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Vaporization Behavior of Ir$_4$(CO)$_{12}$ and Re$_2$(CO)$_{10}$ Measured by Torsion Effusion Gravimetric Method

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Abstract

Metal carbonyls are of great importance in chemical vapor deposition (CVD), composite materials fabrication, and other near-net shape technologies. Carbonyl CVD application applies to deposition of high-purity metallic/alloy coatings for which vapor pressure data is essential. The vapor pressure data is used for many low and high temperature CVD applications. In this study, we report vapor pressures of solid Ir$_4$(CO)$_{12}$ and Re$_2$(CO)$_{10}$ carbonyls, measured by using the Knudsen Cell methodology with a torsion effusion gravimetric system. The equilibrium total vapor pressure determined is given by the equation, $P_{eq}$ = 12.6 - 6615/T(K). The solid Ir$_4$(CO)$_{12}$ exhibited incongruent vaporization, with ~ 66% conversion from a tetramer to metallic iridium, according to Ir$_4$(CO)$_{12}$ (s) $\rightarrow$ Ir (s)+12CO, as suggested by differences in the measured and theoretical molecular weights of the vaporizing species of 128 g/mol and 1105 g/mol, respectively. The Re$_2$(CO)$_{10}$ on the other hand, showed congruent vaporization, Re$_2$(CO)$_{10}$ (s) = Re$_2$(CO)$_{10}$ (g) in the temperature range of measurements. The equilibrium total vapor pressure determined is given by the equation, $P_{eq}$ = 9.396 - 4167/T(K). We measured a molecular weight of 675 g/mol whereas the theoretical value is 625 g/mol. In both cases we used Whitman-Motzfeldt methodology to obtain equilibrium vapor pressures. The total vapor pressures of these carbonyls, partial pressures of gas species, average molecular weights of the effusing gases, equilibrium constants for the vaporization reactions, their enthalpies, entropies, and Gibbs energies of the Ir and Re carbonyls as well comparison of vaporization thermodynamics with other carbonyls from Group VIA to VIIIA are presented in this paper.

Keywords: Vaporization Thermodynamics, Metal Carbonyls, Torsion effusion method, CVD

1. Introduction.

Metal carbonyls have important applications in the chemical vapor deposition (CVD) of metals and alloys, fabrication of composite materials, and other technologies [1]. Chandra et al. [2,3] and Shorovshrov et al. [4,5], reported depositing metallic coatings on fibers. Vaporization thermodynamics of metal carbonyls are important for CVD processes [1,6]. Vapor pressure measurements have been made on metal carbonyls such as, Ni(CO)$_4$, Fe(CO)$_5$, Cr(CO)$_6$, W(CO)$_6$, Os$_5$(CO)$_{12}$, Co$_2$(CO)$_3$, Mo(CO)$_6$, Re$_2$(CO)$_{10}$, Mn(CO)$_5$, Rh$_6$(CO)$_{16}$, and Ru$_3$(CO)$_{12}$ and others. Amongst these, Ni(CO)$_4$ and Fe(CO)$_5$ are liquid at room temperature in their stable form, and the rest of them are crystalline solids. Some of the solid carbonyl compounds exhibit congruent vaporization behavior, and others exhibit non-congruency, irrespective their molecular weight. Non-congruency is associated either direct carbonyl decomposition or disproportionation to metal/CO gas, or to metal/gas/carbonyl gas species. For example, Co$_4$(CO)$_8$ (M=341.95 g/mol), Rh(CO)$_{16}$ (M=1065.6 g/mol) disproportionate, whereas, W(CO)$_6$ (M=351.92 g/mol) and Os$_5$(CO)$_{12}$ (M=906.7 g/mol) do not disproportionate. Due to the toxicity of the above mentioned materials, safety precautions have to be taken while conducting vaporization experiments. Using Knudsen cell thermogravimetric torsion effusion method, our group has performed vapor pressure measurements, on Cr(CO)$_6$, W(CO)$_6$, Co$_2$(CO)$_3$, Os$_5$(CO)$_{12}$, Rh$_6$(CO)$_{16}$, and Ru$_3$(CO)$_{12}$ in low temperature regime [7, 8].

In this paper, we report details of vaporization thermodynamics on Re$_2$(CO)$_{10}$ and Ir$_4$(CO)$_{12}$ that include measuring non-equilibrium total vapor pressures ($P_T$), then calculate equilibrium vapor pressure ($P_e$), true molecular weights of the effusing species ($M$), and the true fraction carbonyl decomposed ($b$ or $m_i$) by the...
Whitman-Motzfeldt method. In addition, we compare selected vaporization thermodynamics of the Group VIA to VIIIA metal carbonyls.

II. Experimental

Thermodynamic properties of vapors are determined by torsion effusion thermogravimetric Knudsen effusion method [9] who established a method to determine vapor pressure by using kinetic theory of dilute gases and molecular flux of the effusing gas in low pressure regimes. Specifically, we measured the total pressure exerted by vapors in a Knudsen cell (a small cylinder of a closed system with very small orifices drilled perpendicular to the wall of the cell that allows vapors to escape in form of a molecular flow in the $10^{-4}$ to $10^{-8}$ atm. regime, Concurrently, we measured the rate of weight loss of the carbonyls from the Knudsen cell, by gravimetric method that gives the molecular weights (M) of the vaporizing species at different temperatures. Details of theory of measurements are given in Margrave’s book [10]. In this method, the molecular weight of the effusing species are measured by weight loss measurements [10, 11]. Using these sets of experimental data, one can calculate the equilibrium vapor pressures using Whitman-Motzfeldt method [12-13].

