KINETICS OF AQUEOUS CORROSION

Electrode Kinetics;

* $M - ne^- \rightarrow M^{n+}$

One mole of metal gives out $n N_A$ electrons which is a charge of $n N_A e$

$\therefore I = \frac{dQ}{dt} = n N_A e \left(\frac{dN}{dt}\right)$ where N is the moles of material

$\Rightarrow I = nF\left(\frac{-dN}{dt}\right)$

* Current density $i = \frac{I}{A} = \frac{nF}{A}\left(\frac{-dN}{dt}\right)$ where A = electrode area

Polarisation;

* For a half-cell reaction at one electrode; Ox. Species + $ne^- \leftrightarrow$ Red. Specie
* At equilibrium the rates of reaction forwards and backwards are equal $\therefore i_a = i_c = i_o$ (exchange current density). ← can't obtain directly
* i_o depends on surface chemistry so it is different for different metals, because $2H^+ + 2e^- \rightarrow H_2$ involves e^- transfer, H atom diffusion, and formation of H_2.
* In the above condition the electrode potential is $E_o^\bullet$ which is the standard E adjusted according to the Nernst equation.
* Polarisation is difference between actual E and $E_o^\bullet$;

$\eta = E - E_o$ so $\eta > 0$, $E > E_o$ so this will cause $i_a > i_c$

$\eta < 0$, $E < E_o$ which will cause $i_c > i_a$

Activation Polarisation;

* When chemical reaction is the slowest step in the corrosion mechanism, the activation energy of the reaction is the most sig. step (activation polarisation).

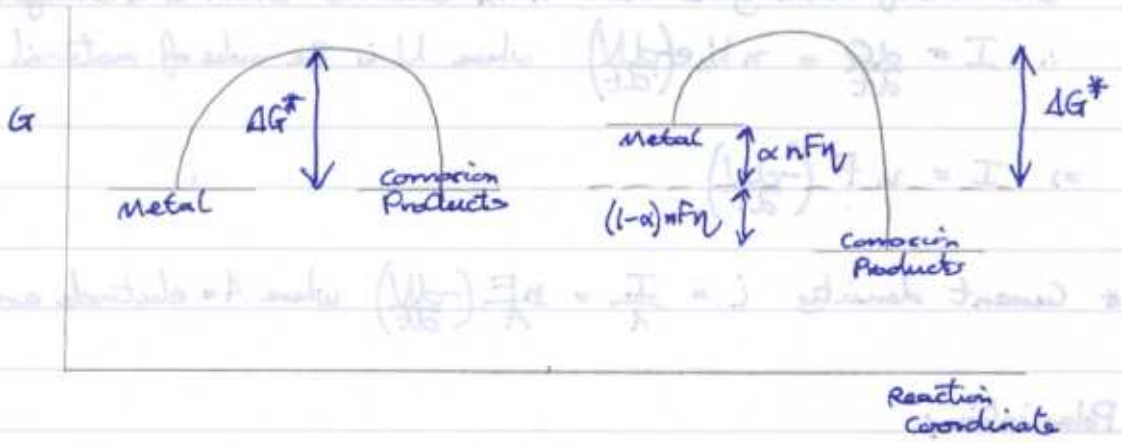
* At eq. $i_o = i_a = i_c = A_o \exp\left(\frac{-\Delta G^*}{RT}\right)$

Now $\Delta G_R = -nFE_{cell}$ $\therefore \Delta G = nF\eta$

* As $i = i_a - i_c$;

$$i = A_0 \exp\left(-\frac{(\Delta G^* - \alpha n F\eta)}{RT}\right) - A_0 \exp\left(-\frac{(\Delta G^* + (1-\alpha) n F\eta)}{RT}\right)$$

$$\Rightarrow i = i_0\left[\exp\left(\frac{\alpha n F\eta}{RT}\right) - \exp\left(\frac{-(1-\alpha) n F\eta}{RT}\right)\right]$$ Butler – Volmer



* If $\eta > 50mV$, then $i_a >> i_c$ so ;

$$\eta = \beta_a \log\left(\frac{i}{i_0}\right)$$ Tafel Eq. (for anodic reaction)

