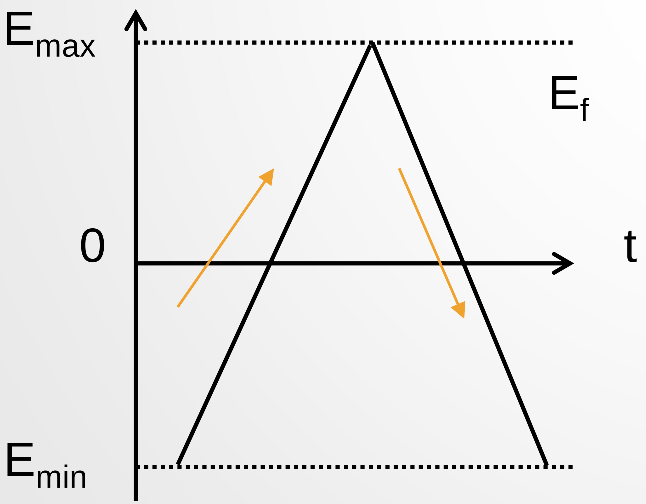
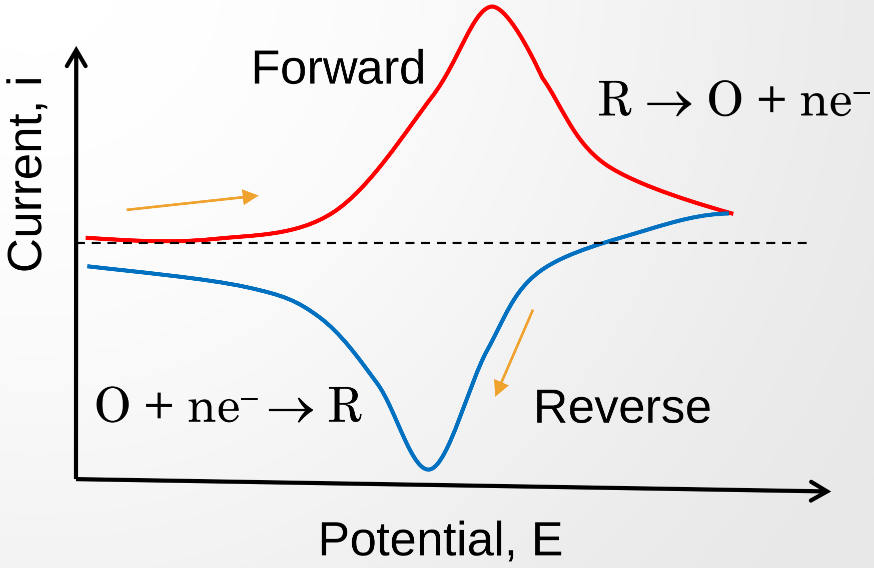
CYCLIC VOLTAMMETRY (CV)

- **Principle:** Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode (in an unstirred solution), using a triangular potential waveform. During the potential sweep, the potentiostat measures the current resulting from the applied potential. The resulting current–potential plot is termed a *cyclic voltammogram*.



Triangular Waveform



Cyclic Voltammogram

CYCLIC VOLTAMMETRY (CV)

- **Point to be remembered:**

Redox couple	Initial Concentration of Reduced form (R)	Initial Concentration of Oxidized form (O)	Initial potential	Sweep direction
R/O	100%	0%	$E_i < E^0$	Positive (Anodic)
	0%	100%	$E_i > E^0$	Negative (Cathodic)
	50%	50%	$E_i < E^0$ / $E_i > E^0$	Positive/ Negative

CYCLIC VOLTAMMETRY (CV)

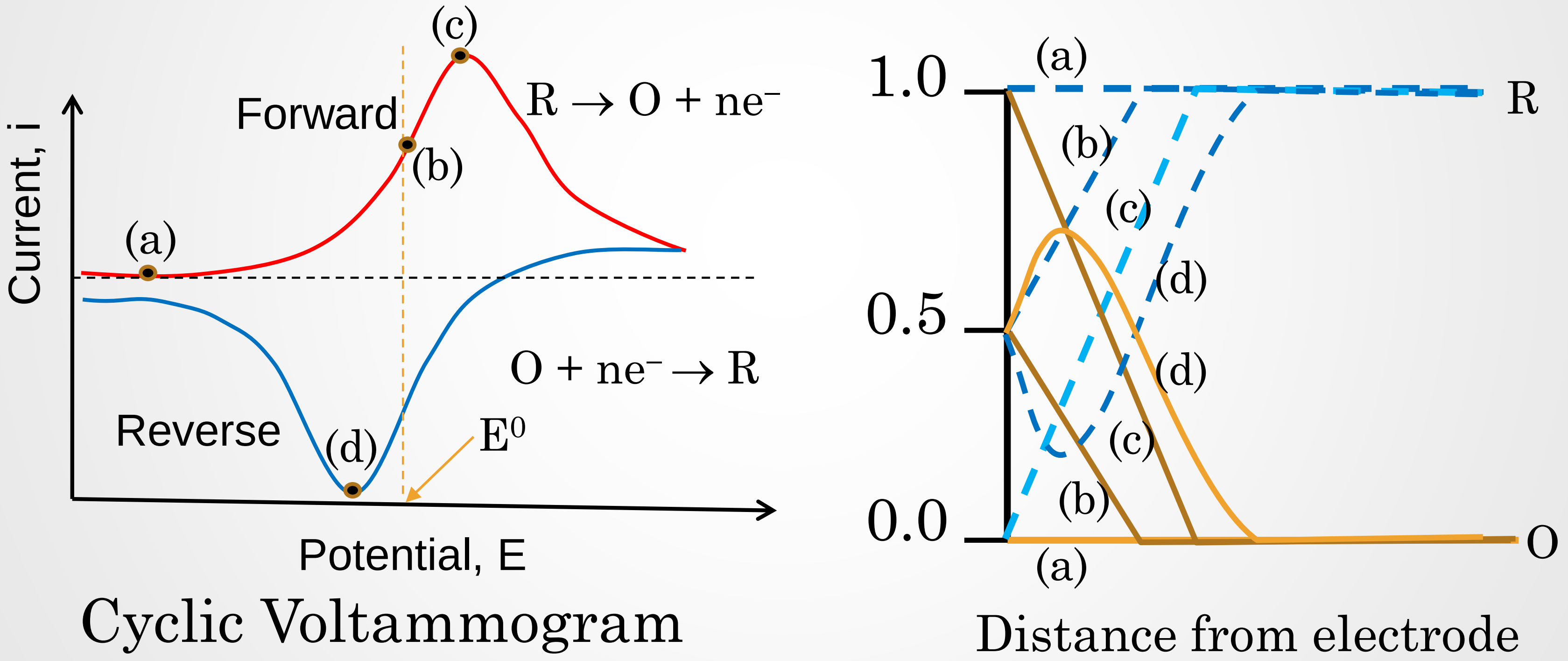
- It is assumed that only the oxidized form R is present initially. Thus, a positive-going potential scan is chosen for the first half-cycle, starting from a value where no oxidation occurs.

- As the applied potential approaches the characteristic $E°$ for the redox process, an anodic current begins to increase, until a peak is reached.

