CEE 597T

Electrochemical Water and Wastewater Treatment

BASIC CONCEPTS IN ELECTROCHEMISTRY

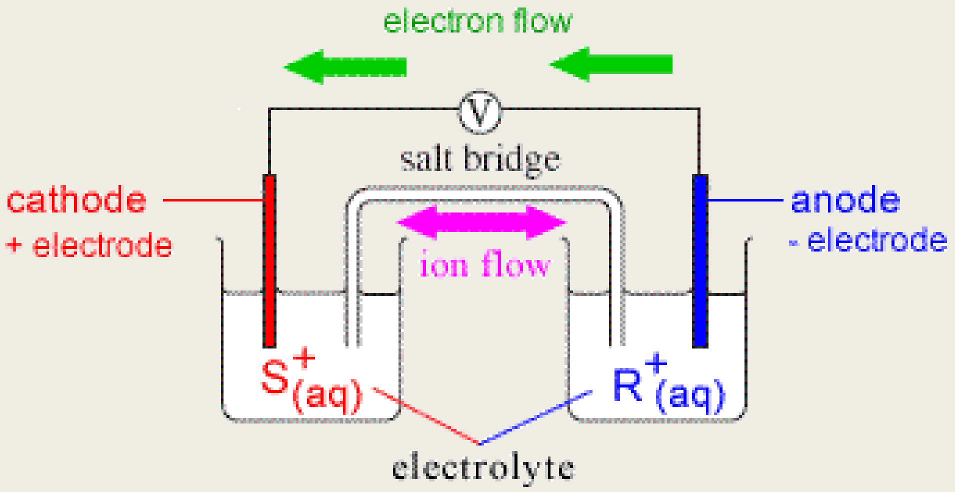
What is electrochemistry?

- Electrochemistry is defined as the branch of chemistry that examines the phenomena resulting from combined chemical and electrical effects.
- Chemical transformation occurring owing to the external applied electrical current or leading to generation of electrical current is studied in electrochemistry.

Electrochemical Cell

An electrochemical cell typically consists of

- Two electronic conductors (also called electrodes)
- An ionic conductor (called an electrolyte)
- the electron conductor used to link the electrodes is often a metal wire, such as copper wiring



Types of Cell

Electrolytic process

Reactions in which chemical changes occur on the passage of an electrical current. Electrolytic cells are driven by an external source of electrical energy.

A flow of electrons drives non-spontaneous ($\Delta G \geq 0$) redox reactions.

Galvanic or Voltaic Processes

Chemical reactions that result in the production of electrical energy. Galvanic cells convert chemical potential energy into electrical energy.

The energy conversion is achieved by spontaneous ($\Delta G < 0$) redox reactions producing a flow of electrons.

Galvanic (Voltaic) Cells

The operation of a galvanic (or voltaic) cell is opposite to that of an electrolytic cell. In a galvanic cell, electrical energy is produced by a chemical redox reaction, instead of a chemical reaction being produced by electricity. The classic example of a redox reaction for a galvanic cell is the reaction between aqueous solutions of zinc (Zn) and copper (Cu):

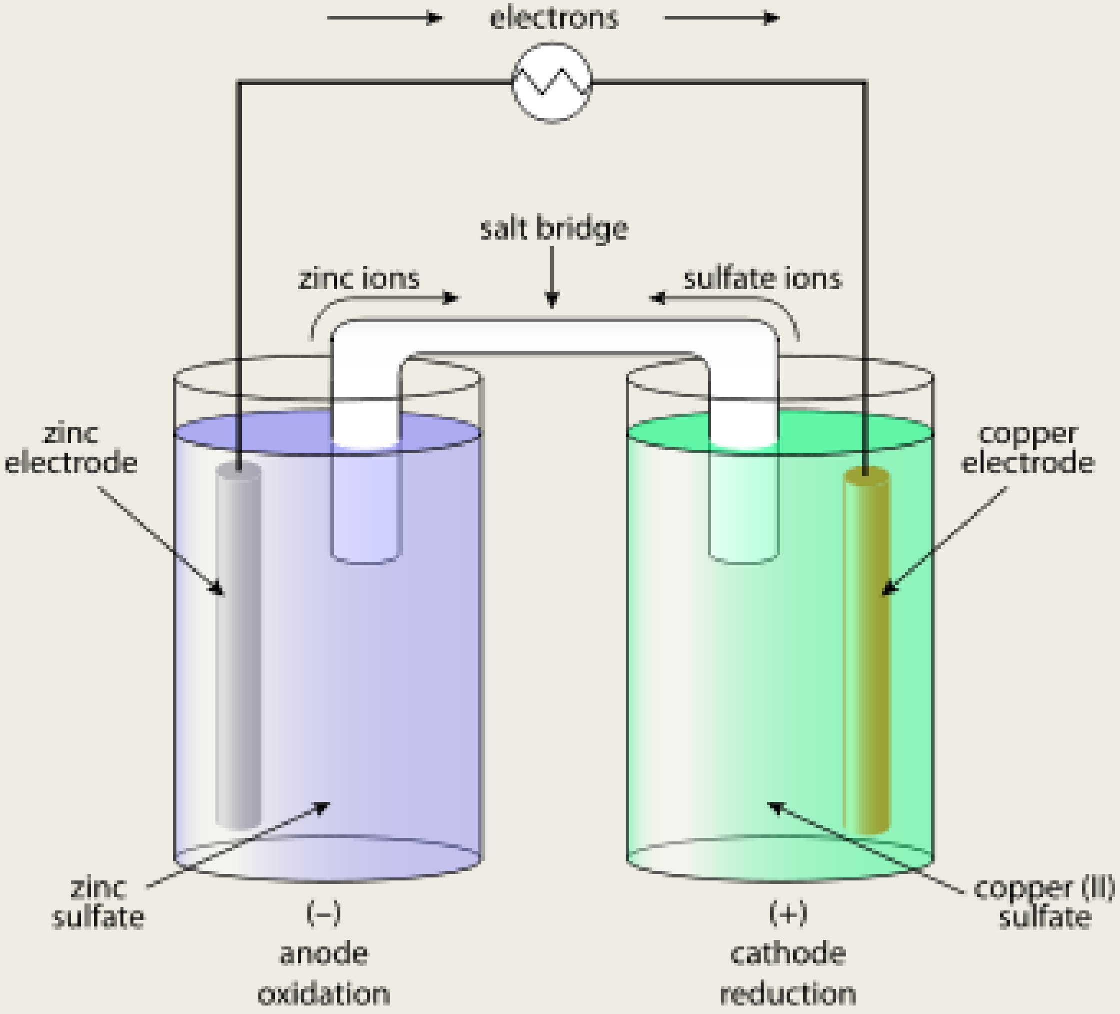
$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

In this cell, the zinc is oxidized, and the copper is reduced. Initially, this produces a flow of electrons across a wire connected to the two separate electrode solutions, but as the zinc solution becomes positively charged from losing electrons and the copper solution becomes negatively charged from gaining them, that flow stops. No more negatively charged electrons want to flow toward the negatively charged copper solution!

Galvanic Cells (conc.)

Salt Bridge

- To solve this problem, and to provide a continuous flow of electrons (which means a source of electricity), the electrode solutions must remain electrically neutral. This can be done with a **salt bridge**.
- The salt bridge is usually a U-shaped tube filled with a concentrated salt solution. The solution in this tube provides a way for ions to travel between the two electrode solutions so that they can remain electrically neutral in charge. This enables the continuous flow of electrons.



