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Corrosion

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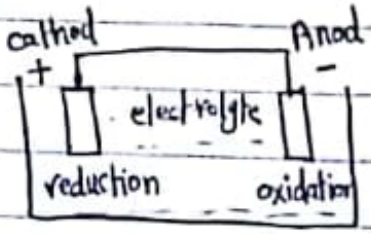
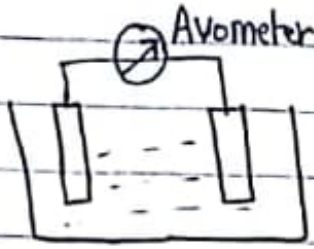
* gases corrosion

Cl_2, Br_2, Sox (SO, SO_2, SO_3), Nox (NO, NO_2, NO_3)

* electrical conductivity ⇒ Ms/cm (Micro simines / cm)



* تنتقل الالكترونات من الاقل للاعلى



electric work

electric energy

energy = E * A * t

volt * $\frac{\text{Amper} * \text{time}}{\text{colom}}$

$Q = nF$ n: # of $\bar{e}$, F: faraday constant = 96500 colom/g. equivilant

$\Delta G = -nFE$

example:- $\overset{+2}{Pb}\overset{-2}{S} + \frac{3}{2}\overset{zero}{O_2} \longrightarrow \overset{+2}{Pb}\overset{-2}{O} + \overset{+4}{S}\overset{-2}{O_2}$

$E = 0.285\ V$

$zero = S + 2*-2$

$S = +4$

$-2 \rightarrow +4 \Rightarrow n = 6$

$\Delta G = -nFE$

$= -6 * 96500 * 0.285$

example :- non-spo درجة الحرارة يلي بتكون عندها التفاعل

$\Delta G = 0$ (at equilibrium)

$\Delta G = \Delta H - T\Delta S$

$T = \frac{\Delta H}{\Delta S} = 5971\ K$

example :-

$$ZnS + \frac{3}{2}O_2 \rightarrow ZnO + SO_2$$

ΔH (kJ/mol)	ΔS (J/mol)
$ZnS = -205.98$	$ZnS = 57.74$
$SO_2 = -269.83$	$SO_2 = 43.64$
$ZnO = -348.8$	$ZnO = 248.11$
	$O_2 = 205.03$

$\Delta G = \Delta H - T\Delta S$

ΔH = Product − reactant

$= (-269.83 + -348.8) - (-205.98) = -312.13$ kJ/mol

$\Delta S = (43.64 + 248.11) - (\frac{3}{2} * 205.03 + 57.74) = 73.535$ J/mol

$\Delta G = -312.13 - 298(73.535 * 1000) =$ - spontaneous

example :- Cu^{+2} (cathod) + Zn (Anode) $\rightarrow Cu + Zn^{+2}$

$-0.76 \quad 0.43$

$E_{cell} = E_{cathod} - E_{Anode}$

$= -0.76 - 0.43$

$= -1.19$

example:- $Fe(s) + \frac{1}{2} O_2 \rightarrow FeO(s)$

ΔG = Gibbs energy < 0 Spontenuos

$= 0$ at equilibrium

$\Delta H = -271$ kJ/mol

$\Delta S = -71$ J/mol

$\Delta G = -271 - 298 * -71 * 1000 = -249.8$ Spontenuos.

example:- $\overset{0}{Zn} + 2\overset{+1}{H}\overset{-1}{Cl} \rightarrow \overset{+2}{Zn}\overset{-1}{Cl_2} + H_2$

$Zn \rightarrow Zn^{+2} + 2\bar{e}$ (oxidation).

$2H^{+1} + 2\bar{e} \rightarrow H_2$ (reduction) $n = 2$

* Nerst equation :-

$aA + bB \rightarrow cC + dD$

$\Delta G = \Delta G_\circ + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$

$-nFE = -nFE_\circ + RT \ln$ ____

$E = E_\circ$ at 1 molar

$E = E_\circ - 2.303 \frac{RT}{} \log \frac{[Product]}{[reactant]}$

$= E_\circ - \frac{0.0592}{n} \log$ ____ at 25°C

* at equilibrium $\Delta G = 0 \Rightarrow \Delta G_\circ = -RT \ln K$

example: $K = ?!$ if $\Delta G_\circ = 65.4\ KJ/mol$

$T = 1300\ K$

$\Delta G = \Delta G_\circ + RT \ln K$

at equ $\Delta G = 0$

$0 = 65.4 * 1000 + 8.314 * 1300 \ln K$

$K = 2.3 \times 10^{-3}$

example: $Cr_2O_7^{-2} + 14H^+ + 6Ag(s) \rightarrow 6Ag^+ + 2Cr^{+3} + 7H_2O$

0.1 M, 0.01 M, zero, 0.01 M, 0.1 M

$E, E_\circ$?! $\quad Ag(s) \rightarrow 6Ag^+ + 6e^-$, $E_\circ = 0.8\ V$

$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{+3}_2 + 7H_2O$, $E_\circ = 1.53\ V$

$$E = E_\circ - \frac{0.0592}{n} \log \frac{[Product]}{[reactant]}$$

$E_\circ = E_\circ$ cathod (reduction) $- E_\circ$ Anode (oxidation)

$E_\circ = 1.53 - 0.8 = 0.73$

$$E = 0.73 - \frac{0.0592}{6} \log \left[\frac{(0.1)^7 (0.01)^2}{(0.01)^{14} (0.1)} \right]$$

$E = 0.5524\ V$

example e- $Cu^{+2} + Zn \rightarrow Cu + Zn^{+2}$

2M 3M

$Cu^{+2} + 2\bar{e} \rightarrow Cu \quad E_o = 0.337$ cathod

$Zn \rightarrow Zn^{+2} + 2\bar{e} \quad E_o = 0.763$ Anode

if $Cu^{+2} \rightarrow [0.2M]$ what will happen?

if $Zn^{+2} \rightarrow [0.3M]$ " " " "

$$E = E_o - \frac{0.0592}{n} \log \frac{[Zn]}{[Cu]}$$

$E_o = E_o$ cathod $- E_o$ Anode

$= 0.337 - 0.763 = -0.426$

$$E = -0.426 - \frac{0.0592}{2} \log \frac{[3]}{[2]} = -0.43\ V$$

$$E = -0.426 - \frac{0.0592}{2} \log \frac{[3]}{[0.2]} = -0.46\ V$$

$$E = -0.426 - \frac{0.0592}{2} \log \frac{[0.3]}{[2]} = -0.40V$$

- wight with time - thickness loss Per unit area

* Faraday law

1st law ⇒ mass of Primary Product (g) is Proportional to quantit of electricity Passed. $m = z I t$ → time (S)

mass (g) constant current (A)

(It) ⇒ current density

2nd law ⇒ mass of Product are Proportional with thier Mwt

$$m = \frac{1}{Fn} Mw\ I\ t$$

Col/mol

* corrosion rate

$$\frac{m}{tA} = \frac{Mw\, I t}{Fn\, A t}$$

(I = current density (A/cm^2))

$$CR = \frac{Mw\ i}{Fn}$$

example :-

current effecing ? if 25 A.h Passes acell ⇒ 20g (Actual) of $CuSO_4$

$Cu^{++} + 2\bar{e} \rightarrow Cu$, $F = 26.8$ A.h /mole

$= 96500$ c/mol

current ? = $\frac{\text{actual chemical change}}{\text{theo} \quad " \quad "}$

$$m = \frac{Mw_{(Cu)}\, I\, t}{n F}$$

$$= \frac{63.6 * 25\ A.h}{2 * 26.8\ \frac{A.h}{mol}}$$

$m = 29.69$

$\frac{20}{29.6} = 67\%$.

mol / m². h
g / m². h
mg / dm². day (standered) mdd
} units of corrosion rate

mm / Year ⇒ (mmy)
mils / Year = 1/1000 inch ⇒ (mpy)
} units of Penetration rate

example :-
steel ⇒ corrosion current = 0.1 A/cm²

$Fe \longrightarrow Fe^{+2} + 2\bar{e}$

corrosion rate ?

