University of Nevada, Reno

Vapor Pressures and Thermodynamic Properties of Tungsten, Chromium, Cobalt and Rhodium Carbonyls

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering

- submitted by -
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ABSTRACT

Low temperature vapor pressures of four metal carbonyls; tungsten hexacarbonyl, chromium hexacarbonyl, dicobalt octacarbonyl and hexarhodium hexadecacarbonyl were determined by using gravimetric torsion effusion method. The vaporization behavior of dicobalt octacarbonyl was complex and it decomposed at room temperature, in vacuo. Just below room temperature at about 270K this decomposition did not occur, but the dimer disproportionated to other forms as revealed by the differences in the measured molecular weight of vaporization of dicobalt octacarbonyl of 226 g/mol as compared to the theoretical value of 342 g/mol. It is proposed that the dimer, Co₂(CO)₈, under goes partial disproportionation to tetramer, Co₄(CO)₁₂, monomer, Co(CO)₄, and carbon monoxide gas. The solid hexarhodium hexadecacarbonyl exhibited unexpected vaporization behavior and did not vaporize to hexarhodium hexadecacarbonyl gas of some disproportioned species. The solid hexarhodium hexadecacarbonyl decomposed directly in the Knudsen cell itself in the temperature range of 325K to 361K, leaving residual porous rhodium particles and carbon monoxide gas; the measured molecular weight of the effusing gas matched that of carbon monoxide. The formation of metallic rhodium was confirmed by X-ray diffraction analyses and scanning electron microscopy/X-ray energy dispersive micro-analyses. The Bragg peaks of rhodium showed extensive broadening as compared to those obtained from the annealed materials. Although, the size of the rhodium particles ranges approximately between 50 to 90 microns, the actual crystallite size of these porous rhodium particles was measured to be about 4.8 nm and the average microstrain, \( <e>^{1/2} \approx 7 \times 10^{-3} \), using the Warren-Averbach method. The fine particle size of the rhodium is suggestive of large surface area and may have possible practical catalyst applications. Lastly, there was virtually no disproportionation in tungsten and chromium hexacarbonyls in this low temperature study and the measured molecular weights of these compounds were very close to the actual values. The vapor pressure of each of the above mentioned carbonyls, the molecular weights of the effusing gases, proposed disproportionation mechanisms in the dicobalt octacarbonyl and the decomposition of hexarhodium hexadecacarbonyl, equilibrium constants for the vaporization reactions, their enthalpies and Gibbs energies are presented.
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I. Introduction

Metal carbonyls are of great interest in metal recovery, chemical vapor deposition (CVD), composite materials fabrication and other near net shape technologies [1], [2]. The carbonyls must be reasonably volatile at temperatures below the decomposition temperatures for the CVD application of high purity metallic deposits. Thus, CVD from metal carbonyls is very suitable for the deposition of cobalt, chromium, nickel, iron and transition metals. Nickel carbonyl is most extensively used for the production of high purity nickel [3]. Molybdenum and tungsten have been investigated in the application of electronic devices and ceramic coatings [4]. For example, tungsten carbonyl decomposition has been used for fusing tungsten filaments. Powell [5] reported formation of adherent ductile coatings by thermal decomposition of nickel and iron carbonyl to form metallic nickel and iron. Clements and Sale [6] successfully decomposed vapors of nickel and iron carbonyls to form Ni-Fe coatings on copper disks. Chandra [7,8] deposited uniform thin coatings of nickel on graphite fibers for composite fabrication application. Deposition methods have been developed for coating molybdenum, rhenium and tungsten [9,10] on carbon fibers for composite applications.

Predictions of conditions for the formation and decomposition of carbonyls in CVD processes are important. For example, the thermodynamics of nickel and iron carbonyls are such that the carbonyl may be formed at high pressure and decomposed at low pressure [11,12] slightly higher than room temperature regime; thus there is flexibility of processing. The tungsten and molybdenum carbonyls yield their respective carbides as the decomposition product rather than the pure metal, however deposition of pure metals is possible with the addition of small amounts of hydrogen.

Carbonyls are produced by reacting metal-halides with carbon monoxide gas at elevated pressures rather than direct reaction with the metal. The partial reduction process is coupled with valence disproportionation which indicates ligands such as cyanide of ammonia readily form coordination compounds. For example in the syntheses of nickel and monoiron carbonyls by metal and carbon monoxide, large increases in the rates of formation are observed in the presence of sulfur, ammonia, and other compounds. This may be used in the optimization of volatilization of carbonyls.
In a similar manner chromium carbide coatings can be deposited, however methods of deposition of pure chromium coating using carbonyl decomposition requires further investigation [13]. There are several binary carbonyls that can be used for CVD purposes but the thermodynamic data is lacking in many cases. Some important carbonyls for CVD applications are vanadium V(CO)₆, chromium Cr(CO)₆, molybdenum Mo(CO)₆, tungsten W(CO)₆, manganese Mn₂(CO)₁₀, dicobalt Co₂(CO)₈, tetracobalt Co₄(CO)₁₂, tetrarhodium Rh₄(CO)₁₂, hexarhodium Rh₆(CO)₁₆, triiron Fe₃(CO)₁₂, diiron Fe₂(CO)₉, monoiron Fe(CO)₅, and nickel Ni(CO)₄; the last two are liquid at room temperature [13] and the compounds are listed in Table 1. The nickel carbonyl threshold limit value (TLV) is 0.05 ppm while for monoiron carbonyl we have (TLV 0.1 ppm). These are very toxic but their TLV is three to four orders of magnitude lower than carbon monoxide. Leadbetter and Spice [14] explored the thermodynamic properties of iron pentacarbonyl.

The carbonyl CVD process, is a low temperature process in which adhesion of high purity metallic coatings on substrates of a complex shaped object may be made for many applications. Moreover the alloy coatings may be of an alloy form which has great potential for metal matrix composite application. The coating thickness can range from a few angstroms to micron size and complex shaped objects can be uniformly coated. The uniformity and the purity is unparalleled provided that the decomposition rates are controlled as compared to the other electrolytic deposition methods. However low temperature thermodynamic properties, such as the vapor pressures of tungsten, chromium and other carbonyls have not been determined. Even in the extensively studied nickel and monoiron carbonyls [6,15] some differences in the thermodynamic data and common practice of depositing need to be resolved. Moreover the properties of the different vapor species of some of the above mentioned carbonyls have not been determined although some species have been recently reported [16]. In particular the data for low temperature dicobalt, tungsten and chromium carbonyl species are not available, and for hexarhodium hexadecacarbonyl vapor pressure no data are available.

Various other researchers have determined the vapor pressures of some of the metal carbonyls at temperatures of around 400K. Windsor and Blanchard [17] found the vapor pressure of chromium carbonyl to be log P = 9.756 -3285/T in Torr. A few years later
Lander and Germer [4] found log P = 11.832 -3755.2/T for chromium carbonyl in the same temperature range. Lander and Germer also studied molybdenum and tungsten carbonyls in this temperature range and found that their vapor pressures to be very close to the vapor pressure of chromium carbonyl.

In the late sixties Baev et al. [18], [19] studied the carbonyls of nickel, iron, molybdenum, manganese, chromium, tungsten, and cobalt. In the temperature range of 400K they found for chromium and tungsten, log P = 10.47 - 3575.9/T and log P = 10.66 - 3886.4/T respectively, both of these pressures are in Torr. The above studies have two things in common. The first is that the measurements were taken at above room temperature at around 400K and secondly all data was acquired by some type of manometer device.

In this study low temperature thermodynamic data of dicobalt octacarbonyl, Co$_2$(CO)$_8$, tungsten hexacarbonyl, W(CO)$_6$, chromium hexacarbonyl, Cr(CO)$_6$, and hexarhodium hexadecacarbonyl, Rh$_6$(CO)$_{16}$, have been determined by using the Knudsen torsion-effusion method. The total vapor pressures of gaseous metal carbonyls at zero degrees centigrade have been determined. The torsion effusion-gravimetric method was selected to measure vapor pressures. Knudsen effusion cells were used for vapor pressure measurements with concurrent weight loss which allowed the determination of measurement of average molecular weights of the effusing vapor phase. The assumption that was made for each of the experiments in this study is that inside the cell the solid and the vapor are in equilibrium. We believe this assumption to be valid because the orifice size is quite small, 0.6 mm, and the amount of vapor escaping the cell is therefore extremely small. It is important to note at this point that at a pressure of only three Torr inside of the apparatus all effusion stops, the torsion oscillation ceases completely and data can no longer be acquired. Also when the background pressure is raised to three Torr all weight loss stops. This the basis for the assumption that the inside of the cell maintains a solid-vapor equilibrium.

The rate of weight loss was taken from the chart recorder which is interfaced with the microbalance. The rate of weight loss is a relatively simple calculation. Once the system has reached thermal equilibrium the slope of the line on the chart recorder becomes straight
because the weight loss per time, $\Delta M/\Delta t$, has become constant. $\Delta M$ is simply the slope of the line and $\Delta t$ is the change in time. This number is the weight loss and is then used to calculate the average molecular weight of the effusing gas.

A mirror assembly is attached to the ribbon and a meter stick is positioned such that its reflection can be viewed via a cathedometer which is a telescope. As the torsion-effusion cell assembly rotates a torque is developed in the ribbon which in turn oscillates the mirror assembly. At thermal equilibrium these minimum and maximum readings from the meter stick do not change, once thermal equilibrium has been attained data can then be taken.

The microbalance from which this cell has been suspended is extremely sensitive. It can detect a change of one tenth of a microgram. As the effusate exits the cell the balance detects this weight loss. This weight loss is combined with the angular displacement to give the molecular weight of the effusate.

When these data are plotted as logarithm of pressure versus reciprocal temperature a straight line is obtained and its equation can be determined. At this point many thermodynamic quantities can be determined, the Gibbs energy, the enthalpy, and the entropy. Species using mass spectrometry, although attempted, was not successful possibly due to room temperature decomposition of cobalt carbonyl under vacuum. However, we have calculated the partial pressures of these gas species, which show a good corroboration with the data.

In the temperature range that the measurements were made, tungsten carbonyl did not show formation of any dimers in vapor phase, because the measured molecular weight matched that of the solid. The molecular weight of chromium carbonyl showed some deviation but it was within the experimental error, suggesting some disproportionation even at low temperatures. Hexarhodium hexadecacarbonyl, showed virtually complete decomposition to metallic rhodium and carbon monoxide.

The study of the physical properties of metal carbonyls has been dormant for approximately thirty years. There is now a renewed interest in these compounds. This study expands the data for the physical properties of several carbonyl compounds.
Table 1. Classification of Transition Metal Carbylons [16]

<table>
<thead>
<tr>
<th>Group VB</th>
<th>Group VIIB</th>
<th>Group VIII(a)</th>
<th>Group VIII(b)</th>
<th>Group VIII(c)</th>
</tr>
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<tr>
<td>V(CO)₆</td>
<td>Mn₃(CO)₁₀</td>
<td>Fe(CO)₅</td>
<td>Co₄(CO)₁₂</td>
<td>Ni(CO)₄</td>
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<td>Yellow crystals</td>
<td>Yellow liquid</td>
<td>Orange crystals</td>
<td>Colorless liq.</td>
</tr>
<tr>
<td>mw 219.0</td>
<td>mw 390.0</td>
<td>mw 195.9</td>
<td>mw 571.9</td>
<td>mw 342.0</td>
</tr>
<tr>
<td>mp 60°C</td>
<td>mp 154°C</td>
<td>mp -20°C</td>
<td>mp 60°C</td>
<td>mp 51°C</td>
</tr>
<tr>
<td>AS very</td>
<td>AS moderately</td>
<td>AS mildly</td>
<td>AS mod.</td>
<td>AS mod.</td>
</tr>
<tr>
<td>Cr(CO)₆</td>
<td>Tc₂(CO)₁₀</td>
<td>Ru(CO)₅</td>
<td>Ru₃(CO)₁₂</td>
<td>Rh₄(CO)₁₂</td>
</tr>
<tr>
<td>White crystals</td>
<td>White crystals</td>
<td>Yellow liquid</td>
<td>Orange crystals</td>
<td>Dark red crys.</td>
</tr>
<tr>
<td>mw 220.1</td>
<td>mw 476.1</td>
<td>mw 195.9</td>
<td>mw 639.3</td>
<td>mw 571.9</td>
</tr>
<tr>
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<td>mp 159°C</td>
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<td>mp 60°C</td>
</tr>
<tr>
<td>Mn₂(CO)₁₀</td>
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<td>Ru(CO)₅</td>
<td>Ru₃(CO)₁₂</td>
<td>Rh₄(CO)₁₂</td>
</tr>
<tr>
<td>Yellow crystals</td>
<td>Yellow crystals</td>
<td>Yellow liquid</td>
<td>Orange crystals</td>
<td>Dark red crys.</td>
</tr>
<tr>
<td>mw 390.0</td>
<td>mw 476.1</td>
<td>mw 195.9</td>
<td>mw 639.3</td>
<td>mw 571.9</td>
</tr>
<tr>
<td>mp 154°C</td>
<td>mp 159°C</td>
<td>mp -20°C</td>
<td>mp 154°C</td>
<td>mp 60°C</td>
</tr>
<tr>
<td>Fe(CO)₅</td>
<td>Fe₂(CO)₉</td>
<td>Co₂(CO)₈</td>
<td>Co₄(CO)₁₂</td>
<td>Ni(CO)₄</td>
</tr>
<tr>
<td>Yellow liquid</td>
<td>Brown plates</td>
<td>Orange crys.</td>
<td>Orange crystals</td>
<td>Colorless liq.</td>
</tr>
<tr>
<td>mw 195.9</td>
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<td>mw 342.0</td>
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<tr>
<td>mp -20°C</td>
<td>mp 100°C</td>
<td>mp 60°C</td>
<td>mp 51°C</td>
<td>mp -19.3°C</td>
</tr>
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<td>AS mildly</td>
<td>AS mildly</td>
<td>AS mod.</td>
<td>AS mod.</td>
<td>AS mod.</td>
</tr>
<tr>
<td>Fe₂(CO)₉</td>
<td>Fe₄(CO)₁₂</td>
<td>Co₂(CO)₈</td>
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<td>Ni(CO)₄</td>
</tr>
<tr>
<td>Brown plates</td>
<td>Orange crys.</td>
<td>Orange crystals</td>
<td>Orange crystals</td>
<td>Colorless liq.</td>
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<tr>
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<td>mw 342.0</td>
<td>mw 342.0</td>
<td>mw 342.0</td>
</tr>
<tr>
<td>mp 100°C</td>
<td>mp 60°C</td>
<td>mp 51°C</td>
<td>mp 51°C</td>
<td>mp -19.3°C</td>
</tr>
<tr>
<td>AS mildly</td>
<td>AS mildly</td>
<td>AS mod.</td>
<td>AS mod.</td>
<td>AS mod.</td>
</tr>
<tr>
<td>Ru(CO)₅</td>
<td>Ru₃(CO)₁₂</td>
<td>Rh₄(CO)₁₂</td>
<td>Rh₆(CO)₁₆</td>
<td>Ru₄(CO)₁₂</td>
</tr>
<tr>
<td>Yellow crystals</td>
<td>Orange crystals</td>
<td>Dark red crys.</td>
<td>Black solid</td>
<td>Yellow solid</td>
</tr>
<tr>
<td>mw 639.3</td>
<td>mw 571.9</td>
<td>mw 1065.6</td>
<td>mw 1104.9</td>
<td>mw 1104.9</td>
</tr>
<tr>
<td>mp 154°C</td>
<td>mp 60°C</td>
<td>mp 220°C</td>
<td>mp 230°C</td>
<td>mp 220°C</td>
</tr>
<tr>
<td>Ru₃(CO)₁₂</td>
<td>Rh₄(CO)₁₂</td>
<td>Rh₆(CO)₁₆</td>
<td>Ru₄(CO)₁₂</td>
<td>Ru₄(CO)₁₂</td>
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<tr>
<td>Orange crystals</td>
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<td>Black solid</td>
<td>Yellow solid</td>
<td>Yellow solid</td>
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<tr>
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<td>mp 60°C</td>
<td>mp 220°C</td>
<td>mp 230°C</td>
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</table>

AS = air sensitive
II. Thermodynamics of Vaporization and Line Profile Analysis

2.1 Thermodynamics of Solid-Gas Phase Equilibria

A. Solid-Gas Equilibrium

Consider a solid-gas equilibrium the total differential for the two phases in equilibrium for each phase is \( \partial \Gamma = V dP - S dT \), where \( \Gamma, V \) and \( S \) are Gibbs energy, volume and entropy of the system and the change in pressure with temperature is given by the following equation:

\[
\left( \frac{dP}{dT} \right)_{eq} = \frac{\Delta S}{\Delta V}
\]  

(1)

At equilibrium \( \Delta G = 0 \) and hence \( \Delta H = T \Delta S \); substituting this the following Clapeyron equation is obtained which gives the temperature and pressure relationships. But the volume of the vapor is much greater than that of the solid and therefore the molar volume change \( \Delta V \) Vapor and the solid-gas equilibria may be represented by the following:

\[
\left( \frac{dP}{dT} \right)_{eq} = \frac{\Delta H_v}{T V_v}
\]  

(2)

If the vapor behaves ideally, then \( PV = RT \) and if the \( \Delta H \) is temperature independent or if the specific heat of the vapor and gas are equal then we can write:

\[
d \ln P = \left( \frac{\Delta H_v}{R T^2} \right) dT
\]  

(3)

For pure solids, \( \Delta G^o = 0 = G^o_S(T) + RT \ln P G^o_\delta(P,T) \)

By rearranging, \( \Delta G^o_v = G^o_v - G^o_S = -RT \ln P \)

and by definition: \( G^o_S(T) = G^o_v(P,T) = \Delta H^o_v - T \Delta S^o_v \)

By integrating equation (2), or by using the above argument we obtain Clausius-Clapeyron equation (7):

\[
\ln P = -\frac{\Delta H^o_v}{RT} - \frac{\Delta S^o_v}{R}
\]  

(7)

where \( \Delta H^o_v \) and \( \Delta S^o_v \) are the enthalpy and entropy of vaporization. Equation (7) is the Clausius Clapeyron equation or may be referred to as the van’t Hoff equation which is
used to determine the heats of sublimation.

