SEM IV: GE & Prog

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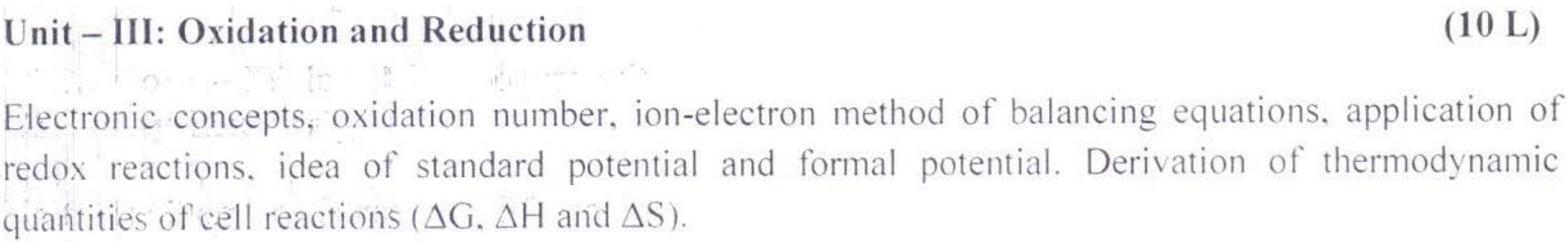
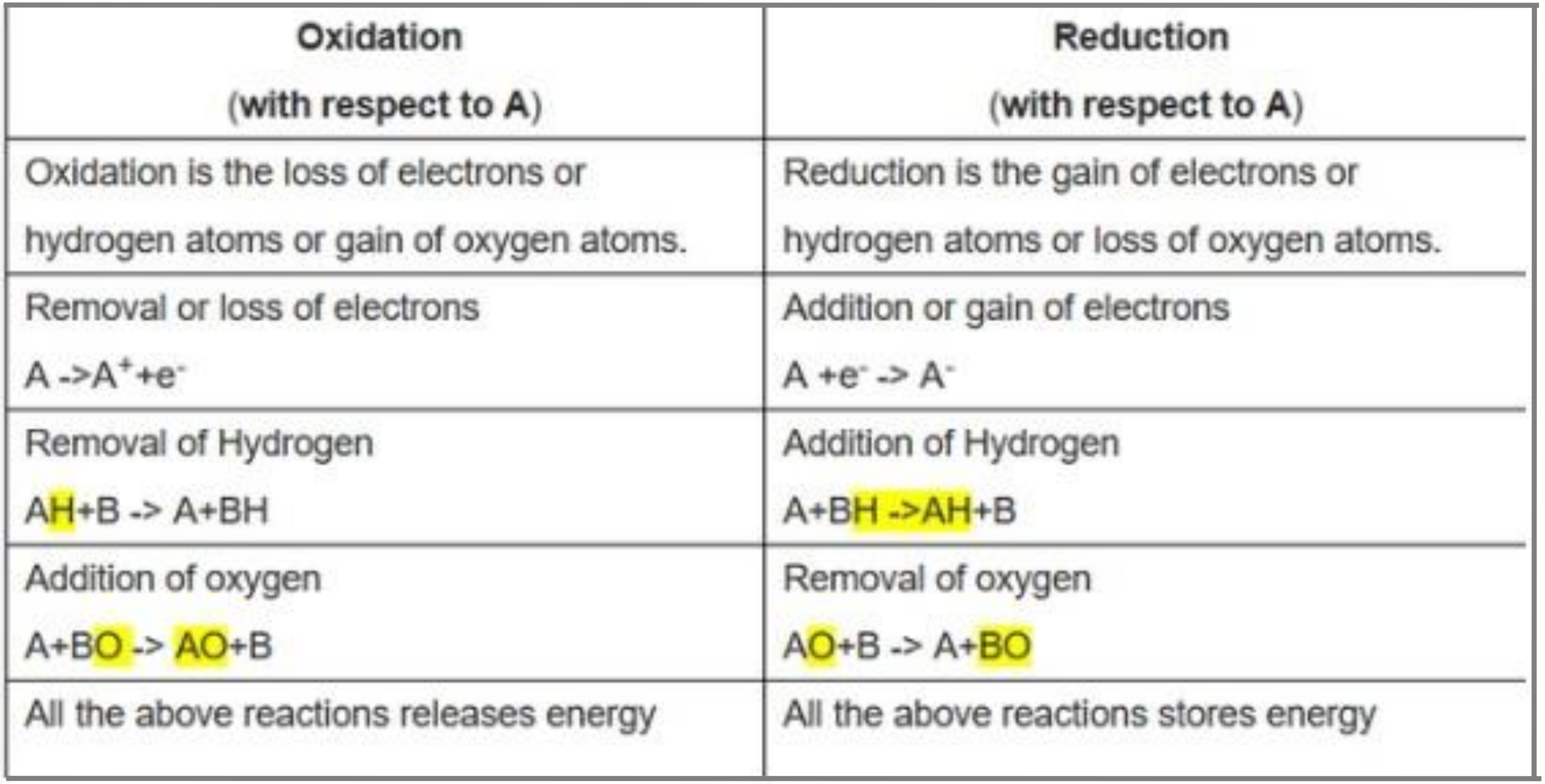
Oxidation & Reduction

