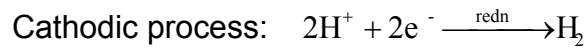
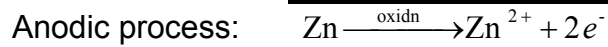
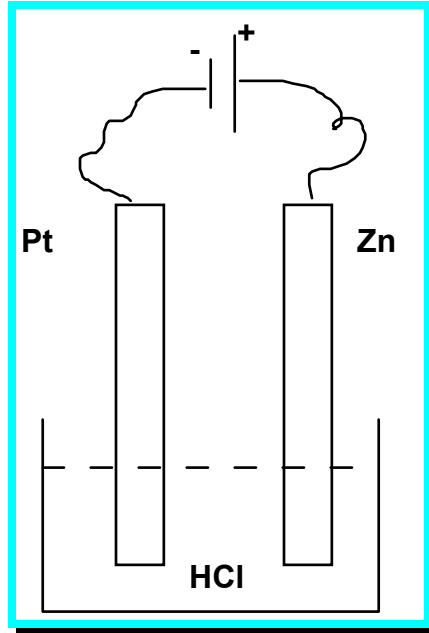


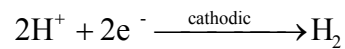
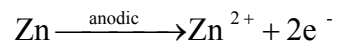
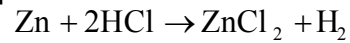
## CORROSION

Corrosion: Is the deterioration of metal due to its interaction with the surrounding environment.

### Electrochemical Nature of Corrosion

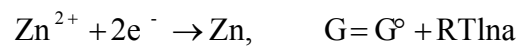


Example



#### (1) Metal-metal ion electrode

Example  $\text{Zn}/\text{Zn}^{2+}$



$\Delta G = G_{\text{products}} - G_{\text{reactants}}$  where  $a$  is the activity

$$\begin{aligned}
&= (G^{\circ}_{Zn} + RT \ln a_{Zn}) - (G^{\circ}_{Zn} + RT \ln a_{Zn^{2+}}) \\
&= (G^{\circ}_{Zn} - G^{\circ}_{Zn^{2+}}) + RT(\ln a_{Zn} - \ln a_{Zn^{2+}}) \\
&= \Delta G^{\circ} + RT \ln \frac{a_{Zn}}{a_{Zn^{2+}}}
\end{aligned}$$

If  $w = -\Delta G$  where "w" is the electrical work  
 $w = \text{charge} \times \text{potential}$  Example  $Zn^{2+} + 2e^{-} \rightarrow Zn$   
 $w = 2F \cdot e$   
 In general  $w = ZF \cdot e$   
 where Z is the valency  
 e is the electrode potential  
 and  $\Delta G = -ZF e$

Since we have  $\frac{\Delta G}{ZF} = -\frac{\Delta G^{\circ}}{ZF} + RT \ln \frac{a_{Zn}}{a_{Zn^{2+}}}$  divided by -ZF

$$-\frac{\Delta G}{ZF} = -\frac{\Delta G^{\circ}}{ZF} - \frac{RT}{ZF} \ln a_{Zn}/a_{Zn^{2+}}$$

$$e = e^{\circ} - \frac{RT}{ZF} \ln a_{Zn}/a_{Zn^{2+}}$$

Since the activity of pure solid = 1

$$e = e^{\circ} + \frac{RT}{ZF} \ln a_{Zn^{2+}} \quad \text{The Nernst equation for the zinc electrode}$$

## (2) The Chlorine Electrode



$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

$$\Delta G = [G^\circ_{\text{Cl}^-} + RT \ln a_{\text{Cl}^-}] - [G^\circ_{\text{Cl}} + RT \ln a_{\text{Cl}}]$$

$$\Delta G = [G^\circ_{\text{Cl}^-} + RT \ln a_{\text{Cl}^-}] - [G^\circ_{\text{Cl}} + RT \ln a_{\text{Cl}}]$$

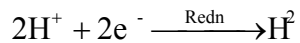
$$\Delta G = DG^\circ + RT \ln \frac{a_{\text{Cl}^-}}{a_{\text{Cl}}}$$

$$\Delta G = -w = -Zfe$$

$$\therefore e = -\frac{\Delta G^\circ}{ZF} - \frac{RT}{ZF} \ln \frac{a_{\text{Cl}^-}}{a_{\text{Cl}}} \quad \text{but } a_{\text{Cl}} = 1$$

$$e = e^\circ - \frac{RT}{ZF} \ln a_{\text{Cl}^-}$$

### (3) The Hydrogen electrode



$$DG = DG^\circ + RT \ln \frac{P_{\text{H}_2}}{(a_{\text{H}^+})^2}$$

$$-\frac{\Delta G}{ZF} = -\frac{\Delta G^\circ}{ZF} - \frac{RT}{ZF} \ln \frac{P_{\text{H}_2}}{(a_{\text{H}^+})^2}$$

$$-\frac{\Delta G}{ZF} = -\frac{\Delta G^\circ}{ZF} - \frac{RT}{ZF} \ln \frac{P_{\text{H}_2}}{(a_{\text{H}^+})^2}$$

$$e = e^\circ - \frac{RT}{ZF} \ln \frac{1}{(a_{\text{H}^+})^2} \quad \text{where } P_{\text{H}_2} = 1$$

since  $e^0$  of hydrogen electrode = Zero

$$e = \frac{RT}{ZF} \ln (a_{H^+})^2$$

$$= \frac{2.303RT}{2F} \log (a_{H^+})^2 \quad \frac{2.303RT}{F} = 0.06V \quad \text{at } 30^\circ C$$

$$e = 0.06 \log a_{H^+}$$

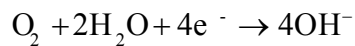
but  $pH = -\log a_{H^+}$

and thus  $e = -0.06 pH$  Nernst equation for hydrogen electrode in terms of pH.

N.B.

Electromotive series according to $e^0$		Values of $2.303 RT/F$	
Zn	$e^0 = -0.76 V$	1) AT $18^\circ C, 20^\circ C$	0.058 V
		2) AT $25^\circ C$	0.059 V
H <sub>2</sub>	$e^0 = \text{Zero}$	3) AT $30^\circ C$	0.060 V
		4) AT $35^\circ C$	0.061 V
Cu	$e^0 = +0.34 V$	i.e. for each $5^\circ C$ rise add 0.001V	

#### (4) The Oxygen Electrode



$$\Delta G = \Delta G^\circ + RT \ln \frac{(a_{OH^-})^4}{(P_{O_2})(a_{H_2O})^2}$$

