

Chemistry 2720 Fall 2001 Assignment 7 Solutions

1. (a) This is a fairly straightforward exercise, except that step 4 generates one equivalent of each of dihydroxyacetone phosphate and of glyceraldehyde-3-phosphate, the former being converted to the latter in step 5. Steps 4 and 5 can therefore be replaced by



We therefore need to double up all the following reactions in order to use up the glyceraldehyde-3-phosphate produced in these steps. The overall reaction is therefore found by adding the following reactions:

	$\Delta\bar{G}^{\circ'}$ (kJ/mol)
1. D-glucose + ATP \rightarrow D-glucose-6-phosphate + ADP	-16.7
2. D-glucose-6-phosphate \rightarrow D-fructose-6-phosphate	1.7
3. D-fructose-6-phosphate + ATP \rightarrow D-fructose-1,6-diphosphate + ADP	-14.2
4 + 5. D-fructose-1,6-diphosphate \rightarrow 2 glyceraldehyde-3-phosphate	31.3
6. 2 glyceraldehyde-3-phosphate + 2 phosphate + 2 NAD ⁺ \rightarrow 2 (1,3-diphosphoglycerate) + 2 NADH + 2 H ⁺	12.6
7. 2 (1,3-diphosphoglycerate) + 2 ADP \rightarrow 2 (3-phosphoglycerate) + 2 ATP	-37.6
8. 2 (3-phosphoglycerate) \rightarrow 2 (2-phosphoglycerate)	9.2
9. 2 (2-phosphoglycerate) \rightarrow 2 (2-phosphoenolpyruvate) + 2 H ₂ O	3.4
10. 2 (2-phosphoenolpyruvate) + 2 ADP \rightarrow 2 pyruvate + 2 ATP	-62.8
D-glucose + 2 phosphate + 2 NAD ⁺ + 2 ADP \rightarrow 2 pyruvate + 2 NADH + 2 H ⁺ + 2 ATP + 2 H ₂ O	-73.1

- (b) The reaction will produce the maximum ATP to ADP ratio when there is no excess free energy, i.e. when $\Delta\bar{G} = 0$.

$$\begin{aligned} \Delta\bar{G} &= \Delta\bar{G}^{\circ'} + RT \ln Q' = 0. \\ \therefore Q'_{\max} &= e^{-\Delta\bar{G}^{\circ'}/(RT)} = \exp\left(\frac{73100 \text{ J/mol}}{(8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right) \\ &= 6.40 \times 10^{12}. \end{aligned}$$

Since $Q' = \frac{(a'_{\text{pyr}})^2 (a'_{\text{NADH}})^2 (a'_{\text{H}^+})^2 (a'_{\text{ATP}})^2 (a'_{\text{H}_2\text{O}})^2}{(a'_{\text{gluc}}) (a'_{\text{P}_i})^2 (a'_{\text{NAD}^+})^2 (a'_{\text{ADP}})^2}$,

$$\left(\frac{a_{\text{ATP}}}{a_{\text{ADP}}}\right)^2 \Bigg|_{\max} = Q'_{\max} \frac{(a'_{\text{gluc}}) (a'_{\text{P}_i})^2}{(a'_{\text{pyr}})^2 (a'_{\text{H}^+})^2 (a'_{\text{H}_2\text{O}})^2} \left(\frac{a'_{\text{NAD}^+}}{a'_{\text{NADH}}}\right)^2.$$

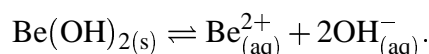
The terms appearing in this equation are mostly straightforward, except for the activity of H^+ . Since the pH is 7 in the biochemists' standard state, the standard concentration of protons is 10^{-7} mol/L. The activity of H^+ is therefore

$$a'_{H^+} = \frac{[H^+]}{10^{-7} \text{ mol/L}} = 1.$$

$$\therefore \left(\frac{a_{ATP}}{a_{ADP}} \right)_{\max}^2 = (6.40 \times 10^{12}) \frac{(0.01)(0.002)^2}{(6 \times 10^{-5})^2 (1)^2 (1)^2} (0.25)^2 = 4.44 \times 10^{14}.$$

$$\therefore \frac{a_{ATP}}{a_{ADP}}_{\max} = 2.11 \times 10^6.$$

2. (a) The solubility equilibrium is



When 4.3×10^{-8} mol/L of beryllium hydroxide dissolve in water, 8.6×10^{-8} mol/L of hydroxide ions are released. Since this is similar to the amount of hydroxide generated by the autoionization of water, we can't neglect either source of hydroxide.

