

M.Sc (Chemistry)

ELECTRODE KINETICS (ELECTRODICS)-I

01-BUTLER – VOLMER Equation (Elementary Electrode Reaction)

1. Recall the following concepts:

- (i) Coulomb.
- (ii) Faraday.
- (iii) Chemical equivalent
- (iv) Electrochemical equivalent.

2. Faraday's laws of electrolysis (Electrolytic Cell)

First law: $w \propto Q$;

Second law: $w \propto z$.

Combination of both laws $w = zIt$.

(DC current of required potential (makes the discharge feasible) and then only current I (rate of the reaction faster). cf: Photoelectric effect)

3. Charge transfer at an electrode.

- (i) Diffusion or the migration of the electroactive species.
- (ii) Adsorption of the electroactive species
- (iii) Change in hydration (primary, secondary and coordinated water molecules)
- (iv) Transfer of e to or from the electroactive species. Discharge or charging
- (v) Any chemical reaction like
Gas evolution
Decomposition. E.g., $\text{VO}_3^- + 4 \text{H}^+ + e \rightarrow \text{VO}^{2+} + 2\text{H}_2\text{O}$
- (vi) Diffusion or migration of the discharged or charged species to or away from the electrode.

4. Rate of an electro-chemical process

$$z = \frac{\text{Chem.Eqwt}}{F} = \frac{M}{nF}$$

M = molecular weight; n = no of electron(s) involved.

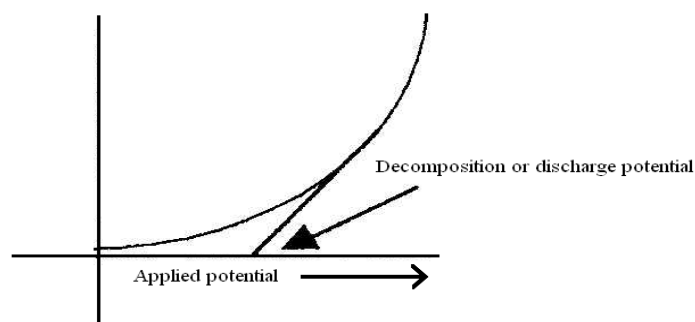
$w = zIt$ (Faraday's Laws)

$$\frac{M}{n} = \frac{It}{F}$$

Where, I = current in ampere; t = time in seconds; F = 96495 c

$$I = \frac{nFw}{Mt} = nF(\text{Rate}) ; \text{ which means that Rate} \propto \text{current}$$

- Ohm's law** (when there are no chemical reactions), $V=IR$. I vs V (applied potential) is linear passing through origin (**Metallic conductors**: slope = $1/R$) - What will be the actual behavior of electrode towards ohmic behavior.....????
- Electrolytic conductors**: Plot of **I vs V**(applied potential) is linear at the beginning passing through origin followed by a steep increase in slope-**decomposition or discharge potential** (i.e., The system obeys Ohm's law up to decomposition or discharge potential afterwards does not.



- Need for relation between i and V** for an electrode process - Butler-Volmer(1930 - Noble Prize) equation.
- Over potential, η**

$$\eta = \Delta\Phi - \Delta\Phi_e \{ \eta \text{ negative for cathodic \& positive for anodic process} \}$$

9. Study of the electrode process [Three electrode system]

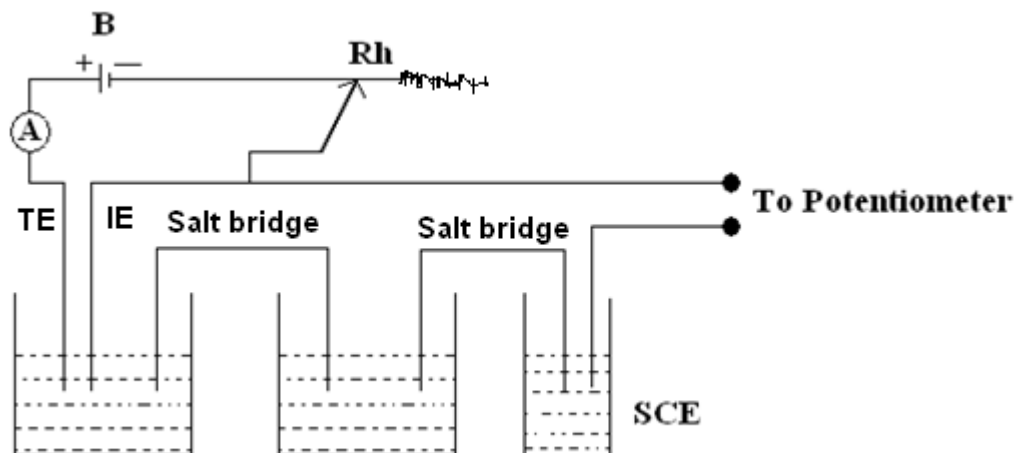


Fig-1: Three electrode system: Two cells (IE&TE and TE&SCE) with TE as Common electrode) - *The present setup is for the study of a anodic reaction.*

