Chemistry 2720 Fall 2005 Quiz 3 Solution

We could adjust the entropies of all the substances in this reaction to 90°, then calculate the entropy change, but it's actually a better idea to use the same technique for this problem as we used for enthalpy changes:

$$\begin{array}{ccc} \mathrm{TiO_{2(s)}} + 2\mathrm{Cl_{2(g)}}(90^\circ\mathrm{C}) & \longrightarrow & \mathrm{TiCl_{4(g)}} + \mathrm{O_{2(g)}}(90^\circ\mathrm{C}) \\ {\scriptstyle 1}\big\downarrow & & \big\uparrow{\scriptstyle 3} \\ \mathrm{TiO_{2(s)}} + 2\mathrm{Cl_{2(g)}}(25^\circ\mathrm{C}) & \xrightarrow{2} & \mathrm{TiCl_{4(g)}} + \mathrm{O_{2(g)}}(25^\circ\mathrm{C}) \end{array}$$

Now calculate the entropy changes for each of the steps:

$$\begin{aligned} \Delta\bar{S}_1 &= \int_{363.15}^{298.15\,\mathrm{K}} \frac{\left(\bar{C}_{P(\mathrm{TiO_2})} + 2\bar{C}_{P(\mathrm{Cl_2})}\right) dT}{T} = \left[55.18 + 2(33.91\,\mathrm{J\,K^{-1}mol^{-1}})\right] \ln \frac{298.15\,\mathrm{K}}{363.15\,\mathrm{K}} \\ &= -24.26\,\mathrm{J\,K^{-1}mol^{-1}}. \\ \Delta\bar{S}_2 &= \bar{S}^\circ_{\mathrm{O_2}} + \bar{S}^\circ_{\mathrm{TiCl_4}} - \left(\bar{S}^\circ_{\mathrm{TiO_2}} + 2\bar{S}^\circ_{\mathrm{Cl_2}}\right) \\ &= 205.152 + 353.2 - \left[50.62 + 2(223.081\,\mathrm{J\,K^{-1}mol^{-1}})\right] = 61.57\,\mathrm{J\,K^{-1}mol^{-1}}. \\ \Delta\bar{S}_3 &= \int_{298.15\,\mathrm{K}}^{363.15} \frac{\left(\bar{C}_{P(\mathrm{TiCl_4})} + \bar{C}_{P(\mathrm{O_2})}\right) dT}{T} = \left(95.4 + 29.35\,\mathrm{J\,K^{-1}mol^{-1}}\right) \ln \frac{363.15\,\mathrm{K}}{298.15\,\mathrm{K}} \\ &= 24.6\,\mathrm{J\,K^{-1}mol^{-1}}. \end{aligned}$$

The overall entropy change is the sum of the entropy changes in processes 1, 2 and 3:

$$\Delta\bar{S} = \Delta\bar{S}_1 + \Delta\bar{S}_2 + \Delta\bar{S}_3 = -24.26 + 61.57 + 24.6\,\mathrm{J\,K^{-1}mol^{-1}} = 61.9\,\mathrm{J\,K^{-1}mol^{-1}}.$$