Homework Set #8 (Mar 22)

7.2 Calculate the emf of the Daniell cell at 298 K when the concentrations of $CuSO_4$ and $ZnSO_4$ are 0.50 *M* and 0.10 *M*, respectively. What would the emf be if activities were used instead of concentrations? (The $\gamma_\pm$ values for $CuSO_4$ and $ZnSO_4$ at their respective concentrations are 0.068 and 0.15, respectively.)

The half reactions for the Daniell cell are

$$\text{Anode:} \quad Zn \rightarrow Zn^{2+} + 2e^-$$

$$\text{Cathode:} \quad Cu^{2+} + 2e^- \rightarrow Cu$$

Thus, for the cell,

$$E^\circ = 0.342\ V - (-0.762\ V) = 1.104\ V$$

The emf at the specified Cu^{2+} and Zn^{2+} concentrations is

$$E = E^\circ - \frac{0.0257\ V}{\nu} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]} = 1.104\ V - \frac{0.0257\ V}{2} \ln \frac{0.10}{0.50} = 1.125\ V$$

Using activities,

$$\begin{aligned} E &= E^\circ - \frac{0.0257\ V}{\nu} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \\ &= E^\circ - \frac{0.0257\ V}{\nu} \ln \frac{\gamma_{\pm,ZnSO_4}[Zn^{2+}]}{\gamma_{\pm,CuSO_4}[Cu^{2+}]} \\ &= 1.104\ V - \frac{0.0257\ V}{2} \ln \frac{(0.15)(0.10)}{(0.068)(0.50)} \\ &= 1.115\ V \end{aligned}$$

7.4 **(a)** None. *E* is an intensive property, **(b)** none. E° is an intensive property, **(c)** squared, **(d)** doubled, **(e)** doubled.

7.8 Calculate the values of E°, $\Delta_r G^\circ$, and *K* for the following reactions at 25° C:

(a) $Zn + Sn^{4+} \rightleftharpoons Zn^{2+} + Sn^{2+}$

(b) $Cl_2 + 2I^- \rightleftharpoons 2Cl^- + I_2$

(c) $5Fe^{2+} + MnO_4^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O + 5Fe^{3+}$

(a)

$$\text{Anode:} \quad Zn \rightarrow Zn^{2+} + 2e^-$$

$$\text{Cathode:} \quad Sn^{4+} + 2e^- \rightarrow Sn^{2+}$$

$$E^\circ = 0.151\ V - (-0.762\ V) = 0.913\ V$$

$$\Delta_r G^\circ = -\nu F E^\circ = -2\left(96500\ C\ mol^{-1}\right)(0.913\ V) = -1.762 \times 10^5\ J\ mol^{-1} = -1.76 \times 10^5\ J\ mol^{-1}$$

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left[-\frac{(-1.762 \times 10^5\ J\ mol^{-1})}{(8.314\ J\ K^{-1}\ mol^{-1})\ (298.2\ K)}\right] = 7.34 \times 10^{30}$$

(b)

$$\text{Anode:} \quad 2I^- \rightarrow I_2 + 2e^-$$

$$\text{Cathode:} \quad Cl_2 + 2e^- \rightarrow 2Cl^-$$

$$E^\circ = 1.368\ \text{V} - 0.536\ \text{V} = 0.824\ \text{V}$$

$$\Delta_r G^\circ = -\nu F E^\circ = -2\left(96500\ \text{C mol}^{-1}\right)(0.824\ \text{V}) = -1.590\times 10^5\ \text{J mol}^{-1} = -1.59\times 10^5\ \text{J mol}^{-1}$$

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left[-\frac{(-1.590\times 10^5\ \text{J mol}^{-1})}{(8.314\ \text{J K}^{-1}\text{mol}^{-1})\ (298.2\ \text{K})}\right] = 7.12\times 10^{27}$$

(c) Anode: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$

Cathode: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^2{+} + 4\text{H}_2\text{O}$

$$E^\circ = 1.507\ \text{V} - 0.771\ \text{V} = 0.736\ \text{V}$$

$$\Delta_r G^\circ = -\nu F E^\circ = -5\left(96500\ \text{C mol}^{-1}\right)(0.739\ \text{V}) = -3.551\times 10^5\ \text{J mol}^{-1} = -3.55\times 10^5\ \text{J mol}^{-1}$$

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left[-\frac{(-3.551\times 10^5\ \text{J mol}^{-1})}{(8.314\ \text{J K}^{-1}\text{mol}^{-1})\ (298.2\ \text{K})}\right] = 1.60\times 10^{62}$$

7.11 An electrochemical cell consists of a half-cell in which a piece of platinum wire is dipped into a solution that is 2.0 M in KBr and 0.050 M in Br_2. The other half-cell consists of magnesium metal immersed in a 0.38 M Mg^{2+} solution. **(a)** Which electrode is the anode and which is the cathode? **(b)** What is the emf of the cell? **(c)** What is the spontaneous cell reaction? **(d)** What is the equilibrium constant of the cell reaction? Assume that the temperature is 25° C.

