Chapter 20 - Electron Transfer Reactions (Electrochemistry)

Recall from Chapter 5:

oxidation: an increase in oxidation number or a process in which e^- are lost
reduction: a decrease in oxidation number or a process in which e^- are gained

oxidizing agent: a substance that oxidizes another substance; it itself gets REDUCED
reducing agent: a substance that reduces another substance; it itself gets OXIDIZED

In a redox reaction, both oxidation and reduction occur at the same time.

Oxidation Number Rules:
(1) The oxidation number of any free element is $\emptyset$.
(2) For a compound, the sum of all the oxidation numbers = $\emptyset$.
(3) For an ion, the sum of the oxidation numbers is the charge on the ion.
(4) For specific elements

IA metals	+1	IIIA	+3
IIA	+2	oxygen	−2 (except for H_2O_2 and a few others)

(5) For simple binary IONIC compounds: VA −3; VIA −2 VIIA −1
(metal + nonmetal)

Examples:

NaCl	Na +1	Cl −1	
NaClO	Na +1	O −2	so Cl must be +1, $+1+x+-2=0$
Fe^{3+}	Fe +3		
$\underline{Cr}_2O_7^{2-}$	set up algebra	$2x+7(-2)=-2$	

$$2x = +12$$
$$x = +6$$

$\underline{N}H_4^+$ $\quad x+4(+1)=+1$; $x=-3$

Note on net ionic equations - Chapter 5

Formula Unit Equation $2AgNO_{3(aq)} + Cu_{(s)} \rightarrow Cu(NO_3)_{2(aq)} + 2Ag_{(s)}$

then break up strong electrolytes (strong acids, strong bases, soluble salts)

Total Ionic Equation $2Ag^+_{(aq)} + 2NO_3^-{}_{(aq)} + Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2NO_3^-{}_{(aq)} + 2Ag_{(s)}$

then cancel out spectator ions (ions <u>identical</u> on both sides of equation)

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

Note: mass <u>and</u> charges balance.

This is a redox reaction: It can be recognized as such after assigning oxidation numbers to all elements.

$$\overset{+1}{2\,Ag^+_{(aq)}} + \overset{0}{Cu_{(s)}} \rightarrow \overset{+2}{Cu^{2+}_{(aq)}} + \overset{0}{2\,Ag_{(s)}}$$

reduction: $\overset{+1}{Ag^+} \rightarrow \overset{0}{Ag}$ $\therefore$ Ag^+ is the oxidizing agent

oxidation: $\overset{0}{Cu} \rightarrow \overset{+2}{Cu^{2+}}$ Cu is the reducing agent

These two reactions are called "half-reactions." To balance them charge-wise, we need to add electrons to one side or the other.

reduction half-rxn: $e^- + Ag^+ \rightarrow Ag$

oxidation half-rxn: $Cu \rightarrow Cu^{2+} + 2e^-$

<u>But</u> the electrons involved in oxidation must equal the electrons involved in reduction, so we multiply the reduction half rxn by 2.

$$2(e^- + Ag^+ \rightarrow Ag)$$
$$Cu \rightarrow Cu^{2+} + 2e^-$$
$$\cancel{2e^-} + 2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+} + \cancel{2e}$$

And the equation is balanced!

I'm going to show you how to balance redox net ionic equations using a variation of the half-rxn method.

Note: in acidic solution, you can add as many H^+ or H_2O as you need
in basic solution, you can add as many OH^- or H_2O as you need.

Balance in acidic solution: $MnO_4^- + HSO_4^- \rightarrow Mn^{2+} + SO_4^{2-}$

(1) Assign oxidation numbers:

$$\overset{+7\ -2}{MnO_4^-} + \overset{+1\,+4\,-2}{HSO_3^-} \rightarrow \overset{+2}{Mn^{2+}} + \overset{+6\ -2}{SO_4^{2-}}$$

reduction ($\downarrow 5$)

oxidation ($\uparrow 2$)

$\therefore$ MnO_4^- is oxidizing agent
HSO_3^- is reducing agent

(2)

reduction: $\underset{\text{Step3}}{5e^-} + \underset{\text{Step2}}{8H^+} + MnO_4^- \rightarrow Mn^{2+} + \underset{\text{step ①}}{4H_2O}$

matches change in oxidation number

$+8-1 = +7$ $\therefore$ need $5e^-$ $\qquad$ $+2+0 = +2$ $\qquad$ charge balance to figure out # electrons

oxidation: $\underset{\text{Step 1}}{H_2O} + HSO_3^- \rightarrow SO_4^{2-} + \underset{\text{Step2}}{3H^+} + \underset{\text{Step3}}{2e^-}$

$0-1 = -1$ $\qquad$ $-2+3 = +1$ need $2e^-$ $\qquad$ matches charge in oxidation number

to balance transfer of electrons

rewriting $\quad 2(5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O)$
$\quad 5(H_2O + HSO_3^- \rightarrow SO_4^{2-} + 3H^+ + 2e^-)$

$$\cancel{10e^-} + \overset{1}{\cancel{16}}H^+ + 2MnO_4^- + \cancel{5H_2O} + 5HSO_3^- \rightarrow 2Mn^{2+} + \underset{3}{\cancel{8}}H_2O + 5SO_4^{2-} + \cancel{15H^+} + \cancel{10e^-}$$

$$H^+ + 2MnO_4^- + 5HSO_3^- \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$$

charge balance $\qquad +1-2-5 = -6 \qquad\qquad +4-10 = -6$

Note: In acidic solution: Step 0 – balance non-O/H elements
Step 1 – balance O with H_2O
Step 2 – balance H with H^+
Step 3 – balance charge with e^-

Balance in basic solution: $HS^- + ClO_3^- \rightarrow S(s) + Cl^-$

Assign oxidation numbers:

$$\overset{+1\ -2}{HS^-} + \overset{+5\ -2}{ClO_3^-} \rightarrow \overset{0}{S(s)} + \overset{-1}{Cl^-}$$

loss of $2e^-$ in half rxn — oxidation ↑2

reduction ↓6 — gain of $6e^-$ in half rxn

∴ HS^- is reducing agent and ClO_3^- is oxidizing agent

reduction: $\underset{\text{Step 3}}{3H_2O} + \underset{\text{Step 1}}{6e^-} + ClO_3^- \rightarrow Cl^- + \underset{\text{Step 2}}{6OH^-}$

Step 1: use change in oxidation # to determine e^-
Step 2: use OH^- to balance charge
Step 3: finish balancing using H_2O.

oxidation: $\underset{\text{Step 2}}{OH^-} + HS^- \rightarrow S + \underset{\text{step 1}}{2e^-} + \underset{\text{step 3}}{H_2O}$

Rewrite:

$$6e^- + 3H_2O + ClO_3^- \rightarrow Cl^- + 6OH^-$$
$$+\ 3\,(OH^- + HS^- \rightarrow S + H_2O + 2e^-)$$

to balance transfer of electrons

$$\cancel{6e^-} + \cancel{3H_2O} + ClO_3^- + \cancel{3OH^-} + 3HS^- \rightarrow Cl^- + \overset{3}{\cancel{6}}OH^- + 3S + \cancel{3H_2O} + \cancel{6e^-}$$

Balanced Net Ionic Equation $\quad ClO_3^- + 3HS^- \rightarrow Cl^- + 3OH^- + 3S$

Question: How (Where) do these reactions happen?

Answer: In electrochemical cells!