Preliminary communication

A NOTE ON THE THERMODYNAMICS OF DIMANGANESE AND DIRHENIUM DECACARBONYLS*

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Summary

The results of low temperature heat capacity studies on $Mn_2(CO)_{10}(s)$ and $Re_2(CO)_{10}(s)$ are compared with literature reports. It is shown that the values of vaporization enthalpies and entropies correspond with those of the low temperature stable phase.

Investigations using DTA [1—3], X-ray diffraction [2,4] drop calorimetry [5], and quadrupole resonance techniques [6] show that $Mn_2(CO)_{10}(s)$ and $Re_2(CO)_{10}(s)$ undergo a reversible phase transition at 341 and 371 K, respectively, with $\Delta H_t[Mn_2(CO)_{10}] = (3.5 \pm 0.1)\ kcal_{th}\ mol^{-1}$ and $\Delta H_t[Re_2(CO)_{10}] = (3.8 \pm 0.1)\ kcal_{th}\ mol^{-1}$ **. However, vapor pressure measurements on $Re_2(CO)_{10}(s)$ between 351—409 [1] and 363—454 K [7] give no indication of a phase transition at 371 K (vapor pressures for $Mn_2(CO)_{10}(s)$ are reported [7,8] for temperatures above the transition point). DTA and TGA studies [3] indicate the low temperature phase of each solid is metastable above the transition temperature and readily sublimes under 0.1 Torr vacuum. These latter two results suggest that reported vapor pressures for $Mn_2(CO)_{10}(s)$ and $Re_2(CO)_{10}(s)$ may be those for the low temperature stable phases. As such, enthalpies of formation for $Mn_2(CO)_{10}(g)$ and $Re_2(CO)_{10}(g)$ calculated [5,9] using literature vaporization enthalpies referred to the high temperature phases may be in error by 3—4 $kcal_{th}\ mol^{-1}$. Entropies of formation, $\Delta S_f^\circ(298.15\ K)$, calculated in a similar manner would be in error by 10—15 $cal_{th}\ K^{-1}\ mol^{-1}$.

A second discrepancy also exists in the thermodynamic data for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. Reports of two independent low temperature heat capacity studies [10,11] on both $Mn_2(CO)_{10}(s)$ and $Re_2(CO)_{10}(s)$ yield entropies at 298.15 K in disagreement by 8 to 11 $cal_{th}\ K^{-1}\ mol^{-1}$.

**Throughout this note: cal_{th} = 4.184 J; Torr = (101.325/760) kPa.

To clarify these discrepancies, vaporization entropies for both the low and high temperature stable phases were computed using third-law entropies. The entropy for each solid phase was obtained from $S°(298.15 \text{ K})$ [10,11] and extrapolated values of $S°(T) - S°(298.15 \text{ K})$ [5]. Entropies for the gaseous molecules were calculated using the rigid-rotator, harmonic oscillator approximation. Principal moments of inertia were calculated from reported structural data [12–15]. Incomplete vibrational wave number assignments for both $Mn_2(CO)_{10}(g)$ [16,17] and $Re_2(CO)_{10}(g)$ [16,18] necessitated estimation of several wave numbers using the concept of an average vibrational wave number [19]. Entropies calculated in this manner are in accord with values previously reported at 298.15 K [20].

TABLE 1

THIRD-LAW ENTROPIES FOR $Mn_2(CO)_{10}$ AND $Re_2(CO)_{10}$

T(K)	$S°(T)$ (cal$_{th}$ K^{-1} mol^{-1})		$S°(T)$ (cal$_{th}$ K^{-1} mol^{-1})
	Low temperature phase	High temperature phase	
	$Mn_2(CO)_{10}(s)$		$Mn_2(CO)_{10}(g)$
390	155.5[a], 147.2[b]	169.5[a], 161.2[b]	176.4 ± 5
397	157.7[a], 149.4[b]	172.3[a], 164.0[b]	178.1 ± 5
	$Re_2(CO)_{10}(s)$		$Re_2(CO)_{10}(g)$
380	159.5[c], 148.7[d]	170.6[c], 159.8[d]	186.0 ± 5
409	168.3[c], 157.5[d]	181.6[c], 170.8[d]	193.0 ± 5

[a]Based on $S°(298.15\text{K}) = 125.9$ cal$_{th}$ K^{-1} mol^{-1} [10].
[b]Based on $S°(298.15\text{K}) = 117.6$ cal$_{th}$ K^{-1} mol^{-1} [11].
[c]Based on $S°(298.15\text{K}) = 133.6$ cal$_{th}$ K^{-1} mol^{-1} [10].
[d]Based on $S°(298.15\text{K}) = 122.8$ cal$_{th}$ K^{-1} mol^{-1} [11].

Third-law entropies used in the calculations are summarized in Table 1. Calculated vaporization entropies are compared with experimental values in Table 2. The results in Table 2 clearly indicate that literature vapor pressures and associated vaporization enthalpies and entropies for both $Mn_2(CO)_{10}(s)$

TABLE 2

COMPARISON OF CALCULATED AND EXPERIMENTAL VAPORIZATION ENTROPIES FOR $Mn_2(CO)_{10}(s)$ AND $Re_2(CO)_{10}(s)$

T(K)	$\Delta S°(T)$, experimental (cal$_{th}$ K^{-1} mol^{-1})	$\Delta S°(T)$, third-law (cal$_{th}$ K^{-1} mol^{-1})	
		Low temperature phase	High temperature phase
$Mn_2(CO)_{10}(s) = Mn_2(CO)_{10}(g)$			
390	31.2 ± 0.9[c]	20.9[a], 29.2[b]	6.9[a], 15.2[b]
397	29.0[d]	20.4[a], 28.7[b]	5.8[a], 14.1[b]
$Re_2(CO)_{10}(s) = Re_2(CO)_{10}(g)$			
380	35.7[e]	26.5[a], 37.3[b]	15.4[a], 26.2[b]
409	35.0 ± 0.5[c]	24.7[a], 35.5[b]	11.4[a], 22.2[b]

[a]Calculated using $S°(298.15\text{K})$ [10]. [b]Calculated using $S°(298.15\text{K})$ [11]. [c]Ref. 7. [d]Ref. 8. [e]Ref. 1.

and $Re_2(CO)_{10}(s)$ correspond to the low temperature stable phase. The results also show that vaporization entropies calculated using the lower $S°(298.15 \text{ K})$ values [11] for both $Mn_2(CO)_{10}(s)$ and $Re_2(CO)_{10}(s)$ are in excellent agreement with the measured values.

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