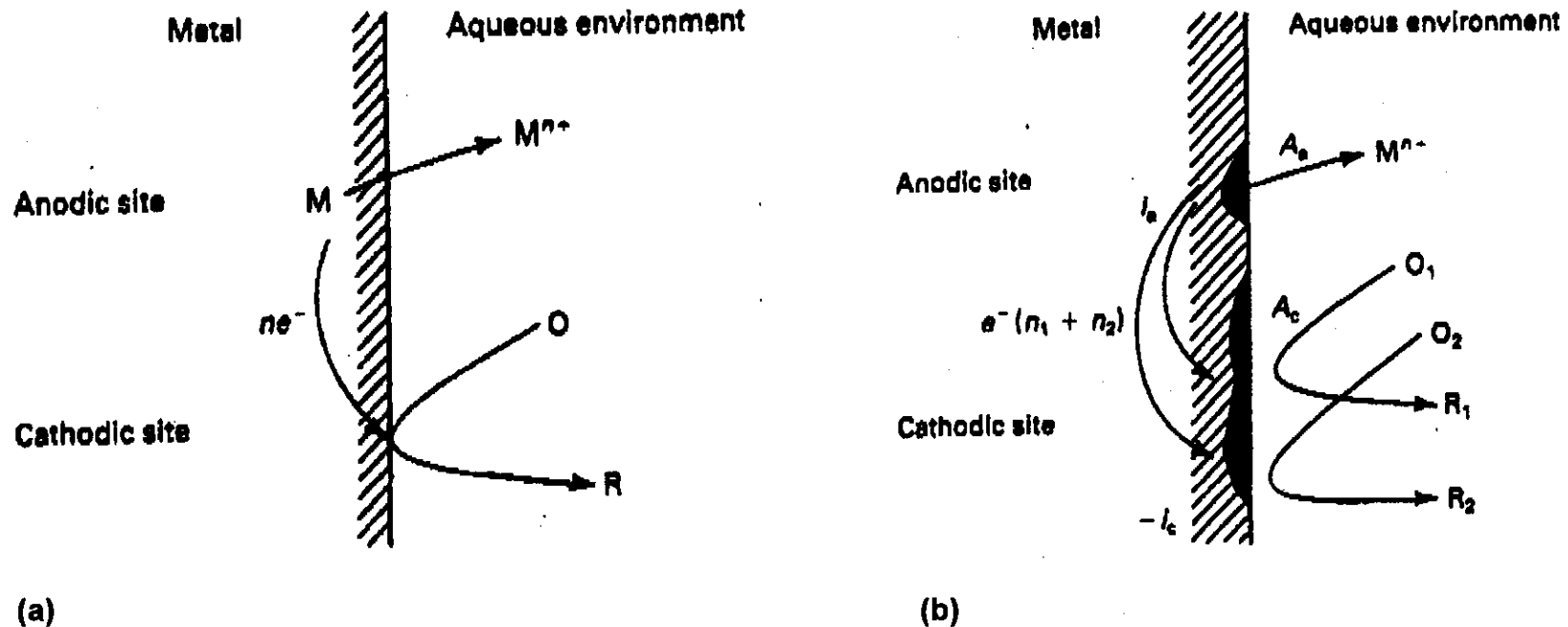# KINETICS OF AQUEOUS CORROSION

Anodic and cathodic reactions are coupled at a corroding metal surface:

(a)　　　　　　　　　　　　　　　　　(b)

Schematics of two distinct corrosion processes.

(a)　The corrosion process $M + O \rightarrow M^{n+} + R$ showing the separation of anodic and cathodic sites.

(b)　The corrosion process involving two cathodic reactions.

The "corrosion current" . . . i_{corr} . . . related to amount of metal corroded by Faraday's Law . . .

$$i_{corr}\, t \;=\; \frac{nFw}{M}$$

n   = number electrons involved in metal dissolution ($\rightarrow$ valency);

F   = Faraday constant (96,500 coulomb/mol);

w   = mass corroded metal;

M   = molecular weight of metal.

<u>Note</u>: there may be more than one cathodic reaction (i.e., more than one "i_c") and more than one anodic reaction (i.e., more than one "i_a" . . . e.g., for alloy);

$$i_{corr} \;=\; \Sigma i_a \;=\; -\Sigma i_c$$

Also: because areas of anodic regions, A_a, are generally different from areas of cathodic regions, A_c, CURRENT DENSITIES are generally not equal . . . thus . . .
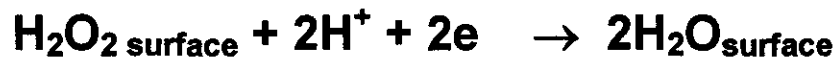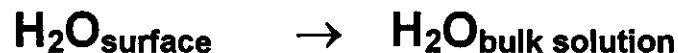
while i_a = $-i_c$

A_a ≠ A_c

so I_a = $\dfrac{i_a}{A_a}$ ≠ $\dfrac{i_c}{A_c}$ = I_c ...

(remember examples of rapid perforation arising from large cathode vs small anode combinations).

Corrosion consists of charge transfer reactions . . . e.g., . . .

anodic $M_{lattice} \rightarrow M^+_{surface} + e \rightarrow M^{n+}_{surface} + (n-1)e$

cathodic $O_{2\ surface} + 2H^+ + e \rightarrow H_2O_{2\ surface}$

              $H_2O_{2\ surface} + 2H^+ + 2e \rightarrow 2H_2O_{surface}$

and mass transport . . . e.g., . . .

anodic $M^{n+}_{surface} \rightarrow M^{n+}_{solution}$

cathodic $O_{2\ solution} \rightarrow O_{2\ surface}$

              $H_2O_{surface} \rightarrow H_2O_{bulk\ solution}$

At equilibrium, $\eta = 0$, $E = E_e$, $i = 0$ **but** $i_a = -i_c = i_o$ (i.e., the forward and backward reactions are equal and the rate corresponds to the **exchange current**, i_o).

The expression relating the OVERPOTENTIAL, η, to the **net** current, i, is the Butler-Volmer equation:

$$i = i_o\{\exp(\beta.\underline{\frac{nF}{RT}}.\eta) - \exp(-[1 - \beta].\underline{\frac{nF}{RT}}.\eta)\}$$

where
- R = gas constant;
- T = absolute temperature;
- n = number of charges transferred (valency);
- F = Faraday constant (96,500 coulomb/mol);
- β = "symmetry coefficient" ($\rightarrow 0.5$).

The first term in { } in B-V describes the forward (metal dissolution, anodic) reaction; the second term in { } describes the backward (metal deposition, cathodic) reaction.

ACTIVATION CONTROL is when the corrosion is controlled by charge transfer reactions . . .

**EITHER the anodic charge transfer OR the cathodic charge transfer can control.**

The anodic reactions and the cathodic reactions in a system can be studied INDIVIDUALLY by electrochemical methods . . . e.g., the changes in potential of an electrode caused by changes in the current flowing through it (or vice versa) can be measured . . . i.e., we can measure the POLARIZATION.

Consider metal dissolution and metal deposition . . .

$$M \quad \overset{\text{anodic}}{\underset{\text{cathodic}}{\rightleftharpoons}} \quad M^{n+} + ne$$
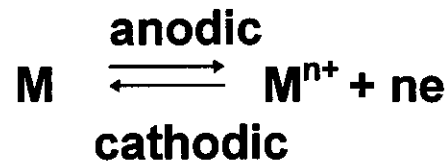
If we "drive" the reaction (with our electrochemical apparatus) in the anodic direction, we can measure the "overpotential" η (the difference between the applied potential, E, required to give a net dissolution of metal and the equilibrium potential, E_e) and the net current, i.

A plot of the B-V equation for the metal dissolution/deposition reaction gives the polarization curve:

Current-potential relationship for a metal dissolution (M → M^{n+})/deposition (M^{n+} → M) process
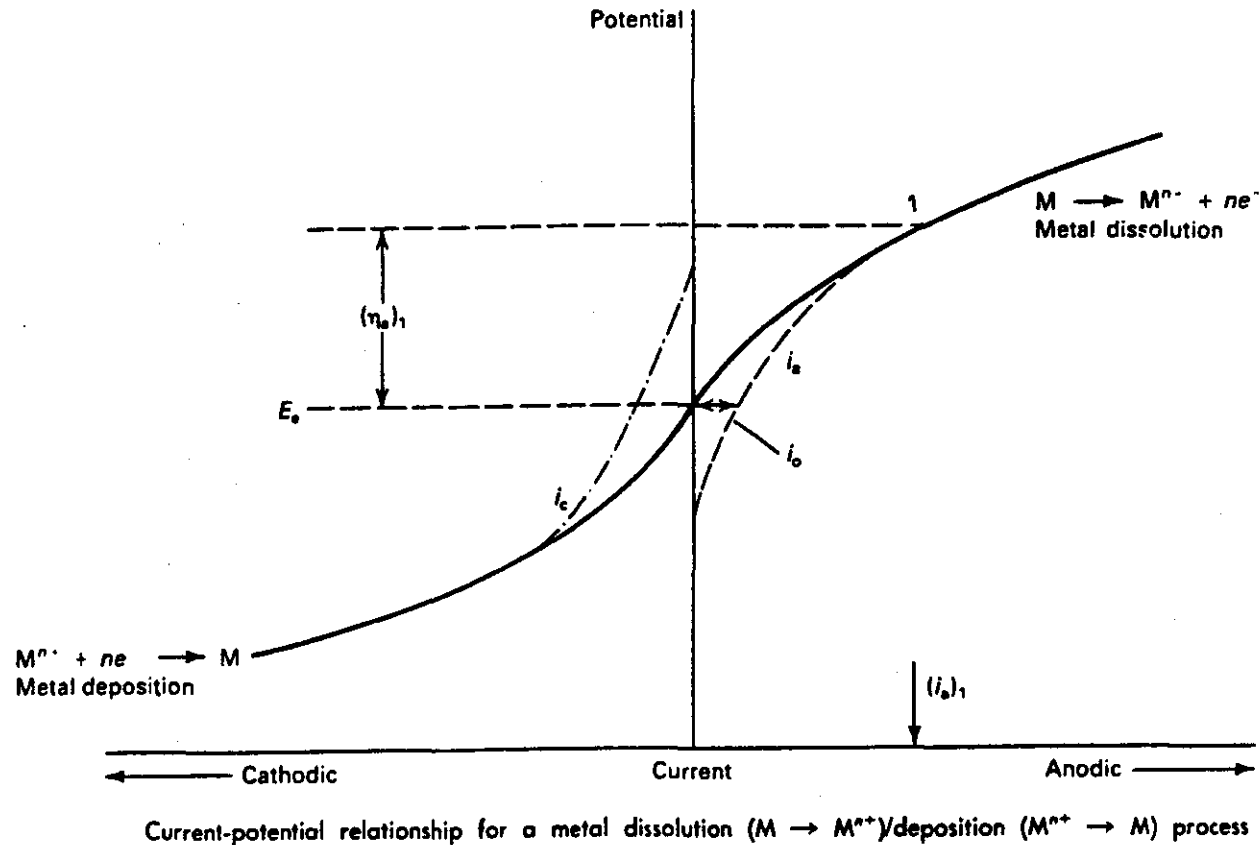
If the symmetry coefficient β = 0.5, the curve is symmetrical about (i=0, E$_e$) and the B-V equation has a sinh form.

Note: At large enough overpotentials, the reaction is essentially all in one direction . . . one of the terms in the B-V-E is negligible and can be dropped.

