Electrochemistry

RedOx Pt 1

Many chemical reactions belong to a large class called electrochemistry or reduction/oxidation reactions commonly called RedOx reactions

<u>Oxidation:</u>
Historically referred to combining substances with oxygen.
Now refer to reactions involving a *loss of electrons*

Ex. $Fe_{(s)} \rightarrow Fe^{3+}_{(aq)} + 3e^-$

Because e^- are lost we have an increase in positive charge = oxidation

<u>Reduction:</u>
Historically referred to refining of metal ore into pure metal
Now refer to reactions involving a *gain of electrons*

Ex. $Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$

e^- are gained we have an decrease in positive charge = reduction

RedOx

Since these reactions are an *exchange* of electrons they have to occur simultaneously. So a reduction has to occur together with an oxidation = RedOx

Ex. The two half reactions from above together:

$Fe_{(s)} + Al^{3+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Al_{(s)}$

Most single replacement reactions (from sci 10) are RedOx reactions.

Mnemonic – ***Le$^-$O*** *the lion says* ***Ge$^-$R*** (Oil Rig)

Oxidizing agent vs Oxidation

Terminology is a little funny here: an "*oxidizing agent*" refers to something that *causes* oxidation, therefore the thing that is undergoing reduction (which causes something else to oxidize) Same thing goes for the reducing agent; it's actually being oxidized.

Ex.

$Fe_{(s)} + Al^{3+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Al_{(s)}$

In this case the oxidizing agent is undergoing reduction ($Ge^{-}R$) gaining electrons, so that's Al^{3+}. The reducing agent is Fe.

Ex.

$$Cu + Br_2 \rightarrow CuBr_2$$

Cu = R.A.
Br_2 = O.A.

Spontaneity of RedOx reactions

Just as not all acid/base reactions occur just because you write them down on paper, not all RedOx reactions occur as written, we have to use another table, very similar to the table used in the AB unit. The table of ***Standard Reduction Potentials***:

Reaction always proceeds assuming that the stronger OA is the reactant.

Ex.

$Sn_{(s)} + Al^{3+}_{(aq)} \rightarrow Sn^{2+}_{(aq)} + Al_{(s)}$

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

$Au_{(s)} + Pb^{2+}_{(aq)} \rightarrow Au^{3+}_{(aq)} + Pb_{(s)}$

Go over handouts… study, get back into the swing of things ☺

Balancing half-reactions

Overall reaction for a simple single replacement reaction (gr 10):

$$2\ Al_{(s)} + 3\ CuCl_{2(aq)} \rightarrow 2\ AlCl_3 + 3\ Cu$$

Net reaction:

$$2\ Al_{(s)} + 3\ Cu^{2+}_{(aq)} \rightarrow 2\ Al^{3+}_{(aq)} + 3\ Cu_{(s)}$$

Oxidation ½ reaction:

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3\ e^-$$

Reduction ½ reaction:

$$2\ e^- + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)}$$

Process of balancing ½ reactions

MAJOR OH^- (Major atoms first, Oxygens, Hydrogens, charge)

Major atoms: everything except hydrogen, and oxygen

Ex.

$$RuO_2 \rightleftharpoons Ru$$

Major atoms (simple)

$$RuO_2 \rightleftharpoons Ru$$

Oxygen (add water)

$$RuO_2 \rightleftharpoons Ru + \mathbf{2\ H_2O}$$

Hydrogen (add H^+)

$$\mathbf{4H^+} + RuO_2 \rightleftharpoons Ru + 2\ H_2O$$

Charge (add e^-)

$$\mathbf{4e^-} + 4H^+ + RuO_2 \rightleftharpoons Ru + 2\ H_2O$$

IF Under basic conditions

Add enough OH^- to both sides of equation to neutralize H^+ and simplify out excess water, check balance of charge for accuracy.

Ex.

$$Pb \rightleftharpoons HPbO_2^- \text{ (under acidic conditions)}$$

Ex.

$$Pb \rightleftharpoons HPbO_2^- \text{ (under basic conditions***)}$$

Ex.

$$Fe \rightleftharpoons Fe_2O_3 \text{ (basic)}$$

Practice: Hebden pg 203 #19 - all

Balancing overall reactions using ½ reactions

There are two methods of balancing a RedOx reaction, by using ½ reactions and by using oxidation number; here we will discuss the former. When looking at an overall RedOx reaction we can break it up into its constituent ½ reactions and subsequently balance.

Ex.

$$Os + IO_3^- \rightarrow OsO_4 + I_2$$

Find the MAJOR atoms that are in common and separate.

1) $Os \rightarrow OsO_4$

2) $IO_3^- \rightarrow I_2$

Balance (as per above)

Have to get electrons to balance; find lowest common multiple (LCM)

$$(4H_2O + Os \rightarrow OsO_4 + 8H^+ + 8e^-) \text{ X } 5$$

$$(10e^- + 12H^+ + 2IO_3^- \rightarrow I_2 + 6H_2O) \text{ X } 4$$

Bring it all together…

$$40e^- + 48H^+ + 8IO_3^- + 20H_2O + 5Os \rightarrow 4I_2 + 24H_2O + 5OsO_4 + 40H^+ + 40e^-$$

Clean it up…

$$8H^+ + 8IO_3^- + 5Os \rightarrow 4I_2 + 4H_2O + 5OsO_4$$

Check that the charges and make sure it's all balanced.