Gibbs energy is derived as the maximum work $\Delta G$ done in a system when the reactants in a chemical process pass reversibly from their initial state to one in which they are in equilibrium with and are transformed to the products which are brought in turn to their final state. The Gibbs energy is then given by the relation:

$$
\Delta G = -RT \ln K_p + RT \Sigma n \ln P
$$

in which the term $\Sigma n \ln P$ defines the initial and final states of the system. $n$ and $P$ represent respectively the number of moles and the pressure of the participant in the reaction. If the pressures are all fixed at unity, the term $RT \Sigma n \ln P$ vanishes and we have $\Delta G = -RT \ln K_p$ remaining.

In the above equation (8) we have substituted, $\ln P = \ln K_p$, where $K_p$ is the equilibrium constant. By using the second law method we just need to know a few equilibrium constants, $K_p$, and knowledge of entropies is not needed. In this equation the $\Delta H^o$ and $\Delta S^o$ are assumed to be temperature independent in this temperature range. Plotting $\ln K_p$ against $1/T$ gives a straight line whose slope is $-\Delta H^o/RT$ for the vaporization equilibrium. The equation for the straight is obtained by least square method with standard deviation. If the enthalpies are known then extrapolation of $H^o_T$ to 298K can be made by using the following approximation (9):

$$
\Delta(H^o_T - H^o_{298}) = \Delta H^o_T - H^o_{298}
$$

The Gibbs energies of the vaporization may be calculated for example for a particular hexacarbonyl may be calculated for example for a particular equilibrium:

$$
M(C0)_6 (s) = M(C0)_6 (g)
$$

by knowing the total pressure the Gibbs energy variation as function of temperature may be determined by the following equation:

$$
\Delta G^o = -RT \ln K_p = -RT \ln P_{eq. M(C0)_6(g)}
$$
B. Vapor Pressure Measurement Methods

The measurement of vapor pressure may be classified into the following categories as per Margrave [20]:

(a) Static manometric methods
(b) Transpiration method
(c) Boiling point method
(d) Knudsen effusion method
(e) Langmuir method

The static method has been commonly used in which the pressure of a system is measured in an closed loop system isothermally. A manometer or Bourdon gauge tube is generally used in this static method. In the transpiration method a carrying gas is passed over a sample and the vapor is condensed in the cooler portion of the reactor tube; the solid is then analyzed. In the boiling point method the pressure is kept constant by a manostat and the temperature is increased until the boiling point. When the pressure is one atmosphere, the temperature, \( T = T_b \), and \( \Delta S_v = \frac{\Delta H_v}{T_b} \). In this case Trouton’s rule [22] may be used which yields \( \Delta S^0/R = 10.56 \), giving a modified Clausius-Clapeyron’s equation:

\[
\ln P = 10.56 \frac{(T - T_b)}{T} \quad (12)
\]

This equation allows calculation of vapor pressure using the known boiling points and is useful when the solid or liquid is very volatile.

The Knudsen and Langmuir methods are useful for measuring low vapor pressures at very high temperatures where the vapor is not very volatile. High vacuum is required in these methods. In the Knudsen method which is the subject of this research a cell with a orifice is used; if the orifice diameter is very small then equilibrium is established within the cell. The rate of gases effusing through the orifice is established by vapor pressure, molecular weight and temperature [20]. In the Langmuir method therefore free evaporation of the sample is used. The pressure \( P \) in an ideal case where the vaporization coefficient, \( \alpha = 1 \), is given by the following equation in both cases:

\[
P_{Knudsen} \text{(dynes/cm}^2) = (2\pi R t M)^{1/2} (n/AT) \quad (13)
\]

where \( n \) is the number of moles of gas leaving area, \( A \text{(cm}^2) \), per time, \( t \text{(sec)} \) with a
molecular weight of \( M \). In the case of Knudsen the \( A \) is the area of the orifice but in the case of the Langmuir method the entire area of the sample is considered and the pressure is given below (14):

\[
P_{\text{Langmuir}} \text{ (atm.)} = \frac{m}{44.33 \text{ At}}(T/M)^{1/2}
\]  

(14)

The Knudsen cell method of pressure measurement is discussed in more detail later in this section. The effusing gases from either of these methods may dissociate and the identification of the species is made by mass spectrometer, velocity and momentum detector [20] but these measurements are rather complicated and successful accurate analyses are dependent on the system.

C. Static Method of Measuring Vapor Pressure [20]

Vapor pressure measurement by direct method static is used to measure relatively high vapor pressures. This apparatus consists of a closed vessel maintained at a fixed temperature with a pressure monitoring system which can consist of anything from a simple U-tube manometer containing mercury to a highly complicated gauge. The sensitivity of the U-tube manometer can be enhanced appreciably by using a tilting differential manometer whereby the difference in the levels of the mercury meniscus is adjusted by tilting the apparatus to equalize the levels and then measuring the amount of pointer deflection that the tilt produces. For low pressure applications a system with a known volume of gas at a known pressure is compressed into a smaller volume by using Boyle's law the pressure generated may then be measured.

The compensation method is another variation of the static method. It employs an auxiliary manometer and a source of gas at various known pressures to balance the pressure in the main manometer. This is especially useful because the temperature of the entire system need not be kept constant. The pressure can be adjusted easily and evaporation of liquid from a free surface insures that the liquid in the thermometer bulb is at the actual boiling temperature. There is a possible superheating of the vapor but the problems of reaction with the moisture or air in the system are eliminated.

Spiral and membrane manometers are also used for pressure Measurements. Principle
of mechanical deformation of a thin of spiral membrane in shape or positions used in these methods. A pressure differential is observed when the vapor evaporate form the solid or liquid. The mechanism consists of a glass or quartz spiral membrane or bulb being sealed into the vacuum system with the specimen and the deformation produced by the pressure of the sample’s vapor is translated in terms of motion measured by magnifying the rotation of a pointer or by amplifying the deflection of a galvanometers mirror. These type of manometers and spiral gauges are especially useful when the vaporizing species is chemically reactive toward mercury, and/or where thermal decomposition is more likely to occur than vaporization. Pressures ranging from one millimeter to one atmosphere at relatively high temperatures may be measure. A thin glass bulb which is shaped like a thick spoon and registers the amount of distortion by moving an attached pointer. This glass is replaced by a thin copper membrane if the pressures are in the range of 0.001 atm. sub-ambient temperatures. Errors may result in measurements from gases or impurities being trapped in the sealed containers, and these which are enhanced significantly at low pressures. Thus more sophisticated methods such Knudsen methods may have to used for the vapor pressure measurement in these cases.

Viscosity manometers are used when vapor pressure are less that 10^{-3} atmospheres. This method works by suspending a quartz fiber which is set in oscillating motion. The rate of damping of the oscillatory motion is a function of the gas viscosity. The rate of decrease in the amplitude of oscillation may be considered to be the result of an energy equilibrium between the moving surface and the incident gas molecules. This type of measuring system is useful for pressures of 5x10^{-4} to 2x10^{-2} Torr. Along these same lines a design of a gas viscosity manometer involving two moving surfaces can be used. Such a device involves a pair of disks with a twist being imparted to the upper disk by a continuously rotating lower disk. This twist is a function of the lower disks velocity and hence a measure of the gas pressure.

Knudsen Radiometer gauge is based on the fact that a gas molecule imparts a greater momentum and kinetic energy as it reflects off of a hotter surface than for a colder surface. The Knudsen gauge has two parallel plates maintained at different temperatures and at a
distance less the mean free path between the gas molecules. Molecules rebounding from
the hotter surface transfer momentum at a faster rate than to the colder surface thereby
exerting an unequal force on the two sides of the plate which are repelled or caused to
rotate accordingly.

Heat Conductivity “Hot Wire” Manometers are used in static methods which are similar
to Knudsen gauge and depend on the transfer of energy from a hot body to a gas. The
energy loss being directly related to the pressure which are used for low pressure systems.
At normal pressures thermal conductivity is independent of the pressure. However, at low
pressures where the mean free path of the molecule is greater than the distance between the
hot and cold surfaces, the energy losses from radiation can be minimized by low emissivity
and a low “cold surface” temperature. The energy from the filament which is heated at a
constant rate is transferred to a surface which is held at a constant temperature so that a
drop in temperature in the filament is related to the increase in pressure of the surrounding
gas. The temperature changes may be determined by a thermocouple on the wire, a
resistance thermometer or by observation of the linear expansion of the filament with
temperature.

Ionization Gauges which are widely used for monitoring residual gas pressure in
vacuum systems may sometime be used in the measurement of vapor pressure for very low
pressure applications. But this method is rarely used for vapor pressure measurements
because recalibration for each species is necessary, pressure greater than a few microns
leads to inefficiency of the ion collector, a complex electrical setup is needed, the
sensitivity is dependent on the nature of the vapor species investigated and the filament is
subject to burnout, poisoning, etc.

The isoteniscope is a convenient and widely used method for the measurement of vapor
pressure of a variety of compounds. For a liquid sample, it is first thoroughly degased by
boiling it until air bubbles cease to form on the sample side of the U-tube manometer. A
solid substance can be studied, provided that a suitable inert nonvolatile containing liquid
can be found. This apparatus is connected to an air reservoir with an auxiliary manometer
and is immersed in a thermostat. The liquid is then allowed to boil and air is supplied to
readjust the liquid levels in the U-tube and simultaneously to make the liquid stop boiling
when the external pressure very exceeds the vapor pressure at the bath temperature. The external pressure applied and the corresponding bath temperature are recorded. This method is especially useful when only small quantities of sample liquid are available or when the sample must be kept anhydrous.

Optical absorption method involves the fact that light absorbed by the vapor species can be related to vapor density and related to vapor pressure. The magnetic rotation of plane of polarized light is related to the number of dispersion electrons and to the number of atoms in the vapor, and therefore the vapor pressure at low optical densities may be obtained. The absorption is a linear function of the optical density, whereas at higher densities absorption is proportional to the square root of the density. Extrapolation from one region to the other is based on the Clapeyron equation which gives a functional relationship between temperature, a conveniently measured property, and pressure which is a more difficult to measure. This method is very useful in measuring the vapor pressure of zinc-cadmium alloys, cesium, sodium, potassium, tellurides, selenides, etc.

The vapor density measurements may be made by filling a weighed sample in a glass bulb and evacuating it. A similar second bulb of approximately equal volume is used as a counterpoise. A weighted quantity of sample is introduced into the barometer and allowed to rise through the mercury and vaporize in the space above the mercury so that the level of the mercury is lowered. The amount of lowering is then a measure of the vapor pressure of the substance. Since the temperature of the system is known the molecular weight can be calculated.

The dew point method is a technique for vapor pressure measurements that is especially useful for determining the partial pressure of the more volatile component of a multicomponent system. It involves the measuring of the “dew point” or condensation temperature. For a single component system consisting of vapor, the temperature at which condensation just begins as the temperature is lowered in some part of the system is known as the dew point. However, in alloy or multicomponent system, the dew point or temperature at which the vapor pressure of the pure condensable component is equal to its partial pressure over the multicomponent system is lower than the temperature of the system because the component is present at less than unit activity. In practice, the alloy is
sealed in a long evacuated tub, one end of which is heated to the desired temperature while the temperature of the other end is gradually lowered until droplets of the more volatile component condense on the inner wall. A slight increase in the temperature results in the evaporation of the droplets. By carefully narrowing the temperature interval between condensation on and evaporation from the area of variable temperature, one may fix the dew point, the vapor pressure of the pure more volatile component, and thus its partial pressure over the system. This technique is especially suitable to systems involving binary components which decompose to give elements whose vapor pressures are widely differing in magnitude. An independent measurement of the vapor pressure of pure volatile constituents must be made initially in order to establish the partial pressure over the alloy.

Quasi-static technique is also used in vaporization studies in which the sample is placed in a shallow vessel connected by long narrow tubes which leads to a supply of inert gas to a manometer and the other to a vacuum system. The sample is allowed to vaporize and cause a reflux action in the colder portions of the tubes. The inert gas pressure, initially greater than the expected vapor pressure, is gradually reduced by a constant pumping action until the vapor pressure if the sample is equal to the pressure of the inert gas is indicated by the differential manometer. As soon as the pressure of the inert gas falls below the vapor pressure, the sample vapor acts as a valve to cut off any further flow of gas from the reservoir tube to the pumps. Thereby creating a permanent difference in the level of the differential manometer limbs. The action depends on the fact that as long as the pressure in the manometer tube is greater than the vapor pressure, gas will flow through the system to equalize any pressure difference. When the pressure in the manometer tube becomes less than the vapor pressure, however, the flow of gas is blocked by the upstreaming vapor. Results obtained by this technique on both mercury and lead are in fairly good agreement with data derived from other static and dynamic methods. Although there is a slight danger of interdiffusion over an extended periods of time thus giving somewhat low results. Application of this technique is limited by two fundamental disadvantages. The first is the difficulty and uncertainty in removing all absorbed gases before sealing of the sample and secondly the difficulty of finding suitable refractory
materials for constructing the high-temperature element of the apparatus. At elevated temperatures the manometer tube may become opaque, thus obscuring the liquid level.

The boiling point method is used for determining vapor pressure which consists of a liquid boiling under a fixed pressure and measuring the temperature of the vapor with the boiling liquid, gives the equilibrium. This method is useful over a wide range of pressures and is inherently simple to carry out. It can be considered a reliable and valuable technique for measuring high vapor pressures provided that boiling point is accurately identified. Since a liquid readily boils when its saturation vapor pressure just exceeds the external press on the liquid, precise determination of the boiling point gives rise to reliable and reproducible data. Although small amounts of gaseous impurities do not affect reliability as in the static method, they can create serious difficulties in determining the boiling temperature and in preventing superheating. At moderate temperatures, i.e. for liquids with fairly high vapor pressures the effects of superheating of the liquid are avoided by measuring the temperature with a thermocouple surrounded by the condensing vapor of the boiling liquid. A thermocouple set into the boiling liquid itself would not give a reliable indication of the temperature at which the liquid and vapor are in equilibrium. However, by placing the temperature measuring device in the vapor phase just above the liquid surface one can obtain reliable results. The temperature of the condensing vapor which may be initially superheated on forming but readily cools and condenses as in a slow distillation, is very near to the true boiling point at the given pressure and is not influenced by bumping in the boiling liquid. At high temperature or with less volatile materials such as liquid metals it is difficult to determine the exact boiling point temperature because superheating of the vapor is appreciable, thermal conductivity of the molten metal is sufficiently great that gas bubbles do not form with in the boiling liquid and operations under reduced pressures may cause significant radiation losses from the thermocouple.

Two possible approaches to boiling point determination have been explored. The first is maintaining a constant external pressure and varying the temperature or second keeping the temperature constant and varying the pressure. Experimental research has resulted in many refinements in types and position of the temperature measuring instruments in the criteria used to judge the initiation of boiling, and in the precise control of temperature and
external pressure.

D. The Knudsen Effusion Method

Thermodynamic properties of vapors and condensed phases may be determined very accurately using Knudsen effusion method. The measurement of vapor pressure of carbonyl have been performed by using the Knudsen effusion method. The method is based on the kinetic theory of dilute gases and the molecular flux of the gases may be calculated [20]. In this system the vapor pressure of the condensed phase is is given as follows:

\[ P_{\text{Knudsen}} \text{(dynes/cm}^2\text{)} = \frac{(2\pi k T/m)^{1/2}}{a} \left( \frac{dW}{dt} \right) \]  \hspace{1cm} (15)

where, \( dW/dt \) is the rate of effusion or weight loss, \( a \) is the area of the orifice, \( m \) is the mass of the molecular gas. Knudsen established an expression for effusion of vapor in low pressure regimes for molecules passing through an orifice without collisions with other molecules such that the equilibrium is for the flux density, \( \phi \), relationship with the molecular density, \( \rho \), given by the expression is valid:

\[ \phi = \rho (2\pi kT/m)^{1/2} \]  \hspace{1cm} (16)

At higher pressures the mean free path is smaller than the orifice and the gas behaves like a fluid effusing following the mass effusion equation of:

\[ \frac{dW}{dt} = 2\rho_2 K_2 \left[ \int \left( \frac{dP}{p} \right) \right]^{1/2} \]  \hspace{1cm} (17)

The integral is between the inlet pressure \( p_1 \) and the outlet pressure \( p_2 \) of a tube configuration and \( K_2 \) is the area of venturi at the exit, where the fluid density is \( \rho_2 \). Thus the vaporization pressures may be determined as independent of the mechanism of materials with very low vapor pressures.

The law of evaporation and a law of reflection of molecules at the boundaries of the container are obtained from the equilibrium as described by the equations (15-16). Consider a closed chamber at a constant temperature with the materials evaporating but the gas phase collisions are absent. The gas molecules move in all directions and the probability that a molecule leaves the surface element \( dp_1 \) in a particular direction is defined by the solid angle, \( d\omega_1 \), subtended is \( d\omega_1/4\pi \), the random probability. The flux of
molecules, $\phi_{ij}$, from $dp_i$ in the direction $d\omega_j$ is the same as cosine law given below:

$$\phi_{ij} dp_j = (vC/4\pi)[\cos \theta_{ij} \cos \theta_{ji}] dp_i dp_j l_{ij}^2$$  \hspace{1cm} (18)

where $v$ is the probable frequency of collisions in $[vC \cos \theta_{ji} dp_i]$, where $\theta_{ij}$ is the angle between the normal to $dp_i$ and the line of direction to $d\omega_j$ and $l$ is the length of the line of projection.

