Intro to Electrochemistry

Electron Transfer Reactions:
- electron transfer reactions are oxidation-reduction or redox reactions
- redox reactions can result in:
  - generation of an electric current, or
  - be caused by imposing an electric current
- when external electric current is involved, this field of chemistry is called ELECTROCHEMISTRY

Terminology:
* oxidation - loss of electron(s) by a species; increase in oxidation number
* reduction - gain of electron(s); decrease in oxidation #
* oxidizing agent - electron acceptor; species is reduced
* reducing agent - electron donor; species is oxidized

Example:

Balanced chemical: $Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$

Total Net Ionic Eq.: $Zn_{(s)} + Cu^{2+}_{(aq)} + SO^{2-}_{4(aq)} \rightarrow Zn^{2+}_{(aq)} + SO^{2-}_{4} + Cu_{(s)}$

Net Ionic Equation: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ Cu-reduced, Zn - oxidized

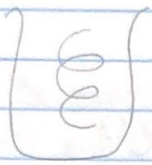
* Reactions in which one reactant is oxidized (lose e^-) and the other reactant is reduced (gains e^-) are called oxidation-reduction reaction, or REDOX

- e^- gained by one reactant are the e^- lost by the other one

Direct Redox Reactions

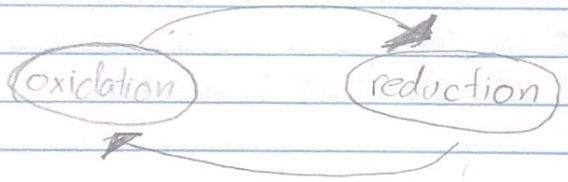
- oxidizing and reducing agents are in direct contact

$$Cu_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$



Indirect Redox Reaction

- A battery functions by transferring electrons through an external wire from the reducing agent to the oxidizing agent



Predicting Redox Reactions:

- Which of the following SD reactions will be spontaneous

1) $Zn + Cu^{2+}$ - spontaneous
2) $Cu + Zn^{2+}$ - non spontaneous
3) $Ag + Pb^{+2}$ - non spontaneous
4) $Ca + H^{+}$ - spontaneous

Rule:

- the redox reaction will be spontaneous if the oxidizing agent in the reaction is higher than the reducing agent

Oxidation Number

- is the oxidation state, is defined as the apparent net electric charge that the atom would have if electron pairs in covalent bonds belonged entirely to the more electronegative atom

- the oxidation number system is a useful way to keep track of electrons but it does not usually represent an actual charge on atom. An oxidation number

* Oxidation Number: a number equal to the charge that an atom would have if no electrons were shared but instead were possessed by the atom with the greatest electronegativity

Rules for Assigning Oxidation Number:

1. Pure element has ON of 0	Na, Br in Br_2, P in P_4
2. the ON of an element in a monoatomic ion equals the charge on the ion	ON of Al^{3+} is 3, ON of Se^{2-} is 2-
3. the ON of H in compounds is +1, except in metal hydrides where ON is -1	the ON of H in $H_2S_{(g)}$ or in CH_4 is +1. The ON of H in NaH or CaH_2 is -1
4. The ON of O in a compound is usually -2	The ON of O in Li_2O or KNO_3 is -2
5. in molecular comp. without O & H, the ON is assigned to the more EN element. it is the negative charge it usually has in ionic comp.	The ON of Cl in PCl_3 is -1 The ON of S in CS_2 is -2
6. The sum of the ON of all atoms in a neutral is 0	
7. The sum of ON of all atoms in a polyatomic ion equals charge on ION	

Examples:

1) $Cl_2 \rightarrow ON = 0$

2) $Na_2O \rightarrow Na = +2 \quad O = -2$

3) $Fe_2O_3 \rightarrow Fe = +3 \quad O = -3$

4) $PbSO_4 \rightarrow Pb = +2$

5) $K\overset{-1}{NO_2} \rightarrow NO_2^- : (+3) + 2(-2) = -1 \quad K = 0$

6) $Fe(NO_3)_3$

6) $\frac{\overset{-1}{(NO_3)}}{-3}$ $\frac{Fe}{+3}$ $\overset{3}{Fe}(\overset{x}{N}\overset{-2}{O_3})_3$

$3 + [x + 3(-2)]3$

$3 + 3x - 18 = 0$

$3x = 15$

$x = 5$

7) $Zn_3(\overset{-3}{PO_4})_2$ $\frac{3}{2}$ -6 $\overset{2}{Zn_3}\overset{-6}{(\overset{-3}{PO_4})_2}$

