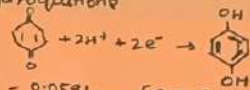


quinhydrone electrode
consists of inert metal in a soln containing
quinone and hydroquinone



$$E_{PQH_2/QH_2} = E^0 - \frac{0.0591}{2} \log \frac{[QH_2]}{[Q][H^+]^2}$$

ELECTROCHEM

Galvanic cell + chemical to electrical
electrolytic cell + electrical to chemical

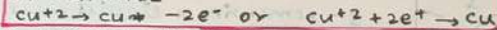
DANIEL CELL

Zn in ZnSO₄ & Cu in CuSO₄

Zn oxidises to become Zn²⁺ ions and results in ZnSO₄ soln which is rich in Zn²⁺ ions. **Anode**

Cu²⁺ from soln reduces to deposit around the copper electrode **cathode**

→ Zn becomes rich in e⁻ hence acts as anode. e⁻ flows from Zn → Cu when connected. One px of cell where anode is +ve and cathode is +ve.



the electrical potential difference b/w two electrodes of a galvanic cell which cause flow of current from higher to lower potential → **EMF, cell potential**

• EMF depends on nature, temperature, concentration of electrolytic soln. **Electrode**

• **Standard emf** → emf of cell when concentrations of products and reactants are at unity at 298 K and 1 atm.

$$\Delta G = -nFE$$

when metal in contact with its own ion soln → 2 types

• **deposition** tendency of M to gain e⁻ and get deposited on surface of electrode

• **ionisation** tendency of M to lose e⁻ and go into the soln. depending on metal causes EP to be formed. the rate of either deposition or ionisation is more. as time passes by, the faster reaction slows down and slower reac speeds up and state of equilibrium is reached.

• This forms double layer which gives rise to electrode potential. **Standard electrode P** → EP when electrode is in contact with a soln of unit concentration at 298 K. If electrode involves gas → atm. E⁰.

All SEPs & EPs are calculated w.r.t SHE (hydrogen)
SHE → hydrogen gas at 1 atm is bubbled through a soln of hydrogen ions of unit conc [1M] at 298 K.

decrease in free energy → reaction quotient
 $\Delta G = \Delta G^0 + RT \ln Q$

EMF of a cell can be measured by a

① as current is drawn from cell that alters conc of electrolytes and thereby changes EP

Electrode potential → potential developed at the interface of electrode and its ion soln.

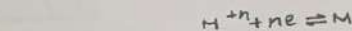
→ indicates a measure of tendency of a electrode to gain electrons → SEP

① If ionisation > deposition

when equilibrium is attained, a few metal atoms have dissolved into the soln, liberating e⁻. making electrode -vely charged. the e⁻ accumulate on surface, these e⁻ attract a layer of +ve charged ions at interface → developing double layer → causes EP → single EP

② deposition > ionisation → metal acquires the metal atoms. ions deposit on electrode as metal atoms by consuming e⁻. As a result, +ve layer of charges is formed which attracts a layer of +ve charged ions. double layer → EP → SEP

Helmholtz double layer



$$\text{Nernst eq} \rightarrow nFE = nFE^0 - RT \ln [M]$$

$$E = E^0 + \frac{0.0591}{n} \log \frac{[M]}{[M^{n+}]} \quad [M] = 1 \rightarrow \text{at } 298 K$$

else

$$\text{cell } E = E^0 - \frac{RT}{n} \ln [M]$$

Electrode potential nF cell representation

$$M_1 / M^{n+}(aq) // M_2^{n+}(aq) / M_2 \quad F = 96500 \text{ Cmol}^{-1}$$

Anode || Cathode

Salt bridge prevents → liquid junction potential provides contact b/w two soln. (saturated salts of KCl or NH₄NO₃)

TYPES OF ELECTRODES

① **Metal-metal ion**

metal dipped in a soln of its own ions.