- After traversing the potential region in which the oxidation process takes place (at least $90/n$ mV beyond the peak), the direction of the potential sweep is reversed. During the reverse scan, O molecules (generated in the forward half-cycle, and accumulated near the surface) are reduced back to R, resulting in a cathodic peak.

CHARACTERISTIC PEAK IN CV

- The characteristic peaks in the cycle voltammogram are caused by the formation of the diffusion layer near the electrode surface.



Cyclic Voltammogram

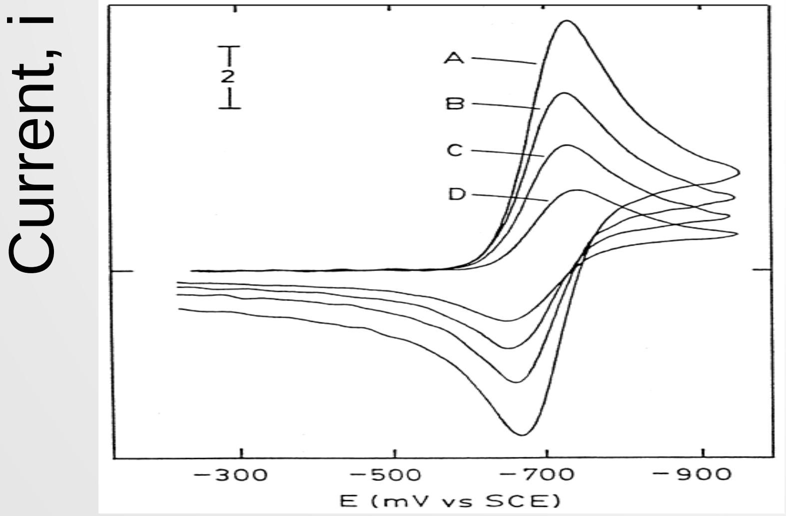
Fig. Concentration distribution of redox forms (a) initial potential, (b,d) formal potential of the couple during the forward and reversed scans, and (c) achievement of a zero-reactant surface concentration

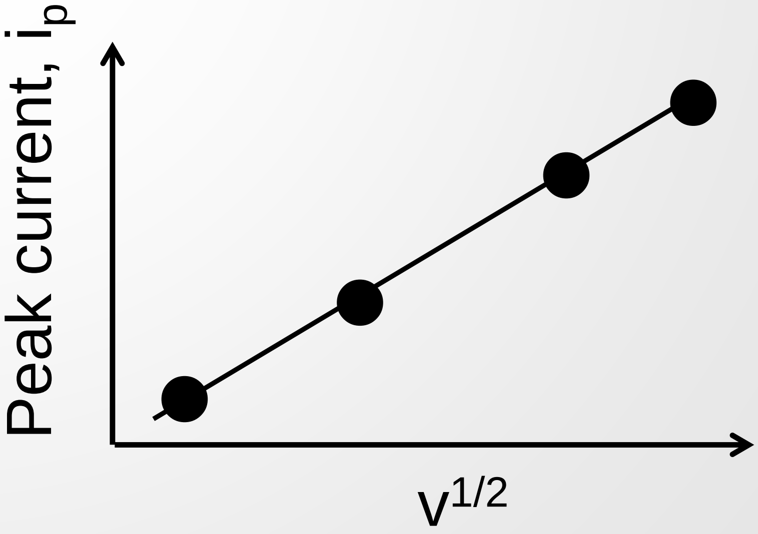
REVERSIBLE SYSTEMS

- **Peak Current:** Peak current, i_p follows the Randles-Sevcik equation

$$i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2}$$

where *n* is the number of electrons, *A* the electrode area (in cm2), *C* the concentration (in mol/cm3), *D* the diffusion coefficient (in cm2/s), and *v* the potential scan rate (in V/s).





REVERSIBLE SYSTEMS

- **Formal potential, E^0:** The formal potential for a reversible couple is centered between $E_{p,a}$ and $E_{p,c}$:

$$E^\circ = \frac{E_{p,a} + E_{p,c}}{2}$$

- **Peak separation, ΔE:** The separation between the peak potentials (for a reversible couple) is given by

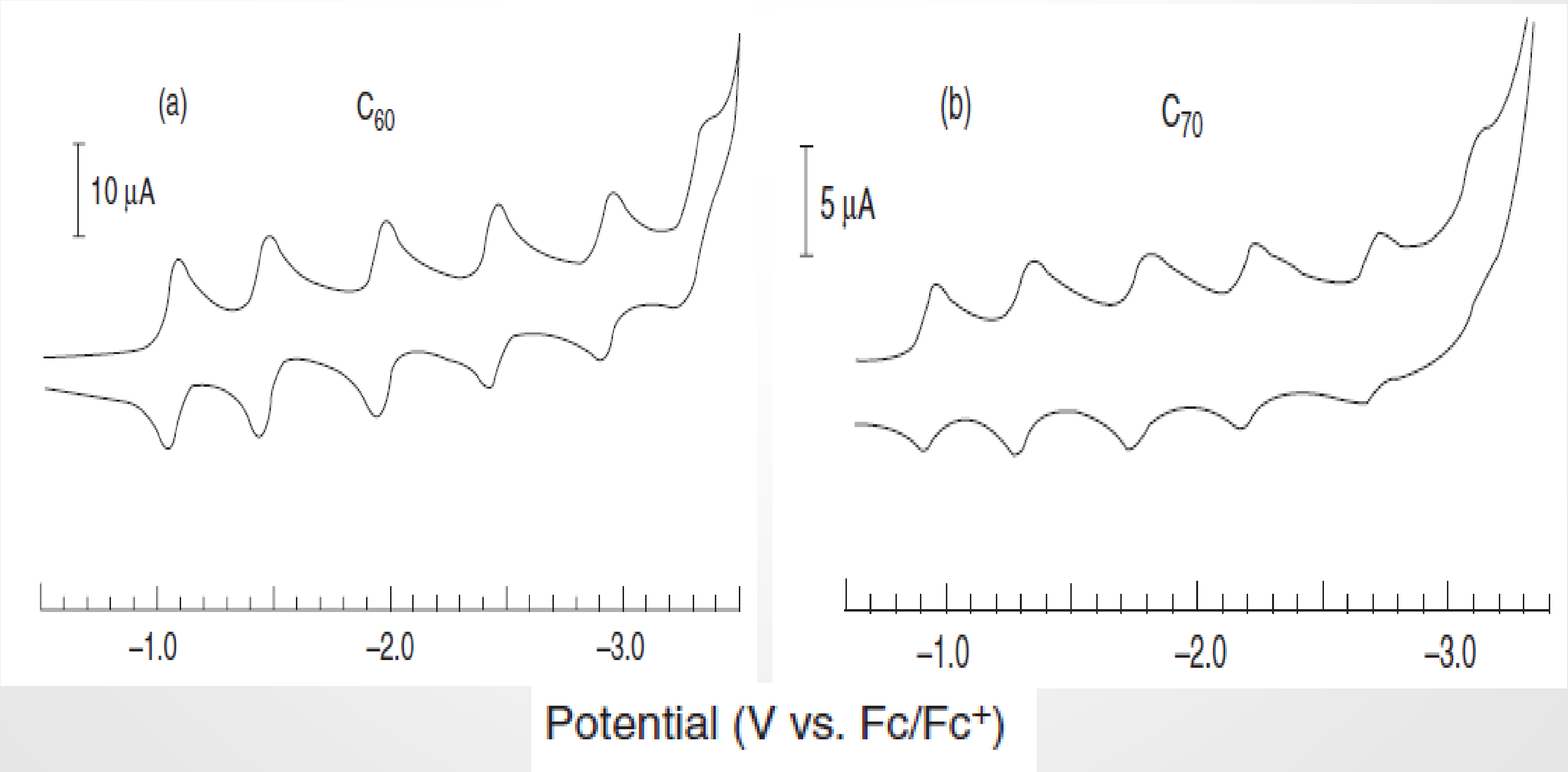
$$\Delta E_p = E_{p,a} - E_{p,c} = \frac{0.059}{n} \quad \text{V}$$