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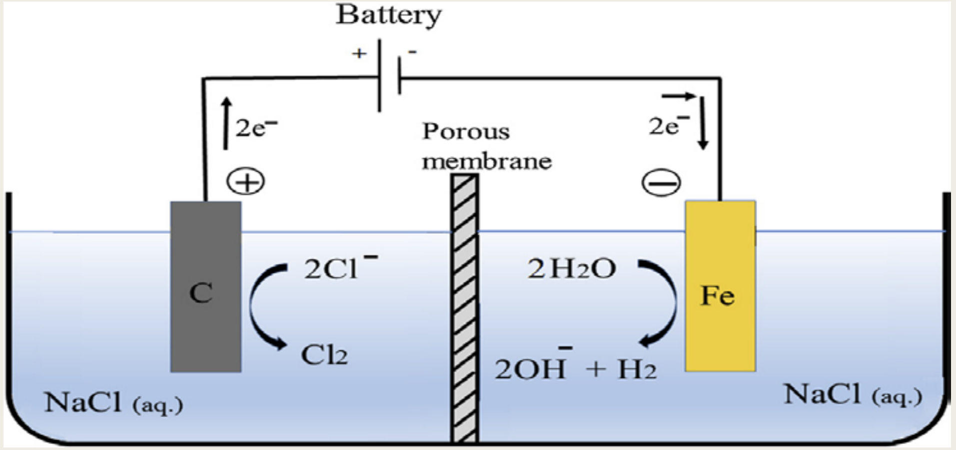
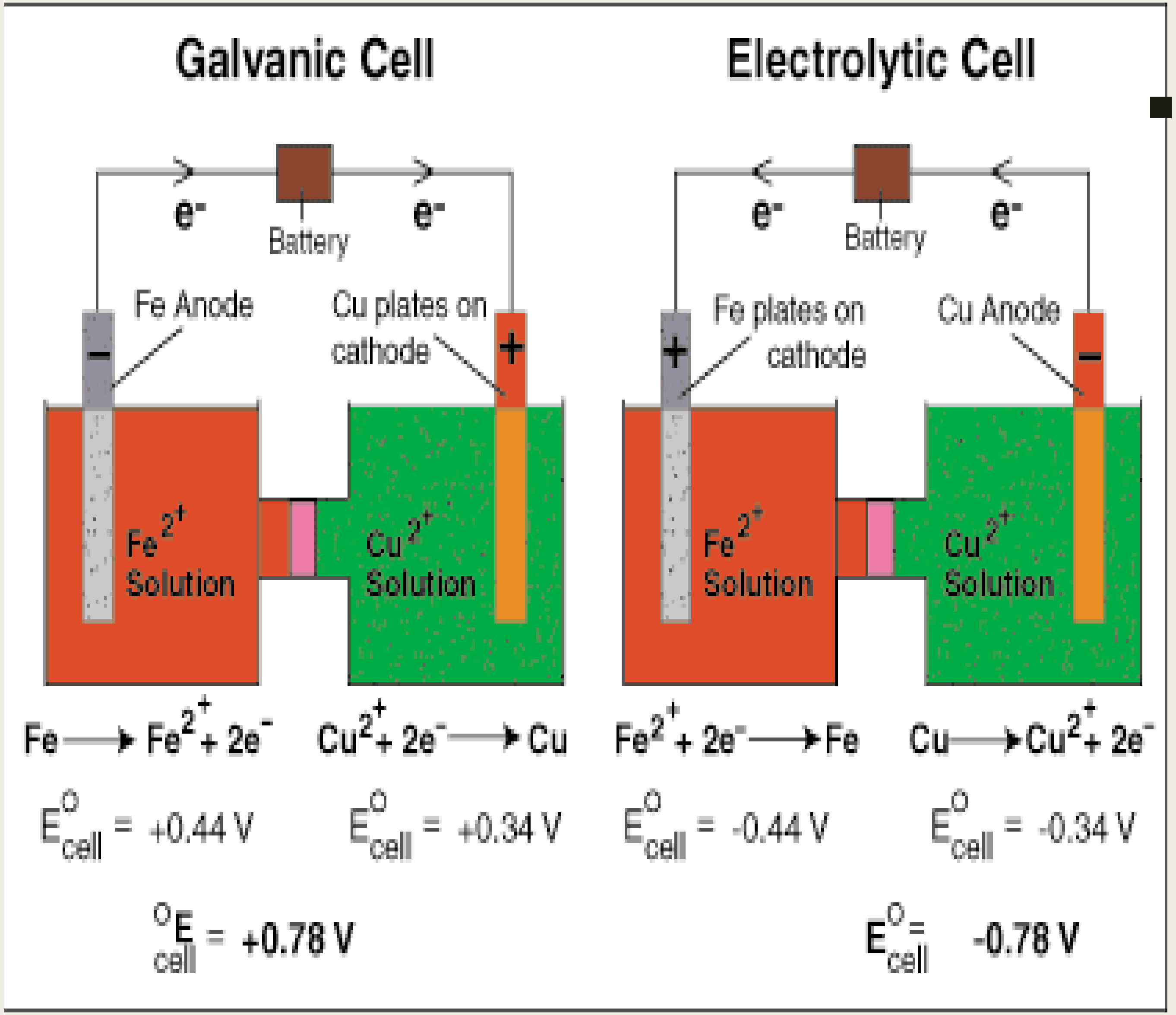
Electrolytic Cells

- Electrolysis is used to drive an oxidation-reduction reaction in a direction in which it does not occur spontaneously.
- The concept of reversing the direction of the spontaneous reaction in a galvanic cell through the input of electricity is at the heart of the idea of electrolysis.
- Electrolytic cells, like galvanic cells, are composed of two half-cells--one is a reduction half-cell, the other is an oxidation half-cell.
- Though the direction of electron flow in electrolytic cells may be reversed from the direction of spontaneous electron flow in galvanic cells, the definition of both cathode and anode remain the same--reduction takes place at the cathode and oxidation occurs at the anode.





- When comparing a galvanic cell to its electrolytic counterpart, occurs on the right-hand half-cell. Because the directions of both half-reactions have been reversed, the sign, but not the magnitude, of the cell potential has been reversed. Note that copper is spontaneously plated onto the copper cathode in the galvanic cell whereas it requires a voltage greater than 0.78 V from the battery to plate iron on its cathode in the electrolytic cell.

Anode and Cathode

- The electrode at which electrons are lost is known as the **anode**, and the one at which electrons are gained is the **cathode**.
- **At the anode:**

***Oxidation**, or loss of electrons, is the process which occurs at the anode

*Negative ions from the electrolyte are discharged if they are halide ions such as I^-, Br^-, and Cl^-.

*SO_4^{2-} and NO_3^- ions are not discharged. Instead, OH^- ions from water are discharged and O_2 gas is produced.

- **At the cathode:**

***Reduction**, or gain of electrons, occurs at the cathode.

*Positive ions from the electrolyte are discharged if they are H^+ ions or ions less reactive metals such as Cu^{2+}, Pb^{2+} or Ag^+.

*Positive ions of reactive metals such as Na^+, K^+ and Ca^{2+} are not discharged in the presence of water. Instead, H^+ ions from water are discharged and H_2 gas is produced.

Inert and Reactive Electrode

- Inert Electrodes do not react with the product produced or dissolved in the electrolyte. Carbon and platinum are examples of inert electrodes.
- Reactive electrodes can react or dissolve in the electrolyte. Copper, silver and mercury are examples of reactive electrodes

Working and Counter Electrodes

- The electrode at which the reaction of interest occurs is called the working electrode
- The electrode at which the other (coupled) reaction occurs is called the counter electrode
- A third electrode, called the reference electrode may also be used

Reactions – half cell and overall

- At each electrode, an electrochemical reaction occurs. This reaction is called a half cell reaction (since there are two electrodes in a typical cell at which reactions occur) The overall chemical reaction of the cell is given by combining the two individual half cell reactions
- There are two fundamental types of half cell reactions:
- - Oxidation reactions
- - Reduction reactions
- A reaction is classified as oxidation or reduction depending on the direction of electron transfer

Oxidation

- Involves the loss of an electron
- Involves the transfer of electrons from the species to the electrode