$CR = \frac{Mw\, i}{Fn} = \frac{55 * 0.1}{26.8 * 2} = 0.104$ g/m² h

examples:-
Zinc anode corrods with a current density $4.27 * 10^{-7}$ A/cm²
corrosion rate in mdd ?

$$CR = \frac{65.38 \text{ g/mol} * 4.27 * 10^{-7} \text{ A/cm}^2 * \frac{1}{10^2} \text{ cm}^2/\text{dm}^2}{2 * 24 * 3600 \frac{\text{s.h}}{\text{day}} * 10^3 \frac{\text{mg}}{\text{g}} * \frac{1}{96500 \frac{\text{A.s}}{\text{mole}}}}$$

= 1.25 mdd

constant, g/mol

$$CR = \frac{C\, Mw\, i}{n\, \rho} \rightarrow \mu A/cm^2$$

n ← e ; ρ → density g/m³

C = 0.129 ⇒ mpy (mils / Year)
C = 3.27 ⇒ mmy (mm / Year)

example:-

Iron $\rho = 7.86$ kg/L

what is the corrosion rate if 1 MA/cm² is passed?

$$CR = \frac{0.129 \left(55.8 \frac{g}{mol}\right)(1)\frac{MA}{cm^2}}{(2)(7.86)\, g/cm^3} = 0.46 \text{ mpy}$$

example:-

corrosion rate in mpy of st.st. 316, 1 MA/cm²

	%	n	ρ	Mw
Cr	18%	1	7.1	52.01
Ni	8%	2	8.9	58.68
Mo	4%	1	10.2	95.95
Fe	balanced → 70%	2	7.86	55.85

$$CR = \frac{0.129\, Mwi}{n\rho}$$

$$= 0.129 \left[\frac{52.01}{1*7.1} * 0.18\right] + \left[\frac{58.68}{2*8.9} * 0.08\right] + \left[\frac{95.95}{1*10.2} * 0.04\right] + \left[\frac{55.85}{2*7.86} * 0.7\right] * \frac{1MA}{cm^2}$$

$$= 0.57 \text{ mpy}$$

example:- Prove that for Al alloy 1100 i the Penetration rate of alloy equ. to 1MA/cm² is 0.43 mpy.

$\rho = 2.71\ g/cm^3$

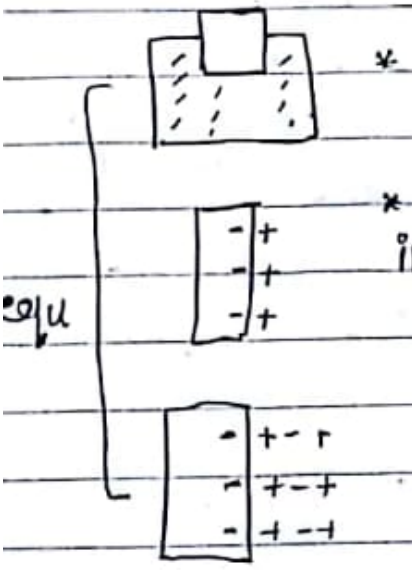
$n = 3$

$Mw = 26.98\ g/mol$

$$CR = \frac{0.129 * 26.98 * 1\ MA/cm^2}{3 * 2.71} = 0.43\ mpy$$

$$CR = \frac{m}{A t \rho}$$

* Reversible electrode Potential



* dissolve of metal
* electrons density increased in the metal surface.
* metal ions attached back to the metal

$R_f = R_b$

* reversible Potential of metal immersed in its solution
* Standered Potential : Potential of Pure metal measured with refrence to H_2 electrod

$E_{H_2} = 0$

Zn metal | $^{1}_{2}M\ Zn^{+2}$ || $M\ Cu^{+2}$ | Cu metal

molarity
1 mol $ZnSO_4$

1 mol
$CuSO_4$

left side
anode
oxidation

right side
cathod
reduction

$Zn \rightarrow Zn^{+2} + 2e^-$

$Cu^{+2} + 2e^- \rightarrow Cu$

example:-

Reversible Potential for zinc electrode in contact with $ZnCl_2$ when the activity of zinc is $a_{Zn^{+2}} = 5 \times 10^{-2}$

$Zn^{+2} + 2e^- \rightarrow Zn$ $\quad E^\circ_{Zn} = -0.76\ V$

E ?!

$$E = E_\circ - \frac{RT}{nF} \ln \left[\frac{1}{a_{Zn^{+2}}} \right]$$

activity of Pure metal = 1 (not ion)

$$= -0.76 - \frac{8.314 \times 298}{96500 \times 2} \ln \left[\frac{1}{5 \times 10^{-2}} \right]$$

or

$$E = -0.76 - \frac{0.059}{2} \log \frac{1}{5 \times 10^{-2}}$$

$$E = -0.799$$

reversible Potential for zinc

Example: Show that for Rxn

$O_2 + 2H_2O + 4\bar{e} \rightarrow 4\bar{O}H$

$E = E_o - 0.0591 \log a_{\bar{O}H}$ ↳ activity

Sol: $E = E_o - \frac{RT}{nF} \ln \frac{[\bar{O}H]^4}{[O_2][H_2O]^2}$

$a = \gamma [\ ]$ (a: activity, γ: activity coeff, [ ]: molar)

$E = E_o - \frac{RT}{nF} \ln \frac{a_{\bar{O}H}^4}{a_{O_2}^1 a_{H_2O}^2}$ → activity ≠ 1 for ions

$E = E_o - \frac{8.314 * 298}{4 * 96500} \ln a_{\bar{O}H}^4$

$E = E_o - \frac{8.314 * 298}{96500} * 2.3 \log a_{\bar{O}H}$ ↳ factor to convert from ln to log

$E = E_o - 0.0591 \log a_{\bar{O}H}$

Example: the emf of cell made from Zn anode and H_2 cathod immeured in 0.7 M $ZnCl_2$ is 0.690 V, what is the pH of sol?

$E = 0.690V$, $[ZnCl_2] = 0.7M$, PH?

$\gamma_{Zn}^{+2} = 0.6133$

$Zn \rightarrow Zn^{+2} + 2\bar{e} \rightarrow E^\circ = 0.763$

$2H^+ + 2\bar{e} \rightarrow H_2 \rightarrow E^\circ = ? = 0$ (H = 0 ولأن)

$Zn + 2H^+ \rightarrow Zn^{+2} + H_2$

$a_{Zn}^{+2} = \gamma [\ ] = 0.6133 * 0.7 = 0.422$

$E = E_o - \frac{0.591}{n} \log \frac{a_{Zn} a_{H_2}^1}{a_{Zn}^1 a_{H}^{+2}}$

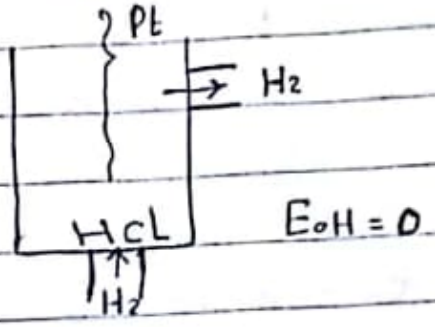
$0.690 = 0.763 - \frac{0.591}{2} \log \frac{0.422}{a_H^{+2}}$

$2PH = 2.8$

$PH = 1.2$

* Refrence electrode

1. Hydrogen electrode



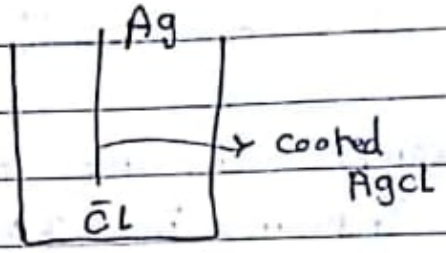
$$2\overset{+}{H} + 2\bar{e} \rightleftharpoons H_2$$

$$E = E_0 - \frac{RT}{nF} \ln \frac{a_{H_2}^{1}}{a_{H^+}^{2}}$$

$$E = 0 - \frac{0.591}{2} \log \frac{1}{a_{H^+}^{2}}$$

$$\boxed{E = -0.591\ PH}$$

2. Silver → Silver chlorid electrodes



$$AgCl \rightleftharpoons \overset{+}{A}g + \bar{C}l$$

$$\overset{+}{A}g + \bar{e} \rightarrow Ag$$

$$AgCl + \bar{e} \rightarrow Ag_{(s)} + \bar{C}l \qquad E = 0.224\ V$$

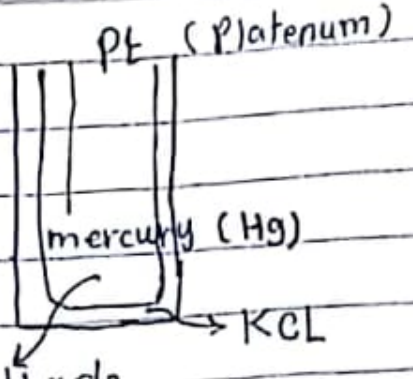
$$E = E_0 - \frac{0.0591}{1} \log \frac{a_{Ag^+}^{1}\ a_{\bar{C}l}}{a_{AgCl}}$$

$$E = 0.224 - 0.0591 \log [\bar{C}L]$$

In diluted sol
$[\bar{C}l] = [\overset{+}{H}]$

$$\boxed{E = 0.224 - 0.0591 \log [\overset{+}{H}]}$$

3. calonel electrode



$Hg^{+2} + 2\bar{e} \rightarrow Hg$

$Hg_2Cl_2 + 2\bar{e} \rightarrow 2Hg + 2\bar{C}l$

$$E = E_o - \frac{0.0591}{2} \log \frac{a_{Hg}\, a_{\bar{C}l}^{2}}{a_{Hg_2Cl_2}}$$

$$E = 0.267 - 0.296 \log a_{\bar{C}l}$$

4. copper-copper sulfate electrode

$Cu^{+2} + 2\bar{e} \rightarrow Cu$

$$E = E_o - \frac{0.0591}{2} \log \frac{a_{C\bar{u}}}{a_{Cu^{+2}}}$$

$$E = 0.34 + \frac{0.0591}{2} \log a_{Cu^{+2}}$$

* reversible Process

$$r_f = r_b = \frac{Mwi}{nF}$$

r_f ← forward, r_b → backward

at equ

$M \rightarrow M^{+2} + 2\bar{e}$ (irreversible Process)

