Chemistry 2740 Spring 2008 Test 1 Solutions

1. The system must only be capable of doing pressure-volume work, and be held at constant volume.

2. (a) True by convention
   (b) False. ΔS, without any special notations, usually refers specifically to the system. It is the entropy change of the universe as a whole which must increase.
   (c) True. This is a consequence of the third law.

3. There are no intermolecular forces in an ideal gas. If there are no forces acting at a distance, it does not matter how far apart the molecules are, and therefore the internal energy cannot depend on the volume.

4. (a)

$$\begin{aligned}
\Delta_r\bar{G} &= \Delta_r\bar{G}^{\circ\prime} + RT\ln Q' \\
&= \Delta_r\bar{G}^{\circ\prime} + RT\ln\left(\frac{a_{\text{3-phosphoglycerate}}}{(a_{\text{glycerol}})(a_{\mathrm{P_i}})}\right) \\
&= 10.0\,\mathrm{kJ/mol} + (8.314\,472\times10^{-3}\,\mathrm{kJ\,K^{-1}mol^{-1}})(298.15\,\mathrm{K}) \\
&\qquad \times\ln\left(\frac{0.35\times10^{-3}}{(1.0\times10^{-3})(18\times10^{-3})}\right) \\
&= 17.4\,\mathrm{kJ/mol}.
\end{aligned}$$

   $\Delta_r\bar{G} > 0$ therefore the reaction is *not* spontaneous.

   (b) In the biochemists' standard state, we do not distinguish between different ionization states of phosphate (PO_4^{3-}, HPO_4^{2-}, etc.).

5. The formation reaction is

$$\mathrm{U_{(s)} + O_{2(g)} + 2H^+_{(aq)} \to UO^{2+}_{2(aq)} + H_{2(g)}}.$$

   For this reaction,

$$\begin{aligned}
\Delta_f\bar{S}^\circ_{\mathrm{UO_2^{2+}}} &= \bar{S}^\circ_{\mathrm{UO_2^{2+}}} + \bar{S}^\circ_{\mathrm{H_2}} - \left(\bar{S}^\circ_{\mathrm{U}} + \bar{S}^\circ_{\mathrm{O_2}} + 2\bar{S}^\circ_{\mathrm{H^+}}\right) \\
&= -98.2 + 130.680 - [50.20 + 205.152 + 2(0)]\ \mathrm{J\,K^{-1}mol^{-1}} \\
&= -222.9\,\mathrm{J\,K^{-1}mol^{-1}}. \\
\therefore \Delta_f\bar{G}^\circ_{\mathrm{UO_2^{2+}}} &= \Delta_f\bar{H}^\circ_{\mathrm{UO_2^{2+}}} - T\Delta_f\bar{S}^\circ_{\mathrm{UO_2^{2+}}} \\
&= -1019.0\,\mathrm{kJ/mol} - (298.15\,\mathrm{K})(-0.2229\,\mathrm{kJ\,K^{-1}mol^{-1}}) \\
&= -952.6\,\mathrm{kJ/mol}.
\end{aligned}$$

6. (a) There are two possible values for each bit, so

$$\begin{aligned}
\Omega &= 2\times2\times2 = 2^3. \\
S &= k_B\ln\Omega = k_B\ln(2^3) = 3k_B\ln 2.
\end{aligned}$$

(b) If there are n bits, then $\Omega = 2^n$, so we get $S = nk_B \ln 2$.

(c) If we double the size of the system (in this case the number of random bits generated), the entropy should double. Note that S is proportional to the number of random bits, so the entropy of these n-bit random number generators is an extensive quantity.

7. (a) The process is

$$\mathrm{H_2O_{(l)}} \to \mathrm{H_2O_{(g)}}.$$

$$\begin{aligned}
\Delta_{\text{vap}}\bar{H}^\circ_{\mathrm{H_2O}} &= \Delta_f\bar{H}^\circ_{(\mathrm{g})} - \Delta_f\bar{H}^\circ_{(\mathrm{l})} \\
&= -241.826 - (-285.830)\,\mathrm{kJ/mol} = 44.004\,\mathrm{kJ/mol}. \\
n_{\mathrm{H_2O}} &= \frac{5000\,\mathrm{g/h}}{18.0153\,\mathrm{g/mol}} = 277.5\,\mathrm{mol/h}.
\end{aligned}$$

Note that the heat lost by the air is the negative of the heat gained by the water during the vaporization process:

$$\begin{aligned}
q_{\text{air}} &= -n_{\mathrm{H_2O}}\Delta_{\text{vap}}\bar{H}^\circ_{\mathrm{H_2O}} \\
&= -(277.5\,\mathrm{mol/h})(44.004\,\mathrm{kJ/mol}) \\
&= -12\,213\,\mathrm{kJ/h} \\
&= -12\,213\,\mathrm{kJ/h}\frac{1\,\mathrm{h}}{3600\,\mathrm{s}} = -3.392\,\mathrm{kW}.
\end{aligned}$$

(b)

$$\begin{aligned}
V &= (10\,\mathrm{m})(10\,\mathrm{m})(4\,\mathrm{m}) = 400\,\mathrm{m}^3. \\
n_{\text{air}} &= \frac{PV}{RT} \\
&= \frac{(100\times 10^3\,\mathrm{Pa})(400\,\mathrm{m}^3)}{(8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}})(291\,\mathrm{K})} \\
&= 16.5\,\mathrm{kmol}. \\
q_{\text{air}} &= n_{\text{air}}\bar{C}_p\Delta T. \\
\therefore \Delta T &= \frac{q_{\text{air}}}{n_{\text{air}}\bar{C}_p} \\
&= \frac{-12\,213\,\mathrm{kJ/h}}{(16.5\,\mathrm{kmol})(29\,\mathrm{J\,K^{-1}mol^{-1}})} \\
&= -25\,\mathrm{K/h}.
\end{aligned}$$

The temperature would decrease by 25 K per hour under these conditions.