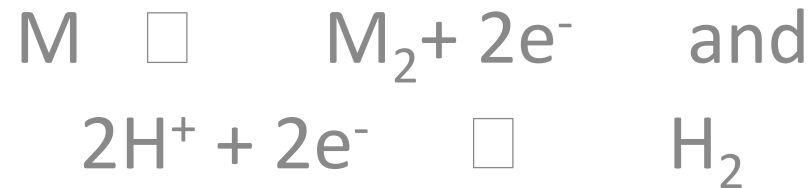


Kinetics of corrosion

consider the E/pH diagram for two metal/ water systems

at pH of x, in M/H₂O system two electrochemical reactions,



are attempting to co-exist . This is irreversible = Corrosion

E-pH diagram for M & M₁ /water

- Draw diagram

Reversible electrode

At pH X,

- If there is no oxygen, metal M will corrode whereas, for metal M_1 corrosion can only occur in the presence of oxygen or some oxidants added to the M_1/H_2O system.
- For M_1/H_2O system, in the absence of oxygen, corrosion will not occur and only one equilibrium will try to establish itself.
- $M_1 \rightleftharpoons M_1^{2+} + 2e^-$

This is a reversible electrode, No corrosion

Irreversible electrode

- For



2 equilibria trying to establish themselves on the electrode = Irreversible.

This is CORROSION.

It has been proved beyond par adventure that Corrosion is electrochemical. Hence Current, I is a measure of its rate of rxn.

Equilibrium condition

- NOTE: $I = \text{current}$ and $I/A = \text{current density} = i$,
where $A = \text{area of electrode}$

At eqbm,

$\square \square M^+$ electronation i

$\square \square M^+ + e^-$ de-electronation, i

$i = i = i_0$ (exchange current density)

Exchange current density, i_0

- i_0 is characteristic of the rxn on a particular metal
- $\Delta \phi_e = P. D @$ eqbm, this is characteristic of the rxn
- When there is departure from eqbm, we have Drift current density, i_{net} . Hence, either i_c or i_a becomes higher than the other a net current will flow $i_{net} = i_c - i_a$

Departure from Eqbm

- $\Delta\phi$ is P.D @ departure from eqbm.
- D4, $\Delta\phi - \Delta\phi_e = \varepsilon$; xtra potential by which electrode departs from eqbm., called
OVERPOTENTIAL .
- If ε is +ve, i increases & i decreases, D4
- $i \gg i$ there will be net anodic current, if ε is – ve, converse is true.

Anodic & Cathodic current

- If ε is large and +ve, ε can be called ε_a anodic overpotential,
- $i = i_o \exp^{\beta Z F \varepsilon / R T}$ 1 also,
- $i = i_o \exp^{-(1-\beta) Z F \varepsilon / R T}$ 2 when ε is large and
-ve

Eqns 1 & 2 are BUTLER- VOLMER EQUATIONS

- ε can be obtained experimentally.
- β = symmetry factor, all other symbols have their usual meanings.

Anodic & Cathodic rxns

- From eqns 1 & 2,
- $\log i = \log i_o + \beta Z F \epsilon_a / 2.3 RT \quad \dots 3$
- $\log i = \log i_o - (1-\beta) Z F \epsilon_c / 2.3 RT \quad \dots 4$
- Let $2.3 RT / \beta Z F = b_a$ and $- 2.3 RT / (1-\beta) Z F = b_c$
- $\log i = \log i_o + \epsilon_a / b_a \quad \dots\dots 5$
- $\log i = \log i_o + \epsilon_c / b_c \quad \dots\dots 6$ from 5&6,

Tafel Eqns

From 5& 6, we obtain,

- $b_a \log i = b_a \log i_o + \epsilon_a \dots\dots\dots 7$

- $b_c \log i = b_c \log i_o + \epsilon_c \dots\dots\dots 8$

- Simplifies further,

- $b_a \log i = a_a + \epsilon_a$ (7a) & $b_c \log i = a_c + \epsilon_c$ (8a)

- Equations 7 & 8 are called TAFEL EQUATIONS

- A plot of ϵ_a versus $\log i_{a \text{ nett}}$ will give a curve, the extrapolation of the linear portion to the y axis will give a_a and the slope b_a

Non- reversible electrodes

- Process of corrosion is irreversible
- Consider Fe in HCl, given by eqn.,
- $\text{Fe} + 2\text{HCl} \rightleftharpoons \text{FeCl}_2 + \text{H}_2$ or
- $\text{Fe} + 2\text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{H}_2$
- At metal or electrode surface there are,
- PD as a result of Fe in solid and Fe^{2+} in soln
- PD as a result of hydrogen evolution
- Corrosion occurs when the 2 equilibria try to compromise each other.

MIXED POTENTIAL THEORY

- The 2 equilibria polarise toward each other
- The compromise potential attained is termed
- MIXED POTENTIAL = Corrosion potential