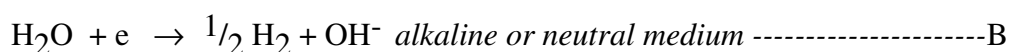
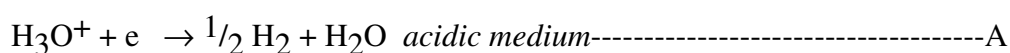


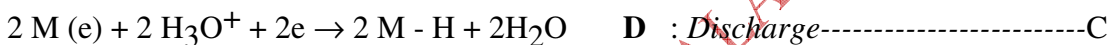
5.6: Evolution Of Hydrogen

5.6: EVOLUTION OF HYDROGEN

1. Standard method of producing H₂ & D₂O
2. Hydrogen evolution in metal deposition - need to understand the mechanism.
3. Plays role in corrosion
4. Explains electrochemicals in greater details- Charge - transfer, consecutive steps, adsorbed intermediate.
5. The evolution of hydrogen can occur from different media.



REACTIONS:



Parameters normally determined.

- (i) i_0 (ii) α (iii) order w.r.t. H_3O^+ (iv) Stoichiometric number
 (v) Surface coverage, θ

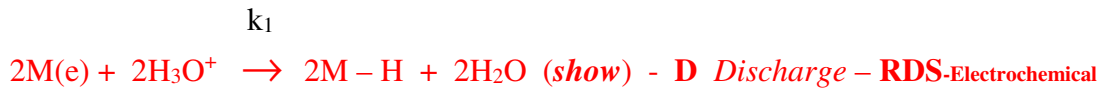
(i) Exchange current density, i_0

Determination of i_0 permits the classification of metals as good or bad electrocatalyst for H₂ evolution.

- Hg, Pb, Tl are **poor** electrocatalyst for H₂ evolution low i_0 (*High resistance*)
- Pd, Pt, Rh **good** electro catalyst for H₂ evolution high i_0 (*Low resistance*)
- **NOTE:** Exchange c.d is a measure of the reaction resistance, $\rho = RT/i_0F$

5.6: Evolution Of Hydrogen

(a) MECHANISM-1.



The Butler Volmer Equation for the electrochemical RDS step is

$$\text{Rate} = \text{Rate of rds} = i = i_c = 2Fk_1(1-\theta_H) [H_3O^+]e^{-\beta\Delta\phi F/RT} \dots\dots\dots 1$$

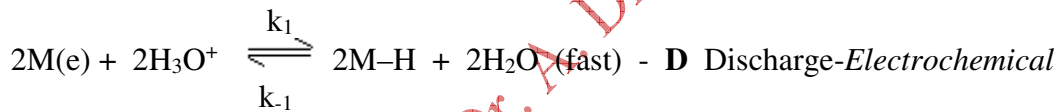
The cathodic order is one with respect to H₃O⁺

θ_H : Adsorbed metal surface involved in the electron transfer and subsequent H₂ formation

$$i = 2 Fk_1 [H_3O^+]e^{-\beta\Delta\phi F/RT} \text{ (if } \theta \ll 1) \dots\dots\dots 2$$

$$= i_0 e^{-\beta\eta F/RT} \therefore \alpha \text{ (Cathodic)} = \beta = 0.5$$

(b) MECHANISM-2.



$$\text{Rate} = \text{Rate of rds} = i = 2Fv_2 = 2F \times \text{chemical rate} = 2Fk_2 [H_{\text{adsorbed}}]^2 = 2Fk_2(\theta_H)^2 \dots\dots\dots 3$$

Any chemical step will have its influence on the c.d of the reaction, hence the incorporation of F.

Applying equilibrium condition for the fast electrochemical Eq. Step $\vec{i} = \overset{\leftarrow}{i}$

$$k_1 (1-\theta_H) [H_3O^+]e^{-\beta\Delta\phi F} = k_{-1} (\theta) e^{(1-\beta)\Delta\phi F/RT} \dots\dots\dots 4$$

$$\therefore \theta_H = \frac{k_1 [H_3O^+]e^{-\Delta\phi F /RT}}{k_{-1}} \text{ For } \theta \ll 1 \dots\dots\dots 5$$

5.6: Evolution Of Hydrogen

Substitute the value of θ_H in the above equation for i we get

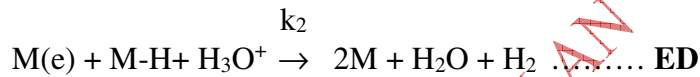
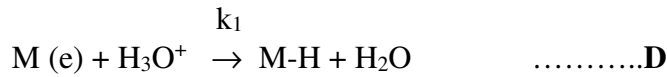
$$i = 2Fk_2 \left[\frac{k_1 [H_3O^+] e^{-\Delta\phi F / RT}}{k_{-1}} \right]^2 \dots\dots\dots 6$$

$$= 2Fk_2 K_1^2 [H_3O^+]^2 e^{-2\Delta\phi F / RT} \dots\dots\dots 7$$

$$= k [H_3O^+]^2 e^{-2\Delta\phi F / RT} \{ \text{The cathodic order is one with respect to } H_3O^+ \}$$

$$= i_0 e^{-2\eta F / RT}; \therefore \alpha = 2$$

(c) MECHANISM-3 (*The speed of both steps are comparable*)