We will provide a general description of the apparatus in this paper. A schematic of the apparatus and procedures are given in references [14,15]. This apparatus consists of a 9 cms. diameter and ~63.5 cms. Long, one end closed, quartz tube. The other end of the quartz tube interfaces with a stainless steel flange connecting to the high vacuum system and a Cahn D100 (RH) electro-balance that is mounted on top of a frame. The high vacuum system consists of turbo molecular pump that provide vacuum levels to $10^{-7}$ atm. A torsion wire/mirror assembly is suspended from one arm of the Cahn balance to measure weight loss that allows calculation of molecular weights of vapors effusing from the sample during measurements. The torsion wire (in form of a fine ribbon) made of Pt-10%Ni (10-1 aspect ratio, 58.6 cm long with a torque constant of 0.0947 cm/rad.) is suspended from the balance arm to a mirror/damping disk at the bottom, that allows pressure measurements. At the bottom of the mirror assembly a long (~2 mm diameter) tungsten rod is suspended inside the quartz tube to which the Knudsen cell are attached. We used two barrel Pt-30%Rh Knudsen cells, these have small apertures (orifices) that are arranged diametrically opposite so that the vapor exerts a torque on the ribbon, which in turn gives angular motion to the mirror allowing $2\theta$ angle measurement substituted in Eq.1. This instrument is checked for accuracies by making vapor pressure measurements on standards such as, KCl and C$_{10}$H$_{18}$. In our experiments, there was very good agreement with the measured and literature values of these standards [14].

The measurements were made using the following equations; the total pressures of the effusing gases were measured using Eq.1[16,17]

$$P_T = K \frac{2\theta}{\sum_{i=1}^{n} a_i d_i f_i},$$  \hspace{1cm} (1)

where $P_T$ is the measured total pressure; $K$, the fiber torsion constant, torque angle, $2\theta$ is the measured angular deflection; $f_i$ the force factor (ratio of force from the effusion of vapors from the orifice ‘i’ of finite wall thickness to the expected force if the orifice had an infinitesimal width) [16]; $a_i$, the area of the orifice; $d_i$, the moment arm of effusion orifice; and $i$ is the number of Knudsen cells ranging from $i =1$ to $n$, in our case $n=2$, [10,15].

The average measured molecular weight ($M$) is obtained from the thermogravimetric experiments, and the value of $M$ is given by the Eq. 2:
where, \( T (K) \) is the temperature, \( W \) is the total rate of weight loss, \( R \) is the gas constant; \( m_i = b_i \), mass fraction of the vapor species \( i \); and \( M_i \) is the molecular weight of the species. \( C_i \) is the orifice Clausing factor [18], and \( a_i \) = area of the orifice. Two different measurements are made using different orifice diameters. If more than one molecular species effuses out due to molecular disproportionation, then Eq. (2b) is used. Two sets of experiments on one sample, the smallest orifice diameter of the Knudsen cells is 0.06 cm, and a larger size of 0.1 cm. The Whitman-Motzfeldt equation is used to calculate the total equilibrium pressure (\( P_e \)) using Eq. 3 [12-13]:

\[
P_e = P_T \left[ 1 + \beta \sum_{i=1}^{n} C_i a_i \right]
\]

(3)

where, \( P_T \) is the measured total pressure from Knudsen cells with different orifice sizes; \( \beta \) is the cell constant for a particular cell configuration, \( C_i \) is the Clausing factor (C) [18], the factor \( C_i a_i \) is related to orifice size effect, in our case, for the double barrel, \( i=2 \). Pressure equations are obtained by plotting \( \log P_T \) vs.1000/T from the two orifice size Knudsen cells. In our case, for Cell #1, the pressure equation is \( \log P_{T1} \) (atm) = B-A/T. It should be noted that the as the orifice size approaches zero the effusion pressure approaches \( P_e \). The equilibrium, \( P_e \) is obtained by using the Whitman –Motzfeldt method by plotting \( 1/P_T \) vs. \( \Sigma C_i a_i \). The intercept of the plot gives the \( 1/P_e \) and the slope gives the \( \beta/P_e \). The \( \beta \) is related to the kinetic hindrances during the vaporization.

Equal amount of the crystalline carbonyl powders are placed in the Knudsen cells, and sealed in an argon glove box. The orifices are sealed by melting \( C_{10}H_8 \). The two barrels of the Knudsen cell (~6 mm. diameter each) are welded with small plate, and attached to the tungsten rod inside the quartz tube. The \( d \) is the distance from the center of the plate to the orifice. A furnace is placed near the Knudsen cells. After attaining a vacuum of \( \sim 1 \times 10^{-7} \) atm. in the system, the sample is heated and the \( C_{10}H_8 \) sealing the orifices evaporates. Due to the torsion effect on the ribbon, there is a deflection in the position of the mirror that gives the \( 2\theta \) angle, which is measured by using a meter scale, the values are substituted in Eq.1. In this paper, we usually measure the pressures in atm. then convert to kPa. Usually, 15-20 pressure readings are acquired at different temperatures from each orifice size Knudsen cell.

III. Results

3.1 Vaporization of solid Iridium Carbonyl - Ir(4(CO))12

The crystalline Ir4(CO)12 exhibits canary yellow color, with MW of 1105 g/mol and melting point of 195 °C (468 K). The vaporization properties were measured using two-barrel Knudsen effusion cells, referred to as Cell #1 (orifice sizes of 0.1 cm), and Cell #2 (0.06 cm.). Results from these measurements showed a complex vaporization behavior. The measured total pressures (\( P_T \)) from the Cell #1 and #2 are listed in Table 1. The measured total pressures measured are plotted as \( \log P_T \) vs.1000/T (K) in Figure 1, and the following equations are obtained:

Total vapor pressures from Cell #1
\[ \log P_{T1} \text{(atm)} = (9.516 \pm 0.233) - \frac{6393 \pm 94}{T} \]  
\[ \log P_{T1} \text{(kPa)} = (11.525 \pm 0.234) - \frac{6393 \pm 94}{T} \]  
\[ b_1 = 0.2185 \]  

**Total vapor pressures from Cell #2**

\[ \log P_{T2} \text{(atm)} = (10.124 \pm 0.127) - \frac{6491 \pm 52}{T} \]  
\[ \log P_{T2} \text{(kPa)} = (12.130 \pm 0.127) - \frac{6491 \pm 52}{T} \]  
\[ b_2 = 0.5539 \]

It can be observed from Table 1 that the average molecular weight (M) obtained from the experiments using the weight loss measurements from Cells #1 and #2 and Eq. 2a,b, show \( M_{\text{Ir}_4 \text{CO}_{12} \text{g}} \) = 452 g/mol (orifice size=0.11 mm), and from Cell #2 is \( M_{\text{Ir}_4 \text{CO}_{12} \text{g}} \) = 206 g/mol (orifice size=0.06 cm). The true equilibrium molecular weight (M) of the effusing gases is 128 g/mol. However, the crystalline Ir\(_4\)(CO)\(_{12}\) has a molecular weight, \( M_{\text{Ir}_4 \text{CO}_{12} \text{g}} \) = 1106.005 g/mol. Thus, we have incongruent vaporization indicating metallic Ir or decomposition to another iridium gas species.

