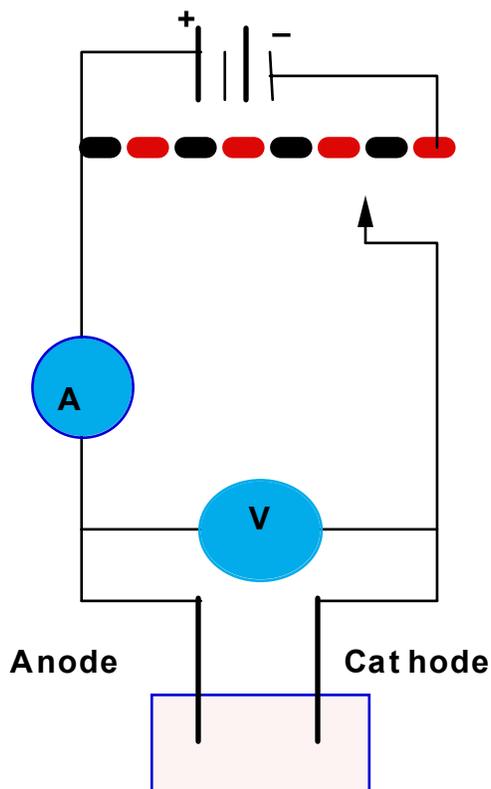


## POLAROGRAPHY

Polarography is the study of the electrolysis of solutions of electrooxidizable and or electroreducible substances between a **dropping mercury electrode (DME)** and some reference electrode (RE) . The potential between these electrodes is varied and the consequent changes in the flow of current is measured Fig. 1. On plotting the changes in current flow versus the potential variation, one obtains an **i - E** curve known as **polarogram**. The first scientist who discovered the use of the DME in electrolysis is Jaroslave Heyrovsky in 1922 and received the Nobel Prize in Chemistry in 1959.



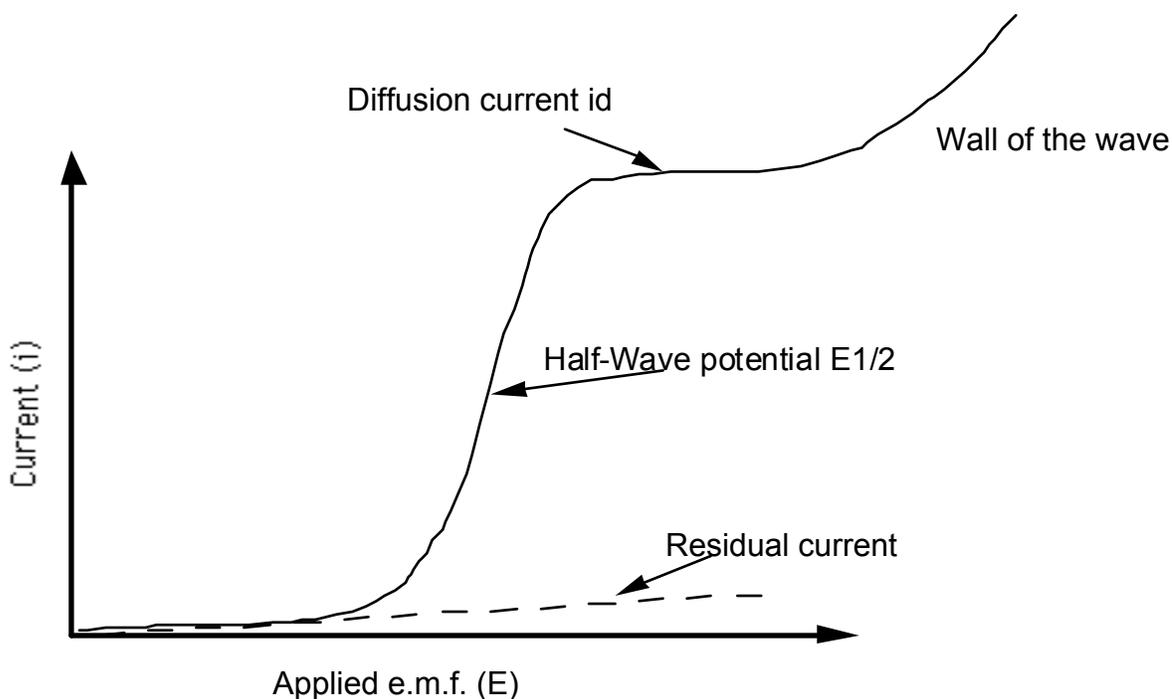
**Fig. 1 The Polarographic Circuit**

From the measurements of the current - potential curves resulting from electron transfer processes at the surface of a **DME**, the identity and concentration of the reactant substance can be determined. One of the virtues of polarography is that solutions as dilute as  $10^{-8}$  M can be analyzed and sample volumes as small as **0.05 ml** can be manipulated. Thus, the position of a wave in a polarogram along the potential axis gives the identity of the substance while the magnitude of the limiting current gives picture of the concentration variation of this material.

A very pure mercury patch can be obtained through distillation under vacuum ( 99.99 % pure ) . Each drop represents a fresh electrode with a new exposed surface. The

reproducibility of geometry of each drop with the laps of time is another advantage of the DME over other electrodes. The large **activation overpotential** for hydrogen gas evolution makes this electrode valuable for the study of cathodic processes. One of the most important drawbacks of the Hg as electrode is its **ease of oxidation**. Thus, Hg undergoes **anodic dissolution at +0.25 V vs. SCE** and is oxidized to insoluble  $\text{Hg}_2\text{Cl}_2$  in presence of chloride ions at zero V vs. SCE so it cannot be used for anodic oxidation above +0.25 V vs. SCE. Also it is important to mention that **Mercury vapors are very poisonous** besides Hg itself is considered to be one of the major **pollutants of the environment**.

A **polarogram** or better a polarographic wave has the S shape illustrated in Fig. 1



**Fig.2 The i - E Curve ( Polarogram )**

The slowly increasing current at the foot of the wave is known as the residual current. This current is non faradaic in nature. The diffusion current  $i_d$  is, as shown, the distance between the limiting diffusion plateau and the residual current. The potential at the mid-point of the wave, where the current is exactly half its limiting value, is known as the half-wave potential  $E^{1/2}$  and its quantity is characteristic of a particular species under fixed experimental conditions. Thus  $E^{1/2}$  value serves as finger-print for the species

undergoing redox. Furthermore, the limiting current is usually proportional to concentration of the species being reduced or oxidized and thus serves for quantitative analyses. Over the diffusion current plateau region the DME is behaving as a completely polarized electrode since it adopts any applied potential to it with no change in current flow. It is interesting to notify that polarization always results from slow stage in the overall electrode process. The slow stage here is the diffusion process which occurs very much slower than the electron transfer. This type of polarization is known as concentration polarization and the DME is said to be concentration polarized. At potentials corresponding to the rising part of the wave the electrode is depolarized since here the current flow is strongly dependent on the applied potential. At this stage it is important to emphasize that in any electrolysis two types of processes are encountered.

**i-** Mass transfer process which brings the electroactive material to the electrode surface

**ii-** Electrochemical process which involves the act of electron transfer between the surface of electrode and the electroactive species.

The mass transfer is usually achieved through **a-** migration, **b-** diffusion and **d-** convection. **Migration** is an electric field effect and depends upon the charge on the species, concentration and mobility in a field of force. **Diffusion** depends upon differences in concentration between species at the surface of the electrode and in the bulk of solution. Finally **convection** arises from any mechanical or thermal disturbance in the solution. For a redox process to occur it is essential that electrons pass between the electrode and the species in solution. However, by no means electron transfer in its crude definition acts alone, thus adsorption, rearrangement of electronic configuration within the species to give a suitable form for the electron exchange is a normal observable sequence. After the electron exchange a primary product is formed which re-undergoes an electronic rearrangement, desorption and may suffer further side reactions to form the final product. These electrolytic processes may be reversible or irreversible in nature depending on the activation energy values.

### **Diffusion Current**

According to Fick's first law of diffusion, the rate of diffusion is proportional to the concentration gradient. Since diffusion in polarography is the rate controlling (determining) step, consequently the rate of diffusion is thus equal to the rate of electrode reaction and therefore the rate of the electrode reaction is proportional to the concentration gradient.

**Rate of Diffusion  $\propto (dC/dx)_{x=0}$**

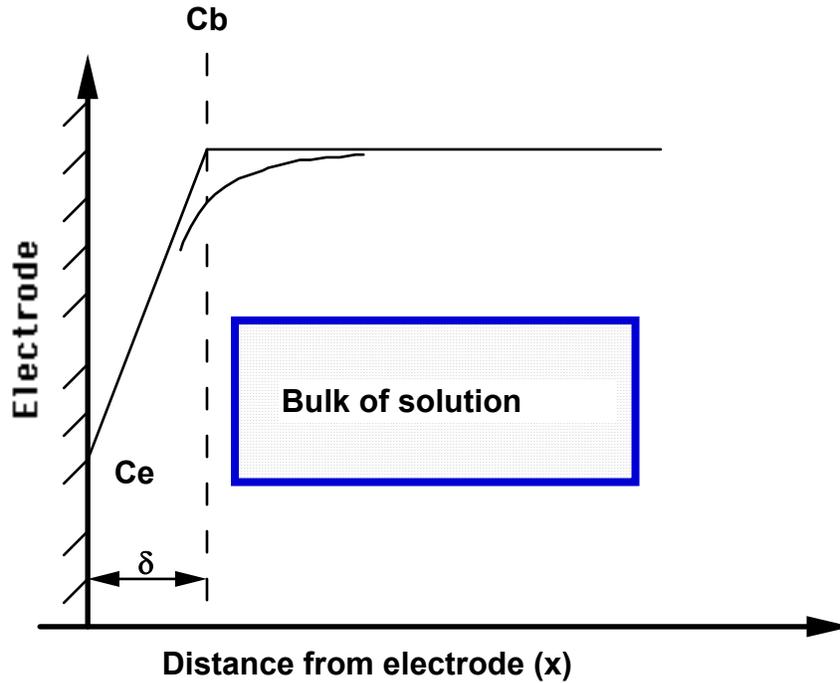
$$i / n F A \propto (dC / dx)_{x=0} \quad \text{For a plane electrode}$$

$$i / n F A = D (dC / dx)_{x=0} \quad \mathbf{1}$$

$$i = n F A D (dC / dx)_{x=0} \quad \mathbf{2}$$

[ Plane electrode of surface area A across which a current i passes due to the impressed emf, n is the number of electrons, F is the faraday, D is the diffusion coefficient in cm<sup>2</sup> / sec., C is the concentration, x = 0 means at the electrode surface ].

We can picture the situation near to the electrode by the model illustrated in Fig. 3.



