Unit 5:
REDOX REACTION

Concepts of Oxidation and Reduction.

*) Oxidation	*) Reduction
Classical: addition of oxygen/electronega-tive radical.	removal of oxygen/electronegative radical.
removal of hydrogen/electro-positive radical.	addition of hydrogen/electropositive radical.
Modern: loss of electrons	gain of electrons
Oxidation number. increase in oxidation number.	decrease in oxidation number.

*) Oxidizing agent (Oxidant):
The reagent that oxidizes others but itself undergoes reduction is called oxidant.

*) Reducing agent (Reductant)
The reagent that reduces others but itself oxidizes is called reductant.

*) Oxidation number:
The residual charge left on an atom when other atoms of the molecules are removed is called oxidation number.

Balancing Reaction Using Ion-electron Method:

i) Divide the equation into oxidation half and reduction half.

ii) Balance oxidation and reduction half separately.

iii) At first, balance all elements except hydrogen and oxygen.

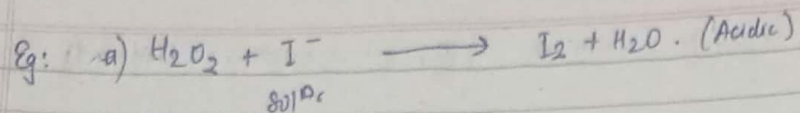iv) Balance oxygen by addition water molecule on either side.

v) Balance hydrogen by adding H^+ ion on required side.

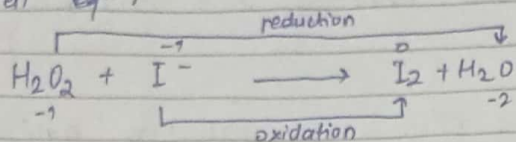vi) Finally charge is balanced by adding electron on either side.

vii) After separate balancing, the oxidation and reduction half are added and then electrons are cancelled out.

viii) If the reaction is in acidic medium, it is balanced reaction but if it occurs in basic medium,
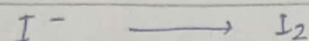a) OH^- ions equal to H^+ ions are added.

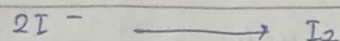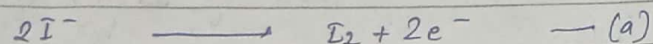b) OH^- and H^+ ions give water molecules that are eliminated from both sides giving balanced equation.
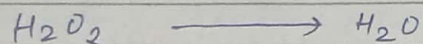
Eg: a) $H_2O_2 + I^- \longrightarrow I_2 + H_2O$. (Acidic)

sol^n

Given eq^n,

$$\overset{-1}{H_2O_2} + \overset{-1}{I^-} \longrightarrow \overset{o}{I_2} + \overset{-2}{H_2O}$$

reduction

oxidation

for oxidation half,

$$I^- \longrightarrow I_2$$

Balancing elements other than oxygen and hydrogen

$$2I^- \longrightarrow I_2$$

Balancing charge on product side,

$$2I^- \longrightarrow I_2 + 2e^- \quad — (a)$$

for reduction half,

$$H_2O_2 \longrightarrow H_2O$$

Balancing oxygen on product side,

$$H_2O_2 \longrightarrow 2H_2O$$

Balancing hydrogen on reactant side,

$$2H^+ + H_2O_2 \longrightarrow 2H_2O$$

Balancing charge on reactant side,

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O \quad —(b).$$

Here, adding (a) and (b),

$$2I^- \longrightarrow I_2 + 2e^-$$
$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$$
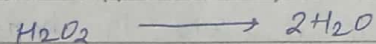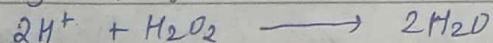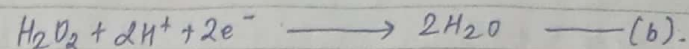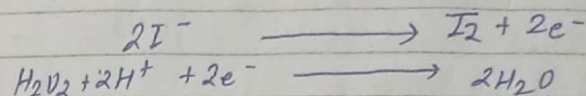
The overall balanced reaction is,

$$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + \cancel{2e^-} 2H_2O$$

b): $ClO^- + CrO_2^- = CrO_4^{2-} + Cl^-$ (Basic)

Soln.

