

Chemistry 2740 Spring 2016 Test 3 solutions

1. (a) We are given $\Delta_r H^\circ$ and $\Delta_r S^\circ$, so we can directly calculate $\Delta_r G^\circ$ at 37°C :

$$\begin{aligned}\Delta_r G^\circ &= \Delta_r H^\circ - T\Delta_r S^\circ \\ &= -138 \text{ kJ mol}^{-1} - (310.15 \text{ K})(-0.305 \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= -43 \text{ kJ mol}^{-1}.\end{aligned}$$

$$\begin{aligned}\therefore K &= \exp\left(\frac{-\Delta_r G^\circ}{RT}\right) \\ &= \exp\left(\frac{43 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(310.15 \text{ K})}\right) \\ &= 2.0 \times 10^7.\end{aligned}$$

- (b) Because the standard state is 1 mol L^{-1} , we have to be careful to convert from $\mu\text{mol L}^{-1}$: I'm going to use an initial/change/final table here:

	Hp	Hb	Hp · Hb
Initial:	2.5×10^{-5}	6×10^{-6}	0
Change:	$-x$	$-x$	x
Final:	$2.5 \times 10^{-5} - x$	$6 \times 10^{-6} - x$	x

$$K = 2.0 \times 10^7 = \frac{a_{\text{Hp} \cdot \text{Hb}}}{(a_{\text{Hp}})(a_{\text{Hb}})} = \frac{x}{(2.5 \times 10^{-5} - x)(6 \times 10^{-6} - x)}.$$

I solved this equation using the equation solver in my calculator and got

$$x = 5.985 \times 10^{-6}.$$

The percentage of free hemoglobin is

$$\frac{6 \times 10^{-6} - x}{6 \times 10^{-6}} \times 100\% = 0.26\%.$$

If you're a bit more daring, you can short-cut this problem. The equilibrium constant is very large. Therefore, almost all of the Hb will be bound up by Hp. This implies that $[\text{Hp} \cdot \text{Hb}] \approx 6 \mu\text{mol L}^{-1}$ and $[\text{Hp}] \approx 25 - 6 \mu\text{mol L}^{-1} = 19 \mu\text{mol L}^{-1}$. Substituting these in the equilibrium relationship, we have

$$K = 2.0 \times 10^7 = \frac{a_{\text{Hp} \cdot \text{Hb}}}{(a_{\text{Hp}})(a_{\text{Hb}})} = \frac{6 \times 10^{-6}}{19 \times 10^{-6} a_{\text{Hb}}}.$$

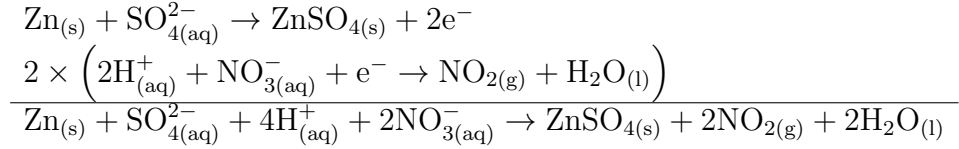
We solve this equation for a_{Hb} :

$$a_{\text{Hb}} = \frac{6 \times 10^{-6}}{(19 \times 10^{-6})(2.0 \times 10^7)} = 1.5 \times 10^{-8},$$

corresponding to 0.26% of the total hemoglobin.

Very little free hemoglobin remains in the bloodstream, so the danger posed by free hemoglobin is greatly reduced by haptoglobin.

2. (a)



(b) Electrons flow from the zinc to the platinum electrode.

(c)

$$\begin{aligned} \Delta_r G_m^\circ &= \Delta_f G^\circ(\text{ZnSO}_4) + 2\Delta_f G^\circ(\text{NO}_2) + 2\Delta_f G^\circ(\text{H}_2\text{O}) - [\Delta_f G^\circ(\text{SO}_4^{2-}) + 2\Delta_f G^\circ(\text{NO}_3^-)] \\ &= -874.4 + 2(51.32) + 2(-237.140) - [-744.00 + 2(-111.4)] \text{ kJ mol}^{-1} \\ &= -279.2 \text{ kJ mol}^{-1}. \end{aligned}$$

From the balancing, we have $\nu_e = 2$.

$$\begin{aligned} E^\circ &= -\Delta_r G_m^\circ / (\nu_e F) \\ &= \frac{279.2 \times 10^3 \text{ J mol}^{-1}}{(2)(96485.342 \text{ C mol}^{-1})} \\ &= 1.447 \text{ V}. \end{aligned}$$

(d) We need the activity of H^+ and NO_3^- in the right half-cell. (Look at where these species appear in the half-reactions.)

$$\begin{aligned} I_{c,\text{right}} &= \frac{1}{2} [(+1)^2(0.0078) + (-1)^2(0.0078)] \\ &= 0.0078 \text{ mol L}^{-1}. \end{aligned}$$

$$\begin{aligned} \ln \gamma_{\text{H}^+} &= -(1.107 \times 10^{-10})(+1)^2 [(6.939 \times 10^{-10})(298.15 \text{ K})]^{-3/2} \sqrt{0.0078 \text{ mol L}^{-1}} \\ &= -0.10. \end{aligned}$$

$$\therefore \gamma_{\text{H}^+} = e^{-0.10} = 0.90 = \gamma_{\text{NO}_3^-}.$$

The last equality holds because H^+ and NO_3^- have the same charge and are in the same solution (same ionic strength).