**Fig. 3 Schematic Representation of the Concentration Gradient**

$C_b$  is the concentration in the bulk of solution and  $C_e$  is the concentration at the surface of the electrode. Thus, the value  $(C_b - C_e)$  represents the fall across the diffusion layer  $\delta$  which is known as the Nernst diffusion layer ( $10^{-2}$  -  $10^{-3}$ ).

$$[C_b - C_e] / \delta = (dC / dx)_{x=0} \quad \mathbf{3}$$

$$i = n F A D (C_b - C_e / \delta) \quad \mathbf{4}$$

$C_b \gg C_e$  &  $C_e$  at a certain time tends to zero

$$i_d = [n F A D C_b] / \delta \quad \mathbf{5}$$

where  $i_d$  is the maximum limiting current. Fick's first law is limited only for the cases where the diffusion layer is of constant thickness and where the conditions are stationary. In other cases when the diffusion layer thickness alters with time and concentration is varying with both time and distance, Fick's second law must be introduced .

$$dC / dt = D [d^2C / dx^2] \quad 6$$

This second order equation can only be solved mathematically by Laplace integral transform resulting in the famous **Cottrell equation**. This equation shows that  $i_t$  decreases with time due to a broadening of the diffusion layer and a decrease in the diffusion rate. Noteworthy that this equation is the backbone of the **Ilkovic equation**.

$$i_t = n F A (\sqrt{D})C_b \sqrt{(\pi t)} \quad 7$$

To convert 7 into Ilkovic equation one assumes both that the drop is spherical and that the mercury flow rate is uniform, that is , that the drop volume increases linearly with time.

$$A = 4 \pi r^2 \quad 8$$

$$V = 4 / 3 \pi r^3 \quad 9$$

$$d = W / V \quad 10$$

$$V = W / d = 10^{-3}m t / d \quad 11$$

Combining 9, 11 equation 12 is obtained

$$r = [(3 \times 10^{-3}m t) / 4d]^{1/3} \quad 12$$

Replacing r value in 8 by 12 and by combining the terms one obtains 13

$$A = \{ [ 6 \times 10^{-3} \times \sqrt{\pi} m t ] / d \}^{2/3} \quad 13$$

Substituting A value in 7 14



$$i = k_o C_o^b - k_o C_o^e \quad 21$$

$$C_o^e = (k_o C_o^b - i) / k_o = (i_d - i) / k_o \quad 22$$

$$\text{Where } k_o = 708 n D_o^{1/2} m^{2/3} t^{1/6}$$

For the anodic process occurring at the electrode surface

$$i = -k_r (C_r^b - C_r^e) \quad 23$$

$$\text{Where } k_r = 708 n D_r^{1/2} m^{2/3} t^{1/6}$$

$$i = k_r C_r^e \quad \text{since } C_r^b \text{ is equal to zero}$$

$$E = E_o - RT / nF \ln [i / k_r] / [i_d - i / k_o] = E_o - RT / nF \ln [i / i_d - i \cdot k_o / k_r]$$

$$E = E_o - [RT / nF \ln i / i_d - i + RT / nF \ln k_o / k_r] \quad 24$$

$$E = E_o - RT / nF \ln \sqrt{D_o} / \sqrt{D_r} - RT / nF \ln i / i_d - i \quad 25$$

When  $i = 1/2 i_d$

$$E = E_{1/2} = E_o - RT / nF \ln \sqrt{D_o} / \sqrt{D_r}$$

$$\text{and hence } E = E_{1/2} - RT / nF \ln i / i_d - i \quad 26$$

at 25 °C

$$E = E_{1/2} - .0592 / n \log i / i_d - i \quad 27$$

From equation 27 the number of electrons can be obtained by plotting the what so called logarithmic plots or well known practically as test of reversibility.

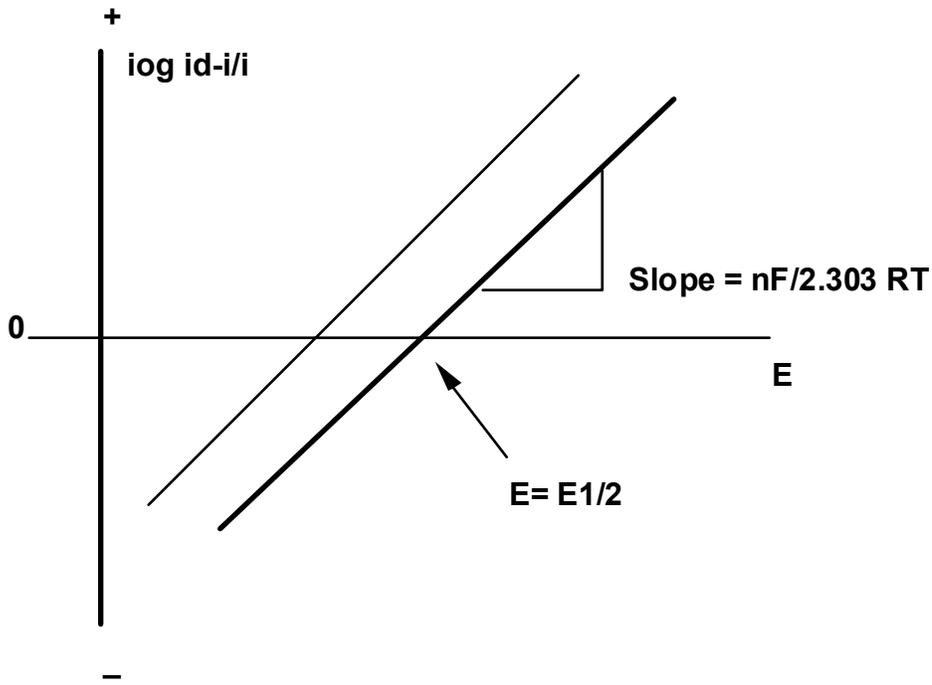
Equation 28 describes the irreversible process where  $\alpha$  is the transfer coefficient  $0 < \alpha < 1$

$$E = E_{1/2} - .0592 / \alpha n \log i / i_d - i \quad 28$$

### Determination of the Number of Electrons in Voltammetry

The actual number of transferred electrons in a reversible electrode process can be determined from the logarithmic plots which simply consist of plotting  $\log i_d - i / i$  versus  $E$  as illustrated in Fig. 4. The slope of the obtained straight line is equal to  $n F / 2.303 RT$

from which  $n$  is determined. These calculations are valid for low electron transfer reaction i.e. one to two electron process. If the obtained  $n$  number is a meaningless fraction, the reaction should be irreversible and  $n$  is obtained through **Faraday's law**, the basics of **coulometry**



**Fig. 4 Logarithmic Analysis**

$$Q = i_t \times t \quad \mathbf{29}$$

The total quantity of electricity  $Q$  in coulombs passed in an electrolysis is given by

$$Q = \int i_t dt \quad \mathbf{30}$$

Current decays in accordance with

$$i_t = i_0 e^{-kt} \quad \mathbf{31}$$

Solving 30

$$Q = \int i_0 e^{-kt} dt \quad \mathbf{32}$$

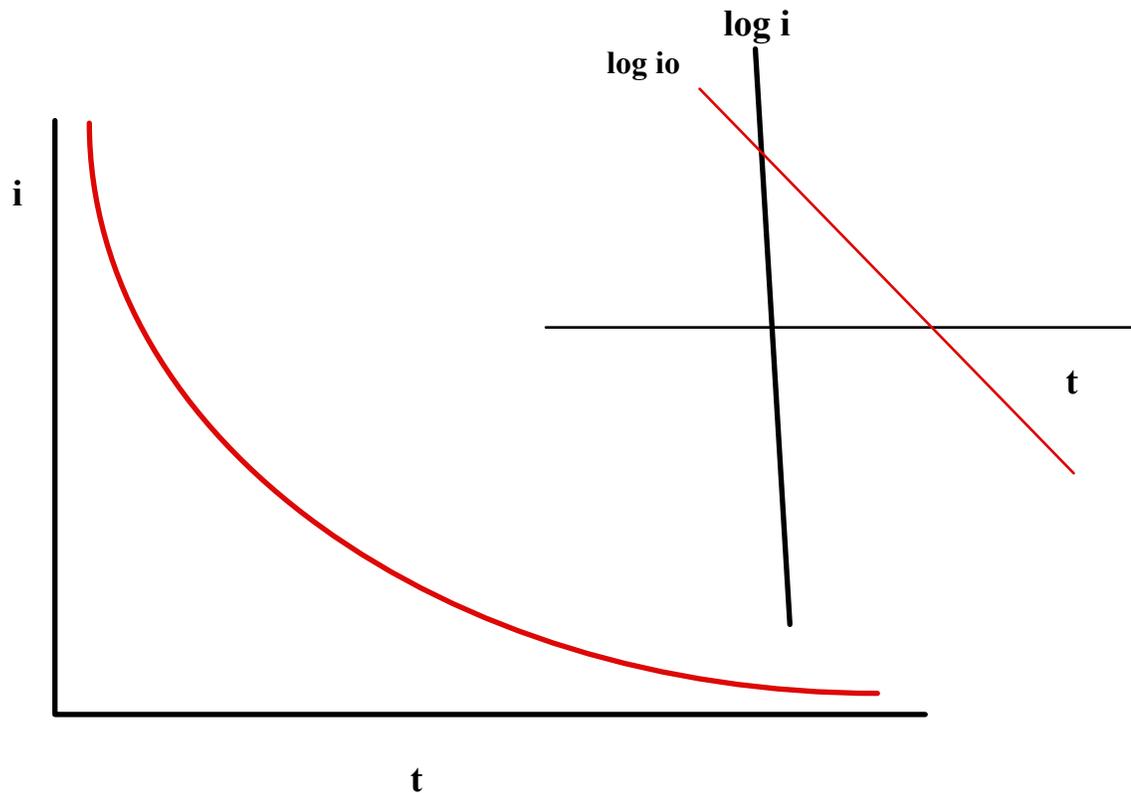
$$Q = i_0 \int e^{-kt} dt \quad 33$$

$$Q = i_0 \left[ e^{-kt} / -k \right] \text{ limits of } i \text{ from } 0 \text{ to } \infty \quad 34$$

$$Q = i_0 \left[ e^{-k\infty} / -k - e^{-k0} / -k \right] \quad 35$$

$$Q = i_0 / k \quad 36$$

Taking the natural logarithm of equation 31 one obtains



**Fig. 5 The i - t relation**

$$\ln i_t = \ln i_0 - kt \quad 37$$

$$2.303 \log i_t = 2.303 \log i_0 - kt \quad 38$$

$$\log i_t = \log i_0 - [k / 2.303] t \quad 39$$

Once Q is measured, the weight W in grams be determined n can be calculated from Faraday's law of electrolysis