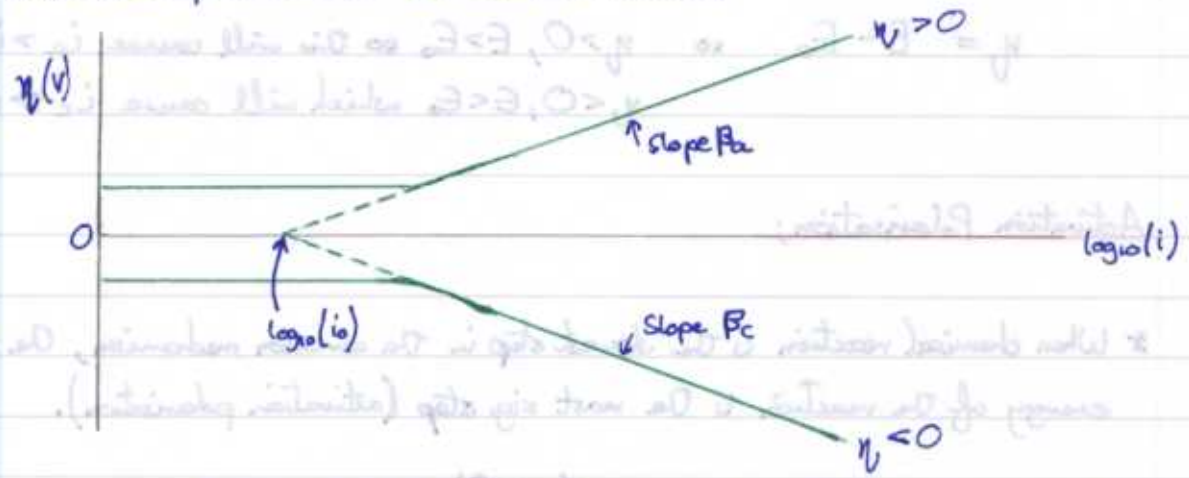
($\beta_a = \frac{2.303RT}{\alpha nF}$)

* If $\eta < -50mV$, then $i_c >> i_a$ so ;

$$\eta = \beta_c \log\left(\frac{i}{i_0}\right)$$ Tafel Eq. (for cathodic reaction)

($\beta_c = \frac{-2.303RT}{(1-\alpha)nF}$)

* At low polarisations behaviour is linear.



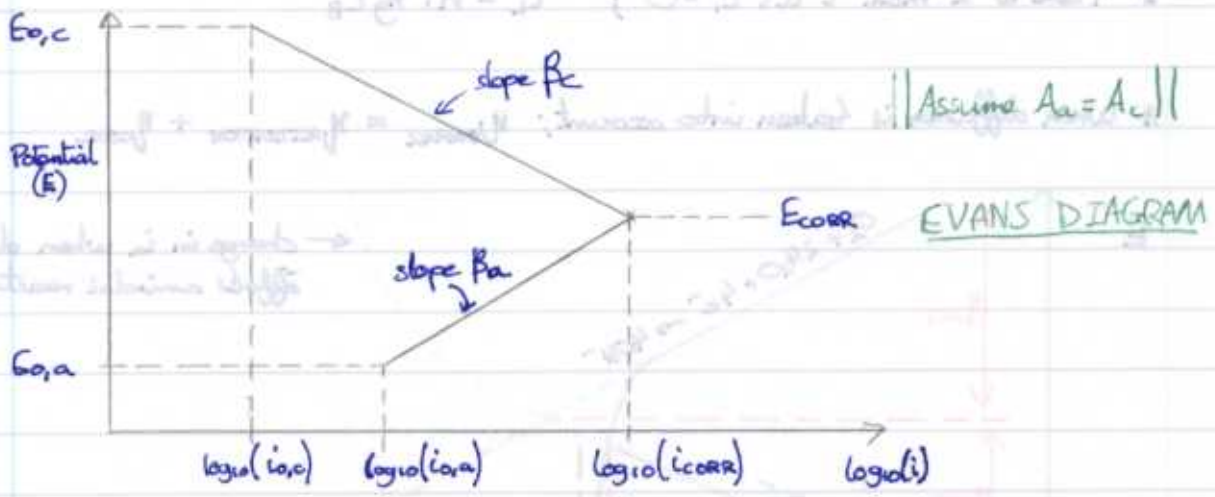
EVANS DIAGRAM → combines thermodynamic and kinetic info

