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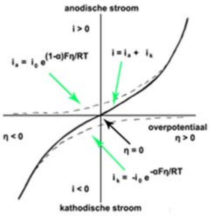
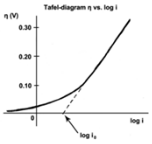
Physical and Interfacial Electrochemistry 2013

Lecture 6.

Phenomenological electrode kinetics:
The Butler-Volmer Equation.





$$i = i_0\left\{\exp\left[\frac{\beta F\eta}{RT}\right] - \exp\left[-\frac{(1-\beta)F\eta}{RT}\right]\right\}$$
$$= i_{ox} - i_{red}$$

Kinetics of interfacial ET.

- Estimation of equilibrium redox potentials provides a quantitative measure for the tendency for a specific redox reaction to occur. Kinetic information is not derived.
- ET reactions at electrode/solution interfaces are activated processes.
  - ET rate effected by:
    - Applied electrode potential
    - Temperature
  - Activation energy barrier height can be effected by applied potential. This is in contrast to ordinary chemical reactions.
- We seek an answer to the following questions:
  - How can we quantitatively model the rate of an ET process which occurs at the interface between a metallic electrode and an aqueous solution containing a redox active couple?
  - How can kinetic information about ET processes be derived?
- We shall also investigate the influence of material transport, and double layer structure on interfacial ET processes.

Basic concepts of electrode kinetics.

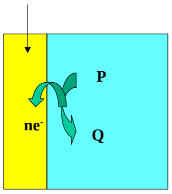
- For an interfacial ET process:
  - current flow is proportional to reaction flux (rate).
- Reaction rate is proportional to reactant concentration at interface.
- As in chemical kinetics:
  - the constant of proportionality between reaction rate f_S (molcm^{-2}s^{-1}) and reactant concentration c (molcm^{-3}) is termed the *rate constant* k (cms^{-1}).
- All chemical and electrochemical reactions are activated processes.
- An activation energy barrier exists which must be overcome in order that the chemical reaction may proceed.
  - Energy must be supplied to surmount the activation energy barrier.
  - This energy may be supplied thermally or also (for ET processes at electrodes) via the application of a potential to the metallic electrode.

The electrode potential drives ET processes at interfaces.

- Application of a potential to an electrode generates a large electric field at the electrode/solution interface which reduces the height of the activation energy barrier and thereby increases the rate of the ET reaction.
- Hence the applied potential acts as a driving force for the ET reaction.
- We intuitively expect that the current should increase with increasing driving force. This can be understood using a simple pictorial approach.

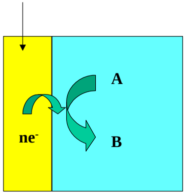
Interfacial electron transfer at electrode/solution interfaces: oxidation and reduction processes.

Electron sink electrode
(Anode).



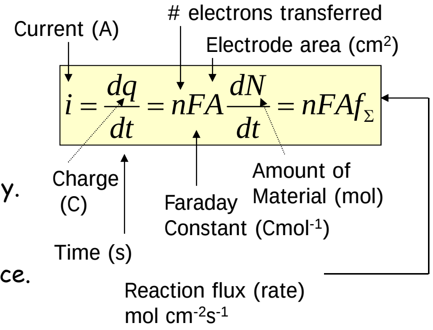
Oxidation or de-electronation.
P = reductant (electron donor)
Q = Product

Electron source electrode
(Cathode).



Reduction or electronation.
A = oxidant (electron acceptor)
B = Product

- The greater the applied voltage, the larger the resulting current flow, and the greater the rate of the chemical reaction.
- The rate at which charge is moved across the M/S interface = the rate at which chemistry is accomplished at the M/S interface.



Current (A)

\# electrons transferred

Electrode area (cm^2)

$$i = \frac{dq}{dt} = nFA\frac{dN}{dt} = nFAf_{\Sigma}$$

Charge (C)

Time (s)

Faraday Constant ($Cmol^{-1}$)

Amount of Material (mol)

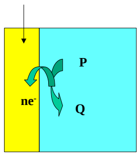
Reaction flux (rate) mol $cm^{-2}s^{-1}$

- In electrolysis we use an applied voltage to perform chemistry at a M/S interface.
- The applied voltage drives the chemical reaction which does not occur spontaneously.
- The current flowing across the M/S interface is a measure of the rate of the chemical transformation at the interface.

Interfacial electron transfer processes are of two types : oxidation or de-electronation , and reduction or electronation. In oxidation, a species present in the electrolyte (termed a reductant or electron donor) may donate an electron to the electrode and in so doing become chemically transformed. The electrode acts as an electron sink and is termed an anode (fig. 1(a)). In reduction, an oxidant present in the electrolyte accepts an electron from the adjacent electrode, and in so doing becomes chemically transformed. In this case the electrode acts as an electron source and is termed a cathode (fig.1(b)) . Hence interfacial electron transfer has a chemical implication. Substances may be transformed and chemistry done at interfaces via application of an external electrical potential.

Fig. 1(a)

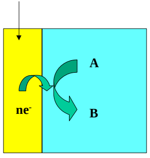
Electron sink electrode
(Anode).



Oxidation or de-electronation.
P = reductant (electron donor)
Q = Product

Fig. 1(b)

Electron source electrode
(Cathode).



Reduction or electronation.
A = oxidant (electron acceptor)
B = Product

We present some typical examples of oxidation and reduction reactions in the table across. We note from table 1 that redox reactions may be of many different types, and can vary from simple single step processes involving the transfer of a single electron, to complex multistep processes involving the transfer of many electrons. A further point should be noted here. Besides the elementary act of electron transfer itself, one must in many cases consider further complicating processes such as the occurence of chemical reactions preceding or following the electron transfer step (CE or EC processes), adsorption processes involving reactants, intermediates or products, and electrochemical nucleation and phase formation reactions. Furthermore the process of reactant transport to the electrode and product transport from the electrode will be important especially when the rate of electron transport is high.

Table 1. Representative oxidation and reduction reactions.

Cathodic reduction process	Anodic oxidation process
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)^{(a)}$	$Ce^{3+}(aq) \rightarrow Ce^{4+}(aq) + e^{-\ (a)}$
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^{-\ (b)}$	$Pt + H_2O \rightarrow PtO + 2H^+ + 2e^{-\ (f)}$
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O^{(c)}$	$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^{-\ (g)}$
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)^{(d)}$	$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-\ (h)}$
$2CH_2 = CHCN + 2H_2O + 2e^-$ $\rightarrow (CH_2CH_2CN)_2 + 2OH^{-\ (e)}$	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^{-\ (i)}$

(a) Simple outer sphere single step single electron transfer reaction. This reaction type serves as a prototype in fundamental kinetic studies.

(b) The cathodic evolution of hydrogen. A much studied multistep, multielectron transfer reaction which involves the formation of intermediate species adsorbed on the electrode surface.

(c) The electrochemical reduction of dioxygen. Much studied in fuel cell technology. Again a complex reaction involving multiple electron transfer and the involvement of adsorbed intermediates.

(d) Metal electrodeposition. An example of an electrochemical phase formation reaction involving nucleation and growth processes.

(e) Conversion of acrylonitrile (AN) to adiponitrile (ADN). An example of electrochemistry applied to organic synthesis.

(f) Metal oxidation. An example of a surface electrochemical redox transformation. Again this involves the generation of transient intermediates.

(g) Chlorine gas evolution. Important in the chlor-alkali industry. This is the anodic analogue to hydrogen evolution. Again adsorbed intermediates are involved in the reaction mechanism.

(h) Metal dissolution reaction. Fundamental basis of low temperature corrosion.

(i) Oxidation of methanol. Much studied in fuel cell research. Typical example of a complex multistep , multielectron transfer process.

In short, one may classify electrode processes into two general classes : simple single step charge transfer processes involving inorganic complex ions , and complex multistep multi-electron transfer reactions which consist of a number of elementary electron transfer and chemical reactions which can occur either in a consecutive or a parallel manner. Parallel electrode reactions are not common and are usually encountered in the anodic oxidation of certain organic compounds such as methanol in acidic or alkaline media. Consecutive processes are much more common. Typical examples of the latter type of processes are the cathodic oxygen reduction reaction, metal dissolution processes and various electro-organic transformations. Now analysis of the kinetics of simple single step reactions (i.e. outer sphere reactions involving inorganic complex ions which do not involve bond breaking) at a phenomenological level is relatively simple and is well understood. In contrast, the kinetics of multistep processes is generally complicated particularly for the case of electro-organic reactions. However some consecutive electrode reactions are particularly suitable for detailed attention since the number of steps involved is not too large. A particular example of the latter is the cathodic hydrogen evolution reaction.

