

Corrosion and oxidation II

- Recap – electrochemistry at E°
- Electrode kinetics
- Polarization and overpotential
- Mixed potential theory
- Corrosion

Electrochemical Cell

Standard electrode potential (pure metal, activity in solution = 1, pressure 1 atm and T is 25°C) is defined as

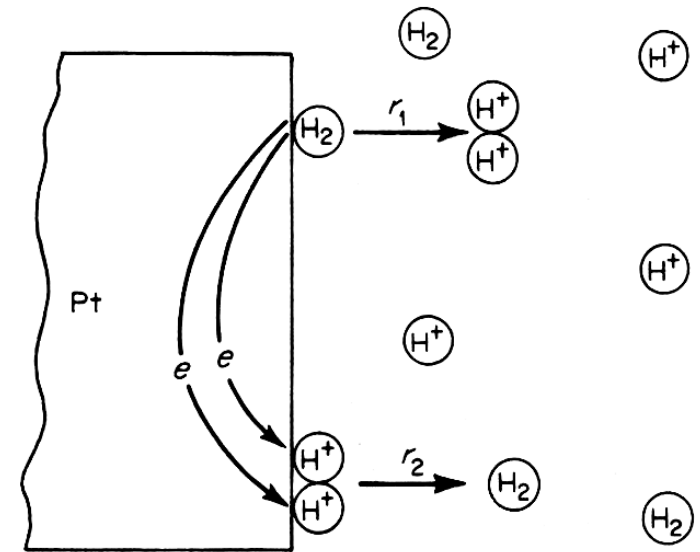
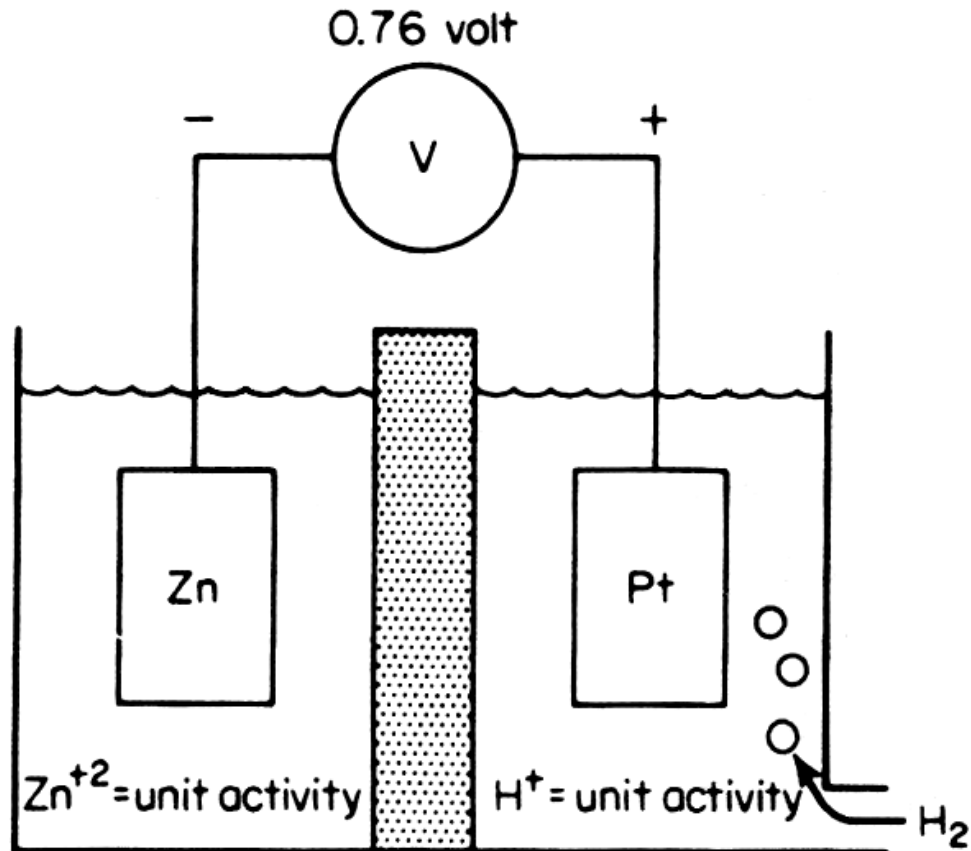
$$E^{\theta} = -\frac{\Delta G^{\theta}}{zF}$$

Electrode potential cannot be measured, because in order to close the circuit we need another electrode → only differences can be measured

System containing two electrodes immersed into the solution is called **electrochemical cell**.

The measurable potential differences between the two electrodes is called **cell potential**.

Electrochemical Cell



Standard emf series of metals

	Metal-metal ion equilibrium (unit activity)	Electrode potential vs. normal hydrogen electrode at 25°C, volts
↑ Noble or cathodic	Au-Au ⁺³	+1.498
	Pt-Pt ⁺²	+1.2
	Pd-Pd ⁺²	+0.987
	Ag-Ag ⁺	+0.799
	Hg-Hg ₂ ⁺²	+0.788
	Cu-Cu ⁺²	+0.337
	H ₂ -H ⁺	0.000
↓ Active or anodic	Pb-Pb ⁺²	-0.126
	Sn-Sn ⁺²	-0.136
	Ni-Ni ⁺²	-0.250
	Co-Co ⁺²	-0.277
	Cd-Cd ⁺²	-0.403
	Fe-Fe ⁺²	-0.440
	Cr-Cr ⁺³	-0.744
	Zn-Zn ⁺²	-0.763
	Al-Al ⁺³	-1.662
	Mg-Mg ⁺²	-2.363
Na-Na ⁺	-2.714	
K-K ⁺	-2.925	

Nernst Equation

- Electrodes potential in other conditions than standard (25°C ja $a_i = 1$) ones be calculated by using the standard electrode potential and the Nernst equation:

$$E = E_0 + \frac{RT}{zF} \ln \left(\frac{a_{\text{oxid}}}{a_{\text{red}}} \right)$$

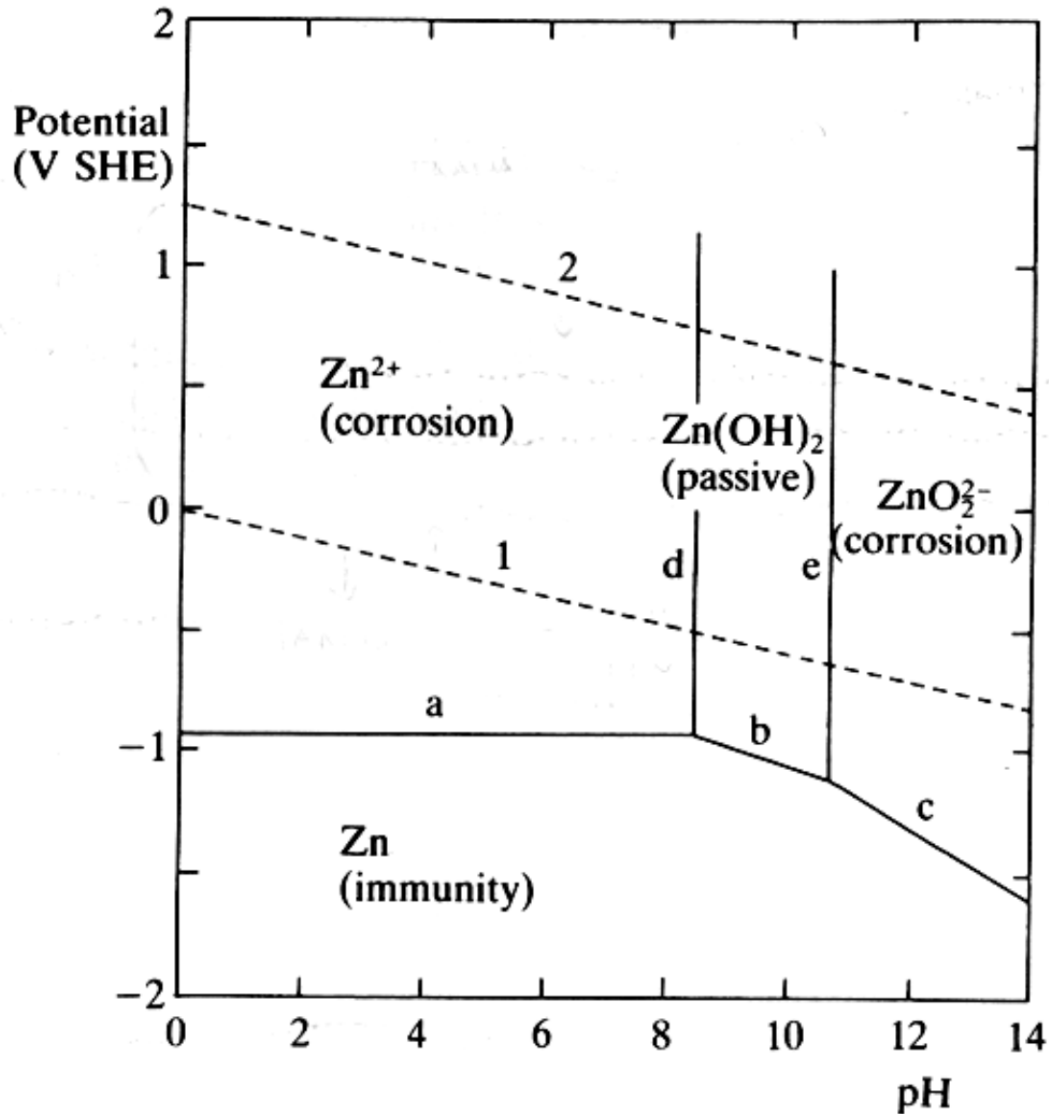
where E° = electrodes standard potential, a_{oxid} = activity of oxidized form, a_{red} = activity of reduced form, R = universal gas constant, T = temperature (K) and F = Faraday's constant (96500 C/mol)

$$\Delta G = -zFE$$

Emf- Sea water

↑ Noble or cathodic	Platinum	Tin
	Gold	Lead
	Graphite	Lead-tin solders
	Titanium	[18-8 Mo stainless steel (active)]
	Silver	[18-8 stainless steel (active)]
	[Chlorimet 3 (62 Ni, 18 Cr, 18 Mo)	Ni-Resist (high Ni cast iron)
	[Hastelloy C (62 Ni, 17 Cr, 15 Mo)	Chromium stainless steel, 13% Cr (active)
	[18-8 Mo stainless steel (passive)	[Cast iron
	[18-8 stainless steel (passive)	[Steel or iron
	[Chromium stainless steel 11-30% Cr (passive)	2024 aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn)
	[Inconel (passive) (80 Ni, 13 Cr, 7 Fe)	Cadmium
	[Nickel (passive)	Commercially pure aluminum (1100)
	Silver solder	Zinc
	[Monel (70 Ni, 30 Cu)	Magnesium and magnesium alloys
	Cupronickels (60-90 Cu, 40-10 Ni)	
	Bronzes (Cu-Sn)	
	Copper	
	Brasses (Cu-Zn)	
	[Chlorimet 2 (66 Ni, 32 Mo, 1 Fe)	
	[Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)	
[Inconel (active)		
[Nickel (active)		
	Active or anodic ↓	

Pourbaix – diagrams



(Source: Tretheway
et.al. Corrosion, Longman,
1996.)