Given eq reaction,

$$\cancel{ClO_2} \quad \overset{1}{Cl}O^- + \overset{+3}{Cr}O_2^- \longrightarrow \overset{+6}{Cr}O_4^{\,2-} + \overset{-1}{Cl^-}$$
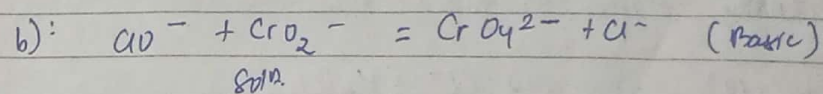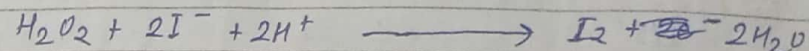
oxidation

reduction.

For oxidation half,

$$CrO_2^- \longrightarrow CrO_4^{--}$$
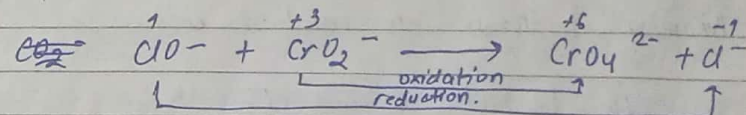
Balancing oxygen on reactant side.

$$CrO_2^- + 2H_2O \longrightarrow CrO_4^{--}$$
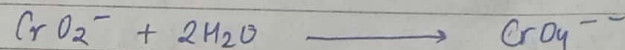
Balancing hydrogen on product side,
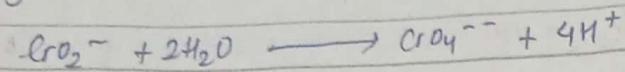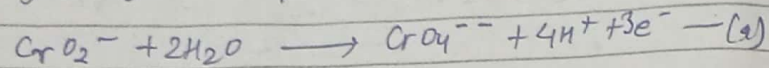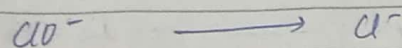
$$CrO_2^- + 2H_2O \longrightarrow CrO_4^{--} + 4H^+$$

Balancing charge on product side,

$$CrO_2^- + 2H_2O \longrightarrow CrO_4^{--} + 4H^+ + 3e^- \quad —(a)$$

for reduction half,

$$ClO^- \longrightarrow Cl^-$$

Balancing oxygen on product side,

$$ClO^- \longrightarrow Cl^- + H_2O$$

Balancing hydrogen on reactant side,

$$ClO^- + 2H^+ \longrightarrow Cl^- + H_2O$$

Balancing charge on reactant side,

$$ClO^- + 2H^+ + 2e^- \longrightarrow Cl^- + H_2O \quad —(b).$$

So,

$$2CrO_2^- + 4H_2O \longrightarrow 2CrO_4^- + 8H^+ + 2e^-$$
$$ClO^- + 2H^+ + 2e^- \longrightarrow Cl^- + H_2O$$

Adding we get,

$$2CrO_2^- + ClO^- + \cancel{2H^+} + \overset{3}{\cancel{4}}H_2O \longrightarrow 2CrO_4^{--} + \overset{6}{\cancel{8}}H^+ + Cl^-$$
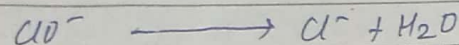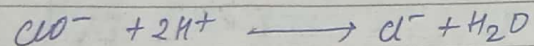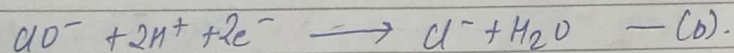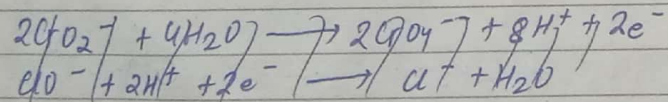
Since reaction occurs in basic medium,
adding 6 OH^- on both sides

$$2CrO_2^- + ClO^- + 3H_2O + \cancel{6}OH^- \longrightarrow 2CrO_4^{--} + Cl^- + \cancel{6}H^+ + 6OH^-$$

or, $2CrO_2^- + ClO^- + 3H_2O + 6OH^- \longrightarrow 2CrO_4^{--} + Cl^- + \cancel{6}H_2O$