Since H<sub>2</sub>O is present in excess therefore  $a_{H_2O} = 1$

$$e = e^\circ - \frac{RT}{4F} \ln \frac{(a_{\text{OH}^-})^4}{P_{\text{O}_2}} \quad P_{\text{O}_2} = 1$$

$$e = 0.401 - 0.06 \log a_{\text{OH}^-} \quad \text{where } e^\circ = 0.401 \text{ for } \text{O}_2/\text{elec.}$$

$$e = 0.401 - 0.06 \log \frac{10^{-14}}{a_{\text{H}^+}} \quad [\text{H}^+][\text{OH}^-] = K_w = 10^{-14}$$

$$= 0.401 - 0.06 \log 10^{-14} + 0.06 \log a_{\text{H}^+} \quad \therefore [\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]}$$

$$= 1.241 + 0.06 \text{ pH}$$

$e = 1.241 - 0.06 \text{ pH}$  Is the Nernst equation of oxygen electrode

### (5) The Oxygen Hydrogen Cell [O<sub>2</sub>/H<sub>2</sub> Cell]

$$e_{(\text{H}_2)} = -0.06 \text{ pH} \quad e_{(\text{O}_2)} = 1.241 - 0.06 \text{ pH}$$

$$\begin{aligned} \text{EMF} &= e_{\text{cathode}} - e_{\text{anode}} \\ &= (1.241 - 0.06 \text{ pH}) - (-0.06 \text{ pH}) \\ \text{EMF} &= 1.241 \text{ V} \end{aligned}$$

and hence one may say that the EMF of O<sub>2</sub>/H<sub>2</sub> cell is pH-independent.

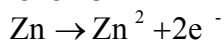
### Potential / pH Diagrams

The two lines in the potential -pH diagram represent the reduction of oxygen and hydrogen ions and they are parallel. The distance between the two lines is "1.241 V" which is the EMF of O<sub>2</sub>/H<sub>2</sub> cell.

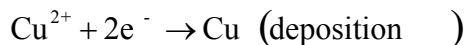
According to the electromotive series

	Zn <sup>2+</sup> /Zn	e° = -0.76	anodic active
Displacement	H <sup>+</sup> /H <sub>2</sub>	e° = Zero	
	Cu <sup>2+</sup> /Cu	e° = +0.34	Noble

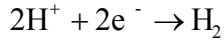
When Zn is contact with copper in HCl Zn will go always into dissolution as follows



On the other hand Cu will deposit as follows



If the medium is acidic hydrogen evolution will occur

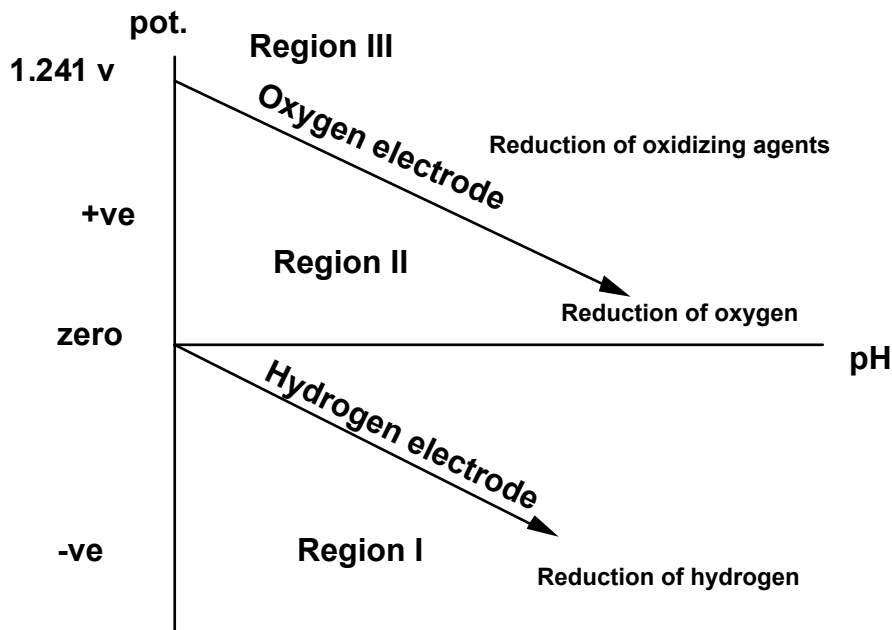
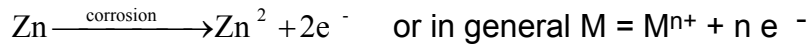


### Condition for Corrosion to occur

The potential of the anode of galvanic cell of corrosion (active) must be "more negative" than the potential of the cathode (noble).

### Anodic Reaction (Corrosion)

There is only one possibility

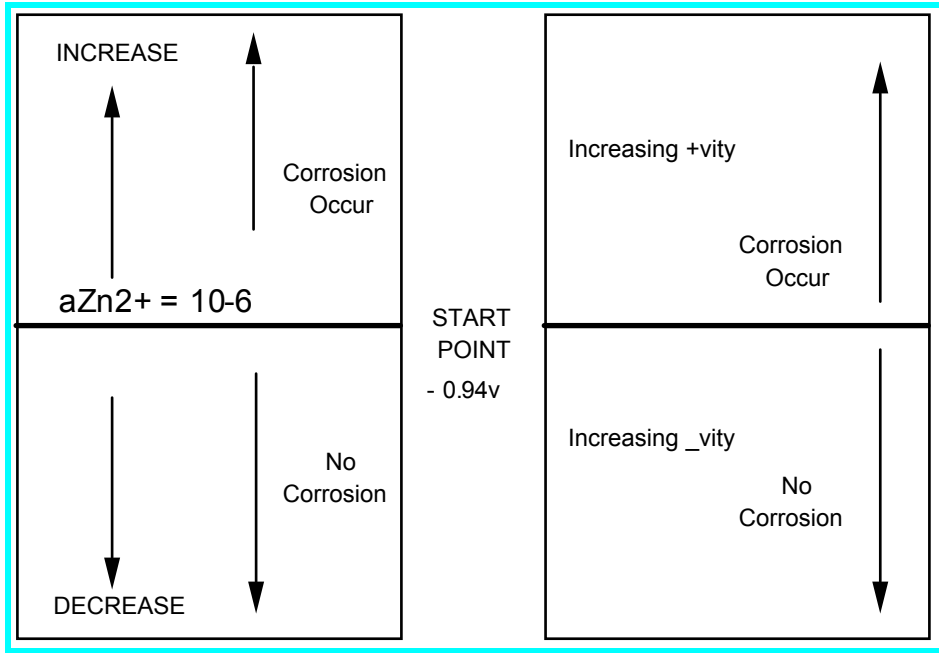


### Cathodic Reaction

According to the outlined diagram There are three possibilities

- (1) If the potential of the active anode is present in region I  
The Cathodic processes are:
  - Reduction of hydrogen ion ( $\text{H}^+$ )
  - Reduction of oxygen ( $\text{O}_2$ )
  - Reduction of the oxidizing agent
- (2) If the potential of the active anode is present in region II  
Cathodic processes are:
  - Reduction of oxygen
  - Reduction of the oxidizing agent
- (3) Finally if the potential of the active anode is present in region III  
Only reduction of the oxidizing agent can occur.