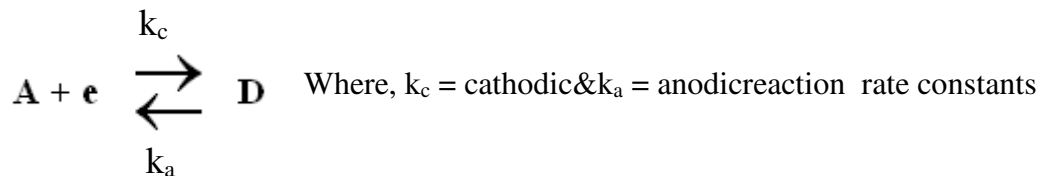
TE = Test electrode; **IE** = inert electrode; **SCE** = Ref electrode; **B** = DC in put;

A = Ammeter;

Rh = Rheostat to adjust the external resistance and thereby to adjust the external applied potential, $\Delta\phi$.

The electrode (**TE**) can be made -ve or +ve by connecting it to the -ve or +ve terminal of the external input followed by the adjustment of the rheostat

10. BUTLER- VOLMER equation - Elementary one electron process



Symbols and sign conventions:

Cathodic: Electrode connected to the -ve terminal of the external input, k_c , $-\Delta\phi$, $-\eta$, $-i$, i_c , i_{forward} , β

Anodic: Electrode connected to the + ve terminal of the external input, k_a , $+\Delta\phi$, $+\eta$, $+i$, i_a , i_{backward} , $(1 - \beta)$

Reactions occur within the Double layer 10^{-8}cm [Very high potential gradient]

Faradic process: Charge transfer

Non - Faradic process:

Adsorption, desorption, hydration,dehydration.... etc

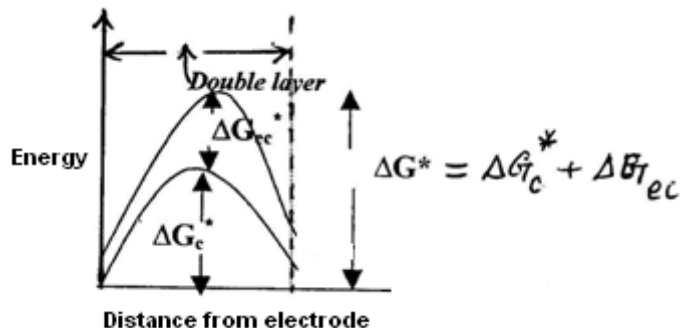


Fig-2: Energy level diagram for a reaction at an electrode

ΔG_c^* = Chemical free energy of activation

ΔG_{ec}^* = Electro-chemical free energy of activation

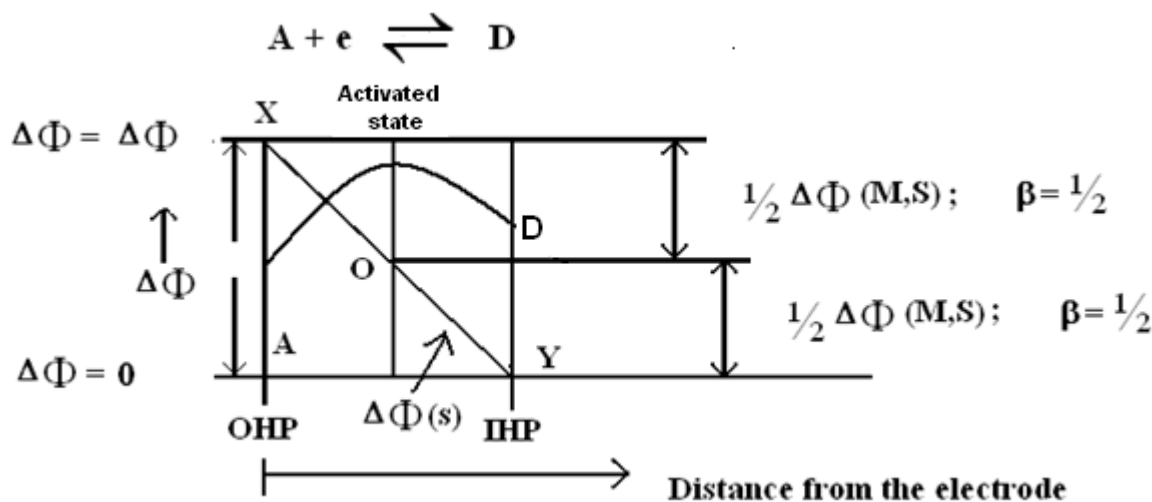
ΔG^* = Total free energy of activation = $\Delta G_c^* + \Delta G_{ec}^*$