Thus, for metal **dissolution**:

$$i_a = i_o \exp\left(\beta . \frac{nF}{RT} . \eta_a\right)$$

or

$$\eta_a = b_a \log \frac{i}{i_o}$$
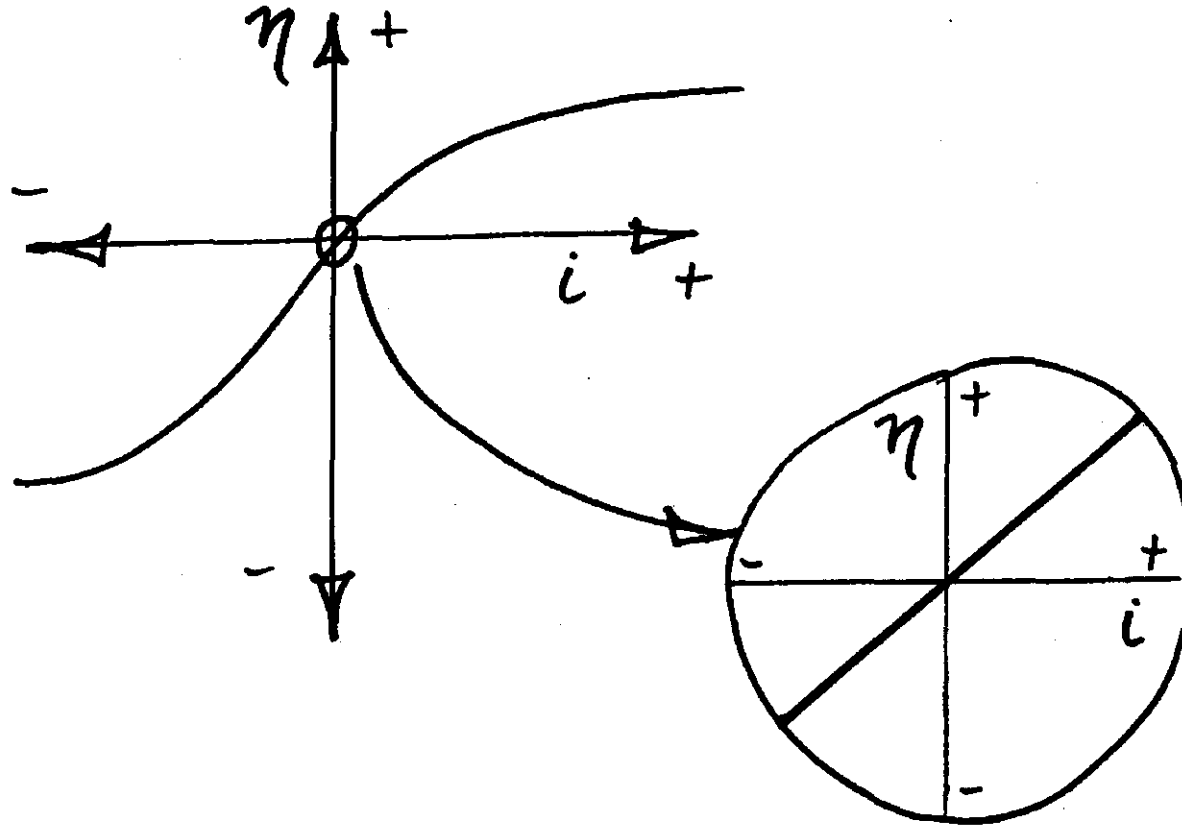
(high overpotential or "high-field" approximation)

where

$$b_a = \frac{2.303RT}{\beta nF}$$

. . . "Tafel coefficient".

The Tafel coefficient for metal **deposition**:
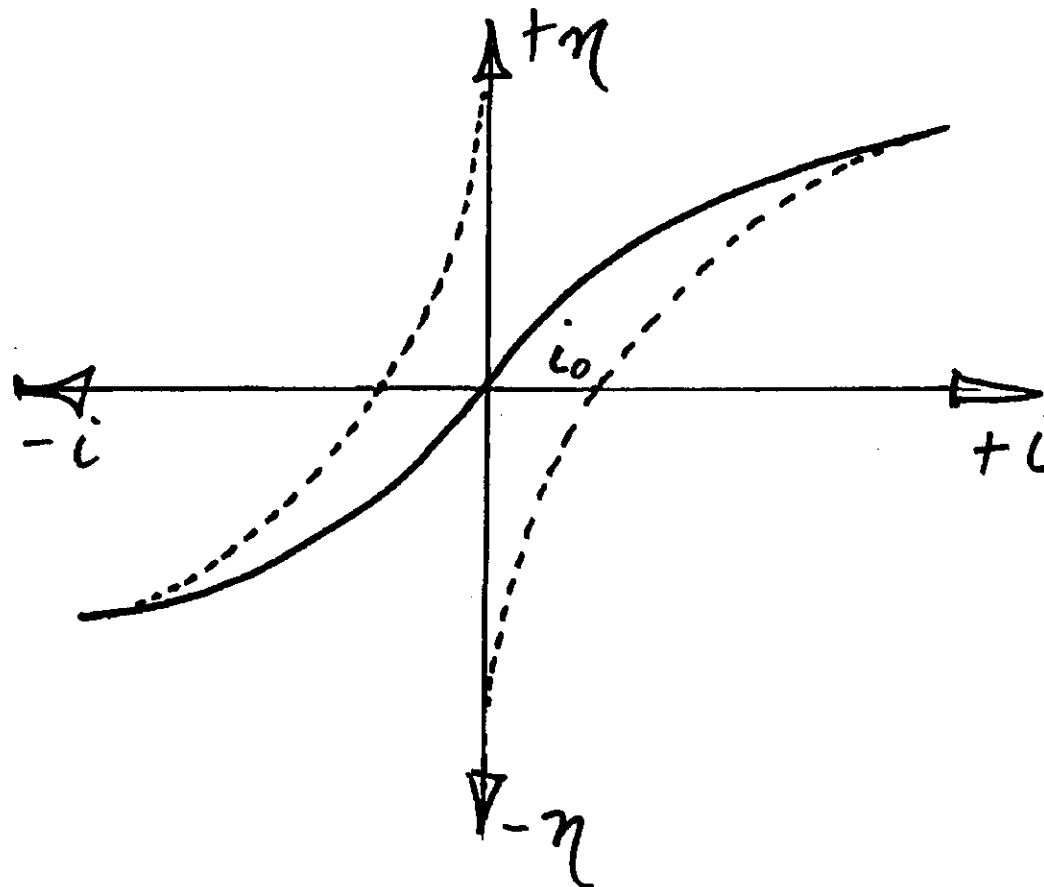
$$b_c = -\frac{2.303RT}{(1 - \beta)nF} .$$

<u>Note Also</u>: In the narrow region of small overpotentials, the relation becomes linear . . .


In the linear region . . .

$$i = i_o \cdot \frac{nF}{RT} \cdot \eta$$

(low-overpotential or "low-field" approximation).

If a reaction has a large exchange current, i_o, the curve is shallow and a large current is obtained for a small overpotential . . .
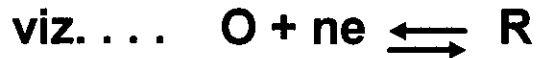

the reaction is not easily polarized (approaching "non-polarizable").

If a reaction has a small exchange current, i_o, the curve is steep and a large overpotential is needed for a small current . . .
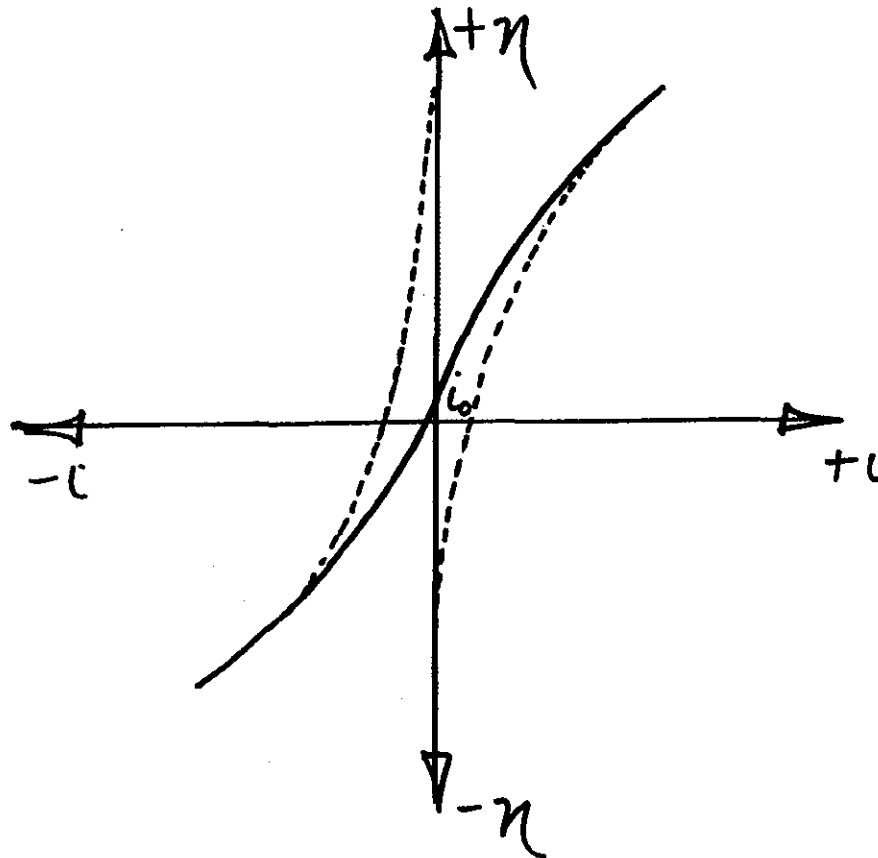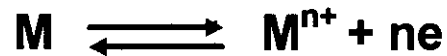

the reaction is readily polarized.

Consider now a reaction that is cathodic to the metal dissolution . . .

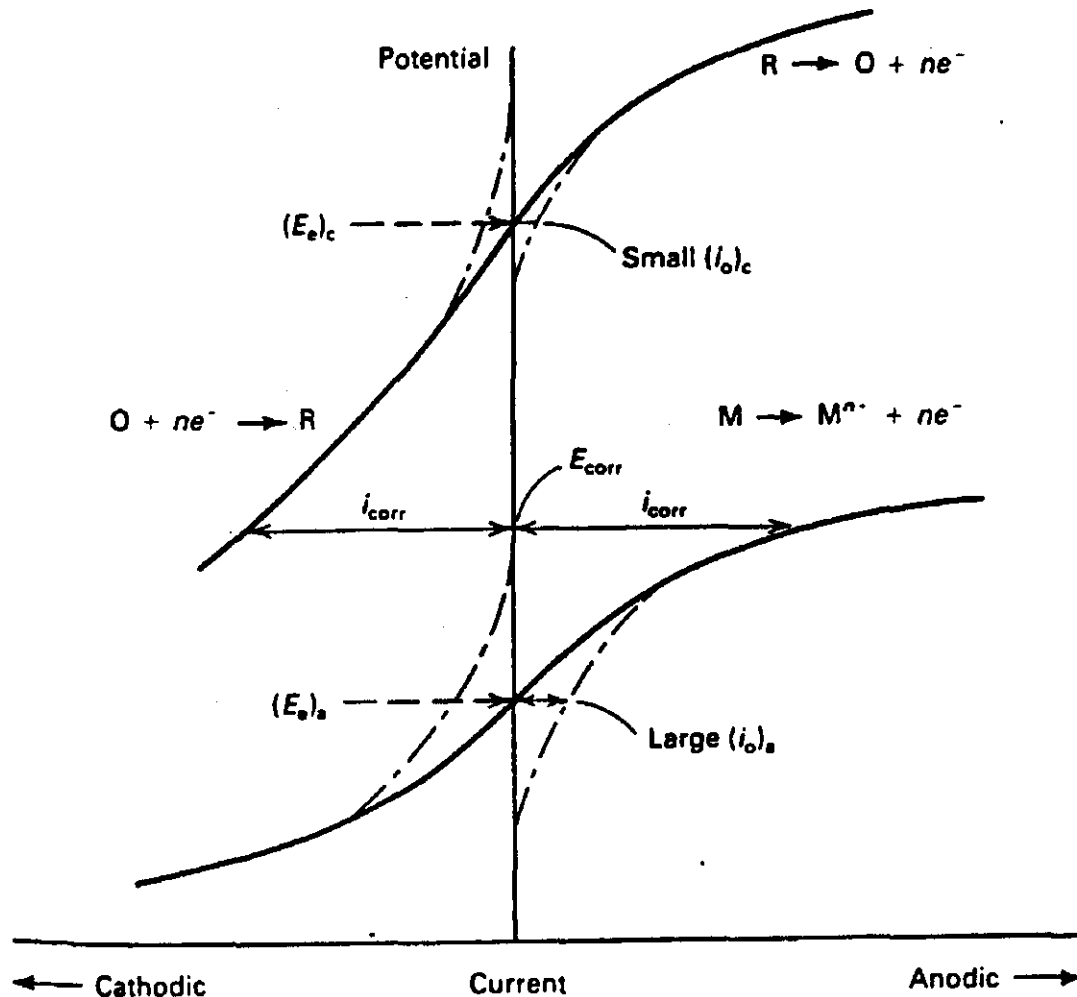viz. . . . $O + ne \rightleftharpoons R$

If this is coupled to metal dissolution in the corrosion process, then the reaction must move away from equilibrium so that a net <u>cathodic</u> current, $-i_c$, flows . . . similarly, the metal dissolution . . .