**Table 1.** Total pressure over solid crystalline Ir\(_4\)(CO)\(_{12}\) measured by Thermogravimetric Torsion Effusion system, using two sets of Knudsen Cells. Molecular weights measured are also included.

<table>
<thead>
<tr>
<th>XT1(K)</th>
<th>1000/T1(K)</th>
<th>PT1(atm)</th>
<th>PT1(kPa)</th>
<th>( \log ) PT1(kPa)</th>
<th>M</th>
</tr>
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<tr>
<td><strong>Cell #1 (0.1 cm.)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>410.10</td>
<td>2.44</td>
<td>8.24E-07</td>
<td>8.35E-05</td>
<td>-4.08</td>
<td>696</td>
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<tr>
<td>418.50</td>
<td>2.39</td>
<td>1.70E-06</td>
<td>1.72E-04</td>
<td>-3.76</td>
<td>757</td>
</tr>
<tr>
<td>415.10</td>
<td>2.41</td>
<td>1.20E-06</td>
<td>1.22E-04</td>
<td>-3.91</td>
<td>730</td>
</tr>
<tr>
<td>418.80</td>
<td>2.39</td>
<td>1.78E-06</td>
<td>1.80E-04</td>
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<td>716</td>
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<td>416.80</td>
<td>2.40</td>
<td>1.55E-06</td>
<td>1.57E-04</td>
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<td>620</td>
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<td>382.10</td>
<td>2.62</td>
<td>5.44E-08</td>
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<td>-5.26</td>
<td>429</td>
</tr>
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<td>397.10</td>
<td>2.52</td>
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<td>2.61E-05</td>
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<td>467</td>
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<td>4.00E-05</td>
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<td>456</td>
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<tr>
<td>394.40</td>
<td>2.54</td>
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<td>2.68E-05</td>
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<td>1.37E-05</td>
<td>-4.86</td>
<td>365</td>
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<tr>
<td>405.00</td>
<td>2.47</td>
<td>5.85E-07</td>
<td>5.93E-05</td>
<td>-4.23</td>
<td>366</td>
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<tr>
<td>399.60</td>
<td>2.50</td>
<td>3.46E-07</td>
<td>3.50E-05</td>
<td>-4.46</td>
<td>366</td>
</tr>
<tr>
<td>393.30</td>
<td>2.54</td>
<td>1.88E-07</td>
<td>1.90E-05</td>
<td>-4.72</td>
<td>353</td>
</tr>
<tr>
<td>381.70</td>
<td>2.62</td>
<td>5.96E-08</td>
<td>6.04E-06</td>
<td>-5.22</td>
<td>356</td>
</tr>
<tr>
<td>414.10</td>
<td>2.41</td>
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<td>1.25E-04</td>
<td>-3.90</td>
<td>342</td>
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<td>409.30</td>
<td>2.44</td>
<td>8.10E-07</td>
<td>8.21E-05</td>
<td>-4.09</td>
<td>325</td>
</tr>
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<td>403.50</td>
<td>2.48</td>
<td>4.98E-07</td>
<td>5.04E-05</td>
<td>-4.30</td>
<td>346</td>
</tr>
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<td>416.40</td>
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<td>1.43E-06</td>
<td>1.45E-04</td>
<td>-3.84</td>
<td>325</td>
</tr>
<tr>
<td>419.10</td>
<td>2.39</td>
<td>1.77E-06</td>
<td>1.79E-04</td>
<td>-3.75</td>
<td>312</td>
</tr>
<tr>
<td>418.60</td>
<td>2.39</td>
<td>1.62E-06</td>
<td>1.64E-04</td>
<td>-3.78</td>
<td>303</td>
</tr>
<tr>
<td></td>
<td>Av. M(_1)</td>
<td>452</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cell #2 (.06 cm)</strong></td>
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<td></td>
<td></td>
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<td></td>
</tr>
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<td>388.00</td>
<td>2.58</td>
<td>2.43E-07</td>
<td>2.46E-05</td>
<td>-4.61</td>
<td>-</td>
</tr>
<tr>
<td>400.60</td>
<td>2.50</td>
<td>8.06E-07</td>
<td>8.16E-05</td>
<td>-4.09</td>
<td>201</td>
</tr>
</tbody>
</table>
At this point, we need to know how much of the crystalline Ir₄(CO)₁₂ decomposed to gas, given by the \( b=m_r \) in Eq. 2b. Three possible decomposition pathways are proposed, according to Eqs. (10-12):

\[
\text{Ir}_4(CO)_{12} (s) = (1-b) \text{Ir}_4(CO)_{12} (g) + b. \text{Ir}_2(CO)_{8} + 2b. \text{Ir} (s) + 4 b CO (g) \quad (10)
\]

\[
2 \text{Ir}_4(CO)_{12} (s) = (1-b) \text{Ir}_4(CO)_{12} (g) + b. \text{Ir}_6CO_{16} + 2b. \text{Ir} (s) + 8 b CO (g) \quad (11)
\]

\[
\text{Ir}_4(CO)_{12} (s) = (1-b) \text{Ir}_4(CO)_{12} (g) + 4 b. \text{Ir} (s) +12 b CO (g) \quad (12)
\]

