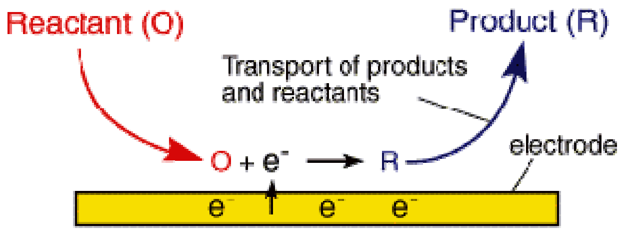
# Lecture 12 and 13 – Mass Transfer Effects in Interfacial Electrochemistry

## Introduction

In interfacial electrochemistry it is important to appreciate the difference between the bulk and the surface. Reactants are often at very different concentrations in these two regions, indeed it is frequently this concentration difference that drives the transfer of molecules from the bulk to the surface.

Consider again the simple situation:



Reactant R has to be transported to the surface from the bulk, in order that it might react and a current flow. Moreover, the product then needs to be transported back into the bulk.

## Mass transport Mechanisms

There are essentially three mechanisms for transporting molecules through space:

- Diffusion
- Migration
- Convection

**Diffusion** is the movement of molecules along a concentration gradient, from an area of high concentration to an area of low concentration.
**Migration** is the transport of a charged species under the influence of an electric field.
**Convection** is the transport of species by hydrodynamic transport (e.g. natural thermal motion and/or stirring).

Generally, in most electrochemical experiments, a background electrolyte of a salt that does not participate directly in the reaction is present. This is typically one or two orders of magnitude higher in concentration than the reactive species and is used to remove the effects of migration in experiments. Therefore, normally only the effects of diffusion and convection need to be considered. Indeed, if a system is changed quickly (i.e. a potential step is applied to an electrode), then diffusion becomes the principal mechanism of mass transport, provided the solution is not externally stirred or agitated.

## Current flow at Electrode Surface

The current that flows from a surface electrochemical reaction can be defined as (using the above example of reduction of O:

$$i_c = nFAk_{red}\lfloor O\rfloor_o$$

This can be empirically easily understood. *n* is the number of electrons (normally 1 or 2), *A* is the electrode area, $k_{red}$ the rate constant of the cathodic reaction and $[O]_o$ the **surface** concentration of O. *F* is Faraday's constant:

$F = N_A e \ \ = 96485\ C mol^{-1}$ The amount of charge in C transferred for 1 mole of reactant.

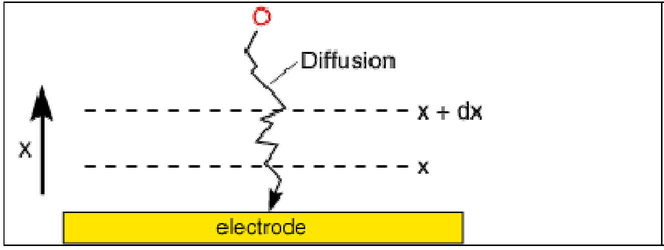
Remember: $i = \frac{dq}{dt}$

## Diffusion limited electrode reactions

So, in order to understand an electrochemical reaction it is necessary to have a feeling for the surface concentration of the reactant $C_o$ (note: $C_o = [O]$) as a function of distance from electrode *and* with respect to time as a reaction progresses.

The flux of a species, *J* is the rate of movement of a species per unit time and per unit area. *J* has the units mol $s^{-1}$ $cm^{-2}$. *J(x)* is the flux at a distance *x* from an electrode.

**Fick's first law** quantifies the movement of a species (under diffusion control) with respect to distance *x* from an electrode with the flux, *J*.



$$J_o = -D_o \frac{\partial C_o}{\partial x}$$

$D_o$ is the diffusion constant of the species O. It is a function of the mobility of an ion in a specific medium. It has a negative sign as molecules always diffuse from areas of high concentration to low concentration.

However, we are more interested in how the $C_o$ changes with time – since this will be more directly related to the current. This can be found and is **Fick's second law:**

$$\frac{\partial C_o}{\partial t} = D_o \left( \frac{\partial^2 C_o}{\partial x^2} \right)$$

In words, this says that the rate of change of the concentration of O with respect to time is proportional to the rate of change of the concentration gradient, $\frac{\partial C_o}{\partial x}$. (the rate of change (w.r.t. time) of the rate of change of O w.r.t. distance, *x*).