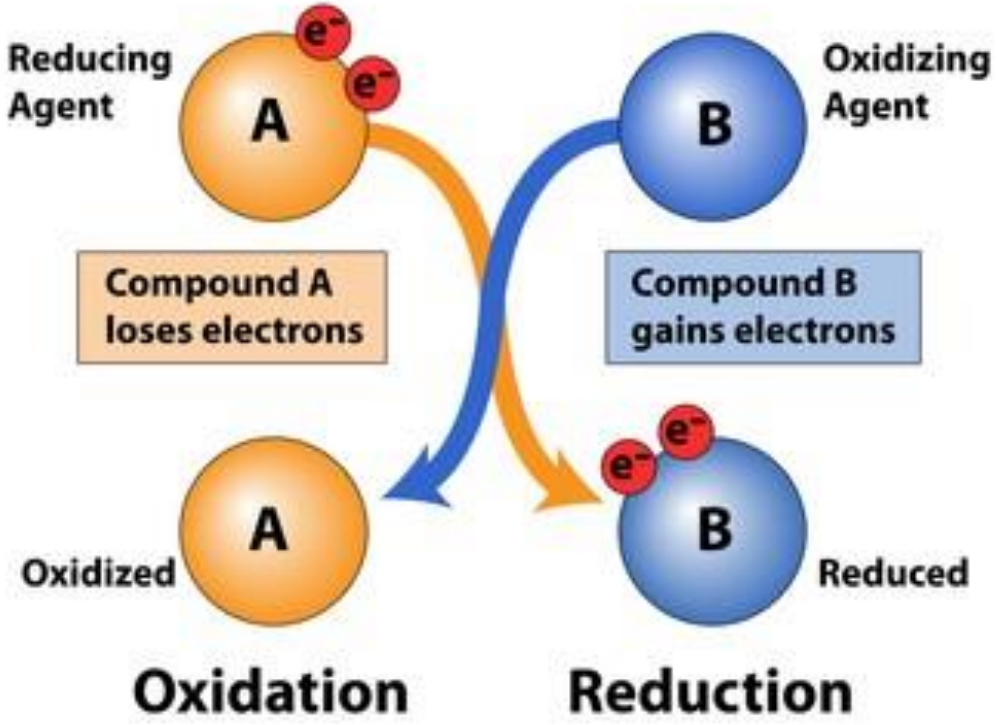


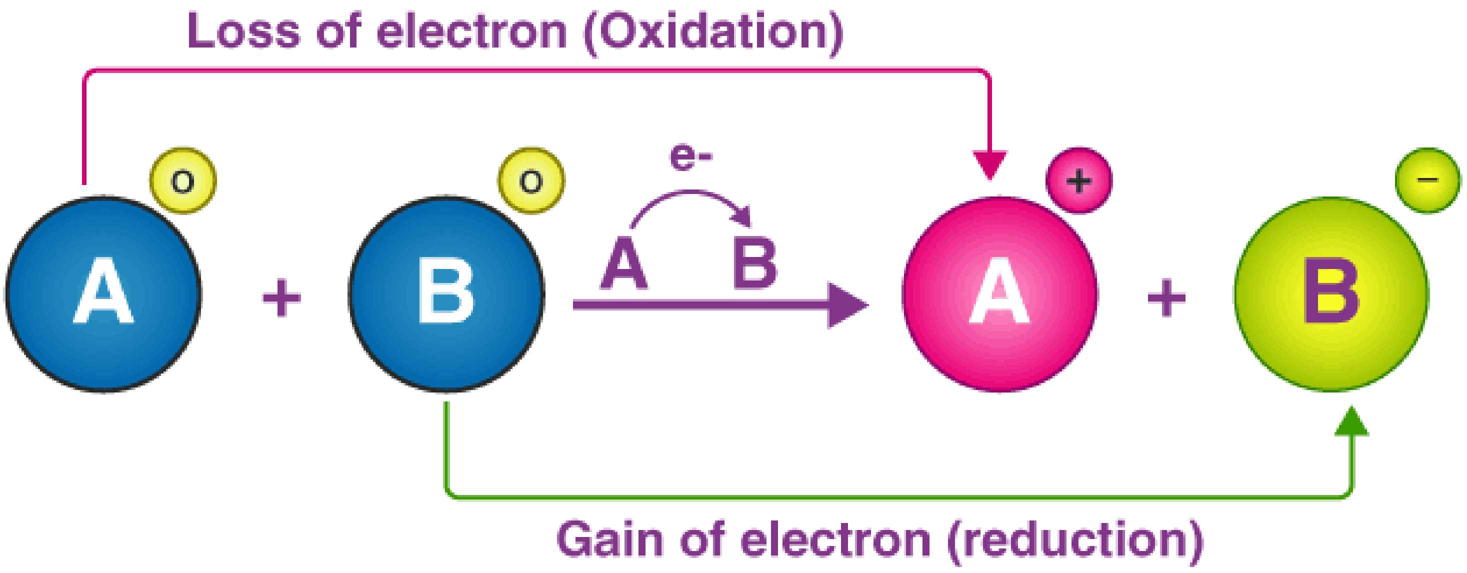
Unit – III: Oxidation and Reduction **(10 L)**

Electronic concepts, oxidation number, ion-electron method of balancing equations, application of redox reactions, idea of standard potential and formal potential. Derivation of thermodynamic quantities of cell reactions (ΔG, ΔH and ΔS).



Oxidation (**with respect to A**)	**Reduction** (**with respect to A**)
Oxidation is the loss of electrons or hydrogen atoms or gain of oxygen atoms.	Reduction is the gain of electrons or hydrogen atoms or loss of oxygen atoms.
Removal or loss of electrons $A \rightarrow A^{+}+e^{-}$	Addition or gain of electrons $A + e^{-} \rightarrow A^{-}$
Removal of Hydrogen AH+B -> A+BH	Addition of Hydrogen A+BH ->AH+B
Addition of oxygen A+BO -> AO+B	Removal of oxygen AO+B -> A+BO
All the above reactions releases energy	All the above reactions stores energy


Reducing Agent
e⁻
e⁻
A
B
Oxidizing Agent
Compound A loses electrons
Compound B gains electrons
e⁻
e⁻
A
Oxidized
B
Reduced
Oxidation
Reduction


Loss of electron (Oxidation)
A
O
+
B
O
e-
A B
A
+
+
B
–
Gain of electron (reduction)