## Thermodynamic Calculations



For example Zinc at 30 °C  
Nernst equation:

$$e = e^\circ + \frac{0.060}{2} \log a_{Zn^{2+}}$$

$$= 0.76 + 0.03 \log a_{Zn^{2+}}$$

At "the beginning of corrosion"

$$e = -0.76 + 0.03 \log 10^{-6}$$

$$e = -0.76 - 0.18 = -0.94 \text{ v}$$

Reversible equilibrium potential of Zn electrode at the beginning of corrosion is = -0.94 v.

No Corrosion

- $a_{Zn^{2+}} \ 10^{-7}$
- $10^{-8}$
- $10^{-9}$
- $10^{-10}$

For example

$$e = -0.76 + 0.03 \log 10^{-10}$$

$$e = -0.76 - 0.3 = -1.06 \text{ v}$$

Corrosion occur

$$a_{Zn^{2+}} = 10^{-6}, 10^{-5}, 10^{-4}, \dots$$

$$e = -0.76 + 0.03 \log 10^{-4}$$

$$e = -0.76 - 0.12 = -0.88 \text{ v.}$$

### Thermodynamic Predictions for Corrosion

Can zinc corrode with H<sub>2</sub> evolution in solutions of pH 2, 7 and 10?

Beginning of corrosion

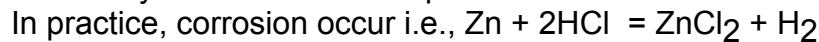
$$e_{(\text{anode})\text{Zn}} = -0.94\text{V.}$$

#### (i) In Acidic Solution pH 2

$$e_{\text{cathode(H)}} = -0.06 \text{ pH} = -0.06 \times 2 = 0.12 \text{ v.}$$

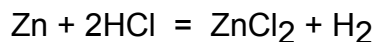
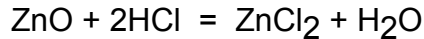
$e_{\text{anode}}$  is more negative than  $e_{\text{cathode}}$

Thermodynamic calculations predict corrosion



Thermodynamic prediction is correct

Even if zinc metal is covered by a layer of ZnO



#### (ii) In Neutral Solution pH 7

$$e_{\text{cathode(H)}} = -0.06 \text{ pH} = -0.06 \times 7 = -0.42 \text{ v.}$$

$e_{\text{anode}}$  is more negative than  $e_{\text{cathode}}$

Thermodynamic calculations predict corrosion

In practice, no corrosion occur.

Thus thermodynamic prediction is not correct, why?

Zinc in neutral medium is covered by a layer of oxide that is insoluble in neutral medium. This oxide layer protects the metal against corrosion.

#### (iii) In Alkaline Solution pH 10

$$e_{\text{cathode(H)}} = -0.06 \text{ pH} = -0.06 \times 10 = -0.6 \text{ v.}$$

$e_{\text{anode}}$  is more negative than  $e_{\text{cathode}}$

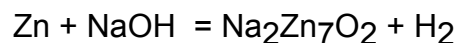
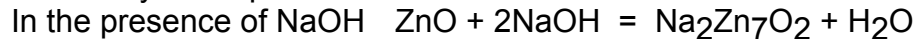
Thermodynamic calculations predict corrosion.

In practice, corrosion occur



Sodium Zincate

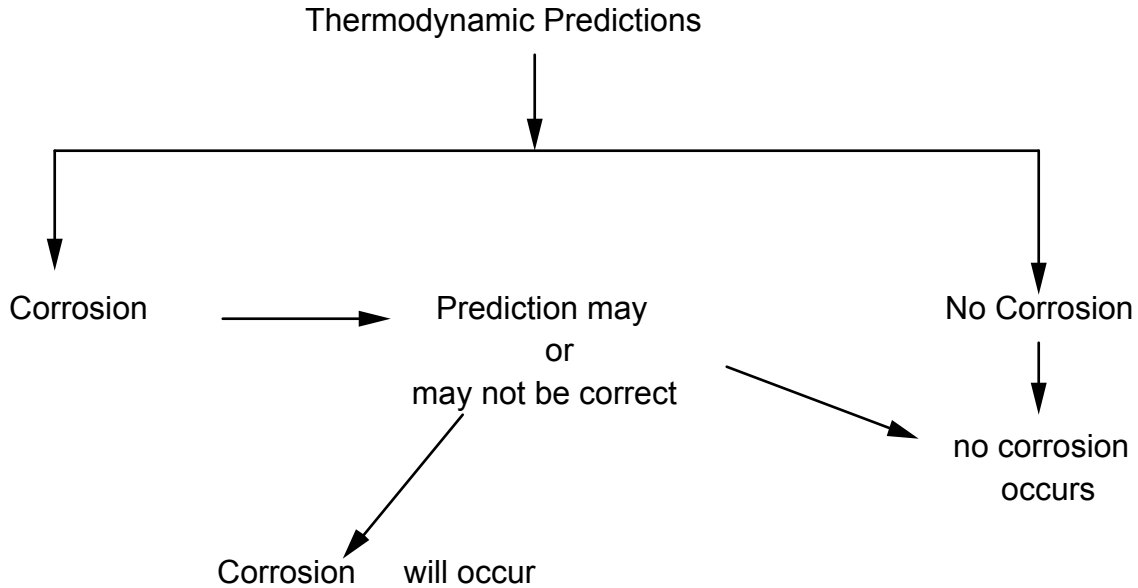
Thermodynamic prediction is correct



\* *Are thermodynamic predictions always correct? No, not always.*

### Thermodynamic Calculations Predicts





### Thermodynamic Calculation with Cu

Can Cu corrode with H<sub>2</sub> evolution in acid, neutral and alkaline media (pH values 2, 7 and 10).

#### Beginning of Corrosion

$$\begin{aligned}
 e_{\text{anode (Cu)}} &= +0.34 + 0.06 / 2 \log 10^{-6} \\
 &= 0.34 - 0.18 \\
 e &= +0.16 \text{ v}
 \end{aligned}$$

#### Acid Solution pH 2

$$\begin{aligned}
 e_{\text{cathode (H}_2)} &= -0.06 \text{ pH} \\
 &= -0.12 \text{ V}
 \end{aligned}$$

$e_{\text{anode}}$  is more positive than  $e_{\text{cathode}}$

Thus Thermodynamic calculations predict "no corrosion" and in practice this is true. Thus Thermodynamic prediction is correct.

#### Neutral Solution pH 7

$$\begin{aligned}
 e_{\text{cathode (H}_2)} &= -0.06 \text{ pH} \\
 &= -0.06 \times 7 = -0.42 \text{ V}
 \end{aligned}$$

$e_{\text{anode}}$  is more positive than  $e_{\text{cathode}}$

Thermodynamic predicts "no corrosion" and in practice, this is true. Thermodynamic prediction is correct.

