

POST-MINOR 1

LECTURE 11 (14/02/2023)

21] For a reaction:



We can write forward & backward rates:

$$\frac{r_f}{r_b} = \frac{k_f [A]}{k_b [B]}$$

For equilibrium, the net rate, $r = r_f - r_b = 0$

$$\Rightarrow \frac{k_f}{k_b} = \frac{[B]}{[A]}$$

22] Now, we know that:

$$\mu = \mu^\circ + k_B T \ln(a)$$

where, $a \rightarrow$ activity

$$\text{and } a = \gamma c$$

$$\text{Thus, } \mu = \underbrace{\mu^\circ + k_B T \ln \gamma}_{\text{this can be expressed as}} + k_B T \ln(c)$$

$$\mu^{\text{ex}} \rightarrow (\text{"}\mu\text{-excess"})$$

$$\therefore \ln \gamma = \frac{\mu^{\text{ex}} - \mu^\circ}{k_B T} \Rightarrow \gamma \text{ can be thus expressed as:}$$

$$\gamma = \exp\left(\frac{\mu^{\text{ex}} - \mu^\circ}{k_B T}\right)$$

$$= \exp\left(-\frac{\Delta \mu}{k_B T}\right)$$

Using this we can write rates as:

$$r_f = k_f c \exp\left(-\frac{\Delta \mu}{k_B T}\right) \leftarrow \text{in general}$$

$$\{ \text{where } \Delta \mu = \mu^\circ - \mu^{\text{ex}} \}$$

So we can thus write:

$$r_f = k_f c_1 \exp\left(-\frac{(\mu^{ex} - \mu_1)}{k_B T}\right)$$

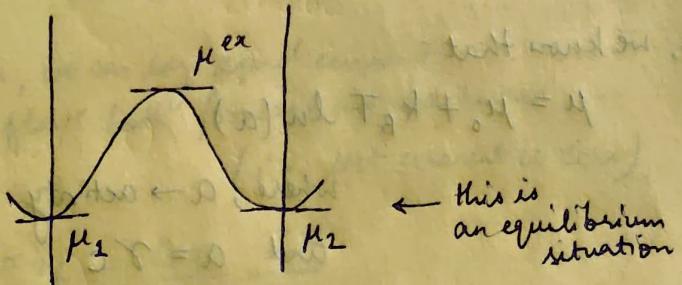
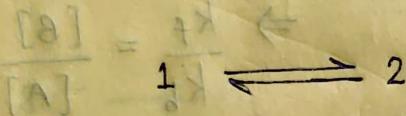
$$r_b = k_b c_2 \exp\left(-\frac{(\mu^{ex} - \mu_2)}{k_B T}\right)$$

At equilibrium:

$$k_f c_1 \exp\left(-\frac{(\mu^{ex} - \mu_1)}{k_B T}\right) = k_b c_2 \exp\left(-\frac{(\mu^{ex} - \mu_2)}{k_B T}\right)$$

In general, this gives us (i.e. at equilibrium, we must take)

$$\mu_1 = \mu_2$$



LECTURE 12

(15/02/2023)

* NOTE: When doing for 1 atom/molecule $\Rightarrow k_B T$
When doing for 1 mol $\Rightarrow RT$

23]



$$(\mu_1 = \mu_2)$$

Here, $1 \rightleftharpoons 2$

We can write:

$$r_f = k_f c_1 \exp\left[-\frac{\Delta \mu^*}{RT}\right]$$

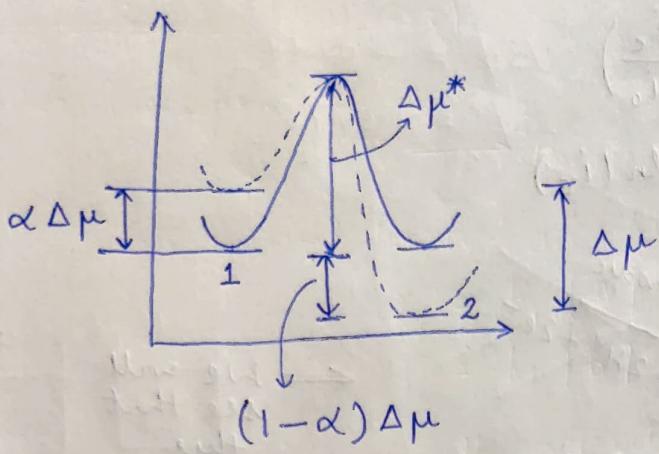
$$r_b = k_b c_2 \exp\left[-\frac{\Delta \mu^*}{RT}\right]$$

$$\therefore r = r_f - r_b = 0 \quad (\text{at eq, bm.})$$

$$\Rightarrow [k_f c_1 = k_b c_2]$$

* this relation is thus true for eq^{bm} only

24] For Non-Equilibrium case:



$$\text{changed to: } \exp\left[-\frac{(\Delta\mu^* - \alpha\Delta\mu)}{RT}\right]$$

$$\therefore \text{We have here: } r_f = k_f c_1 \exp\left[-\frac{\Delta\mu^*}{RT}\right]$$

$$r_b = k_b c_2 \exp\left[-\frac{(\Delta\mu^* + (1-\alpha)\Delta\mu)}{RT}\right]$$