Consider a closed Knudsen cell in which is shown in Figure 1. The area $A_0$ is the area of the circular orifice with a radius $r_0$ shown ideally as knife edge. The area where the sample is placed is $A_1$ which defines the evaporating surface and the remaining areas of the top and side walls are designated as $A_2$. The elemental areas $dp_1$, $dp_0$ etc. are also shown in the schematic. The mass and energy balance for total collision density on an elemental area $dp_2$ of the wall of the cylindrical container is given by the equation:

$$\phi_e dp_2 = \int_{A_1} \phi_e g_{12} dp_1 dp_2 + \int_{A_2} \phi_e g_{22} dp_2 dp_2 + \int_{A_0} \phi_e g_{02} dp_0 dp_2$$  \hspace{1cm} (19)

where the flux density, $\phi_e$, throughout the $2\pi$ solid angle at $dp$ is equal to $vC/4$. The symmetrical geometrical factor, $g_{ij}$, is given by the equation:

$$g_{ij} = [\cos \theta_{ij} \cos \theta_{ji}/\pi]_{ij}^2$$  \hspace{1cm} (20)

and therefore the equation:

$$\phi_{ij} dp_j = \phi_e g_{ij} dp_i dp_j$$  \hspace{1cm} (21)

The first term in the equation (19) is the contribution from the evaporating area $A_1$ and the second term form the rest of the walls and the third term is from the closed orifice area. It is assumed that the vapor phase once departing from the sample either emerges from the orifice or recondenses back into the evaporating sample. The total vapor density is constant and is the sum of these two densities of the vapors. But if one considers a cell with a orifice, however small, then the recondensation of molecules from the $A_0$ to $A_1$ may not occur.
The collision rate at $A_o$ for the gas molecules leaving the evaporating area $A_1$ to the orifice $A_o$ is given by the following equation:

$$\phi_e G = \frac{dn}{dt} = \phi_e \left( \int_{A_1} \int_{A_o} g_{10} \, dp_1 \, dp_0 + \int_{A_2} \int_{A_o} [n \, (dp_2)] \, g_{20} \, dp_2 \, dp_0 \right)$$  \hspace{1cm} (22)$$

This equation actually gives the actual rate of effusion and not the equilibrium rate expressed by the equation $\phi_e A_o = \frac{P_e A_o}{(2 \pi k T m)^{1/2}}$ unless $G = A_o$. The normalized emission density is given by the equation:

$$n \, (dp_2) = \int_{A_1} g_{12} \, dp_1 + \int_{A_2} [n \, (dp_2)] \, g_{22} \, dp_2$$  \hspace{1cm} (23)$$

and by definition the source emission density, $\phi_e$, is uniform at every elemental area of the surface, i.e. $n \, (dp_1) = 1$. If the $n \, (dp_2)$ is known from the equation:

$$\phi_e = \phi_e [n \, (dp_2)] + \delta (dp_2) \, \phi_e$$  \hspace{1cm} (24)$$

where $n(dp_2) =$ normalized boundary emission density from the source $A_1$ and sink $A_o$. 

---

**Figure 1.** Knudsen Cell in closed configuration with thin knife edge type ideal orifice. Also shown to the right is the non ideal channelled orifice which is close to the real systems.
and $\delta(dp_2)$ = normalized boundary emission density from the source $A_o$ and sink $A_1$. The rate of effusion is $\phi_e G$ and the fraction of molecules leaving $A_1$ and passing through the orifice, $A_o$, is a the “transmission coefficient” given by the equation (25):

$$\alpha = \frac{G}{A_1}$$

(25)

Now if we consider the real orifices which have a finite thickness such as shown in Figure 1 with thickness of $H_o$. The $n$ (equation 24) gives a different geometric factor $G'/E$ the transmission coefficient is called the **Clausing factor** for this cylindrical orifice is given by the equation:

$$\alpha = \frac{G'}{A_o}$$

(26)

Thus the equation 15 is modified by using the above argument as follows:

$$P_{Knudsen} \, (\text{dynes/cm}^2) = \frac{(2\pi kT/m)^{1/2}}{M}(1/A_o)(dW/dt)$$

(27)

In the Knudsen technique a good approximation of the equilibrium vapor pressure can be found if the orifice area is not too large or if the condensation coefficient, $\alpha_c$, is not too small. The Knudsen cell shown in Figure 2 is nonideal but under isothermal conditions measurements of vapor pressure and equilibrium vapor pressure can be related. Resistance to gaseous flow is accounted for by Clausing factors $W_A$ and $W_B$. The values for the Clausing factor vary from zero to one and are characteristic of the cell and of the orifice hole. Equation (28) is the measured vapor pressure for a nonideal Knudsen cell:

$$P_M = \frac{dW}{BW_Bdt}(2\pi RT/M)^{1/2}$$

(28)

For a finite hole size the upward pressure, $u$, exerted by the upward flux on planes 1 and 2 will be different from the downward pressure, $d$, exerted by the downward flux on planes 1 and 2. Several assumptions are made at this point. The first is that the rate of evaporation is equal to the rate of condensation plus the rate of escape of vapor through the hole. The second is that the upward pressure, $u_2$, above the surface be composed of the evaporated sample from this surface and the rebound molecules coming from above. The third is that the downward pressure just below the lid is caused by reflection of the
downward moving molecules minus the fraction that escapes through the hole. The fourth assumption is that the upward pressure, $u_2$, at the top of the cell is caused by the fraction $W_A$ of the molecules that are heading upward from the bottom of the cell and the fraction $(1-W_A)$ of molecules that are heading downward from the top of the cell, because this fraction is reflected upward again by the walls of the cell. The fifth assumption is that there is no net condensation of vapor molecules on the cell wall. This assumption comes from having an isothermal cell. The sixth assumption is that there are no radical inhomogeneities. The seventh assumption is that there are no pressure discontinuities in the cell. For this assumption to be valid the orifice must be much smaller than the cell diameter. The eighth assumption is that the pressures are uniform across any one of the horizontal planes which like assumption seven cannot be strictly true with the orifice in the cell. The ninth assumption is that the calculation of the Clausing coefficients are which implicitly presupposes a truly random condensation and re-evaporation of the molecules at the walls and may not always occur. The last assumption is that the gas phase collision are not important because only a few percent of the molecules leaving the orifice are involved in such collisions. Given these assumptions equation (28) becomes:

$$P_M[1+BW_B/A(1/\alpha_L-1)] = P_{eq},$$

If $(BW_B/A)(1/\alpha_L - 1)$ is made small compared to unity then $P_M$ can be set equal to $P_{eq}$. This is the primary assumption for the research in this study. We have assumed that if the diameter of the orifice is quite small compared the diameter of the cell then the measured pressure is the equilibrium pressure.
2.2 Crystal Structure Properties of The Carbonyls:

A. X-ray Microstrain and Domain Size Analyses

The crystal structure for each of the metal carbonyls that were used for this study is known. It turns out that both the tungsten hexacarbonyl and the chromium hexacarbonyl have the same crystal structure, and both the dicobalt octacarbonyl and the hexarhodium hexadecacarbonyl have the same structure. The crystal structure of tungsten hexacarbonyl [23] and chromium carbonyl [24] is orthorhombic. While the crystal structure of dicobalt octacarbonyl [25] and hexarhodium hexadecacarbonyl [26] is monoclinic. All of these structures were verified by running samples of each compound through the diffractometer. Table 2 gives the lattice parameters for each crystal structure.

Table 2. Lattice Parameters of Metal Carbonyls [23],[24],[25],[26].

<table>
<thead>
<tr>
<th>Carbonyl</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(β)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>11.505</td>
<td>10.916</td>
<td>6.203</td>
<td>---</td>
</tr>
<tr>
<td>Cr</td>
<td>11.944</td>
<td>11.370</td>
<td>6.459</td>
<td>---</td>
</tr>
<tr>
<td>Co</td>
<td>6.22</td>
<td>15.59</td>
<td>11.31</td>
<td>90°±20°</td>
</tr>
<tr>
<td>Rh</td>
<td>17.00</td>
<td>9.78</td>
<td>17.53</td>
<td>121°±45°</td>
</tr>
</tbody>
</table>
B. Effects of Molecular Bonding

The effects of molecular bonding on vapor pressure can be very profound. Along with molecular weight, molecular bonding is the most important factor. As the sample vaporizes bonds must be broken. Depending on the individual carbonyl it can either sublime or it can completely dissociate into metal and carbon monoxide. When the carbonyl sublimes it can decompose into the form of monomer, dimer, trimer, etc. plus carbon monoxide. Upon heating these mers can be decomposed into metal and carbon monoxide. The microbalance can give the average weight of effusing gas. With this average weight an equation can be developed to calculate the proportion of each mer in the total effusate. Lau, Cubicciotti and Hildenbrand [27] found that potassium sulfate, $\text{K}_2\text{SO}_4$, dissociated into a combination of potassium sulfate, potassium, sulfur dioxide and oxygen. The calculation of the amount of each individual member will be discussed in results section.
Figure 3. Molecular structure of W(CO)$_6$[23].

Figure 4. The crystal unit cell of Cr(CO)$_6$ at 78K. Thermal ellipsoids are for a 50% probability [24].

Figure 5. Dicobalt octacarbonyl, Co$_2$(CO)$_8$ intramolecular bond distances and angles based on the final parameters of least-squares and differential synthesis refinement [25].

Figure 6. Diagram of the projection down [001] for Co$_2$(CO)$_8$: numbers in parentheses indicate cobalt z coordinates [25].

Figure 7. Molecular structure of Rh$_6$(CO)$_{16}$[26].
2.3 X-ray Microstrain and Domain Size Analyses

A. Fourier Analyses of Peak Shapes:

The strain and particle size effect can be measured by the line profile analyses of peak shapes. The analyses of these broadened Bragg peaks will be discussed in this section. It is well established [28,29,30] that the cold worked metals produce dislocation arrays, such as small angle boundaries which subdivide the original grains into small domains or mosaics. Substitutional or interstitial atoms and dislocations contribute to the broadening of the peaks.

In general, the breadth of the diffraction peak depends inversely on the number of unit cells. If a mosaic is N cells thick normal to [001'] diffracting planes, then the h is a continuous variable in reciprocal space and \( h = \frac{2\sin\theta}{\lambda} \) and \( \Delta2\theta = (\Delta h_b \lambda / \cos\theta) \lambda \). The line profile broadening (\( \Delta h_b \)) varies inversely with \( \cos\theta \) in \( 2\theta \) space and is given by the equation \( \Delta2\theta = \frac{\lambda}{N a_3} \cos\theta \); where N is the number of unit cells normal to a diffracting plane of the mosaic. If the distortions are uniform then the d-spacings change and not the shape of the peak. However if the distortions are not uniform the position of the nth unit cell, given by vector \( r_n \), becomes \( (r_n + \Delta r_n) \) near an imperfection where \( \Delta r_n \) allows for distortions in a domain. The power per unit length of the diffracting cone is given by:

\[
P_{eu} = K(\theta) \sum_{h_1, h_2, h_3} \frac{(N_{h_1}N_{h_2}N_{h_3})}{N} \left\{ \cos 2\pi l' z_n > x \cos 2\pi n / 3 \cdot (N_{h_1}N_{h_2}) \sin 2\pi n' > x \sin 2\pi n' / 3 \right\}
\]

A_n = (N_n/N_{h_3})<\cos 2\pi l' z_n> and B_n = (N_n/N_{h_3})<\sin 2\pi l' z_n>

The Fourier coefficients of broadened peak are due to distortions. A new unit cell is defined such that the diffraction peak hkl is [001'] from the new cell. \( N' \) are the average number of columns in a plane perpendicular to [001'] in a mosaic region. \( N_n \) are the average number of cells having neighboring cell n cells away along [001']. \( N'_{h_3}, a_3 \) is the \( D_{eff} \) i.e. effective mosaic or domain size along [001']. The \( z_n = n \varepsilon_n \), where \( \varepsilon_n \) is the strain along \( a_3' \) over n cells, oriented to diffract, related to the average distance normal to the diffracting planes [001'] shown above.

The instrumental broadening due to slits etc. can be corrected by the Stokes method [29]. In this method the annealed (\( G_r \)) and broadened (\( H_r \)) functions are given by the
following equations:

\[ G_r(n) = \sum_{j=-Y/2}^{Y/2} g(j)(\cos 2\pi nj/Y)Dx \]  
\[ H_r(m) = \sum_{k=-X/2}^{X/2} h(j)(\cos 2\pi nk/X)Dx \]

where the annealed peak has been divided into Y intervals and the broadened peak into X intervals. Similar expressions can be written for sine coefficients \( G_j(n) \) and \( H_j(m) \). The relationship between the harmonic numbers \( n \) and \( m \) of the above equations (31) and (32) is necessary to perform Stokes correction. Warren [31] has shown the true normal (column) length of the diffracting planes as:

\[ L_{\text{annealed}} = nb_3 \quad \text{or} \quad L_{\text{broadened}} = ma'\]

where the \( a'_3 \) is a fictitious cell parameter. The coefficients of the annealed and the broadened peaks must be compared with equal values of \( L \) that is say \( L_{\text{annealed}} = L_{\text{broadened}} = L \) and the sine \( \{F_r(L)\} \) and cosine \( \{F_l(L)\} \) coefficients are given by the following equations:

\[ F_l(L) = \frac{Gr(L) H_l(L) - G_l(L) H_r(L)}{Gr^2(L) + Gl^2(L)} \]  
\[ F_r(L) = \frac{Gr(L) H_r(L) + G_l(L) H_l(L)}{Gr^2(L) + Gl^2(L)} \]

The Fourier cosine coefficients of harmonic number \( n \) is \( A_n = A^S_n A^D_n \), where \( A^S_n \) are the particle size coefficients and \( A^D_n \) are the distortion coefficients. These are the first and second terms, respectively, in the following working equation (35) for line profile analyses [29,30]:

\[ \text{Line profile analysis} \]
In An = ln(Nn/N_h^3) - (2\pi^2L^2/d^2_{hkl})\langle\varepsilon_n^2\rangle (36)

where \langle\varepsilon_n^2\rangle is the root mean square strain and the related \langle z_n^2 \rangle the reduced displacement disorder. A plot of \ln A_n vs. \hbar^2+k^2+l^2 for a constant L=na_3 is expected to give a straight line for a set of parallel planes. The intercept, b, is \{\ln (N_n/N'_h^3)\} which is related to the mosaic sizes and a plot of n(N_n/N'_h^3) vs. L, where l=0 intercept is unity, gives the average \text{D}_{\text{eff}}. There are Hook effects associated with this line profile analyses due to background selection problems, which can also be corrected. The slope, m, gives the microstrain at a constant column length, L. These slopes can be obtained for various L values in the same plot. Appropriate equations can be developed for various structures to take into account all reflections. The intercepts from these plots for each value of L value can be plotted i.e. ln (N_n/N'_h^3) vs. L to obtain particle sizes (Warren-Averbach method). In general two reflections are are used for the final analyses. A single line may be used and the cosine coefficient:

\[ A_n = 1 - n \{ a_3/D_{\text{eff}} + 2\pi^2 a_3' G^2/d^2_{hkl} \} + n^2 \{ 2\pi^2 a_3'' G^2/d^2_{hkl} D_{\text{eff}} \} \]  (37)

where \langle\varepsilon_n^2\rangle = G^2/na_3'.

In many cases there are faults observed in metals which have imperfections. These faults may selectively broaden certain X-ray diffraction peaks. The stacking sequence in FCC crystals is three atomic layers stacking ABCABC... for planes parallel to \{111\}[101]. A stacking fault is created by insertion of two atomic planes and the order becomes ABCBCABC indicating a small increase in d-spacing will be required to accommodate these extra layers. However the faulting actually occurs by a dissociation of dislocations. The following is the proposed reaction for (112) plane with Burgers vector in the [111] direction [32]:

\[ \frac{1}{2}a[111] \rightarrow \frac{1}{3}a[112] + \frac{1}{6}a[111] \]  (38)

B. Torsion-Effusion Vapor Pressure Measurements

The definition of torsion is the shear stress from an applied torque. Effusion is simply mass passing through an orifice. For the torsion-effusion method a sample is placed inside
a Knudsen cell. This cell has a small aperture in its wall. When a vacuum is maintained around this cell the sample will sublime. The vapor or vapors of this sublimation will then become effusate. As this effusate escapes from the cell a net force is applied to the cell. The cell is suspended from a microbalance by a ribbon which is made of a platinum-nickel alloy and this net force causes the cell to rotate. The cell is configured such that the orifice will direct the effusion flow perpendicular to the ribbon. This configuration is shown in Figure 9. As the effusate leaves the cell the net force generated causes the cell to rotate from Newton’s third law. When the cell moves the rotation causes the ribbon to store both energy and momentum. This process continues until the stiffness of the ribbon and the force of the vapor jet balance. At this point the cell starts to rotate back the other way until the vapor jet causes the whole process to start all over again.

III Experimental

3.1 Carbonyls Investigated

In this research project four metal carbonyls were investigated; tungsten carbonyl W(CO)\(_6\), chromium carbonyl Cr(CO)\(_6\), dicobalt octacarbonyl Co\(_2\)(CO)\(_8\), and hexarhodium hexadecacarbonyl Rh\(_6\)(CO)\(_{16}\). Several batches of these carbonyls were obtained for commercially from the following companies:

1. Cr(CO)\(_6\) 99% purity, Aldrich Chemical, New York.
2. W(CO)\(_6\) 99% purity, Johnson-Matthey, New York.
3. Co\(_2\)(CO)\(_8\) 93% purity, Johnson-Matthey, New York.
4. Rh\(_6\)(CO)\(_{16}\) NA purity, Strem Chemical Co, New York.

The tungsten carbonyl, chromium carbonyl and hexarhodium hexadecacarbonyl were in powder form, and these compounds appeared relatively stable at room temperature and under ambient pressure. The first two above mentioned carbonyls are stable at relatively high temperatures and have to be heated far above room temperature for decomposition. Tungsten and chromium are white in color while rhodium is a dark color. The hexarhodium hexadecacarbonyl appeared to be stable under ambient conditions. The dicobalt octacarbonyl appeared orange in color and appeared to be of plastic crystal form and was a highly volatile carbonyl which decomposed at room temperature under vacuum.
The handling of dicobalt octacarbonyl was very difficult because it easily oxidized in air. These materials were ground and purified in the glove box.

All the preliminary experiments relating to the rough estimation of vapor pressures to determine the suitability of the method, crystal structure X-ray diffraction experiments pertained to the phase identification were performed at UNR. The microstrain measurements were performed at the Reno Research Center, USBM. The torsion effusion experiments were performed by the author at the SRI International, Menlo Park, California and the thermodynamic analyses were performed at UNR.

Before the vapor pressure experiments were performed, tests were made in a Pyrex apparatus at UNR to determine the general physical characteristics of the carbonyls. A schematic of this apparatus is shown in Figure 8. This system consists of a sample holder, which is a vacuum crystallization chamber for growing single crystals. Transducers of 0-2 Torr range with necessary Datametric electronic metering devices were used to measure pressure. A large volume reservoir was attached to a Veeco vacuum system with a small diffusion pump, backed by a mechanical pump.