#### Alkaline Solution pH 10

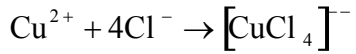
$$\begin{aligned}
 e_{\text{cathode (H)}} &= -0.06 \text{ pH} \\
 &= -0.06 \times 10 = -0.6 \text{ v}
 \end{aligned}$$

$e_{\text{anode}}$  is more positive than  $e_{\text{cathode}}$

Thermodynamic predicts "no corrosion" and this is true in practice. Thermodynamic prediction is correct.

### Special Case for Corrosion of Cu with H<sub>2</sub> evolution

If Cu is present in a very strong acid it will form a complex and hence little corrosion of Cu by H<sub>2</sub> evolution will occur.



Cu<sup>2+</sup> with conc. = 10<sup>-12</sup>

$$e_{\text{anode}}(\text{Cu}) = +0.34 + \frac{0.06}{2} \log 10^{-12}$$
$$= 0.34 - 12 \times 0.03 = -0.02 \text{ V}$$

$$e_{\text{cathode}}(\text{H}_2) = -0.06 \text{ pH}$$

In very strong acid pH = Zero

$$e_{\text{cathode}}(\text{H}_2) = \text{Zero}$$

$e_{\text{anode}}$  is more negative than  $e_{\text{cathode}}$

Therefore little corrosion of Cu with H<sub>2</sub> evolution can occur and in practice there is little corrosion.

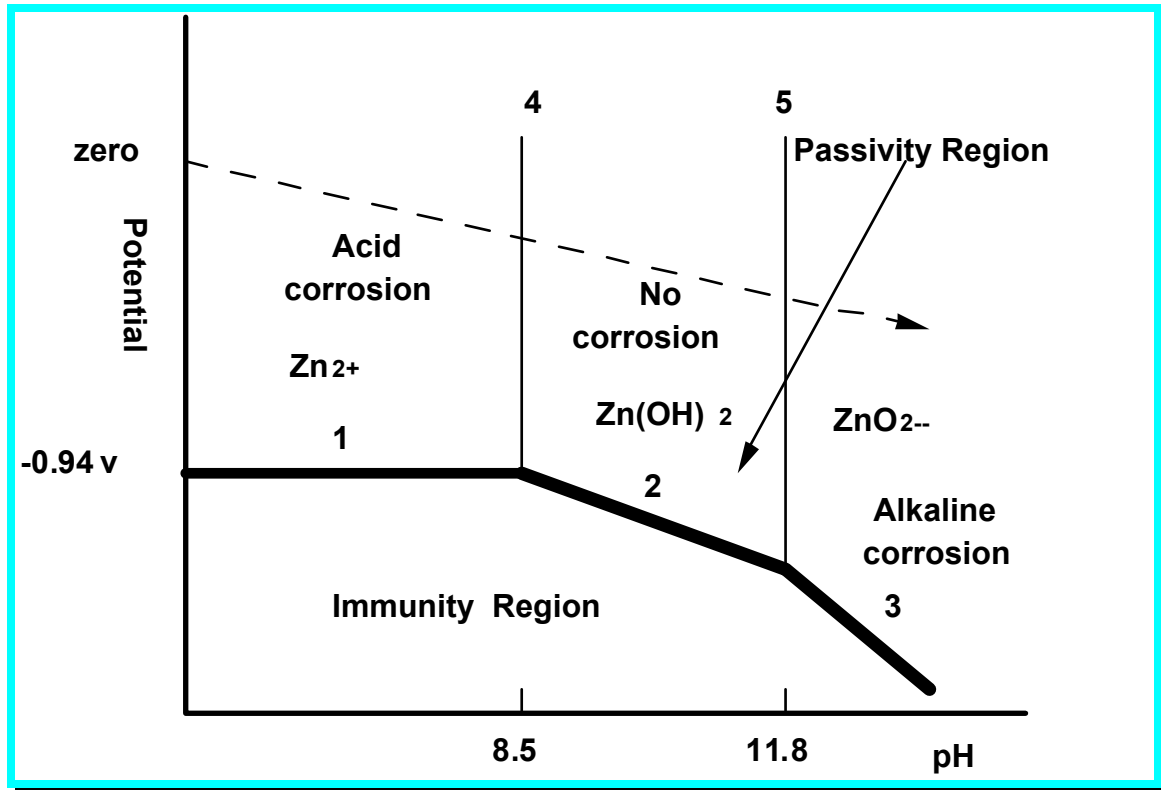
## The Pourbaix Diagram (Potential / pH diagram)

Interaction between Metal and H<sub>2</sub>O

Example: Zn / H<sub>2</sub>O system

Types of interactions

**(A) Electrochemical** (Electrons evolved)



- (1)  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$  independent of pH
- (2)  $\text{Zn} + 2\text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2 + 2e^- + \text{H}^+$  pH dependent
- (3)  $\text{Zn} + 2\text{H}_2\text{O} \rightarrow \text{ZnO}_2^{--} + 4\text{H}^+ + 2e^-$  pH dependent

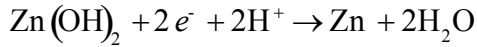
**(B) Chemical reactions (No electrons)**

- (4)  $\text{Zn}(\text{OH})_2 + 2\text{H}^+ = \text{Zn}^{2+} + 2\text{H}_2\text{O}$
- (5)  $\text{Zn}(\text{OH})_2 \rightarrow \text{ZnO}_2^{--} + 2\text{H}^+$

**Reaction (1)**

$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$   
 $e_{(\text{Zn})}$  at the beginning of corrosion = -0.94 v

**Reaction (2)**



$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Zn}][\text{H}_2\text{O}]^2}{[\text{Zn}(\text{OH})_2][\text{H}^+]^2}$$

but  $\Delta G = -ZFe$

$$e = \frac{DE^\circ}{2F} - \frac{RT}{2F} \ln \frac{[\text{Zn}][\text{H}_2\text{O}]^2}{[\text{Zn}(\text{OH})_2][\text{H}^+]^2}$$

$$= e^\circ - \frac{RT}{2F} \ln \frac{[\text{Zn}]}{[\text{Zn}(\text{OH})_2]} + \frac{RT}{2F} \ln [\text{H}^+]^2$$

$$= \text{Const.} + \frac{2.303RT}{F} \log [\text{H}^+]$$

at 30 °C

$$e = \text{Const.} - 0.06\text{pH}$$

$$\frac{de}{d\text{pH}} = -0.06\text{V}$$

The increase of pH by "1" unit makes the electrode potential of reaction (2) more negative by -0.06 V.

