OXIDATION REDUCTION

Section I

Example 1: $Na \rightarrow Na^+ + e$

Example 2: $2C1^- \rightarrow Cl^2 + 2e$

Example 3: $K^+ + e \rightarrow K$

Example 4: $C1^2 + 2e \rightarrow 2Cl^-$

1. The oxidation number of group I A is always (+) 1.

2. The oxidation number of group II A is always (+) 2.

3. The oxidation number of oxygen is -2 exception peroxides. In peroxides the oxidation number of oxygen is -l. Example of peroxides: H_20_2, Na_20_2.

4. The oxidation number of hydrogen is +1 except in hydrides. In hydrides the oxidation number of H is -1. Example of hydrides: NaH, LiH.

5. The algebraic sum of the oxidation number of all atoms in a neutral compound is zero.

6. The oxidation number of elements in its free state is zero.

7. The oxidation number of the halogens is -1 when they combine with hydrogen or with a metal in a binary compound.

We will discuss the ion-electron method first. The following steps are recommended.

1. Write the redox reaction as 2 half-cell reactions. A half-cell reaction representing oxidation and the other half-cell reaction representing reduction.

2. Balance each half-cell individually.

3. To balance oxygen, add H_20 molecules to the side where oxygen needs to be added.

4. To balance hydrogen add H^+ to the opposite side where water molecules were added.

5. The charge on each half-cell reaction is balanced by adding electrons to the appropriate side (usually on the same side where H^+ are added).

6. To balance the two half-cell reactions we need to make the number of e's lost equal number of e's gained by multiplying the two half-cell reactions by the appropriate number and adding:

Example 5: $Fe + C1^2 \rightarrow Fe^{+2} + C1^-$

A: $C1_2 \rightarrow C1^-$ red.

B: $Fe \rightarrow Fe^{+2}$ ox.

Now we balance each half-cell reaction individually.

C: $2e + Cl_2 \rightarrow 2C1$

D: $Fe \rightarrow Fe^{+2} + 2e$

Note that half-cell reaction C gained 2e while half-cell reaction D lost 2e. Therefore, the number of e's lost is equal to the number of e's gained. To get the total reaction we simply add reactions C and D.

C: $2e + Cl^- \rightarrow 2C1$

D: $Fe \rightarrow Fe^{+2} + 2e$

$Fe + C1_2 \rightarrow Fe^{+2} + 2C1^-$

Note: $C1_2$ is the oxidation agent; it oxidizad Fe from oxidation state of zero to +2. The Fe is the reducing agent; it reduced the oxidation number of chlorine from 0 to -1.

Also, note that the reducing agent (Fe) was oxidized and the oxidizing agent ($C1_2$) was reduced.

Example 6: $MnO_4^- + C1^- \rightarrow Mn^{+2} + C1_2$

A: $C1^- \rightarrow C1_2$ ox.

B: $MnO_4^- \rightarrow Mn^{+2}$ red.

Balance each half-cell reaction. To balance A multiply C1 by 2; then add 2e to the right side of the reaction to obtain reaction C.

C: $2C1^- \rightarrow Cl^2 + 2e$

B: $MnO_4^- \rightarrow Mn^{+2}$

To balance oxygen in half-cell reaction B, add 4 moles of H_20 to the right side to obtain reaction D.

D: $MnO_4^- \rightarrow Mn^{+2} + 4H_20$

To balance the hydrogen add $8H^+$ to the opposite side where H_20 molecules were added and obtain E.

E: $8H^+ + MnO_4^- \rightarrow Mn^{+2} + 4H_20$

The net charge on the left side of the half-cell reaction E is +7 and on the right side is +2. To balance the charge add 5e to the left side of the reaction to obtain F.

F: $5e + 8H^+ + MnO_4^- \rightarrow Mn^{+2} + 4H_20$

C: $2Cl^- \rightarrow C1_2 + 2e$

Half-cell reaction F gained 5e, while half-cell reaction C lost 2e. To balance the gain and loss **multiply** half-cell reaction F by 2 and half-cell reaction C by 5 and add.

$10e + 16H^+ + 2MnO_4^- \rightarrow 2Mn^{+2} + 8H_2O$

$10Cl^- \rightarrow 5C1_2 + 10e$

$16H^+ + 2MnO_4^- + 10C1^- \rightarrow 2Mn^{+2} + 8H_2O + 5C1_2$

Example 7: $Cr_2O_7^{2-} + I^- \rightarrow Cr^{+3} + I_2$

A: $Cr_2O_7^{2-} \rightarrow Cr^{+3}$

B: $I^- \rightarrow I_2$

C: $Cr_2O_7^{2-} \rightarrow 2Cr^{+3}$

D: $Cr_2O_7^{2-} \rightarrow 2Cr^{+3} + 7H_2O$

E: $14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{+3} + 7H_2O$

The net charge on the left side of the half-cell reaction is +12 (14 - 2 = 12), while on the right side is +6 (2 x 3). To balance the charge add 6e to the left side and obtain Reaction F.