If $i_f > i_b$

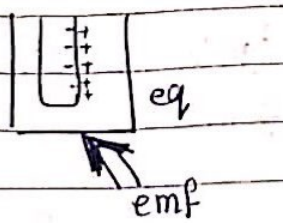
$i_q^{net} = i_f - |i_b|$

$\eta_{over\ Potential} = E - E_{rev}$

E → applied Potential, E_{rev} → reversible Potential

* Electrode Potential vs reaction rate

- Polarization :- the change of Potential from stabilitized state as aresult of Possin a current (over Potential)



(Polarization)

- the ratio between Polarization and rate of reaction

Tafel eq

$\eta A = \beta_A \log \frac{i_A}{i_o}$ (β_A constant, i_A → Anode, i_o → Applid)

$\eta C = \beta_C \log \frac{i_c}{i_o}$ (β_C constant, i_c → cathod, i_o → exchange current density)

~~Tafelss~~ Tafeles slope (β_A, β_C)

$$i_a = i_o e^{\frac{B z f \eta a}{RT}}$$

$$i_c = i_o e^{\frac{(1-B) z f \eta c}{RT}}$$

$$\frac{i_a}{i_o} = e^{\frac{B z f \eta a}{RT}}$$

$$\ln \frac{i_a}{i_o} = \frac{B z f \eta a}{RT}$$

$$\ln i_a = \ln i_o \frac{B z f \eta a}{RT}$$

$$\eta = \frac{RT}{Bzf} \ln i_a - \frac{RT}{Bzf} \ln i_o$$

$$\frac{2.3 RT}{Bzf} \log i_a - \frac{2.3}{Bzf} \log i_o$$

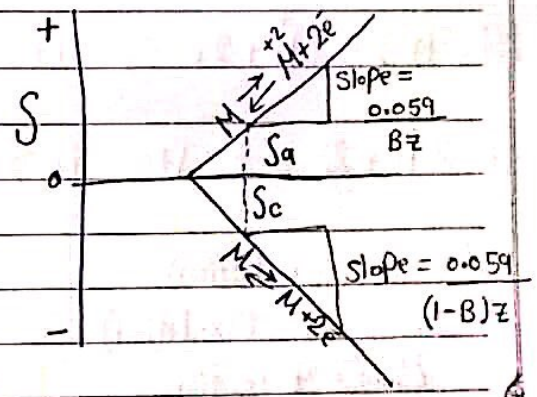
$$S_a = \frac{0.059}{Bz} \log i_a - \frac{0.059}{Bz} \log i_o$$

$$S_a = \frac{0.059}{Bz} (\log i_a - \log i_o)$$

$$S_a = \boxed{\frac{0.059}{Bz}} \log \frac{i_a}{i_o}$$

↳ slope

$$S_c = \frac{0.059}{(1-B)z} \log \frac{i_c}{i_o}$$

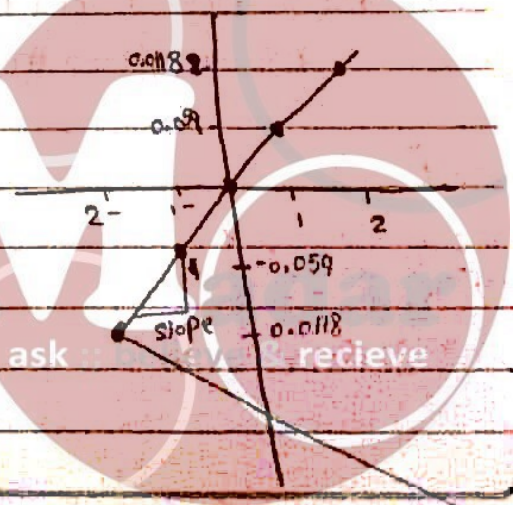


example& (Anode Plot)

$i_o = 10^{-3}$, $z = 0.2$, $B = 0.5$

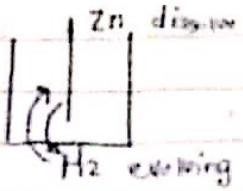
S_A Grafically ?!

i_a	$\log i_a$	S_a	$\log i_o$	$\log(\frac{i_a}{i_o}) = \log i_a - \log i_a$
10^{-5}	-5	-0.0118	-3	-2
10^{-4}	-4	-0.059	-3	-1
10^{-3}	-3	0	-3	0
10^{-2}	-2	0.059	-3	1
10^{-1}	-1	0.118	-3	2



* Evans diagrame

$E_{Zn} = -0.763$



RXN

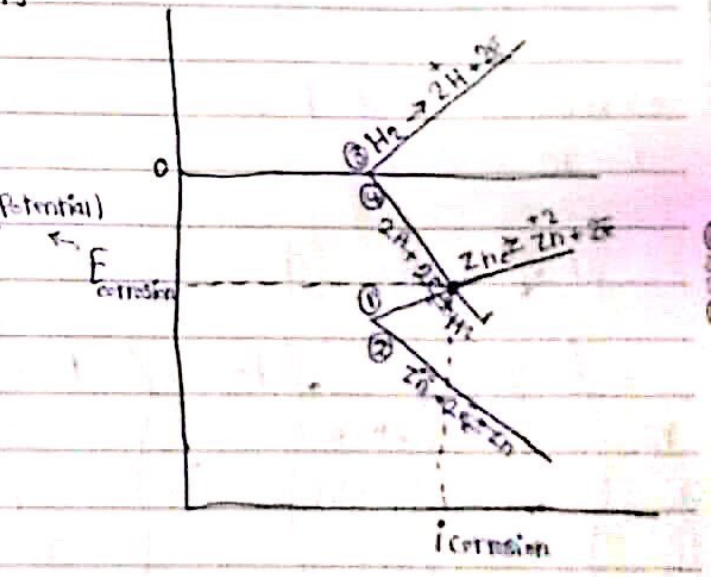
1. $Zn \rightleftarrows Zn^{+2} + 2e^-$ $i_f > i_r$
2. $Zn^{+2} + 2e^- \rightleftarrows Zn$ $i_r > i_f$
3. $H_2 \rightleftarrows 2H^+ + 2e^-$ $i_f > i_r$
4. $2H^+ + 2e^- \rightleftarrows H_2$ $i_r > i_f$

يتغير عندك تفاعلين

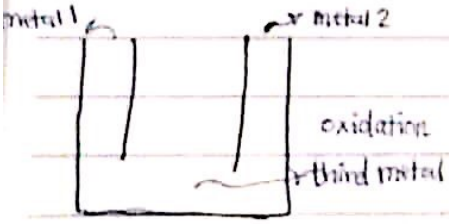
$E_H = 0$ (reduction)

$E_{Zn} = -0.76$ (oxidation)

1 and 4 reaction



* mixed Potential



metal lower E_o and higher i_o will corrods fastly ← i_o is more proportional

$E^\circ_{H_2/H} = 0$

$E^\circ_{Zn/Zn^{+2}} = 0.76$

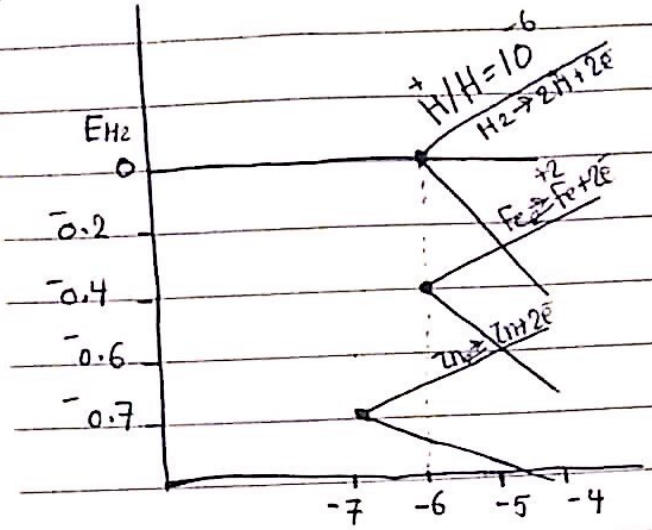
$E^\circ_{Fe/Fe^{+2}} = 0.49$

which corrods faster?