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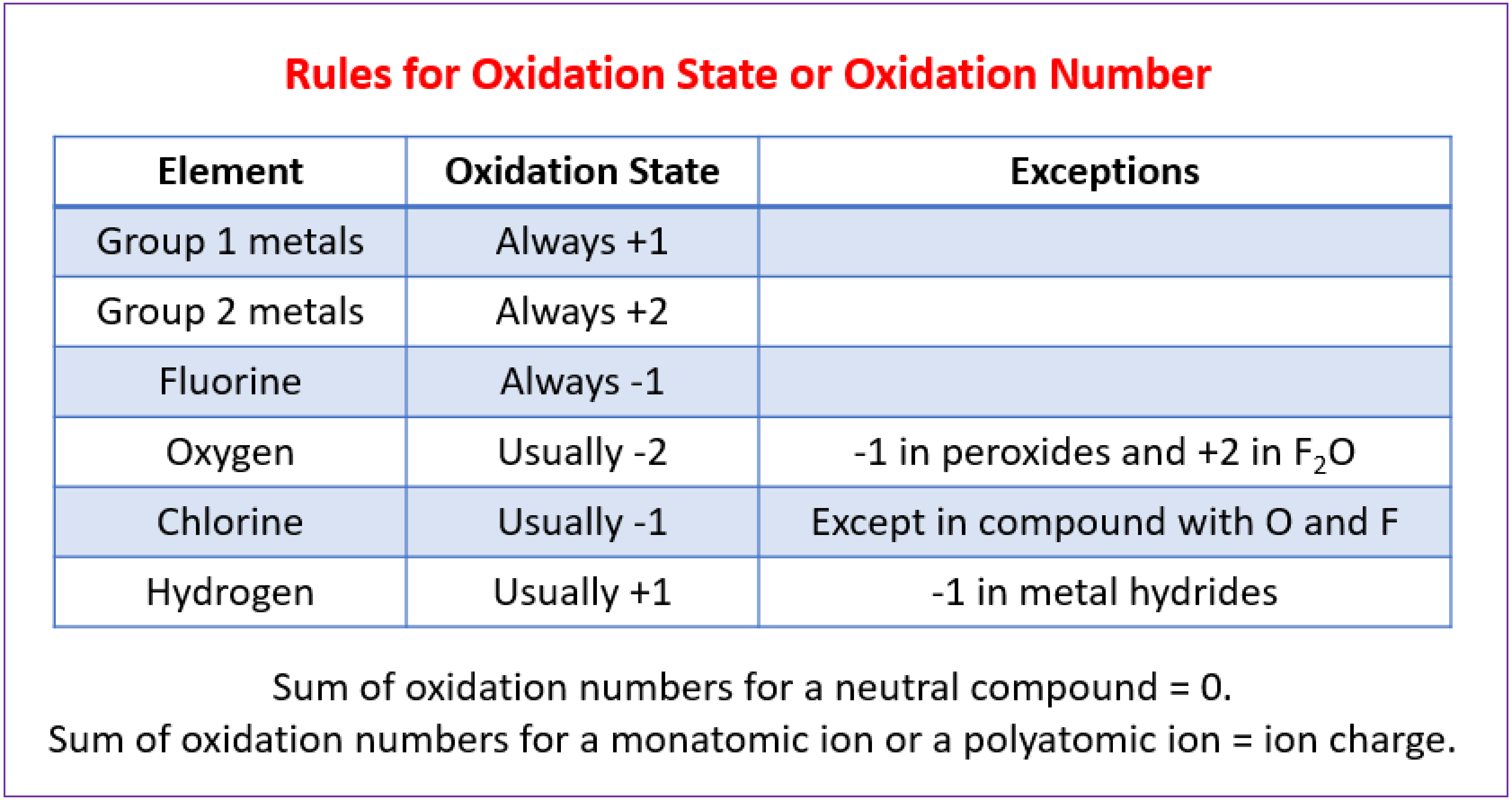
Oxidation number

Oxidation number in simple terms can be described as the **number** that is allocated to elements in a chemical combination. The **oxidation number** is basically the count of electrons that atoms in a molecule can share, lose or gain while forming chemical bonds with other atoms of a different element.



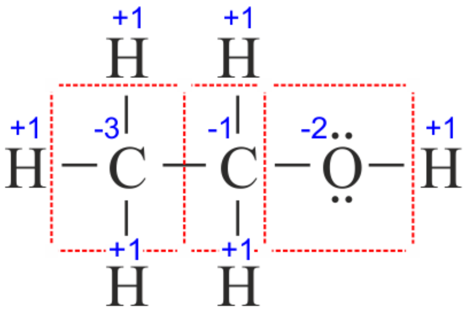
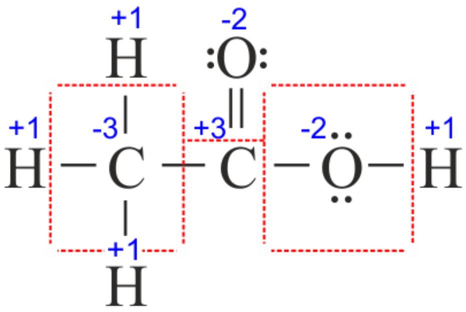
Rules for Oxidation State or Oxidation Number

Element	Oxidation State	Exceptions
Group 1 metals	Always +1	
Group 2 metals	Always +2	
Fluorine	Always -1	
Oxygen	Usually -2	-1 in peroxides and +2 in F_2O
Chlorine	Usually -1	Except in compound with O and F
Hydrogen	Usually +1	-1 in metal hydrides

Sum of oxidation numbers for a neutral compound = 0.
Sum of oxidation numbers for a monatomic ion or a polyatomic ion = ion charge.

Sl.No	Oxidation number of the element	In the compound	Calculation
1	C	CO_2	$x + 2(-2) = 0$ $x = +4$
2	S	H_2SO_4	$2(+1) + x + 4(-2) = 0$ $2 + x - 8 = 0$ $x = +6$
3	Cr	$Cr_2O_7^{2-}$	$2x + 7(-2) = -2$ $2x - 14 = -2$ $x = +6$
4	C	CH_2F_2	$x + 2(+1) + 2(-1) = 0$ $x = 0$
5	S	SO_2	$x + 2(-2) = 0$ $x = +4$