Coparable rate means , the over all rate of the reaction is equal to the rate of any one of the step

For the discharge (**D**) cathodic step we have.

$$\begin{aligned} \rightarrow i &= F k_1 (1-\theta_H) [H_3O^+] e^{-\beta\Delta\phi F / RT} \\ &= F k_1 [H_3O^+] e^{-\beta\Delta\phi F / RT}; \text{ for } \theta_H \ll 1 \dots\dots\dots 8 \end{aligned}$$

$$= i_0 e^{-\beta\eta F / RT} \dots\dots\dots \mathbf{8(a)}$$

Hence, the cathodic order with respect to H_3O^+ one

$1-\theta_H$: Empty metal surface involved in the electron transfer

For the **ED** step

$$\rightarrow i = F k_2 (\theta_H) [H_3O^+] e^{-\beta\Delta\phi F / RT} \dots\dots\dots 9$$

According to steady state approximation the above two rates (and hence the corresponding currents from equations-8 & 9) are equal

5.6: Evolution Of Hydrogen

$$\therefore \theta_H = \frac{k_1}{k_2}$$

Substituting for θ_H in the later expression we get

$$i = 2Fk_2(k_1/k_2) [H_3O^+]e^{-\beta\Delta\phi F/RT} \dots\dots\dots 10$$

{ The reaction is first-order with respect to H_3O^+ is one}

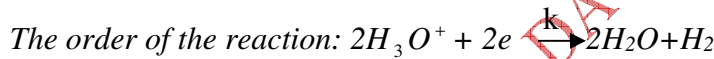
$$\cong i_0 e^{-\beta\eta F/RT} \dots\dots\dots 10(a)$$

→

$$\therefore \alpha = \beta \cong 0.5$$

NOTE: Equations-8(a) & 10(a) lead to the same result

(iii) Determination of reaction order w.r.t. $[H^+]$



is $1/2$ in acid solution & $-1/2$ in alkaline solution.

$$\vec{i} = 2Fk e^{-\beta\Delta\phi_e F/RT} (H_3O^+)$$

$$\ln \vec{i} = \ln 2Fk - \frac{\beta\eta F}{RT} - \frac{\beta\Delta\phi_e F}{RT} + \ln(H_3O^+) \dots\dots\dots 11$$

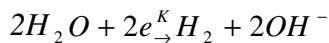
$$\left(\frac{\partial \ln \vec{i}}{\partial \ln H_3O^+} \right)_\eta = -\frac{\beta F}{RT} \frac{\partial \Delta\phi_e}{\partial \ln H_3O^+} + 1$$

But, $\Delta\phi_e = \Delta\phi_e^o + \frac{RT}{F} \ln\{ H_3O^+ \}$ Nernst equation

$$\frac{\partial \Delta\phi_e}{\partial \ln(H_3O^+)} = \frac{RT}{F}$$

$$\therefore \left(\frac{\partial \ln \vec{i}}{\partial \ln H_3O^+} \right)_\eta = 1 - \beta = \frac{1}{2}$$

Consider discharge in alkali solution or neutral medium



5.6: Evulution Of Hydrogen

$$i = 2F k e^{-\beta\Delta\phi_e F / RT} e^{-\beta\eta F / RT} (H_2O)^2 \dots\dots\dots 12$$

$$\ln i = \ln \{2F k (H_2O)^2\} - \frac{\beta\Delta\phi_e F}{RT} - \frac{\beta\eta F}{RT}$$

But, $\Delta\phi_e = \Delta\phi_e^\circ + \frac{RT}{2F} \ln \frac{(H_2O)^2}{(H_2)(OH^-)^2}$ **Nernst equation**

$$= \Delta\phi_e^\circ + \frac{RT}{2F} \ln \frac{1}{OH} \dots\dots\dots 13$$

$$= \Delta\phi_e^\circ + \frac{RT}{2F} \ln \frac{H_3O^+}{K_w}$$

$$\text{But, } [OH^-] = \frac{K_w}{[H_3O^+]}$$

$$\ln i = \ln \{2Fk [H_2 O]^2\} - \frac{\beta F}{RT} \left(\Delta\phi_e^\circ + \frac{RT}{F} \ln \frac{H_3O^+}{K_w} \right) - \frac{\beta\eta F}{RT}$$

.....14

Differentiating both sides with respect to $\ln H_3O^+$

$$\left(\frac{\partial \ln i}{\partial \ln H_3O^+} \right)_\eta = -\beta = -\frac{1}{2}$$

Therefore the order of the reaction with respect to H_3O^+ is $-\beta = -1/2$