**M.Sc (Chemistry)**

**ELECTRODE KINETICS – ELECTRODICS-I**

# 4. PROBLEMS & SOLUTION (Butler-Volmer Equation)

**1 High field approximation (HFA) :** $|\eta| > 0.1$ V

Anodic current for +ve $\eta$ ; **$i = i_o \exp\{(1-\beta)\eta F/RT\}$**

Cathodic current for -ve $\eta$ **; $i = i_o \exp\{-\beta\eta F/RT\}$**

**2 Low field approximation (LFA) :** $|\eta| < 0.01$ V

$$i = 2i_o \sin \frac{F\eta}{2RT} \approx 2i_o \frac{F\eta}{2RT} = i_o \frac{F\eta}{RT}$$

**3 For $\eta \approx$ 0.01 V - 0.1V**

**Use the BV-equation.**

**4. BV equation can be used as it is under any circumstances.**



## PROBLEM-1

**Compare the rates of the reaction: $Ag^+ + e \rightarrow Ag$ at $\eta$ = - 0.2V & $\eta$ = 0.2 V.**

i = nF x Rate

Hence , rate of a reaction α current density

Therefore, we have to compare the cathodic rate in both η

**Cathodic rate α $i_c$ ; $i_c = i_o \exp\{-\beta\eta F/RT\}$**

$$\text{Ratio of rates} = \text{Ratio of the cds} = \frac{(i_c)\eta = -0.2}{(i_c)\eta = +0.2} = \frac{e^{-0.5 X (-0.2)\frac{96500}{8.314 X 298}}}{e^{-0.5 X (0.2)\frac{96500}{8.31 X 298}}}$$

$$= \frac{49}{0.02} = 2450$$

**N.B:** A small change in potential – 0.2 to +2V (0.4 unit) increases the rate by 2450 times.

## PROBLEM-2

**For $\eta$=10mV , i = 0.62mA through 2cm$^2$ Pt electrode in $H^+/H_2$. What will be i for (a) $\eta$=100 mV (b)-100mV .Assume the symmetry factor as 0.5**

$H^+ + e \rightarrow \frac{1}{2} H_2$

BV equation to be used as such without any modification for given over potential range.

For $\eta$ = 10 mV = 0.01V; I/A = 0.62/2 = 0.31 mAcm$^{-2}$

$$i = i_o \left(e^{(1-\beta)\,\eta F / RT} - e^{-\beta\,\eta F / RT}\right)$$

$$\therefore 0.31 = i_o \left[e^{0.5 \times 0.01 / F / RT} - e^{-0.5 \times 0.01 \; F / RT}\right]$$

$$\therefore i_o = 0.79 \text{ mA cm}^{-2}$$

**(a) $\eta$= 100 mV = 0.1V**

$$i = 0.79 \left(e^{0.5 \times 0.1 \times 96500 / 8.314 \times 298} - e^{-0..5 \times 0.1 \times 96500 / 8.314 \times 298}\right)$$

$$i = -5.42 \text{ mA cm}^{-2}$$

**(b) Similarly** , i = + 5.42 mA cm$^{-2}$

## PROBLEM-3

**The exchange current density of $Pt/H_2,H^+$ is 0.79 mAcm$^{-2}$ at 25$^0$C. Calculate the current density across it when the over potential is (a) 10 mV (b) –200 mV**

**a)** $\eta$ = 10 mV = 0.01 V

$i = i_0\eta F/RT$ = 0.79x10/25.68 = **0.308mAcm$^{-2}$**

**b)** $\eta$ = – 200 mV = – 0.2 V, negative ( net cathodic current)

$$i = i_0\, e^{-\beta\eta F/RT}$$

$$= 0.79\, e^{-0.5 \times 0.2 \times 96{,}500 / RT} = 38.79 \text{ mAcm}^{-2}$$

$i = i_a - i_c = - i_c =$ **-38.79 mAcm$^{-2}$**

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## PROBLEM-4

**The exchange current density of Pt / $H_2$, $H^+_{(aq)}$ is 0.79 mA $cm^{-2}$. What current will flow through SHE when the p.d. across the electrode is 5mV at 298K?**