Faraday's laws

1. Electrochemical reactions **"take place on the surface of an electrode", where "amount of reacting substance is directly related to the amount of charge put into the system"** and
2. "Amount of material that has been reacted on the electrode surface because of the current flow can be obtained as follows:

$$It = Q = z \cdot n \cdot F = \frac{m \cdot z \cdot F}{M}$$

where m is the mass of the reaction product [g], I = current [A], t = time [s], M = atomic weight of the element [g/mol], $F \approx 96\,500$ C/mol or As/mol

- Efficiency of the electrolysis:

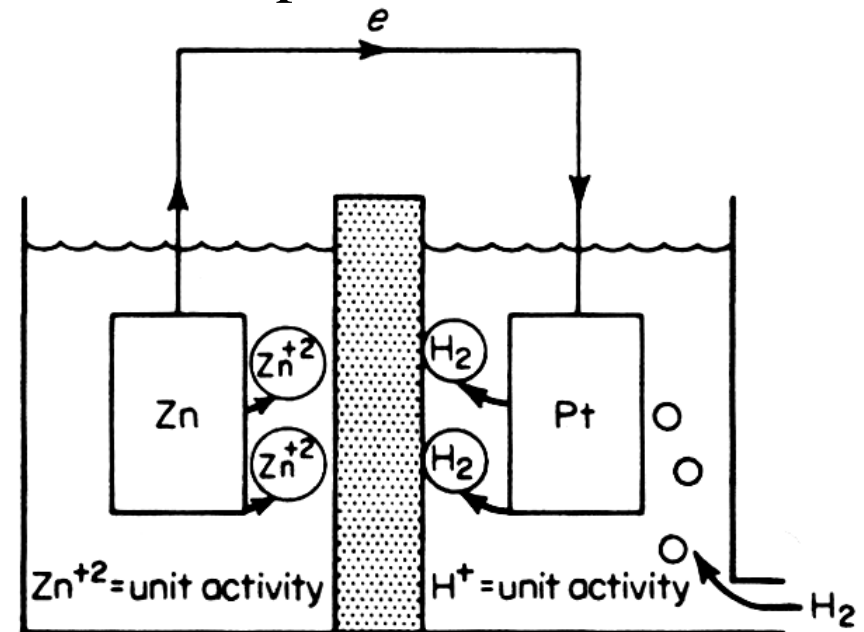
$$\eta = \frac{Q}{Q_{kok}}$$

Electrode kinetics

- In practice **kinetics of the electrode reactions** is especially important, and for example in corrosion the system is **not in equilibrium**, we need kinetic considerations to complement the thermodynamic reasoning.

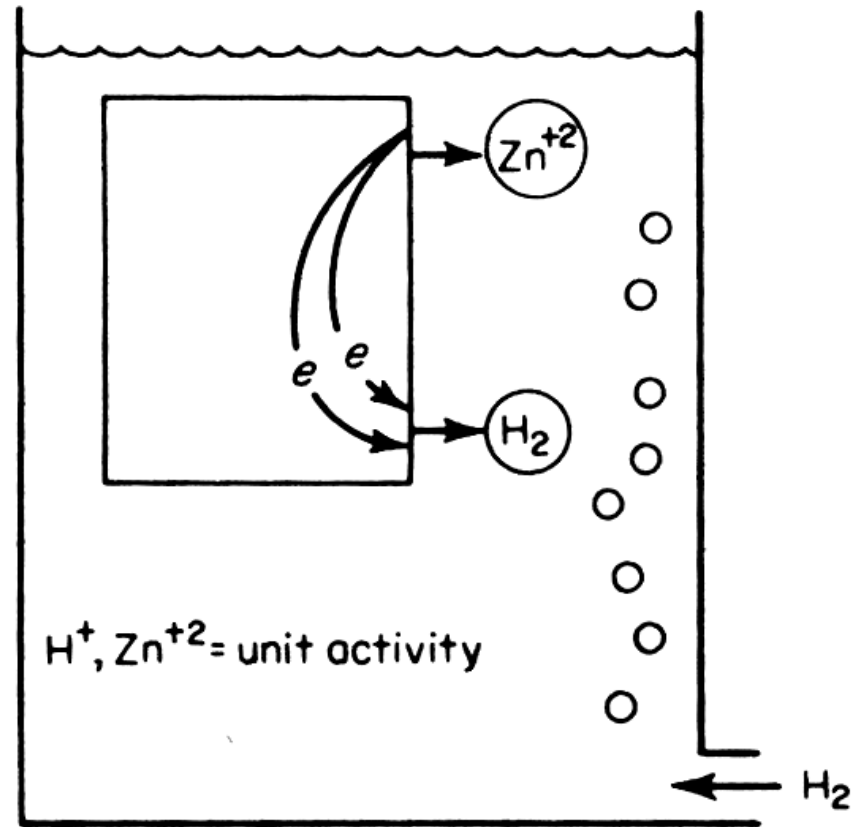
☞ When a cell is short circuited fast dissolution of Zn and strong evolution of hydrogen at the Pt-electrode take place

☞ Electrons, which are released at Zn-electrode travel along the wire to Pt-electrode, where they are used for hydrogen reduction.



Electrode kinetics

- Similar reaction takes place when a piece of Zn is placed into a acidic solution containing Zn-ions.
 - 📄 The reactions take place at the same metal surface (on Zn) and ΔG is same as before.
 - 📄 **Anode** is the electrode **or location of the metal surface**, where net **oxidation** takes place
 - 📄 Similarly on **cathode** (which is local) reduction takes place
 - 📄 “under short-circuit” electrodes are no longer in the their equilibrium potentials and the difference is called **polarization**, which is expressed as **over potential, η**



Polarization and overpotential

If the potential of the metal electrode in the cell is biased to positive direction (by outside potential source) electrons are withdrawn from the metal -> dissolution rate increases.

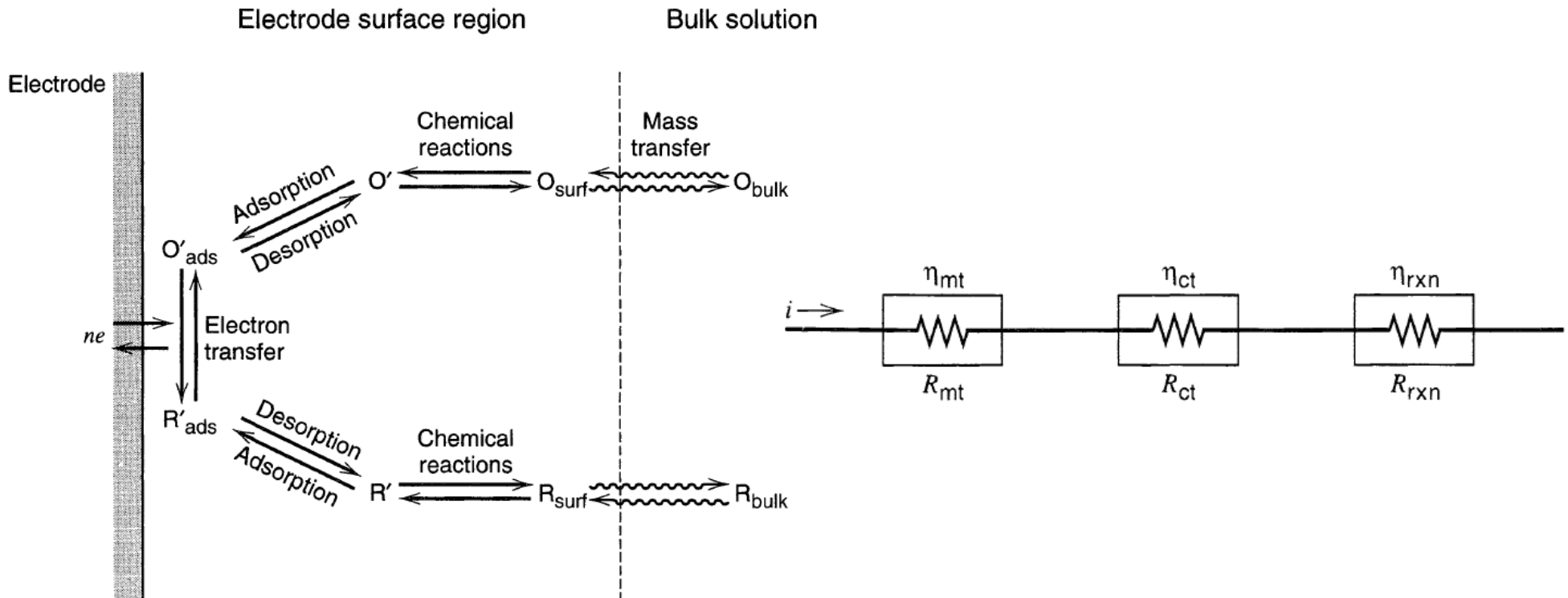
If **dissolution reaction is not fast enough** to balance the charge of the withdrawn electrons, the potential of the metal electrode becomes more positive with respect to eq. situation and **electrode has been polarized anodically**.

Similarly, when metal electrode is biased to negative direction and not enough metal is precipitated on the electrode surface, **electrode becomes cathodically polarized**.