(b) $[\text{OH}^-] = [\text{H}^+] + 2[\text{Be}^{2+}]$

- (c) Since $K_w = (a_{H^+})(a_{OH^-})$, the hydrogen ion concentration can be written as

$$[\text{H}^+] = \frac{K_w}{a_{OH^-}} c^\circ$$

where $c^\circ = 1$ mol/L is the standard concentration. Substituting this expression into the charge balance equation and recalling that $[\text{Be}^{2+}] = 4.3 \times 10^{-8}$ mol/L, we get

$$[\text{OH}^-] = \frac{K_w}{a_{OH^-}} c^\circ + 2[\text{Be}^{2+}].$$

$$\therefore 0 = [\text{OH}^-]^2 - 2[\text{Be}^{2+}][\text{OH}^-] - K_w c^\circ$$

$$= [\text{OH}^-]^2 - 8.6 \times 10^{-8} [\text{OH}^-] - 10^{-14}.$$

$$\therefore [\text{OH}^-] = \frac{1}{2} \left\{ 8.6 \times 10^{-8} \pm \sqrt{(8.6 \times 10^{-8})^2 - 4(-10^{-14})} \right\}$$

$$= 1.5 \times 10^{-7} \text{ mol/L}.$$

(d) $K_{sp} = (a_{\text{Be}^{2+}})(a_{\text{OH}^-})^2 = (4.3 \times 10^{-8})(1.5 \times 10^{-7})^2 = 9.9 \times 10^{-22}.$

- (e) Since the only source of beryllium ions in solution is the beryllium hydroxide, the solubility is just equal to the concentration of beryllium ions in solution.

$$a_{\text{Be}^{2+}} = \frac{K_{sp}}{(a_{\text{OH}^-})^2} = \frac{K_{sp}(a_{\text{H}^+})^2}{K_w^2} = \frac{K_{sp}(10^{-pH})^2}{K_w^2} = \frac{K_{sp}10^{-2pH}}{K_w^2}.$$

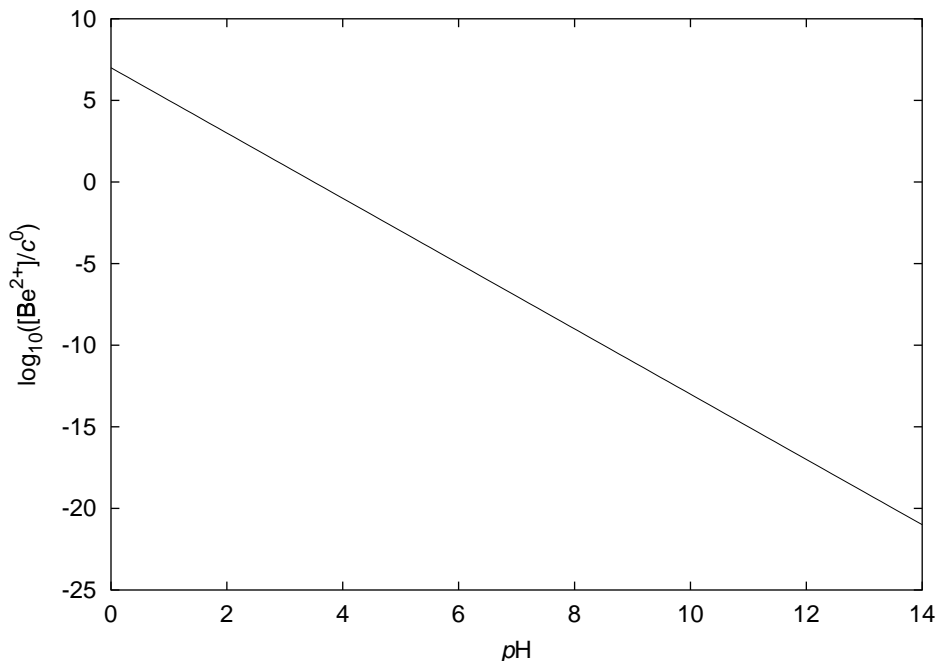
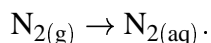


Figure 1: Base-10 logarithm of the solubility of $\text{Be}(\text{OH})_2$ in water at 25°C as a function of $p\text{H}$. Note that the solubilities at very low $p\text{H}$ are unrealistically high and would no doubt be limited by other factors than those considered in our calculation.

$$\begin{aligned} \therefore \log_{10} \left(\frac{[\text{Be}^{2+}]}{c^\circ} \right) &= \log_{10} \left(\frac{K_{\text{sp}}}{K_w^2} \right) - 2p\text{H} \\ &= 7.0 - 2p\text{H}. \end{aligned}$$

Remarkably, the relationship between solubility and $p\text{H}$ is linear. The result is shown in Fig. 1.

