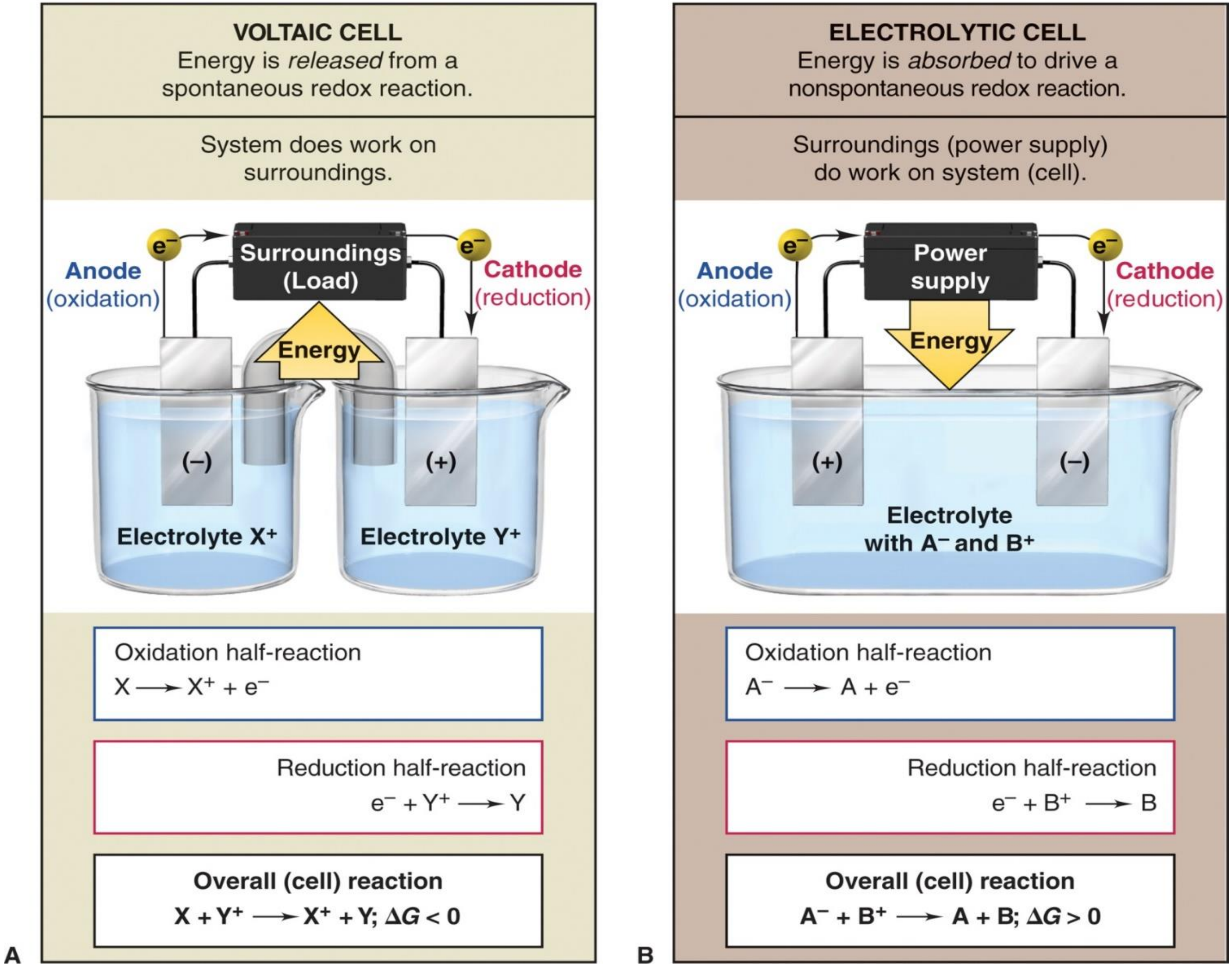
CHAPTER (2)

Review of Electrochemical Process Fundamentals

Part-1

General characteristics of (A) Galvanic (voltaic) and (B) Electrolytic cells



VOLTAIC CELL
Energy is *released* from a spontaneous redox reaction.

System does work on surroundings.

Oxidation half-reaction
$X \longrightarrow X^+ + e^-$

Reduction half-reaction
$e^- + Y^+ \longrightarrow Y$

Overall (cell) reaction
$\mathbf{X + Y^+ \longrightarrow X^+ + Y;\ \Delta G < 0}$

ELECTROLYTIC CELL
Energy is *absorbed* to drive a nonspontaneous redox reaction.

Surroundings (power supply) do work on system (cell).

Oxidation half-reaction
$A^- \longrightarrow A + e^-$

Reduction half-reaction
$e^- + B^+ \longrightarrow B$

Overall (cell) reaction
$\mathbf{A^- + B^+ \longrightarrow A + B;\ \Delta G > 0}$

Fundamental concepts: EC Reactions

- An electrochemical reaction is a heterogeneous chemical process involving the transfer of charge to or from an electrode, generally a metal, carbon or a semiconductor.
- The charge transfer may be a **cathodic process** in which an otherwise stable species is reduced by the transfer of electrons from an electrode.
- Examples of cathodic reactions important in electrochemical technology:

Hydrogen gas production: $2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$ (1.1)

Metal electrodeposition: $Cu^{2+} + 2\,e^- \rightarrow Cu$ (1.2)

Amalgam electrode formation: $Na^+ + e^- + Hg \rightarrow NaHg$ (1.3)

Automobile batteries: $PbO_2 + 4\,H^+ + SO_4^{2-} + 2\,e^- \rightarrow PbSO_4 + 2\,H_2O$ (1.4)

Fundamental concepts: EC Reactions

Conversely, the charge transfer may be an anodic process where an otherwise stable species is oxidized by the removal of electrons to the electrode. Examples of anodic reactions important in electrochemical technology:

Oxygen gas production: $2H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ (1.5)

Chlorine gas production: $2Cl^- \rightarrow Cl_2 + 2e^-$ (1.6)

Electrolytic thickening of metal oxide layer:

$2Al + 3H_2O \rightarrow Al_2O_3 + 6\ H^+ + 6\ e^-$ (1.7)

Methanol Fuel Cell: $CH_3OH + H_2O \rightarrow CO_2 + 6\ H^+ + 6\ e^-$ (1.8)

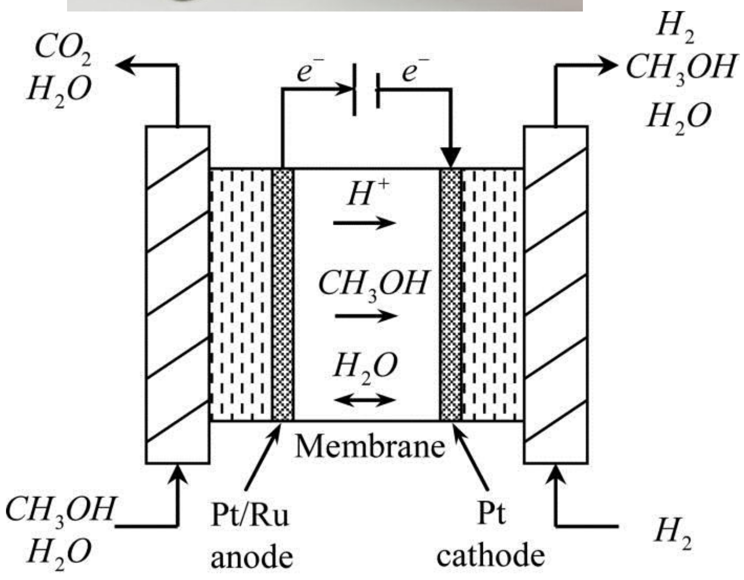
Other industrially important reactions (both cathodic and anodic) are given in the following Tables.

