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Torsion effusion vapor pressure determinations of Os, Rh, Ru, W, Co, and Cr solid carbonyls[☆]

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Abstract

Vaporization thermodynamics of low and high (>400 g/mol) molecular weight (MW) carbonyls is compared in this study. A gravimetrictorsion effusion method was used to measure vapor pressures of carbonyls such $Os_3(CO)_{12}$, $Rh_6(CO)_{16}$, $Ru_3(CO)_{12}$, $Co_2(CO)_8$, $Cr(CO)_6$, and $W(CO)_6$ carbonyls. The vapor pressure thermodynamic data is used for many low and high temperature CVD applications. Disproportionation of solid carbonyls was found to be virtually independent of molecular weight of the species. Vaporization studies of $Rh_6(CO)_{16}$ showed complete decomposition to nano-structured porous metallic Rh metal; the measured $MW_{Rh6(CO)16(effusing gas)}$ is 27.75 g/mol was close to that of carbon monoxide as compared to $MW_{Rh6(CO)16(solid)}$ of 1065.56 g/mol for the value of solid $Rh_6(CO)_{16}$. However, $Ru_3(CO)_{12}$ and $Co_2(CO)_8$ show very complex behavior. The molecular weights of the vaporizing species have been estimated and the numbers of vaporizing species are proposed. For example, there was partial decomposition of $Ru_3(CO)_{12}$ to (approx. 52%) metallic Ru and CO gas during vaporization as suggested by the difference in the molecular weight of the vaporizing species of 107.58 g/mol compared to the actual value of 639.33 g/mol. The dimer $Co_2(CO)_8$ partially disproportionates to tetramer $Co_4(CO)_{12}$, monomer $Co(CO)_4$, and CO gas. Whereas, the $Os_3(CO)_{12}$, $Cr(CO)_6$, and $W(CO)_6$ have shown virtually no disproportionation. The total vapor pressures of all the abovementioned carbonyls, partial pressures of various species, average molecular weights of the effusing gases, equilibrium constants for the vaporization reactions, their enthalpies, entropies, and Gibbs energies have been determined. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Vapor pressure of solid carbonyls; Torsion effusion; VCD; Os, Rh, Ru, W, Cu, Cr carbonyls

1. Introduction

Metal carbonyls are used in chemical vapor deposition (CVD) of metals and alloys, in the formation of composite materials fabrication, and other technologies [1]. Carbonyl CVD application applies to deposition of high-purity metallic/alloy coatings. Chandra et al. [2,3] and Shorovshrov [4,5], reported depositing metallic coating on fibers. High temperature vapor pressure measurements on W(CO)₆ were reported by Baev [6], Windsor and Blanchard [7], Hieber and Romberg [8], Lander and Germer [9], and low temperature by Garner and Chandra [2]. Hieber and

Romberg [8] and Chandra et al. [10] reported vaporization of Cr carbonyls. Hagihara et al. [11], Windsor and Blanchard [7] reported early total vapor pressures of $Co_2(CO)_8$, later Chandra et al. [12] reported details of disproportionation of $Co_2(CO)_8$.

2. Experimental

A gravimetric-torsion effusion apparatus was used to measure the vaporization behavior of the above-mentioned carbonyls. A schematic of the apparatus is shown in Fig. 1. This consists of an opposed dual-orifice Pt-30%Rh Knudsen cell suspended on Pt-10%Ni torsion element ribbon (58.6 cm long with a torque constant of 0.0947 cm/rad.). Two orifice sizes were used in the cases where disproportionation behavior was suspected due variation of the molecular weight of the effusing species. The ribbon was attached to mirror assembly to take angular torque pressure

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Fig. 1. A schematic of the gravimetric torsion effusion system used to measure the vapor pressures of the carbonyls (left). Also shown is the mirror assembly for suspension of the torsion cells (right).

measurements and suspended from an arm of the Cahn-D100 (RH) electro-balance. A Quartz tube, 9 cm in diameter was used to accommodate the Knudsen cell assembly. A high vacuum system was interfaced with the Knudsen cell assembly shown in Fig. 1. Vapor pressure measurements were made on standards such as, KCl and $C_{10}H_8$ to check the instrument accuracy; there was very good agreement with the measured and literature values of these standards [13].

