

Intro:

- **Redox Reactions** – chemical reactions in which oxidation state of one or more substances changes
- Atom that loses electrons is **oxidized**; atom that gains electrons is **reduced**

## 20.1 Oxidation-Reduction Reactions

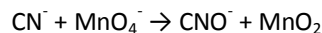
- Find unknown oxidation states based on what is known, such as: atoms in their elemental form (0), fluorine (-1), hydrogen (+1 except when bonded to metal, then -1), and oxygen (-2 except when in peroxide like H<sub>2</sub>O<sub>2</sub>) and known oxidation states based on group on the periodic table (group 1 (+1), group 2 (+2), group 15 (-3), group 16 (-2), and group 17 (-1))

## 20.2 Balancing Oxidation-Reduction Reaction Equations

1. Divide reaction into its corresponding half reactions
2. Balance elements other than H and O
3. Add H<sub>2</sub>O to one side until O atoms are balanced
4. Add H<sup>+</sup> to one side until H atoms are balanced
5. Add e<sup>-</sup> to one side until charge is balanced
6. Multiply each half reaction by integer so equal number of electrons are transferred in reaction
7. Add two half reactions and simplify

\*For redox reactions that are basic, follow same steps, neutralize the H<sup>+</sup> ions by adding same number of OH<sup>-</sup> ions to both sides of the reaction\*

Ex. Reaction is basic which will show how to do acidic reaction balancing as well as extra basic reaction steps (starting at step 3)



1.  $\text{CN}^- \rightarrow \text{CNO}^-$  and  $\text{MnO}_4^- \rightarrow \text{MnO}_2$
2.  $\text{CN}^- + \text{H}_2\text{O} \rightarrow \text{CNO}^- + \text{H}^+ + 2\text{e}^-$  and  $3\text{e}^- + 4\text{H}^+ + \text{MnO}_4^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$
3.  $2\text{OH}^- + \text{CN}^- + \text{H}_2\text{O} \rightarrow \text{CNO}^- + 2\text{H}_2\text{O} + 2\text{e}^-$  or  $2\text{OH}^- + \text{CN}^- \rightarrow \text{CNO}^- + 2\text{e}^-$   
 $3\text{e}^- + 4\text{H}_2\text{O} + \text{MnO}_4^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} + 4\text{OH}^-$  or  $3\text{e}^- + \text{MnO}_4^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$
4.  $3\text{CN}^- + \text{H}_2\text{O} + 2\text{MnO}_4^- \rightarrow 2\text{MnO}_2 + 2\text{OH}^- + 3\text{CNO}^-$

## 20.3 Voltaic Cells

- **Voltaic (or galvanic) cell** – device in which transfer of electrons occurs in external pathway; used to harness energy released in spontaneous redox reactions so it can be used to perform electrical work
- **Anode** - negative; oxidation half reaction takes place at the anode; **Cathode** – positive; reduction half reaction takes place at cathode
- Electrical neutrality is maintained by migration of ions through porous glass disc separating two compartments or a **salt bridge** (U-shaped tube that contains electrolyte solution whose ions do not react with other ions in cell or electrode material)
- Electrons flow from anode to cathode through external circuit

## 20.4 Cell EMF

- Potential energy of electrons is higher in anode than in cathode, they spontaneously flow through external circuit
- **Potential Difference** – difference in potential energy per electrical charge
- Potential difference between two electrodes (measured in volts) of a voltaic cell provides the driving force that pushes electron through external circuit (called **electromotive force**, or **emf**)
- **Cell potential** – electromotive force of a cell; will be positive in cell reactions that are spontaneous (like voltaic cell)
- The voltage V in volts (V) is equal to the energy E in joules (J), divided by the charge Q in coulombs (C):

$$V = J / C$$

- **Standard emf (Standard Cell Potential, or E<sup>o</sup><sub>cell</sub>)** – electromotive force under standard conditions (1 M concentrations for reactants and products in solution, 1 atm pressure for those that are gases)
- **Standard Reduction Potential (E<sup>o</sup><sub>red</sub>)** -  $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}}(\text{cathode}) - E^{\circ}_{\text{red}}(\text{anode})$
- **Standard Hydrogen Electrode (SHE)** – electrode designed to produce this half reaction:  $2\text{H}^+(\text{aq}, 1\text{M}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}, 1\text{atm})$   $E^{\circ}_{\text{red}} = 0\text{ V}$
- Since the oxidation potential of hydrogen is zero, the cell potential of any electrode used in conjunction with SHE will be exactly equal to the reduction potential of the half reaction occurring at the other electrode