or $2CrO_2^- + ClO^- + 6OH^- \longrightarrow 2CrO_4^{--} + Cl^-$
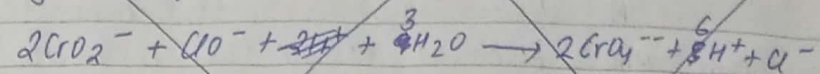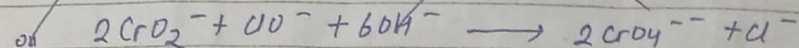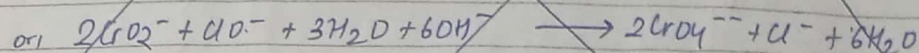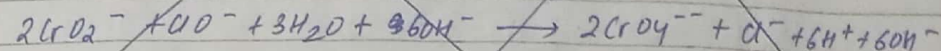
So, multiplying (a) by 2 and (b) by 3,

$$2CrO_2^- + 2H_2O \longrightarrow 2CrO_4^{--} + 8H^+ + 6e^-$$
$$3ClO^- + 6H^+ + 6e^- \longrightarrow 3Cl^- + 3H_2O$$

Adding we get

$$2CrO_2^- + 3ClO^- + H_2O + \cancel{6H^+} \longrightarrow 2CrO_4^{--} + 3Cl^- + 2H^+$$

Adding 2OH^- on both sides

$$2CrO_2^- + 3ClO^- + H_2O + 2OH^- \longrightarrow 2CrO_4^{--} + 3Cl^- + 2H^+ + 2OH^-$$

or, $2CrO_2^- + 3ClO^- + 2OH^- \longrightarrow 2CrO_4^{--} + 3Cl^- + H_2O$
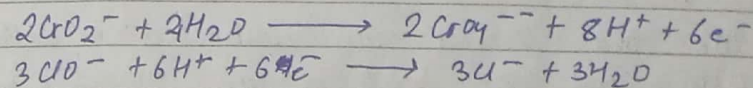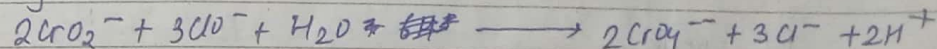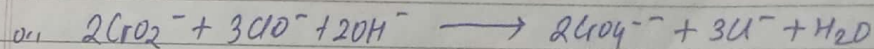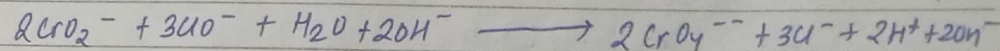
This is the balanced equation.

Galvanic Cell / Voltaic Cell / Electrochemical Cell

A device that converts chemical energy into electrical energy as a result of spontaneous redox reaction is called galvanic cell.

The two beakers are connected by salt bridge and the electrodes are connected by copper wire with an ammeter.

At anode,
→ oxidation occurs
$$Zn \longrightarrow Zn^{2+} + 2e^-$$

At cathode,
— reduction occurs.
$$Cu^{2+} + 2e^- \longrightarrow Cu.$$

Net redox reaction:
$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

Representation of cell:

phase boundary ↓   ↙ salt bridge   → phase boundary

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

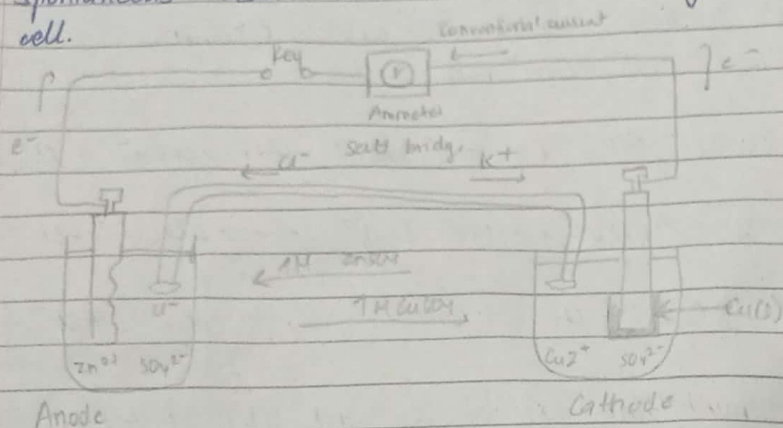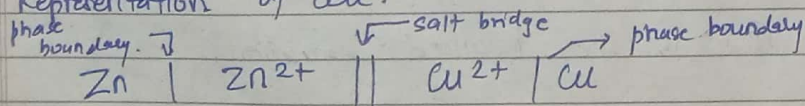# Salt bridge:

Salt bridge is U-shaped tube containing KCl, KNO_3 or NH_4NO_3 solution in agar-agar gel.