$$\therefore r = r_f - r_b$$

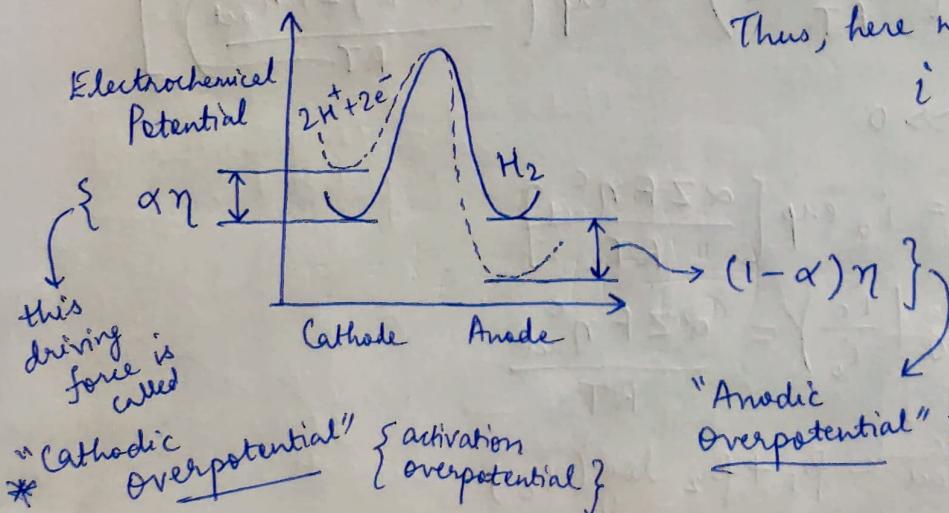
$$= k_f c_1 \exp\left(-\frac{\Delta\mu^*}{RT}\right) \exp\left(\frac{\alpha\Delta\mu}{RT}\right)$$

$$- k_b c_2 \exp\left(-\frac{\Delta\mu^*}{RT}\right) \exp\left(-\frac{(1-\alpha)\Delta\mu}{RT}\right)$$

Here we can approximately say $\Rightarrow k_f c_1 = k_b c_2 = k_0$ (constant)

$$\therefore r = k_0 \exp\left(-\frac{\Delta\mu^*}{RT}\right) \left[\exp\left(\frac{\alpha\Delta\mu}{RT}\right) - \exp\left(-\frac{(1-\alpha)\Delta\mu}{RT}\right) \right]$$

25] Now, considering the case of Electrochemical potential:



Thus, here we obtain:

$$i = i_c - i_a$$

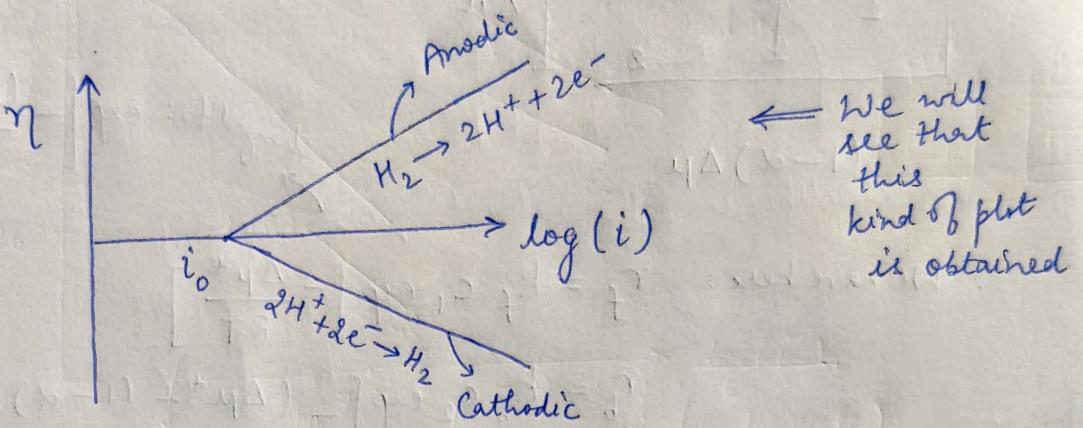
$$= i_0 \left[\exp\left(\frac{\alpha\eta_c}{RT}\right) - \exp\left(-\frac{(1-\alpha)\eta_c}{RT}\right) \right]$$

"Anodic Overpotential" { if this is taken as: $\alpha\eta_a$ }

$$\text{Now, } i_c = i_0 \exp\left(\frac{\alpha \eta_c}{RT}\right)$$

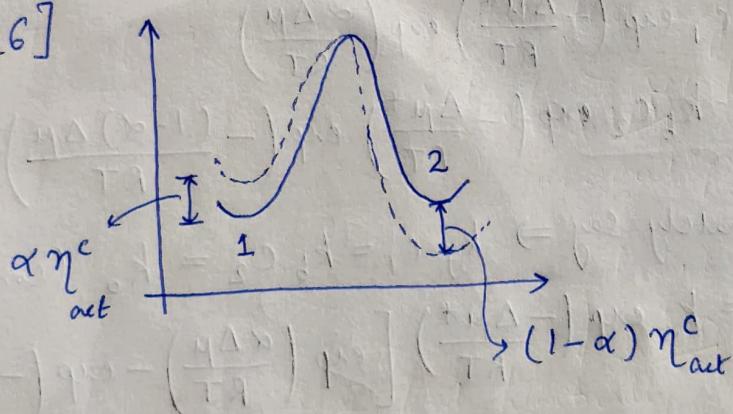
$$\Rightarrow \eta_c = \frac{RT}{\alpha} \ln\left(\frac{i_c}{i_0}\right)$$

$$\Rightarrow \eta_c = \beta_1 + \beta_2 \ln(i_c)$$



LECTURE 13 (17/02/2023)

26]



$$i = i_c - i_a$$

required to convert electric potⁿ to chemical potential

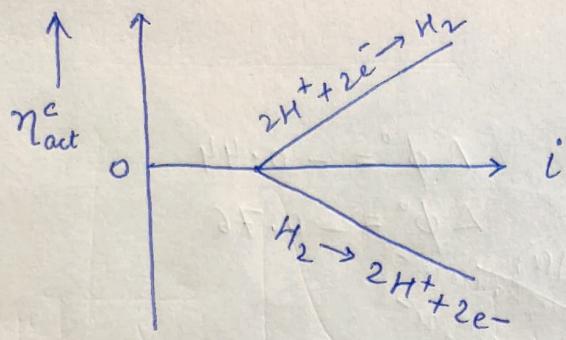
$$= i_0 \left[\exp\left(\frac{\alpha ZF \eta_{act}^c}{RT}\right) - \exp\left(-\frac{(1-\alpha) ZF \eta_{act}^c}{RT}\right) \right]$$