(a) The reduction reaction for the Pt | Br_2, Br^- half cell is

$$\text{Br}_2(aq) + 2\text{e}^- \rightarrow 2\text{Br}^-(aq) \qquad E^\circ = 1.087\ \text{V}$$

The emf for this half cell is

$$E = E^\circ - \frac{0.0257\ \text{V}}{\nu}\ \ln\frac{\left[\text{Br}^-\right]^2}{\left[\text{Br}_2\right]} = 1.087\ \text{V} - \frac{0.0257\ \text{V}}{2}\ \ln\frac{(2.0)^2}{0.050} = 1.0307\ \text{V}$$

The reduction reaction for the Mg^{2+} | Mg half cell is

$$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg} \qquad E^\circ = -2.372\ \text{V}$$

The emf for this half cell is

$$E = E^\circ - \frac{0.0257\ \text{V}}{\nu}\ \ln\frac{1}{\left[\text{Mg}^{2+}\right]} = -2.372\ \text{V} - \frac{0.0257\ \text{V}}{2}\ \ln\frac{1}{0.38} = -2.3844\ \text{V}$$

The cell reaction that would occur is one with a positive E. This is possible if Mg^{2+} | Mg is the anode and Pt | Br_2, Br^- is the cathode.

(b) $E = 1.0307\ \text{V} - (-2.3844\ \text{V}) = 3.415\ \text{V}$

(c) The spontaneous cell reaction is

$$\text{Br}_2 + \text{Mg} \rightarrow 2\text{Br}^- + \text{Mg}^{2+}$$

(d) E° for the cell is

$$E^\circ = 1.087\ \text{V} - (-2.372\ \text{V}) = 3.459\ \text{V}$$

Therefore, the equilibrium constant is

$$K = \exp\left(\frac{\nu F E^\circ}{RT}\right) = \exp\left[\frac{2\ (96500\ \text{C mol}^{-1})\ (3.459\ \text{V})}{(8.314\ \text{J K}^{-1}\text{mol}^{-1})\ (298.2\ \text{K})}\right] = e^{269.3} = 9.03\times 10^{116}$$

7.12 From the standard reduction potentials listed in Table 7.1 for $Sn^{2+} \mid Sn$ and $Pb^{2+} \mid Pb$, calculate the ratio of $[Sn^{2+}]$ to $[Pb^{2+}]$ at equilibrium at 25° C and the $\Delta_r G^\circ$ value for the reaction.

The reduction potentials for the half cells are

$$\begin{aligned} &Sn^{2+} + 2e^- \rightarrow Sn \qquad E^\circ = -0.138\ \text{V} \\ &Pb^{2+} + 2e^- \rightarrow Pb \qquad E^\circ = -0.126\ \text{V} \end{aligned}$$

The standard emf for the reaction $Sn + Pb^{2+} \rightarrow Sn^{2+} + Pb$ is

$$E^\circ = -0.126\ \text{V} - (-0.138\ \text{V}) = 0.012\ \text{V}$$

The ratio of $[Sn^{2+}]$ to $[Pb^{2+}]$ at equilibrium is directly related to the equilibrium constant, which can be calculated from E°.

$$K = \frac{[Sn^{2+}]}{[Pb^{2+}]} = \exp\left(\frac{\nu F E^\circ}{RT}\right) = \exp\left[\frac{2\,(96500\ \text{C mol}^{-1})\ (0.012\ \text{V})}{(8.314\ \text{J K}^{-1}\text{mol}^{-1})\ (298.2\ \text{K})}\right] = 2.55$$

The standard Gibbs energy is

$$\Delta_r G^\circ = -\nu F E^\circ = -2\left(96500\ \text{C mol}^{-1}\right)(0.012\ \text{V}) = -2.32 \times 10^3\ \text{J mol}^{-1}$$

8.16 A solution of methylamine (CH_3NH_2) has a pH of 10.64. How many grams of methylamine are in 100.0 mL of the solution?

