

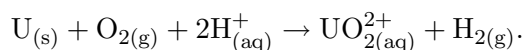
Chemistry 2740 Spring 2008 Test 1 Solutions

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)

$$\begin{aligned}
 \Delta_r \bar{G} &= \Delta_r \bar{G}^{\circ'} + RT \ln Q' \\
 &= \Delta_r \bar{G}^{\circ'} + RT \ln \left(\frac{a_{\text{3-phosphoglycerate}}}{(a_{\text{glycerol}})(a_{\text{P}_i})} \right) \\
 &= 10.0 \text{ kJ/mol} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \\
 &\quad \times \ln \left(\frac{0.35 \times 10^{-3}}{(1.0 \times 10^{-3})(18 \times 10^{-3})} \right) \\
 &= 17.4 \text{ kJ/mol.}
 \end{aligned}$$

$\Delta_r \bar{G} > 0$ 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



For this reaction,

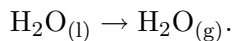
$$\begin{aligned}
 \Delta_f \bar{S}_{\text{UO}_2^{2+}}^{\circ} &= \bar{S}_{\text{UO}_2^{2+}}^{\circ} + \bar{S}_{\text{H}_2}^{\circ} - (\bar{S}_{\text{U}}^{\circ} + \bar{S}_{\text{O}_2}^{\circ} + 2\bar{S}_{\text{H}^+}^{\circ}) \\
 &= -98.2 + 130.680 - [50.20 + 205.152 + 2(0)] \text{ J K}^{-1} \text{ mol}^{-1} \\
 &= -222.9 \text{ J K}^{-1} \text{ mol}^{-1}. \\
 \therefore \Delta_f \bar{G}_{\text{UO}_2^{2+}}^{\circ} &= \Delta_f \bar{H}_{\text{UO}_2^{2+}}^{\circ} - T \Delta_f \bar{S}_{\text{UO}_2^{2+}}^{\circ} \\
 &= -1019.0 \text{ kJ/mol} - (298.15 \text{ K})(-0.2229 \text{ kJ K}^{-1} \text{ mol}^{-1}) \\
 &= -952.6 \text{ kJ/mol.}
 \end{aligned}$$

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

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

- (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



$$\begin{aligned}\Delta_{\text{vap}} \bar{H}_{\text{H}_2\text{O}}^\circ &= \Delta_f \bar{H}_{(\text{g})}^\circ - \Delta_f \bar{H}_{(\text{l})}^\circ \\ &= -241.826 - (-285.830) \text{ kJ/mol} = 44.004 \text{ kJ/mol.} \\ n_{\text{H}_2\text{O}} &= \frac{5000 \text{ g/h}}{18.0153 \text{ g/mol}} = 277.5 \text{ mol/h.}\end{aligned}$$

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

$$\begin{aligned}q_{\text{air}} &= -n_{\text{H}_2\text{O}} \Delta_{\text{vap}} \bar{H}_{\text{H}_2\text{O}}^\circ \\ &= -(277.5 \text{ mol/h})(44.004 \text{ kJ/mol}) \\ &= -12\,213 \text{ kJ/h} \\ &= -12\,213 \text{ kJ/h} \frac{1 \text{ h}}{3600 \text{ s}} = -3.392 \text{ kW.}\end{aligned}$$

- (b)

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

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