$$M \rightleftharpoons M^{n+} + ne$$

must move away from equilibrium so that a net anodic current, $-i_a$, flows.

We know that . . . $i_a = -i_c$ $(= i_{corr})$.

We plot the cathodic reaction on the same diagram as the anodic reaction . . . à La Butler-Volmer . . .

Potential

$R \longrightarrow O + ne^-$

$(E_e)_c$ ---- Small $(i_o)_c$

$O + ne^- \longrightarrow R$

$M \longrightarrow M^{n \cdot} + ne^-$

E_{corr}

i_{corr} i_{corr}

$(E_e)_a$ ---- Large $(i_o)_a$

Note: $i_a = -i_c$ ($= i_{corr}$) at one spot on the diagram - the "corrosion potential", E_{corr}.

← Cathodic   Current   Anodic →

Current-potential relationship for a metal dissolution/deposition and an accompanying redox showing how the two reactions couple together at the corrosion potential, E_{corr}.

E_{corr} is the mixed potential . . .

$$(E_e)_a < E_{corr} < (E_e)_c$$

Metal dissolution is driven by the ANODIC ACTIVATION OVERPOTENTIAL:

$$\eta_a^A = E_{corr} - (E_e)_a$$

**and the cathodic reaction is driven by the CATHODIC ACTIVATION OVERPOTENTIAL:**

$$\eta_c^A = (E_e)_a - E_{corr}$$

<u>**Note**</u>: the thermodynamic driving force for corrosion, ΔE_{therm} . . .

$$\Delta E_{therm} = (E_e)_c - (E_e)_a .$$

Usually, ΔE_{therm} is large enough to put E_{corr} in the Tafel regions for both reactions (i.e., the reverse reactions are negligible) - unless oxide films interfere.

The coupled portions of the curves for the anodic and cathodic reactions (i.e., i_a + ve, i_c + re) are usually plotted as potential vs. logarithm of the current, with the -ve sign of the cathodic current neglected . . .
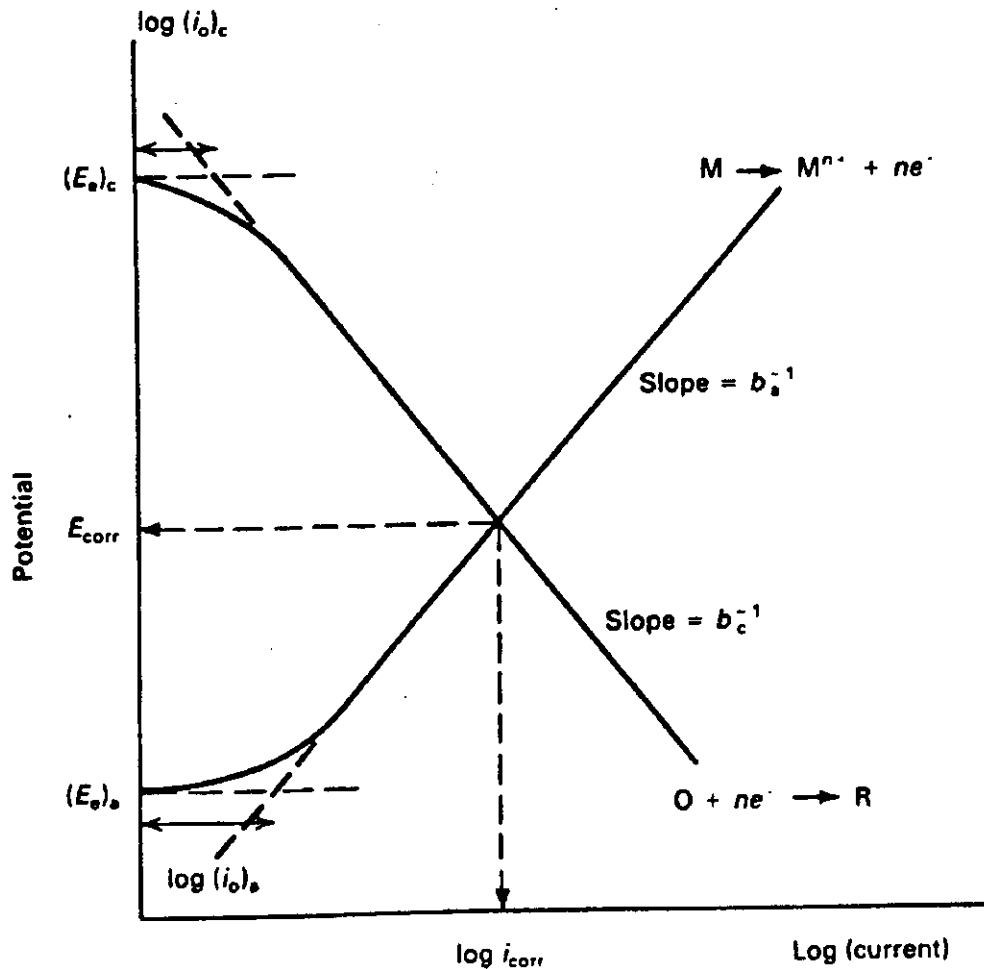
Both curves appear in the +ve quadrant. This is the "EVANS DIAGRAM".

Evans diagram for the corrosion process
M + O $\longrightarrow$ M^{n+} + R

The straight-line portions of the curves are the TAFEL REGIONS, with Tafel slopes indicated earlier.

The exchange currents $(i_o)_a$ and $(i_o)_c$, can be obtained by extrapolating the Tafel lines back to the equilibrium potentials $(E_e)_a$ and $(E_e)_c$ . . .

<u>N.B.</u> don't forget that the origin (i=0) cannot be shown on a logarithmic plot.

The intersection of the two curves in the Evans diagram occurs at the corrosion current, i_{corr}.

<u>N.B.</u> the bigger the difference in equilibrium potentials (i.e., the bigger the value of ΔE_{therm}), the bigger the value of i_{corr} (i.e., the greater the corrosion).

Two possible cathodic reactions
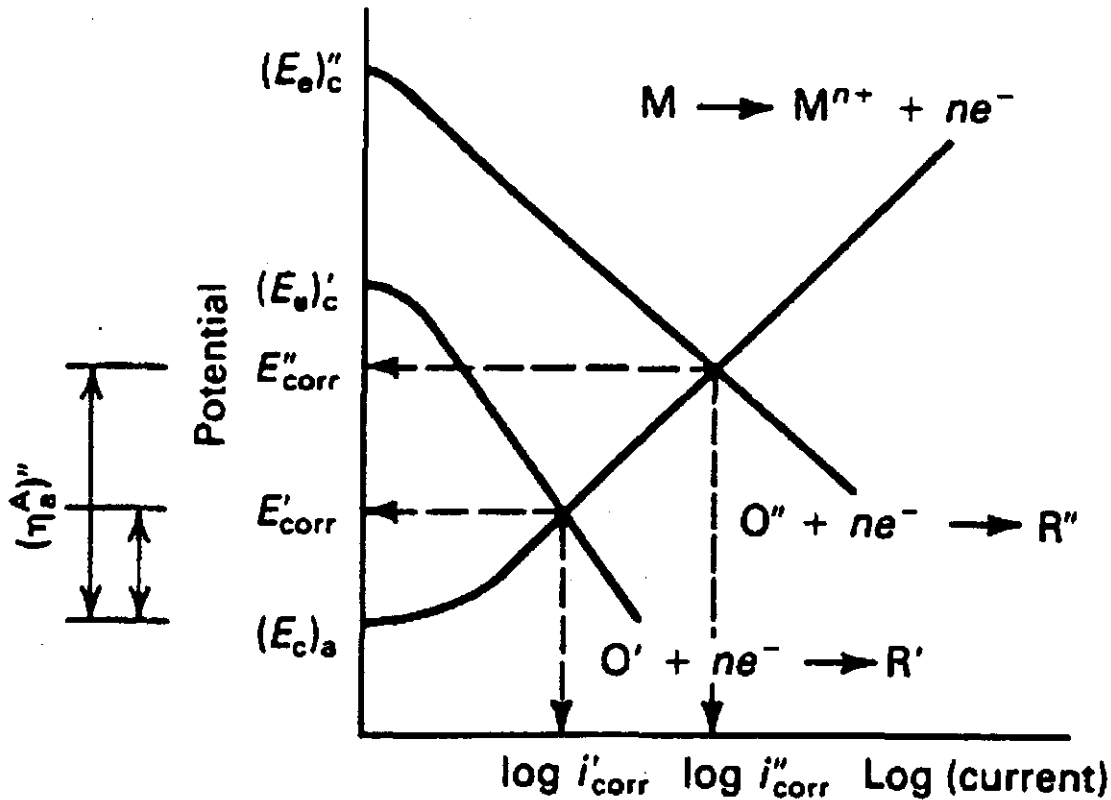
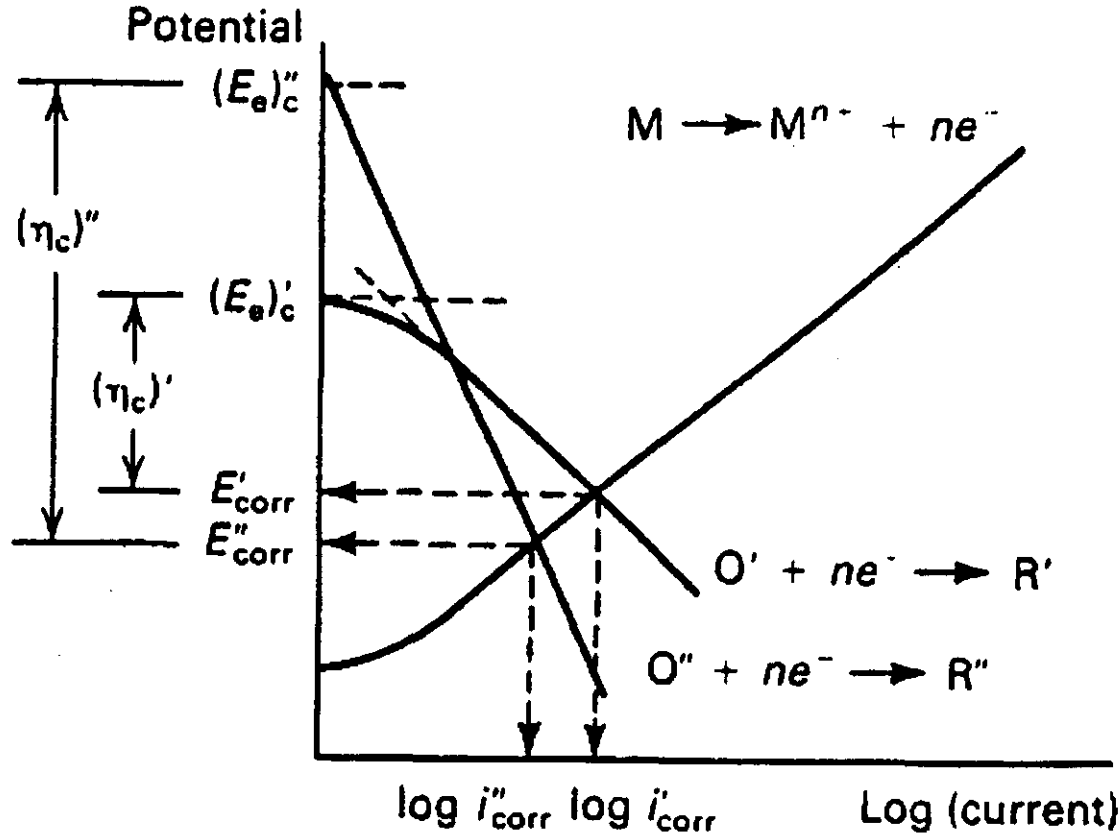**NOTE:**