Fig-3: Electro-chemical activation- Activation occurring at the “mid-point of the potential drop” giving a symmetrical curve, $\beta = 1/2$

OHP = Outer Helmholtz plane; IHP = Inner Helmholtz plane

$\Delta\Phi(s)$ = Potential at the electrode.

$\Delta\Phi_{(M,S)}$ = Potential at solution at distance, Y from the electrode



01-BV Equation (Elementary Electrode Reaction)

XY = Potential drop across the double layer At "O"

$\Delta\Phi = \frac{1}{2} \Delta\Phi$ (Activation occurs at the midpoint of the potential drop).

$\Delta\Phi_{(s)} = \Delta\Phi$ (at the electrode)

$\Delta\Phi_{(Ms)} = 0$ (outside the double layer)

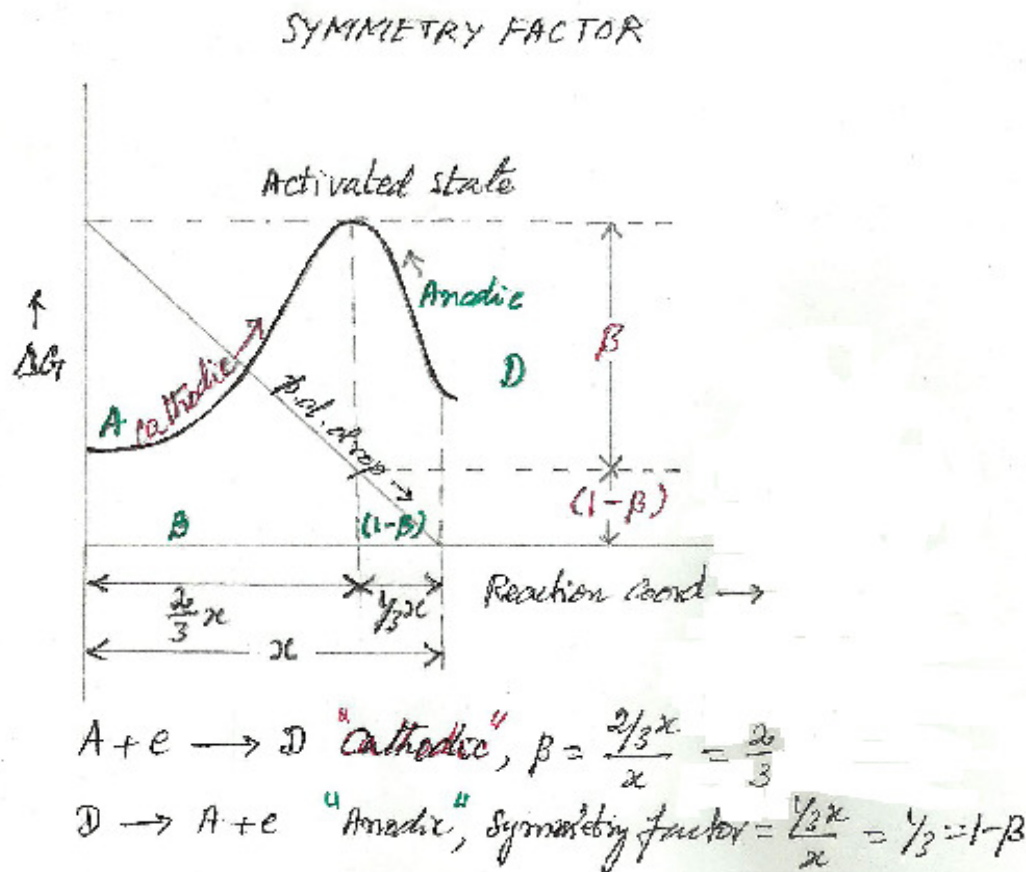


Fig-4: Electro-chemical activation- Activation occurring away from the "mid-point of the potential drop" giving a non-symmetrical curve, $\beta \neq \frac{1}{2}$

