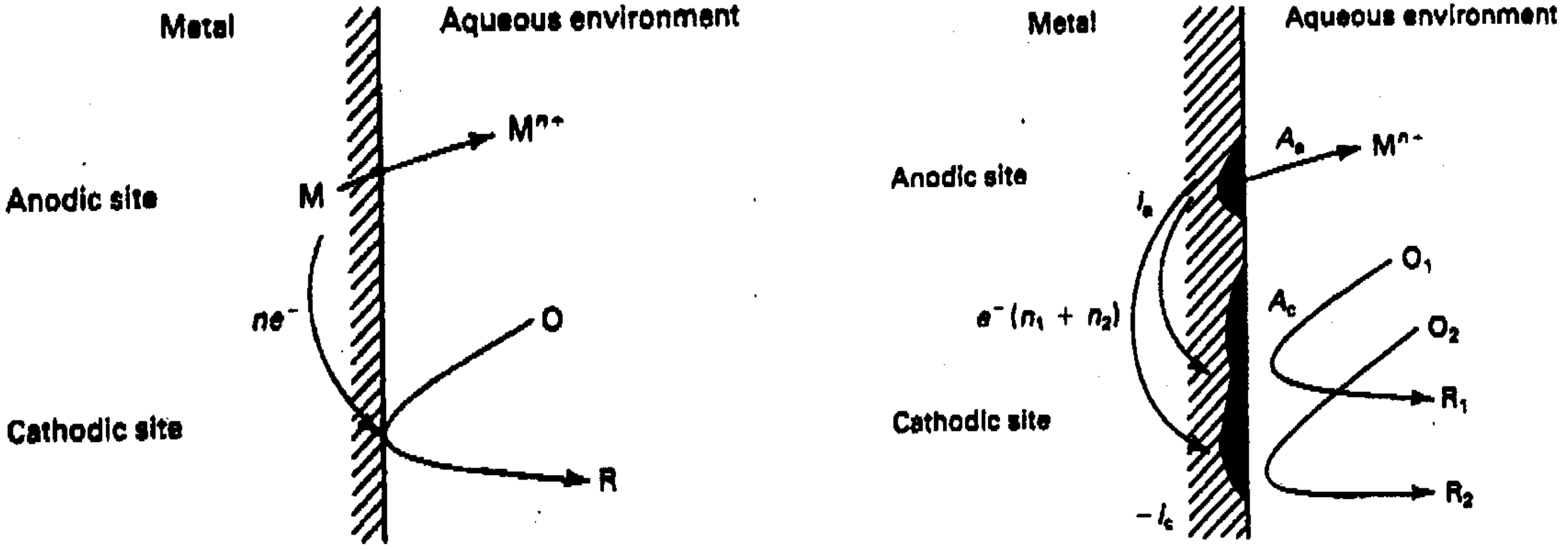
# KINETICS OF AQUEOUS CORROSION

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



(a) (b)

Schematics of two distinct corrosion processes.

(a) The corrosion process $M + O \longrightarrow M^{n+} + R$ 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 (→ valency);**
**F = Faraday constant (96,500 coulomb/mol);**
**w = mass corroded metal;**
**M = molecular weight of metal.**

**Note: 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);**

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

**<u>Also</u>: because areas of anodic regions, $A_a$, are generally different from areas of cathodic regions, $A_c$, CURRENT DENSITIES are generally not equal . . . thus . . .**

$$\text{while} \quad i_a = -i_c$$

$$A_a \neq A_c$$

$$\text{so} \quad I_a = \frac{i_a}{A_a} \neq \frac{i_c}{A_c} = I_c \ \ldots$$

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

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

**<u>anodic</u>** $M_{lattice} \rightarrow M^{+}_{surface} + e \rightarrow M^{n+}_{surface} + (n-1)e$

**<u>cathodic</u>** $O_{2\,surface} + 2H^{+} + e \rightarrow H_2O_{2\,surface}$

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

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

**<u>anodic</u>** $M^{n+}_{surface} \rightarrow M^{n+}_{solution}$

**<u>cathodic</u>** $O_{2\,solution} \rightarrow O_{2\,surface}$

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

**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, $\eta$, to the net current, i, is the Butler-Volmer equation:**

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

**where**

$R$ = gas constant;
$T$ = absolute temperature;
$n$ = number of charges transferred (valency);
$F$ = Faraday constant (96,500 coulomb/mol);
$\beta$ = "symmetry coefficient" (→ 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.**

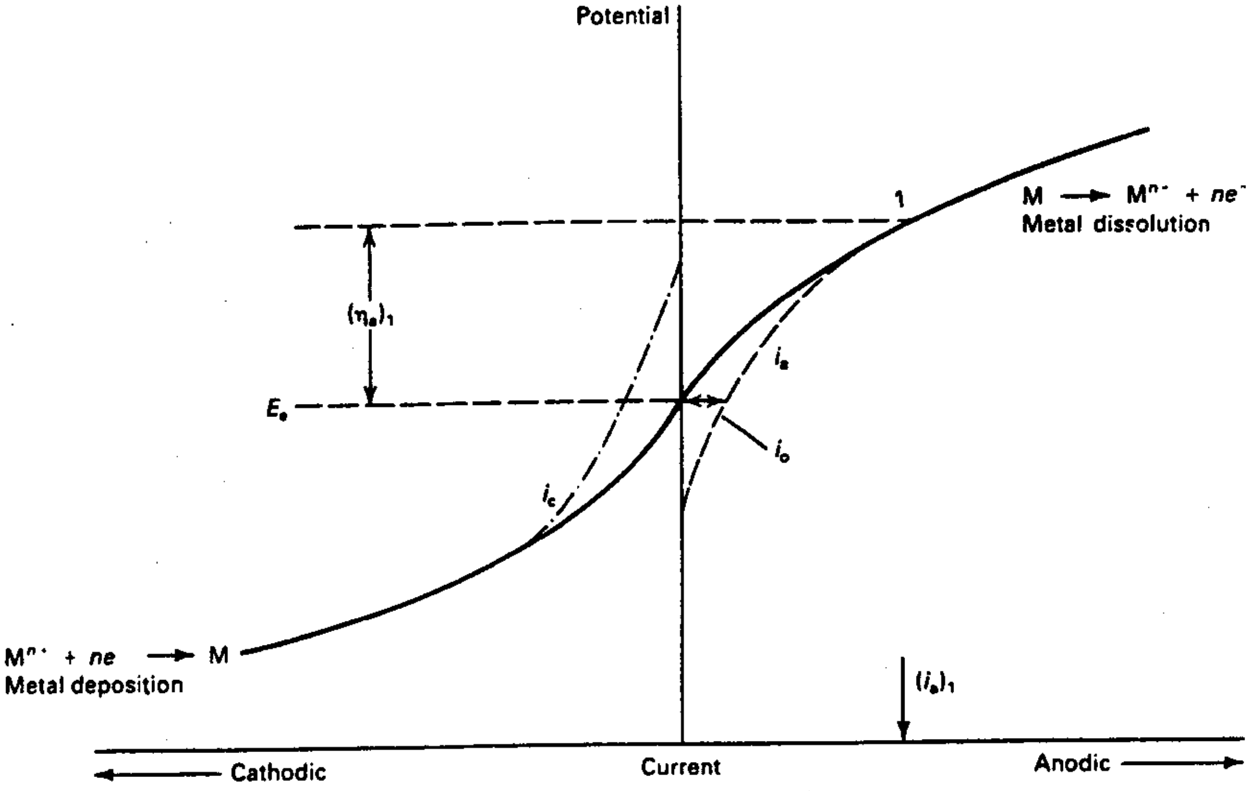
**The anodic reactions and the cathodic reactions in a system can be studied INDIVIDUALLY by electrochemical methods . . . e.g., the changes in potential of an electrode caused by changes in the current flowing through it (or vice versa) can be measured . . . i.e., we can measure the POLARIZATION.**

**Consider metal dissolution and metal deposition . . .**

$$M \underset{\text{cathodic}}{\overset{\text{anodic}}{\rightleftharpoons}} M^{n+} + ne$$

**If we "drive" the reaction (with our electrochemical apparatus) in the anodic direction, we can measure the "overpotential" $\eta$ (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 ($M \rightarrow M^{n+}$)/deposition ($M^{n+} \rightarrow M$) process