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

② **Gas electrode**

gas bubbled about an inert metal wire dipped in a solution containing ions to which gas is

reversible. metal provides electric contact and establishes equilibrium. (H₂ electrode)

P(H₂) (H₂ electrode)

$$E = E^0 - \frac{0.0591}{2} \log \frac{P(H_2)}{[H^+]^2}$$

③ **Ion selective electrode**

consists of membrane in contact with soln with which it can exchange ions.

$$E = E^0 + \log [H^+] \times 0.0591 \rightarrow \text{GLASS ELECTRODE}$$

disadv of glass electrode

alkaline error → for pH > 9, electrode reacts to Na⁺, and gives value lesser than actual

• fragile

• glass has high resistance.

Adv easy to set up

works well from pH 4

(1-7)

② **Metal-metal salt ion**

metal in contact with insoluble salt of same metal

dipped in soln of the anion of salt. (Ag/AgCl/Cl⁻) (calomel)

③ **Amalgam electrode**

metal amalgam in contact with soln of metal ions.

④ **Redox electrode**

consists of inert metal dipped in soln containing approp. oxidised & reduced forms of redox sys.

metal provides electric contact

potential arises due to tendency of one form to change into another.

• Pt/Fe²⁺, Fe³⁺, Pt/Ce³⁺, Ce⁴⁺

REFERENCE ELECTRODES

whose potentials are accurately known, stable and with ref to which the EP of any electrode can be measured.

Primary SHE

Secondary calomel (Hg), Ag/AgCl/Cl⁻

electrode with very thin glass bulb immersed in soln of H⁺ ions. with internal reference soln of H⁺ and electrode ref of metal-insoluble salt. (ref. soln of 0.1M) lined

boundary potential $H^+ + Na^+ \rightleftharpoons Na^+ + H^+$

potential developed when ion exchange b/w singly charged cations (Na⁺) in glass

and protons from soln. $C_2 \rightarrow \text{const}$

$$E_b = \frac{2.303RT}{nF} \log \frac{C_1}{C_2} \quad L' = \frac{2.303RT}{nF} \log \frac{C_1}{C_2}$$

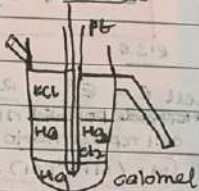
$$E_b = L' + \frac{2.303RT}{nF} \log C_1 \quad \text{Easy to error in potential}$$

$$E_{eq} = E_b + E_{asy} + E_{ref} = L' + \frac{2.303RT}{nF} \log C_1 + E_{asy}$$

$$= L' + \frac{0.0591}{n} \log C_1 + E_{asy} + E_{ref} \quad \text{works well from pH 4}$$

$$E_{CM} = 0.24 - 0.0591 \log [H^+]$$

SHE
electrode potential = 0.0V
gas electrode - Pt / H₂ / H⁺
disadv. have to maintain conc of H⁺ ions at 1M and P(H₂) at 1 atm
Pt is highly susceptible to poisoning by impurities in gas
cant be used with redox environment
CALOMEL
metal insoluble salt
glass tube containing a layer of mercury over which a paste of Hg₂Cl₂ + Hg is added. Next layer is a solution of KCl.
Pt wire dipped in Hg provides electric contact.



anode: $2Hg \rightleftharpoons Hg_2^{2+} + 2e^-$
cathode: $Hg_2^{2+} + 2e^- \rightleftharpoons Hg$
overall: $2Hg + 2Cl^- \rightleftharpoons Hg_2Cl_2 + 2e^-$