[Cathodic, β ; Anodic, $(1 - \beta)$]

$$\Delta\Phi(s) = \beta\Delta\Phi + (1-\beta)\Delta\Phi$$

∴ The **symmetry factor, β** is a measure of the symmetry of energy profile curve of $\Delta\Phi(s)$ vs. distance

∴ The symmetry factor β is the fractional contribution to $\Delta\Phi$ for the cathodic electrode process.

• ∴ Activation cannot occur at A or at D (i.e., neither at the reactant nor at the product)

.Hence, β or $(1 - \beta)$ cannot be zero or one. $0 < \beta < 1$

- ∴ Symmetry factor, β is called transfer coefficient, α for multi step multi electron reactions (To be discussed later)

The Symmetry factor, β can also be defined as

$$\beta = \frac{\text{Distance along the reaction coordinate between initial and activated state}}{\text{Distance along the reaction coordinate between initial and final state (Prodt)}}$$

Once the activated state is attained, the rest of the job of getting converted in to product becomes a spontaneous process.

CATHODIC (Reduction) REACTION

Consider the electrode reaction: $A + eD \longrightarrow$

$$i = nF \text{ Rate} = nFk[A]$$

(Charge transfer at the electrode is fast & hence considered as first-order)

According to stat. Mech., $k = (k_b T / h) e^{-\Delta G^*/RT}$; k_b : Boltzmann constant

$$i_c = nF \text{ Rate} = nF k[A] = nF(k_b T / h) e^{-\Delta G^*/RT}[A]$$

NB: The orders of most of the electro-chemical process are unity. The chemical reaction before or after the electro - chemical process may have all other possible orders.

Hence,

For the forward (cathodic) process: $A + eD \longrightarrow$

$$\Delta G_c^* = \Delta G_{\text{chem}}^* + \Delta G_{\text{ele.chem}}^*$$

$$= \Delta G_{\text{chem}}^* + \beta \Delta \Phi F; \beta = \text{symmetry factor for cathodic process}$$

$$\text{NB: } \Delta G_{\text{ele.chem}}^* = nFE = FE \text{ (one 'e' process)} = \Delta \Phi F = \beta \Delta \Phi F$$

$$i_c = nF(k_b T / h) e^{-\Delta G^*/RT}[A]$$

$$= nF(k_b T / h) e^{-\Delta G_{\text{chem}}^*/RT} e^{-\beta \Delta \Phi F / RT}[A]$$

But, $\Delta \Phi = \Delta \Phi_e + \eta$; where, $\Delta \Phi_e = \Delta \Phi_e^0 + RT \ln[A]$Nernst Eq

$$i_c = nF(k_b T / h) e^{-G_{\text{chem}}^*/RT} e^{-\beta \Delta \Phi_e F / RT} e^{-\beta \eta F / RT} [A] = i_0 e^{-\beta \eta F / RT}$$

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

Where, $i_o = nF(k_b T/h) e^{-G^*_{chem}/RT} e^{-\beta \Delta \Phi_e F/RT} [A]$

i_o = exchange or equilibrium current density.

ii) ANODIC (Oxidation ;Reverse) REACTION: $D \rightarrow A + e$

$\Delta G_a^* = -\Delta G^*_{chem} - \Delta G^*_{ele.chem}$; If ΔG^* +ve for cathodic it will be -ve for anodic

$= -\Delta G^*_{chem} - (1-\beta)\Delta \Phi F$; $(1-\beta)$ = symmetry factor for anodic process

Therefore, $i_a = nF(k_b T/h) e^{\Delta G^*_{chem}/RT} e^{(1-\beta)\Delta \Phi F/RT} [D]$;