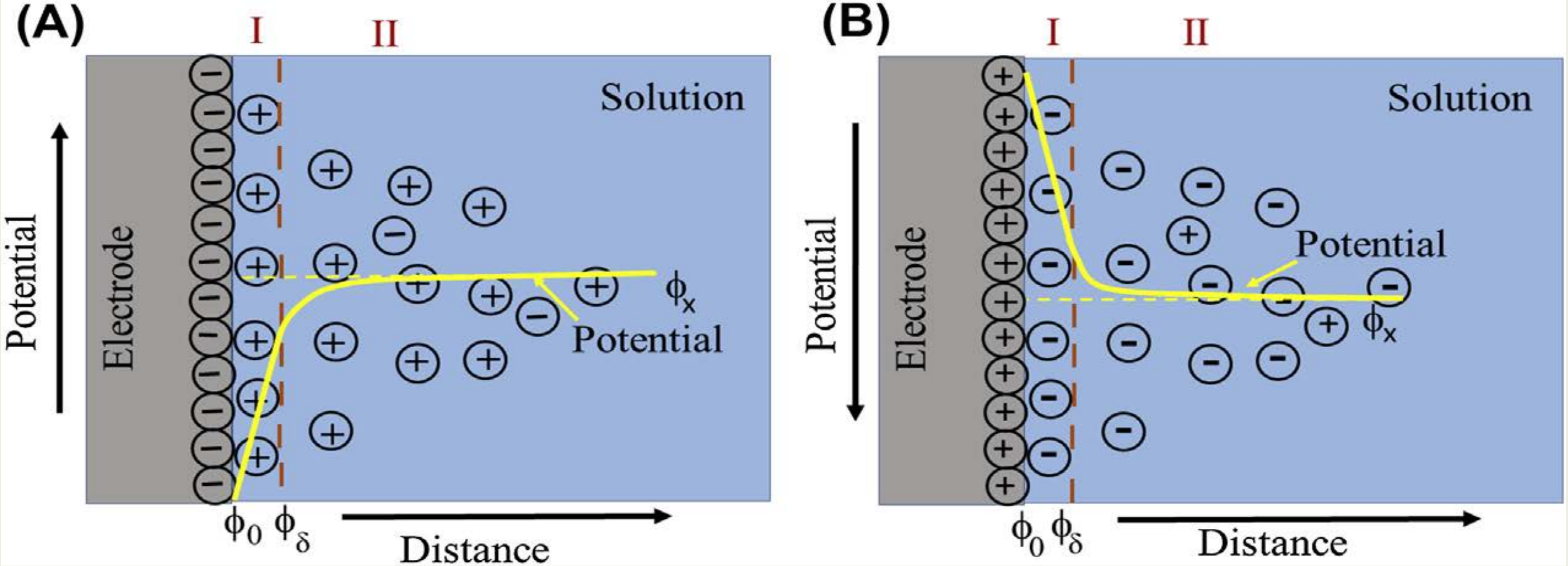
  $R = O + ne$

Reduction

- Involves the gain of an electron
- Involves the transfer of electrons from the electrode to the species

  O + ne = R

Electrode Potential



Schematic representation of the electrode potential development in the case of active (A) and less active (B) metal electrodes. Electrical double layer. ϕ0 is the surface potential, ϕd is the Stern potential, and ϕx is the potential at distance x from the surface, I is the dense part of the EDL (Helmholtz/Stern layer), and II is the diffuse part of the ELD

- The major part of the released cations into solutions (Fig. A; the case of active metals) or left in the solution anions (Fig. B; the case of less active metals) accumulates near the surface of the electrode. As the distance from the surface of the electrode increases, the concentration of cations/anions decreases and becomes equal to the concentration in solution. As a result the electrical double layer (EDL) is formed.
- While EDL is formed, the potential difference between the electrode surface (ϕ_0) and solution at distance x from the electrode surface (ϕ_x) is called electrode potential (E)
- $E = \phi_0 - \phi_x$

Nerst equation

- The value of electrode potential depends on the material of electrode, the nature of the solvent, temperature, and concentration of the electrode exchange ions. Therefore, the electrode potential is measured by comparing with the reference electrode potential. Typically, this is the standard hydrogen electrode (SHE), whose potential is stable and is assumed to be zero ($E^{o}_{2H^{+}/H_2} = 0\,V$)
- The theoretical value of electrode potential can be calculated using the Nernst equation.

$$E = E^{0} - \frac{RT}{zF} ln \frac{[a_{ox}]}{[a_{red}]}$$

where E is the electrode potential at a given temperature, E^0 is the standard electrode potential, R is the universal gas constant, T is the temperature, z is the number of electrons participating in the process, a_{ox} and a_{red} are activities of oxidized and reduced forms of the substance, respectively.

- The difference in potential is given in units of volts (V).

1 Volt = 1 Joule / 1 Coulomb; units of energy / units of charge

Potentials are usually tabulated at standard conditions: 25°C (298 K), 1 M concentrations of reactants and products, 1 atm pressure for species that are in the gas phase.

- The potential is a quantitative description of the driving force behind an electrochemical reaction.
- The electrode potential for a reaction is derived directly from the free energy change for that reaction
- $\Delta G = - NFE$
- The standard oxidation potential is equal in magnitude, but opposite in sign to the std. reduction potential

$\Delta G_{cell} = - NFE_{cell}$

What is normally tabulated is the standard reduction potential E^o_{red} (that is, measured under standard conditions). The standard oxidation potential is simply the negative of the standard reduction potential. Therefore, for any electrochemical cell, the potential is given by:

$E^o_{cell} = E^o_{reduction}(\text{cathode reaction}) - E^o_{reduction}(\text{anode reaction})$

For a feasible reaction: Ecell must be positive (so that ΔGcell is negative)

If $E^o_{cell} > 0$, we have a spontaneous process (galvanic cell)
If $E^o_{cell} < 0$, we have a nonspontaneous process (electrolytic cell)