It establishes electrical contact between two half cells and doesn't participate in chemical reaction.

→ It prevents the any net charge accumulation in either half cell.

Here, voltage of glalvanic cell is the function of

(a): the ratio of concentration of zinc and copper cupric ions.

voltage increases if reactant concentration increases voltage decreases if product concentration decreases.

(b): It is the characteristic of both of the chemical substance involved in cell reactions and their concentration.

(x): Types of Electrodes:
The common types of electrodes that are used in galvanic cells are: active metal, inert, gas electrodes.

(a): Active metal electrodes:
They are active metals and dissolved or formed during cell reaction.
Eg: Zn-Cu electrodes.

(b): Inert/sensing electrode:
They remain unchanged by net cell reaction.
Eg: Platinum (Pt) and Graphite (C) electrode.

(c): Gas Electrodes:
They also remain unchanged by cell reaction.
Eg: standard hydrogen electrode.

Cell potential / Standard Cell Potential (ΔE°)
Cell potential is the difference between the electrodes present in the two half cells of electrochemical cell.

Standard cell Potential is the cell potential of galvanic cell measured at conditions of
1-M concentrations for all dissolved materials
1-atm pressure for all gases.
at $25^\circ C$.

Standard Cell Potential (ΔE°) is driving force of the cell potential.

(x) Illustration:
A Zn-Cu standard cell $(\Delta E^\circ = 1.1 V)$ is connected to external variable voltage that opposes the cell voltage and ammeter indicates direction of flow.
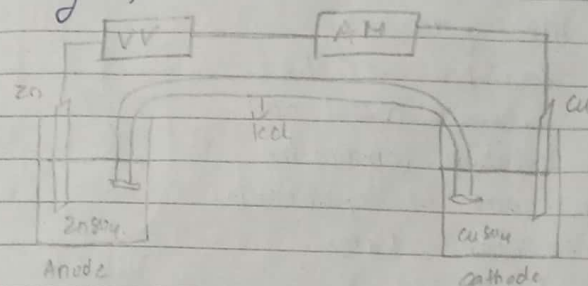
There are three distinct cases.

(a): $EV < 1.1 V$

→ Ammeter shows electron flow from Zn to Cu.
Spontaneous cell reaction: $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$

(b): $EV > 1.1V$

→ Ammeter shows electron flow from Cu to Zn.
Spontaneous cell reaction: $Cu + Zn^{2+} \longrightarrow Zn + Cu^{2+}$

(c): $EV = 1.1 V$

→ No electron flow through ammeter
→No net cell reaction.
→ the std driving force is opposed by equal amount of external voltage.

Mathematically,

$$\Delta E^° = \Delta E^°_{cathode} - \Delta E^°_{anode}$$

if $\Delta E^° = +ve$, reaction feasible
if $\Delta E^° = -ve$, reaction non-feasible.

Standard Electrode Potential,

The potential difference developed at the interface between metal and electrolyte solution containing its own ions at equilibrium in 1M solution, 1 atm pressure and 298 K.
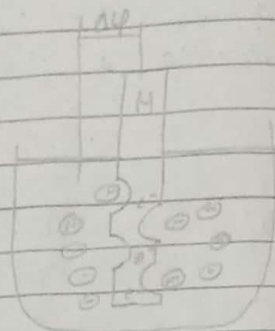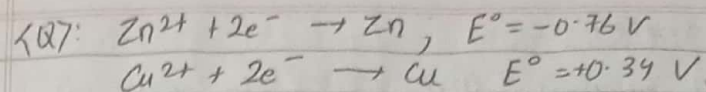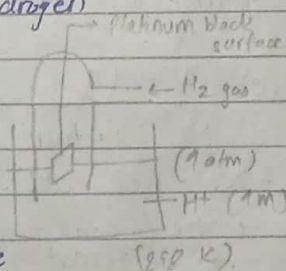
Fig: Half cell.