- **Peak current ratio, $i_{p,a}/i_{p,c}$:** For reversible redox couple

$$\frac{i_{p,a}}{i_{p.c}} = 1$$

MULTIELECTRON TRANSFER REVERSIBLE SYSTEMS

- For multielectron transfer (reversible) processes, the cyclic voltammogram consists of several distinct peaks, if the $E°$ values for the individual steps are successively higher and are well separated.



IRREVERSIBLE & QUASI-REVERSIBLE SYSTEMS

- For irreversible processes (those with sluggish electron exchange), the individual peaks are reduced in size and widely separated

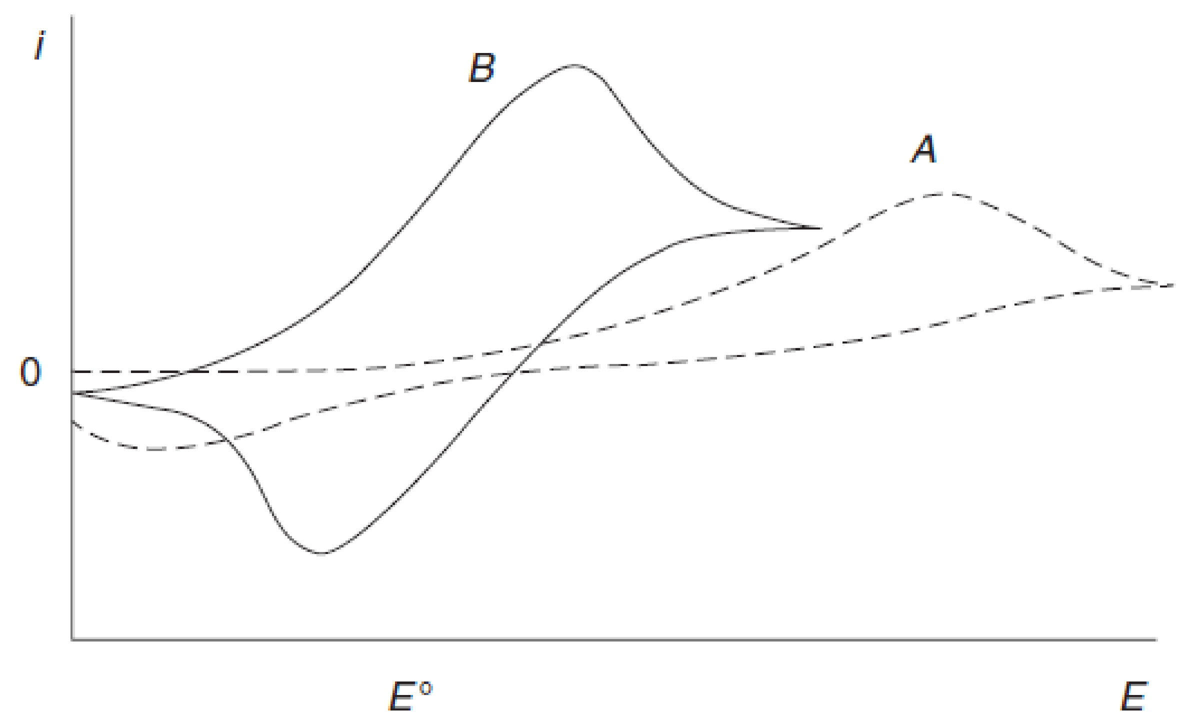


Fig. Cyclic voltammograms for irreversible (curve A) and quasi-reversible (curve B) redox processes.

IRREVERSIBLE & QUASI-REVERSIBLE SYSTEMS

- **Peak potential:** Totally irreversible systems are characterized by a shift of the peak potential with the scan rate:

$$E_p = E^\circ - \frac{RT}{\alpha n_a F}\left[0.78 - \ln\frac{k^\circ}{D^{1/2}} + \ln\left(\frac{\alpha n_a F v}{RT}\right)^{1/2}\right]$$

- **Peak c**

$$i_p = (2.99 \times 10^5) n (\alpha n_a)^{1/2} A C D^{1/2} v^{1/2}$$

WHAT DICTATES REVERSIBLE AND IRREVERSIBLE BEHAVIOR?

- **Mass transfer rate,**

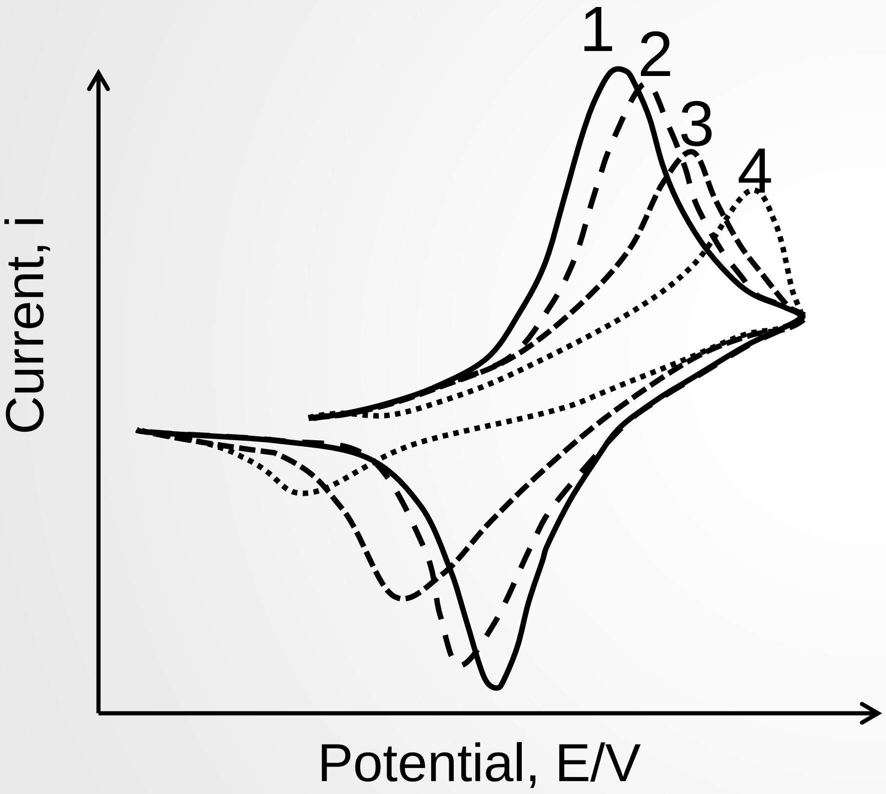
$$m_T = \frac{D}{\delta} = \frac{D}{\sqrt{Dt}} = \sqrt{\frac{D}{t}} = \sqrt{\frac{D}{\frac{RT}{nFv}}} = \sqrt{\frac{nvFD}{RT}}$$

- **Dimensionless rate constant,**

$$\Lambda = \frac{k^0}{m_T} = \frac{k^0}{\sqrt{\frac{nvFD}{RT}}}$$

- **Λ becomes large for large values of k^0 and small scan rate.**
- **Λ is small for small values of k^0 and large scan rate.**

WHAT DICTATES REVERSIBLE AND IRREVERSIBLE BEHAVIOR?