By solving Fick's second law, and then rearranging: $i_c = nFAk_{red}[O]_o$ one obtains a relationship between the measured current and time, when a potential step is applied to an electrode. This is what Cottrell did. Fortunately, you don't have to!

$$|i| = \frac{nFA[O]\sqrt{D}}{\sqrt{\pi}\sqrt{t}}$$ (Cottrell's equation)

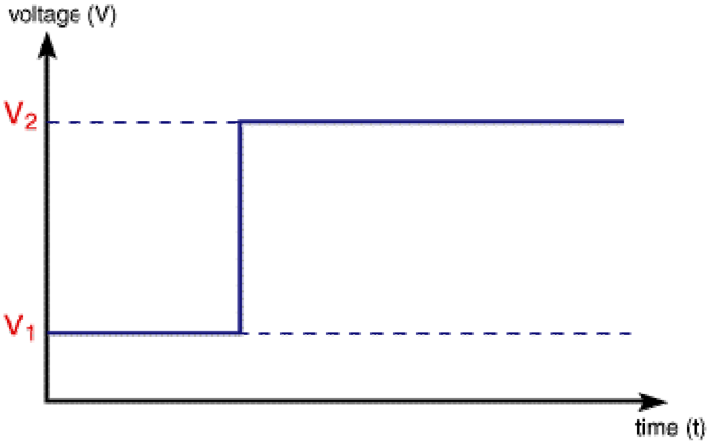
note [O] is now the *bulk* concentration of O.

**Examples**
So far, so theoretical. In labs you will all have the opportunity to see the Cotrell equation and effect of diffusion control (or not) in action.

A good „worked example“ is taken from the Web:

**Potential Step Voltammetry**

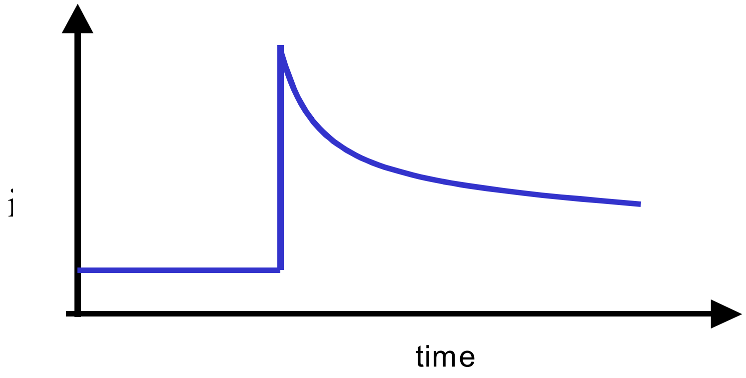
Imagine having a pot containing $Fe^{3+}$ and some electrodes and a background electrolyte of 0.1M KCl.
In a potential step measurement the applied voltage is instantaneously jumped from one value $\mathbf{V_1}$ to another $\mathbf{V_2}$



The resulting current is then measured as a function time. If we consider the reaction

$$Fe^{3+}(s) \; + \; e^{-}(m) \xrightarrow{k_{red}} Fe^{2+}(s)$$

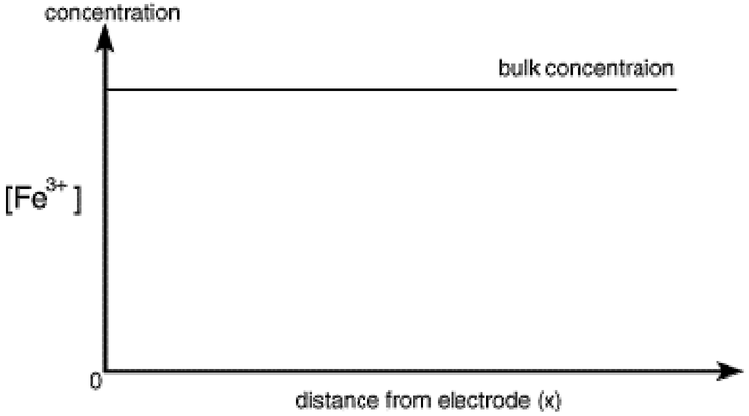
Usually the voltage range is set such that at $\mathbf{V_1}$ the reduction of ($\mathbf{Fe^{3+}}$ ) is thermodynamically unfavourable. The second value of voltage ($\mathbf{V_2}$) is selected so that any ($\mathbf{Fe^{3+}}$) close to the electrode surface is converted to product ($\mathbf{Fe^{2+}}$ ). Under these conditions the current response is shown below:



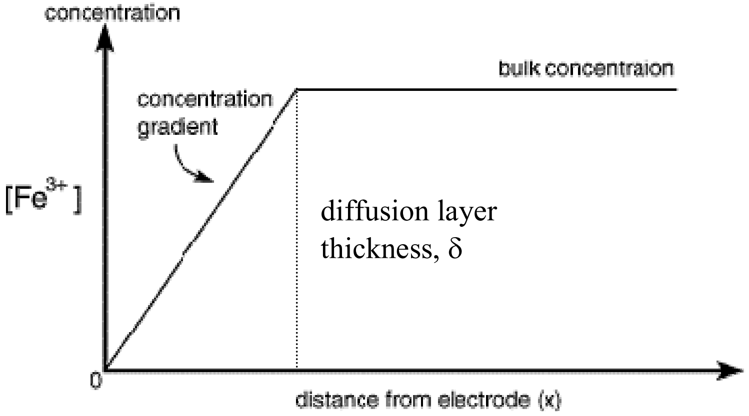
The current rises instantaneously after the change in voltage and then begins to drop as a function of time. This is because immediately after the voltage step, all reactant close by the surface gets used up. The reaction can only proceed if further reactant ($Fe^{3+}$) is transported to the electrode surface. Naturally, it is, and if the system is not stirred and a background electrolyte is used then **diffusion** is the transport mechanism that dominates.

The shape of the above curve is better explained by considering what happens to the concentration of $Fe^{3+}$ w.r.t. distance *x* from the electrode (Fick's 1st law).

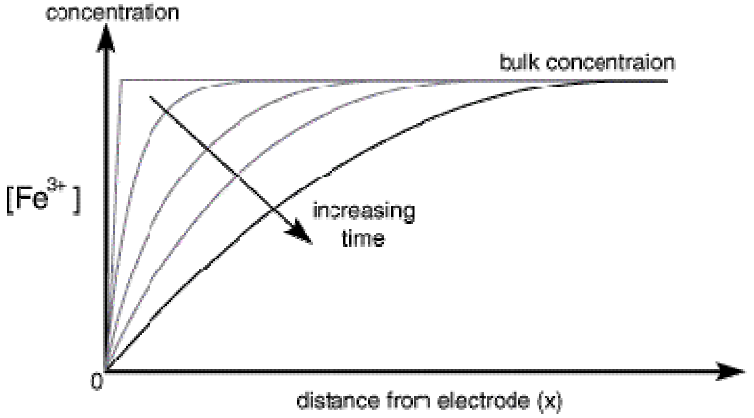
***Concentration verses distance above the electrode before voltage step***



***Concentration verses distance above the electrode a short time after a voltage step***



As the electrode reaction continues, material can diffuse further from the electrode and therefore the concentration gradient drops. As the concentration gradient drops (see concentration profiles below) so does the supply of fresh reactant to the surface and therefore the current also decreases.



So, the individual concentration curves w.r.t. distance *x* are described by Fick' 1st law. But, the change in gradient (represented by the arrow saying „increasing time") is a representation of Fick´s $2^{nd}$ law:

$$\frac{\partial[Fe^{3+}]}{\partial t} = D_o\left(\frac{\partial^2[Fe^{3+}]}{\partial x^2}\right)$$

The Cottrell equation (obtained by solving Fick' $2^{nd}$ law) is a formalisation of what happens to the current with time:

$$|i| = \frac{nFA[Fe^{3+}][\sqrt{D}}{\sqrt{\pi}\sqrt{t}} \quad \text{so,} \quad i \propto \frac{1}{\sqrt{t}}$$

or re-arrange, and plot 1 / $i^2$ vs. t

Clearly current is a maximum at t = 0, and as t increases so i decreases.

These concepts are very important, and will be considered in more detail in next lecture where Linear Sweep Voltammetry is studied.