$i_o\ H_2/H^+ = 10^{-6}$ V

$i_o\ Fe/Fe^{+2} = 10^{-6}$ V

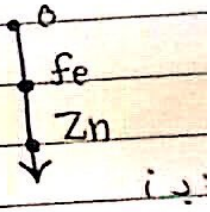
$i_o\ Zn/Zn^{+2} = 10^{-7}$ V



Fe $i = 10^{-6}$

- ready to oxidiz first faster than zn

-



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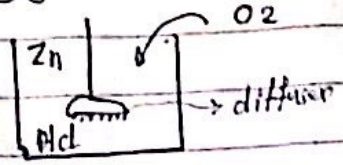
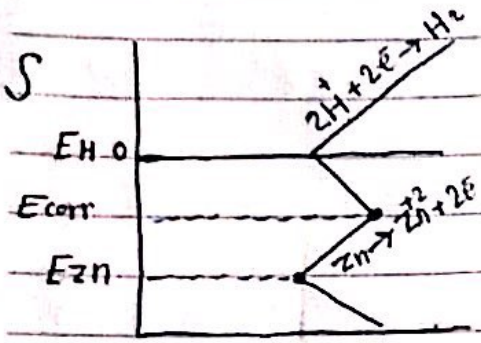
2) effect of ~~hydrogen~~ oxygen:-

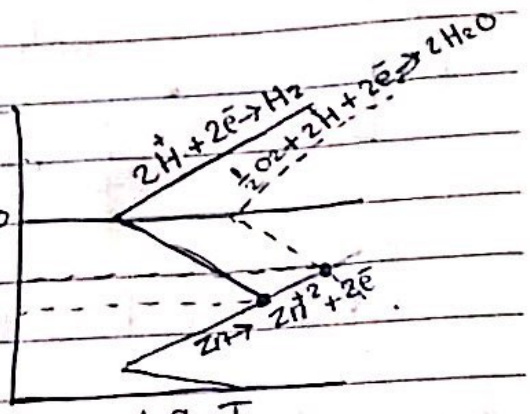
Zn → HCL



Zn oxidation
$2H^+$ reduction
O_2 reduction



(deareation)



(Areation)

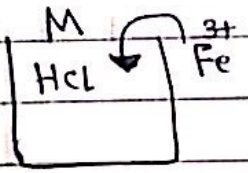
3) effect of oxidizer

Fe^{+3}

case 1 :- befor addition of fe^{+3}

→ $2H^+ / H_2$

→ M / M^+ (metal)



case 2 :- after addition fe^{+3}

i_{corr} shiftting ↑ rate value

E_{corr} shiftting → more nobel value (EH) = 0

* Results :-

1) corrosion rate ↑

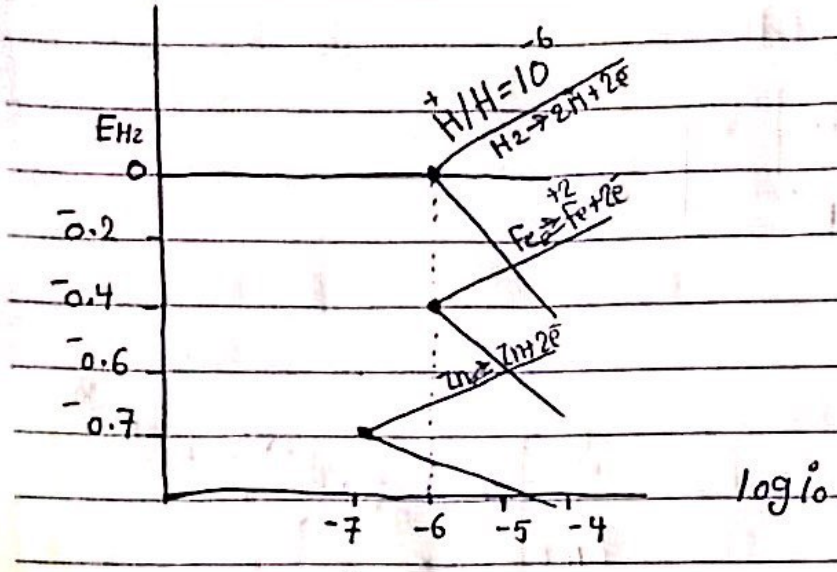
2) E_{corr} ↓↑

3) corr. shiftting ↑

4) rate of H_2 evolution ↓

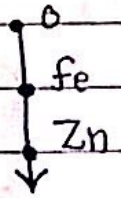
most of changes

$fe^{+3} \rightarrow Fe^{+2}$



Fe $i = 10^{-6}$

- ready to oxidiz first faster than zn



بقارن بـ i
اذا تساوو بـ E

* mixed Potential

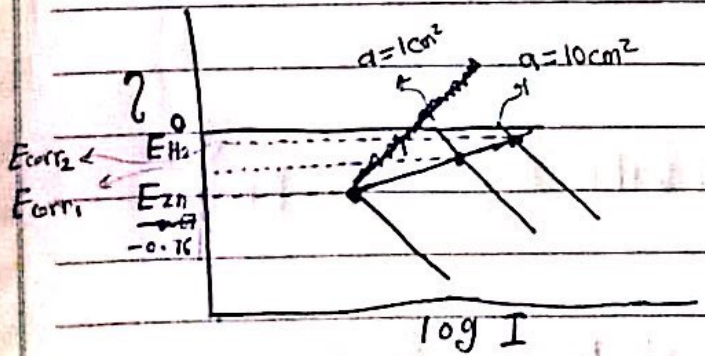
1) effect of Area ratio of anode and cathod

corroded metal ↘ reduced metal (nobel mdd)

Area ratio — Anode Area / cathod Area ↑ — corrosion rate ↓

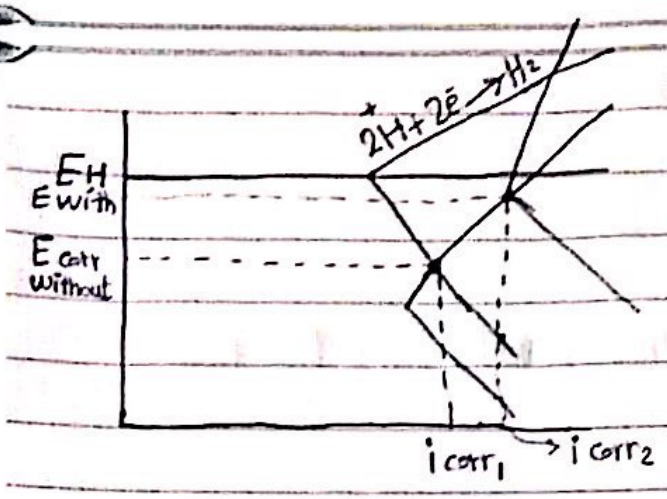
كل ما الرقم بيزيد بكبر

Area zn / Area Pt ↓ — corrosion rate ↑

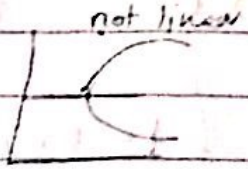


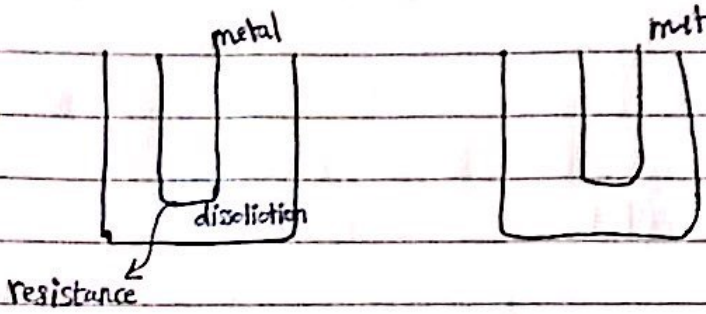
cathod Area - 1 cm²

cathod Area 10 cm²

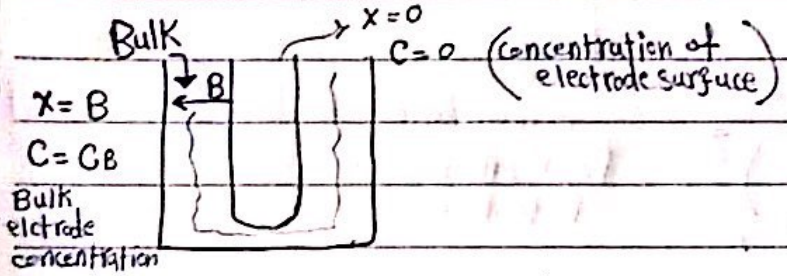


* Concentration - Polarization





dissolution and flux of ions linear



on Surface ↗ Potential

Then reduction $C_{x=0} < C_B$ and $E_{x=0} < E_B$

oxidation $C_{x=0} > C_B$ and $E_{x=0} > E_B$

applying Nernest equ

$$\int_{con} = E_{x=0} - E_B = \frac{RT}{nF} \ln\left[\frac{C_{x=0}}{C_B}\right]$$