The measurements were made using the following equations; the total pressures of the effusing gases may be obtained using the following equation:

$$P_{\rm T} = \frac{K2\theta}{\sum_{i=1}^{n} (a_i f_i d_i)} \tag{1}$$

where $P_{\rm T}$ is the total pressure; K, torsion constant, θ , the measured angular deflection; f_i , the force factor; 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 [10,13], in our case n = 2

$$M = 2\pi RT \left[\frac{W \sum_{i=1}^{n} (a_i f_i d_i)}{(K2\theta) \sum_{i=1}^{n} (Ca)_i} \right]^2$$
(2)

$$M = \left(\sum_{i=1}^{n} m_i M_i^{-1/2}\right)^{-2}$$
(3)

M is the average molecular weight; *T*, absolute temperature; *W*, the total rate of weight loss; *R*, the gas constant; m_i , mass fraction of the species *i*; and M_i is the molecular weight of the species. If more than one molecular species effuses out due to molecular disproportionation, then Eq. (2) is used. We did two sets of experiments whenever disproportionation was suspected, using 0.06 and 0.11 cm orifice diameter of the Knudsen cells

$$P_{\rm eq} = P \left[1 + \beta \sum_{i=1}^{n} (Ca)_i \right]$$
(4)

 P_{eq} is the equilibrium pressure; *P*, the measured total pressure; β , cell configuration constant; *C*, the clausing factor; and *a* is the area of the orifice. More details may be found in Ref. [14].

3. Results and discussions

3.1. Thermodynamic vaporization properties of rhodium, ruthenium, and osmium carbonyls

Vapor pressure results of high molecular weight (MW, > 400 g/mol) carbonyls are present below. Vaporization of $Rh_6(CO)_{16}(s)$ showed complete disproportionation at relatively low temperatures, ranging from 320 to 370 K. Gravimetric data showed a vast discrepancy between the molecular weight of pure $Rh_6(CO)_{16}(s)$ (1065.6 g/mol) and the effusing species; in this case, molecular weights of 27.1 (1.8) g/mol with 0.11 cm orifice cell, and 29.7 (3.6) g/mol with 0.06 cm, were measured suggesting that the effusing species is carbon monoxide. The total pressure measured using cell no.1 (0.11 cm) and cell no. 2 (0.06 cm) was obtained using second law method. The decomposition may be represented as:

$$Rh_6(CO)_{16}(s) = 6Rh(s) + 16CO(g)$$
 (5)

$$\log P_1 \text{ (kPa)} = 11.6149(0.063) - 5467(22)/T \text{ (cell no. 1)}$$
(6)

$$\log P_2 \text{ (kPa)} = 12.1096(0.087) - 5494(31)/T \text{ (cell no. 2)}$$
(7)

The equilibrium decomposition pressure, P_{eq} , for Eq. (4) was extrapolated by using Whitman–Motzfeldt plot (1/*P* vs $\sum C_i a_i$) to take in account the effect of orifice size and temperature [13,14] giving the following equation

$$\log P_{\rm eq \ Rh6(CO)16(s)} \ (\text{kPa}) = 12.553 - 5540/T \tag{8}$$

The vapor pressures obtained using the two cells and the equilibrium pressures are plotted in Fig. 2A. The Gibbs energy for Eq. (5) of decomposition of $Rh_6(CO)_{16}(s)$ is given as follows

$$\Delta G_{\rm Rh6(CO)16}^{\circ} = -RT \ln K_{\rm p} = 1697.1 - 3.23T \,(\rm kJ/mol) \qquad (9)$$

where, K_p is the equilibrium constant, and $\Delta H^\circ = +$ 1697.1 kJ/mol.

