

Cyclic voltammetry principle

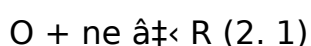


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Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions [34, 35]. The power of cyclic voltammetry results from its ability to provide considerable information on the thermodynamics and kinetics of heterogeneous electron transfer reactions [47, 48], and coupled chemical reactions [36, 37]. It also provides mathematical analysis of an electron transfer process at an electrode [41, 49, 50].

Basic Principle of Cyclic voltammetry

An electron transfer process with a single step may be represented as;



where O and R are oxidized and reduced form of electroactive species respectively, which either is soluble in solution or absorbed on the electrode surface and are transported by diffusion alone.

Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode (in an unstirred solution), using a triangular potential waveform. Depending on the information sought, single or multiple cycles can be used. During the potential sweep, the potentiostat measures the current resulting from the applied potential. The resulting plot of current vs. potential is termed as cyclic voltammogram.

The excitation signal in cyclic voltammetry is given in Fig. 2. 1a. Initially the potential of the electrode is E_i . Then the potential is swept linearly at the rate of \hat{v} volts per second. In cyclic voltammetry reversal technique is

carried out by reversing direction of scan after a certain time $t = \hat{v}$. The potential at any time $E(t)$ is given by

$$E(t) = E_i - \hat{v}^{1/2} t \quad (2.2a)$$

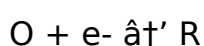
$$E(t) = E_i - 2\hat{v}^{1/2} t + \hat{v}^{1/2} t \quad (2.2b)$$

Here " \hat{v} " is scan rate in V/s.

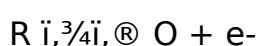
The shape of the resulting cyclic voltammogram can be qualitatively explained as follows:

When potential is increased from the region where oxidized form "O" is stable, cathodic current starts to flow as potential approaches E_0 for R/O couple until a cathodic peak is reached. After traversing the potential region in which the reduction process takes place, the direction of potential sweep is reversed.

The reaction-taking place in the forward scan can be expressed as



During the reverse scan, R molecule (generated in the forward half cycle, and accumulated near the surface) is reoxidized back to O and anodic peak results.



In the forward scan as potential moves past E_0 , the near-electrode concentration of O falls to zero, the mass transfer of O reaches a maximum rate, in unstirred solution, this rate then declines as the depletion of O

further and further from electrode takes place. Before dropping again current passes through a maximum. Reversal of scan repeats the above sequence of events for the oxidation of electrochemically generated R that now predominates in near-electrode region.

The continuous change in the surface concentration is coupled with an expansion of the diffusion layer thickness (as expected in the quiescent solutions). The resulting current peaks thus reflect the continuous change of the concentration gradient with time, hence, the increase to the peak current corresponds to the achievement of diffusion control, while the current drop (beyond the peak) exhibits a $t^{-1/2}$ dependence (independent of the applied potential). For the above reasons, the reversal current has the same shape as the forward one.

Electrochemical Cell

Electrochemical cell is a sealed vessel which is designed to prevent the entry of air. It has an inlet and outlet to allow the saturation of solution with an inert gas, N₂ or Ar. Removal of O₂ is usually necessary to prevent currents due to the reduction of O₂ interfering with response from system under study. The standard electrochemical cell consists of three electrodes immersed in an electrolyte;

- Working electrode (WE)
- Reference electrode (RE)
- Counter electrode (CE)

Working Electrode (WE)

The performance of the voltammetric procedure is strongly influenced by the working electrode material. Since the reaction of interest (reduction or oxidation) takes place on working electrode, it should provide high signal to noise characteristics, as well as a reproducible response. Thus, its selection depends primarily on two factors: the redox behaviour of the target analyte and the background current over the potential region required for the measurement. Other considerations include the potential window, electrical conductivity, surface reproducibility, mechanical properties, cost, availability and toxicity. A range of materials have found application as working electrodes for electroanalysis, the most popular are those involving mercury, carbon or noble metals (particularly platinum and gold).

Reference Electrode (RE)

This functional electrode has a constant potential so it can be used as reference standard against which potential of other electrode present in the cell can be measured. Commonly used reference electrodes are silver-silver chloride or the calomel electrode.