We will use the disproportionation of \( \text{Ir}_4(CO)_{12} \) (Eq. 12) and the average measured molecular weight, \( M_{\text{Ir}_4(CO)_{12}} = 452 \text{ g/mol} \) and \( M_{\text{Ir}_4(CO)_{12}} = 206 \text{ g/mol} \), from Table 1 to calculate \( b \) values. The measured molecular weights are substituted on the left hand side of the Eq. 13 to calculate \( b \) values for each cell, ranging from 0 to 1. If \( b=0 \) only one vaporization species \( \text{Ir}_4(CO)_{12} (g) \) forms, in any of the above cases shown in Eqs. 10-12. The theoretical molecular weights of the gases; \( M_{\text{Ir}_4(CO)_{12}} = 1106.005 \text{ g/mol} \) and \( M_{CO(g)} = 28.01 \text{ g/mol} \) are substituted in the right hand side of the Eq. 13, the unknown value \( b_2 = 0.2185 \) for Cell #1 and \( b_2 = 0.5539 \) for Cell #2 are calculated.

\[
M_{\text{Ir}_4(CO)_{12}} = \sum_{i=1}^{n} b_i M_i^{1/2} - 2 = \frac{(1-b) M_{\text{Ir}_4(CO)_{12}}^{1/2} + 12 b. M_{CO(g)}^{1/2}}{1-b M_{\text{Ir}_4(CO)_{12}}^{1/2} + 12 b. M_{CO(g)}^{1/2}}
\]

(13)

We also attempted to calculate the \( b \) values for Eqs. 10 and 11, assuming partial decomposition to \( \text{Ir}_4(CO)_{6} \) (g) with \( M = 608.52 \text{ g/mol} \) and \( \text{Ir}_4(CO)_{6} \) (g), however, we did not find any solutions for these equations. Thus, we propose Eq.12 for the partial decomposition mechanism to \( \text{Ir}_4(CO)_{12} (g) \), \( \text{Ir} (s) \) and CO gas.

The equilibrium vapor pressures (\( P_r \)), true \( b \) values, and true molecular weights (\( M \)) are calculated by plotting...
1/P vs. $\sum_{i=1}^{n} C_i \cdot a_i$, b vs. $\sum_{i=1}^{n} C_i \cdot a_i$, and M vs. $\sum_{i=1}^{n} C_i \cdot a_i$, respectively, using the data obtained from the two cells. Figure 2 shows the Whitman–Motzfeldt plot for the Ir$_4$(CO)$_{12}$ effusion. The slope of each line plotted for different temperature in Figure 2 gives $\beta/Peq$. The average value of $\beta$ =134 = (1/$\alpha$.A), where $\alpha$~0.012 (evaporation constant), and A= 0.63 cm$^2$ (cross sectional area of the Knudsen cell). The intercepts of each line give inverse total equilibrium pressure for Ir$_4$(CO)$_{12}$. An equation for ($P_e$) is given in Eq.14, these are also listed in Table 2.

$$\log P_e [kPa] = 12.673 - \frac{6615}{T(K)}$$

(14)

The true values of $b$ for the vapor pressure of Ir$_4$(CO)$_{12}$ were also extracted by plotting $b$ vs. $\sum_{i=1}^{n} C_i \cdot a_i$, whose intercept gives the true value of $b$=0.6604. The plot is not shown for brevity but from the linear regression, we obtain the following equilibrium $b$ value or $b_e$ in the equation Eq.15 (note, x = slope of the line):

$$b_e = 0.6604 - 19.8 x$$

(15)

In a similar manner the true values of the molecular weights (M) of the effusing gas were obtain by plotting M vs. $\sum_{i=1}^{n} C_i \cdot a_i$ as shown in Figure 3. The intercept gives the true M =128 g/mol for the decomposition of Ir$_4$(CO)$_{12}$ using Eq.16 (note, x= slope of the line):

$$M_e = 127.89 - 14523 x$$

(16)

The measured $P_{T1}$ and $P_{T2}$ measured from Knudsen cells with different orifices and the calculated $P_e$ at different temperatures are tabulated in Table 2.

**Table 2.** The measured total pressures ($P_{T1}$ and $P_{T2}$ ) and the calculated equilibrium pressures ($P_e$) from the intercept (1/Pe) of the Whitman-Motzfeldt plot for the reaction Ir4(CO)12(s) =(1-b) Ir4(CO$_{12}$ (g) +4 b.Ir (s) +12 b.CO(g).

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P_{T1}$(atm)</th>
<th>$P_{T2}$(atm)</th>
<th>1/$P_e$ (atm$^{-1}$)</th>
<th>$P_e$ (atm)</th>
<th>$P_e$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>380</td>
<td>4.9374 x10$^{-8}$</td>
<td>1.1034 x10$^{-7}$</td>
<td>5.5094 x10$^6$</td>
<td>1.815 x10$^7$</td>
<td>1.839 x10$^5$</td>
</tr>
<tr>
<td>390</td>
<td>1.3330 x10$^{-7}$</td>
<td>3.0249 x10$^{-7}$</td>
<td>1.9735 x10$^6$</td>
<td>5.067 x10$^7$</td>
<td>5.134 x10$^5$</td>
</tr>
<tr>
<td>400</td>
<td>3.4247 x10$^{-7}$</td>
<td>7.8850 x10$^{-7}$</td>
<td>7.4376 x10$^5$</td>
<td>1.345 x10$^6$</td>
<td>1.362 x10$^4$</td>
</tr>
<tr>
<td>410</td>
<td>8.4206 x10$^{-7}$</td>
<td>1.9615 x10$^{-6}$</td>
<td>2.9380 x10$^5$</td>
<td>3.404 x10$^6$</td>
<td>3.449 x10$^4$</td>
</tr>
<tr>
<td>420</td>
<td>1.9753 x10$^{-6}$</td>
<td>4.6722 x10$^{-6}$</td>
<td>1.2124 x10$^5$</td>
<td>8.248 x10$^6$</td>
<td>8.357 x10$^4$</td>
</tr>
<tr>
<td>430</td>
<td>4.4628 x10$^{-6}$</td>
<td>1.0689 x10$^{-6}$</td>
<td>5.2111 x10$^4$</td>
<td>1.919 x10$^5$</td>
<td>1.944 x10$^3$</td>
</tr>
</tbody>
</table>