The magnitude of the difference between actual and equilibrium potential is called **overpotential**, $\eta = E' - E$.

Polarization and overpotential

Overpotential can be divided into different parts depending on the rds



Polarization

- Two most important forms of polarization are:

- ★ Activation polarization (in corrosion controls kinetics of anodic dissolution)
- ★ Concentration polarization

☰ Activation polarization caused by

- ☐ Electron transfer step
- ☐ Formation of hydrogen molecules

☰ Under activation polarization relation between reaction speed (current density) and over potential is given by

Tafel equation ($|\eta| > 50 \text{ mV}$)

$$\eta_a = \pm b \log\left(\frac{i}{i_0}\right)$$
$$b_{anodic} = \frac{2.303RT}{\alpha zF}$$
$$b_{cathodic} = -\frac{2.303RT}{(1-\alpha)zF}$$
$$b_c = \left(\frac{\partial \eta}{\partial \log j}\right)$$

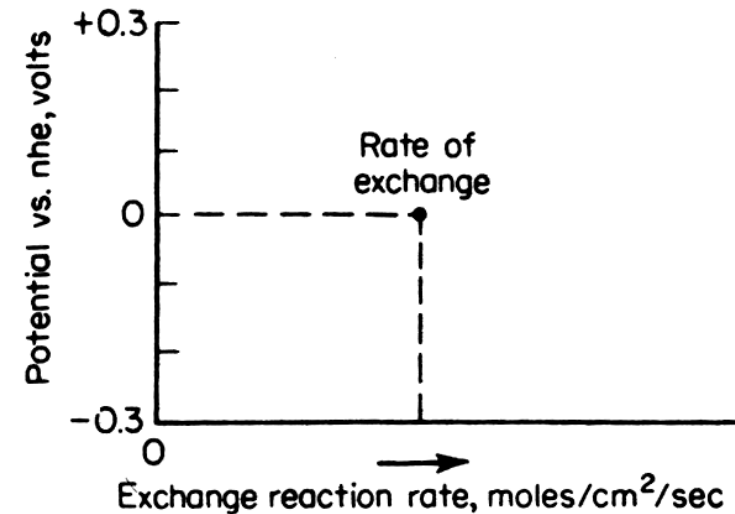
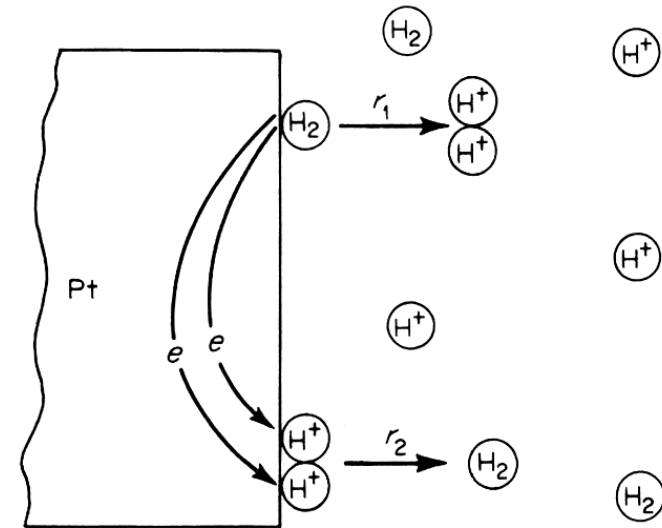
where η_a is **overpotential**, b is constant and i current density and i_0 **exchange current density**

Exchange current density, i_0

- At equilibrium $r_{\text{anodic}} = r_{\text{cathodic}}$
 - 📄 At equilibrium the rate of reaction is finite
 - 📄 Electrode potential plotted as a function of exchange reaction rate \Rightarrow point that corresponds to hydrogen reaction at Pt electrode
 - 📄 Give the speed of exchange reaction [mol/cm²s]
 - 📄 Correlation between speed of the reaction and current density is given by **Faraday's law**

$$r_{\text{oxid}} = r_{\text{red}} = \frac{i_0}{zF}$$

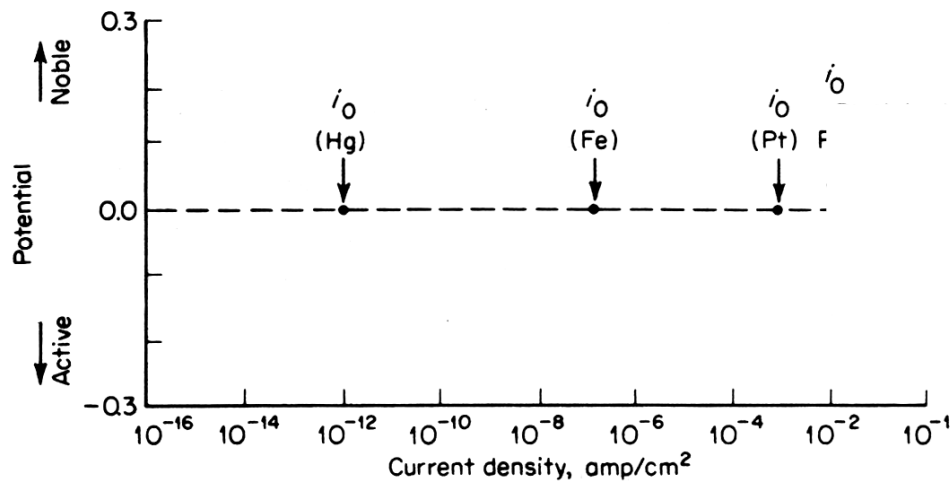
- where i_0 is the exchange current density (flux) and z is the number of electrons participating in the reaction



Exchange current density, i_0

Exchange current for a given reaction depends on the electrode and temperature.

It can (only) be determined experimentally



Reaction	Electrode	Solution	i_0 , A/cm ²
$2\text{H}^+ + 2e = \text{H}_2$	Al	2N H ₂ SO ₄	10^{-10}
$2\text{H}^+ + 2e = \text{H}_2$	Au	1N HCl	10^{-6}
$2\text{H}^+ + 2e = \text{H}_2$	Cu	0.1N HCl	2×10^{-7}
$2\text{H}^+ + 2e = \text{H}_2$	Fe	2N H ₂ SO ₄	10^{-6}
$2\text{H}^+ + 2e = \text{H}_2$	Hg	1N HCl	2×10^{-12}
$2\text{H}^+ + 2e = \text{H}_2$	Hg	5N HCl	4×10^{-11}
$2\text{H}^+ + 2e = \text{H}_2$	Ni	1N HCl	4×10^{-6}
$2\text{H}^+ + 2e = \text{H}_2$	Pb	1N HCl	2×10^{-13}
$2\text{H}^+ + 2e = \text{H}_2$	Pt	1N HCl	10^{-3}
$2\text{H}^+ + 2e = \text{H}_2$	Pd	0.6N HCl	2×10^{-4}
$2\text{H}^+ + 2e = \text{H}_2$	Sn	1N HCl	10^{-8}
$\text{O}_2 + 4\text{H}^+ + 4e = 2\text{H}_2\text{O}$	Au	0.1N NaOH	5×10^{-13}
$\text{O}_2 + 4\text{H}^+ + 4e = 2\text{H}_2\text{O}$	Pt	0.1N NaOH	4×10^{-13}
$\text{Fe}^{3+} + e = \text{Fe}^{2+}$	Pt		2×10^{-3}
$\text{Ni} = \text{Ni}^{2+} + 2e$	Ni	0.5N NiSO ₄	10^{-6}

Butler-Volmer

$$i = i_0 \cdot \left\{ \exp \left[\frac{\alpha_a n F \eta}{RT} \right] - \exp \left[-\frac{\alpha_c n F \eta}{RT} \right] \right\}$$

- Valid under activation polarization control (and explicitly only for outer sphere redox couples)
- Three limiting cases:
 - $\eta = 0$ (Nernst)
 - $\eta < 10$ mV (linear response)
 - $\eta \gg 50$ mV (Tafel)

Activation polarization

if $|\eta| < 10 \text{ mV}$

\Downarrow

$$i = i_0 \frac{nF}{RT} \eta$$

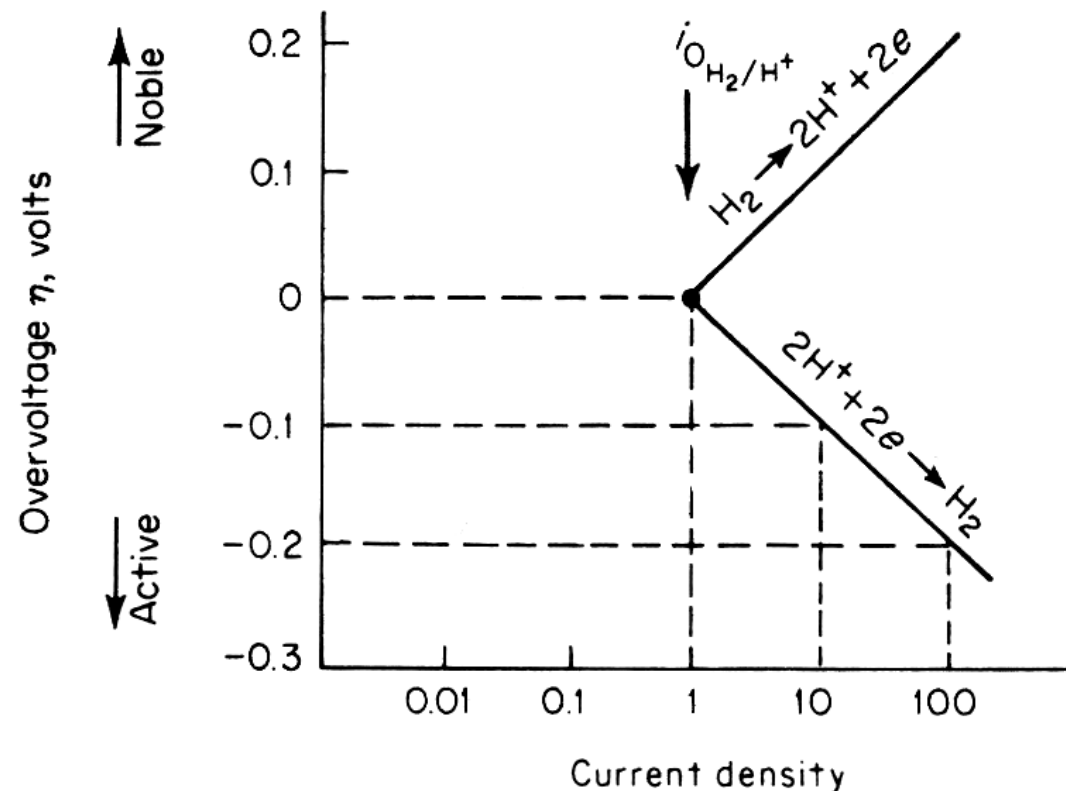
- b in Tafel's equation is called Tafel slope