Counter of Auxiliary Electrode (CE)

It is also termed as auxiliary electrode and serves as source or sink for electrons so that current can be passed from external circuit through the cell.

The potential at WE is monitored and controlled very precisely with respect to RE via potentiostat. This may be controlled in turn via interfacing with a computer. The desired waveform is imposed on the potential at the WE by a <https://assignbuster.com/cyclic-voltammetry-principle/>

waveform generator. The potential drop V is usually measured by the current flowing between the WE and CE across a resistor R (from which $I = V/R$), the latter connected in series with the two electrodes. The resulting I/V trace, termed as a voltammogram is then either plotted out via an XY chart recorder or, where possible, retained in a computer to allow any desired data manipulation prior to hard copy being taken.

Single Electron Transfer Process

Three types of single electron transfer process can be studied.

- Reversible process
- Irreversible process
- Quasi-reversible process

Based on values of electrochemical parameters, i. e. peak potential E_p , half peak potential ($E_{p/2}$), half wave potential ($E_{1/2}$), peak current (i_p), anodic peak potential E_{pa} , cathodic peak potential E_{pc} etc, it can be ascertained whether a reaction is reversible, irreversible or quasi-reversible. E_p is the potential corresponding to peak current i_p , $E_{p/2}$ is the potential corresponding to $0.5 i_p$, $E_{1/2}$ is the potential corresponding to $0.85 i_p$. These electrochemical parameters can be graphically obtained from the voltammogram as shown in the Fig. 2. 2.

Reversible Process

The heterogeneous transfer of electron from an electrode to a reducible species and vice versa



is a form of Nernstian electrode reaction with assumption that at the surface of electrode, rate of electron transfer is so rapid that a dynamic equilibrium is established and Nernstian condition holds i. e.

$$C_O(0, t) \hat{=} C_R(0, t) = \text{Exp}[(nF\hat{=} \cdot RT)(E_i - \hat{=}^{1/2}t - E_o)] \quad (2. 3)$$

In equation (2. 3), C_O and C_R are concentration of oxidized and reduced species at the surface of electrode as a function of time, E_o is the standard electrode potential, E_i is the initial potential and $\hat{=}^{1/2}$ is the scan rate in volts per second. Under these conditions, the oxidized and reduced species involved in an electrode reaction are in equilibrium at the electrode surface and such an electrode reaction is termed as a “ reversible reaction”.

Current Expression

Due to difference in concentration of electroactive species at the surface of electrode and the concentration in the bulk, diffusion controlled mass transport takes place. Fick's second law can be applied to obtain time dependent concentration distribution in one dimension of expanding diffusion layer.

$$\hat{=} \frac{\partial C_i(x, t)}{\partial t} = D_i \frac{\partial^2 C_i(x, t)}{\partial x^2} \quad (2. 4)$$

Peak current is a characteristic quantity in reversible cyclic voltammetric process. The current expression is obtained by solving Fick's law [51].

$$i = nFA C_o^* (\hat{=} D_o a)^{1/2} \hat{=} (at) \quad (2. 5)$$

where i = current, n = number of electrons transferred, A is the area of electrode, C_o^* is the bulk concentration of oxidized species, D_o is the diffusion coefficient, i_p (at) is the current function and $a = nFv^{1/2}/RT$

At 298K, function i_p (at) and the current potential curve reaches their maximum for the reduction process at a potential which is 28.5/n mV more negative than the half wave potential i. e. at $n(E_p - E_{1/2}) = -28.50$ mV, $i_{p1/2}/i_p$ (at) = 0.4463 (Table 2. 1). Then the current expression for the forward potential scan becomes

$$(2. 6)$$

where i_p is the peak current or maximum current.

Using $T = 298K$, Area (A) in cm^2 , Diffusion coefficient (D_o) in cm^2/s , concentration of species O (C_o^*) in $moles\ dm^{-3}$ and Scan rate ($v^{1/2}$) in $volts\ sec^{-1}$, equation (2. 6) takes the following form,

$$(2. 7)$$

Equation (2. 7) is called Randle's Sevcik equation [39, 40].