Ex.

$$Zn + As_2O_3 \rightarrow AsH_3 + Zn^{2+} \text{ (Acidic/Neutral)}$$

Ex.

$$MnO_4^- + C_2O_4^{2-} \rightarrow MnO_2 + CO_2 \text{ (Basic)}$$

Disproportionation

A reaction in which the same species is BOTH reduced and oxidized:

Ex.

$$Br_{2(aq)} \rightarrow Br^-_{(aq)} + BrO_3^-{}_{(aq)}$$

In this case Br_2 is both oxidized and reduced, so you need to create two half reactions that BOTH have Br_2 as the sole reactant.

1) $Br_2 \rightarrow BrO_3^-{}_{(aq)}$

2) $Br_2 \rightarrow Br^-_{(aq)}$

Balance (as per above)

Practice: Hebden pg 207 #24 – all

Balancing with Oxidation numbers

Oxidation number is just a fancy way of saying the charge on a given element. For a molecule the sum of all the negative and positive oxidation numbers MUST equal the overall charge of the molecule.

Some elements have a common charge that is usually assumed*

Alkali metals	always = +1
Alkali Earth metals	always = +2
Halogens	usually[A] = -1
Oxygen	usually[B] = -2
Hydrogen	usually[C] = +1
In elemental form (diatomic or otherwise) = 0	

A – Fluorine is always -1, but all other halogens CAN take a positive charge if interacting with an element with a stronger electronegativity

B – Sometimes oxygen can take on a -1 charge, this is called a *peroxide* and should be noted in the question

C – Hydrogen can take on a -1 charge, this is called a *hydride* and should be noted in the question

Ex. What is the oxidation number of the element in BOLD?

Mg^{2+}

Cu

H**Cl**O_2

H_4**P**$_2O_7$

Practice: Hebden pg 194 #3-6

Balancing

Some equations are actually much easier to balance using one method or the other (Oxidation No. vs. ½ reaction)

For example:

$CuF_2 + NH_3 \rightarrow Cu_3N + NH_4F + N_2$ – this question is a PAIN to balance using the ½ reaction method… let's TRY it anyways.

$$CuF_2 + NH_3 \rightarrow Cu_3N + NH_4F + N_2$$

But with oxidation numbers it's actually much simpler…. Let's try that too!

$$CuF_2 + NH_3 \rightarrow Cu_3N + NH_4F + N_2$$

Some practice examples:

Ex 1. $Cu + MnO_4 \rightarrow CuO + Mn^{2+}$ (acidic conditions)

Ex 2. $Zn + As_2O_3 \rightarrow AsH_3 + Zn^{2+}$ (basic conditions)

Ex 3. $Br_2 + NH_3 \rightarrow BrO_3^- + Br^-$ (acidic conditions)

HW Hebden #25 pg 210

RedOx Titrations (Titrations, just like zombies, you thought they were dead… but Nooooooooooooo, They're BACK!)

As with acids and bases, RedOx reactions can also be titrated; that is, the oxidizing agent can be titrated against the reducing agent until an endpoint is reached. The purpose would be to determine the concentration of a solution.

Ex 1. Titrating iodine (I_2) with a thiosulphate ($S_2O_3^{2-}$) solution to form iodide (I^-) and tetrathionate ($S_4O_6^{2-}$)

Such a reaction consumes I_2 and can be used to:
1. determine the *amount of iodine* in a sample.
2. determine the *concentration of oxidizing agent* used to prepare the iodine from a solution of iodide.

Amount of Iodine

A solution containing I_2 is titrated to the endpoint using 18.0 mL of 0.13 M $Na_2S_2O_3$ solution. How many moles of I_2 were present?

Usually, the I^- is oxidized when in contact with an oxidizing agent such as IO_3^-, Fe^{3+}, Ag^+ or Br_2. Similarly, the Cu^{2+} ion is an oxidizing agent that, under the right conditions, can oxidize the I^- into I_2.

Concentration of Oxidizing Agent

First, a solution containing Cu^{2+} is mixed with excess I^- (KI solution) to reduce all Cu^{2+} ions into Cu^+

The I_2 that formed is then titrated with a standardized $Na_2S_2O_3$ solution until the end point is reached.

The amount of standardized solution required depends only on the amount of I_2 present. Also, the I^- ions that are formed during the titration are precipitated by the Cu^+ as CuI. The end point is determined by the disappearance of the blue color of I_2 in starch.

Ex 2. Concentration of Cu^{2+} oxidizing agent.
Excess 0.10 M KI solution is added to 50 mL of $CuSO_4$ solution to reduce the Cu^{2+} into Cu^+. The mixture is titrated with 43 mL of 0.10 M $Na_2S_2O_3$ until an end point is reached. Find the concentration of the copper (II)sulphate solution.

Ex 3. 0.67 g hydrated $Cu(N0_3)_2$ is made into solution to which is added excess KI. The resulting mixture is titrated with 17.7 mL of 0.128 M Na2S2O3 to the starch endpoint.
Find the moles of water to anhydride ratio.

End of sub-unit Study for Electrochemistry Pt 1 Test

Test Date on: _____