$E^0 = 0$; $\alpha = 0.5$; $A = 1\ \mathrm{cm}^2$;
$[A]_0 = 1\ \mathrm{mM}$; $D_A = D_B = 10^{-5}\ \mathrm{cm^2 s^{-1}}$

Redox reaction : $A \pm e \rightleftharpoons B$

Value of ʌ parameter

1. 100
2. 1
3. 0.1
4. 0.01

Reversible: $\Lambda \geq 15$ or $\Lambda \geq 0.3\sqrt{v}$

Quasi-reversible:

$15 > \Lambda > 10^{-3}$

Or $0.3\sqrt{v} > k^0 > 2 \times 10^{-5}\sqrt{v}$

Irreversible:

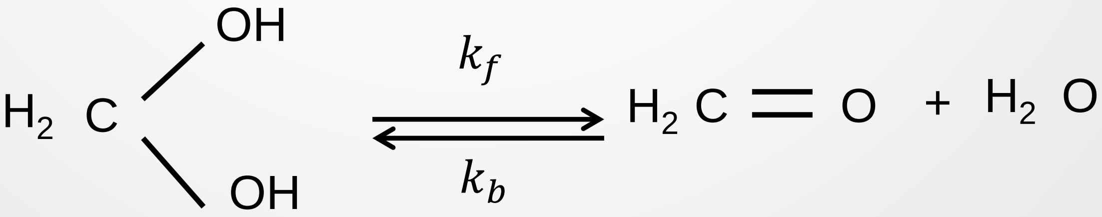
$\Lambda \leq 10^{-3}$ or $k^0 \leq 2 \times 10^{-5}\sqrt{v}$

STUDY OF REACTION MECHANISM

- **Homogeneous coupled reactions**
- $A(aq) + e^{-} \rightleftharpoons B(aq)$ **(1)**

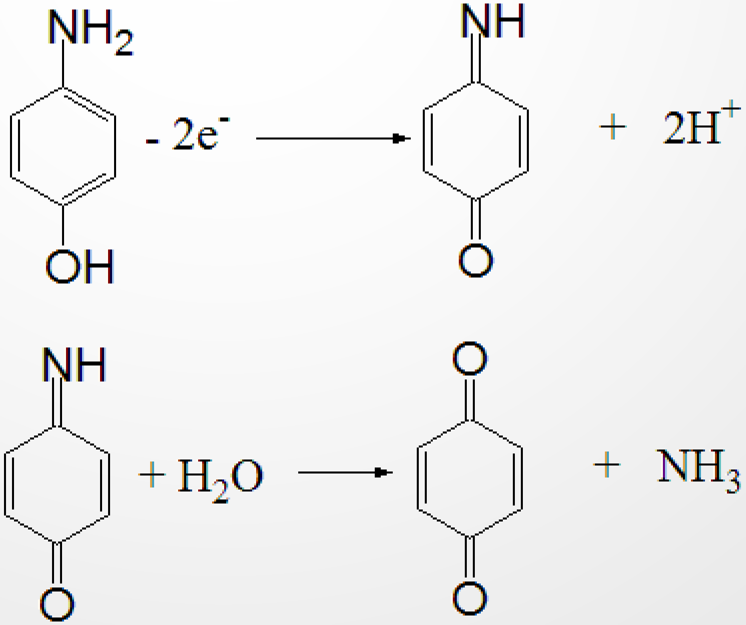
where A and B both are chemically stable on the timescale of the experiment.

- However, in real case the product B are not so much stable, even in some cases reactant A itself undergoes heterogeneous electron transfer reaction followed by structural changes such as solvation, bond breaking and so on.
- Example:



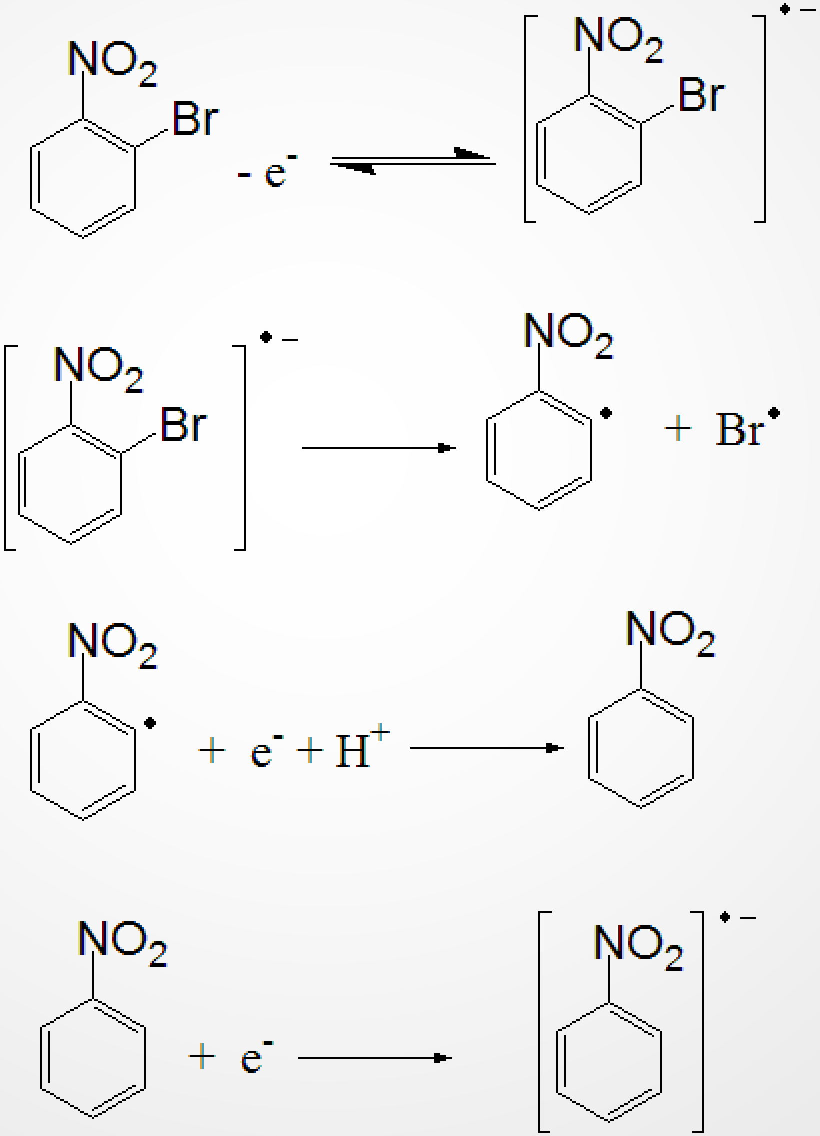
NOTATION AND EXAMPLES

- Heterogeneous electron transfer reactions → E
- Homogeneous chemical reactions → C
- Subscripts r and ir are used for reversible and irreversible reactions
- Notation of mechanisms: E_rC_r, E_rC_{ir}, C_rE_r, C_rE_{ir}, ECE
- Example EC reaction:



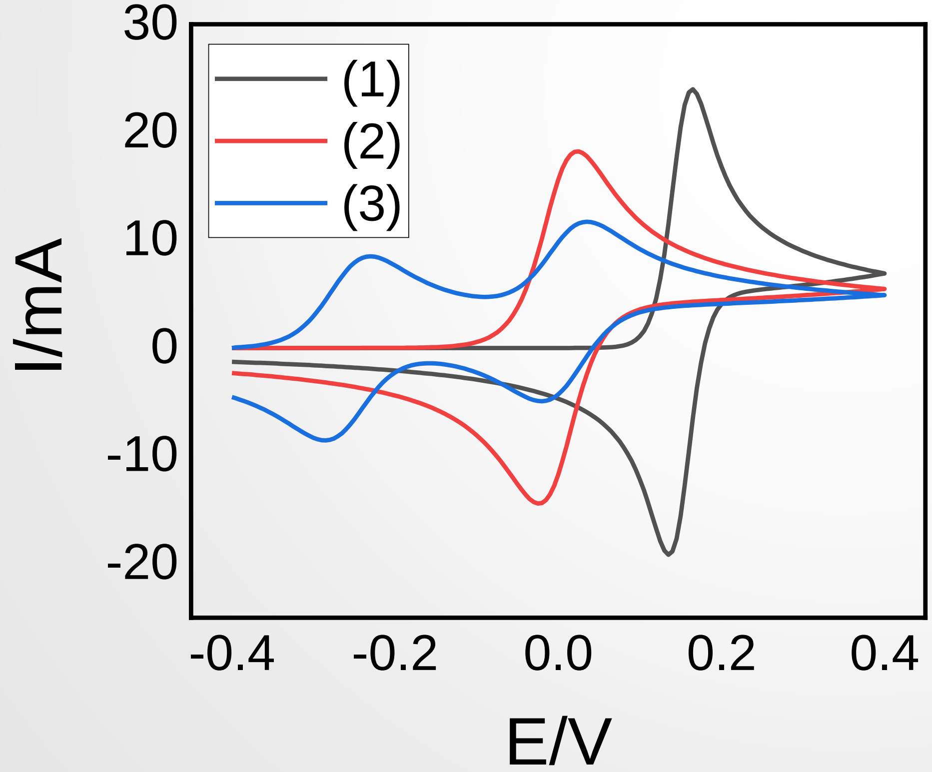
NOTATION AND EXAMPLES

- **ECE reactions**



MULTIELECTRON TRANSFER

- $A + e \rightleftharpoons B \qquad E_f^0\ (A/B)$
- $B + e \rightleftharpoons C \qquad E_f^0\ (B/C)$
- $k_1^0 = k_2^0 = 1 \times 10^2\ \mathrm{cm/s}$



- What will be the nature of cyclic voltammogram?
- How many redox waves will be observed?

Index	$\mathbf{E_f^0}$**(A/B)**	$\mathbf{E_f^0}$**(B/C)**
(1)	0.0 V	0.3 V
(2)	0.0 V	0.0 V
(3)	0.0 V	– 0.3 V

$$E_f^0\ (B/C) \gg E_f^0(A/B)$$

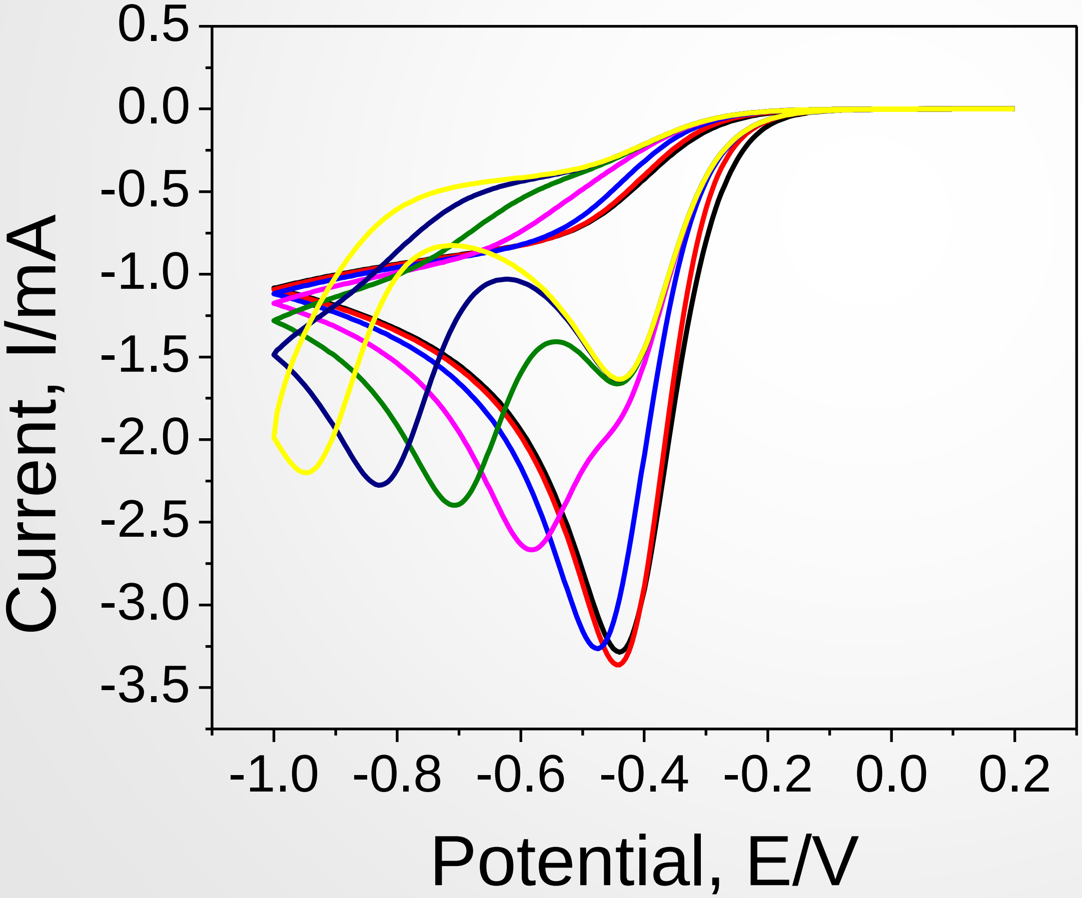
– One redox wave

$$E_f^0\ (B/C) \ll E_f^0(A/B)$$

– two redox waves

MULTIELECTRON TRANSFER (IRREVERSIBLE

- $A + e \rightarrow B \quad E_f^0\,(A/B)$; **slow**
- $B + e \rightarrow C \quad E_f^0\,(B/C)$; **fast**



- What will be the nature of cyclic voltammogram?
- How many redox waves will be observed?

k_2^0 *is relatively large*

– One redox wave

k_2^0 *is very small*

– two redox waves

CV OF EC REACTION

- **$A + e \rightleftharpoons B$**

$$B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C,\ K = \frac{k_f}{k_b}$$