Example Application of EC Reactions

Amalgam electrode :

Sodium amalgam Electrode ($Na(Hg) \mid Na^+$)
$Na(Hg) \rightarrow Na^+ + e^-$

1) More readily reversible
2) Do not react with water
3) Avoid impurities formation
4) Pt wire dipping into the amalgam pool



Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode: $6H^+ + 6e^- \rightarrow 3H_2$

Overall: $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$

- Anodized Aluminum has a naturally formed layer of aluminum oxide which is then thickened by an electrolytic process.
- This makes the metal harder and non-reactive.

Examples of Important Inorganic EC Reactions

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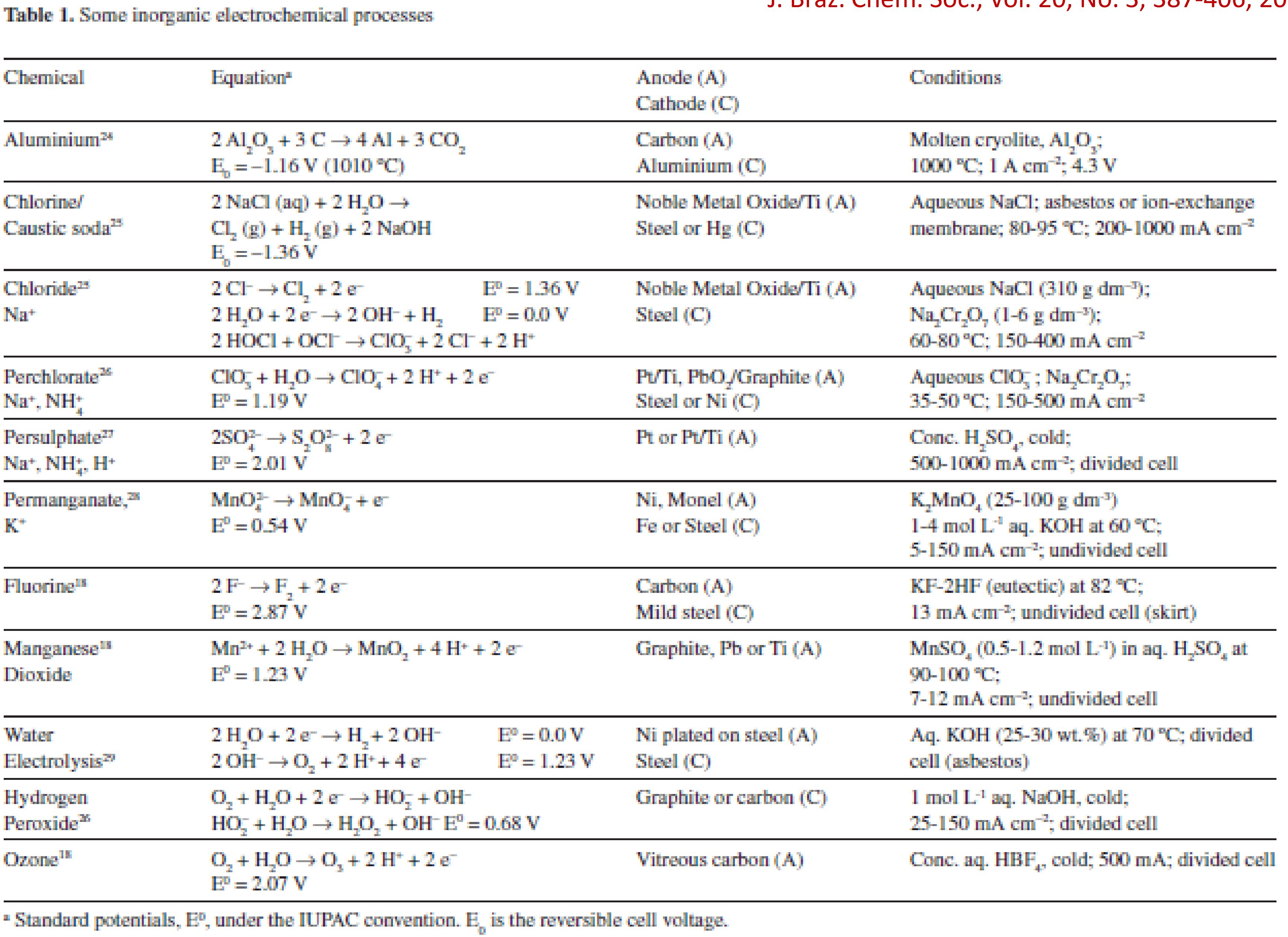

Table 1. Some inorganic electrochemical processes

Chemical	Equation[a]	Anode (A) Cathode (C)	Conditions
Aluminium[24]	$2\ Al_2O_3 + 3\ C \rightarrow 4\ Al + 3\ CO_2$ $E_0 = -1.16$ V (1010 °C)	Carbon (A) Aluminium (C)	Molten cryolite, Al_2O_3; 1000 °C; 1 A cm^{-2}; 4.3 V
Chlorine/ Caustic soda[25]	$2\ NaCl\ (aq) + 2\ H_2O \rightarrow$ $Cl_2\ (g) + H_2\ (g) + 2\ NaOH$ $E_0 = -1.36$ V	Noble Metal Oxide/Ti (A) Steel or Hg (C)	Aqueous NaCl; asbestos or ion-exchange membrane; 80-95 °C; 200-1000 mA cm^{-2}
Chloride[25] Na^+	$2\ Cl^- \rightarrow Cl_2 + 2\ e^-$ $E^0 = 1.36$ V $2\ H_2O + 2\ e^- \rightarrow 2\ OH^- + H_2$ $E^0 = 0.0$ V $2\ HOCl + OCl^- \rightarrow ClO_3^- + 2\ Cl^- + 2\ H^+$	Noble Metal Oxide/Ti (A) Steel (C)	Aqueous NaCl (310 g dm^{-3}); $Na_2Cr_2O_7$ (1-6 g dm^{-3}); 60-80 °C; 150-400 mA cm^{-2}
Perchlorate[26] Na^+, NH_4^+	$ClO_3^- + H_2O \rightarrow ClO_4^- + 2\ H^+ + 2\ e^-$ $E^0 = 1.19$ V	Pt/Ti, PbO_2/Graphite (A) Steel or Ni (C)	Aqueous ClO_3^- ; $Na_2Cr_2O_7$; 35-50 °C; 150-500 mA cm^{-2}
Persulphate[27] Na^+, NH_4^+, H^+	$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\ e^-$ $E^0 = 2.01$ V	Pt or Pt/Ti (A)	Conc. H_2SO_4, cold; 500-1000 mA cm^{-2}; divided cell
Permanganate,[28] K^+	$MnO_4^{2-} \rightarrow MnO_4^- + e^-$ $E^0 = 0.54$ V	Ni, Monel (A) Fe or Steel (C)	K_2MnO_4 (25-100 g dm^{-3}) 1-4 mol L^{-1} aq. KOH at 60 °C; 5-150 mA cm^{-2}; undivided cell
Fluorine[18]	$2\ F^- \rightarrow F_2 + 2\ e^-$ $E^0 = 2.87$ V	Carbon (A) Mild steel (C)	KF-2HF (eutectic) at 82 °C; 13 mA cm^{-2}; undivided cell (skirt)
Manganese[18] Dioxide	$Mn^{2+} + 2\ H_2O \rightarrow MnO_2 + 4\ H^+ + 2\ e^-$ $E^0 = 1.23$ V	Graphite, Pb or Ti (A)	$MnSO_4$ (0.5-1.2 mol L^{-1}) in aq. H_2SO_4 at 90-100 °C; 7-12 mA cm^{-2}; undivided cell
Water Electrolysis[29]	$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ $E^0 = 0.0$ V $2\ OH^- \rightarrow O_2 + 2\ H^+ + 4\ e^-$ $E^0 = 1.23$ V	Ni plated on steel (A) Steel (C)	Aq. KOH (25-30 wt.%) at 70 °C; divided cell (asbestos)
Hydrogen Peroxide[26]	$O_2 + H_2O + 2\ e^- \rightarrow HO_2^- + OH^-$ $HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$ $E^0 = 0.68$ V	Graphite or carbon (C)	1 mol L^{-1} aq. NaOH, cold; 25-150 mA cm^{-2}; divided cell
Ozone[18]	$O_2 + H_2O \rightarrow O_3 + 2\ H^+ + 2\ e^-$ $E^0 = 2.07$ V	Vitreous carbon (A)	Conc. aq. HBF_4, cold; 500 mA; divided cell

[a] Standard potentials, E^0, under the IUPAC convention. E_0 is the reversible cell voltage.