By using log scale there is a linear correlation between current density and potential ($\eta > \pm 50 \text{ mV}$)

More noble potentials with respect to equilibrium one induce oxidation and less noble ones reduction

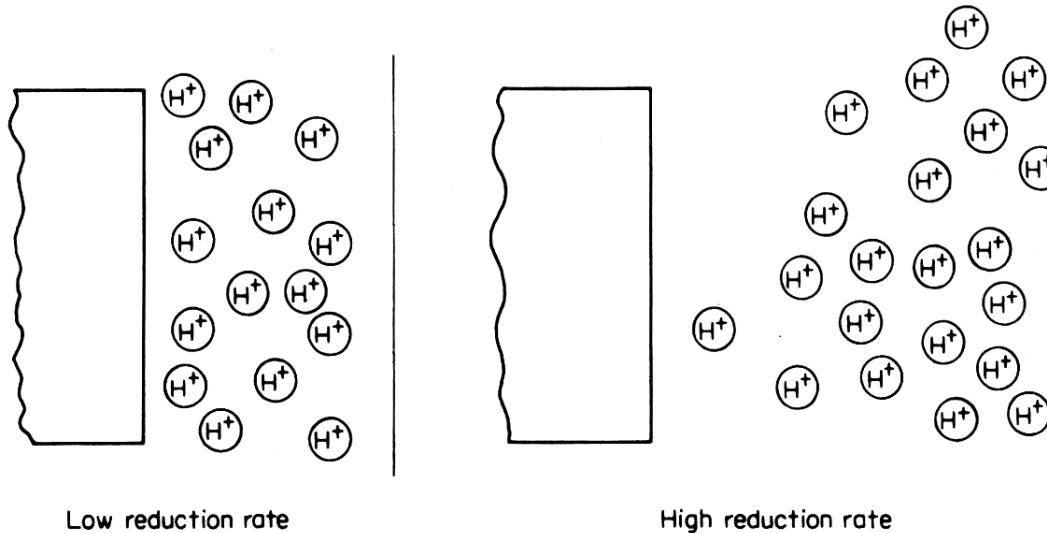
Reaction speed (current density) depends exponentially on the potential

$$\eta_a = \pm b \log\left(\frac{i}{i_0}\right)$$



Concentration polarization

- Let us look at hydrogen evolution reaction



- 📖 At low reduction rates the distribution of protons near the electrode is relatively uniform
- 📖 At high reduction rates the protons become consumed near the electrode and **the diffusion of protons** becomes the rate limiting step → concentration difference between the electrode surface and the bulk solution

Concentration polarization

- Limiting diffusion current density i_L describes the maximum velocity of the **redox reaction**

$$i_L = \frac{D_B z F C_B}{x}$$

where i_L is limiting current density, D_B is intrinsic diffusion coefficient, C_B concentration of B in the bulk and x is the thickness of the diffusion boundary layer

☞ Thickness of the diffusion boundary layer is affected by:

- ☐ Shape and size of the electrode
- ☐ Mixing → decreases (x) → increases i_L !
- ☐ The geometry of the whole system

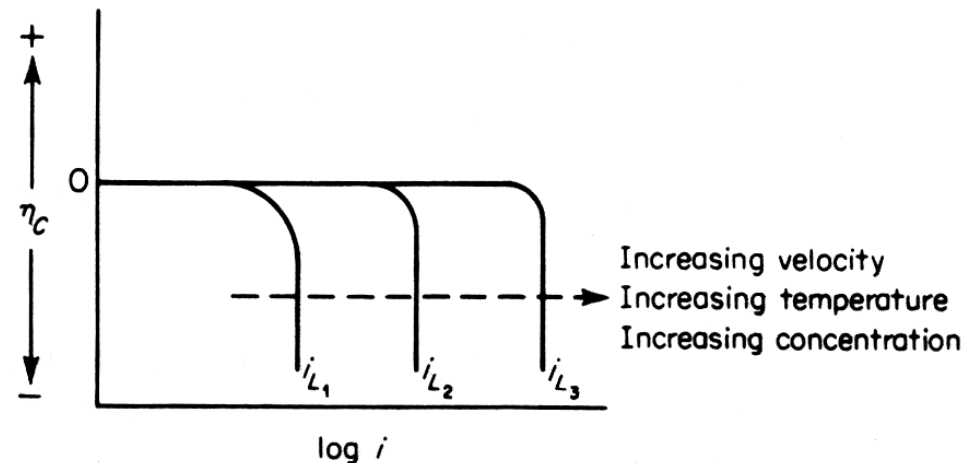
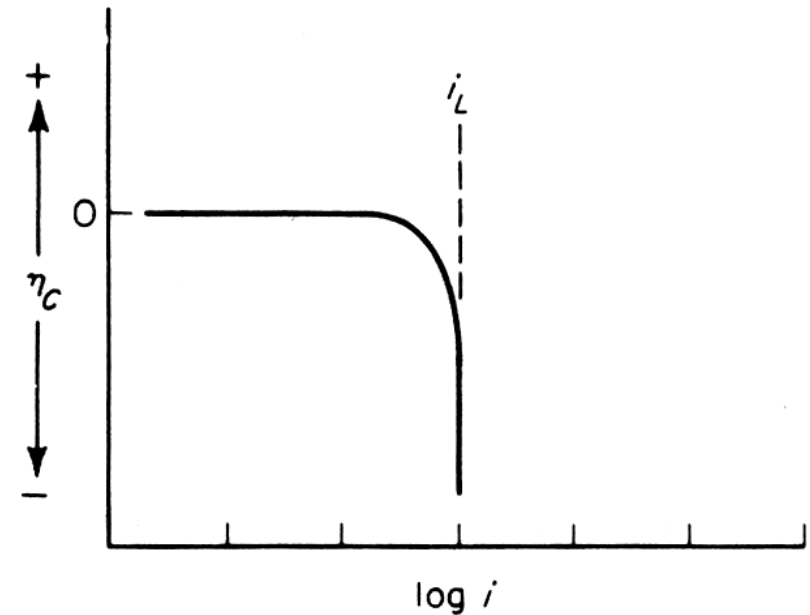
☞ **Limiting current is important in cathodic reactions but for example in anodic dissolution it does not have any role.**

Concentration polarization

- Formula for concentration polarization (only)

$$\eta_c = 2.3 \frac{RT}{zF} \log \left(1 - \frac{i}{i_L} \right)$$

- Concentration polarization becomes significant only when **limiting current density i_L** is approached
- Cathodic current approaches asymptotically the limiting current
→ overpotential increases to infinity ($\ll 0$)
- Influencing factors: mixing, temperature and higher concentration increase i_L



Combined activation and concentration polarization

- Typically **redox reaction** is controlled by both concentration and activation polarization
- At low rates activation and at high rates concentration polarization dominates.
- Total polarization is the sum:

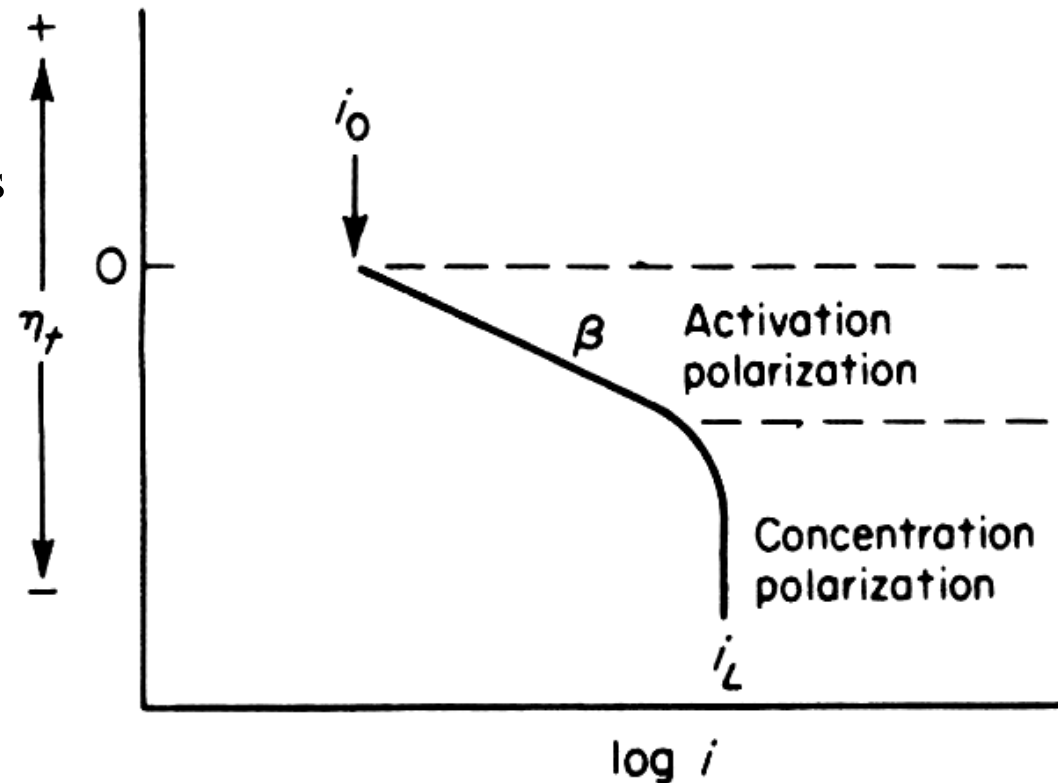
$$\eta_T = \eta_a + \eta_c$$

where η_T is total overpotential,

Thus, for the redox reaction

$$\eta_{red} = -\beta \log\left(\frac{i}{i_o}\right) + 2.3 \frac{RT}{zF} \log\left(1 - \frac{i}{i_L}\right)$$

$$\eta_{diss} = \beta \log \frac{i}{i_o}$$



Mixed potential theory

- Mixed potential theory (Wagner and Traud, 1938) is based on the following postulates:
 - 1. Electrochemical reactions can be divided into two or more partial reactions*
 - 2. Conservation of charge (charge cannot accumulate into the system)*