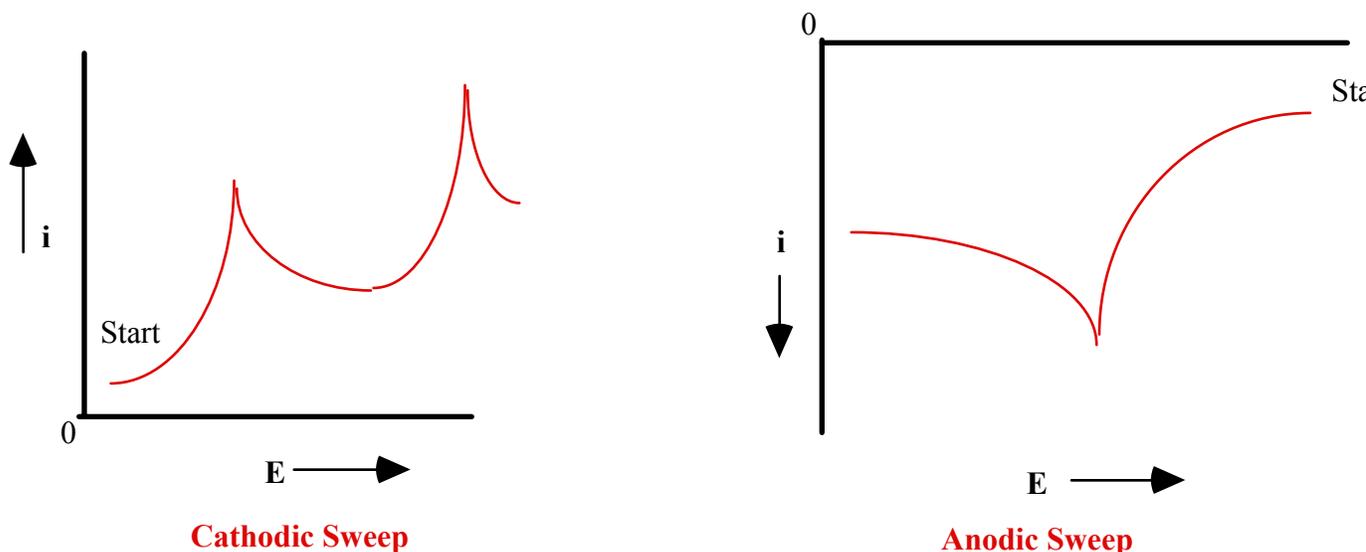
$$W = Q M / n F \quad 40$$

## CYCLIC VOLTAMMETRY

Cyclic voltammetry is a variant of a technique called stationary electrode voltammetry. This technique is also known as cyclic triangular wave voltammetry. Typical stationary electrode voltammograms are illustrated in Fig. 6. Notice that the potential may be swept either anodically or cathodically, and that, unlike polarography, the curves are peaked. As the potential moves into the region where the substrate is reduced or oxidized, the region adjacent to the electrode becomes depleted of material and the current decreases. The relation relating the peak current  $i_p$  to the experiment parameters of a stationary electrode is given by equation 41

$$i_p = 2.687 \times 10^5 n^{2/3} A D^{1/2} C \nu^{1/2} \quad 41$$

$n$ ,  $A$ ,  $D$ , and  $C$  have their usual significance.  $\nu$  is the potential sweep rate expressed in volt per second. Equation 41 ( the **Randles- Cevcik equation**) is based on the assumptions that the electrode process is reversible and linear diffusion, when these conditions are fulfilled the ratio  $i_p / \nu^{1/2}$  is constant.



**Fig. 6 Stationary Electrode Voltammogram**

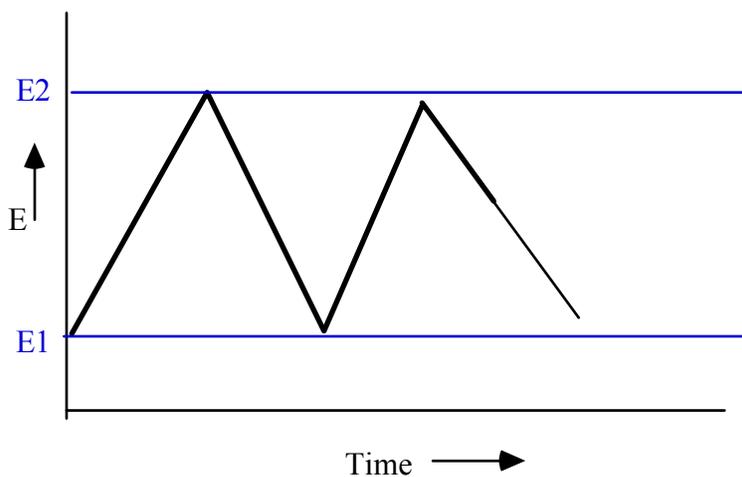
The experimental feature of interest in cyclic voltammetry is the variation of the potential of the working electrode as a triangular wave ( Fig. 7 ) i. e. after the stationary

electrode voltammogram of a substance has been measured by sweeping past the potential  $E_p$  the direction of voltage scan is reversed. Either a single cycle [ from  $E_1$  to  $E_2$  and back to  $E_1$  ] or many cycles may be carried out. Typical CV are shown in Fig. 8 where it is obvious that cyclic voltammetric behavior can exhibit a variety of forms. The shape of the CV curve is highly dependent on the relative rates of electron transfer, mass transport, and any chemical reactions occurring at the electrode surface. Scan rates can be varied over a wide range .

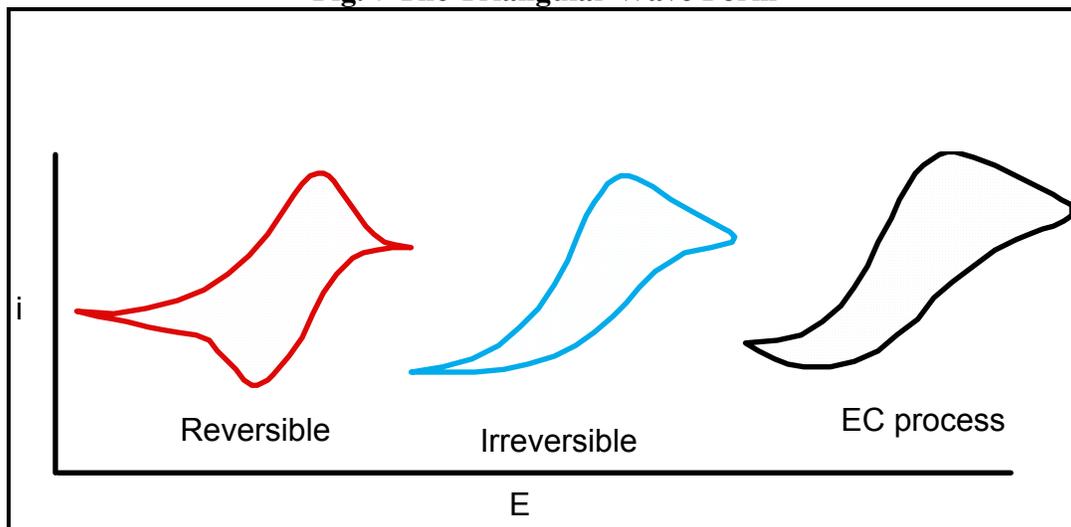
Cyclic voltammetry serves nicely as a tool for the test of reversibility. Consider the reversible reduction of a species O to R.



the CV showing this behavior is illustrated in Fig.8 and expanded in Fig. 9



**Fig. 7 The Triangular Wave Form**



### Fig. 8 Representative CV Curves

Reduction of O takes place at a certain potential  $E_{pc}$  when the voltage scan direction is reversed an anodic peak due to the oxidation of R is observed . Now if  $E_{pa}$  and  $E_{pc}$  are the potential corresponding to the anodic and cathodic peak currents and  $E_{pa/2}$  and  $E_{pc/2}$  are the potentials corresponding to the half peak currents it may be shown that  $E_{pa} - E_{pc}$  and  $E_{pc/2} - E_{pa/2}$  will be each equal to  $0.056 / n$  for a reversible process. Also the following expressions are valid within experimental error ( Fig 9 ).

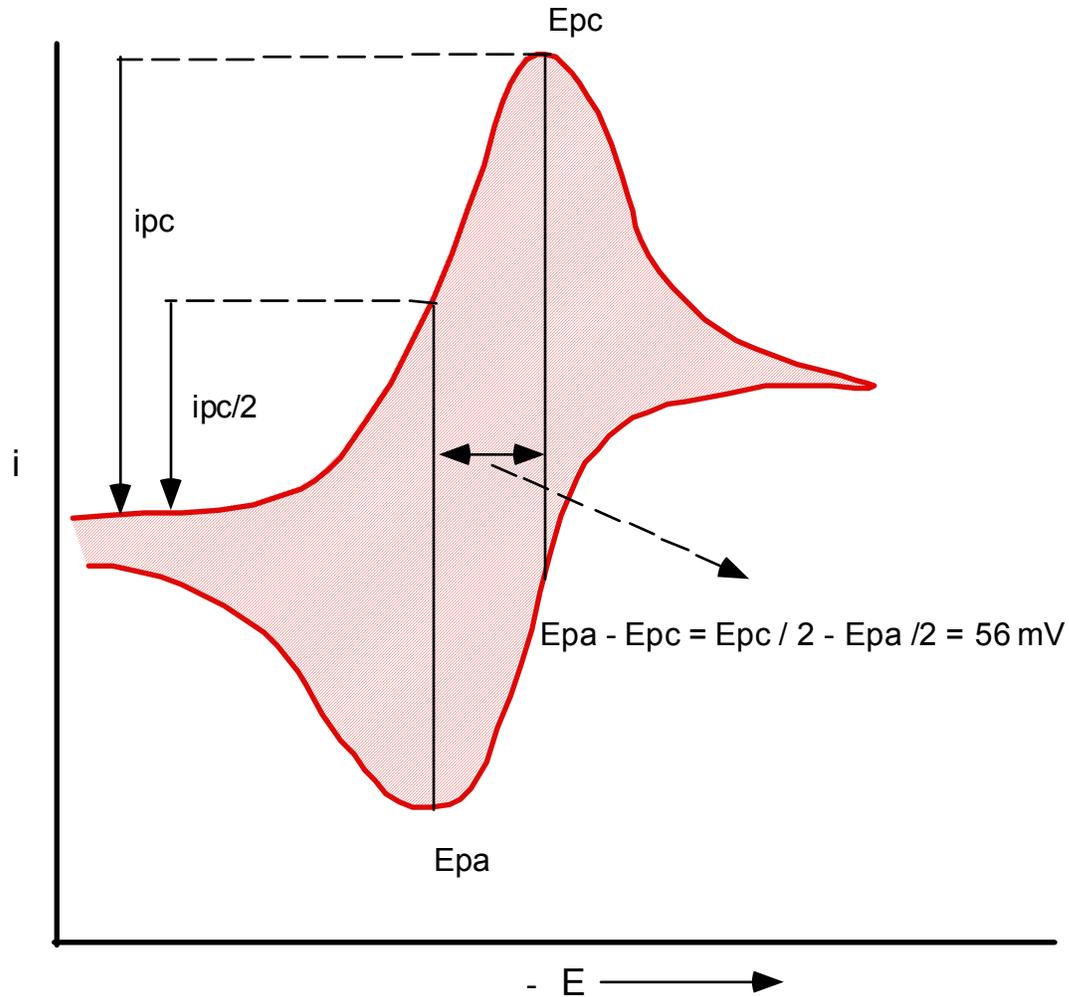
$$E_{pc/2} = E_{pa} = E_o + 0.028 / n$$

$$E_{pa/2} = E_{pc} = E_o - 0.028 / n$$

Suppose that the electrode process of interest is totally irreversible



The CV curve as illustrated in Fig. 8 will have no anodic peak upon scan reversal past the peak potential. This is consistent with a very low rate of reoxidation of R and is a conclusive evidence of irreversibility.



**Fig. 9 CV Curve of a One Electron Reversible Process**

These simple electron transfers are known as the E mechanisms and as previously pointed out the CV shapes are determined both by the heterogeneous charge transfer and the diffusional mass transfer. The heterogeneous charge transfer is described by the Butler - Volmer equation [ the basic equation in electrokinetics ].