K	k_f	k_b	**Index**
10^6	3.9×10^4	3.9×10^{-2}	(1)
	1.2×10^0	1.2×10^{-6}	(2)
	3.9×10^{-3}	3.9×10^{-9}	(3)

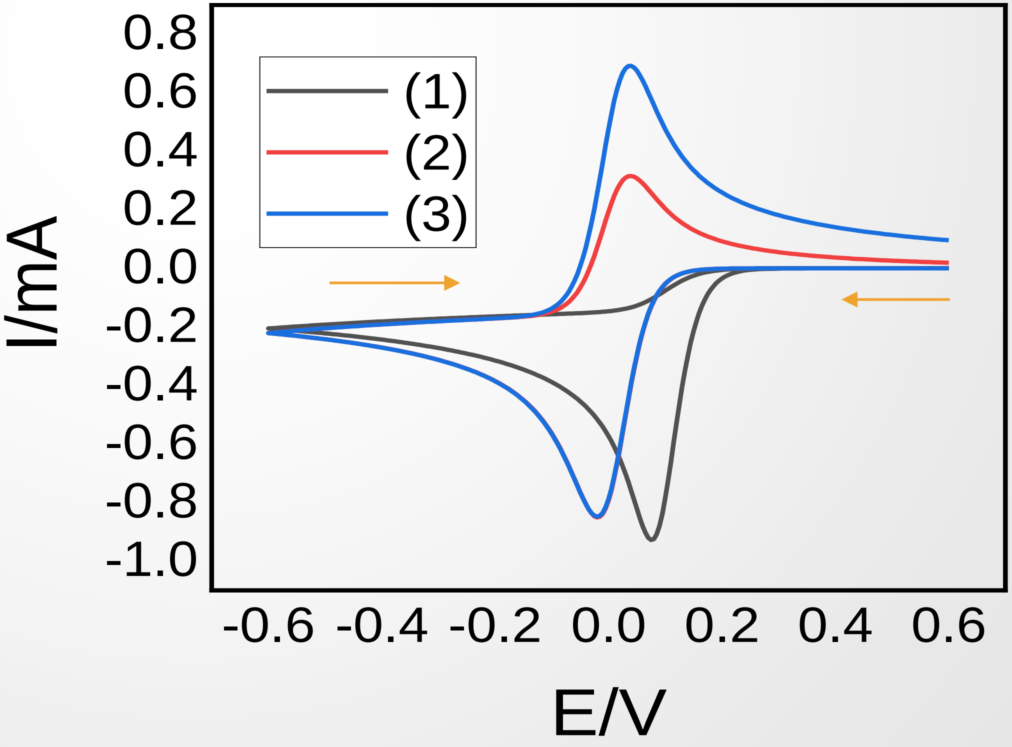
$[A]=1$ mM;

$k^0=1.973$;

$v = 1\ Vs^{-1}$;

$D_A=D_B=D_C=D=10^{-5}$;

area = 1 cm^2



CV FOR $E_{IR}C$ REACTION

- **A + e → B**

$$B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{products}$$

K	k_f	k_b	**Index**
10^6	3.9×10^3	3.9×10^{-3}	(1)
	3.9×10^{-2}	3.9×10^{-8}	(2)
	3.9×10^{-4}	3.9×10^{-10}	(3)

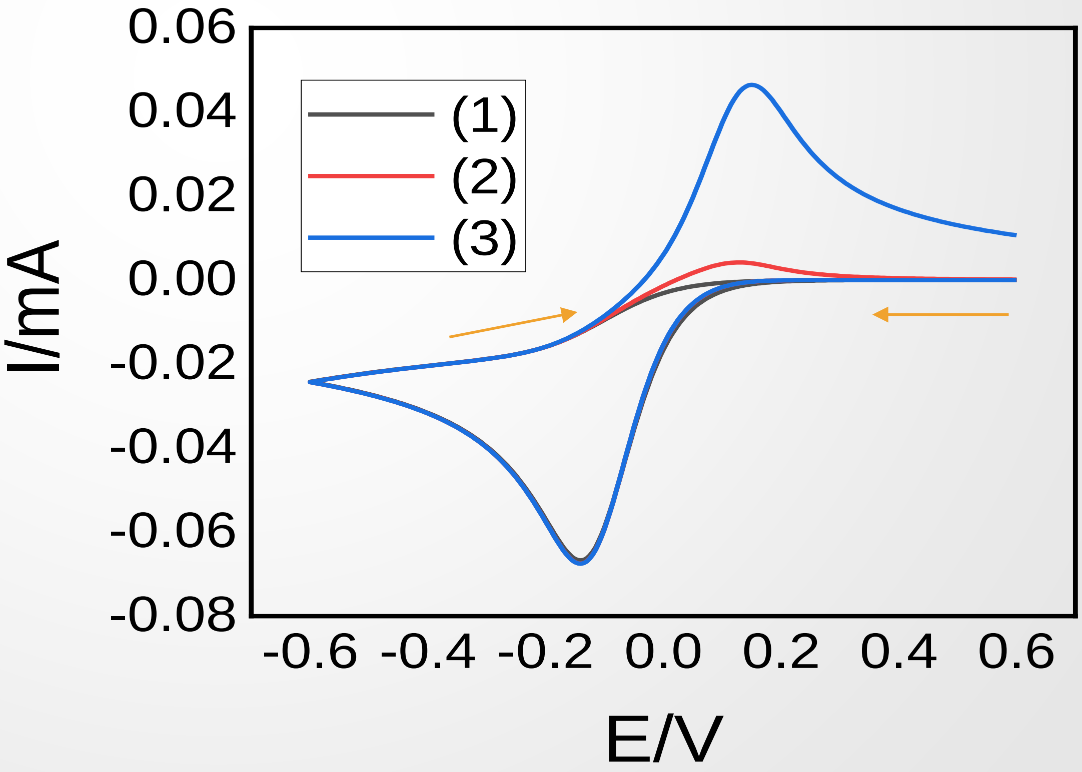
$[A]=1$ mM;

$k^0=1.973\times10^{-4}$;

$v = 0.01\ Vs^{-1}$;

$D_A=D_B=D_C=D=10^{-5}$;

area = 1 cm^2



EFFECT OF PH ON CV

- $A + mH^{+} + ne^{-} \rightleftharpoons B$
- Case I: Reversible reaction
- Nernst equation

$$E = E_{f}^{0}(A/B) - \frac{RT}{nF}\ln\frac{[B]}{[A][H^{+}]^{m}}$$

$$E = E_{f}^{0}(A/B) + \frac{RT}{nF}\ln[H^{+}]^{m} - \frac{RT}{nF}\ln\frac{[B]}{[A]}$$

