S^o_{298} = (47._5 \pm 3._9)$ eu; ΔH^o_{298} (3rd law) = $(72._3 \pm 1._5)$ kcal/mole. The overall consistency of the data was shown by the lack of a trend in third law values of ΔH^o_{298} over the 324 degree range of the experiment. From the reduced second law values, the enthalpy and entropy and literature values, free energies of formation were calculated as: ΔH^o_{f298} $YbBr_2(g) = -(90.2 \pm 0.2)$ kcal/mole, ΔH^o_{f298} $YbBr_2(s) = -(170._0 \pm 4._4)$ kcal/mole. The second law absolute entropy was determined from the entropy of vaporization and entropy of $YbBr_2$ gas (estimated from $HgBr_2$ values) as: S^o_{298} $YbBr_2(s) = (29._0 \pm 3._9)$ eu, which combined with literature values of entropy for Yb(s) and $Br_2(\ell)$ allowed calculation of ΔS^o_{f298} $YbBr_2(s) = -(21._7 \pm 3._9)$ eu. Values of ΔG^o_{f298} $YbBr_2(s) = -(163._5 \pm 4._6)$ kcal/mole and ΔS^o_{f298} $YbBr_2(g) = (25._8 \pm 3._9)$ eu were determined and subsequently ΔG^o_{f298} $YbBr_2(g) = -(97._9 \pm 1._2)$ kcal/mole was estimated. By resorting to a $PbBr_2$ model system to obtain thermodynamic functions for $YbBr_2(\ell)$ calculation of $\Delta H^o_v = (58._6 \pm 4._4)$ kcal/mole was made at the normal boiling point of $(2.0_3 \pm 0.1_1) \times 10^3$ K. $\Delta S^o_v = (28._9 \pm 2._2)$ eu was then calculated.

VAPORIZATION THERMODYNAMICS OF $YbBr_2$

By

Michael Daniel Gebler

A THESIS

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DEDICATION

To My Parents

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The assistance of former members of the High Temperature Group, especially Sandra Bacon and Drs. John Haschke and Alleppey Hariharan, is gratefully acknowledged. Unfortunate lack of close personal contact with them can only be counted as loss but their writings proved immensely rewarding.

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CHAPTER I

INTRODUCTION

Experimentally determined values for such thermodynamic parameters as enthalpies of fusion, vaporization and formation, as well as for heat capacities are not available for many of the rare earth halides. Indeed, as late as 1964 Novikov and Polychenok[1] observed the lack of experimental conformation for many values found in tables of estimates such as those by Brewer _et_ _al_.[2,3] especially for divalent compounds. Since then much interest has centered around the trivalent state. Vapor pressure values and sublimation thermodynamics for most of the lanthanide(III) fluorides have been established.[4-10] Some vapor pressure values are known for lanthanide trichlorides and tribromides.[11-15]

For lanthanide halides in the less common divalent state Polychenok and Novikov[16] have reported thermodynamic values for $SmCl_2$, $EuCl_2$, and $YbCl_2$ but they assert that the "boiling point" method they used tends to be inherently inaccurate. Haschke and Eick[17] and Hariharan[18] have used the Knudsen effusion method to determine the vaporization thermodynamics of $EuCl_2$, EuI_2, and $EuBr_2$ and Hariharan, Fishel, and Eick[19] used the same technique to describe the $YbCl_2$ system.

It was the intention of the present work to establish experimental values of the enthalpy of vaporization and entropy of vaporization of $YbBr_2$ by the use of procedures similar to those applied by Haschke, Eick, and Hariharan to the analogous $EuBr_2$ system.

CHAPTER II

THEORETICAL CONSIDERATIONS NECESSARY TO VAPORIZATION STUDIES

A. Modes of Vaporization and Phase Rule Considerations

1. Modes of Vaporization

When heated to a specific temperature a substance will vaporize in either a congruent or incongruent manner. A substance which vaporizes congruently yields a vapor that has the same chemical composition as that of the condensed phase from which it was obtained; incongruent vaporization results when a condensed phase gives rise to a vapor of different composition from that of the condensed phase.

2. Phase Rule

The phase rule:

$$F = C - P + 2 \qquad \text{(II-1)}$$

establishes many useful relationships for vaporization studies. In II-1 the number of degrees of freedom, F, is related to the number of components in a system, C, and the number of phases, P.

For a binary system of a condensed (either liquid or solid) phase and a congruently derived vapor, P will equal two in II-1 above. The number of components, C, will equal one since the vapor and condensed phase are chemically equivalent so that the number of degrees of freedom for the system will be one. Therefore, to obtain a parameter such as vapor pressure it is only necessary to fix one experimental condition such as temperature.

B. Methods of Vapor Pressure Measurement

A number of methods are available to establish the vapor pressure of a system.[20] These fall into two classifications, the absolute, which include the static and boiling point methods, and the non-absolute which are the effusion and transpiration techniques. The non-absolute procedures rely on the kinetic theory of gases which necessitates the assumption of a molecular weight of the vapors, hence they are not applicable in those systems where vaporization of fragmented or polymeric components invalidates the assumption. However, for less volatile or chemically reactive substances they are the usual methods of choice because they allow the vaporizing system to operate at lower overall temperature than the absolute methods and because they operate at high vacuum.

The effusion techniques include an open, the Langmuir free evaporation, and a closed method, the Knudsen effusion procedure. Both are theoretically and in essence the same. The former relies on vaporization from a surface of known area and the latter on the amount of effusate which can be lost from an otherwise closed system without significantly shifting the equilibrium which is established between the condensed phase and the vapor. Both have advantages and disadvantages, but since the surface area of a vaporizing substance is difficult to determine accurately the latter method, the Knudsen Effusion technique, was chosen for our vapor pressure determinations.

C. Vapor Pressure Determinations by the Knudsen Effusion Method; the Use of Target Collection Procedures

When certain conditions (see below) are met the kinetic theory of gases allows establishment of vapor pressures according to a method first put forth by Knudsen.[21,22] The Knudsen Effusion technique requires that a small "ideal" (see below) orifice be placed in a sample cell which contains a condensed phase and its vapor in equilibrium such that the amount of effusate which escapes from the orifice does not appreciably shift the equilibrium. The number of molecules striking a unit area of the interior of the cell per unit time, Z, is proportional to the number of molecules per unit volume, n, and the average molecular velocity, $\bar{v}$. Precisely:

$$Z = n\bar{v}/4 \text{ molecules cm}^{-2}\text{sec}^{-1} \qquad \text{(II-2)}$$

If an "ideal" orifice, that is, a small, infinitesmally thin, circular orifice is placed in the container so that a small portion of the vapor can escape into a perfect void (guaranteed by high vacuum) in such a way as not to affect equilibrium within the cell, then the number of molecules escaping through the orifice of area A_o per second will be given by:

$$N_o = A_o Z \qquad \text{(II-3)}$$

Now if a circular target is placed at a distance d above the orifice so that the center of the target is coaxial with the center of the orifice, and if the target has radius r, then the fraction of molecules striking the target can be determined since the effusing vapor follows the cosine distribution law:

$$dN = \pi^{-1} N_o \cos \theta d\omega \qquad \text{(II-4)}$$

Here N_o is the total flux at the orifice, θ is the angle between the perpendicular and the axis of $d\omega$ (see Figure 1), the solid angle formed by the effusate which is subtended by a target of area dN. Upon substitution in terms of r, d, A_o, and Z into the cosine distribution law and integration of the value over the space above the orifice one obtains:

$$N = ZA_o(r^2/(d^2+r^2)) \text{ molecules sec}^{-1} \qquad \text{(II-5)}$$

and as long as pressure remains below 10^{-3} atm in the sample cell to meet Knudsen conditions the gas can be assumed ideal so that the ideal gas law can be applied.

When $\bar{v} = (8RT/\pi M)^{1/2}$ is substituted into II-2 and the Z so obtained used in II-5 above, multiplication of II-5 by the total time effusate is allowed to strike the container, t, allows the inclusion of the ideal gas law assumption to yield the following equation for equilibrium vapor pressure.

$$P = [W/A_o t]\ [2\pi RT/M]^{1/2}\ [(d^2+r^2)/r^2] \qquad \text{(II-6)}$$

If W, the mass in grams of effusate of molecular weight M, is collected in t minutes on a circular target of radius r cm placed d cm above an orifice of A_o cm^2 area, and R is