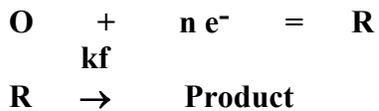
$$J_e(0, t) = i/nFA = C_e(0,t) k_0 e^{[-\alpha nF(E-E_0)/RT]} - C_b(0, t) k_0 e^{[1-\alpha]nF(E - E_0) / RT}$$

$k_0$  is the heterogeneous standard rate constant,  $E_0$  the standard electrode potential  $A$  the surface area of the electrode and  $J$  is the flux at the electrode interface. If  $k_0 > 10^{-1} \text{ cm s}^{-1}$

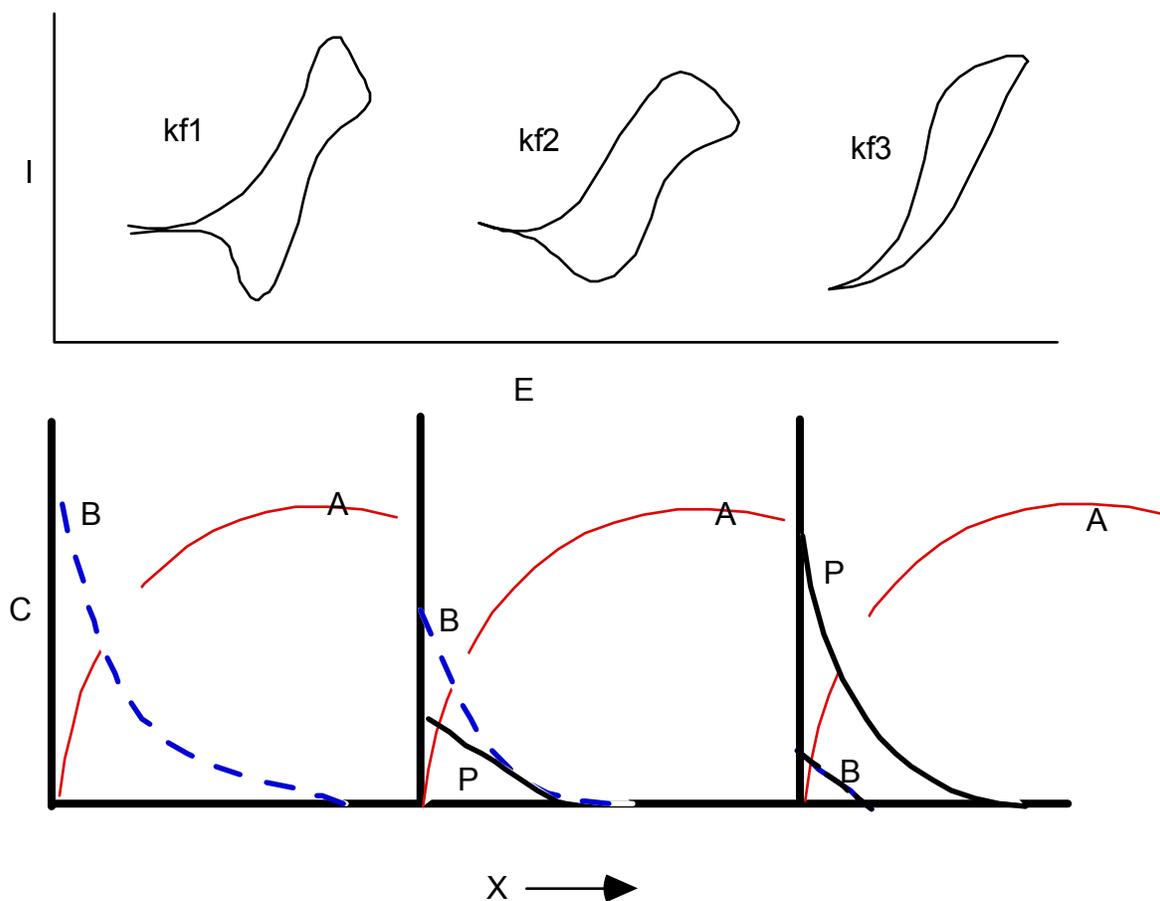
$k_0$  is considered to be very high and a dynamic equilibrium is established at the electrode interface and the Butler - Volmer equation is reduced to Nernst equation and  $C_e$  and  $C_b$  will depend only on the actual applied electrode potential and are no longer influenced by

heterogeneous kinetic effects and a thermodynamic equilibrium exists at the phase boundary. The current is thus influenced solely by the mass transport which is the slowest step ( diffusion ). If  $k_0 < 10^{-5} \text{ cm s}^{-1}$  the reaction is very slow and the term  $i / nFAk_0$  cannot be neglected and depending on the potential only one of the cathodic or the anodic heterogeneous reactions has a measurable rate, the current is thus largely controlled by the rate of charge transfer reaction. In this case Nernst equation as is does not apply and one speaks of an irreversible process.

The third frequently encountered type of behaviour is the EC process shown in Fig. 8 . An anodic peak is observed in the reversal scanning but this peak is diminished considerably in height relative to the cathodic peak. Furthermore, A faster scan rate will increase the relative height of this anodic peak and could reach at any instant the height of the cathodic peak. on the other hand at very low scan rates the anodic peak can completely disappear. This behaviour is usually associated with a chemical reaction subsequent to electron transfer such that a fraction of the R reacts chemically and is not available for reoxidation upon scan reversal. If the scan rate is very high relative to  $k_f$  little R will be lost to the



succeeding chemical reaction, and the the CV curve will resemble the reversible case. Conversely if the scan rate is low relative to  $k_f$  the chemical reaction will be completed before reversal of scan and the electrode process will be totally irreversible. This mechanism is known as the EC mechanism. Fig. 10 illustrates the profile of an EC



**Fig. 10 Concentration Profile of an EC Mechanism**

$$k_{f1} \ll k_{f2} \ll k_{f3}$$

mechanism. In the follow - up reaction the initially formed anion R decays and a new product is formed P, only a small amount of R is available for oxidation in the reverse sweep depending on the rate of the following up reaction and the scan rate . Accordingly the anodic current in the cyclic voltammogram decreases until it disappears at high rate constants and low scan rates. The rate of the follow - up reaction can be determined from the ratio of  $i_p$  and  $i_c$  of the CV curves at an appropriate scan rate .

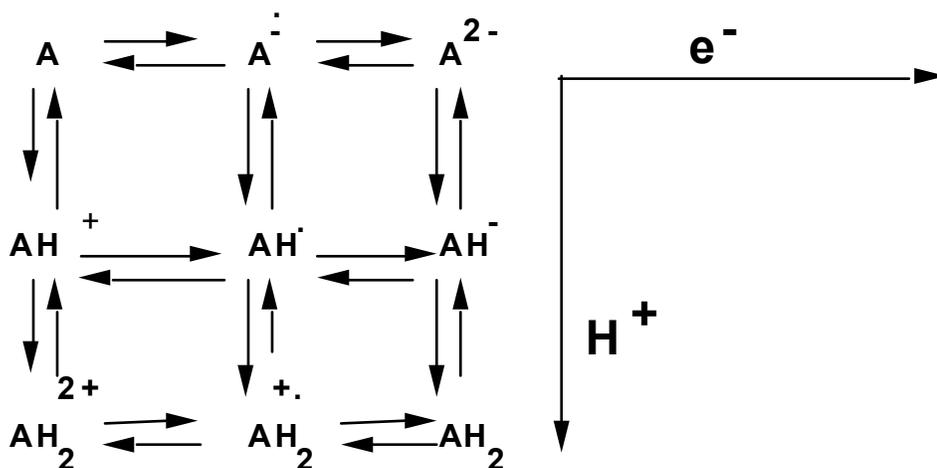
## APPLICATION OF VOLTAMMETRY IN ORGANIC ELECTRODE PROCESSES

### The Square Diagram

Let us undertake a detailed examination of a relatively simple system in which two electrons and two protons are gained or lost during an electrochemical process. This type of reaction is very common in electroorganic mechanism. It is obvious to chemists

accustomed with reaction mechanisms that this process can occur only in stages . In principle there could be seven intermediates involved in such process . In the scheme diagrammed below all electron transfers are given by horizontal lines and all chemical changes are given by vertical lines

The computer analysis of such diagram leads to the following conclusions.



- i- The reaction path which is followed depends on the acid-base equilibrium constants which are involved in the scheme and on the kinetics of electron transfers and chemical reactions.
- ii- For a given electrode potential, several pathways may be simultaneously followed. The relative importance of each depends on the applied potential.
- iii- Reaction paths may be different in oxidation and in reduction.

### Protons in Organic Electroreduction Processes

In electrode processes involving Organic species the  $E_{1/2}$  is usually dependent on the variation of  $\text{H}^+$  concentration and thus is shifted towards negative values. The variation of  $E_{1/2}$  with pH is usually linear . The slope of this linear dependence is given by

$$d E_{1/2} / d \text{pH} = -0.0592 / n \times P$$

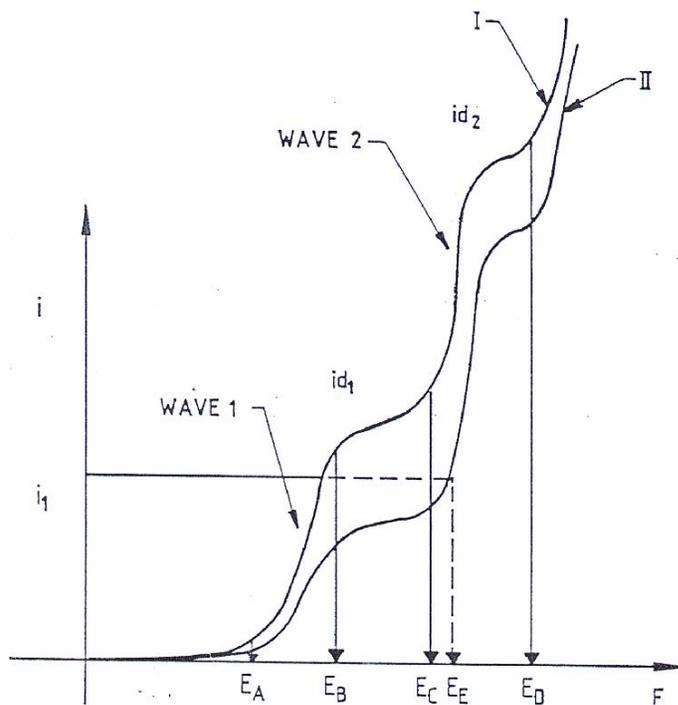
where P is the number of protons in the rate determining step in a reversible reaction according to Mairanovskii. On the other hand for an irreversible reaction the shift can be described by

$$d E_{1/2} / d \text{pH} = -0.0592 / \alpha n \times P$$

## ELECTROLYSIS

### Controlled Electrolysis and Selectivity

The practical quantities to be controlled in an electrolysis is the current measured in amperes or the potential of the working electrode expressed in volts. The differences in these two ways are illustrated in Fig. 11 . In this figure curve I depicts schematically the



**Fig. 11 Schematic Illustration of the Deformation of Waves During Electrolysis** connection between the current through the cell and the potential of the working electrode. Consider a solution containing two reducible species or one molecule with two electroactive sites (waves 1 and 2). When the potential at the cathode is varied between 0