***Estimation of the diffusion layer thickness***

If the diffusion coefficient of an electroactive species is known, or has been calculated, the diffusion layer thickness can be estimated using this equation:

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

It can clearly be seen that the diffusion layer extends into the bulk solution more and more slowly after application of a potential step. Hence for a molecule with a diffusion coefficient of $1 \times 10^{-10}$ $m^2s^{-1}$, the diffusion layer thickness is around 20 μm after 1 second.

The fraction of molecules oxidised or reduced can also be estimated by calculating the volume of a hemispherical diffusion layer around a circular electrode as a fraction of the total solution.

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## Linear Sweep and Cyclic Voltammetry

### Introduction

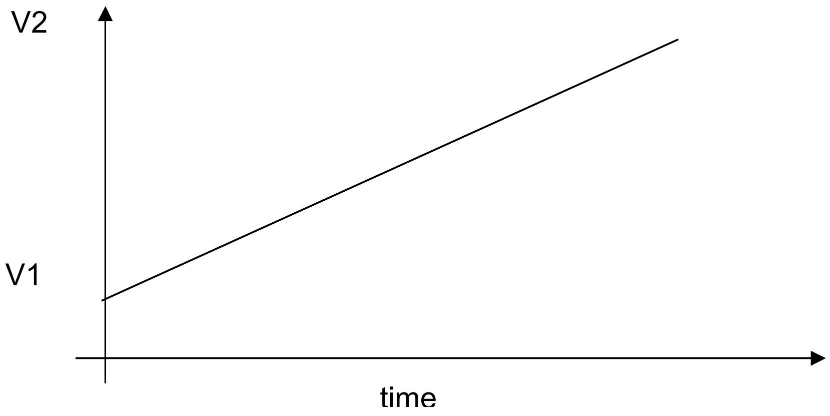
The last lecture considered a situation where an electrode suddenly had a voltage applied to it, in order to make a surface reaction happen. The voltage was supplied suddenly – as an off / on pulse. Moreover, the examples and discussion assumed that the electrode kinetics were facile and that therefore the overall rate of electrode reaction was controlled by mass transport of species to the electrode, and that diffusion was the principal method of mass transport.

This lecture will extend these ideas and consider what happens if instead of applying a sudden pulse of voltage to the electrode, the voltage is slowly increased at a predetermined rate linear with time. Once again, it will be assumed (generally) that the electrode reaction is under diffusion limited conditions. A number of effects will be considered:

- What is happening in terms of mass transport as the voltage is increased.
- Whats the effect of scan rate?
- What happens if one sweeps the voltage back again (cyclic voltammetry).

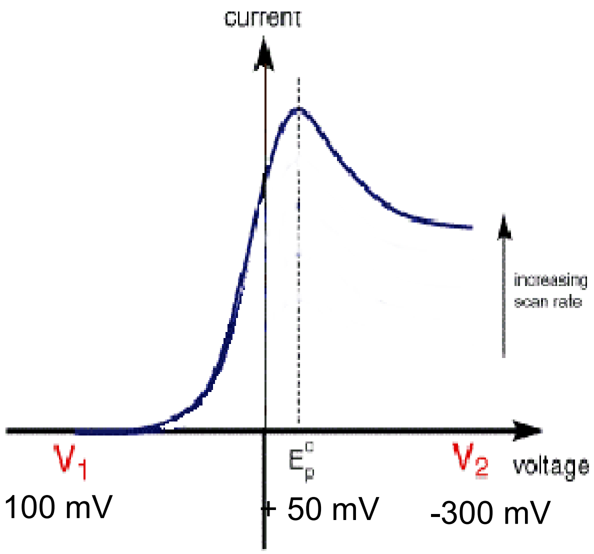
**Linear Sweep Voltammetry**

Sweep voltage between V1 (no electrode reaction) and V2 at a set rate and measure current.



Consider the same situation as last lecture, also with a background electrolyte:

$$Fe^{3+}(s) + e^{-}(m) \xrightarrow{k_{red}} Fe^{2+}(s)$$



### Interpretation of results

The two graphs above show the applied voltage sweep vs. time and the current response vs. voltage. It is very important to remember when interpreting such data, that since the voltage is being swept at a constant rate, then the voltage axis in the current – voltage curve is **also** a time axis.

For example, sweeping at 10 mV $s^{-1}$, between +100 mV and –300 mV means that the voltage axis above is also a measurement of time between 0 s at +100 mV and 40 s at –300 mV.