### Reaction (3)

Equilibrium between Zn and Zincate ions ( $\text{ZnO}_2^{--}$ )



$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Zn}][\text{H}_2\text{O}]^2}{[\text{ZnO}_2^{--}][\text{H}^+]^4}$$

$$\Delta G = -2Fe$$

$$e = e^\circ - \frac{RT}{2F} \ln \frac{[\text{Zn}][\text{H}_2\text{O}]^2}{[\text{ZnO}_2^{--}][\text{H}^+]^4}$$

$$\Delta G = -2Fe$$

$$e = e^\circ - \frac{RT}{2F} \ln \frac{[\text{Zn}][\text{H}_2\text{O}]^2}{[\text{ZnO}_2^{--}]} + \frac{RT}{2F} \ln [\text{H}^+]^4$$

$$e = \text{const.} + \frac{2.303RT}{2F} \log [\text{H}^+]^4$$

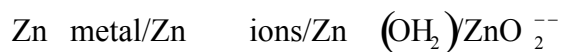
$$= \text{const.} + 0.12 \log [\text{H}^+]$$

$$= \text{const.} - 0.12 \text{ pH}$$

$$\frac{de}{dpH} = -0.12V$$

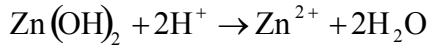
Thus increase of pH by one unit makes the electrode potential of reaction (3) more negative by -0.12.

In aqueous solution may be present as:



### Chemical Reactions

Reaction (4) equilibrium between  $\text{Zn}^{2+}/\text{Zn}(\text{OH})_2$   
(independent of potential)



$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Zn}^{2+}][\text{H}_2\text{O}]^2}{[\text{Zn(OH)}_2][\text{H}^+]^2}$$

At equilibrium  $\Delta G = \text{Zero}$

$$\frac{-\Delta G^\circ}{2.303RT} = \log \frac{[\text{Zn}^{2+}]}{[\text{Zn(OH)}_2]} - \log [\text{H}^+]^2$$

$$= \log \frac{[\text{Zn}^{2+}]}{[\text{Z(OH)}_2]} + 2\text{pH}$$

Now we want to calculate the pH at which equilibrium between  $\text{Zn}^{2+}$  and  $\text{Zn(OH)}_2$  takes place.

This pH is independent of potential (chemical reaction).

$\Delta G^\circ$  can be calculated from thermodynamic tables.

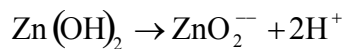
$[\text{Zn}^{2+}] = 10^{-6}$  at the beginning of corrosion of  $[\text{Zn(OH)}_2] = 1$

The resulting value of pH = 8.5.

### Chemical Reaction (5)

Equilibrium between

Equilibrium between  $\text{Zn(OH)}_2/\text{ZnO}_2^{--}$



$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{ZnO}_2^{--}][\text{H}^+]^2}{[\text{Z(OH)}_2]}$$

At equilibrium  $\Delta G = \text{Zero}$

$$\begin{aligned}
-\frac{\Delta G^\circ}{2.303RT} &= \log \frac{[\text{ZnO}_2^{--}][\text{H}^+]^2}{[\text{Zn}(\text{OH})_2]} \\
&= \log \frac{[\text{ZnO}_2^{--}]}{[\text{Zn}(\text{OH})_2]} + 2 \log \text{H}^+ \\
&= \log \frac{[\text{ZnO}_2^{--}]}{[\text{Zn}(\text{OH})_2]} - 2\text{pH}
\end{aligned}$$

$\Delta G^\circ$  is calculated from the thermodynamic tables.

$[\text{ZnO}_2^{--}] = 10^{-6}$  at the beginning of corrosion and  $[\text{Zn}(\text{OH})_2] = 1$

The pH value calculated for this equilibrium = 11.8.

### Uses of Pourbaix Diagram

#### (1) Determination of the Stable Species

If we know the potential and pH then the intersection indicates that the stable species are  $\text{ZnO}_2^{--}$  as shown in the diagram.

#### (2) Cathodic Protection

- (i) Keep pH constant
- (ii) Change the potential in the negative direction to the immunity region.

#### (3) Anodic Protection

- (i) Keep the potential constant
- (ii) Increase pH to the passivity region.

### Limitation of Thermodynamic Treatment of Corrosion

#### (1) Thermodynamic predictions are not always correct.

If Predictions say No

This is definite No

If Predictions say Yes

This may be or may not

#### (2) Thermodynamic calculations give no information on "Rate of Corrosion".

There are two possibilities for  $\Delta G$

(a)  $\Delta G$  is -ve then E is +ve where  $\Delta G = ZFE$

Spontaneous corrosion will occur

(b)  $\Delta G$  is +ve then E is -ve

Non spontaneous corrosion

This means that thermodynamic gives tendency for corrosion if  $\Delta G$  is -ve and no corrosion if  $\Delta G$  is +ve.

But this is wrong as shown from the following example. Suppose that we have Zn and Fe in 1 N HCl

and  $e_{Zn}^{\circ} = -0.76V$ ,  $e_{Fe}^{-} = -0.44V$  and  $e_{H_2}^{-} = \text{Zero}$

and Zn in HCl gives the following reactions

$$e_{Zn} = -0.76 + 0.03 \log 1 = -0.76V$$

$$e_{H_2} = \text{Zero}$$

$$\therefore \text{EMF} = e_{\text{cath.}} - e_{\text{anode}} = 0 - (-0.76) = +0.76V$$

Fe in HCl will give the following

$$E_{Fe} = -0.44 + 0.03 \log 1 = -0.44V$$

$$e_{H_2} = \text{Zero}$$

If corrosion rate —  $\Delta G$  or EMF

One expects that the rate of corrosion of Zn is higher than that of Fe, but actually the inverse is the correct.

- (3) Thermodynamic calculations consider only the interaction between the metal and  $H_2O$  (as illustrated in Pourbaix diagram) and neglect the interaction between the metal and anions as for example  $Cl^{-}$ ,  $SO_4^{--}$ ,  $PO_4^{3-}$ , etc.
- (4) Thermodynamic calculations depend on pH in the bulk of solution where it is different from the pH near the corroding metal.
- (5) Thermodynamics consider the range of hydroxide ( $Zn(OH)_2$ ) as a range of passivity but actually hydroxide may or may not protect the metal according to the nature of hydroxide itself.

<u>Hydroxides</u>	
May be compact Metal	may not be compact Metal
No contact between the metal and solution which cause passivity	hydroxide porous There is a contact between the metal and the solution and hence corrosion occurs

- (6) **It is not correct to use Nernst equation** (equilibrium equation) to a corrosion system (not at equilibrium)  
For example Daniel Cell.

