Chemistry 2720 Fall 2005 Quiz 4 Solution

There are two different solutions to this problem, but they both start the same way:

$$\begin{aligned} \Delta \bar{G}^{\circ} &= \Delta \bar{G}^{\circ}_{f(\mathrm{HSO}_{4}^{-})} - \left(\Delta \bar{G}^{\circ}_{f(\mathrm{SO}_{3})} + \Delta \bar{G}^{\circ}_{f(\mathrm{H}_{2}\mathrm{O})}\right) \\ &= -677 - \left[-371.1 + \left(-237.140\right)\right] \,\mathrm{kJ/mol} = -69 \,\mathrm{kJ/mol}. \\ \Delta \bar{H}^{\circ} &= \Delta \bar{H}^{\circ}_{f(\mathrm{HSO}_{4}^{-})} - \left(\Delta \bar{H}^{\circ}_{f(\mathrm{SO}_{3})} + \Delta \bar{H}^{\circ}_{f(\mathrm{H}_{2}\mathrm{O})}\right) \\ &= -887 - \left[-395.7 + \left(-285.830\right)\right] \,\mathrm{kJ/mol} = -205 \,\mathrm{kJ/mol}. \end{aligned}$$

From here, they diverge:

1.

$$\begin{split} \Delta \bar{S}^{\circ} &= \frac{\Delta \bar{H}^{\circ} - \Delta \bar{G}^{\circ}}{T} \\ &= \frac{-205 - (-69) \,\text{kJ/mol}}{298.15 \,\text{K}} = -0.459 \,\text{kJ} \,\text{K}^{-1} \text{mol}^{-1}. \\ \therefore \Delta \bar{G}^{\circ}_{323} &= \Delta \bar{H}^{\circ} - T \Delta \bar{S}^{\circ} \\ &= -205 \,\text{kJ/mol} - (323.15 \,\text{K})(-0.459 \,\text{kJ} \,\text{K}^{-1} \text{mol}^{-1}) = -57 \,\text{kJ/mol} \\ \therefore K_{323} &= e^{-\Delta \bar{G}^{\circ}_{323}/(RT)} \\ &= \exp\left(\frac{57 \times 10^3 \,\text{J/mol}}{(8.314 \,472 \,\text{J} \,\text{K}^{-1} \text{mol}^{-1})(323.15 \,\text{K})}\right) \\ &= 1.8 \times 10^9. \end{split}$$

2.

$$K_{298} = e^{-\Delta \bar{G}^{\circ}/(RT)}$$

= $\exp\left(\frac{69 \times 10^{3} \text{ J/mol}}{(8.314 \, 472 \, \text{J K}^{-1} \text{mol}^{-1})(298.15 \, \text{K})}\right)$
= 1.1×10^{12} .
$$\ln\left(\frac{K_{323}}{K_{298}}\right) = \frac{-205 \times 10^{3} \, \text{J/mol}}{8.314 \, 472 \, \text{J K}^{-1} \text{mol}^{-1}} \left(\frac{1}{298.15 \, \text{K}} - \frac{1}{323.15 \, \text{K}}\right)$$

= -6.41
 $\therefore K_{323} = (1.1 \times 10^{12})e^{-6.41} = 1.8 \times 10^{9}.$

The equilibrium constant is very large, which suggests that SO_3 is extremely soluble in water.