Comproportionation Rxn :

Comproportionation rxn is the reverse of the disproportionation rxn. In this rxn two different oxidation states of the same element give a product with intermediate oxidation state.

Examples :-

① $\overset{+2}{Ag}(aq) + \overset{0}{Ag}(s) \rightarrow 2\overset{+1}{Ag}(aq)$

② $\overset{-3}{N}H_4\overset{+3}{N}O_2 \rightarrow \overset{0}{N_2} + 2H_2O$

Complementary and Non-complementary rxns :-

- The redox rxns in which oxidant gains the same no. of electrons as the reductant losses are called Complementary redox rxn.
- When the no. of electrons gained and lossed are different, the redox rxns are called non-complementary redox rxn

The complementary rxns are generally faster than the non-complementary rxns.

Examples :- ① $Sn^{2+} + Ti^{3+} = Sn^{4+} + Ti^{+}$

② $Sn^{2+} + Hg^{2+} = Sn^{4+} + \overset{0}{Hg}$

③ $Ce^{4+} + Fe^{2+} = Ce^{3+} + Fe^{3+}$

} Complementary redox rxns

④ $Sn^{2+} + 2Fe^{3+} = Sn^{4+} + 2Fe^{2+}$

⑤ $2Fe^{3+} + Ti^{+} = 2Fe^{2+} + Ti^{3+}$

} Non-complementary redox rxns

Auto-oxidation -Reduction rxn.

Redox rxn in which one compound partially oxidised & reduced.

Reduction

Ex. 1) $2K\overset{+5}{Cl}\overset{-2}{O_3}(s) \longrightarrow 2K\overset{-1}{Cl}(s) + 3\overset{0}{O_2}(g)$

oxidation

Reduction

2) $2\overset{-3}{N}H_4\overset{+5}{N}O_3(s) \longrightarrow 2\overset{0}{N_2}(g) + 4H_2O(g) + O_2(g)$

oxidation

8. What is meant by redox potential? or What is meant by standard reduction potential

⊛ Standard Redox potential:

The standard electrode potential of a metal-metal ion electrode is the e.m.f of a cell made by coupling a normal hydrogen electrode with the metal-metal ion electrode obtained by immersing the metal in its salt soln of 1 (M) concentration at 25°C. The potential of normal hydrogen electrode with the metal-metal ~~ion electrode obtained by~~ is taken as zero.

The standard ~~electrode~~ reduction potential gives a measure of the tendency of metal ions (at unit concentration) to get reduced by gain of electrons.

Metal ions + electrons ⇌ Metal

e.g; $Cu^{2+} + 2e \rightleftharpoons Cu$; $E^{0}_{Cu^{2+}/Cu} = 0.34$ volt.

The standard oxidation potential gives a measure of the tendency of a metal (at unit concentration) to get oxidised by loss of electrons. ~~Capacity of a metal to lose electrons from a soln of its ions at unit concentration.~~

Metal ⇌ Metal ions + electrons

e.g; $Zn \rightleftharpoons Zn^{2+} + 2e$, $E^{0}_{Zn/Zn^{2+}} = +0.763$ volt.

⊛⊛ $\boxed{\text{Reduction potential} = -\text{ Oxidation potential}}$

⊛ Standard e.m.f of a Galvanic cell:

When all the reactants and the products involved in the cell rxn of a Galvanic cell are at unit concentration (1M), the e.m.f of the cell is called standard e.m.f of the cell which is represented as E^{0}_{cell}. It is also called standard cell potential.

⊛ Relation betn free energy and e.m.f of the cell:

We know that, one equivalent of any substance corresponds to 1 Faraday of F coulombs of electricity. Suppose n equivalents of the reactants in a chemical cell are present per mole. For each mole of the converted to products, nF coulombs of electric charge pass through the cell. If E is the e.m.f developed by the cell rxn, the net electrical work

The change in free energy for the overall ~~cell~~ rxn is expressed as

$$\Delta G = \Sigma G_{product} - \Sigma G_{reactant}$$

$$= \Delta G^{\circ} + RT \ln \frac{a_C^{\gamma} \cdot a_D^{\delta}}{a_A^{\alpha} \cdot a_B^{\beta}} \text{ ------------- } ①$$

[where ΔG° = standard free energy change]

We know,

$$\Delta G = -nFE \text{ and } \Delta G^{\circ} = -nFE^{\circ}$$

[where E° = standard e.m.f of the cell]

Thus equation (1) becomes

$$-nFE = -nFE^{\circ} + RT \ln \frac{a_C^{\gamma}\, a_D^{\delta}}{a_A^{\alpha}\, a_B^{\beta}}$$

or,

$$\boxed{E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_C^{\gamma} \cdot a_D^{\delta}}{a_A^{\alpha} \cdot a_B^{\beta}}} \text{ ---------- } ②$$

This equation is known as Nernst equn.

From equation (2) we can write

$$E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{a_C^{\gamma}\, a_D^{\delta}}{a_A^{\alpha} \cdot a_B^{\beta}}$$

or,

$$E = E^{\circ} - \frac{0.059}{n} \log \frac{a_C^{\gamma} \cdot a_D^{\delta}}{a_A^{\alpha} \cdot a_B^{\beta}} \text{ [at 25°C]}$$

[where $\frac{2.303RT}{F} = 0.059$ at 25°C]

This is also the another form of Nernst equn.

For dilute solun equn (2) can be written as

$$E = E^{\circ} - \frac{\overset{RT}{\cancel{0.059}}}{nF} \ln \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha}[B]^{\beta}} \text{ ------- } ③$$

Since ~~At~~ equillibrium, the cell could not perform any work, e.m.f will be zero.

Hence equn (3) becomes

$$E^{\circ} = \frac{RT}{nF} \ln K_{eq.} \quad \left[\text{where } K_{eq.} = \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha} \cdot [B]^{\beta}}\right]$$

or, $nFE^{\circ} = RT \ln K_{eq.}$

or, $-\Delta G^{\circ} = RT \ln K_{eq.}$

available would be nFE joules. When the cell operates, this ~~equal~~ work is equal to the decrease in free energy per mole of the reactant.

Denoting this by $-\Delta G$ we obtain the relation

$$-\Delta G = nFE$$

or, $\boxed{\Delta G = -nFE}$ ①

For thermodynamic principles, we know that at constant temperature and pressure,

ΔG is

1. negative for any spontaneous process.
2. positive for any non-spontaneous process.
3. equal to zero for any system at equillibrium.

Since $\Delta G = -nFE$, we may readily conclude that the e.m.f of a cell will be

1. positive when the cell rxn is spontaneous
2. negative when the cell rxn is non-spontaneous.
3. Equal to zero when the cell rxn reaches at eqm.

At standard state i.e; when the activity of all species appearing in electrode rxn are unity.

$$\boxed{\Delta G^0 = -nFE^0}$$

where ΔG^0 = standard free energy change.
and E^0 = standard e.m.f of the cell.

Q. Derive Nernst equation for an electrochemical cell and establish the relation betn the standard free energy change and equillibrim constant for a given cell rxn.

Let us consider an electrochemical rxn

$$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$$

Where the activities of all species undergo change.

For species A, the free energy for α-moles is

$$G_A = G_A^0 + \alpha RT \ln a_A$$
$$= G_A^0 + RT \ln a_A^{\alpha}$$

Similarly, the expressions for species B, C and D are

$$G_B = G_B^0 + RT \ln a_B^{\beta}$$
$$G_C = G_C^0 + RT \ln a_C^{\gamma}$$
$$G_D = G_D^0 + RT \ln a_D^{\delta}$$