



Lecture 18

Electrolysis: Electrosynthesis and Electroplating.

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Electrolysis.

- Redox reactions in which the change in Gibbs energy ΔG is positive do not occur spontaneously.
- However they can be driven via application of either a known voltage or a known current.
- Electrolysis is the process of driving a reaction in a non spontaneous direction by using an electric current.
- Hence an electrolytic or driven cell is an electrochemical device in which an electric current from an external source is used to drive a non spontaneous chemical reaction.
- Electrolysis provides the basis of electrosynthesis and industrial electrochemistry.

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Michael Faraday

1791-1867



Originated the terms anode, cathode, anion, cation, electrode.

Discoverer of

- electrolysis
- magnetic props. of matter
- electromagnetic induction
- benzene and other organic chemicals

Was a popular lecturer.

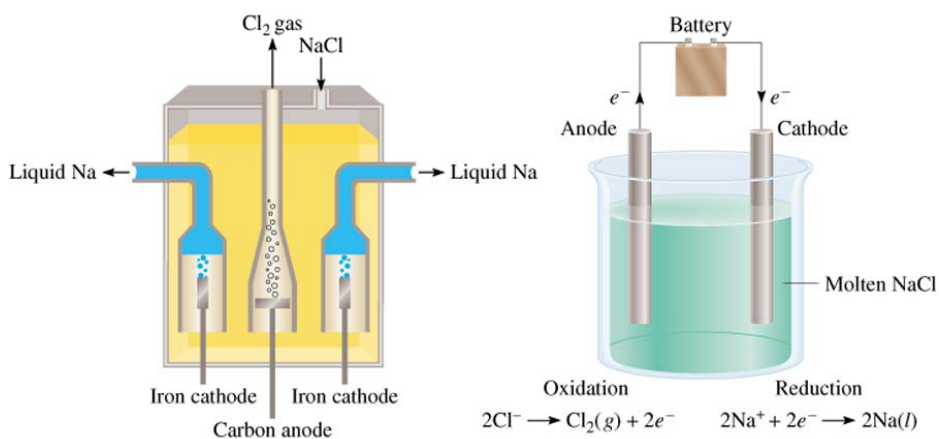
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Table 21.4 Comparison of Voltaic and Electrolytic Cells

Cell Type	ΔG	E_{cell}	Electrode		
			Name	Process	Sign
Voltaic	< 0	> 0	Anode	Oxidation	-
Voltaic	< 0	> 0	Cathode	Reduction	+
Electrolytic	> 0	< 0	Anode	Oxidation	+
Electrolytic	> 0	< 0	Cathode	Reduction	-

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Electrolysis is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.



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Sample Problem 21.8: Predicting the Electrolysis Products of a Molten Salt Mixture

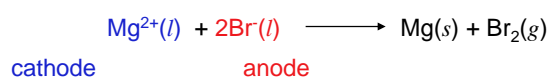
PROBLEM: A chemical engineer melts a naturally occurring mixture of NaBr and MgCl₂ and decomposes it in an electrolytic cell. Predict the substance formed at each electrode, and write balanced half-reactions and the overall cell reaction.

PLAN: Consider the metal and nonmetal components of each compound and then determine which will recover electrons (be reduced; strength as an oxidizing agent) better. This is the converse to which of the elements will lose electrons more easily (lower ionization energy).

SOLUTION: Possible oxidizing agents: Na⁺, Mg²⁺
Possible reducing agents: Br⁻, Cl⁻

Na, the element, is to the left of Mg in the periodic table, therefore the IE of Mg is higher than that of Na. So Mg²⁺ will more easily gain electrons and is the stronger oxidizing agent.

Br, as an element, has a lower IE than does Cl, and therefore will give up electrons as Br more easily than will Cl⁻.



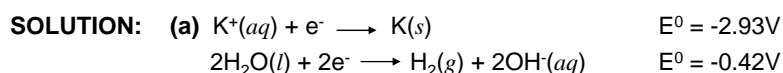
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Sample Problem 21.9: Predicting the Electrolysis Products of Aqueous Ionic Solutions

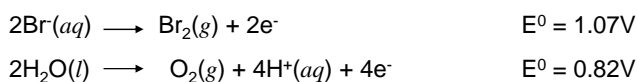
PROBLEM: What products form during electrolysis of aqueous solution of the following salts: **(a)** KBr; **(b)** AgNO₃; **(c)** MgSO₄?

