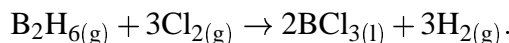# Chemistry 2720 Fall 2001 Assignment 6 Solutions

1. (a) The reaction is spontaneous (i.e. thermodynamics predicts that it will proceed) if the free energy change is negative. The balanced reaction is

$$B_2H_{6(g)} + 3Cl_{2(g)} \rightarrow 2BCl_{3(l)} + 3H_{2(g)}.$$

For this reaction,

$$
\begin{aligned}
\Delta \bar{G}^\circ &= 2\Delta \bar{G}^\circ_{f(BCl_{3(l)})} + 3\Delta \bar{G}^\circ_{f(H_2)} - \left(\Delta \bar{G}^\circ_{f(B_2H_6)} + 3\Delta \bar{G}^\circ_{f(Cl_2)} \right) \\
&= 2(-387) + 3(0) - [86.7 + 3(0)] \, \text{kJ/mol} \\
&= -861 \, \text{kJ/mol}.
\end{aligned}
$$

Because the pressures are all given in bars and the standard pressure is 1 bar, the activities of the gases are numerically equal to the pressures. The activity of liquid BCl_3 is 1 since no solutes are mentioned.

$$
\begin{aligned}
\Delta \bar{G} &= \Delta \bar{G}^\circ + RT \ln Q \\
&= \Delta \bar{G}^\circ + RT \ln \left(\frac{(a_{BCl_{3(l)}})^2 (a_{H_2})^3}{(a_{B_2H_6})(a_{Cl_2})^3} \right) \\
&= -861 \, \text{kJ/mol} + (8.314\,510 \times 10^{-3} \, \text{kJ K}^{-1}\text{mol}^{-1})(298.15\,\text{K}) \ln \left(\frac{(1)^2(0.03)^3}{(0.5)(0.5)^3} \right) \\
&= -880 \, \text{kJ/mol}.
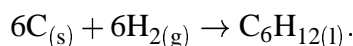\end{aligned}
$$

Since $\Delta \bar{G}$ is negative, the reaction is spontaneous under the stated conditions and could in principle be used to produce boron trichloride.

(b)

$$
\begin{aligned}
\Delta \bar{H}^\circ &= 2\Delta \bar{H}^\circ_{f(BCl_{3(l)})} + 3\Delta \bar{H}^\circ_{f(H_2)} - \left(\Delta \bar{H}^\circ_{f(B_2H_6)} + 3\Delta \bar{H}^\circ_{f(Cl_2)} \right) \\
&= 2(-427) + 3(0) - [36 + 3(0)] \, \text{kJ/mol} \\
&= -890 \, \text{kJ/mol}.
\end{aligned}
$$

$$
\therefore \Delta \bar{S}^\circ = \frac{\Delta \bar{H}^\circ - \Delta \bar{G}^\circ}{T} = \frac{-890 - (-861)\,\text{kJ/mol}}{298.15\,\text{K}} = -0.0983 \, \text{kJ K}^{-1}\text{mol}^{-1}.
$$

$$
\therefore \Delta \bar{G}^\circ_{263.15} \approx -890 \, \text{kJ/mol} - (263.15\,\text{K})(-0.0983\,\text{kJ K}^{-1}\text{mol}^{-1}) = -864 \, \text{kJ/mol}.
$$

$$
\begin{aligned}
\therefore \Delta \bar{G} &= \Delta \bar{G}^\circ + RT \ln \left(\frac{(a_{BCl_{3(l)}})^2 (a_{H_2})^3}{(a_{B_2H_6})(a_{Cl_2})^3} \right) \\
&= -864 \, \text{kJ/mol} \\
&\quad + (8.314\,510 \times 10^{-3} \, \text{kJ K}^{-1}\text{mol}^{-1})(263.15\,\text{K}) \ln \left(\frac{(1)^2(0.03)^3}{(0.5)(0.5)^3} \right) \\
&= -881 \, \text{kJ/mol}.
\end{aligned}
$$

The free energy change is still negative, so the reaction is still spontaneous at this temperature.
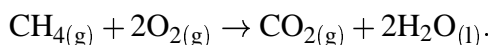
2. The formation reaction is
$$6C_{(s)} + 6H_{2(g)} \rightarrow C_6H_{12(l)}.$$

We know that $\Delta \bar{G}^{\phi} = 26.7\,\text{kJ/mol}$ and we want to calculate $\Delta \bar{G}^{\circ}$. $\Delta \bar{G}^{\phi}$ is the free energy change when the gases have an activity of $1\,\text{atm}/1\,\text{bar} = 1.013\,25$ and all other species are at unit activity. Therefore

$$
\begin{aligned}
\Delta \bar{G}^{\circ} &= \Delta \bar{G}^{\phi} - RT \ln \left(\frac{a_{C_6H_{12}}}{(a_C)^6 (a_{H_2})^6} \right) \\
&= \Delta \bar{G}^{\phi} - RT \ln \left(\frac{1}{(1)^6 (1.013\,25)^6} \right) \\
&= 26.7\,\text{kJ/mol} - (8.314\,510 \times 10^{-3}\,\text{kJ}\,\text{K}^{-1}\text{mol}^{-1})(298.15\,\text{K}) \ln \left(\frac{1}{(1.013\,25)^6} \right) \\
&= 26.9\,\text{kJ/mol}.
\end{aligned}
$$