- *During the corrosion of electrically isolated metal sample the total rate of oxidation must equal the total rate of reduction (if the areas of cathode and anode are the same) [more generally the number of electrons generated by metal dissolution must exactly balance the number of electrons being consumed by the cathodic reduction]*

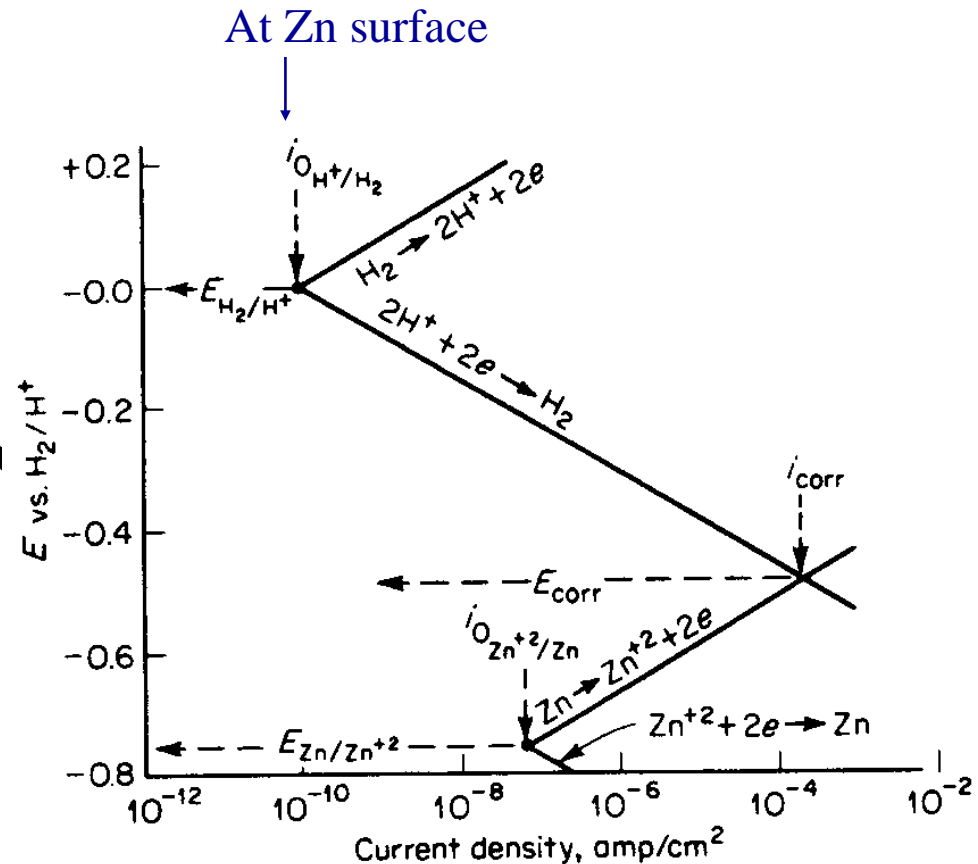
- Mixed electrodes are used in the mixed potential theory .

Mixed electrode is an electrode (for example metal wire), which is in contact with one or more redox systems

- When Zn/Zn^{2+} -reaction is in dynamic equilibrium it can be described by equilibrium potential and exchange current density $i_o(\text{Zn}/\text{Zn}^{2+})$
- Similarly when hydrogen evolution reaction **at the surface of the zinc** is in dynamic equilibrium it can be described by the equilibrium potential and exchange current density $i_o(\text{H}^+/\text{H}_2)$
- However, when Zn is immersed into a acidic solution (example HCl), electrodes **on the surface of the Zn will polarize**, and the overall potential of the Zn surface moves to a new value (mixed potential)
- Zn is a good electrical conductor and this takes place rapidly and thus **mixed or corrosion potential at the Zn surface is established**. This is the only potential where charge is conserved
- $i_{\text{ox}}(\text{Zn} \rightarrow \text{Zn}^{2+}) = i_{\text{red}}(2\text{H}^+ \rightarrow \text{H}_2)$
- Current density i_{corr} corresponding to potential E_{corr} gives the dissolution rate of Zn and rate of hydrogen evolution. ($1 \mu\text{A}/\text{cm}^2 =$

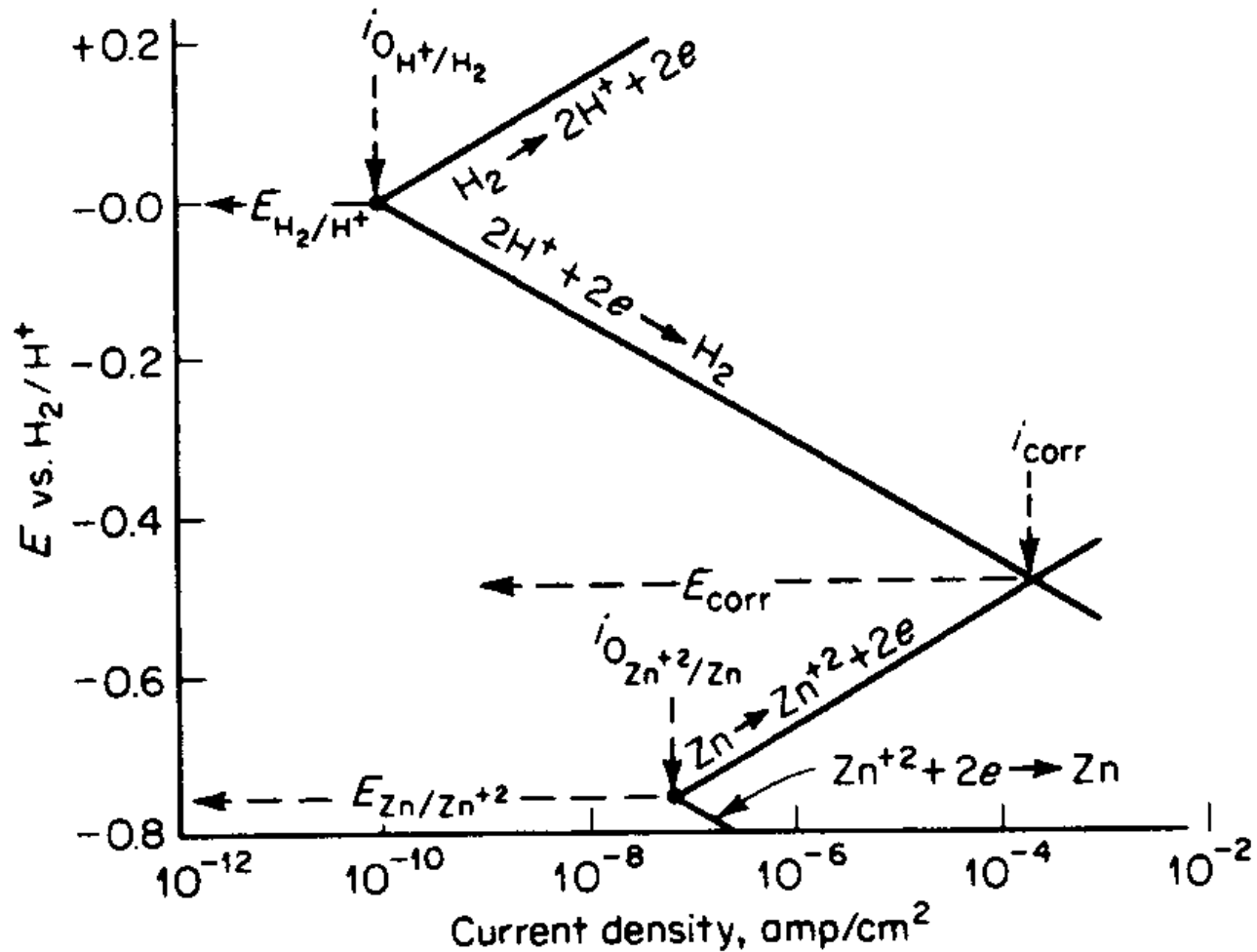
Mixed potential theory

Metal in contact with one redox system



Zn immersed to HCl

$$i_{\text{ox}}(\text{Zn} \rightarrow \text{Zn}^{2+}) = i_{\text{red}}(2\text{H}^+ \rightarrow \text{H}_2)$$

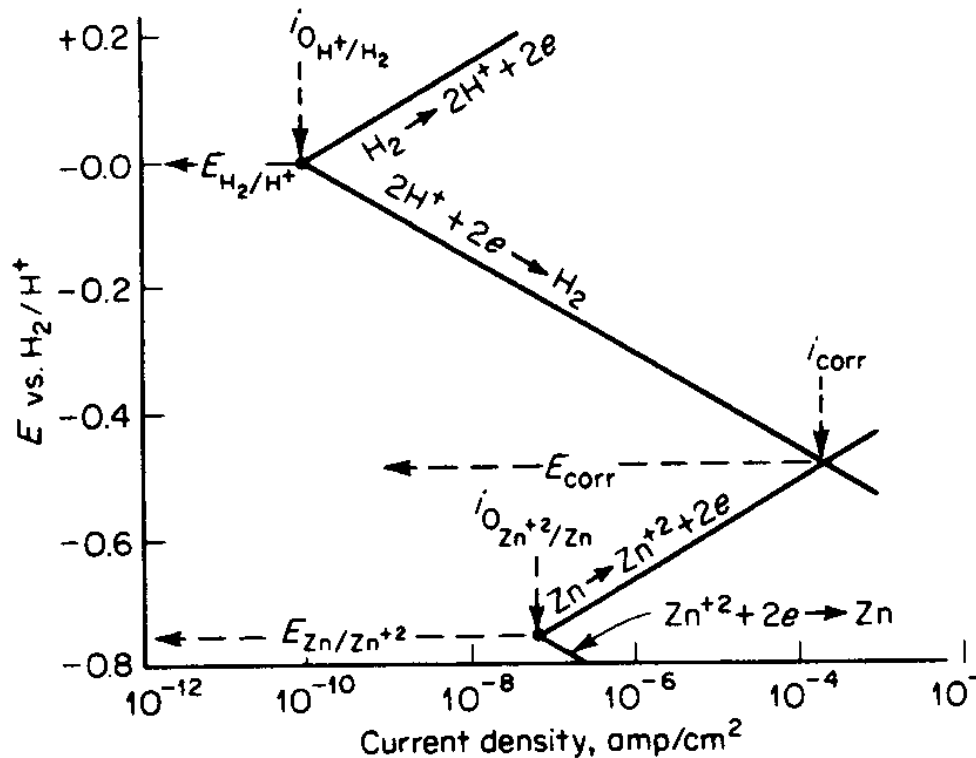


Charge conservation takes place only at E_{corr} !