PLAN: Compare the potentials of the reacting ions with those of water, remembering to consider the 0.4 to 0.6V overvoltage.

The reduction half-reaction with the less negative potential, and the oxidation half-reaction with the less positive potential will occur at their respective electrodes.



The overvoltage would make the water reduction -0.82 to -1.02 but the reduction of K⁺ is still a higher potential so H₂(g) is produced at the cathode.

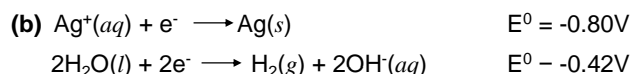


The overvoltage would give the water half-cell more potential than the Br⁻, so the Br⁻ will be oxidized. Br₂(g) forms at the anode.

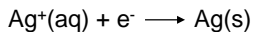
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Sample Problem 21.9: Predicting the Electrolysis Products of Aqueous Ionic Solutions

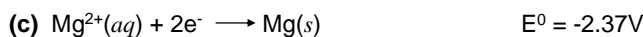
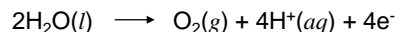
continued



Ag⁺ is the cation of an inactive metal and therefore will be reduced to Ag at the cathode.



The N in NO₃⁻ is already in its most oxidized form so water will have to be oxidized to produce O₂ at the anode.



Mg is an active metal and its cation cannot be reduced in the presence of water. So as in (a) water is reduced and H₂(g) is produced at the cathode.

The S in SO₄²⁻ is in its highest oxidation state; therefore water must be oxidized and O₂(g) will be produced at the anode.

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Faraday's laws of electrolysis.

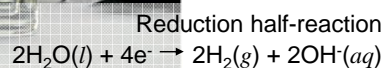
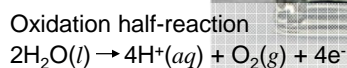
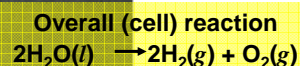
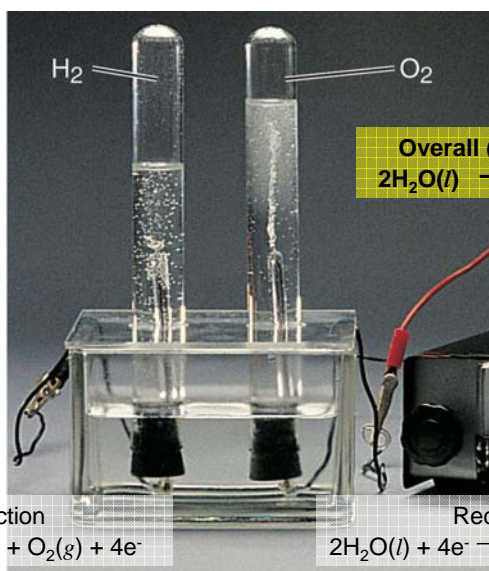
- The quantity (moles) of product formed by the passage of an electric current is stoichiometrically equivalent to the amount (moles) of electrons supplied.
- The amount of product formed during an electrolysis process is calculated from the stoichiometry of the reaction, the magnitude of the current flowing, and the time during which the current flows.