$E^°$ is generally standard reduction potential.

Standard Hydrogen Electrode:

A hydrogen electrode in which the pressure of hydrogen gas is maintained at 1 atm, concentration of H^+ ions is 1M at 298 K is called standard hydrogen electrode.

Since it has potential $0.00 V$ at all temperature, it is used as reference electrode.
It can be used as cathode or anode depending on other half cell.

Platinum black surface
$e^- H_2$ gas
(1 atm)
H^+ (1M)
(298 K)

< Q7: $Zn^{2+} + 2e^- \rightarrow Zn$, $E^° = -0.76 V$
$Cu^{2+} + 2e^- \rightarrow Cu$ $E^° = +0.34 V$

a) Write net cell reaction.
b) Write cell oxe representation.
c) Calculate $\Delta E^°$ cell.

Sol^n:

Given,
$E^°$ Zn^{++}/Zn = $-0.76 V$
$E^°$ Cu^{++}/Cu = $+0.34 V$

Since, $E^° Cu^{++}/Cu > E^° Zn^{++}/Zn$,
Cu is cathode and Zn is anode.

(a): Net cell reaction:

$$Zn \longrightarrow Zn^{++} 2e^-$$
$$Cu^{++} + 2e^- \longrightarrow Cu^{++}$$

Net cell reaction: $Zn + Cu^{++} \longrightarrow Cu + Zn^{++}$
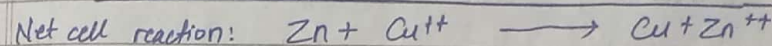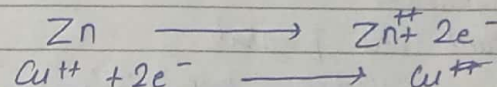
(b). Net cell representation:
$$Zn | Zn^{++} || Cu^{++} | Cu.$$
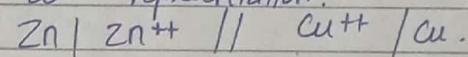
(c): $\Delta E^°$ cell = $\Delta E^°_{cathode} - \Delta E^°_{anode}$
= $+0.34 - (-0.76)$
= $+1.1 V$.

The reaction is feasible.

Nernst Equation:

An equation that relates the reduction potential of a reactant to the standard electrode potential, temperature and activities of concentration of chemical species undergoing react of redox process.

Consider a reaction,

$$aA + bB \rightleftharpoons -cC + dD$$

Sol,

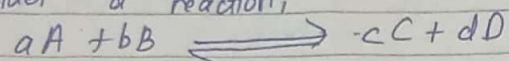$$\Delta E = \Delta E^\circ - \frac{0.059}{n} \log \left[\frac{[C]^c [D]^d}{[A]^a [B]^b}\right]_{eqm.}$$
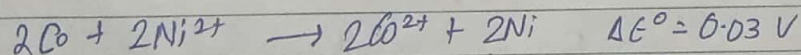
Here,

ΔE = cell potential
ΔE° = standard cell potential.
n = number of electron transferred.

*) Applications:

i): Cell potential of a reaction remains unaffected by multiplying the reaction by any positive number.

$$2Co + 2Ni^{2+} \longrightarrow 2Co^{2+} + 2Ni \qquad \Delta E^\circ = 0.03 \, V$$

$$\Delta E = \Delta E^\circ - \frac{0.059}{4} \log \left(\frac{[Co^{2+}]^2}{[Ni^{2+}]^2}\right) \Rightarrow \Delta G = \Delta G^\circ - \frac{0.059}{2} \log \left(\frac{[Co^{++}]}{[Ni^{++}]}\right)$$

Here, the form of Nernst equation is consistent.

(ii): To predict spontaneity of reaction:

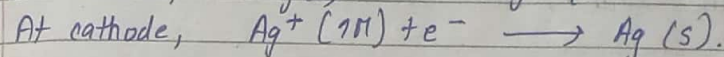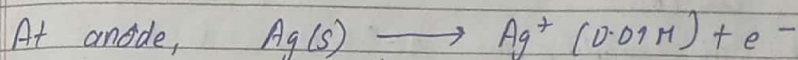If $\Delta E = +ve$, reaction spontaneous in forward direction
if $\Delta E = -ve$, reaction spontaneous in backward direction.