$$\Delta E'_{therm} \ (= (E_e')_c - (E_e)_a)$$
$$< \Delta E''_{therm} \ (= (E_e'')_c - (E_e)_a)$$
$$\text{so} \qquad i'_{corr} < i''_{corr}.$$

Also: anodic activation overpotential for reaction'
$(E'_{corr} - (E_e)_a) <$ for reaction"
$(\eta_a^A)' < (\eta_a^A)''$.

Evans diagram for a metal dissolution coupled separately to two cathodic reactions with distinctly different equilibrium potentials, $(E_e)_c''$ and $(E_e)_c'$.

Two possible cathodic reactions - different kinetic factors.

Even though $(E_e)''_c > (E_e)'_c$, activation overpotential $(\eta_a^A)'' < (\eta_a^A)'$, so that $i''_{corr} < i'_{corr}$ ...i.e., the corrosion couple with the smaller thermodynamic driving force $(\Delta E'_{therm})$ produces the larger corrosion current . . .
"Kinetics are controlling".

Evans diagram for a metal dissolution coupled separately to two cathodic reactions, in which the impact of relative kinetics is greater than the thermodynamic driving force, ΔE_{therm}.

This situation often occurs for a metal corroding in acid, compared with corroding in dissolved oxygen . . . though the thermodynamic driving force is greater in oxygen (remember, Pourbaix Diagram for Ni), acid corrosion is faster.

Arises from kinetic factors . . .

$$(I_o)_{H^+/H_2} = 10^{-3} - 10^{-2} \text{ A/m}^2$$

and $(b_c)_{H^+/H_2} \approx 120$ mV/decade (. . . depending on metal surface)

<u>while</u> . . .

$$(I_o)_{O_2/H_2O} \approx 10^{-10} \text{ A/m}^2$$

and $(b_c)_{O_2/H_2O} = 120$ mV/decade (. . . depending on metal surface).

Corrosion Rate Controlled by Anodic or Cathodic Reactions

Overall corrosion rate controlled by SLOWEST reaction . . . i.e., reaction with smallest exchange current, i_o, and/or largest Tafel coefficient, b.

(Remember, small i_o means that curve close to vertical axis, large b also means curve close to axis - with steep slope).

Differences in steepness of curves means that activation overpotentials are different . . . and polarizations are different (steep curve → strongly polarized).
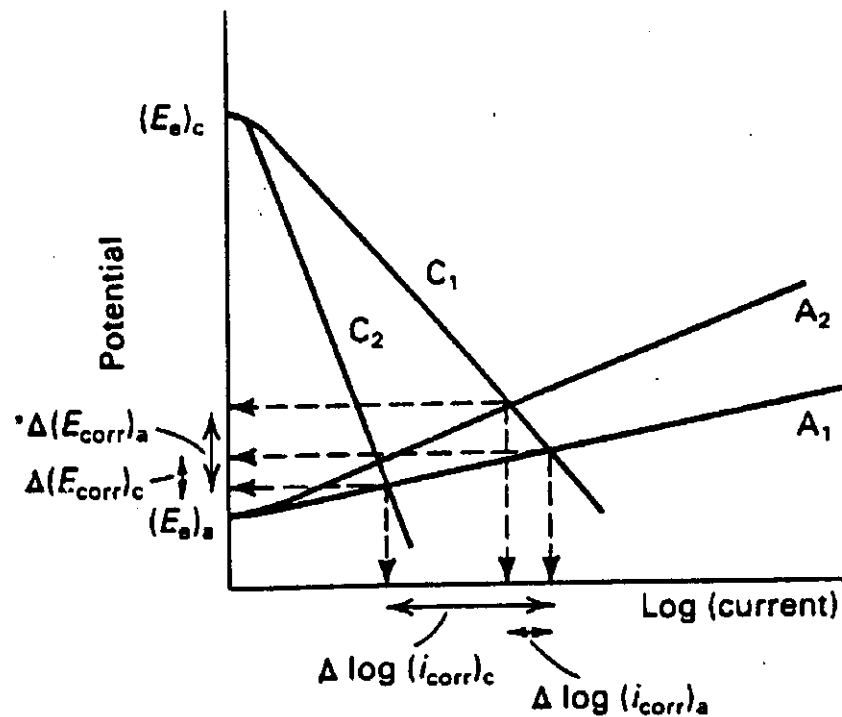
Evans diagram showing the impact on the corrosion current, i_{corr}, and potential, E_{corr}, of varying the kinetics of a fast metal dissolution (A_1, A_2) or a slow cathodic process (C_1, C_2).

Cathode reaction in diagram strongly polarized . . . controls corrosion . . . small changes in kinetics of cathode have <u>large</u> effect on corrosion rate, small changes in kinetics of anode have <u>small</u> effect on corrosion rate.

Mass Transfer Control (not to be confused with EROSION-CORROSION in which film formation is involved).

 If the cathode reagent at the corrosion site (e.g., dissolved O_2 in the O_2 reduction reaction) is in short supply, mass transfer of the reagent can become rate limiting.

Then, the cathodic charge-transfer reaction is fast enough to reduce the concentration of the reagent at the surface corrosion site to a value less than that in the bulk solution.
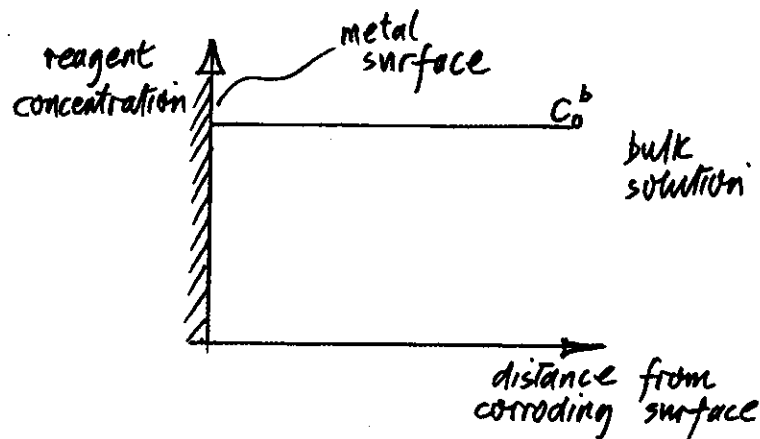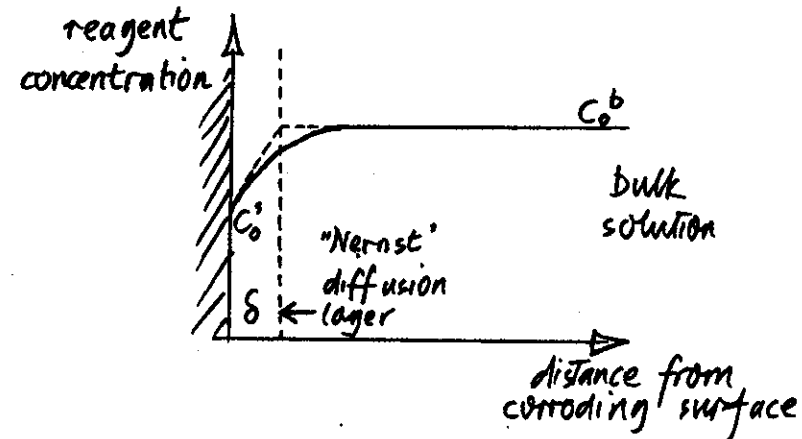
ACTIVATION CONTROL   **MASS TRANSFER CONTROL**

From the simple "Nernst Diffusion Layer" model . . . flux of cathodic reagent to surface, J, given by ...

$$J = -\frac{D(C_o{}^s - C_o{}^b)}{\delta}$$
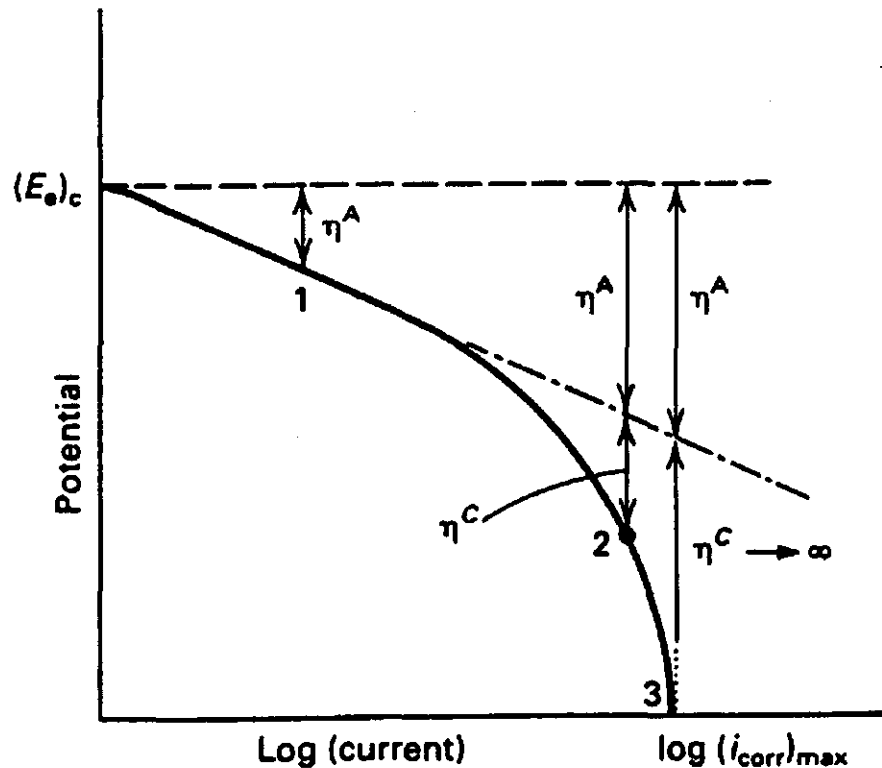
so that, at steady state,

$$\frac{i_c}{nF} = -\frac{D(C_o{}^s - C_o{}^b)}{\delta}$$

* In the limit, $C_o{}^s \to 0$

$$(i_c)_{lim} = \frac{nFDC_o{}^b}{\delta} = (i_{corr})_{max} \,.$$

When corrosion rate is at this limit, it can only be changed by altering the bulk concentration, $C_o{}^b$, and/or the diffusion layer thickness, δ, (by flow, etc.).