**If the symmetry coefficient $\beta = 0.5$, 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:**

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

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

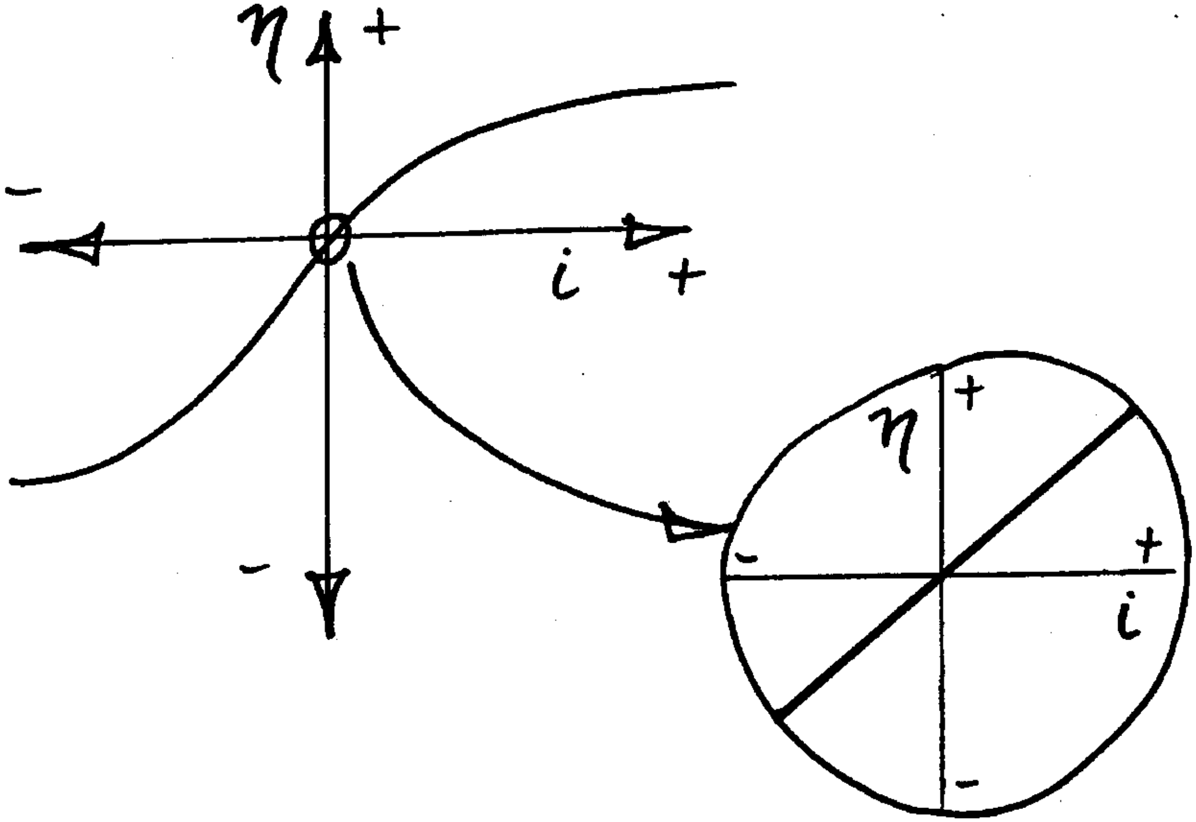
**where**

$$b_a = \frac{2.303RT}{\beta nF}$$ **. . . "Tafel coefficient".**

**The Tafel coefficient for metal deposition:**

$$b_c = -\frac{2.303RT}{(1-\beta)nF} \quad .$$

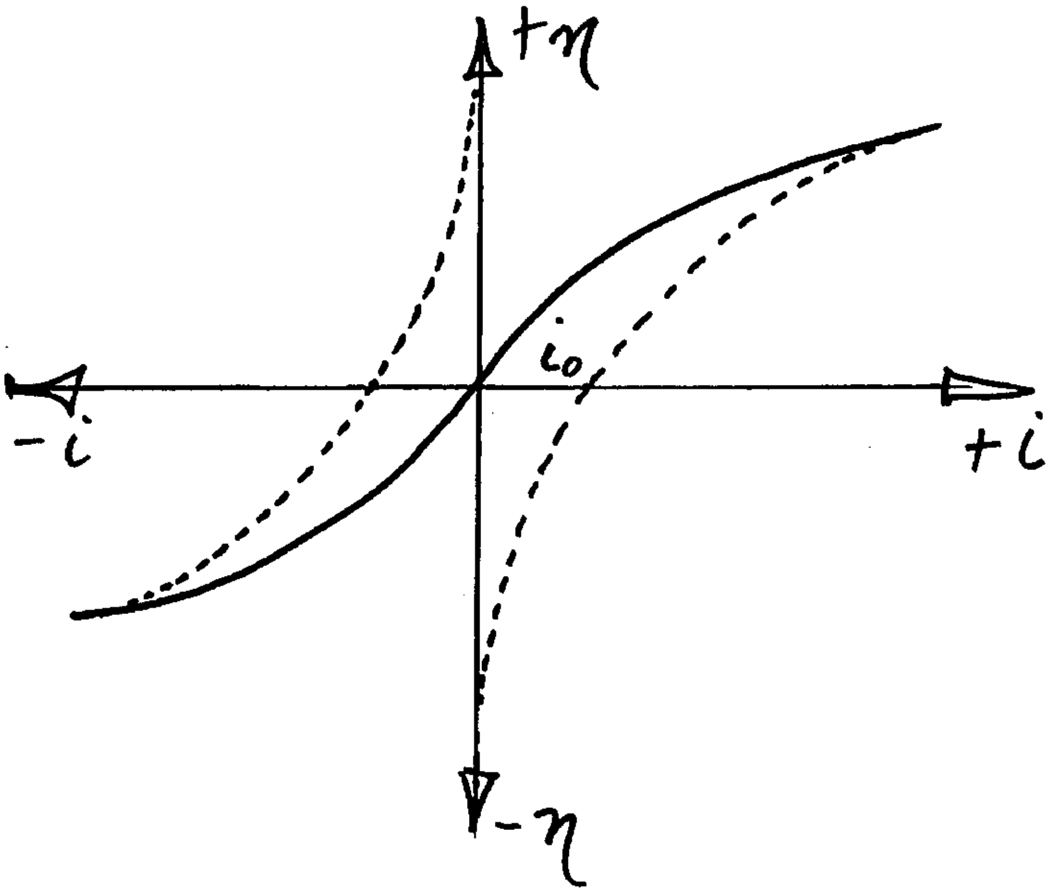
**Note Also**: In the narrow region of small overpotentials, the relation becomes linear . . .



In the linear region . . .

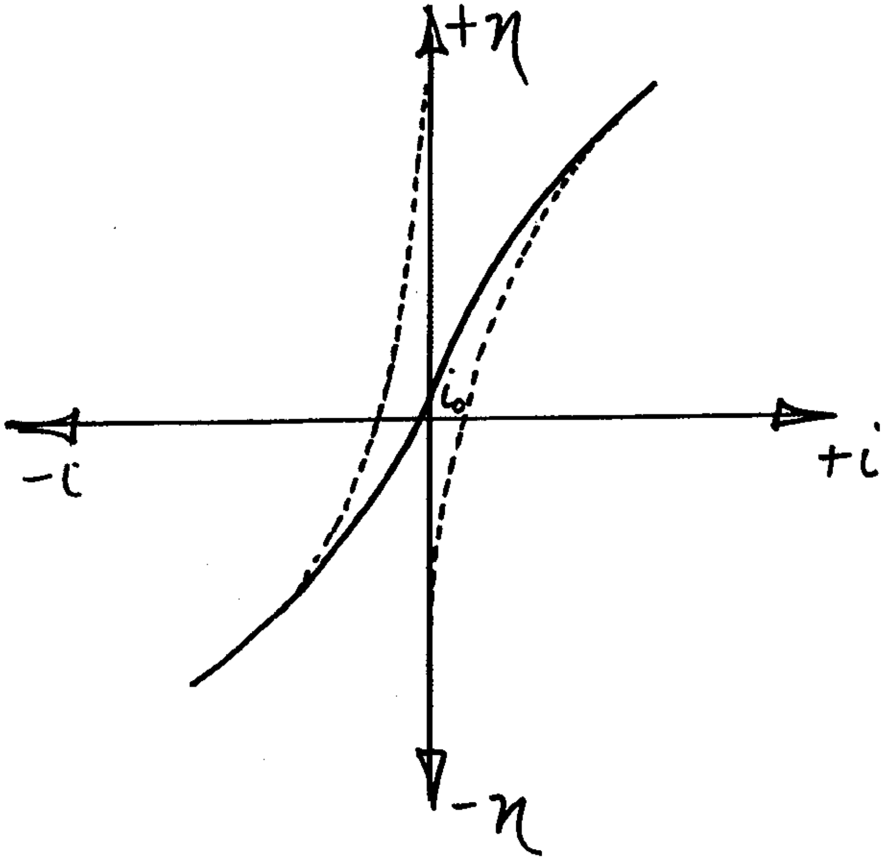
$$i = i_o . \frac{nF}{RT} . \eta$$ (low-overpotential or "low-field" approximation).

**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. . . . $O + ne \leftrightarrows R$

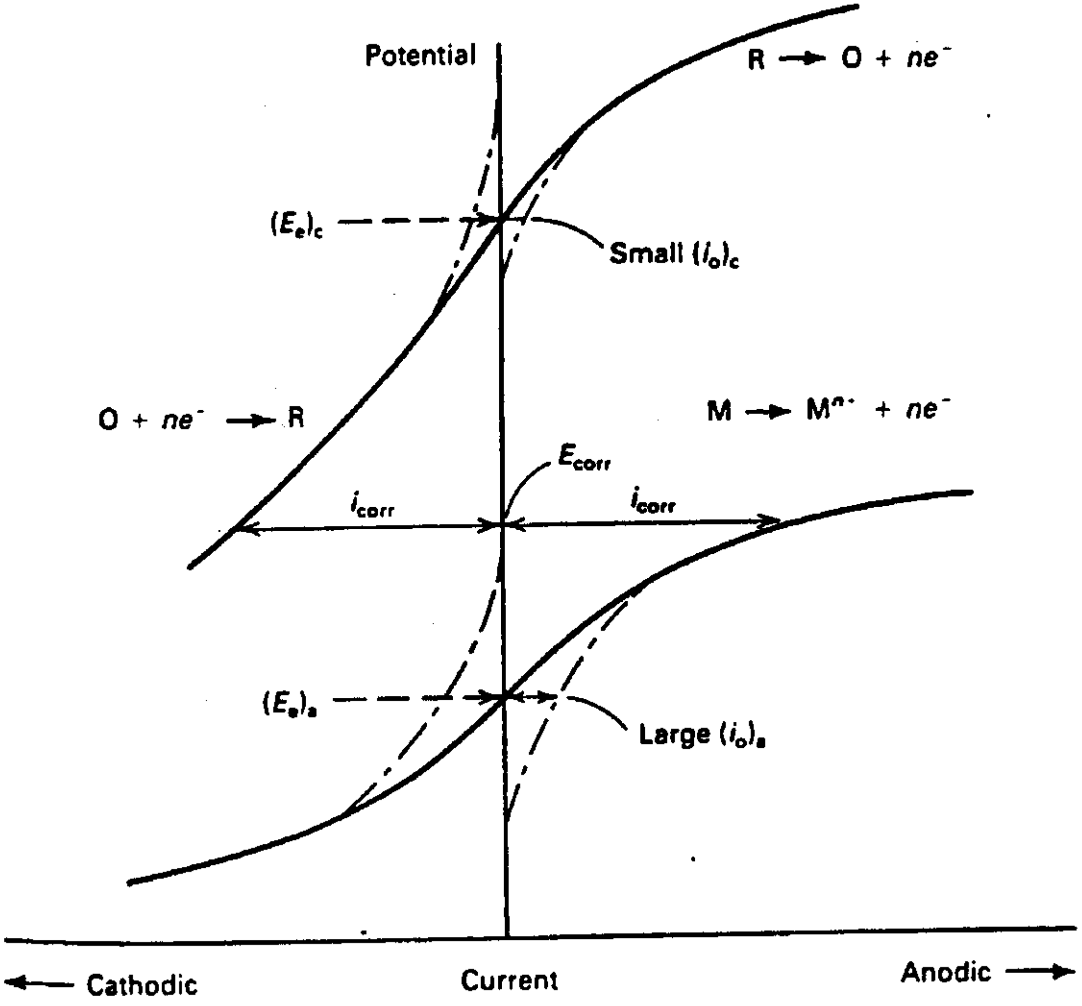
If this is coupled to metal dissolution in the corrosion process, then the reaction must move away from equilibrium so that a net cathodic current, $-i_c$, flows . . . similarly, the metal dissolution . . .