The partial pressures of Ir$_4$(CO)$_{12}$ (g) and the CO gas, are determined by Eq. 17 and 18 for the reaction in Eq.12 by substituting, $b$=0.6604; $P_{Ir_4(CO)_{12}}/P_e$ = 0.21207 for the Ir$_4$(CO)$_{12}$ (g), and for the iridium metal formation with the evolution of carbon monoxide gas, $P_{CO_2}/P_e$ = 0.7879.
The partial pressures at different temperatures are tabulated in Table 3 along with total equilibrium pressures ($P_e$) between 380 and 430K. From the total equilibrium vapor pressure ($P_e$) and the $b$ value, we calculated, the partial pressure of the Ir$_4$(CO)$_{12}$ (g) and CO gas (Eqs. 17, 18) and the equilibrium constant, $K_P$ for each vaporization reaction. The solid-gas equilibrium for the Ir$_4$(CO)$_{12}$ (Eq. 19) is represented as:

$$\text{Ir}_4(\text{CO})_{12} \text{(s)} = \text{Ir}_3(\text{CO})_{12} \text{(g)}$$

(19)
Table 3. Partial pressures of $P_{Ir_4(CO)_{12}}$ and $P_{CO}$ as a function of temperature for the reaction
$Ir_4(CO)_{12} (s) = (1-b) Ir_4(CO)_{12} (g) + 4b.Ir (s) + 12b .CO (g)$

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$1/T$ (1/K)</th>
<th>Equilibrium Pressure ($P_e$) (kPa)</th>
<th>Partial Pressures (kPa) $P_{Ir_4(CO)_{12}}$</th>
<th>$P_{CO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>380</td>
<td>2.632x10^{-3}</td>
<td>1.839x10^{-5}</td>
<td>3.900x10^{-6}</td>
<td>1.449x10^{-5}</td>
</tr>
<tr>
<td>390</td>
<td>2.564x10^{-3}</td>
<td>5.134x10^{-5}</td>
<td>1.089x10^{-6}</td>
<td>4.045x10^{-5}</td>
</tr>
<tr>
<td>400</td>
<td>2.500x10^{-3}</td>
<td>1.362x10^{-4}</td>
<td>2.888x10^{-5}</td>
<td>1.073x10^{-4}</td>
</tr>
<tr>
<td>410</td>
<td>2.439x10^{-3}</td>
<td>3.449x10^{-4}</td>
<td>7.314x10^{-5}</td>
<td>2.718x10^{-4}</td>
</tr>
<tr>
<td>420</td>
<td>2.381x10^{-3}</td>
<td>8.357x10^{-4}</td>
<td>1.772x10^{-4}</td>
<td>6.585x10^{-4}</td>
</tr>
<tr>
<td>430</td>
<td>2.326x10^{-3}</td>
<td>1.944x10^{-3}</td>
<td>4.123x10^{-4}</td>
<td>1.523x10^{-3}</td>
</tr>
</tbody>
</table>

Using the equilibrium constant, $K_p(Eq.19) = P_{Ir_4(CO)_{12}} = 0.21207 P_e$. (20)

The Gibbs energy change ($\Delta G^o=-RT\ln K_p$) for the reaction (Eq.19) is determined by using Eq. 20 as follows from the plot in Figure 3(a):

$$\Delta G_{Eq.19}^o = 126.7 - 0.2298 T \text{ (kJ/mol)}$$

(21)

Eq. 22 gives the decomposition of the iridium carbonyl to metallic Ir and CO gas, from the plot in Figure 3(b):

$Ir_4CO_{12} (s) = 4 Ir (s) + 12 CO (g)$

(22)

For which, $K_p = P_{CO}^{12} \cdot (0.7879 P_e)^{12}$

(23)

The Gibbs energy change for the reaction (Eq. 22) is determined as follows:

$$\Delta G_{Eq.22}^o = 2000 - 2.888T \text{ (kJ/mol)}$$

(24)

Thus, using the Knudsen cell and Whitman–Motzfeldt methodology it is possible to determine the equilibrium thermodynamic properties of $Ir_4(CO)_{12}$. 

8
3.2 Vaporization behavior of Re$_2$(CO)$_{10}$

The vapor pressure measurements for crystalline Re$_2$(CO)$_{10}$ (s), that exhibit white color, with MW of 625.5 g/mol and melting point of 170°C (443K), were also measured in a similar manner as those for Ir$_4$(CO)$_{12}$, but the results obtained were quite different as compared to Ir$_4$(CO)$_{12}$ in terms of orifice size dependence. There was negligible orifice size effect similar that obtained in the vaporization of KCl(s). The Re$_2$(CO)$_{10}$ did not decompose to Re metal nor particulate soot was observed in the quartz glass tube during the vaporization experiments of Re$_2$(CO)$_{10}$ in the temperature range of 298K to 320K. The equilibrium vaporization of Re$_2$(CO)$_{10}$ is given by the following equation:

$$\text{Re}_2\text{(CO)}_{10}\text{(s)} = \text{Re}_2\text{(CO)}_{10}\text{(g)}$$  \hspace{1cm} (25)

The measured vapor pressure data from solid Re$_2$(CO)$_{10}$ (s) using two different orifice sizes are shown in Table 4 and plotted in Figure 4, indicating virtual congruency.

**Total Vapor pressure using Cell #1**

$$\log P_{T_1} \text{(atm)} = 9.283 - 4745.3/T \text{ (K)}$$  \hspace{1cm} (26)

$$\log P_{T_1} \text{(kPa)} = 11.288 - 4745.3/T \text{ (K)}$$  \hspace{1cm} (27)

**Total vapor pressures from Cell #2**

$$\log P_{T_2} \text{(atm)} = (10.392 \pm 0.092) - (5089.7 \pm 28)/T$$  \hspace{1cm} (28)

$$\log P_{T_2} \text{(kPa)} = (12.397 \pm 0.092) - (5089.7 \pm 28)/T$$  \hspace{1cm} (29)
Table 4. Total pressure over solid crystalline Re₂(CO)₁₀ measured by Thermogravimetric Torsion Effusion system, using two sets of 2-Barrel Knudsen Cells with different orifice sizes of 0.1 cm (Cell #1) and 0.06 cm (Cell #2).