Considering $\eta_{act}^c \gg 0$

$$\text{Now, } i_c = i_0 \exp\left[\frac{\alpha ZF \eta_{act}^c}{RT}\right]$$

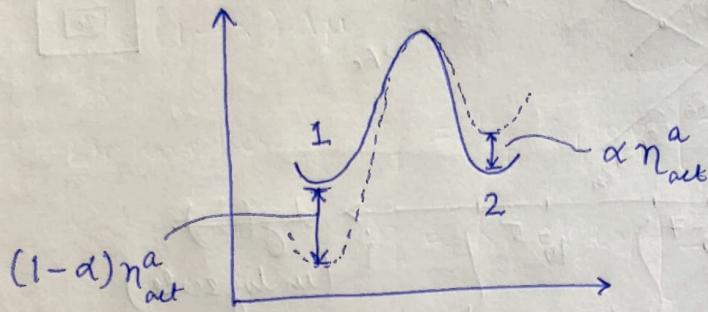
$$\Rightarrow \log\left(\frac{i_c}{i_0}\right) = \frac{\alpha ZF \eta_{act}^c}{RT}$$

$$\Rightarrow \eta_{act}^c = \beta_1 + \beta_2 \log(i_c)$$



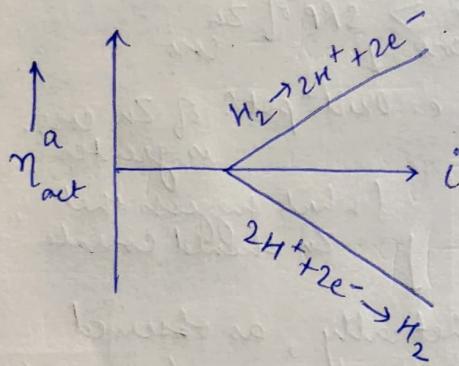
called
TAFEL DIAGRAM

NOTE: In some textbooks we may see instead anodic case:

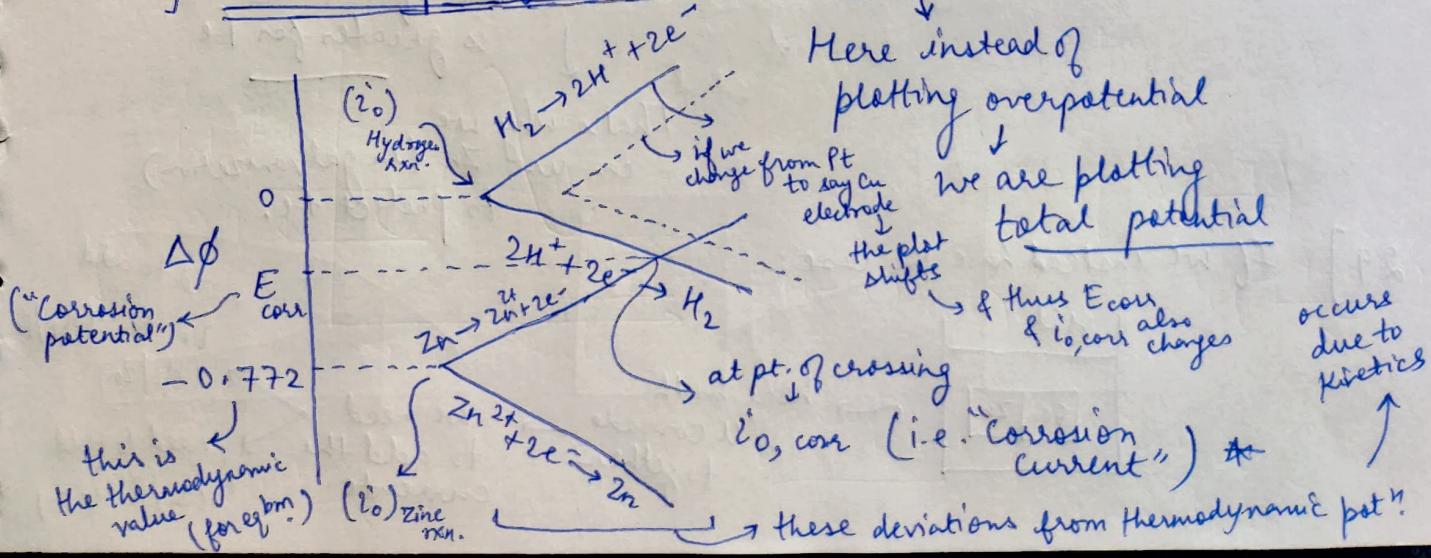


* NOTE: All machines generally mostly measure the overpotential in the anodic form

$$\text{We get: } i = i_a - i_c \\ = i_0 \left[\exp\left(\frac{\alpha \eta_{act}^a ZF}{RT}\right) - \exp\left(-\frac{(1-\alpha) \eta_{act}^a ZF}{RT}\right) \right]$$