Such "CONCENTRATION POLARIZATION" is shown on the Evans diagram (partial):

Polarization curve for the cathodic process showing activation polarization (point 1), joint activation-concentration polarization (point 2), and transport-limited corrosion control (point 3).

Point 1: Small shift from equilibrium potential . . . no limitation on reagent supply - activation control.

Point 2: Control: activation + concentration . . . overpotential $\eta_{total} = \eta^A + \eta^C$

Point 3: Large shift from equilibrium: - reaction rate maximum, η^c **infinite.**

Effect of increasing mass transport rate (e.g., by stirring the solution surrounding a corroding surface) . ..

$(E_e)_c$

Potential

$M \longrightarrow M^{n+} + ne^-$
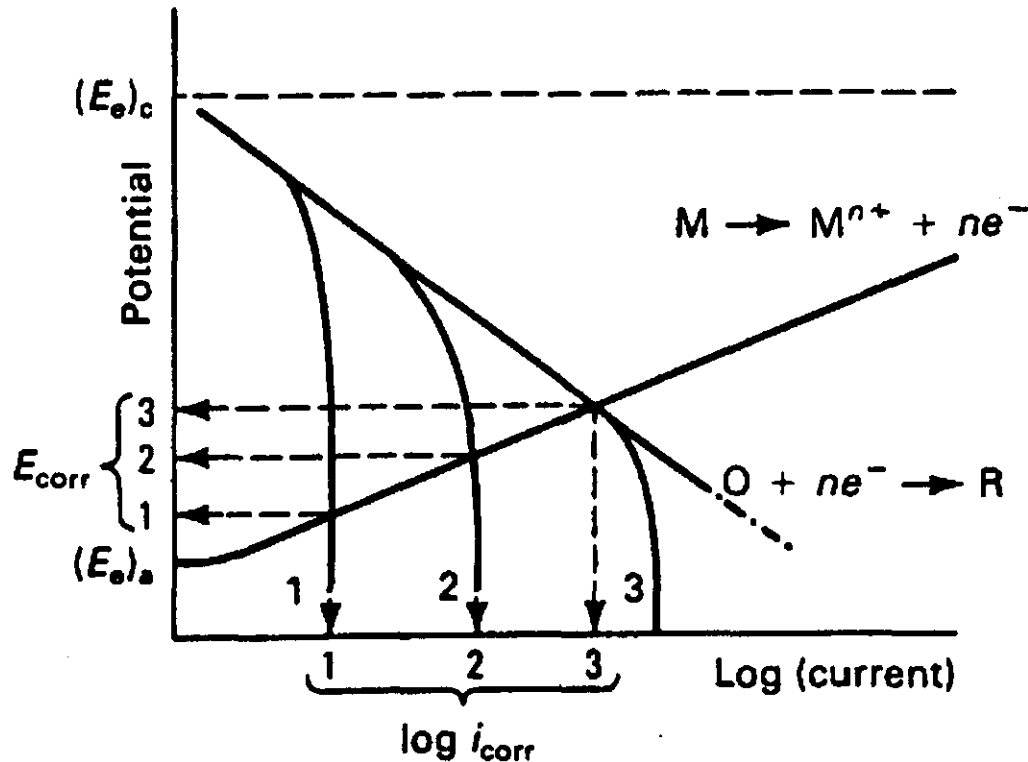
Evans diagram for a corrosion process initially controlled by the transport of cathodic reagent to the corroding surface (line 1). Lines 2 and 3 show the effect of increasing the transport rate of reagent.

E_{corr}
3
2
1

$(E_e)_a$

1   2   3

$O + ne^- \longrightarrow R$

1   2   3   Log (current)

log i_{corr}

Increase in corrosion potential, E_{corr}, caused by decrease in cathodic overpotential as concentration polarization decreased.

If anodic reaction were mass-transfer controlled (difficulty of metal ions diffusing away), improved stirring would DECREASE E_{corr} .

| DISCUSS |

Electrochemical methods for studying corrosion (e.g., evaluating the performance of a metal specimen in a test solution) often involve the construction of POTENTIAL vs CURRENT curves . . . i.e., they involve the study of polarization characteristics.

Polarization Measurements
The simple potentiostat for applying a fixed potential (relative to a reference electrode) and measuring the current (flowing from the "working" electrode to the "counter" or "auxiliary" electrode):
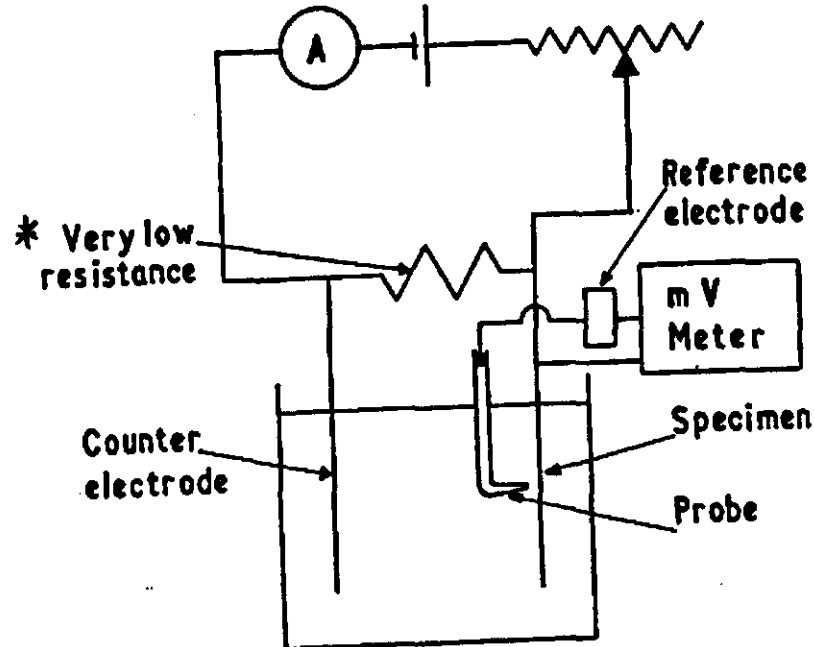
A typical arrangement of a classical potentiostat.

* ensures specimen potential (w.r.t. counter) constant . . . even though solution resistance might alter.

REMEMBER : We can only measure the <u>net</u> current across the specimen electrode - at the corrosion potential there is no net current (only local anode-cathode currents which constitute the corrosion current). WE CANNOT MEASURE CORROSION RATE DIRECTLY . . .although i_{corr} is what we need!

Tafel Method

Measure potential and current at some distance on either side of E_{corr} and extrapolate E - log i curves (in same quadrant) back to E_{corr} . . .
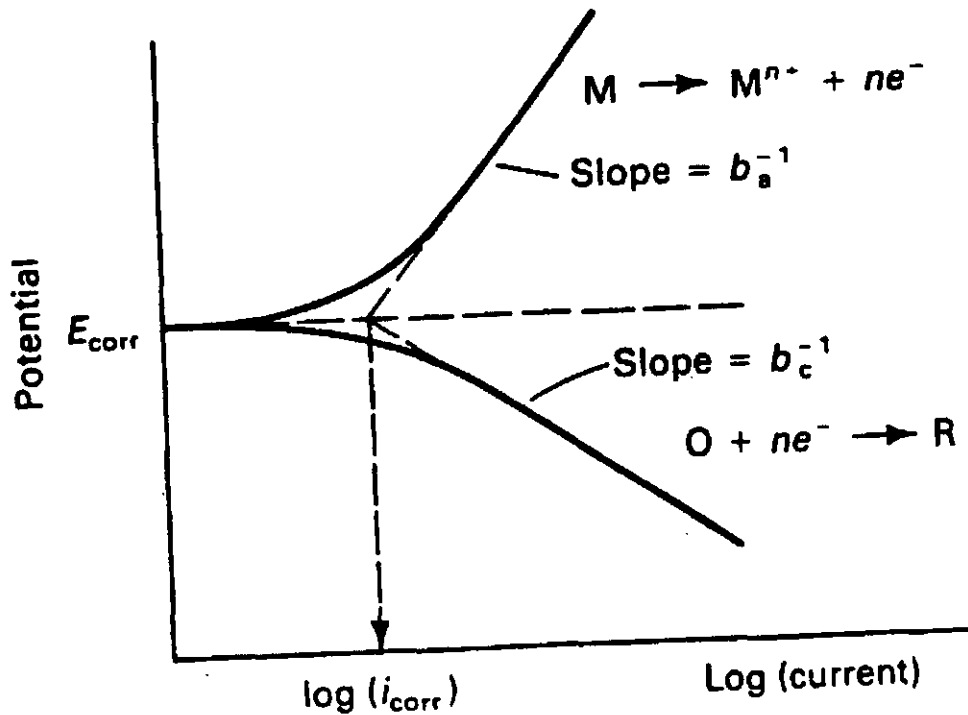
Plot of the total current ($i_T = i_o + i_c$) versus potential showing the extrapolation of the Tafel regions to the corrosion potential, E_{corr}, to yield the corrosion current, i_{corr}.

N.B.   If we know . . . (for the anodic or cathodic reaction)

- the exchange current, $(i_o)_a$, say;

- the equilibrium potential, $(E_e)_a$;

- the Tafel coefficient, b_a,

then from one measurement (of the corrosion potential, E_{corr}) we can calculate the corrosion rate . . .
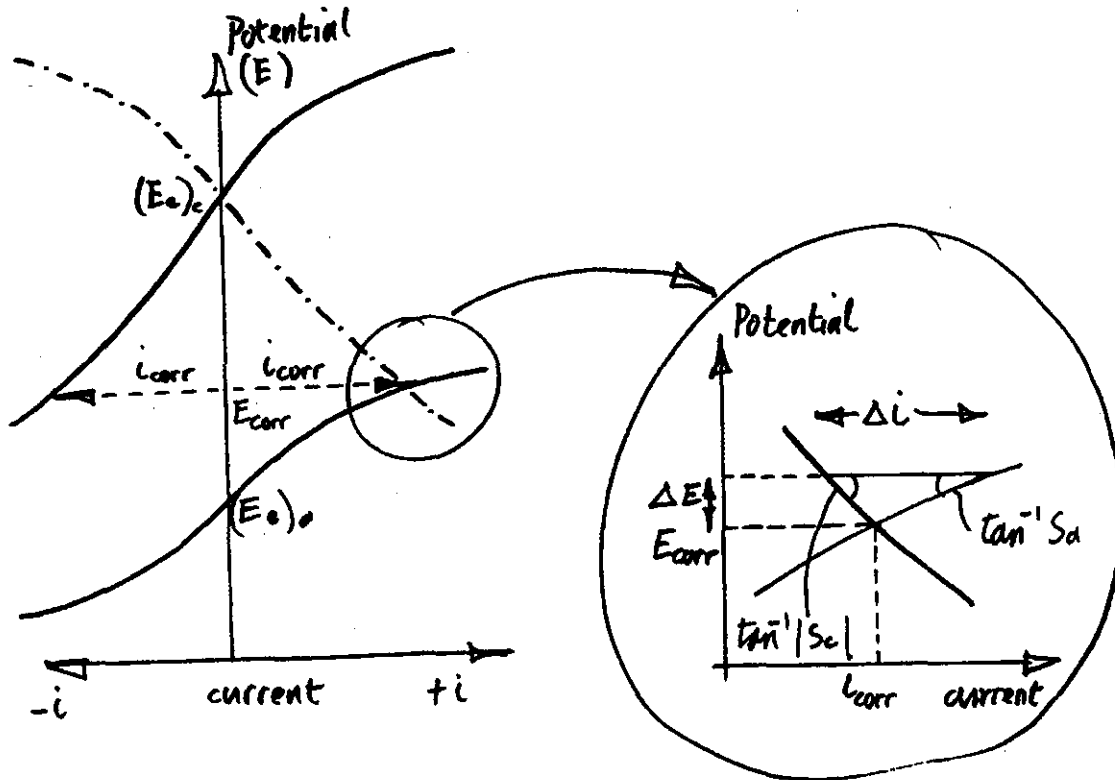
$$i_{corr} = i_o \exp\left\{\frac{2.303(E_{corr} - (E_e)_a)}{b_a}\right\}$$

We don't usually know these, though.

