SMM 3622

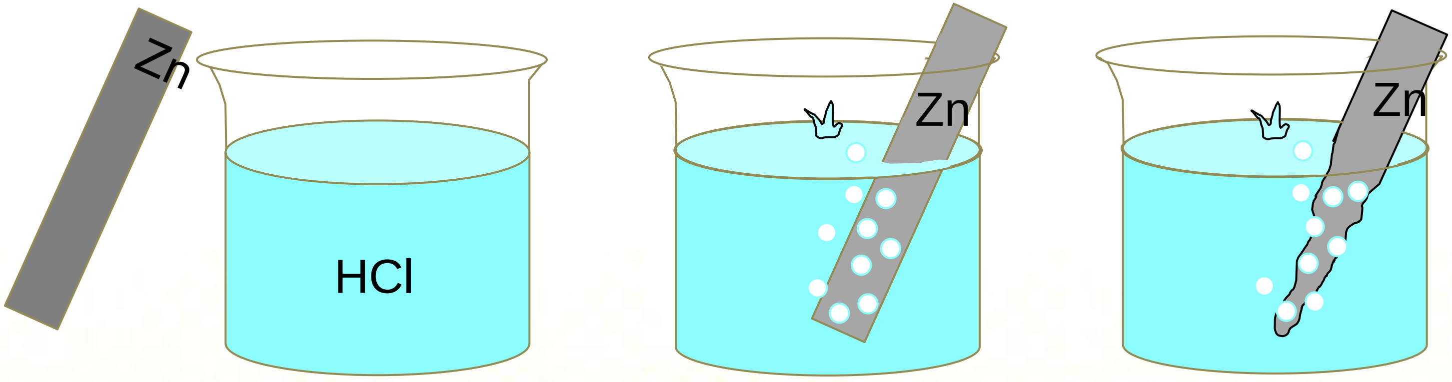
Materials Technology

4.2 Corrosion

Aqueous Corrosion:

Electrochemical reactions:

- ❑ Aqueous corrosion can be best described by this simple example:
    - ❑ If we take a piece of zinc (Zn) and place it in HCl, we will quickly notice a vigorous reaction and formation of bubbles on the surface of the Zn.



Corrosion of platinum (Pt) in HCl

- ☐ Now if we place a piece of Pt in HCl, what will happen?
- ☐ Pt does not corrode – does not take part in the electrochemical reaction
- ☐ Pt is a noble metal
- ☐ Pt acts as a reference to calculate emf value for other metals

What happens if we connect Zn and Pt in HCl solution?

1. If Zn and Pt are not connected

- ☐ There will be no reaction on Pt
- ☐ Dissolution of Zn

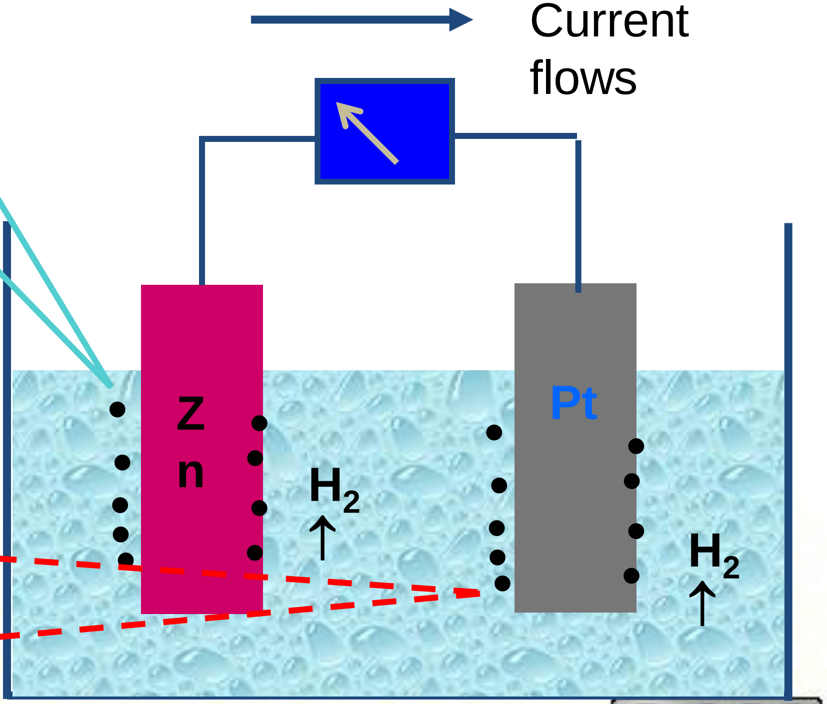
$Zn \rightarrow Zn^{+2} + 2e^-$

- ☐ H_2 evolution on Zn

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

2. If Zn and Pt are connected

- ☐ Current flows
- ☐ Dissolution of Zn
- ☐ Evolution of H_2 on Pt



Thermodynamics of aqueous Corrosion:

- ☐ Free energy changes provide *the driving force* and control the spontaneous direction for a chemical reaction.

- ☐ Corrosion reactions being electrochemical in nature, by calculating the free energy change it is possible to indicate whether or not the corrosion occurs.