![Figure 8. Recrystallizer apparatus for preliminary work. The valves used to keep the sample for being contaminated by vacuum pump oil.](image)

Since the vapor pressures of metal carbonyls have not been explored in the lower temperature range circa zero degrees centigrade. We have chosen this temperature region for our study. Because there is very little information about these compounds in this temperature region it is for this reason that we built a small recrystalizer in order to perform some preliminary studies. Data cannot be acquired from this apparatus but one can get a feel for the behavior of the compound. For example how long it takes to sublime a given amount of a compound at a certain temperature. If the sublimation occurs too quickly then the vapor pressure is very likely too high for the torsion effusion method. Also this
preliminary work can tell us if the compound decomposes and how readily it does so at any given temperature.

The mechanism that is shown in Figure 9 is seen suspended from the arm of the microbalance and extending down into the quartz tube. The system is evacuated and the quartz tube is lowered into a temperature controlled region. This region can either be a tube furnace or some kind of chilled bath. A thermocouple is positioned as close to the sample as is possible.

As is shown in Figure 10 one sights through a spotting scope and marks the extreme points on a meter stick. From the two end points one can determine the angle $\theta$. The angle is later used in equation (39) to calculate the total pressure.

Figure 11 shows the overall apparatus. The mechanism that was shown in Figure 9 can be seen suspended from the arm of the microbalance and extending down into the quartz tube. The system is evacuated and the quartz tube is lowered into a temperature controlled
region. This region can either be a tube furnace or some kind of chilled bath or a tube furnace. A thermocouple is positioned as close to the sample as is possible.

Figure 10. Schematic of the spotting scope arrangement for the deflection measurement

The total pressure is given by equation (39):

$$P_T = \frac{2K\theta}{\sum (af_d_i)}$$  \hspace{1cm} (39)

where $K$ is torsion constant for ribbon, $\theta$ is the measured angular deflection, $a$ is the area of the orifice, $f$ is the force factor, $d$ is the moment arm of the effusion orifice, and $i$ is the number of chambers which for these measurements was always two.

The molecular weight ($M$) of the effusing gas can be calculated from the weight loss of the cell and the angular displacement by using this equation:

$$M = \frac{2\pi RT W^2}{[2P_T \Sigma (Ca)i]^2}$$  \hspace{1cm} (40)

total pressure from equation (39), $T$ is the absolute temperature, $R$ is the gas constant, $W$ is total rate of weight loss, $a$ is the area of the orifice and $C$ is the Clausing factor. The Clausing factor is the probability that once a molecule has entered the orifice it will in fact exit the cell. The calculation of the molecular weight comes from simultaneous torsion and Knudsen effusion. Details of this method are described in references [20] and [21].
The instrument was calibrated with potassium chloride but a final calibration using naphthalene, C₁₀H₈, was performed which showed close agreement with the literature value [33]. This is shown in Figure 12.

The assumption that was made for each of the experiments in this study is that inside the cell the solid and the vapor are in equilibrium. We believe this assumption to be valid because the orifice size is quite small, 0.6 mm, in comparison to the diameter of the orifice and the amount of vapor escaping the cell is therefore extremely small. It is important to note at this point that at a pressure of only three Torr inside of the apparatus all effusion stops, the torsion oscillation ceases completely and data can no longer be acquired. Also when the background pressure is raised to three Torr all weight loss stops. This the basis for the assumption that the inside of the cell maintains a solid-vapor equilibrium.

The microbalance from which this cell has been suspended is extremely sensitive. It can detect a change of one tenth of a microgram. As the effusate exits the cell the balance
detects this weight loss. This weight loss is combined with the angular displacement to give the molecular weight of the effusate.

When these data are plotted as logarithm of pressure versus reciprocal temperature a straight line is obtained and its equation can be determined. At this point many thermodynamic quantities can be determined, the Gibbs energy the enthalpy, and the entropy. Species using mass spectrometry, although attempted, was not successful possibly due to room temperature decomposition of cobalt carbonyl under vacuum. However, we have calculated the partial pressures of these gas species, which show a good corroboration with the data.

![Graph](image)

**Figure 12. Calibration data for the microbalance [33].**

In the temperature range that the measurements were made, tungsten carbonyl did not show formation of any dimers in vapor phase, because the measured molecular weight matched that of the solid. The molecular weight of chromium carbonyl showed some deviation but it was within the experimental error, suggesting some disproportionation even at low temperatures. Hexarhodium hexadecacarbonyl, showed virtually complete
decomposition to metallic rhodium and carbon monoxide.

3.2 Environmentally Safe Handling of The Carbonyls and Sample Preparation:

The metal carbonyls are well known as hazardous materials. The vapors of carbonyls decompose easily when heated; generally to metal and carbon monoxide at very low temperatures. The toxicity of the decomposed products carbon monoxide and metals are also well known; both chromium and cobalt are proven carcinogens and must be handled in a MSDS prescribed manner. The threshold limit value (TLV) for chromium (IV) is 0.05 ppm [34] and for cobalt is 0.01 ppm [35]. Tungsten and rhodium while being less also need to be handled carefully and the TLV's are 0.1 ppm [36] and 0.01 ppm [35], respectively. The human contact or breathing of the fumes may result in deposition of metal in lungs beside or known physiological effects. Thus all the carbonyls were considered hazardous and handled in an argon atmosphere dedicated glove box. Argon gas was chosen because its inert properties would keep it from reacting with the carbonyls. Fresh argon gas was introduced into the glove box in order to flush the carbonyl vapors. The exiting gases were bubbled through a sodium hypochlorite solution and then passed over a bed of ceramic beryl saddles in a tubular furnace maintained at 550° C to decompose the carbonyls to metal. After which these exiting gases were subjected to a flame to oxidize any remaining residual carbonyl and keep it from escaping to the atmosphere. Enclosed with each carbonyl from the vendor, was an MSDS literature which provided pertinent safety information for handling. It was assumed that these were adequate precautions for environmental safety.

The carbonyl powders were ground in a mortar and pestal in the glove box and transferred to the respective apparatus for experiments. Wax seals were used in many cases. For the final torsion effusion runs napthalene was used for sealing the Knudsen cells.

3.3 Vapor Pressure Measurements By Torsion Effusion Gravimetric Method

A. Principles and Calculations

The primary objective of this research was to determinate the vapor pressures of
tungsten hexacarbonyl, chromium hexacarbonyl, dicobalt octacarbonyl and hexarhodium hexadecacarbonyl. Total pressure of vaporization was measured to obtain the equilibrium constant which allowed calculation of the Gibbs energy. Using the second law, the Gibbs energies, enthalpies and entropies for different systems were calculated.

Let us consider a metal carbonyl vaporizing for which the equilibrium reaction is given by the following:

\[ \text{M(CO)}_6(s) = \text{M(CO)}_6(g) \]  

(41)

The basic principles of the Knudsen effusion method have already been described in section 2. The specifics of the calculations required in the torsion-effusion/gravimetric effusion methods used to determine vapor pressure and molecular weights are described in this section. Knittel et al. used this method to study thermal decomposition of magnesium sulfate [37]. This method is used to measure pressures below the molecular flow region (10^-4 atm. and less). The weight loss (dW/dt) of the vapor effusing in unit time through an area \(A\). The Knudsen effusion pressure \(P_x\) is related to (dW/dt) by the following equation (42):

\[ P_x = \left( \frac{2\pi k T/m}{\sum_{i=1}^{n} A_i C_i} \right)^{1/2} \left( \frac{dW/dt}{\sum_{i=1}^{n} A_i C_i} \right) \]  

(42)

where, \(m\) is the molecular weight of the effusing species, \(k\) is Plank’s constant, \(T\) is the temperature, and \(C_i\) is the orifice Clausing factor. The sum is carried over all the \(n\) orifices with the assumption that it is proportional to \(A_i\) times the probability term \(C_i\). The molecular weight of the vaporizing species, if more than one species is evaporating is calculated by the following equation (43):

\[ M = \left[ \sum_{i=1}^{n} m_i M_i^{1/2} \right]^{-2} \]  

(43)

where, \(m_i\) is the mass fraction of species \(i\) and \(M_i\) is its molecular weight. The summation is over all the vapor species effusing from the sample. An obvious limitation to vapor pressure determination by this method is the required knowledge of the vapor molecular weight. If the system has torque measuring capability the knowledge of the molecular
weight of the evaporating species is not required. We made the measurement using torsion-effusion system in which a torque resulting from effusion of vapor through orifice area $A_i$ and at distances $d_i$ from the suspension axis of the cell is determined from the angle $\theta$ through which the torque twisted the torsion suspension ribbon. The torsion pressure, $P_T$ of the effusing species is related to angle $\theta$ by the following equations (44):

$$P_T = \frac{2k\theta}{\sum_{i=1}^{n} A_i d_i f_i}$$

(44)

where $k$ is the fiber torsion constant, $f_i$ is the ratio of the force from the effusing vapor from the orifice $i$ of infinite length. Equation (42) used to determine the torsion pressure is the same as the Knudsen pressure that was defined in equation (15). The weighted average molecular weight is obtained by determine the total pressure from equation (42) and the rate of weight loss given by equation (45):

$$\frac{dw}{dt} = \sum_{i=1}^{n} \frac{dw}{dt} P_i$$

(45)

and the rate of weight loss is given by (46):

$$M = (2\pi RT)^2 \left[ \frac{\sum_{i=1}^{n} A_i d_i f_i}{2k\theta \sum_{i=1}^{n} A_i C_i} \right]$$

(46)

The measured vapor pressure $P$ is a steady-state pressure and will be equal to the equilibrium pressure $P_{eq}$. In order to interpret $P$ in terms of $P_{eq}$, the vaporization coefficients and resistance of gas flow through the effusion cell and out the orifice must be evaluated. The Whitman [38] and Motzfeldt [39] approach is used for this purpose and the equilibrium pressure is given by the equation (47):

$$P_{eq} = P (1+\beta) \sum_{i=1}^{n} A_i C_i$$

(47)

where, $\beta$ is a constant for a certain type of cell. The total pressure from the above equation
is used to obtain equilibrium pressures from effusion data and existing pressure dependence on orifice size. This is necessary when the disproportionation reaction occurs. In such cases, we used a zero orifice extrapolation to obtain the effusion pressure by plotting $1/P$ against the $\Sigma C_i A_i$, where the intercept is $1/P_{eq}$ and the slope is $\beta/P_{eq}$. In cases where there is no orifice dependence, such as, thermal decomposition of KCl which has virtually no kinetic barrier but other system that will be discussed in the results sections shows dependence [21].

B. The Torsion Effusion-Gravimetric Apparatus

A schematic of the apparatus used in this study was shown in Figure 11. This instrument is a combination of two types of apparatuses: the first is the torsion effusion component which measures the vapor pressure from angular displacement. The second is the gravimetric component which measures the average molecular weight of the effusing gas. A high vacuum system to the order of $10^{-6}$ to $10^{-9}$ Torr was used with oil diffusion pumps backed by a mechanical forepump with all the necessary valving and cold traps for safe and efficient operation of the high vacuum system.

The torsion component consists of a the sample chamber, which is a double barrel platinum Knudsen cells with orifices in the opposite directions in order to develop a moment when the effusing vapors are generated. The sample chamber was suspended by a tungsten rod to a mirror assembly as shown in Figure 9. The mirror assembly also has a damping disk. Generally a permanent magnet was used to damp the oscillation before starting the experiments. The damping mechanism was suspended by Pt-Ni torsion ribbon to the pan of the balance. The modulus and torsion coefficient of the ribbon were furnished by the manufacturer. A meter stick is positioned horizontally in front of the apparatus such that the scale is reflected on the mirror as shown in Figure 10. A spotting scope was positioned beneath the meter stick. The gravimetric measurements were made by a Cahn D-100 microbalance. The torsion ribbon was suspended from the pan of the balance. This system is extremely sensitive to changes in weight and is capable of detecting one tenth of a microgram change. A standard strip chart recorder was used to
record the weight loss.

C. Experimental Procedure

The carbonyl samples were carefully weighed in a glove box with argon atmosphere. Equal amount of carbonyl sample was placed in the either side of the Knudsen cell. The orifices were previously sealed by using naphthalene, which has a very high vapor pressure. This sealed assembly was later transferred to the torsion effusion apparatus and suspended on the torsion wire/damping assembly. A quartz tube was then placed in position so that an o-ring would seal and a vacuum could then be made. This apparatus is shown in Figure 11. The quartz tube was immersed in an ethylene glycol bath chilled by a standard refrigeration system. In certain experiment such as that of hexarhodium hexadecacarbonyl the sample was heated above room temperature and therefore a tubular furnace was used for this purpose.

The system was later evacuated to 10^-7 Torr and the temperature was set via a controller. When the system temperature reached equilibrium the vapors from the solid escape the Knudsen cell. This escaping flux causes the cell to rotate which in turn rotates the mirror. As the vapor leaves the cell it causes the assembly to oscillate to a minimum and a maximum angular displacement. The minima and maxima are observed as one sights through the spotting scope and observes the positions on the meter stick. At thermal equilibrium these minima and maxima stabilize and the data for angular displacement was taken. When thermal equilibrium is attained the minimum and maximum may change slightly but their arithmetic average does not. Because this entire process is carried out under vacuum there is virtually no damping and the cell will oscillate until the sample is exhausted and probable thereafter, never attaining a steady reading on the meter stick. Concurrently, as the effusate exits the cell the balance detects this weight loss. The weight loss is recorded on a chart recorder. At thermal equilibrium the line on the chart will have not curve to it. It will be perfectly straight. This combined weight loss with the angular displacement to gives the molecular weight of the effusate.

The apparatus was first calibrated with potassium chloride with naphthalene being used for the final calibration because these data are available and were used as a primary standard [33]. The equilibrium vapor pressure was determined using the smallest orifice.
In cases where there was no decomposition to metal and the reactions were congruent, the smallest orifice (0.06 cm) yielded results very close to the equilibrium pressure. A typical plot for naphthalene calibration of the system was shown Figure 12.

D. Calculations of Vapor Pressure and Molecular Weights:

The deflection is measured by using the arrangement shown in Figure 10. By sighting through a spotting scope one can measure the minimum and maximum points attained on the meter stick. This then yields the deflection, $2\theta$. Therefore, this measured angle is divided by two when used in equation (39) to calculate the total pressure:

$$P_T = \frac{(2K\theta)\Sigma(afd)}{I}$$  \hspace{1cm} (39)

The total pressure is obtained by the equation (44) and the molecular weight by equation (47). The molecular weight of the effusing gas can be calculated from the weight loss of the cell and the angular displacement by using this equation:

$$M = \frac{2\pi RTW^2}{[2PT\Sigma(Ca)i]_2}$$  \hspace{1cm} (40)

$P$ is the total pressure from equation (44), $T$ is the absolute temperature, $R$ is the gas constant, $W$ is total rate of weight loss, $a$ is the area of the orifice and $C$ is the Clausing factor. The Clausing factor is the probability that once a molecule has entered the orifice it will in fact exit the cell. Details of this method are described in references [20] and [21].

The assumption that was made for each of the experiments in this study is that inside the cell the solid and the vapor are in equilibrium. We believe this assumption to be valid because the orifice size is quite small, 0.6 mm, and the amount of vapor escaping the cell is therefore extremely small. If solid-gas equilibrium is not established then the system torque is not obtained. The rate of weight loss, obtained from the Cahn balance chart recorder slope ($\Delta W/\Delta t$) is a linear function and is constant. This $\Delta W/\Delta t$ is used to calculate the molecular weight of the effusing gas. When these data are plotted as logarithm of pressure versus reciprocal temperature a straight line is obtained and its equation can be determined. The thermodynamic quantities, the Gibbs energy the enthalpy, and the entropy for each
species can be determined.

The total pressure determined in this study was assumed to fit Antoine's equation:

$$\log P = A + B/T + C/T^2 + \ldots \ldots .$$  \hspace{1cm} (48)

where the constants A and B were found by using a Claussuis-Calpyeron/van't Hoff plot which is log P versus 1/T with the higher order terms not considered. For the temperature range in which this study was conducted all of our data was linear and therefore the higher order terms in Antoine's equation were neglected.

The equilibrium constant $K_p$ for a given chemical reaction is defined as the product of the concentrations of the products that were produced in the reaction divided by the product of the the concentrations of the reactants that were consumed in the reaction. For gases the activities are used but if ideal behavior is assumed then the partial pressures can be substituted for the activities. Since this work deals with sublimation the $K_p$ was taken as the vapor pressure of the compound because the partial pressure of a solid is the same as its activity and therefore was taken to be one. Equation (49) shows the calculation of $K_p$:

$$K_p = \frac{P_{vapor}}{a_{solid}}$$  \hspace{1cm} (49)

Since we were dealing with sublimation the partial pressure of the solid cannot be known and therefore the activity was used instead. The value of the activity for the solid was then taken to be one. $K_p$ therefore becomes the pressure of the vapor that was measured. Having the equilibrium constant allows the calculation of the Gibbs energy. This calculation was made by using equation (50).

$$\Delta G^\circ = -RT\ln K_p$$  \hspace{1cm} (50)

Equation (51) is the second law of thermodynamics. Once the Gibbs energy has been computed we then used this equation to find both the enthalpy and the entropy at a given temperature in the range that was studied.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$  \hspace{1cm} (51)

3.4 Microstrain and Particle Size Determinations of Rhodium Carbonyl

The broadened Bragg peaks of the vanadium monohydride phase which had overlaps
with the annealed vanadium peaks were analyzed in this study. If we consider a two peaks, one of them is broadened peak and the other gives intrinsic instrumental broadening, the period $a_3$ in the Figure 13 below is the same for both of these peaks.