### Chemical behaviour

As potential is applied, the ratio of $Fe^{3+}$ to $Fe^{2+}$ changes, as $Fe^{3+}$ starts to be reduced. This can be shown clearly:

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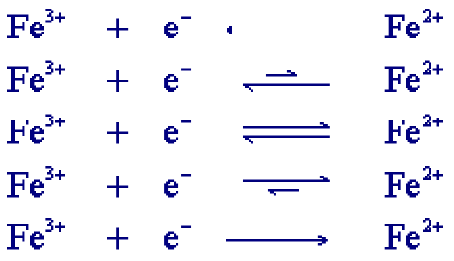
|  | V1<br><br>~ $E_p$<br><br>V2 |

This can be understood ny using the Nernnst equation (again!). The Nernst equation, as well as being useful for calculating the expected potential of reference electrodes can also be used to rationalise the change in *surface* (electrode) concentration of electroactive species when a potential, E is applied.

To remind you:

$$E = E^o + \frac{RT}{nF}\ln\left(\frac{C_{ox}}{C_{red}}\right)$$

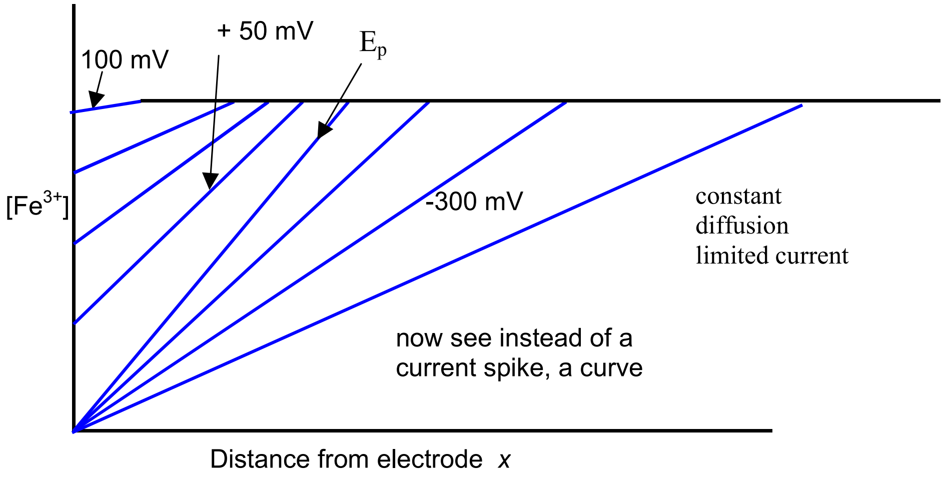
So, in the above case, reducing $Fe^{3+}$ to $Fe^{2+}$, when the applied potential E is equal to the standard potental of reduction of $Fe^{3+}$ ($E^o$), then $C_{Fe3+} = C_{Fe2+}$ at the surface of the electrode, i.e. $Fe^{3+}$ and $Fe^{2+}$ are in balanced equailbrium. This is at a potential just before the peak potential.

### Current behaviour

Note how the current rises with applied voltage, reaches a maximum at $E_p$ and then decreases to a limiting value.

Why does the current not just rise with applied voltage?

To understand this, it is necessary to consider the last lecture, where a voltage step is applied. Here also a maximum current is found that then deceases. As before, to really understand the current behaviour we need to consider the movement of ions to the electrode.

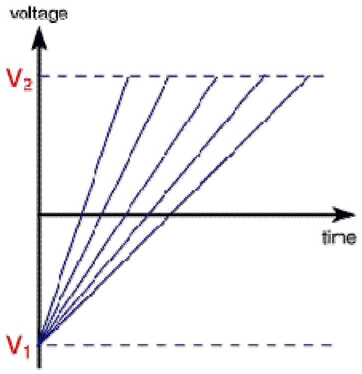


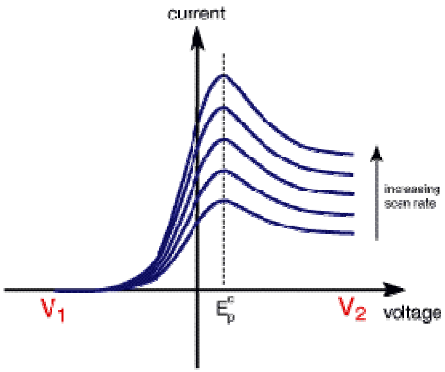
The situation is almost like with the voltage step experiment, except since the applied voltage is increased, the currrent rises as the diffusion gradient increases, between +100 mV → $E_p$. At $E_p$, the voltage at which maximum current is flowing, the diffusion gradient is at its most steep.