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

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 . . .



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

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:

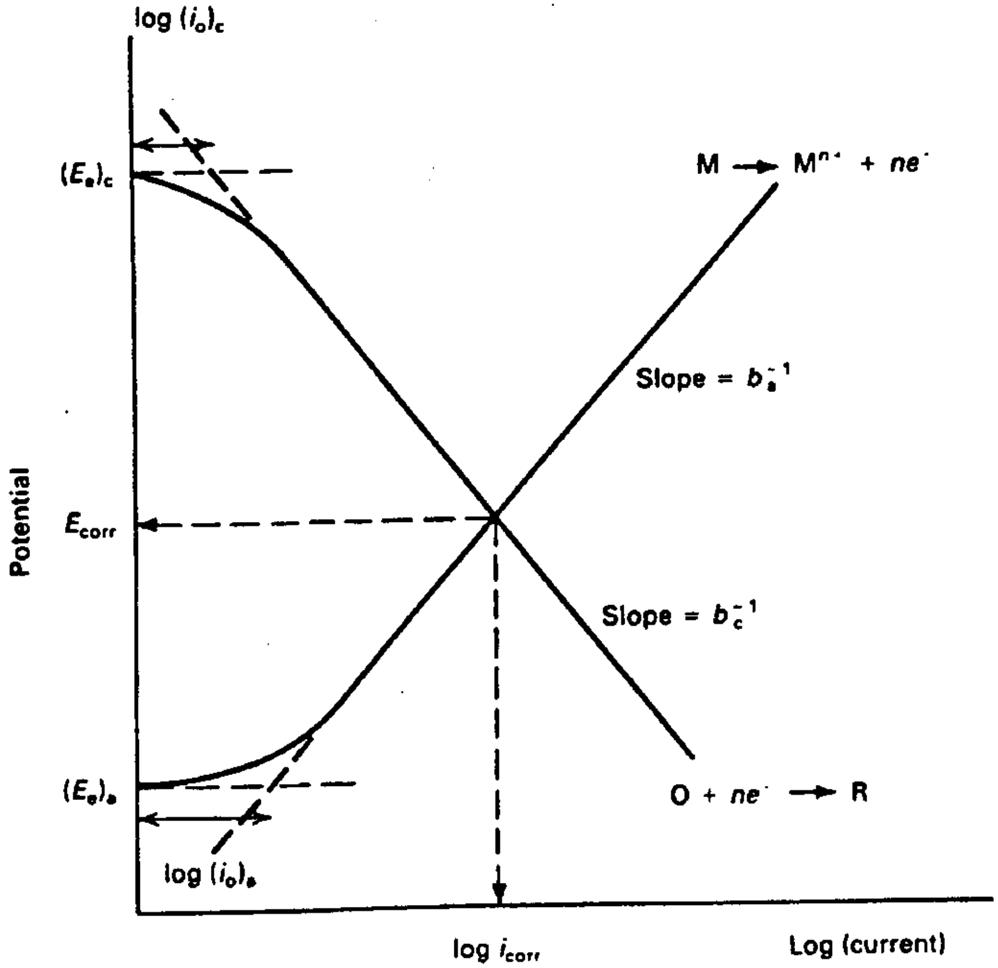
$$\eta_c^A = (E_e)_a - E_{corr}$$

Note: the thermodynamic driving force for corrosion, $\Delta E_{therm}$ . . .

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

Usually, $\Delta E_{therm}$ 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.**

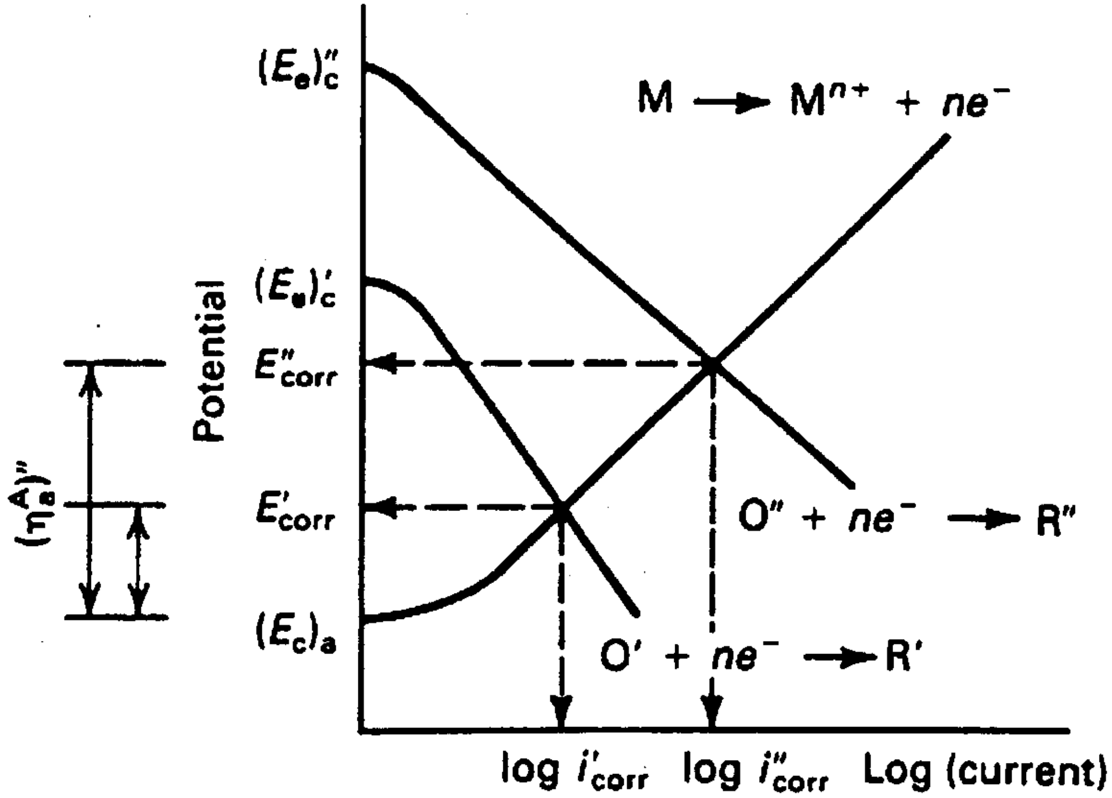
**The exchange currents $(i_o)_a$ and $(i_o)_c$, can be obtained by extrapolating the Tafel lines back to the equilibrium potentials $(E_e)_a$ and $(E_e)_c$ . . .**

**N.B. 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, $i_{corr}$.**

**N.B. the bigger the difference in equilibrium potentials (i.e., the bigger the value of $\Delta E_{therm}$), the bigger the value of $i_{corr}$ (i.e., the greater the corrosion).**