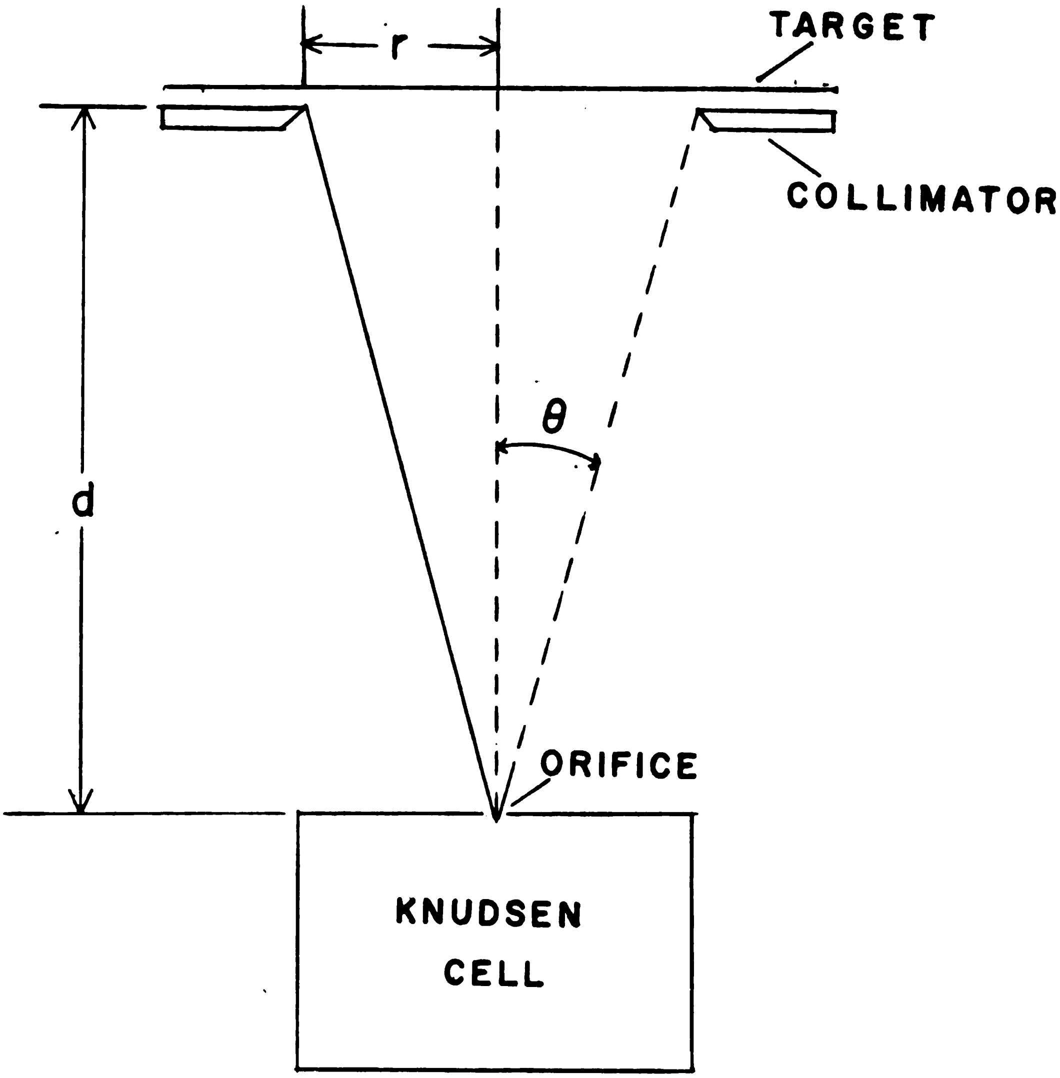


Figure 1. Effusion cell-target collection geometry.

defined in ergs deg^{-1} $mole^{-1}$, then P is obtained in units of dynes cm^{-2}, a unit which is easily converted into atmospheres. Substitution of appropriate constants into II-6 yields:

$$P_{atm} = [3.76\times10^{-4}\ W/A_o t]\ [T/M]^{1/2}\ [(d^2+r^2)/r^2] \qquad (II-7)$$

If a molecular weight of the effusate is known or can be assumed, and if the weight of effusate plated on a target can be determined, then measurement of time in minutes, area of the orifice in cm^2, and temperature in degrees Kelvin will yield the vapor pressure of the system when the geometry of the system (hence d and r) is known.

D. Assumptions of the Knudsen Method

Aside from the fundamental assumption that the orifice is "ideal" the system for Knudsen effusion relies on other assumptions many of which are required by the kinetic theory of gases. These include:

1. Isothermal conditions exist about and within the cell.
2. Molecules are point masses.
3. Isotropy of gas exists in the cell.
4. Molecular velocity distribution is Maxwellian.
5. There are no molecular interactions in the gas phase.

6. Orifice walls do not return any molecules to the cell.

7. Molecules do not return to the cell once through the orifice.

8. Loss of effusate occurs by vapor transport only.

9. Equilibrium pressure is maintained within the cell.

10. No molecular collisions occur in the orifice.

E. Limitations of the Knudsen Effusion Method

All of the assumptions stated above would be valid in an ideal system. However, in a real system some of the assumptions can only be approximated and the resulting error must be corrected for by changing equation II-7 so that it includes a number of correction factors.

1. Non-Ideal Cells

a. Clausing Correction Factor

The basic assumption that the orifice is ideal, which implies infinitesmally thin, is violated immediately in a real system since it is impossible to obtain such an opening in an absolute sense. Therefore, a certain resistance to molecular flow occurs, the so-called channeling effect. Clausing demonstrated[23] that the effect is a function of orifice geometry and that one can apply a correction factor (the Clausing Factor), W_o, to the usual vapor pressure equations, II-6, II-7. He obtained these correction factors in terms of orifice radius and orifice length. Inclusion of W_o in II-7 makes the vapor pressure equation:

$$P_{atm} = [3.76\times10^{-4}\ W/A_o t]\ [T/M]^{1/2}\ [(d^2+r^2)/r^2]\ [1/W_o] \qquad \text{(II-8)}$$

b. Correction for Orifice Effects by Proper Choice of Collection Geometry

The limits of the cosine distribution law for real knife-edged conical orifices have been examined by Ward.[24] He demonstrates through experiment and calculation that when a target geometry is chosen such that only small angles of θ are subtended there is little or no effect on the cosine distribution law for conical orifices. Therefore, by simply choosing the target geometry such that θ remains small and by using a conical orifice one need not apply a correction factor. Indeed, if the target is small enough or at great enough distance to receive about 1% or less[24] of the effusate the Clausing correction factor can be taken as unity and vapor pressures will be given directly by II-7.

2. Vaporization Coefficient

Another of the Knudsen assumptions requires that the vaporizing system be at equilibrium. That is, the vaporization coefficient α_v, defined as the rate of vaporization compared to the equilibrium rate, is equal to the condensation coefficient α_c, defined as the fraction of vapor molecules which recondense. Since the Knudsen effusion procedure allows a certain portion of vapor to escape a steady state loss might arise. The pressure given by II-7, P_m, as measured will not be equal to the true equilibrium vapor pressure P_e. Motzfeldt[25] has derived an expression to relate P_m to P_e assuming that $\alpha_v = \alpha_c$ and that a resistance similar to a Clausing orifice factor develops along the cell wall. In its mathematical form the equation is:

$$P_e = P_m[1 + f(\frac{1}{\alpha} + \frac{1}{W_a} - 2)] \qquad \text{(II-9)}$$

Here $f = W_oA_o/A$ with A_o being the orifice area and A the sample surface area, W_o is the Clausing orifice factor, W_a is a "Clausing factor" of the cell body and $\alpha = \alpha_v = \alpha_c$. From equation II-9 it is evident that when $A_o/A \leq .01$, $P_m \approx P_e$ provided α, the vaporization coefficient does not differ significantly from unity. Indeed, early work by Rosenblatt[26] has established that finely divided samples (or those with large surface areas) usually have vaporization coefficients which approach unity. However, it appears that the vaporization coefficient need not strictly approach unity with increasing sample size but is dependent on a number of experimental and system factors which include surface effects of the samples. An extensive review of the vaporization coefficient problem was given by Work.[27]

3. Striking Coefficient

If all the effusate striking a target does not adhere to it another source of error arises. One can determine the amount of material which does strike to the target by placing a chilled disc with a hole in its center in front of the target. Any molecules not striking to the target will be reflected back by the cosine law and a fraction of these will adhere to the disc. By measurement of the amount on the target and the amount on the disc a correction factor can be obtained.

4. Interactions with Knudsen Cells

Steps must be taken to insure that the vaporizing compounds do not interact with the cell material. Simple mass difference determinations of an empty cell before vaporization and after 100% vaporization of the cell's content will lend more qualitative insight but the method is limited by the sensitivity of the balance used for mass determination.

Usually it is sufficient to rely on X-ray powder diffraction patterns (hereafter called "patterns") of the material remaining in the cell after the vaporization. By comparing the patterns of the residue after vaporization to those of the starting material two determinations can be made. If the patterns before and after vaporization are the same then, reasonably, one can assume no interaction between the cell and the sample. Further, the vaporization was probably congruent. If they are not the same then chemical analysis (using wet chemical and/or X-ray fluorescence methods) is necessary to establish what materials are present in the residue. If analysis shows that the residue is simply the starting material's elements in different mole fractions then incongruent vaporization should be suspected, but if the residual material contains a compound composed in part of the cell's elements then one must try to describe the chemical process taking place to ascertain a correction factor. If a correlation cannot be found, then measured values of vapor pressure cannot be related to a specific reaction.

5. Non-Ideal Gas

Since the kinetic theory of gases is fundamental to the Knudsen effusion theory most of the assumptions mentioned in Section D are required to insure that its principles are not violated. Many of these assumptions center around pressure build-ups in the cell. If free molecular flow is to be maintained the pressure must not reach the point that molecular interactions occur and a "viscous flow" of molecules results in the molecular flux. Experiments conducted by Meyer[28] show that for orifices of areas between 10^{-4} and 10^{-5} cm^2 the pressure should not exceed 5×10^{-3} atm if free molecular flow is to be maintained.

F. Analysis of Targets; X-Ray Fluorescence

One must ascertain the amount (mass) of material plated on the targets during the vaporization process before II-7 can be used to compute vapor pressures. Since the amount of plated material is usually maintained in the microgram region to avoid adhesion problems, X-ray fluorescence is uniquely suited to the task of mass determination.

1. X-Ray Fluorescence: Basic Method

When white X-radiation is allowed to shine on a sample it excites inner shell electrons to higher energy levels. Those electrons which return to the ground state emit photons of characteristic wavelength -- the basic fluorescence. The radiation thus given off can be analysed by allowing it to diffract from a suitable crystal and by arranging a detector (such as a scintillation counter) such that it picks up the particular wavelength given off by the element being analysed for. The fluorescence X-radiation is analysed according to the Bragg equation:

$$n\lambda = 2d\sin\theta \qquad \text{(II-9)}$$

where n is the order of diffraction (usually $n=1$), λ is the wavelength of the characteristic radiation, d is the inner planar spacing of the analysing crystal and θ is the angle of incidence. Placement of the detector at 2θ allows the correct geometry for analysis (see Figure 2).