Linear Polarization Method

Valid for corrosion under activation control.

Involves applying small perturbations to the potential around E_{corr} (i.e., $\pm\Delta E \leq 10$ mV).

Over small ΔE ($\leq$ 20mV) the curves are approximately linear with slopes:

$$S_a = \frac{dE}{di} = \frac{b_a}{2.303\ i_{corr}}$$

and $$|S_c| = \frac{dE}{di} = \frac{b_c}{2.303\ i_{corr}}$$

and from the linear geometry ...

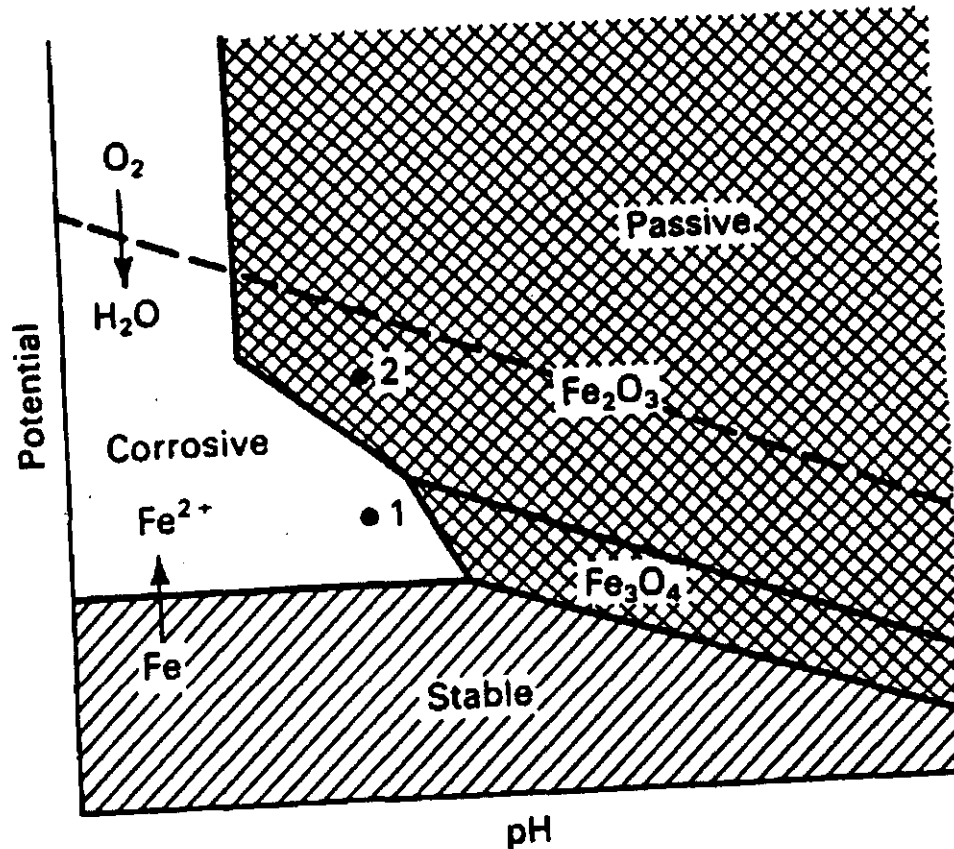$$\frac{\Delta i}{\Delta E} = \frac{S_a - |S_c|}{S_a|S_c|}$$

which gives . . .

$$i_{corr} = \frac{1}{2..303} \cdot \frac{b_a|b_c|}{b_a + |b_c|} \cdot \frac{\Delta i}{\Delta E}$$

The "polarization resistance", $\Delta i/\Delta E$, is measured: the Tafel coefficients b_a and b_c must be known.
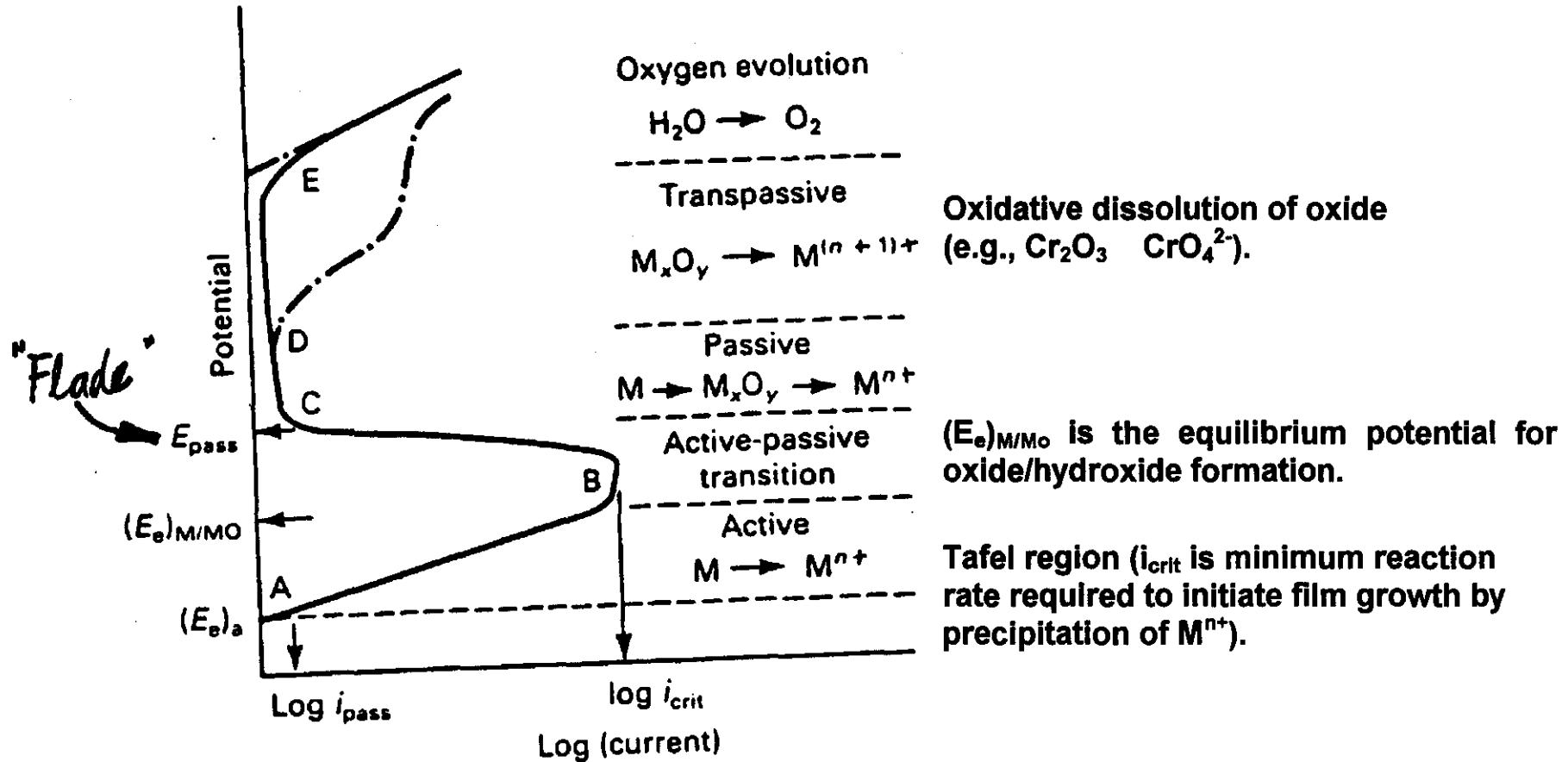
Passivation

Under certain conditions of potential and pH, some metals form protective films . . . i.e., they "passivate":
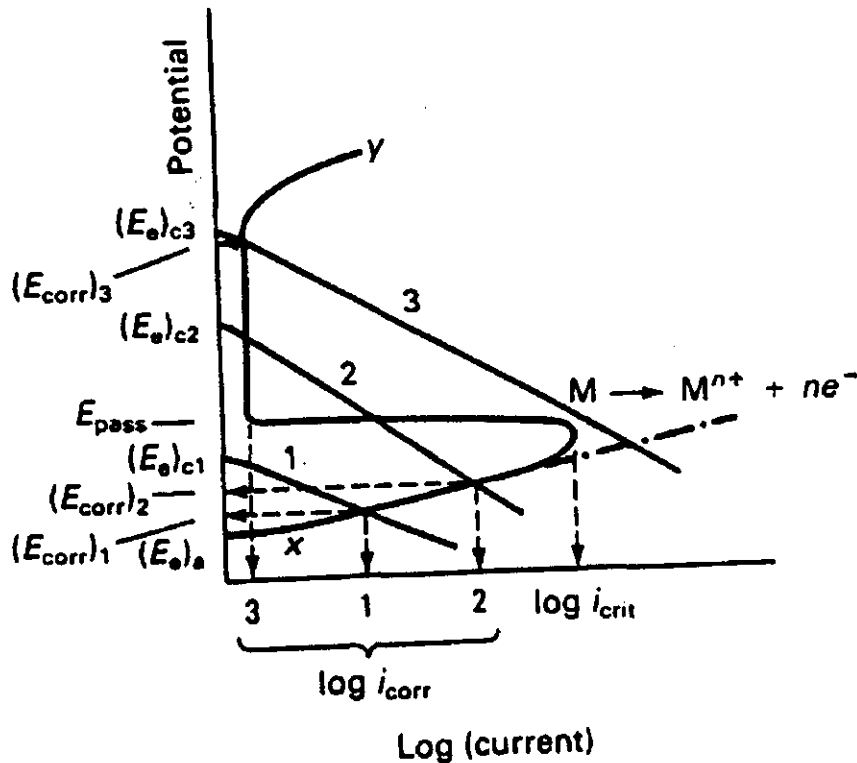
Pourbaix diagram for the iron/water/dissolved oxygen system showing the effect of potential in moving the system from a corrosive (active) region (point 1) to a passive region (point 2).

We can examine the KINETICS via an Evans diagram . . .

The polarization curve for the ANODIC reaction of a passivating metal drawn for potentials more noble than the equilibrium potential $(E_e)_a$ . . .

Oxygen evolution

$$H_2O \longrightarrow O_2$$

Transpassive

$$M_xO_y \longrightarrow M^{(n+1)+}$$

Passive

$$M \longrightarrow M_xO_y \longrightarrow M^{n+}$$

Active-passive transition

Active

$$M \longrightarrow M^{n+}$$

"Flade"

E_{pass}

$(E_e)_{M/MO}$

$(E_e)_a$

Potential

Log i_{pass}

log i_{crit}

Log (current)

Oxidative dissolution of oxide (e.g., Cr_2O_3 CrO_4^{2-}).

$(E_e)_{M/MO}$ is the equilibrium potential for oxide/hydroxide formation.

Tafel region (i_{crit} is minimum reaction rate required to initiate film growth by precipitation of M^{n+}).

The region attained by the metal in a given environment depends upon the cathodic reaction . . . i.e., where the cathodic curve "cuts" the above anodic curve.

Impact of various cathodic reactions on the corrosion current and potential for a metal capable of undergoing an active-passive transition.