Diagnostic Criteria of Reversibility

Certain well-defined characteristic values can be obtained from the voltammogram, for a reversible electrochemical reaction.

Relationship between peak potential (E_p) and half wave potential ($E_{1/2}$) for a reversible reaction is given by,

$$(2. 8a)$$

(2. 8b)

Where $E_{1/2}$ is potential corresponding to $i = 0.8817i_p$ [41].

At 298 K

(2. 8c)

From equations (2. 8a) and (2. 8b) one obtains,

(2. 9a)

At 298K

(2. 9b)

The peak voltage position does not alter as scan rate varies. In some cases, the precise determination of peak potential E_p is not easy because the observed CV peak is somewhat broader. So it is sometimes more convenient to report the potential at $i = 0.5i_p$ called half peak potential, which can be used for $E_{1/2}$ determination [52].

(2. 10a)

At 298 K

(2. 10b)

(2. 10c)

From equations (2. 8a) and (2. 10a) we obtain,

(2. 11a)

At 298K

(2. 11b)

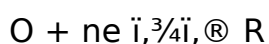
The diagnostic criterion of single electron transfer reversible reaction is often sufficient to get qualitative as well as quantitative information about the thermodynamic and kinetic parameters of the system.

For a reversible system, should be independent of the scan rate, however, it is found that generally increases with ν . This is due to presence of finite solution resistance between the reference and the working electrode.

Irreversible Process

For a totally irreversible process, reverse reaction of the electrode process does not occur. Actually for this type of reaction the charge transfer rate constant is quite small, i. e. $k_{ct} \approx 10^{-5} \text{ cm sec}^{-1}$, hence charge transfer is extremely low and current is mainly controlled by the rate of charge transfer reaction. Nernst equation is not applicable for such type of reaction.

The process can be best described by the following reaction



Delahay [51] and later on Mastuda, Ayabe [48], and Reinmuth [53] described the stationary electrode voltammetric curves of the irreversible process.

Irreversibility can be diagnosed by three major criteria.

A shift in peak potential occurs as the scan rate varies.

Half peak width for an irreversible process is given by

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(2. 12)

Here α is transfer coefficient and n_a is the number of electrons involved in rate determining step of charge transfer process.

At 298K

(2. 13)

Current expression is given as,

$$i = nFAc_0^*(D\nu)^{1/2} f(\alpha, \nu) \quad (2. 14)$$

The function $f(\alpha, \nu)$ goes through a maximum at $\alpha = 1/2$, $f(\alpha, \nu) = 0.4958$. (Table 2. 2).

Introduction of this value in equation (2. 14) yields the expression (2. 15) for the peak current.

A plot of $\ln i_p$ vs. $(E_p - E_0)$ for different scan rates would be a straight line with a slope proportional to $-\alpha n_a F$ and an intercept proportional to k_s, h .

Quasi-reversible Process

Quasi-reversible process is termed as a process which shows intermediate behaviour between reversible and irreversible processes. Both charge transfer and mass transfer control current of the reaction. For quasi-reversible process value of standard heterogeneous electron transfer rate constant, k_s, h lies between 10^{-1} to 10^{-5} cm sec⁻¹ [42]. Cyclic voltammogram for quasi-reversible process is shown in Fig. 2. 3.

An expression relating the current to potential dependent charge transfer rate was first provided by Matsuda and Ayabe [48].

(2. 17)

where, k_{sh} is the heterogeneous electron transfer rate constant at standard potential E^0 of redox system, α is the transfer coefficient and $\alpha + \beta = 1$.

In this case, the shape of the peak and the various peak parameters are functions of α and the dimensionless parameter $\alpha n F E^0 / RT$, defined as [54]

(2. 18)

For quasi-reversible process current value is expressed as a function of.

(2. 19)

where is expressed as

(2. 20)

is shown in Fig. 2. 4. It is observed that when $\alpha n F E^0 / RT > 10$, the behavior approaches that of a reversible system.

