

Lecture 6 : Chrono“metric” Techniques

Section 6-1 : Introduction

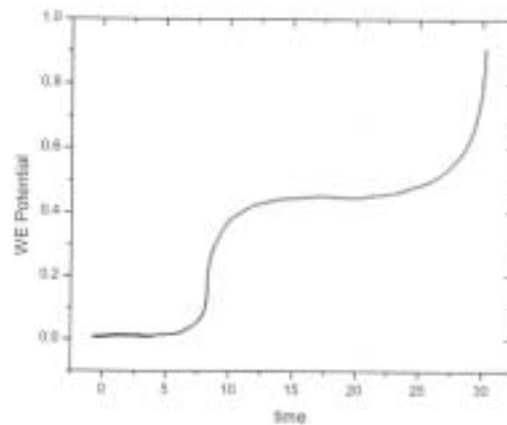
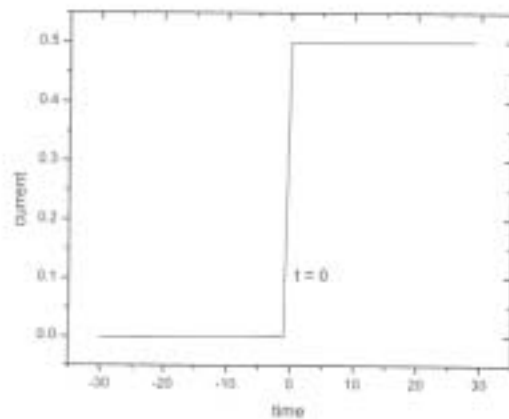
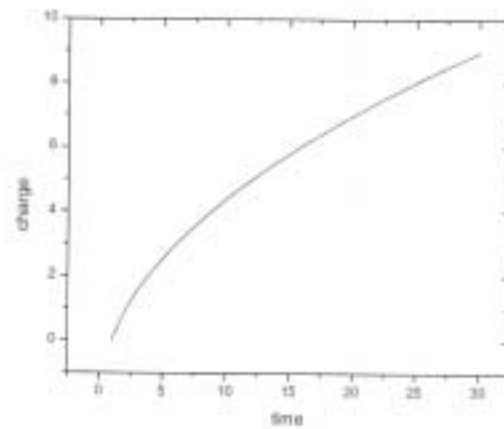
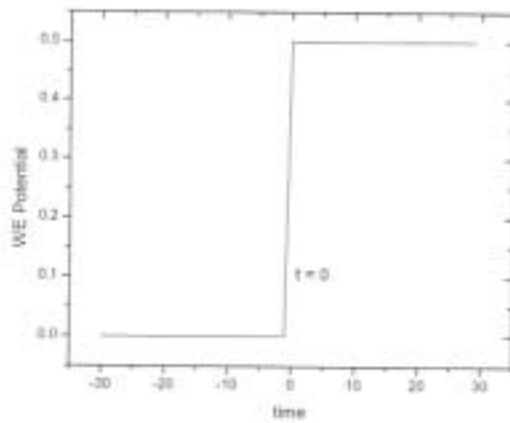
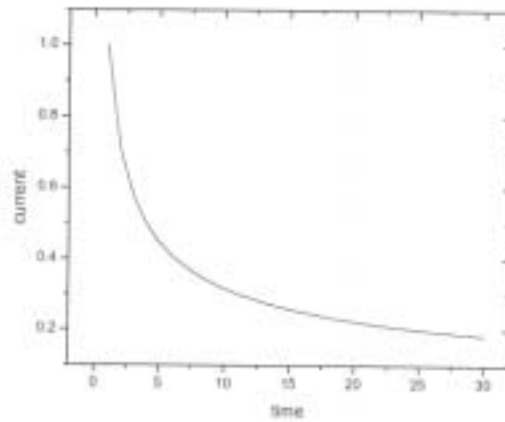
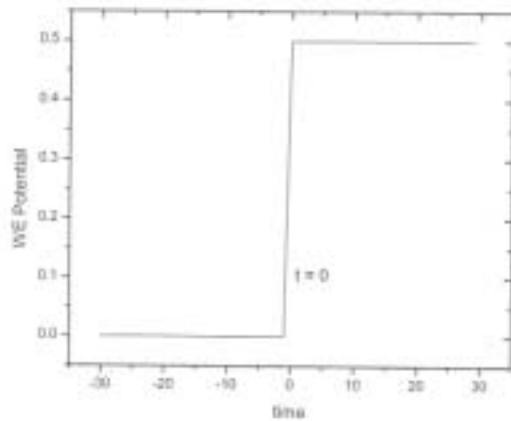
Chrono = Greek for time

- Chronometric techniques are those that involve following a time dependent (transient) electrical signal
- Good for studying kinetic processes but can also give very important thermodynamic information.

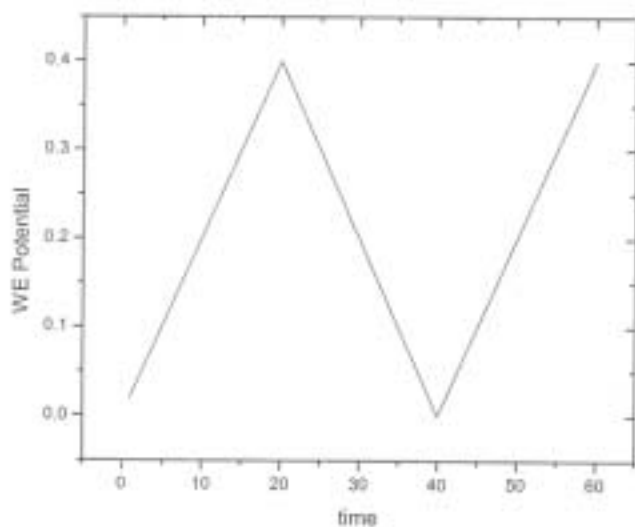
Different Chronometric techniques

Controlled Variable	Measured Variable	Title
WE potential	Current $I(t)$	<i>chronoamperometry</i>
WE potential	Charge $Q(t)$	<i>chronocoulometry</i>
Current flowing through the cell	WE Potential $E(t)$	<i>chronopotentiometry</i>