The number of intervals $a$, about the center of gravity of the instrumental broadened peak ($a_{ins}$) and the peak broadened by the sample strain effects ($a_{br}$) are different, as shown below. The value $a_{ins}$ is usually $1/2(a_{br})$ and the Fourier cosine coefficients are given by:

$$A_n = \frac{1}{a} \sum_{x=-a/2}^{a/2} f(x) \cos(2\pi nx/a) Dx$$

where $f(x)$ is the value of intensity at $x$, where $x$ is the interval number between $-a/2...0...+a/2$, $Dx=1$, and $n=\text{harmonic number}(0, .25, .5, ..., 30)$. For each $n$, say $n=0, 1, 2$ sum over all values of $x$ and obtain $A_0$. In the computer program this $A_0$ is set equal to 1 for normalization purposes. Similarly the values for $A_1, A_2$ etc. were obtained. Normalized values of $A_1/A_0$ for $n=1, A_2/A_0$ for $n=2$, etc. were obtained. The Fourier sine coefficients are given by:

$$B_n = \frac{1}{a} \sum_{x=-a/2}^{a/2} f(x) \sin(2\pi nx/a) Dx$$

These are generally equal to zero if the peak is symmetric but have values if there is asymmetry. Both the sin and cos coefficients are obtained from the computer program. The column length, $L=na_3$, where $a_3=[\lambda/4(\sin \theta_2-\sin \theta_0)]$. If a fictitious plane [001] is chosen then in one dimensional reciprocal space the $b_3=1/a_3$. The Fourier series reproduces the peak along the sin $\theta$ axis with a period $a_3$. The instrumental broadening has been obtained by Stokes [24].
IV Results and Observations

4.1 Vaporization of Tungsten Hexacarbonyl

The vapor pressures of tungsten hexacarbonyl were measured in the temperature range of 265K to 288K using a torsion effusion apparatus. The total pressure measurements of tungsten hexacarbonyl obtained at various temperatures are listed in Table 3 along with the calculated average molecular weight of the effusing gaseous species. The total pressures of the effusing gases of the above mentioned species was obtained by this equation (39).

The measured average molecular weight for tungsten hexacarbonyl vapor which was calculated using equation (40) is 351 g/mol. This value correlates closely with the theoretical value of 351.9 g/mol, with a negligible error of 0.0026%. From this we concluded that there is no disproportionation of tungsten hexacarbonyl in this temperature range. Therefore, because there is no disproportionation of tungsten hexacarbonyl gas in the temperature range of these experiments the vaporization reaction may be written as equation (54).

$$W(CO)_6(s) = W(CO)_6(g)$$  \hspace{1cm} (54)

Figure 14 shows a plot the data in Table 3. The assumption that was made for all of these
experiments is that inside the cell the solid and the vapor are in equilibrium. We believe this assumption to be valid because the orifice size is quite small, 0.6mm, and the amount of vapor escaping the cell is therefore extremely small.

Table 3. Total pressures ($P_T$) of the effusing vapors of tungsten hexacarbonyl, W(CO)$_6$(g) measured by torsion effusion method, using 0.06 cm. orifice diameter in a platinum cell, at various temperatures. The average measured molecular weight is 351 g/mol.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$P_T$ (Pa)</th>
<th>log $P_T$ (Pa)</th>
<th>M (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>287.8</td>
<td>0.957</td>
<td>-0.01931</td>
<td>360</td>
</tr>
<tr>
<td>280.7</td>
<td>0.445</td>
<td>-0.3518</td>
<td>347</td>
</tr>
<tr>
<td>266.1</td>
<td>0.0669</td>
<td>-1.175</td>
<td>343</td>
</tr>
<tr>
<td>272.6</td>
<td>0.149</td>
<td>-0.8270</td>
<td>342</td>
</tr>
<tr>
<td>286.2</td>
<td>0.789</td>
<td>-0.1027</td>
<td>352</td>
</tr>
<tr>
<td>277.2</td>
<td>0.288</td>
<td>-0.5410</td>
<td>364</td>
</tr>
<tr>
<td>278.7</td>
<td>0.326</td>
<td>-0.4864</td>
<td>357</td>
</tr>
<tr>
<td>265.4</td>
<td>0.0618</td>
<td>-1.209</td>
<td>367</td>
</tr>
<tr>
<td>267.9</td>
<td>0.861</td>
<td>-1.065</td>
<td>351</td>
</tr>
<tr>
<td>269.9</td>
<td>0.116</td>
<td>-0.9374</td>
<td>335</td>
</tr>
<tr>
<td>283.2</td>
<td>0.566</td>
<td>-0.2469</td>
<td>343</td>
</tr>
<tr>
<td>288.0</td>
<td>0.976</td>
<td>-0.01021</td>
<td>354</td>
</tr>
</tbody>
</table>

Equation (55) is the Antoine equation for the vapor pressure of tungsten hexacarbonyl in the temperature range of 265K to 288K:

$$\log P_T\ (Pa) = (14.106 \pm 0.11) - (4064.4 \pm 31)/T$$ (55)

and the estimated enthalpies of vaporization in the same temperature range:

$$\Delta H^{°}_{277K} = 77.714 \pm 0.59 \text{ kJ/mol}$$ (56)

The standard Gibbs energy change obtained using the equilibrium constant, $K_p$, which was calculated by using equation (49). Equation (57) is equations (50) and (51) combined together:

$$\Delta G^{°}_{W(CO)_6}= -RT \ln K_p = 77,714 - 173.93T \text{ J/mol}$$ (57)

In comparing our data with literature, we note that Hieber and Romberg [40] reported the vapor pressures at higher temperature range of 310K to 375K:
Lander and Germer [4] reported the vapor pressure of tungsten hexacarbonyl in the temperature range of 310K to 375K:

$$\log P_T (\text{kPa})_{[\text{W(CO)}_6]} = 10.65 - 3872 / T$$  \hspace{1cm} (58a)

Baev [18] also reported in the temperature range of 416K to 432K:

$$\log P_T (\text{kPa})_{[\text{W(CO)}_6]} = 10.66 - 3886 / T$$  \hspace{1cm} (58c)

4.2 Vaporization of Chromium Hexacarbonyl:

The vapor pressures of chromium hexacarbonyl, Cr(CO)$_6$, were obtained in exactly the same manner as that of tungsten hexacarbonyl, W(CO)$_6$, and are tabulated in Table 4. The experimental average molecular weight, from Table 4, was calculated as 229 g/mol as compared to the theoretical value of 220.1 g/mol which shows an error of 3.93%. This
suggests that there may be some disproportionation of chromium hexacarbonyl to dichromium dodecacarbonyl may have occurred, but its partial pressure is very low. Moreover allowing for experimental error, it may be concluded that there is virtually no disproportionation or decomposition of chromium hexacarbonyl in the temperature range that we studied. We will therefore use the same representation for solid-vapor equilibrium which is:

\[
\text{Cr(CO)}_6(s) = \text{Cr(CO)}_6(g)
\]  

Visual experimental observation in the quartz tube did not reveal any deposition of either shiny metallic coating or other condensed matter in the quartz tube or the copper baffles in the system.

Using the second law we obtain the equation for vapor pressure and enthalpy change as the follows:

\[
\log P_T (\text{Pa}) = (12.755 \pm 0.25) - (3468.3 \pm 68)/T
\]  

and the estimated enthalpies in the temperature range of 266K to 272K:

\[
\Delta H_{269K} = (64.921 \pm 1.30) \text{kJ/mol}
\]  

Figure 15 is a plot of the data from Table 4.

The standard Gibbs energy change obtained using the equilibrium constant, \( K_p \), which was calculated by using equation (49). Equation (62) is equations (50) and (51) combined together:

\[
\Delta G^o_{\text{[Cr(CO)}_6]} = -RT \ln K_p = 64,921 - 144.08 T \text{ J/mol}
\]  

Windsor and Blanchard [17] reported data for chromium hexacarbonyl in the temperature range of 264K to 279K:

\[
\log P_T (\text{kPa})_{\text{[Cr(CO)}_6]} = 9.756 - 3285 / T
\]  

Hieber and Romberg [40] also reported vapor pressures of chromium hexacarbonyl in the temperature range of 310K to 375K, and their vapor pressures were close to our measured values in this study:

\[
\log P_T (\text{kPa})_{\text{[Cr(CO)}_6]} = 10.95 - 3775.2 / T
\]
Baev [18] also reported vapor pressures of chromium hexacarbonyl in the temperature range of 374K to 415K and they have suggested disproportionation of monomer to dimer in vapor phase and the vapor pressure equation is the following:

$$\log P_T \text{(kPa)}_{\text{Cr(CO)}_6} = 10.47 - \frac{3575.9}{T} \quad (63c)$$

Table 4. The total pressures ($P_T$) of the effusing vapors of Cr(CO)$_6$(c) measured by torsion effusion method, using 0.06 cm. orifice diameter in a platinum cells, at various temperatures. The average measured molecular weight is 229 g/mol.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$P_T$ (Pa)</th>
<th>log $P_T$ (Pa)</th>
<th>$M$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>266.4</td>
<td>0.541</td>
<td>-0.2667</td>
<td>-</td>
</tr>
<tr>
<td>266.0</td>
<td>0.519</td>
<td>-0.2850</td>
<td>238</td>
</tr>
<tr>
<td>271.4</td>
<td>0.944</td>
<td>-0.02487</td>
<td>231</td>
</tr>
<tr>
<td>269.0</td>
<td>0.736</td>
<td>-0.1333</td>
<td>228</td>
</tr>
<tr>
<td>269.0</td>
<td>0.731</td>
<td>-0.1363</td>
<td>232</td>
</tr>
<tr>
<td>271.9</td>
<td>1.01</td>
<td>-0.004847</td>
<td>238</td>
</tr>
<tr>
<td>270.7</td>
<td>0.888</td>
<td>-0.5029</td>
<td>226</td>
</tr>
<tr>
<td>267.3</td>
<td>0.609</td>
<td>-0.2154</td>
<td>209</td>
</tr>
<tr>
<td>270.0</td>
<td>0.802</td>
<td>-0.9556</td>
<td>233</td>
</tr>
<tr>
<td>267.9</td>
<td>0.647</td>
<td>-0.1888</td>
<td>225</td>
</tr>
<tr>
<td>270.8</td>
<td>0.854</td>
<td>-0.06846</td>
<td>229</td>
</tr>
</tbody>
</table>

Figure 15: Plot of the total pressure of vaporization of Cr(CO)$_6$ according to the reaction Cr(CO)$_6$(s) = Cr(CO)$_6$(g) in the temperature range of 266K to 272K.
4.3 Vaporization of Dicobalt Octacarbonyl

Dicobalt octacarbonyl, $\text{Co}_2(\text{CO})_8$, is the most interesting of the four compounds studied in this report. It was first discovered in 1910 by Mond et al. [41]. When we were doing the preliminary work in the recrystalizer we noticed that the sublimation process was quite slow and a black film coated the whole inside of the apparatus. When this compound was placed in the torsion-effusion cell again this black film coated every thing except those parts that were gold plated and the coldest section of the quartz tube. This film bonded quite strongly to the surfaces in which it came in contact, and could not be removed with acetone. We found that the best thing to remove this coating was concentrated nitric acid.

The vapor pressure data for the vaporization of solid dicobalt octacarbonyl are listed in Table 5. These data were then used to generate a plot of the logarithm of the pressure versus the reciprocal temperature. This is shown in Figure 16. By using the second law, equation (51), the vapor pressure equation number (48), the enthalpy change was obtained from Figure 16 for the reaction number (64).

$$\text{Co}_2(\text{CO})_8(\text{s}) = \text{Co}_2(\text{CO})_8(\text{g})$$  \hspace{1cm} (64)

Table 5. Total pressures ($P_T$) of the effusing vapors of, dicobalt octacarbonyl, $\text{Co}_2(\text{CO})_8(\text{c})$ measured by torsion effusion method, using 0.06 cm. orifice diameter in a platinum cell, at various temperatures. The average measured molecular weight is 226 g/mol.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$P_T$ (Pa)</th>
<th>log $P_T$ (Pa)</th>
<th>$M$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>263.6</td>
<td>0.122</td>
<td>-0.9151</td>
<td>219</td>
</tr>
<tr>
<td>263.6</td>
<td>0.123</td>
<td>-0.9115</td>
<td>221</td>
</tr>
<tr>
<td>263.8</td>
<td>0.124</td>
<td>-0.9079</td>
<td>209</td>
</tr>
<tr>
<td>263.9</td>
<td>0.127</td>
<td>-0.8974</td>
<td>239</td>
</tr>
<tr>
<td>266.1</td>
<td>0.170</td>
<td>-0.7689</td>
<td>232</td>
</tr>
<tr>
<td>268.4</td>
<td>0.235</td>
<td>-0.6288</td>
<td>218</td>
</tr>
<tr>
<td>269.6</td>
<td>0.291</td>
<td>-0.5364</td>
<td>235</td>
</tr>
<tr>
<td>272.8</td>
<td>0.444</td>
<td>-0.3528</td>
<td>221</td>
</tr>
<tr>
<td>276.8</td>
<td>0.758</td>
<td>-0.1204</td>
<td>235</td>
</tr>
<tr>
<td>277.9</td>
<td>0.874</td>
<td>-0.05827</td>
<td>235</td>
</tr>
</tbody>
</table>

The total vapor pressure of dicobalt octacarbonyl, crystals are reported in Table 5 in the temperature range of 264K to 278K along with the molecular weight measurements. The molecular weight of the effusing vapor for this compound turned out to be very different
from its theoretical value. This observation will discussed in a few paragraphs. From the
total pressure of the system $P_T$ and from Figure 15, we obtained Antoine’s equation (65):

$$\log P_T (\text{Pa}) = 15.776(\pm0.102) - 4400.2(\pm27)/T$$  \hspace{1cm} (65)

and the estimated enthalpy in the temperature range 263K to 278K is shown in equation
(66):

$$\Delta H^\circ_{(267\text{K})} = 84.27 (\pm0.5) \text{ kJ/mol}$$  \hspace{1cm} (66)

Baev [19] explored the temperature range of 288K to 315K and found $\log P_T (\text{Pa}) = 18.59 - 4380/T$. This shows fairly close agreement with this study when the data from each is
extrapolated into the other temperature region. Figure 16 is a plot of the data in Table 5.

The measured molecular weight of dicobalt octacarbonyl turned out to average 226
g/mol which differed significantly, 40.83% lower, from the molecular weight of dicobalt
octacarbonyl which is 341.95 g/mol, suggesting that the effusing species were not pure
dicobalt octacarbonyl. We developed two different mechanisms to explain this discrepancy. Mass spectrometric measurements have been attempted to positively identify the gas species, however problems were encountered in the measurements due to low temperature decomposition of this carbonyl in the chamber. As the gaseous carbonyl species pass through the ionizer they are literally torn apart and therefore proved little if any useful information about their decomposition mechanisms or species. For the first mechanism, case A, we have proposed that dicobalt octacarbonyl partially disproportionates to monocobalt tetracarbonyl during the vaporization process from the dicobalt octacarbonyl solid phase. An estimation of the mass fraction (m) of gaseous monocobalt tetracarbonyl in the mixture is designated as b in the following equation:

$$\text{Co}_2\text{(CO)}_8 (c) = (1-b)\text{Co}_2\text{(CO)}_8(g) + 2b \text{Co(CO)}_4(g)$$  \hspace{1cm} (67)

The average molecular weight, $M$, of a multicomponent effusing vapor is given by:

$$M = \frac{\sum m_i (M_i)^{1/2}}{\sum m_i}$$

$$= \left[ \left( (1-b)\frac{M_{\text{Dimer} (g)}}{M_{\text{Dimer} (g)}} + 2b \frac{M_{\text{Monomer} (g)}}{M_{\text{Monomer} (g)}} \right) / M_{\text{Dimer} (g)} \right]^{-2}$$

$$= 226 \text{ g/mol}$$  \hspace{1cm} (68)

where $m_i$ and $M_i$ are mass fractions and molecular weight of the gas species, respectively. Inserting the molecular weights of pure gases in equation (68) a general polynomial relating to the mass fraction of the dimer and monomer is obtained:

$$M=341.82 - 278.17b + 147.39b^2 - 40.177b^3$$  \hspace{1cm} (69)

By substituting our measured value of $M$ of 226 g/mol in this equation we obtain $b=0.555$. The partial pressure of dicobalt octacarbonyl may be expressed as:

$$P_{\text{Co}_2\text{(CO)}_8}/P_T = \left( (1-b)\frac{M_{\text{Dimer} (g)}}{M_{\text{Dimer} (g)}} + 2b \frac{M_{\text{Monomer} (g)}}{M_{\text{Monomer} (g)}} \right)$$

$$= 0.362P_T$$

and by substituting $b=0.555$ we obtain $P_{\text{Co}_2\text{(CO)}_8} = 0.362P_T$ and $P_{\text{Co(CO)}_4} = 0.638P_T$. These partial pressures along with the total pressures are tabulated in Table 6.
In a similar manner we can write an equation for the overall reaction (71) as well as the dimer subliming (72) and the dimer decomposing to monomer (73):

\[
\begin{align*}
1 & \text{ Co}_2(\text{CO})_8 (s) = 1/2 \text{ Co}_2(\text{CO})_8 (g) + \text{Co}(\text{CO})_4 (g) \\
2 & \text{Co}_2(\text{CO})_8 (s) = \text{Co}_2(\text{CO})_8 (g) \\
3 & \text{Co}_2(\text{CO})_8 (s) = 2 \text{Co}(\text{CO})_4(g)
\end{align*}
\]

The reaction (73) was suggested by Bor [42] in 1963 and confirmed by Keller et al. 1965 [43].