An important point to note from the table presented and from the previous discussion , is that many redox processes which underline important technological applications are *complex*. . Hence their study requires considerable ingenuity and the use of a broad arsenal of electrochemical and in situ spectroscopic techniques which are surface specific. Hence the modern approach to the study of electrode kinetics involves the use of electrochemical and non-electrochemical techniques.

Indeed one may state that the examination of the kinetics and mechanisms of electrochemical reactions is one specific aspect of the broader area of surface science.

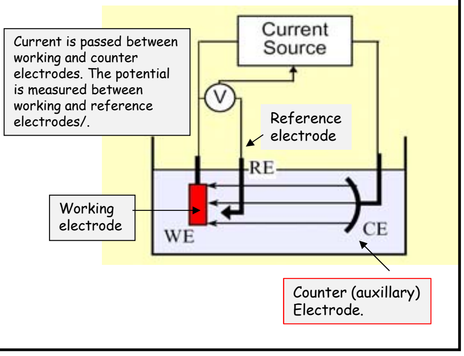
The fundamental act in electrode kinetics, the interfacial electron transfer reaction, can be described in two ways. Firstly, one may adopt a macroscopic phenomenological approach, which results in the formal description of electron transfer kinetics in terms of rate equations and current / potential relationships. It is based largely on the activated complex theory of chemical reactions.

Alternatively, one may consider a microscopic molecular based approach. This pathway leads to the subject of quantum electrode kinetics . Here an attempt is made to examine the molecular basis of interfacial electron transfer, and one seeks to describe the effect of the molecular structure of the reactant molecules and the electronic band structure of the electrode, on the kinetics of the electrode process. Quantum electrode kinetics was discovered early on in the development of electrochemistry, but was neglected for many years and consequently has not undergone the same degree of development as its more traditional macroscopic counterpart. At the present time there is little broad consensus in this topic.

In this section we consider , in a very qualitative way, the kinetic description of a simple single step, single electron transfer process. A typical example might be the $Fe^{2+}(aq)$ / $Fe^{3+}(aq)$ redox reaction at a Pt electrode in an aqueous electrolyte solution . The latter type of reaction is termed an *outer sphere electron transfer process since no bonds are broken or made during the course of* the reaction. Consequently, we neglect complicating factors such as diffusional transport of reactants and products , and adsorption effects.

How are the electron transfer kinetics examined experimentally ? It is obvious that one must do the measurement using an electrochemical cell containing at least two electrodes. Indeed it is conventional to use a three electrode arrangement as outlined across. The electrode of interest is termed the working or indicator electrode. The redox chemistry occurs at the interface between the working electrode and the electrolytic solution. A second electrode , termed the counter or auxiliary electrode, is required to complete the circuit . Current is passed in a circuit containing the working and the counter electrodes. Finally , one wishes to determine the potential difference $\Delta\phi$ across the working electrode / solution interface. The latter cannot be experimentally determined.

What one can do however, is to measure changes in the potential of the working electrode with respect to a third electrode, the reference electrode, placed in the solution near the working electrode. The latter will have a very high impedance to current flow and so the potential of the reference electrode can be considered to be constant, irrespective of the current passed through the working and counter electrodes. Thus, the measured change in potential between the working and reference electrodes will be equal to the change in potential at the working electrode / solution interface. Hence in a typical experiment a potential waveform is applied to the working electrode , chemistry is done, and the resultant current response is monitored using a suitable output device .



Current is passed between working and counter electrodes. The potential is measured between working and reference electrodes/.

Reference electrode

Working electrode

Counter (auxillary) Electrode.

The potential applied to the electrode is controlled using an electronic device called a potentiostat. It is now common practice to perform experiments under microcomputer control and to use the processing capabilities of modern microcomputers to collect, store and process the resultant data. How are the electron transfer kinetics examined experimentally ? It is obvious that one must do the measurement using an electrochemical cell containing at least two electrodes. Indeed it is conventional to use a three electrode arrangement .The electrode of interest is termed the working or indicator electrode. The redox chemistry occurs at the interface between the working electrode and the electrolytic solution. A second electrode , termed the counter or auxiliary electrode, is required to complete the circuit . Current is passed in a circuit containing the working and the counter electrodes. Finally , one wishes to determine the potential difference $\Delta\phi$ across the working electrode / solution interface. The latter cannot be experimentally determined.

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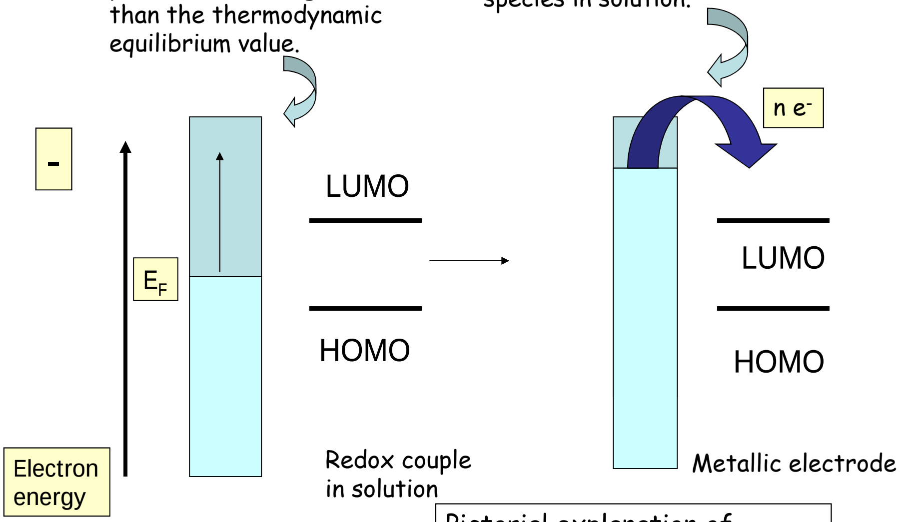
$$\boxed{A(aq)\xrightarrow{\mp e^-}B(aq)}$$

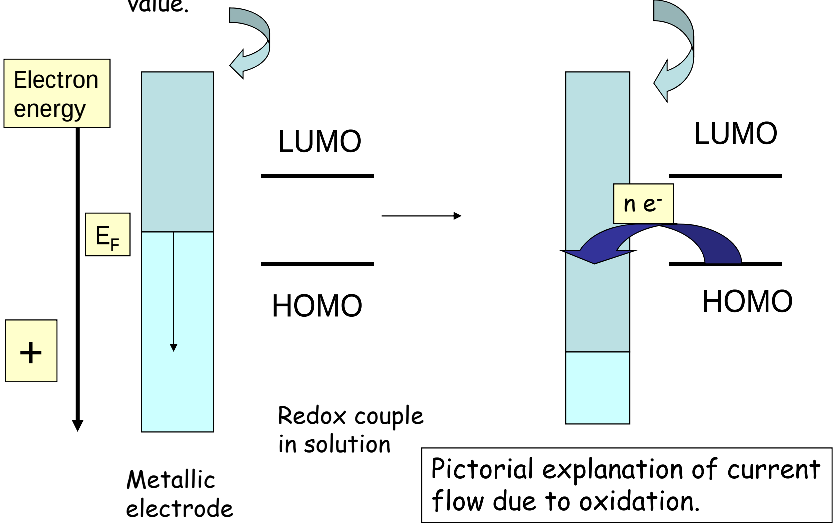
We consider the latter reaction which occurs at the interface between a metal and a solution. Let us assume that both A and B are present in the bulk of the solution with concentrations a^{∞} and b^{∞}. We now consider the effect that charging the electrode (via application of an external potential) has on the rate of electron transfer. Let us firstly approach the situation at a qualitative level before we begin detailed kinetic analysis.

Energy of electrons in metal ***increases*** upon application of a potential more negative than the thermodynamic equilibrium value.

A net reduction (cathodic) current flows from metal to LUMO levels of redox active species in solution.



Pictorial explanation of current flow due to reduction.



Energy of electrons in metal ***decreases*** upon application of a potential more positive than the thermodynamic equilibrium value.