Michael Faraday : 1791-1867¹⁰³

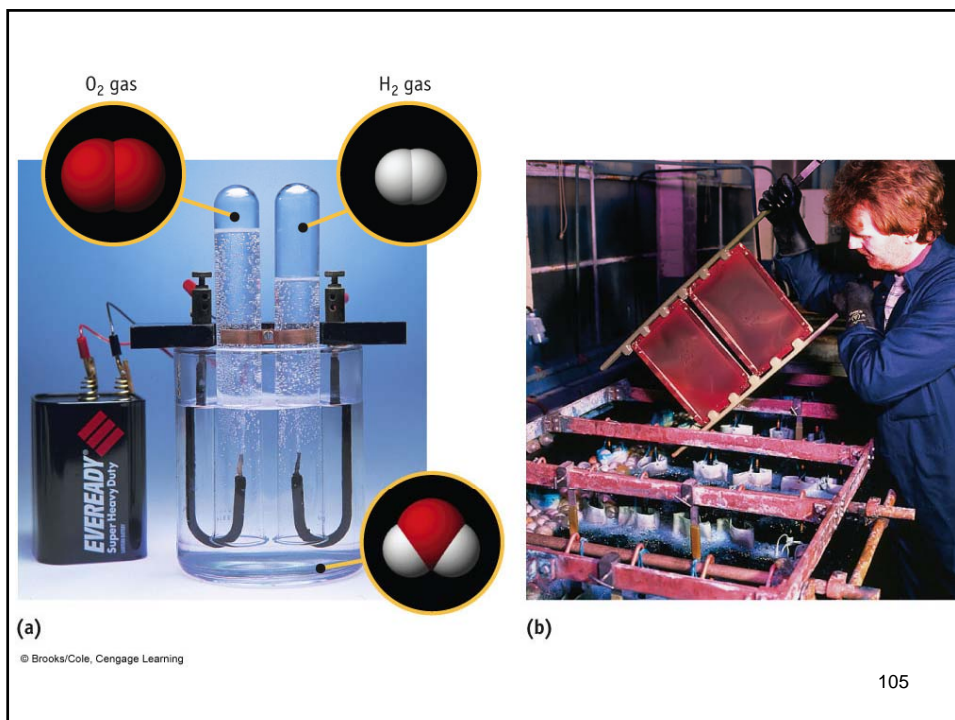
Figure 21.19

The electrolysis of water



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Electrolysis of Water

Battery

e^- ↑ ↓ e^-

Anode Cathode

Dilute H₂SO₄ solution

Oxidation

$$2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$$

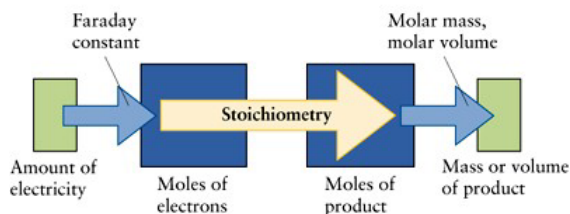
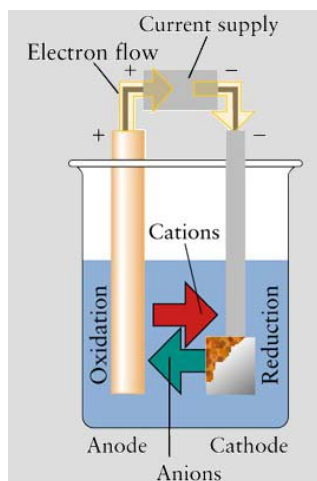
Reduction

$$4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2(g)$$

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Quantitative electrolysis.

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We will focus a lot on metal plating or metal electrodeposition reactions.



Required equations. $n \text{ mol } e^- = 1 \text{ mol } M$

Charge = current flowing \times time taken

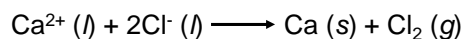
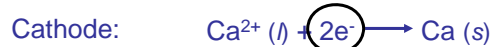
Coulombs C Amperes A Seconds s

Charge passed by 1 mole electrons = 1F
= 96,500 C.

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How much Ca will be produced in an electrolytic cell of molten CaCl_2 if a current of 0.452 A is passed through the cell for 1.5 hours?



2 mole $e^- = 1 \text{ mole Ca}$

$$\text{mol Ca} = 0.452 \frac{\cancel{\text{C}}}{\cancel{\text{s}}} \times 1.5 \cancel{\text{hr}} \times 3600 \frac{\cancel{\text{s}}}{\cancel{\text{hr}}} \times \frac{1 \text{ mol } e^-}{96,500 \cancel{\text{C}}} \times \frac{1 \text{ mol Ca}}{2 \text{ mol } e^-}$$

$$= 0.0126 \text{ mol Ca}$$

$$= 0.50 \text{ g Ca}$$

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Sample Problem 21.10: Applying the Relationship Among Current, Time, and Amount of Substance

PROBLEM: A technician is plating a faucet with 0.86g of Cr from an electrolytic bath containing aqueous $\text{Cr}_2(\text{SO}_4)_3$. If 12.5 min is allowed for the plating, what current is needed?