But, $\Delta \Phi = \Delta \Phi_e + \eta$

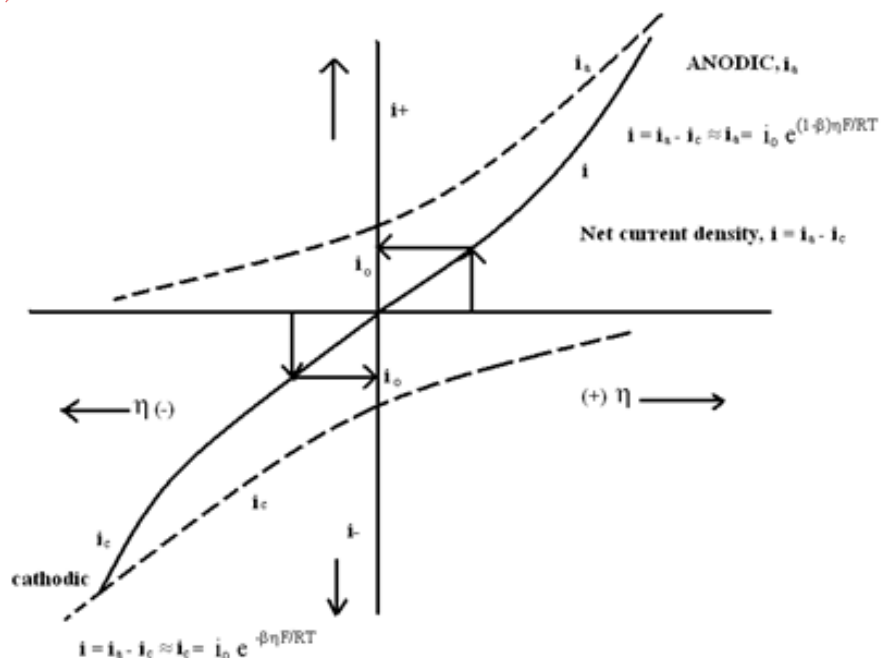
$i_a = nF(k_b T/h) e^{-G^*_{chem}/RT} e^{(1-\beta)\Delta \Phi_e F/RT} e^{(1-\beta)\eta F/RT} [D]$

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

Where ; $i_o = nF(k_b T/h) e^{-G^*_{chem}/RT} e^{(1-\beta)\Delta \Phi_e F/RT} [D]$ = exchange or equilibrium current density.

Net current density, $i = i_a - i_c = i_o [e^{(1-\beta)\eta F/RT} - e^{-\beta \eta F/RT}]$ BUTLER – VOLMER Equation

Fig-5: Butler-Volmer Plot



01-BV Equation (Elementary Electrode Reaction)

Metal	System	Medium	i_0	β
Mercury	H ⁺ /H ₂	H ₂ SO ₄	7.9x10 ⁻¹³	0.50
Lead	H ⁺ /H ²	H ₂ SO ₄	5.01 x 10 ⁻¹²	-
Nickel	H ⁺ /H ₂	H ₂ SO ₄	6.3 x 10 ⁻⁶	0.58
Tungsten	H ⁺ /H ₂	H ₂ SO ₄	1.25 x 10 ⁻⁶	-
Platinum	H ⁺ /H ₂	H ₂ SO ₄	7.9 x 10 ⁻⁴	-
Gold	H ⁺ /H ₂	H ₂ SO ₄	2.51 x 10 ⁻⁴	-
Mercury	Cr ³⁺ /Cr ²⁺	KCl	1 x 10 ⁻⁶	-
Platinum	Ce ⁴⁺ /Ce ³⁺	H ₂ SO ₄	3.98 x 10 ⁻⁵	0.75
Iridium	Fe ³⁺ /Fe ²⁺	H ₂ SO ₄	1.58 x 10 ⁻³	-
Rhodium	Fe ³⁺ /Fe ²⁺	H ₂ SO ₄	1.73 x 10 ⁻³	-
Platinum	Fe ³⁺ /Fe ²⁺	H ₂ SO ₄	2.51 x 10 ⁻³	0.58
Palladium	Fe ³⁺ /Fe ²⁺	H ₂ SO ₄	6.3 x 10 ⁻³	-
Calomel	Hg, Hg ₂ Cl ₂	KCl		

- Highly **polarisable**. Does not allow charge (e⁻) to pass through ; e.g., Hg/H⁺/H₂
- Discharge of H⁺ is difficult on Hg surface
- Highly **non-polarisable**. Allows charge (e⁻) to pass through easily ; e.g., *Calomel electrode*



NB: $i_0 = nF(k_b T/h) e^{\Delta G^+_{\text{chem.}}/RT} e^{-\beta \Delta \Phi_e} F/RT [A] \quad \text{OR}$
 $= nF(k_b T/h) e^{\Delta G^+_{\text{chem.}}/RT} e^{(1-\beta) \Delta \Phi_e} F/RT [D]$, called exchange or equilibrium c.d

- Exchange means exchange of electrons between reactants and products at equilibrium
- Exchange c.d depends on T, concentration of the reactants & products and the equilibrium potential, Φ_e . At equilibrium, they act suitably in order cancel their effect on i_0 , so that at equilibrium, $i_a = i_c = i_0$
- Exchange c.ds normally refers at 1 M concentrations unless otherwise stated.