The equilibrium constant for reactions (71), (72), and (73) are given by equations (74), (75), and (76) respectively:

\[
\begin{align*}
K_{P1} &= (P_{\text{Co}_2(\text{CO})_8})^{1/2} (P_{\text{Co}(\text{CO})_4}) \\
K_{P2} &= P_{\text{Co}_2(\text{CO})_8} \\
K_{P3} &= (P_{\text{Co}(\text{CO})_4})^2
\end{align*}
\]

The standard Gibbs energy change were obtained by using these equilibrium constants, Kp, which were calculated by using equation (49). The Gibbs energies for the reactions in equations (71), (72), and (73), are given by equations (77), (78), and (79). They are equations (50) and (51) combined together:

\[
\begin{align*}
\Delta G^0_1 &= -RT \ln K_{P1} = 125985 - 441.34T \ J/\text{mol} \\
\Delta G^0_2 &= -RT \ln K_{P2} = 84271 - 293.68T \ J/\text{mol} \\
\Delta G^0_3 &= -RT \ln K_{P3} = 168492 - 596.59T \ J/\text{mol}
\end{align*}
\]

Table 6. The measured total pressure (P_T) and the calculated partial pressures, (P), of the effusing vapors of Co_2(CO)_8(c) and Co(CO)_4(c) measured by torsion effusion method using 0.06 cm. orifice diameter in a platinum cell. The average measured molecular weight is 226 g/mol.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>P_T (P_a)</th>
<th>log P_T</th>
<th>M (g/mol)</th>
<th>P_{Co(CO)_4} (Pa)</th>
<th>P_{Co_2(CO)_8} (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>263.6</td>
<td>0.122</td>
<td>-0.9151</td>
<td>219</td>
<td>0.0440</td>
<td>0.0776</td>
</tr>
<tr>
<td>263.6</td>
<td>0.123</td>
<td>-0.9115</td>
<td>221</td>
<td>0.0444</td>
<td>0.0782</td>
</tr>
<tr>
<td>263.8</td>
<td>0.124</td>
<td>-0.9079</td>
<td>209</td>
<td>0.0458</td>
<td>0.0808</td>
</tr>
<tr>
<td>266.1</td>
<td>0.170</td>
<td>-0.7690</td>
<td>232</td>
<td>0.0616</td>
<td>0.0108</td>
</tr>
<tr>
<td>268.4</td>
<td>0.235</td>
<td>-0.6288</td>
<td>218</td>
<td>0.0851</td>
<td>0.0150</td>
</tr>
<tr>
<td>269.6</td>
<td>0.291</td>
<td>-0.5364</td>
<td>235</td>
<td>0.105</td>
<td>0.185</td>
</tr>
<tr>
<td>272.8</td>
<td>0.444</td>
<td>-0.3528</td>
<td>235</td>
<td>0.161</td>
<td>0.283</td>
</tr>
<tr>
<td>276.8</td>
<td>0.758</td>
<td>-0.1204</td>
<td>235</td>
<td>0.275</td>
<td>0.483</td>
</tr>
<tr>
<td>277.9</td>
<td>0.874</td>
<td>-0.05827</td>
<td>235</td>
<td>0.316</td>
<td>0.558</td>
</tr>
</tbody>
</table>
Figure 17 shows a plot of the vapor pressures of both the monocobalt and the dicobalt from data Table 6.

\[ \log P_{\text{dimer}} (\text{Pa}) = 15.340 - 4401.8/T \]

\[ \log P_{\text{monomer}} (\text{Pa}) = 15.581 - 4400.5/T \]

\[ \log P_{\text{dimer}} (\text{Pa}) = 15.340 - 4401.8/T \]

The second possibility, case B, is that the dicobalt octacarbonyl solid is changing into a combination of monocobalt, Co(CO)_4, dicobalt, Co_2(CO)_8, tetracobalt, Co_4(CO)_{12}, carboxyls and carbon monoxide, CO. This relationship is given by the following equations:

\[ \text{Co}_2\text{(CO)}_8(c) = (1-b)\text{Co}_2\text{(CO)}_8(g) + b/4 \text{Co}_4\text{(CO)}_{12}(g) + b\text{Co(CO)}_4(g) + b\text{CO}(g) \] (80)

For equation (80) it was found that for b equal to 0.727 it gave the same molecular weight that was found in the experiment, 226 g/mol. Equation (81) represents the mole fraction of dicobalt octacarbonyl for the dissociation into monomer, dimer, and tetramer:
\[ M = \left[ \sum_{i=1}^{N} m_i \left( M_i \right)^{1/2} \right]^{-2} \]

\[ \frac{\left[ \frac{(1-b)/M^{1/2}_{\text{Co}_2(\text{CO})_8(\text{g})} + b/4 M^{1/2}_{\text{Co}_4(\text{CO})_{12}(\text{g})} + b M^{1/2}_{\text{Co}(\text{CO})_4(\text{g})} + b M^{1/2}_{\text{CO}(\text{g})}}{(1-b)/M^{1/2}_{\text{Co}_2(\text{CO})_8(\text{g})} + b/4 M^{1/2}_{\text{Co}_4(\text{CO})_{12}(\text{g})} + b M^{1/2}_{\text{Co}(\text{CO})_4(\text{g})} + b M^{1/2}_{\text{CO}(\text{g})}} \right]^{-2}}{(81)} \]

\[ = 226 \text{ g/mol} \]

\[ \frac{P_{\text{CO}_2(\text{CO})_8}}{P_T} = \frac{(1-b) M^{1/2}_{\text{Dimer}(\text{g})}}{(1-b) M^{1/2}_{\text{Dimer}(\text{g})} + b/4 M^{1/2}_{\text{Tetramer}(\text{g})} + b M^{1/2}_{\text{Monomer}(\text{g})} + b M^{1/2}_{\text{CO}(\text{g})}} \quad (82) \]

For \( b \) equal to 0.727 and inserted into equation (82) the partial pressures for the individual species are given as:

\[ P_{\text{CO}_2(\text{CO})_8} = 0.143 P_T \quad (83) \]
\[ P_{\text{Co}_4(\text{CO})_{12}} = 0.0952 P_T \quad (84) \]
\[ P_{\text{Co}(\text{CO})_4} = 0.381 P_T \quad (85) \]
\[ P_{\text{CO}} = 0.381 P_T \quad (86) \]

By using equations (83) through (86) the numbers in Table 7 were generated.

Considering the partial pressures of the effusing gases are known for the dicobalt octacarbonyl system, we find the Gibbs energy change for the equilibrium of these reactions:

\[ \text{Co}_7(\text{CO})_8(\text{c}) = (1-b)\text{Co}_2(\text{CO})_8(\text{g}) + b/4 \text{Co}_4(\text{CO})_{12}(\text{g}) + b\text{Co}(\text{CO})_4(\text{g}) + b\text{CO}(\text{g}) \quad (80) \]

the equilibrium constant for equation (80):

For case B we can write an equation for the overall reaction (87) as well as the dimer subliming (88), the dimer decomposing to monomer (89), and the dimer dissociating to tetramer and carbon monoxide (90):

\[ \begin{align*}
1 \text{Co}_2(\text{CO})_8(\text{s}) &= 1/4\text{Co}_4(\text{CO})_{12}(\text{g}) + 1/4\text{Co}_2(\text{CO})_8(\text{g}) + 1/2\text{Co}(\text{CO})_4(\text{g}) + \text{CO}(\text{g}) \\
2 \text{Co}_2(\text{CO})_8(\text{s}) &= \text{Co}_2(\text{CO})_8(\text{g}) \\
3 \text{Co}_2(\text{CO})_8(\text{s}) &= 2 \text{Co}(\text{CO})_4(\text{g}) \\
4 \text{Co}_2(\text{CO})_8(\text{s}) &= 1/2 \text{Co}_4(\text{CO})_{12}(\text{g}) + 4\text{CO}(\text{g})
\end{align*} \quad (87) \]

(88)

(89)

(90)
The equilibrium constant for reactions (87), (88), (89), and (90) are given by equations (91), (92), (93), and (94) respectively:

\[
\begin{align*}
K_{P_1} &= (P_{Co_4(CO)_1})^{1/4}(P_{Co_2(CO)_8})^{1/4} (P_{Co(CO)_4})^{1/2} P_{CO} \\
K_{P_2} &= P_{Co_2(CO)_8} \\
K_{P_3} &= (P_{Co(CO)_4})^2 \\
K_{P_4} &= (P_{Co_4(CO)_1})^{1/2} (P_{CO})^4
\end{align*}
\]  

The change in Gibbs energies for the reactions (87), (88), (89), and (90) were obtained by using the equilibrium constants, \(K_p\), which were calculated by using equation (49). Equations (91), (92), (93), and (94) are equations (50) and (51) combined together:

\[
\begin{align*}
\Delta G_1^0 &= -RT \ln K_{P_1} = 168040 - 581.48T \ J/mol \\
\Delta G_2^0 &= -RT \ln K_{P_2} = 84244 - 286.04T \ J/mol \\
\Delta G_3^0 &= -RT \ln K_{P_3} = 168458 - 587.93T \ J/mol \\
\Delta G_4^0 &= -RT \ln K_{P_4} = 378121 - 1313.7T \ J/mol
\end{align*}
\]

These values come from assuming that the equilibrium temperature is 361.58K and \(b\) equal to 0.727 in equation (80). By using equation (82) and setting \(b\) equal to 0.727:

\[
P_{Co_2(CO)_8} = 0.272 \ P_T
\]

The other partial pressures were not possible because there were to many unknowns. Table 7 shows the partial pressure of each specie. Figure 18 is a plot of the partial pressures of all the species, mono, di, tetra cobalt and carbon monoxide.

Baev [19] also reported vapor pressures of dicobalt octacarbonyl at higher temperatures and also suggested the conversion of the dicobalt to the tetracobalt. Their equation gave a slightly higher vapor pressure than what we found in our work. Baev [19] et al. found:

\[
\log P (Pa) = 20.16 - 5559/T
\]

in a temperature range of 288K to 315 K.

The dissociation of dicobalt octacarbonyl to tetracobalt dodecacarbonyl was discovered in the thirties [44]. It was synthesized by heating dicobalt octacarbonyl. This reaction is shown in equation (101):
2[Co(CO)₄]₂ \rightarrow [Co(CO)₃]₄ + 4CO \quad (101)

Table 7. The measured total pressure (Pₜ) and the calculated partial pressures, (P), of the effusing vapors of Co₂(CO)₈(c), Co₄(CO)₁₂, Co(CO)₄ and CO measured by torsion effusion method using 0.06 cm. orifice diameter in a platinum cell. The average measured molecular weight is 226 g/mol.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Pₜ</th>
<th>log Pₜ</th>
<th>P_CO</th>
<th>P_{Co(CO)₄}</th>
<th>P_{Co₂(CO)₁₂}</th>
<th>P_{Co₄(CO)₁₂}</th>
</tr>
</thead>
<tbody>
<tr>
<td>263.6</td>
<td>0.122</td>
<td>-0.9151</td>
<td>0.0463</td>
<td>0.0463</td>
<td>0.0174</td>
<td>0.0116</td>
</tr>
<tr>
<td>263.6</td>
<td>0.123</td>
<td>-0.9115</td>
<td>0.0467</td>
<td>0.0467</td>
<td>0.0175</td>
<td>0.0117</td>
</tr>
<tr>
<td>263.8</td>
<td>0.124</td>
<td>-0.9079</td>
<td>0.0471</td>
<td>0.0471</td>
<td>0.0177</td>
<td>0.0118</td>
</tr>
<tr>
<td>263.9</td>
<td>0.127</td>
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<td>0.0482</td>
<td>0.0482</td>
<td>0.0181</td>
<td>0.0121</td>
</tr>
<tr>
<td>266.1</td>
<td>0.170</td>
<td>-0.7690</td>
<td>0.0648</td>
<td>0.0648</td>
<td>0.0243</td>
<td>0.0162</td>
</tr>
<tr>
<td>268.4</td>
<td>0.235</td>
<td>-0.6288</td>
<td>0.0895</td>
<td>0.0895</td>
<td>0.0336</td>
<td>0.0224</td>
</tr>
<tr>
<td>269.6</td>
<td>0.291</td>
<td>-0.5364</td>
<td>0.1111</td>
<td>0.1111</td>
<td>0.0416</td>
<td>0.0276</td>
</tr>
<tr>
<td>272.8</td>
<td>0.444</td>
<td>-0.3528</td>
<td>0.1699</td>
<td>0.1699</td>
<td>0.0635</td>
<td>0.0423</td>
</tr>
<tr>
<td>276.8</td>
<td>0.758</td>
<td>-0.1204</td>
<td>0.2892</td>
<td>0.2892</td>
<td>0.1080</td>
<td>0.0722</td>
</tr>
<tr>
<td>277.9</td>
<td>0.874</td>
<td>-0.05827</td>
<td>0.3323</td>
<td>0.3323</td>
<td>0.1250</td>
<td>0.0833</td>
</tr>
</tbody>
</table>

\[ A \rightarrow \log Pₜ ( Pa ) = 15.776 - 4400.2/T \]
\[ B \rightarrow \log P_{\text{mono}} ( Pa ) = 15.355 - 4399.6/T \]
\[ C \rightarrow \log P_{\text{di}} ( Pa ) = 14.941 - 4400.4/T \]
\[ D \rightarrow \log P_{\text{tetra}} ( Pa ) = 14.752 - 4399.5/T \]

Figure 18: Plot of the total pressure of Co₂(CO)₈ and the partial pressure of the monomer, dimer and tetramer in the temperature range of 263K to 278K.
A plot of the total pressure of vaporization of dicobalt octacarbonyl and the partial pressures of the dissociated gases, monocobalt tetracarbonyl, dicobalt octacarbonyl, tetracobalt dodecacarbonyl are shown in Figure 18. These data come from Table 7.

4.4 Vaporization of Hexarhodium Hexadecacarbonyl

A. Vapor Pressure Measurements

Hexarhodium hexadecacarbonyl was first discovered by Hieber and Lagally in 1943 [46]. Since that time not much work has been done with this compound. As before the vapor pressure was calculated by using equation (39). However for hexarhodium hexadecacarbonyl the vapor pressure and the decomposition pressure are one and the same in the temperature range of 325.3K to 360.7K. The molecular weight of the effusing gas was calculated from equation (40). For both orifices the molecular weight of the effusate averaged 27.7 g/mol. The molecular weight of hexarhodium hexadecacarbonyl is 1065.6 g/mol so we know that the effusate is not hexarhodium hexadecacarbonyl and with a molecular weight of 27.7 g/mol the effusate is definitely carbon monoxide. The evidence that hexarhodium hexadecacarbonyl decomposes is also enhanced by the X-ray pattern of the decomposition residue. This substance has an X-ray pattern that matches both a rhodium standard and the JCPDS file pattern, 05-0685. This will be discussed more fully in section B.

The sublimation of hexarhodium hexadecacarbonyl, \( \text{Rh}_6(\text{CO})_{16} \), is given by equation (90):

\[
\text{Rh}_6(\text{CO})_{16}(s) = \text{Rh}_6(\text{CO})_{16}(g)
\]

The vapor pressure, decomposition pressure, data for the vaporization of solid hexarhodium hexadecacarbonyl are listed in Tables 8 and 9. However it was found that this compound does not sublime, it decomposes in the temperature range that was studied. This decomposition was verified by the molecular weight of the effusing gas. Because of this decomposition two different orifices were used for the study of this compound. There was no discrepancy in the molecular weights of the effusing gases for either orifice. Each gave a molecular weight of about 28 g/mol. The molecular weight of the effusing gas from
the smaller orifice averaged 28.3 g/mol. While the molecular weight of the effusing gas from the larger orifice averaged 27.2 g/mol. The difference between these two is only 3.96%. From these molecular weights it is quite apparent that the effusate is carbon monoxide and that therefore hexarhodium hexadecacarbonyl decomposes without subliming in the temperature range of 325.3K to 360.7K.

The sublimation of hexarhodium hexadecacarbonyl is represented by equation (101) but since this compound decomposes its sublimation is best represented by equation (102):

$$\text{Rh}_6(\text{CO})_{16}(s) = 6\text{Rh}(s) + 16\text{CO}(g) \quad (102)$$

From the data that is shown in Table 9 a graph was generated. The line that connected these data points was made to fit Antoine’s equation (103). The slope of equation one gives the vapor pressure of the compound:

$$\log P_T (\text{Pa}) = (14.64 \pm 0.063) - (5467 \pm 22)/T \quad (103)$$

and the estimated enthalpy and Gibbs energy in the temperature range 326K to 361K:

$$\Delta H_{342K} = 104.7 \pm 0.42 \text{ kJ/mol} \quad (104)$$

Equations (103) and (104) are for the larger orifice.

The standard Gibbs energy change for the larger orifice was obtained using the equilibrium constant, $K_p$, which was calculated by using equation (49). Equation (105) is equations (50) and (51) combined together:

$$\Delta G^\circ_{342K}^{\text{Rh}_6(\text{CO})_{16}} = -RT \ln K_p = 104,700 - 280 T \text{ J/mol} \quad (105)$$

The Antoine’s equation for the slope from the data in Table 9 is equation (106).

$$\log P_T (\text{Pa}) = (15.14 \pm 0.087) - (5502 \pm 31)/T \quad (106)$$

and the estimated enthalpy and Gibbs energy in the temperature range 326K to 365K for the smaller orifice:

$$\Delta G^\circ_{[\text{Rh}_6(\text{CO})_{16}]} = -RT \ln K_p = 105,200 - 290T \text{ J/mol} \quad (107)$$
Table 8. Total pressures ($P_T$) of the effusing vapors of hexarhodium hexadecacarbonyl, Rh$_6$(CO)$_{16}$, measured by torsion effusion method, using 0.11 cm. orifice diameter in a platinum cell, at various temperatures. The average measured molecular weight is 27.2 g/mol.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$P_T$ (Pa)</th>
<th>log $P_T$ (Pa)</th>
<th>$M$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325.5</td>
<td>0.00638</td>
<td>-2.1949</td>
<td>---</td>
</tr>
<tr>
<td>328.6</td>
<td>0.00942</td>
<td>-2.0258</td>
<td>---</td>
</tr>
<tr>
<td>333.3</td>
<td>0.0160</td>
<td>-1.7956</td>
<td>27.8</td>
</tr>
<tr>
<td>335.0</td>
<td>0.0200</td>
<td>-1.6976</td>
<td>29.0</td>
</tr>
<tr>
<td>337.3</td>
<td>0.0258</td>
<td>-1.5877</td>
<td>---</td>
</tr>
<tr>
<td>344.0</td>
<td>0.0544</td>
<td>-1.2643</td>
<td>28.4</td>
</tr>
<tr>
<td>348.6</td>
<td>0.0856</td>
<td>-1.0674</td>
<td>23.6</td>
</tr>
<tr>
<td>349.0</td>
<td>0.0874</td>
<td>-1.0583</td>
<td>26.5</td>
</tr>
<tr>
<td>357.2</td>
<td>0.204</td>
<td>-0.6911</td>
<td>28.1</td>
</tr>
<tr>
<td>360.7</td>
<td>0.285</td>
<td>-0.5454</td>
<td>26.7</td>
</tr>
</tbody>
</table>

The standard Gibbs energy change for the smaller orifice was obtained using the equilibrium constant, $K_p$, which was calculated by using equation (49). Equation (107) is equations (50) and (51) combined together:

$$
\Delta H_{345K} = 105,200 \pm 0.59 \text{ kJ/mol} \quad (108)
$$

The enthalpy for the reaction is given in equation (108). These data are from the smaller orifice that was used for hexarhodium hexadecacarbonyl, these data are plotted in Figure 19.