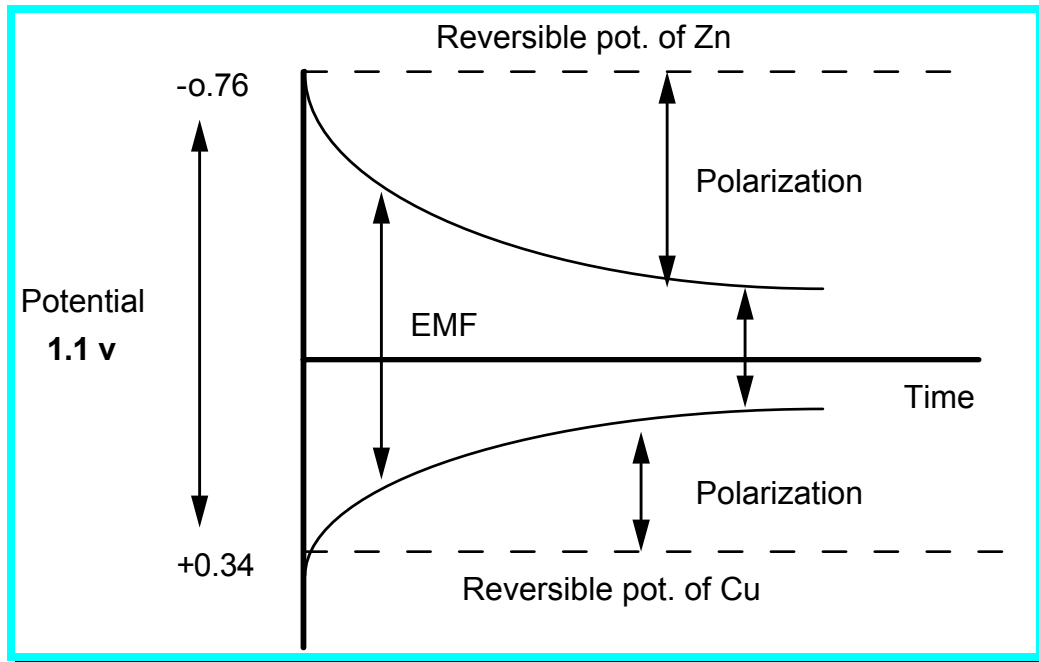
**For Zinc Electrode**



$$e = 0.76 + 0.03 \log 1$$

Since there is a dissolution of Zn, the activity of  $Zn^{2+}$  will increase i.e.,  $e$  will shift to more +ve direction.

### For Copper Electrode



$$e = +0.34 + 0.03 \log 1$$

$Cu^{2+}$  will deposit on the Cu electrode and the activity of  $Cu^{2+}$  will decrease i.e.,  $e$  will shift to more -ve direction.

EMF of the cell decreases as the current passes at the beginning where there is no current passes  $EMF = e_{cathode} - e_{anode} = +0.34 - (-0.76) = 1.10$

$\eta$ : is the overpotential  
or overvoltage  
or polarization

$\eta$ : is the difference between polarized and reversible potentials and its value increases with increasing of the current passing.

Finally if there is a connection between Cu and Zn electrodes, the equilibrium or reversible value of EMF (1.1V) can be obtained only at "Zero Current".

### Conclusion

To treat corrosion we have to consider the polarization or overvoltage occurring on the cathode and anode due to current passing. This will be the subject of "Electrode Kinetics".

### Electrochemical Kinetics of Corrosion

In electrochemistry we use current or current density (current/area) instead of rate.

If "i" is current density (c.d)

cathodic transfer current density,  
anodic transfer current density.

The reaction:  $\text{Cu} \xrightarrow{\text{oxidn.}} \text{Cu}^{2+} + ze^{-}$   
Redn

Rate of oxidation = Rate of reduction

i.e., we have equilibrium

$\bar{i} = \bar{i} = i_o$  where "i<sub>o</sub>" is the exchange current density.

Definition of Equilibrium (electro)

Transfer cathodic c.d  $\bar{i}$  = transfer anodic c.d  $\bar{i}$  = exchange c.d i.o

Electrochemical Kinetic Treatment of Polarization (current is passing)

$i_a = i_c$  only when the cathode and the anode have the same area i.e., current passing in the circuit is the same.

$i_a \neq i_c$  if areas are different

Let us consider two different cases

Cathode

- i) Low polarization  
 $\bar{i}_c$  increases and  $\bar{i}_a$  decreases and hence  $i_c$  increases ( $i_c = \bar{i}_c - \bar{i}_a$ ).
- ii) High polarization  
 $\bar{i}_c$  increases and  $\bar{i}_a$  decreases to reach zero and hence  $i_c = \bar{i}_c$ .

Anode

- i) Low polarization  
 $i_a = \bar{i}_c - \bar{i}_a$  where  $\bar{i}_a$  decreases  
 $\emptyset$              $\emptyset$   
 increase      increase
- ii) High polarization  
 $i_a = \bar{i}_c$  where  $\bar{i}_a$  reaches to Zero as current passing increases.

Polarization, Overpotential, Overvoltage "h"

h is the difference between polarized and reversible potentials.

There are two types of polarization:

- i)  $h_a$  (anodic) = potential of polarized anode - Rev. potential (P1 reading).
- ii)  $h_c$  (cathodic) = potential of polarized cathode - Rev. potential (P2 reading).

Factors Affecting on h

- (1) Nature of metal            (2) Nature of solution and its composition
- (3) Temperature                (4) Current density

The relation between h and current density is described by TAFEL line (polarization curve).

Mixed Potential or Corrosion Potential

Corrosion of Zn/Acid

To get the mixed or corrosion potential we have to plot the polarization curves (TAFEL lines) for each system (Zn and  $H_2$ ). To plot the polarization curve we must know:

- 1) Reversible potential.
- 2) TAFEL slope (constant b of the TAFEL equation).
- 3) Exchange current density,  $i_0$ .

(1) Reversible Potential

- a) For Zn system  
 If  $a_{Zn^{2+}} = 1$      $\bar{u}$  Reversible potential     $e^- = -0.76V$
- b) For  $H_2$  system  
 If  $a_{H^+} = 1$      $\bar{u}$  Reversible potential     $e^- = \text{zero}$

## (2) Tafel Slopes

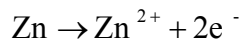
Slope of Tafel depends on: nature of the metal, nature and concentration of solution, temperature and other factors.

In corrosion we take Tafel slope "b" equal to 0.1 and 0.12 V (this is an approximation).

## (3) Exchange Current Density $i_0$

$i_0$  depends on: metal, solution, temperature, etc.

For H<sub>2</sub> system:  $i_0$  is different for different metals on which hydrogen gas is evolved,  $i_0$  for H<sub>2</sub> on Zn =  $10^{-10}$  A/cm<sup>2</sup>.



For Zn system:

$$i_0 = 10^{-7} \text{ A/cm}^2$$

At Point X

The intersection of anodic Zn with cathodic H<sub>2</sub> where the rate of dissolution of anodic Zn = rate of cathodic hydrogen evolution i.e., at point X there is a "steady state of corrosion".

At Point Y

Log corrosion current density = log I cor.