- ☐ Thermodynamics. However, cannot predict the rate of the corrosion reaction (corrosion rate)

- The magnitude of the change in free energy (ΔG) is a measure of the tendency of the reaction.

- The more negative the value of ΔG the greater is the tendency for the reaction to proceed.

$$Mg + H_2O + {}^{1}\!/_{2}O_2 = Mg(OH)_2,\ \Delta G = -596 KJmol^{-1}$$

$$Cu + H_2O + {}^{1}\!/_{2}O_2 = Cu(OH)_2,\ \Delta G = -119 KJmol^{-1}$$

$$Au + {}^{3}\!/_{2}H_2O + {}^{3}\!/_{4}O_2 = Au(OH)_3,\ \Delta G = +66 KJmol^{-1}$$

- The free energy change accompanying a corrosion reaction can be calculated as follows:

$$\Delta G = -nFE$$

- E is known as the "*electrochemical cell potential*" in volts.

- Since an electrochemical reaction has 2 electrodes (anode and cathode), each of this electrode has its own potential developed at the electrode – electrolyte interface, called "half-cell potential".

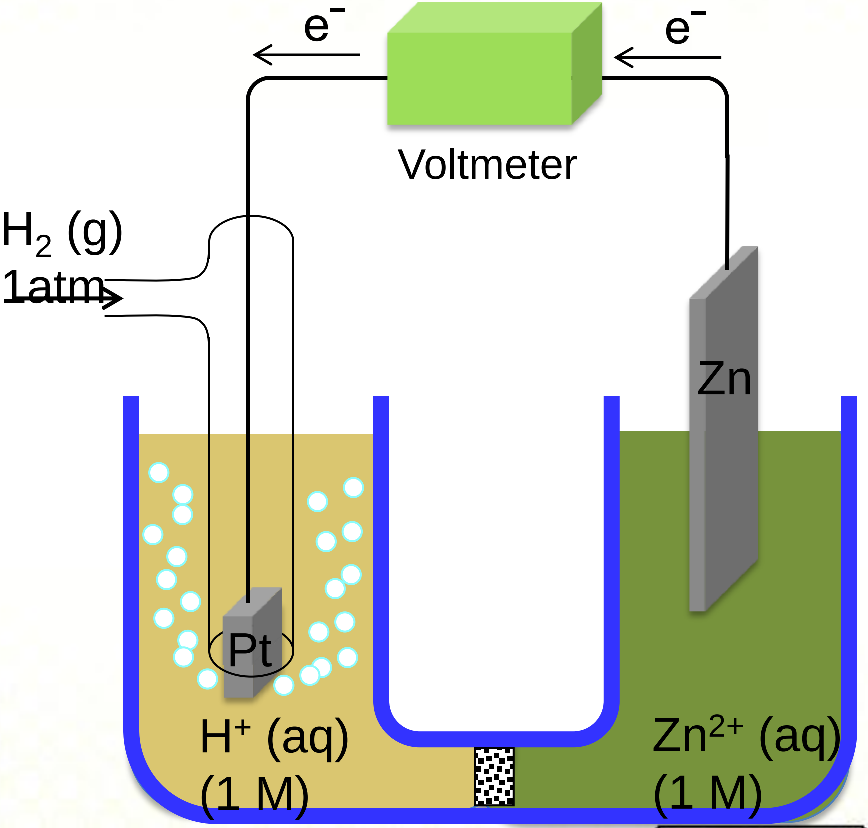
$$E = E_a + E_c$$

Electrochemical Force or EMF series:

- ❑ The *emf* series is an arrangement of the standard (unit activity or 1M conditions) half-cell potentials.

- ❑ The standard emf series is very useful to rank general resistance of metals to corrosion, but more practical rankings must be developed for each electrolyte of interest.

- ❑ Since it is impossible to measure the absolute value of any half-cell electrode potential, the values of half-cell potentials found in the emf series have been measured against a reference electrode (H_2).



The Standard emf Series

Increasingly inert (cathodic)

Increasingly active (anodic)

Electrode Reaction	*Standard Electrode Potential, V^0 (V)*
$Au^{3+} + 3e^- \longrightarrow Au$	+1.420
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
$Pt^{2+} + 2e^- \longrightarrow Pt$	~+1.2
$Ag^+ + e^- \longrightarrow Ag$	+0.800
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.771
$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH^-)$	+0.401
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.340
$2H^+ + 2e^- \longrightarrow H_2$	0.000
$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.126
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.136
$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.250
$Co^{2+} + 2e^- \longrightarrow Co$	−0.277
$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.403
$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.440
$Cr^{3+} + 3e^- \longrightarrow Cr$	−0.744
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.763
$Al^{3+} + 3e^- \longrightarrow Al$	−1.662
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.363
$Na^+ + e^- \longrightarrow Na$	−2.714
$K^+ + e^- \longrightarrow K$	−2.924

Anodic reaction:

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

Cathodic reaction:

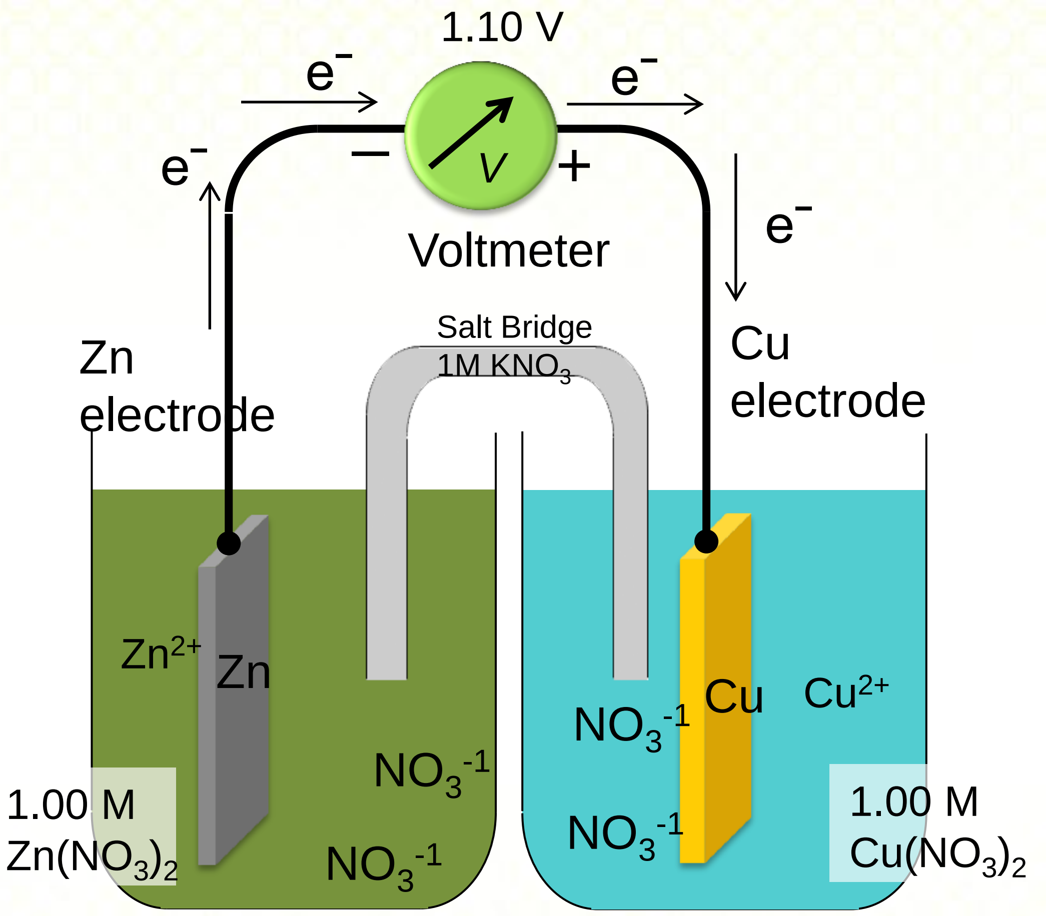
$Cu^{+2} + 2e^{-} \rightarrow Cu$

Overall reaction:

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

$E = E_a + E_c = -(-0.76) + 0.34$
$= 1.10 \text{ V}$

Electrochemical cell



Anode reaction
$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^{-}$

Cathode reaction
$Cu\ (aq) + 2e^{-} \rightarrow Cu^{2+}\ (s)$

This is also called Galvanic Cell

The direction of the reaction is reversed than the reduction reactions shown in emf table. So the

Dependence of cell potential on concentration:

- ❑ What happens to the cell potential when the concentration is not standard (not 1M)?

- ❑ We use the Nernst equation:

$$\boxed{E = E^o + \frac{0.0592}{n}\log C_{ion}}$$

Standard potential

E = *new emf of half-cell*
E^o = *standard electrode potential, emf of half cell*
n = *number of electrons transferred (e.g.* $M \rightarrow M^{n+} + ne^-$*)*
C_{ion} = *molar concentration of ions*

example

- One-half of an electrochemical cell consists of a pure nickel electrode in a solution of Ni^{2+} ions; the other half is a cadmium electrode immersed in a Cd^{2+} solution.

Compute the cell potential at 25°C if the Cd^{2+} and Ni^{2+} concentrations are 0.5 and 10^{-3} M respectively.

solution

First, assume the dilutions from 1M solutions will not affect the order of the potentials of Ni and Cd in the standard electrode potential series. Thus, Cd with more negative potential, -0.403 V will be the anode of the Ni-Cd electrochemical cell and Ni will be cathode.

Next use Nernst equation

$$\boxed{E = E^{o} + \frac{0.0592}{n} \log C_{ion}}$$

$E_A = - \{-0.403 \text{ V} + (0.0592/2) \log 0.5\} = 0.4119 \text{ V}$

$E_C = -0.250 + (0.0592/2) \log 10^{-3} \} = - 0.3388 \text{ V}$

$E_{cell} = E_A + E_C = 0.4119 + (-0.3388) = 0.0731 \text{ V}$

***The cadmium is oxidized and nickel is reduced.

Kinetics of Corrosion:

- ☐ Thermodynamics tell whether the metal will corrode under the given conditions or not
- ☐ Kinetics of corrosion tell the rate at which corrosion will occur
- ☐ Understanding of the fundamental laws of electrochemical reaction kinetics is essential to develop more corrosion-resistant materials and improve the methods of protection against corrosion.