Excitation and Response Signals

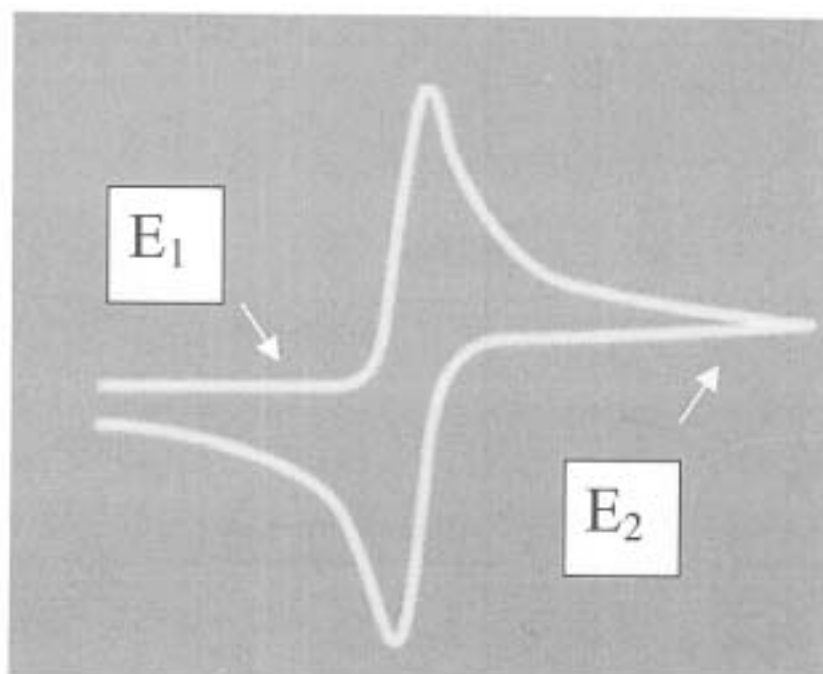


Compare to these to the excitation signal of voltammetric experiments.



General Discussion

Let's start with the simplest chronometric experiment.
We have a reversible redox system ($Ox + n\bar{e} \rightarrow Red$)



- If we step the potential from E_1 (where no net current flows) to E_2 where the reduced species becomes oxidized what influences the observed current ?

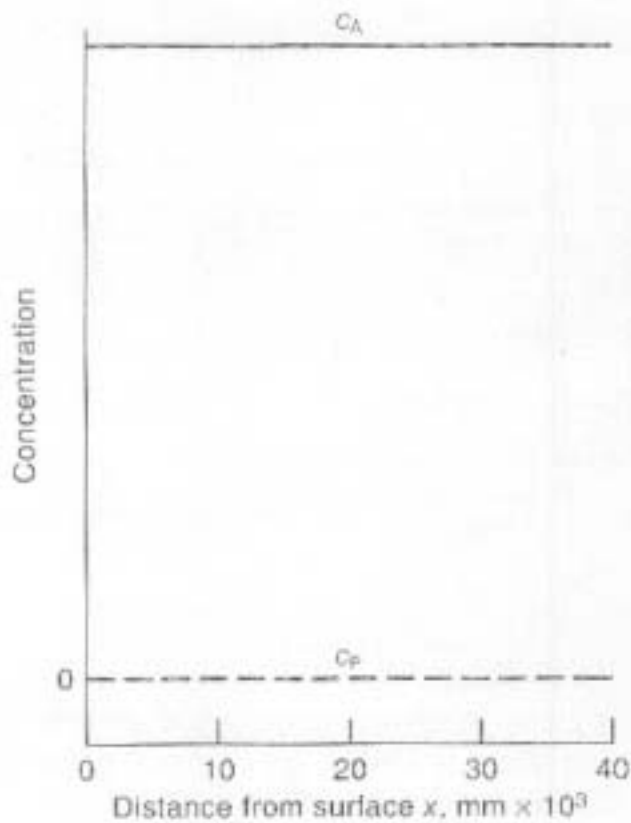
1. Mass transport
2. The rate of electron transfer.