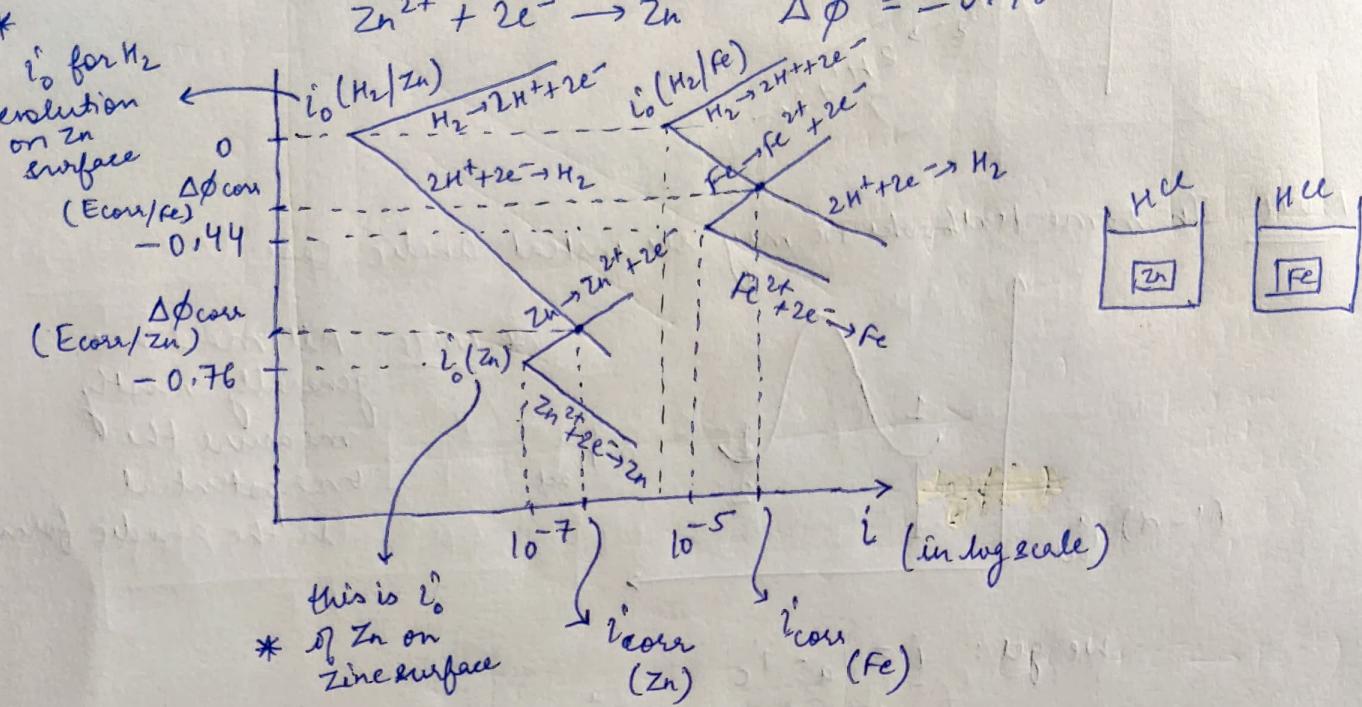


27] Some examples of Total Potential plot



LECTURE 14 (21/02/2023)

$$28] \quad \text{eg: } \text{Fe}^{2+} + 2e^- \rightarrow \text{Fe} \quad \Delta\phi^\circ = -0.44$$



Thus from here we see that thermodynamically

$$\text{SRP of Fe} > \text{SRP of Zn}$$

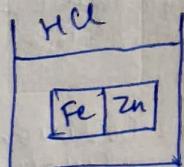
i.e. Oxid."pot." of Zn corr.
is greater

(which suggests that
 τ should correlate "more")

* But kinetically, as observed from τ_{corr} values we see that the real rate of corrosion is greater for Fe

That's why we can use Zn (galvanization) to protect fe.

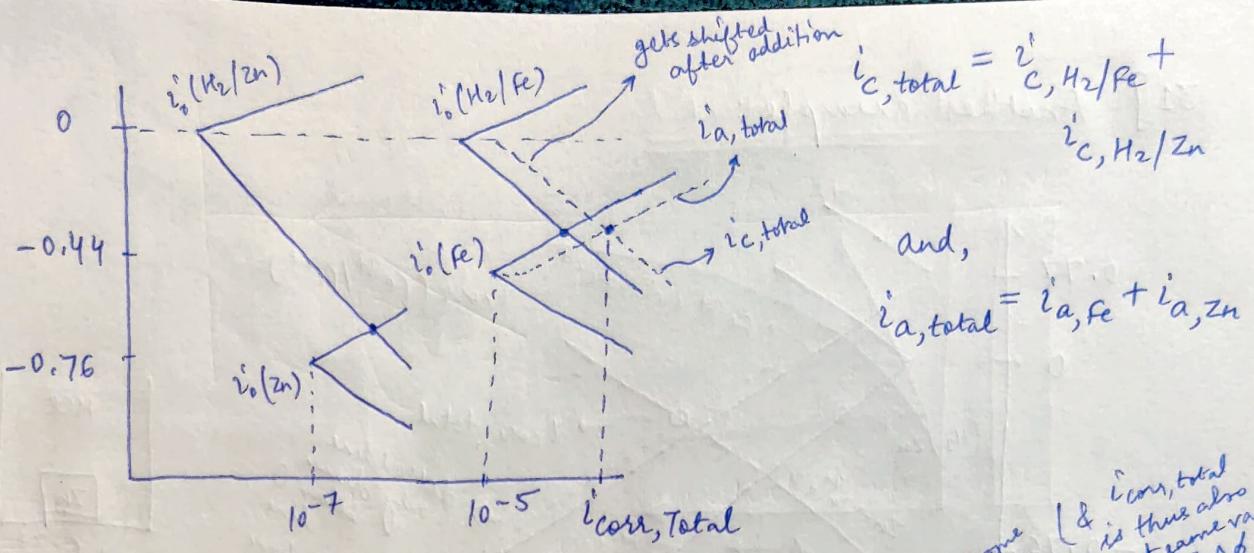
29.] If we instead have the case:



→ here both
will correlate
together

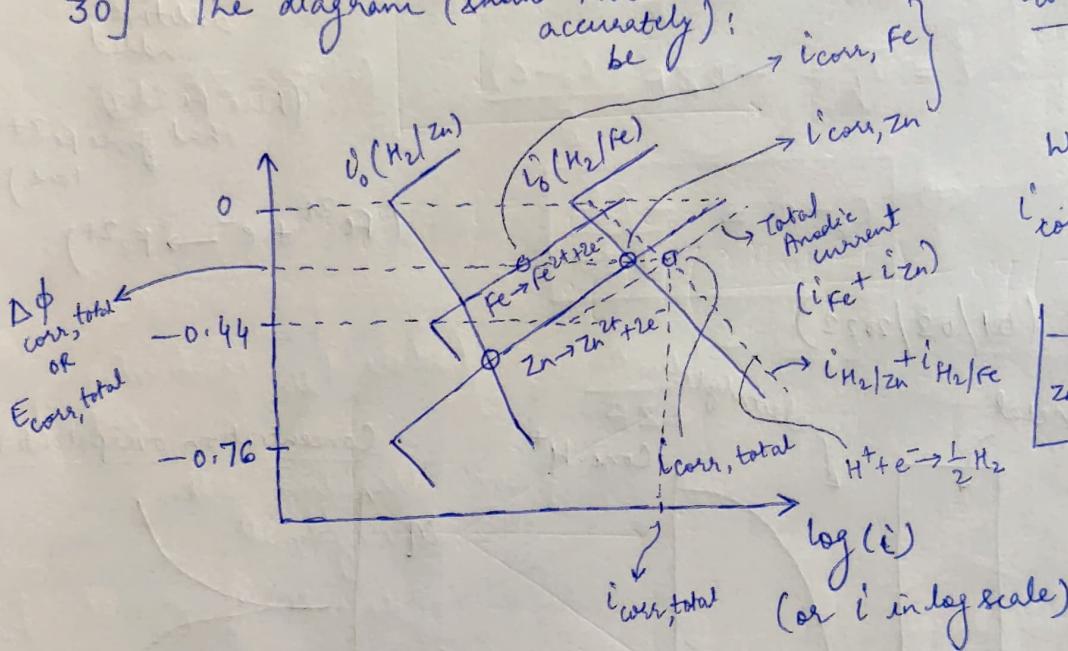
ill corrode together \rightarrow we need to add the currents