(a): If reactant concentration is increased or product concentration is decreased, the cell voltage becomes more positive.

(b): If reactant concentration is decreased or product concentration is increased, the cell voltage becomes more negative.

(iii): Concentration Cell:

The more dilute solution is anode and more concentrated solution is cathode.

At anode, $Ag(s) \longrightarrow Ag^+ (0.01M) + e^-$
At cathode, $Ag^+ (1M) + e^- \longrightarrow Ag(s)$.

Net cell reaction.

$$Ag^+ (1M) \longrightarrow Ag^+ (0.01 M).$$
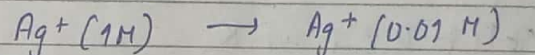
until Until anode and cathode have equal concentration, cell reaction is spontaneous.
for concentrat

For concentration cell, $\Delta E^\circ = 0$.
Using Nernst equation,

$$\Delta E = \Delta E^\circ - \frac{0.059}{1} \log \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right) \frac{(Ag^+)_{dilute}}{[Ag^+] \, concentrated}$$

$$= 0 - \frac{0.059}{1} \log \left(\frac{0.01}{1} \right)$$

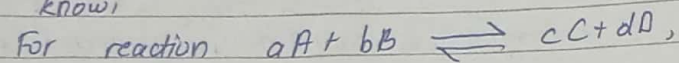$$\therefore \Delta E = 0.12 \, V.$$

(iv): Calculating equilibrium constant.

We know,

For reaction $aA + bB \rightleftharpoons cC + dD$,

Nernst eqn is:

$$\Delta E = \Delta E^\circ - \frac{0.059}{n} \log \left[\frac{[C]^c [D]^d}{[A]^a [B]^b} \right] \quad eq^n$$

We know,

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = K$$

and at equilibrium, $\Delta E^\circ = 0$.

or So, eq^n (1) becomes.

$$0 = \Delta E^\circ - \frac{0.059}{n} \log K$$

or $\frac{\Delta E^\circ \times n}{0.059} = \log K$

$$\therefore K = 10^{\frac{n \Delta E^\circ}{0.059}}$$

Here, if $\Delta E^\circ = +ve$, $K > 1$, forward reaction spontaneous.
if $\Delta E^\circ = -ve$, $K < 1$, backward reaction is spontaneous.

Electrolysis:

The process in which the dissociation of electrolyte occurs when electricity is provided resulting in the migration of these particles towards electrodes.

1 Faraday $\Rightarrow$ Total charge of one mole of electrons.
$= (1.6 \times 10^{-19}) \times (6.023 \times 10^{-23}) = 96,500 \, C$

Charge = current × time.

$$\therefore Q = It \qquad W = \frac{E}{F} It = ZIt.$$

$\angle Q7$: $CuSO_4$ solution is electrolyzed for 7 minutes with 0.6 A current. How much Cu is deposited?

soln.

Here,

$$Cu^{2+} + 2e^- \longrightarrow Cu$$
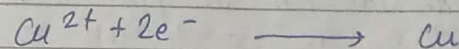
Charge $(Q) = 0.6 \times 7 \times 60$

$$= 252 \, C \qquad = 2.6 \times 10^{-3} \, F$$

$$\therefore \text{Weight deposited} = \frac{Q}{n} = \frac{2.6 \times 10^{-3}}{2}$$

$$= 1.3 \times 10^{-3} \, mol.$$

Rusting of Iron:

When iron is exposed to moist air, a brown coloured substance $(Fe_2O_3 \cdot xH_2O)$ deposits on its surface which is called rusting.

The most convincing theory is electrochemical theory of rusting.

Due to heterogeneous distribution of impurities, some portions of Fe are at lower electrical potential whereas some are at higher electrode potential.
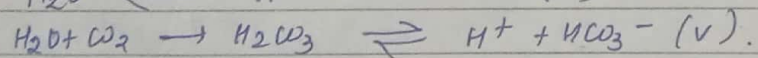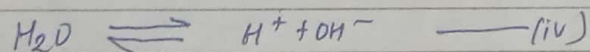
So, some region acts as anode and some region acts as cathode.

