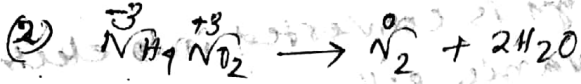
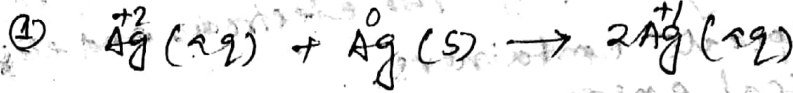


Comproportionation Rxn:

✓✓✓

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.

Example:

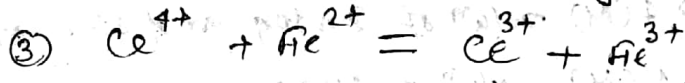
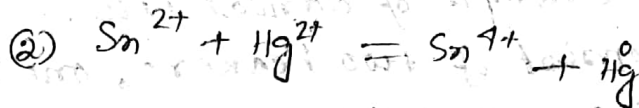
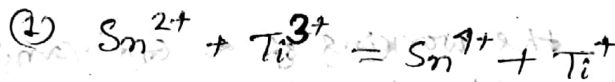


Complementary and Non-complementary rxns:-

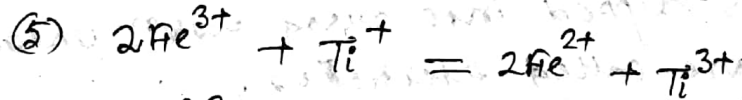
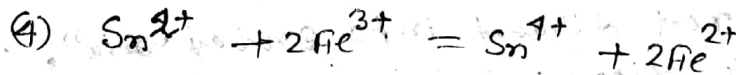
- ⊗ The redox rxns in which oxidant gains the same no. of electrons as the reductant loses are called Complementary redox rxn.
- ⊗ When the no. of electrons gained and lost are different, the redox rxns are called non-complementary redox rxn.

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

Examples:



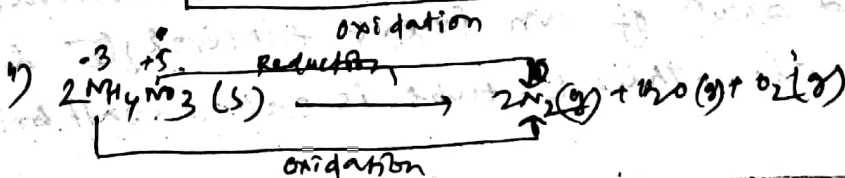
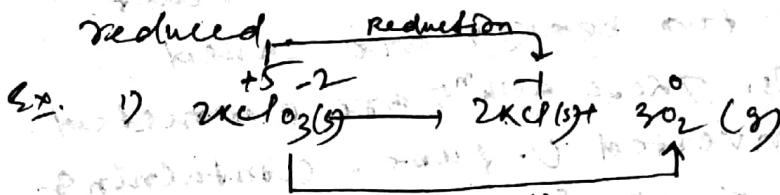
Complementary redox rxns



Non-complementary redox rxns

Auto-oxidation-Reduction rxn

Redox rxn in which one compound partially oxidised & reduced.

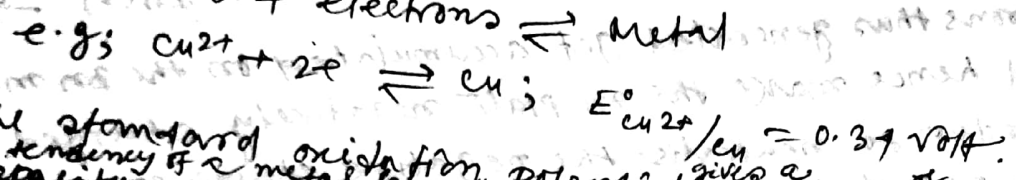
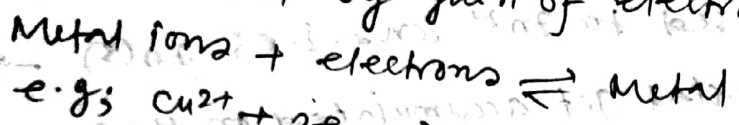


3. What is meant by redox potential? or What is meant by standard reduction potential?

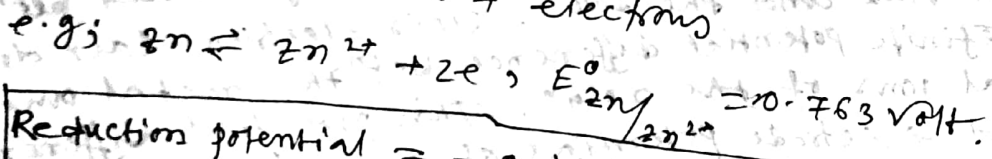
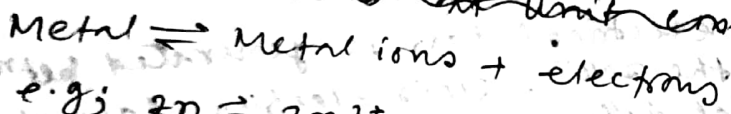
⊗ Standard Redox potential:

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



The standard oxidation potential gives a measure of the tendency of a metal at unit concentration to get oxidised by loss of electrons.



Reduction potential = - 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°_{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 reactants 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

$$\Delta G = \sum G_{\text{product}} - \sum G_{\text{reactant}}$$

$$= \Delta G^\circ + RT \ln \frac{a_c^\gamma \cdot a_d^\delta}{a_A^\alpha \cdot a_B^\beta} \quad \text{--- (1)}$$

[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

$$-nFE = -nFE^\circ + RT \ln \frac{a_c^\gamma \cdot a_d^\delta}{a_A^\alpha \cdot a_B^\beta}$$

$$\text{or, } E = E^\circ - \frac{RT}{nF} \ln \frac{a_c^\gamma \cdot a_d^\delta}{a_A^\alpha \cdot a_B^\beta} \quad \text{--- (2)}$$

This equation is known as Nernst equⁿ.

From equation (2) we can write

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

$$\text{or, } E = E^\circ - \frac{0.059}{n} \log \frac{a_c^\gamma \cdot a_d^\delta}{a_A^\alpha \cdot a_B^\beta} \quad \text{[at } 25^\circ\text{C]}$$

[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

$$E = E^\circ - \frac{RT}{nF} \log \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta} \quad \text{--- (3)}$$

Since at equilibrium, the cell could not perform any work, e.m.f will be zero.

Hence equⁿ (3) becomes

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

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

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

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

$$-\Delta G = nFE$$

$$\text{or, } \boxed{\Delta G = -nFE}$$

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 equilibrium.

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,

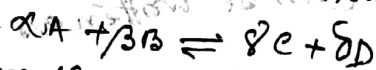
$$\boxed{\Delta G^\circ = -nFE^\circ}$$

where ΔG° = standard free energy change.

and E° = 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 equilibrium constant for a given cell rxn.

Let us consider an electrochemical rxn



where the activities of all species undergo change.

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

$$\begin{aligned} G_A &= G_A^\circ + \alpha RT \ln a_A \\ &= G_A^\circ + RT \ln a_A^\alpha \end{aligned}$$

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

$$G_B = G_B^\circ + RT \ln a_B^\beta$$

$$G_C = G_C^\circ + RT \ln a_C^\gamma$$

$$G_D = G_D^\circ + RT \ln a_D^\delta$$