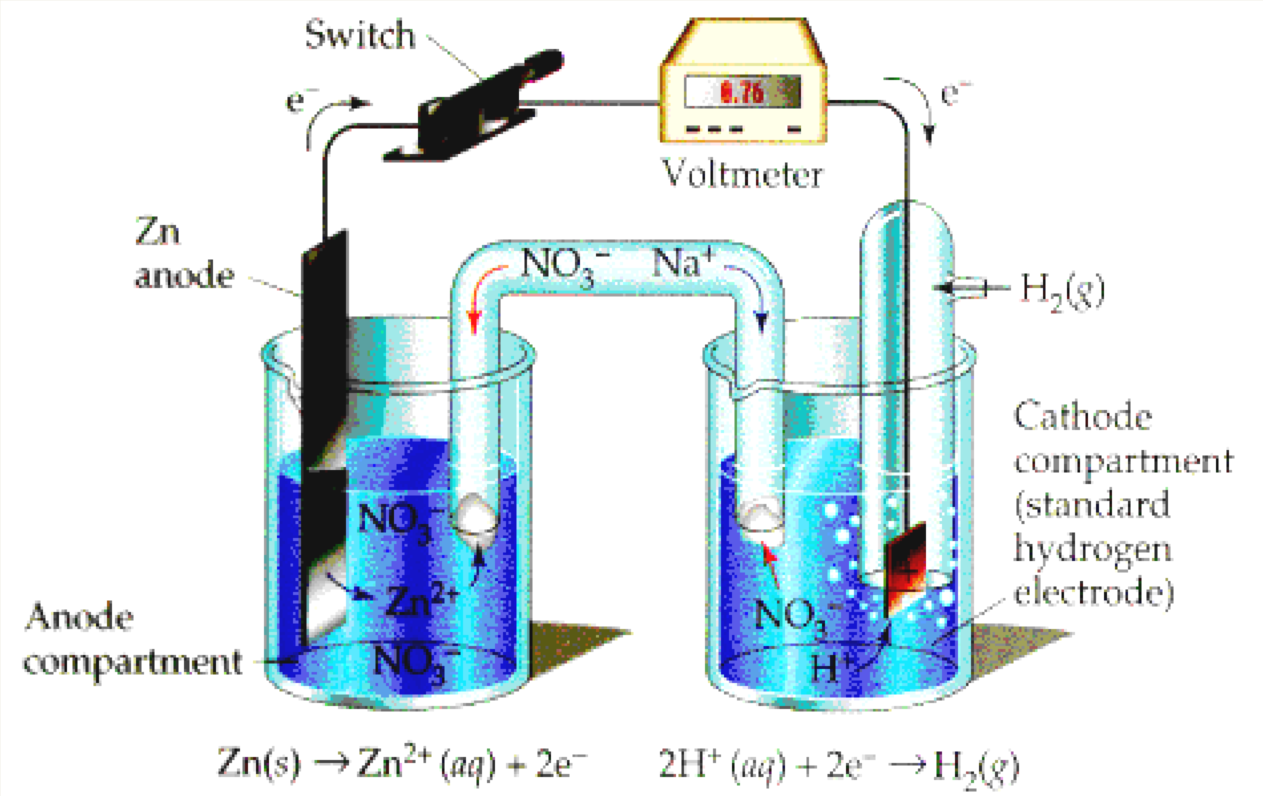
Standard hydrogen electrode

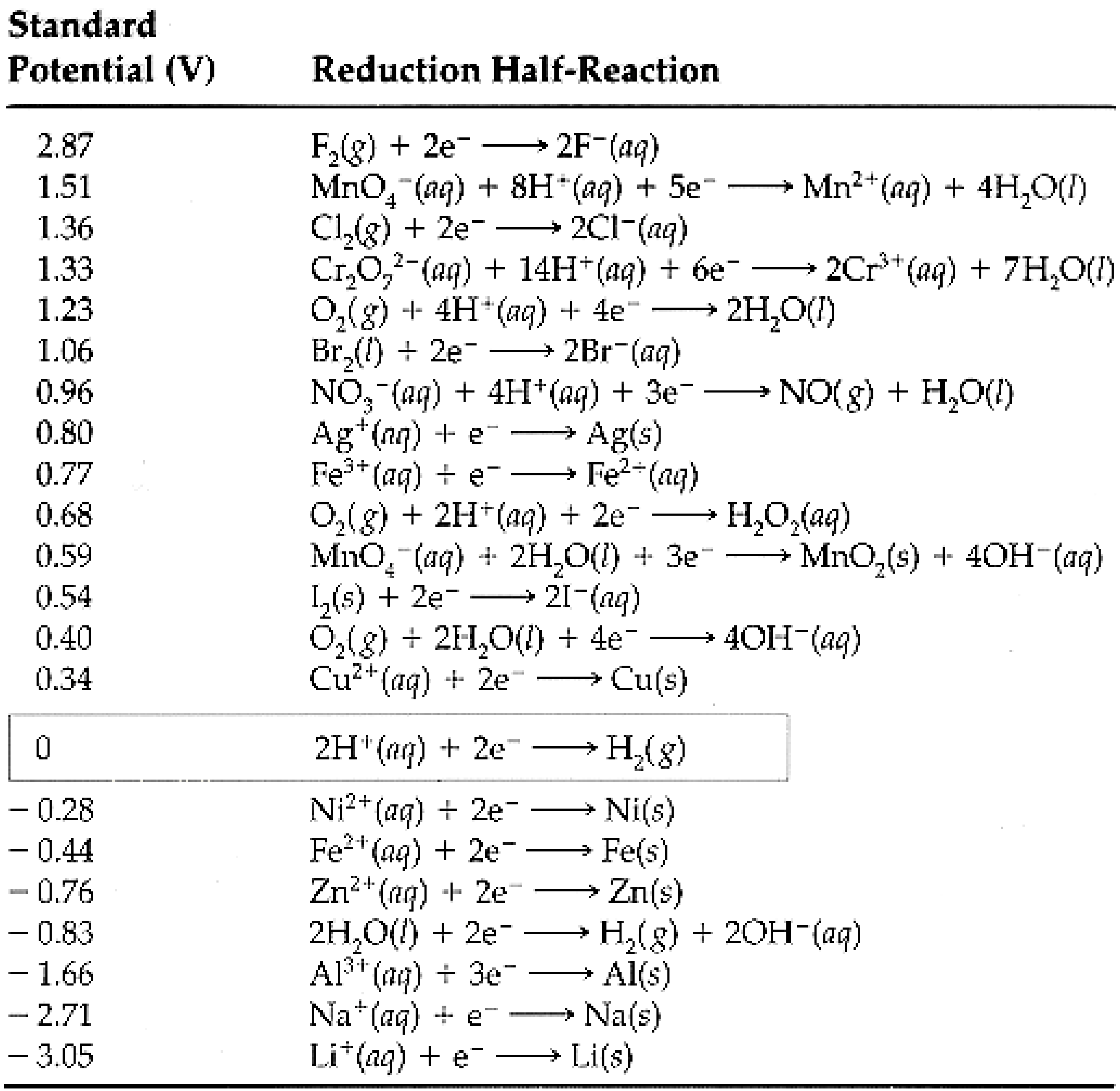
- Since every electrochemical cell involves two-half-cells, it is not possible to measure directly the standard reduction potential of a half-reaction. Hence, we choose one half-cell reaction as a standard against which all other half cells will be measured.

- The standard, E^o_{red} = 0 Volt exactly for:

  $2\ H^+\ (aq,1\ M) + 2e^- \rightarrow\ H_2\ (gas,1\ atm)$

  - The cell whose potential is to be measured is placed against the standard half-cell. The voltmeter reads 0.76 V. However, it turns out that the spontaneous flow of electrons is occurring from the Zn electrode to the standard cell. Thus, the reduction potential of $Zn^{2+}(aq)$ is -0.76 V.

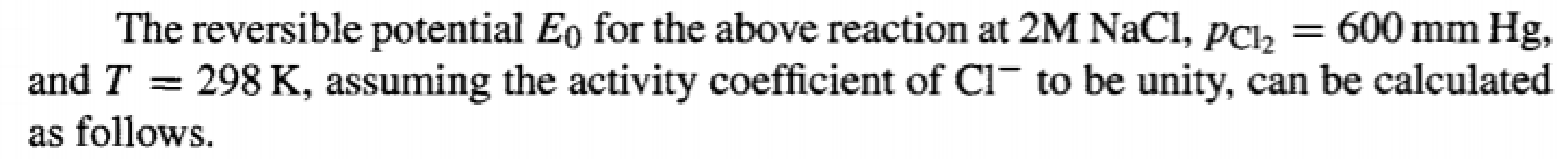




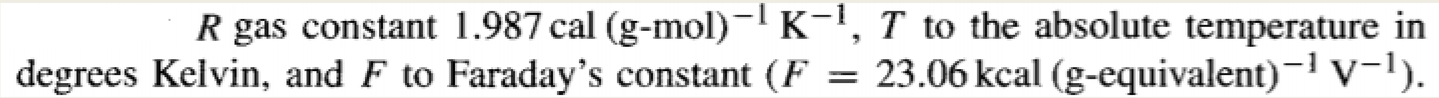
Standard Potential (V)	Reduction Half-Reaction
2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + H_2O(l)$
0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
− 0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
− 0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
− 0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
− 0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
− 1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
− 2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
− 3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

- The species near the top of the list prefer to be reduced (good oxidizing agents)
  while the species near the bottom prefer to be oxidized (good reducing agents.

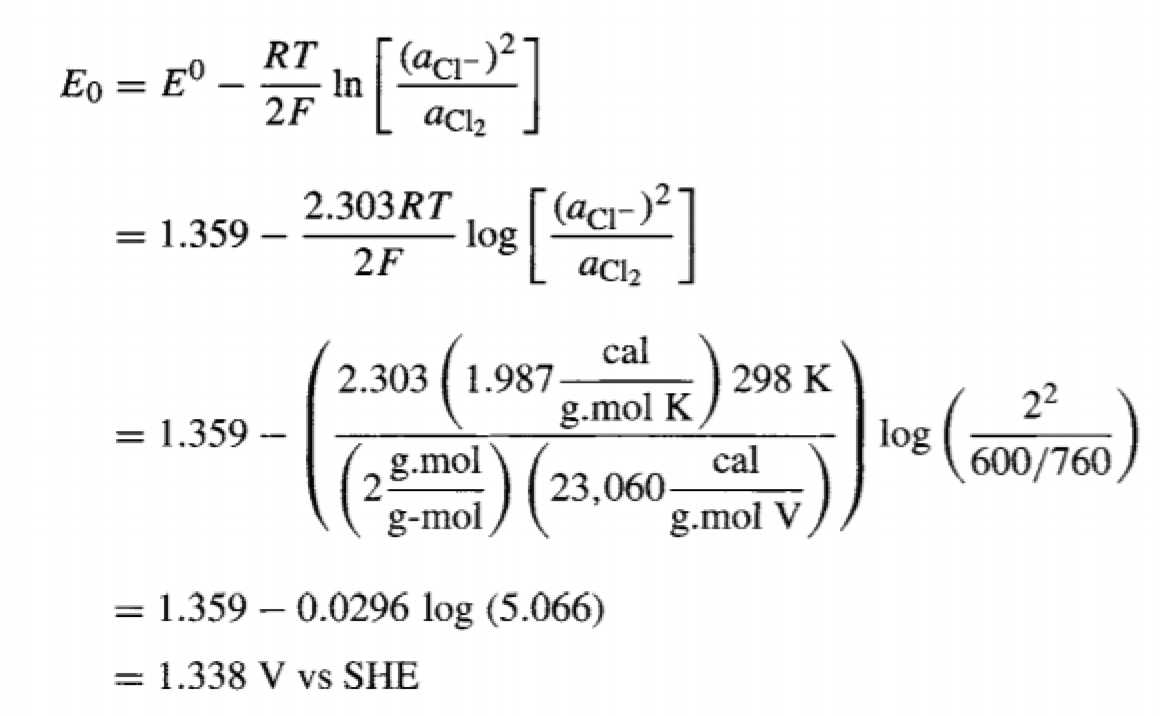
- **Example:**
- Cl_2 + 2e- → 2C1$^-$



The reversible potential E_0 for the above reaction at 2M NaCl, $p_{Cl_2} = 600$ mm Hg, and $T = 298$ K, assuming the activity coefficient of Cl^- to be unity, can be calculated as follows.