\*Changing the stoichiometric coefficient in a half reaction does not affect value of standard reduction potential\*

Ex. For a Zn-Cu<sup>2+</sup> the E<sup>o</sup><sub>cell</sub> = 1.10 V and the Zn electrode is the anode. Given standard reduction potential of Zn<sup>2+</sup> is -.76 V, find E<sup>o</sup><sub>red</sub> for reduction of Cu<sup>2+</sup> to Cu

$$\begin{aligned} \text{Cu}^{2+}(\text{aq}, 1\text{M}) + 2\text{e}^- &\rightarrow \text{Cu}(\text{s}) \\ E^{\circ} &= E^{\circ}_{\text{red}}(\text{cathode}) - E^{\circ}_{\text{red}}(\text{anode}) \\ 1.10\text{V} &= E^{\circ}_{\text{red}}(\text{cathode}) - (-0.76\text{V}) \\ E^{\circ}_{\text{red}}(\text{cathode}) &= 0.34\text{V} \end{aligned}$$

## 20.5 Spontaneity of Redox Reactions

$$E^{\circ} = E^{\circ}_{\text{red}}(\text{reduction process}) - E^{\circ}_{\text{red}}(\text{oxidation process})$$

- Gibbs free energy (ΔG) – measure of spontaneity of process that occurs at constant temperature and pressure

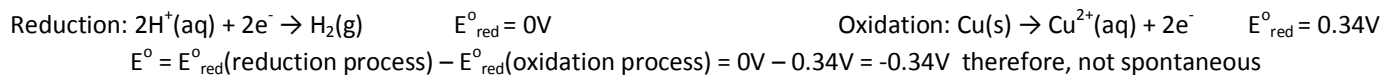
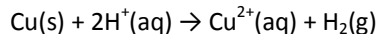
$$\Delta G = -nFE$$

## Chapter 20 Electrochemistry

Nicholas DiLosa

- $n$  is positive number without units that represents number of electrons transferred in reaction,  $F$  is Faraday's constant = 96,500 C/mol or 96,500 J/V-mol,  $E$  is electromotive force or emf
- A positive value of  $E$  and a negative value of  $\Delta G$  both indicate that a reaction is spontaneous

Ex. Using standard reduction potentials listed in Table 20.1, determine whether reaction is spontaneous under standard conditions



### 20.6 Effect of Concentration on Cell EMF

- Nernst Equation

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad \text{or} \quad E = E^\circ - \frac{.0592\text{ V}}{n} \log Q \quad \text{at } T = 298$$

- **Concentration Cell** – cell based solely on the emf generated because of a difference in concentration
- Compartment with more dilute solution will be the anode compartments; more concentrated solution will be the cathode compartment

Ex. Consider cell in which one compartment consists of a strip of nickel metal immersed in 1.00 M solution of  $\text{Ni}^{2+}(\text{aq})$  and the other compartment has  $\text{Ni(s)}$  electrode, but immersed in  $1.00 \times 10^{-3}$  M solution of  $\text{Ni}^{2+}(\text{aq})$ , connected by salt bridge and exterior wire with voltmeter



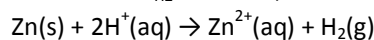
Cell operates in nonstandard conditions because of difference in concentration of  $\text{Ni}^{2+}(\text{aq})$  in two compartments, so use the Nernst equation:

$$E = E^\circ - \frac{.0592\text{ V}}{n} \log Q = 0 - \frac{.0592}{2} \log \frac{[\text{Ni}^{2+}]_{\text{dilute}}}{[\text{Ni}^{2+}]_{\text{concentrated}}} = -\frac{.0592}{2} \log \frac{1.00 \times 10^{-3}\text{ M}}{1.00\text{ M}} = .0888\text{ V}$$