PLAN:

- mass of Cr needed
- divide by M
- mol of Cr needed
- $3\text{mol e}^-/\text{mol Cr}$
- mol of e^- transferred
- $9.65 \times 10^4 \text{C/mol e}^-$
- charge (C)
- divide by time
- current (A)

SOLUTION: $\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Cr}(\text{s})$

$$0.86\text{g} \frac{(\text{mol Cr})}{(52.00\text{gCr})} \frac{(3\text{mol e}^-)}{(\text{mol Cr})} = 0.050\text{mol e}^-$$

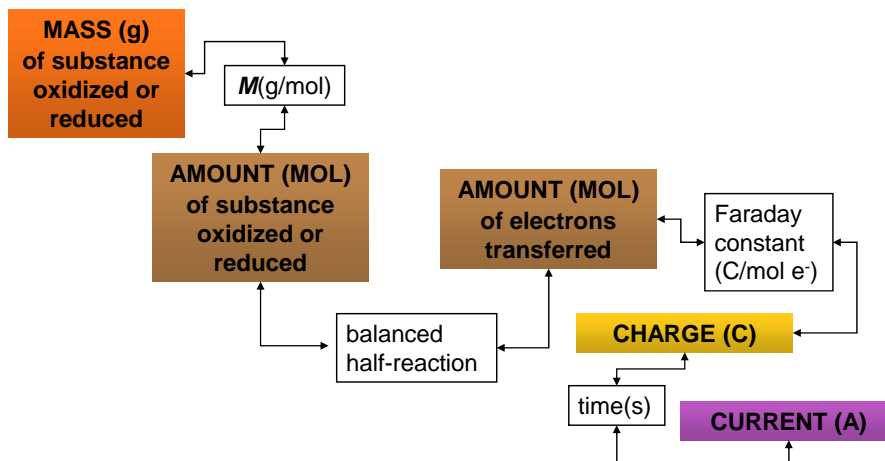
$$0.050\text{mol e}^- (9.65 \times 10^4 \text{C/mol e}^-) = 4.8 \times 10^3 \text{C}$$

$$\frac{4.8 \times 10^3 \text{C}}{12.5\text{min}} \frac{(\text{min})}{(60\text{s})} = 6.4 \text{C/s} = 6.4 \text{ A}$$

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Figure 21.20

A summary diagram for the stoichiometry of electrolysis



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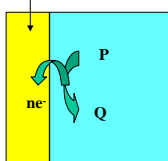
Kinetics of interfacial ET.

- Estimation of equilibrium redox potentials provides a quantitative measure for the **tendency** for a specific redox reaction to occur. **Kinetic information** is not derived.
- In short thermodynamics provides the tools by which the possibility of an oxidation or reduction event can be established. To determine the speed at which the oxidation or reduction process occurs a kinetic approach is required.
- 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?
- This information will enable us to obtain a modern quantitative picture of electrolysis at electrodes, and to recast Faraday's ideas in a compact modern form.

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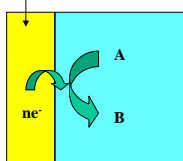
Interfacial electron transfer at electrode/solution interfaces: oxidation and reduction processes.

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

- 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.

- 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.

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

Current (A) # electrons transferred
Electrode area (cm²)

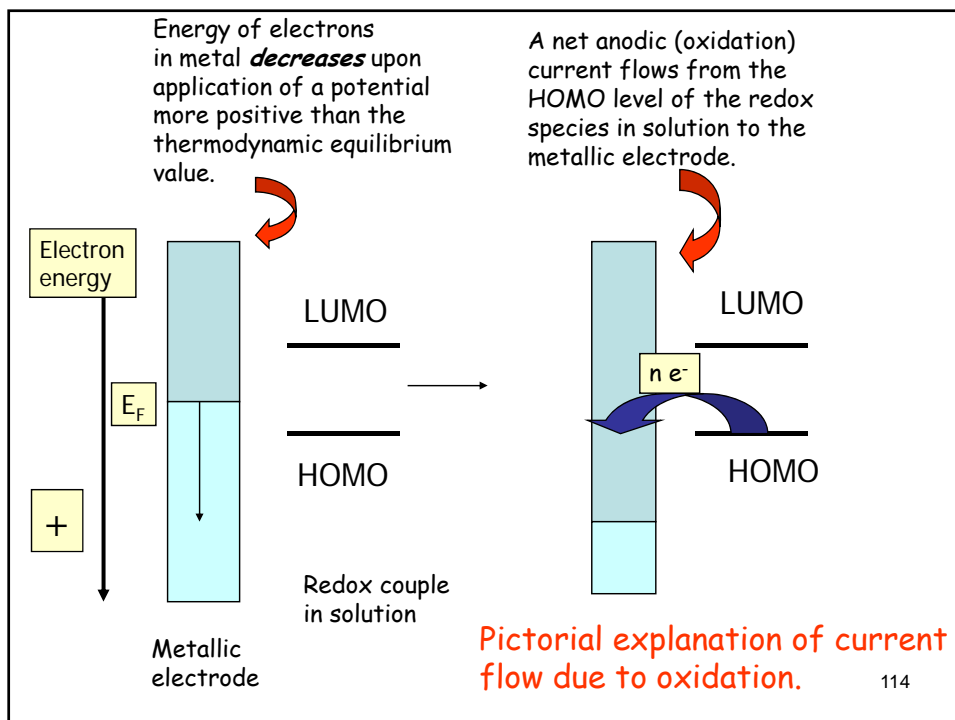
Charge (C) Faraday Constant (Cmol⁻¹)
Time (s) Amount of Material (mol)

