Chemistry 2740 Spring 2022 Test 1 Solutions

1. (a) Since the process is adiabatic, $q = 0$.

   (b) Since the external pressure is constant, $w = -p_{\text{ext}}\Delta V$. We need all of the relevant quantities in SI units to do this calculation.

$$\begin{aligned} p_{\text{ext}} &= (1.18\,\text{bar})(10^5\,\text{Pa}\,\text{bar}^{-1}) = 1.18 \times 10^5\,\text{Pa} \\ V_i &= \frac{10.0\,\text{L}}{1000\,\text{L}\,\text{m}^{-3}} = 0.0100\,\text{m}^3 \\ V_f &= \frac{20.0\,\text{L}}{1000\,\text{L}\,\text{m}^{-3}} = 0.0200\,\text{m}^3 \\ w &= -(1.18 \times 10^5\,\text{Pa})(0.0200 - 0.0100\,\text{m}^3) \\ &= -1.18 \times 10^3\,\text{J} \equiv -1.18\,\text{kJ} \end{aligned}$$

   (c) $\Delta U = q + w = -1.18\,\text{kJ}$

2. To get from liquid dodecane at $T_1 = 298.15\,\text{K}$ to the solid at $T_2 = 263.1\,\text{K}$, we need to first cool the liquid to the melting point, and then freeze the liquid. Thus,

$$\begin{aligned} S^\circ(\text{s}, 263.1\,\text{K}) &= S^\circ(\text{l}, 298.15\,\text{K}) + \Delta_{298\to263}S^\circ + \Delta_{\text{freeze}}S^\circ \\ \Delta_{298\to263}S^\circ &= \int_{T_1}^{T_2} \frac{C_{p,m}dT}{T} = C_{p,m}\ln\left(\frac{T_2}{T_1}\right) \\ &= \left(375.1\,\text{J}\,\text{K}^{-1}\text{mol}^{-1}\right)\ln\left(\frac{263.1\,\text{K}}{298.15\,\text{K}}\right) \\ &= -46.91\,\text{J}\,\text{K}^{-1}\text{mol}^{-1} \\ \Delta_{\text{freeze}}S^\circ &= \frac{\Delta_{\text{freeze}}H^\circ}{T_2} \\ &= \frac{-35.7 \times 10^3\,\text{J}\,\text{mol}^{-1}}{263.1\,\text{K}} = -136\,\text{J}\,\text{K}^{-1}\text{mol}^{-1} \\ \therefore S^\circ(\text{s}, 263.1\,\text{K}) &= 490.66 - 46.91 - 136\,\text{J}\,\text{K}^{-1}\text{mol}^{-1} \\ &= 308\,\text{J}\,\text{K}^{-1}\text{mol}^{-1} \end{aligned}$$

3. (a) Muscle work is non-pV work, which we get from ΔG. The balanced reaction is

$$\text{C}_{12}\text{H}_{22}\text{O}_{11(\text{aq})} + 12\,\text{O}_{2(\text{aq})} \rightarrow 12\,\text{CO}_{2(\text{aq})} + 11\,\text{H}_2\text{O}_{(\text{l})}$$

$$\begin{aligned} \Delta_r G_m^\circ &= 12\Delta_f G^\circ(\text{CO}_2, \text{aq}) + 11\Delta_f G^\circ(\text{H}_2\text{O}) - [\Delta_f G^\circ(\text{sucrose}, \text{aq}) + 12\Delta_f G^\circ(\text{O}_2, \text{aq})] \\ &= 12(-386.05) + 11(-237.140) - [-1550.89 + 12(16.35)]\ \text{kJ}\,\text{mol}^{-1} \\ &= -5886.45\,\text{kJ}\,\text{mol}^{-1} \end{aligned}$$

We will be using the equation

$$\Delta_r G_m = \Delta_r G_m^\circ + RT \ln Q.$$

To calculate Q, note that the concentrations are given in $\mathrm{mmol\,L^{-1}}$. The standard concentration is $1\,\mathrm{mol\,L^{-1}}$, so we need to make sure that the two are in the same units to calculate activities, e.g.

$$a_{\text{sucrose}} = \frac{[\text{sucrose}]}{c^\circ} = \frac{2.2 \times 10^{-3}\,\mathrm{mol\,L^{-1}}}{1\,\mathrm{mol\,L^{-1}}} = 2.2 \times 10^{-3}.$$