Faraday’s Law:

- ☐ Electrochemical reactions either produce electrons (oxidation) or consume electrons (reduction).
- ☐ The rate of electron flow to or from a reaction interface is a measure of reaction rate.

- ☐ Electron flow is measured as current, I, in amperes.

$$\boxed{m = \frac{Ita}{nF}}$$

Q: charge (C),
F: Faraday’s number = 96,500 C/mol
n: number of electrons transferred,
m: mass of metal oxidised (corroded) (weight loss),
a or M: atomic weight of metal (g/mol) (***some ref sign as M for atomic weight)
I: current (A),
t: time (s)

- The corrosion rate ,r, can also be obtained by dividing the above equation by the surface area (dm^2 – (decimeter)^2) of the metal, A,

$$\boxed{r = \frac{m}{tA} = \frac{ia}{nF}}$$

(mdd: mg/dm^2/day)

- The corrosion rate in *mpy* (mils per year or millimeters per year mm/year) is given by:

$$\boxed{r = 0.129\frac{ia}{nD}}$$

(mpy: mills per year)

- Where D: density of the metal (g/cm^3)

$$r = \frac{m}{tA} = \frac{\frac{Ita}{nF}}{tA}$$

Sometimes the uniform aqueous corrosion of a metal is expressed in terms of a current density, *i which is often expressed in amperes per square centimeter. Now replacing I by iA*

$$r = \frac{m}{tA} = \frac{\frac{iAta}{nF}}{tA} = \frac{ia}{nF}$$

☐ The corrosion rate depends on the following:

1. *Electrode potential of anode*
2. *Electrode potential of cathode*
3. *Presence of intermediary resistive material (passive layer) – (protective surface layer). Corrosion resistance like Ni, stainless steel, Ni alloy etc.*
4. *Areas of electrode surfaces*
5. *Temperature*

High Temperature Corrosion

- The products of high temperature corrosion can potentially be turned to the advantage of the engineer.

- The formation of oxides on stainless steels, for example, can provide a protective layer preventing further atmospheric attack, allowing for a material to be used for sustained periods at both room and high temperature in hostile conditions.

POLARISATION:

- ☐ If equilibrium electrode is disturbed, a net current flows across its surface displacing the potential in a direction and to an extent depending on the direction and magnitude of the current.

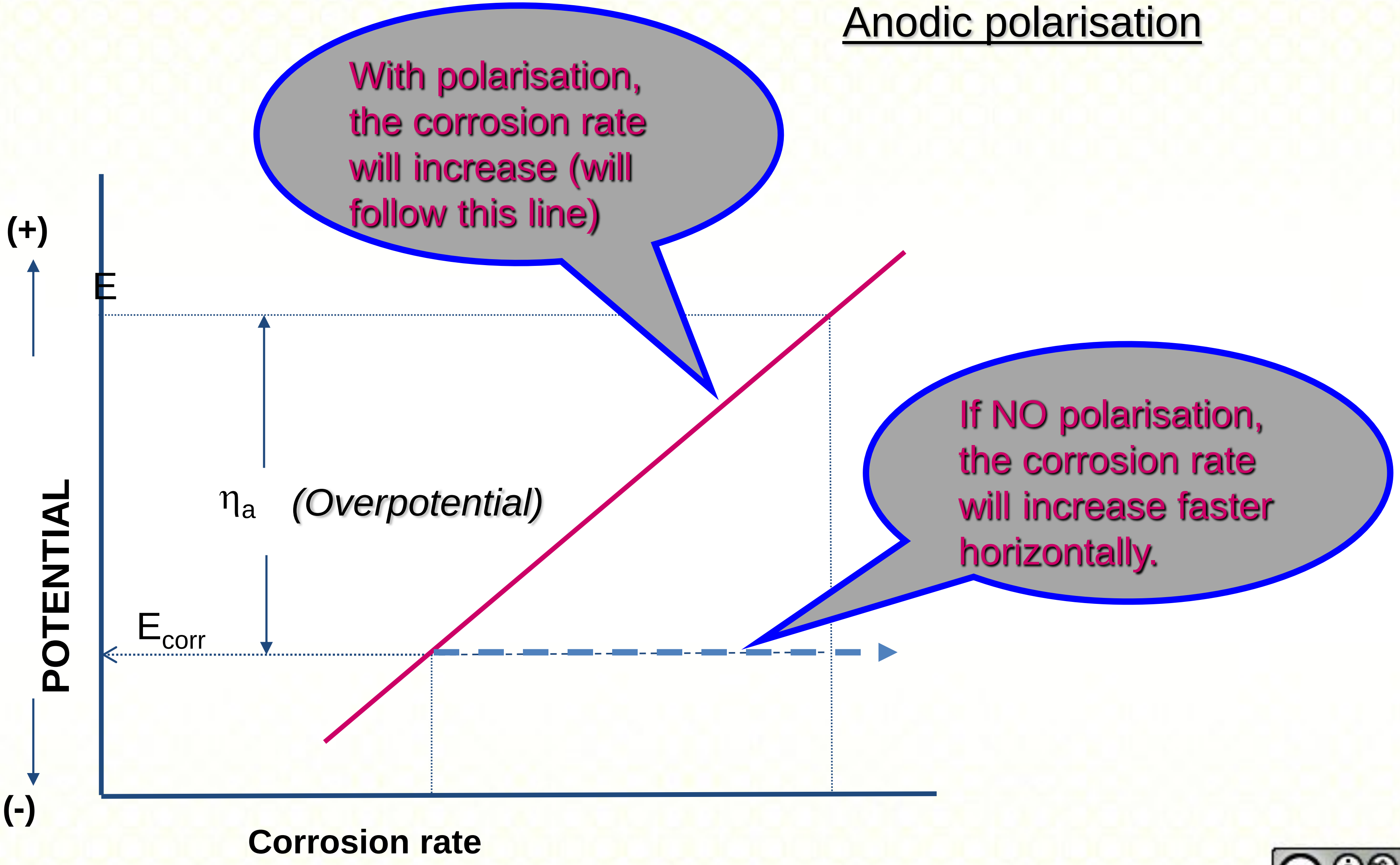
- ☐ This shift in potential is called *polarisation* and its value, η, is called *overpotential*.