The distance between where the concentration of $[Fe^{3+}]$ changes with distance and where it is fairly constant is known as the ***diffusion layer thickness.*** This changes more slowly than the rate at which $Fe^{3+}$ is used up at the electrode as the voltage is changed, and therefore the gradient increases quickly until $E_p$. At $E_p$, the any $Fe^{3+}$ close by the electrode is immediately reduced, so there is effectivelly zero concentration of $Fe^{3+}$ at the electrode. But, the diffusion layer thickness continues to increase ($E_p$ → +300 mV), so the diffusion gradient decreases, and therefore so does the current (as shown in last lecture). Note also, that the Cottrell equation descibes the decreases in current from the current maximum.

**Effect of scan rate**

Following on from the argument given above it might seem reasonable to think that the current at $E_p$, that is to say the maximum peak current, will be related in some way to the scan rate. This is indeed the case. The following diagram illustrates this effect:





Intuitivelly this should make sense – the faster one scans the applied voltage, the less time the duffusion layer has to extend into the bulk solution and consequently the larger the diffusion gradient.

Quantitativelly, this can be described by a sister equation of the Cottrell equation:

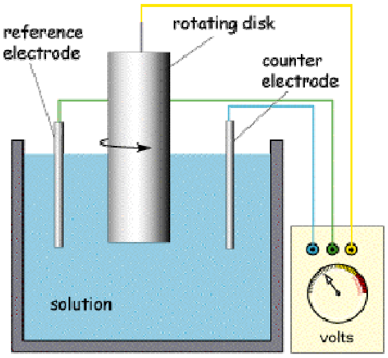
$$i_p = -(2.69x10^5)n^{3/2}FAD^{1/2}[O]\upsilon^{1/2}$$

In the above example, [O] is the concentration of bulk $Fe^{3+}$. This square root of scan rate relationship to the peak current is a property of all reversible reactions. Such so called „diagnostics“ will be considered in more detail in the next section.

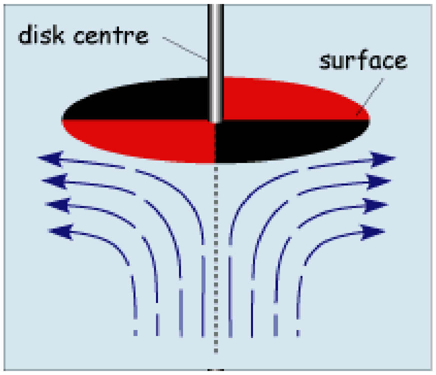
**Electrochemistry under conditions of controlled mass transport – forced convection: The Rotating Disc Electrode (RDE).**

So, far the situation where diffusion is the rate limiting mass transport step in an electrode reaction has been considered. However, it is also possible to control the movement of material to the electrode via convection.

This can be achieved by encasing the electrode in a Teflon outer layer and rotating in a controlled fashion.



Experimental setup



Laminar flow at electrode centre

The rotating electrode draws electrolyte from the bulk onto its surface. Within certain limits, the rotation rate is directly related to the rate of transport to the surface.

In fact, in the mass transport taking place in such systems is dependent both on diffusion and convection. So one can write:

$$\frac{\partial[C]}{\partial t} = D_C \frac{\partial^2[C]}{\partial x^2} - v_x \frac{\partial[C]}{\partial x}$$

which is like Fick´s 2nd law, but has an additional term, $-v_x \frac{\partial[C]}{\partial x}$ that relates to the convection component. $v_x$ is the velocity of the flow at some distance $x$ normal to the electrode surface.

### Experimental effect

The experimental manifestation of this convection effect can be seen if one ramps a voltage on an electrode.