Examples of Industrial Organic EC Reactions

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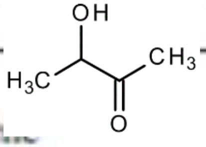
Table 2. Examples of industrial organic electrosynthesis processes



Product	Starting Material	Company
Acetoin	Butanone	BASF
1-Acetoxynaphthale	Naphthalene	BASF
Acetylenedicarboxylic acid	1,4-Butynediol	BASF
Adipoin dimethyl acetal	Cyclohexanone	BASF
Adiponitrile	Acrylonitrile	Monsanto (Solutia), BASF,
2-Aminobenzyl alcohol	Anthranilic acid	BASF
4-Aminomethylpyridine	4-Cyanopyridine	Reilly Tar
Anthraquinone	Anthracene	L. B. Holliday, ECRC
Anthraquinone	Naphthalene, butadiene	Hydro Quebec
Arabinose	Gluconate	Electrosynthesis Co.
Azobenzene	Nitrobenzene	Johnson Matthey Company
Bleached montan wax	Raw montan wax	Clariant
1,2,3,4-Butanetetracarboxylic acid	Dimethyl maleate	Monsanto
p-*t*-Butylbenzaldehyde	*p*-*t*-Butyltoluene	BASF, Givaudan
Calcium gluconate	Glucose	Sandoz, India

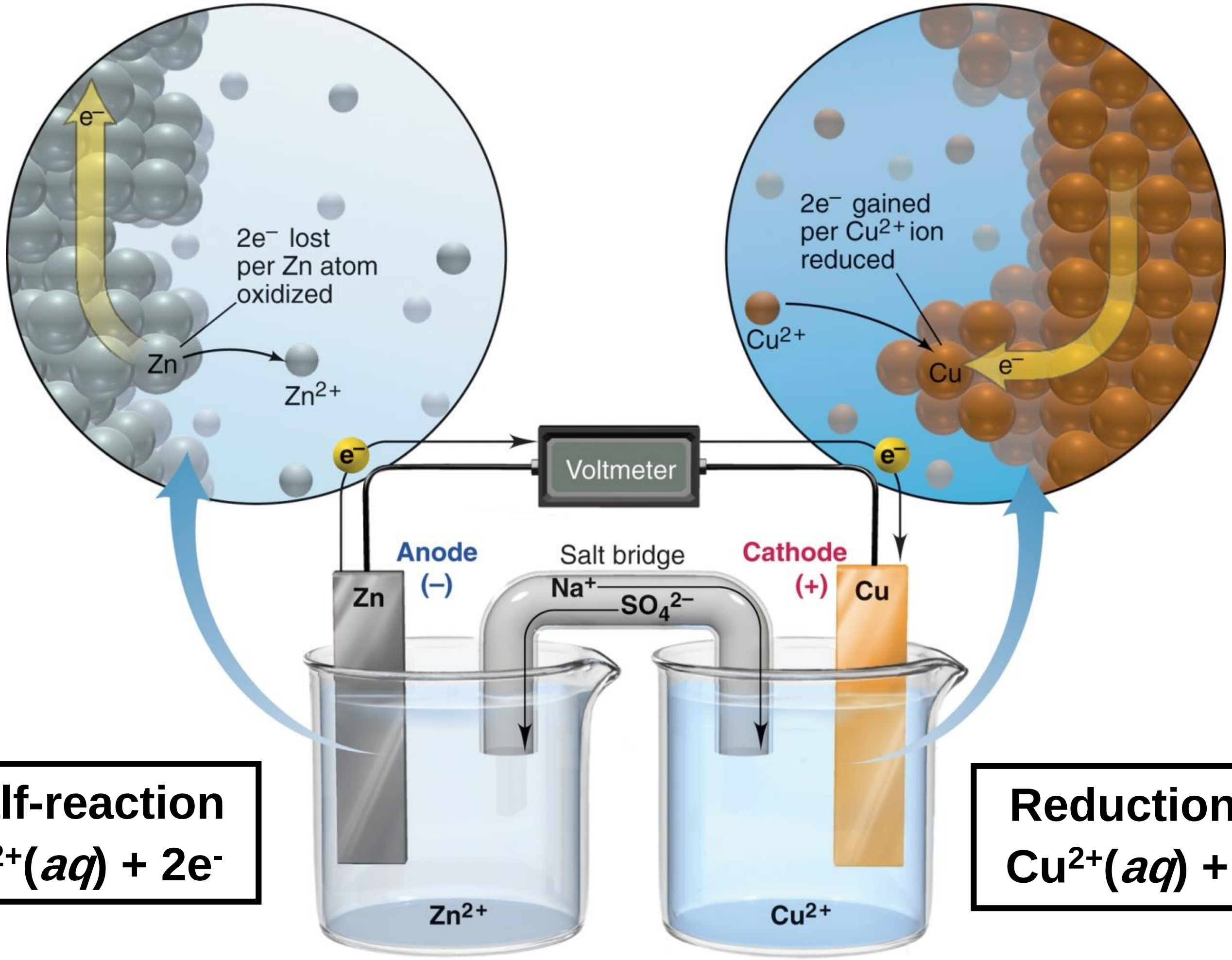
Active and Inactive Electrodes

- An *active* electrode is an active component in its half-cell and is a *reactant or product* in the overall reaction.

- An *inactive* electrode provides a surface for the reaction and completes the circuit. It does not participate actively in the overall reaction.

- Inactive electrodes are necessary when none of the reaction components can be used as an electrode.
- Inactive electrodes are usually unreactive substances such as ***graphite*** **or** ***platinum*.**

A Galvanic cell using active electrodes (Cu, Zn)



Oxidation half-reaction

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

Reduction half-reaction

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

Overall (cell) reaction

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

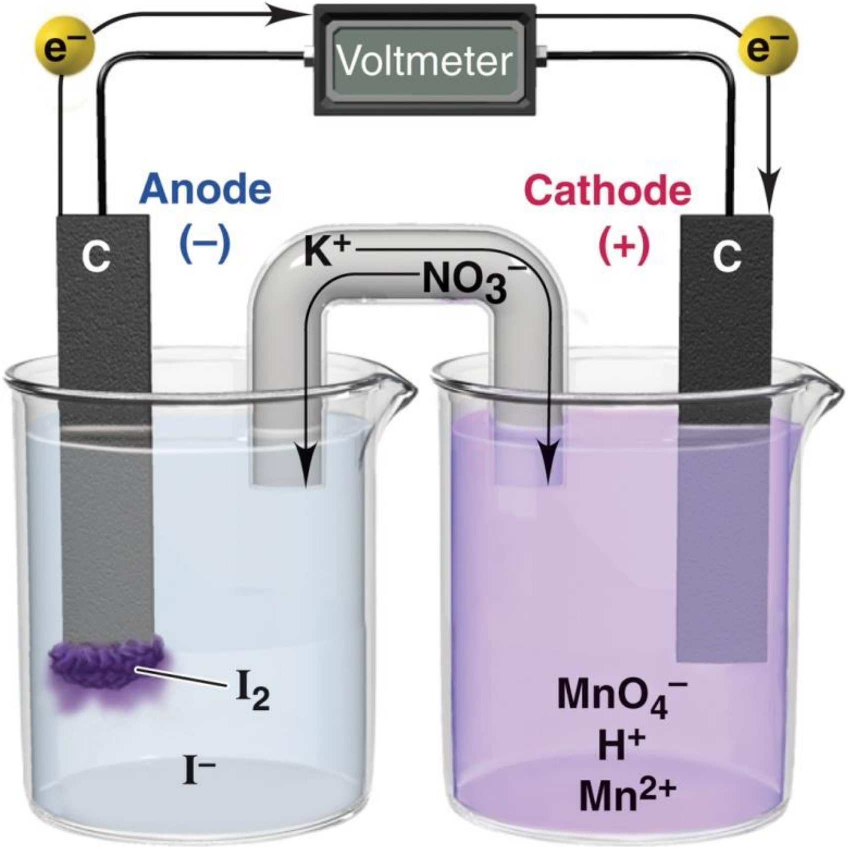
A Galvanic cell using inactive electrodes (Carbon)