$\Delta\Phi = \Delta\Phi + \eta$

$5mV = 0 + \eta \quad \therefore \eta = 5mV = 0.005$ V (< 0.01V)

Use linear approximation

$$i = i_o \frac{\eta F}{RT} = \frac{0.00079 x 0.005 x 96{,}495}{8{,}314 x 298} = 0.154 mAcm^{-2}$$

Over potential is positive. Therefore , the net current across the electrode is due to net anodic process.: ½ $H_2 \rightarrow H^+$ +e.

## PROBLEM-5

**Calculate the effective resistance across 1$cm^2$ of**

**(a) Pt, $H_2$, $H^+$ ; $i_0$ = 0.79 mA $cm^{-2}$**

**(b) Hg, $H_2$, $H^+$ $i_o$ = 0.79 x $10^{-12}$ A $cm^2$**

***What conclusion you can draw from the result?***

When $\eta < 0.01$ V

$$I = i_o \frac{\eta F}{RT} \quad \therefore \eta = \frac{RT}{i_o F} i \quad (V = IR) \quad \therefore Reisance = \frac{RT}{i_o F}$$

(a)Resistance, $\rho = \dfrac{8.314 x 298}{0.790 x 10^{-3} x 96{,}495} = 32.5 ohmcm$

Less resistance, the electrode can be less polarisable (***non-polsrisable***)

(b)Similarly, $\rho = \dfrac{8.314 x 298}{0.790 x 10^{-12} x 96495} = 3.2 x 10^{10} ohm$

Greater resistance, the electrode can be more ***polarisable***

## PROBLEM-6

**In an experiment involving Pt, $H_2$, $H^+$ electrode , the following data were obtained. Determine $\beta$ and $i_0$**

**$\eta$/mV : 50 100 150 200 250**

**$i/mAcm^{-2}$ : 2.66 8.91 29.9 100 335 evaluate β and $i_o$**

**Ans :** $\beta = 0.38$ ; $i_0 = 0.78 mAcm^{-2}$

## PROBLEM-7

**For the system Pt /$Fe^{3+}$, $Fe^{2+}$ at 298K the i were measured as shown below:**

**$\eta$ (mV) : -80 -100 -120 -150 -200 50 80 100 120 150 200**

**$i$ (mA $cm^{-2}$) : 8.01 16.1 25.17 41 82.4 264 5.45 -8.71 -11.9 -16.3 -26 -56.6**

**Calculate $i_o$ and β**

$$i = i_a = i_0 e^{(1-\beta)\eta F/RT}$$

$$\ln i = \ln i_0 + \frac{(1-\beta)\eta F}{RT} \; for \eta > 0$$ (anodic ,+ve over potential)

$$\ln i = \ln i_0 - \frac{\beta \eta F}{RT} \; for \eta < 0$$ (cathodic –ve over potential

Plot ln i vs η . Evaluate $i_o$ and β from slope & intercept.

**Ans :** $\beta = 0.60$ ; $i_0 = 2.51 mAcm^{-2}$



## PROBLEM-8

**The data given below refer to C.D. through 2$cm^2$ Pt electrode in contact with $Fe^{2+}$ ,$Fe^{3+}$ at 298K.**

**Find $i_o$ and β for the process : $Fe^{3+} + e \rightarrow Fe^{2+}$**

| $\eta(mV)$ | 50 | 100 | 150 | 200 | 250 |
|---|---|---|---|---|---|
| **I(mA)** | 8.8 | 25 | 58 | 131 | 298 |

Note : $\eta$ =50 x $10^{-3}$ to 250 x $10^{-3}$ ; i.e. > 0.1V

$$i = i_0 \, e^{(1-\beta)\eta F/RT}$$

$$\ln i = \ln i_0 + \frac{(1-\beta)\eta F}{RT}$$ ; Plot ln i vs $\eta$

| | | | | | |
|---|---|---|---|---|---|
| $\eta$(mV) | : 50 | 100 | 150 | 200 | 250 |
| $i = \frac{I}{A}$ | : 4.4 | 12.5 | 29 | 65.5 | 149 |
| ln i | : 1.50 | 2.53 | 3.37 | 4.18 | 5.00 |

The high $\eta$ values give straight line.

