18.23 Calculate $K_p$ for the following reaction at 25°C:
\[
\text{H}_2(g) + I_2(g) \rightleftharpoons 2 \text{HI}(g)
\]
\[\Delta G^\circ = 2.60 \text{ kJ/mol} \]
\[K_p = e^{-\frac{-\Delta G^\circ}{RT}} = e^{-\frac{-2.60 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K mol}(298 \text{ K})}} = e^{-1.05} = 0.35\]

18.25 Calculate $\Delta G^\circ$ for the following reaction at 25°C: \(\text{Fe(OH)}_3(s) \rightleftharpoons \text{Fe}^{2+}(aq) + 2 \text{OH}^-(aq)\)

\[K_{sp} = 1.6 \times 10^{-14}.\]
\[\Delta G^\circ = -RT \ln K_{sp} = -(8.314 \text{ J/K mol})(298 \text{ K}) \ln (1.6 \times 10^{-14}) = 7.9 \times 10^4 \text{ J/mol} = 79 \text{ kJ/mol}\]

18.27 (a) Calculate $\Delta G^\circ$ and $K_p$ for the following equilibrium reaction at 25°C:
\[
\text{PCl}_3(g) \rightleftharpoons \text{PCl}_5(g) + \text{Cl}_2(g)
\]
The $\Delta G_i$ values are 0 for Cl$_2$(g), −286 kJ/mol for PCl$_3$(g), and −325 kJ/mol for PCl$_5$(g).

\[\Delta G^\circ_{\text{rxn}} = \Delta G_i^0[\text{PCl}_3(g)] + \Delta G_i^0[\text{Cl}_2(g)] - \Delta G_i^0[\text{PCl}_5(g)]
= (-286 \text{ kJ/mol})(1) + (0)(1) - (325 \text{ kJ/mol})(1) = 39 \text{ kJ/mol}\]
\[K_p = e^{-\frac{-\Delta G^\circ}{RT}} = e^{-\frac{-39 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K mol}(298 \text{ K})}} = e^{-15.7} = 1.5 \times 10^{-7}\]

(b) Calculate $\Delta G$ for the reaction if the partial pressures of the initial mixture are $P_{\text{PCl}_3} = 0.0029 \text{ atm},$
\[P_{\text{PCl}_5} = 0.27 \text{ atm, and } P_{\text{Cl}_2} = 0.40 \text{ atm.}\]
\[Q_p = \frac{P_{\text{PCl}_3}P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{(0.27)(0.40)}{0.0029} = 37\]
\[\Delta G = \Delta G^0 + RT \ln Q = (39 \times 10^3 \text{ J/mol}) + (8.314 \text{ J/K mol})(298 \text{ K}) \ln (37) = 48 \text{ kJ/mol}\]

(c) What is the direction of spontaneous change for this system? Is it more or less spontaneous than at standard conditions? Explain.

Since $\Delta G > 0$, this reaction is spontaneous in the reverse direction. It is less spontaneous than standard conditions since $\Delta G$ is more positive than $\Delta G^\circ$. We can also tell that the system will spontaneously move to the left since $Q > K$.

*Note: do not use the term “shift” in this situation since we are not applying a change to a system at equilibrium (this is NOT a “Le Châtelier” situation).*

(d) What would be the value of $\Delta G$ if the given data were equilibrium pressures? What would be the value of $Q_p$ in that case?

At equilibrium, $Q = K$, so $\Delta G = 0$.

18.29 Consider the decomposition of calcium carbonate: \(\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)\)

$\Delta H^\circ = 177.8 \text{ kJ/mol}$ and $\Delta S^\circ = 160.5 \text{ J/K mol}$.