- ☐ Polarization is the displacement of an electrode potential from its equilibrium value as a result of current flow.

- ☐ If electrons are made available (excess of electrons) to the cathode, the potential becomes <u>more negative</u>, meaning the reaction is not fast enough to accommodate all the available electrons. This is called *cathodic polarisation*.

- ☐ If there is a deficiency of electrons liberated by the anode, a <u>positive potential</u> is produced and is called *anodic polarisation* (represents a driving force for corrosion)

Anodic polarisation



With polarisation, the corrosion rate will increase (will follow this line)

If NO polarisation, the corrosion rate will increase faster horizontally.

PASSIVITY OF METALS

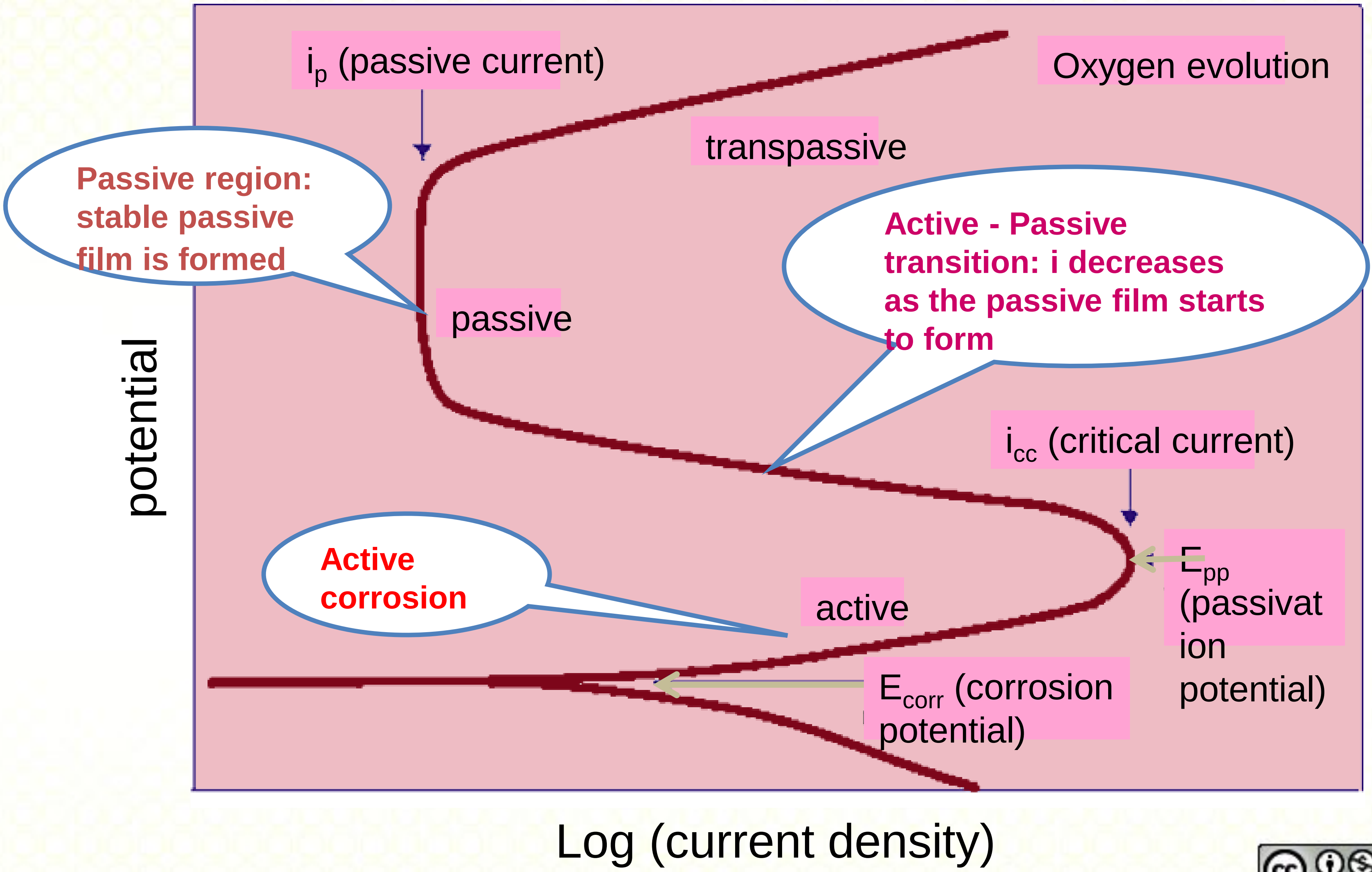
- ☐ Passivity refers to the phenomenon of *loss of chemical reactivity* of a metal in an environment where thermodynamically the reaction ought to have occurred.
- ☐ A passive metal is one that is active in the emf series but which corrodes a very low rate.
- ☐ Passivity results from the formation of a thin, oxidised and protective film on the metal surface
- ☐ Important engineering alloys such as Al, Ti, Ni, Cr can be passivated by direct exposure to oxidising media or by anodic polarisation.
- ☐ When a passive film is formed, the current density drops markedly due to the resistance of the film and its effect as a barrier to corrosion.