3. (a) Henry's law has to do with the equilibrium



Give or take the units, the Henry's law constant is the equilibrium constant for this process. Thus $K = 6.2 \times 10^{-4}$ and

$$\Delta \bar{G}^\circ = -RT \ln K = -(8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(6.2 \times 10^{-4}) = 18.3 \text{ kJ/mol}.$$

Since $\Delta \bar{G}^\circ = \Delta \bar{G}_{f(\text{aq})}^\circ - \Delta \bar{G}_{f(\text{g})}^\circ$ and the standard free energy of formation of gaseous N_2 is zero, $\Delta \bar{G}_{f(\text{aq})}^\circ = 18.3 \text{ kJ/mol}$.

- (b) Again, k_H is just an equilibrium constant. Equation 5.1 is (slightly rewritten)

$$\ln k_H - \ln k_{H(2)} = \frac{\Delta \bar{H}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \quad (5.1)$$

where $k_{H(2)}$ is the Henry's law constant at a reference temperature T_2 (e.g. 298.15 K). It follows, by direct evaluation of the derivative, that

$$\frac{d(\ln k_H)}{d(1/T)} = -\frac{\Delta\bar{H}^\circ}{R}.$$

Therefore,

$$\Delta\bar{H}^\circ = -(8.314510\text{JK}^{-1}\text{mol}^{-1})(1300\text{K}) = -10.8\text{kJ/mol}.$$

Again, since the enthalpy of formation of gaseous nitrogen is zero $\Delta\bar{H}_{f(\text{aq})}^\circ = -10.8\text{kJ/mol}$.

- (c) This is a straightforward application of equation 5.1. We know the Henry's law constant at 298.15 and $\Delta\bar{H}^\circ/R$, so we can calculate k_H at any other temperature:

$$\begin{aligned}\ln k_H &= \ln k_{H(298)} + \frac{\Delta\bar{H}^\circ}{R} \left(\frac{1}{298.15\text{K}} - \frac{1}{T} \right) \\ &= \ln(6.2 \times 10^{-4}) - (1300\text{K}) \left(\frac{1}{298.15\text{K}} - \frac{1}{310.15\text{K}} \right) \\ &= -7.55. \\ \therefore k_H &= e^{-7.55} = 5.2 \times 10^{-4} \text{molL}^{-1}\text{bar}^{-1}.\end{aligned}$$

- (d) $[\text{N}_2] = (5.2 \times 10^{-4} \text{molL}^{-1}\text{bar}^{-1})(5 \text{bar}) = 2.6 \times 10^{-3} \text{mol/L}$.

- (e) At 1 bar, the solubility is $5.2 \times 10^{-4} \text{mol/L}$. The difference between the solubilities at 5 and at 1 bar is therefore $2.1 \times 10^{-3} \text{mol/L}$. For 5.7 L of blood, this would represent

$$n_{\text{N}_2} = (2.1 \times 10^{-3} \text{mol/L})(5.7\text{L}) = 1.2 \times 10^{-2} \text{mol}.$$

This much gas at a pressure of 1 bar and a temperature of 37°C occupies a volume of

$$\begin{aligned}V &= \frac{nRT}{P} = \frac{(1.2 \times 10^{-2} \text{mol})(8.314510\text{JK}^{-1}\text{mol}^{-1})(310.15\text{K})}{100000\text{Pa}} = 3.08 \times 10^{-4} \text{m}^3. \\ &\equiv (3.08 \times 10^{-4} \text{m}^3)(100\text{cm/m})^3 = 308 \text{cm}^3.\end{aligned}$$

- (f) 308cm^3 is almost a third of a litre. Large bubbles will almost certainly be formed almost everywhere in the bloodstream. This could indeed cause serious problems.