Session 11: **LECTURE OUTLINE (SECTION K pp F73 – F79)**

I. Oxidation Reactions
   a. Definition
II. Oxidation and Reduction
   a. Definitions
III. Oxidation Numbers
   a. What are they?
IV. Oxidizing and Reducing Agents
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V. How are oxidation numbers assigned?
   a. Rules
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VI. Balancing Ox/Red Reactions
   a. Steps in acidic solution
   b. Steps in basic solution
   c. Examples

Suggested Problems: pp F74-F77 K.1A, K.1B, K.2A, K.2B, K.3A, K.3B,.
pp F78-F79 K.4A. K.4B, K.1, K.3, K.5, K.7, K.9, K.11, K.13, K.15, K17

REDOX REACTIONS

- Redox reactions or oxidation-reduction reactions involve transfer of electrons. As the electron transfer occurs, substances undergo changes in oxidation number.

OXIDATION AND REDUCTION

- Oxidation: the process by which a compound looses or appears to loose electrons. It corresponds to an increase in the oxidation number.
- Reduction: the process by which a compound gains or appears to gain electrons. It corresponds to a decrease in oxidation number

OXIDATION NUMBERS

- Oxidation numbers are used to keep track of electron transfer.
- Oxidation numbers are assigned to ionic as well as molecular compounds.
- Oxidation numbers are assigned per atom.

OXIDIZING AND REDUCING AGENTS

- Oxidizing agent: species that causes oxidation. An oxidizing agent accepts electrons from the species it oxidizes and therefore, an oxidizing agent is always reduced.
- Reducing agents: species that causes reduction. A reducing agent donates electrons to the species it reduces and therefore, a reducing agent is always oxidized.

Example

Zinc, Zn, reacts with copper (II) ions, Cu^{2+}, to give Zn^{2+} and copper, Cu.

-----Zn----------- is being oxidized and --- Cu^{2+}------------ is being reduced. The oxidizing agent is ----- Cu^{2+}------------- and the reducing agent is --Zn--

The oxidation number of Zn is zero (free element). As it reacts and turns into the Zn ion, its oxidation number changes to +2. This is an oxidation. The oxidation number of copper changes from +2 to 0. This is a reduction. Because Zn metal was oxidized, it is the reducing agent and Copper (II) is the oxidizing agent.

HOW ARE OXIDATION NUMBERS ASSIGNED?

1.

The oxidation number of a free element is zero.

2.

The oxidation number of an element in a monatomic ion is the charge on the ion.

3.

When combined, Grp IA elements have ox. number of +1.

4.

When combined, Grp IIA elements have ox. number of +2.

5.

When combined, Grp IIIA elements have ox. number of +3.

6.

When combined, fluorine has an ox. number of –1.

7.

When combined, Oxygen has an ox. number = –2 except in peroxides and superoxides.

8.

When combined, hydrogen has an ox. number = +1 except in hydrides.

9. In a polyatomic ion, the sum of the ox. numbers of the elements in the ion is equal to the charge of the ion.

10. The sum of the oxidation numbers of all elements in a compound is zero.

Example1

Assign an oxidation number to each atom in the following:

NaCl Na O_2 $H_2PO_4^-$

NaCl (a compound)
Ox # Na + Ox # Cl = 0 (rule 10)
Ox # Na = +1 (rule 3) therefore, the ox # of Cl = -1.

Na (a free element)
ox # = 0 (rule 1)

O_2 (a free element)
ox # = 0 (rule 1)

$H_2PO_4^-$ (a polyatomic ion)
Ox # H = +1 (rule 8)
Ox # O = -2 (rule 7)
Ox # P = x (unknown)
2(ox # H) + ox # P + 4(ox # O) = -1 (rule 9)
2(+1) + (x) + 4(-2) = -1
x = +5

Example 2 (answers will be provided by TA)
Assign an oxidation number to each atom in the following:

$\mathbf{H_2}$ $\mathbf{NH_4^+}$ $\mathbf{SO_4^{2-}}$ $\mathbf{H_2CO_3}$ $\mathbf{Cr_2O_7^{2-}}$

BALANCING OX/RED EQUATIONS, the Half-Reaction Method:

1. Identify the species being oxidized and reduced.

2. Construct two unbalanced half-reactions, one for oxidation and one for reduction

3. Balance by inspection all elements in each half-reaction, except H and O.

4. Balance O and H as follows:
   <u>In acidic solution:</u> (Balance O first)
   For each missing O, add one H_2O to the side that is missing it.
   For each missing H, add one H^+ to the side that is missing it.
   <u>In basic solution:</u> (Balance O first)
   For each missing O, add one H_2O to the side that is missing it.
   For each missing H, add one H_2O to the side that is missing it, then go to the other side and add one OH^-.
   Before you move on, cancel common terms (species) that appear on both sides of the equation.

5. In each half-reaction, balance the charge by adding electrons to the side that is more positive.

6. Balance the electron transfer by multiplying the balanced half-reactions by appropriate integers.

7. Add the resulting half-reactions and eliminate any common terms.

8. Check to make sure that charges as well as number of atoms are balanced!

Example 1

In acidic solution, dichromate ions $Cr_2O_7^{2-}$ oxidize iodide ions, I^-, to free iodine, I_2, and are reduced to chromium (III) ions. Balance the corresponding equation.

Reduction half-reaction (Cr goes from +7 to +3, this is a reduction)

$Cr_2O_7^{2-}$ -----------------→ Cr^{3+}

- We need to multiply the product side by 2 to balance Cr.