## Two possible cathodic reactions



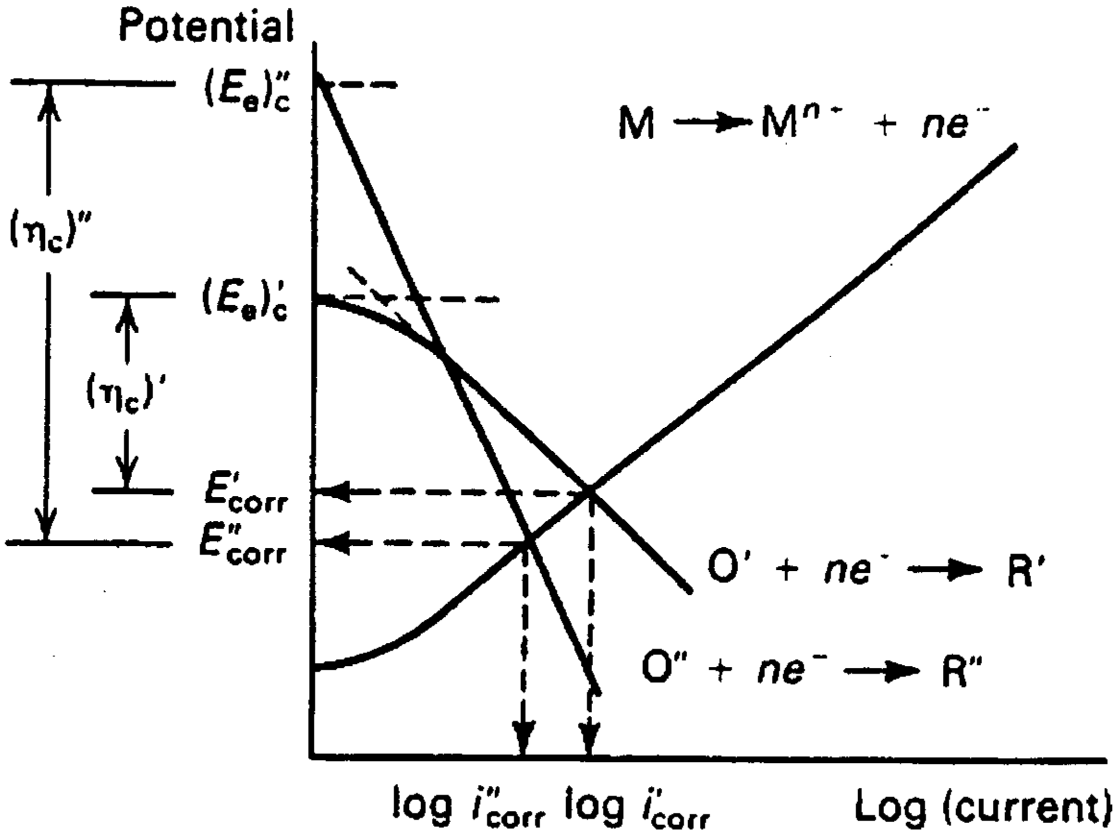
**NOTE:**

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

**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, $\Delta E_{therm}$.**

**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 . . .**

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

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

**<u>while</u> . . .**

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

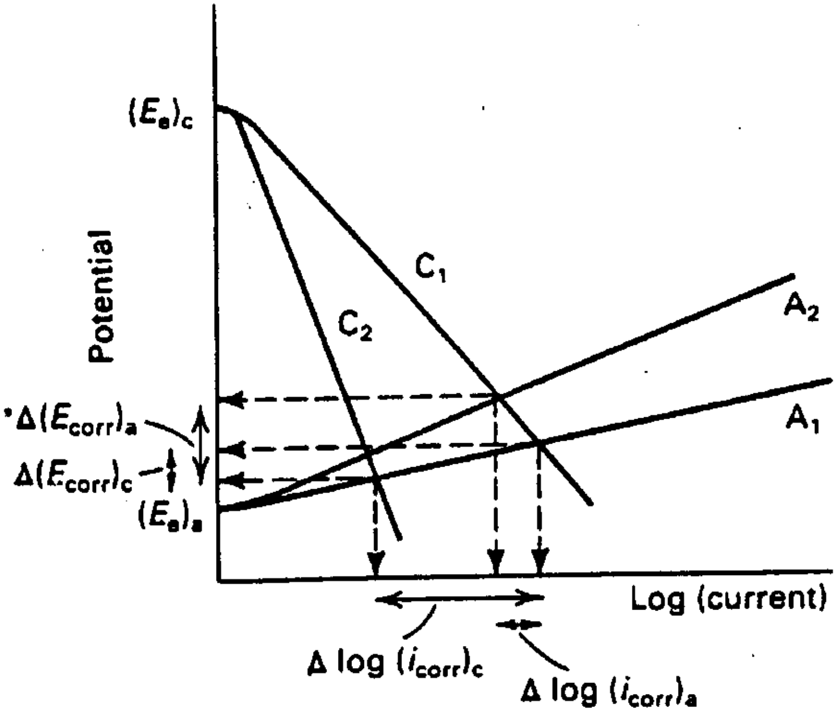
**and** $(b_c)_{O_2/H_2O} = 120$ mV/decade (. . . depending on metal surface).

# 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).**



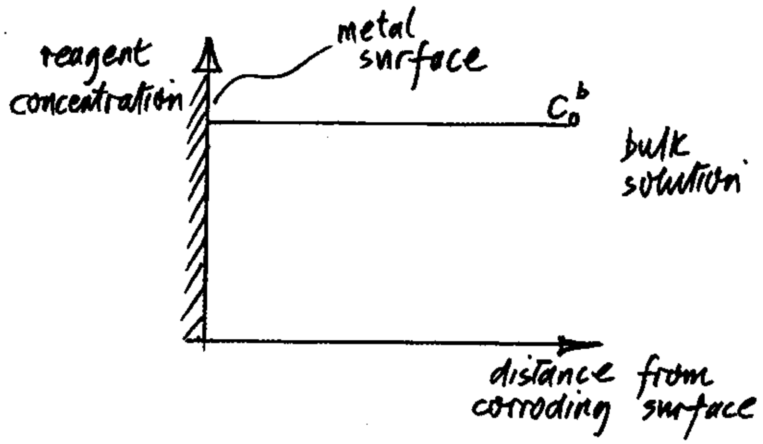
**Evans diagram showing the impact on the corrosion current, $i_{corr}$, and potential, $E_{corr}$, of varying the kinetics of a fast metal dissolution ($A_1$, $A_2$) or a slow cathodic process ($C_1$, $C_2$).**

**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.**

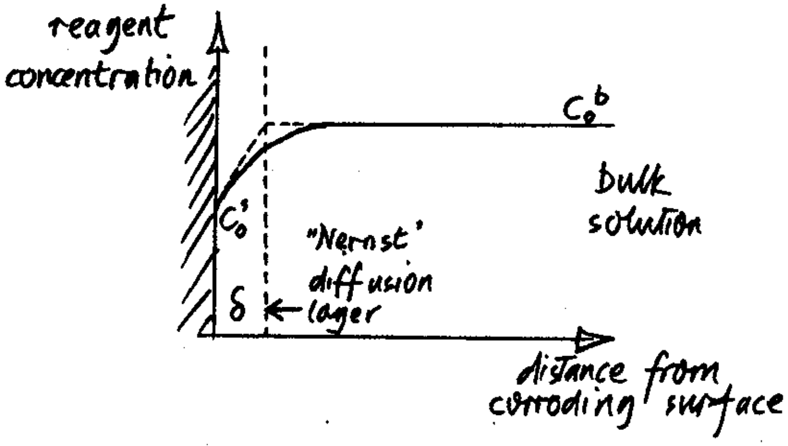
**Mass Transfer Control** (not to be confused with EROSION-CORROSION in which film formation is involved).

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,**

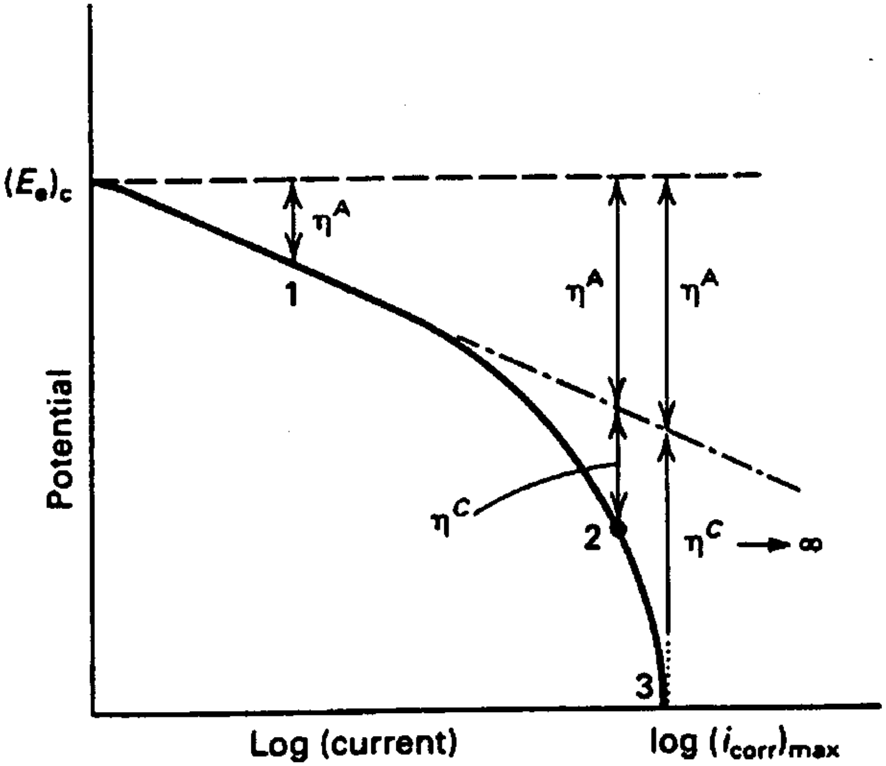
$$\frac{i_c}{nF} = -\frac{D(C_o^s - C_o^b)}{\delta}$$

*** In the limit, $C_o^s \rightarrow 0$**

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

**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, $\delta$, (by flow, etc.).**

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



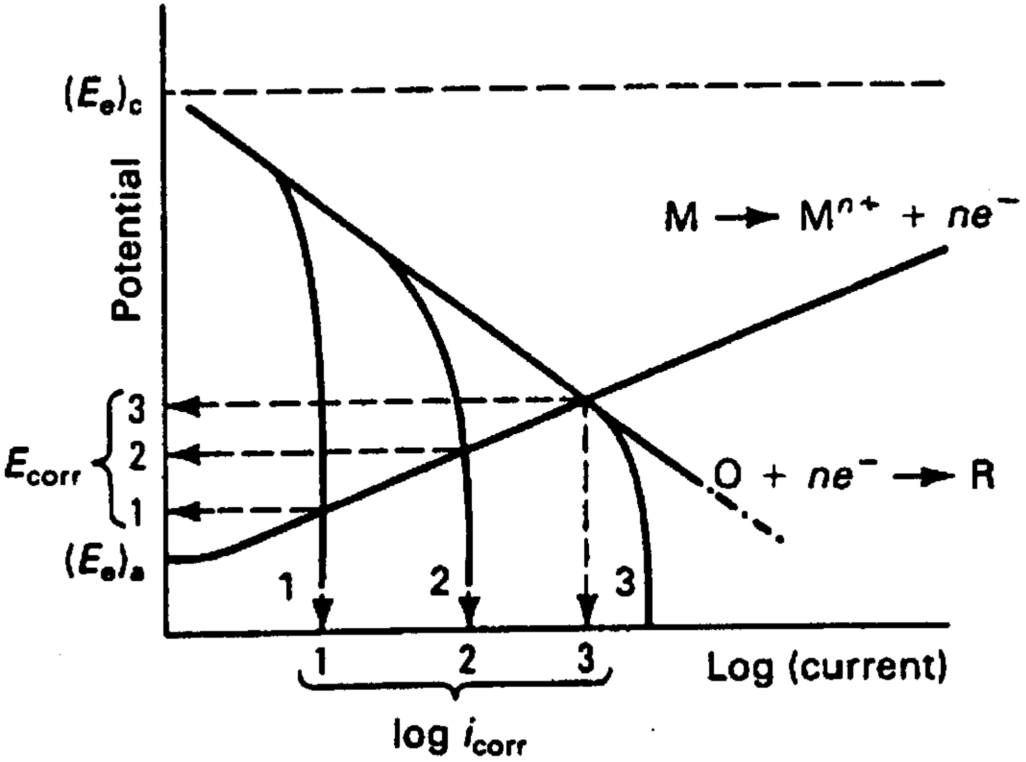
Polarization curve for the cathodic process showing activation polarization (point 1), joint activation-concentration polarization (point 2), and transport-limited corrosion control (point 3).

