4. Free Energy and Redox Reactions

A. Any reaction that can occur in a voltaic (galvanic) cell to produce a +emf must be spontaneous.

(1) You can use half-cell potentials (w/ general redox reactions, not just voltaic cells) to determine if a reaction is spontaneous

$$E^\circ = E^\circ_{red\ (reduction)} - E^\circ_{red\ (oxidation)}$$

- a $+E^\circ$ - spontaneous process
- a $-E^\circ$ - nonspontaneous process

Ex (15) Using appendix E, determine which of the following are spontaneous under standard conditions

(A) $I_2(s) + 5Cu^{2+}(aq) + 6H_2O(l) \rightarrow 2IO_3^-(aq) + 5Cu(s) + 12H^+(aq)$

ox: I_2 (0) → IO_3^- (+5); red: Cu^{2+} (+2) → Cu (0)

$E^\circ = +.337V - +1.195V = -.858\ V$ nonspontaneous

(B) $Hg^{2+}(aq) + 2I^-(aq) \rightarrow Hg(l) + I_2(s)$

red: Hg^{2+} (+2) → Hg (0); ox: I^- (−1) → I_2 (0)

$E^\circ_{cell} = (+.854V) - (+.536V) \rightarrow E^\circ_{cell} = .318V$ spontaneous

(C) $H_2SO_3(aq) + 2Mn(s) + 4H^+(aq) \rightarrow S_8(s) + 2Mn^{2+}(aq) + 3H_2O(l)$

red: H_2SO_3 (+4) → S_8 (0); ox: Mn (0) → Mn^{2+} (+2)

$E^\circ = 0.45 - (-1.18) = 1.63V \rightarrow$ spontaneous

B. EMF and ΔG (for a redox reaction)

$$\Delta G = -nFE$$

n = #moles of e^- transferred
F = Faraday constant (F)

$1F = 96485\ C/mol = 96485\ J/V\,mol$

under standard conditions

$$\Delta G^\circ = -nFE^\circ$$

Ex (16) For the reaction

$$3Ni^{2+}(aq) + 2Cr(OH)_3(s) + 10OH^-(aq) \rightarrow 3Ni(s) + 2CrO_4^{2-}(aq) + 8H_2O(l)$$

(A) what is the value of n?

ox. $2Cr^{+3} \rightarrow 2CrO_4^{-} + 6e^-$

red. $3Ni^{2+} + 6e^- \rightarrow 3Ni^0$

$n = 6e^-$

(B) use Appendix E to calculate ΔG°.

$E^\circ = E^\circ_{reduction} - E^\circ_{oxidation}$

$E^\circ = -.28V - -.13V = -.15V$

$\Delta G^\circ = -nFE^\circ = (6 mol)(96485 J/mol)(-.15V) = 86836.8$

(C) calculate K at 298K.

$K = e^{-\frac{\Delta G^\circ}{RT}}$ $\quad R = 8.314 \ J/mol\,K$

$K = e^{-\frac{86836.8}{(8.314)(298)}}$

$K = 6 \times 10^{-16}$

Ex (17) If the equilibrium constant for a ~~one~~ two electron redox reaction at 298K is 1.5×10^{-4}, calculate ΔG° and E°_{cell}.

$$\Delta G^\circ = -RT \ln K = -(8.314\ J/mol\,K)(298\,K)(\ln 1.5 \times 10^{-4})$$

$$\boxed{\Delta G^\circ = 21814.7\ J/mol}$$

$$\Delta G^\circ = -nFE^\circ$$

$$21814.7 = -2(96485)E^\circ$$

$$\boxed{-.113V = E^\circ}$$

5. Cell EMF under nonstandard conditions

As a voltaic (galvanic) cell is discharged, the concentrations change. The emf drops to 0, at which point we say the cell is "dead". The concentrations stop changing, they are at equilibrium.

A. The Nernst Equation

remember $\Delta G = \Delta G^\circ + RT \ln Q$

substitute in $\Delta G = -nFE$ & get

$$-nFE = -nFE^\circ + RT \ln Q$$

divide both sides by $-nF$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

or

$$E = E^\circ - \frac{2.303\,RT}{nF} \log Q$$

at room temp., 298K the equation becomes:

$$E = E^\circ - \frac{.0592}{n} \log Q$$

Ex (18) Calculate the emf generated by the cell with an overall cell reaction:

$$2Al(s) + 3I_2(s) \rightarrow 2Al^{3+}(aq) + 6I^-(aq)$$

when $[Al^{3+}] = 4.0 \times 10^{-3} M$ and $[I^-] = .010 M$.