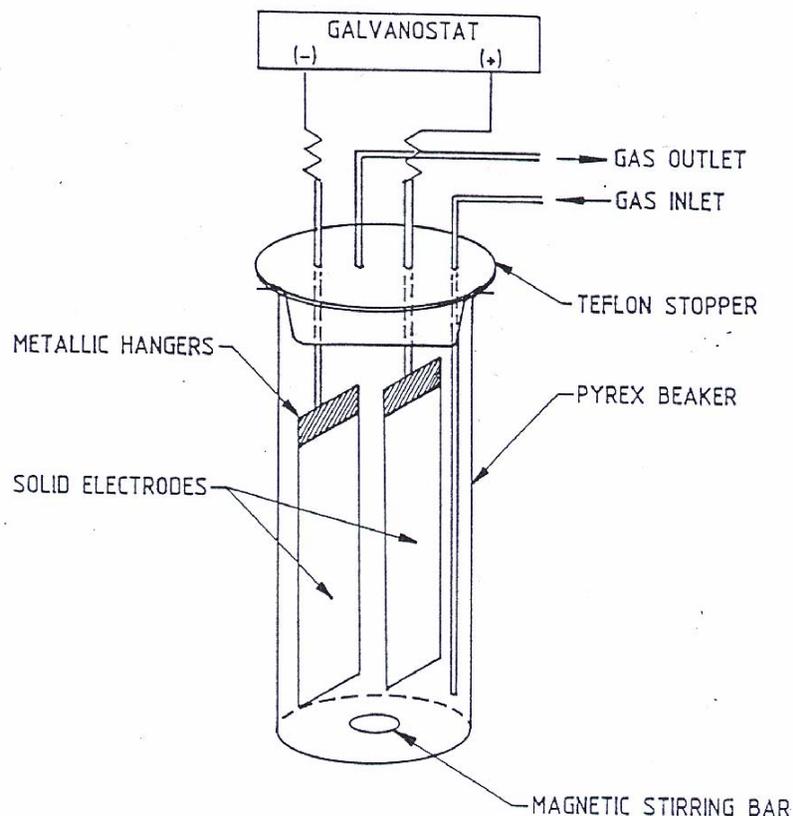
and  $E_A$ , no electron transfer across the electrical double layer can take place and thus no current runs through the cell. If the cathode potential is made more negative, the electron transfer becomes possible; that is, the reduction of the most easily reducible compound or group starts. Between  $E_A$  and  $E_B$  the current rises in dependence on the potential, but when the value  $E_B$  has been reached, all the molecules that arrive at the electrode and which can undergo the first reduction are reduced as soon as they reach the electrode. In the potential interval  $E_B$  to  $E_C$  the current is limited by the transport of the reducible compound to the cathode. This current is called the limiting current  $i_l^{1,2}$  and under fixed conditions it is proportional to the concentration of the electroactive compound and known as the diffusion current  $i_d$ .

A further change of the electrode potential in the negative direction results in the occurrence of the second electrode reaction and the current rises; a similar S-shaped curve results from this reduction. At more negative potentials ( $>E_D$ ) a third reaction the reduction of the medium takes place ( Wall of the electrolyte ).

If a suitable current  $i_l$  [ $i_l < i_{d1}$ ] is sent through the cell, the cathode potential assumes the value  $E_1$  between  $E_A$  and  $E_B$ , and when  $i_l < i_{d1}$  is well below the potential ( $E_C$ ) at which the second electrode reaction starts; a selective reduction thus occurs at the beginning of the electrolysis. During the electrolysis the concentration of the reducible compound, and thus its limiting current, diminishes and after a while (curve II) the limiting current becomes smaller than the applied current [ $i_l > i_{d1}$ ]. The cathode potential has then, by necessity, reached the value  $E$  in between  $E_C$   $E_D$  and at this potential the second electrode reaction also takes place; the electrolysis is no longer selective. When the electrode potential is the factor controlled and is kept at a suitable value, eg. on the limiting current plateau of the first wave, the second electrode process cannot take place, and the reduction remains selective to the end of electrolysis. The current through the cell is never higher than the limiting current corresponding to the first electrode reaction. This means that the current decreases during the reduction and becomes very small toward the end of the reaction, as the limiting current is proportional to the concentration of the electroactive material .

### **Controlled Current Electrolysis ( CCE ) Manipulation**

This electrolysis preparation is usually carried out in a simple two electrode cell. The cell and circuit are illustrated in Fig.1 2 . The basic components for the circuit are :  
The  
constant current supply with a stable current output of maximum 10 A ( for a laboratory scale electrolysis ), the voltage and current measuring devices, and the cell, which can be

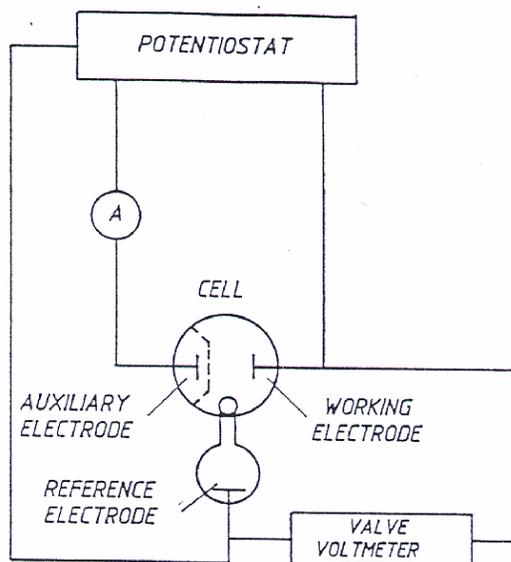


**Fig. 12 Control Current Electrolysis Cell**

simply a pyrex beaker with a working (WE) and a counter (CE) electrode. To minimize the IR drop in the cell the distance between the electrodes should be very small. The choice of the WE material depends mainly on the actual type of electrolysis and medium. In classical electrooxidation processes the Platinum and Carbon electrodes are widely used. In indirect electrooxidation large scale electrolytic preparations the Nickel oxide hydroxide anode is used. Mercury and Lead electrodes are the commonly used cathodes in electroreduction processes. The reduction of Oxygen leading to the superoxide ion in aprotic media using Hg, Au, Pt and C cathodes with the proper supporting electrolyte is another powerful indirect electrolysis technique.

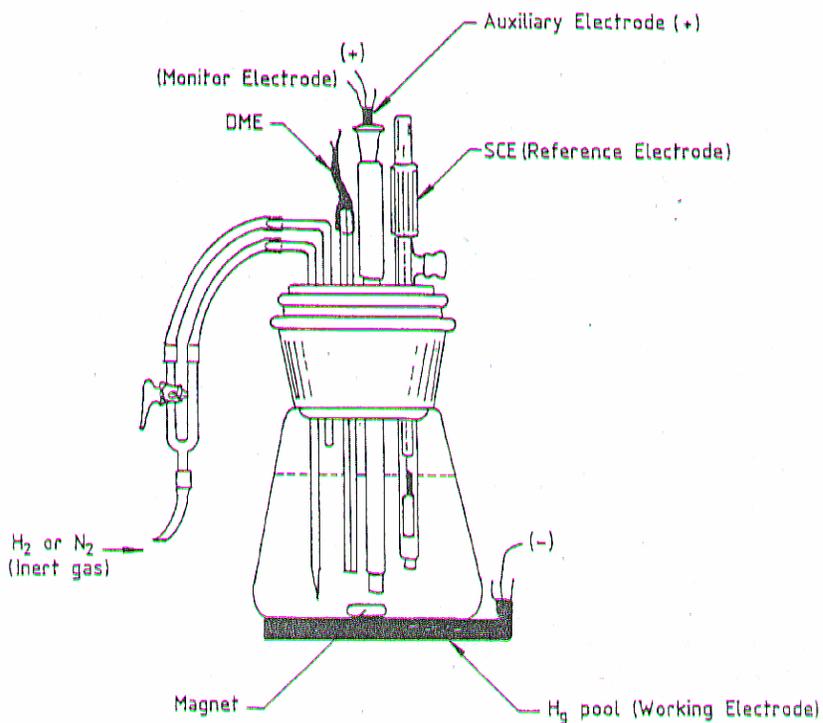
#### **Controlled Potential Electrolysis ( CPE ) Manipulation**

A circuit as the one illustrated in Fig. 13 is fairly sufficient for performing such CPE experiments together with the help of a classical DC polarograph a must for finding out the optimum experimental conditions through routine analyses of the compound to



**Fig. 13 Circuit Used in Controlled Potential Electrolysis**

be electrolyzed. The circuit consists in its simple form of a potentiostat (used for controlling the applied potential), galvanometer (used as current measurement device) and a valve voltmeter to check the accuracy of the applied potential and to detect any resistance in the cell during the course of electrolysis. A 250 ml conical or flat bottom flask (Fig. 14)



### Fig.14 Controlled Potential Electrolysis Cell

in which the reference (RE) and auxiliary (AE) electrodes have been inserted by means of a cork or Teflon stopper, is a practical cell for this purpose. The working electrode (WE) in electroreduction processes is usually mercury which has been previously purified by classical methods. Finally, a magnetic stirrer is used for agitation of mercury with the help of a stream of purified N<sub>2</sub> or H<sub>2</sub> gas which is continuously bubbled through the mixture. This stream repels and prevents contamination of the solution with atmospheric O<sub>2</sub>. The number of electrons consumed in the electrochemical reaction is usually calculated either directly by inserting an electronic integrator into the circuit or simply by recording the decay in current with time using Lingane's method of analysis emphasized further on.

For this purpose a complete detailed study of the half-wave potential ( $E_{1/2}$ ) and limiting current ( $i_l$ ) versus pH dependence of the compound to be electrolyzed must be undertaken using different solvent compositions. A plot of  $i_l$  versus time  $t$  curve, from which a knowledge about the stability of a certain species towards a certain medium, is also of great value. In the following are summarized some important hints for carrying out large scale laboratory preparative electrolysis:

(1) The choice of electrolysis potential must be taken in the medium where  $i_l$  is practically pH and time independent (Fig.15).

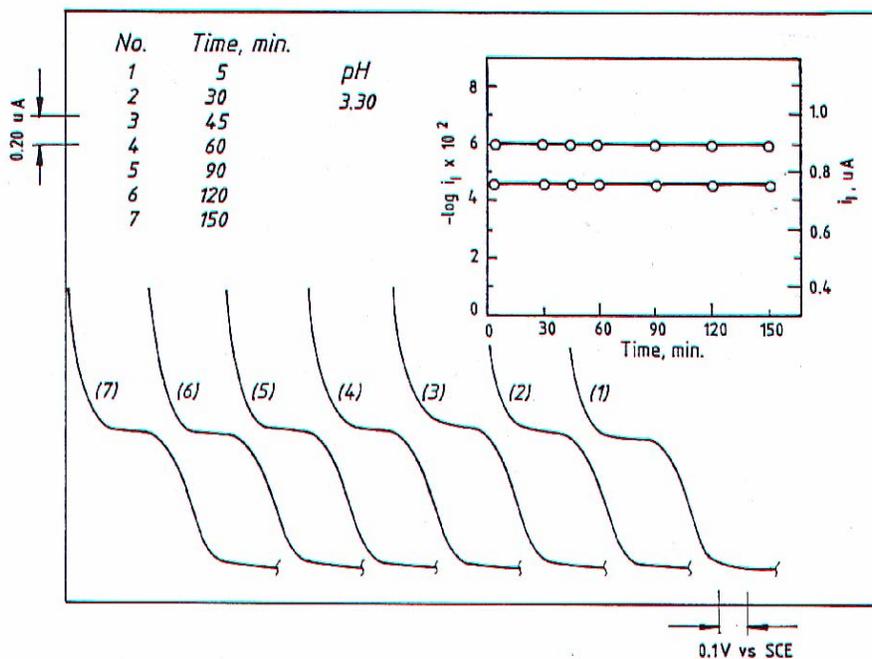


Fig. 15 Effect of Time on Limiting Current of a Polarographic Wave

(2) In molecules displaying well defined polarographic waves the potential of electrolysis must be chosen in a way that it covers the beginning of the limiting current i.e.  $-0.2 \text{ V} > E_{1/2}$  value. On the other hand, if the wave is located at very negative potential i.e. near hydrogen evolution in acid media or near the limiting wall of supporting electrolyte, the potential must be fixed at value within the beginning of the rising portion of the wave in question.