$-4 + x = -3$

$x = 1$

(8) $Na(NO_2^{-1})$

$2(-2) + x = -1$

$-4 + x = -1$

$x = 3 = N$

(9) $SnBr_2^{-1}$

$2(-1) + x = 0$

$-2 + x = 0$

$x = 2$

(10) $\overset{-1}{H}Sb\overset{-2}{O_2}$

$-1 + x + 2(-2) = 0$

$x = 4 + 1$

$x = 5$

(11) $\overset{2+}{Mg}(\overset{3}{Mn}\overset{-2}{O_4})_2$ -1 -2

$2(-2) + x = -1$

$-4 + x = -1$

$x = 3$

Redox Reaction:

- a redox reaction is a reaction in which the oxidation numbers of atleast two atoms change
- oxidation is an increase in oxidation number
- reduction is a decrease in oxidation number

Ex: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$

O.N: $0 \quad +2 \quad 0 \quad +2$

-2 reduced

$+2$ oxidized

Ex:

① $3O_2^{2-} \rightarrow 2O_3^{2-}$

$-12 \quad -12$

NO

② $\overset{+1\ +5\ -2}{AgNO_3} + \overset{+1\ -1}{NaCl} \rightarrow \overset{+1\ -1}{AgCl} + \overset{+1\ +5\ -2}{NaNO_3}$

NOT REDOX REACTION
NO CHANGE

③ $\overset{0}{4Na} + \overset{0}{O_2} \rightarrow \overset{+1\ -2}{2Na_2O}$

Na oxidized
O reduced

$+1 \times 2 = +2$

-2

④ $\overset{+1\ -1}{KI} \rightarrow K^+ + I^-$

NO CHANGE

Ballancing Redox Reaction s with O.N

Using Oxidation Numbers

Ex 1: $\overset{+2\ -1}{CuCl_2} + \overset{0}{Al} \rightarrow \overset{0}{Cu} + \overset{3\ -1}{AlCl_3}$

*oxidation half reaction: $Al \rightarrow AlCl_3 + 3e^-$

*Reduction half reaction: $2e^- + CuCl_2 \rightarrow Cl$

OHR:

$(Al \rightarrow AlCl_3 + 3e^-) \times 2$

$= 2Al \rightarrow 2AlCl_3 + 6e^-$

RHR

$(2e^- + CuCl_2 \rightarrow Cu) \times 3$

$\rightarrow 6e^- + 3CuCl_2 \rightarrow 3Cu$

Ex 2: $\overset{+5\ -2}{HNO_3} + \overset{1\ 3\ -2}{H_3AsO_3} \rightarrow \overset{+2\ -2}{NO} + \overset{1\ +5\ -2}{H_3AsO_4} + \overset{+1\ -2}{H_2O}$

N: 5 to 3

As: 3 → 5

OHR:

$(H_3AsO_3 \rightarrow H_3AsO_4 + 2e^-) \times 3$

$= 3H_3AsO_3 \rightarrow 3H_3AsO_4 + 6e^-$

RHR:

$(3e^- + HNO_3 \rightarrow NO) \times 2$

$= 6e^- + 2HNO_3 \rightarrow 2NO$

Steps:

1. write unbalanced half-reactions that show the formulas for the given reactant(s) and product(s)
2. Balance only atoms other than Oxygen and Hydrogen
3. Balance O atoms by adding water molecules
4. Balance H atoms by adding H ions
5. Balance charges by adding electrons

Ex 4: $\overset{5\ -2}{2IO_3^-} + \overset{1\ 4\ -2}{HSO_3^-} \longrightarrow \overset{+6\ -2}{SO_4^{2-}} + \overset{0}{I_2}$

OHR:

$(HSO_3^- \rightarrow SO_4^{2-} + 2e^-) \times 5$

$5HSO_3^- \rightarrow 5SO_4^{2-} + 10e^-$

RHR:

$(10e^- + 2IO_3 \rightarrow I_2) \times 1$

Practice:

1) $\overset{0}{Cl_2} + \overset{4\ -2}{SO_2} \rightarrow \overset{-1}{Cl^-} + \overset{6\ -2}{SO_4^{-2}}$

OHR:

$SO_2 \rightarrow SO_4^{-2} + 2e^-$

$4(-2)$

$x + -8 = -2$

$x = 6$

RHR:

$(Cl_2 + e^- \rightarrow Cl_2^-)2$

$= 2Cl_2 + 2e^- \longrightarrow 2Cl_2^-$

$SO_2 + 2Cl_2 + 2e^- \longrightarrow 2Cl_2^- + SO_4^{-2} + 2e^-$

$SO_2 + 2Cl_2 \rightarrow 2Cl_2^- + SO_4^{-2}$

$2H_2O + SO_2 + 2Cl_2 \rightarrow 2Cl_2^- + SO_4^{-2} + 4H^+$