Note that:

- (1) E<sub>cor.</sub> lies between the two reversible potentials.
- (2) I<sub>cor.</sub> >  $i_0$  of H<sub>2</sub> system  
>  $i_0$  of Zn system

Corrosion of Fe in acid medium

(1) Reversible potentials

- a) For H<sub>2</sub> system  $a_{\text{H}^+} = 1$   $\text{e}^- = \text{zero}$
- b) For Fe system  $a_{\text{Fe}} = 1$   $\text{e}^- = -0.44\text{V}$

(2) Tafel slopes 0.1 and 0.12 V

(3) Exchange current density  $i_0$

- a) For Fe system  $10^{-6}$  a/cm<sup>2</sup>
- b) For H<sub>2</sub> system  $10^{-6}$  A/cm<sup>2</sup>

Rate of Corrosion

- (1) Loss in Weight
  - (a) Determine the area

- (b) If  $w_1$  is the weight of metal before corrosion
- (c) Leave the metal to corrode for sometime [from one day to several days].
- (d) Remove the metal, dry and weight.
- (e) If  $w_2$  is the weight of the metal after corrosion

$$\text{Rate of corrosion} = \frac{W_1 - W_2}{\text{area.time}}$$

- (2) Change  $I_{cor}$  in mdd i.e., mg per day per decimeter.

$$\text{Standard units of the rate of corrosion} = \frac{\text{mg}}{\text{dm}^2 \cdot \text{day}} = \text{mdd}$$

( $\text{dm}^2 = 100 \text{ cm}^2$ ).

### Electrochemical Methods of Corrosion Rate Determination

- (1) Tafel Extrapolation

$E_{co}$  lies between the two reversible potentials

$I_{co} > i_0$  for the two systems.

#### Step (1)

Leave the metal to corrode and measure the potential against reference electrode until the potential becomes steady ( $E_{cor}$ ).

#### Step (2)

- (i) Determine the cathodic polarization of the corroding metal after reaching  $E_{cor}$ .
- (ii) Start from low current density to high current density and measure the potential at each current density.
- (iii) Plot potential against log current density to get Tafel line A which joins the Tafel line or cathodic hydrogen line.

#### Step (3)

- (i) Determine the anodic polarization of corroding metal (change the polarity of the battery) after reaching  $E_{cor}$ .
- (ii) Start from low current density to high current density and measure the potential in each case.
- (iii) Plot the relation between the potential and log current density to get line B which joins the anodic metal.

#### Step (4)

Extrapolate the linear parts of A and B to meet at point X, where X corresponds to  $E_{cor}$  and  $I_{cor}$ .

From the antilog of  $\log I_{cor}$  we can obtain  $I_{cor}$ .

N.B.

We can determine point X from the cathodic polarization only i.e., from Tafel line A.

Linear Polarization (Polarization Resistance)  
 Consider the non linear region A (cathodic) where  
 for hydrogen system  
 for metal system

$$i_c = \bar{i} - \bar{i}$$

$$= I_{cor} \left[ e^{-\frac{\alpha ZFE}{RT}} - e^{\frac{\alpha' Z'FE}{RT}} \right]$$

where E is the difference between the electrode potential and  $E_{co}$ .  
 Note that for one system

$$i_c = i_o \left[ e^{-\alpha \frac{ZF\eta_c}{RT}} - e^{(1-\alpha) \frac{ZF\eta_c}{RT}} \right]$$

if  $X$  is small

$$e^x = 1 + X$$

$$e^{-x} = 1 - X$$

In the non linear region (cathodic A) E is small (low polarization).

$$i_c = I_{cor} \left[ 1 - \frac{\alpha ZFE}{RT} - \left\{ 1 + \frac{\alpha' Z'FE}{RT} \right\} \right]$$

$$= -I_{cor} E \left[ \frac{\alpha ZF}{RT} + \frac{\alpha' Z'F}{RT} \right]$$

Since for the same system  
 Tafel slopes

$$bc = \frac{2.303RT}{\alpha ZF}$$

$$ba = \frac{2.303RT}{(1-\alpha)ZF}$$

$$\therefore \frac{2.303}{bc} = \frac{\alpha ZF}{RT} \quad \text{and} \quad \frac{2.303}{ba} = \frac{\alpha' Z' F}{RT}$$

$$\therefore i_c = -I_{cor} \cdot E \left[ \frac{2.303}{bc} + \frac{2.303}{ba} \right]$$

$$= -I_{cor} \cdot E \cdot 2.303 \left[ \frac{ba + bc}{bc \cdot ba} \right]$$

To get the relation between E and  $i_c$

$$\therefore E = \frac{i_c}{-2.303 I_{cor}} \left( \frac{bc \cdot ba}{bc + ba} \right)$$

$$\left( \frac{dE}{di_c} \right)_{E \rightarrow 0} = \frac{1}{I_{cor} \times 2.303} \frac{bc \cdot ba}{bc + ba}$$

$$= \frac{\text{Constant}}{E_{Cor}} = R_p$$

polarization resistance

$E \propto i_c$  means that we are in the non linear part (cathodic low polarization).

From  $R_p$  and by knowing the constants we can calculate  $I_{co}$ .

This method is very useful to monitor corrosion rates in the industry.

### Protection against Corrosion

The methods of controlling corrosion are divided into the following:

- 1) Changing the process variables as for example:
  - a) Concentration of the main constituent
  - b) Concentration of impurities e.g.  $Cl^-$  ions, complexing agents, etc.
  - c) Temperature
- 2) Cathodic Protection
- 3) Anodic protection.

### Cathodic Protection

#### Principle

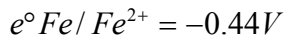
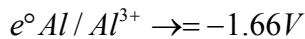
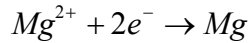
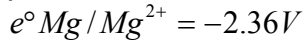
At constant pH, change the potential to the -ve direction from the corrosion region to immunity.

Experimental

There are two methods:

(1) Galvanic Coupling (Sacrificial anode).

The Mg anodes are replaced periodically with new ones after certain period of time.



2) Impressed Current

The pipeline must be in the immunity region, so the potential of this pipeline must be in suitable -ve potential. This is done by shifting the potential to:

a) The upper end of immunity region (line 1), but it is not sufficient, i.e., corrosion may occur.

b) The lower end of the immunity region (line 2), but it is very costly.

c) The best condition is between line (1) and (2).

The best condition for steel:

Adjust D.C. source such that the potential difference between the pipeline (steel) and Cu/CuSO<sub>4</sub> (reference electrode) = -0.85V.

Problem

The pipelines passing between the anode and the tank will suffer from corrosion. This is due to the "Stray Current".

In this way we protect the tank and destroy the pipelines.

Stray Current

To solve this problem connect the circuit as shown in Fig. (2). By this way the pipeline is completely protected from the effect of stray currents.

Anodic Protection

Principle

Bring the metal to the passivity region.

Pourbaix Diagram

Keep the potential constant and increase the pH from the corrosion region to the passivity region.

Passivity (Electrokinetics)



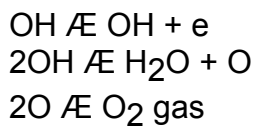
If we increase the potential to the +ve direction, the c.d. will increase till point "b", and if the potential increased beyond point "b", the c.d will drop sharply to point "c". This is due to the formation of an oxide film which resist the passing of the current.

Due to the resistance of the oxide film, the current passing decreases from point "b" to "c" 1/100000 times.

The oxide film has the following characteristics:

The thickness is about 60 Å, transparent, compact, covering all the surface, prevents contact between the metal and solution (true passivity).