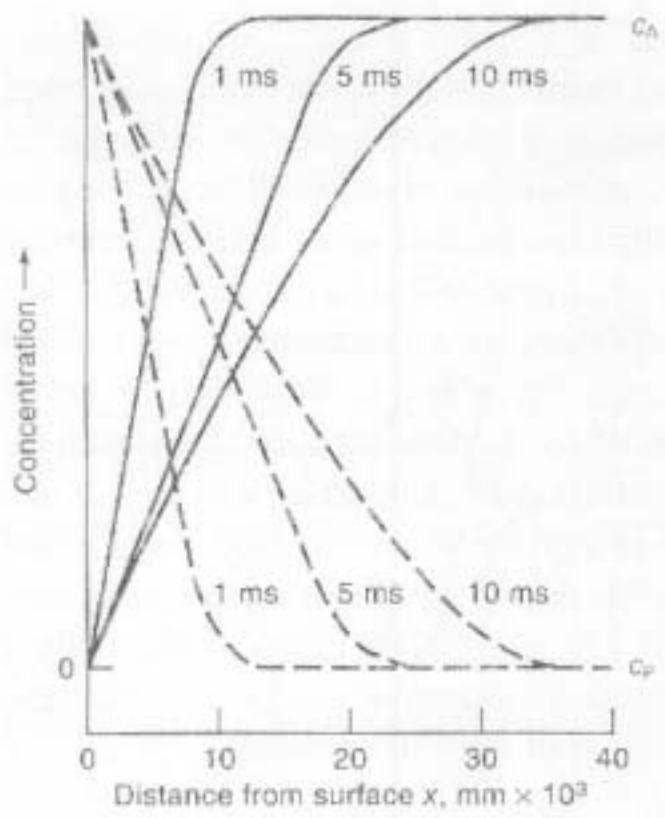
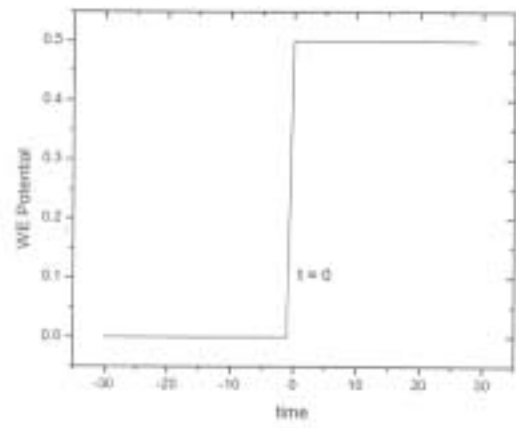
3. The rate of any chemical reactions coupled to either the reduced or oxidized species.
4. The nature and quantity of any species initially adsorbed on the working electrode prior to the perturbation.

Section 6-2 : Mass Transport Limited Chronoamperometry

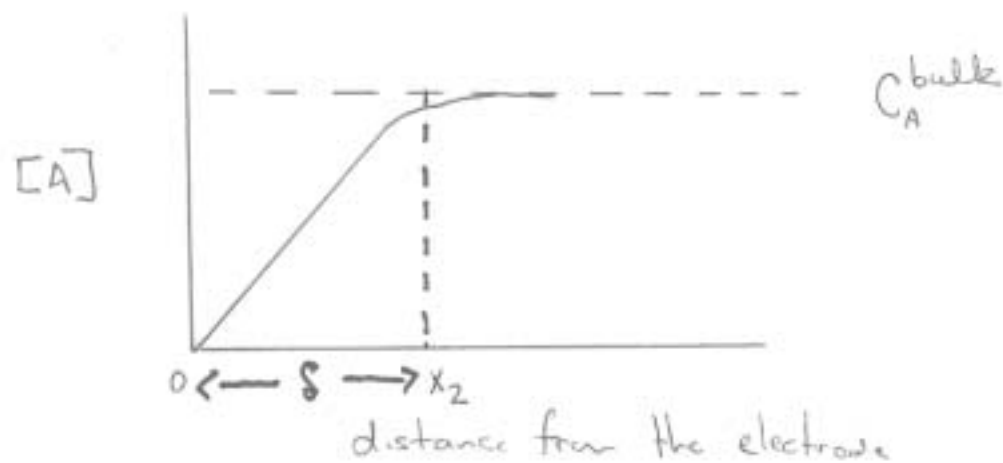
- There is no stirring
- No convection
- Presence of a large excess of supporting electrolyte \therefore no migration.



$t = 0$
(before the step)



Derivation of the Cottrell Eqn.



Fick's First Law : $J = D \frac{\partial C_A}{\partial x}$

flux in $\frac{\text{moles}}{\text{cm}^2 \cdot \text{s}}$

Making the approximation that $\frac{\partial C_A}{\partial x} = \frac{\Delta C_A}{\Delta x}$

$$J = \frac{D [C_A^{\text{bulk}} - C_A^{x=0}]}{x_2 - x_1} = \frac{D C_A^{\text{bulk}}}{\delta}$$

Looking at the units . . .

$$J \left(\frac{\text{moles}}{\text{cm}^2 \cdot \text{s}} \right) \times nF \left(\frac{\text{coulombs}}{\text{mole}} \right) \times A \left(\text{cm}^2 \right) = \frac{\text{coulombs}}{\text{s}}$$

$$JFA n = i$$

$$\therefore \frac{i}{FA n} = \frac{D C_A^{\text{bulk}}}{\delta} \Rightarrow i = \frac{nFA D C_A^{\text{bulk}}}{\delta}$$

CONT'D

For a planar electrode

$$\delta = \sqrt{\pi D t}$$

$$\therefore \dot{i} = n F A c_A^{\text{bulk}} \left(\frac{D}{\pi t} \right)^{1/2}$$

The Rigorous Approach

Fick's Second Law is the basic eqn. of linear diffusional motion:

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2}$$

"All" we need to do is solve this second-order partial differential eqn under the following boundary conditions.

$$C(x,0) = C^{\text{bulk}} \quad \text{B.C. \#1}$$

$$C(\infty, t) = C^{\text{bulk}} \quad \text{B.C. \#2}$$

$$C(0, t) = 0 \quad \text{B.C. \#3 (semi-infinite diffusion)}$$

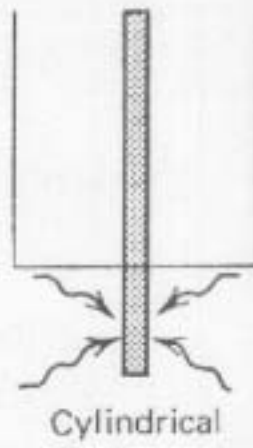
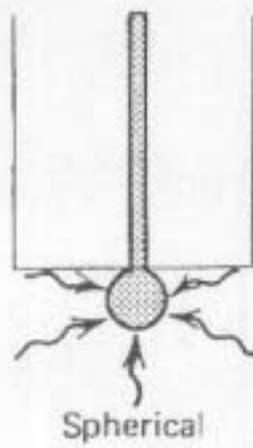
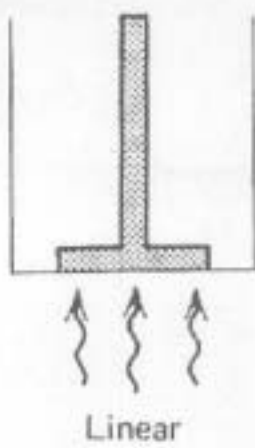
If you solve this differential eqn. you'll get

$$C(x,t) = C^{\text{bulk}} \operatorname{erf} \left[\frac{x}{2D^{1/2}t^{1/2}} \right]$$