Mixed Potential Theory (2 half-cell reactions):

* Due to differences in microstructure 2 half-cell reaction can occur on the same surface.
* e.g. $M \rightarrow M^{n+} + ne^-$ (anode)
  $2H^+ + 2e^- \rightarrow H_2$ (cathodic)
  } Ignore back-reactions
* The difference in E between the above reactions causes a flow of e^-. This will reduce the potential of the cathode and increase that of the anode.

* Charge conservation applies; $I_{cell} = i_a A_a = i_c A_c$ where i_a, i_c depend on the potential of the metal.

* [FREE MIXED CORROSION POTENTIAL; potential at which charge conservation is obeyed, in the absence of an external current source.



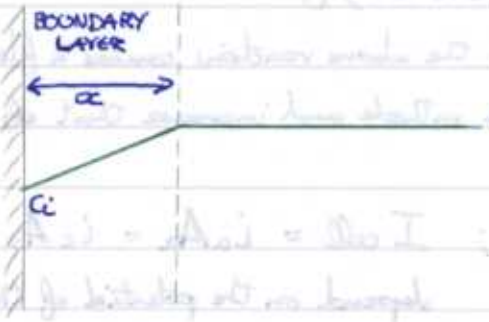
||Assume $A_a = A_c$||

EVANS DIAGRAM

* $E_{o,c}$ and $E_{o,a}$ are standard electrode potentials adjusted by Nernst Equation.
* Use above diagram and Tafel equations to find E_{CORR}.
* i_{CORR} depends on
  - electrode potentials
  - exchange current densities (which depend on surface chemistry)
  - Tafel parameters
  - external applied potentials.
* Due to charge conservation, corrosion will be faster if $A_a << A_c$

Diffusional Limitations ; (concentration polarisation)

* Diffusion of species to and from the electrode surface may be the rate determining step, not activation polarisation, particularly for reactions involving transport of GASES to the CATHODE.



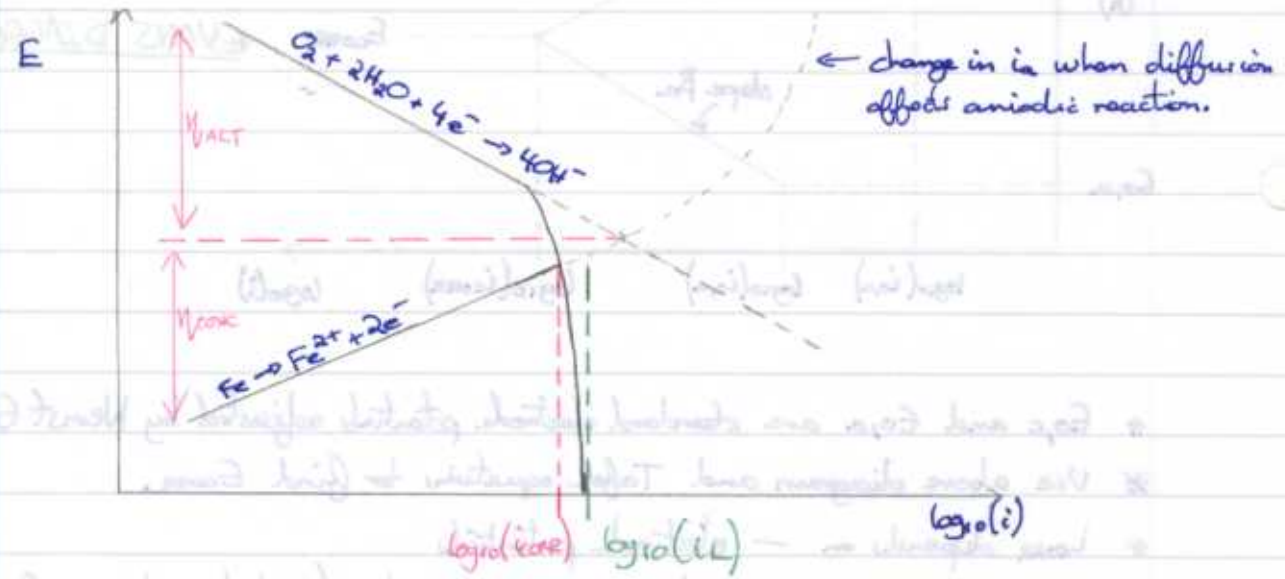
so $\frac{1}{A}\left(\frac{-dN}{dt}\right) = k_g (C_B - C_i)$