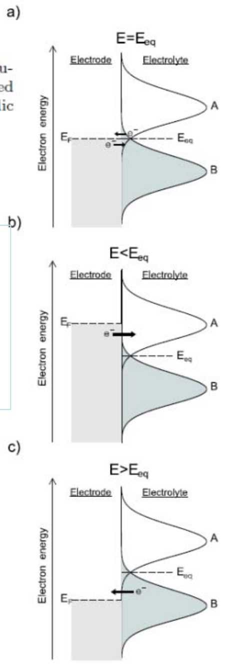
A net anodic (oxidation) current flows from the HOMO level of the redox species in solution to the metallic electrode.

Metallic electrode

Redox couple in solution

Pictorial explanation of current flow due to oxidation.

Fig. 1.1. Electronic states at the interface between a metal electrode and a redox couple A/B in solution at equal concentrations of the electroactive species. The applied potential corresponds to (a) equilibrium, (b) cathodic (electroreduction) and (c) anodic (electrooxidation) conditions.



Metal : energy band picture for electronic energy Levels.
Redox active solute in solution: Fluctuating Gaussian model for electronic energy levels.
Marcus Gerisher Theory allows one to compute ET rate constant at interface.

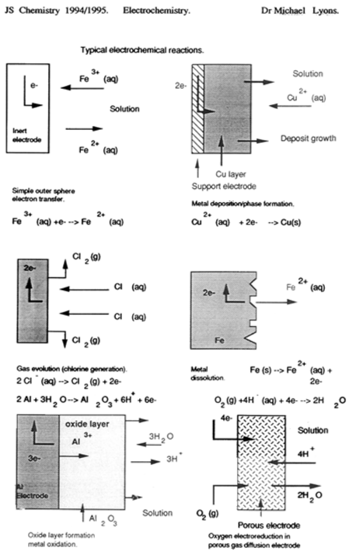
Consider the situation depicted in the previous two slides, obne for a net reduction process and the other or a net oxidation process.

In this picture we indicate, in a very schematic way, the filled and empty electronic states in the metallic electrode and the highest occupied and lowest unoccupied energy levels of the donor species A and acceptor species B in the solution. The demarcation line between filled and empty electronic states in the metal is designated the Fermi energy E_F. Now if species A and B are both present in solution and if no external potential is applied to the working electrode, then after a certain time a steady open circuit potential termed the equilibrium potential E_e may be measured. Indeed the value of this potential will depend on the logarithm of ratio of the concentrations of A and B via the Nernst equation as discussed previously in lecture 4. Under such conditions we may set $E_F = E_e$.

In contrast, when the working electrode becomes positively charged via application of an external potential more positive than E_e then the energy of the electrons in the metal will be lowered and E_F shifts downwards in energy. If the applied potential is sufficiently positive then a stage will be reached such that E_F is lower in energy than the HOMO level of the donor species A and one can obtain a net flow of electrons from the donor to the metal. An anodic oxidation current flows. Conversely, if a potential more negative than the equilibrium value is applied to the electrode then the energy of the electrons in the filled levels of the metal will be raised. A stage will be reached when E_F is now higher in energy than the LUMO level of the acceptor species B and electrons will be transferred from the metal to B in solution. A cathodic reduction current will flow. We shall consider this picture in greater detail in the next chapter when we discuss the microscopic quantum mechanical approach to interfacial electron transfer.

A survey of electrochemical reaction types.

- Electrochemical reactions are usually complex multistep processes involving the
- transfer of more than one electron.
- In this course we focus on simple single step ET processes involving the transfer of a single electron.
- The kinetics of simple ET processes can be understood using the activated complex theory of chemical kinetics (see SF Kinetics notes).



JS Chemistry 1994/1995. Electrochemistry. Dr Michael Lyons.

Typical electrochemical reactions.

Simple outer sphere electron transfer.

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$

Metal deposition/phase formation.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Gas evolution (chlorine generation).

$2\,Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Metal dissolution. $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

$2\,Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$

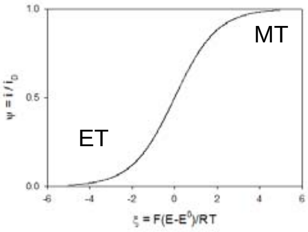
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$

Oxide layer formation metal oxidation.

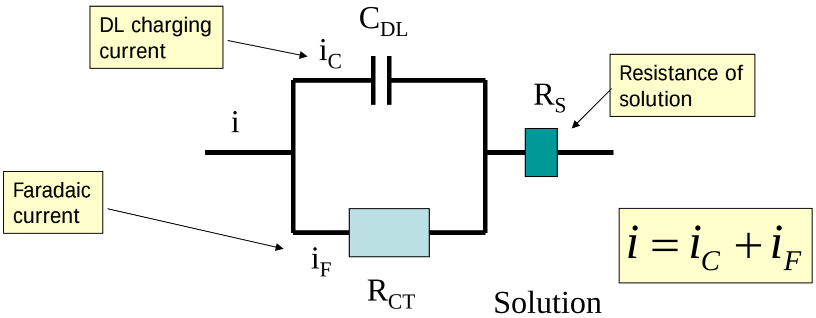
Oxygen electroreduction in porous gas diffusion electrode

Factors effecting the current/potential response at electrode/solution interfaces.

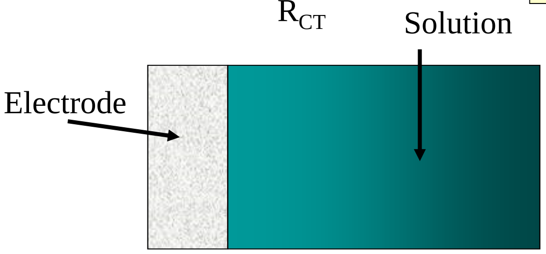
- The current observed at an electrode/solution interface reflects two quantities:
  - Charging of electrical double layer : non Faradaic charging current i_C
  - Interfacial ET across electrode/solution interface : Faradaic current i_F.
- We initially focus attention on the Faradaic component.
- The Faradaic current i_F in turn can have components:
  - at low potentials : arising from rate determining interfacial ET,
  - at high potentials : arising from material transport (MT) due to diffusion mechanisms.
  - These components can be quantified in terms of characteristic rate constants : k^0 (units: cms^{-1}) for ET and k_D (units: cms^{-1}) for MT.
- Our aim is to be able to understand the shape that the general current/potential curve adopts and to be able to interpret the voltammogram in terms of ET and MT effects.



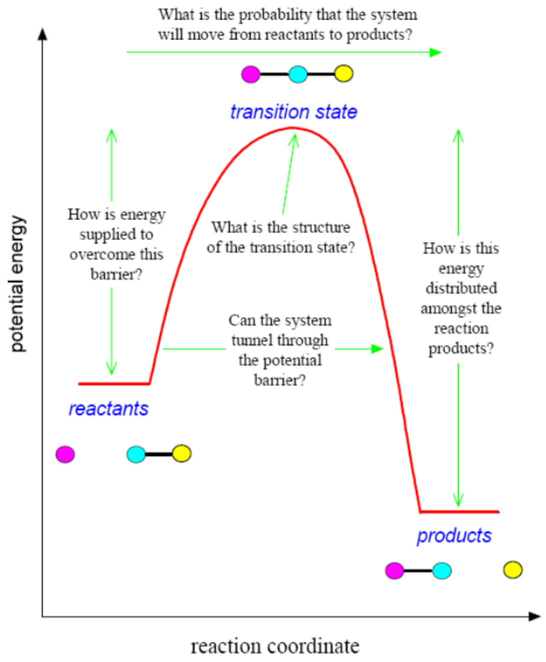
Simple equivalent circuit representation of electrode/solution interface region.



$$i = i_C + i_F$$



Double layer charging current always presen in addition to Faradaic current in electrochemical measurements.



What is the probability that the system will move from reactants to products?

transition state

How is energy supplied to overcome this barrier?

What is the structure of the transition state?

Can the system tunnel through the potential barrier?

How is this energy distributed amongst the reaction products?

reactants

products

potential energy

reaction coordinate

We begin by noting that chemical reactions are thermally activated processes. Consequently in order for chemical to occur, the reactant species must initially come together in a molecular encounter and then gain enough thermal energy to subsequently pass over the activation energy energy barrier . We recall that the activation energy is simply the energy required to bring the reactants to some critical configuration from which they can rearrange to form products. It is clear that during the course of a chemical reaction bonds will be stretched and broken in the reactants and new bonds will be formed. Hence we see that the potential energy of the system will vary during the course of the reaction. Hence a more complete and rigorous description involves the examination of potential energy changes during the course of a chemical reaction. This approach leads to the development of multidimensional potential energy surfaces where the potential energy of the system is plotted as a function of various bond distances and bond angles.