Cathodic Reaction 1: $(E_e)_{c1} < E_{pass}$, so $(E_{corr})_1$ must also $< E_{pass}$ . . . corrodes actively.
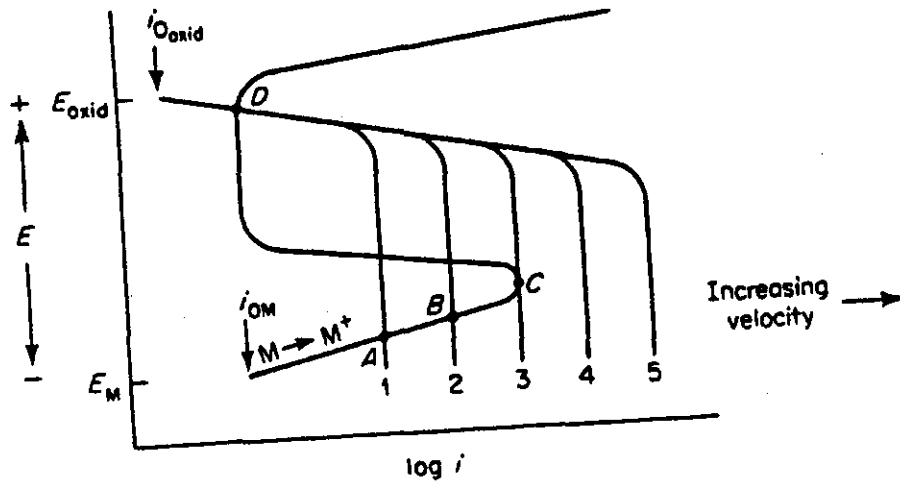
Cathodic Reaction 2: $(E_e)_{c2} > E_{pass}$; HOWEVER, curve intersects Tafel line for anodic reaction BELOW i_{crit} . . . passive film cannot form, corrodes actively.

Cathodic Reaction 3: both passivating condition are met $((E_e)_{c3} > E_{pass}$; $i_{initial}$ (intersecting Tafel line) $> i_{crit})$ . . . passivates.

Other Corrosion Examples on Evans Diagrams (from Fontana)

Velocity Effects

Effect of velocity on the electrochemical behaviour of an active-passive metal corroding under diffusion control.
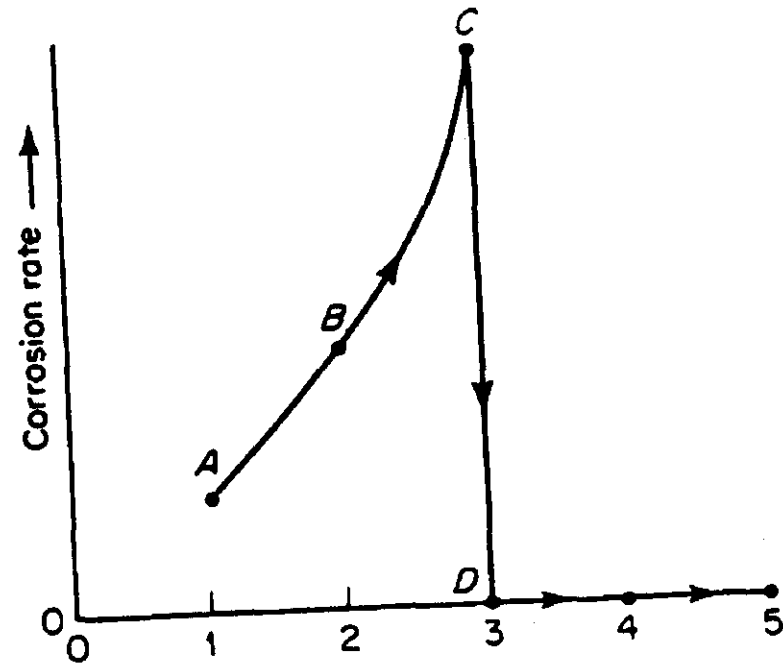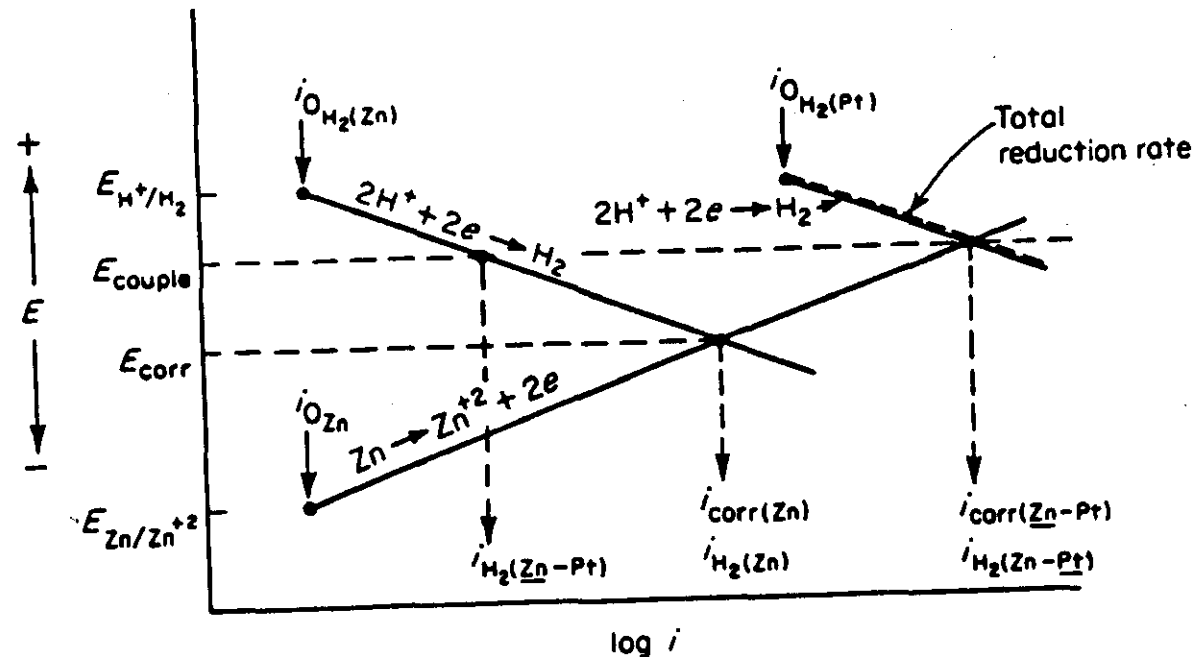
Effect of velocity on the corrosion rate of an active-passive metal corroding under diffusion control.

Galvanic Effects

Isolated zinc corrodes in acid . . .

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

$$2H^+ + 2e \rightarrow H_2$$

Platinum is inert in acid, BUT, when coupled . . . zinc corrosion increases,

H2 evolution occurs on platinum . . .

NOTE:
the <u>thermodynamic</u> driving force remains the same
($\Delta E_{therm} = (E_e)_{H^+/H_2} - (E_e)_{Zn/Zn^{2+}}$)
but the kinetics change - EXCHANGE CURRENTS on Zn and Pt are different: Potential increases, H_2 evolution on Zn decreases, total reaction increases.

Effect of galvanically coupling zinc to platinum (equal areas).
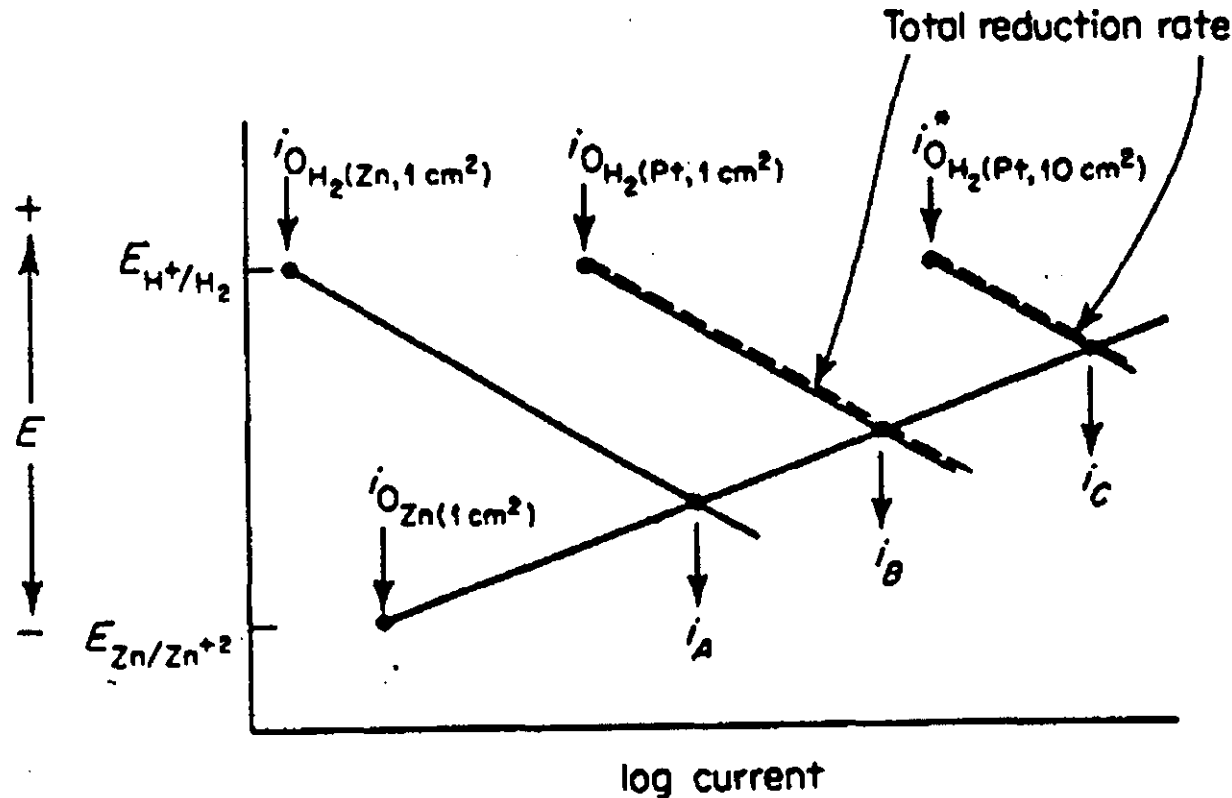
Effect of H⁺/H₂ Exchange Current