(3) Calculated amounts, not exceeding 100 mg, of starting material are practical in CPE experiments to decrease as much as possible electrolysis time and in turn side chemical (CR) and secondary electrochemical reactions (ECR). In addition, the use of calculated amounts help controlling the efficiency of experiment.

(4) It is preferable to use a medium in which the compound to be electrolyzed is completely soluble. However, if the products of electrolysis are soluble in the medium, suspensions of the starting materials may be used. Preferable to use acid medium or faintly acidified medium to minimize as much as possible conductance problems.

(5) pH-control (Cf, further ) is mandatory since, in some processes molecules of basic character are obtained as main products of electrolysis and thus will change the pH of solution in the course of electrolysis.

(6) Room temperature is suitable for most CPE experiments if not otherwise specified for a certain reaction.

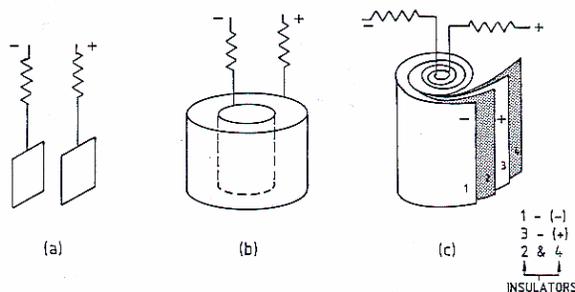
Finally, before carrying out a large scale electrolysis a researcher needs to emphasize in a way or another to overall picture occurring inside his electrochemical cell and thus it is wise to perform an experiment on a small scale say  $10^{-4} \text{ mol dm}^{-3}$  depolarizer, in which the electrochemical reactions are closely monitored through periodic plotting of  $i$ - $E$  curves using classical DC-voltammetric techniques using a DME, HMDE or a RDE. This will help to shed light on the mechanism and kinetics of the electrode processes. At the end of electrolysis products are identified via spot tests or an other convenient analytical technique. The purpose of this low concentration CPE is to improve the experimental conditions, to get information as much as possible on the stability of the resulting products, the intermediates (if any) and to estimate the average total time that will be consumed in a large scale preparative electrolysis.

## **Best Cell Geometry**

### **Potential Distribution**

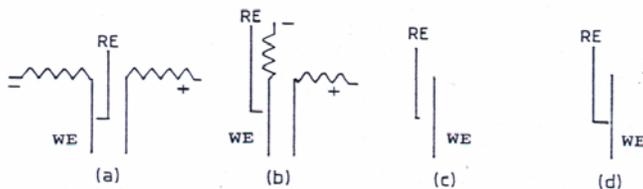
Potential gradient should be the same all over the electrode surface so as to obtain a uniform density distribution. The design of electrodes help to improve the potential distribution in a certain cell thus a good distribution is obtained in concentric electrodes

such as Swiss-roll (Cf. further) and cylindrical electrodes followed by the plane parallel electrodes. (Fig.16).



**Fig. 16 Common Electrodes a-Plane Parallel b- Cylindrical C-Swiss-Roll**  
**Position of a Reference Electrode**

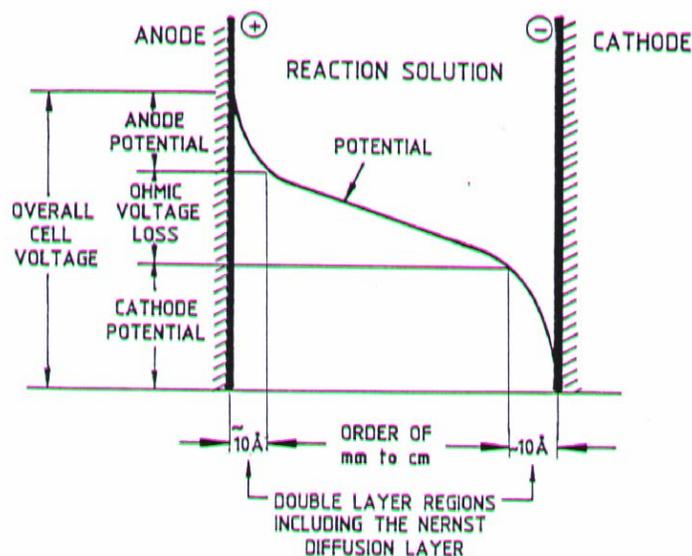
Electrochemists generally approved the position concept which states that "In the general case the best approach is to place the reference electrode as near as possible to the working electrode surface on the line of minimum distance between the counter and working electrode" (cf. Fig. 17).



**Fig. 7 Location of the Reference Electrode in an Electrolysis Cell**  
**a- Best Position b- Not Advisable Position b- Error Caused by IR Drop**  
**d- Minimal IR Drop Position**

**Ohmic Resistance**

The diagram in Fig. 18 illustrates schematically the potential distribution in an electrochemical cell. If one wishes to diminish the ohmic resistance the first approach is to minimize the distance between the working and counter electrodes [in some cases one may reach a value of 0.1 to 0.2 mm (Swiss-roll electrodes)]. Secondly is to increase the surface of the electrodes and finally diaphragms should be used only when unavoidable.



**Fig. 18 Potential Distribution in an Electrolytic Cell**

### **Diaphragms**

These should be used only when the products of the auxiliary electrode may interfere with the desired electrode reaction occurring on the working electrode.

### **Mass Transfer**

An efficient mass transfer must be acting all the time through electrolysis by either stirring (mechanically or magnetically), recycling pumping or heating.

### **Heat Transfer**

Excess heating resulting from electrochemical processes in resisting solutions should be avoided by proper cooling procedures or the use of flow cells.

### **Closed System**

In electrolytic reduction processes closed systems should be used to avoid contamination with atmospheric oxygen which is reduced at the surface of the electrode causing an indefinite number of problems. Also, when dealing with non-aqueous media, contamination with H<sub>2</sub>O vapors is also avoided by the use of closed systems.

### **Difference between Micro and Macro Scales Electrolyses**

Shifting from micro to macro scale preparative electrolysis requires some skills due to the interference of few newly borned factors such as .

**(a) Prolonged time of electrolysis**

Usually macro scale electrolysis consumes longer time ranging from several hours to 7 days a time which is long enough to allow consecutive chemical reactions to occur between solvent and products or between reagent and starting molecules or the interference of known common chemical reactions such as hydrolysis or hydration.

**(b) Enlarged surface area of electrode**

Increasing the concentration of the substrate requires the immediate increase of the available surface area of the electrode and this by turn causes the following.

- i) Adsorption phenomena resulting in the blocking of the electrode surface.
- ii) Increase of the rate of chemical surface reactions of species adsorbed on the surface of the electrode.

**(c) Higher concentrations**

The high concentration of electrolysable material causes higher order reactions such as dimerization, oligomerization and polymerization. This can clearly be observed in some cases from the variation of the uptake number of electrons by the same species at higher and lower concentrations.

**(d) pH-control**

The pH in macro scale electrolysis vary in the vicinity of the electrode according to the obtained electrolysis products and hence is difficult to be controlled with high degree of accuracy. Thus in the CPR of hydrazones amines are produced as main products of electrolysis and hence the pH will increases drastically and the solution becomes highly alkaline.

**(e) Difference in  $E_{1/2}$  measured by a micro electrode and a large surface electrode (macro electrode)**

For an irreversible reaction at a stirred pool. The half-wave potential of a Hg pool electrode as compared to that of a DME is given by the following relation.

$$E_{1/2}(\text{Hg pool}) = E(\text{DME}) + \frac{RT}{\alpha nF} \ln 1.349 \sqrt{Dt} / \delta$$

D is the diffusion coefficient, t is the drop time,  $\delta$  is the diffusion layer thickness. (D is  $\sim 6 \times 10^{-6}$  cm<sup>2</sup>/s for a t of 4 s for a medium sized molecule and  $\delta$  is  $\sim 3 \times 10^{-3}$  cm)

For a reversible system

$$E_{1/2}(\text{Hg pool}) = E_{1/2}(\text{DME}) - \frac{RT}{nF} \ln \delta R / \delta O$$

and hence the two are nearly equal.

**Efficiency of an Electrochemical Process**

According to the first Faraday law of electricity "For any electrode process the amount of material converted by electrolysis is proportional to the product of current and time of its passage, that is, the total electric charge". On the other hand the Second Faraday's law describes the effect of nature of ions. Accordingly this law states that "the amounts of different substances produced by the passage of the same electric charge are proportional to their equivalent masses". The electric charge required to liberate 1 equivalent of any substance by electrolysis is 96500 coulombs or 26.8 Ah. In practice the amount of substance liberated by electrolysis is always smaller than the theoretical amount calculated from Faraday's laws.

The efficiency of a certain electrochemical process is basically defined by its current yield (in percentage) and by the coefficient of energy. The current yield or efficiency  $\eta$  (CE) is the ratio of the actual amount  $w_a$  of matter obtained by electrolysis to the theoretical amount  $w_{th}$  which should be obtained with the same energy consumption according to Faraday's Law.

$$\eta(\text{CE}) = w_a / w_{th} \quad \text{or} \quad \text{Actual Ah} / \text{Theoretical Ah.}$$

but  $w_{th} = (I \times t \times w_0) / 1000$

where I is the current in amperes, t is the duration of electrolysis in hours and  $w_0$  is the amount of material liberated at the working electrode with the passage of 1Ah charge.

The coefficient of energy  $\mu$  is equal to the ratio of the theoretical amount of energy  $\varepsilon_{th}$  to the actual consumed amount of energy in the electrolysis process  $\varepsilon_a$ .

$$\mu = \varepsilon_{th} / \varepsilon_a$$

the theoretical consumed amount of energy in an electrolysis (kW/Kg of product) is given by

$$\varepsilon_{th} = E_{th} \times I \times t / w_{th}$$

where  $E_{th}$  is the theoretical applied voltage which is the difference between the equilibrium potentials of the anodic  $e_a$  and  $e_c$  potentials in volts.

$$E_{th} = e_a - e_c$$

The equilibrium electrode potentials are given by Nernst equation as follows.

$$e_c = e_0 + RT/nF \ln a_1$$

$$e_a = e_0 + RT/nF \ln a_2$$

where  $e_0$  is the standard electrode potential, R is the gas constant, n is the number of electrons, F the Faraday, T the absolute temperature. On the other hand the actual operating voltage  $E_a$  is higher than  $E_{th}$  owing to polarization and overvoltage, as well as to the losses due to the ohmic resistances of electrolyte and current leads. The actual operating voltage equation will take the following form.

$$E_a = (e_a - e_c) + \Delta e_a + \Delta e_c + \Sigma IR$$

where  $\Delta e_a$  and  $\Delta e_c$  are the voltage compensating terms for both electrochemical polarizations at the anode and cathode respectively and  $\Sigma IR$  is the voltage drop compensation. The actual consumption of energy (Energy efficiency) in an electrolysis process is given by

$$\epsilon_a = E_a \times I \times t / w_a$$

and  $\mu$  will be equal to  $E_{th} / E_a \eta$ .