Factors deciding the magnitude of exchange (equilibrium) current density, i_0

$$\text{NB: } i_0 = nF(k_b T/h) e^{\Delta G^*_{\text{chem}}/RT} e^{-\beta \Delta \Phi_e F/RT} [A] \quad \text{OR}$$

$$= nF(k_b T/h) e^{\Delta G^*_{\text{chem}}/RT} e^{(1-\beta)\Delta \Phi_e F/RT} [D], \text{ called exchange or equilibrium c.d.}$$

$$i_0 = nF \text{cathodic rate} = nF \text{anodic rate} = i_c = i_a$$

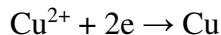
- (i) Rate constant of the chemical reaction as decided by $k_{\text{chem}} = k_b T/h) e^{\Delta G^*_{\text{chem}}/RT}$
- (ii) Concentration of the electro-active species
- (iii) Mobility of the ion on either side of the double layer
- (iv) Equilibrium potential, $\Delta \Phi_e$, which in turn depends on the concentration and nature of the electrode
- (v) Temperature

Factors affecting the magnitude of current density, i :

- The magnitude of the current density across an electrode depends on the magnitude of the **over voltage** rather than the applied potential even though over voltage depends on applied potential.
- The magnitude of the current density increases **exponentially with η** . The electrode is non-ohmic. However, it can show ohmic behavior at very low η as it could be shown latter here.
- The magnitude of the current density depends on **T** as $e^{(1-\beta)\eta F/RT}$ or $e^{-\beta \eta F/RT}$
- The current density, is directly proportional to exchange or equilibrium current density, **i_0** , which in turn depends on several factors as indicated above.

Problem:1

A potential of 0.2 V is applied to Cu/Cu²⁺(0.01M) electrode. Calculate the cathodic over potential



$$\eta = \Delta\Phi - \Delta\Phi_e \{ \eta \text{ negative for cathodic \& positive for anodic process} \}$$

$$\Delta\Phi_e = \Delta\Phi_e^\circ + (RT/nF) \ln(R_{xt}/P_{dt})$$

$$\Delta\Phi_e = 0.34 + (RT/nF) \ln(10^{-2}) = 0.28\text{V}$$

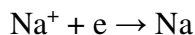
{ more negative & less spontaneous, $\Delta G = -nFE$ }

Reduction: RP positive & η negative

$$\eta = 0.2 - 0.28 = -0.08 \text{ The reduction reaction will undergo.}$$

Problem: 2

A potential of 0.2 V is applied to Na/Na⁺(0.01M) electrode. Calculate the cathodic over potential



$$\eta = \Delta\Phi - \Delta\Phi_e \{ \eta \text{ negative for cathodic \& positive for anodic process} \}$$

$$\Delta\Phi_e = \Delta\Phi_e^\circ + (RT/nF) \ln(R_{xt}/P_{dt})$$

$$\Delta\Phi_e = -2.71 + (RT/nF) \ln(10^{-2})$$

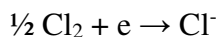
$$= -2.83\text{V} \{ \text{more negative \& less spontaneous, } \Delta G = -nFE \}$$

Reduction: RP positive & η negative

$$\eta = 0.2 - (-2.83) = 3.03 \text{ The reduction reaction will not undergo}$$

Problem: 3

A potential of 0.2 V is applied to Cl₂/Cl⁻ (0.01M) electrode. Calculate the cathodic over potential



$$\eta = \Delta\Phi - \Delta\Phi_e \{ \eta \text{ negative for cathodic \& positive for anodic process} \}$$

$$\Delta\Phi_e = \Delta\Phi_e^\circ + (RT/nF) \ln(R_{xt}/P_{dt})$$

$$\Delta\Phi_e = 1.36 + (RT/nF) \ln(1/10^{-2})$$

$$= 1.48\text{V} \{ \text{more positive \& more spontaneous, } \Delta G = -nFE \}$$

Reduction: RP positive & η negative

$$\eta = 0.2 - (1.48) = -1.28 \text{ The reduction reaction will undergo.}$$