G. Temperature Measurement

Figure 3 shows a symmetric effusion cell. When the top cavity is used as a sample container and the entire

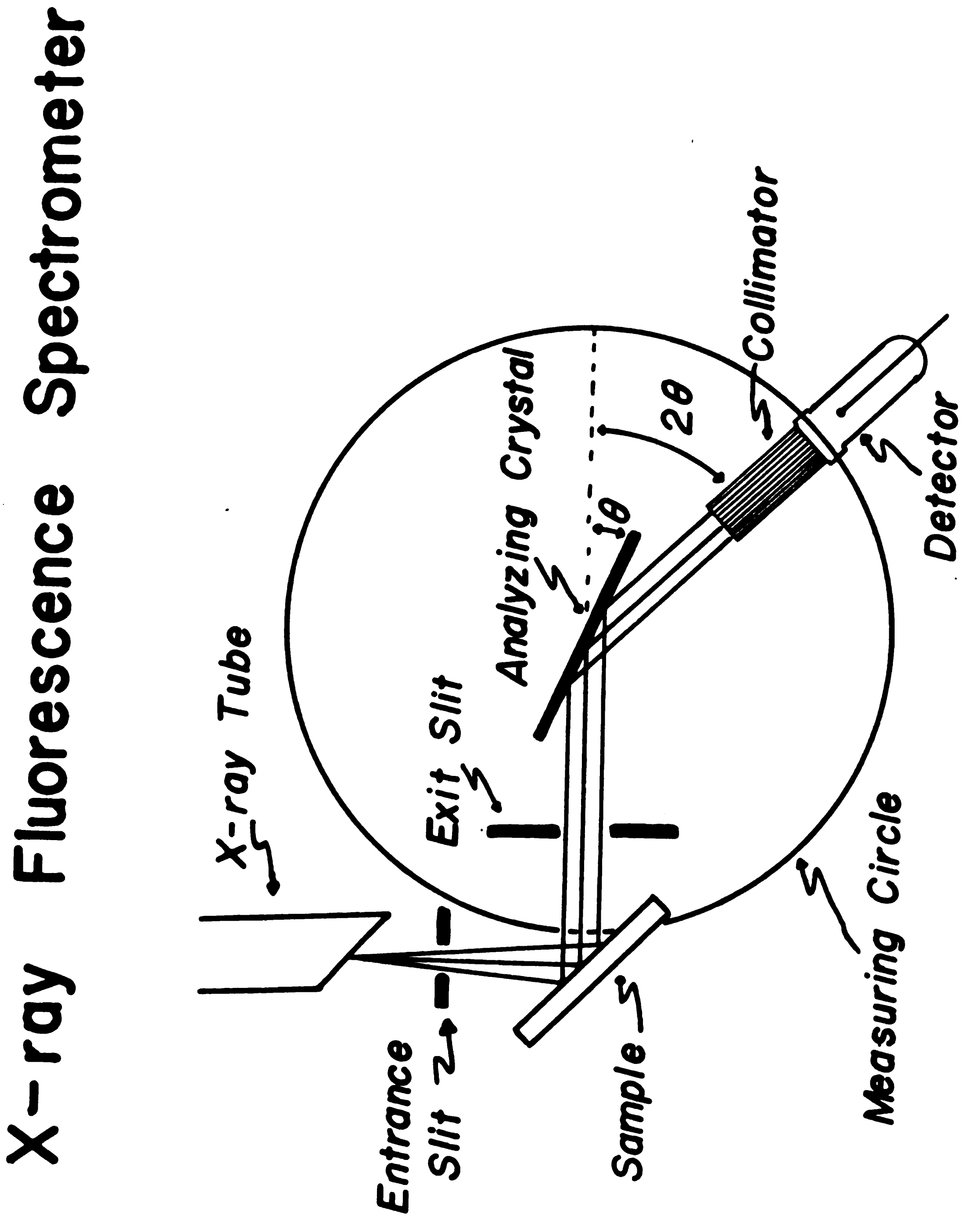
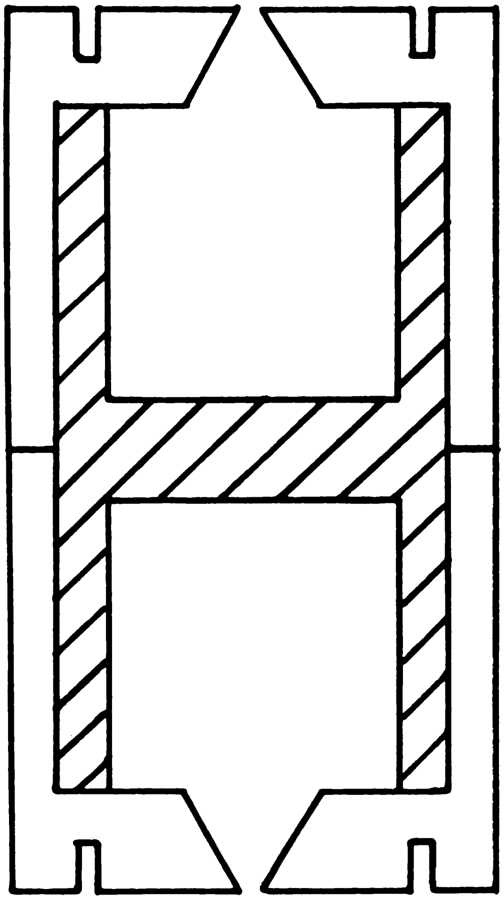


Figure 2. X-ray fluorescence spectrometer.



SYMMETRICAL EFFUSION CELL WITH SAMPLE AND OPTICAL CAVITIES

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Figure 3. Symmetric effusion cell.

cell maintained in an isothermal environment the bottom cavity should display a temperature identical to that of the top cavity. By placing a thermocouple in the bottom cavity the temperature of the vaporization process can be determined directly.

H. Thermodynamic Calculations

1. Second-Law Calculations

With only one degree of freedom available to a vaporizing system a free energy relationship would be expected between temperature and vapor pressure. That is since:

$$\Delta G_T^o = -RT\ell nP_T \qquad \text{(II-10)}$$

and

$$\Delta G_T^o = \Delta H_T^o - T\Delta S_T^o \qquad \text{(II-11)}$$

we have

$$-\ell nP_T = (\Delta H_T^o/RT) - \Delta S_T^o/R \qquad \text{(II-12)}$$

where P_T is the equilibrium vapor pressure given by II-7 above. From II-12 it can be seen that a plot of ℓnP_T versus 1/T by least squares regression will yield the relationship of $\ell nP_T = m/T = b$ so that enthalpies are given by the slope of the line:

$$\Delta H_T^o = -Rm \qquad \text{(II-13)}$$

and entropies are given by the y-intercept:

$$\Delta S_T^o = Rb \qquad \text{(II-14)}$$

The entropy and enthalpy values thus obtained are usually considered those of the mean temperature of the study.[29]

These values are reduced to a reference temperature according to the following:

$$\Delta H_{298}^o = \Delta H_T^o + \int_T^{298} CpdT \qquad \text{(II-15)}$$

and

$$\Delta S_{298}^o = \Delta S_T^o + \int_T^{298} Cp/T\ dT \qquad \text{(II-16)}$$

where it is usually necessary to express the heat capacities in their analytical forms:

$$C_p = a + bT \qquad \text{(II-17)}$$

$$C_p = a + bT + cT^{-2}$$

2. Third Law Calculations

The third law treatment utilizes a free energy function, fef, to reduce thermodynamic data to a reference temperature which results in a value of ΔH^o_{298} for each data point. The fef can be defined as:

$$\text{fef} = (G^o_T - H^o_{298})/T \qquad \text{(II-18)}$$

or

$$\text{fef} = (H^o_T - H^o_{298})/T - S^o_T \qquad \text{(II-19)}$$

Δfef values are calculated from those of fef for each product and reactant by:

$$\Delta\text{fef} = \sum_i \nu_i\ \text{fef}_i - \sum_j \nu_j\ \text{fef}_j \qquad \text{(II-20)}$$

where i refers to the products and j refers to the reactants. Once determined, Δfef values lead to ΔH^o_{298} values from:

$$\Delta fef = (\Delta G^o_T - \Delta H^o_{298})/T \qquad \text{(II-21)}$$

or through

$$\Delta H^o_{298} = -(\Delta fef + R\ell nP_T)T \qquad \text{(II-22)}$$

when II-10 is substituted into II-21. The advantage of the use of third law treatment is that, although it does not give values of ΔS^o_{298} as the second law does, the treatment results in a value of ΔH^o_{298} for each data point. Analysis of the values thus obtained allows any trend in ΔH^o_{298} to be displayed. A trend might arise from systematic error in either pressure or temperature measurement or in the computation of free energy function changes. A large difference in second-law and third law values indicates error in measurement of the parameters of vaporization or indeed, in the basis definition of the vaporization process itself.

CHAPTER III

EXPERIMENTAL

A. Preparation of $YbBr_2$

$YbBr_2$ was produced by following the general procedure for rare earth dichloride preparation put forth by DeKock and Radtke.[30] The sesquioxide of ytterbium (99.99% Research Chemicals, P.O. Box 14588, Phoenix, Arizona) was dissolved in approximately 150-200 ml of 4.5 N HBr along with NH_4Br (Matheson Coleman and Bell) and metallic zinc (Baker). One to three grams of the oxide was used with sufficient quantities of the other reagents to give a ratio of twelve moles to ammonium salt and one and two tenths mole of zinc bromide per mole of rare earth tribromide formed in the first step of the reaction. The solution was evaporated to dryness and the dried material transferred to a carbon boat which contained an excess of zinc metal as a reducing agent. After drying under vacuum and low (200°C) temperature, the material was melted in an inert atmosphere to effect reduction. The excess NH_4Br was sublimed off and a second attempt was made to remelt the remaining contents of the boat by heating to 500-600°C to insure all of the tribromide was reduced to the dibromide. Next the Zn and $ZnBr_2$ were vaporized under high vacuum. The greenish-yellow crude $YbBr_2$ remaining was transferred to an outgassed molydenum crucible and heated by induction in a high vacuum so that it distilled onto a high vacuum so that it distilled onto a quartz condenser (distillation temperature approximately 1145°C).

B. Chemical Analysis

1. For Ytterbium

A 50-80 mg sample of distilled $YbBr_2$ was placed in a crucible and fired directly to the oxide by heating to 1000°C in a muffle oven (Thermolyne Model F-A1620) for 2-3 hours.

2. For Bromide

A 60-80 mg sample of $YbBr_2$ was dissolved in dilute nitric acid solution. A 0.1 N solution of silver nitrate was stirred into precipitate Br^- as AgBr. The solution was heated to boiling for 1-2 minutes and allowed to settle overnight. A few drops of $AgNO_3$ were added to the solution above the precipitate to insure complete precipitation before the solution was filtered into a sintered glass crucible. The material so collected was dried at 110°C for 1½ hours and then weighed as the bromide of silver.

C. X-Ray Powder Diffraction Analysis

Samples of $YbBr_2$ and the residue left in sample cells after vaporization were prepared for powder X-ray diffraction analysis by sealing small amounts of each substance in plastic bags in a dry box. A Haegg Type Guiner forward focusing camera of 80 mm radius and a Ca $K_{\alpha}1$ radiation source ($\lambda_{\alpha 1} = 1.54051$ Å, $t = 24 \pm 1°C$) powered by a Picker 80913 generator was used to obtain the powder patterns.