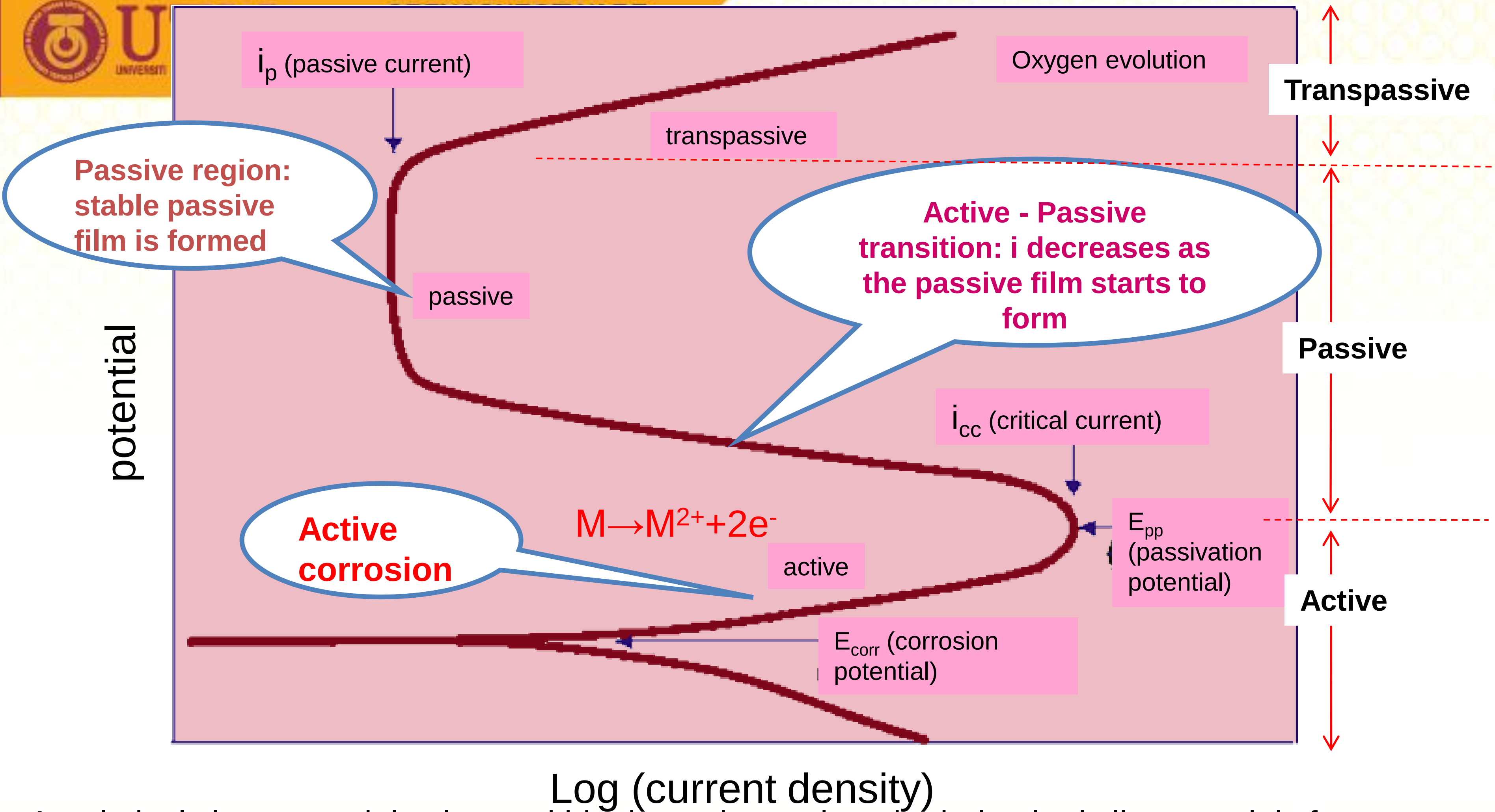
Passive metals and alloys– means very corrosion resistant

Active – Passive Corrosion Behaviour

- ☐ When the potential of a metal is anodically polarised, the current required for the shift has the polarisation curve as shown in the Figure below. The metal is in the active – passive state.