KCl	Name	EP at 298	disadv
0.1M	decinormal	0.3358V	mercury is toxic
1M	normal	0.2824V	works only until 50°C.
saturated soln of KCl	saturated calomel electrode (SCE)	0.2422V	

concentration cell
cell with identical electrodes dipped in identical soln of identical species but of diff. concentration
current moves from higher conc to lower.
driving force → electrolyte tendency to diffuse from a soln of higher conc to a soln of lower conc.
higher conc → cathode
lower conc → anode
emf +ve only when $C_2 > C_1$ (cathode > anode)

same electrodes dipped in same electrolyte but with diff conc of electrolytes
electrode conc. consists of two same electrodes of different activity dipped in same electrolyte.
 $E = \frac{2.303RT}{nF} \log \frac{a_1 - HgCl}{a_2 - HgCl}$
 $E_c = \frac{2.303RT}{nF} \log \frac{C_1}{C_2}$

types of ion selective elec

- crystalline: single crystal, LaF₃ selective to F⁻
polycrystalline such as Ag₂S → S²⁻
- non-crystalline: glass membrane → H⁺, Na⁺
- liquid membrane: ion exchanger in viscous organic liquid
- membrane: used for Ca²⁺, K⁺
- immobilised "liquid" in a rigid polymer
- immobilized ion exchanger in PVC matrix

CORROSION

- destruction (deterioration and consequent loss of metal through direct chemical or electrochemical attack)
- rushing: brownish/reddish scale formation on iron & steel obj due to Fe hydrated ferric oxide (Fe₂O₃·xH₂O)
- scaling of copper: green scales on copper due to cupric carbonate (CuCO₃·Cu(OH)₂)
- metals occur in nature in form of their compounds (oxides, sulfides, carbonates, chlorides)

DRY CORROSION: direct chemical attack due to affinity of metal to some gases.
WET CORROSION: presence of moisture or conducting medium

WET CORROSION
anode → undergoes oxidation
undergoes corrosion
cathode → unaffected
e⁻ from anode migrate towards cathode → small corrosion current
metal ions formed at anode and some anions formed at cathode diffuse towards each other forming corrosion product somewhere b/w anode and cathode.

Anode: undergoes corrosion
cathode: absorption of oxygen
liberation of hydrogen
Acidic: $M \rightarrow M^{2+} + 2e^-$
 $2H^+ + 2e^- \rightarrow H_2$
Neutral or basic: $M \rightarrow M^{2+} + 2e^-$
 $2H_2O + 2e^- \rightarrow 2OH^- + H_2$
 $M + 2H_2O \rightarrow M^{2+} + 2OH^- + H_2$
Acidic: $2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O$
BASIC or Neutral: $\frac{1}{2}O_2 + 2e^- + H_2O \rightarrow 2OH^-$
 $M + \frac{1}{2}O_2 + H_2O \rightarrow M(OH)_2$

Anodic of Humidity

Articles cleaned, degreased & polished.
 Immersed in electrolyte soln of 5-10% chromic acid, sulphuric acid, phosphoric acid, oxalic acid or their mixtures → maintained at 40°C.
 - Pb or steel + cathode
 - voltage above 40V
 - extra layer oxidized to Al_2O_3
 $2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$
 - Al_2O_3 slightly porous → can be made compact by immersing article in boiling water or steam. → $4H_2O_3 \cdot H_2O \rightarrow$ occupies higher volume → pores → sealed

Aluminizing

coating of Zn on Fe.
 Process:
 1) dipped or passed through organic solvents or caustic soln to remove oil or grease & washed with dil. H_2SO_4 to remove rust or scale or dirt → pickling
 2) treated with $ZnCl_2$ and NH_4Cl which prevents oxidation → dried and dipped in molten Zn at 425-450°C.
 3) excess removed by hot rollers.
 Adv.
 - Zn film 2mils thick, Fe does not corrode.
 - Fe acts as cathode.
 DAD used for pre-painting & storing food because zinc dissolves in dilute acids.

cathodic polarisation: due to retarded movement of cathodic reactions towards surface or retarded removal of products formed in cathodic region.

anodic rate, moderate → corrosion
 due to depletion of ions
 polarisation can be reduced by → anodic + completing eqn.
 increase in temp. cathodic + cupric ions.