D. Target Collection Apparatus

Kent[31] has described the general setup used during the work. Basicly it is a glass vacuum line (Figure 4) in which the effusion cell is supported above a boron nitride table by tungsten rods. A similar set of rods support a molydenum oven arranged symmetrically about the cell (Figure 5). Directly above the oven-cell arrangement the glass line supports a target magazine fitted with a liquid nitrogen dewar so that the targets can be cooled. The line has apparati which allow target changes while the

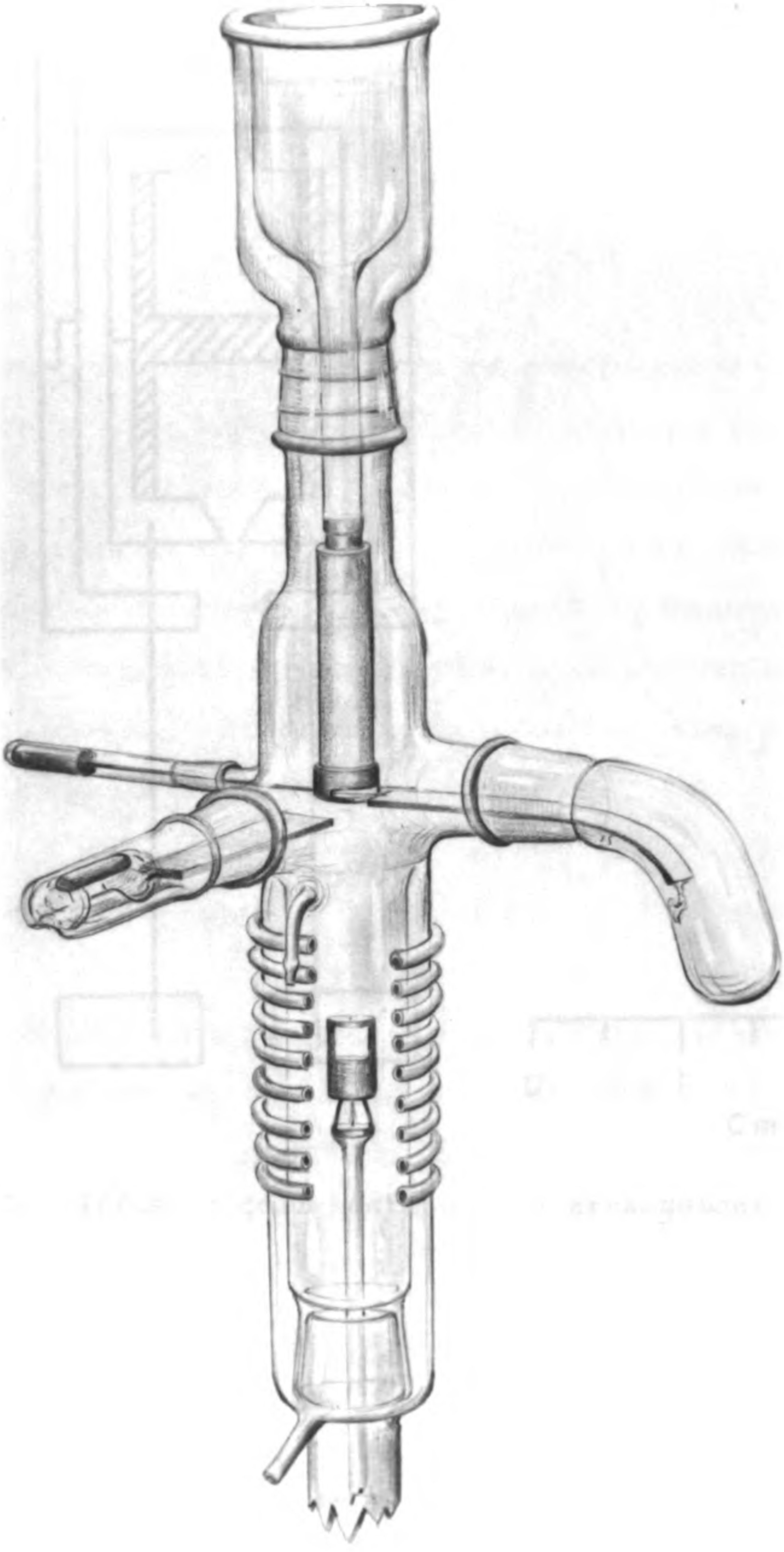

Figure 4. High vacuum Knudsen effusion apparatus.

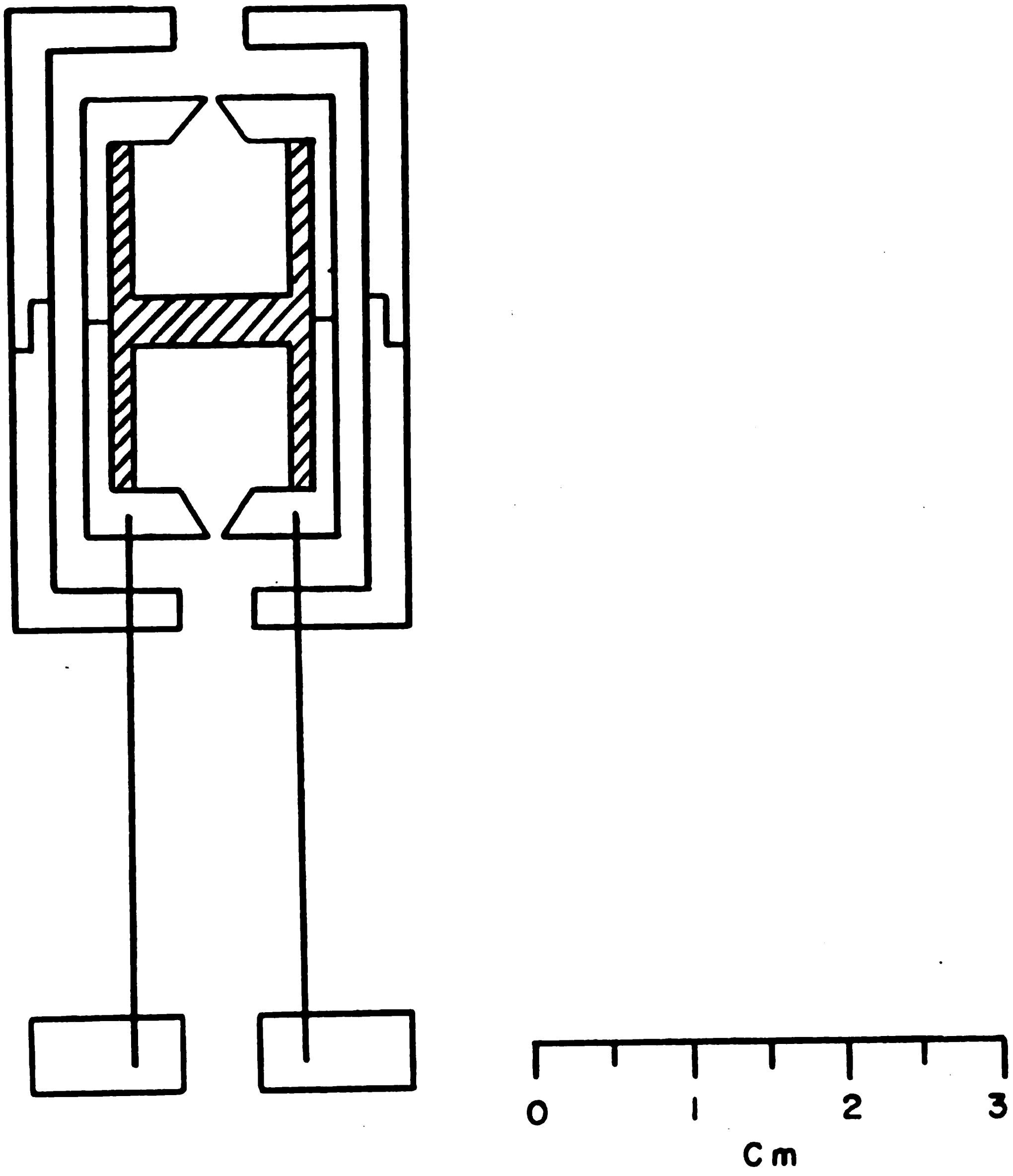

Figure 5. Effusion cell-heating oven arrangement.

system is closed by the use of magnets and iron mechanical parts built into its side. A mercury diffusion pump provides the high vacuum necessary for the experiments.

E. Effusion Cells

In every vaporization experiment except one the effusion cells were made of molydenum; the basic design of which was given in Figure 3. As stated before, their symmetric nature allows the bottom cavity to be used as a chamber into which the temperature sensing thermocouple is placed while vaporization occurs from an identical top cavity. In one case a carbon insert was used with molydenum end caps in the usual cell arrangement.

F. Temperature Measurement

A two foot thermocouple supplied by Omega Engineering was calibrated against the melting point of National Bureau of Standards copper, and the boiling point and ice point of water. The thermocouple was then used in conjunction with a Numetron 914 Numeric Display digital potentiometer (Leeds and Northrup) to read temperatures directly in degrees centigrade.

G. Heat Source

The oven cell arrangement was heated to and held at constant temperature by a 20-kva Thermonic induction generator coil which was situated as symmetrically as possible about the cell.

H. Targets

Targets for the vapor study were made of an aluminum backing 2.7 cm in diameter and 0.46 cm thick with a 2.08×0.19 cm circular recession machined in one side. A thin platinum disc was supported in the recession by a stainless steel retaining ring. The platinum discs were cleaned prior to vaporization runs by degreasing with petroleum ether, washing with detergent, scouring with steel wool, and boiling in dilute nitric acid. The aluminum backings were treated in a similar manner except they were boiled in distilled water. The retaining clips were scoured with detergent and steel wool. All parts were rinsed in distilled water and dried at 130°C.

I. Orifice Measurement

The area of the orifices used in the experiments was measured precisely by finding the area of an enlarged photomicrograph (Bausch and Lamb Dynazoom Metallograph fitted with Polaroid attachment) with a polar planimeter (Keffel and Esser) and then multiplying by an enlargement factor of 0.25×10^{-4}. The enlargement factor had been found by calibrating the Metallograph's internal scale with a micrometer slide (American Optical Co.).

