The standard entropies of CO, CO_2, and O_2 at 298.15 K are

$$S^{\ominus}_{298.15}(CO, g) = 197.67 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^{\ominus}_{298.15}(CO_2, g) = 213.74 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^{\ominus}_{298.15}(O_2, g) = 205.138 \text{ J K}^{-1} \text{ mol}^{-1}$$
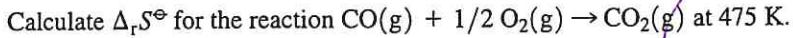
The temperature dependence of constant pressure heat capacity for CO, CO_2, and O_2 is given by

$$\frac{C_{P,m}(CO, g)}{\text{J K}^{-1} \text{ mol}^{-1}} = 31.08 - 1.452 \times 10^{-2}\frac{T}{K} + 3.1415 \times 10^{-5}\frac{T^2}{K^2} - 1.4973 \times 10^{-8}\frac{T^3}{K^3}$$

$$\frac{C_{P,m}(CO_2, g)}{\text{J K}^{-1} \text{ mol}^{-1}} = 18.86 + 7.937 \times 10^{-2}\frac{T}{K} - 6.7834 \times 10^{-5}\frac{T^2}{K^2} + 2.4426 \times 10^{-8}\frac{T^3}{K^3}$$

$$\frac{C_{P,m}(O_2, g)}{\text{J K}^{-1} \text{ mol}^{-1}} = 30.81 - 1.187 \times 10^{-2}\frac{T}{K} + 2.3968 \times 10^{-5}\frac{T^2}{K^2}$$

Rxn → Calculate $\Delta_r S^{\ominus}$ for the reaction $CO(g) + 1/2\, O_2(g) \rightarrow CO_2(g)$ at 475 K.

Solution

$$\frac{\Delta C_{P,m}}{\text{J K}^{-1} \text{ mol}^{-1}} = \left(18.86 - 31.08 - \frac{1}{2} \times 30.81\right)$$

$$+ \left(7.937 + 1.452 + \frac{1}{2} \times 1.187\right) \times 10^{-2}\frac{T}{K}$$

$$- \left(6.7834 + 3.1415 + \frac{1}{2} \times 2.3968\right) \times 10^{-5}\frac{T^2}{K^2}$$

$$+ (2.4426 + 1.4973) \times 10^{-8}\frac{T^3}{K^3}$$

$\Delta C_{P,m}$

$$= -27.63 + 9.983 \times 10^{-2}\frac{T}{K} - 1.112 \times 10^{-4}\frac{T^2}{K^2} + 3.940 \times 10^{-8}\frac{T^3}{K^3}$$

$\Delta S^{\circ}_{rxn} =$

$$\Delta_r S^{\ominus} = S^{\ominus}(CO_2, g, 298.15 \text{ K}) - S^{\ominus}(CO, g, 298.15 \text{ K}) - \frac{1}{2} \times S^{\ominus}(O_2, g, 298.15 \text{ K})$$

$$= 213.74 \text{ J K}^{-1} \text{ mol}^{-1} - 197.67 \text{ J K}^{-1} \text{ mol}^{-1} - \frac{1}{2} \times 205.138 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= -86.50 \text{ J K}^{-1} \text{ mol}^{-1}$$

correction

$$\Delta_r S^{\ominus}(T) = \Delta_r S^{\ominus}(298.15 \text{ K}) + \int_{298.15 \text{ K}}^{T} \frac{\Delta C_p}{T'} dT'$$

$$= -86.50 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$+ \int_{298.15 \text{ K}}^{475 \text{ K}} \frac{\left(-27.63 + 9.983 \times 10^{-2}\frac{T}{K} - 1.112 \times 10^{-4}\frac{T^2}{K^2} + 3.940 \times 10^{-8}\frac{T^3}{K^3}\right)}{T} dT \text{ J K}^{-1} \text{ mol}^{-1}$$

ΔS°_{rxn}

$$= -86.50 \text{ J K}^{-1} \text{ mol}^{-1} + (-12.866 + 17.654 - 7.605 + 1.0594) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= -86.50 \text{ J K}^{-1} \text{ mol}^{-1} - 1.757 \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{-88.3 \text{ J K}^{-1} \text{ mol}^{-1}} \leftarrow \text{final answer}$$

correction

The value of $\Delta_r S^{\ominus}$ is negative at both temperatures because the number of moles of gaseous species is reduced in the reaction.