It is observed that for a quasi-reversible reaction, i_p is not proportional to $\nu^{1/2}$. For half peak potential we have

at 298K (2. 21)

This implies,

These parameters attain limiting values characteristic of reversible or totally irreversible processes as $\nu \Delta E$ varies. For $\nu \Delta E > 10$, $i_p / i_{p,c} = 2.2$ which gives $E_p - E_{p/2} = 56.5 \text{ mV}$ (value characteristic of a reversible wave). For $\nu \Delta E < 10$, $i_p / i_{p,c} = 0.5$, $i_p / i_{p,c} = 3.7$, which yields totally irreversible characteristics. Thus a system may show Nernstian, quasi-reversible, or totally irreversible behaviour depending on $\nu \Delta E$, or experimentally on the scan rate employed. At small $\nu \Delta E$ (or long times), systems may yield reversible waves, while at large (or short times), irreversible behaviour is observed [54].

Variation of i_p with ν and ΔE is shown in Fig. 2.5.

For three types of electrode processes Matsuda and Ayabe [48] suggested following zone boundaries.

a) Reversible (Nernstian)

$$\nu \Delta E > 15; \text{ ksh } \nu \Delta E > 0.3 \sqrt{1/2} \text{ cm s}^{-1}$$

b) Quasi-Reversible

$$15 \leq \nu \Delta E \leq 10^{-2} (1 + \Delta E); \text{ ksh } \nu \Delta E \leq 2 \cdot 10^{-5} \sqrt{1/2} \text{ cm s}^{-1}$$

c) Totally Irreversible

$$\nu \Delta E < 10^{-2} (1 + \Delta E); \text{ ksh } < 2 \cdot 10^{-5} \sqrt{1/2} \text{ cm s}^{-1}$$

Source: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*, John Wiley, New York, 1980, pp 225.

Source: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*, John Wiley, New York, 1980, pp 227.

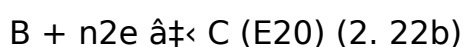
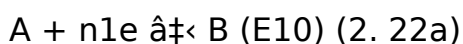
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Multi Electron Transfer Process

Multi-electron transfer process usually takes place in two separate steps.

Two-steps mechanism, each step characterized by its own electrochemical parameters is called "EE mechanism".

Stepwise reversible "EE mechanism" is given by following reaction,



where, A and B are electroactive species and n_1 and n_2 are the number of electrons involved in successive steps. If A and B react at sufficiently separated potentials with A more easily reducible than B, the voltammogram for overall reduction of A to C consists of two separated waves. The first wave corresponds to the reduction of A to B with n_1 electrons and in this potential range the substance B diffuses into the solution. As potential is scanned towards more cathodic values, a second wave appears which is made up of two superimposed parts. The current related to substance A, which is still diffusing toward electrode increases since this species now is reduced directly to substance C by (n_1+n_2) electrons. In addition, substance B, which was the product of the first wave, can be reduced in this potential region and a portion of this material diffuses back towards the electrode and reacts.

Each heterogeneous electron transfer step is associated with its own electrochemical parameters i. e. k_s , h_i and $\hat{I}_{\pm i}$, where $i = 1, 2$ for the 1st and 2nd electron transfer respectively.

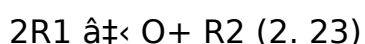
Based on the value of i_p , E_o , we come across three different types of cases [50] as shown in the Fig. 2. 6.

Types of Two Electron Transfer Reactions [50]

Case 1: Separate Peaks

When i_p , E_o , $E_{1/2}$ -150mV the EE mechanism is termed as “ disproportionate mechanism [55]. Cyclic voltammogram consists of two typical one-electron reduction waves. The heterogeneous electron transfer reaction may simultaneously be accompanied by homogenous electron transfer reactions, which in multi-electron system leads to

disproportionation. Each disproportionation reaction can be described as,



The equilibrium constant K (disproportionation constant) is given by

$$(2. 24)$$

It can be derived from the difference between the standard potentials using

$$(2. 25)$$

Case 2: < 100mV ----Peaks Overlapped

In this case, the individual waves merge into one broad distorted wave whose peak height and shape are no longer characteristics of a reversible wave. The wave is broadened similar to an irreversible wave, but can be distinguished from the irreversible voltammogram, in that the distorted wave does not shift on the potential axis as a function of the scan rate.