Oxidation half-reaction

$2I^-(aq) \rightarrow I_2(s) + 2e^-$

Reduction half-reaction

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$



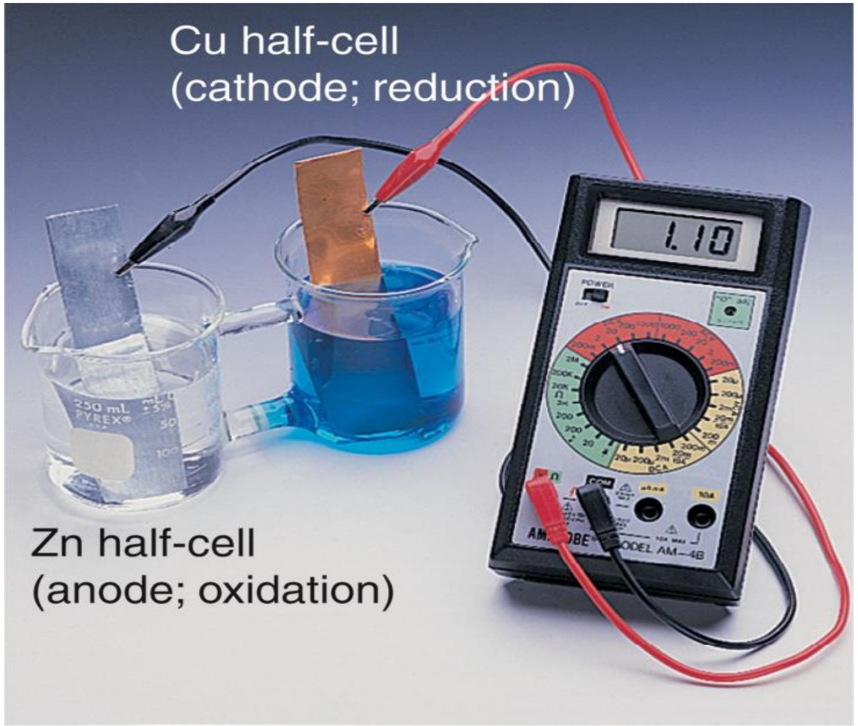
Overall (cell) reaction

$2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(s) + 8H_2O(l)$

Table 21.1 Voltages of Some Galvanic* Cells

Galvanic Cell	Voltage (V)
Common alkaline flashlight battery	1.5
Lead-acid car battery (6 cells ≈ 12 V)	2.1
Calculator battery (mercury)	1.3
Lithium-ion laptop battery	3.7

The standard cell potential is designated E°_{cell} and is measured at a specified temperature with no current flowing and all components in their standard states.



***Also known as Voltaic cells.**

Cell Thermodynamics: Efficiency

- The electrochemical parameters we have explored so far are linked with the Gibbs' Free Energy to establish the thermodynamic model of galvanic cells. Work is the negative of charge times potential:

$$w = -Q.E$$

where Q is the charge and can be defined as Q = nF where F is the Faraday constant (96485 C/mol). We are interested in the maximum work since this can be related to the thermodynamic parameter ΔG.

- Thus, for the case where the work is done infinitely slowly (chemical system is always at equilibrium with the electrodes, electrical resistance is zero since current is essentially zero, etc…) we have: $w_{max} = -Q.E_{max}$

where Emax for standard conditions is simply E° as calculated from the tabulated half-cell potentials.

Example:

- A cell with a maximum cell potential of 2.50 V. If 1.33 mol of electrons passes through the cell at an average potential E = 2.10 V. What is the **cell efficiency**?

Solution:

$w = – Q E = – nFE = 1.33 \text{ mol} × 96485 \text{ C/mol} × 2.10 \text{ V}$ (V = J/C)

$w = – 2.69 × 105 \text{ J} = – 269 \text{ kJ}$

$w_{max} = – nFE_{max} = 1.33 \text{ mol} × 96485 \text{ C/mol} × 2.50 \text{ V} = – 321 \text{ kJ}$

- **Efficiency** = $w/w_{max} × 100\% = –269/–321 × 100\% = 83.8\ \%$

- Of course, since w_{max} is only achievable if the work is done reversibly (infinitely slowly), we can never reach 100% efficiency in any system in the real world.

Cell Thermodynamics:
Cell Potential and Electrolyte Concentration

Nernst Equation

$$E_{cell} = E°_{cell} - \frac{RT}{nF} \ln Q$$

- When Q < 1, [reactant] > [product], ln Q < 0, so $E_{cell} > E°_{cell}$
- When Q = 1, [reactant] = [product], ln Q = 0, so $E_{cell} = E°_{cell}$
- When Q > 1, [reactant] < [product], ln Q > 0, so $E_{cell} < E°_{cell}$

We can simplify the equation as before for *T* = 298.15 K:

$$E_{cell} = E°_{cell} - \frac{0.0592\ \mathrm{V}}{n} \log Q$$

Cell Thermodynamics: Interrelationship of $\Delta G°$, $E°_{cell}$ and K

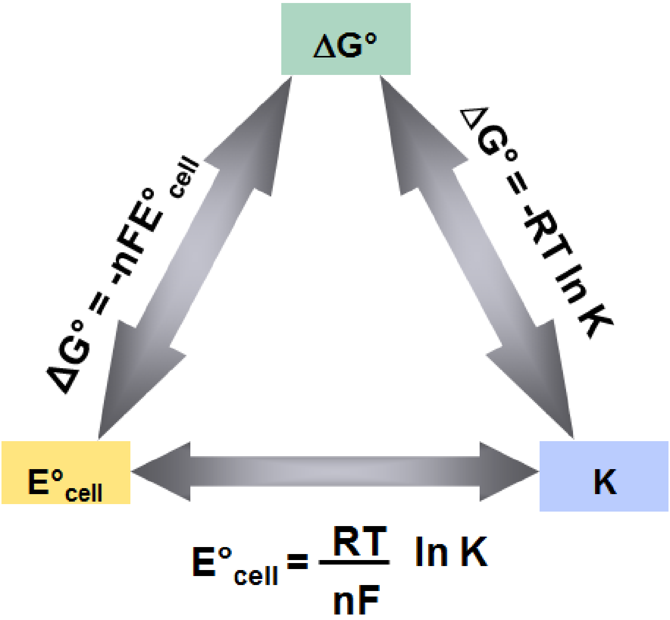
- We already have seen that ΔG is a measure of the maximum work obtainable from a system. Thus:

$$\Delta G = w_{max} \quad \text{and} \quad \Delta G = -QE = -nFE$$

- In this case, the potential is the cell potential E_{cell}.

$$\Delta G° = -RT \ln K = -nFE°_{cell}.$$

- Thus, we now have a link between free-energy, equilibrium and electrochemical thermodynamic parameters.



Reaction Parameters at the Standard State

$\Delta G°$	K	$E°_{cell}$	Reaction at standard-state conditions
< 0	> 1	> 0	spontaneous
0	1	0	at equilibrium
> 0	< 1	< 0	Non-spontaneous

Cell Thermodynamics: Application of Nernst Equation

Example: In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a Zn/Zn^{2+} half-cell and an H_2/H^+ half-cell under the following conditions:

$[Zn^{2+}] = 0.010$ M $[H^+] = 2.5$ M $P_{H_2} = 0.30$ atm

Calculate E_{cell} at 298 K.

