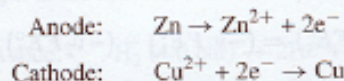


Homework Set #8 (Mar 22)

- 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 γ_{\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



Thus, for the cell,

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

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

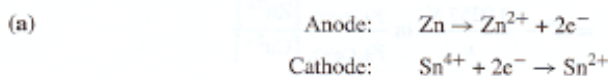
$$E = E^\circ - \frac{0.0257 \text{ V}}{\nu} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.104 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.10}{0.50} = 1.125 \text{ V}$$

Using activities,

$$\begin{aligned}E &= E^\circ - \frac{0.0257 \text{ V}}{\nu} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \\ &= E^\circ - \frac{0.0257 \text{ V}}{\nu} \ln \frac{\gamma_{\pm, \text{ZnSO}_4} [\text{Zn}^{2+}]}{\gamma_{\pm, \text{CuSO}_4} [\text{Cu}^{2+}]} \\ &= 1.104 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(0.15)(0.10)}{(0.068)(0.50)} \\ &= 1.115 \text{ V}\end{aligned}$$

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

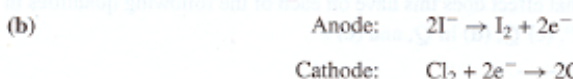
- 7.8 Calculate the values of E° , $\Delta_r G^\circ$, and K for the following reactions at 25°C:



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

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

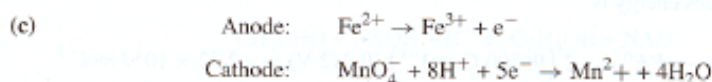
$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left[\frac{(-1.762 \times 10^5 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298.2 \text{ K})}\right] = 7.34 \times 10^{30}$$



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

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

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



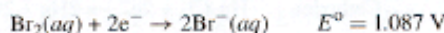
$$E^{\circ} = 1.507 \text{ V} - 0.771 \text{ V} = 0.736 \text{ V}$$

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

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

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 Br₂. The other half-cell consists of magnesium metal immersed in a 0.38 M Mg²⁺ 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 | Br₂, Br⁻ half cell is



The emf for this half cell is

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

The reduction reaction for the Mg²⁺ | Mg half cell is



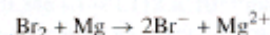
The emf for this half cell is

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

The cell reaction that would occur is one with a positive E . This is possible if Mg²⁺ | Mg is the anode and Pt | Br₂, Br⁻ is the cathode.

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

(c) The spontaneous cell reaction is



(d) E° for the cell is

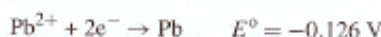
$$E^{\circ} = 1.087 \text{ V} - (-2.372 \text{ V}) = 3.459 \text{ V}$$

Therefore, the equilibrium constant is

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

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

The reduction potentials for the half cells are



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

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

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

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

The standard Gibbs energy is

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

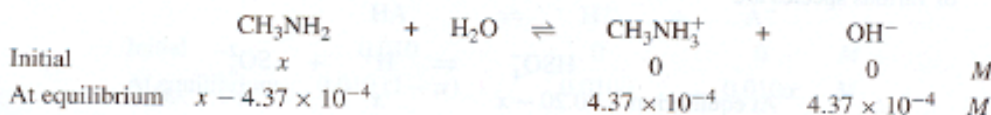
- 8.16 A solution of methylamine (CH_3NH_2) has a pH of 10.64. How many grams of methylamine are in 100.0 mL of the solution?

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.

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

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

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



$$K_b = 4.38 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(4.37 \times 10^{-4})^2}{x - 4.37 \times 10^{-4}}$$

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

where x represents the initial concentration of CH_3NH_2 in solution.

The mass of methylamine can now be calculated.

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

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

8.6 At equilibrium,

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

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

The dissociation constant, K_a , of the acid is therefore

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

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	H ⁺	+	A ⁻	
Initial	0.010		0		0	M
At equilibrium	0.010(1 - α)		0.010 α		0.010 α	M

(a)

$$K_a = 1.47 \times 10^{-3} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.010\alpha)^2}{0.010(1 - \alpha)}$$
$$1.0 \times 10^{-4}\alpha^2 + 1.47 \times 10^{-5}\alpha - 1.47 \times 10^{-5} = 0$$
$$\alpha = 0.32$$

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

(b)

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

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

$$K_a = 1.47 \times 10^{-3} = \frac{[\text{H}^+][\text{A}^-]\gamma_{\pm}^2}{[\text{HA}]} = \frac{(0.010\alpha)^2(0.93)^2}{0.010(1 - \alpha)}$$
$$8.65 \times 10^{-5}\alpha^2 + 1.47 \times 10^{-5}\alpha - 1.47 \times 10^{-5} = 0$$
$$\alpha = 0.34$$

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