F: $6e+ 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{+3} + 7H_2O$

G: $2I^- \rightarrow I_2$

H: $2I^- \rightarrow I_2 + 2e$

To balance the gain and the loss of e's, multiply Reaction H by 3 obtaining Reaction I. Add I and F.

I: $6I^- \rightarrow 3I_2 + 6e$

F: $6e + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{+3} + 7H_2O$

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

BALANCING REDOX REACTIONS BY CHANGE IN OXIDATION NUMBER METHOD:

Example 8: $Fe + C1_2 \rightarrow FeCl_2$

Oxidation number of Fe = 0

Oxidation number of Cl_2 + O

Oxidation number of Fe in $FeCl_2$ = +2

Oxidation number of C1 in $FeCl_2$ = -1

The summary is given by Reaction A:

0 gain of le/atom or a total of 2e

Reaction A: $Fe + C1_2 \rightarrow FeC1_2$

0 loss of 2e +2

The loss of e's is equal to the gain of e's.

Example 9: $H_2SO_4 + HI \rightarrow H_2S + I_2 + H_2O$

Establish the oxidation number of each atom in the equation.

S in H_2SO_4 = +6

I in HI = -1

S in H_2S = -2

The summary is shown by Reaction B.

-1 loss of le 0

Reaction B: $H_2SO_4 + 8HI \rightarrow H_2S + 4I_2 + 4H_2O$

+6 gain of 8 -2

On the left side we have 8HI; therefore, multiply I_2 on the right side by 4 to balance the I. Left side 4 oxygen; therefore, multiply H_2O on the right side by 4 to balance the oxygen.

Example 10: $KMnO_4 + HC1 \rightarrow MnCl_2 + KCl + H_2O$

Oxidation number of C1 in HC1 is -1

Oxidation number of Mn in $KMnO_4$ is +7

Oxidation number of Mn in $MnCl_2$ is +2

Oxidation number of $C1_2$ is 0

The summary is shown by Reaction C

Reaction C:

-1 loss le 0

$KMnO_4 + HC1 \rightarrow MnCl_2 + H_2O + KC1 + C1_2$

+2

+7 5e gain of 5e

We multiply the HC1 by 5, but in this case we have to notice that the HC1 was partly used as a reducing agent and partly used to supply the Mn^{+2} and the K^+ with $C1^-$. Therefore, in addition to the 5 molecules we need to add 2 molecules of HC1 to supply $2C1^-$ for the Mn^{+2} and one molecule of HC1 to supply one chloride ion for the K^+. Adding these gives 8 HC1 as shown by Reaction D.

Reaction D: $KMnO_4 + 8HC1 \longrightarrow MnCl_2 + 5/2C1_2 + KC1 + 4H_2O$

The rest of the reaction is balanced by inspection.

On the left side we have 4 oxygens; therefore, multiply the H_20 by 4. On the left side we have 8 chlorines; therefore, multiply the $C1_2$ by 5/2. We already have 3 other chlorine ($MnCl_2$ and KC1). To get rid of the fraction, multiply all compounds in reaction D by 2 to obtain Reaction E.

Reaction E:$2KMnO_4 + 16HC1 \longrightarrow 2MnCl_2 + 5C1_2 + 2KCl + 8H_2O$

Compare example 6 with example 10; it is seen that both of these examples are the same.

Example 6: $16H^+ + 2MnO_4^- + 10C1^- \longrightarrow 2Mn^{+2} + 5C1_2 + 8H_2O$

Example 10: $2KMnO_4 + 16HC1 \longrightarrow 2MnCl_2 + 5C1_2 + 8H_2O + 2KC1$

The reason why we have $16H^+$ and $10C1^-$ in the ion-electron method is because we did not add the $4C1^-$ for $2Mn^{+2}$ nor did we add the $C1^-$ attached to the K^+.

The equivalent weight of oxidizing or a reducing agent is equal to its molecular weight divided by the number of transferred e' s.

Equivalent weight of $KMnO_4$ in example 10 = $\frac{158}{5}$ = 31.6

Equivalent weight of H_2SO_4 in example 9 of $\frac{98}{8}$ = 12.25

So then to prepare 1N solution of $KMnO_4$ used in example 10, dissolve 31.6 g of $KMnO_4$ in 1 liter of solution.