Back to Fick's first law.

$$\dot{i} = nFAD \left(\frac{\partial C(x,t)}{\partial x} \right)$$

$$\Rightarrow \boxed{\frac{\dot{i}}{A} = nFC^{\text{bulk}} \left(\frac{D}{\pi t} \right)^{1/2}}$$



Spherical Diffusion

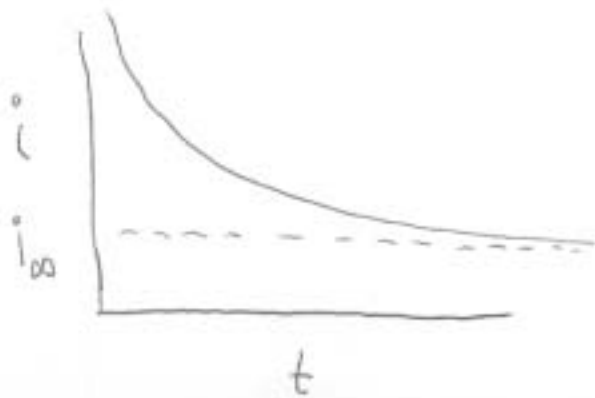
$$\frac{\partial C(r,t)}{\partial t} = D \left\{ \frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial C(r,t)}{\partial r} \right\}$$



Boundary Conditions

1. $C_{r_0} = C_{\text{bulk}} \quad (r > r_0)$
2. $C_{(\infty,t)} = C_{\text{bulk}}$
3. $C(r_0,t) = 0 \quad (t > 0)$

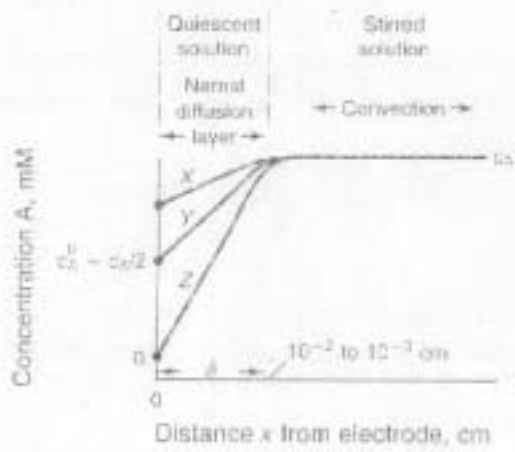
$$i = nFAD C^{\text{bulk}} \left[\frac{1}{(\pi D t)^{1/2}} + \frac{1}{r_0} \right]$$



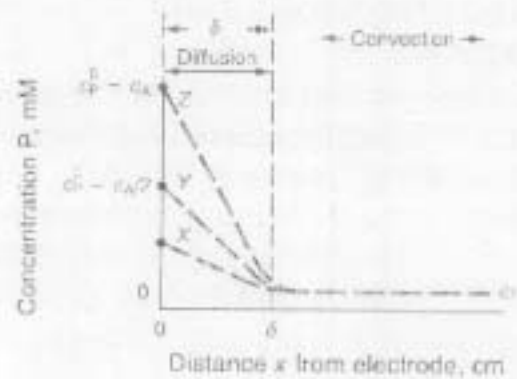
$$\lim_{t \rightarrow \infty} i = \frac{nFAD C^{\text{bulk}}}{r_0}$$

Relating Chronoamperometry to Voltammetry

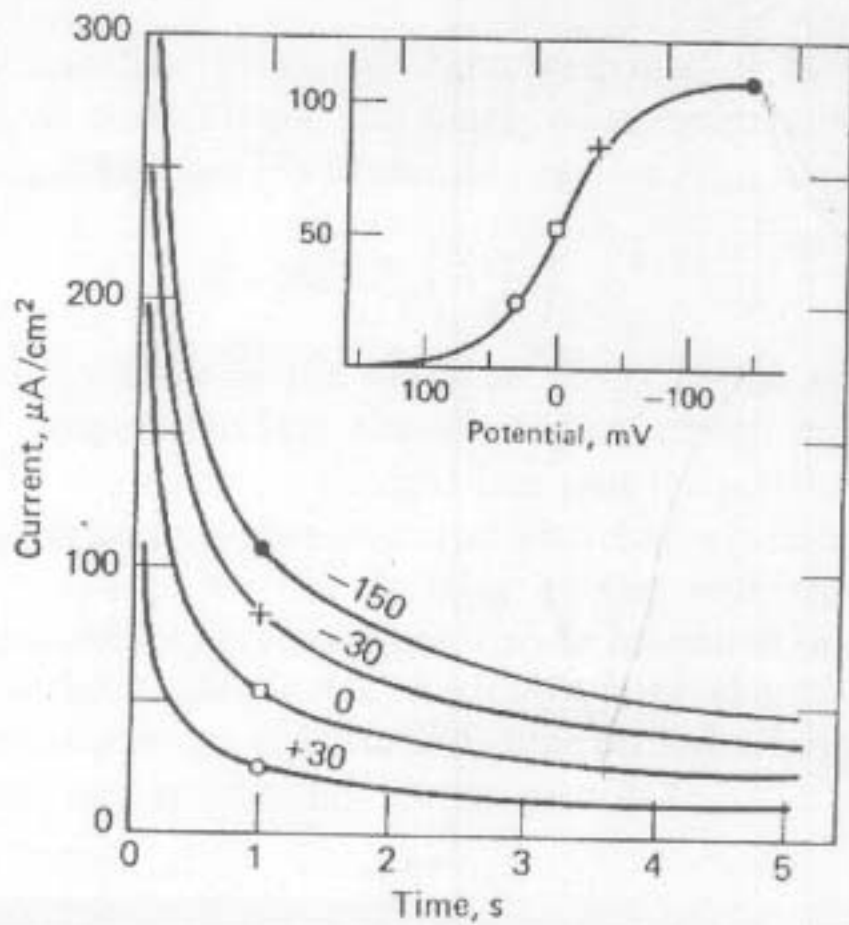
Hydrodynamic Voltammetry



(a)