Consider the following simple reaction between an atom A and a diatomic molecule BC in the gas phase :

$$\boxed{A + BC \rightarrow [ABC]^* \rightarrow AB + C}$$

In the latter expression the reactants are transformed to products via formation of a high energy activated complex [ABC]* . If a potential energy surface is to be calculated for this reaction then the potential energy V should be plotted as a function of the two bond distances R_{AB} and R_{BC} and the bond angle $\theta = A\hat{B}C$.

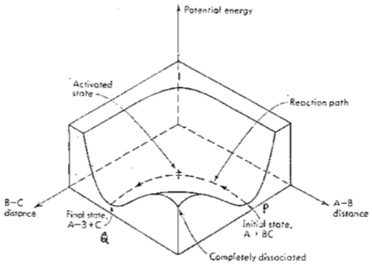
Of course, this procedure would necessitate use of a four dimensional diagram. However to make matters less complicated, one usually fixes one of the parameters, say θ, at a particular value, and then one examines the corresponding three dimensional surface defined by the axes V(R), R_{AB} and R_{BC} . The latter is a particular three dimensional cut from the four dimensional energy hypersurface. A particular three dimensional potential energy surface corresponding to a fixed θ value is presented in the next slide. We note that the course of the reaction is represented by a trajectory on the potential energy surface from P to Q, where P denotes the classical ground state of the diatomic molecule BC and Q represents the ground state of the diatomic molecule AB. Note that the variation of V(R) with bond distance R is described by the Morse potential energy function :

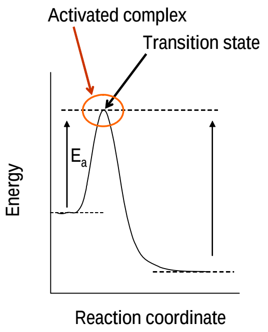
$$\boxed{V(R) = D_o \left\{1 - \exp\left[-a\left(R - R_e\right)\right]\right\}^2}$$

where D_o denotes the bond dissociation energy , R_e is the equilibrium bond separation distance, and a is the anharmonicity constant.

Now the system will tend to describe a trajectory of relatively low energy along the potential energy surface. Typically, this pathway involves two valleys meeting at a saddle point or col (labelled †) located in the interior of the potential energy surface. This pathway is outlined in more detail in the figure. Hence we see that in order for the system to pass from the reactant state to the product state, it will tend to travel along the bottom of the first valley (reactant region), over the col, and down into the second valley (product region). This minimum energy trajectory, termed the *reaction coordinate , q,* is illustrated as a dashed line in the figure presented across. This represents the most probable pathway along the three dimensional energy surface for the P / Q transformation. Finally, a cross section through this minimum energy path, known as a reaction profile is illustrated in the fig. outlined below. We pay particular attention to the point at the top of the V(q) profile. This point corresponds to the saddle point on the potential energy surface, and corresponds not only to a position of maximum energy with respect to the reaction co-ordinate, but also defines a position of minimum energy with respect to trajectories at right angles with respect to the reaction coordinate.

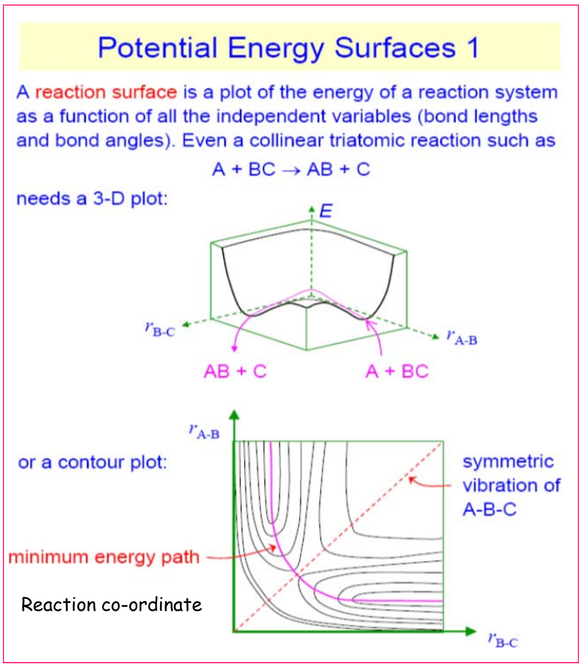
Hence the activated complex or transition state theory focuses attention on the chemical species at the saddle point, i.e., at the point where the reactants are just about to transform into products. At this point one has the activated complex which is that special configuration of atoms of a system in transit between reactants and products.





Henry Eyring
1901-1981

Developed (in 1935) the Transition State Theory (TST)
or
Activated Complex Theory (ACT)
of Chemical Kinetics.



Potential Energy Surfaces 1

A reaction surface is a plot of the energy of a reaction system as a function of all the independent variables (bond lengths and bond angles). Even a collinear triatomic reaction such as

$$A + BC \rightarrow AB + C$$

needs a 3-D plot:

or a contour plot:

Our presentation to date has been couched in qualitative terms. We can of course get more quantitative but this has already been covered adequately earlier on in the module by Prof. Bridge. Now we have stated that chemical activation occurs via collisions between molecules and that reaction involves formation of a discrete activated complex of transient existence. The latter species represents a configuration in which the reactant molecules have been brought to a degree of closeness and distortion, such that a small perturbation due to a molecular vibration in an appropriate direction will transform the complex to products. The overall rate of reaction is then equal to the rate of passage of the activated complex through the transition state. The Activated Complex Theory has been discussed earlier on but we will deal with a special case of a unimolecular reaction at an electrode surface. Since the reaction is heterogeneous we must include a characteristic reaction layer thickness which we label δ (the length of which is of the order of a molecular diameter).
Hence for an interfacial electron transfer reaction we have the following.

$$\boxed{k' = \kappa\delta\frac{k_B T}{h}\exp\left[-\frac{\Delta\bar{G}^{0\ddagger}}{RT}\right]}$$

Where $\Delta\bar{G}^{0\ddagger}$ denotes the electrochemical Gibbs energy of activation. Note that the pre-factor term $k_B T/h$ has got units of s^{-1} and δ is expressed in cm.
Hence k ' has got units of cm s^{-1} as it should.

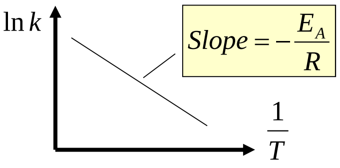
Temperature effects in chemical kinetics.

- Chemical reactions are activated processes : they require an energy input in order to occur.
- Many chemical reactions are activated via thermal means.
- The relationship between rate constant k and temperature T is given by the empirical **Arrhenius equation**.
- The activation energy E_A is determined from experiment, by measuring the rate constant k at a number of different temperatures. The Arrhenius equation is used to construct an Arrhenius plot of ln k versus 1/T. The activation energy is determined from the slope of this plot.

$$\boxed{k = A\exp\left[-\frac{E_A}{RT}\right]}$$

Pre-exponential factor

$$\boxed{E_A = -R\left(\frac{d\ln k}{d(1/T)}\right) = RT^2\left(\frac{d\ln k}{dT}\right)}$$



$$\boxed{Slope = -\frac{E_A}{R}}$$

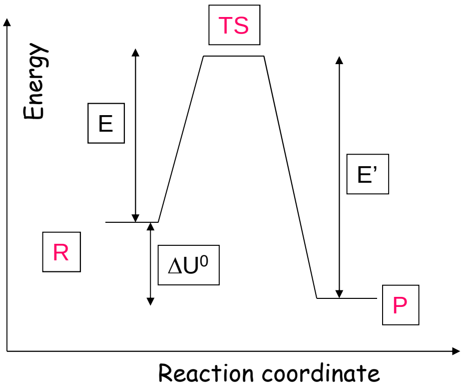
Van't Hoff expression:

$$\boxed{\left(\frac{d\ln K_c}{dT}\right)_P = \frac{\Delta U^0}{RT^2}}$$

Standard change in internal energy:

$$\boxed{\Delta U^0 = E - E'}$$

$$\boxed{\begin{array}{l} R \underset{k'}{\overset{k}{\rightleftarrows}} P \\ K_c = \dfrac{k}{k'} \end{array}}$$



$$\boxed{\left(\frac{d}{dT}\ln\left(\frac{k}{k'}\right)\right)_P = \frac{d\ln k}{dT} - \frac{d\ln k'}{dT} = \frac{\Delta U^0}{RT^2}}$$

$$\boxed{\begin{array}{l} \dfrac{d\ln k}{dT} = \dfrac{E}{RT^2} \\ \dfrac{d\ln k'}{dT} = \dfrac{E'}{RT^2} \end{array}}$$

This leads to formal definition of Activation Energy.