Incept = 0.916 = ln $i_0$ ; Slope = 0.0163 = $\frac{(1-\beta)F}{RT}$

**Ans :** $i_0$ = 2.5 mA $\beta = 0.58$

Note : The plot will be non-linear for η < 100 mV

## PROBLEM-9

**The exchange current density of Pt/$Fe^{3+}$, $Fe^{2+}_{aq}$ is 2.5 mA $cm^{-2}$. Calculate the current density across the electrode at 25$^o$ C maintained at 1V when [$Fe^{2+}$] = 0.1 M and [$Fe^{+3}$]= 0.2 M (SRP = 0.771V, β = 0.58)**

$Fe^{3+}$ +e → $Fe^{2+}$

$$\Delta\phi_e = \Delta\phi_e^o - \frac{0.05915}{n}\log\frac{Fe^{2+}}{Fe^{3+}} = 0.771 - 0.05915 \log \frac{1}{2} = 0.788 \text{ V.}$$

$$\Delta\phi = \Delta\phi_e + \eta$$

$$1.0 = 0.788 + \eta$$

$$\therefore \quad \eta = 0.212 \text{ V. (+ve, >0.01 V)}$$

$$\therefore \quad i \cong i_a = i_0 e^{(1-\beta)\eta F/RT} = 2.5 \text{ e}^{0.42 \text{ x } 0.212 \text{ F/ RT}}$$

$$= 80 \text{ mA cm}^{-2}$$



## PROBLEM-10

**What are the minimum potential at which (a) Zn (b) Cu can be deposited from aqueous solutions when their concentrations are (i) 1.0 M (ii) 0.01 M ; (SRP : Zn/$Zn^{2+}$ = -0.76 , Cu/$Cu^{2+}$ = 0.34V)**

**(a)** (i) 1 M $Zn^{2+}$

$$\Delta\phi = \Delta\phi_e + \eta = -0.76 + \eta$$

$$\eta = \Delta\phi + 0.76 < 0$$

$\therefore \Delta\phi < -0.76V$

(ii) 0.01M $Zn^{2+}$

$$\Delta\phi = -0.76 - \frac{0.05915}{2}\log\frac{1}{10^{-2}} = -0.82.$$

$$\Delta\phi = \Delta\phi_e + \eta = -0.82 + \eta$$

$$\therefore \eta = \Delta\phi + 0.82 < 0$$

$$\therefore \Delta\phi < -0.82$$

**(b)** (i) $\Delta\phi_e = 0.34$

$$\Delta\phi = \Delta\phi_e + \eta = 0.34 + \eta$$

$$\therefore \eta = \Delta\phi - 0.34$$

For $\eta$ to be –ve for cathodic process $\Delta\phi < 0.34$

Note : Even if $\Delta\phi = 0$ no potential is applied Cu will get deposited.

(ii) 0.01 M

$$\Delta\phi e = \Delta\phi_e - \tfrac{0.05915}{2}\log Cu^{2+} = 0.34 - \frac{0.05915}{2}\log\frac{1}{10^{-2}} = 0.28 \text{ V}$$

$\Delta\phi = \Delta\phi_e + \eta = 0.28 + \eta$ ; $\therefore \eta = \Delta\phi - 0.28 < 0$

For copper to be deposited (cathodic process) $\eta$ must be negative. $\therefore \Delta\phi < 0.28$