The effect of applying a linear voltage sweep to an electrode can be seen in the above diagrams:

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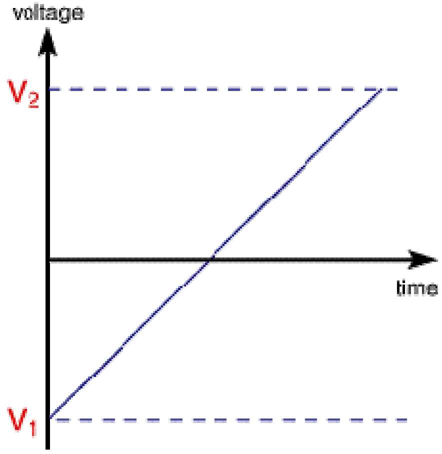
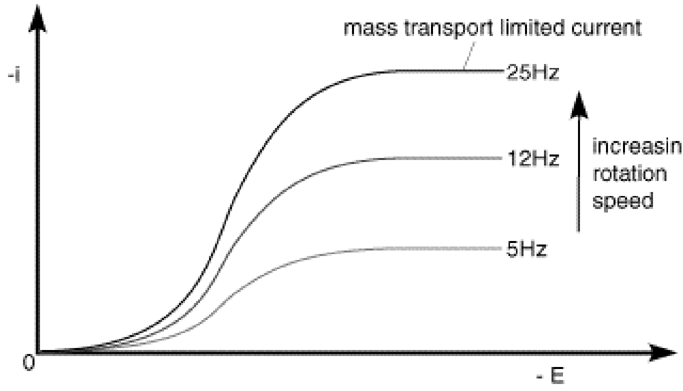
|  |  |
| Slow linear sweep | Resultant current at different rotation rates |

Note, that unlike systems under just diffusion control, there is no current peak. This time the rate of reaction – that is the limiting current is influenced by how fast one can transport material to the electrode by rotation.

Quantitatively, the above diffusion equations can be solved and the following equation obtained:

$$i_L = 0.62nFA[C]_{BULK}D^{2/3}\nu^{-1/6}\omega^{1/2}$$ The Levich equation

where $i_L$ is the limiting current, $[C]_{bulk}$ the bulk concentration of species to be reduced (or oxidised), D the diffusion constant, A electrode area, $\nu$ a kinematic viscosity of the solution and $\omega = 2\pi f$, where f is the rotation rate.

So, by plotting $i_L$ vs. $\omega^{1/2}$ for different rotation rates, and knowing (looking up $\nu$), it is possible to obtain the diffusion constant of the electroactive species.

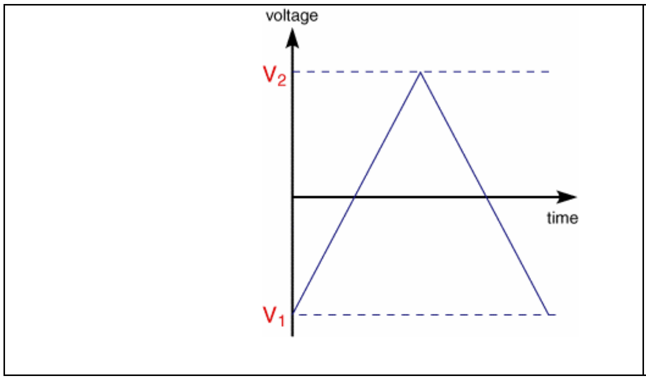
**Note**: be careful about units! For example, when switching between concentration in mol $dm^{-3}$ to diffusion constant D in $m^2\ s^{-1}$.

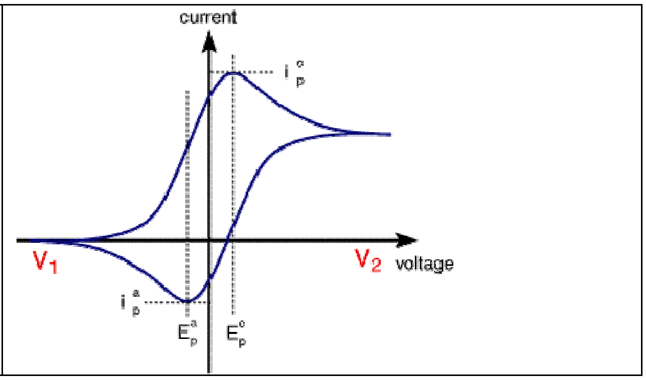
### The diffusion constant D

As already shown, the diffusion constant (or coefficient) relates the flux, J of a spies moving along a concentration gradient, $\frac{\partial c}{\partial x}$.