Arrhenius equation: more elaborate situations.

In some circumstances the Arrhenius Plot is curved which implies that the Activation energy is a function of temperature.
Hence the rate constant may be expected to vary with temperature according to the following expression.

$$\boxed{k = aT^m \exp\left[-\frac{E}{RT}\right]}$$

We can relate the latter expression to the Arrhenius parameters A and E_A as follows.

$$\ln k = \ln a + m\ln T - \frac{E}{RT}$$

$$E_A = RT^2\left(\frac{d\ln k}{dT}\right) = RT^2\left\{\frac{m}{T} + \frac{E}{RT^2}\right\} = E + mRT$$

$$E = E_A - mRT$$

Hence

$$k = aT^m e^m \exp\left[-\frac{E_A}{RT}\right] = A\exp\left[-\frac{E_A}{RT}\right]$$

$$A = aT^m e^m$$

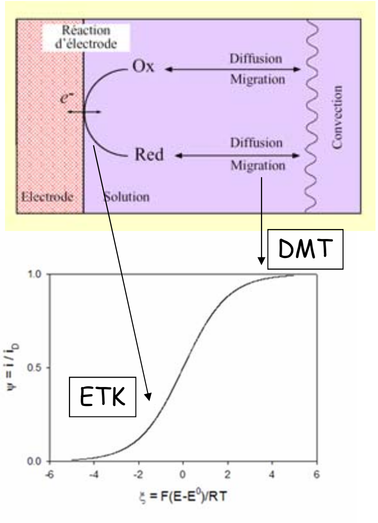
Svante August Arrhenius

Microscopic theories of chemical reaction kinetics.

- A basic aim is to calculate the rate constant for a chemical reaction from first principles using fundamental physics.
- Any microscopic level theory of chemical reaction kinetics must result in the derivation of an expression for the rate constant that is consistent with the empirical Arrhenius equation.
- A microscopic model should furthermore provide a reasonable interpretation of the pre-exponential factor A and the activation energy E_A in the Arrhenius equation.
- We will examine the activated complex theory of chemical reactions and see how this model is applied to electron transfer reactions at interfaces.

Transport and kinetics at electrode/solution interface

- We consider two fundamental processes when considering dynamic events at electrode/solution interfaces:
  - Reactant /product transport to/from electrode surface
  - Electron transfer (ET) kinetics at electrode surface.
- We first consider the kinetics of interfacial ET from a classical, macroscopic and phenomenological (non quantum) viewpoint.
- This approach is based on classical Transition State Theory, and results in the Butler-Volmer Equation.



- In electrochemistry the rate constant k varies with applied potential E because the Gibbs energy of activation ΔG^* varies with applied potential.

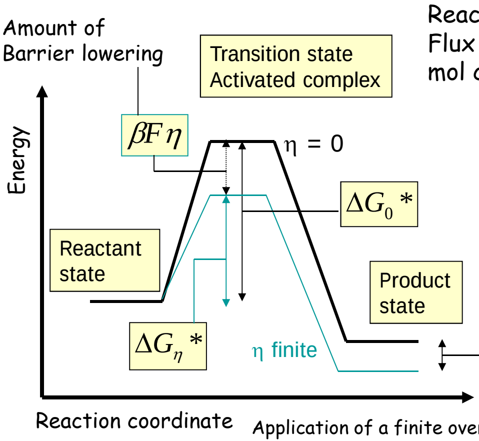
$$i = \frac{dq}{dt} = nFA\frac{dN}{dt} = nFAf_\Sigma$$

$$f_\Sigma = k'_{ET}\, c_0$$

Reaction Flux mol $cm^{-2}\, s^{-1}$

Heterogeneous ET rate constant cm s^{-1}

Interfacial reactant concentration mol cm^{-3}



Application of a finite overpotential η lowers the activation energy barrier by a fixed fraction β .

Total added Electrical energy

$F\eta$

Symmetry factor

$$\Delta G_\eta * = \Delta G_0 * - \beta F\eta$$

overpotential

$$\eta = E - E_N$$

Applied potential

Thermodynamic Nernst potential

We use the result of TST to obtain a value for the ET rate constant.

overpotential

$$f_\Sigma = k'_{ET}\, c_0$$

$$\Delta G_\eta * = \Delta G_0 * - \beta F\eta$$

Apply Eyring eqn. from TST

Electrochemical Gibbs energy of activation

$$k'_{ET} = Z\exp\left[-\frac{\Delta G_\eta *}{RT}\right]$$

Symmetry factor

$$Z = \kappa\left(\frac{k_B T}{h}\right)\sigma$$

Characteristic ET distance (molecular diameter).

Transmission coefficient

$$k'_{ET} = Z\exp\left[-\frac{\Delta G_0 *}{RT}\right]\exp\left[\frac{\beta F\eta}{RT}\right] = k^0_{ET}\exp\left[\frac{\beta F\eta}{RT}\right]$$

The important result is that the rate constant for heterogeneous ET at the interface depends in a marked manner with applied electrode potential. As the potential is increased the larger will be the rate constant for ET.

$$i = nFAf_\Sigma$$

Butler-Volmer Equation.

For the moment we neglect the fact that mass transport may be rate limiting and focus attention on the act of electron transfer at the electrode/ solution interface.
We examine the kinetics of a simple ET process in which bonds are not broken or made, involving the transfer of a single electron in a single step.

$$A(aq) \xrightarrow{-e^-} B(aq)$$
$$B(aq) \xrightarrow{+e^-} A(aq)$$

- Oxidation and Reduction processes are microscopically reversible.
- Net current i at interface reflects a balance between i_{ox} and i_{red} .
- Symmetry factor β determines how much of the input electrical energy fed into the system will affect the activation energy barrier for the redox process. Note 0< β < 1 and typically β = 0.5.

Net rate

$$i = i_{ox} - i_{red}$$

Symmetry factor

Normalised potential

$$i = i_0 \{\exp[\beta\theta] - \exp[-(1-\beta)\theta]\}$$

BV equation

Exchange current

Oxidation component

Reduction component

- Exchange current provides a measure of kinetic facility of ET process.

overpotential

Thermodynamic Nernst potential

$$\theta = \frac{F\eta}{RT} = \frac{F(E - E_N)}{RT}$$

Applied potential

Exchange current →

$$i_0 = FAk^0 a^{\infty 1-\beta} b^{\infty \beta}$$

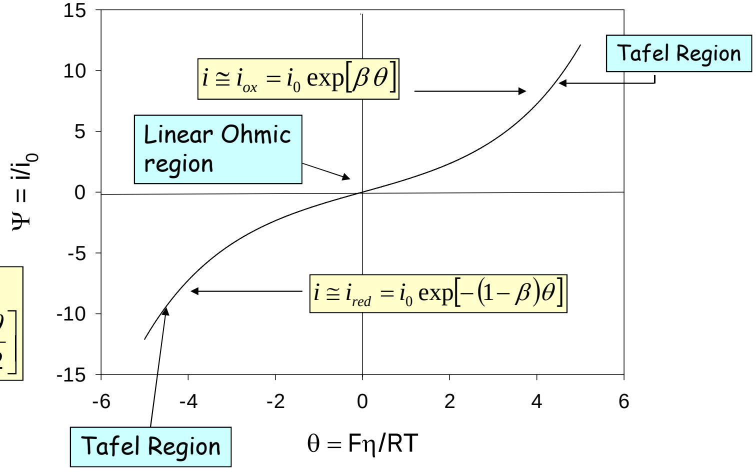
Standard rate constant

Delineating the regions of the simple Butler-Volmer Equation.