fick's law for diffusion

$$J = -D\frac{dc}{dx} = -D\frac{C_B - 0}{x}$$

D: diffusivity coeff

$$J = \frac{i}{nF} = \frac{dc}{dx}$$

$$i = -Dnf \frac{(C_B - C_{x=0})}{X}$$

$$i = -Dnf \frac{C_B}{X}$$

When $C_{x=0} \Rightarrow i = i_L \rightarrow$ (Limiting current)

$$\frac{C_B - C_x}{C_B} = \frac{i_x}{Dnf} \Big/ \frac{-i_L X}{Dnf}$$

$$1 - \frac{C_{x=0}}{C_B} = \frac{i}{i_L}$$

$$\frac{C_{x=0}}{C_B} = 1 - \frac{i}{i_L}$$

$$\int_{Conc} = \frac{RT}{nf} \ln\left(1 - \frac{i}{i_L}\right)$$

Concentration Polarization Potential

Example :-

Ni, electrode is corroted electrolyte sol which has PH = 2 and $[Ni^{+2}] = 0.003$ @ 25°C

1) Determine the i_{corr} of Ni

2) E_{corr}

Given : $i_{o\,anode}(Ni) = 10^{-7}$ A/cm²

cathod i_o (H on Ni) $= 10^{-6}$ A/cm²

$\beta_a = 0.04$, $\beta_c = -0.13$

Anode $Ni \longrightarrow Ni^{+2} + 2\bar{e}$

cathod $2H^{+} + 2\bar{e} \longrightarrow H_2$

$Ni + 2H^{+} \longrightarrow Ni^{+2} + H_2 \Rightarrow E^{\circ} = -0.25V$

Sol:-

By Applying Nernest equ

$$E = E_o + \frac{RT}{nf} \ln \frac{a_{Ni^{+2}}}{a_{Ni}}$$

$$= -0.25 - \frac{0.059}{2} \log \frac{[0.003]}{1}$$

$$E = -0.325\ V$$

$$S_A = \beta_a \log \frac{i_{corr}}{i_o}$$

$$S_c = \beta_c \log \frac{i_{corr}}{i_o}$$

$$E_{H_2} = E_o - \frac{0.059}{2} \log a_{H^{+2}} = -0.059\ PH = -0.1184$$

$$S_A = 0.04\ (\log i_{corr} - \log 10^{-7})$$

$$S_A = -0.045 + 0.04 \log i_{corr} \rightarrow (1)$$

$S_c = -0.13\ (\log i_{corr} - \log 10^{-6})$

$S_c = -0.848 - 0.13 \log i_{corr}$ → ②

$0.045 + 0.04 \log i_{corr} = -0.848 - 0.13 \log i_{corr}$

$i_{corr} = 9.6 * 10^{-6}\ A/cm^3$

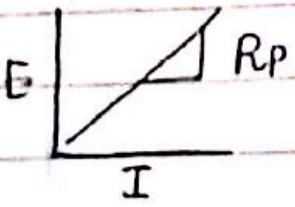
$E_{corr} = -0.045 + 0.04 \log i_{corr}$

$E_{corr} = -0.246\ V$

* Polarization Resistance (RP)

$$RP = \frac{\Delta E}{\Delta I}$$

$$= \frac{\beta_a \beta_c}{2.3\, i_{corr} (\beta_a + \beta_c)}$$



$$i_{corr} = \frac{1}{2.3 R_p} \left[\frac{\beta_a \beta_c}{\beta_a + \beta_c} \right]$$

example:-

From agivin Plot calculate i_{corr}

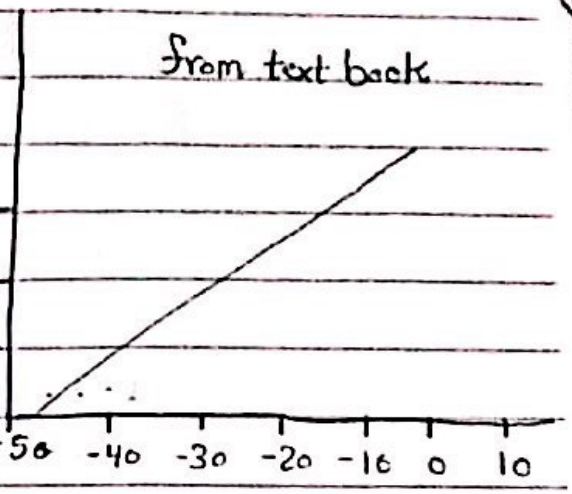
$\beta_a = 100$, $\beta_c = 100$

From slope

$R_P = 1.11 \times 10^2$ ohm. cm^2

$$i_{corr} = \frac{1}{2.3 * 1.11 * 10^2} \left[\frac{100 * 100}{100 + 100} \right]$$

$i_{corr} = 1.959 \times 10^{-4}$ A/cm^2



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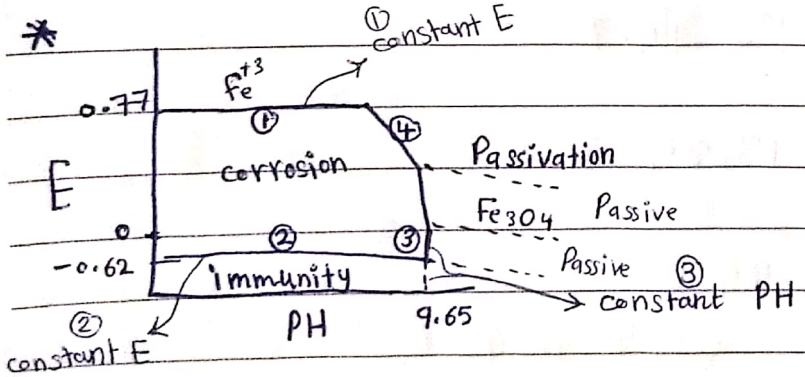


corrosion region

E: -0.62 - 0.77

PH: 9.65

immunity

PH: 0 - 9.65

E: 0.62

Passivation

* using activity Fe 10^{-6} where the corrosion exists at 25°C, 1 atm Pressure

* line ① independent of PH $E^{\circ}_{Fe^{+3}/Fe^{+3}} = 0.77$

$Fe^{+2} \longrightarrow Fe^{+3} + \bar{e}$ $a_{Fe^{+2}} = 10^{-6}$

$a_{Fe^{+3}} = 10^{-6}$

$$E_{Fe^{+2}/Fe^{+3}} = E^{\circ}_{Fe^{+2}/Fe^{+3}} - \frac{0.059}{n} \log \frac{a_{Fe^{+3}}}{a_{Fe^{+2}}}$$

* line ② independent of PH

$Fe \longrightarrow Fe^{+3} + 2\bar{e}$ $E^{\circ}_{Fe/Fe^{+2}} = -0.44$

$= -0.62$

no corrosion of fe below -0.62

* line ③

$Fe + 2H_2O \longrightarrow Fe(OH)_2 + 2\overset{+}{H}$, $Fe^{+2} + 2OH \rightleftharpoons Fe(OH)_2$

Pricipetation $Fe(OH)_2$

$K_{sp} = [a_{Fe^{+2}}][a_{O\bar{H}}]^2$

$= 10^{-14.71}$

$\log[a_{Fe^{+2}}] + 2\log[a_{O\bar{H}}]^2 = -14.71$

$\log[a_{O\bar{H}}] = -2PH + 13.29$

$a = 10^{-6}$ givin

$-6 = -2PH + 13.29$

$PH = 9.65$

* line ④

$2Fe^{+2} + 3H_2O \longrightarrow Fe_2O_3 + 6\overset{+}{H} + 2\bar{e}$

$E_{Fe^{+2}/Fe_2O_3} = 1.089 - 0.177PH$ $E^{\circ} = 0.73$

$a_{Fe^{+3}} = 10^{-6}$, $n = 2$

$a_{Fe_2O_3} = 1$

$a_{H_2O} = 1$

* line ⑤

$Fe_3O_4 + 8H^+ + 2e^- \rightleftharpoons Fe^{+2} + 4H_2O$

$E^\circ = 0.98$

$E = 0.98 - 0.88 \log [a\, Fe^{+2}]$ → ماديصير أخد 10^{-6} لدنها في Passivating region

* Corrosion inhibitors

- inorganic
  - Anodic
  - Cathodic
    - Poisining
    - Precipitators
    - oxygen Scavergor
- organic
  - Adsorbent