**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, $\eta^c$ infinite.

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



**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.**

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

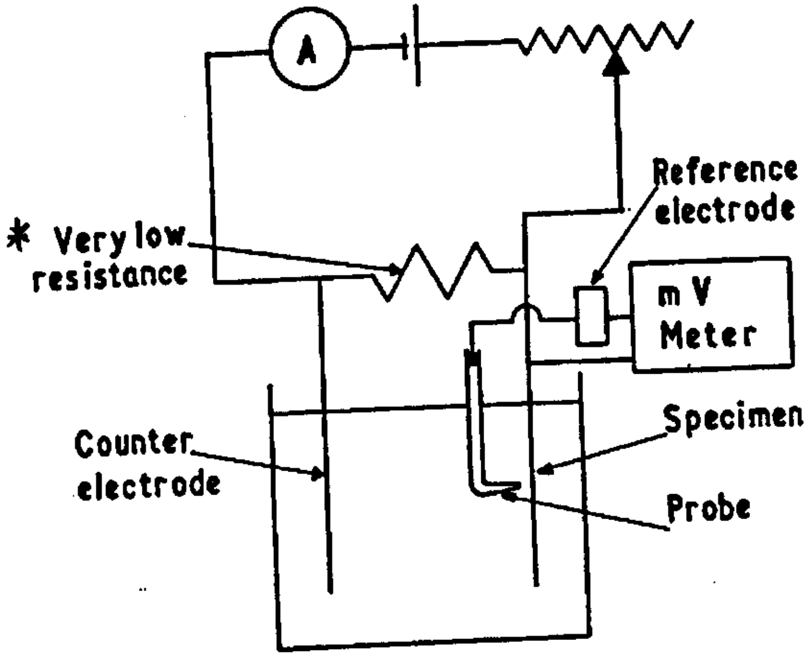
**If anodic reaction were mass-transfer controlled (difficulty of metal ions diffusing away), improved stirring would DECREASE $E_{corr}$ .**

**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):**



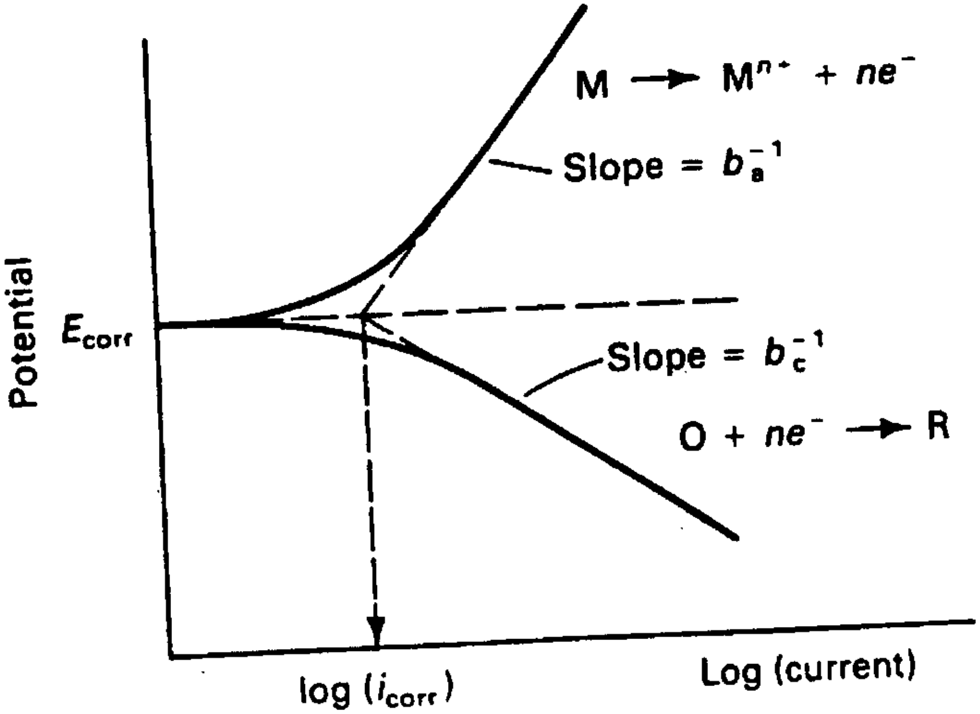
A typical arrangement of a classical potentiostat.

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

**REMEMBER : We can only measure the net 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, $b_a$,

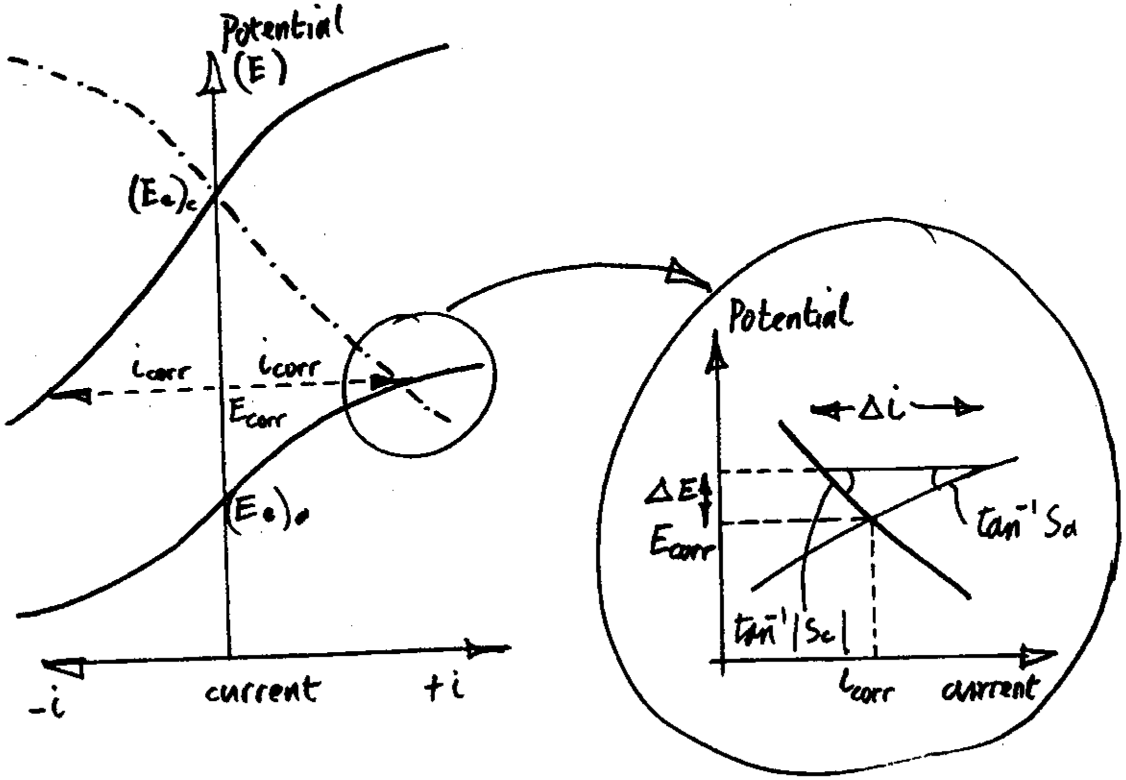
then from one measurement (of the corrosion potential, $E_{corr}$) we can calculate the corrosion rate . . .

$$i_{corr} = i_o \exp\left\{2.303\frac{E_{corr} - (E_e)_a}{b_a}\right\}$$

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., $\pm\Delta E \lesssim 10$ mV).**