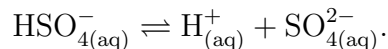
$$\therefore a_{\text{H}^+} = \gamma_{\text{H}^+}[\text{H}^+]/c^\circ = 0.90(0.0078) = 0.0070 = a_{\text{NO}_3^-}.$$

$$a_{\text{NO}_2} = p/p^\circ = \frac{0.38 \text{ bar}}{1 \text{ bar}} = 0.38.$$

$$\begin{aligned} E &= E^\circ - \frac{RT}{\nu_e F} \ln Q \\ &= E^\circ - \frac{RT}{\nu_e F} \ln \left(\frac{(a_{\text{NO}_2})^2}{(a_{\text{SO}_4^{2-}})(a_{\text{H}^+})^4(a_{\text{NO}_3^-})^2} \right) \\ &= 1.447 \text{ V} - \frac{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{(2)(96485.342 \text{ C mol}^{-1})} \ln \left(\frac{(0.38)^2}{(0.0013)(0.0070)^4(0.0070)^2} \right) \\ &= 1.004 \text{ V}. \end{aligned}$$

Bonus: Note that I'm going to give a lot more detail than I would have needed in order to award a bonus mark.

We need the activity of the sulfate ion. H_2SO_4 is a strong acid, but HSO_4^- is not. However, the $\text{p}K_a$ of the second proton is very low (1.96). A quick, back-of-the-envelope calculation should convince you that the pH will lie somewhere between 2.6 (full dissociation of the first proton) and 2.3 (full dissociation of both protons). This is close to the $\text{p}K_a$ so, in order to determine the concentration of free sulfate, we have to consider the equilibrium



Let's start with an initial/change/final table. The first proton of H_2SO_4 dissociates completely, leading to the first line of the table:

	HSO_4^-	H^+	SO_4^{2-}
Initial:	0.0025	0.0025	0
Change:	$-x$	$+x$	$+x$
Final:	$0.0025 - x$	$0.0025 + x$	x

Now let's develop the K_a expression for the second proton:

$$K_{a,2} = \frac{(a_{\text{H}^+})(a_{\text{SO}_4^{2-}})}{a_{\text{HSO}_4^-}} = \frac{(\gamma_{\text{H}^+})(\gamma_{\text{SO}_4^{2-}})}{\gamma_{\text{HSO}_4^-}} \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}, \quad (1)$$

leaving out the usual factors of c° . Using our table, we get

$$K_{a,2} = \frac{(\gamma_{\text{H}^+})(\gamma_{\text{SO}_4^{2-}})}{\gamma_{\text{HSO}_4^-}} \frac{x(0.0025 + x)}{0.0025 - x}. \quad (2)$$

We now need to deal with the ionic activity coefficients. The ionic strength is

$$\begin{aligned} I_c &= \frac{1}{2} ([\text{H}^+] + [\text{HSO}_4^-] + 4[\text{SO}_4^{2-}]) \\ &= \frac{1}{2} (0.0025 + x + 0.0025 - x + 4x) = 0.0025 + 2x. \end{aligned}$$

We can then use the equation

$$\ln \gamma_i = -Az_i^2(\varepsilon T)^{-3/2} \sqrt{I_c}$$

to obtain equations for the activities of each of the ions in terms of x . Note that we will have $\gamma_{\text{H}^+} = \gamma_{\text{HSO}_4^-}$ since their charges are equal in magnitude, so equation (2) will simplify a little:

$$K_{a,2} = \gamma_{\text{SO}_4^{2-}} \frac{x(0.0025 + x)}{0.0025 - x}. \quad (3)$$

We therefore just need

$$\gamma_{\text{SO}_4^{2-}} = \exp \left(-4A(\varepsilon T)^{-3/2} \sqrt{0.0025 + 2x} \right).$$

After substituting the activity coefficient into equation (3), we can solve for x . Once we have x , we calculate $\gamma_{\text{SO}_4^{2-}}$, and finally the activity of the ion by

$$a_{\text{SO}_4^{2-}} = \gamma_{\text{SO}_4^{2-}} x / c^\circ.$$