* Anodic inhibitors

Shifting corrosion Potential corrosion region → Passivation region

- hydroxide
- oxide

Anodic inhibitors

- oxidizing anions (absence of O_2)
- non-oxidizing anions (Presence of O_2)

* oxidizing

1) Chromate: $Cr_2O_7^{-2}$, $Cr_2O_4^-$
2) Nitrite : NO_2^-
3) Nitrate : NO_3^-

* non- oxidizing

1) Phosphate : PO_4^{-2}

2) molybdate : $MO O_4^{-2}$

* mechanisim

Steel Nitrite inhepetor

$$N\bar{O}_2 + 6\bar{e} \longrightarrow NH_4^+ + 2H_2O$$

$$9\,Fe(OH)_2 \longrightarrow 3Fe_3O_4 + 6H_2O + 6\overset{+}{H} + 6\bar{e}$$

$$2H_2O \longrightarrow 2\overset{+}{H} + 2o\bar{H}$$

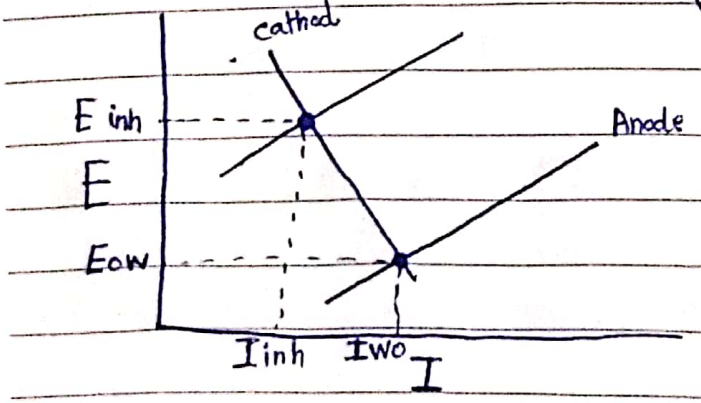
$$9\,Fe(oH)_2 + N\bar{O}_2 \longrightarrow 3Fe_3O_4 + \overset{+}{N}H_4 + 2o\bar{H} + 6H_2O$$

Fe	NaCl	Na NO_2 (inhepetor)			
C_{NaCl}	C_{NaNO_2}	Ratio	t(h)	E(mv)	state
0.5	0.2	0.4	20	-11	corrosion
0.5	0.35	0.7	99.5	271	inhibition
0.5	0.45	0.9	48.5	285	"
0.5	1	2	3122	300	"

* chromat

- less expensive (0.04 → 0.1%)
- internal combustion engine

(anodic inhipitors)



Shifting up and left

* non oxidizing

$7MoO_4^{-2} + 8H^+ \rightarrow Mo_7O_{24}^{-6} + 4H_2O$ at PH = 6

$Mo_7O_{24}^{-6} + HMoO_4^- + 3H^+ \rightarrow MoO_{26}^{-4} + 2H_2O$ at PH = 4.5

* corrosion inhibtor S

$$S = \frac{CR_o - CR_i}{CR_o}$$

CR_o : corrosion rate without inhibition

CR_i : corrosion rate with inhibition

* Quantity of inhibitor

$$Q(kg) = V(sol) * C_{inh}(PPm) * 10^{-6}$$

V: L, C_{inh}: mg/L, PPm = mg/L

Example: calculate the amount of sodium chromate required to be added to 500,000 Liters of water, if the concentration of sodium chromate is 5PPm.

$$Q_{(kg)} = 500{,}000 * 5 * 10^{-6} = 2.5\ kg$$

* cathodic inhibitors

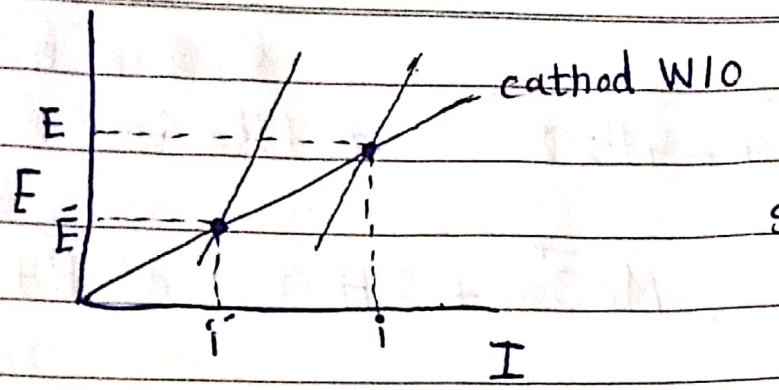
1) Slowing the cathodic reaction
2) Precipetate on cathodic area
3) increasing the impedance of surface
4) limit the diffusion of reducible (reduced metals) species to cathod area.

* cathodic Poising: (low PH, Acidic solution)

[1]

[2] shifting cathodic reaction → (Preventing hydrogen from ing H_2)

AS, CN (cyanid) heavy metals (toxic) ⇒ disadvantage.



shifting down and left

2) Precipitor (at high PH)

Ca^{2+}, zinc, Mg

Participitation ⇒ surface (Protection layer)

$Mg(OH)_2$, $Zn(OH)_2$, $Ni(OH)_2$ -- or $CaCO_3$

* oxygn scavenger

Preventing cathodic Polarization caused by oxygen

[Ammonium sulfite, Sodium sulfite, hydrazin (toxic)]

↳ low cost

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

sulfite → sulfate

$$(NH_4)_2SO_3 + \frac{1}{2}O_2 \rightarrow (NH_4)_2SO_4$$

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

hydrazine.

* organic inhibitor
- oil and gas industry
- most common types $C_{18}-H$, $C_{18}-N$
- Aeither anodic or cathodic but inhibit both

Types

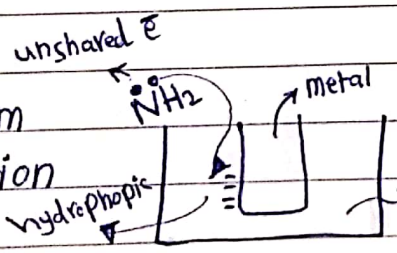
monoamines
Primary → $R-NH_2$
Secondry → R_2-NH
tertiary → $R-N(CH_3)_2$

Di amines
$-R-NH(CH_2)_3NH_2$

Amides
$R-CO-NH_2$

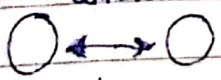
Polyethoxy lated compounds
$R-N$ → $(CH_2CH_2O)_xH$
→ $(CH_2CH_2O)_yX$

* mechanism
- Adsorption



1. metal surface → covering sol
2. Polar $\ddot{N}H_2$ denoted $2\bar{e}$ to the metal surface.
3. Large hydrocarbon chain orianted towards the sol (replce H_2O from metal surface)
4. attachment (adsorption) (chemosorption)

adhesion



hydrophobic

- Vanderwall
- Newtons

* Synergistic inhibitors
- combination between anodic and cathodic inhibitors → to obtain better corrosion inhibition
- chromate - Phosphate
- chromate - orthophosphate

* Scale inhibitors

Scale ⟶ Mg, Ca ⟶ hardness

$CaCO_3$, $Mg(OH)_2$

Scales :-

1 $CaCO_3$

- by increased temp ⇒ solubility of $CaCO_3$ decrease.

$2HCO_3^- \longrightarrow CO_2\uparrow + CO_3^{-2} + H_2O$

$CO_2\uparrow \Rightarrow PH\uparrow \Rightarrow [CO_3^{-2}]\uparrow$

- Ca^{+2} in water ⇒ formation $CaCO_3$

↙

e.g. NaCl ⇒ scale ↓

less than 150 g/L ⟶ scale ↓

more than " " ⟶ scale ↑

- Further heating

$CO_3^{-2} + H_2O \longrightarrow CO_2\uparrow + 2(OH^-)$

$Mg^{+2} + 2(OH^-) \longrightarrow Mg(OH)_2$

→ more than 82°C

→ less than 82°C

2 $CaSO_4 . 2H_2O$ (gypsum)

- max. solubility (Ksp)
- at 40°C

* Scale inhibitors :-

(1) Sodium hexameta Phosphate
or " tripoly "
using when $CaCO_3$ (2-5) PPm
and $CaSO_4$ (10-12) PPm

(2) Aminotrimethylene Phosphoric Acid (ATMP)
- stable at 120° C and at all PH values

* Scale removal
$CaCO_3$ بواسطة → [Hcl, formic acid, acetic acid, H_2SO_4]

Hcl, H_2SO_4 → strong acid
(sequestering agent), (oxalic acid) (EDTA)
(chalating agent) لازم تجيب
example.

* Coating
- material applied to metal surface to Prevent being exposed to the enviroment.