Polarization curve of a passive metal





-At relatively low potential values, within the active region, the behavior is linear as it is for normal metals.

- With increasing potential, the current density suddenly decreases to a very low values that remains independent of potential; this is termed the “passive” region.

- Finally even at higher potentials values, the current density again increases with potential in the “transpassive” region.

- ☐ Two types of Passivation exist:

1. Spontaneous Passivation:

- ☐ Some metals passivate in water if the pH is within ranges corresponding to potential – independent domains of stability for oxides or hydroxides (these domains appear in the *Pourbaix* diagrams).

- ☐ This passivation is due to the formation of thin protective oxide film.

- ☐ This oxide film must be coherent and adherent to the metal surface and must not be impaired by impurities (in the metal or environment).

2. Anodic Passivation:

- ❑ For some metals and their alloys, passivation is both pH and potential dependent.
- ❑ In this case, the metal may corrode at low potentials but can passivate by increasing its potential to a more positive value.

Pourbaix Diagram (E – pH diagram)

- a **Pourbaix diagram**, also known as a **potential/pH diagram**, maps out possible stable (equilibrium) phases of an aqueous electrochemical system.

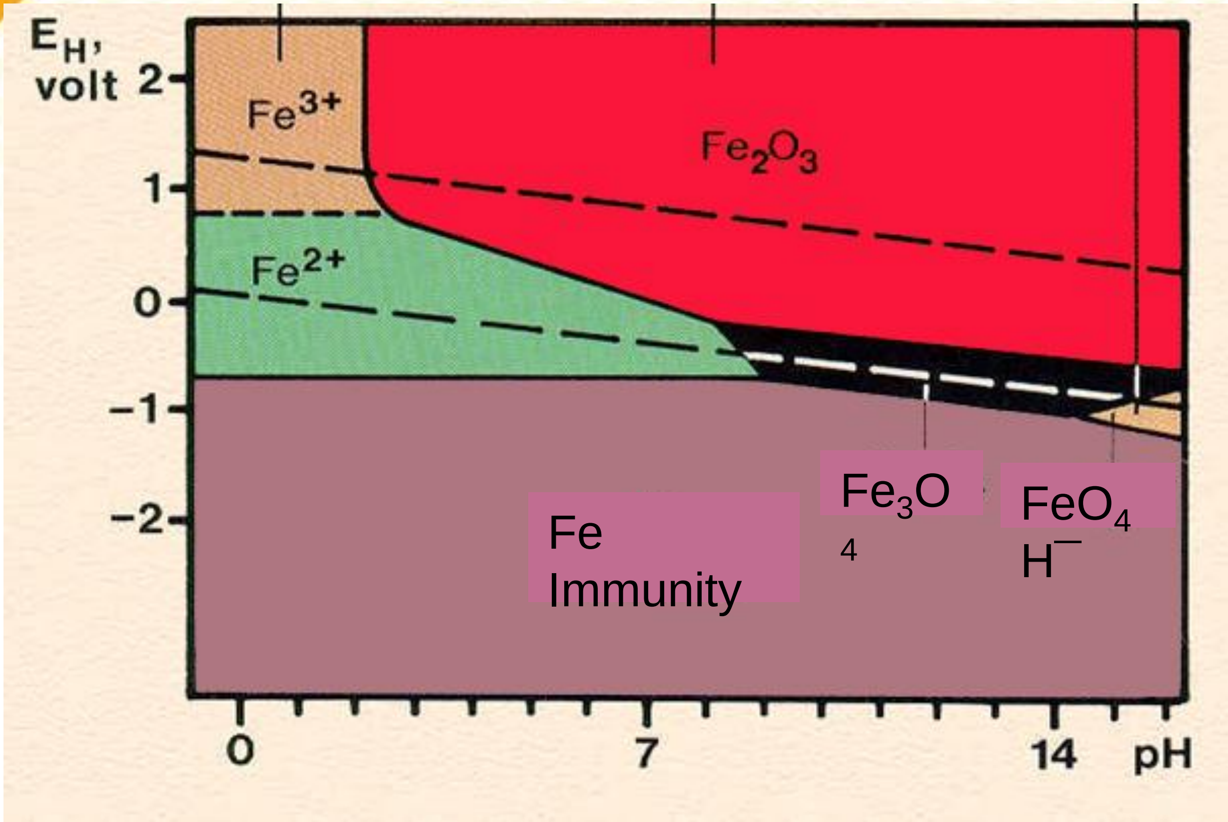
- *Pourbaix* diagrams are charts based on thermodynamic calculations which can be used to distinguish a corroding condition from a non-corroding condition.