Case 3: = 0mV Single peak

In this case, in cyclic voltammogram, only a single wave would appear with peak current intermediate between those of a single step one electron and two electron transfer reactions and $E_p - E_p/2 = 21 \text{ mV}$.

Case 4: $E_{1o} < E_{2o}$ ---2nd Reduction is Easy than 1st one

If the energy required for the first second electron transfer is less than that for the first, one wave is observed having peak height equal to $2^{3/2}$ times that of a single electron transfer process. In this case, $E_p - E_{1/2} = 14.25 \text{ mV}$. The effective E_0 for the composite two electron wave is given by [50].

Source: Polcyn, D. S.; Shain, I. J. Anal. Chem. 1966, 38, 370.

Cyclic Voltammetric Methods for the Determination of Heterogeneous Electron Transfer Rate Constant

Cyclic voltammetry provides a systematic approach to solution of diffusion problems and determination of different kinetic parameters including k_s , h . Various methods are reported in literature to determine heterogeneous rate constants. Nicholson [41, 42], Gileadi [56] and Kochi [37] developed different equations to calculate heterogeneous electron transfer rate constants.

Nicholson's Method [41, 42]

Nicholson derived an expression for determination of heterogeneous electron transfer rate constant k_{sh} . This method is based on correlation between k_s , h through a dimensionless parameter by following equation,

(2. 26)

where ν is scan rate.

for different values of \hat{v} E_p can be obtained from the Table 2. 3. Hence, if \hat{v} E_p ($E_{pa}-E_{pc}$) is determined from the voltammogram, can be known from Table 2. 3. From the knowledge of, , k_{sh} can be calculated using equation (2. 27).

If $D_o = D_R$ then $\hat{v} = 1$

(2. 27)

This method is applied for voltammograms having peak separation in the range of 57mV to 250mV, and between this range, the electrode process progresses from reversible to irreversible. With increasing scan rate, the peak separation and hence \hat{v} decreases.

It can be seen from the Table 2. 3, that for reversible reactions i. e. for the current voltage curves and is independent of . For totally irreversible reaction i. e. for the back reaction becomes unimportant, anodic peak and is not observed. For quasi-reaction i. e. for $0.001 \ll \hat{v} < 7$, the form of current curves and depends upon .

Separation of cathodic and anodic peak potential as a function of the kinetic parameter \hat{v}^{-1} in the cyclic voltammogram at room temperature.

Kochi's Method

Kochi and Klinger [37] formulated another correlation between the rate constant for heterogeneous electron transfer and peak separation.

The expression for k_{sh} given by Kochi was

(2. 28)

The standard rate constant k^0 can be calculated from the difference of peak potentials and the sweep rates directly. This equation applies only to sweep rates which are large enough to induce electrode irreversibility. The relation derived by Koshi is based on following expressions derived by Nicholson and Shain [41].

(2. 29a)

(2. 29b)

where $\hat{I}^2 = 1 - \hat{I}^2$, and \dot{I} is the scan rate.

Equations (2. 29a) and (2. 29b) yield

(2. 30)

This expression is used for the determination of the transfer coefficient.

Assuming that (for reversible reaction).

We have,

(2. 31)

Gileadi's Method

Gileadi [56] formulated a more sophisticated method for the determination of heterogeneous electron transfer rate constant, k_s , h , using the idea of critical scan rate, c . This method can be used in the case where anodic peak is not observed.

When reversible heterogeneous electron transfer process is studied at increasing scan rates, peak potential values also vary and process

progresses towards irreversible. If are plotted against the logarithm of scan rates, a straight line at low scan rates and ascending curve at higher scan rate is obtained. Extrapolation of both curves intersects them at a point known as "toe". This "toe" corresponds to the logarithm of critical scan rate, c , as shown in Fig. 2. 7. Hence critical scan rate can be calculated experimentally.

k_s , h can be calculated as,

(2. 32)

where \dot{c} is the critical scan rate, $\hat{\alpha}$ is a dimensionless parameter, called transfer coefficient and D_0 is the diffusion coefficient.

Coupled Chemical Reactions

Although charge transfer processes are an important part of entire spectrum of chemical reactions, they seldom occur as isolated elementary steps.

