# Chemistry 2720 Fall 2002 Test 1 Solutions

1.

$$
\begin{aligned}
dw &= -P_{\text{ext}}\,dV, \text{ but in a reversible process, } P_{\text{ext}} = P, \\
\therefore w &= -\int_{V_i}^{V_f} P\,dV = -nRT\int_{V_i}^{V_f}\frac{dV}{V} = -nRT\ln\left(\frac{V_f}{V_i}\right) = nRT\ln\left(\frac{V_i}{V_f}\right). \\
T &= 300 + 273.15\,\text{K} = 573.15\,\text{K}. \\
V_i &= \frac{1\,\text{L}}{1000\,\text{L/m}^3} = 1\times 10^{-3}\,\text{m}^3. \\
V_f &= \frac{30\times 10^{-3}\,\text{L}}{1000\,\text{L/m}^3} = 3.0\times 10^{-5}\,\text{m}^3. \\
\therefore w &= (8\,\text{mol})(8.314472\,\text{J K}^{-1}\text{mol}^{-1})(573.15\,\text{K})\ln\left(\frac{1\times 10^{-3}\,\text{m}^3}{3.0\times 10^{-5}\,\text{m}^3}\right) \\
&= 1.3\times 10^5\,\text{J}.
\end{aligned}
$$

The work is positive, which indicates that work is being done *on* the system, which makes sense since the gas is being compressed.

2. The reaction is

$$
\text{CaO}_{(s)} + \text{CO}_{2(g)} \rightarrow \text{CaCO}_{3(s)}.
$$
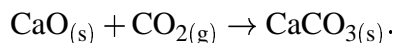
The heat at constant volume is ΔE. To get ΔE, we first calculate $\Delta \bar{H}$.

$$
\begin{aligned}
\Delta\bar{H} &= \Delta\bar{H}^{\circ}_{f(\text{CaCO}_3)} - \left(\Delta\bar{H}^{\circ}_{f(\text{CaO})} + \Delta\bar{H}^{\circ}_{f(\text{CO}_2)}\right) \\
&= -1206.9 - [-634.92 + (-393.51)]\,\text{kJ/mol} = -178.5\,\text{kJ/mol}. \\
\Delta\bar{n}_{\text{gas}} &= 0 - 1 = -1. \\
\therefore \Delta\bar{E} &= \Delta\bar{H} - RT\Delta\bar{n}_{\text{gas}} \\
&= -178.5\,\text{kJ/mol} - (8.314472\times 10^{-3}\,\text{kJ K}^{-1}\text{mol}^{-1})(298.15\,\text{K})(-1) \\
&= -176.0\,\text{kJ/mol}. \\
n_{\text{CaO}} &= \frac{18\,\text{g}}{56.077\,\text{g/mol}} = 0.32\,\text{mol}. \\
\therefore q &= \Delta E = n\Delta\bar{E} \\
&= (0.32\,\text{mol})(-176.0\,\text{kJ/mol}) = -56.5\,\text{kJ}.
\end{aligned}
$$

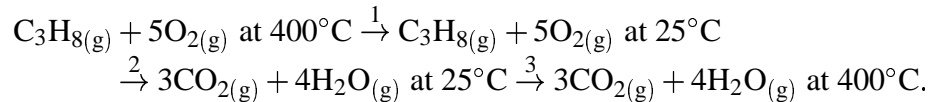q is negative, therefore heat is produced in the course of this reaction.

3. The reaction is
$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}.$$
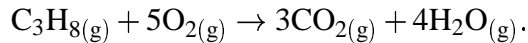
At 25°C, we have

$$
\begin{aligned}
\Delta\bar{H}_{25} &= 3\Delta\bar{H}^{\circ}_{f(CO_2)} + 4\Delta\bar{H}^{\circ}_{f(H_2O)} - \Delta\bar{H}^{\circ}_{f(C_3H_8)} \\
&= 3(-393.51) + 4(-241.826) - (-103.85)\,\mathrm{kJ/mol} = -2043.98\,\mathrm{kJ/mol}.
\end{aligned}
$$

To calculate the heat at 400°C, we imagine the following sequence of steps:

$$C_3H_{8(g)} + 5O_{2(g)} \text{ at } 400°C \xrightarrow{1} C_3H_{8(g)} + 5O_{2(g)} \text{ at } 25°C$$
$$\xrightarrow{2} 3CO_{2(g)} + 4H_2O_{(g)} \text{ at } 25°C \xrightarrow{3} 3CO_{2(g)} + 4H_2O_{(g)} \text{ at } 400°C.$$