At anode, iron oxidizes: $\quad Fe \longrightarrow Fe^{++} + 2e^- \quad —(1)$

Electrodes migrate to anode and reduce oxygen to hydroxide ion in presence of moisture.

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad —(ii)$$
$$2H^+ + 2e^- \longrightarrow H_2 \quad —(iii).$$
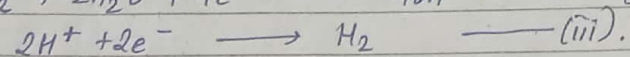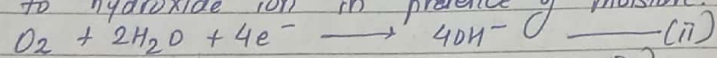
H^+ ions required for reaction (iii) produced by ionization of water or dissociation of H_2CO_3 formed by CO_2 and H_2O on iron surface.

$$H_2O \rightleftharpoons H^+ + OH^- \quad —(iv)$$
$$H_2O + CO_2 \longrightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad —(v).$$

Fe^{++} from anode and OH^- from cathode combines forming ferrous hydroxide.

$$Fe^{++} + 2OH^- \longrightarrow Fe(OH)_2 \quad —(vi)$$
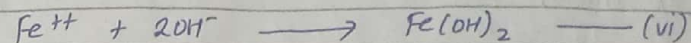
Ferrous hydroxide is oxidized to ferric hydroxide by air in moisture presence which is unstable and thus decomposes to ferric oxide.

$$4Fe(OH)_2 + O_2 + H_2O \longrightarrow 4Fe(OH)_3 \quad —(vii)$$
$$2Fe(OH)_3 \longrightarrow Fe_2O_3 + 3H_2O \quad —(viii).$$
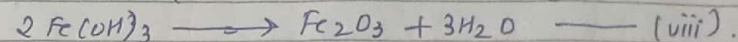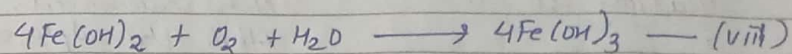
Ferric oxide absorbs moisture, thus forming rust.

$$Fe_2O_3 \cdot xH_2O \longrightarrow Fe_2O_3 \cdot xH_2O \quad \{Rust\}.$$
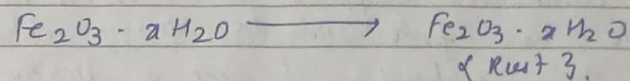
*) Prevention:

i) Coating with paints, enamel.
ii) Coating with noble metals Au, Ag, Cu.
iii) Using sacrificial anode i.e, galvanization

Types of Cells:

a): Primary Cell	b) Secondary Cell
→ redox reaction only one	→ redox reaction more than once
→ can't be recharged	→ can be recharged
Eg: Lechlanche dry cell,	Eg: Lead-acid cell,
Mercury cell.	Nickel-cadmium cell,
	Alkali metal-sulphus cell, etc.

c) Fuel cells

The primary cells in which reactants are continuously supplied to electrodes from outside as fuel and the energy obtained from the combustion of fuel is directly converted to electrical energy is fuel cells.
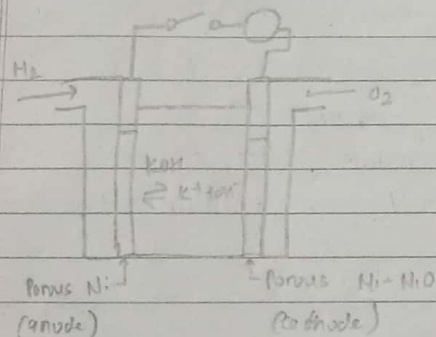

Fig: Hydrogen fuel cell.

Porous Ni
(anode)

Porous Ni - NiO
(Cathode)

At anode, oxidation of H_2 to water.

$$H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$$

At cathode, reduction of O_2 to OH^-.

$$\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

So, net cell reaction: $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$.

Cell works at high pressure (40 atm).