* characterstics of coating
1) high degree of adhesion
2) minimum Porosity
3) high resistance to flow of e
4) Sufficient thickness
5) low diffusion rate for H_2O

* classification

- Barrier coating
- conversion coating
- Anodic coating
- cathodic coating

1) Barrier coating

* Anodic oxide

high Porosity

Al_2O_3 (Alumina) Al by electrolysis

Scaling by using $K_2Cr_2O_7$ add to electrolyte solution to Prevent Porosity of Al_2O_3

* classification

- Barrier coating
- conversion coating
- Anodic coating
- cathodic coating

1) Barrier coating

A) * Anodic oxide

high Porosity

Al_2O_3 (Alumina) Al by electrolysis

Scaling by using $K_2Cr_2O_7$ add to electrolyte solution to Prevent Porosity of Al_2O_3

~~1) Barrier coating~~

B) Inorganic coating

cermic, glass

SiO_2 SiO_2 high Protective material

c) inhibitive coating

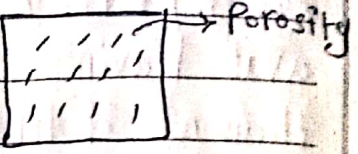
layer inhibitive material

d) organic coating

Epoxy, chloronated compounds

(Poly vinyl chloride Pue)

2) conversion coating
surface of metal is converted into adesired compound having Porosity to act as agood base for Paint.



3) Anodic coating
the coating becomes Anodic to the surface such as Al, Zn, cd coating

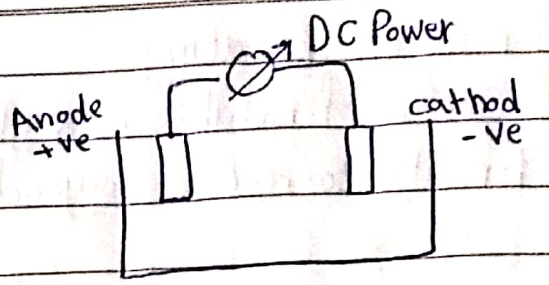
4) cathodic coating
metals are deposited on surface of material (to be coated) such as steel and becomes electropositive to the substract.
copper coated steel.

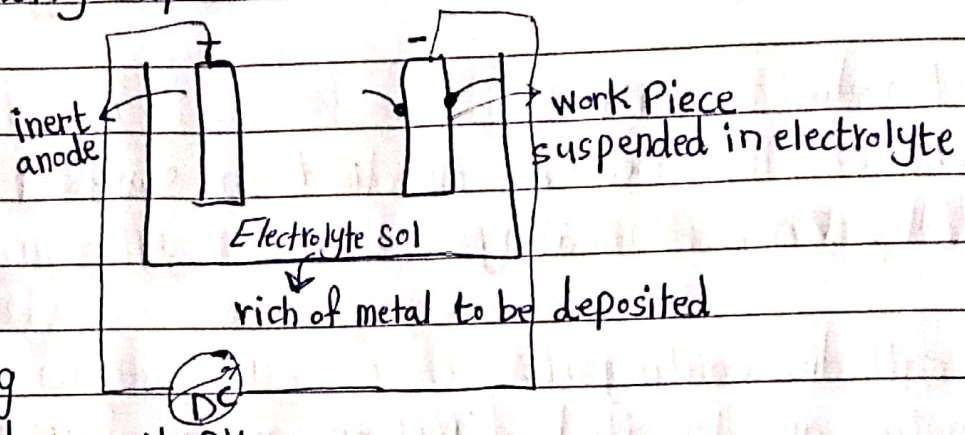
* Paint coating systems
- Paint coating
1) Primer coating
2) intermediate
3) top coating.
- Primer coating
Red Lead (Pb_3O_4), in linseed oil
Red lead reacts with oil ⇒ Protection steel
- Primer coating should be:
1) strongly bonded to the surface
2) Resists corrosive envi
3) Having good adhesion to the intermediate coating
examples: chromate salts, red lead.

* Electroplating

A) Vat Plating :-

Electroposition is performed in a vat having capacity up to thousands of liters.



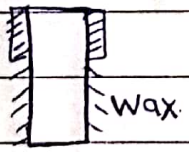


Used:

1) Full coating
2) Dense coating
(thickness of coating layer is proportional to the current density)

b) Selective coating

electroposition can be made to selected areas without need of masking (waxing) used in decoration



Advanteges:-

1) selective Plating
2) electro deposition is higher than vat Plating
3) Portability

c) Electroless Plating

- Reduction of metal ions to Produced metal atoms which deposited on cathod (work Piece)
  copper, nickel, cobalt, gold, silver (+ve charge)
- is conducted in PTFE (Poly tetra floro ethylene) ⇒ (Teflon) lined st.st tanks at 90°C.

* Different coating :-

A) Diffusion coating
surface of metal is modified by diffusion of coating into it at high temp.
↳ metal to be diffused
ex: Zinc diffusion coating
AL " "

B) flame spraying
melt the coating material and blow it into the surface of metal

c) Hot dipping galvanizing (most common)
- steel is dipped in to molten bath (450°C)
- Zinc reacts with steel and form Protection layer.

steps :-
1) cleaning from agrease باستخدام → Alkali Sol لإزالة
2) scale and oxides removal by HCl, H_2SO_4, blasting
3) steel is dipped in moltten Zn and forms iron-zinc layer (chemically bonded)
4) Galvanizing Process Performed at 445-465°C for 1-5 min
5) This layer is called unalloyed layer طبقة غير مسبوكة
6) Alloyed layer is used to enhance the dictiliting of steel.

* Galvanizing

Hot dipping — alloy بقدر أعمل فيها

Electro Galvanizing — alloyed ما بقدر أعمل فيها

Electro Galvanizing

- Hot dipping is replaced by series of electrolytes cells through which steel strips passes.
- in each cell, electrical current flow through zinc sol (Anode) to the cathod (steel)
- zinc is electrochemically bonded to the steel

* Galvanizing

Hot dipping — Electro galvanizing

alloy بقدر أعمل فيها — alloyed ما بقدر أعمل فيها

Electro galvanizing

- Hot dipping is replaced by series of electrolytes cells through which steel strips passes.
- in each cell, electrical current flow through zinc sol (Anode) to the cathod (steel)
- zinc is electrochemically bonded to the steel

* 8 forms of corrosions :-

1) Uniform corrosion

ex: corrosion of iron

* mechanism

1) Very thin layer of electrolyte is Present of the metal surface

2) Anodic Area, Anodic reaction

$$Fe \longrightarrow Fe^{+2} + 2\bar{e} \quad \text{(oxidation)}$$

3) at cathodic Area, reduction of oxygen takes Place

$$O_2 + 2H_2O + 4\bar{e} \longrightarrow 4\,o\bar{H} \quad \text{(Reduction)}$$

4) The ions of $o\bar{H}$ react with Fe^{+2} to Produce iron hydrooxide

$$Fe^{+2} + 2\,o\bar{H} \rightarrow Fe(oH)_2 \rightarrow \text{corrosion}$$

5) with more access to hydrogen in the air

$$Fe(oH)_2 + O_2 + 2H_2O \rightarrow 4\,Fe(oH)_3 \rightarrow \text{corrosion}$$

6) $Fe(oH)_2$, Furrous hydroxide, is converted to hydrated ferric oxide or Rust.

$$4\,Fe(oH)_2 + O_2 \rightarrow \underbrace{2\,Fe_2O_3 \cdot H_2O}_{\text{Rust}} + 2\,H_2O$$

2) Galvanic corrosion

- ↳ galvanic cell ⇒ cathod, Anode, electrolyte, metalic Path
- two different metals in contact with each other.
- examples copper, iron
- more nobel → cathod
  less nobel → Anode

	emf (V)	
copper	+0.337	(more nobel)
iron	-0.44	

- moisture (water) ⇒ electrolyte
- metal surface ⇒ metalic Path

1) Fe^{+2} flows from anode (iron) to the cathod (copper) through electrolyte (water)
2) hydrogen ions (H^+) are discharged at copper cathode → H_2 is released
3) Fe^{+2} travels towards cathod and $o\bar{H}$ toward Anode.
4) combination between Fe^{+2}, $o\bar{H}$ to form $fe(oH)_2$ → corrosion
5) iron corrods and copper will not

	emf (V)	
Ag	+0.8	cathod (more nobel)
Au	+1.5	Anode (corrosion)

3) crevice corrosion

Different ions exisists between crevice and out side; corrosion cell is formed

* the site at crevice is formed (Anode)
* outside the crevice is the cathod
* Anode (crevice) . $M^{\text{metal}} \rightarrow M^{+2} + 2\bar{e}$
  cathod (oxygen reduction) $O_2 + 2H_2O + 2\bar{e} \rightarrow 4\,o\bar{H}$

* after sometimes, the oxygen in the crevice is consumed.
* the concentration of O_2 at cathod remain unchanged hence, reaction ~~continue~~ continues
* the anodic dissolution continues and the cavity becomes deeper and depper.