We can calculate $\Delta\bar{H}$ for each of the steps:

$$
\begin{aligned}
\Delta\bar{H}_1 &= \left(\bar{C}_{P(C_3H_8)} + 5\bar{C}_{P(O_2)}\right)\Delta T_1 \\
&= \left[73.6 + 5(29.35)\,\mathrm{J\,K^{-1}mol^{-1}}\right](25 - 400°C) \\
&= -82.63\,\mathrm{kJ/mol}. \\
\Delta\bar{H}_2 &= \Delta\bar{H}_{25} = -2043.98\,\mathrm{kJ/mol}. \\
\Delta\bar{H}_3 &= \left(3\bar{C}_{P(CO_2)} + 4\bar{C}_{P(H_2O)}\right)\Delta T_2 \\
&= \left[3(37.1) + 4(33.58)\,\mathrm{J\,K^{-1}mol^{-1}}\right](400 - 25°C) \\
&= 92.11\,\mathrm{kJ/mol} \\
\therefore \Delta\bar{H}_{400} &= -82.63 + (-2043.98) + 92.11\,\mathrm{kJ/mol} = -2034.50\,\mathrm{kJ/mol}.
\end{aligned}
$$

The reaction liberates less heat ($\Delta\bar{H}$ is less negative) at 400°C.

4. At least some of the ice will melt. This will cool the dichloroacetic acid (DCA). We first need to determine if the DCA will reach its freezing point. The thermodynamic data for DCA is given on a molar basis, so we will need to determine the number of moles of DCA:

$$n_{DCA} = \frac{150\,g}{128.94\,g/mol} = 1.16\,mol.$$

To get from its initial temperature to its freezing point, the DCA will release

$$
\begin{aligned}
q_{293.15 \to 286.5} &= n_{DCA}\bar{C}_{P(DCA_{(l)})}\Delta T \\
&= (1.16\,mol)(207\,\mathrm{J\,K^{-1}mol^{-1}})(286.5 - 293.15\,K) \\
&= -1601\,J.
\end{aligned}
$$

On the other hand, 50 g of ice can absorb

$$q_{\text{melt 50g ice}} = (333.4\,J/g)(50\,g) = 16\,670\,J$$

while melting. The DCA will clearly reach its melting point. Will it all freeze?

$$q_{\text{freeze 150g DCA}} = (1.16\,\text{mol})(-12.34\,\text{kJ/mol}) = -14\,355\,\text{J}.$$

The sum of the heats released by cooling and freezing the DCA are

$$q_{\text{liquid DCA@293.15}^\circ \rightarrow \text{solid DCA@286.5}} = -1601 + (-14\,355)\,\text{J} = -15\,957\,\text{J}.$$

This is just slightly *less* than the amount of heat absorbed by melting 50 g of ice. This means that all the DCA will freeze. However, it now seems likely that all of the ice will melt as well. To verify this, we calculate the heat required to cool all of the DCA down to 0°C from its freezing point:

$$
\begin{aligned}
q_{\text{cool 150g solid DCA to 0}^\circ} &= n_{\text{DCA}}\bar{C}_{P(\text{DCA}_{(s)})}\Delta T \\
&= (1.16\,\text{mol})(182.30\,\text{J}\,\text{K}^{-1}\text{mol}^{-1})(273.15 - 286.5\,\text{K}) \\
&= -2831\,\text{J}.
\end{aligned}
$$
$$\therefore q_{\text{liquid DCA@293.15}^\circ \rightarrow \text{solid DCA@273.15}} = -1601 + (-14\,355) + (-2831)\,\text{J} = -18\,788\,\text{J}.$$

There clearly isn't enough heat to be liberated by melting the ice to cool the liquid DCA, freeze it, and then cool all of the solid DCA to zero. This means that all of the ice will melt. The final state of the system will consist of 150 g solid DCA and 50 g liquid water at a temperature between the freezing points of water and DCA. We just need to solve for the final temperature T_f. The heat balance equation to be solved is

$$
\begin{aligned}
q = 0 &= \left\{ \begin{array}{c} \text{cool} \\ \text{liquid DCA} \end{array} \right\} + \left\{ \text{freeze DCA} \right\} + \left\{ \begin{array}{c} \text{cool} \\ \text{solid DCA} \end{array} \right\} \\
&\quad + \left\{ \text{melt ice} \right\} + \left\{ \begin{array}{c} \text{warm} \\ \text{liquid water} \end{array} \right\} \\
&= -1601\,\text{J} + (-14\,355\,\text{J}) + n_{\text{DCA}}\bar{C}_{P(\text{DCA}_{(s)})}(T_f - 286.5\,\text{K}) \\
&\quad + 16\,670\,\text{J} + m_{\text{H}_2\text{O}}\tilde{C}_{P(\text{H}_2\text{O}_{(l)})}(T_f - 273.15\,\text{K}).
\end{aligned}
$$
$$\therefore 421 T_f = 117\,189.$$
$$\therefore T_f = 278\,\text{K}.$$