$$E = E^\circ - \frac{.0592}{n} \log Q \qquad Q = [Al^{3+}]^2 [I^-]^6$$

$$Q = [4.0 \times 10^{-3}]^2 [.010]^6$$

$$Q = 1.6 \times 10^{-17}$$

ox. $2Al \rightarrow 2Al^{3+} + 6e^-$

red. $3I_2 + 6e^- \rightarrow 6I^-$

$E^\circ = +.536V + +1.66V$

$E^\circ = 2.196V$

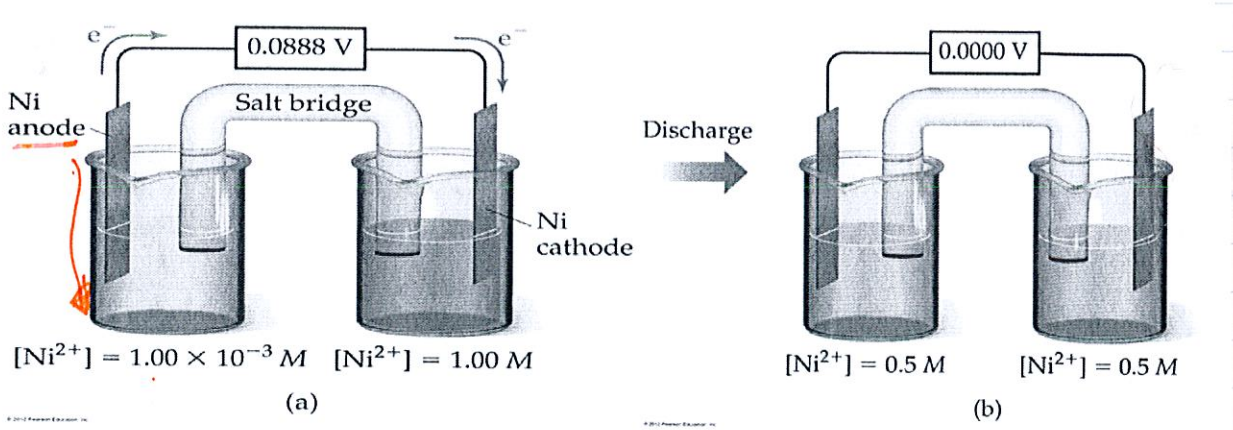
$n = 6e^-$

$$E = +2.196V - \frac{.0592}{6} \log 1.6 \times 10^{-17}$$

$$E = +2.196V - -.166 = \boxed{2.362V}$$

(1). Concentration Cells

A voltaic cell can be constructed using the same species in both the anode and the cathode as long as the concentrations are different.



$E^\circ_{cell} = \emptyset$

$Q \neq \emptyset$

∴ As long as the concentrations are different, $E \neq 0$

$$E = E^\circ - \frac{.0592}{n} \log Q$$

· oxidation occurs in the anode half cell w/ lesser concentration

Ex (19) A voltaic cell is constructed with two Zn^{2+} - Zn electrodes. The two cell compartments have $[Zn^{2+}] = 1.8M$ and $[Zn^{2+}] = 1.00 \times 10^{-2} M$, respectively.

(A) which electrode is the anode?

$[Zn^{2+}] = 1 \times 10^{-2} M$

(B) what is the standard emf of the cell? $E^\circ = 0$

(C) what is the cell emf for the concentrations given.

(D) For each electrode, predict whether $[Zn^{2+}]$ will increase, decrease, or stay the same as the cell operates.

$E = \cancel{E^\circ}^{0} - \frac{.0592}{n} \log(Q)$

anode $Zn \rightarrow Zn^{+2} + 2e^-$ Reactant Zn anode

cathode $Zn^{+2} + 2e^- \rightarrow Zn(s)$ Product Zn^{+2} cathode

$Q = \frac{[Zn^{2+}]_{cathode}}{[Zn^{2+}]_{anode}} = \frac{1.8}{1.00 \times 10^{-2}} = 180$

$E = \cancel{E^\circ}^{0} - \frac{.0592}{2} \log 180$

$E = -.0668 V$

Ex (20) The cell in Figure 20.11 (p 857) could be used to provide a measure of the pH in the cathode. Calculate the pH in the cathode if the cell emf at 298K is measured to be +.684V when $[Zn^{2+}] = .30M$ and $P_{H_2} = .90$ atm

$$Zn(s) + 2H^+(aq) + 2e^- \rightarrow Zn^{+2}(aq) + H_2(g) + 2e^-$$

$$E = E^\circ - \frac{.0592}{n} \log Q$$

.684V = E, +.76V = E°, 2 = n

$$Q = \frac{[Zn^{2+}][H_2]^{P_{H_2}}}{[H^+]^2}$$

$$Q = \frac{[Zn^{2+}]\,P_{H_2}}{[H^+]^2}$$

$$.684 = .76 - \frac{.0592}{2} \log Q$$

$$-.076 = -\frac{.0592}{2} \log Q$$

$$2.568 = \log Q$$

$$10^{2.568} = Q$$

$$369.8 = Q$$

$E^\circ = 0V - -.76V$

$E^\circ = +.76$

$$pH = -\log[H^+]$$

$$[H^+]^2\ 369.8 = \frac{[.30][.90]}{[H^+]^2}$$

$$7.30 \times 10^{-4} = [H^+]^2$$

$$.0270 = [H^+]$$

$$pH = -\log .0270 = 1.57$$

HW p 887–888 #52, 54a:b, 56, 62, 64, 68.