To summarize one can conclude that the energy efficiency of an electrochemical process can be developed from observation of the cell operating voltage and the efficiency of the current in converting the substrate to the desired product. It should be always remembered that the cell current efficiency is increased usually by decreasing resistance losses, selection of electrode material and avoiding as much as possible secondary reactions.

## Recent Trends in Electrolysis

### Mediated Electrochemical Reactions

Two types of mediated or what so called regenerative electrochemical reactions have been thoroughly investigated in this decade. The first type is known as the internal mediation which consists of an electrochemically generated reactive species which reacts with the substrate to form a product and this mediator is electroregenerated (reformed). The second type involves the electrochemical generation of an oxidizing or reducing reagent within the cell, reaction of the reagent with the substrate externally to the cell, and return of the reduced or oxidized reagent to the electrolysis cell for regeneration.

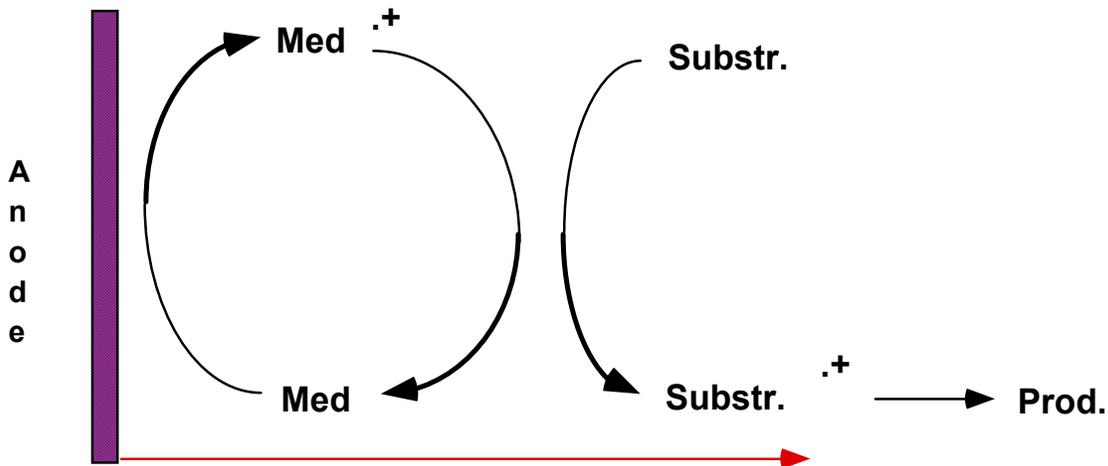
#### Internally mediated reactions

Figure 19 illustrates the principle of the internally mediated reaction. The radical ion formed at the anode reacts with the substrate, transforming the latter to the radical anion. The deactivated mediator is recycled at the anode, and the substrate radical anion is transformed into the reaction product. The mediator thus acts as a catalyst for the electrochemical transformation. Four cases in which mediated reactions may be attractive alternatives to classical electrochemical reactions.

i- To obtain products of an electrochemical reaction that are not obtainable during direct electrolysis.

ii- To conduct electrochemical reactions at potentials lower than those required for direct electrolysis.

iii- To conduct electrochemical reactions of substrates who are not obtainable under classical electrolysis conditions.



**Fig.19 Principle of Mediated Electrolysis with Internal Mediators**

iv- To conduct reactions using catalytic amounts of metallic redox reagents with reduction of the required inventory of the redox agent required for the direct reaction.

### Case i example

An example of this case is the reaction of benzene with electrochemically generated hydroxyl ion via the Fenton reaction. Classically this reaction gives very poor yields but electrochemically the yield reaches 64%. It is important to draw attention that ferrous ions are both chemically and electrochemically regenerated during the electrolysis.

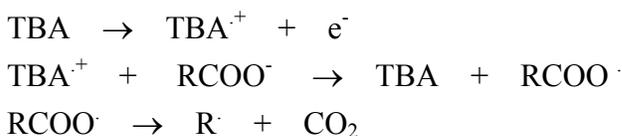


### Case ii example

The use of an electrochemically generated intermediate to reduce the voltage required to drive electrochemical reaction has been illustrated in a modification of the Kolbe reaction

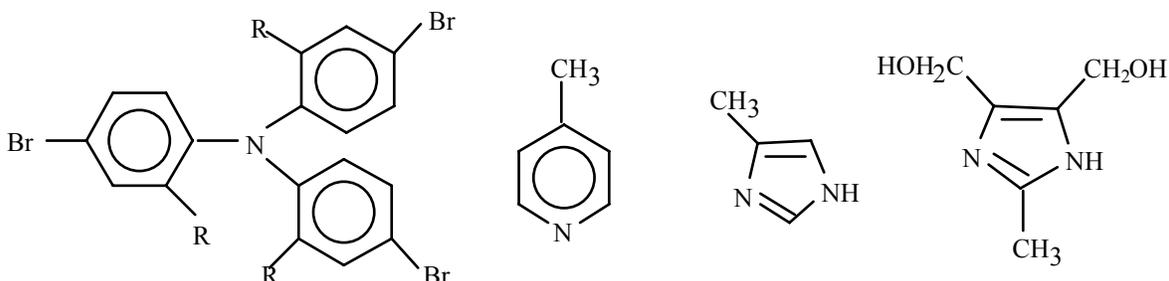


The observed potential of this initial step of the Kolbe synthesis is 2.46 V vs Hydrogen reference electrode. By the use of mediator the formation of the alkyl radical can occur at 1.3 V. This has been accomplished by using tris-(p-bromophenyl) amine (TBA) and lead to the following mechanism requiring only 1.3 V.

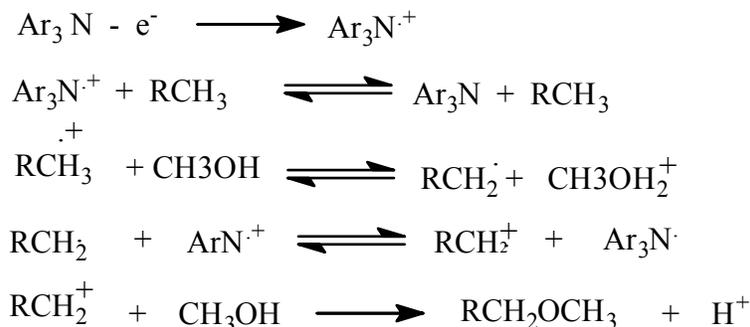


### Case iii example

The technically important side-chain oxidation of three heterocyclic compounds, such as 4-Picoline, 4-methylimidazol and 2-methyl-4,5-dihydromethylimidazol, can be performed electrochemically at low potentials, in CH<sub>3</sub>CN / MeOH / LiClO<sub>4</sub> system, using catalytic amounts of electrogenerated and regenerated triarylamine cation radicals as organic mediators. It is important to attract attention to the fact that direct electrochemical oxidation of Picolines, because of the electron-poor heteroaromatic ring, can only occur under acidic conditions.



The applicability of triarylamines (TAA) as redox catalyst was first demonstrated in the oxidation of cyanide ions. The advantage of triarylamine as mediator is the possibility to adjust their oxidation potential by the selection of the ortho and para substituents. A large spectrum of substituted triarylamine has been developed and applied as mild and selective oxidizing agents. The electrogenerated and regenerated triarylamine cation radicals are usually used for the side-chain oxidation of alkyl-substituted aromatic compounds and benzyl alcohol oxidations. The following scheme is postulated for the indirect mediated electrooxidation.



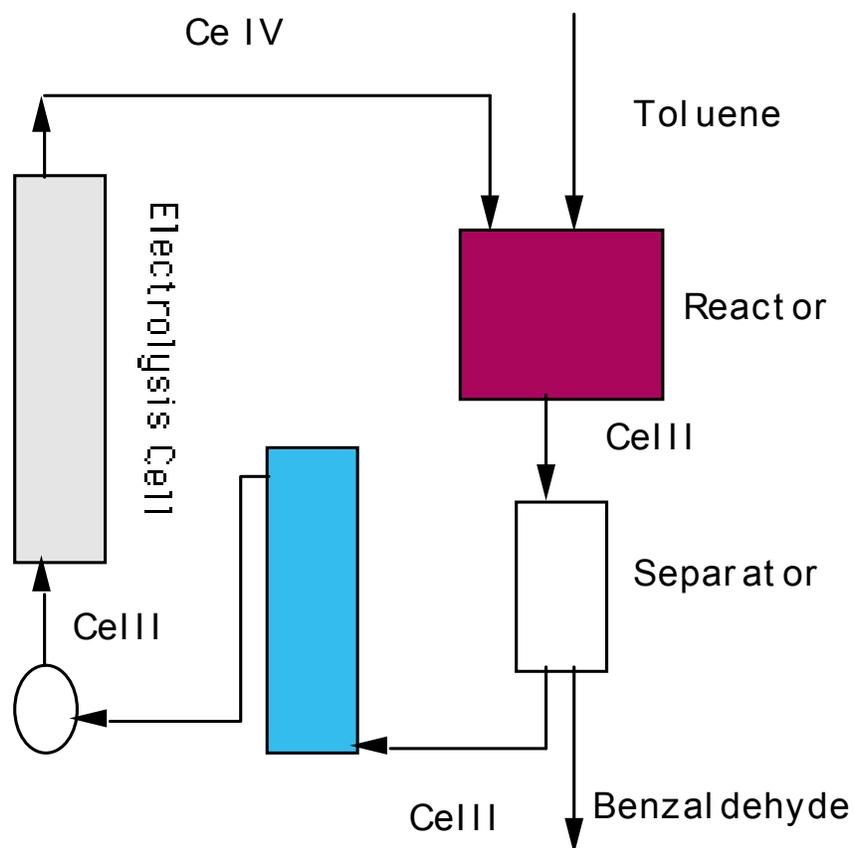
### Modified electrodes

Modified electrodes are considered as the most ideal form of internal mediators, the process consists mainly of coating the working electrode with a metal complex in which the metal will act as the mediator. This technique is considered very attractive since it protects the electrode, and helps in using various types of low cost material electrode and improves the purity of the obtained product and the film can be easily regenerated.

### Externally mediated reactions

The block diagram for carrying out an industrial scale electrochemical reaction is given in Fig.20. The reducing or oxidizing reagent, is regenerated in the electrolysis cell and then transferred to the chemical reactor, where reaction with the desired compound occurs. Following the reaction, the product is extracted from the reaction mixture. The unreacted substrate can be recovered and returned back to the reactor. The reacted oxidizing or reducing agent is returned to the electrolysis cell for regeneration. The oxidation of toluene to benzaldehyde by an external mediator is well known. In 5 M  $\text{HClO}_4$  in the presence of  $\text{Ce(IV)}$  benzaldehyde yields were around 98.8%.