Section II

1. Balance the following redox reactions using the ion electron method:

a. $Zn + NO_3^- \longrightarrow Zn^{2+} + NO_2$

b. $Zn + NO_3^- \longrightarrow Zn^{2+} + N_2O$

c. $Zn + NO_3^- \longrightarrow Zn^{2+} + N_2$

d. $Fe^{2+} + MnO_4^- \longrightarrow Fe^{3+} + Mn^{+2}$

e. $Ag + NO_3^- \longrightarrow Ag^+ + NO$

f. $PbO_2 + C1^- \longrightarrow Pb^{2+} + C1_2$

g. $Fe^{+2} + Cr_2O_7^{2-} \longrightarrow Fe^{3+} + Cr^{3+}$

h. $Cr_2O_7^{2-} + I^- \longrightarrow Cr^{3+} + I^2$

i. $A1 + H^+ \longrightarrow A1^{+3} + H_2$

j. $C1O_3^- \longrightarrow C1O_4^- + C1O_2$

2. Balance the following redox reactions using the change in oxidation number method.

a. $NH_3 + O_2 \longrightarrow NO + H_2O$

b. $CuO + NH_3 \longrightarrow N_2 + H_2O + Cu$

c. $H_2S + H_2O_2 \longrightarrow S + H_2O$

d. $Sn + HNO_3 \longrightarrow SnO_2 + NO_2 + H_2O$

e. $CuS + HNO_3 \longrightarrow Cu(NO_3)_2 + S + NO + H_2O$

f. $KMnO_4 + HC1 \longrightarrow KC1 + MnCl_2 + C1_2 + H_2O$

g. $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$

h. $CdS + I_2 + HC1 \longrightarrow CdCl_2 + HI + S$

i. $HC1O_3 \longrightarrow HC1O_4 + C1O_2 + H_2O$

j. $KBr + H_2SO_4 \longrightarrow K_2SO_4 + Br_2 + SO_2 + H_2O$

3. Calculate the equivalent weight of:

a. $KMnO_4$ in f of number 2

b. HNO_3 in e of number 2

c. $HC1O_3$ in i of number 2

4. Balance the following redox reactions using both the change in oxidation number method and the electron method.

(a) $Fe_2O_3 + S \longrightarrow Fe + SO_2$

(b) $NH_3 + O_2 \longrightarrow NO + H_2O$

(c) $N_2O + H_2 \longrightarrow H_2O + NH_3$

(d) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$

(e) $FeS + HNO_3 \longrightarrow Fe(NO_3)_3 + S + NO_2 + H_2O$

(f) $KMnO_4 + SnF_2 + HF \longrightarrow MnF_2 + SnF_4 + KF + H_2O$

(g) $Cr_2O_3 + Na_2CO_3 + KNO_3 \longrightarrow Na_2CrO_4 + CO_2 + KNO_2$

(h) $Na_2SO_3 + H_2SO_4 + KMnO_4 \longrightarrow K_2SO_4 + MnSO_4 + Na_2SO_4 + H_2O$

(i) $KBrO_3 + Fe(NO_3)_2 + HNO_3 \longrightarrow KBr + Fe(NO_3)_3 + H_2O$

(j) $HgS + HNO_3 + HCl \longrightarrow HgCl_2 + NO + S + H_2O$

ANSWERS

l. a. $Zn \longrightarrow Zn^{+2} + 2e$

$[e + 2H^{+} + NO_3^{-} \longrightarrow NO_2 + H_2O]\ 2$

$2/ + Zn + 4H^{+} + 2N03^{-} \longrightarrow Zn^{+2} + 2NO_2 + 2H_2O + 2/e$

b. $[Zn \longrightarrow Zn^{+2} + 2e]\ 4$

$8e + l0H^{+} + 2NO_3^{-} \longrightarrow N_2O + 5H_2O$

$4Zn + 8e + l0H^{+} + 2NO_3^{-} \longrightarrow 4Zn^{+2} + N_2O + 5H_2O + 8e$

c. $[Zn \longrightarrow Zn^{+2} + 2e]\ 5$

$l0e + 12H^{+} + 2NO_3^{-} \longrightarrow N_2 + 6H_2O$

$10e + 5Zn + 12H^{+} + 2NO_3^{-} \longrightarrow 5Zn^{+2} + N_2 + 6H_2O + 10e$

d. $[Fe^{+2} \longrightarrow Fe^{+3} + e]\ 5$

$5e + 8H^{+} + MnO_4^{-} \longrightarrow Mn^{+2} + 4H_2O$

$5e + 5Fe^{+2} + 8H^{+} + MnO_4^{-} \longrightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O + 5e$