4) Pitting corrosion

* local corrosion cell is formed

Causes:-

1) lack homoginity of metal surface (impurities, rough surface)
2) Destruction of Passive film (cause formation anodic area)

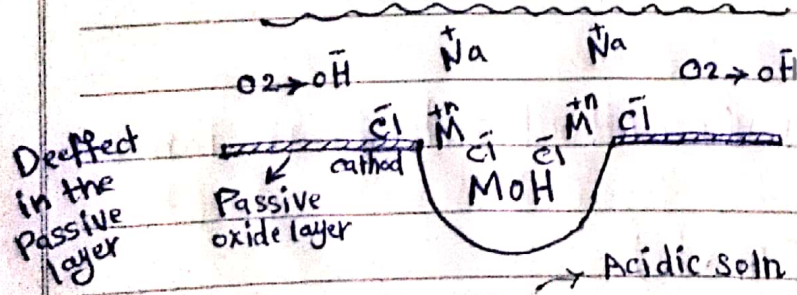
mechanism:-

a) formation anodic sites (destruction of Passive film)
b) Pitting is initiated $M \rightarrow M^{+n} + n\bar{e}$
c) cathodic reaction, oxygen reduction

$$O_2 + 2H_2O + 4\bar{e} \rightarrow 4\,o\bar{H}$$

whole surface is in contact with electrolyte containing O_2

d) due to metal dissolution continuting, the Process is self Propagated and Producing apit



Acidic soln, bottom of the Pit

$MCl + H_2O \rightarrow MoH + HCl$

(hydrolysis)

PH 1-1.5

* Propagation corrosion

5. stress corrosion (سريعة التآكل)

Couses :- 1. susceptible material.
2. specific material
3. Tensil strength

- copper is a susceptible material to ammonia solution and its compounds.

- A) Adsorption model
specific chemicals adsorb on the crack surface and lower fracture stress. (قوة الكسر)

B) Film rupture model (repetitive cycle)
- Localized film rupturing (caused by stress)
- Film repair (Passive film)
- a new Passive film is ruptured again by stress atack
- The cycle continues until failure.

C) Pre-exsisting active Path
(boundary grain)
impurities such as (S, P) on
intermetalic and new compounds are formed.

D) imbrittlement model
↳ (less of ductility)
↳ (بسبب) hydrogen immbrittlement
Example : hydrogen atom diffue to the crack tip and embrittle the metal.

6. Errosion - corrosion

Mechanical effect of fluid flow combined with corrosive action of the fluid.

mechanisim:-

- mechanical removal of metal Protective layer.
- corrosion of metal by flowing corrosive fluid.
- the Process is cyclic until Pitforation occurs.

7. intergranular corrosion

* caused by:-

Micro segregation of impurities and alloying element on grain boundary

- Driving force of corrosion difference between electrode Potential of the grain boundary and the grain itself.
- corrosion cell is formed in Presence of electrolyte solution.

8. Selective - leaching corrosion

cause:-

selective Removal of element from alloy by corrosion

* two Proposed mechanisims:-

① two metals in alloy are dissolved and one redeposited on the surface

② one metal is selectively dissolved leaving the other behined.

* Corrosion control by design

1) Metalic contact (galvanic corrosion)

Control :-

Avoid direct contact between metals by using insulating material

Applying Protective coating

* insulation material :-

rubber, glass wool (fiber), Polyurethane foam.

Why insulator leads to corrosion ?

* Moisture in the insulator (fiber, foam), resulting in leaching of soluble material

Even insulator → PH (2-3) ⇝ corrosive medium.

* Destruction of Passivity by chloride ion and initiate a pit

cholinated compounds (PVC)

* Crevice corrosion caused by insulator

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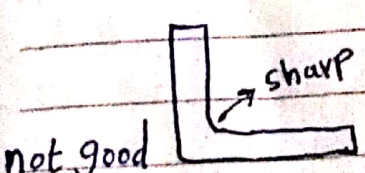
2) Impurities

- Caused Adsorption of moisture which leads to corrosion
- Passive surface destroyed by such deposits.
- the surface under deposits become anodic and lead to Pitting
- Prevention by design
- Good design shold not allowed the built up of impurities on surface



not good

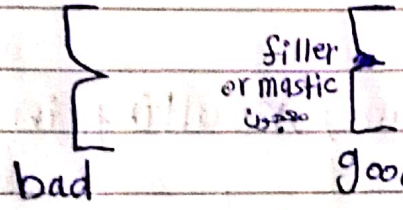
dirt not easily removed

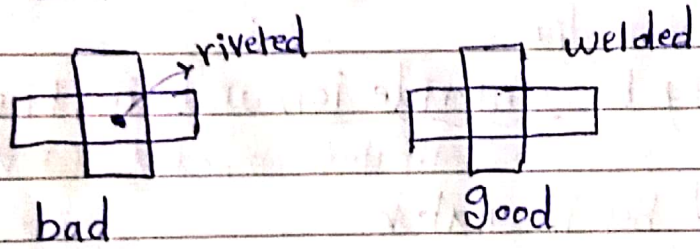
good

dirt easily removed

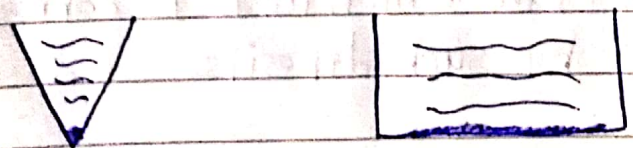
3) crevice corrosion
narrow gaps
- moisture enters the gaps by capillary action

Preventing :- البرشام
- use welded joints in Preferences to botted or ~~nia~~ riveted
- minimize contact between metals and non-metals
- Avoid sharp corners
- use of fillers and mastics to fill the gaps





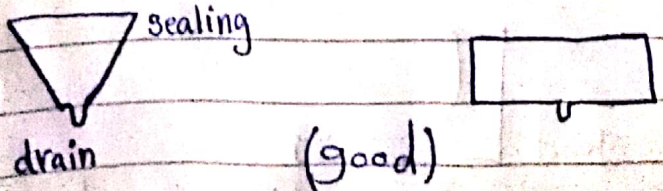
4) ~~Draing~~ Drainage and ventilation



(bad design) water trap

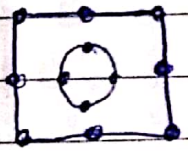
* rust will be found after water has evaporated

Prevention



5) Soldring and threading
- Soldring is aprocess in which two or more Parts are joint together. (welding), by melting and Puting a filler metal into the joint.
- threading :- separable joints which are used to hold machine Parts together (elbow, valve, flanges) (corrosion Join)
- soldring is preferable than threading
threaded joints cannt be avoided for assembling and disassembling reasons.
- threaded joints should be treated for corrosion Prevention.

6) Flowing water stream in Pipe



cause :- turbulent flow
↙
errosion-corrosion

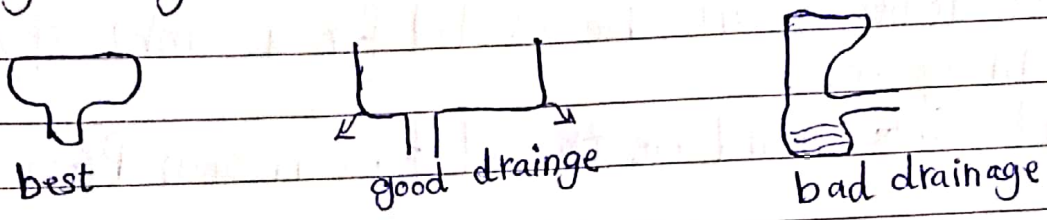
* to minimize corrosion by water flowing :-
a- design replacable Parts for the system areas which are mostly likely to corrode.
b. select materials which are compatible and dont offer risk of bimetalic corrosion.
c- the Pipe should be designed for smooth flow and all valves, elbows and other fittings should be installed in accordance with design to allow min. disturbance in flow
d. decrease the velocity of flow and use of baffles is effective
E. increase the Pipe diameter
f. Reguler maintenance and cleaning of Pipes to avoid accumilation of impurities which lead to change flow Pattern
g. Avoid Placing Pipe in direct contact with sand.

laminar
turbulent
both

7) Tanks and Piping system

Problems :-

- Galvanic cell ⇒ various material of construction
- crevice corrosion ⇒ behined gaskets
- bad drairange ⇒ traping electrolyte
- Poorly desinged bends and junctions



8) Design of liquid containers must offer the following :-

a- freedom from sharp corner and edges
b- smooth flow of liquid
c- freedom from build up of water traps
d. complete drainage
e. min bimetalic corrosion by joining compatible materials.
f. complete external and internal coating.