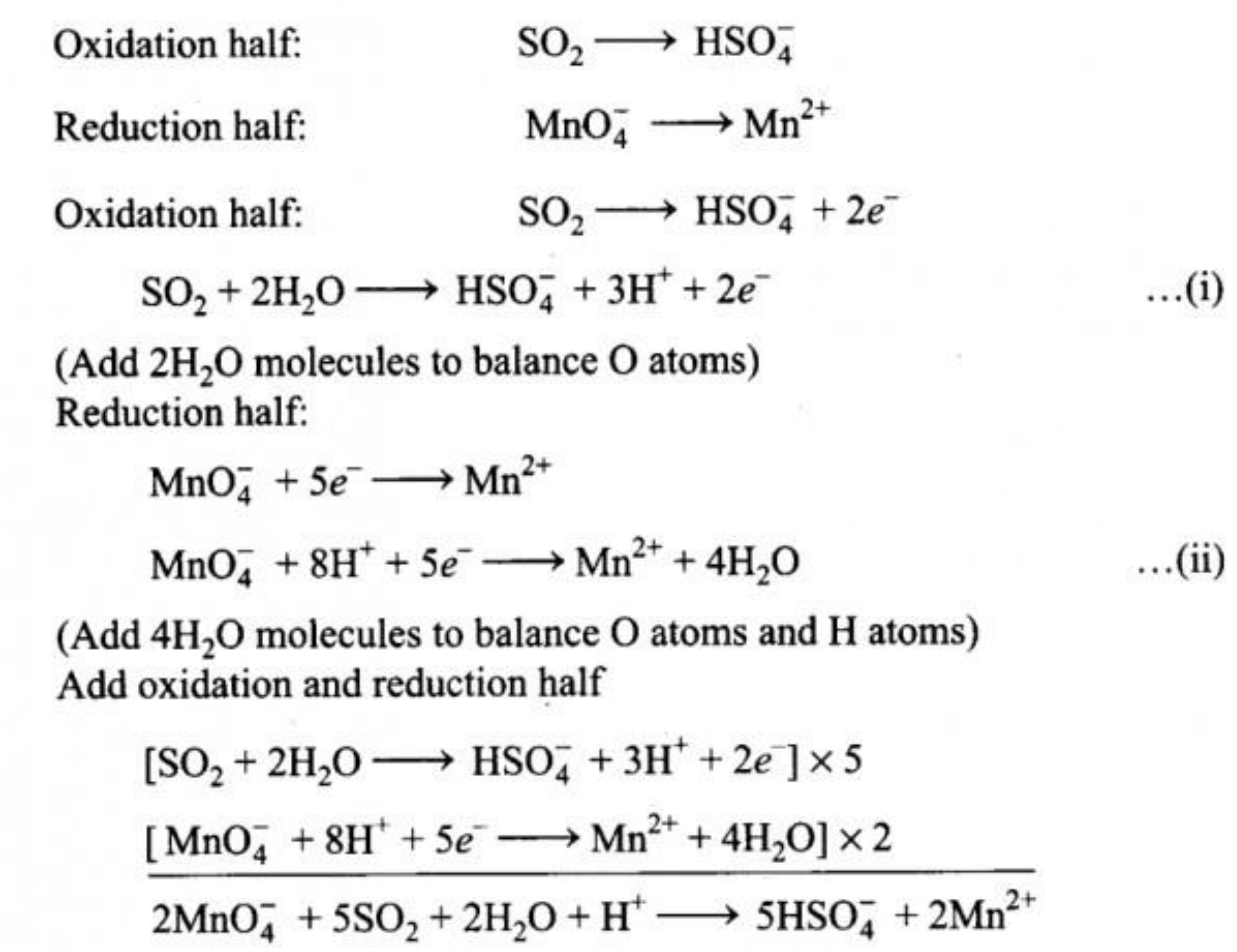
CH_3OH oxidation state of ‘C’?

	Ethanol	Acetic acid
a)		
b)	$\overset{-3}{C}\overset{+1}{H_3}-\overset{-1}{C}\overset{+1}{H_2}\overset{-2}{O}\overset{+1}{H}$	$\overset{-3}{C}\overset{+1}{H_3}-\overset{+3}{C}\overset{-2}{O}\overset{-2}{O}\overset{+1}{H}$
c)	$\overset{0}{R}-\overset{-1}{C}\overset{+1}{H_2}\overset{-2}{O}\overset{+1}{H}$	$\overset{0}{R}-\overset{+3}{C}\overset{-2}{O}\overset{-2}{O}\overset{+1}{H}$
d)	$\overset{-2}{C_2}\overset{+1}{H_6}\overset{-2}{O}$	$\overset{0}{C_2}\overset{+1}{H_4}\overset{-2}{O_2}$

Ion Electron Method –Acidic solution

- Divide the equation into two Half-reactions
- Balance atoms other than H & O
- Balance O by adding H_2O to side that needs O
- Balance H by adding H+ to side that needs H
- Balance charge by adding electrons
- Make electron gain equal electron loss; then add half reactions
- Cancel everything that is same on both sides

$$SO_2 + MnO_4^- \longrightarrow Mn^{2+} + HSO_4^-$$



Oxidation half: $SO_2 \longrightarrow HSO_4^-$

Reduction half: $MnO_4^- \longrightarrow Mn^{2+}$

Oxidation half: $SO_2 \longrightarrow HSO_4^- + 2e^-$

$$SO_2 + 2H_2O \longrightarrow HSO_4^- + 3H^+ + 2e^- \quad \ldots(i)$$

(Add $2H_2O$ molecules to balance O atoms)

Reduction half:

$$MnO_4^- + 5e^- \longrightarrow Mn^{2+}$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad \ldots(ii)$$

(Add $4H_2O$ molecules to balance O atoms and H atoms)