From point "c" to "d" the c.d. is constant and very small = 6-10  $\mu$  A/cm<sup>2</sup>. At point "d" we reach the thermodynamic potential of O<sub>2</sub> evolution. Since the passive oxide film passes electrons, OH<sup>-</sup> ions are discharged on the oxide.



#### Experiment

- \* Bring the metal to the passivity region i.e., to point Y.
- \* Change the potential using a potentiostat until the potential of the anode (pipeline) reach point Y on the passivity region.

## Protection against Corrosion

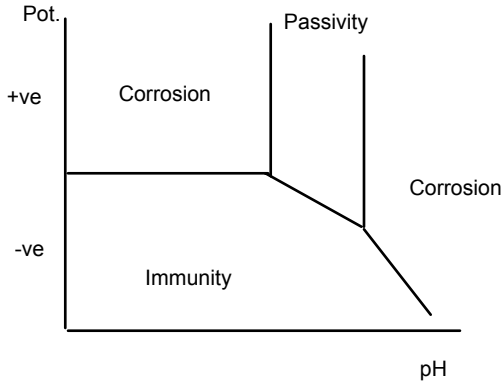
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### Cathodic Protection

#### Principle

At constant pH, change the potential to the -ve direction from the corrosion region to immunity.



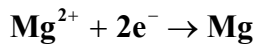
## Experimental

There are two methods:

### (1) Galvanic Coupling (Sacrificial anode).

The Mg anodes are replaced periodically with new ones after certain

$$e^{\circ}_{\text{Mg}/\text{Mg}^{2+}} = -2.36\text{V}$$

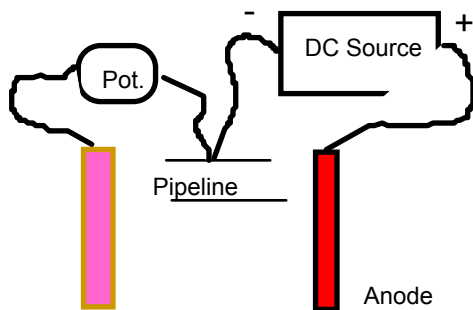


$$e^{\circ}_{\text{Al}/\text{Al}^{3+}} = -1.66\text{V}$$

$$e^{\circ}_{\text{Fe}/\text{Fe}^{2+}} = -0.44\text{V}$$

period of time.

### (2) Impressed Current



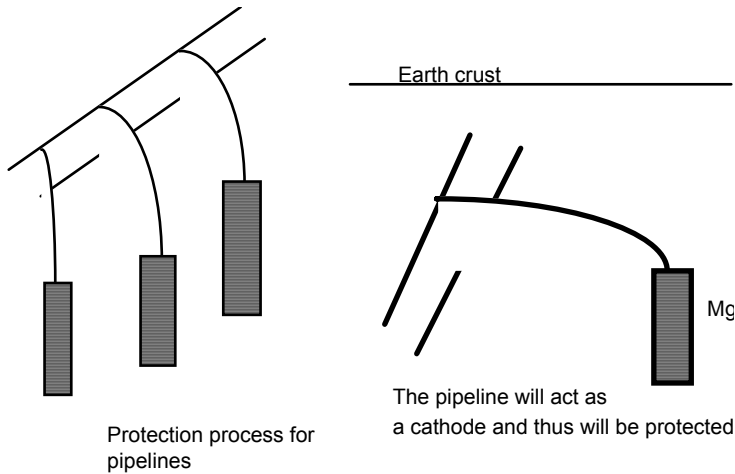
Reference Electrode

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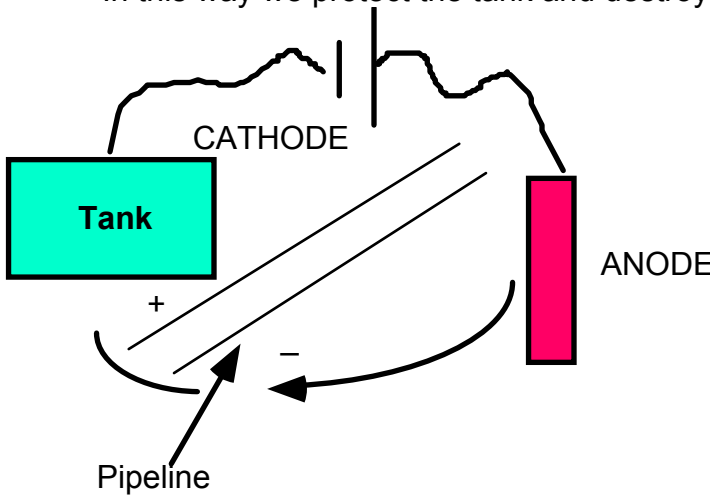
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If we increase the potential to the +ve direction, the c.d. will increase till point "b", and if the potential increased beyond point "b", the c.d will drop

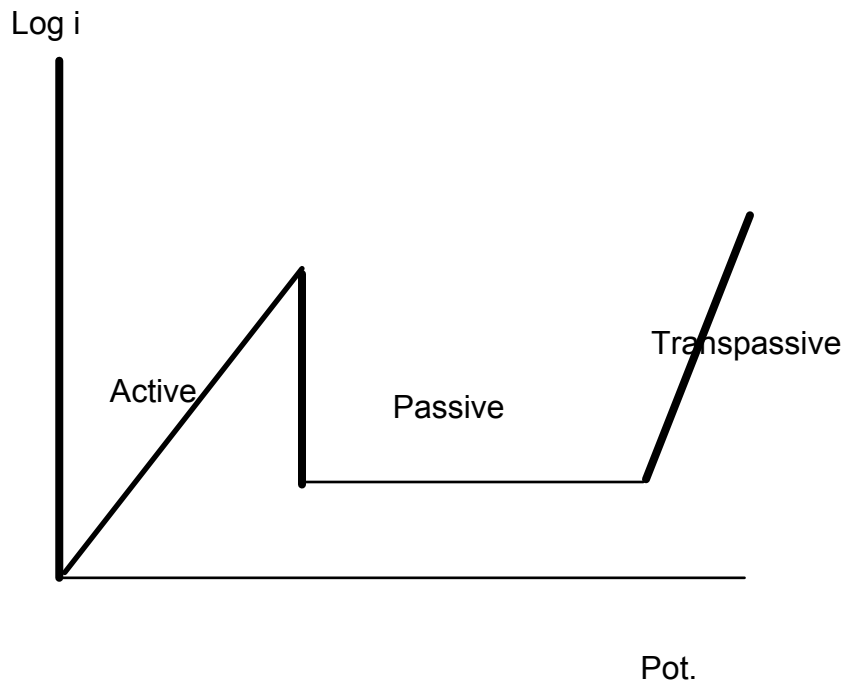
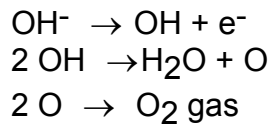
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