R gas constant 1.987 cal (g-mol)$^{-1}$ K^{-1}, T to the absolute temperature in degrees Kelvin, and F to Faraday's constant ($F = 23.06$ kcal (g-equivalent)$^{-1}$ V^{-1}).



$$E_0 = E^0 - \frac{RT}{2F}\ln\left[\frac{(a_{Cl^-})^2}{a_{Cl_2}}\right]$$

$$= 1.359 - \frac{2.303RT}{2F}\log\left[\frac{(a_{Cl^-})^2}{a_{Cl_2}}\right]$$

$$= 1.359 - \left(\frac{2.303\left(1.987\frac{\text{cal}}{\text{g.mol K}}\right)298\text{ K}}{\left(2\frac{\text{g.mol}}{\text{g-mol}}\right)\left(23{,}060\frac{\text{cal}}{\text{g.mol V}}\right)}\right)\log\left(\frac{2^2}{600/760}\right)$$

$$= 1.359 - 0.0296\log(5.066)$$

$$= 1.338\text{ V vs SHE}$$

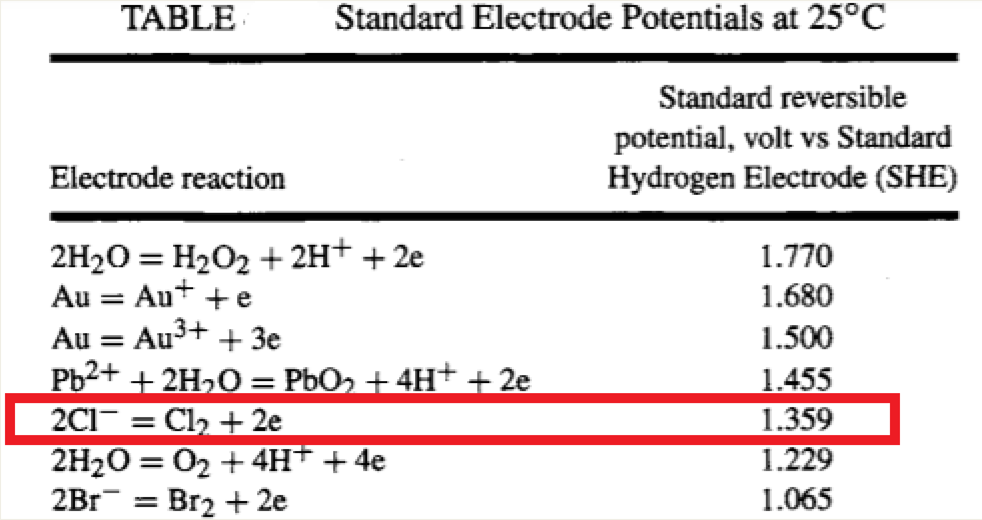
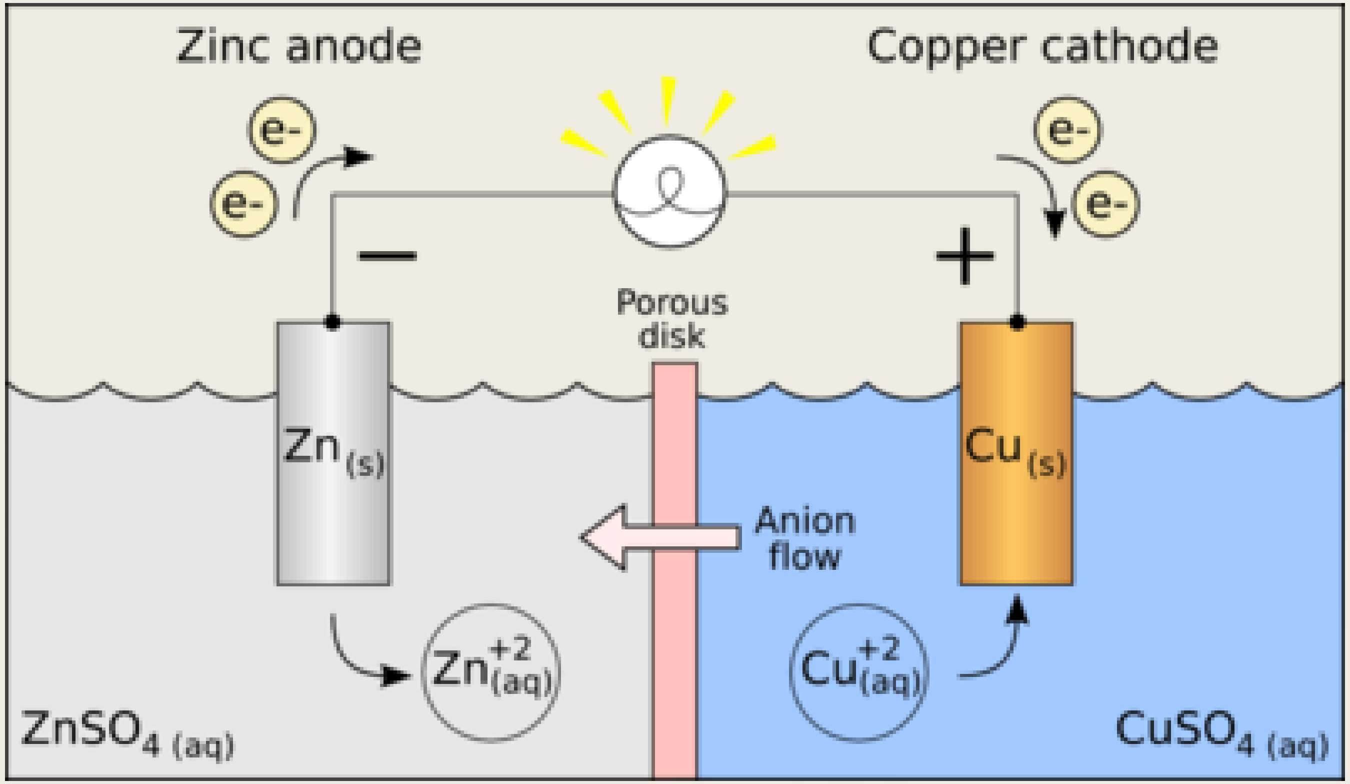


TABLE Standard Electrode Potentials at 25°C

Electrode reaction	Standard reversible potential, volt vs Standard Hydrogen Electrode (SHE)
$2H_2O = H_2O_2 + 2H^+ + 2e$	1.770
$Au = Au^+ + e$	1.680
$Au = Au^{3+} + 3e$	1.500
$Pb^{2+} + 2H_2O = PbO_2 + 4H^+ + 2e$	1.455
$2Cl^- = Cl_2 + 2e$	1.359
$2H_2O = O_2 + 4H^+ + 4e$	1.229
$2Br^- = Br_2 + 2e$	1.065



- Zinc and copper metals placed in a solution of their respective sulfates, and separated by a semi permeable membrane
- Zinc metal gets oxidized - goes into solution: $Zn = Zn^{2+} + 2e$ (1)
- Copper ions in solution – reduced; copper metal - deposited on the copper electrode $Cu^{2+} + 2e = Cu$ (2)
- Electrons for reduction obtained from the zinc electrode - external wire
- Sulfate ions (reaction 2)migrate through the membrane, - react with the zinc ions [from (1)] - zinc sulfate

Competing reactions

- For a set of 2 competing reactions:
- The reaction with the lower standard reduction potential gets oxidized - the other reaction proceeds as a reduction
- $Zn \Rightarrow Zn^{2+} + 2e$ $E°_{red} = -0.7618$ V
- $Cu^{2+} + 2e \Rightarrow Cu$ $E°_{red} = 0.341$ V
- Thus, in the above example, Zn is oxidized, and Cu is reduced
- Since oxidation occurs at the anode – the species with the lower reduction potential will get oxidized
- This is to ensure that ΔG_{cell} is negative ($\Delta G = - NFE$)
- This is why Zn got oxidized (and Cu reduced) in the above example.
- In this case: $E_{cell} = E^o red\ (cathode) - E^o red(anode) = 1.102$.
- If the reverse were to occur, E_{cell} would be: -1.102, leading to a positive ΔG_{cell}

Faraday’s Law

- The amount of a substance consumed or produced at one of the electrodes in an electrolytic cell is directly proportional to the amount of electricity that passes through the cell.
- By definition, one coulomb of charge is transferred when a 1-amp current flows for 1 second.