J. Miscellaneous Measurements and Equipment

Time was measured to ±0.01 minutes by a Lab Con timer.

A precision cathetometer with a readibility of 0.005 cm (Gaertner Scientific) was used to measure the cell to target distance.

K. Procedure for Vaporization

Approximately 0.25 g of $YbBr_2$ was placed in the sample cavity of an outgassed effusion cell in an argon atmosphere glove box. A drop of dried fluorolube oil was placed over the orifice and the cell quickly transferred to the vacuum line. The cathetometer was used to obtain the height of the top of the cell before the remainder of the glass vacuum system was assembled. After the apparatus had pumped down to $<10^{-4}$ torr a reading was made of the height of the flat spot on the target magazine. The assembly was heated to 200-300°C to insure outgassing before the actual vaporization experiment began. When the vacuum had reached $<10^{-5}$ torr liquid nitrogen was added to the target magazine's trap and the system heated to vaporization run temperatures. Targets were exposed for periods of time sufficient to plate between two and twelve micrograms (as ytterbium) on them (times were found by trial and error).

L. X-Ray Fluorescence Analysis of Mass of Effusate

1. X-Ray Fluorescence Unit

The targets were analysed by a 4-position Norelco Universal Vacuum spectrograph with a broad focus tungsten X-ray tube powered by a Norelco XRG 5000 X-ray generator. The spectrograph was set at a 2θ value of 28.88°, the optimum setting for the $L_{\alpha 1}$ radiation of Yb for our particular instrument.

2. Calibration of X-Ray Fluorescence Unit

Since the targets collect between 2 and 12 micrograms of effusate it is necessary to know how many counts per microgram of Yb the detector will "see". To find the value each of six targets was counted blank to determine its background fluorescence at the particular settings used in the experiments. Next each target was plated with 49.6 λ of solution delivered by a precision micropipet (Misco). The solutions thus deposited contained between 2.7 and 12.11 micrograms of Yb made up as a six member series from a stock solution obtained by dissolving a carefully weighed sample of Yb_2O_3 (99.99% Research Chemicals) in HCl, boiling the majority of acid off, and then diluting to 500 ml. The solutions deposited on the target were evaporated to dryness under a high intensity light. Much skill was necessary to perfect the art of plating so that consistent values were obtained target to target, but the remainder of the procedure was trivial. The targets were counted after plating, the value of the targets' background fluorescence subtracted, a correction of a "standard blank" applied (see Section 3 below) and then the number of counts remaining was divided by the number of micrograms of Yb in the solution that was used to plate the individual targets. The average value of these six targets became the "standard" number of counts per microgram Yb used in the analysis of vaporization-plated targets.

3. Target Analysis

The method of analysis for vaporization-plated targets is essentially the same as that for the calibration targets given above. That is, it is necessary to find the background fluorescence of the targets before the vaporization run. Once plated the targets are counted again. The difference between the background fluorescence and the plated target's fluorescence should give the fluorescence (as indicated by number of counts the detector sees). Due to instrumental and environmental conditions which change from day to day it is necessary to apply a correction factor in the analysis. One obtains the correction factor by counting one particular target blank (unplated) both before the vaporization run (with the other blank targets) and after the experiment is complete when all the other targets are plated. The difference of its background fluorescence is a direct measure of systematic changes so that the standard blank correction can be defined as the value of (standard blank fluorescence counts before vaporization experiment -- standard blank fluorescence count after vaporization experiment). The so-called "standard blank" correction is then added to the value of the fluorescence of Yb on each individual target to ascertain the correct value of mass of Yb on each target.

CHAPTER IV

RESULTS AND DATA REDUCTION

A. Elemental Analysis of $YbBr_2$

Table I shows the results of chemical analyses of $YbBr_2$ prepared for the vaporization experiments.

Table I. Analytical Results

Analysis #	wt % Yb		wt % Br	
		Theoretical		Theoretical
1	50.46	51.99	48.74	48.01
2	50.48		48.63	
3	51.61		48.90	
Average	$50.8_5 \pm 0.7_0$		$48.7_6 \pm 0.1$	

These values correspond to the formula $YbBr_{2.0_8 \pm 0.1_1}$.

B. X-Ray Fluorescence Calibration

A plot of counts of $L_{\alpha 1}$ radiation from Yb versus μg of Yb was linear over the range of 2-12 μg ytterbium.

Table II shows the data collected at each concentration and the average number of counts per microgram ytterbium. The average value was used to obtain mass values used in II-7 which subsequently generated the equilibrium vapor pressures listed in Appendix A.

Table II. X-Ray Fluorescence Calibration Results

μg Yb	Counts 1 μg Yb
2.8	1857.1
4.7	1599.8
6.5	2076.2
8.4	2506.9
10.3	2516.7
12.1	1662.8
Average value = 2037±405	

C. Thermocouple Calibration

Numerous attempts were made to calibrate the chromel-alumel thermocouple against the melting points of aluminum, silver, lead, and copper. In the first three cases either the heating rate could not be slowed enough to observe the melting point transition or the metal interacted (alloyed) with the molyendum crucible. With copper a transition was seen in the temperature versus time plot which corresponded well with the melting point reported for the copper sample by the National Bureau of Standards (1083.3°C). Three separate meltings were made with deviations of 0.8, 0.6, and 0.3°C. It is believed that some interaction was beginning between the sample and the crucible and that the first value of 0.8°C represented the true deviation. Since no other metals were readily available a quick qualitative check calibration was made against the ice point and boiling point of water. The thermocouple showed readings which averaged approximately +1.5° and it was judged that no significant error in temperature measurement would occur if readings were taken directly with no correction applied for the vaporization experiments (±1.5° presents only a 0.1% error in temperature at 1360°).

D. Vaporization Experiments

Six independent vaporization experiments were carried out with two different Knudsen cells (different size orifice). All of the experiments were effected in a molyendum cell except number 6 in which the sample was placed in a graphite holder with the usual molyendum end caps. Table III lists the orifice size and temperature range of each vaporization experiment.

Table III. Vaporization Experiments

Experiment #	Area of Orifice ($x10^4$)	Temperature Range
1	9.37±0.01 cm^2	1207-1296 K
2	9.37±0.01	1190-1279
3	2.94±0.02	1337-1359
4	3.01±0.01	1300-1478
5	2.78±0.00	1309-1514
6	2.90±0.02	1407-1482

The results of the vaporization experiments are graphically represented in Figure 6.

E. Mode of Vaporization

Inspection of the X-ray powder diffraction patterns for the sample of starting material and product remaining in the cell after vaporization cataloged in Appendix E shows that $YbBr_2$ was the predominate chemical substance both before and after the experiments. Indeed the pattern showing spurious lines is that of the starting material. These lines seem to have disappeared in the product left after vaporization; indicating that, whatever their cause, the substance has been destroyed by the heating process. By looking at known powder patterns of $Yb(BrO_3)_3 \cdot 9H_2O$,

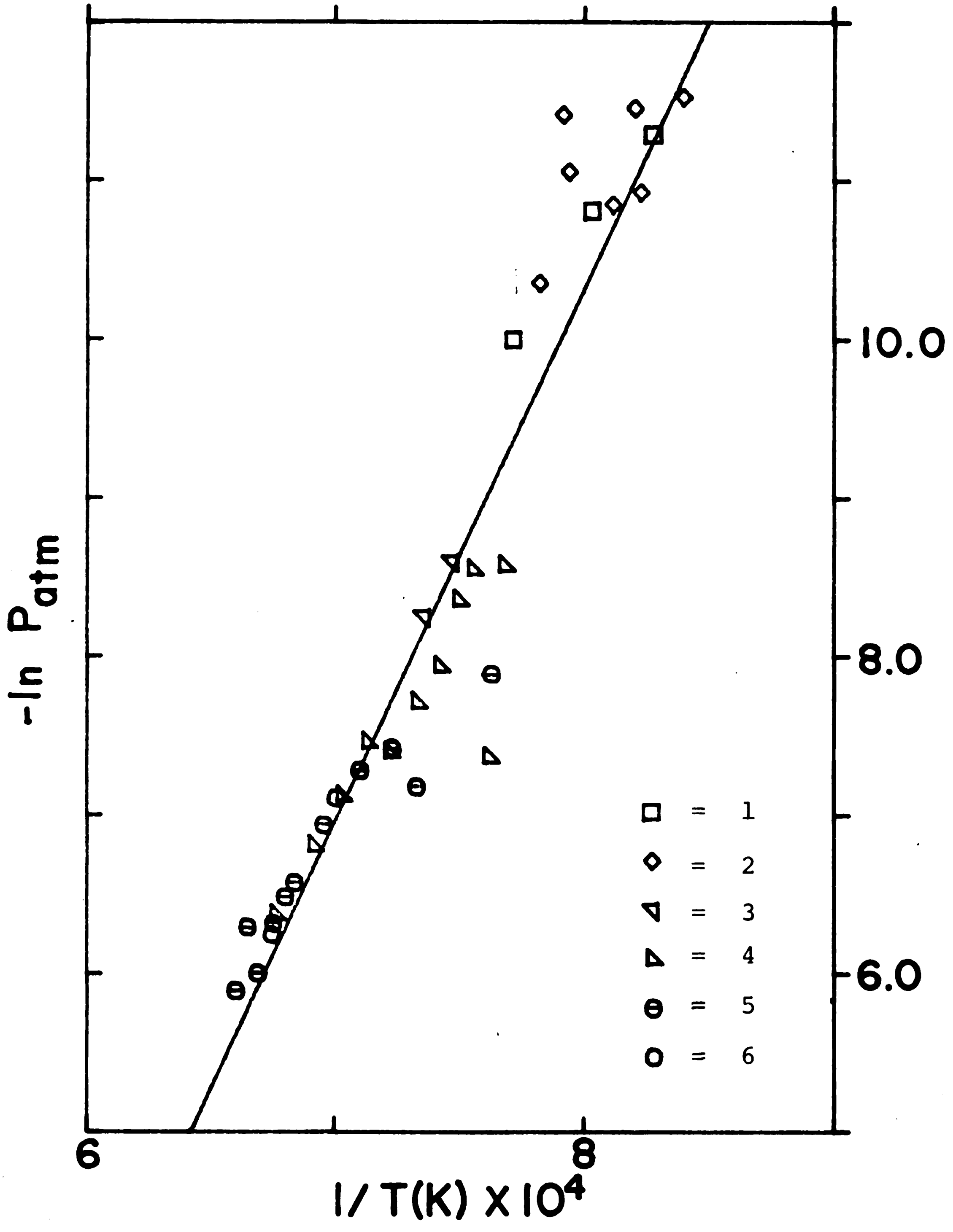

Figure 6. Pressure of $YbBr_2$(g) in equilibrium with $YbBr_2$(s).