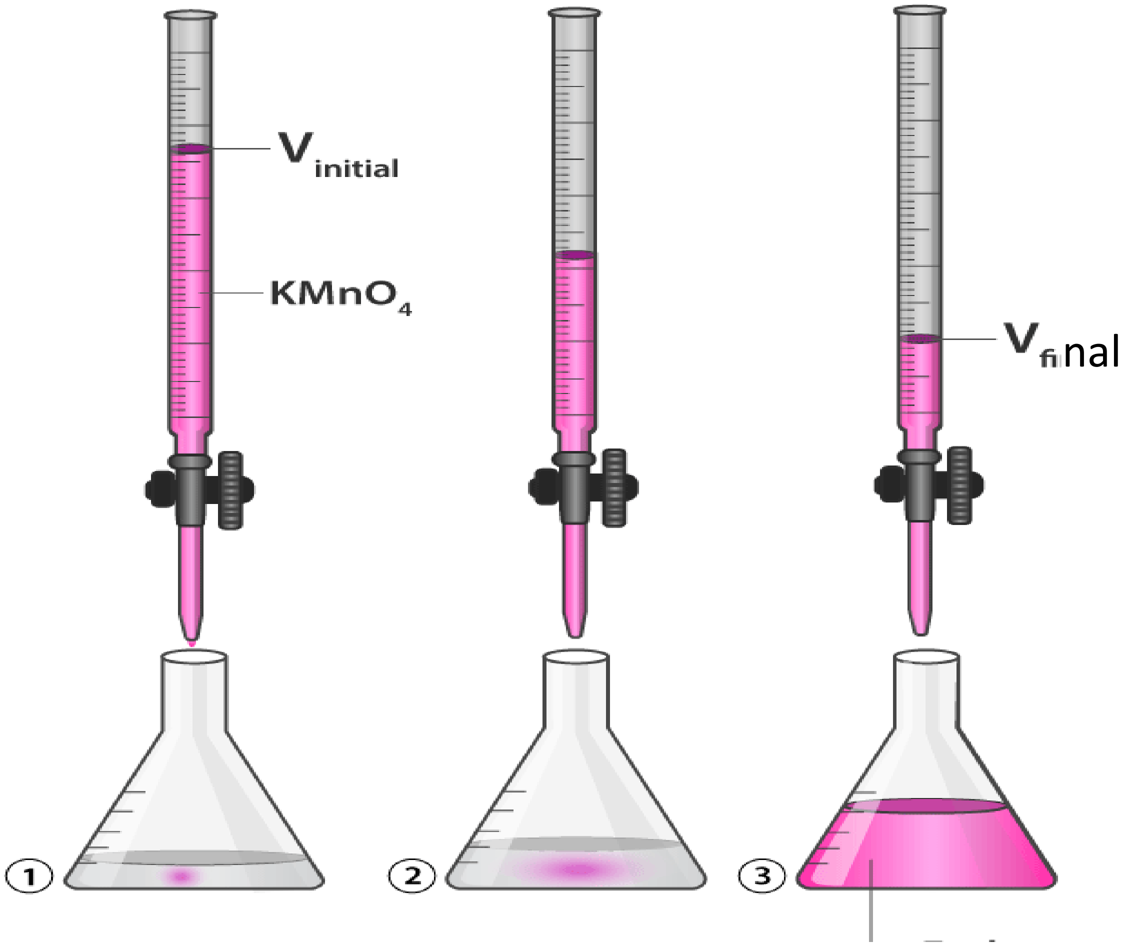
Add oxidation and reduction half

$$[SO_2 + 2H_2O \longrightarrow HSO_4^- + 3H^+ + 2e^-] \times 5$$

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

$$2MnO_4^- + 5SO_2 + 2H_2O + H^+ \longrightarrow 5HSO_4^- + 2Mn^{2+}$$

TITRATION OF OXALIC ACID VS KMnO4



End Point
Pale Violet colour

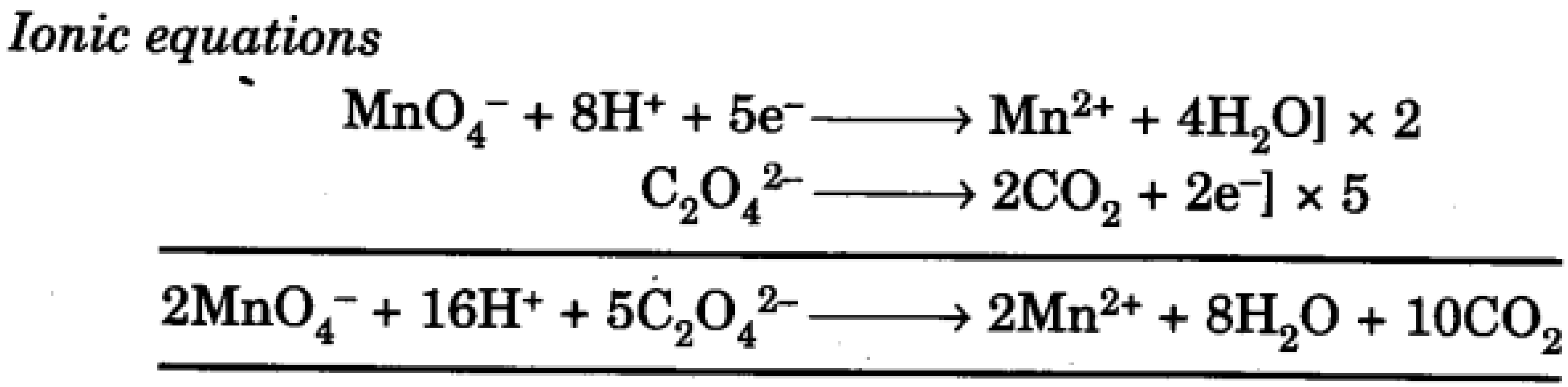
$$V_1S_1=V_2S_2$$

$$V_{final}-V_{initial}=V_2$$

Strength of $KMNO_4=S_2$?

Balance the equation in acid medium

$$MnO_4^- + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2$$

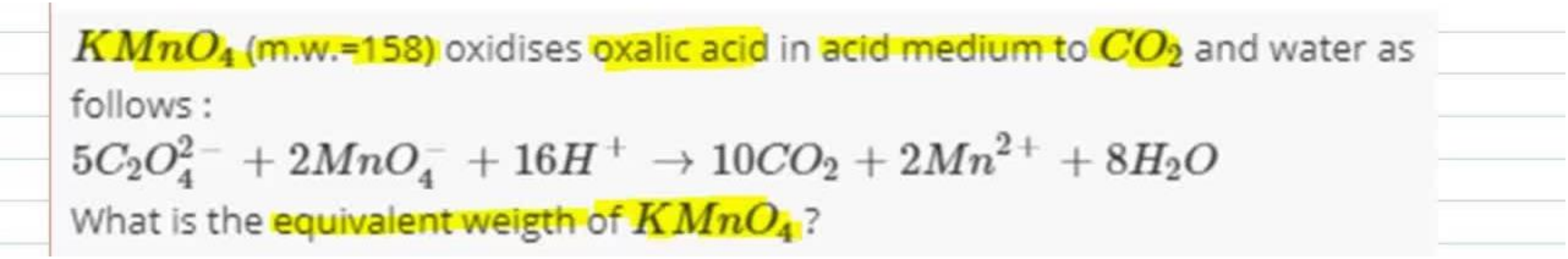


Ionic equations

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

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$



$KMnO_4$ (m.w.=158) oxidises oxalic acid in acid medium to CO_2 and water as follows :