**Over small $\Delta E$ ($\lesssim$ 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 ...**

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

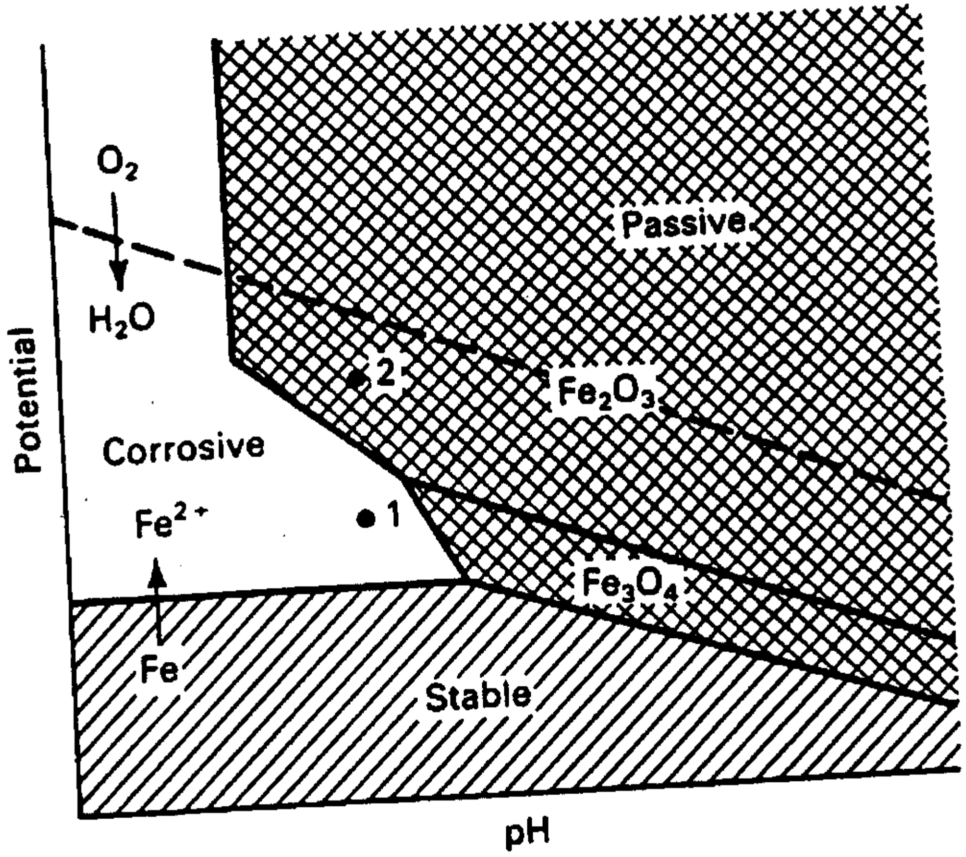
**which gives . . .**

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

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

## Passivation

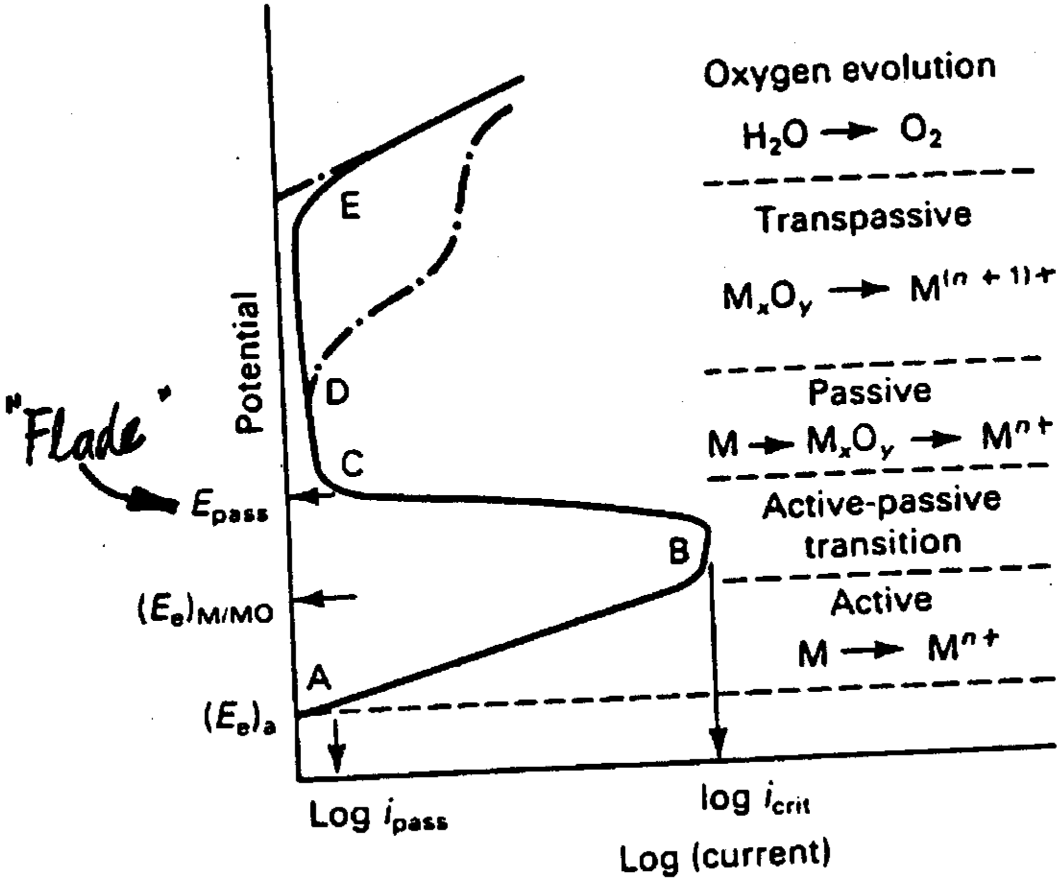
**Under certain conditions of potential and pH, some metals form protective films . . . i.e., they "passivate":**



**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 $(E_e)_a$ . . .**

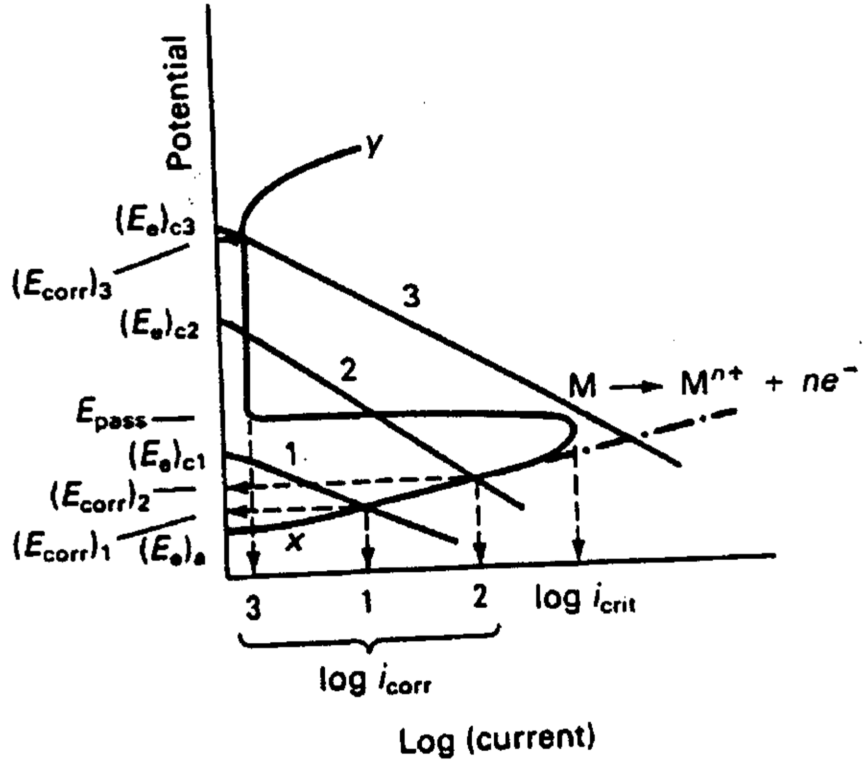


**Oxidative dissolution of oxide (e.g., $Cr_2O_3$ $CrO_4^{2-}$).**

**$(E_e)_{M/Mo}$ 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.**

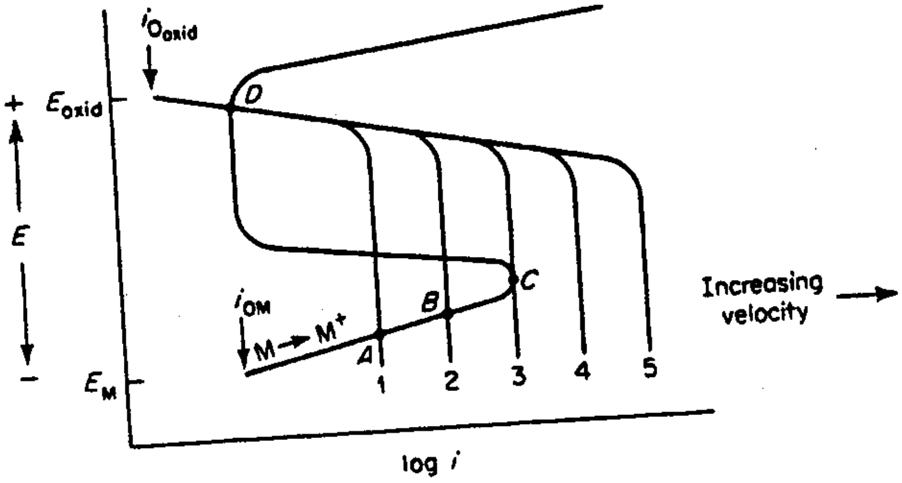
**<u>Cathodic Reaction 1</u>: $(E_e)_{c1} < E_{pass}$, so $(E_{corr})_1$ must also $< E_{pass}$ . . . corrodes actively.**

**<u>Cathodic Reaction 2</u>: $(E_e)_{c2} > E_{pass}$; HOWEVER, curve intersects Tafel line for anodic reaction BELOW $i_{crit}$ . . . passive film cannot form, corrodes actively.**

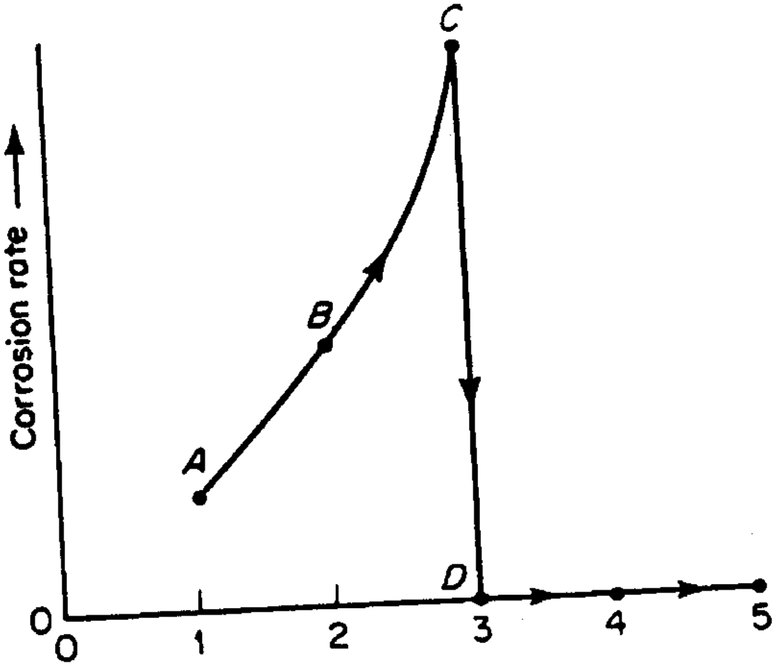
**<u>Cathodic Reaction 3</u>: both passivating condition are met ($(E_e)_{c3} > E_{pass}$; $i_{initial}$ (intersecting Tafel line) $> i_{crit}$) . . . passivates.**