need to add
 i_o & $i_o(H_2/Fe)$
 $\rightarrow (H_2/Zn)$



LECTURE 15 (28/02/2023)

30] The diagram (should more accurately):

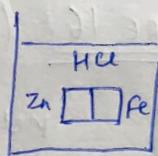


There are taken at some $\Delta\phi$ value (& $i_{\text{corr, total}}$ is thus also at same value $\Delta\phi$)

$$i_{\text{corr, Zn}} > i_{\text{corr, Fe}}$$

But here we see usually:

$$i_{\text{corr, Fe}} > i_{\text{corr, Zn}}$$



* ∵ $i_{\text{corr, Zn}}$ is greater than $i_{\text{corr, Fe}}$ when Zn & Fe are placed together

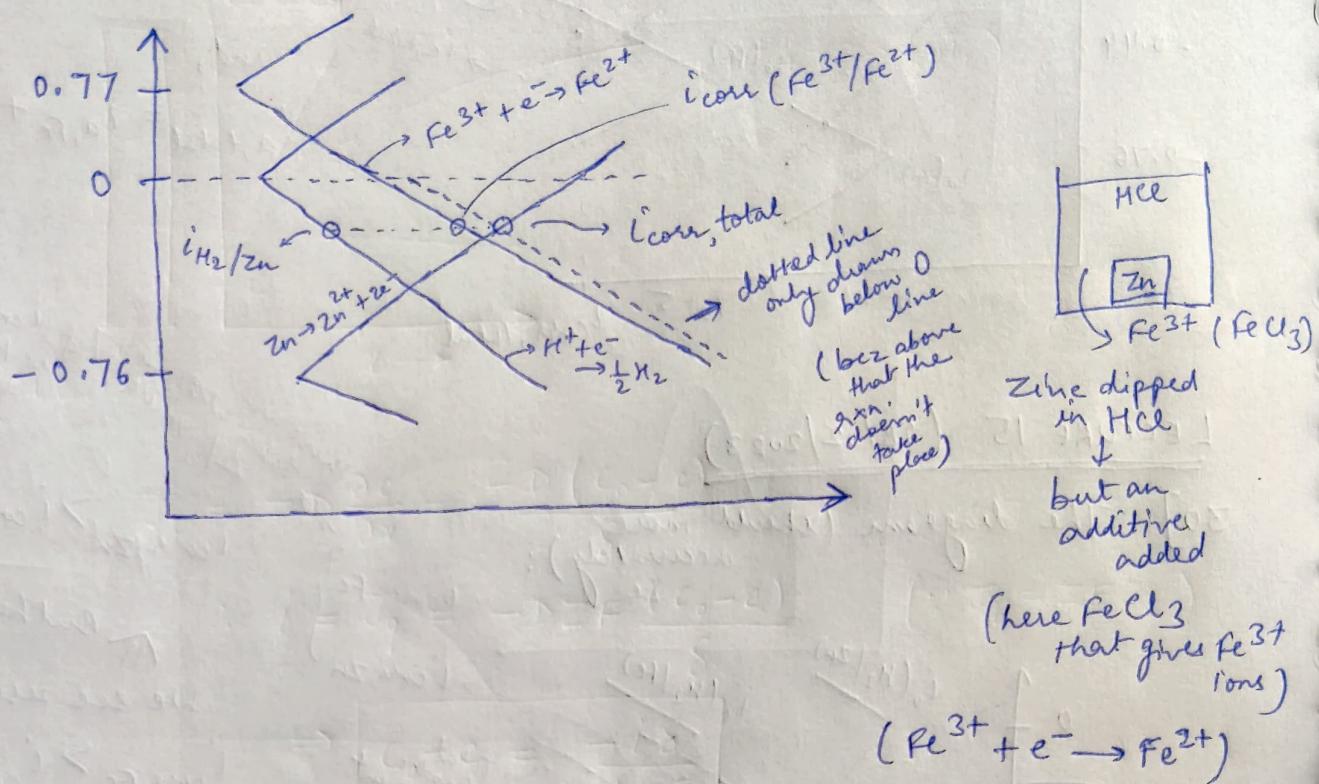
↓
that is why it can be used to protect Fe

NOTE: We can add currents bcz i is extensive property (whereas $\Delta\phi$ is intensive property).

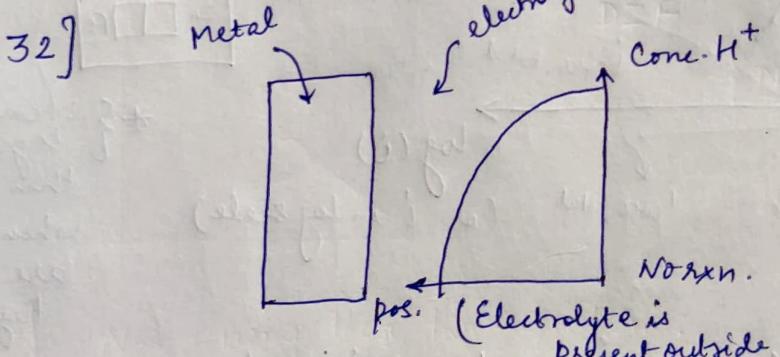
NOTE: Since $i_0(\text{H}_2/\text{Fe}) \gg i_0(\text{H}_2/\text{Zn})$, thus H_2 is mostly evolved on Fe surface here.