Reaction flux (rate) — 112
mol cm⁻²s⁻¹

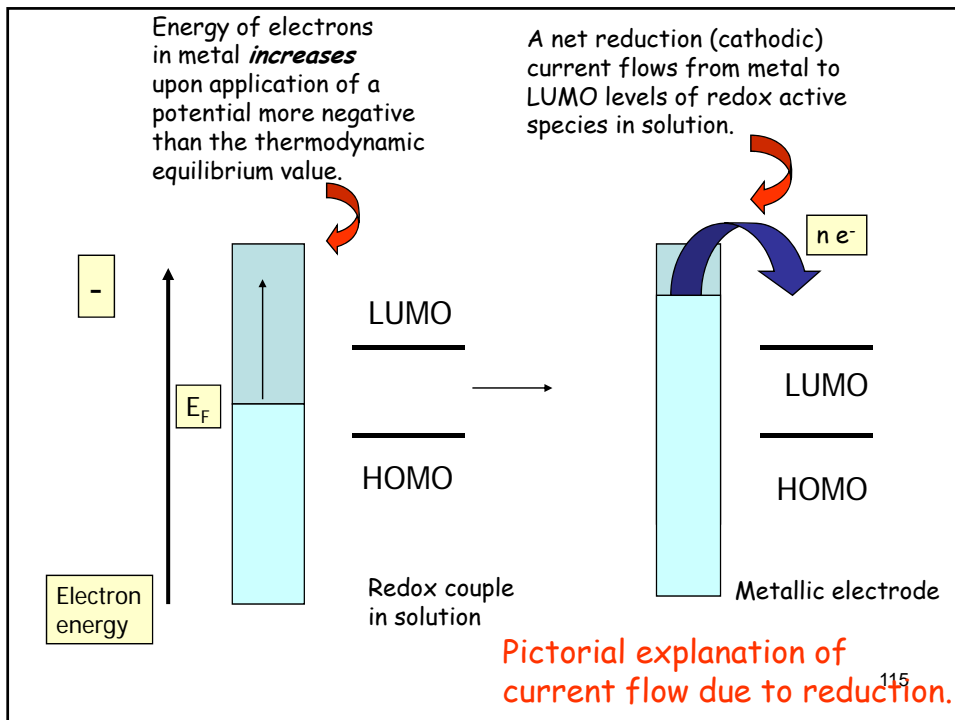
Basic concepts of electrode kinetics.

- 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 ($\text{molcm}^{-2}\text{s}^{-1}$) 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.
 - 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.

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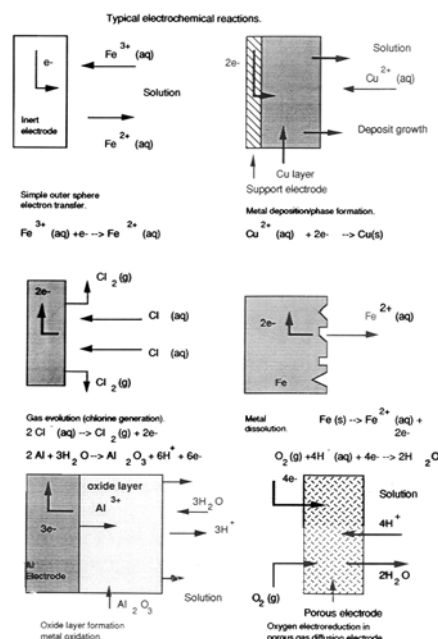
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A survey of electrochemical reaction types.