$Cr_2O_7^{2-}$ -----------------→ $2Cr^{3+}$

- Balancing O:

We have 7 more oxygen on the reactants side and therefore, we need to add 7 water molecules to the products side.

$Cr_2O_7^{2-}$ -----------------→ $2Cr^{3+}$ + $7H_2O$

- Balancing H (in acidic solution)

We have 14 H on the products side. Therefore, we add 14 H^+ to the reactants side.

$Cr_2O_7^{2-}$ + $14H^+$ -----------------→ $2Cr^{3+}$ + $7H_2O$

- Balancing charges by adding electrons:

We have 12 positive charges on the reactant side and 6 positive charges on the products side. We add 6 electrons to the reactants side.

$Cr_2O_7^{2-}$ + $14H^+$ + $6e^-$ ----------------→ $2Cr^{3+}$ + $7H_2O$

At this point it is a good idea to verify that atoms and charges are really balanced!

Oxidation half-reaction (I goes from -1 to 0, this is an oxidation)

I^- ----------------→ I_2

- We need to multiply the reactant side by 2 to balance I.

$2I^-$ ----------------→ I_2

- There are no oxygen to balance, we move on!

- There are no H to balance, we move on!

- Balancing charges by adding electrons:

We have 2 negative charges on the reactants side and a neutral charge on the products side. We add 2 electrons to the products side.

$2I^-$ ----------------→ $I_2 + 2e^-$

At this point it is a good idea to verify that atoms and charges are really balanced!

We now need to add the two reactions. However, in the reduction half-reaction, 6 electrons are gained and in the oxidation half reaction, 2 electrons are lost. So, we need to multiply the oxidation half-reaction by 3 to balance the electron transfer. We obtain:

Ox: $6I^-$ ----------------→ $3I_2 + 6e^-$

Red: $Cr_2O_7^{2-} + 14H^+ + 6e^-$ ----------------→ $2Cr^{3+} + 7H_2O$

We now add the two equations and cancel the electrons. There are no other common terms to be canceled!

$6I^- + Cr_2O_7^{2-} + 14H^+$ ----------------→ $3I_2 + 2Cr^{3+} + 7H_2O$

Check one last time to make sure that charges and atoms are balanced!

Example 2

Bromide ions, Br^-, react with permanganate ions, MnO_4^-, in basic aqueous solution to give manganese (IV) oxide, MnO_2, and bromate ions, BrO_3^-. Balance the corresponding equation.

Reduction half-reaction (Mn goes from +7 to +4, this is a reduction)

MnO_4^- ----------------→ MnO_2

- The Mn is balanced.

- Balancing O:

We have two more oxygen on the reactants side and therefore, we need to add 2 water molecules to the products side.

MnO_4^- -----------------→ $MnO_2 + 2H_2O$

- Balancing H (in basic solution)

We have 4 H on the product side. Therefore, we add four H_2O to the reactants side and go back to the products side and add 4 OH^-.

$4H_2O + MnO_4^-$ -----------------→ $MnO_2 + 2H_2O + 4OH^-$

- By canceling like species on both sides, we obtain:

$2H_2O + MnO_4^-$ ----------------→ $MnO_2 + 4OH^-$

- Balancing charges by adding electrons:
We have one negative charge on the reactants side and 4 negative charges on the products side. We add 3 electrons to the reactants side.
$2H_2O + MnO_4^- + 3e^- \text{----------------}\rightarrow MnO_2 + 4OH^-$

At this point it is a good idea to verify that atoms and charges are really balanced!

Oxidation half-reaction (Br goes from -1 to +5, this is an oxidation)

$Br^- \text{----------------}\rightarrow BrO_3^-$
- Here again, the Br is balanced, so we move to balance O.

- Balancing O:
We have three more O on the products side and therefore, we need to add 3 H_2O to the reactants side.

$3H_2O + Br^- \text{----------------}\rightarrow BrO_3^-$

- Balancing H (in basic solution):
We have 6 H on the reactants side. Therefore, we add 6 H_2O to the products side and go back to the reactants side and add 6 OH^-.
$6OH^- + 3H_2O + Br^- \text{---------------}\rightarrow BrO_3^- + 6H_2O$

- By canceling like species on both sides, we obtain:
$6OH^- + Br^- \text{---------------}\rightarrow BrO_3^- + 3H_2O$

- Balancing charges by adding electrons:
We have 7 negative charges on the reactants side and 1 negative charge on the products side. We add 6 electrons to the product side.
$6OH^- + Br^- \text{---------------}\rightarrow BrO_3^- + 3H_2O + 6e^-$

At this point it is a good idea to verify that atoms and charges are really balanced!

- We now need to add the two half-reactions. However, in the reduction half-reaction, 3 electrons are gained and in the oxidation half reaction, 6 electrons are lost. So, we need to multiply the reduction half-reaction by 2 to balance the electron transfer. We obtain:

Ox: $4H_2O + 2MnO_4^- + 6e^-$ ----------------→ $2MnO_2 + 8OH^-$

Red: $6OH^- + Br^-$ ---------------→ $BrO_3^- + 3H_2O + 6e^-$

We now add the two equations and cancel the electrons as well as the terms that are the same on both sides:

$H_2O + 2MnO_4^- + Br^-$ ----------------→ $2MnO_2 + 2OH^- + BrO_3^-$

Check one last time to make sure that charges and atoms are balanced!