# 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

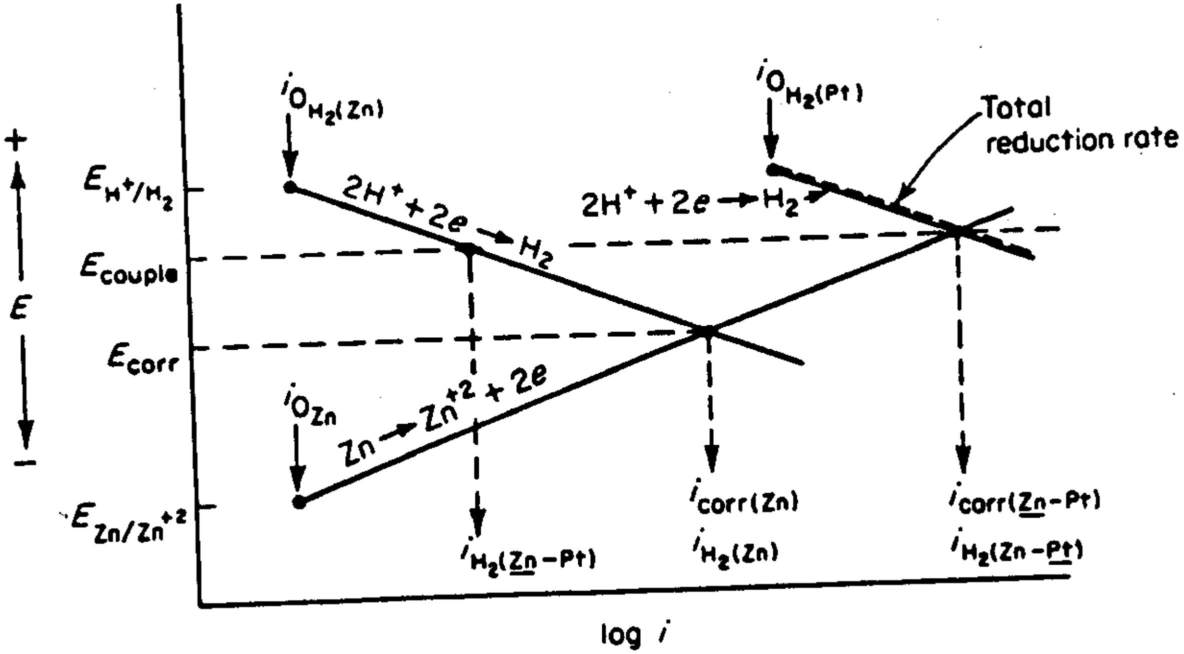
**Isolated zinc corrodes in acid . . .**

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

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

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

**H2 evolution occurs on platinum . . .**

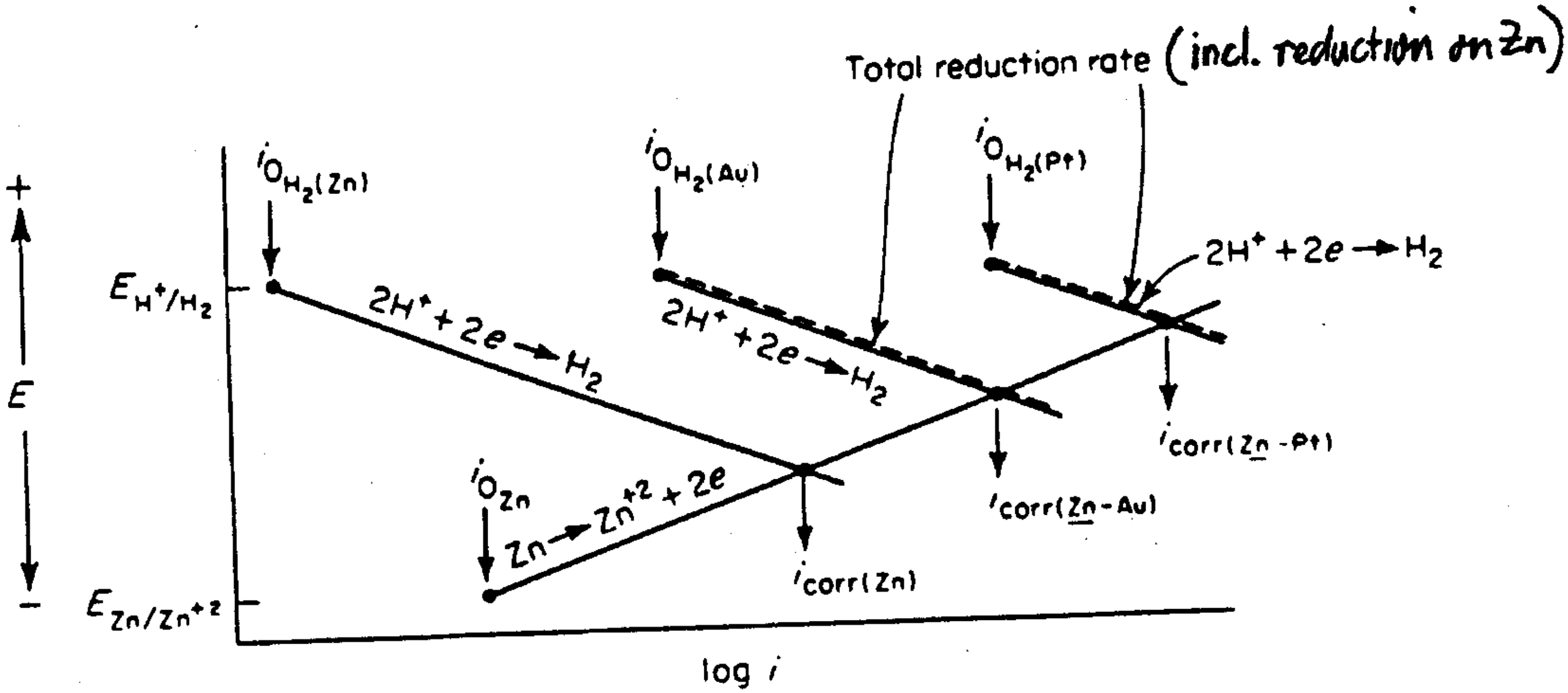


**NOTE:**
**the thermodynamic driving force remains the same**
**($\Delta E_{therm} = (E_e)_{H^+/H_2} - (E_e)_{Zn/Zn^{2+}}$)**
**but the kinetics change - EXCHANGE CURRENTS on Zn and Pt are different:**
**Potential increases,**
**$H_2$ evolution on Zn decreases, total reaction increases.**

Effect of galvanically coupling zinc to platinum (equal areas).

## Effect of $H^+/H_2$ Exchange Current

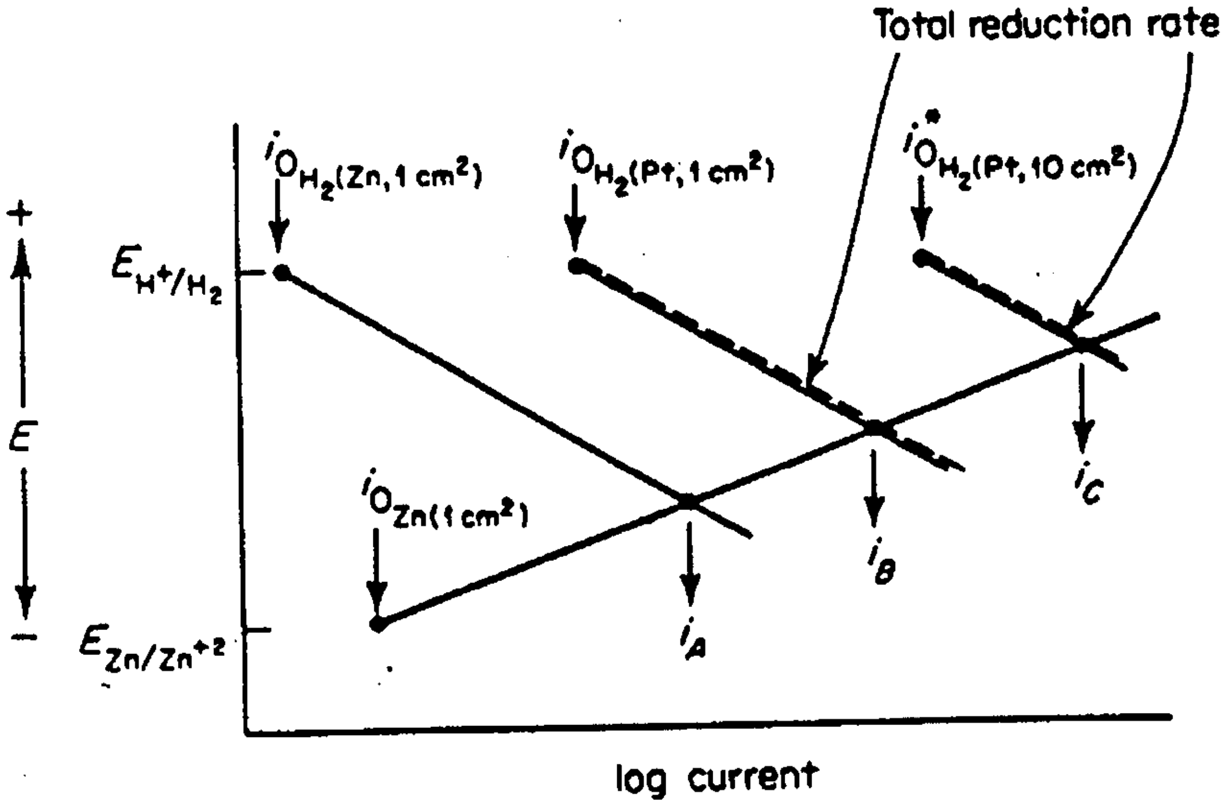
**The more efficient the hydrogen evolution process (i.e., the higher the exchange current), the larger the effect of galvanic coupling . . .**