3. (a) The overall reaction is
$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}.$$

The maximum electrical work is the change in the Gibbs free energy:

$$\Delta \bar{G} = \Delta \bar{G}^{\circ} + RT \ln Q = \Delta \bar{G}^{\circ} + RT \ln \left(\frac{(a_{CO_2})(a_{H_2O_{(l)}})^2}{(a_{CH_4})(a_{O_2})^2} \right).$$

For this reaction,

$$
\begin{aligned}
\Delta \bar{G}^{\circ} &= \Delta \bar{G}^{\circ}_{f(CO_2)} + 2\Delta \bar{G}^{\circ}_{f(H_2O_{(l)})} - \left(\Delta \bar{G}^{\circ}_{f(CH_4)} + 2\Delta \bar{G}^{\circ}_{f(O_2)} \right) \\
&= -394.37 + 2(-237.140) - [-50.72 + 2(0)]\,\text{kJ/mol} \\
&= -817.93\,\text{kJ/mol}.
\end{aligned}
$$

The activities of the gases are all calculated by $a_i = P_i/P^{\circ}$, where $P^{\circ} = 1\,\text{bar}$. Since pure water is assumed, the activity of the liquid water is 1. Thus we have

$$
\begin{aligned}
\Delta \bar{G} &= -817.93\,\text{kJ/mol} \\
&\quad + (8.314\,510 \times 10^{-3}\,\text{kJ}\,\text{K}^{-1}\text{mol}^{-1})(298.15\,\text{K}) \ln \left(\frac{(0.0003)(1)^2}{(0.7)(0.2)^2} \right) \\
&= -829.18\,\text{kJ/mol}.
\end{aligned}
$$

A methane fuel cell operating under these conditions might therefore produce as much as 829.18 kJ/mol of methane oxidized.

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(b) The activity of a solvent like water is (to a first approximation) its mole fraction. In a concentrated solution, the mole fraction of water would be significantly less than 1. This would reduce Q which would make $\Delta \bar{G}$ more negative. In other words, more useful work could be produced.

Note: If you have trouble following this argument, try a few calculations with $a_{H_2O} < 1$.

(c) If we reduce the partial pressure of oxygen, we increase Q. Increasing Q makes $\Delta \bar{G}$ less negative. In other words, less useful work could be obtained.

(d) If we burn methane in a heat engine, the amount of work obtained is $\eta \bar{q}_{comb}$, where $\bar{q}_{comb}$ is the molar heat of combustion of methane under the reaction conditions and η is the efficiency of the heat engine. For any real heat engine, $\eta < 1$. The heat of combustion of course depends on a number of factors (temperature, whether the reaction is at constant pressure or volume, etc.). However, we can get a rough idea of the magnitude of this number by computing the standard enthalpy of combustion, which tells us the heat of combustion at $25°C$ and 1 bar constant pressure. This is

$$
\begin{aligned}
\Delta \bar{H}° &= \Delta \bar{H}°_{f(CO_2)} + 2\Delta \bar{H}°_{f(H_2O_{(l)})} - \left(\Delta \bar{H}°_{f(CH_4)} + 2\Delta \bar{H}°_{f(O_2)} \right) \\
&= -393.51 + 2(-285.830) - [-74.81 + 2(0)] \, \text{kJ/mol} \\
&= -890.36 \, \text{kJ/mol}.
\end{aligned}
$$

This particular reaction generates a little more heat than free energy. However, just to match the power output of the fuel cell calculated in question 3a, the efficiency of the heat engine would have to be

$$
\eta = \frac{829.18 \, \text{kJ/mol}}{890.36 \, \text{kJ/mol}} = 0.931.
$$

This is an extraordinarily high efficiency for a heat engine. It requires the ratio of the upper and lower operating temperatures to be $T_{low}/T_{high} = 0.069$. For instance, if the upper operating temperature is $800\,K$ (which would of course require a recalculation of $\Delta \bar{H}$), the lower temperature would have to be $55\,\text{K}$ ($-218°C$). In order for the lower temperature to approach room temperature (293 K), the upper temperature would have to be over $4000\,\text{K}$. All of these calculations assume that both the fuel cell and heat engine operate at the maximum theoretical efficiency, but it does give us some idea of the relative efficiencies of the two kinds of machines. The answer is therefore that while it is theoretically possible for a heat engine burning methane to operate with a similar or better efficiency as a methane fuel cell, the required operating conditions for the heat engine make it impractical. A fuel cell is therefore a better alternative environmentally since it will use less fuel (and thus produce less of the greenhouse gas carbon dioxide) to produce a given amount of work.