Since there were two orifices used for the study of hexarhodium hexadecacarbonyl a Whitman-Motzfeld plot was constructed, Figure 20. This is a plot of reciprocal pressure versus the sum of the force constant times the distance of the orifice to the pivot point. Table 10 is the data that was used to construct the plot of Figure 20. The Whitman-Motzfeld plot allows the calculation of the true equilibrium vapor pressure. This equilibrium pressure is then plotted in Figure 21 along with the measured pressures of the larger and smaller orifices. The plot shows that the pressure determined by the smaller orifice is in fact very close to the equilibrium pressure.
The average measured molecular weight is 28.3 g/mol.

Table 9. Total pressures ($P_T$) of the effusing vapors of hexarhodium hexadecacarbonyl, $\text{Rh}_6(\text{CO})_{16}$, measured by torsion effusion method, using 0.06 cm. orifice diameter in a platinum cell, at various temperatures. The average measured molecular weight is 28.3 g/mol.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$P_T$ (Pa)</th>
<th>log $P_T$ (Pa)</th>
<th>$M$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>326.3</td>
<td>0.0193</td>
<td>-1.7155</td>
<td>---</td>
</tr>
<tr>
<td>330.0</td>
<td>0.0284</td>
<td>-1.5471</td>
<td>---</td>
</tr>
<tr>
<td>331.9</td>
<td>0.0345</td>
<td>-1.4628</td>
<td>---</td>
</tr>
<tr>
<td>332.2</td>
<td>0.0375</td>
<td>-1.4261</td>
<td>---</td>
</tr>
<tr>
<td>340.3</td>
<td>0.0912</td>
<td>-1.0400</td>
<td>---</td>
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<tr>
<td>345.0</td>
<td>0.156</td>
<td>-0.8068</td>
<td>29.7</td>
</tr>
<tr>
<td>347.5</td>
<td>0.154</td>
<td>-0.8124</td>
<td>27.0</td>
</tr>
<tr>
<td>352.0</td>
<td>0.327</td>
<td>-0.4758</td>
<td>30.5</td>
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<tr>
<td>352.4</td>
<td>0.334</td>
<td>-0.4758</td>
<td>30.3</td>
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<td>356.4</td>
<td>0.500</td>
<td>-0.3014</td>
<td>27.1</td>
</tr>
<tr>
<td>361.7</td>
<td>0.825</td>
<td>-0.08366</td>
<td>26.5</td>
</tr>
<tr>
<td>363.0</td>
<td>0.925</td>
<td>-0.03381</td>
<td>---</td>
</tr>
<tr>
<td>364.9</td>
<td>1.0153</td>
<td>0.006584</td>
<td>27.0</td>
</tr>
</tbody>
</table>

Figure 19: Plot of the vaporization of $\text{Rh}_6(\text{CO})_{16}$ according to the reaction $\text{Rh}_6(\text{CO})_{16} = 6\text{Rh}(s) + 16\text{CO}(g)$ in the temperature range of 325K to 365K. Both a large and a small orifice were used.
Hexarhodium hexadecacarbonyl has not been studied very much in the last 30 years. In fact an extensive literature search revealed that no papers have been published on this compound since 1963. There was no data for the vapor pressure of this compound available. These are the first such data collected in the last three decades.

As can be seen in Figure 20 the vapor pressure equation (109) and the Gibbs energy equation is (110) for hexarhodium hexadecacarbonyl.

\[
\log P \text{ (Pa)} = 15.573 - \frac{5551.0}{T} \quad (109)
\]

\[
\Delta G^\circ_{[Rh_6(CO)_{16}]} = -RT \ln K_P = 106271.9 - 298T \text{ J/mol} \quad (110)
\]

The equilibrium pressure from the Whitman-Motzfeld plot Figure 20 is included with the pressures theta were obtained from cells one and two. This plot is shown in Figure 21.

Table 10. Vaporization pressures using two different orifices at four different temperatures using the Whitman-Motzfeld approach.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>P1 (Pa)</th>
<th>P2 (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>0.91844</td>
<td>0.35507</td>
</tr>
<tr>
<td>340</td>
<td>0.29909</td>
<td>0.11499</td>
</tr>
<tr>
<td>350</td>
<td>0.10385</td>
<td>0.03972</td>
</tr>
<tr>
<td>360</td>
<td>0.03824</td>
<td>0.01455</td>
</tr>
<tr>
<td>(\Sigma fd cm^2)</td>
<td>2.23180</td>
<td>0.53788</td>
</tr>
</tbody>
</table>

Table 11. Equilibrium pressure calculated from zero orifice extrapolation from the Whitman-Motzfeld plot.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>P (Pa)</th>
<th>log P (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>0.1773</td>
<td>0.75124</td>
</tr>
<tr>
<td>340</td>
<td>0.05624</td>
<td>1.2450</td>
</tr>
<tr>
<td>350</td>
<td>0.01976</td>
<td>1.7042</td>
</tr>
<tr>
<td>360</td>
<td>0.009666</td>
<td>2.1474</td>
</tr>
</tbody>
</table>
Figure 20: Whitman-Motzfeld plot to determine the equilibrium pressure for Rh₆(CO)₁₆.

A -> \log P_{eq} (\text{Pa}) = 15.573 - \frac{5551.0}{T} \quad T = 330K
B -> \log P (\text{Pa}) = 14.951 - \frac{5443.1}{T} \quad T = 340K
C -> \log P (\text{Pa}) = 14.609 - \frac{5465.4}{T} \quad T = 350K
D -> \log P (\text{Pa}) = 14.609 - \frac{5465.4}{T} \quad T = 360K

Figure 21: Plot of the equilibrium pressure of Rh₆(CO)₁₆ along with the pressures for the large and small orifices.
B. Domain or Crystallite Size and Microstrain Determination of the Decomposed Hexarhodium Hexadecacarbonyl

The hexarhodium hexadecacarbonyl obtained from the residue, after the torsion effusion experiment, were examined and this material appeared metallic and shiny, suggesting decomposition to metal. X-ray diffraction patterns in Figure 22 show the Bragg peaks obtained in a 2\(\theta\) range of 10°-90° for the decomposition of hexarhodium hexadecacarbonyl to rhodium which matched exactly the rhodium metal listed in the JCPDS file 05-0685. The decomposition mechanism has already been suggested earlier in this section.

The Bragg peaks of rhodium metal obtained from decomposition of hexarhodium hexadecacarbonyl in Figure 22 are very broad compared to those of the annealed peaks which are superimposed in this figure. This suggests that there are either microstrain and/or domain size effects in the residual rhodium particles. Line profile analyses were performed on all the Bragg peaks, but only a few reflections were selected for Warren-Averbach analysis because these calculations require at least two reflections in each crystal direction; for example, if we choose 311 then we need 440 reflection, which we did not observe in the 2\(\theta\) range examined.

The 200 and 400 reflections were selected for microstrain calculations. The peak position, FWHM, and integral breadth of the 200 Bragg peak are listed in Table 12. Also shown in Table 12 are Fourier coefficients obtained for this 200 reflection. The peak position, FWHM, and integral breadth, Fourier coefficients of the 400 Bragg peak are listed in Table 13. The Fourier size coefficients and the microstrains at each column length are listed in Table 14 were obtained by using Warren-Averbach analyses. Also listed are the cosine size coefficients for 200 and 400 peaks as a function of column length. It was observed that there was Hook effect in the size coefficient vs. column length plot and therefore Hook correction was applied and the results are presented in Table 15 and plotted in Figures 23 and 24. Details of the analyses are discussed in section III.

It was originally thought that the broadening of the Bragg peaks was primarily due to small crystallite size effects. However Warren-Averbach analyses revealed that significant microstrains were present in lattice and the distribution of strain
$\langle \varepsilon_2 \rangle^{1/2}$, as a function of column length (L) are shown in Figure 23. The Fourier cosine size coefficients were then plotted against L (Å) as shown in Figure 24. A straight line was drawn tangent to the initial slope of the curve and the intercept on the x-axis according to equation (36) in section II yielded $D=4.8\text{nm}$. It is proposed that when the hexarhodium hexadecacarbonyl decomposes to metallic rhodium with the evolution of carbon monoxide which collapses the crystal lattice to form small clusters of face centered cubic (FCC) rhodium metal. This yielded large porosity in the particles which was confirmed by SEM analyses. The residual microstrain in the lattice was observed because annealing did not take place during decomposition of this carbonyl at such low temperature of 230K to 259K. This observation has implications in the production of a very porous crystallite size rhodium catalyst; perhaps a simple carbonyl decomposition approach can be used to produce a catalyst.
Figure 22. Bragg peaks of rhodium metal obtained from decomposition of hexarhodium hexadecacarbonyl.
<table>
<thead>
<tr>
<th>Data and corrections</th>
<th>Standard Profile</th>
<th>Analyzed Profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>File Name</td>
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<td>UNRRHB.RD</td>
</tr>
<tr>
<td>Identification</td>
<td>anlrhb</td>
<td>unrhh</td>
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<tr>
<td>Start Angle (deg)</td>
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<td>43.995</td>
</tr>
<tr>
<td>Final Angle (deg)</td>
<td>50.500</td>
<td>59.340</td>
</tr>
<tr>
<td>Step Size (deg)</td>
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<td>0.015</td>
</tr>
<tr>
<td>Number of Data Points</td>
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<td>1024</td>
</tr>
<tr>
<td>Background Correction</td>
<td>Parabolic</td>
<td>Parabolic</td>
</tr>
<tr>
<td>Fitted from (deg)</td>
<td>45.500 to 45.5745</td>
<td>43.995 to 44.505</td>
</tr>
<tr>
<td>and from (deg)</td>
<td>50.255 to 50.500</td>
<td>53.895 to 54.495</td>
</tr>
<tr>
<td>A +B 20</td>
<td>2925.004</td>
<td>76690.086</td>
</tr>
<tr>
<td>+C 20</td>
<td>-113.391</td>
<td>-2718.344</td>
</tr>
<tr>
<td>Peak Position (deg)</td>
<td>47.909</td>
<td>47.711</td>
</tr>
<tr>
<td>Estimated Error (deg)</td>
<td>0.001</td>
<td>0.0074</td>
</tr>
<tr>
<td>Lattice Spacing</td>
<td>1.89724</td>
<td>1.90465</td>
</tr>
<tr>
<td>Fitted Function</td>
<td>Cauchy</td>
<td>Parabola</td>
</tr>
<tr>
<td>Fitted from (deg)</td>
<td>47.870 to 47.950</td>
<td>47.355 to 48.105</td>
</tr>
<tr>
<td>to</td>
<td>10641.00</td>
<td>9466.00</td>
</tr>
<tr>
<td>Maximum Intensity (cts)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full Width at Half Max. (deg)</td>
<td>0.174</td>
<td>1.822</td>
</tr>
<tr>
<td>Asym. of FWHM (high/low)</td>
<td>1.080</td>
<td>0.932</td>
</tr>
<tr>
<td>Integral Breadth (deg)</td>
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</tr>
<tr>
<td>Asym. of Integral Breadth</td>
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<td>0.942</td>
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<tr>
<th>Column Length</th>
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<th>Broadened 200 Profile</th>
<th>Stokes corrected 200 Profile</th>
</tr>
</thead>
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<td>n</td>
<td>L(Å)</td>
<td>cos G</td>
<td>sin G</td>
</tr>
<tr>
<td>0</td>
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<td>1.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1</td>
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</tr>
<tr>
<td>2</td>
<td>14.25</td>
<td>0.9905</td>
<td>-0.0012</td>
</tr>
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<td>3</td>
<td>21.38</td>
<td>0.9780</td>
<td>-0.0021</td>
</tr>
<tr>
<td>4</td>
<td>28.50</td>
<td>0.9609</td>
<td>-0.0026</td>
</tr>
<tr>
<td>5</td>
<td>35.63</td>
<td>0.9412</td>
<td>-0.0019</td>
</tr>
<tr>
<td>6</td>
<td>42.76</td>
<td>0.9213</td>
<td>0.0003</td>
</tr>
<tr>
<td>7</td>
<td>49.88</td>
<td>0.9023</td>
<td>0.0037</td>
</tr>
<tr>
<td>8</td>
<td>57.01</td>
<td>0.8837</td>
<td>0.0069</td>
</tr>
<tr>
<td>9</td>
<td>64.14</td>
<td>0.8643</td>
<td>0.0092</td>
</tr>
<tr>
<td>10</td>
<td>71.26</td>
<td>0.8433</td>
<td>0.0103</td>
</tr>
</tbody>
</table>
Table 13. Standard and Analyzed Profiles Obtained From (400) Nano-crystalline Rhodium Reflection.

<table>
<thead>
<tr>
<th>Data and corrections</th>
<th>Standard Profile</th>
<th>Analyzed Profile</th>
</tr>
</thead>
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<td><strong>File Name</strong></td>
<td>ANLRHBJ02</td>
<td>UNRRHB.RD</td>
</tr>
<tr>
<td><strong>Identification</strong></td>
<td>anlrhf</td>
<td>unrrhh</td>
</tr>
<tr>
<td><strong>Start Angle (deg)</strong></td>
<td>105.700</td>
<td>95.000</td>
</tr>
<tr>
<td><strong>Final Angle (deg)</strong></td>
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<td>119.960</td>
</tr>
<tr>
<td><strong>Step Size (deg)</strong></td>
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<td>0.040</td>
</tr>
<tr>
<td><strong>Number of Data Points</strong></td>
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<td>625</td>
</tr>
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<td><strong>Background Correction</strong></td>
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<td>Linear</td>
</tr>
<tr>
<td><strong>Fitted from (deg)</strong></td>
<td>105.700</td>
<td>95.000</td>
</tr>
<tr>
<td></td>
<td>to 105.945</td>
<td>96.200</td>
</tr>
<tr>
<td></td>
<td>and from 110.455</td>
<td>113.520</td>
</tr>
<tr>
<td></td>
<td>to 110.700</td>
<td>114.000</td>
</tr>
<tr>
<td><strong>A</strong></td>
<td>399.336</td>
<td>1026.007</td>
</tr>
<tr>
<td><strong>+B 2θ</strong></td>
<td>0.317</td>
<td>31.187</td>
</tr>
<tr>
<td><strong>Peak Position (deg)</strong></td>
<td>108.189</td>
<td>108.257</td>
</tr>
<tr>
<td><strong>Estimated Error (deg)</strong></td>
<td>0.004</td>
<td>0.154</td>
</tr>
<tr>
<td><strong>Lattice Spacing</strong></td>
<td>0.95101</td>
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</tr>
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Table 14. Fourier Cosine Size Coefficients (size F.C.) and microstrain $\langle \varepsilon \rangle^{1/2}$ Calculated using 200 and 400 Profiles Obtained from Rhodium Metal. These values are plotted in Figure 23 and are not corrected for Hook Effect.

<table>
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Table 15. Fourier Cosine Size Coefficients (size F.C.) and microstrain $\langle \varepsilon \rangle^{1/2}$ Calculated using 200 and 400 Profiles Obtained from Rhodium Metal. These values are plotted in Figure 24 and are corrected for Hook Effect.

<table>
<thead>
<tr>
<th>L-Value</th>
<th>Size F.C.</th>
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Figure 23. Root mean square strain in <200> direction of FCC rhodium obtained by decomposition of rhodium carbonyl.

Figure 24. Fourier size coefficient in <200> direction of FCC rhodium obtained by decomposition of rhodium carbonyl.
V. Summary and Discussion

The thermodynamics of vaporization of tungsten, chromium, dicobalt, and hexarhodium carbonyls have been determined in this study. The primary objective of this research project was to determine the vapor pressures of the above mentioned metal carbonyls at temperatures around zero degrees centigrade by using the Knudsen torsion effusion method. The total pressures of these carbonyls and the average molecular weights of their vaporizing gases were measured experimentally at various temperatures and by using the second law the vapor pressure equations were determined. In some cases disproportionation of the vaporizing species was observed and in these cases the partial pressures of the mixture of the gases have been calculated. Gibbs energies of vaporization or decomposition in certain cases have also been determined. The key results are summarized below.

Low temperature vaporization of solid tungsten hexacarbonyl, W(CO)₆, monomer revealed solid-gas equilibria of carbonyl and the equilibrium vapor pressure was determined as \( \log P_T (\text{Pa}) = 14.106 - 4064.4/T \). The average enthalpy \( \Delta H_{277^K}^{\circ} = 77.714 \pm 0.59 \text{ kJ/mol} \) and Gibbs energy for the reaction; \( \Delta G_{[W(CO)_6]}^{\circ} (\text{J/mol}) = 77,714 - 173.93T \).

Disproportionation of tungsten hexacarbonyl gas in this temperature range of 265K - 288K of these experiments was not observed because the average molecular weight for tungsten hexacarbonyl from the vapor pressure measurement were 351 g/mol which is almost equal to the theoretical value of 351.9 g/mol. X-ray diffraction analyses confirmed the structure of the crystals to be orthorhombic and lattice spacings matched with that of the literature [18]. In addition the measured value correlate well the higher temperature range 310K to 375K in the literature of Hieber and Romberg [35], Lander and Germer [4] in the temperature range of 310K to 375K and also Baev [36] in the temperature range of 416K to 432K. In the temperature range that the measurements were made, tungsten carbonyl did not show formation of any dimers in vapor phase, because the measured molecular weight matched that of the solid.

Another monomer, chromium hexacarbonyl, Cr(CO)₆, was investigated and the equilibrium vapor pressure was determined as, \( \log P_T (\text{Pa}) = 12.755 - 3468.3/T \) in the
temperature range of 266K to 272K. This equation for the vapor pressure of chromium hexacarbonyl matched well with the work of Windsor and Blander [37] in the temperature range of 264K to 279K, Hieber and Romberg [35] in the temperature range of 310K to 375K, and Baev [36] in the temperature range of 374K to 415K. The enthalpy change: 
\[ \Delta H^\circ_{269K} = 64.92 \text{ kJ/mol} \] and the Gibbs energy: 
\[ \Delta G^\circ_{[Cr(CO)_6]} = 64.921 - 144.01T \text{ (J/mol)} \]

The average molecular weight was measured as 229 g/mol as compared to the theoretical value of 220.1 g/mol (±3.93%). This suggests that there may be slight disproportionation of Cr(CO)_6 to Cr_2(CO)_12 as suggested by Baev [36] for high temperature but these partial pressures were not estimated. Allowing for experimental error, it may be concluded that there is virtually no disproportionation or decomposition of chromium hexacarbonyl. Structural analyses has revealed that the structure is orthorhombic [20].