<table>
<thead>
<tr>
<th>T(K)</th>
<th>1000/ T</th>
<th>P(T) (atm)</th>
<th>P(T) (kPa)</th>
<th>logP(T) (kPa)</th>
<th>MW(g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell #1 (0.1 cm.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>302.17</td>
<td>3.31</td>
<td>3.54 x10⁻⁷</td>
<td>3.59 x10⁻⁵</td>
<td>-4.45</td>
<td>-</td>
</tr>
<tr>
<td>321.50</td>
<td>3.11</td>
<td>3.55 x10⁻⁶</td>
<td>3.60E-04</td>
<td>-3.44</td>
<td>787</td>
</tr>
<tr>
<td>321.65</td>
<td>3.11</td>
<td>3.68 x10⁻⁶</td>
<td>3.73E-04</td>
<td>-3.43</td>
<td>795</td>
</tr>
<tr>
<td>324.90</td>
<td>3.08</td>
<td>5.47 x10⁻⁶</td>
<td>5.54E-04</td>
<td>-3.26</td>
<td>795</td>
</tr>
<tr>
<td>325.69</td>
<td>3.07</td>
<td>5.90 x10⁻⁶</td>
<td>5.97E-04</td>
<td>-3.22</td>
<td>782</td>
</tr>
<tr>
<td>329.35</td>
<td>3.04</td>
<td>8.60 x10⁻⁶</td>
<td>8.72E-04</td>
<td>-3.06</td>
<td>806</td>
</tr>
<tr>
<td>329.35</td>
<td>3.04</td>
<td>8.56 x10⁻⁶</td>
<td>8.67E-04</td>
<td>-3.06</td>
<td>817</td>
</tr>
<tr>
<td>331.00</td>
<td>3.02</td>
<td>1.06 x10⁻⁶</td>
<td>1.07E-03</td>
<td>-2.97</td>
<td>827</td>
</tr>
<tr>
<td>330.10</td>
<td>3.03</td>
<td>9.13 x10⁻⁶</td>
<td>9.25E-04</td>
<td>-3.03</td>
<td>820</td>
</tr>
<tr>
<td>309.51</td>
<td>3.23</td>
<td>8.99 x10⁻⁷</td>
<td>9.11E-05</td>
<td>-4.04</td>
<td>775</td>
</tr>
<tr>
<td>307.91</td>
<td>3.25</td>
<td>7.33 x10⁻⁷</td>
<td>7.43E-05</td>
<td>-4.13</td>
<td>804</td>
</tr>
<tr>
<td>316.87</td>
<td>3.16</td>
<td>2.18 x10⁻⁷</td>
<td>2.21E-04</td>
<td>-3.66</td>
<td>791</td>
</tr>
<tr>
<td>311.75</td>
<td>3.21</td>
<td>1.15 x10⁻⁶</td>
<td>1.17E-04</td>
<td>-3.93</td>
<td>791</td>
</tr>
<tr>
<td>309.70</td>
<td>3.23</td>
<td>8.71 x10⁻⁷</td>
<td>8.82 x10⁻⁵</td>
<td>-4.05</td>
<td>813</td>
</tr>
<tr>
<td>Av. M₁</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>800</td>
</tr>
</tbody>
</table>

| Cell #2 (.06 cm) |          |            |            |               |           |
| 298.53 | 3.35     | 2.48 x10⁻⁷ | 2.51 x10⁻⁵ | -4.60         | 670       |
| 298.70 | 3.35     | 2.52 x10⁻⁷ | 2.55 x10⁻⁵ | -4.59         | 693       |
| 313.83 | 3.19     | 1.50 x10⁻⁶ | 1.52 x10⁻⁴ | -3.82         | 704       |
| 314.95 | 3.18     | 1.69 x10⁻⁷ | 1.72 x10⁻⁴ | -3.77         | 727       |
The Whitman-Motzfeldt plot (1/P vs. $\sum_i C_i \alpha_i$, not shown, were made from the measured total vapor pressures (Eqs. (26) and (28)). The equilibrium vapor pressures are shown in Table 5 and plotted in Figure 4. The $b = 0$ as well as the $\beta = 0$. The equation for the equilibrium total vapor pressure is calculated as follows:

$$\log(P_e (\text{kPa})) = 9.396 - 4167/T (\text{K})$$

(30)

The extrapolated true $M = 675$ (g/mol) which is closer to the theoretical value (within experimental error), as compared to the measured $M$ (Cell#1) = 800 g/mol, and from Cell No.2 = 705 g/mol. From Table.

Using the equilibrium constant, $K_p = P_{Re_2(CO)_{10}} (b = 0)$, the Gibbs energy change for the vaporization is obtained represented by the following Eq. (31) which is obtained by plotting Figure 5:

$$\Delta G^o (\text{kJ/mol}) = 80.0 - 0.180 T$$

(31)

Table 5. Total equilibrium pressure ($P_e$) extracted by using Whitman Motzfeldt solid $Re_2(CO)_{10}$ model using Cell #1 (0.1 cm) and Cell #2 (0.06 cm) orifice diameter Knudsen cells.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1000/</th>
<th>1/Pe (atm)</th>
<th>Pe (atm)</th>
<th>Pe (kPa)</th>
<th>log (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>3.45</td>
<td>1.00E-07</td>
<td>1.01E-05</td>
<td>-4.9943</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>3.33</td>
<td>3.33E-07</td>
<td>3.38E-05</td>
<td>-4.4714</td>
<td></td>
</tr>
<tr>
<td>310</td>
<td>3.23</td>
<td>3.00E-06</td>
<td>1.01E-04</td>
<td>-3.9943</td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>3.13</td>
<td>2.81E-07</td>
<td>2.85E-05</td>
<td>-4.545</td>
<td></td>
</tr>
<tr>
<td>330</td>
<td>3.03</td>
<td>7.83E-06</td>
<td>7.94E-04</td>
<td>-3.1003</td>
<td></td>
</tr>
</tbody>
</table>
IV. Discussion

The vaporization behavior of solid carbonyls in Group VIA to VIII A (in Table 6; Mo (42), Ru (44), Rh (45), W (74), Re (75), Os (76) and Ir (77)) is compared with Ir$_4$(CO)$_{12}$ (M = 1105.6 g/mol) and Re$_2$(CO)$_{10}$ (M = 625.5 g/mol). Our measurements were made at lower temperatures and pressures using thermogravimetric torsion effusion Knudsen cell method, and the data for the higher temperature is from the literature. Table as shown in the Table 6.