Solution: To apply the Nernst equation and determine E_{cell}, we must know E°_{cell} and Q. We write the equation for the spontaneous reaction and calculate E°_{cell} from standard electrode potentials. We must convert the given pressure to molarity in order to have consistent units.

$$\begin{array}{lll} (1)\ \ 2H^+(aq) + 2e^- & \rightarrow H_2(g) & E^\circ = 0.00\text{ V} \\ (2)\ \ Zn(s) & \rightarrow Zn^{2+}(aq) + 2e^- & E^\circ = -0.76\text{ V} \\ \hline \end{array}$$

$$2H^+(aq) + Zn(s) \rightarrow H_2(g) + Zn^{2+}(aq) \quad E^\circ_{cell} = 0.00 - (-0.76) = 0.76\text{ V}$$

Cell Thermodynamics: Application of Nernst Equation

Solution (Cont'd):

Converting pressure to molarity:

$$\frac{n}{V} = \frac{P}{RT} = \frac{0.30\ \text{atm}}{0.0821\ \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}}\ \text{x}\ 298.15\ \text{K}} = 1.2\text{x}10^{-2}\ M$$

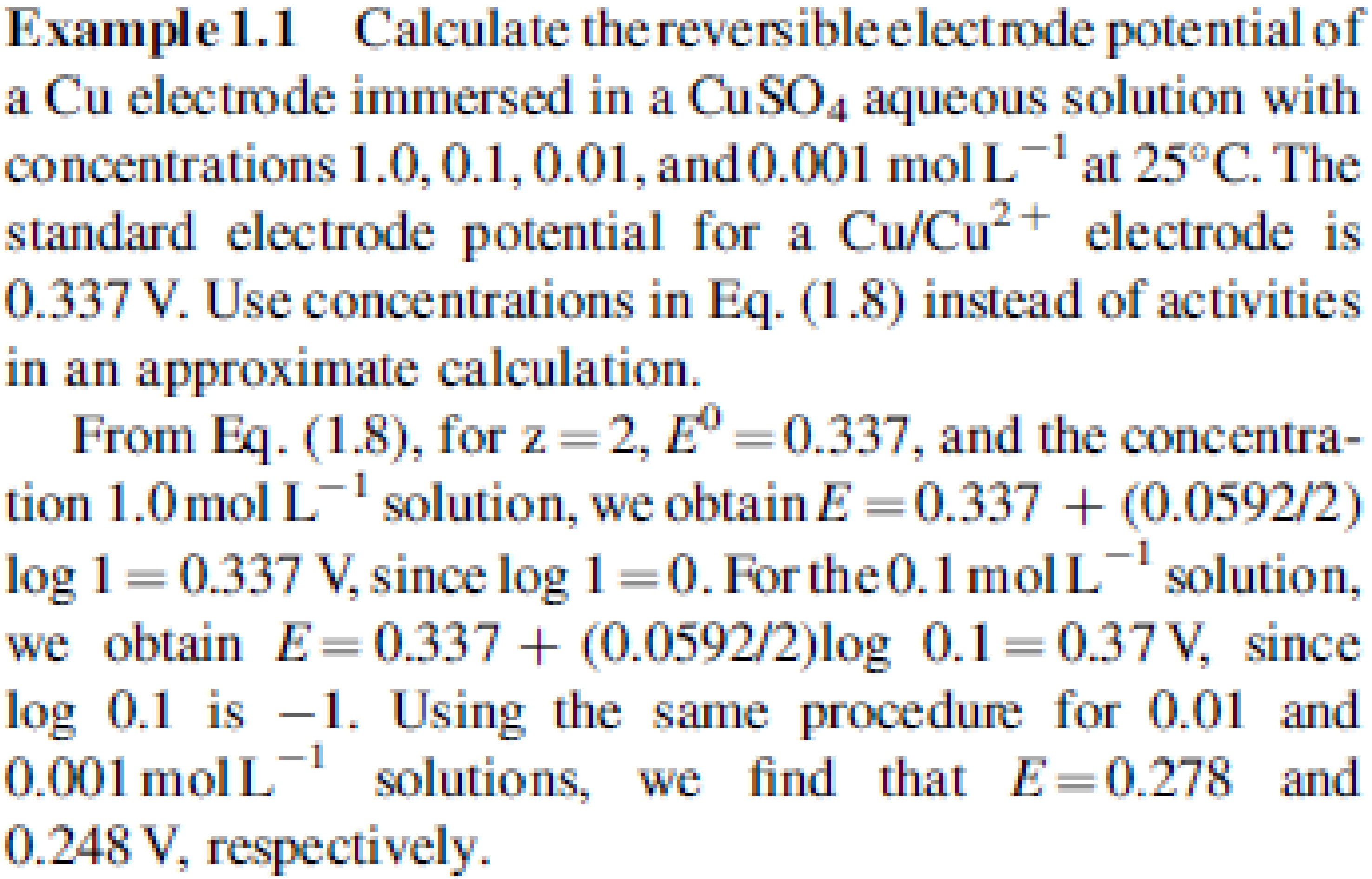
$$Q = \frac{[H_2][Zn^{2+}]}{[H^+]^2} = \frac{0.012\ \text{x}\ 0.010}{(2.5)^2} = 1.9\text{x}10^{-5}$$

Solving for E_{cell} at 25°C (298.15 K), with $n = 2$:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592\ \text{V}}{n} \log Q$$

$$= 0.76\ \text{V} - \left(\frac{0.0592\ \text{V}}{2} \log(1.9\text{x}10^{-5})\right) = 0.76 - (-0.14\ \text{V})\ \boxed{\mathbf{= 0.90\ V}}$$

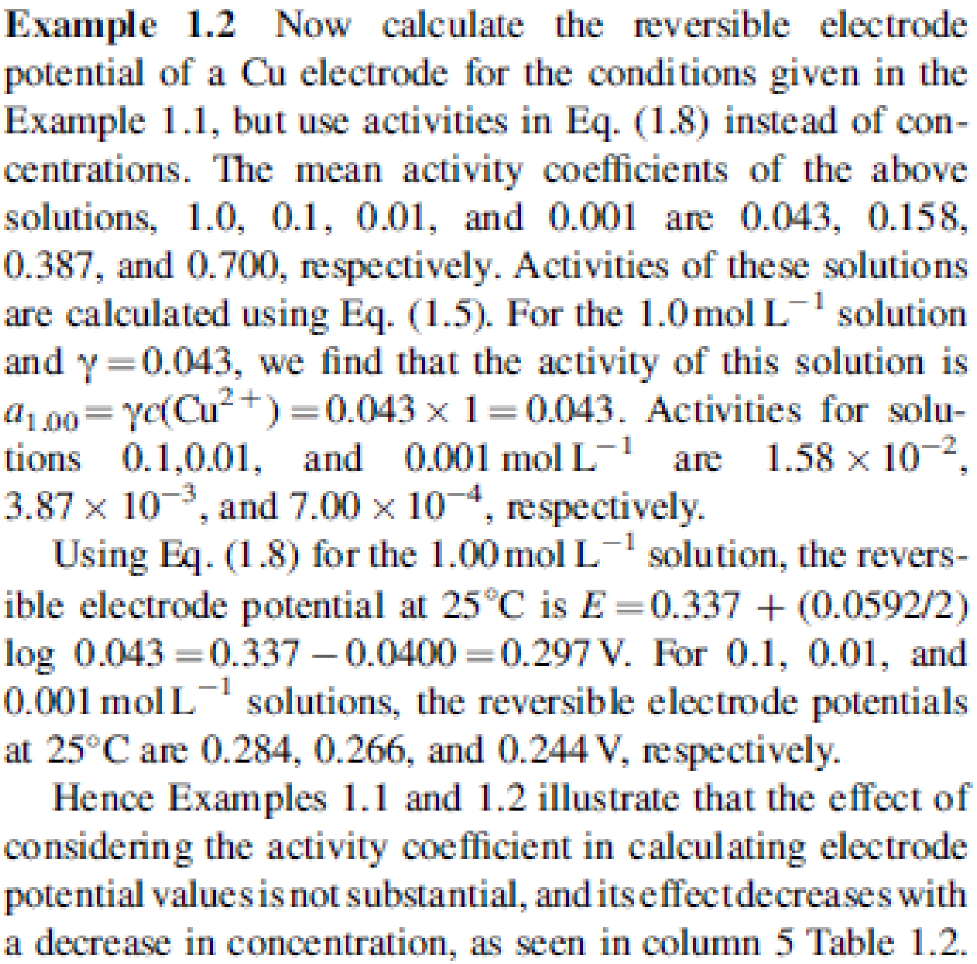
Cell Thermodynamics: Reversible Potential



Example 1.1 Calculate the reversible electrode potential of a Cu electrode immersed in a $CuSO_4$ aqueous solution with concentrations 1.0, 0.1, 0.01, and 0.001 mol L^{-1} at 25°C. The standard electrode potential for a Cu/Cu^{2+} electrode is 0.337 V. Use concentrations in Eq. (1.8) instead of activities in an approximate calculation.