(a) Calculate the pressure in atm of CO$_2$ in an equilibrium process at 25°C
\[\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (177.8 \times 10^3 \text{ J/mol}) - (298 \text{ K})(160.5 \text{ J/K mol}) = 130.0 \times 10^3 \text{ J/mol}\]
The expression of $K_p$ is:
\[K_p = P_{\text{CO}_2}, \text{ so } P_{\text{CO}_2} = \frac{-\Delta G}{RT} = e^{\frac{-130.0 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K mol}(298 \text{ K})}} = e^{-52.47} = 1.6 \times 10^{-23} \text{ atm}\]
(b) Calculate the pressure at 800°C (assume that $\Delta H^\circ$ and $\Delta S^\circ$ are independent of T)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (177.8 \times 10^3 \text{ J/mol}) - (1073 \text{ K})(160.5 \text{ J/K-mol}) = 5.58 \times 10^3 \text{ J/mol}$$

$$P_{\text{CO}_2} = K_p = e^{-\frac{\Delta G^\circ}{RT}} = e^{-\frac{-5.58 \times 10^3}{(8.314 \text{ J/K-mol})(298 \text{ K})}} = e^{-0.625} = 0.535 \text{ atm}$$

18.31 At 25°C, $\Delta G^\circ$ for the process

$$\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$$

is 8.5 kJ/mol.

(a) Write the $K_p$ expression and calculate the vapor pressure of water at this temperature.

The equilibrium constant expression is:

$$K_p = P_{\text{H}_2\text{O}}$$

$$P_{\text{H}_2\text{O}} = K_p = e^{-\frac{\Delta G^\circ}{RT}} = e^{-\frac{-8.6 \times 10^3}{(8.314 \text{ J/K-mol})(298 \text{ K})}} = e^{-3.47} = 3.1 \times 10^{-2} \text{ atm}$$

(b) What does the value of $K_p$ imply about the favorability of the forward reaction at this temperature? How is this consistent with increasing vapor pressure as T increases to the boiling point (think about the signs of $\Delta H^\circ$ and $\Delta S^\circ$)?

The positive value of $\Delta G^\circ$ implies that reactants are favored at equilibrium at 25°C. This process becomes more spontaneous as T increases because $\Delta S^\circ$ is positive, so the $-T\Delta S^\circ$ term becomes more negative as T increases, slowly overcoming the endothermic $\Delta H^\circ$. At the boiling point, $\Delta H^\circ = T\Delta S^\circ$, $\Delta G^\circ = 0$, and the system is at equilibrium.

18.36 In the metabolism of glucose, the first step is the conversion of glucose to glucose 6-phosphate:

$$\text{glucose} + \text{H}_3\text{PO}_4 \rightarrow \text{glucose 6-phosphate} + \text{H}_2\text{O} \quad \Delta G^\circ = 13.4 \text{ kJ/mol}$$

Because $\Delta G^\circ$ is positive, this reaction does not favor the formation of products. Show how this reaction can be made to proceed by coupling it with the hydrolysis of ATP (see #35).

(a) Write an equation for the coupled reaction and determine the value of $\Delta G^\circ$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>glucose + H$_3$PO$_4$ → glucose 6-phosphate + H$_2$O</td>
<td>13.4 kJ/mol</td>
</tr>
<tr>
<td>ATP + H$_2$O → ADP + H$_3$PO$_4$</td>
<td>−31 kJ/mol</td>
</tr>
<tr>
<td>glucose + ATP → glucose 6-phosphate + ADP</td>
<td>$\Delta G^\circ = 13.4 \text{ kJ/mol} + (-31 \text{ kJ/mol}) = -18 \text{ kJ/mol}$</td>
</tr>
</tbody>
</table>

(b) Estimate the equilibrium constant for the coupled process.

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-18 \times 10^3 \text{ J/mol})}{(8.314 \text{ J/K-mol})(298 \text{ K})} = 7.3, \text{ so } K = e^{-\frac{(-18 \times 10^3 \text{ J/mol})}{(8.314 \text{ J/K-mol})(298 \text{ K})}} = 1.4 \times 10^3$$