Yb_2O_3, Yb_3O_4Br, and YbOBr[32] it was evident that the extra lines in the starting material could not be ascribed to any of these compounds. Comparison of the process which yield the starting material revealed that the only other possible contaminates would be $ZnBr_2$ or $YbBr_3$. Of these the first would be eliminated from a $YbBr_2$ melt very early in the vaporization process because of its appreciable vapor pressure (just such a process of heating under high vacuum was used to supposedly preferentially remove $ZnBr_2$ from the crude $YbBr_2$ in the reaction sequence used to produce $YbBr_2$). Most probably the contaminate is $YbBr_3$ which "bumped" over during the distillation process used to purify crude $YbBr_2$ in production of the starting material. As a measure of its possible quantative contamination of the starting material one need only look to the elemental analysis of $YbBr_2$ described in IV-A. Here it is shown that the starting material is slightly bromine rich (compare molecular formula $YbBr_{2.0_8}$) but a possibility exists for contamination by slight amounts of $YbBr_3$. Indications are the $YbBr_3$ decomposes under heat[2] thus giving a possible explanation to the pattern of $YbBr_2$ after the vaporization process has been accomplished.

In view of the powder patterns, elemental analysis, and lack of a trend in third law measurements (see IV-K) the mode of vaporization can be ascribed to a congruent process whereby $YbBr_2(\ell)$ vaporizes to $YbBr_2(g)$.

F. Vapor Pressure Equation -- ΔH^{o} and ΔS^{o} at Mean Temperature of Vaporization Experiments

When data of vapor pressure and reciprocal temperature are treated by least squares regression equation (IV-1) results:

$$\ell n\ P_{YbBr_2} = -(3.3_7 \pm 0.1_8) \times 10^4/T + 16.6_1 \pm 1.3_2 \qquad \text{(IV-1)}$$

in the temperature range 1190 < T < 1514 K. For comparative purposes the vapor pressure equation for the experiments with the larger orifice (numbers 1 and 2) is presented as:

$$\ell n\ P_{YbBr_2} = -(1.7_0 \pm 0.5_4) \times 10^4/T + 2._8 \pm 4._4 \qquad \text{(IV-1a)}$$

$$1190 < T < 1295\ K$$

and the vapor pressure equation obtained by the remainder of the experiments with the smaller orifice is:

$$\ell n\ P_{YbBr_2} = -(2.2_4 \pm 0.1_9 \times 10^4)/T + 8._7 \pm 1._3 \qquad \text{(IV-1b)}$$

$$1300 < T < 1514\ K$$

however, it is equation IV-1 which is used in all subsequent data treatments since, indeed, the third law data treatment (Section IV-K) shows that the values between the two sets of data represented by IV-1a and IV-1b are coherent with no observable temperature trend. The mean temperature is 1360 K so that through II-13 and II-14 ΔH^o_{1360} and ΔS^o_{1360} are calculated as

$$\Delta H^o_{1360} = 66._9 \pm 3._5 \text{ kcal/mole}$$

$$\Delta S^o_{1360} = 33._0 \pm 2._6 \text{ eu}$$

G. Estimation of Thermodynamic Values

The absence of experimentally determined enthalpies and entropies makes it necessary to resort to estimates of these values for the data reduction process.

If $(H^o_T - H^o_{298})$ and $(S^o_T - S^o_{298})$ functions are available for the various phases or can be estimated reasonably then the relationships:

$$(H^o_T - H^o_{298}) = \int_{298}^{T} Cp\ dT \qquad \text{(IV-2)}$$

and

$$(S^o_T - S^o_{298}) = \int_{298}^{T} Cp/T\ dT \qquad \text{(IV-3)}$$

allow substitution into II-15 and II-16 to give:

$$\Delta H^{o}_{298} = \Delta H^{o}_{T} + [\sum_{i} \nu_{i} \; (H^{o}_{T} - H^{o}_{298})_{i} - \sum_{j} \nu_{j} \; (H^{o}_{T} - H^{o}_{298})_{j}] \qquad \text{(IV-4)}$$

and

$$\Delta S^{o}_{298} = \Delta S^{o}_{T} + [\sum_{i} \nu_{i} \; (S^{o}_{T} - S^{o}_{298}) - \sum_{j} \nu_{j} \; (S^{o}_{T} - S^{o}_{298})_{j}] \qquad \text{(IV-5)}$$

where ν_i refers to coefficients on products i, and ν_j refers to reactants j.

When necessary entropies can be found in a similar manner by:

$$\Delta S^{o}_{298} = \sum_{i} \nu_{i} \; S^{o}_{298_{i}} - \sum_{j} \nu_{j} \; S^{o}_{298_{j}} \qquad \text{(IV-6)}$$

In vaporization reactions only one reactant exists so that the summation on j is dropped:

$$S^{o}_{298_{j}} = 1/\nu_{j} (\sum_{i} \nu_{i} \; S^{o}_{298_{i}} - \Delta S^{o}_{298}) \qquad \text{(IV-7)}$$

Absolute entropy can also be calculated in a purely estimative manner by the following relationship due to Latimer[33] as reinvestigated by Gronwold and Westrum.[34] It is:

$$S^{o}_{298} = \sum_{i} \nu_{i} \; S^{o}_{i} + \sum_{i} \nu_{i} \; M_{i} \qquad \text{(IV-8)}$$

where S_i^o's are the lattice contributions and Mi's are the magnetic contributions to entropy.

Finally thermodynamic values for gases can be estimated by choice of a proper model system. Haschke[35] reviews the method as applied to rare earth systems, where basically it is established that thermodynamic functions for gases rely mostly on molecular symmetry and not mass effects. Following his arguments for $EuBr_2$, $YbBr_2$ is assumed to have $D_{\infty h}$ symmetry, and, therefore, values of $HgBr_2(g)$ are chosen for the model system.

Estimated values for gases are those given in the JANAF[36] table, while $(H_T^o - H_{298}^o)$ and $(S_T^o - S_{298}^o)$ for solids were found by graphical interpolation of estimates for $YbBr_2$ found in Brewer <u>et al.</u>[2] and Bulletin 605 of the National Bureau of Mines[37] (see Appendix B).

H. Second Law Data Reduction to 298 K

Data from the second law treatment is reduced to from the mean temperature of 1360 K to a reference temperature of 298 K through the use of values compiled in Appendix B and similar values for $HgBr_2(g)$ by application of IV-4 and IV-5:

$$\Delta H_{298}^o = 66.89 + 28.64 - 15.70 = 79._8 \pm 4._4 \text{ kcal/mole}$$

$$\Delta S^{o}_{298} = 33.01 + 36.9 - 22.36 = 47._{5} \pm 3._{9} \text{ eu}$$

where errors were assumed to be 20% in the values in Appendix B.

I. Value of Absolute Entropy

The absolute entropy of $YbBr_2$ was found from IV-8 by the use of Latimer's[33] value for Br^- lattice contribution (10.9 eu) and Westrum's[38] value for Yb(II) lattice contribution (13.1 eu). No magnetic contribution was assumed since Yb(II) has a fully filled 4f shell.

The value of absolute entropy thus obtained was, $S^{o}_{298} = 13.1 + 2(10.9) = 34.9$ eu.

J. Estimation of fef and Δfef for $YbBr_2$

So that the tabulated data computed in Appendix B can be used for data reductions by the third law technique it is necessary to rewrite II-19 as:

$$\text{fef} = (H^{o}_{T} - H^{o}_{298})T - (S^{o}_{T} - S^{o}_{298}) - S^{o}_{298} \qquad \text{(IV-9)}$$

Use of absolute entropy and values of $(H^{o}_{T} - H^{o}_{298})$ and $(S^{o}_{T} - S^{o}_{298})$ from Appendix B generates $-(G^{o}_{T} - H^{o}_{298})/T$ data since it is just equal to fef (see II-18). The use of

II-20, through combination of $(G^o_T - H^o_{298})/T$ data of $YbBr_2(s)$ in Appendix B and similar data for the vapor assumed equal to that of $HgBr_2(g)$[36] allows calculation of estimated Δfef for $YbBr_2$ vaporizations (Appendix C).

K. Data Reduction by the Third Law Procedure

Values of Δfef from Appendix C were fitted by least squares regression to a parabola of the form:

$$\Delta fef = aT^2 + bT + c \qquad \text{(IV-10)}$$

to yield; $a = -1.2 \times 10^{-5}$, $b = 3.78 \times 10^{-2}$, $c = -66.12$. An excellent fit of data was obtained with the largest deviation for any data point being 0.51 eu. Thus obtained, a, b, c along with equation IV-10 when coupled with $\ell n\ P_T$ and temperature values in equation II-22 yield ΔH^o_{298} values according to the third law treatment. The resulting average value, $\langle H^o_{298} \rangle = 72._3 \pm 1._5$ kcal/mole with no apparent trend with temperature over the 324 degree range of the vaporization.

L. Other Thermodynamic Parameters for $YbBr_2$

1. From Literature Estimates and Measured Data

Knowledge of $\Delta H^{o}_{298,v}$ from the $\ell n\ P_T$-inverse temperature plot along with literature values of enthalpies of formation of Yb(g)[39] and Br(g)[39] combined with the dissociation energy of $YbBr_2$[40] permits calculation of the estimated enthalpy of formation of $YbBr_2(g)$:

$$\Delta H^{o}_{f298} = \sum_i \nu_i\ \Delta H^{o}_{298_i} - \sum_j \nu_j\ \Delta H^{o}_{f298_j} \qquad \text{(IV-11)}$$

where, again, ν_i refers to coefficients of products and ν_j to those of the reactants: ΔH^{o}_{298} $YbBr_2(g) = -90.2 \pm 0.2$ kcal/mole.