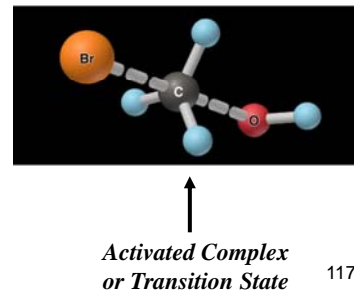
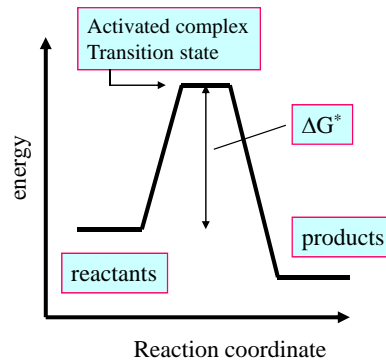
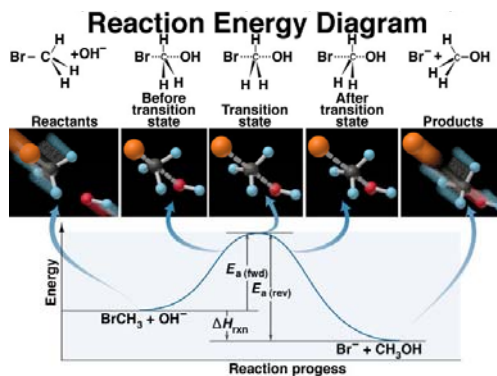
- Electrochemical reactions are usually complex multistep processes involving the transfer of more than one electron.
- In this course we focus on simple single step ET processes involving the transfer of a single electron.
- The kinetics of simple ET processes can be understood using the activated complex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

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



Activated Complex Theory (ACT) of chemical reaction kinetics.

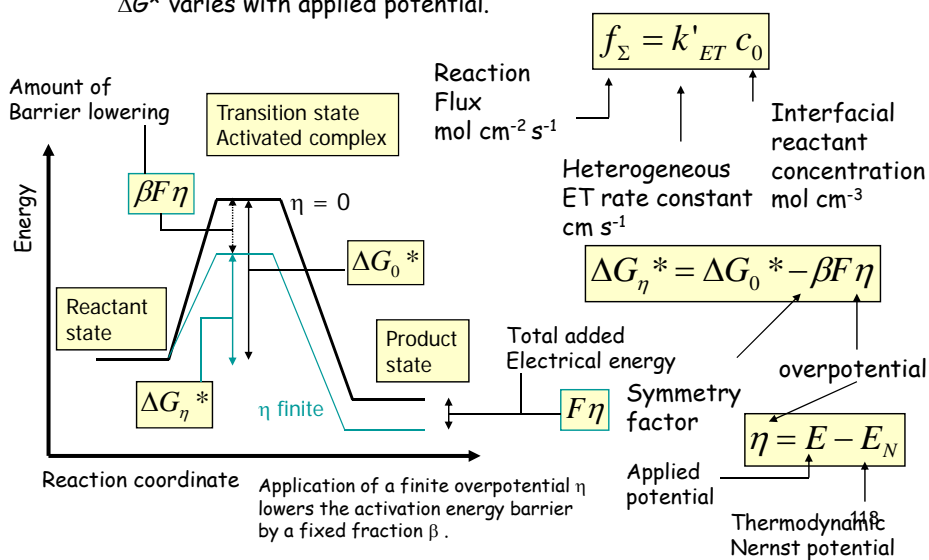
Progress of a chemical reaction can be expressed in terms of a plot of energy versus reaction co-ordinate. The reaction coordinate may be described in terms of changes in particular bond lengths since these will vary as the reaction progresses.



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

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



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

overpotential

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

$$\Delta G_{\eta}^* = \Delta G_0^* - \beta F \eta$$

Electrochemical Gibbs energy of activation

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

Symmetry factor

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

$$= k_{ET}^0 \exp\left[\frac{\beta F \eta}{RT}\right]$$

Characteristic ET distance (molecular diameter).

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

Transmission coefficient

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.

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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 $0 < \beta < 1$ and typically $\beta = 0.5$.

Net rate

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

Exchange current

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

Symmetry factor

Normalized potential

BV equation

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

$$i_0 = F A k^0 a^{\alpha(1-\beta)} b^{\alpha\beta}$$

Standard rate constant