⑧ Humidity
 moisture provides conducting medium
 corrosion ↑ with ↑ in humidity

⑨ Conductivity of medium
 as conductivity of medium increases, corrosion rate also increases.
 → conductivity, faster reactions can migrate, anodic and cathodic regions.
 corrosion is more in saline water.

CORROSION CONTROL
 → protective coating: metals coating → corrosion of base metal more over Fe. Anodic metal coating → coating with metal than anodic to base → Fe → Zn. Cathodic metal coating → coating with metal → cathodic to base → Zn → Fe. Fe → Sn. Cathodic coating → base metal is completely covered. If base metal is uncovered then in case of anodic due to demagnetization coating, corrosion, inhibition, Sn over Fe (cathodic protection, anodic protection).

→ inorganic coating → anodizing & phosphating
 chemical conversion coating: surface of metal is converted into protective coating.
 anodizing: induced oxidation in a oxidizing environment making the article anode & passing current. It converts outer layer of metal to its metal oxide which covers the metal surface → protective layer.
 works for all non-ferrous metals.

→ organic coating
 coating of metal surface with organic materials like paint or lacquers. Coating serves to keep out air and moisture from the metal surface & serve as barrier b/w the metal surface & corrosion environment.

CORROSION INHIBITORS
 chemical substances which are added in small quantities to corrosive environment to decrease the rate of corrosion. Inhibitors slow down the anodic or cathodic reactions and control corrosion.
 action depends on nature of metal to be protected and corrosive environment.

Anodic inhibitors → formation of Mn is prevented, the corrosion process slows down.

→ achieved by adding large anions such as chromate, tungstate (WO_4^{2-}), thio ions combine with Mn to form a precipitate layer.
 → we need to add sufficient quantity of inhibitors.

- Na_2CrO_4 , Na_2SO_4
Cathodic Inhibitors
 aimed by inhibiting liberation of hydrogen or absorption of O_2

→ to prevent liberation of H_2 → add organic compounds which contain nitrogen & sulphur → liberation they form protective films preventing hydrogen evolution. Hydrogen overvoltage is high, liberation H_2 is less → organic compounds containing N or S like sodium molybdate, arsenite (arsenous) → overvoltage is high for these metals.

→ to remove oxygen from corrosive media.
 by adding oxygen scavengers like hydrazine.
 $NH_4OH \rightarrow N_2 + 2H_2O$

By adding reducing agents → sodium sulphite
 $2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$
 → by adding large cations like $ZnSO_4$, $MgSO_4$, $NiSO_4$ etc. carries react with OH^- and form $Zn(OH)_2$, $Mg(OH)_2$ → protective layer impermeable to oxygen is formed → restricts diffusion of O_2 to cathode.

Inhibitors contaminate the environment, they are toxic. can only be used in closed systems.
CATHODIC PROTECTION
 by completely covering the metal to cathode.

Sacrificial
 metal is connected to a more reactive metal making it the anode. The more reactive metal corrodes, protecting the base metal → preferential corrosion.
 Since anode is sacrificed → anodic & unaffected. Exhausted anodes have to be replaced periodically. Adv.
 Accepting expenditure. one installation expensive, high protect large area. If current is not uniform → localised corrosion.

Impressed current
 DC is applied. the metal is connected to cathode of battery → unused anode is connected to inert electrode (Si, Pt, graphite) used to improve efficiency → electrolytic reduces electrical conductivity.
 → metal is unaffected. Exhausted anodes have to be replaced periodically. Adv.
 one installation expensive, high protect large area. If current is not uniform → localised corrosion.

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Disadv continued
 If hydrogen liberation occurs at cathode, then metal undergoes → cathodic → hydrogen embrittlement.
 → H_2 more easily being small & diffusing (diffusion) through metal (weakened), it causes blister & makes metal brittle.

in oxidising environment, Fe(OH)_2 is oxidised to ferric oxide \rightarrow yellow rust. A and water

in presence of limited oxygen, black rust: Fe_3O_4

WET CORROSION

a differential metal corrosion or galvanic corrosion
when 2 dissimilar metals are in contact with each other and are exposed to a corrosive environment.