Methylamine is a base. It ionizes to give equal concentrations of $CH_3NH_3^+$ and OH^-, which can be calculated from the pH of the solution.

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.64 = 3.36$$

$$\left[OH^-\right] = 10^{-3.36} = 4.37 \times 10^{-4}\ M$$

Let x M of methylamine be present initially. The equilibrium concentration is then $x - 4.37 \times 10^{-4}\ M$. The concentrations of various species are written below the chemical equation.

$$\begin{array}{llcccccc} & CH_3NH_2 & + & H_2O & \rightleftharpoons & CH_3NH_3^+ & + & OH^- & \\ \text{Initial} & x & & & & 0 & & 0 & M \\ \text{At equilibrium} & x - 4.37 \times 10^{-4} & & & & 4.37 \times 10^{-4} & & 4.37 \times 10^{-4} & M \end{array}$$

$$K_b = 4.38 \times 10^{-4} = \frac{[CH_3NH_3^+]\,[OH^-]}{[CH_3NH_2]} = \frac{(4.37 \times 10^{-4})^2}{x - 4.37 \times 10^{-4}}$$

$$x = 8.73 \times 10^{-4}$$

where x represents the initial concentration of CH_3NH_2 in solution.

The mass of methylamine can now be calculated.

$$\text{Number of moles of methylamine} = \left(8.73 \times 10^{-4}\ M\right)(0.100\ \text{L}) = 8.73 \times 10^{-5}\ \text{mol}$$

$$\text{Mass of methylamine} = \left(8.73 \times 10^{-5}\ \text{mol}\right)\left(31.06\ \text{g mol}^{-1}\right) = 2.7 \times 10^{-3}\ \text{g}$$

8.6 At equilibrium,

$$[\mathrm{H^+}] = [\mathrm{A^-}] = (0.135)\,(0.040\ M) = 5.40 \times 10^{-3}\ M$$

$$[\mathrm{HA}] = (1 - 0.135)\,(0.040\ M) = 3.46 \times 10^{-2}\ M$$

The dissociation constant, K_a, of the acid is therefore

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{(5.40 \times 10^{-3})^2}{3.46 \times 10^{-2}} = 8.4 \times 10^{-4}$$

8.8 The dissociation constant of a monoprotic acid at 298 K is 1.47×10^{-3}. Calculate the degree of dissociation by **(a)** assuming ideal behavior and **(b)** using a mean activity coefficient $\gamma_\pm = 0.93$. The concentration of the acid is 0.010 M.

Let α be the degree of dissociation of the monoprotic acid. The corresponding concentrations of all species are

	HA	$\rightleftharpoons$	$\mathrm{H^+}$	+	$\mathrm{A^-}$	
Initial	0.010		0		0	M
At equilibrium	$0.010\,(1-\alpha)$		0.010α		0.010α	M

(a)

$$K_a = 1.47 \times 10^{-3} = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{(0.010\alpha)^2}{0.010\,(1-\alpha)}$$

$$1.0 \times 10^{-4}\alpha^2 + 1.47 \times 10^{-5}\alpha - 1.47 \times 10^{-5} = 0$$

$$\alpha = 0.32$$

Therefore, assuming ideal behavior, the acid is 32% dissociated.

(b)

$$K_a = \frac{a_{\mathrm{H^+}} a_{\mathrm{A^-}}}{a_{\mathrm{HA}}} = \frac{[\mathrm{H^+}]\,\gamma_+\,[\mathrm{A^-}]\,\gamma_-}{[\mathrm{HA}]\,\gamma_{\mathrm{HA}}}$$

Since HA is an uncharged species and the solution is dilute, γ_{HA} is approximately 1. Furthermore, $\gamma_+\gamma_- = \gamma_\pm^2$. The K_a expression becomes

$$K_a = 1.47 \times 10^{-3} = \frac{[\mathrm{H^+}][\mathrm{A^-}]\,\gamma_\pm^2}{[\mathrm{HA}]} = \frac{(0.010\alpha)^2\,(0.93)^2}{0.010\,(1-\alpha)}$$

$$8.65 \times 10^{-5}\alpha^2 + 1.47 \times 10^{-5}\alpha - 1.47 \times 10^{-5} = 0$$

$$\alpha = 0.34$$

Therefore, accounting for non-ideality, the acid is 34% dissociated.