From Eq. (1.8), for $z = 2$, $E^0 = 0.337$, and the concentration 1.0 mol L^{-1} solution, we obtain $E = 0.337 + (0.0592/2) \log 1 = 0.337$ V, since $\log 1 = 0$. For the 0.1 mol L^{-1} solution, we obtain $E = 0.337 + (0.0592/2) \log 0.1 = 0.37$ V, since $\log 0.1$ is -1. Using the same procedure for 0.01 and 0.001 mol L^{-1} solutions, we find that $E = 0.278$ and 0.248 V, respectively.

Cell Thermodynamics: Reversible Potential & Activity



Example 1.2 Now calculate the reversible electrode potential of a Cu electrode for the conditions given in the Example 1.1, but use activities in Eq. (1.8) instead of concentrations. The mean activity coefficients of the above solutions, 1.0, 0.1, 0.01, and 0.001 are 0.043, 0.158, 0.387, and 0.700, respectively. Activities of these solutions are calculated using Eq. (1.5). For the 1.0 mol L^{-1} solution and $\gamma = 0.043$, we find that the activity of this solution is $a_{1.00} = \gamma c(\mathrm{Cu}^{2+}) = 0.043 \times 1 = 0.043$. Activities for solutions 0.1,0.01, and 0.001 mol L^{-1} are 1.58×10^{-2}, 3.87×10^{-3}, and 7.00×10^{-4}, respectively.

Using Eq. (1.8) for the 1.00 mol L^{-1} solution, the reversible electrode potential at 25°C is $E = 0.337 + (0.0592/2) \log 0.043 = 0.337 - 0.0400 = 0.297$ V. For 0.1, 0.01, and 0.001 mol L^{-1} solutions, the reversible electrode potentials at 25°C are 0.284, 0.266, and 0.244 V, respectively.

Hence Examples 1.1 and 1.2 illustrate that the effect of considering the activity coefficient in calculating electrode potential values is not substantial, and its effect decreases with a decrease in concentration, as seen in column 5 Table 1.2.

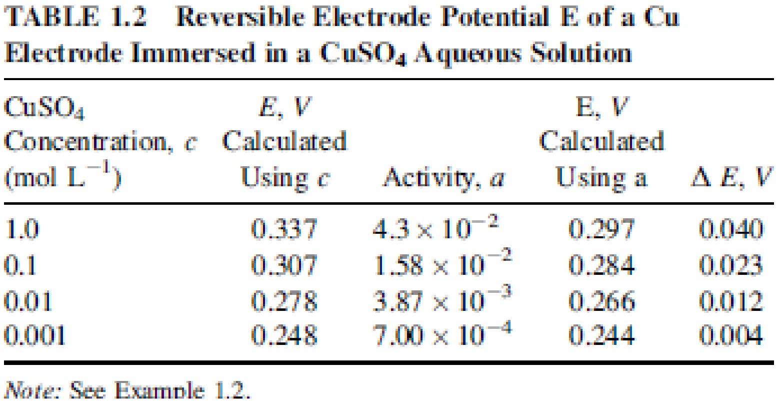
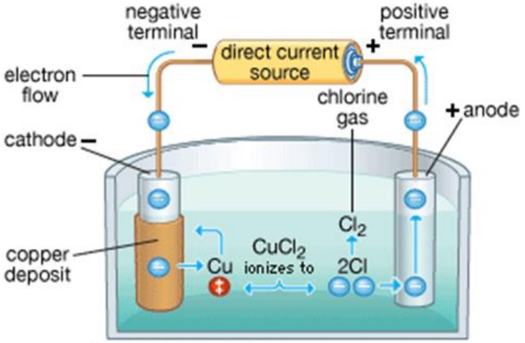


TABLE 1.2 Reversible Electrode Potential E of a Cu Electrode Immersed in a $CuSO_4$ Aqueous Solution

$CuSO_4$ Concentration, c (mol L^{-1})	E, V Calculated Using c	Activity, a	E, V Calculated Using a	ΔE, V
1.0	0.337	4.3×10^{-2}	0.297	0.040
0.1	0.307	1.58×10^{-2}	0.284	0.023
0.01	0.278	3.87×10^{-3}	0.266	0.012
0.001	0.248	7.00×10^{-4}	0.244	0.004

Note: See Example 1.2.

ELECTROLYSIS PRINCIPLES AND PRACTICE



electrolysis of $CuCl_2$

- When an electric current is forced to pass through an electrolyte or electrolyte solution, chemical reactions take place both at the anode and at the cathode.
- The stoichiometry of these reactions obeys Faraday's laws of electrolysis (next Section).
- However, when several different reactions are possible at an electrode of an electrolytic cell then the process which actually does take place will be determined by *the potential of the electrode.*
  - The reactions which take place in electrolytic cells are those reactions which require the *least potential difference* between the two electrodes.

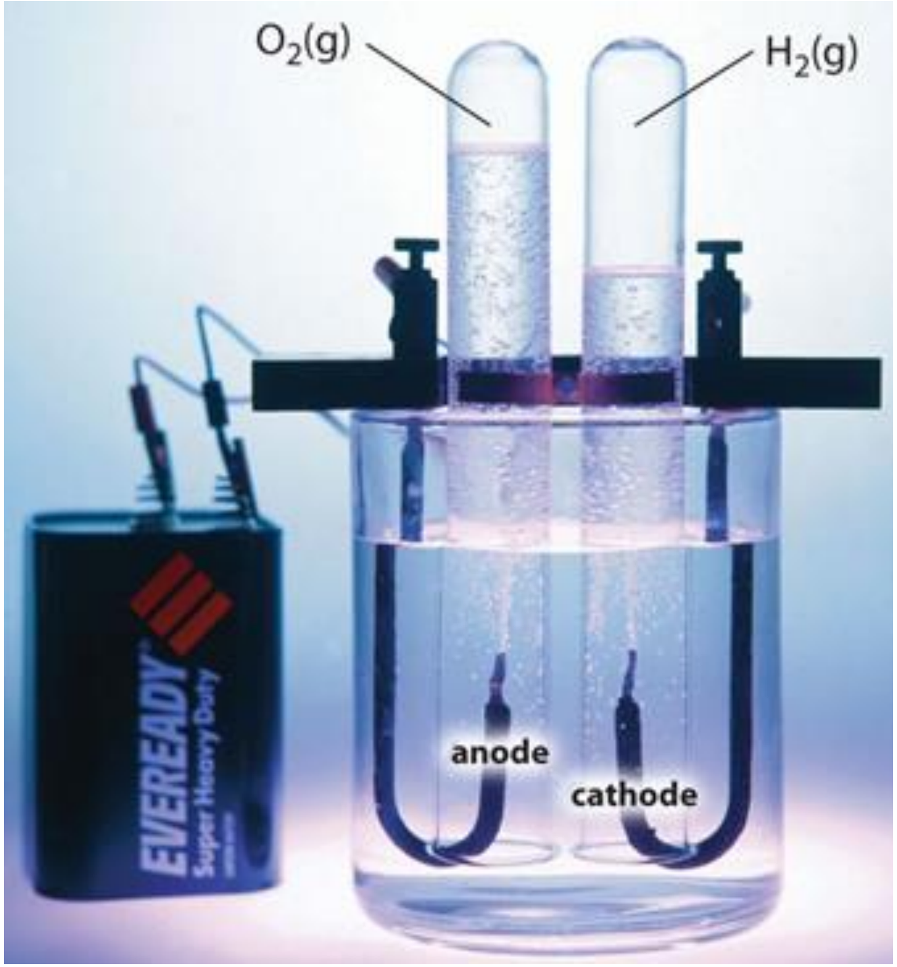
Principles of Electrolysis

The reactions which occur at the electrodes during electrolysis will be the oxidation and the reduction of the solvent (normally water) unless some solute is more easily oxidized or reduced than is the solvent:

a) Electrolysis of an aqueous solution of Na_2SO_4 will produce hydrogen at the cathode and oxygen at the anode because reduction of $H^+(aq)$ is easier than is reduction of $Na^+(aq)$ and oxidation of water is easier than is oxidation of aqueous sulfate ion.