Electron transfer reactions coupled with new bond formation or bond breaking steps are very frequent. The occurrence of such chemical reactions, which directly affect the available surface concentration of the electroactive species, is common to redox processes of many important organic and inorganic compounds. Changes in the shape of the cyclic voltammogram resulting from the chemical competition for the electrochemical reactant or product, can be extremely useful for elucidating the reaction pathways and for providing reliable chemical information about reactive intermediates [35].

It is convenient to classify the different possible reaction schemes in which homogeneous reactions are associated with the heterogeneous electrons

transfer steps by using letters to signify the nature of the step. E represents an electron transfer at the electrode surface, and C represents a homogenous chemical reaction. While O and R indicate oxidized and reduced forms of the electroactive species, other non electroactive species which result from the coupled chemical complication are indicated by W, Y, Z, etc [57]. The order of C with respect to E then follows the chronological order in which the two events occur [58]. So according to sequence of step, the systems are classified as EC, ECE, CE etc. These reactions are further classified on basis of reversibility. For example, subclasses of EC reactions can be distinguished depending on whether the reactions are reversible (r), quasi-reversible (q), or irreversible (i), for example Er Cr, ErCi, EqCi, etc.

Two Steps Coupled Chemical Reactions

In two steps reactions, a variety of possibilities exist, which include chemical reactions following or preceding a reversible or an irreversible electron transfer [59, 60, 61, 62]. The chemical reactions themselves may be reversible or irreversible.

a) Preceding Chemical Reactions (CE)

In a preceding chemical reaction, the species O is the product resulting from a chemical reaction. Such a reaction influences the amount of O to be reduced so forward peak is perturbed. For a preceding chemical reaction, two mechanisms are possible, depending on whether the electron transfer is reversible CrEr or irreversible CrEi [58].

Reversible Electrode Process Preceded by a Reversible Chemical Reaction

(CrEr Reaction)

The process in which a homogeneous chemical reaction precedes a reversible electron transfer is schematized as follows:

(2. 33)

where Y represents the non electroactive species and O and R are the electroactive congeners.

Since the supply of electroactive species O results from the chemical reaction, it is important to know that how much of O is formed during the time scale of cyclic voltammogram. In this connection, it must be noted that the time scale of voltammetry is measured by the parameter

$a = nF\dot{V}/RT$ for a reversible process

and $b = \hat{I} \pm naF\dot{V}/RT$ for a quasi reversible or an irreversible process

It means that the time scale of cyclic voltammetry is a function of the scan rate, in the sense that higher the scan rate, the higher is the competition of the voltammetric intervention with respect to the rate of chemical complication.

The limit at which the chemical complication can proceed is governed either by the equilibrium constant K or the kinetics of the homogeneous reaction ($I = k_f + k_r$). In this regard, it is convenient to distinguish three limiting cases depending on the rate of chemical complication [41].

Slow preceding chemical reaction ($k_f + k_r \ll nF\dot{V}.../RT$)

When K is large (i. e. $K > 20$) most of O will already be present in solution, the response is apparently not disturbed by the latter, i. e. it appears as a simple reversible electron transfer.

When K is small, the small electron transfer again appears as a simple reversible process except that the peak current will be smaller than is expected on the basis of quantity of Y in the solution. This results because the concentration of the electroactive species CO , being determined by the equilibrium of the preceding reaction is equal to a fraction of species Y placed in the solution.

where $C^* = CO(x, 0) + CY(x, 0)$

Fast preceding chemical reaction ($k_f + k_r \gg nF\dot{V}.../RT$)

When K is large, once again the response appears as a simple reversible electron transfer, but the measured standard potential E_o^* is shifted toward more negative values compared to the standard potential $E_o/$ of the couple O/ R by a factor of .

When K is small, because of the fast continuous maintaining of the small equilibrium amount of O , the complete depletion of O at the electrode surface will never be reached, so that the forward profile no longer maintains the peak shape form, rather assumes a sigmoidal S-shaped curve, the height of which remains constant at all scan rates.