- *Pourbaix* diagrams do not predict the kinetics of corrosion (rate of corrosion)

- The *Pourbaix* diagram of Fe in water is shown in the Figure below.

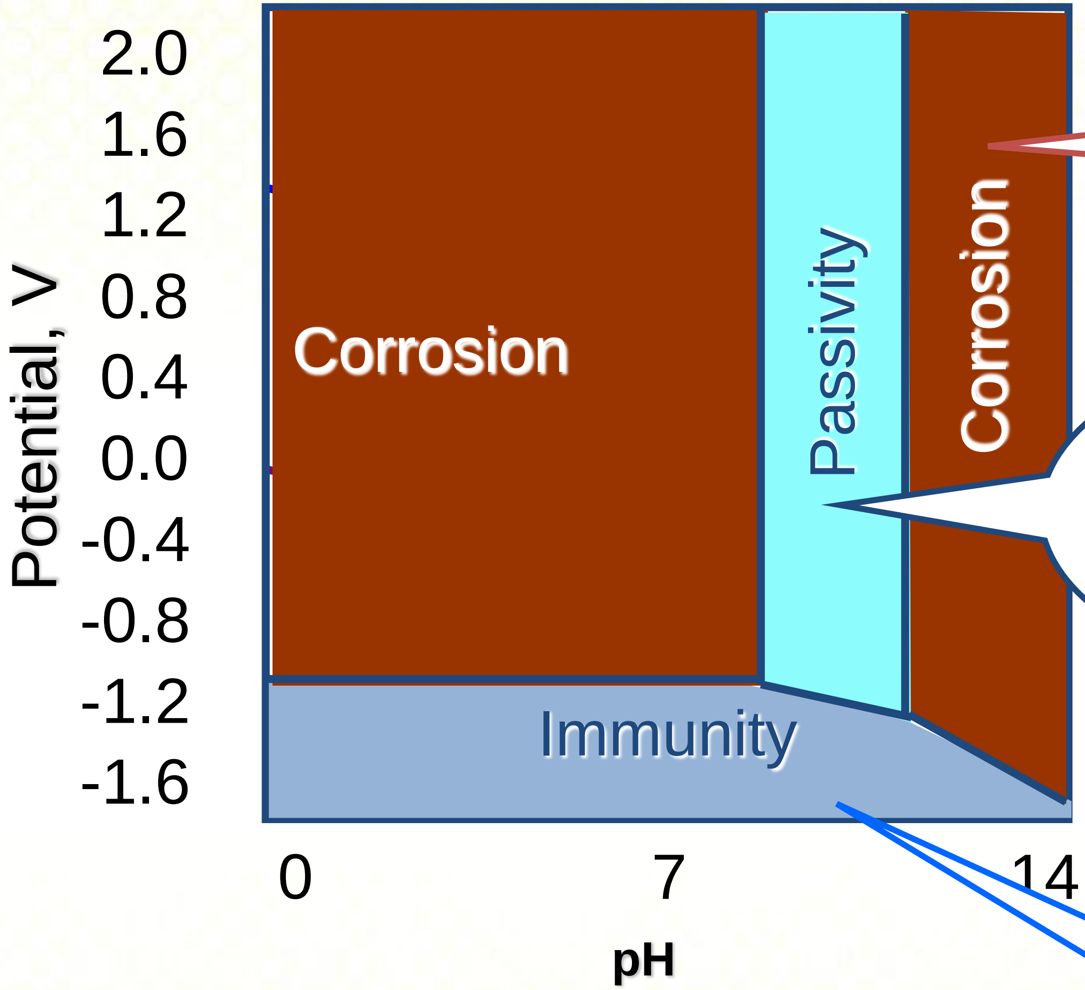
- The dashed lines represent the practical region of stability of water to oxidation or reduction.

Corrosion I **Passivation** **Corrosion II**



Potential-pH diagram for Fe-H_2O at 25°C; 10^{-6} M dissolved Fe

-A Pourbaix diagram indicates regions of "Immunity", "Corrosion" and "Passivity”.
-This diagram give a guide to the stability of a particular metal in a specific environment.
-Immunity means that the metal is not attacked.
-corrosion shows that general attack will occur.
-Passivation occurs when the metal forms a stable coating of an oxide or other salt on its surface, the best example being the relative stability of Al because of the alumina layer formed on its surface when exposed to air.



Corrosion is possible

Corrosion is possible, but likely to be stopped by solid corrosion product

Corrosion is impossible

E – pH diagram for Zn in water

- The possible regions of a Pourbaix diagram are:

1. Immunity: **if the metal is thermodynamically stable**
2. Passivity: **if the soluble ion is thermodynamically most stable**
3. Corrosion: **if an insoluble corrosion product is most stable**

Applications of Pourbaix diagrams

- Formulation of corrosion control techniques ((cathodic protection (CP), anodic protection (AP), Inhibitors (chemical compound to slow down the corrosion rate)
- Identify the possible corroding states of metal – media system

Limitations of Pourbaix diagrams

- Is for pure metals not alloys
- No kinetic information (rate of reaction) is given
- Effect of velocity on the stability of passivity is not taken into account