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

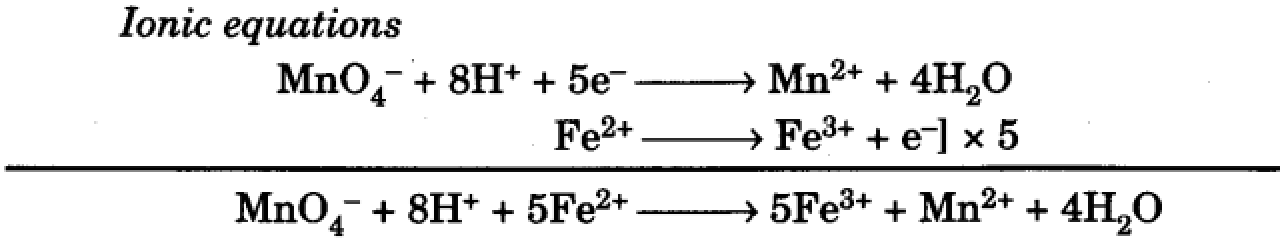
What is the equivalent weigth of $KMnO_4$?

Mohr’s Salt

$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$

$$MnO_4^- + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}$$

Determined by similar way



Ionic equations

$$\begin{array}{r} MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \\ Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5 \\ \hline MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O \end{array}$$

Balance the following rebox reactions by ion electron method:

$MnO_4^{\ominus}(aq) + SO_2(g) \rightarrow Mn^{2+}(aq)$
$+ HSO_4^{\ominus}(aq)$
(in acidic solution)

. $H_2O_2(aq) + Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + H_2O(l)$
(in acidic solution)

$Cr_2O_7^{2-} + SO_2(g) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$ (in acidic solution)

Ion Electron Method –Alkaline solution

- Divide the equation into two Half-reactions
- Balance atoms other than H & O
- Balance O by adding H_2O to side that needs O
- Balance H by adding H+ to side that needs H
- Balance charge by adding electrons
- Add OH- (Alkaline medium) both side, equal number of H^+
- Make electron gain equal electron loss; then add half reactions
- Cancel everything that is same on both sides

$Cl_2 + IO_3^{\ominus} + OH^{\ominus} \rightarrow IO_4^{\ominus} + Cl_2 + H_2O$

Balance the equation in alkaline medium.

Ans:

Reduction: $Cl_2 \rightarrow Cl^{\ominus}$

① Balance Cl atom

$Cl_2 \rightarrow 2Cl^{\ominus}$

② Balance charge by adding electrons

$Cl_2 + 2e^{\ominus} \rightarrow 2Cl^{\ominus}$ —— (I)

Oxidation: $IO_3^{\ominus} \rightarrow IO_4^{\ominus}$

① Balance Oxygen by adding H_2O

$IO_3^{\ominus} + H_2O \rightarrow IO_4^{\ominus}$

② Balance Hydrogen by adding $H^{\oplus}$

$IO_3^{-} + H_2O \rightarrow IO_4^{-} + 2H^{\oplus}$

③ Balance ~~2H+~~ charge by adding ~~2OH-~~ $e^{\ominus}$

$IO_3^{\ominus} + H_2O \rightarrow IO_4^{\ominus} + 2H^{\oplus} + 2e^{\ominus}$

④ Balance $2H^{+}$ by adding $2OH^{-}$

$2OH^{-} + IO_3^{-} + H_2O \rightarrow IO_4^{-} + 2H^{+} + 2OH^{-} + 2e^{\ominus}$

$\Rightarrow IO_3^{\ominus} + 2OH^{\ominus} \rightarrow IO_4^{-} + H_2O + 2e^{\ominus}$ —— (II)

Reduction: $Cl_2 + 2e^{-} \rightarrow 2Cl^{-}$

Oxidation: $IO_3^{-} + 2OH^{-} \rightarrow IO_4^{-} + H_2O + 2e^{-}$

Overall Balanced equation:

$IO_3^{-} + Cl_2 + 2OH^{-} \rightarrow IO_4^{-} + 2Cl^{-} + H_2O$

Balance the following equations in basic medium by ion-electron method and oxidation number methods and identify the oxidising agent and the reducing agent.

(a) $P_4(s) + OH^-(aq) \rightarrow PH_3(g) + HPO_2^-(aq)$

(b) $N_2H_4(1) + ClO_3^-(aq) \rightarrow NO(g) + Cl^-(g)$

(c)
$Cl_2O_7(g) + H_2O_2(aq) \rightarrow ClO_2^-(aq) + O_2(g) + H^+$

Standard Electrode Potential

If a second dissimilar half cell in its standard state is coupled with to a standard hydrogen Electrode (of zero potential) forming a cell, the measured potential difference of the cell Is defined as the standard electrode potential for second electrode (symbol=E^o)

For components of electrochemical cells involved in electrode reactions, the standard State is chosen as 1 atmosphere for gases and 1 M concentration for solutions in the electrode compartments

Oxidation-Reduction Potential

The degree of spontaneity of a reaction is indicated by the change of the reaction. The free Change reflects the driving force of a reaction, and expectedly there is connection between Free energy change and the equilibrium constant of the, expressed as:

$$\Delta G^o = - RT \ln K = - 2.303\ RT \log K$$

A spontaneous reaction is characterised by a negative free energy. The free energy change of a reaction

$$aA + bB \qquad\qquad lL + mM$$

Is given by $\Delta G = \Delta G^o + RT \ln \dfrac{a^l_L\, a^m_M}{a^a_A\, a^b_B}$

Where a's represent the activities of the different species. It follows that when all species are at standard state, that is, unit activity

$$\Delta G = \Delta G^o$$

Now in an electrochemical cell of e.m.f.,E, $\Delta G = -nFE$
ΔG is free energy change in calories, n is the number of moles of electrons transferred in the reaction, F is the Faraday and E is in voltage

At standard state

$$\Delta G^o = -nFE^o$$

Where E^o is the standard potential of the cell. Then we have

$$-nFE = -nFE^o + RT \ln \frac{a^l_L \, a^m_M}{a^a_A \, a^b_B}$$

So that $$E = E^o - \frac{RT}{nF} \ln \frac{a^l_L \, a^m_M}{a^a_A \, a^b_B}$$

An electrode reaction may be written according to international conventions:

$$\text{Oxidant} + ne \rightleftharpoons \text{Reductant}$$

Then we have

$$E = E^o - \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Ox}} = E^o + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}}$$

Our activities may be replaced by concentrations so that

$$\boxed{E = E^{o} + \frac{0.0591}{n} \log \frac{[OX]}{[Red]}}$$

At 25 °C

Where E is observed potential of redox electrode at temperature, T, relative to standard Hydrogen electrode and E^{o} is standard potential.