   The actual potentials will be close to the standard potentials, and the standard potential of $H^+(aq)/H_2(g)$ is less negative than is the standard potential of $Na^+(aq)/Na$, while the standard potential of $O_2(g)/H_2O$ is less positive than the standard potential of sulfate oxidation.

Principles of Electrolysis



The electrolysis of water

Overall (cell) reaction
$2H_2O(l) \rightarrow H_2(g) + O_2(g)$

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

Reduction half-reaction
$2H_2O(l) + 4e^- \rightarrow 2H_2(g) + 2OH^-(aq)$

Principles of Electrolysis

b) Electrolysis of an aqueous solution of copper sulfate will produce copper at the cathode because both the Cu2+/Cu and Cu+/Cu couples have standard potentials which are considerably less negative than the standard potential of hydrogen.

The electrolysis will again produce oxygen at the anode, because Cu2+(aq) cannot be further oxidized in aqueous solution.

c) Electrolysis of an aqueous solution of NaBr will produce hydrogen at the cathode as the aqueous sodium sulfate solution did, but at the anode aqueous NaBr solutions will produce bromine gas because the standard potential of bromide oxidation is less positive than that of the oxidation of water.

Principles of Electrolysis

d) Electrolysis of a solution of aqueous CuBr2 will produce copper at the cathode and bromine at the anode because these are the least negative possible reduction and the least positive possible oxidation reactions in that solution.

In general,

- The anode reaction in any electrolysis will always be the oxidation which occurs at the least positive potential and the cathode reaction will always be the reduction which occurs at the least negative potential.
- In setting up an **electrolysis cell**,
  - we must take into account all possible reactions and make sure the conditions are set so that the desired reaction occurs.
  - We will do this at first by using only inert electrodes and then by using pure electrolyte liquids rather than aqueous (or other) solutions.

Faraday's Laws of Electrolysis

1- The mass of an element discharged at an electrode m is directly proportional to the amount of electrical charge Q passed through the electrode: $\mathbf{m\ \alpha\ Q}$

Since: $\mathbf{Q = I\ t}$ therefore, $\mathbf{m\ \alpha\ I\ t}$

2- If the same amount of electrical charge Q is passed through several electrodes, the mass m of an element discharged at each electrode will be directly proportional to both (a) the atomic mass of the element, and (b) the number of moles of electrons required to discharge one mole of the element from whatever material is being discharged at the electrode (the charge number z):

$$\mathbf{m\ \alpha\ M/z}$$

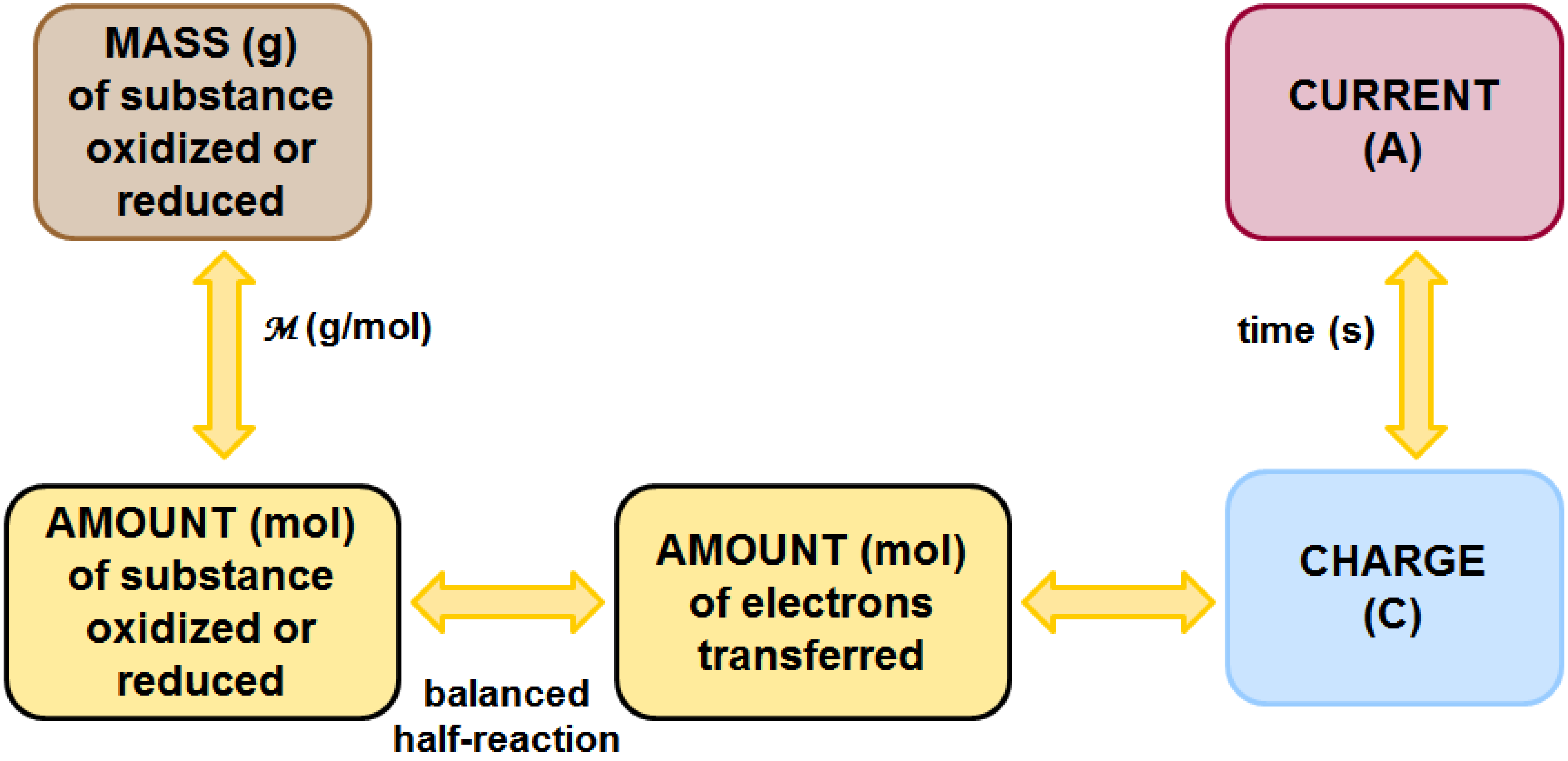
Combining the two laws: $\mathbf{m\ \alpha\ M\ I\ t/z}$ **.**

The proportionality constant was found to be 1/F where F = Faraday, a constant which is equal to 96485 C (Coulomb/mol of electrons):

$\mathbf{m = M\ I\ t/zF}$ Since: $\mathbf{m/M = n}$ (the number of moles),

then: $\mathbf{n = I\ t/zF = Q/zF}$ or $\mathbf{Q = nzF}$

Diagram summarizes the stoichiometry of electrolysis



MASS (g) of substance oxidized or reduced

$\mathcal{M}$ (g/mol)