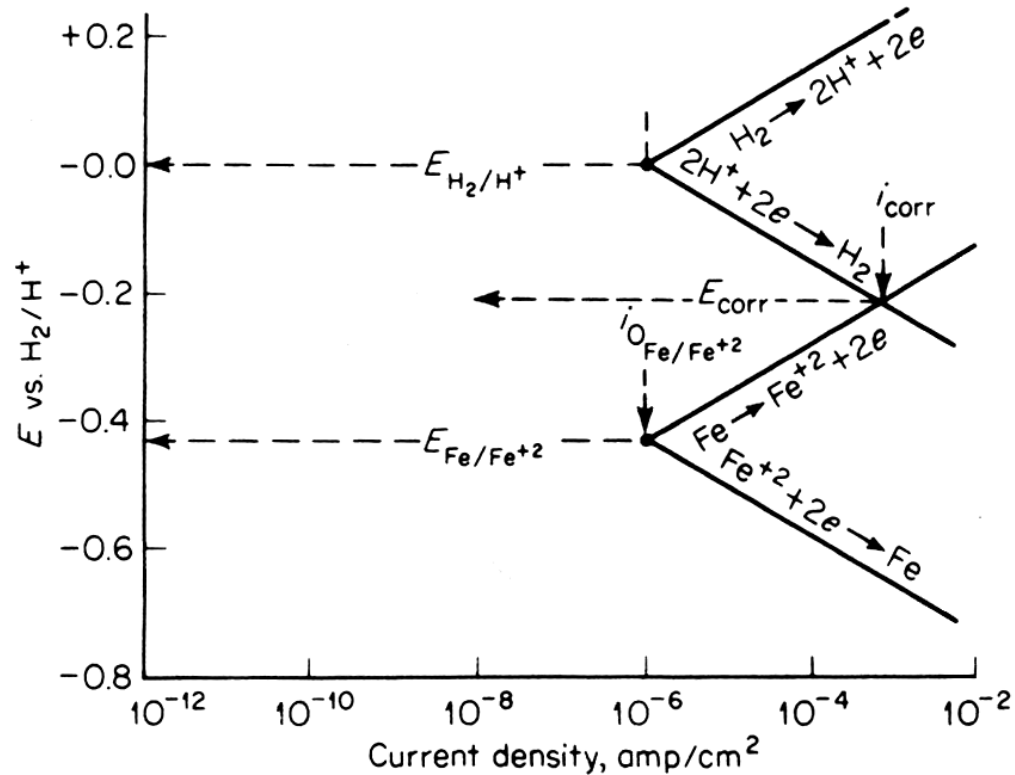
Driving force for corrosion and kinetics