The dicobalt octacarbonyl vaporization behavior was very complex and the disproportion of the gases was observed even in the low temperature range of 267K to 278K. However complete decomposition to metallic cobalt and carbon monoxide was not observed in this temperature range. But an increase in temperature to 298K showed extensive deposition of a black film. This black film adhered to virtually everything except the gold plated parts of the balance and the coldest parts of the quartz tube. The measured molecular weight of the vaporizing species of the dicobalt octacarbonyl, Co_2(CO)_8, was 226 g/mol as compared to the theoretical value of 341.9501 gm/mol. Our measured molecular weight was 40.83% lower than the literature value. The total pressure determined was logP_T (Pa) = 15.776 - 4400.2/T. Baev [39] found logP_T (Pa) = 20.16 - 5559/T for the temperature range of 288K to 315K. Literature review showed investigations by Hagihara, Kumada and Okawara [47], who reported one data point on Co_2(CO)_8, P_T = 9.3x10^3 Pa at 288K. Extrapolation of our data using equation (64), yielded a P_T = 3.1x10^{-3} kPa, which is a factor of three lower than that reported in reference [47], suggesting possible decomposition of the gas to metallic cobalt at 288K. The average 
\[ \Delta H^\circ_{(267K)} = 84.27 \text{ kJ/mol for case A.} \] Preliminary attempts to identify the effusing gaseous form of this dimer by mass spectrometry were not very successful. It was assumed that either partial disproportionation of dicobalt to monocobalt, Co(CO)_4,
referred as case A, according the reaction:

$$\text{Co}_2(\text{CO})_8 (c) = (1-b)\text{Co}_2(\text{CO})_8(g) + 2b \text{Co(CO)}_4(g)$$

or to monocobalt Co(CO)$_4$, dicobalt Co$_2$(CO)$_8$, tetracobalt Co$_4$(CO)$_{12}$, and carbon monoxide, CO referred to as case B, according to the reaction:

$$\text{Co}_2(\text{CO})_8 (c) = (1-b)\text{Co}_2(\text{CO})_8(g) + b/4 \text{Co}_4(\text{CO})_{12}(g) + b\text{Co(CO)}_4(g) + b\text{CO}(g)$$

Case A:

1. Co$_2$(CO)$_8$ (s) = 1/2 Co$_2$(CO)$_8$ (g) + Co$_2$(CO)$_8$ (g)
2. Co$_2$(CO)$_8$ (s) = Co$_2$(CO)$_8$ (g)
3. Co$_2$(CO)$_8$ (s) = 2 Co(CO)$_4$ (g)

$$K_{p1} = (P_{\text{Co}_2(\text{CO})_8})^{1/2} (P_{\text{Co(CO)}_4})$$
$$K_{p2} = P_{\text{Co}_2(\text{CO})_8}$$
$$K_{p3} = (P_{\text{Co(CO)}_4})^2$$

The standard Gibbs energy change were obtained by using these equilibrium constants, $K_p$, which were calculated by using equation (49).

$$\Delta G^o_1 = - RT \ln K_{p1} = 125985 - 441.34T \quad \text{J/mol}$$
$$\Delta G^o_2 = - RT \ln K_{p2} = 84271 - 293.68T \quad \text{J/mol}$$
$$\Delta G^o_3 = - RT \ln K_{p3} = 168492 - 596.59T \quad \text{J/mol}$$

Case B:

1. Co$_2$(CO)$_8$ (s) =1/4Co$_4$(CO)$_{12}$(g)+1/4Co$_2$(CO)$_8$ (g)+1/2Co$_2$(CO)$_8$ (g)
2. Co$_2$(CO)$_8$ (s) = Co$_2$(CO)$_8$ (g)
3. Co$_2$(CO)$_8$ (s) = 2 Co(CO)$_4$(g)
4. Co$_2$(CO)$_8$ (s) = 1/2 Co$_4$(CO)$_{12}$(g) + 4CO

The equilibrium constant for these reactions respectively:
\[ K_{p1} = (P_{CO}(CO)_{12})^{1/4}(P_{CO_{2}}(CO)_{8})^{1/4}(P_{CO}(CO)_{4})^{1/2} \]
\[ K_{p2} = P_{CO_{2}}(CO)_{8} \]
\[ K_{p3} = (P_{CO}(CO)_{4})^{2} \]
\[ K_{p4} = (P_{CO}(CO)_{12})^{1/2}(P_{CO})^{4} \]

The change in Gibbs energies for these reactions were obtained by using the equilibrium constants, \( K_p \), which were calculated by using equation (49):

\[ \Delta G^0_1 = -RT \ln K_{p1} = 168040 - 581.48T \text{ J/mol} \]
\[ \Delta G^0_2 = -RT \ln K_{p2} = 84244 - 286.04T \text{ J/mol} \]
\[ \Delta G^0_3 = -RT \ln K_{p3} = 168458 - 587.93T \text{ J/mol} \]
\[ \Delta G^0_4 = -RT \ln K_{p4} = 378121 - 1313.7T \text{ J/mol} \]

The crystal structure of dicobalt octacarbonyl is monoclinic [25].

The vapor pressure of hexarhodium hexadecacarbonyl, \( Rh_6(CO)_{16} \) was very low and as such it was very difficult to measure below room temperature by the torsion effusion method. These vaporization experiments were in the temperature range of 325K to 365K. Results showed that the vaporization of crystalline hexarhodium hexadecacarbonyl under vacuum was a direct decomposition of hexarhodium hexadecacarbonyl according to the reaction, \( Rh_6(CO)_{16} (s) = 6Rh(s) + 16CO(g) \) at just slightly above room temperatures, and hexarhodium hexadecacarbonyl gas was not detected in this temperature range. The measured molecular weight of vaporizing gas was 27.75 g/mol, which in comparison to the theoretical value of the hexarhodium hexadecacarbonyl of 1065.559 g/mol. Two sets of experiments were performed with different diameters of the Knudsen cell apertures. The vapor pressure equations using cell Nos. 1 and 2 are and the calculated equilibrium vapor pressures are given below:

\[ \log P (\text{Pa}) = (14.609 \pm 0.063) - (5465 \pm 22)/T \quad \Delta H^\circ 342K = 104.6 \pm 0.42 \text{ kJ/mol (P1)} \quad \text{(cell 1)} \]
\[ \log P (\text{Pa}) = (14.951 \pm 0.087) - (5443 \pm 31)/T \quad \Delta H^\circ 345K = 104.2 \pm 0.59 \text{ kJ/mol (P2)} \quad \text{(cell 2)} \]
\[ \log P (\text{Pa}) = (15.573 \pm 0.087) - (5551 \pm 31)/T \quad \Delta H^\circ 345K = 104.2 \pm 0.59 \text{ kJ/mol (equil)} \]

Using the Whitman-Motzfeld model of effusion of gases was used to obtain equilibrium pressures \( P_{eq} \) by extrapolation of the data to zero orifice size. The equilibrium total vapor pressures for decomposition of hexarhodium hexadecacarbonyl is given by the equation, \( \log P_{eq} (\text{Pa}) = 15.573 - 5551/T \). Shiny fine metallic appearing particles were found as
residue in Knudsen cells after termination of the experiment. A scanning electron microscopic/energy dispersive analyses revealed that these were porous identified as rhodium metal. X-ray diffraction analysis revealed a spectrum with extremely broad Bragg peaks due to the crystallite size effect. These pure metallic particles were identified as nanocrystalline rhodium. The average crystallite size $D_{\text{eff}}$ was determined to be about 4.8 nm (48 Å) using the Warren-Averbach method and the microstrain at half the crystallite size is $\langle \varepsilon^2 \rangle^{1/2} = 4.3 \times 10^{-3}$. It is proposed that these porous particles since they have a very large surface area might be useful as a catalyst.

The crystal structure of hexarhodium hexadecacarbonyl is monoclinic [26].

The vapor pressures obtained in this study are compared with those of other investigators in Figure 25. This figure shows the vapor pressure measurements from several researchers for the compound that were studied in this report. The data that was gathered in this study agrees well with the body of previous work done in this field. The behavior of rhodium was completely different as compared to any of the other metal carbonyls investigated in this study. Below room temperature evaluation of the vapor pressures were not measurable using this torsion effusion method. However in the temperature range of 325K to 365K it was observed that the molecular weight of the effusing species was 27.75 g/mol which suggested that the rhodium metal was residual with the evolution of carbon monoxide during the vaporization, rather than vaporization to hexarhodium hexadecacarbonyl gas whose molecular weight is 1065.559 g/mol. Because of direct decomposition of hexarhodium hexadecacarbonyl, there were two sets of apertures for the Knudsen cells used to obtain the equilibrium vapor pressure for the reaction $\text{Rh}_6(\text{CO})_{16} (s) = 6\text{Rh}(s) + 16\text{CO(g)}$ established by Moltzfeldt-Whitman equation (29). The total vapor pressure for the decomposition reaction is given was determined to be; $\log P_T (\text{Pa}) = 15.14 - 5502/T$. The average $\Delta H^\circ_{\text{Rh}_6(\text{CO})_{16}} = 77.74$ kJ/mol. and the $\Delta G^\circ_{\text{Rh}_6(\text{CO})_{16}} = 106,272 - 298T$. Structural analyses by Warren-Averbach method have revealed the crystallite size of rhodium is ~4.8nm and the $\langle \varepsilon^2 \rangle^{1/2}$ at 2.4nm is $7 \times 10^{-3}$.

The low temperature vapor pressure data obtained from dicobalt, chromium, tungsten
and hexarhodium organometallic carbonyls in this study compare reasonably well with high temperature data reported by other investigators [4,17,18,19,40,47]. A log P vs. 1/T plot (Figure 25) shows our results and the results obtained by others. Gibbs energy change (ΔG°) plot obtained for various gas-solid equilibria are shown in Figure 26. In the case of dicobalt octacarbonyl there is partial dissociation of the dimer gas to monomer, carbon monoxide and tetramer carbonyl. Gibbs energies are calculated bases on the assumption that there are only dimer and monomer present in the vapor phase (Case A). It is probably more likely that the dimer dissociates to tetramer, monomer and carbon monoxide gas which is referred to as Case B and the Gibbs energies obtained in this case are also plotted in Figure 26. The hexarhodium hexadecacarbonyl decomposed in the Knudsen cell and the Gibbs energy change for the decomposition is reported in Figure 27.
Figure 25. Summary plot of vapor pressures vs. inverse temperatures for all the carbonyls investigated in this study and also superimposed are the plots from literature.
Figure 26. Gibbs energies of vaporization of tungsten, chromium and cobalt carbonyls. In the case of cobalt, case A represents partial dissociation of dimer to monomer only and case B represents partial dissociation to dimer, monomer and tetramer

A: \( \text{W(CO)}_6(\text{s}) = \text{W(CO)}_6(\text{g}) \)
B: \( \text{Cr(CO)}_6(\text{s}) = \text{Cr(CO)}_6(\text{g}) \)
C: Case A \( \text{Co}_2(\text{CO})_8(\text{s}) = \frac{1}{2}\text{Co}_2(\text{CO})_8(\text{g}) + \text{Co(CO)}_4(\text{g}) \)
D: Case A \( \text{Co}_2(\text{CO})_8(\text{s}) = \text{Co}_2(\text{CO})_8(\text{g}) \)
E: Case A \( \text{Co}_2(\text{CO})_8(\text{s}) = 2\text{Co(CO)}_4(\text{g}) \)
F: Case B \( \text{Co}_2(\text{CO})_8(\text{s}) = \frac{1}{4}\text{Co}_4(\text{CO})_{12}(\text{g}) + \frac{1}{4}\text{Co}_2(\text{CO})_8(\text{g}) + \frac{1}{2}\text{Co(CO)}_4(\text{g}) + \text{CO(g)} \)
G: Case B \( \text{Co}_2(\text{CO})_8(\text{s}) = \text{Co}_2(\text{CO})_8(\text{g}) \)
H: Case B \( \text{Co}_2(\text{CO})_8(\text{s}) = 2\text{Co(CO)}_4(\text{g}) \)
L: Case B \( \text{Co}_2(\text{CO})_8(\text{s}) = \frac{1}{2}\text{Co}_4(\text{CO})_{12}(\text{g}) + 4\text{CO(g)} \)
Figure 27. Gibbs energies for the decomposition of Rh₆(CO)₁₆₋₁₆⁺. 

\[ \text{Rh}_6(\text{CO})_{16} (s) = 6 \text{ Rh} (s) + 16 \text{ CO (g)} \]
Conclusion

The vapor pressures of metal carbonyls have been determined using the Knudsen torsion effusion method. From the vapor pressure data the equilibrium constant was then calculated. When these data were plotted as logarithm of pressure versus reciprocal temperature the slope of the line yielded both the enthalpy and the entropy. From the equilibrium constant the Gibbs energy was calculated. The average molecular weight of the effusing vapor of each compound was determined.

The hexacarbonyls of tungsten and chromium showed no dissociation. The average molecular weight each of these compounds was within experimental error five per cent.

The Antoine equation, enthalpy, and Gibbs energy for vaporization of tungsten hexacarbonyl was found for the temperature range of 265K to 288K:

\[
\log P_T \text{(Pa)} = 14.106 - 4064.4/T
\]

\[
\Delta H^\circ_{277K} = 77.714 \text{ kJ/mol}
\]

\[
\Delta G^\circ\text{[W(CO)\textsubscript{6}]} = -RT \ln K_p = 77,714 - 173.93T \text{ J/mol}
\]

The vapor pressure equation, enthalpy, and Gibbs energy for vaporization of chromium hexacarbonyl was found for the temperature range of 266K to 272K:

\[
\log P_T \text{(Pa)} = 12.755 - 3468.3/T
\]

\[
\Delta H^\circ_{269K} = 64.92 \text{ kJ/mol}
\]

\[
\Delta G^\circ\text{[Cr(CO)\textsubscript{6}]} = -RT \ln K_p = 64.921 - 144.08T \text{ J/mol}
\]

The vaporization behavior dicobalt octacarbonyl was very complex. This compound decomposed. The measured molecular weight was 226 nearly 41% below the theoretical value of 342. A black film coated everything inside of the apparatus except for the coldest parts of the apparatus and the parts that were gold plated. The vapor pressure and enthalpy in the temperature range 263K to 278K are listed below:

\[
\log P_T \text{(Pa)} = 15.776 - 4400.2/T
\]
\[ \Delta H^\circ_{(267K)} = 84.27 \text{ kJ/mol} \]

To explain the disproportionation two mechanism are proposed. Case A has the solid dissociating into dimer and monomer.

\[ \text{Co}_2(\text{CO})_8(\text{c}) = (1-b)\text{Co}_2(\text{CO})_8(\text{g}) + 2b \text{Co(\text{CO})}_4(\text{g}) \]

\[ b = 0.555 \]

The partial pressures and the Gibbs energy for each reaction in the temperature range of 263K to 278K are listed below:

\[ P_{\text{Co_2(CO)_8}} = 0.362P_T \]

\[ P_{\text{Co_4(CO)_4}} = 0.638P_T \]

overall reaction
\[ \Delta G^\circ = -RT \ln K_{P_1} = 125985 - 441.34T \text{ J/mol} \]

sublimation
\[ \Delta G^\circ = -RT \ln K_{P_2} = 84271 - 293.68T \text{ J/mol} \]

decomposition
\[ \Delta G^\circ = -RT \ln K_{P_3} = 168492 - 596.59T \text{ J/mol} \]

Case B has the solid dissociating into monomer, dimer, tetramer, and carbon monoxide.

\[ \text{Co}_2(\text{CO})_8(\text{c}) = (1-b)\text{Co}_2(\text{CO})_8(\text{g}) + b/4 \text{Co}_4(\text{CO})_{12}(\text{g}) + b\text{Co(\text{CO})}_4(\text{g}) + b\text{CO(\text{g})} \]

\[ b = 0.727 \]

For \( b \) equal to 0.727 in the temperature range of 263K to 278K and the partial pressures and Gibbs energy for the individual species are given as:
The change in Gibbs energies for the reactions:

**Overall reaction**  
\[ \Delta G^\circ = - RT \ln K_p = 168040 - 581.48T \text{ J/mol} \]

**Sublimation**  
\[ \Delta G^\circ = - RT \ln K_p = 84244 - 286.04T \text{ J/mol} \]

**Decomposition to monomer**  
\[ \Delta G^\circ = - RT \ln K_p = 168458 - 587.93T \text{ J/mol} \]

**Decomposition to tetramer**  
\[ \Delta G^\circ = - RT \ln K_p = 378121 - 1313.7T \text{ J/mol} \]

Rhodium showed no sublimation only decomposition the the temperature range of 325K to 361K. The average molecular weight of the effusing gas was very close to 28. It was assumed that this gas was carbon monoxide. The residue remaining inside the cell was examined with X-ray diffraction analyses. This residue proved to be FCC metallic rhodium. Its diffraction pattern matched exactly the JCPDS file 05-0685. This residue also was found to be made of porous particles, and composed of crystallites of about 4.8 nm in length. It is proposed that the high surface are of this rhodium residue may make it useful as a catalyst.

The equilibrium vapor pressure equation and the equilibrium Gibbs energy for hexarhodium hexadecacarbonyl are shown below:

\[ \log P (\text{Pa}) = 15.573 - 5551.0/T \]

\[ \Delta G^\circ_{[\text{Rh}_6(\text{CO})_{16}]} = - RT \ln K_p = 106271.9 - 298T \text{ J/mol} \]
VII References


5. Powell C.F., Oxley, J.H and Blocke, J.M. *Vapor Deposition*, John Wiley and Sons Inc. NY.


33. Brown, E., Journ. of Chem. Eng. vol 6, Jan 1963
42. Bor, G., Spectrochim. Acta. 19 1209 1963
44. Heiber, W., Mulbauer, F. and Ehman, E. A., Ber. 65 1090 1932
45. Blanchard, A., Chem. Revs. 21 3 1937