Two metals differ in electrode potentials. The metal with lower potential becomes anode. the other cathode. Anode undergoes oxidation. cathode \rightarrow unaffected.

driving force \rightarrow difference in electrode potential

b differential: Aeration corrosion

when metal is exposed to different concentrations of O_2 , part of metal exposed to lower conc of O_2 becomes anodic \rightarrow corrosion.

concentration cell
anode: $\text{M} \rightarrow \text{M}^{n+} + n\text{e}^-$
cathode: $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$

c waterline corrosion
differential aeration when conduction medium is water. \rightarrow metal half immersed in water.

d pitting corrosion

localised accelerated corrosion
results in pits or pin holes around which metal is comparatively unaffected.

very destructive. characterised by small anodic area & large cathodic area. CASE 1 \rightarrow oil or dust on metal.

the demand for e^- from cathode is high. anode goes under accelerated corrosion to form pits.

CASE 2 \rightarrow breakdown of protective film. Peeling of tin coating on

STRESS CORROSION

when a part of metal is under stress due to mechanical operations and is exposed to corrosive environment.

external stress or residual stress.
due to stress crack is initiated. metals under stress are at higher energy levels. \therefore more reactive. stressed part \rightarrow anode conditions

stress \rightarrow tensile \rightarrow causes breakdown.

specific corrosive environment

Brass \rightarrow ammoniacal soln or ammonia vapours

Steel \rightarrow NaOH and chloride ions

Factors affecting corrosion

• nature of metal, difference in ep, nature of corrosion product, ratio of anodic to cathodic area, overvoltage, polarisation, pH, temperature, conductivity of medium, humidity.

① Nature of metals \rightarrow lower EP metals \rightarrow susceptible to corrosion
 \rightarrow Chromium, Al, Ti exception as they are passive

Galvanic series is a list of metal and alloys in order of their tendency to undergo corrosion.

② difference in potential btw A & C.
larger PD \rightarrow higher the rate of galvanic corrosion.

when PD more, free energy decrease is higher \rightarrow corrosion rate \uparrow .

\rightarrow use of dissimilar metals should be avoided

③ Nature of corrosion product.

Cr, Al corrosion product acts like a protective film if it is insoluble, stable, uniform & non-porous \rightarrow prevents further corrosion.

Iron, Zn, Mg do not form layer. If product is soluble, unstable, nonuniform and porous \rightarrow corrosion \rightarrow unabated.

④ ratio of anode area to cathode area.

when small A \rightarrow big C \rightarrow corrosion more intensive & faster. \rightarrow pitting corrosion. e^- from anode are rapidly consumed.

⑤ hydrogen overvoltage

low overvoltage \rightarrow liberation of gas more \rightarrow corrosion more as cathodic reaction is fast

when high overvoltage \rightarrow reaction is slow and corrosion of metal also slows down.

⑥ Temperature.

rate \uparrow with \uparrow in temp for redox reaction.
rate, conductance of medium, increase in solubility of product all increase, polarisation effects decrease, breakdown of protective film

However, if corrosion is due to dissolved gases like O_2 , CO_2 , etc \rightarrow rate decreases with inc in temp \rightarrow as solubility of gas decreases

⑦ pH
At low pH, rate \uparrow as conc of H^+ is high and increases rate of cathodic reaction. corrosion product more soluble in acidic medium. Al undergoes fast corrosion even in alkaline medium

⑧ polarisation
shift of electrode potential \rightarrow due to change in conc. anode polarisation \rightarrow ions when obstructed and cant move freely towards cathode due to low conductivity med etc... ions get conc in anode and decrease tendency of metal to undergo corrosion. rate falls. accumulation of ions