1 C = 1 amp-s

- $m = M\,I\,t\,/n\,F$

m - mass of substance

M - molecular weight of the substance

I - current passed (A)

t - time for which the current is passed (s)

n - number of electrons transferred

F - Faraday constant (96475 C / eqv)

- **The amount of chemical change is proportional to the amount of current passed**

- Practice problem 1: Calculate the number of grams of sodium metal that will form at the cathode when a 10.0-amp current is passed through molten sodium chloride for a period of 4.00 hours.
- We start by calculating the amount of electric charge that flows through the cell.

$$10.0\ amp\ x\ 4.00\ h\ x\ \frac{60\ \text{min}}{1\ hr}\ x\ \frac{60\ s}{1\ \text{min}}\ x\ \frac{1\ C}{1\ amp-s} = 144{,}000\ C$$

- describes the number of coulombs of charge carried by a mole electrons.

$$\frac{6.022045\ x\ 10^{23}\ e^-}{1\ mol}\ x\ \frac{1.6021892\ x\ 10^{-19}\ C}{1\ e^-} = 96{,}484.56\ C/mol$$

- Thus, the number of moles of electrons transferred when 144,000 coulombs of electric charge flow through the cell can be calculated as follows.

$$144{,}000\ C\ x\ \frac{1\ mol\ e^-}{96{,}485\ C} = 1.49\ mol\ e^-$$

- According to the balanced equation for the reaction that occurs at the cathode of this cell, we get one mole of sodium for every mole of electrons.
- Cathode (-): $Na^+ + e^- \rightarrow Na$
- Thus, we get 1.49 moles, or 34.3 grams, of sodium in 4.00 hours.

$$1.49\ mol\ Na\ x\ \frac{22.99\ g\ Na}{1\ mol\ Na} = 34.3\ g\ Na$$

- Practice Problem 2: Calculate the volume of H_2 gas at 25°C and 1.00 atm that will collect at the cathode when an aqueous solution of Na_2SO_4 is electrolyzed for 2.00 hours with a 10.0-amp current.
- Solution:

We start by calculating the amount of electrical charge that passes through the solution.

$$10.0\ amp \times 2.00\ h \times \frac{60\ \text{min}}{1\ hr} \times \frac{60\ s}{1\ \text{min}} \times \frac{1\ C}{1\ amp\text{-}s} = 72{,}000\ C$$

We then calculate the number of moles of electrons that carry this charge.

$$72{,}000\ C \times \frac{1\ mol\ e^-}{96{,}485\ C} = 0.746\ mol\ e^-$$

The balanced equation for the reaction that produces H_2 gas at the cathode indicates that we get a mole of H_2 gas for every two moles of electrons.

Cathode (-): $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$

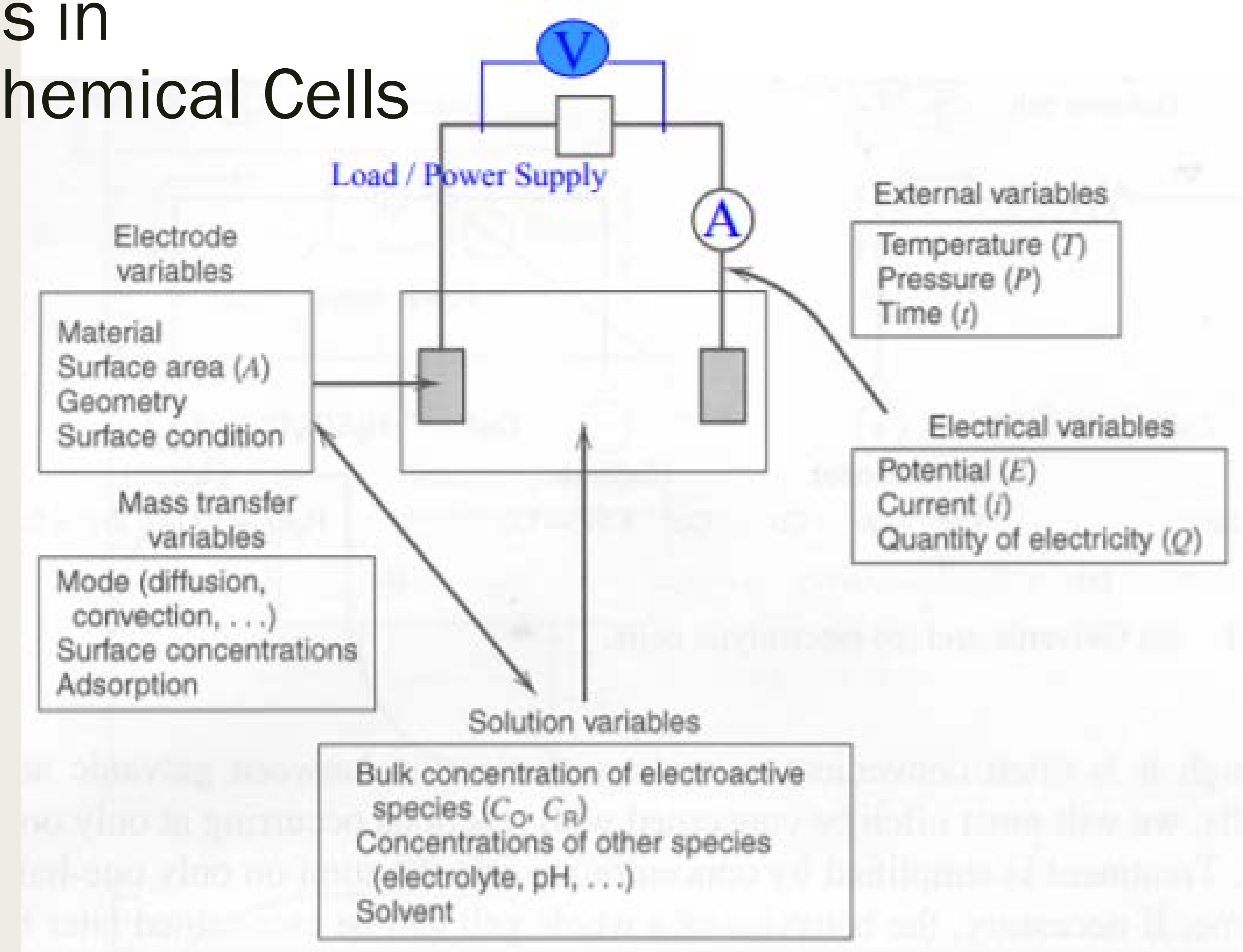
We therefore get one mole of H_2 gas at the cathode for every two moles of electrons that flow through the cell.

$$0.746\ mol\ e^- \times \frac{1\ mol\ H_2}{2\ mol\ e^-} = 0.373\ mol\ H_2$$

We now have the information we need to calculate the volume of the gas produced in this reaction.

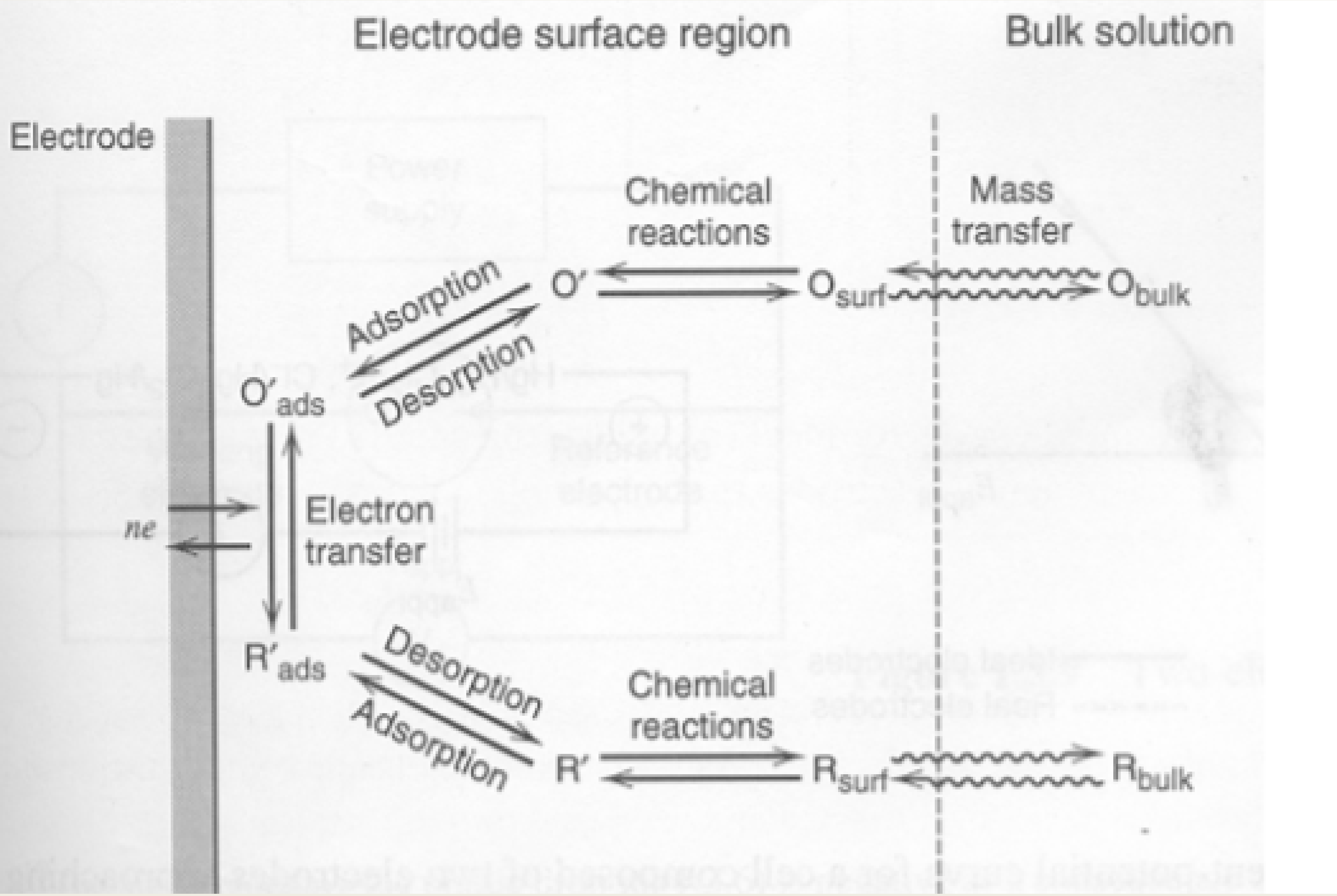
$$V = \frac{nRT}{P} = \frac{(0.373\ mol)(0.08206\ L\text{-}atm/mol\text{-}K)(298\ K)}{(1\ atm)} = 9.12\ L$$