{ continuing on the Next Page }

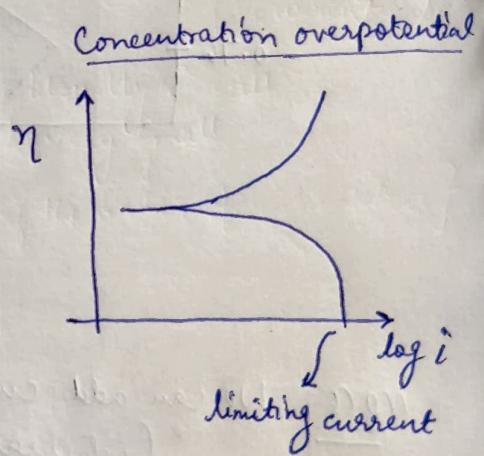
31] Another example:



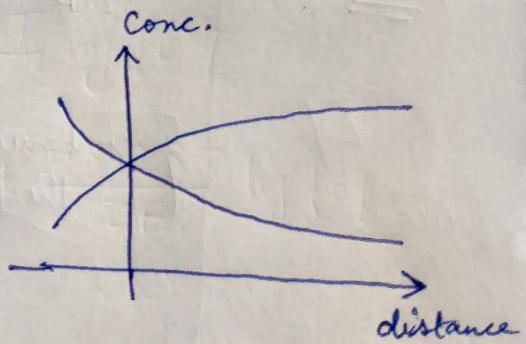
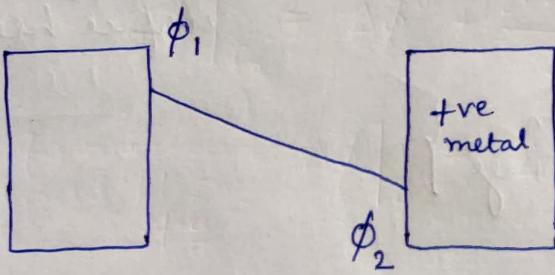
LECTURE 16 (01/03/2023)



* The conc. drops as we move closer towards the metal



33]



Due to repulsion by the charge
on metal, we observe this.

As η changes, the concentration will
↓ dip even further.
Diffusivity is decreasing

34] For current to pass, charges must diffuse
↓
thus we can
write:

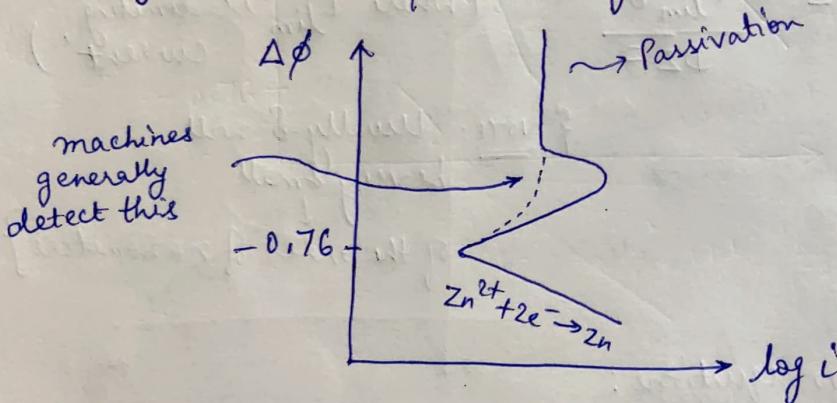
$$J_c = -D \frac{\partial c}{\partial x} = -M \frac{\partial \mu}{\partial x}$$

and, $J_q = -k \frac{\partial \phi}{\partial x}$

(where ϕ = charge density)

LECTURE 17 (03/03/2023)

35] Oxide or product layer:

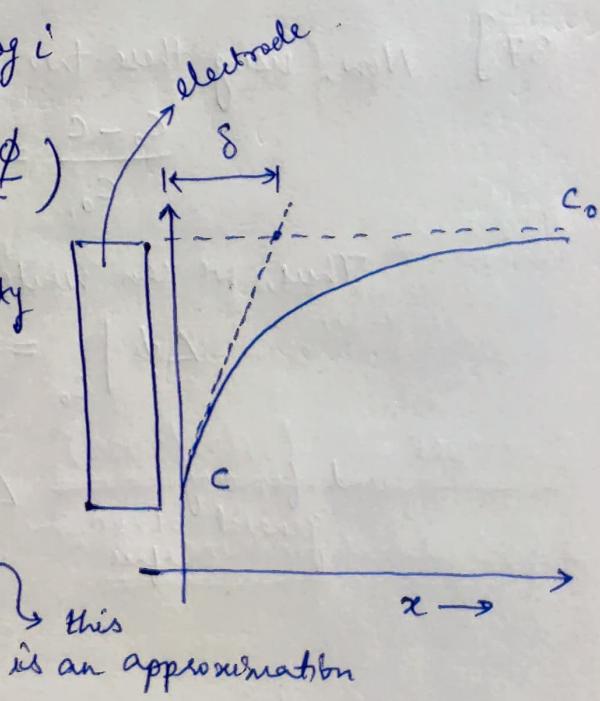


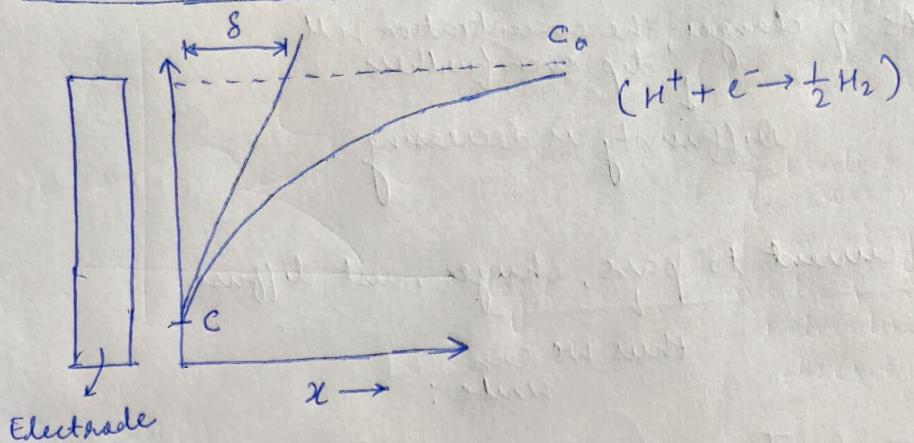
We see: $c = c_0 \exp\left(-\frac{Z F \phi}{R T}\right)$