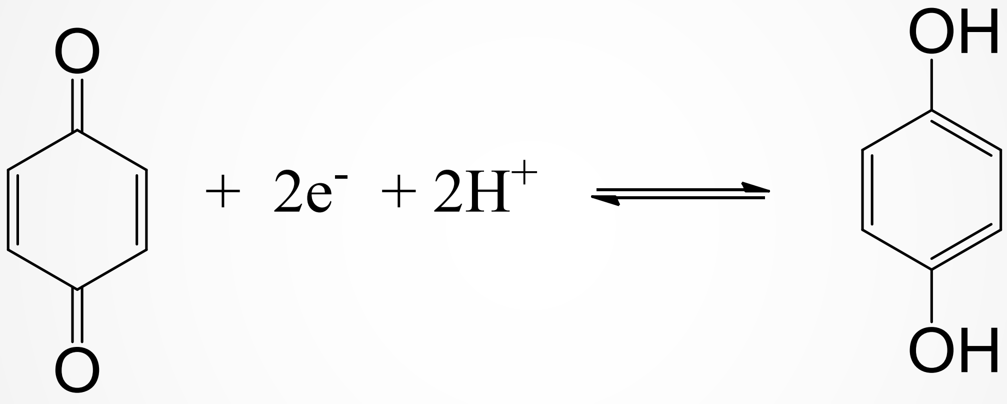
$$E = E_{f}^{0}(A/B) - 2.303\frac{mRT}{nF}pH - \frac{RT}{nF}\ln\frac{[B]}{[A]}$$

$$E = E_{f,eff}^{0}(A/B) - 2.303\frac{mRT}{nF}pH$$

$$E = E_{f,eff}^{0}(A/B) - \frac{0.059\,m}{n}pH \qquad \text{at } 25^{0}\text{C}$$

EFFECT OF PH ON CV

- **For m = n**
- $E^0_{f,eff} = E^0_f(A/B) - 0.059pH \;\; at\; 298\; K$



(BQ) (HQ)

- For the above reaction, redox wave is observed to shifted negative direction by ~59 mV per pH up to pH=~9. pH higher than 9, redox wave does not show any shifting because upper limit corresponds to the appropriate pK_a of HQ.

EFFECT OF PH ON CV

- **Case I: Irreversible reaction**

$$A + mH^+ \rightleftharpoons AH_m^{m+}$$

$$AH_m^{m+} + ne^- \rightleftharpoons B$$

- **Pre-equilibrium can be described**

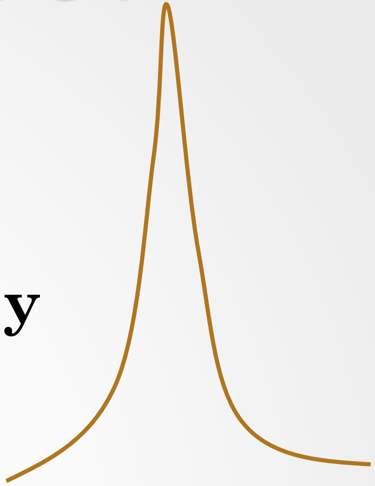
$$K = \frac{[A][H^+]^m}{[AH_m^{m+}]}$$

$$[A]_{total} = [A] + [AH_m^{m+}]$$

$$[A]_{total} = \frac{K[AH_m^{m+}]}{[H^+]^m} + [AH_m^{m+}]$$

$$[AH_m^{m+}] = \frac{[A]_{total}[H^+]^m}{K + [H^+]^m}$$

EFFECT OF PH ON CV



$$I \propto [AH_m^{m+}]_0 \exp\left(-\frac{n'+\alpha}{RT}F\eta\right)$$

- **Where, η is over potential given by**

$$\eta = E - E_f^0(AH_m^{m+}/B)$$

$$I \propto \frac{[A]_{total}[H^+]^m}{K+[H^+]^m} \exp\left(-\frac{n'+\alpha}{RT}F\eta\right)$$

$$I \propto [A]_{total} \exp\left(-\frac{n'+\alpha}{RT}F\eta + ln\frac{[H^+]^m}{K+[H^+]^m}\right)$$

$$I \propto [A]_{total} \exp\left(-\frac{n'+\alpha}{RT}F\eta'\right)$$

$$\eta' = E - E_f^0(AH_m^{m+}/B) + \frac{RT}{(n'+\alpha)F} ln\frac{[H^+]^m}{K+[H^+]^m}$$

EFFECT OF PH ON CV

E_p **will show pH dependence given by**

$$E_p = const + \frac{RT}{(n' + \alpha)F} ln \frac{[H^+]^m}{K + [H^+]^m}$$

Two limiting case

- **Case I:** $[H^+] \ll K$ **i.e.,** $pH \gg pK$

$$E_p = const + \frac{RT}{(n'+\alpha)F} \ln \frac{[H^+]^m}{K}$$

$$E_p = const - \frac{2.303mRT}{(n'+\alpha)F} pH + \frac{2.303RT}{(n'+\alpha)F} pK$$

Case II: $[H^+] \gg K$ **or** $pH \ll pK$

$$E_p = const + \frac{RT}{(n'+\alpha)F} ln1$$

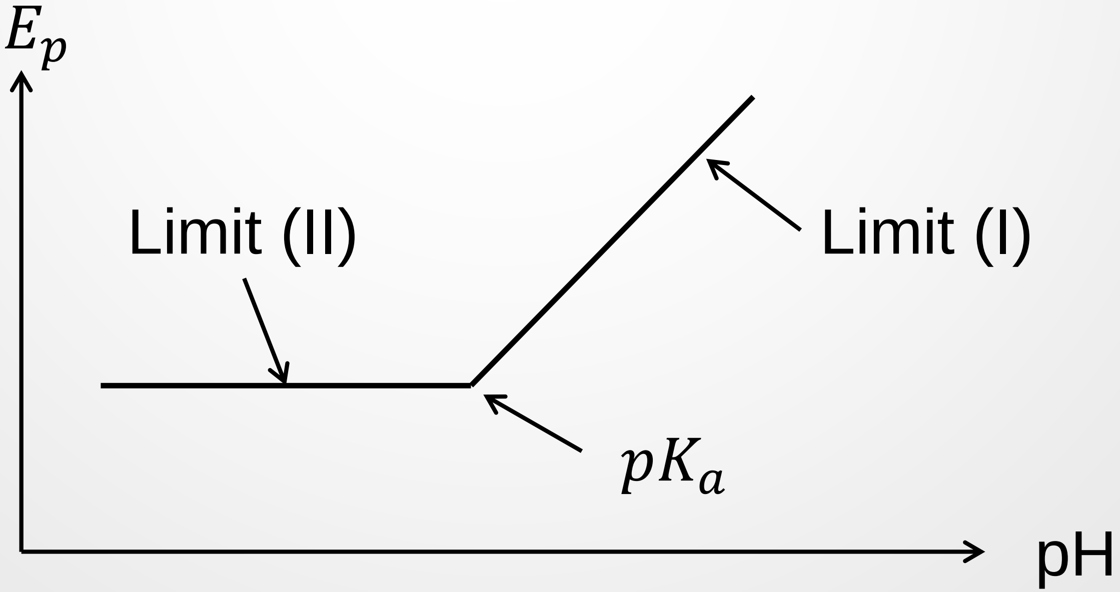
$$E_p = const$$

EFFECT OF PH ON CV

For example,

$$PhCOC^{-}S^{+}R_1R_2 + H^{+} \rightleftharpoons PhCOCH_2S^{+}R_1R_2$$

$$PhCOCH_2S^{+}R_1R_2 + 2e \rightleftharpoons PhCOCH_2^{-} + R_1SR_2$$



ADSORPTION AND CV

$$A(ads) + e^{-} \rightleftharpoons B(ads)$$

$$\Gamma_A(t) + \Gamma_B(t) = \Gamma_{Total}$$

$$\frac{\Gamma_A(t)}{\Gamma_B(t)} = exp\left(-\frac{F}{RT}[E - E_f^0(A/B)]\right)$$

$$\frac{\Gamma_A(t)}{\Gamma_B(t)} = exp(-[\Theta - \Theta_f^0(A/B)])$$

where, $\Theta = \frac{FE}{RT}$ and $\Theta_f^0 = \frac{F}{RT}E_f^0(A/B)$

ADSORPTION AND CV

$$\Gamma_A(t) = \frac{exp\left[-\left\{\Theta - \Theta_f^0(A/B)\right\}\right]}{1 + exp\left[-\left\{\Theta - \Theta_f^0(A/B)\right\}\right]}\Gamma_{Total}$$