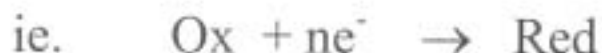


(b)



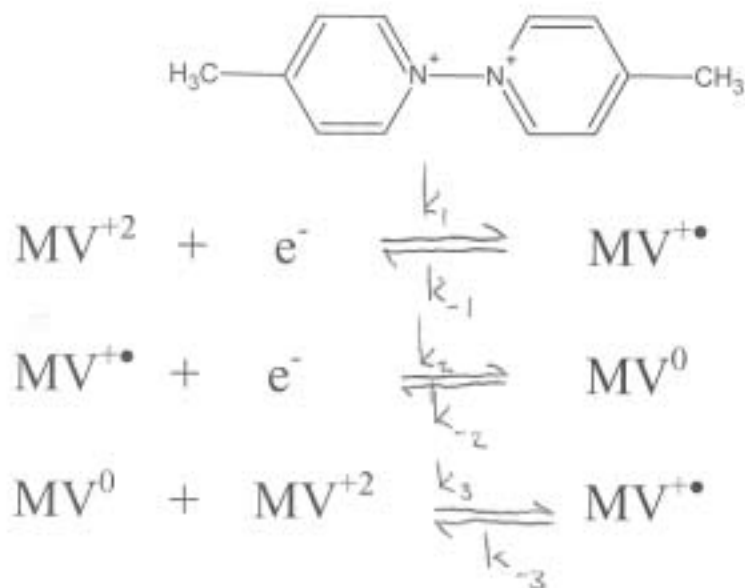
Section 6-3 : Chronoamperometry Coupled to Chemical Reactions

So far we have considered a system where only one electrochemical reaction occurs.

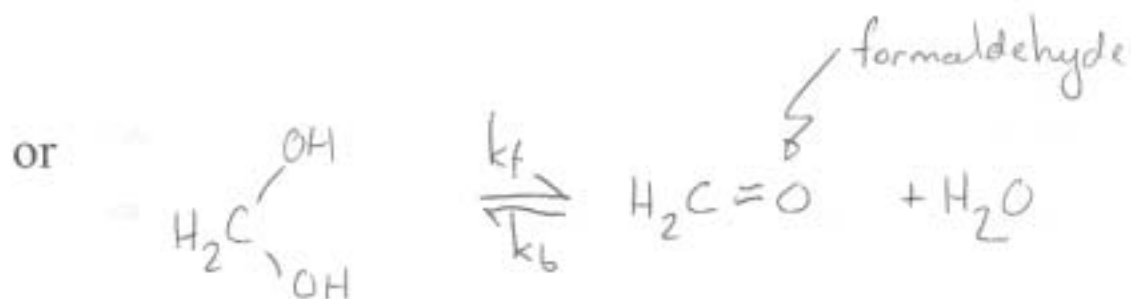
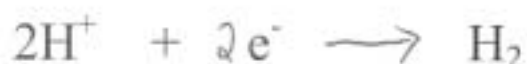
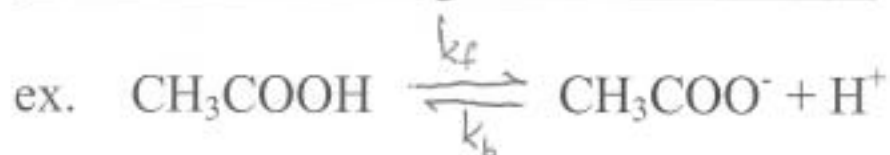


In many instances, especially with organic redox couples, many more and interesting side reactions may occur.

Example : conproportionation of methyl viologen

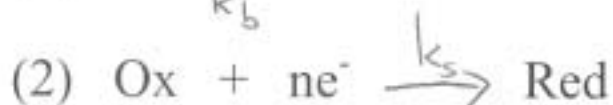
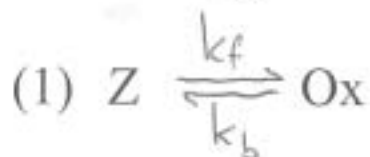


6-3-1 : A Preceding Chemical Reaction



Start with the case of the oxidized species (Ox) lying at equilibrium (current = 0) with an electroinactive species Z.

We are initially at a potential sufficiently positive such that the $C_{\text{red}} = 0$.



As before, we make a potential step to a potential negative enough to immediately reduce all Ox species at the electrode surface to zero.

Initially, we see the decaying diffusion controlled current but now the [Ox] species is inherently coupled to [Z] via equilibrium (1).

What happens depends on the value of k_f .

1) If k_f is very small \rightarrow Cottrellian

If k_f is very small then the [Ox] coming from Z is negligible and on the time scale of the transient, reaction 1 can be ignored.

$$i_0 = nFAc_{Ox}^{bulk} \left(\frac{D}{t\pi} \right)^{1/2}$$

2) If k_f is very large \rightarrow Cottrellian (with a twist)

Reaction (1) proceeds very rapidly.