Intermediate preceding chemical reaction ($k_f + k_r = nF\dot{I}.../RT$)

In this case, the kinetics can be studied using the ratio between the kinetic and the diffusive currents according to the relationship

(2. 34)

Irreversible Electrode Process Preceded by a Reversible Chemical Reaction

(CrEi Reaction)

This process is schematizes as.

(2. 35)

In this case, not only the thermodynamic K (k_f / k_r) and kinetic ($k_f + k_r$) parameters of preceding chemical reaction but also the kinetic parameters of the electron transfer (\hat{I}_{\pm}, k_0) play a role. Obviously the lack of reverse peak is immediately apparent, due to the irreversibility of the charge transfer. The curves are also more drawn out because of the electron transfer coefficient, \hat{I}_{\pm} .

Slow preceding chemical reaction ($k_f + k_r \ll nF\dot{I}.../RT$)

In this case, the process appears as a simple irreversible electron transfer. The peak height of the process depends on the equilibrium constant because, as mentioned in the previous case, the concentration of the active species C_0 is a fraction of the amount C^* put in the solution:

Fast preceding chemical reaction ($k_f + k_r \gg nF\dot{I}.../RT$)

If instead the reaction kinetics is fast, there are two possibilities:

If K is large, again the response appears as if the preceding chemical reaction would be absent. However, the peak potential is shifted towards more negative values than those that would be recorded in the absence of the chemical complication by a factor equal to .

If K is small, as in the preceding case, an easily recognizable S-like curve voltammogram is obtained having a limiting current independent from the scan rate

(2. 36)

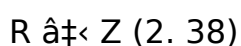
Intermediate preceding chemical reaction ($k_f + k_r = nF\dot{I}.../RT$)

Here again, the kinetics can be studied using the ratio between the kinetic and diffusive currents according to the relationship

(2. 37)

b) Following Chemical Reactions (EC)

The process in which the primary product of an electron transfer becomes involved in a chemical reaction is indicated by EC mechanism. It can be represented by



where O and R are the electroactive congeners and Z represents the non electroactive species.

Several situations are possible depending on the extent of electrochemical reversibility of the electron transfer and on the reversibility or irreversibility of the chemical reaction following the electron transfer.

As a general criterion, in cyclic voltammetry, the presence of a following reaction has little influence on the forward peak, whereas it has a considerable effect on the reverse peak.

Reversible Electrode Process Followed by a Reversible Chemical Reaction

(ErCr Reaction)

ErCr mechanism can be written as

(2. 39)

Once again the voltammetric response will differ to a greater or lesser extent with respect to a simple electron transfer depending on the values of either the equilibrium constant, K , or the kinetics of the chemical complication (k_f+k_r) [58].

Analogously to that discussed for preceding equilibrium reactions, three limiting cases can be distinguished.

Slow following chemical reaction ($k_f+k_r \ll nF\dot{I}\dots/RT$)

If the rate of chemical reaction is low, it has a little effect on the process, thus reducing it a simple reversible electron transfer.

Fast following chemical reaction ($k_f + k_r \gg nF\dot{V}/RT$)

If the rate of the chemical complication is high, the system will always be in equilibrium and the voltammogram will apparently look like a non complicated reversible electron transfer. However, as a consequence of the continual partial removal of the species R from the electrode surface, the reduction occurs at potential values less negative than that of a simple electron transfer by an amount of .

Due to the fast kinetics of the chemical complication, the potential will remain at this value regardless of the scan rate.

Intermediate following chemical reaction ($k_f + k_r = nF\dot{V}/RT$)

If the kinetics of the chemical reaction are intermediate with the scan rate the response gradually shifts from previous value for a fast chemical reaction [which was more anodic by w. r. t. to value of the couple O/R] towards the E_0' value assuming more and more the values predicted by the relationship

(2. 40)

In other words, the response (which for the fast kinetics is more anodic compared to E_0') due to the competitive effects of the potential scan rate moves towards more cathodic values by $30/n$ (mV) for every ten fold increase in the scan rate. However, it is noted that at the same time, the reversible peak tends to disappear, in that on increasing the scan rate, the species Z does not have time to restore R. This is demonstrated by the current ratio which is about one at low scan rates, but it tends to zero at high scan rates.

Reversible Electrode Process Followed by an Irreversible Chemical R