Table 6. Group VIA, VIIA and VIIIA listing of solid carbonyl compounds

<table>
<thead>
<tr>
<th>Group VIA</th>
<th>Group VIIA</th>
<th>Group VIII A</th>
<th>Group VIIIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element/Carbonyl</td>
<td>Atomic Number/Molecular Weight</td>
<td>Element/Carbonyl</td>
<td>Atomic Number/Molecular Weight</td>
</tr>
<tr>
<td>Mo 42- Mo(CO)$_5$ M= 264.01 g/mol</td>
<td>Tc 43 (not studied)</td>
<td>Ru 44 - Ru$<em>3$(CO)$</em>{12}$ M= 639.33 g/mol</td>
<td>Rh 45- Rh$<em>6$(CO)$</em>{16}$ M= 1065.6 g/mol</td>
</tr>
<tr>
<td>W 74- W(CO)$_8$ M=351.92 g/mol</td>
<td>Re 75- Re$<em>2$(CO)$</em>{10}$ M= 632.71 g/mol</td>
<td>Os 76-Os$<em>3$(CO)$</em>{12}$ M= 906.7 g/mol</td>
<td>Ir 77- Ir$<em>4$(CO)$</em>{12}$ M=1105.01 g/mol</td>
</tr>
</tbody>
</table>

4a. Group VIA (W and Mo carbonyls)

The vapor pressure data in the low temperature regime of W(CO)$_8$ showed congruent vaporization and the equilibrium pressure and Gibbs energy are shown in equation are shown Eqs. 32 to 34 [7]:

\[
W_\beta^0(\gamma) = W_\beta^0(\gamma) = \frac{4060(31)}{T(\text{K})} 
\]

\[
\Delta G^o_{\text{Eq.34}} = 77,714 - 173 T \text{kJ/mol} \quad (34)
\]

The high temperature vapor pressure measurements on W(CO)$_8$ were reported by Baev [19], Windsor and Blanchard [20], Hieber and Romberg [21], Ginsburg [22] and Lander and Germer [6]. The data from Rezzukhina and Shvyrev [23] is given by the Eq.35 in the range of 338.76 to 410.13 K:

\[
\log P \text{ (kPa)} = 10.072 - 3640.4/T 
\]

Figure 5  Equilibrium Gibbs energies for solid–gas Ir$_4$(CO)$_{12}$ of Eq. 25.
We did not perform any experiments on vaporization of Mo(CO)$_6$, but we included the values of Rezzukhina and Shvyrev [23] in the range of 323.68 K to 402.77 K.

\[ \log P \text{ (kPa)} = 10.8522 - 3788.3/T \]  

(36)

Figure 6 shows vapor pressures of all the relevant carbonyls for comparison purposes.

4b. **Group VIIA (Re Carbonyl)**

The low temperature data from this study on Re$_2$(CO)$_{10}$ showed congruent vaporization, and equilibrium vapor equation is given in Eq. 30. The higher temperature data on Re$_2$(CO)$_{10}$ were first published in 1961 by Ginzburg [22], Eq. (37), in the range of 351K to 408.5K. In 1971, Baev et al. [25] published equations, in the range of 356K to 454K, Eq. (38) for the crystal-vapor equilibrium in Eq. 25:

\[ \log P \text{ (kPa)} = 9.808 - 4152/T \text{(K)} \]  

(37)

\[ \log P \text{ (kPa)} = 9.6558 - 4054.6/T \text{(K)} \]  

(38)

4c. **Group VIIIA (Ru, Os, Rh, and Ir Carbonyls)**

Thermodynamic vaporization properties of Ru, Rh and Ir carbonyls show disproportionation effects, with the exception of Os$_3$(CO)$_{12}$. Our previous vapor pressure studies [24] showed congruent vaporization, and the equilibrium is represented as Eq. 39:

\[ \text{Os}_3(\text{CO})_{12} \text{ (s)} = \text{Os}_3(\text{CO})_{12} \text{ (g)} \]  

(39)

\[ \log P_{eq, 39} \text{ (kPa)} = 15.00 - 7101/T \text{(K)} \]  

(40)

\[ K_{eq, 39} = 1 \times [P_{\text{Os}_3(\text{CO})_{12}}] = 1 \times (15.00 - 7101/T \text{(K)}) \]  

(41)

\[ \Delta G^\circ_{eq, 39} \text{ (kJ/mol)} = 134.2 - 0.021 \text{ T(K)} \]  

(42)

Gaidym et al. [26] only reported an pressure equation for Os$_3$(CO)$_{12}$ between 423 to 543 K in Eq. 43:

\[ \log P_e \text{ (kPa)} = 14.792 - 5659/T \text{(K)} \]  

(43)

The high temperature data of Giadym et al. [26] does not agree with our results, at this point we cannot comment with regards to the discrepancy without performing experiments. Although, we performed Onnk’s OAR analyses showed that the data does not follow the arc representation in our thermodynamic assessment paper [27].