On the time scale of the transient the current-time response is again given by the Cottrell eqn., but now the total $c_{Ox}^{bulk} + c_Z^{bulk}$ determines the current.

$$i_{\infty} = \frac{nAF}{\pi^{1/2}} [c_{Ox}^{bulk} + c_Z^{bulk}] \left(\frac{D}{t} \right)^{1/2}$$

3) But what if it's neither very fast or very slow?

Again, we start with Fick's Second Law

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2}$$

Boundary conditions

$$C_{Ox}(x,0) = C_{Ox}^{bulk}$$

$$C_{Ox}(\infty, t) = C_{Ox}^{bulk}$$

$$C_{Ox}(0, t) = 0$$

But now we have an additional eqn. to add to the mix

$$K = \frac{k_f}{k_b} = \frac{[Ox]}{[Z]}$$

$$(1) \quad i = nAF \left(C_{Ox}^{bulk} + C_Z^{bulk} \right) (Dk_fK)^{1/2} \exp[k_fKt] \operatorname{erfc}[k_fKt]^{1/2}$$

$$\lim_{t \rightarrow \infty} i = nAF \left[C_{Ox}^{bulk} + C_Z^{bulk} \right] \left[\frac{D}{\pi t} \right]^{1/2}$$

BACK TO THE COTTRELL EQN!

How can you extract the kinetic information from equation (1) ?

1. Measure your transient $i(t)$.

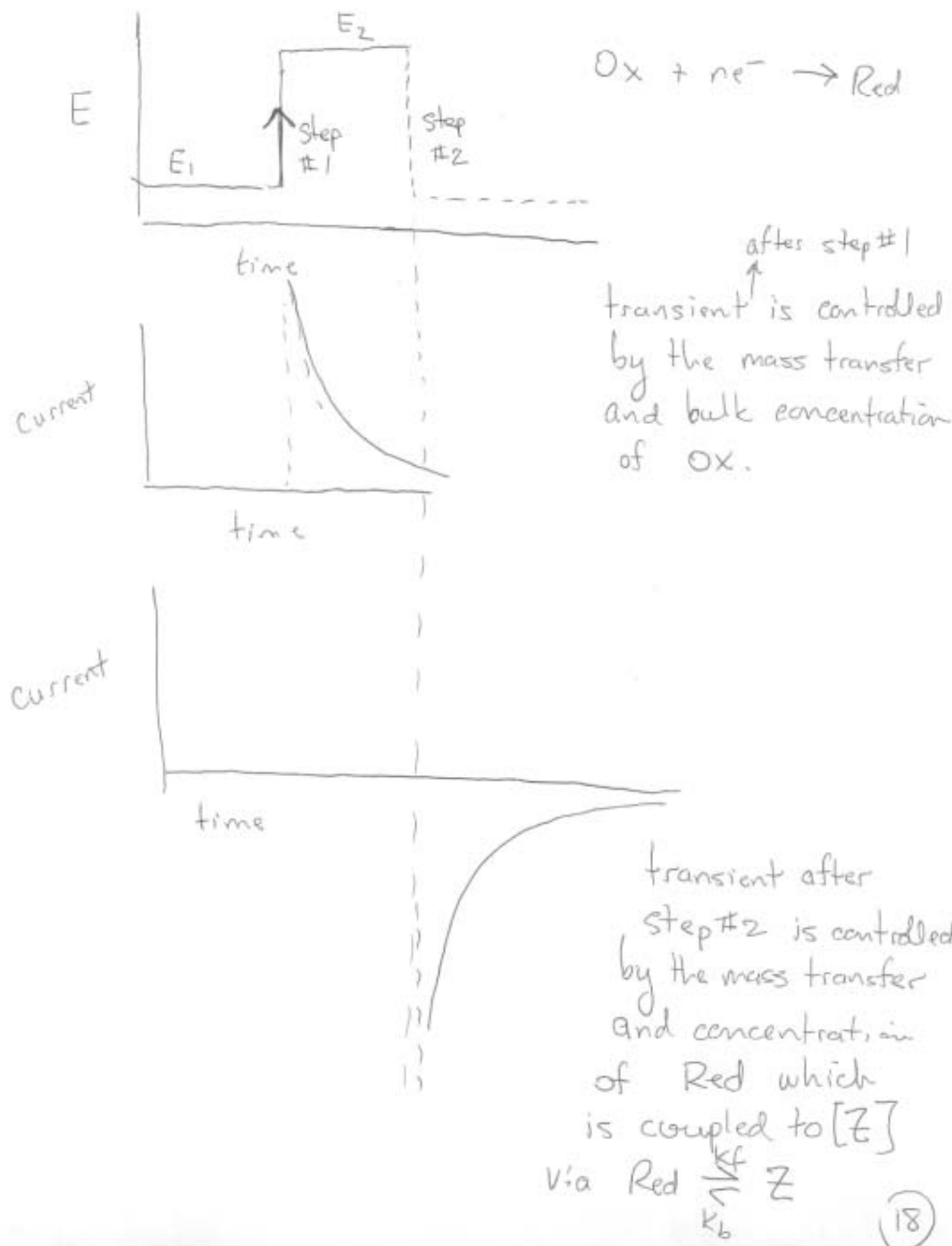
$i_{t=\infty} = i_{\infty}$: Normalize your data (i / i_{∞})

2. Guess a value for $k_f K$
3. Calculate the right hand side of (1) for different times and compare to (i / i_{∞}).
4. Refine your guess of $k_f K$.