Therefore,

$$\begin{aligned}
\Delta_r G_m &= \Delta_r G_m^\circ + RT \ln\left(\frac{(a_{\mathrm{CO_2}})^{12}(a_{\mathrm{H_2O}})^{11}}{a_{\text{sucrose}}(a_{\mathrm{O_2}})^{12})}\right)\\
&= -5886.45\,\mathrm{kJ\,mol^{-1}}\\
&\qquad + (8.314472 \times 10^{-3}\,\mathrm{kJ\,K^{-1}mol^{-1}})(298.15\,\mathrm{K}) \ln\left(\frac{(25 \times 10^{-3})^{12}(1)^{11}}{(2.2 \times 10^{-3})(1.2 \times 10^{-3})^{12}}\right)\\
&= -5780.95\,\mathrm{kJ\,mol^{-1}}\\
n_{\text{sucrose}} &= \frac{33\,\mathrm{g}}{342.30\,\mathrm{g\,mol^{-1}}} = 0.096\,\mathrm{mol}\\
\Delta_r G &= n_{\text{sucrose}} \Delta_r G_m\\
&= (0.096\,\mathrm{mol})(-5780.95\,\mathrm{kJ\,mol^{-1}})\\
&= -557\,\mathrm{kJ}
\end{aligned}$$

The maximum work that could be performed is therefore 557 kJ.

(b)

$$\begin{aligned}
w &= mgh\\
\therefore h &= \frac{w}{mg} = \frac{557 \times 10^3\,\mathrm{J}}{(90\,\mathrm{kg})(9.806\,65\,\mathrm{m\,s^{-2}})}\\
&= 631\,\mathrm{m}
\end{aligned}$$

It's 2.7 m between the ground and second floors in my house, so that's over 200 trips up the stairs... Of course, that's a ridiculous oversimplification of how the body uses energy, but it does give you an idea of how much free energy is stored in that mocha.

(c) The Gibbs free energy is a state function. The change in a state function only depends on the overall change, and not on how that change was accomplished.

Bonus: The biggest issue is that we need $\Delta_r G^\circ$ at 37 °C ≡ 310.15 K. To get this, we first need to calculate $\Delta_r H_m^\circ$ and $\Delta_r S_m^\circ$:

$$\Delta_r H_m^\circ = 12\Delta_f H^\circ(\mathrm{CO_2}, \mathrm{aq}) + 11\Delta_f H^\circ(\mathrm{H_2O}) - [\Delta_f H^\circ(\text{sucrose}, \mathrm{aq}) + 12\Delta_f H^\circ(\mathrm{O_2}, \mathrm{aq})]$$

$$\begin{aligned}
&= 12(-413.26) + 11(-285.830) - [-2215.85 + 12(-12.09)]\ \mathrm{kJ\,mol^{-1}}\\
&= -5742.32\,\mathrm{kJ\,mol^{-1}}\\
\Delta_r S_m^\circ &= \frac{\Delta_r H_m^\circ - \Delta_r G_m^\circ}{T}\\
&= \frac{-5742.32\,\mathrm{kJ\,mol^{-1}} - (-5886.45\,\mathrm{kJ\,mol^{-1}})}{298.15\,\mathrm{K}}\\
&= 0.483\,41\,\mathrm{kJ\,K^{-1}mol^{-1}}\\
\therefore \Delta_r G_{m,37}^\circ &= \Delta_r H_m^\circ - T\Delta_r S_m^\circ\\
&= -5742.32\,\mathrm{kJ\,mol^{-1}} - (310.15\,\mathrm{K})(0.483\,41\,\mathrm{kJ\,K^{-1}mol^{-1}})\\
&= -5892.25\,\mathrm{kJ\,mol^{-1}}\\
\Delta_r G_m &= \Delta_r G_m^\circ + RT\ln\left(\frac{(a_{\mathrm{CO_2}})^{12}(a_{\mathrm{H_2O}})^{11}}{a_{\mathrm{sucrose}}(a_{\mathrm{O_2}})^{12})}\right)\\
&= -5892.25\,\mathrm{kJ\,mol^{-1}}\\
&\qquad + (8.314472\times10^{-3}\,\mathrm{kJ\,K^{-1}mol^{-1}})(310.15\,\mathrm{K})\ln\left(\frac{(25\times10^{-3})^{12}(1)^{11}}{(2.2\times10^{-3})(1.2\times10^{-3})^{12}}\right)\\
&= -5782.51\,\mathrm{kJ\,mol^{-1}}\\
\Delta_r G &= n_{\mathrm{sucrose}}\Delta_r G_m\\
&= (0.096\,\mathrm{mol})(-5782.51\,\mathrm{kJ\,mol^{-1}})\\
&= -557\,\mathrm{kJ}\\
h &= \frac{w}{mg} = \frac{557\times10^3\ \mathrm{J}}{(90\,\mathrm{kg})(9.806\,65\,\mathrm{m\,s^{-2}})}\\
&= 632\,\mathrm{m}
\end{aligned}$$