Formal Electrode Potential

Standard potentials (E^{o})are evaluated with respect to activity and with all ions, expressed in simple ion forms. In practice the solution may be quite concentrated making activities and concentrations unequal and further may contain the ions not in their simple form but in the form of complex

Under such conditions , actual species involved may differ from those to which the standard potentials refer

To recognize such situations, standard redox potentials are replaced by the more practical and useful **formal potentials** (E)

Formal potentials cover the effects of concentrations of the species, pH of the solution, any complexation in solution etc

Applications of Oxidation-Reduction Potential

Prediction of reaction

Consider the standard electrode potentials of the following couples:

$$Cu^{2+} + 2e \rightleftharpoons Cu \qquad E^o = +0.337$$

$$Ag^{+} + e \rightleftharpoons Ag \qquad E^o = +0.799$$

The More negative the potential of the couple the more effective the metal is as reducing agent

Here potential of Cu^{2+}/Cu is less positive than Ag^{+}/Ag couple
So Copper will serve as a better reducing agent

Therefore if Cu wire is dipped into a solution of silver nitrate, there will be a deposit of silver on the copper wire.

But if a silver wire is dipped into a copper (II) solution, there will be no reaction.

Calculation of cell potentials

$$\mathrm{Zn} \left| \, \mathrm{Zn}^{2+} \right\| \mathrm{Ag}^{+} \left| \, \mathrm{Ag} \right.$$

Cell potentials can be calculated by adding algebraically the standard electrode potentials of the electrodes in the cell

The E^o of Zn^{2+}/Zn = -0.763 Volt & The E^o of Ag^{+}/Ag couple = +0.799

Thus the cell potentials of the cell is [–(-0.763) + 0.799] volt=+1.562 Volt

The E^o remains independent of the total number of atoms or ions of the variety.

Applications of Formal Potential

Influence of precipitation

It is common place knowledge that Cu^{2+} can ne estimated iodomaterically by titrating the Iodine liberated from iodide ion:

$$2Cu^{2+} + 4I^- = 2\,CuI \downarrow + I_2$$

A consideration of potentials of the Cu^{2+}/Cu couple and iodine-iodide couple:

$$Cu^{2+} + e \rightleftharpoons Cu^+ \qquad E^o = +0.15 \text{ Volt}$$

$$I_2 + e \rightleftharpoons 2I^- \qquad E^o = +0.54 \text{ Volt}$$

Would indicate a reverse reaction:

$$2Cu^+ + I_2 = 2Cu^{2+} + 2I^-$$

But the anomaly can be explained by taking into consideration the sparing solubility of Cu(I)I. Assuming the iodide concentration as 0.1 M and taking the solubility product of CuI As 10^{-12} we have:

$$K_{SP} = [Cu^+][I^-]; \quad [Cu^+] = \frac{10^{-12}}{10^{-1}} = 10^{-11}\ M$$

The potential of the Cu^{2+}/Cu^+ couple then becomes:

$$E = 0.15 + \frac{0.0591}{1} \log \frac{[Cu^{2+}]}{10^{-11}}$$

$$= 0.15 + 0.0591 \log [Cu^{2+}]$$

Since 0.799 is larger than the E^o of the I_2/I^- couple it follows that the preferred reaction is:

$$2Cu^{2+} + 4I^- = 2\,CuI \downarrow + I_2$$

Influence of precipitation

Under standard conditions, Fe^{2+} reduces Hg^{2+} to Hg_2^{2+}:

$$2Fe^{2+} + Hg^{2+} = Hg_2^{2+} + 2Fe^{3+}$$

A consideration of potentials of the Hg^{2+}/Hg_2^{2+} couple and Fe^{3+}/Fe^{2+} couple:

$$Fe^{3+} + e \rightleftharpoons Fe^{2+} \qquad E^o = +0.77 \text{ Volt}$$

$$Hg^{2+} + e \rightleftharpoons Hg_2^{2+} \qquad E^o = +0.92 \text{ Volt}$$

In presence of thiocyanate ions a reverse reaction occured:

$$Hg_2^{2+} + 2Fe^{3+} = 2Fe^{2+} + Hg^{2+}$$

In presence of thiocyanate ion Hg^{2+} is strongly complexed as $[Hg(SCN)_4]^{2-}$ whereby the Concentration of free Hg^{2+} ion in the solution is lowered.

If the ratio is lowered from 1 to 10^{-3} M, the E will change from E^o=+0.92 Volt to +0.743 Volt.

Thus Hg_2^{2+} becomes a stronger reductant than Fe^{2+}. In practice Hg_2^{2+} can be detected by its ability to force reduction of Fe^{3+} to Fe^{2+} in presence of thiocyanate ion.

It is a common practice to determine copper (II) iodometrically in a mixture of Copper(II) and Iron (III) by prior masking of the iron (III) by excess fluoride. On the addition of excess fluoride ions iron (III) is converted to a strong complex $[FeF_6]^{3-}$ and as a result the redox potential of the Fe^{3+}/Fe^{2+} is substantially reduced from the value of 0.77 volt ,so that iron (III) can no longer oxidise any iodide ion to iodine. But copper (II) does not form such a fluoro complex, so that it can still liberate iodine from iodide ion.