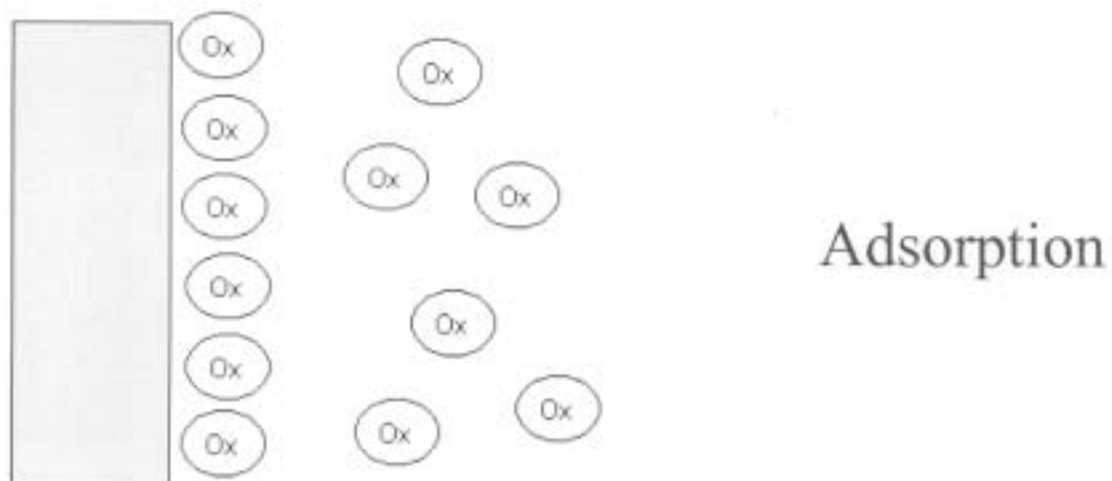
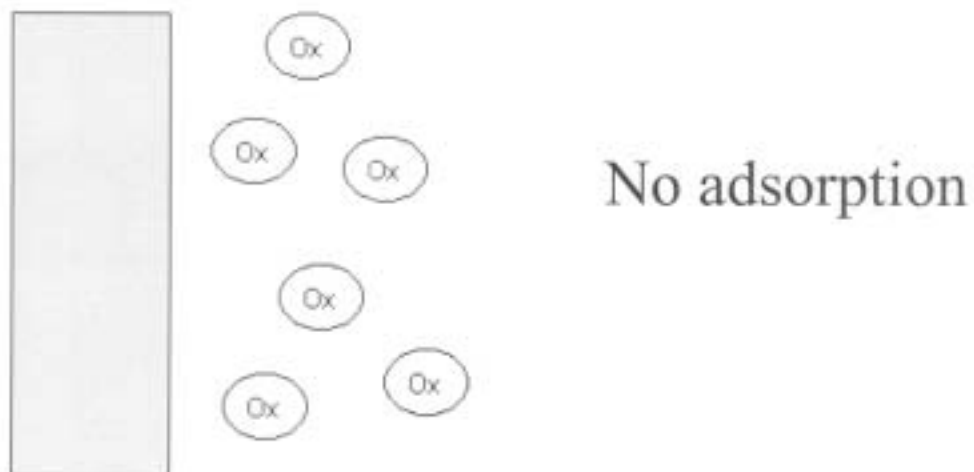
You can only determine the product (called the kinetic parameter) using this analysis.

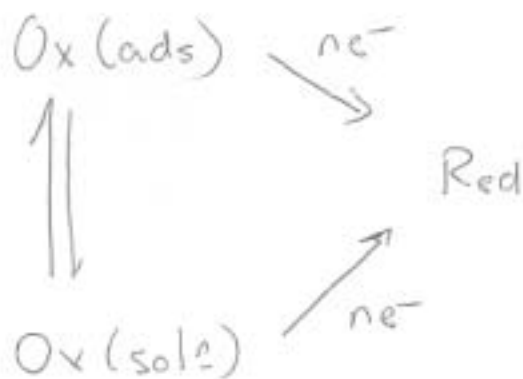
To extract k_f you need to independently determine K .

Because the chemical rxn. is subsequent to the electrochemical rxn. a single step won't work.



Section 6-4 : Determining the Gibbs Excess of an Adsorbed Electroactive Species





What happens if we step the working electrode potential to a value sufficiently negative to produce the condition

$$c_{\text{Ox (sol)}}(0,t) = c_{\text{Ox (ads)}}(0,t) = 0$$

The current-time response for the solution Ox species will be diffusion controlled but the Ox species adsorbed on the electrode requires no mass-transport and the reduction of this species results in a sharp current spike at very small time.

Ignoring double-layer charging, the charge passed in this sharp spike is proportional to the amount of Ox adsorbed on the electrode's surface (Γ_{Ox}).

$$Q_{\text{ads}} = nF\Gamma_{\text{Ox (ads)}}$$

In order to determine Q_{ads} one needs to evaluate the diffusion controlled Q-t transient by integrating the current transient.

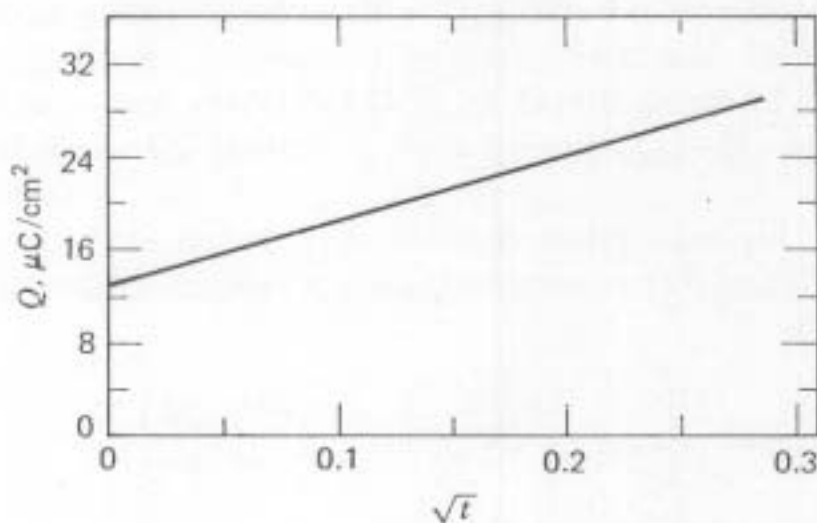
$$i_{dc} = \frac{nFAD^{1/2}C_{ox}^{bulk}}{\pi^{1/2}t^{1/2}} = \frac{dQ_{DC}}{dt}$$