**Cyclic Voltammetry**

Cyclic voltammetry is closely related to linear sweep voltammetry, the only difference being that following the first linear potential sweep from $V_1$ to $V_2$, the sweep is revered and swept back from $V_2$ to $V_1$. This is illustrated below:





For a fully reversible reaction, on the forward sweep, where electrons are put into the electrode (the cathodic sweep) the curve is identiocal to that seen in LSV. On reversing the scan direction, electrons are withdrawn from electrode and the material reduced in the forward sweep are oxidised back.

***Nomenclature***

$i_p^c$ and $i_p^a$ refer to the peak current of the cathodic and anodic sweeps.
$E_p^a$ and $E_p^c$ refer to the potential (voltage) of the anodic and cathodic current peaks.

When investigating an unknown electroactive system, it is generally very important to know of the oxidation – reduction is reversible, or not. To determine this, a series of diagnostic tests can be carried out on the cyclic voltammograms of the system under test.

A CV of a fully reversible system will display the following characteristics:

I) The voltage separation between the current peaks is

$$\Delta E = E_p^a - E_p^c = \frac{59}{n}\text{mV}$$

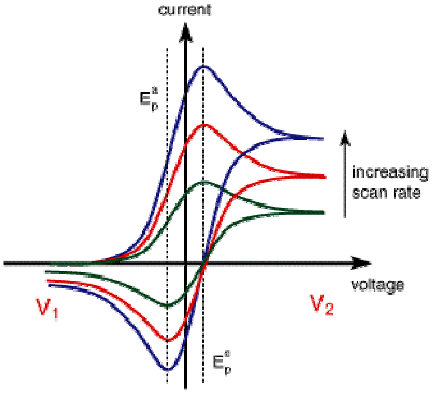
II) The positions of peak voltage do not alter as a function of voltage scan rate
III) The ratio of the peak currents is equal to unity.

$$\left|\frac{i_p^a}{i_p^c}\right| = 1$$

IV) The peak currents are proportional to the square root of the scan rate

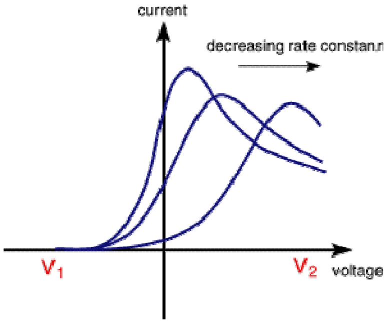
$$i_p^a \text{ and } i_p^c \propto \sqrt{v}$$

The influence of the voltage scan rate on the current for a reversible electron transfer can be seen below:

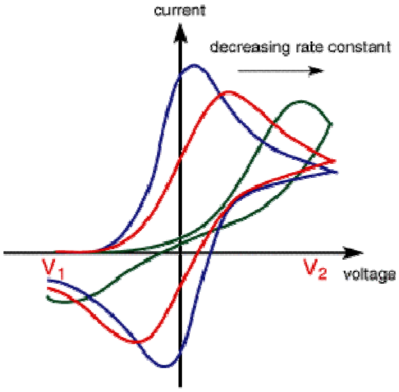


**Effect of electron transfer kinetics.**
The above examples all assume that the electron transfer kinetics are very fast – that is the rate limiting step of the electrode reaction is influenced purely by the ease of getting material to the electrode to react – *mass transport.*

However, in many cases, electron transfer kinetics are not fast. In this case the shape of the LSV or the CV is changed. The effect of differences in the kinetic rate ($k_{red}$) constant for electron transfer on the LSV of a system are schematically illustrated below:



Both $E_p^c$ and $i_p^c$ shift to different values as electron transfer becomes more difficult. In cyclic voltammetry, a system can have different cathodic ($K_{red}$) and anodic ($K_{ox}$) kinetic rate constant. Such systems are known as *quasi-irreversible*. The CV is illustrated below:



Note how the diagnostics for a reversible reaction are no longer fulfilled.

Thus linear sweep and cyclic voltammetry can be used to gain much fundamental information about electron transfer between molecules and electrodes. Therefore it is of use to more than „hardcore” electrochemists, but also inorganic chemists and many biochemists studying electron transfer complexes.