- When concentration of two compartments become the same, the value of  $Q = 1$  and  $E = 0$
- A system at  $\Delta G = 0$  is at equilibrium, thus when  $E = 0$  the cell reaction has reached equilibrium, where  $Q = K$  (equilibrium constant)

$$0 = E^\circ - \frac{RT}{nF} \ln K \quad \text{or} \quad \log K = -\frac{nE^\circ}{.0592} \quad \text{at } T = 298$$

Ex. If voltage of  $\text{Zn-H}^+$  Cell is 0.45 V at 25°C when  $[\text{Zn}^{2+}] = 1.0$  M and  $P_{\text{H}_2} = 1.0$  atm, what is concentration of  $\text{H}^+$ ? (Standard emf is  $E^\circ = +0.76$  V)



$$0.45 = 0.76 - \frac{.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} = 0.76 - \frac{.0592}{2} (-2 \log[\text{H}^+])$$

$$\log[\text{H}^+] = \frac{0.45 - 0.76}{0.0592} = -5.2; \text{ therefore } [\text{H}^+] = 6 \times 10^{-6}\text{ M}$$

Ex. Using standard reduction potentials listed in Appendix E, calculate the equilibrium constant for the oxidation of  $\text{Fe}^{2+}$  by  $\text{O}_2$  in acidic solution according to reaction:  $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{Fe}^{2+}(\text{aq}) \rightarrow 4\text{Fe}^{3+}(\text{aq}) + 2\text{H}_2\text{O(l)}$



$$E^\circ = 1.23 - 0.77 = 0.46\text{ V and } n = 4$$

$$\log K = -\frac{nE^\circ}{.0592} = -\frac{4(0.46\text{V})}{.0592\text{ V}} = 31$$

### 20.7 Batteries

- Portable, self-contained electrochemical power source consisting of one or more voltaic cells
- **Fuel Cells** – voltaic cells that convert thermal energy released by combustion to electrical energy using conventional fuels such as  $\text{H}_2$  and  $\text{CH}_4$

### 20.8 Corrosion

- Spontaneous redox reactions in which metal is attacked by substance in environment, thus converted to unwanted compound
- Corrosion of iron into rust is caused by the presence of water and oxygen, accelerated in presence of electrolytes
- **Cathodic Protection** – protection of a metal by putting it in contact with another metal that more readily undergoes oxidation

### 20.9 Electrolysis

- **Electrolysis Reaction** – process of using electrical energy to cause nonspontaneous redox reactions to occur (take place in **electrolytic cell**)
- Electrolytic cell consists of two electrodes in a molten salt or solution
- Because of high melting points of ionic substances, the electrolysis of molten salts requires very high temperatures
- Negative terminal of external source is connected to cathode of cell, positive to anode
- Products of electrolysis can be predicted by comparing reduction potentials associated with possible oxidation and reduction processes
- Electrodes in electrolytic cell can be active, meaning the electrode can be involved in electrolysis reaction (important in electroplating)
- Quantity of substances formed can be calculated by number of electrons involved in redox and amount of electrical charge passed into cell
- Maximum amount of electrical work produced by voltaic cell is given by:  $E_{w_{\text{max}}} = -nFE$
- Work performed in electrolysis is given by:  $w = -nFE_{\text{ext}}$ , where  $E_{\text{ext}}$  is applied external potential
- Watt is unit of power:  $1\text{W} = 1\text{J/s}$

Ex. Calculate the mass of aluminum produced in 1.00 hr by electrolysis of molten  $\text{AlCl}_3$  if electrical current is 10.0 A

$$\text{Coulombs} = \text{amperes} \times \text{seconds} = (10\text{A})(1\text{hr})(3600\text{s}/1\text{hr})(1\text{C}/1\text{A}\cdot\text{s}) = 3.6 \times 10^4\text{ C}$$

$$\text{Moles } \text{e}^- = 3.6 \times 10^4\text{ C} (1\text{mole}/96,500\text{ C}) = .373\text{ mol } \text{e}^-$$

$$\text{Grams Al} = (.373)(1\text{ mol Al}/3\text{ mol } \text{e}^-) (27.0\text{g Al}/1\text{ mol Al}) = 3.36\text{ g Al}$$