For the special case of vaporization IV-11 reduced to:

$$\Delta H^{o}_{f298} = 1/\nu_j (\sum_i \nu_i\ \Delta H^{o}_{f298_i} - \Delta H^{o}_{298}) \qquad \text{(IV-12)}$$

When i refers to the gas phase and ΔH^{o}_{298} equals the second law enthalpy of vaporization IV-12 yields ΔH^{o}_{f298} $YbBr_2(s) = -170._0 \pm 4._4$ kcal/mole.

The second law absolute entropy of vaporization was determined from the entropy of vaporization and entropy of gaseous $YbBr_2$ (found for the model $HgBr_2$ gas[36]) through IV-7. It is, S^{o}_{298} $YbBr_2(s) = 29._0 \pm 3._9$ eu.

The value of the absolute entropy combined with the entropies of Yb(s) and $Br_2(\ell)$ (see Appendix D) in

$$\Delta S^o_{f298_i} = S^o_{298_i} - \sum_j \nu_j \, S^o_{298_j} \qquad \text{(IV-13)}$$

where ν denotes coefficients on reactants j in formation of compound i, yields ΔS^o_{f298} $YbBr_2(s) = -21._7 \pm 3._9$ eu.

Relationship II-11 allows calculation of ΔG^o_{f298} $YbBr_2(s)$ from ΔH^o_{f298} $YbBr_2(s)$ and ΔS^o_{f298} $YbBr_2(s)$ as; ΔG^o_{f298} $YbBr_2(s) = -163._5 \pm 4._6$ kcal/mole. Further ΔS^o_{f298} $YbBr_2(g)$ can be found from ΔS^o_{f298} $YbBr_2(s)$ and the entropy of vaporization as: ΔS^o_{f298} $YbBr_2(g) = 25._8 \pm 3._9$ eu. Combination of the entropy of formation of $YbBr_2$ gas with the estimated enthalpy of formation gives an approximate value of ΔG^o_{f298} $YbBr_2(g) = -(97._9 \pm 1._2)$ kcal/mole.

2. From Extrapolation of the Vapor Pressure Equation

The normal boiling point of $YbBr_2(\ell)$ was found by extrapolation of IV-1 to one atmosphere. It has the value: $T_b = (2.0_3 \pm 0.1_1) \times 10^3$ K where error is associated with enthalpy only. The data of $(H^o_T - H^o_{298})$ for $YbBr_2(\ell)$ were determined in the 1200-3000 K range by choosing a $PbBr_2$ model system. Graphical interpolation yields $(H^o_{2026} - H^o_{298}) = 46.85$ kcal/mole for the liquid and again by resorting to $HgBr_2$ values for gases, $(H^o_{2026} - H^o_{298}) =$

25.62 kcal/mole for $YbBr_2$ gas. From IV-4 ΔH_v^o is calculated as $58._6 \pm 4._4$ kcal/mole and, since $\Delta S_v^o = H_v^o/Tb$, $\Delta S_v^o = 28.9_2 \pm 2._2$ eu.

M. Note on Errors

The problem of combination of errors in thermodynamic cycles was handled in the preceding sections by a treatment due to Feller.[41] In essence if $Xi(1 \le i \le n)$ is a set of variables with associated standard deviations σi, the deviation in their sum, y, is σy according to:

$$\sigma y = \left(\sum_{i=1}^{n} \sigma_i^{2} \right)^{1/2} \qquad \text{(IV-14)}$$

Since data used in thermochemical cycles are visually independent IV-14 should be a reasonable estimator of error.

CHAPTER V

DISCUSSION AND SUGGESTIONS

A. Preparation of $YbBr_2$

The method followed for the preparation of $YbBr_2$ outlined in III-A provided an adequate source of starting material although one final step was added to the process as outlined by DeKock and Radtke,[30] namely the distillation of the reduced product. It was found that appreciable quantities of the oxide formed if the system leaked air or if the inert gas used during the high temperature reduction contained any O_2 or H_2O. The oxide formed as a crust upon the dark green melt. By distillation the separation of the reduced [Yb(II)] bromide could be effected from the oxide.

B. X-Ray Fluorescence Procedures

The X-ray fluorescence technique theoretically provides a rapid and direct microanalytical determination. However, when operated in a non-vacuum mode the actual number of counts the instrument records is dependent on air pressure. The blank counting procedure should correct for the problem, that is, it should eliminate those systematic errors due to day to day variability of the instrument, but in fact the count rate seemed to vary rapidly -- even during a 20 minute analysis. Surely such changes cannot be ascribed to air pressure but other variables not so easily accounted for come into play. It was found that during a long analysis (of the order of 45 minutes) the number of counts steadily decayed. Although initially the standard blank was counted often during the analysis runs it was decided to count it before and after each target. Still count changes were suspect even during the two minutes needed to analyse each target. In addition the necessity of keeping the counts low (required by remaining in the microgram region) caused any error in counting to be proportionally higher than would the same deviation cause if the counts due to plated material were high. It is my belief that whatever instrumental cause is responsible for the count variation is the weak point of the entire experimental procedure. Mechanical means are at hand to insure that assumptions necessary to the techniques are not violated, but no such mechanism exists to remove the heretofore inexplicable drop in count rate. At best one must count only three or four targets then allow the unit to "rest" for at least one hour before continuing the analysis. Even so, moment to moment changes cannot be accounted for and the most one can hope for is that the variance from the true count not be more than an acceptable percentage.

C. Target Collection Knudsen Effusion Technique

The highest vapor pressure attained during the vaporization experiments was 2.5×10^{-3} atm. The value is of the order of magnitude of the upper pressure limit beyond which molecular flow cannot be maintained but not above the pressure limit given by Mayer.[28] (See Section II-E.5.) As expected no discontinuity was displayed for values obtained by varying the area of the orifice, thus creditability is given to the assumption that Knudsen conditions of equilibrium were maintained in the effusion cell. However satisfying the second law and third law data seem, one problem remained throughout the experiments. Upon inspection of the interior of the effusion cells after the vaporization it was noticed that at least some material had blocked the orifice of the cell. Such behavior is ascribed to a temperature gradient across the cell by Haschke,[35] a condition thought to be corrected by the placement of the cell assembly in a symmetric oven. Indeed, optical pyrometer measurements indicated that no temperature gradient existed across the oven, top to bottom but of course, no such measurement could be made on the cell itself. Lack of a trend in the enthalpies derived by the third law data treatment suggests that even if a temperature gradient did exist it had little effect upon vapor pressure.

An alternative to a temperature gradient could be selective condensation of the vapor on the lid of the cell interior during the cooling process. Direct evidence of such a situation is not at hand but it seems reasonable since a possible mechanism exists whereby the top and bottom of the cell might lose energy more rapidly than the sides of the cell. First, the walls of the cell are at least twice as thick as the lid since the sample container consists of an insert and end caps; the walls are composed of one layer of insert and one of end cap while the lid is formed only from the end cap. If the extra mass of metal in the sides retains its heat longer than the smaller mass of the lid then selective condensation might occur. Secondly the oven which is about the cell has only two openings, one at the top directly above the orifice of the cell and one coaxially placed at the bottom of the oven. Since the system cools in a high vacuum the only possible way for the cell and oven assembly to release energy is through infrared radiation. The oven essentially stops direct radiation of the cell and a back radiation system might be established -- except at the lid and bottom of the

cell where it can lose radiation directly to the external environment. Should either condition lower the temperature of the lid preferentially to the walls then selective condensation could occur.

D. The Use of Thermodynamic Approximation

1. Absolute Entropy Approximation

The value obtained by equation IV-8 for the estimated absolute entropy (34.9 eu) falls outside the range of the calculated absolute entropy ($29._0 \pm 3._9$ eu). The difference could be ascribable to the measured ΔS at the median temperature if one can assume the $HgBr_2$ model system represents $YbBr_2(g)$ accurately since it is a simple combination of these two entropy values in IV-7 which yields the absolute entropy. Indeed, it was because of the probability of variation in these two absolute entropy values that ΔS^o_{298}, the calculated (IV-8) value was used in estimation of fef's for the third law determinations.

2. $YbBr_2$ Data

Most of the determined values are consistent with available estimated values. The equilibrium vapor pressure is within the limits put forth by Brewer.[2] Estimation of the normal boiling point results in a value (2026 K) in good agreement with Brewer's[2] estimate. However the value of ΔS_v^o of 28.9 eu is outside the range of Trouton's rule. However, Gschneidner[42] points out that liquids boiling much higher than room temperature tend to have higher entropy of vaporization values and recommends a value of 25.5 eu for such substances. Even so, a high value such as 28.9 eu could only come from a value of ΔH_v^o which is too large. Indeed, a scan of the JANAF[36] tables shows a definite trend toward increasing $(H_T - H_{298}^o)$ values with increasing molecular weight for liquid compounds of metal dibromides. The $PbBr_2$ model system was chosen for $YbBr_2(\ell)$ to minimize ΔH_v to bring it as closely in line with the estimated value as possible. Lack of proper model systems in the rare earth series precludes the strict application of an estimative system.

The ΔH_{298}^o second law value of $79._8 \pm 4._4$ kcal/mole is some 8 kcal/mole above the value estimated by Feber[40] (71 kcal/mole); the average third law value of $72._3 \pm 1._5$ kcal/mole is in much closer agreement. The ΔH_{f298}^o $YbBr_2(s) = -170._0 \pm 4._4$ kcal/mole is also somewhat lower than the estimated value of -161 kcal/mole[40] again probably due to the use of the ΔH_{298}^o (second law) value which is higher in magnitude than it should be.

The overall magnitude of error in second law values can be shown by examination of IV-1, IV-1a, and IV-1b.

Here one sees that the error in the definition of a least squares line can greatly affect the slope (and hence the enthalpy) and the intercept (thereby the entropy). Indeed even if the slope is known to within a small error probability the variance in intercept could be appreciable since the slope is of so great a magnitude. As stated before, the accuracy of the system rests on the consistency shown by the third law treatment without which one would be hard pressed to find reason to join data which forms the two equations (IV-1a and IV-1b) into an overall vapor pressure equation (IV-1).

Ultimately the correctness of any data set can only be ascertained by comparison to the trends established by other researchers when no mechanism exists to ascertain in an absolute fashion the necessary relationships.