$$i = i_0 \{\exp[\beta\theta] - \exp[-(1-\beta)\theta]\}$$

oxidation

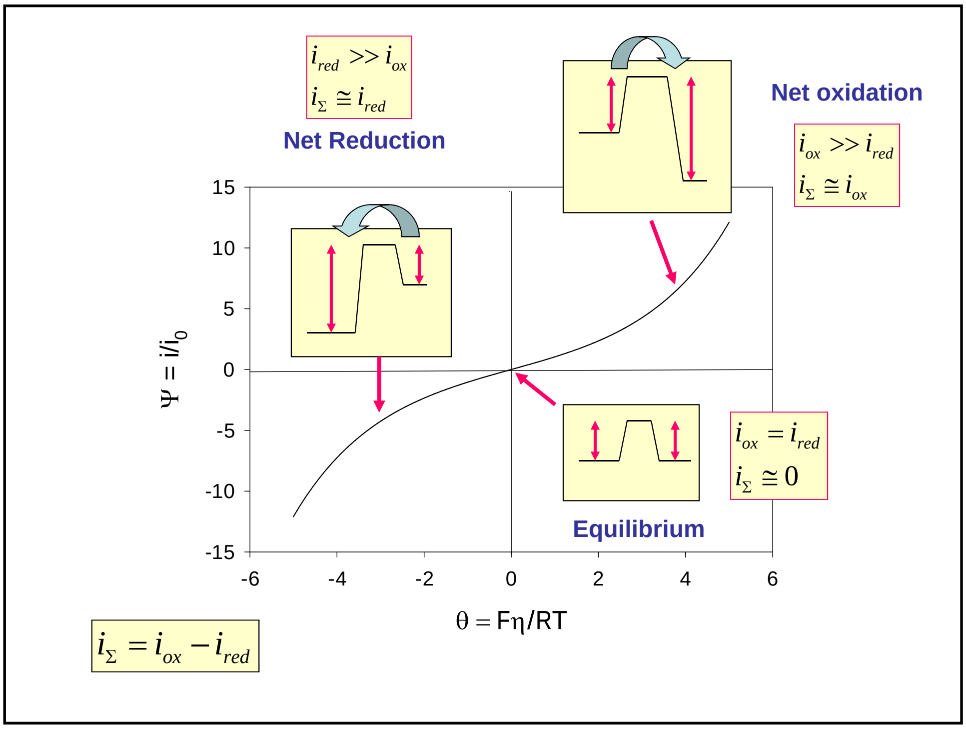
reduction



$$i \cong i_{ox} = i_0 \exp[\beta\theta]$$

$$i \cong i_{red} = i_0 \exp[-(1-\beta)\theta]$$

$$\beta = 1/2$$
$$i = 2i_0 \sinh\left[\frac{\theta}{2}\right]$$



$i_{red} >> i_{ox}$

$i_{\Sigma} \cong i_{red}$

Net Reduction

Net oxidation

$i_{ox} >> i_{red}$

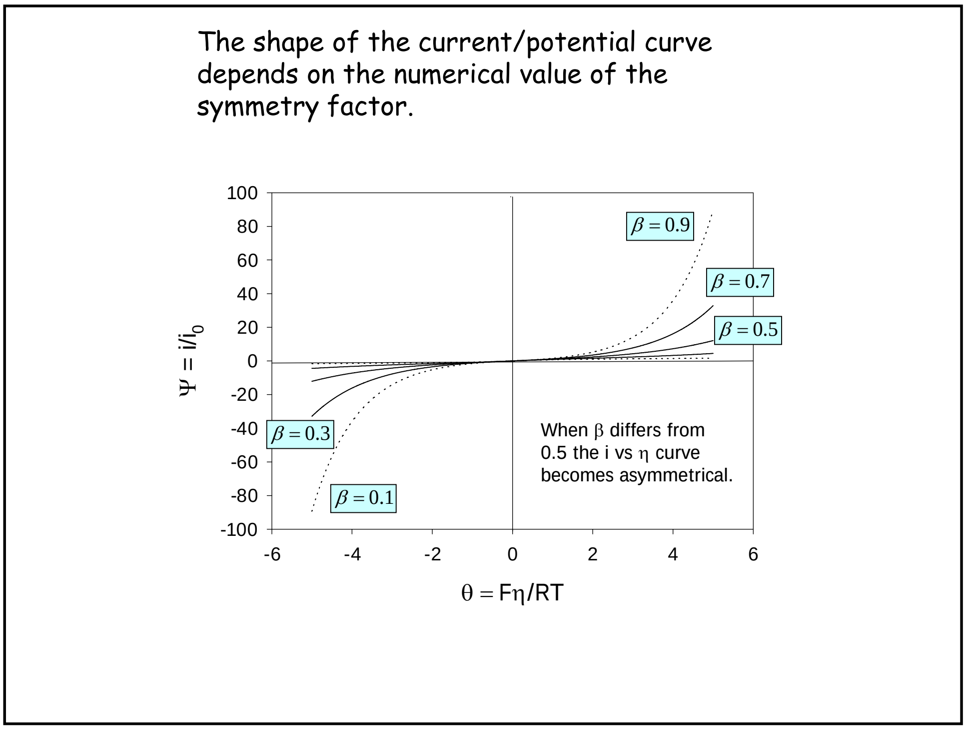
$i_{\Sigma} \cong i_{ox}$

$i_{ox} = i_{red}$

$i_{\Sigma} \cong 0$

Equilibrium

$i_{\Sigma} = i_{ox} - i_{red}$



The shape of the current/potential curve depends on the numerical value of the symmetry factor.

When β differs from 0.5 the i vs η curve becomes asymmetrical.

Approximations to the BV equation (I). High overpotential Tafel Limit.

The BV equation reduces to the Tafel equation when the overpotential η is large, typically η > 120 mV. At high overpotentials we assume that the ET reaction occurs in the forward direction and the reaction occurring in the reverse direction can be neglected. This results in the derivation of a logarithmic relationship between current and overpotential. A plot of ln i vs η is linear. This is called a Tafel plot. Evaluation of the slope of the linear Tafel region enables the symmetry Factor β to be evaluated, whereas the exchange Current i_0 is obtained from the intercept at η = 0.

$$i = i_0\left\{\exp\left[\frac{\beta F\eta}{RT}\right] - \exp\left[-\frac{(1-\beta)F\eta}{RT}\right]\right\}$$
$$= i_{ox} - i_{red}$$

If $\eta >> 0$ then $i \approx i_{ox}$: net de-electronation or oxidation.

$$i \cong i_{ox} = i_0 \exp\left[\frac{\beta F\eta}{RT}\right]$$

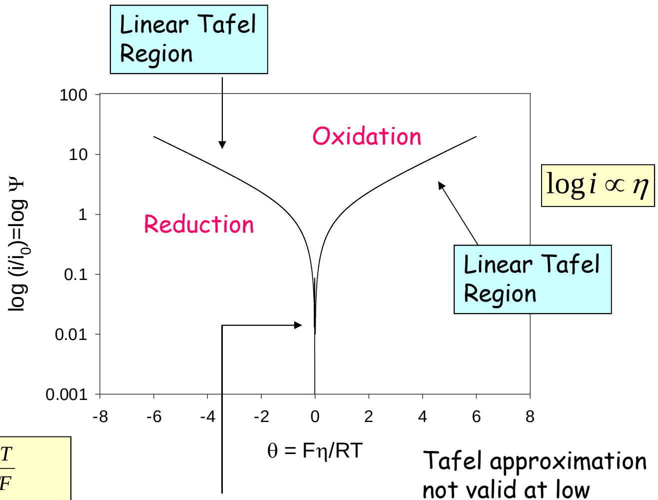
$$\ln i = \ln i_0 + \frac{\beta F\eta}{RT}$$

If $\eta << 0$ then $i \approx i_{red}$: net electronation or reduction.

$$i \cong i_{red} = i_0 \exp\left[-\frac{(1-\beta)F\eta}{RT}\right]$$

$$\ln i = \ln i_0 - \frac{(1-\beta)F\eta}{RT}$$

Tafel Plot Analysis



$$\log i \propto \eta$$

Tafel approximation not valid at low overpotential

Exchange Current evaluated At η = 0

$$b_A = \left(\frac{d\eta}{d\log i}\right) = 2.303\frac{RT}{\beta F}$$

$$b_C = \left(\frac{d\eta}{d\log i}\right) = -2.303\frac{RT}{(1-\beta)F}$$

Approximations to the BV equation (II). The low overpotential linear limit.

We note that the logarithmic Tafel behaviour breaks down as η → 0.

Tafel behaviour is characteristic of totally irreversible (hard driven) ET kinetics and will only be valid if the driving force for the electrode process is very large which will be the case at high overpotentials.