Now, $J_c = -D \frac{\partial c}{\partial x}$

(where, $D = \frac{M R T}{c} \xrightarrow{\text{mobility}}$)

we observe from plot: $J_c = -D \frac{(c_0 - c)}{\delta}$



36] Concentration overpotential


$$J_c = -D \frac{\partial c}{\partial x} = -\frac{D(c_0 - c)}{\delta}$$

$$\therefore i = J_q = -DZF \frac{(c_0 - c)}{\delta} \quad (\because J_q = ZFJ_c)$$

$$\Rightarrow c_0 - c = \frac{-i\delta}{DZF}$$

* and also $\Rightarrow c_0 = -\frac{i_{\lim}\delta}{DZF}$ (where i_{\lim} is 'limiting current')

{ NOTE: Usually δ will be very small
↓ of the order of nanometres }

37] Now, using these two equations:

$$\frac{c_0 - c}{c_0} = \frac{i}{i_{\lim}}$$

Thus, we can write now:

$$\Delta\phi|_{c_0} = \Delta\phi^\circ + \frac{2.303RT}{ZF} \log [c_0]$$

and for any general pt. on surface: $\Delta\phi|_S = \Delta\phi^\circ + \frac{2.303RT}{ZF} \log [c]$

$$\therefore \eta_c = \frac{2.303 RT}{ZF} \log \left(\frac{C}{C_0} \right)$$

$$= \frac{2.303 RT}{ZF} \log \left(1 - \frac{i}{i_{\text{lim}}} \right)$$

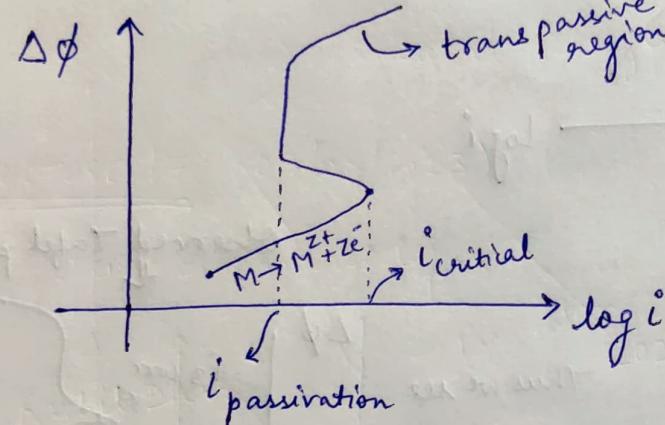
{ NOTE: From Maxwell's First Equation, we will also see that:

$$\vec{\nabla} \cdot \vec{E} = \frac{f}{\epsilon_0} \Rightarrow \nabla \cdot (-\nabla \phi) = \frac{f}{\epsilon_0} \Rightarrow \nabla^2 \phi = -\frac{f}{\epsilon_0}$$

which for one-dimensional case becomes: $\frac{\partial^2 \phi}{\partial x^2} = -\frac{f}{\epsilon_0}$

LECTURE-19 (15/03/2023)

38]

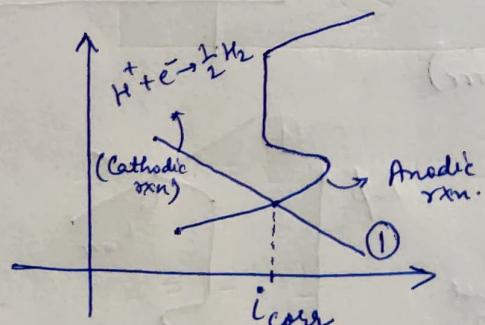


Possible reasons for it are:

- { ① it is porous layer
- ② another compound may form
- ③ Breakdown of oxide layer
- ④ O₂ formation

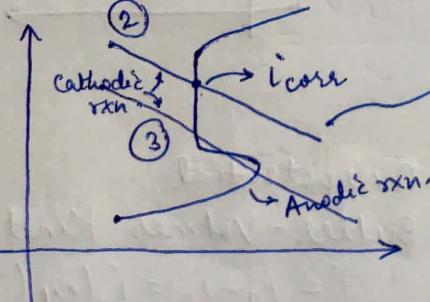
NOTE: $\vec{J}_c = -D \nabla c - \nu c$

39]



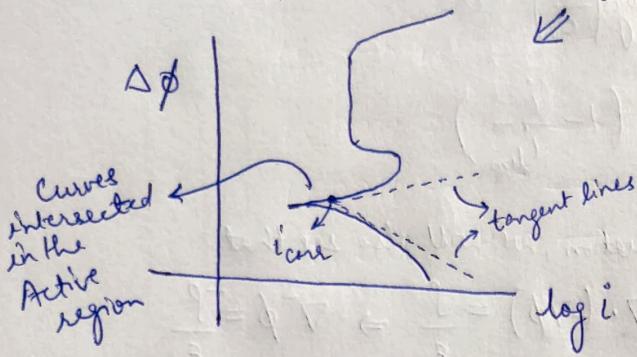
Here passivation does not matter (for case ①)

(i.e. here curve ① has been shifted either to ② or to ③)



Here passivation matters (for ② & ③)
i.e. if the curve shifts upwards then i_core is found here