Variables in Electrochemical Cells



Factor Affecting Electrode Reaction Rate and Current

- Consider an overall reaction, O+ne ⇔ R (O dissolved oxidized species, reduce to form R). In general, the current (or electrode reaction rate) is governed by the rates of processe such as
- 1. Mass transfer (e.g., of O from the bulk solution to the electrode surface)
- 2. Electron transfer at the electrode surface
- 3.Chemical reaction preceding or following the electron transfer.
- 4. Other surface reactions, such as adsorption, desorption, or crystalization (electrodeposition).
- The rate constant for some of these processes (e.g. Electron transfer at the electrode surface or adsoprtion) depend upon the potential.


Electrode surface region
Bulk solution
Electrode
Chemical reactions
Mass transfer
O′
O_{surf}
O_{bulk}
Adsorption
Desorption
O'_{ads}
ne
Electron transfer
R'_{ads}
Desorption
Adsorption
Chemical reactions
R′
R_{surf}
R_{bulk}

Current

- By definition, current is the rate of flow of charge Therefore
- i (amperes) = dQ/dt (coulombs/s)
- $\frac{Q\ (coulombs)}{nF\ (\frac{couloms}{mol})} = N(mol\ electrolyzed)$

where n is the stoichiometric number of electrons consumed in the electrode reaction

- Rate (mol/s)= dN/dt= i/nF
- Homogeneous reaction occurs everywhere within the medium at a uniform rate.
- Heterogeneous reaction occurs only at the electrode-electrolyte interface. Its rate depend on mass transfer to the electrode and various surface effects, in addition to the usual kinetic variables. Since electrode reactions are usually heterogeneous, their reaction rates are usually described in units of mol/s per unit area
- $Rate\ (\frac{mol}{s\ cm^2})=\frac{i}{nFA}=\frac{j}{nF}$

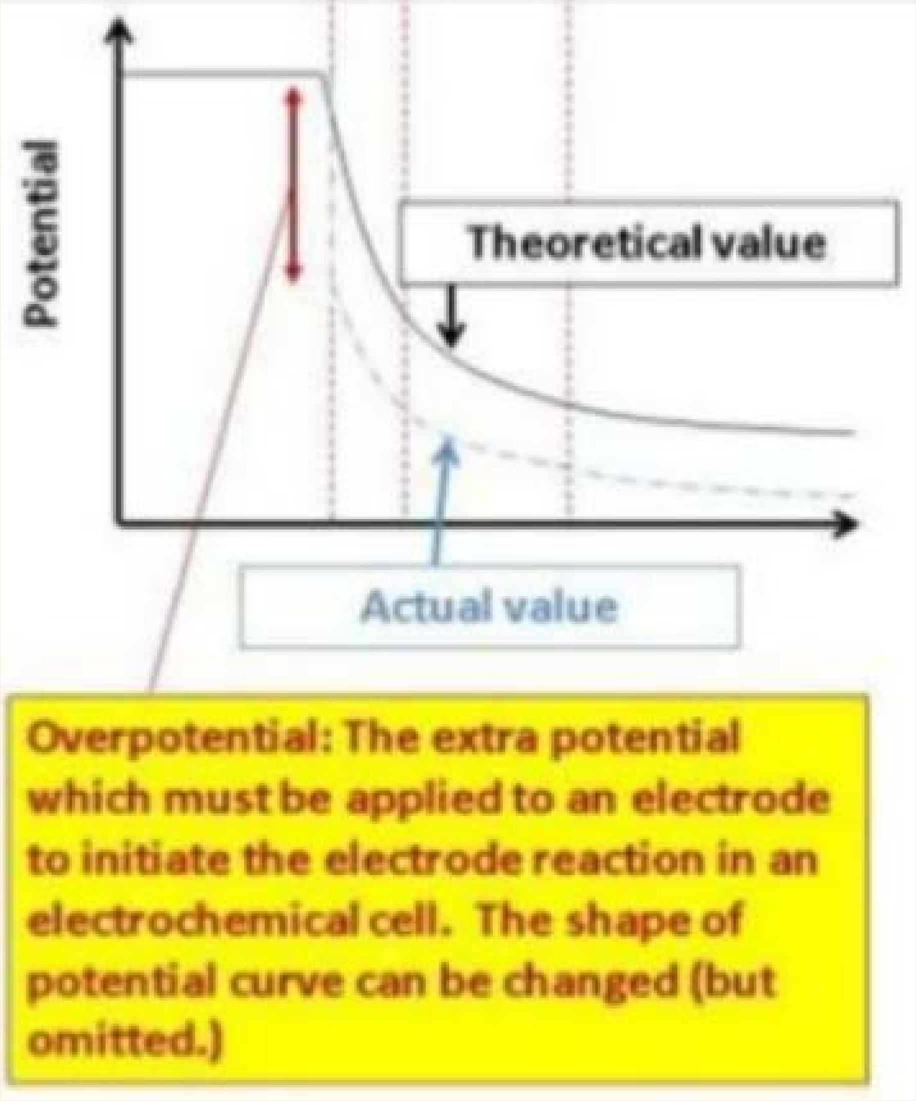
where j is the current density (A/cm^2)

Current Efficiency

- Deviations from Faraday’s law in industrial systems are associated with Faradic current losses appearing as heat or unwanted by-products, loss of material by spraying the solution, etc. The ratio of the actual amount of product (charge/electrons) obtained/spent in electrolysis to the theoretical amount of product (charge/electrons) calculated based on Faraday’s law is typically below one in the technological processes. This relation is called **current efficiency** (CE; faradaic or coulombic efficiency;
- $\mathrm{CE} = \frac{m_{actual}}{m_{theoretical}} = \frac{Q_{actual}}{Q_{theoretical}}$

Overpotential

- The extra potential which must be applied to an electrode to initiate the electrode reaction in an electrochemical cell.
- The difference between equilibrium potential (E) and applied potential (Ej) required to initiate the initiate the electrode reactions is called overpotential (ΔE).
- $\Delta E = Ej - E$
- The cell overpotential is considered to be composed of a number of independent contributions:
- 1) Ohmic drop
- 2) Activation overpotential
- 3) Diffusion overpotential



Overpotential: The extra potential which must be applied to an electrode to initiate the electrode reaction in an electrochemical cell. The shape of potential curve can be changed (but omitted.)

(1) Ohmic drop (IR)

- (1) Ohmic drop(IR) between electrodes results from the fact that the electrolyte solution has finite conductivity. An ohmic potential drop always occurs between the working electrode and the reference electrode. This contribution to polarization is equal to IR, where I is the current density, and R is the resistance.

(2) Activation overpotential

- Activation overpotential at one or both electrodes arising from kinetic inhibition of one of the steps involved in the electrode reaction (desolvation of the reactive ion, chemisorption of the reaction product, etc.).
- Activation polarization is caused by a slow electrode reaction. The reaction at the electrode requires an activation energy in order to proceed.
- The most important example is that of hydrogen ion reduction at a cathode,

$H^+ + e^- \rightarrow 0.5H_2$

For this reaction, the polarization is called hydrogen overpotential. Overpotential is defined as the polarization (=potential change) of an equilibrium electrode that results from current flow across the electrode/solution interface. Hydrogen overpotential can vary with metal, current density, etc.