Vaporization of ruthenium carbonyl showed complex behavior and may be represented as:

$$Ru_{3}(CO)_{12}(s) = (1-b)Ru_{3}(CO)_{12}(g) + 3bRu(s) + 12bCO(g)$$
(10)

The vapor pressure equation is given by:

$$\log P_{\rm T}(\rm kPa) = 12.519(0.03) - 5392(45)/T$$
(11)

The molecular weights of the effusing species were obtained by the derived equation given below:

$$M = \left[\sum_{i=1}^{n} m_i (M_i)^{-1/2}\right]^{-2}$$
$$= \left[\frac{\left[(1-b)M_{\text{Ru3(CO)12(g)}}^{1/2} + 12bM_{(\text{CO)(g)}}^{1/2}\right]}{\left[(1-b)M_{\text{Ru3(CO)12(g)}} + 12bM_{(\text{CO)(g)}}\right]}\right]^{-2}$$
(12)

By substituting the molecular weights of pure gases from Eqs. (11) and (12), a general equation for $b = -0.738 \log M + 2.049$ was obtained, and for the measured molecular weight, M = 92.022 g/mol, and b = 0.5923. The partial pressure of ruthenium carbonyl may be

expressed as:

$$\frac{P_{\text{Ru3(CO)12}}}{P_{\text{T}}} = \left[\frac{(1-b)M_{\text{Ru3(CO)12(g)}}^{1/2}}{(1-b)M_{\text{Ru3(CO)12(g)}}^{1/2} + 12bM_{(\text{CO)(g)}}^{1/2}}\right]$$
(13)

By substituting the above value of *b* in Eq. (13) we obtain $p_{\text{Ru3(CO)12(g)}} = 0.215P_{\text{T}}$ and $p_{(\text{CO})(g)} = 0.785P_{\text{T}}$. The solid-gas equilibrium for direct vaporization of Ru₃(CO)₁₂ solid to gas was also obtained for the following equation:

$$Ru_3(CO)_{12}(s) = Ru_3(CO)_{12}(g)$$
 (14)

For which

$$K_{\rm p} = p_{\rm Ru3(CO)12(gas)} = 0.215 P_{\rm T}$$
 (15)

 $\Delta G_{\text{Ru3(CO)12(g)}}^{\circ} = -RT \ln K_{\text{p}} = 103.2 - 0.214T (\text{kJ/mol})$

Concurrently, the decomposition of metallic Ru was also occurring for which we write the following equation:

$$Ru_3(CO)_{12}(s) = 3Ru(s) + 12CO(g)$$
 (17)

$$K_{\rm p} = (p_{\rm CO})^{12} = (0.785 P_{\rm T})^{12}$$
 (18)

and

$$\Delta G^{\circ} = -RT \ln K_{\rm p} = 1237.8 - 2.39T (\rm kJ/mol)$$
(19)

Thus, solid Ru₃(CO)₁₂ disproportionates to metallic Ru and carbon monoxide near room temperature as shown in Eq. (17). At $P_{\rm T}$ _{298 K}=4.86×10⁻⁷ kPa, and $\Delta G^{\circ}_{298 \rm K}$ = 549.4kJ/mol. The equilibrium (partial) pressures for



Fig. 2. (A) Vapor pressures measured for $Rh_6(CO)_{16}(s) = 6Rh(s) + 16CO(g)$ obtained using Knudsen cells with orifice sizes 0.06 and 0.11 cm. Equilibrium vapor pressure for this reaction was obtained using Whitman–Motzfeldt plot (see Ref. [3]). (B) Vapor pressures showing $Ru_3(CO)_{12}(s) = (1 - b)Ru_3(CO)_{12}(g) + 3bRu(s) + 12bCO(g)$ obtained using torsion effusion cells. The P_{eq} of rhodium carbonyl ($Rh_6(CO)_{16}$) decomposition, and $Os_3(CO)_{12}$ are also plotted in this figure for comparison of the high molecular weight carbonyls.

Ru₃(CO)₁₂ vaporization relationship for solid–gas given in Eq. (14) and the decomposition partial pressure, p_{CO} , given in Eq. (18) are plotted in Fig. 2B as comparison with those of Rh₆(CO)₁₆.

The vaporization of solid to gas $Os_3(CO)_{12}$ was determined and there was no disproportionation and equation may be simply written as:

$$Os_3(CO)_{12}(s) = Os_3(CO)_{12}(g)$$
 (20)

$$P_{\rm T(kPa)} = 15.003(0.05) - 7101(20)/T$$
(21)

$$\Delta G^{\circ}_{(\text{kJ/mol})} = -RT \ln K_{\text{p}} = 134.2 - 0.021T$$
(22)

The plot for the equilibrium vapor pressure of $Os_3(CO)_{12}$ is also shown in Fig. 2B.