To address the question of molecular geometry, DeKock and Wesley[43] have linked the degree of non-linearity in the rare earth halides to the s-d orbital separation through actual measurement of infrared spectra of some divalent rare earth halides. On passing from the difluoride to the dichloride the bond angle opened for samarium and europium by some 20°, but for some unexplained reason ytterbium remains invarient with increasing molecular weight (greater s-d orbital separation) of the attached halide. Nonetheless they point out the strong correlation between the alkaline earth halides and those of the rare earths and it was upon that basis that a linear structure was chosen for $YbBr_2$.

Thermodynamic vaporizations have been carried out on both $YbCl_2$[17] and YbF_2.[44] The latter case proved to be incongruent but many of the vaporization parameters were nonetheless described or estimated. Table IV presents values from these references and those found by Hariharan[18] for the analogous Eu(II) compounds.

Table IV. Data Summary for Vaporization Thermodynamics of Eu(II) and Yb(II) Halides

	MF_2	MCl_2	MBr_2	MI_2
ΔH_{298} kcal/mole Eu(II)	$100._8 \pm 2._5$	$84._9 \pm 1._1$	$79._8 \pm 1._5$	$75._4 \pm 1._1$
ΔH_{298} kcal/mole Yb(II)	$109._0 \pm 8._5$	$84._7 \pm 1._1$	$79._8 \pm 4._4$	
ΔS_{298} eu Eu(II)	$48._9 \pm 2._5$	$48._3 \pm 1._8$	$48._0 \pm 2._0$	$48._1 \pm 1._9$
ΔS_{298} eu Yb(II)	$46._0 \pm 5._6$	$48._0 \pm 1._1$	$47._6 \pm 3._9$	
ΔH_v^o kcal/mole Eu(II)	$79._3 \pm 2._0$	$58._9 \pm 1._8$	$55._3 \pm 2._2$	$53._5 \pm 1._6$
ΔH_v^o kcal/mole Yb(II)		$61._7 \pm 1._0$	$58._6 \pm 4._4$	
ΔS_v^o eu Eu(II)	$31._7 \pm 1._0$	$25._2 \pm 0._7$	$25._1 \pm 1._0$	$26._1 \pm 0._7$
ΔS_v^o eu Yb(II)		$26._7 \pm 0._7$	$28._9 \pm 2._2$	

In view of these data it is evident that the $YbBr_2$ system presents values which are in line with those derived for related systems. Even though the amount of scatter in the data points and the resultant error would indicate that the overall value should be somewhat suspect, the system proved to be well-behaved in that consistent values were obtained which allowed the description of the vaporization parameters of $YbBr_2$.

E. Suggestions for Future Research

Examination of Figure 5 shows considerable variance in the individual data points. In addition those with most average variance are at the lower temperatures. These points were taken early in the experiments before partial remedies were found for the counting technique problem with the X-ray fluorescence unit and before it was determined just how long to expose targets to obtain plated quantities in the calibration region. While there are enough points to establish that no trend in measurement exists I felt it invalid to eliminate any of them through statistical means since such a procedure would have negated the overall importance of the initial experiments which were intended to have equal weight given to them as latter experiments. At present it is unknown whether or not the linearity of the data at higher temperatures is due to a variable in the vaporization process or elimination of some random errors due to improvement in the skills of the investigator. Obviously what is needed is additional experiments at the lower temperatures so that more data can be obtained for that region. Also the gap between the lower and higher temperatures could be filled in since it is the region where one would expect a cell with an orifice of intermediate area between those used to supply data. Regardless of the amount of data obtained the enthalpies and entropies at a reference temperature will only be as reliable as the system used for reduction to that temperature from the operating temperature of the experiments. Since the choice of the $HgBr_2$ model system for $YbBr_2(g)$ was dependent on the necessity for $D_{\infty h}$ symmetry should the $YbBr_2$ molecule prove to be non-linear then revaluation of the system with a new model system would be necessary.

Finally it should be pointed out that at least one other system exists for estimation of the thermodynamic properties of materials. Through theories developed by statistical thermodynamics, known rotational, vibrational and electronic states of a molecule allow calculation of its heat capacity, $(H_T - H^o_{298})$ and S^o_T functions. Although more pleasing in essence, it too is dependent on assumptive techniques when the necessary preliminary data from measured spectra are not known. Hariharan[18] has applied the method to Haschke's[17,35] data for $EuBr_2$ and obtains somewhat differing values. His treatment, while more eloquent in nature than extrapolation of estimated thermodynamic values, is only as reliable as his estimates from the extrapolation of data for the alkaline earth bromides. Of course should the electronic, vibrational and rotational spectra of $YbBr_2$ become available then the system would yield absolute data reduction from median temperatures to any reference temperature.

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APPENDICES

Appendix A: Collected Vaporization Data and Third Law Enthalpies for $YbBr_2$

T(K)	μg $YbBr_2$	$-\ell n\ P_T$	Orifice Area ($x10^4$)	Collection Times	ΔH^o_{298}
1295	19.30	9.999 atm	9.37 cm^2	45.16 min	73.997 kcal/mole
1208	3.67	11.293		30.24	42.949
1245	5.84	10.812		30.18	73.607
1259	4.52	11.061		30.15	74.921
1278	9.09	10.357		30.22	74.085
1231	5.66	10.852		30.30	73.017
1215	5.24	10.931		30.13	72.423
1190	2.91	11.530		30.15	72.616
1219	3.09	11.460		30.21	73.901
1262	3.26	11.418		31.12	75.966
1338	15.93	8.600	2.94	30.13	72.377
1359	22.37	8.256		30.22	72.428
1311	19.55	7.370	3.01	10.455	67.925
1300	8.55	8.576		15.21	70.563
1322	5.84	8.550		10.21	71.504
1346	10.66	7.941		10.22	70.986
1332	7.02	8.359		10.17	71.460
1363	13.24	7.712		10.16	71.140
1384	14.41	7.400		8.16	71.237
1401	8.45	7.464		5.13	72.186

Appendix A (Cont.)

T(K)	μg $YbBr_2$	$-\ell n\ P_T$	Orifice Area ($\times 10^4$)	Collection Times	ΔH^o_{298}
1421	11.91	7.123 atm	3.01 cm^2	5.18 min	72.141 kcal/mole
1445	9.84	6.812		3.16	72.348
1477	14.89	6.374		3.12	72.535
1310	10.42	7.891	2.78	10.16	69.238
1364	16.67	7.181		8.15	69.746
1382	9.85	7.424		6.18	71.213
1407	9.32	7.284		5.13	71.957
1437	8.04	6.943		3.18	72.359
1462	7.73	6.577		2.14	72.444
1470	8.37	6.486		2.12	72.543
1480	7.52	6.320		1.62	72.513
1494	6.46	6.005		1.02	72.219
1514	5.13	5.894		0.73	72.800
1503	4.34	6.296		0.92	73.498
1407	9.89	7.286	2.90	5.12	71.962
1427	9.25	7.110		4.04	72.378
1481	8.12	6.250		1.53	72.353

Appendix B: Enthalpy, Entropy, Free Energy Functions of $YbBr_2(s,\ell)$

T(K)	$(H^o_T - H^o_{298})$	$(S^o_T - S^o_{298})$	$-(G^o_T - H^o_{298})/T$
1000	20,000 cal/mole	29.00 eu	43.90 eu
1100	22,400	31.50	46.04
1200	24,800	34.00	48.23
1300	27,200	36.00	49.98
1400	29,600	37.50	51.26
1500	32,000	39.00	52.57
1600	34,400	40.00	53.4

Appendix C: Free Energy Function Changes For the Vaporization of $YbBr_2(\ell)$

T(K)	$-\Delta$fef
1000	40.061 eu
1100	38.927
1200	37.689
1300	36.839
1400	36.413
1500	35.914
1600	35.855

Appendix D: Thermodynamic Functions

Phase	Thermodynamic Function at 298 K	Value	Reference
Yb(g)	ΔH_f^o kcal/gfw	36.35±0.2	39
Br(g)	ΔH_f^o kcal/gfw	26.740	36
Yb(g)	ΔG_f^o kcal/gfw	28.285	39
Br(g)	ΔG_f^o kcal/gfw	19.700	36
Yb(s)	S^o eu	14.30±0.04	37
$Br_2(\ell)$	S^o eu	36.384	36
$YbBr_2(g)$	D_o kcal/gfw	(180)	40

Appendix E: X-Ray Powder Diffraction Patterns

$YbBr_2$ Sample Before Vap. Exp. d-spacings	Relative Intensity of Reflection	Product Remaining in Cell After Vap. Exp. d-spacings	Relative Intensity of Reflection	Calculated d-spacings for $YbBr_2$*	Calc.* Intensity of Reflection	Reflection $(h\ k\ \ell)$
5.17[a]	40%	5.79	diffuse			
4.78	30	4.76	90%	4.79	100%	110
4.22[a,b]	40	4.24[b]	very weak			
4.10[a]	30					
3.65	20	3.63	40	3.65	24.7	101
3.20	30	3.21	50	3.23	23.6	111
3.12	30	3.00	10	3.07	11.4	120
2.91	20	2.91	20	2.99	0.3	210
2.54[a,b]	40	2.59[b]	40			
2.50	60	2.49	30	2.51	26.3	121
2.45	100	2.45	60	2.47	53.7	211
2.41	60	2.37	20	2.40	21.7	220
2.29	20	2.21	10	2.19	16.1	002
		2.17	20	2.18	7.6	130

Appendix E (Cont.)

$YbBr_2$ Sample Before Vap. Exp. d-spacings	Relative Intensity of Reflection	Product Remaining in Cell After Vap. Exp. d-spacings	Relative Intensity of Reflection	Calculated d-spacings for $YbBr_2$*	Calc.* Intensity of Reflection	Reflection ($h\ k\ \ell$)
2.08	20%			2.11	5.3	310
2.02	15	2.03	20%	2.04	18.9	031
		1.83[b]	30	1.86	1.1	320
		1.60	10	1.61	6.2	222
		1.56[b]	10	1.54	3.1	132

*Calculated from known X-ray parameters for $YbBr_2$ and $CaBr_2$.[45]

[a] Spurious reflection (see V-E).

[b] Possibly due to presence of Yb_2O_3 (see Ref. 32).