- Example: Corrosion rates of Fe and Zn in dilute HCl

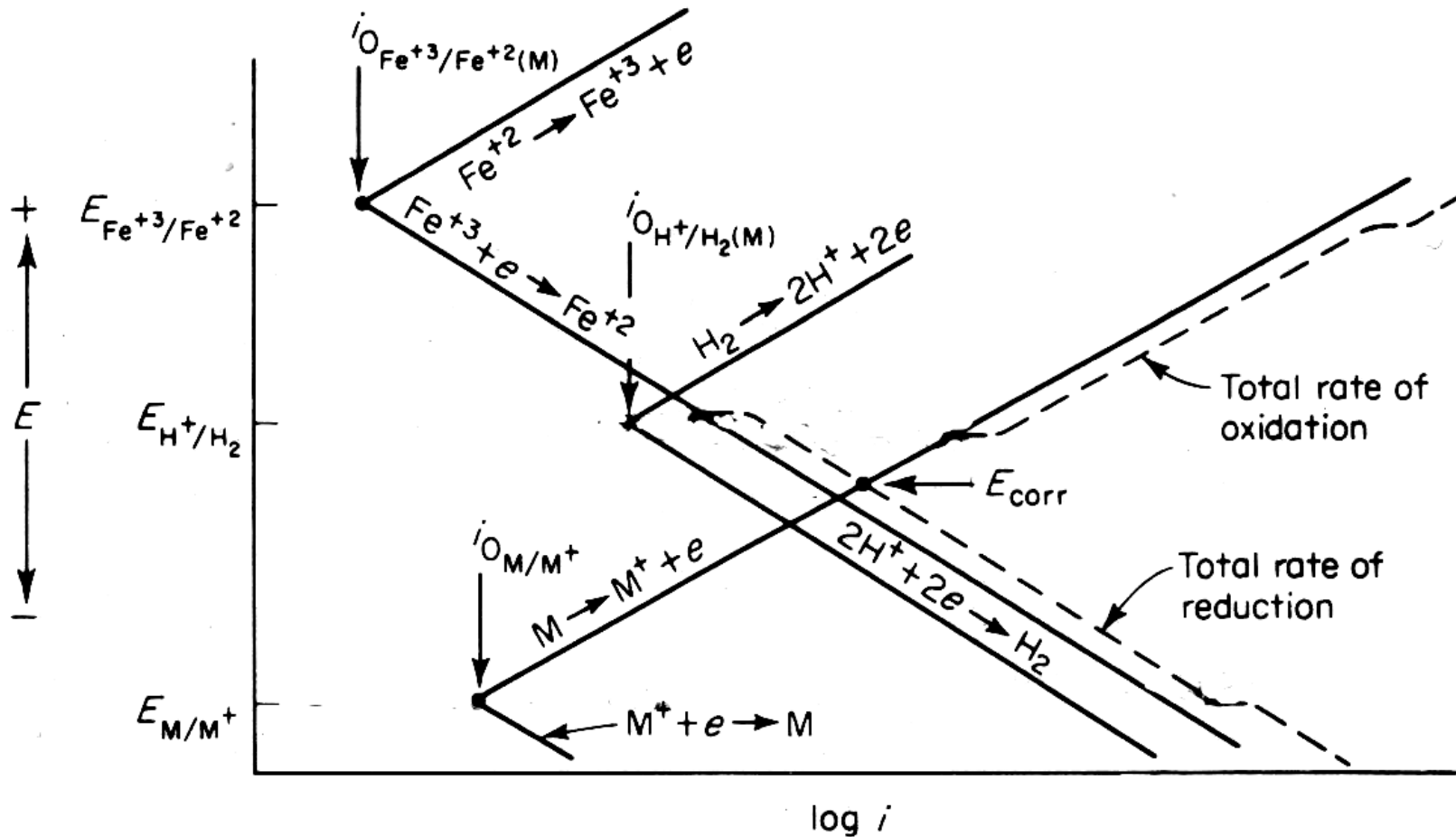
Zn^{2+}/H_2



Fe^{2+}/H_2

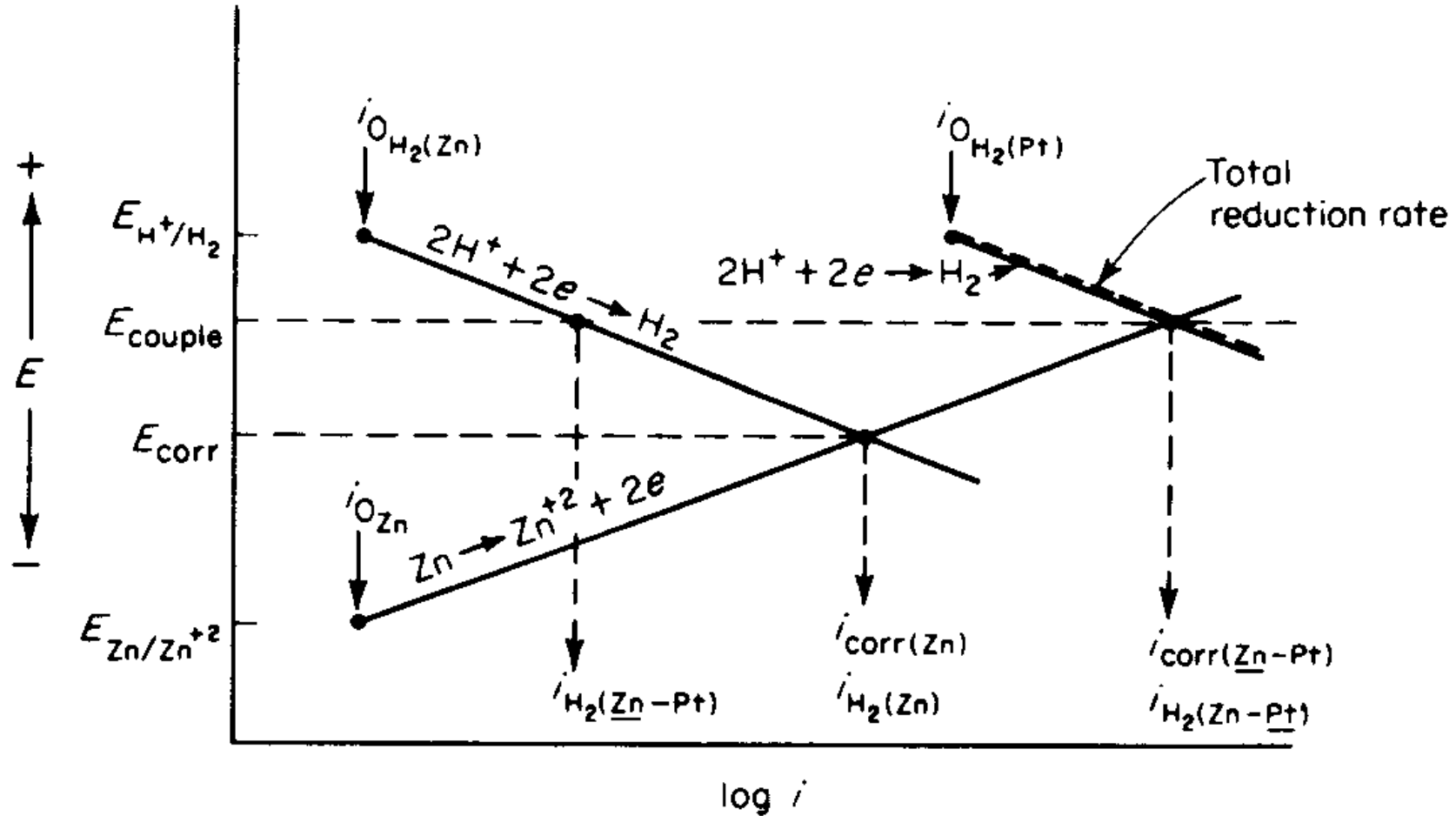


Additional oxidizers



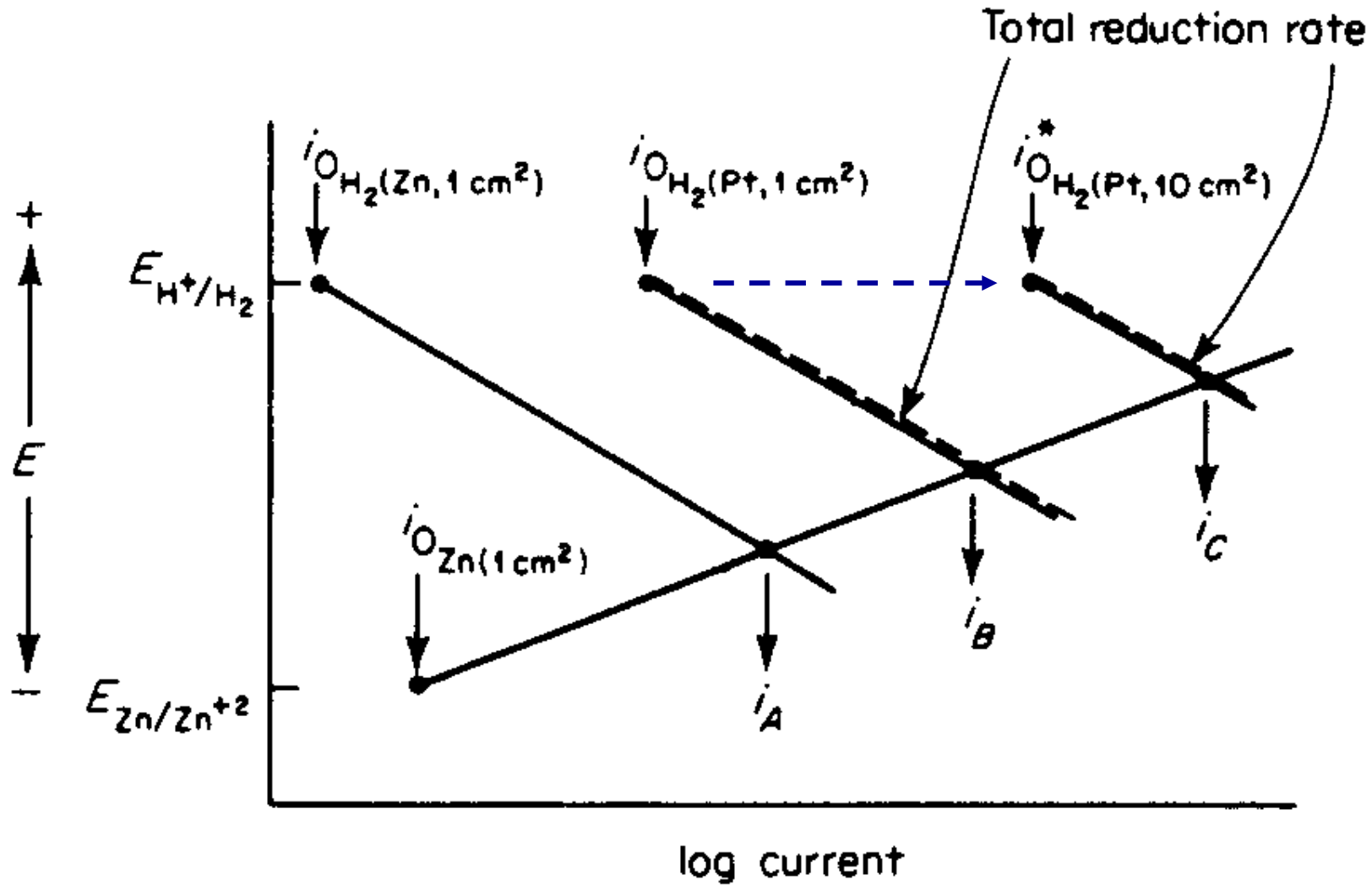
Galvanic coupling

Zn|Pt-bimetal in oxygen depleted acidic solution

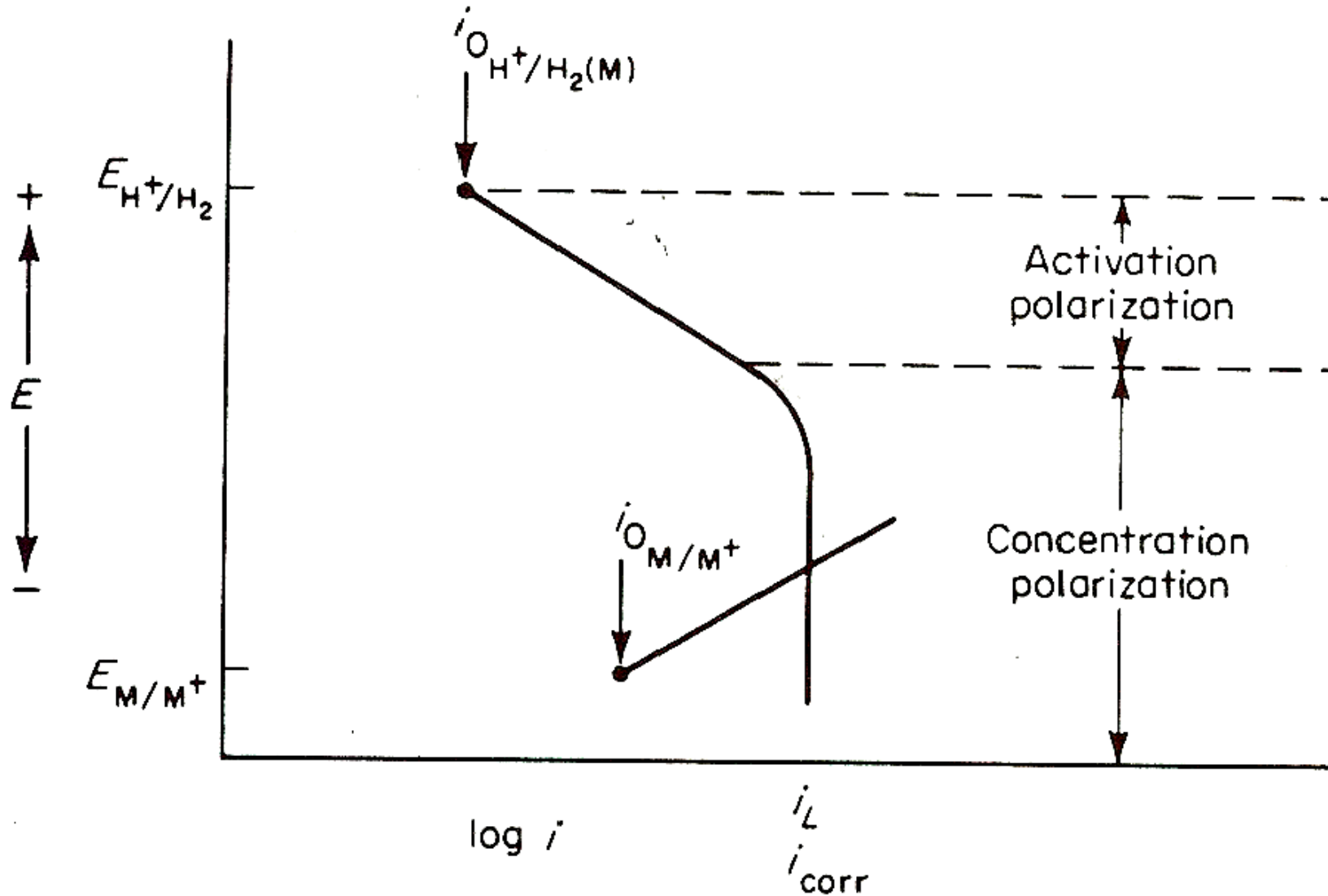


$$E_{corr} \rightarrow E_{couple} \rightarrow (i_{corr}(Zn) \rightarrow i_{corr}(Zn-Pt)) \rightarrow (i_{H_2}(Zn) \rightarrow i_{H_2}(Zn-Pt))$$