3.2. Thermodynamic vaporization properties of cobalt, chromium, and tungsten carbonyls

Vapor pressure results of low molecular weight (MW, <400 g/mol) carbonyls are shown below. Several disproportionation of this solid Co₂(CO)₈ carbonyl was observed. After detailed analyses discussed in Ref. [10,12], we summarize the results leading to the determination of

the following equilibrium equations:

$$Co_2(CO)_8(s) = Co_2(CO)_8(g) \quad \Delta G^\circ (kPa) = 84,270 - 198T$$
(23)

$$Co_{2}(CO)_{8}(s) = 2Co(CO)_{4}(g) \ \Delta G^{\circ} (kPa)$$

= 168,614 - 405.46T (24)

$$Co_{2}(CO)_{8}(s) = 1/2Co_{4}(CO)_{12}(g) + 2CO(g) \Delta G^{\circ} (kPa)$$

= 210,723 - 492.82T (25)

Thus, based on our results it can be concluded that unstable monomer decomposes to metallic cobalt and carbon monoxide gas, and may be represented as $\text{Co}_2(\text{CO})_8(\text{s}) \rightarrow 1/4\text{Co}_4(\text{CO})_{12}(\text{g}) + \text{Co}(\text{CO})_4(\text{g}) + \text{CO}(\text{g}) \rightarrow 2\text{Co}(\text{s}) + 8\text{CO}.$

The vaporization thermodynamics of $Cr(CO)_6$ was also determined and there was no disproportionation and equilibrium equation may be summarized as follows [10,12]:

$$Cr(CO)_6(s) = Cr(CO)_6(g)$$
(26)

The vapor pressure equation is given by:

$$\log P_{\rm T} \,(\rm kPa) = 9.628(0.25) - 3434(68)/T \tag{27}$$



Fig. 3. A van't Hoff summary plot of vaporization studies for Rh, Ru, Os, Co, W, and Cr carbonyls showing the various equilibrium vapor pressures of pure compounds as well as disproportionated species.

 $\Delta G^{\circ}_{\mathrm{Cr(CO)6, s \rightarrow g}}$

$$= 64,888 - 144.01T \text{ (J/mol)}, \text{ where } \Delta H_{269 \text{ K}}^{\circ}$$
$$= 64.82(1.30) \text{ (kJ/mol)}$$
(28)

In the case of vaporization of solid $W(CO)_6$ also there was no disproportionation, and a simple equation may be written as follows:

$$W(CO)_6(s) = W(CO)_6(g)$$
⁽²⁹⁾

The vapor pressure given by:

$$\log P_{\rm T} \,(\rm kPa) = 11.096(0.11) - 4060(31)/T \tag{30}$$

$$\Delta G_{W(CO)_6}^{\circ} = -RT \ln K_p$$

= 77,714 - 173T, where $\Delta H_{277 \text{ K}}^{\circ}$
= 77.74(0.59) (kJ/mol) (31)

In general high molecular weight carbonyls $Rh_6(CO)_{16}$ (MW: 1065.6 g/mol), $Os_3(CO)_{16}$ (MW: 906.7 g/mol), and $Ru_3(CO)_{12}$ (MW: 639.3 g/mol) showed lower vapor pressure than the lower molecular weight carbonyls $Co_2(CO)_8$ (MW: 342 g/mol), W(CO)₆ (MW: 330.3 g/mol), and $Cr(CO)_6$ (MW: 220.1 g/mol) in the temperature range of 312.5–400 K. Vapor pressures of the high and low molecular weight species from our and other investigators data are plotted in Fig. 3; these include disproportionated and decomposed carbonyls.

4. Conclusions

Vaporization thermodynamic measurements, using gravimetric torsion-Knudsen effusion method, of Os, W, Cr, Rh, Ru, Co did not have any dependence on molecular weight on disproportionation or decomposition. The $Rh_6(CO)_{16}$, $Ru_3(CO)_{12}$, and $Co_2(CO)_8$ showed disproportionation or decomposition; equilibrium Gibbs energies for vaporization were obtained and are being tabulated in a database. The vapor pressures of the high molecular weight carbonyls were generally lower than those of lower

molecular weight species in certain temperature range. This trend applies to non-disproportionated species and may not apply to the disproportionated or decomposed species.

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