In the limit of low overpotentials (η < 10 mV) the exponential terms in the BV equation may be simplified via use of a Taylor expansion to produce a linear relationship between current and overpotential (Ohm's Law).

$$
\begin{aligned}
i &= i_0\left\{\exp\left[\frac{\beta F\eta}{RT}\right]-\exp\left[-\frac{(1-\beta)F\eta}{RT}\right]\right\}\\
&= i_{ox}-i_{red}
\end{aligned}
$$

Taylor expansion at small x.

$$
\begin{aligned}
\exp[x] &\cong 1+x+\frac{x^2}{2!}+\cdots\\
\exp[-x] &\cong 1-x+\frac{x^2}{2!}-\cdots
\end{aligned}
$$

$$
\begin{aligned}
\exp\left[\frac{\beta F\eta}{RT}\right] &\cong 1+\frac{\beta F\eta}{RT}\\
\exp\left[-\frac{(1-\beta)F\eta}{RT}\right] &\cong 1-\frac{(1-\beta)F\eta}{RT}=1-\frac{F\eta}{RT}+\frac{\beta F\eta}{RT}
\end{aligned}
$$

$$
i \cong i_0\left\{1+\frac{\beta F\eta}{RT}-1-\frac{\beta F\eta}{RT}+\frac{F\eta}{RT}\right\}
$$

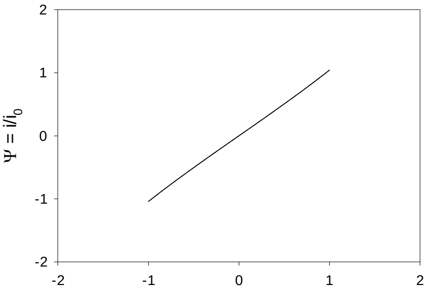
Linear approximation →

$$
i \cong i_0\left\{\frac{F\eta}{RT}\right\}
$$

Charge Transfer Resistance

- We introduce the concept of a **charge transfer resistance** R_{CT} as being a measure of the resistance to ET across the metal/solution interface.
- Since R_{CT} and i_0 are inversely proportional to each other, then a large value of R_{CT} implies a small value of i_0 and vice versa.
- Large R_{CT} implies sluggish ET kinetics, and small R_{CT} implies facile ET kinetics.
- Useful idea : physical act of ET modelled in terms of a resistor of magnitude R_{CT}.
- Hence ET process described using an **electrical equivalent circuit element**.

Linear i versus η relation

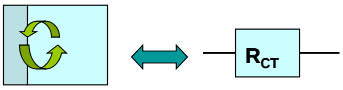


$$
i=\frac{i_0F}{RT}\eta
$$

$$
R_{CT}=\left(\frac{d\eta}{di}\right)_{i\to 0}=\frac{RT}{i_0F}
$$

$$
\eta = iR_{CT}
$$

Ohms Law



Interfacial ET

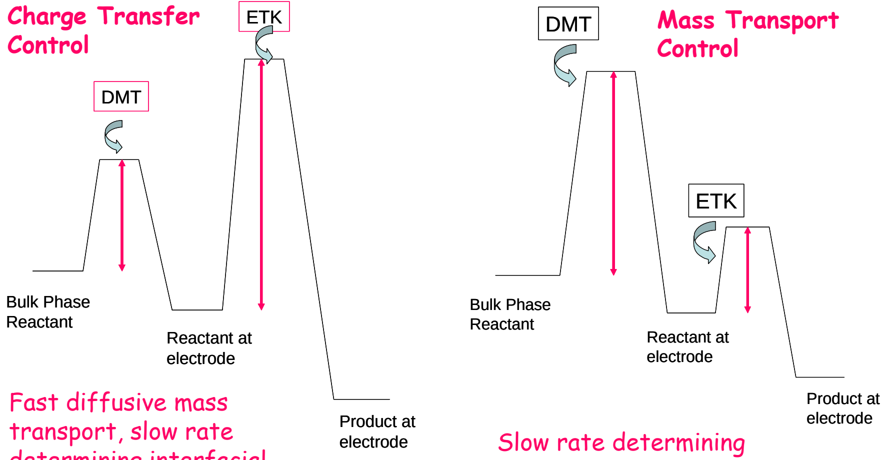
Transport effects in electrode kinetics

- Influence of reactant transport (logistics) becomes important when the applied overpotential becomes very large.
- The current/potential curve "bends over" and a current plateau region is observed.
- This observation is explained in terms of rate control via diffusion of the reactant species to the electrode surface.
- We consider a two step sequence : diffusion to the site of ET at the electrode/solution interface followed by the act of ET itself.
- When the overpotential is very large, the driving force for interfacial ET is very large, and so ET becomes facile and hence no longer controls the rate.
- Matter transport via diffusion (i.e. getting the reactant species to the region of reaction) becomes rate limiting.

Transport and kinetics at electrode/solution interfaces

Low overpotential situation:
Charge Transfer Control

Large overpotential situation :
Mass Transport Control



Fast diffusive mass transport, slow rate determining interfacial ET kinetics

Slow rate determining Diffusive mass transport, Fast interfacial ET kinetics

Transport and kinetics at electrodes.

Diffusion layer approximation used.

Current density

$$f_\Sigma = \frac{i}{nFA} = \frac{J}{nF}$$

Net flux

$$k_D = \frac{D}{\delta}$$

$$f_\Sigma = D\left(\frac{dc}{dx}\right)_0 = k_{ET}c_0 = \frac{D}{\delta}\left\{c^\infty - c_0\right\} = k_D\left\{c^\infty - c_0\right\}$$

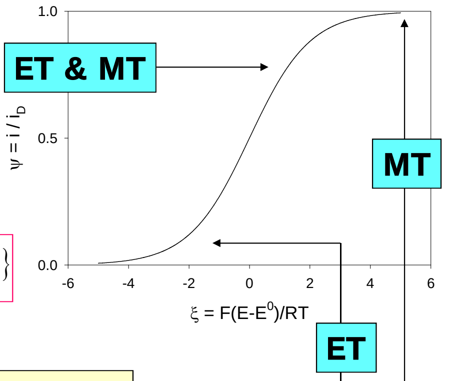
$$c_0 = \frac{c^\infty}{1+\frac{k_{ET}\delta}{D}}$$

$$f_\Sigma = k_{ET}c_0$$

$$k_{ET} = k^0\exp\left[\pm\beta\xi\right]$$

Normalised potential

$$f_\Sigma = \frac{k_{ET}k_Dc^\infty}{k_D+k_{ET}}$$



$$\frac{1}{f_\Sigma} = \frac{1}{k_{ET}c^\infty} + \frac{1}{k_Dc^\infty}$$

Mass transport corrected Tafel Equation

$$f_D = \frac{i_D}{nFA} = k_Dc^\infty$$

$$\frac{i}{nFA} = f_\Sigma = \frac{k_{ET}k_Dc^\infty}{k_{ET}+k_D} = \frac{k_Dc^\infty}{1+\frac{k_D}{k_{ET}}} = \frac{f_D}{1+\frac{k_D}{k_{ET}}}$$

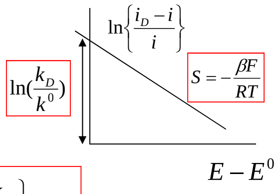
$$\frac{f_D}{f_\Sigma} - 1 = \frac{k_D}{k_{ET}}$$

$$k_{ET} = k^0\exp\left[\frac{\beta F\left(E-E^0\right)}{RT}\right]$$

$$\frac{i_D}{i} - 1 = \frac{f_D}{f_\Sigma} - 1 = \frac{f_D - f_\Sigma}{f_\Sigma} = \frac{k_D}{k^0}\exp\left[-\frac{\beta F\left(E-E^0\right)}{RT}\right]$$

$$\ln\left\{\frac{f_D - f_\Sigma}{f_\Sigma}\right\} = \ln\left\{\frac{i_D - i}{i}\right\} = \ln\left\{\frac{k_D}{k^0}\right\} - \frac{\beta F\left(E-E^0\right)}{RT} = \ln\left\{\frac{k_D}{k^0}\right\} - \beta\xi$$

MT corrected Tafel plot



This is one form of the mass transport corrected Tafel equation. We see that a plot of ln (i_D-i/i) vs $E - E^0$ is linear . The slope of this plot yields - βF/RT whereas the intercept directly yields ln (k_D/k^0). Since k_D may be readily evaluated, then the standard rate constant k^0 may be determined. This form of Tafel plot has been much used in the literature.

Other useful data analysis strategies.

The Tafel analysis may be applied with good accuracy to obtain i_0 and β when the exchange current density for the electrode process is low (typically when $i_0 < 10^{-3}$ A cm^{-2}). In contrast , the low overpotential linear approximation is useful when the exchange current density is large ($i_0 > 10^{-3}$ A cm^{-2}).

$$A \mp ne^- \rightarrow B$$

$$i_0 = FAk^0 a^{\infty 1-\beta} b^{\infty\beta}$$

$$\ln i_0 = \ln\left(FAk^0\right) + (1-\beta)\ln a^\infty + \beta \ln b^\infty$$

$$\left(\frac{\partial \ln i_0}{\partial \ln a^\infty}\right)_{b^\infty} = 1-\beta \qquad \left(\frac{\partial \ln i_0}{\partial \ln b^\infty}\right)_{a^\infty} = \beta$$

Hence we see that a plot of ln i_0 versus either ln a^∞ or ln b^∞ should be linear with slope producing a value for the symmetry factor β.