**Comparison of zinc-platinum and zinc-gold galvanic couples (equal areas).**

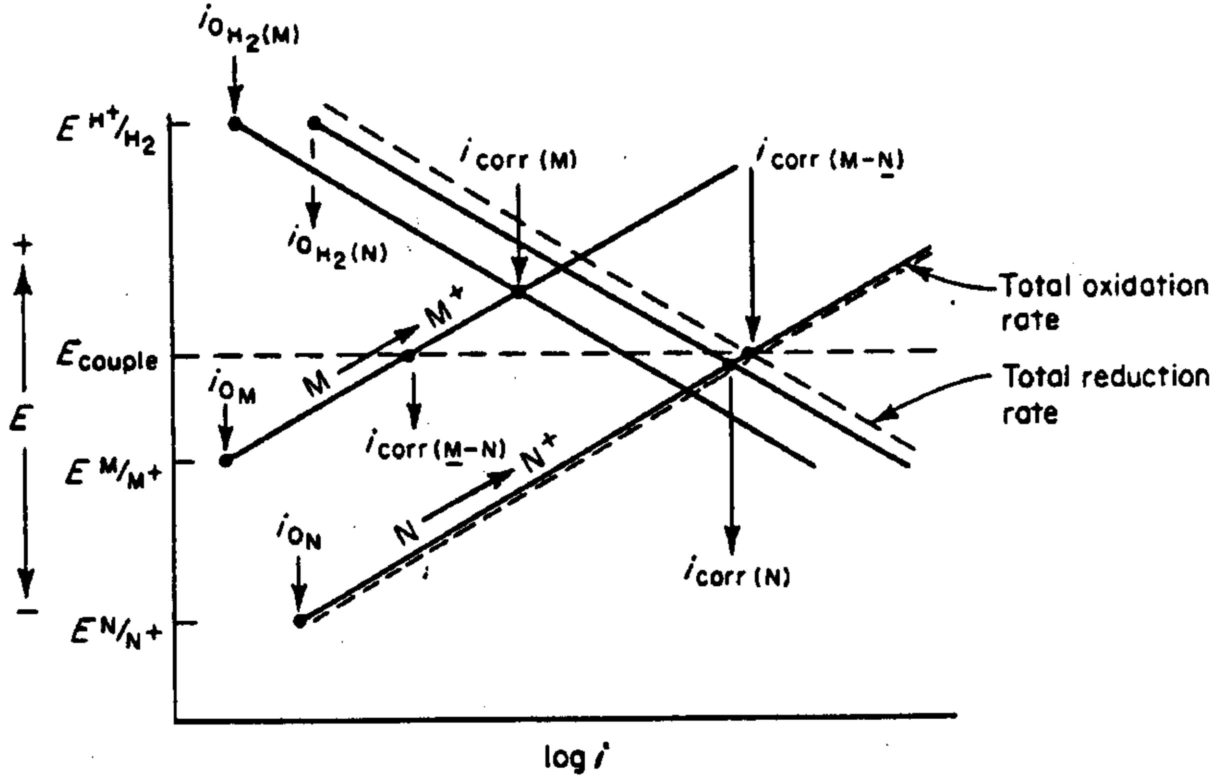
**Pt is a very efficient cathode.**

# 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).

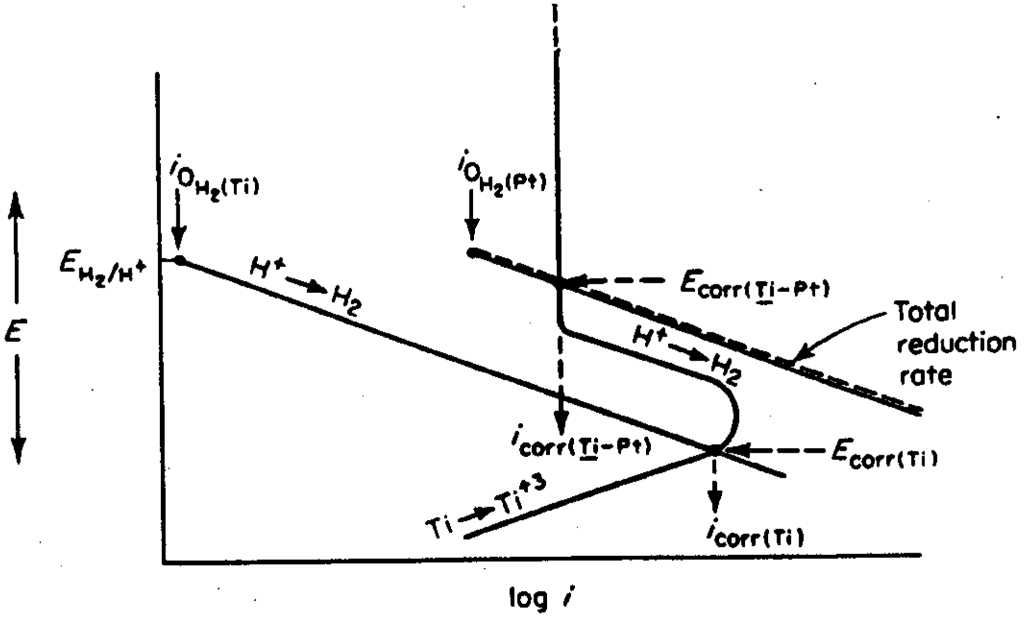


Galvanic couple between two corroding metals.

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

<u>N.B.</u> actual rates depend on Tafel slopes, exchange currents, etc., . . . without detailed information we only predict trends.

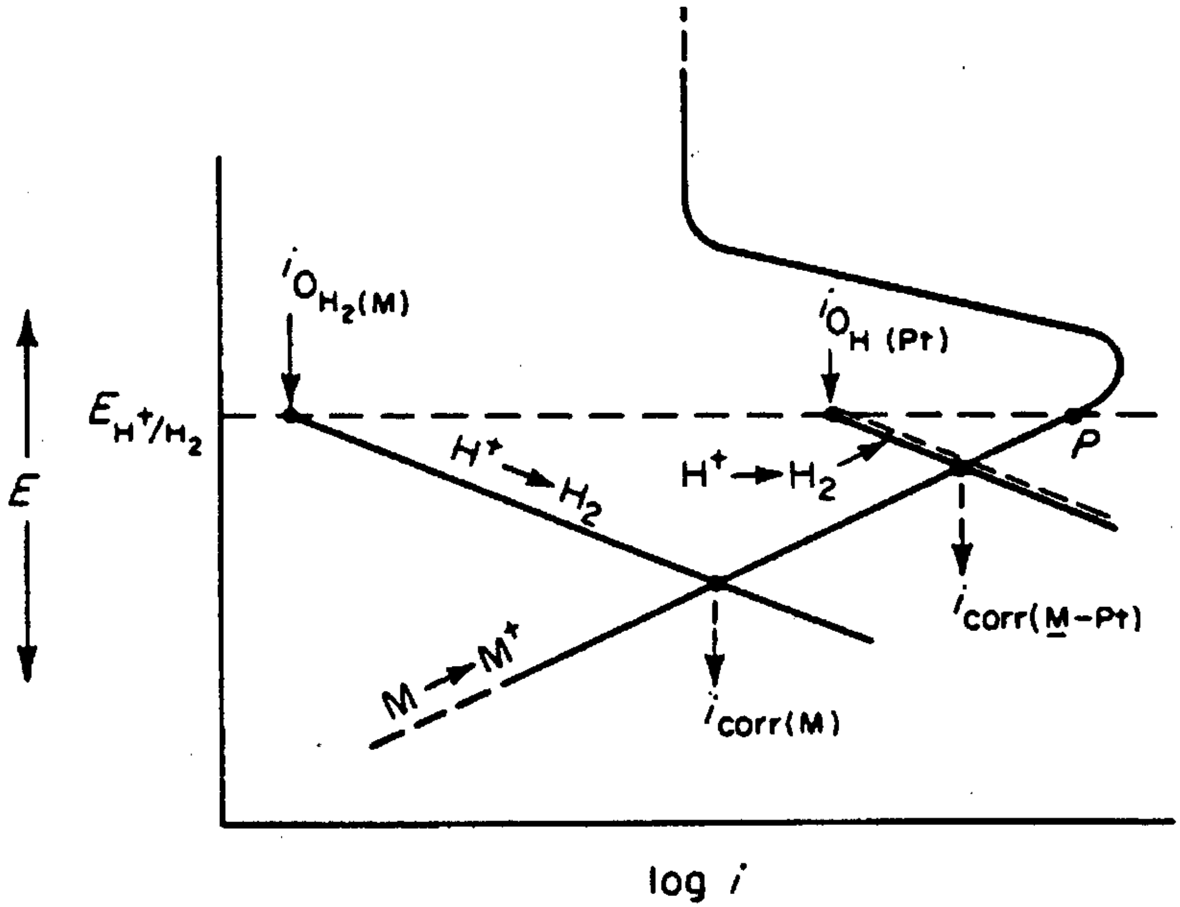
# Effects on Passivating Metals



**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.**