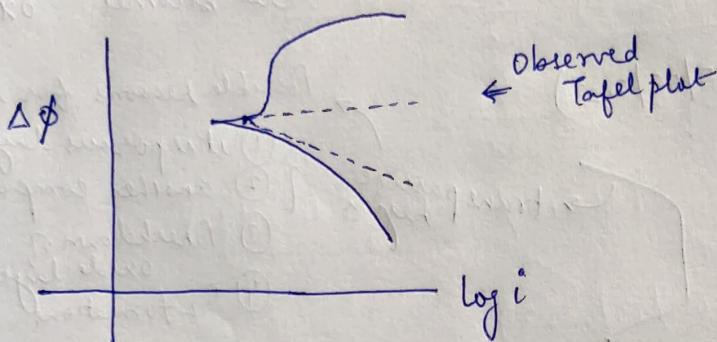
For case ①:



↙ This is going to be
the actual
observed Tafel plot
(for combined
anodic & cathodic)

{ Earlier we
were only
overlaid the
anodic & cathodic curves
individually to
observe each of them }

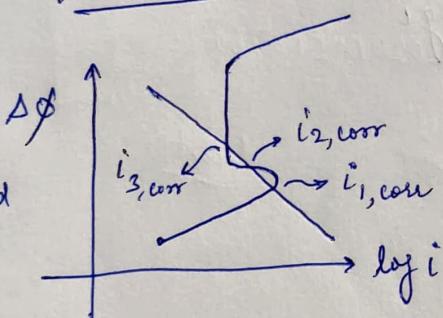
For case ②:



↙ Observed
Tafel plot

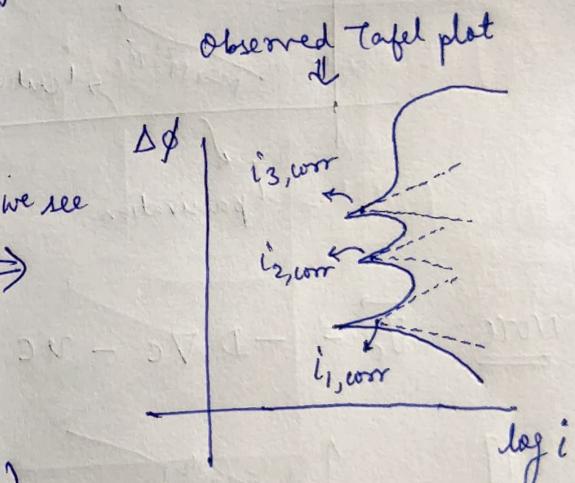
For case ③:

We had
this:

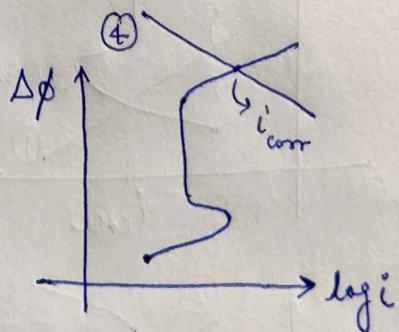


$$(i_1,corr > i_2,corr > i_3,corr)$$

Thus we see



Question: What will be the final plot for this case?
(to think about) as H.W.



LECTURE 20 (17/03/2023)

* { Syllabus for minor-2:

1) Overpotential

2) Butler-Volmer Kinetics

$$i = i_a - i_c = i_0 \left(\exp \left(-\frac{\alpha \eta}{k_B T} + \dots \right) \right)$$

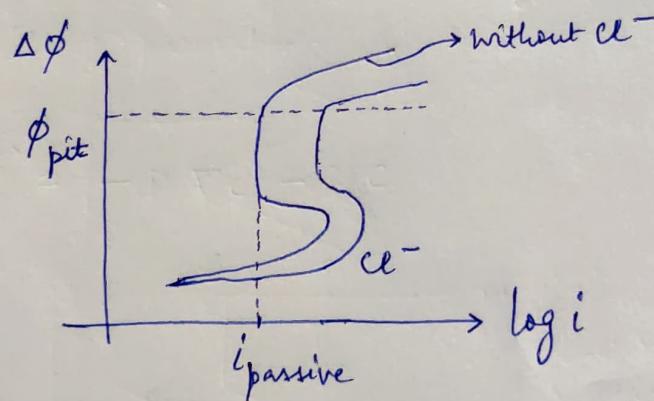
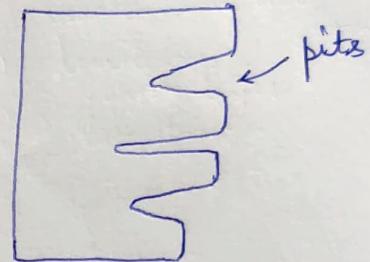
- 3) Tafel plots
- 4) Tafel plots for metallic corrosion
(Fe/HCl, Zn/HCl)
- 5) Galvanic coupling
(Fe/Zn system)
- 6) Concentration overpotential
(Effect of velocity, pH)
- 7) Passivation

Reference : D.A. Jones - Chapters 4, 5, 3, 6.

- 8) Pitting Corrosion

40] Pitting : Localised corrosion

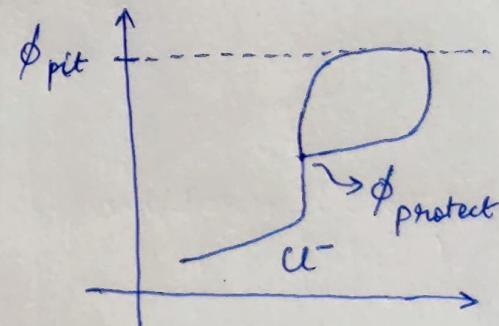
You may not see much of a weight loss
 ↓
 but pitting could be there
 which could lead to Mechanical failure



41] In cyclic corrosion:
 $\Delta\phi \rightarrow$ goes from +ve to -ve

above ϕ_{pit} , more pits will form
 below ϕ_{pit} , no new pits will form

In region θ, such that $\theta \in [\phi_{protect}, \phi_{pit}]$
 there is small chance of pit formation
 but existing pits will grow



Fe examples :