The more efficient the hydrogen evolution process (i.e., the higher the exchange current), the larger the effect of galvanic coupling . . .
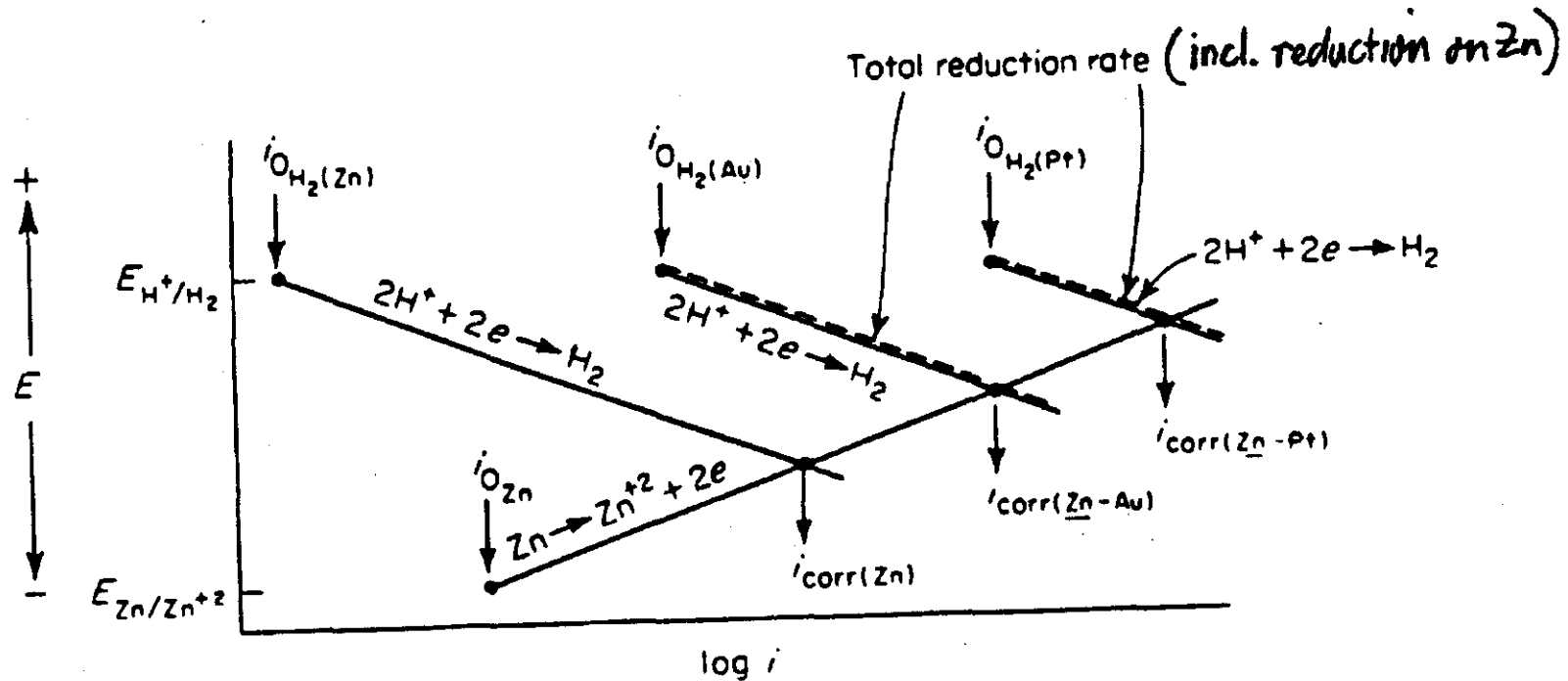
Comparison of zinc-platinum and zinc-gold galvanic couples (equal areas).

Pt is a very efficient cathode.

Effect of Cathode Surface Area

Effect of cathode-anode area ratio on galvanic corrosion of zinc-platinum couples.

Increasing cathode area increases corrosion; (remember, corrosion [mixed] potential determined by point where total oxidation rate equals total reduction rate . . . rates of individual processes determined by mixed potential).
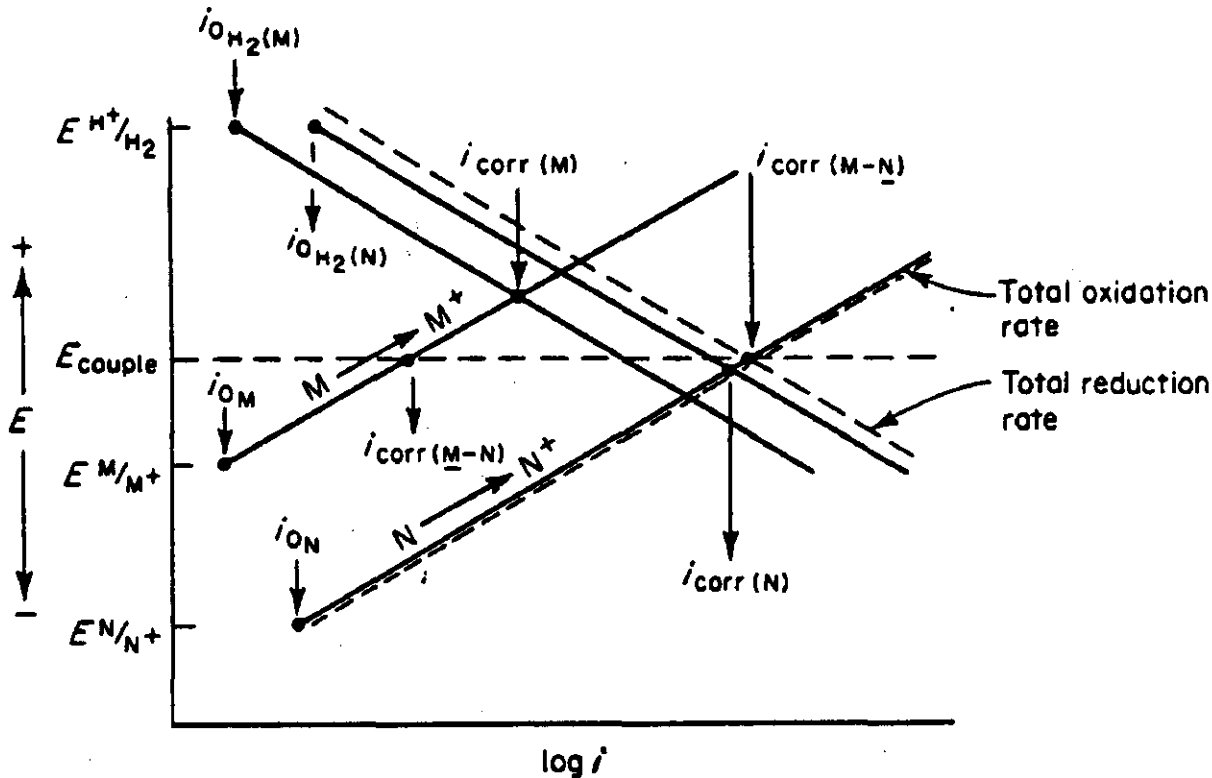
Galvanic couple between two corroding metals.

- more active metal corrodes faster when coupled, more noble metal corrodes slower;

- more active metal becomes anode, more noble becomes cathode;

N.B. actual rates depend on Tafel slopes, exchange currents, etc., . . . without detailed information we only predict trends.
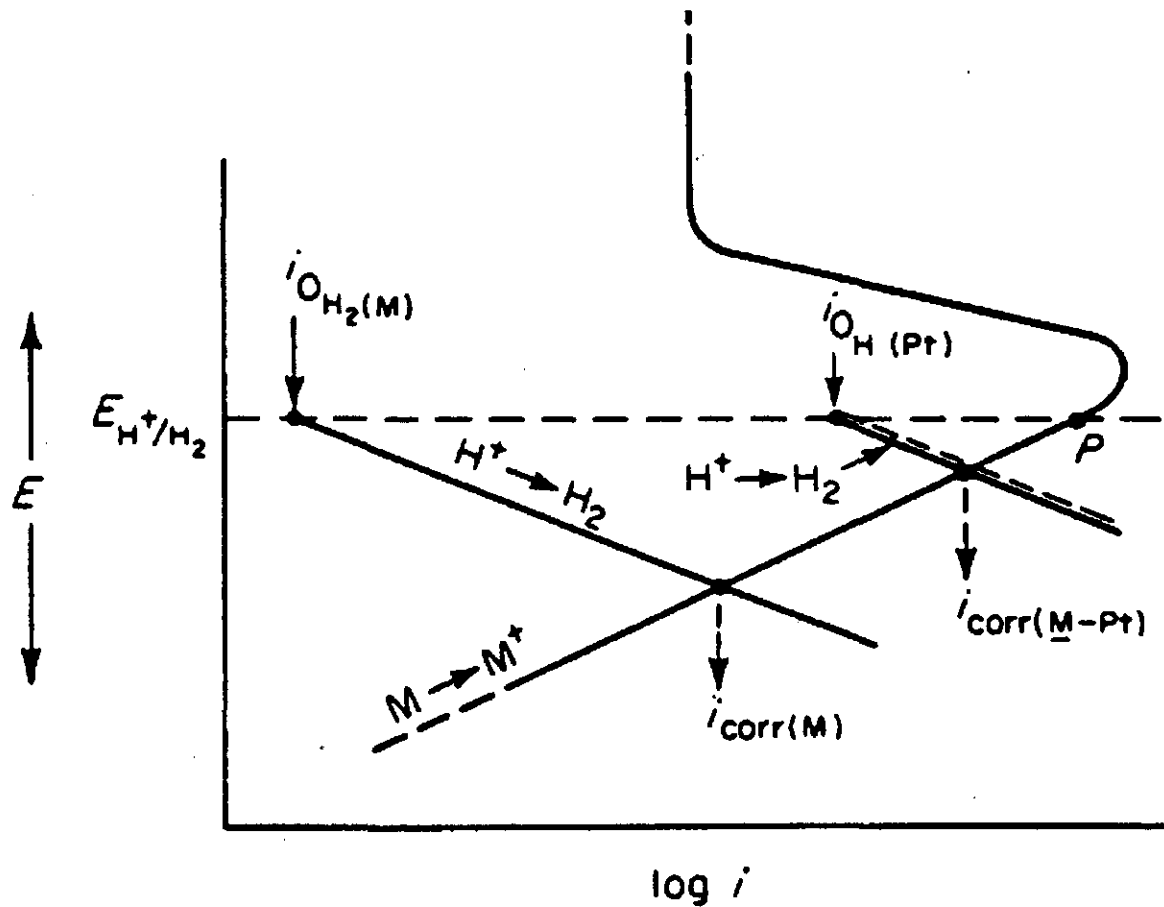
Effects on Passivating Metals
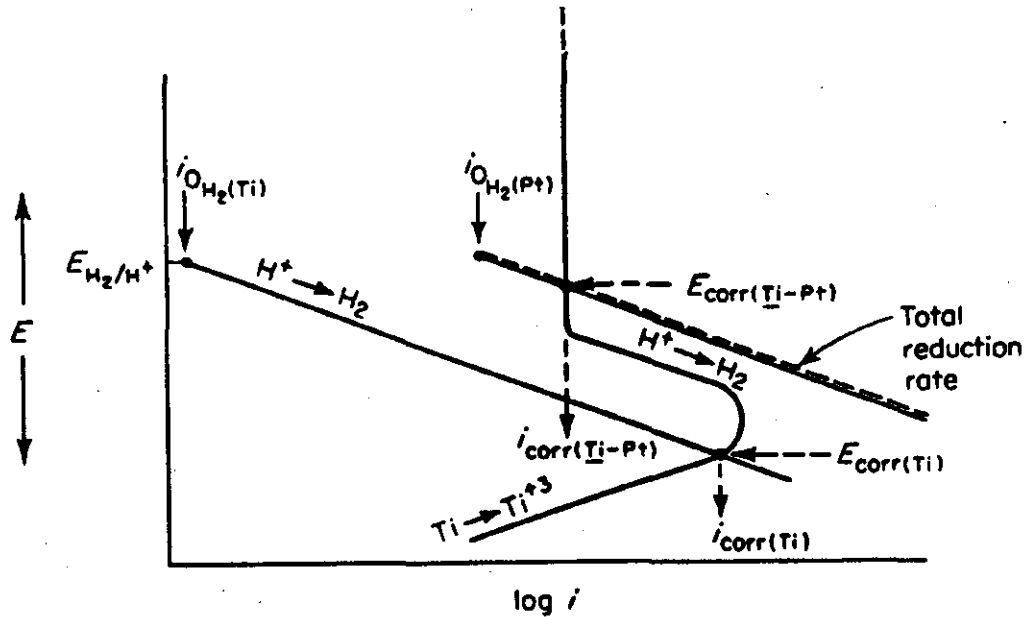
Spontaneous passivation of titanium by galvanically coupling to platinum.

Only works if passivating potential (i.e., Flade potential) less than E_{H_2/H^+}.

NOTE: Raises the possibility of ANODIC PROTECTION.

Galvanic couple between an active-passive metal and platinum in air-free acid solution.

Passivating potential too noble for couple to passivate metal.

If very large Pt cathode coupled, corrosion can be increased to P.