$$dQ_{DC} = \frac{nFAD^{1/2}C_{ox}^{bulk}}{\pi^{1/2}} \frac{dt}{t^{1/2}} \quad \text{INTEGRATE}$$

$$Q_{DC} = \frac{2nFAD^{1/2}C_{ox}^{bulk}}{\pi^{1/2}} t^{1/2}$$

$$Q_{tot} = Q_{DC} + Q_{ads}$$

Plot Q_{tot} vs $t^{1/2}$



Intercept with the ordinate axis yields Q_{ads}

But we've neglected charging currents

Remember our electrode-electrolyte interface is modelled as a capacitor.

$$C = \frac{dQ}{dE} \quad \text{or} \quad dQ = C dE$$

If we make a potential step (dE) a corresponding amount of charge must flow to the electrode's surface, ~~to~~

$$E_x \quad C = 20 \mu\text{F}/\text{cm}^2$$

$$dE = 0.5 \text{ V}$$

$$dQ = \text{approx } 10^{-5} \text{ C}/\text{cm}^2$$

Therefore :

$$Q_{\text{tot}} = Q_{\text{DC}} + Q_{\text{ads}} + Q_{\text{dl}}$$

Our y-axis intercept is really equal to $Q_{\text{ads}} + Q_{\text{dl}}$.

How much influence does Q_{dl} have?

If $\Gamma = 10^{-10} \text{ mol}/\text{cm}^2$ (typical for aromatic adsorbates)

$$Q_{\text{ads}} = nF\Gamma \approx 10^{-5} \text{ C}/\text{cm}^2$$

$$\boxed{Q_{\text{ads}} \approx Q_{\text{dl}} !!}$$

Section 6-5 :Experimental Difficulties

1. Avoiding convection

- any vibrations and the build-up of density gradients will cause convective disruption of the diffusion layer. The measured current at long times following a potential step is often larger than that predicted by the Cottrell equation.

$T > 100$ s are often problematic.

2. R_uC Effects.

- Whenever the potential is stepped, current must flow to charge the electrode. This current contains no analytical information about the Faradaic processes.
- As a rule of thumb the time for full DL charging is $5R_uC$. The initial $5R_uC$ seconds define the time scale of kinetic events you can study.

3. Potentiostat limitations.

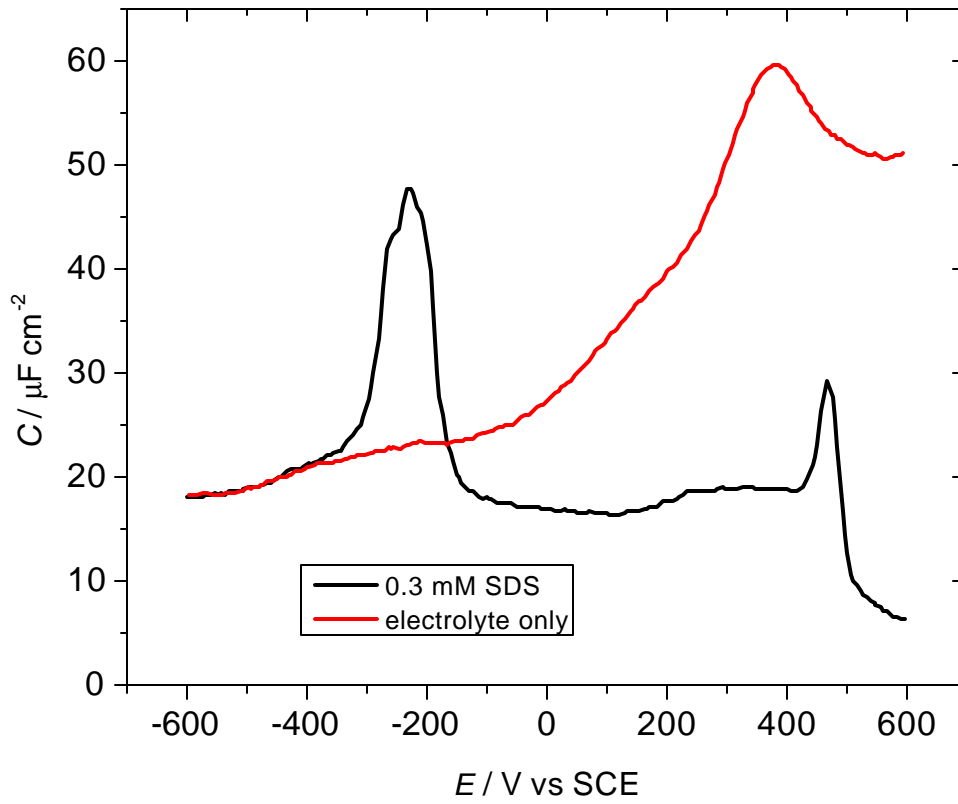
- A potentiostat can not change the potential it applies infinitely fast.
- Rise time : $t_R = (1/\Delta f)$
- Noise versus speed.

4. Recording device limitations

- The initial current is very large but very quickly decays toward zero. It is extremely difficult to precisely measure both the long and short time current (or charge) signals.

Worked Example : Adsorption of Dodecyl Sulfate on a gold electrode.

Differential Capacity



Allows for the selection of $E_0 = -600 \text{ mV}$