as $i = \frac{nF}{A}\left(\frac{-dN}{dt}\right)$

$\therefore i = nF\, k_g (C_B - C_i)$ where $k_g = D/\alpha$

* There is a max. i at $c_i = 0$; $i_L = nF k_g C_B$

* When diffusion is taken into account; $\eta_{OVERALL} = \eta_{ACTIVATION} + \eta_{CONC.}$



← change in i when diffusion affects anodic reaction.

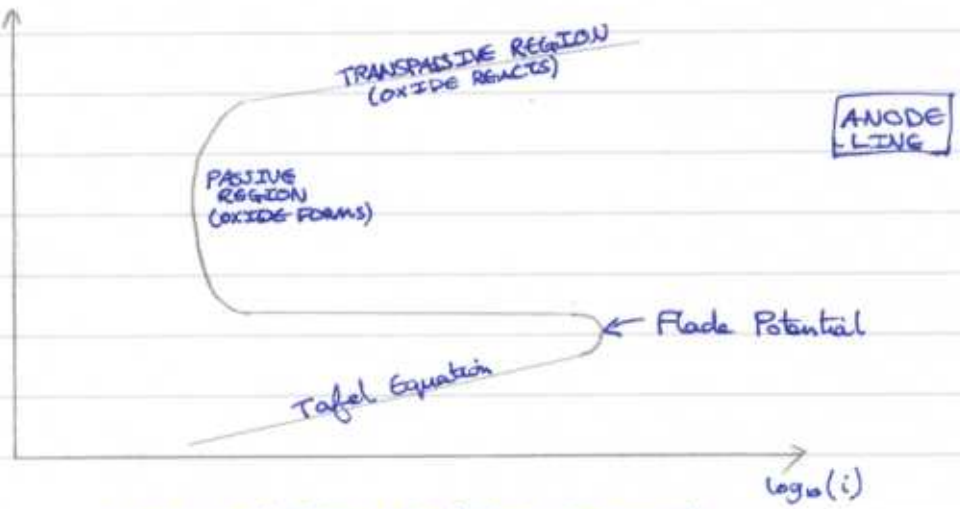
* E_c (bulk conc.) $= E^\circ - \frac{RT}{nF} \ln\left(\frac{1}{C_B}\right)$

E_c (actual) $= E^\circ - \frac{RT}{nF} \ln\left(\frac{1}{C_i}\right)$

$\therefore \eta = E_c(\text{actual}) - E_c(\text{bulk}) = \frac{RT}{nF} \ln\left(\frac{C_i}{C_B}\right)$ ← $1 - \frac{i}{i_L}$

Passivation;

* This is the formation of a protective oxide layer at the surface.



EVANS DIAGRAM FOR ANODIC REACTION

* Alloying causes the curve in the above diagram to shift left.
* If other chemical species are present (e.g. Cl^- attacks passivation layers) then the transpassive line moves downwards.
* Overall corrosion behaviour ~~occurs~~ is a combination of where the anodic line intersects the possible cathodic reactions.

* Cracks in the passivating layer mean that A_a is very small and A_c is large so that corrosion is rapid.
* But e.g. Cr in Fe reacts quicker than Fe so the passivation layer of Cr_2O_3 forms again. Cr > 11% for this to occur.