Influence of pH of the solution

The pH of the solution is nicely demonestrated by oxidation of iodide ion in acid medium by AsO_4^{3-} and oxidation of AsO_3^{3-} by iodine in neutral or alkaline medium.
The relevant oxidation potentials are:

$$AsO_4^{3-} + 2H+ + 2e = AsO_3^{3-} + H_2O \qquad ; E^o = + 0.54 \text{ Volt}$$

$$I_2 + 2e = 2I^- \qquad ; E^o = + 0.54 \text{ Volt}$$

The following reaction takes place when the medium is **sufficiently acidic**:

$$AsO_4^{3-} + 2H^+ + 2I^- = AsO_3^{3-} + H_2O + I_2$$

If the solution is brought to a pH-8 by the addition of NaHCO3, the reverse reaction takes place.

$$AsO_3^{3-} + H_2O + I_2 = AsO_4^{3-} + 2H^+ + 2I^-$$

Reason: The [H+] becomes 10^{-8}. This lowering of [H+] from standard value of 1 to 10^{-8} now entirely changes the direction of the redox reaction . The E of the AsO_4^{3-} /AsO_3^{3-} is given by:

$$E = 0.56 + \frac{0.0591}{2} \log \frac{[AsO_4^{3-}]\,[10^{-8}]^2}{[AsO_3^{3-}]}$$

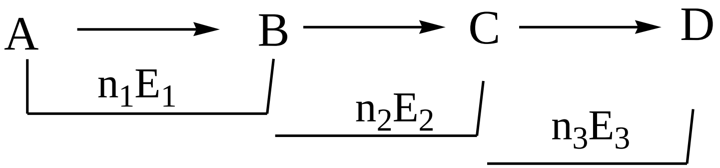
$$= 0.088 + \frac{0.0591}{2} \log \frac{[AsO_4^{3-}]}{[AsO_3^{3-}]}$$

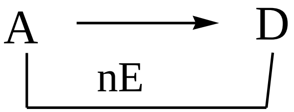
At pH-8, potential value of AsO_4^{3-} /AsO_3^{3-} couple drops far below that of the I2/I- system Making AsO_4^{3-} a far weaker oxidant than iodine.

Computation of Reduction potentials

At standard state

$$\Delta G^{o} = -nFE^{o}$$





$$\Delta G^{o} = -nFE^{o}$$

$$A \longrightarrow B \qquad B \longrightarrow C \qquad C \longrightarrow D$$

$$\Delta G_1{}^{o} = -n_1FE_1{}^{o} \qquad \Delta G_2{}^{o} = -n_2FE_2{}^{o} \qquad \Delta G_3{}^{o} = -n_3FE_3{}^{o}$$

$$\Delta G^{o} = \Delta G_1{}^{o} + \Delta G_2{}^{o} + \Delta G_3{}^{o}$$

$$-nFE^{o} = (-n_1FE_1{}^{o}) + (-n_2FE_2{}^{o}) + (-n_3FE_3{}^{o})$$

$$E^{o} = \frac{nE_1{}^{o} + n_2E_2{}^{o} + n_3E_3{}^{o}}{n}$$

Prediction of reaction spontaneity

From this diagram we can also predict whether the reaction will occur or not .

If $E > o$, then $\Delta G^{o} = (-)$ ve and so the reaction is spontaneous

If $E = o$, then $\Delta G^{o} = 0$ and so the reaction is at equilibrium

If $E < o$, then $\Delta G^{o} = (+)$ ve and so the reaction is **not** spontaneous

Problem XII. : The standard reduction potentials of the Ni^{2+}/Ni and Co^{2+}/Co are –0.25 volt and –0.277 volt. Calculate the equilibrium constant of the reaction

$$Ni^{2+} + Co \rightleftarrows Ni + Co^{2+}$$

and hence draw reasonable conclusion.

The half reactions involved are :

$$Ni^{2+} + 2e \rightleftarrows Ni \; ; \qquad E^{\circ} = -0.25 \text{ volt}$$

$$Co \rightleftarrows Co^{2+} + 2e \; ; \qquad E^{\circ} = +0.277 \text{ volt}$$

The E° of the overall reaction is 0.027 volt. The reaction involves two electrons and hence the equilibrium constant is :

$$\log K = \frac{nE^{\circ}}{0.059} = \frac{2 \times 0.027}{0.059} = 0.915$$

Therefore $K = 8.22$

$$\text{In the reaction } K = \frac{[Ni^{\circ}][Co^{2+}]}{[Ni^{2+}][Co^{\circ}]} = \frac{[Co^{2+}]}{[Ni^{2+}]}$$

Since the equilibrium constant is low not much Ni^{2+} is expected to be reduced by metallic cobalt.

Problem XIII. **:** Consider the following reduction potentials :

$$Cu^{2+} + 2e \rightleftarrows Cu \ ; \qquad E^\circ = 0.337 \text{ volt}$$
$$Zn^{2+} + 2e \rightleftarrows Zn \ ; \qquad E^\circ = -0.763 \text{ volt}$$

and ascertain whether the following reaction will go to completion :

$$Zn(s) + Cu^{2+} \rightleftarrows Zn^{2+} + Cu(s)$$

The E° of the above reaction is $0.337 - (-0.763) = 1.1$ volt. The number of electrons involved i.e. $n = 2$.

$$\therefore \ \log K = \frac{nE^\circ}{0.059} = \frac{2 \times (1.10)}{0.059} = 37 \ ; \ K = 10^{37}$$

Thus $K = \dfrac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{37}$

The equilibrium constant being very large it is certain that the reaction between Cu^{2+} ions and metallic zinc will go to completion.

Problem XIV. **:** From a consideration of the following potentials decide if Mn^{2+} is likely to disproportionate in solution.

$$Mn^{2+} + 2e \rightarrow Mn \ ; \qquad E^\circ = -1.18 \text{ volt}$$
$$Mn^{2+} \rightarrow Mn^{3+} + e \ ; \qquad E^\circ = -1.51 \text{ volt}$$

We multiply the second equation by 2 and then add to get the balanced equation :

$$3Mn^{2+} \rightarrow 2Mn^{3+} + Mn \ ; \ E^\circ = -2.69 \text{ volt}$$

Since the cell voltage turns out to be negative the reaction is not spontaneous and so Mn^{2+} will remain stable in solution.

References:

- Inorganic Chemistry; Part 1: R Sarkar

- www.google.com

- Inorganic Chemistry; Part I: R L Dutta