Since there are only two significant figures in this calculation (limited by the number of significant figures in the mass), the difference is completely negligible, as it turns out.

4. (a) The heat balance for a bomb calorimeter is

$$q = 0 = \left\{\begin{array}{c}\text{combustion}\\ \text{of tyrosine}\end{array}\right\} + \left\{\begin{array}{c}\text{combustion}\\ \text{of fuse wire}\end{array}\right\} + \left\{\begin{array}{c}\text{warming of}\\ \text{calorimeter}\end{array}\right\}$$

Recasting this relationship in symbolic form, we have

$$n_{\mathrm{tyrosine}}\Delta_c U_m^\circ + \ell\Delta_c u_{\mathrm{fuse}} + C_V\Delta T = 0.$$

We can rearrange this equation to solve for the molar energy of combustion of tyrosine. We will also need the number of moles of tyrosine.

$$\begin{aligned}
n_{\mathrm{tyrosine}} &= \frac{1.0832\,\mathrm{g}}{181.1885\,\mathrm{g\,mol^{-1}}}\\
&= 0.005\,9783\,\mathrm{mol}
\end{aligned}$$

$$\begin{aligned}\Delta_c U_m^\circ &= \frac{-\left(\ell\Delta_c u_{\text{fuse}} + C_V\Delta T\right)}{n_{\text{tyrosine}}}\\ &= \frac{-\left[(10.3\,\text{cm})(-9.6\times10^{-3}\,\text{kJ}\,\text{cm}^{-1}) + (10.84\,\text{kJ}\,\text{K}^{-1})(2.436\,\text{K})\right]}{0.005\,9783\,\text{mol}}\\ &= -4400\,\text{kJ}\,\text{mol}^{-1}\end{aligned}$$

To get from a ΔU to a ΔH we need a balanced reaction:

$$\text{C}_9\text{H}_{11}\text{NO}_{3(\text{s})} + \frac{41}{2}\,\text{O}_{2(\text{g})} \to 9\,\text{CO}_{2(\text{g})} + \frac{11}{2}\,\text{H}_2\text{O}_{(\text{l})} + \frac{1}{2}\,\text{N}_{2(\text{g})}$$

$$\begin{aligned}\Delta_c H_m^\circ &= \Delta_c U_m^\circ + RT\Delta_r\nu_{\text{gas}}\\ \Delta_r\nu_{\text{gas}} &= 9 + \frac{1}{2} - \frac{41}{2} = -11\\ \therefore\ \Delta_c H_m^\circ &= -4400\,\text{kJ}\,\text{mol}^{-1} + (8.314472\times10^{-3}\,\text{kJ}\,\text{K}^{-1}\text{mol}^{-1})(298.15\,\text{K})(-11)\\ &= -4427\,\text{kJ}\,\text{mol}^{-1}\end{aligned}$$

(b)

$$\begin{aligned}\Delta_c H_m^\circ &= 9\,\Delta_f H^\circ(\text{CO}_2) + \frac{11}{2}\,\Delta_f H^\circ(\text{H}_2\text{O},\text{l}) - \Delta_f H^\circ(\text{C}_9\text{H}_{11}\text{NO}_3)\\ \therefore\ \Delta_f H^\circ(\text{C}_9\text{H}_{11}\text{NO}_3) &= 9\,\Delta_f H^\circ(\text{CO}_2) + \frac{11}{2}\,\Delta_f H^\circ(\text{H}_2\text{O},\text{l}) - \Delta_c H_m^\circ\\ &= 9(-393.51) + \frac{11}{2}(-285.830) - (-4427)\,\text{kJ}\,\text{mol}^{-1}\\ &= -686\,\text{kJ}\,\text{mol}^{-1}\end{aligned}$$