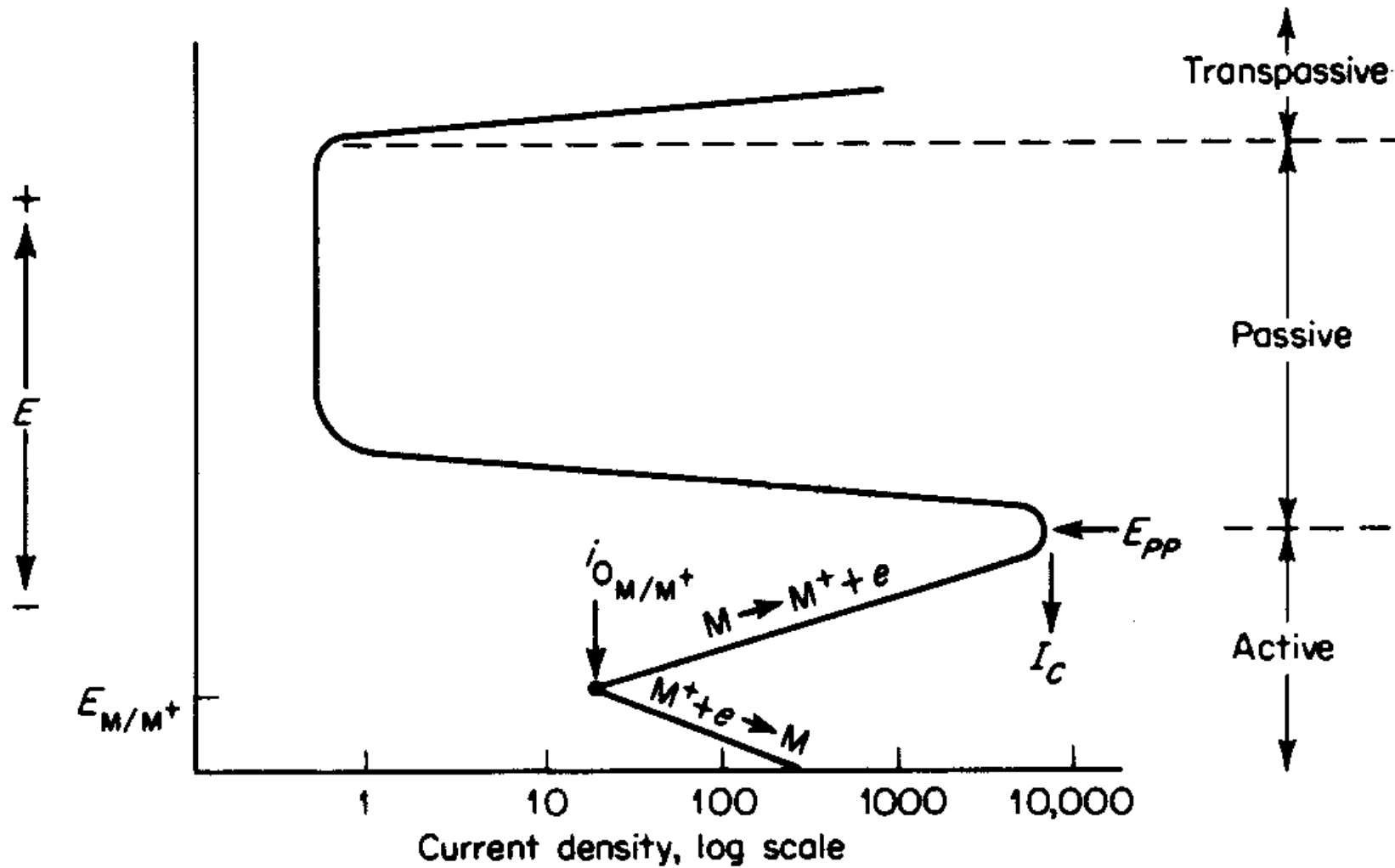
Effect of ratio of anodic and cathodic surface area to galvanic corrosion



Effect of concentration polarization

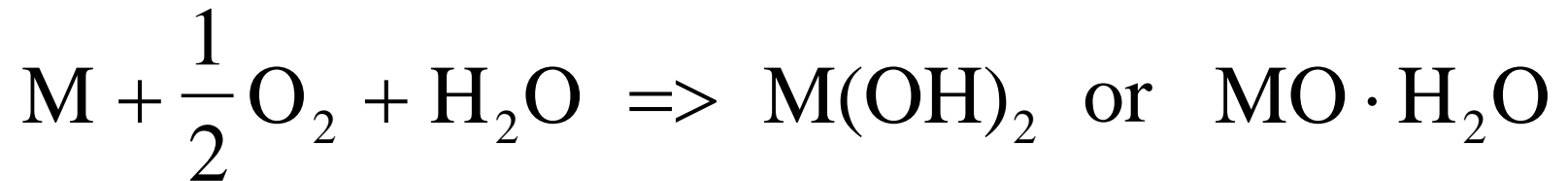


Passivation



Corrosion

- ❑ Corrosion is an electrochemical phenomenon.
- ❑ When a metal is immersed into a solution a dynamic equilibrium is established at the interface
- ❑ In water based solutions the following takes place



Corrosion

- ❑ In corrosion there are always two distinguishable locations (anode and cathode) where half reactions take place.
- ❑ In corrosion studies one can utilize Pourbaix-diagrams and mixed potential diagrams
- ❑ Different forms of corrosion are general corrosion, which includes galvanic corrosion and local corrosion, which includes pitting, crevice corrosion, intergranular corrosion, stress corrosion, erosion corrosion, cavitation corrosion and selective leaching.

Redox reactions

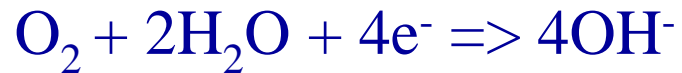
Anodic

$M \Rightarrow M^{n+} + ne^{-}$ so. production of electrons

Cathodic

Hydrogen reduction $2H^{+} + 2e^{-} \Rightarrow 2[H]_{\text{abs}} \text{ tai } H_2 \uparrow$

Oxygen reduction in neutral or basic solutions



Oxygen reduction in acidic solutions



Consumption of electrons

Corrosion

Example 1. $\text{Ni} + \text{H}_2\text{O} + \text{O}_2$

Dissolution: $\text{Ni} \Rightarrow \text{Ni}^{1+} + \text{e}^-$

Cathodic reaction: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \Rightarrow 4\text{OH}^-$

Thus: $2\text{Ni} + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \Rightarrow 2\text{Ni}^{1+} + 2\text{OH}^- \Rightarrow 2\text{Ni}(\text{OH})$

Example 2 Corrosion of Zn in O_2 containing HCl

Because $\text{HCl} \Rightarrow \text{H}^+ + \text{Cl}^-$ and $\text{pH} = -\log c_{\text{H}} < 7$

Following cathodic reactions

$2\text{H}^+ + 2\text{e}^- \Rightarrow \text{H}_2 \uparrow$ and

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \Rightarrow 2\text{H}_2\text{O}$ are possible.

As there are two reactions consuming the electrons and $I_{\text{ox}} = I_{\text{red}}$, then the dissolution rate of Zn increases.

Corrosion prevention = slowing down or preventing the ANODIC or CATHODIC reaction

Corrosion

Factors influencing

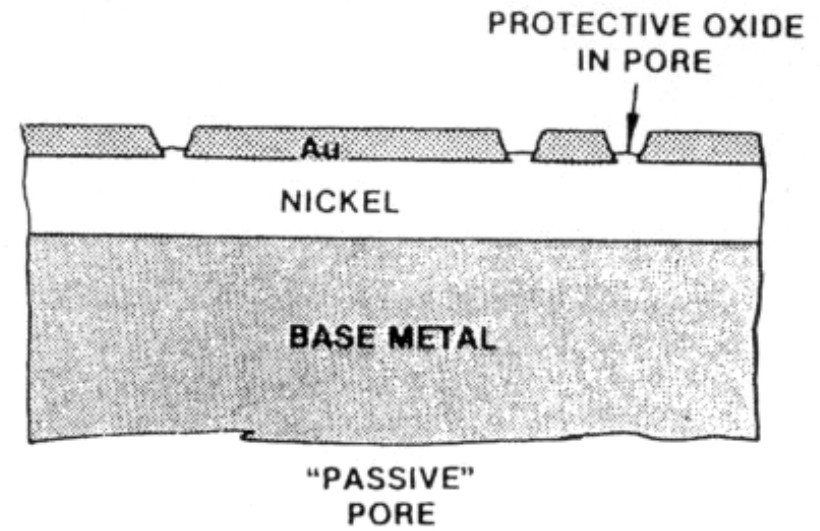
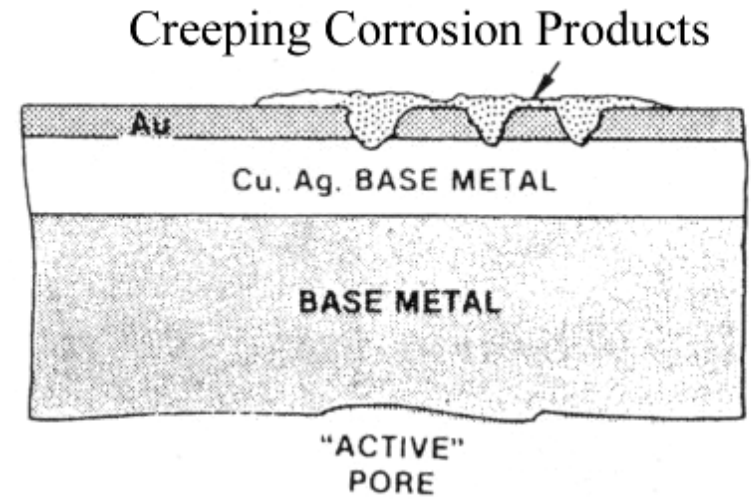
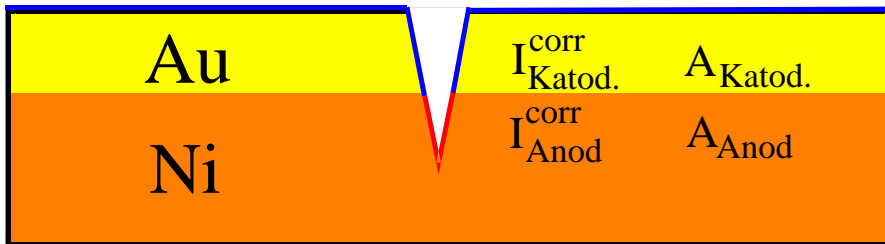
1. Environment

- Chemical composition (including impurities)
- State
- Temperature
- O₂- content
- pH
- Movement

2. Material

- Composition
- Microstructure
- Surface state (active/ passive)
- Stress state (internal and external stresses)
- Coupling to other materials (galvanic series)
- Continuity of the contact between environment (temporally and spatially)

Example



Summary

- Faraday's laws
- Kinetics of electrode reactions
- Exchange current density
- Polarization and overpotential
 - 📄 Activation and concentration overpotential
- Mixed potential theory
 - 📄 Evans diagrams - interpretation
- Corrosion – factors affecting it and prevention