We note that the Butler-Volmer equation may be used to determine i_0 and β regardless of the magnitude of the overpotential η using the following procedure.

$$\begin{aligned} i &= i_0\left\{\exp\left[\frac{\beta F\eta}{RT}\right] - \exp\left[-\frac{F\eta}{RT}\right]\exp\left[\frac{\beta F\eta}{RT}\right]\right\} \\ &= i_0 \exp\left[\frac{\beta F\eta}{RT}\right]\left\{1-\exp\left[-\frac{F\eta}{RT}\right]\right\} \end{aligned}$$

$$\ln\left\{\frac{i}{1-\exp\left[-\frac{F\eta}{RT}\right]}\right\} = \ln i_0 + \frac{\beta F\eta}{RT}$$

Allen-Hickling Equation

Hence we see that a plot of $\ln\{i/1-\exp[-F\eta/RT]\}\ versus\ \eta$

should be linear, the slope yielding β and the intercept at $\eta = 0$ yielding i_0 .

Multistep electron transfer Reactions

Molecular Hydrogen Evolution (HER)

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$
$$2H^+(aq) + 2e^- \rightarrow H_2(g) + 2H_2O$$

Electrochemical water oxidation
Forming molecular oxygen (OER)

$$4OH^-(aq) \rightarrow O_2(g) + 2H_2O + 4e^-$$
$$2H_2O \rightarrow 4H^+(aq) + O_2(g) + 4e^-$$

Electrochemical oxygen reduction
To form water(ORR)

$$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-(aq)$$
$$4H^+(aq) + O_2(g) + 4e^- \rightarrow 2H_2O$$

Organic electro-oxidation reactions (methanol, ethanol & methane oxidation).

$$CH_3OH(aq) + H_2O \rightarrow CO_2 + 6H^+(aq) + 6e^-$$
$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+(aq) + 12e^-$$
$$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+(aq) + 8e^-$$

Electrons transferred one at a time.
Simultaneous multi-electron transfer
Not very probable.
Generation of many intermediates.
Reaction mechanism complex and depends on experimental conditions (solution pH, electrode potential, and electrode composition.
Many multistep reactions of relevance in energy conversion/ storage devices, e.g. fuel cells, electrolysis cells.

Hydrogen evolution reaction (HER)

Simplest multistep multi-electron transfer process.
Most studied.
3 basic steps labeled : Volmer (V) ; Heyrovsky (H); Tafel (T).

$$\text{Volmer (V)}: \quad S + H^+(aq) + e^- \underset{k'_{-V}}{\overset{k'_V}{\rightleftharpoons}} S - H$$

Acid Solution

$$\text{Heyrovsky (H)}: \quad S - H + H^+(aq) + e^- \underset{k'_{-H}}{\overset{k'_H}{\rightleftharpoons}} S + H_2(g)$$

$$\textit{Tafel}\,(T): \quad S - H + S - H \underset{k_{-T}}{\overset{k_T}{\rightleftharpoons}} 2S + H_2(g)$$

Alkaline Solution

$$\text{Volmer (V)}: \quad S + H_2O + e^- \underset{k'_{-V}}{\overset{k'_V}{\rightleftharpoons}} S - H + OH^-$$

$$\text{Heyrovsky (H)}: \quad S - H + H_2O + e^- \underset{k'_{-H}}{\overset{k'_H}{\rightleftharpoons}} S + H_2(g) + OH^-$$

$$\textit{Tafel}\,(T): \quad S - H + S - H \underset{k_{-T}}{\overset{k_T}{\rightleftharpoons}} 2S + H_2(g)$$

Major Mechanisms: VH, VT. Both add to produce desired $2e^-$ reaction.

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$
$$2H^+(aq) + 2e^- \rightarrow H_2(g) + 2H_2O$$

General multistep ET Process

$$A \leftrightarrow B + e^- \; step1$$

. . . . .

$$P \leftrightarrow R + e^- \; step\,\vec{n}$$

$$v(R \rightarrow S + n_r e^-) \; RDS \; repeated \; v \; times$$

$$vS \leftrightarrow T + e^- \; step \; n - \vec{n} - n_r v \equiv \overleftarrow{n}$$

. . . . .

$$Y \leftrightarrow Z + e^- \; step \; n$$

ν = stoichiometric factor
= number of times slow rds
occurs per single act of
net reaction.

$$i = i_0\{exp[\left(\frac{\vec{n}}{v} + n_r\beta\right)\frac{F\eta}{RT}] - \{exp[-\left(\frac{\vec{n}}{v} + n_r\beta\right)\frac{F\eta}{RT}]\}$$

$$\vec{\alpha} = \frac{\vec{n}}{v} + n_r\beta \qquad \overleftarrow{\alpha} = \frac{\overleftarrow{n}}{v} + (1-\beta)n_r$$

$$i = i_0\{exp[\frac{\vec{\alpha}F\eta}{RT}]\} - \{exp[-\frac{\overleftarrow{\alpha}F\eta}{RT}]\}$$

β = symmetry factor (usually ½)

Tafel Approximation

$$i = i_0\{exp[\frac{\vec{\alpha}F\eta}{RT}]\}$$

$$\ln i \cong \ln i_0 + \frac{\vec{\alpha} F}{RT}\eta$$

Tafel Slope got via Linear Tafel Plot.

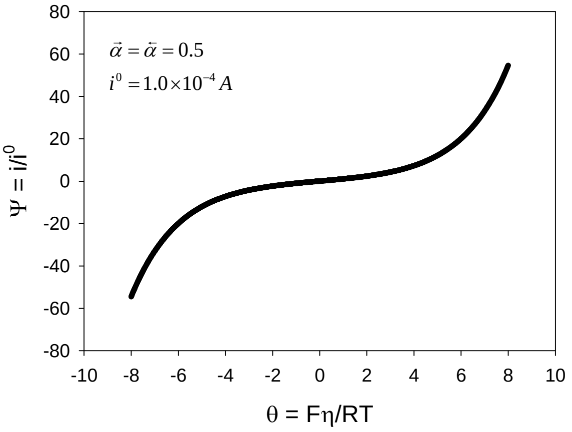
$$b = \frac{d\eta}{d\log i} = 2.303\left(\frac{RT}{\vec{\alpha} F}\right)$$

Tafel Slope b is useful
Mechanistic indicator
Via transfer coefficient term.

$\vec{n}$ = number of electrons transferred before slow rds.

n_r = number of electrons transferred during rds, either 1 or 0 (chemical step).

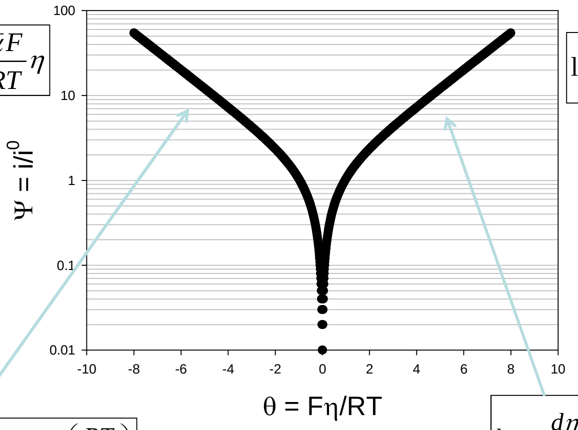
$$i = i_0\{exp[\frac{\vec{\alpha}F\eta}{RT}]\} - \{exp[-\frac{\overleftarrow{\alpha}F\eta}{RT}]\}$$



Tafel Plot General BV Equation

$\vec{\alpha} = \overleftarrow{\alpha} = 0.5$

$i^0 = 1.0\times10^{-4}A$



$$\ln i \cong \ln i_0 - \frac{\overleftarrow{\alpha}F}{RT}\eta$$

$$\ln i \cong \ln i_0 + \frac{\vec{\alpha}F}{RT}\eta$$

$$b = \frac{d\eta}{d\log i} = -2.303\left(\frac{RT}{\overleftarrow{\alpha}F}\right)$$

$$b = \frac{d\eta}{d\log i} = 2.303\left(\frac{RT}{\vec{\alpha}F}\right)$$