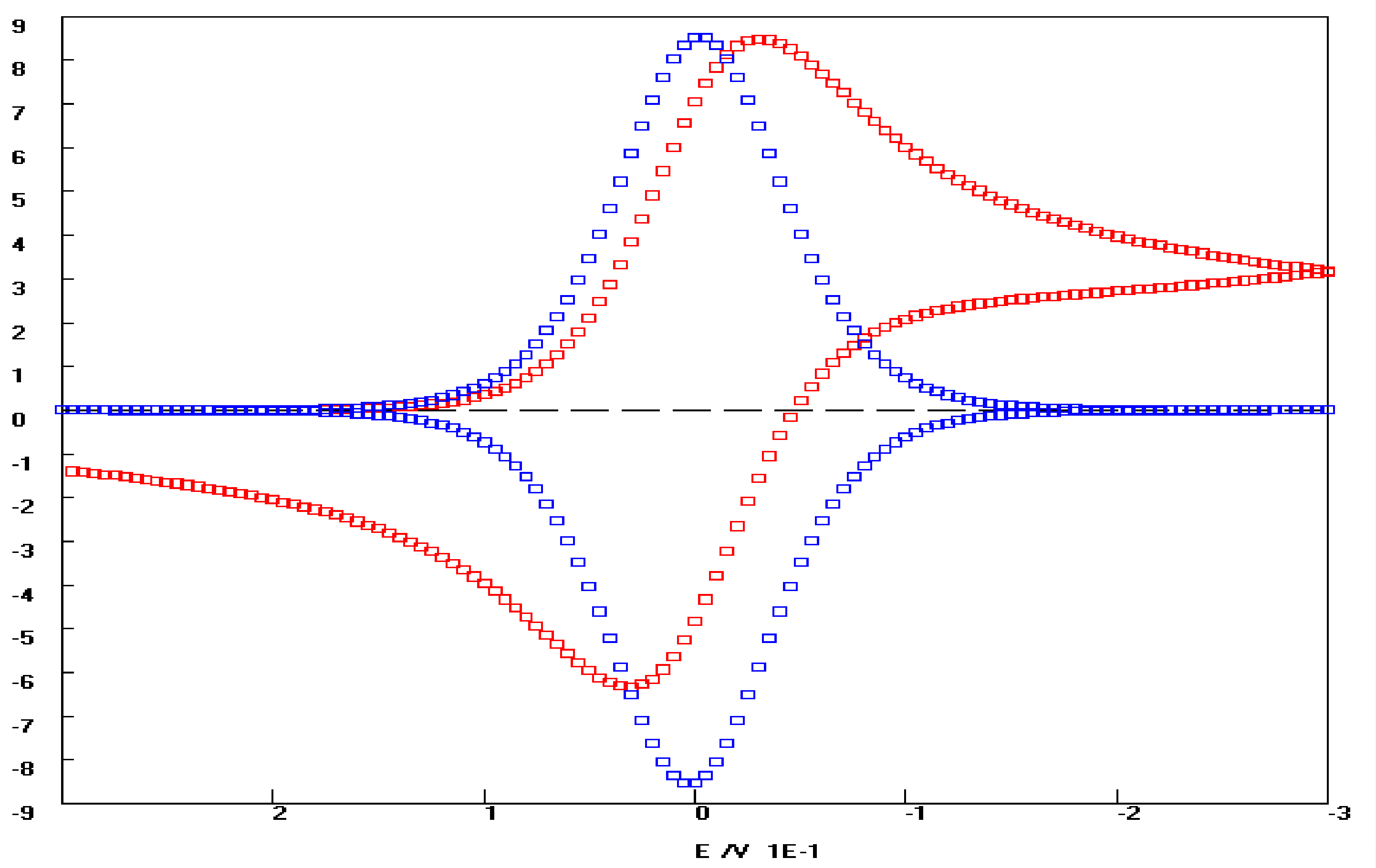
$$\Gamma_B(t) = \frac{1}{1+exp\left[-\left\{\Theta-\Theta_f^0(A/B)\right\}\right]}\Gamma_{Total}$$

The current is given by

$$\frac{I}{FA} = \frac{\partial \Gamma_B(t)}{\partial t} = -\frac{\partial \Gamma_A(t)}{\partial t}$$

$$\frac{I}{FA} = \frac{vF}{RT}\Gamma_{Total}^{*}\frac{exp\left[-\left\{\Theta-\Theta_f^0(A/B)\right\}\right]}{\left(1+exp\left[-\left\{\Theta-\Theta_f^0\left(\frac{A}{B}\right)\right\}\right]\right)^2}$$

ADSORPTION AND CV



$$I_p = \frac{n^2F^2}{4RT} vA\Gamma_{Total}$$

For adsorption

$$I_p = 2.69 \times 10^5 n^{3/2} A\sqrt{D}[A]_{bulk}\sqrt{v}$$

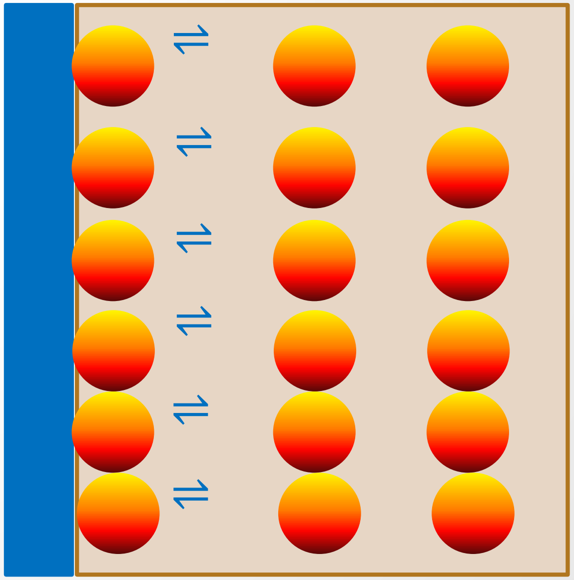
For solution

ADSORPTION AND CV

- The surface coverage

$$\int_0^{t_{switch}} Idt = FA\Gamma_{Total}$$

The relation between formal potential of redox couples in solution and adsorbed at surface



$$\Gamma_A = b_A[A]$$

$$\Gamma_B = b_B[B]$$

$$E_f^0(A/B)(ads) = E_f^0(A/B)(soln) - \frac{RT}{F}\ln\frac{b_A}{b_B}$$

ADSORPTION AND CV