e. $[Ag \longrightarrow Ag^{+} + e]\ 3$

$3e + 4H^{+} + NO_3^{-} \longrightarrow NO + 2H_2O$

$3Ag + 3e + 4H^{+} + NO_3^{-} \longrightarrow 3Ag^{+} + NO + 2H_2O + 3e$

f. $2Cl^{-} \longrightarrow Cl_2 + 2e$

$2e + 4H^{+} + PbO_2 \longrightarrow Pb^{+2} + 2H_2O$

$2e + 2Cl^{-} + 4H^{+} + PbO_2 \longrightarrow Cl_2 + Pb^{+2} + 2H_2O + 2e$

g. $[Fe^{+2} \longrightarrow Fe^{+3} + e]\ 6$

$6e + 14H^{+} + Cr_2O_7^{=} \longrightarrow 2Cr^{+3} + 7H_2O$

$6Fe^{+2} + 6e + 14H^{+} + Cr_2O_7^{=} \longrightarrow 6Fe^{+3} + 2Cr^{+3} + 7H_2O + 6e$

h. $[2I^{-} \longrightarrow I_2 + 2e]\ 3$

$6e + 14H^{+} + Cr_2O_7^{=} \longrightarrow 2Cr^{+3} + 7H_2O$

$6e + 14H^{+} + Cr_2O_7^{=} + 6I^{-} \longrightarrow 2Cr^{+3} + 7H_2O + 3I_2 + 6e$

i. $[A1 \quad A1^{+3} + 3e]\ 2$

$[2e + 2H^{+} \longrightarrow H_2]\ 3$

$2A1 + 6e + 6H^{+} \longrightarrow 2A1^{+3} + 6e + 3H_2$

j. $[H_2O + C1O_3^- \rightarrow C1O_4^- + 2H^+ + 2e]$

$[e + 2H^+ + C1O_3^- \rightarrow C1O_2 + H_2O]\ 2$

$H_2O + 3C1O_3^- + 2e + 4H^+ \rightarrow C1O_4^- + 2H^+ + 2C1O_2 + 2H_2O + 2e$

$3C1O_3^- + 2H^+ \rightarrow H_2O + C1O_4^- + 2C1O_2$

0 gain 2e/at or 4e

2. a. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

-3 loss of 5c(ox) +2

-3 loss of 3e 0(ox)

b. $3CuO + 2NH_3 \rightarrow N_2 + 3H_2O + 3Cu$

+2 +2 gain of 2e (red) 0

-2 loss of 2e 0(ox)

c. $H_2S + H_2O_2 \rightarrow S + 2H_2O$

-1 gain of le/atom or 2 -e

+5 gain of le (red) +4

d. $Sn + 4HNO_3 \rightarrow SnO_2 + 4NO_2 + 2H_2O$

0 loss of 4e (ox) +4

+5 gain of 3e (ox) +2

e. $3CuS + 6HNO_3 \rightarrow 3Cu(NO_3)_2 + 3S + 2NO + 4H_2O$

+
2

-2 loss of 2e (ox) 0

8
"
-l loss of le (ox) 0
+3

f. $KMnO_4 + 5HC1 \rightarrow KC1 + MnC1_2 + 5C1_2 + 4H_2O$

-
+7 gain of 5e (red) +2 2

or

$2KMnO_4 + 16HC1 \rightarrow 2KC1 + 2MnCl_2 + 2MnCl_2 + 2C1_2 + 8H_2O$

+5 gain of 3e (red) +2

g. $3Cu + 8HNO_3 \longrightarrow 3Cu\ (NO_3)_2 + 2NO + 4H_2O$

0 loss of 2e (ox) + 2

0 gain of le/atom or 2 -1

h. $2CdS + 2I_2 + 4HCl \longrightarrow 2CdCl_2 + 4HI + 2S$

-2 -2 loss of 2e (ox) 0

or

$CdS + I_2 + 2HC1 \longrightarrow CdCl_2 + 2HI + S$

+5 gain of le (red) +4

i. $3HClO_3 \longrightarrow HClO_4 + 2C1O_2 + H_2O$

+5 loss of 2e (ox) +7

+6 gain of 2e (red) +4

j. $2KBr + 2H_2SO_4 \longrightarrow K_2SO_4 + Br_2 + SO_2 + 2H_2O$

-1 loss of le (ox) 0

3. a. Equivalent Weight of $KMnO_4$ = 158.1/5=31.62

b. Equivalent Weight of HNO_3 = 63/3 = 21

c. Equivalent Weight of $HC1O_3$ = 84.5/3 = 28.17