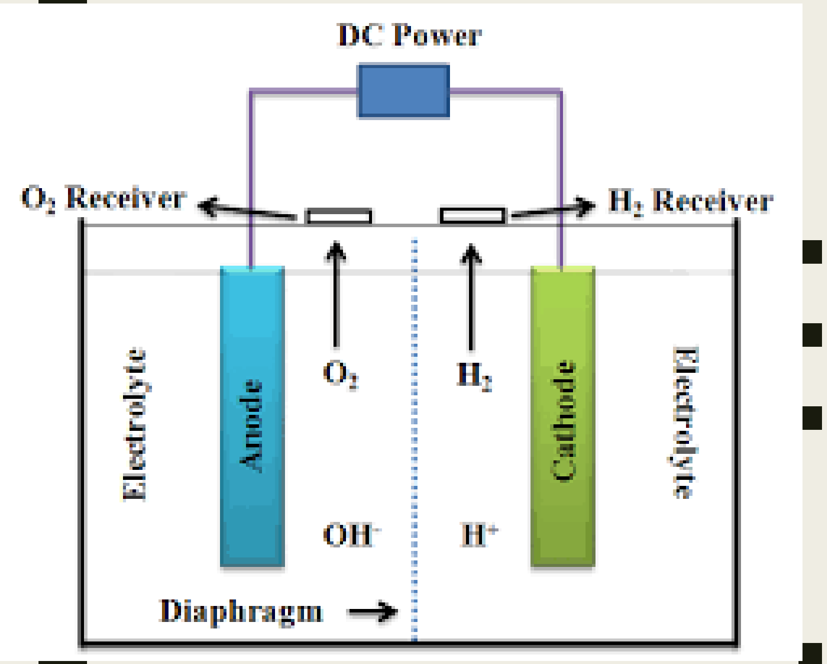
(3) Diffusion overpotential

- Diffusion overpotential at one or both electrodes due to the presence of concentration gradients in the vicinity of the electrode surface. As a result of electrochemical reaction, the concentration at the electrode surface no longer have their equilibrium values. If migration through the electric double layer is very rapid, then diffusion from the bulk of the solution towards the electrode will be unable to replenish the ions at the double layer quickly enough and a concentration gradient will result.
- Concentration polarization decreases with stirring, whereas activation polarization and IR drop are not affected significantly with stirring.

*Diffusion is due to a concentration gradient . Diffusion occurs for all species.

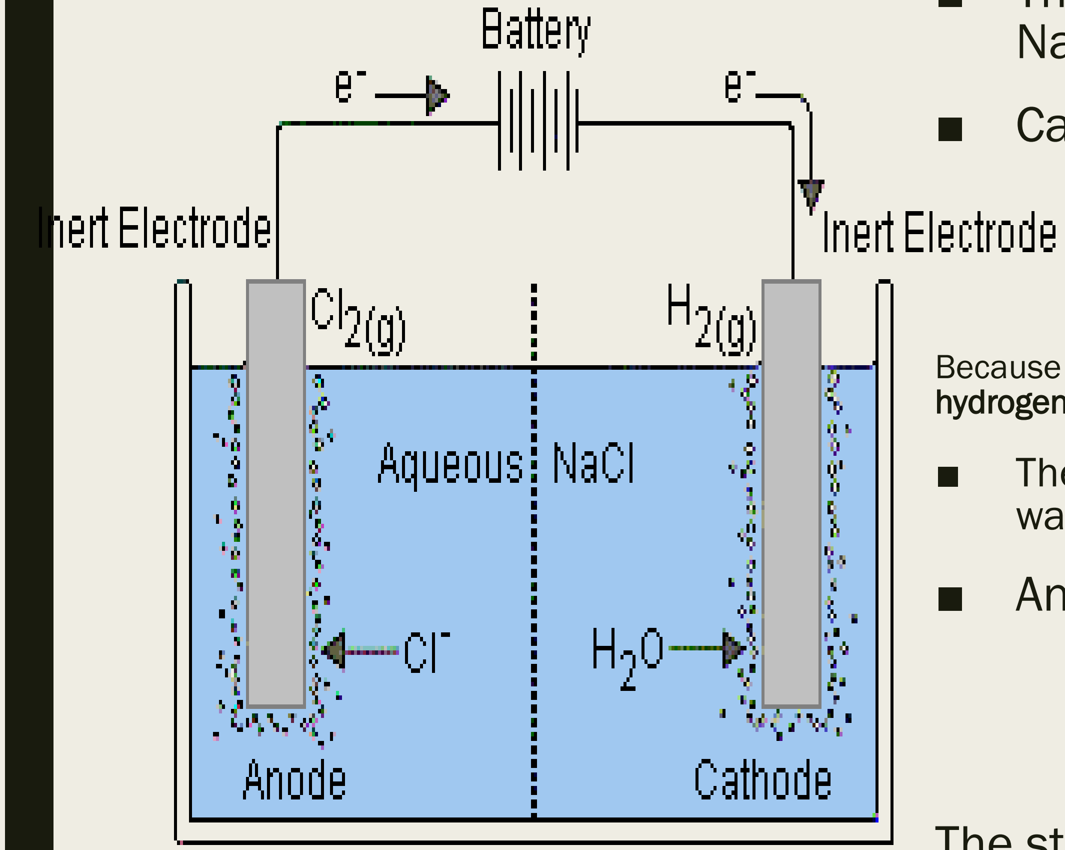
*Migration is due to electric field effects. Thus migration affects only charged species.

Electrolysis of Water



- Water is a very poor conductor of electricity. We therefore add an electrolyte to water to provide ions that can flow through the solution, thereby completing the electric circuit. The electrolyte must be soluble in water. It should also be relatively inexpensive. Most importantly, it must contain ions that are harder to oxidize or reduce than water.
- $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ $E^o_{red} = -0.83$ V
- $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ $E^o_{ox} = -1.23$ V
- The following cations are harder to reduce than water: Li+, Rb+, K+, Cs^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Na^+, and Mg^{2+}. Two of these cations are more likely candidates than the others because they form inexpensive, soluble salts: Na^+ and K^+.
- The SO_4^{2-} ion might be the best anion to use because it is the most difficult anion to oxidize. The potential for oxidation of this ion to the peroxydisulfate ion is -2.05 volts.
- $2\ SO_4^{2-} \rightarrow S_2O_8^{2-} + 2$ e- $E^o_{ox} = -2.05$ V
- When an aqueous solution of either Na_2SO_4 or K_2SO_4 is electrolyzed in the apparatus shown in the above figure, H_2 gas collects at one electrode and O_2 gas collects at the other.

The Electrolysis of Aqueous NaCl



- The Na^+ ions migrate toward the negative electrode and the Cl^- ions migrate toward the positive electrode.
- There are two substances that can be reduced at the cathode: Na^+ ions and water molecules.
- Cathode (-)

$Na^+ + e^- \rightarrow Na$ $\quad E^o_{red} = -2.71$ V

$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ $\quad E^o_{red} = -0.83$ V

Because it is much easier to reduce water than Na^+ ions, the **only product formed at the cathode is hydrogen gas.**

- There are also two substances that can be oxidized at the anode: Cl^- ions and water molecules.
- Anode (+)

$2\ Cl^- \rightarrow Cl_2 + 2$ e- $\quad E^o_{ox} = -1.36$ V

$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ $\quad E^o_{ox} = -1.23$ V

The standard-state potentials for these half-reactions are so close to each other that we might expect to see a mixture of **Cl_2 and O_2 gas collect at the anode.** In practice, the only product of this reaction is **Cl_2.**

- At first glance, it would seem easier to oxidize water (E^o_{ox} = -1.23 volts) than Cl^- ions (E^o_{ox} = -1.36 volts). It is worth noting, however, that the cell is never allowed to reach standard-state conditions. The solution is typically 25% NaCl by mass, which significantly decreases the potential required to oxidize the Cl^- ion. The pH of the cell is also kept very high, which decreases the oxidation potential for water. The deciding factor is a phenomenon known as **overvoltage**, which is the extra voltage that must be applied to a reaction to get it to occur at the rate at which it would occur in an ideal system.
- Under ideal conditions, a potential of 1.23 volts is large enough to oxidize water to O_2 gas. Under real conditions, however, it can take a much larger voltage to initiate this reaction. (The overvoltage for the oxidation of water can be as large as 1 volt.) By carefully choosing the electrode to maximize the overvoltage for the oxidation of water and then carefully controlling the potential at which the cell operates, we can ensure that only chlorine is produced in this reaction.

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