*) Advantage	*) Disadvantage
→ pollution free	→ Handling difficulty
→ more efficient	→ finding suitable fuel difficulty

Q7: An electrode chemical cell is constructed of one half cell in which platinum wire dips into solution containing 1M Fe^{3+} and 1M Fe^{2+}; the other half cell consists of thallum metal immersed in 1M Tl^+ solution.
Given, $E° \quad Tl^+ + e^- \rightleftharpoons Tl$, $\varepsilon° = -0.34$
$$Fe^{3+} + e^- = Fe^{2+}, \quad \varepsilon° = 0.77.$$

a) Which electrode is negative?
b) Which electrode is cathode?
c) What is cell voltage?
d) Write spontaneous cell reaction.
(e): What is equilibrium constant?
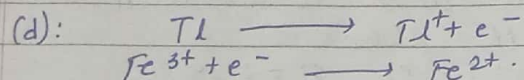(f): How voltage changes if Tl^+ concentration is decreased?

Sol^n:

Given,

$$\mathcal{E}° \; Tl^+/Tl \; = \; -0.34 \; V \qquad \{anode\}$$
$$\mathcal{E}° \; Fe^{3+}/Fe^{2+} \; = \; 0.77 \cdot V \qquad \{cathode\}.$$

(a): The negative ~~therm~~ ~~the~~ terminal is Thallium electrode.

(b): $\mathcal{E}° \; Fe^{3+}/Fe^{2+} \; > \; \mathcal{E}° \; Tl^+/Tl$,

Platinum electrode dipped in Fe^{2+} and Fe^{3+} ion solution is cathode.

(c): $\Delta\mathcal{E}°cell = \mathcal{E}°cathode - \mathcal{E}°anode$
$$= 0.77 - (0 - 34)$$
$$= 1.11 \; V$$

(d):
$$Tl \longrightarrow Tl^+ + e^-$$
$$Fe^{3+} + e^- \longrightarrow Fe^{2+}.$$

The overall reaction: $Tl + Fe^{3+} \longrightarrow Tl^+ + Fe^{2+}$.

(e):
$$K = 10^{\frac{\Delta n \; \mathcal{E}°}{0.059}} = 10^{\frac{1 \times 1.11}{0.059}}$$
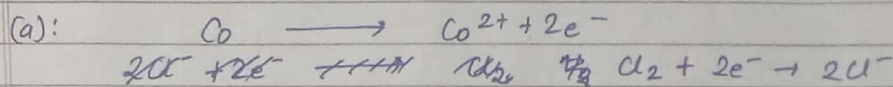
$$\therefore K = 6.5 \times 10^{18}.$$

(f): We know, the decrease in concentration of product, increases voltage.

So, Tl^+ decrease increases voltage of cell.

Q27: A Galvanic cell consists of cobalt metal strip Co dipped into 1 M Co^{2+} solution and another half cell in which a piece of platinum dips into 1 M solution of Cl^-. Chlorine gas at 1-atm pressure is bubbled into solution. Observed cell voltage is 1.63 V and cobalt electrode is negative. Standard potential for chlorine - chloride half cell $\mathcal{E}° = 1.36$.

a) what is spontaneous cell reaction.
b) What is standard potential of cobalt electrode?
c) What happens if Cl_2 pressure is increased?
d) What would cell voltage be if concentration of $[Co^{2+}]$ is reduced to 0.01 M.?

Sol:

$$\Delta\mathcal{E}°cell = 1.63 \; V \qquad \mathcal{E}° \; 2Cl^+/Cl_2 = 1.36 \; V$$
$$\mathcal{E} \; Co^{2+}/Co = negative$$

(a):
$$Co \longrightarrow Co^{2+} + 2e^-$$
$$2Cl^- + 2e^- \longrightarrow Cl_2 \quad \frac{1}{2}Cl_2 + 2e^- \rightarrow 2Cl^-$$

The overall reaction is, $Co + Cl_2 \rightleftharpoons Co^{2+} + 2Cl^-$

(b): $\mathcal{E}°anode = \mathcal{E}cell \; \mathcal{E}°cathode - \mathcal{E}°cell$
$$= 1.36 - 1.63 = -0.27 \; V.$$

(c): If pressure of Cl_2 is increased, the voltage increases

(d): At 0.01 M of Co^{2+},
$$\Delta\mathcal{E} = \Delta\mathcal{E}° - \frac{0.059}{2} \log\left(\frac{0.01}{1}\right) \qquad \therefore \mathcal{E} = 1.689 \; V.$$
$$= 1.63 - \frac{0.059}{2} \log\left(\frac{0.01}{1}\right)$$