**Fig. 20 Diagram for an Externally mediated Process Commercial and Pilot-Plant Synthesis**

### General

Electrochemical preparation of ingredients or precursors of certain pharmaceuticals and perfumes has been of commercial interest for a number of years. However, production of organic chemicals at multithousand- ton- per- year rates is only relatively recent. One of the first large plants was that of Atlas Powder Company, which was built in 1937 for the manufacture of 1400 tons / yr. of sorbitol and mannitol by cathodic reduction of glucose. This early success was rather short-lived and the process was replaced within a few years by a high-pressure catalytic hydrogenation route. It was not until 1964 that a truly largescale electroorganic manufacturing facility was erected the Nalco's tetraalkyllead plant in the USA. The capacity of the original installation was 15,000 tons / yr. tetramethyllead or 18,000 tons / yr. tetraethyllead. The following year Monsanto began production of adiponitrile electrolytically

Electroorganic processes that have been investigated on a pilot-plant or semicommercial scale cover a wide range of reaction types. In addition to the reductive

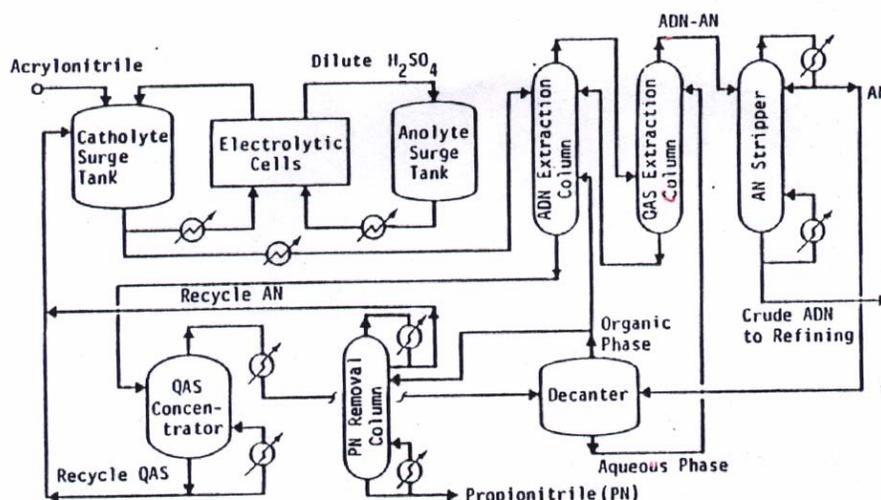
coupling of acrylonitrile and the preparation of sorbitol / mannitol, examples of other cathodic processes considered for commercialization include the reduction of (1) salicylic acid to salicylaldehyde (2) phthalic acids to the corresponding dihydrophthalic acids (3) benzoic acid to benzyl alcohol. Anodic processes claimed to have favorable economics are (1) the oxidation of propylene to propylene oxide, (2) the bromination of hydrogen cyanide to give cyanogen bromide, and (3) the oxidation of starch to the dialdehyde.

### **B. Commercial Process for Adiponitrile**

In excess of a billion pounds per year of adiponitrile is produced worldwide as a precursor to hexamethylenediamine, one of the monomers used in the manufacture of nylon 66 polymer. The importance of the production cost of adiponitrile on the economics of making nylon is well recognized and has been responsible for considerable research activity on the preparation of this intermediate. The possibility of electroreductive coupling of acrylonitrile to adiponitrile was reported in the 1940s, but it was not until the discovery in 1963 of the importance of the supporting electrolyte that commercially attractive selectivities and current efficiencies were realized. It was found that through the use of concentrated solutions of certain quaternary ammonium salts, such as tetraethylammonium p-toluenesulfonate, nearly quantitative yields of adiponitrile could be achieved at lead or mercury cathodes. Following an intensive process development program, Monsanto designed and built a 15,000 ton / yr facility for production of adiponitrile via this technology. This plant has been improved and expanded substantially since startup in 1965 and a new electrolysis facility to produce 90,000 tons / yr of adiponitrile was put into operation in 1978 in England, by Polyamide Intermediates Ltd.

In the Monsanto process a catholyte consisting of an aqueous solution of acrylonitrile, quaternary ammonium salt (QAS). The QAS serves the joint function of increasing the solubility of acrylonitrile in water and improving the electrical conductivity of the solution. The anolyte, a dilute solution of sulfuric acid, is similarly circulated through the opposing anolyte compartments. The cathode is lead; a lead alloy, stable in sulfate electrolysis, is used as the anode material. The electrodes are mounted on polypropylene plates with the anode of one cell joined electrically to the cathode of the next via internal connectors, providing series flow of current through the bank of cells. A cation permselective membrane separates the anode and cathode compartments.

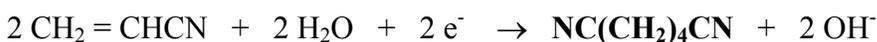
Electrolyte is pumped through each cell in parallel and both anolyte and catholyte are recirculated through external exchangers for removal of the heat generated in the cells. A side stream is withdrawn from the circulating catholyte and sent to an extraction system for removal of the product ADN.



**Fig. 20 Industrial Production of Adiponitrile**

The withdrawn catholyte stream is cooled and countercurrently contacted with excess acrylonitrile in a multistage extraction column. The acrylonitrile/ adiponitrile extract stream is then back-extracted with water in a similar column of dissolved QAS. The organic stream leaving the second extraction column is sent to a stripping column, where the acrylonitrile is distilled overhead and recycled to the process, following removal of by-product propionitrile. The bottoms from the acrylonitrile stripper are further refined by distillation to produce a 99% pure product, suitable for hydrogenation into hexamethylenediamine. (Fig. 20).

The principal cathode reaction is:



Water is decomposed at the anode as follows:



The Monsanto cells can be operated at current densities ranging from 25 to 100 A / dm<sup>2</sup> with cell voltages ranging from 6 to 15 V, corresponding to power consumptions of 3-8 kWh / kg adiponitrile produced.

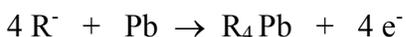
### C. Commercial Process for Tetraalkyllead

Production of lead alkyls exceeded 5000,000 tons per year in the early 1970s in the USA and although the demand has slackened in the United States in more recent years because of environment constraints, the International markets have continued to show modest growth.

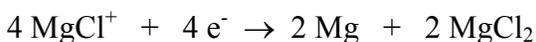
Prior to the introduction by Nalco Chemical in 1964 of its electrolytic process for tetraalkyllead, this important gasoline additive was produced via a 40-year-old process involving the reaction of methyl or ethyl halide with sodium-lead alloy. Nalco combined the large-scale production of Grignard reagent with a novel electrolysis system to pioneer this new process and installed facilities to produce tetramethyllead (TML) or tetraethyllead (TEL) in the USA. A simplified flowsheet of the Nalco TML process is shown in Fig. 2.1

The first step is the production of the Grignard reagent from magnesium metal turnings and alkyl halide in a mixture of anhydrous ethers, such as tetrahydrofuran and the diethyl ether of tetraethylene glycol. The reaction is carried out in several 30 m<sup>3</sup> propane-cooled reactors, operating at about 2 kg / cm<sup>2</sup> pressure and 35 - 40°. Yields above 98% are realized. The reactor product, containing excess alkyl chloride, is fed to ten 30 m<sup>3</sup> electrolysis vessels containing a bank of steel-tube cathodes filled with lead shot. The lead constitutes a sacrificial anode and is replaced through a feed arrangement in the top head of the vessel. The bed of shot is insulated from the retaining steel cathode tubes by porous diaphragms of plastic or ceramic. An improved version of the Nalco cell has been described in which the bed of lead shot fills virtually the entire vessel and a number of rectangular steel bars, covered with fiberglass cloth, are immersed in the bed to serve as cathodes. The electrolysis is conducted at 40-50°, cooling being provided by an ethyl chloride refrigeration system. Current densities are typically 1.5-3.0 A / dm<sup>2</sup> at 15-30 V. The electrode reactions may be written as follows, assuming dissociation of the Grignard reagent into two ions, R<sup>-</sup> and MgCl<sup>+</sup> :

Anode reaction



Cathode reaction

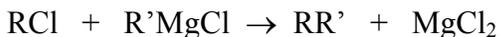


Although the theoretical cathode reaction shows formation of a mole of free magnesium for each mole of magnesium chloride, the excess alkyl halide added to the

feed combines with the magnesium to reform Grignard reagent equivalent to half of the consumed. Thus, the overall reaction is

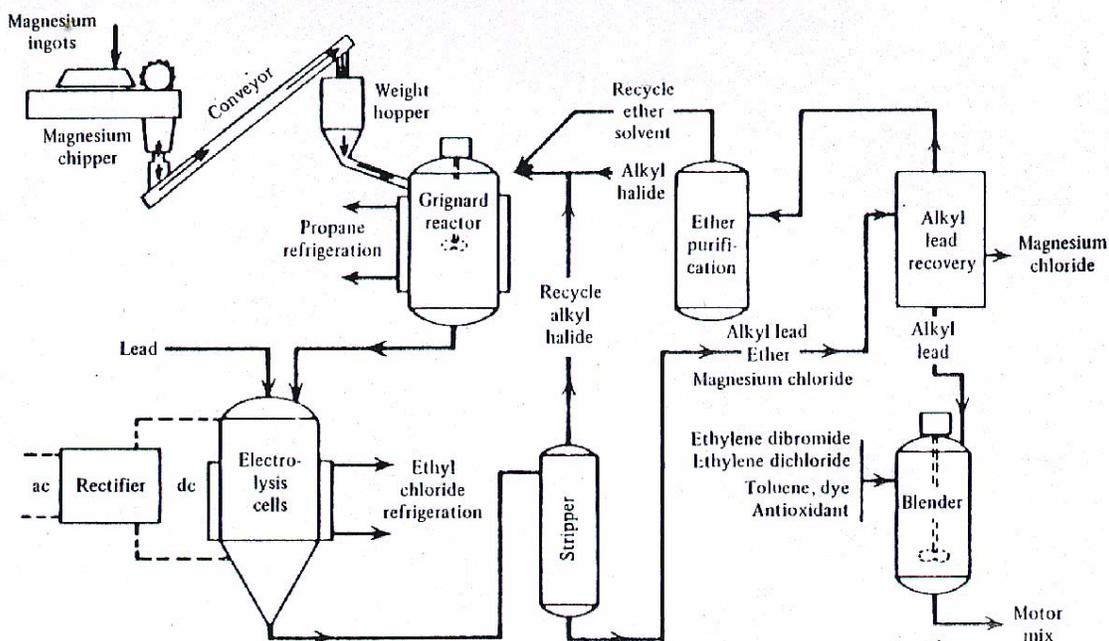


If the concentration of alkyl halide in the electrolyte is too high, there is a loss of reactants through WurtzFittig-type side reactions such as



On the other hand, insufficient levels of alkyl halide allow magnesium to be plated out on the cathode, ultimately bridging the cathode-anode and causing short circuits. By proper control of concentrations, temperature, and flow rate, yields up to 96% on the Grignard reagent can be achieved at conversion levels as high as 99%, with yield based on the magnesium consumed of 95%. The effluent from the cells is stripped with natural gas to remove unreacted methyl chloride, which is subsequently reabsorbed in ether for recycle to the Grignard reactors. The liquid phase from the stripper is contacted with water in a series of extraction stages for separation of the magnesium chloride, TML, and mixed ethers. The ethers are purified by azeotropic distillation and gas drying for recycle to the process. By using different alkyl groups on the Grignard reagent and the alkyl chloride fed to the cells, the process may be employed to prepare mixtures of tetraalkylleads, such as  $\text{Me}_4\text{Pb}$ ,

$\text{Me}_3\text{EtPb}$ ,  $\text{Me}_2\text{Et}_2\text{Pb}$ , and  $\text{Et}_4\text{Pb}$ .



## **Fig. 21 Industrial Production of TML in the USA.**

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