In similar temperature ranges, the Ru$_3$(CO)$_{12}$ with MW of 639.3 (g/mol) and partially disproportionates to metallic Ru, between 314 and 352K. The solid-gas equilibrium is extracted is given below [24]:

\[ \text{Ru}_3(\text{CO})_{10} \text{ (s)} = \text{Ru}_3(\text{CO})_{10} \text{ (s)} \]  

(44)

\[ \log P_{eq, 44} \text{ (kPa)} = 12.51 - 5392/T \text{(K)} \]  

(45)

\[ K_{eq, 44} = [0.215 \times P_{\text{Ru}_3(\text{CO})_{10}}] = [0.215 \times (12.51 - 5392/T) \text{(K)}] \]  

(46)
\[ \Delta G_{\text{eq}, 44} = 103.2 - 0.214 T(K) \] (47)

The decomposition portion of it is represented by the equation [24]:

\[ \text{Ru}_3(\text{CO})_{10} \quad (s) \quad \rightarrow \quad 3 \cdot \text{Ru} \quad (s) \quad + \quad 12 \text{CO} \quad (g) \] (48)

\[ K_{\text{eq}, 48} \quad (\text{kPa}) \quad = \quad [0.785 \times P_{\text{Ru}_3(\text{CO})_{10}}]^{12} = [0.785 \times (12.51 - 5392/T(K))]^{12} \] (49)

\[ \Delta G_{\text{eq}, 48} \quad (\text{kJ/mol}) \quad = \quad 1237.8 \quad - \quad 2.39 \quad T(K) \] (50)

The \( \text{Rh}_6(\text{CO})_{16} \) completely disproportionates and decomposes to metallic Rh and CO gas, in the range of 320 to 370 K [7, 28]. We extracted the Rh metal crystals and performed line broadening x-ray diffraction that showed very broad Bragg peaks, and extremely fine crystallite sizes in the order of \( D_{\text{eff}} \approx 46 \, \text{Å} \) were measured [29]. The following are the equations for vaporization of \( \text{Rh}_6(\text{CO})_{16} \) (s) [8,28,29]:

\[ \text{Rh}_6(\text{CO})_{16} \quad (s) \quad \rightarrow \quad 6 \cdot \text{Rh} \quad (s) \quad + \quad 16 \cdot \text{(CO)} \quad (g) \] (51)

\[ \log K_{\text{eq}, 51} \quad = \quad 12.533 - 5540/T(K) \] (52)

\[ K_{\text{eq}, 51} \quad = \quad [1 \times P_{\text{Rh}_6(\text{CO})_{16}}]^{16} \quad = \quad [1 \times (12.51 - 5392/T(K))]^{16} \] (53)

\[ \Delta G_{\text{eq}, 51} \quad (\text{kJ/mol}) \quad = \quad 1697.1 \quad - \quad 3.23 \quad T(K) \] (54)

In summary, the determination of equilibrium vaporization thermodynamics of crystalline \( \text{Ir}_4(\text{CO})_{12} \) (M=1105.6 g/mol) equations and \( \text{Re}_2(\text{CO})_{10} \) (M=625.5 g/mol) in this study revealed incongruent vaporization of \( \text{Ir}_4(\text{CO})_{12} \) and congruent vaporization of \( \text{Re}_2(\text{CO})_{10} \). To the best our knowledge, we could not find vaporization data on \( \text{Ir}_4(\text{CO})_{12} \), however, we found data on \( \text{Re}_2(\text{CO})_{10} \) at higher temperatures.

**Figure 6** shows comparative data of carbonyls summarized the data from the literature. The vapor pressure with lines with data points are from present and previous studies our group, and ones with only lines are from the literature. As the measurements were made in high vacuum, our pressure range is between ~1x10^{-6} to ~1x10^{-3} kPa. High pressure and temperature data is from the literature ranging from ~2x10^{-4} to ~200 kPa.

Extrapolation of the pressure data, discussed above, at 300K (**Figure 6**), showed that the VIA group Mo and W carbonyls have higher vapor pressures than those of Group VIIA, Re carbonyl, and VIIIA, Ru, Os, Rh, and Ir carbonyls. The equilibrium Gibbs energy functions derived in this study are compared with those of the previously investigated carbonyls and these results are shown in **Figure 7**. In general, the \( \Delta G^o \) of solid to gas equilibrium of the Ir, Os, Ru, and Re carbonyls were lower than those of carbonyls that decomposed to metal and carbon monoxide gas.

V. Conclusions

Vaporization thermodynamic measurements, using gravimetric torsion-Knudsen effusion method, of Os, W, Cr, Rh, Ru, Co showed equilibrium vapor \( (P_e) \) dependence on molecular weights at a particular temperature. Overall, there is reasonable agreement between low temperature studies from our group with studies performed at higher temperature reported in the literature except for the \( \text{Os}_3(\text{CO})_{12} \). Amongst the high molecular weight carbonyls, the \( \text{Rh}_6(\text{CO})_{16} \), \( \text{Ru}_3(\text{CO})_{12} \) and \( \text{Ir}_4(\text{CO})_{12} \) exhibited disproportionation. Whereas, the \( \text{Re}_2(\text{CO})_{10} \) and \( \text{Os}_3(\text{CO})_{12} \) showed congruent vaporization without any disproportion in the temperature of the studies. Extrapolating the total vapor pressure data to room temperature, we conclude that the vapor pressure of various crystalline carbonyls show that total equilibrium pressure \( (P_e) \) follow the trend below:

**Vapor Pressure:** \( P_e \text{Mo(CO)}_6 > P_e \text{W(CO)}_6 > P_e \text{Ru}_2(\text{CO})_{10} > P_e \text{Ru}_3(\text{CO})_{12} > P_e \text{Rh}_6(\text{CO})_{16} > P_e \text{Os}_3(\text{CO})_{12} > P_e \text{Ir}_4(\text{CO})_{12} \)
M (g/mol): 264.01 351.92 632.71 639.32 906.7 1065.6 1106.5

Equilibrium Gibbs energies for decomposition vaporization to metal and CO gas are much higher than for the solid-gas carbonyls reactions.

Figure 6. Comparison of total vapor pressures of group VIA to VIIIA carbonyls. The Ir₄(CO)₁₂ and Re₂(CO)₁₀ plots are from this study.
Figure 7. Comparison of equilibrium and decomposition Gibbs energies of Ir, Os, Ru, and Re carbonyls.

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References

23. T.N. Rezzukhina, V.V. Shvyrev, 7(No. 6 Ser. Fiz.-Mat. i Estestven. Nau No. 4) (1952), 41-46.
28. M. Garner, Vapor pressures and thermodynamics properties tungsten,chromium, cobalt and rhodium