AMOUNT (mol) of substance oxidized or reduced

balanced half-reaction

AMOUNT (mol) of electrons transferred

CHARGE (C)

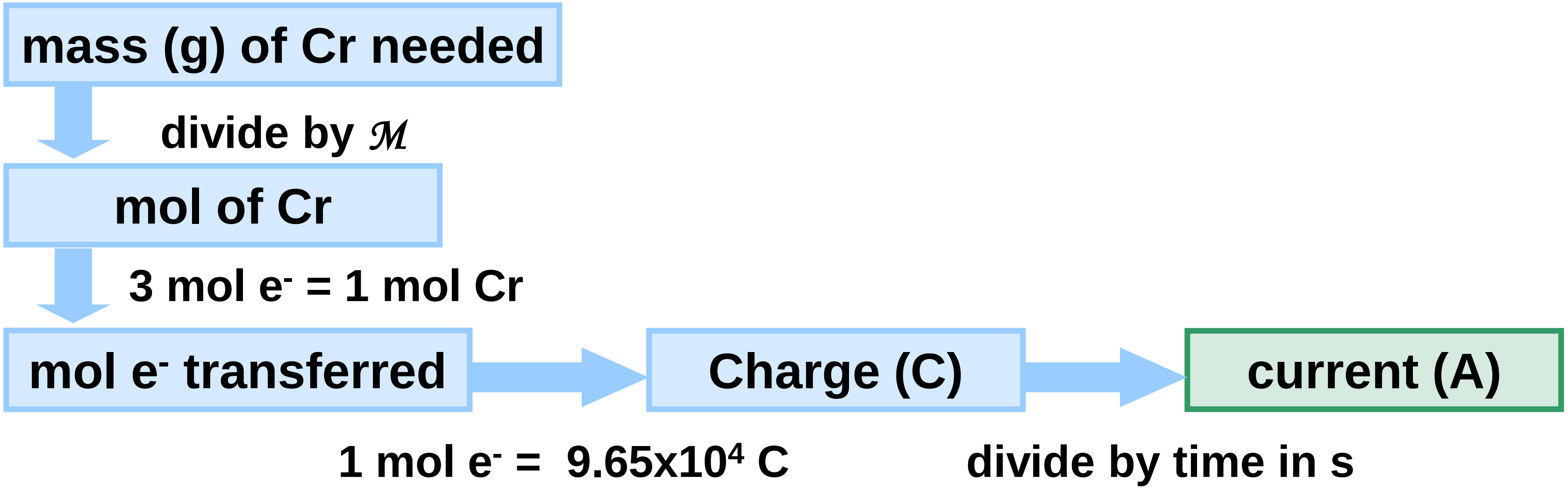
time (s)

CURRENT (A)

Example-1:

A technician plates a faucet with 0.86 g of Cr metal by electrolysis of aqueous $Cr_2(SO_4)_3$. If 12.5 min is allowed for the plating, what current is needed?

Solution To find the current, we divide charge by time, so we need to find the charge. We write the half-reaction for Cr^{3+} reduction to get the amount (mol) of e^- transferred per mole of Cr. We convert mass of Cr needed to amount (mol) of Cr. We can then use the Faraday constant to find charge and current.



mass (g) of Cr needed

divide by $\mathcal{M}$

mol of Cr

3 mol e^- = 1 mol Cr

mol e^- transferred

1 mol e^- = 9.65×10^4 C

Charge (C)

divide by time in s

current (A)

Example-1

Solution

$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$

$$0.86 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Cr}} = 0.050 \text{ mol e}^-$$

$$\text{Charge (C)} = 0.050 \text{ mol e}^- \times \frac{9.65\text{x}10^4 \text{ C}}{1 \text{ mol e}^-} = 4.8\text{x}10^3 \text{ C}$$

$$\text{Current (A)} = \frac{\text{charge (C)}}{\text{time (s)}} = \frac{4.8\text{x}10^3 \text{ C}}{12.5 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 6.4 \text{ C/s} = \mathbf{6.4\ A}$$

Example-2.

- If one kilogram of copper is to be deposited by means of the electrochemical reaction **Cu2+ + 2e- → Cu**, we can calculate how many coulombs will be required. If a constant current of 10 amperes is used to carry out this deposition, we can calculate how long it will take.

Solution:

One kilogram of Cu is 1000/63.456 moles Cu;

since one mole Cu requires two moles of electrons, we need 1000 x 2/63.456 = 31.52 moles of electrons.

Since one mole of electrons equals one Faraday or 96,485 coulombs:

96,485 x 31.6 = 3.041 x 10+6 coulombs are needed.

One ampere is one coulomb/sec, so 10 A = 3.41 x 10+6 coulombs/time (s), therefore, time = 3.041 x 10+5 seconds.

Since 1 hour = 60 x 60 = 3600 s,

the electrolysis will take 3.041 x 10+5/3.6 x 10+3 = 84.47 hours.

Example-3

- A current of 1.375 A flows for 96 s through a silver cathode in an aqueous solution of silver nitrate.

- The mass of silver deposited on the cathode is calculated as follows:

  - The electrical charge Q = 1.375 A x 96 s = 132 coulombs,
  - which is equivalent to 132/96485 = 1.368 mmol of electrons.
  - Since the deposition reaction is: **$Ag^+ + e^- \rightarrow Ag$,**
  - This corresponds to 1.368 mmol of silver metal whose mass is (107.868 g/mol)(0.001368 mol) = 0.1476 g.

Electrolysis of Aqueous Salt Solutions

When an aqueous salt solution is electrolyzed:

- The strongest oxidizing agent (most positive electrode potential) is reduced, and
- The strongest reducing agent (most negative electrode potential) is oxidized.

Overvoltage* is the additional voltage needed (above that predicted by E° values) to produce gases at metal electrodes.

Overvoltage needs to be taken into account when predicting the products of electrolysis for aqueous solutions.

Overvoltage is 0.4 – 0.6 V for $H_2(g)$ or $O_2(g)$.

*Discussed later.

Products of Electrolysis

- Other metals (which are not quite as reactive as Na and Mg, but are sufficiently reactive that they cannot be produced in an aqueous cell), can be also produced this way.
- **Aluminum** is one such metal. The Hall process, developed in 1886, allowed for the production of aluminum on an industrial scale.
- There are three factors that determine product that we will find in any given electrolysis cell:
    1. the electrode material,
    2. the solvent and
    3. the electrolyte.
- Often, we use inert electrodes and/or pure liquids to help alleviate some of the complications from competing chemistry.
- Sometimes, we must simply carefully adjust conditions (concentrations and voltages) to ensure that the desired product is achieved.

Predicting the Electrolysis Products

Example-4: What products form at which electrode during electrolysis of aqueous solution of the following salts?

(a) KBr **(b)** $AgNO_3$ **(c)** $MgSO_4$

Solution:

We identify the reacting ions and compare their electrode potentials with those of water, taking the 0.4 – 0.6 V overvoltage into account. The reduction half-reaction with the less negative $E°$ occurs at the cathode, while the oxidation half-reaction with the less positive $E°$ occurs at the anode.

(a) KBr

$$K^+(aq) + e^- \rightarrow K(s) \qquad E° = -2.93$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.42V$$

Despite the overvoltage, which makes E for the reduction of water between -0.8 and -1.0 V, H_2O is still easier to reduce than K^+, so **$H_2(g)$ forms at the cathode**.

Solution (Cont'd):

$$2Br^{-}(aq) \rightarrow Br_2(l) + 2e^{-} \qquad E^{\circ} = 1.07\ V$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 4e^{-} \qquad E^{\circ} = 0.82\ V$$

The overvoltage makes *E* for the oxidation of water between 1.2 and 1.4 V. Br^{-} is therefore easier to oxidize than water, so **$Br_2(g)$ forms at the anode**.

(b) $AgNO_3$

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s) \qquad E^{\circ} = 0.80\ V$$

$$2H_2O(l) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq) \qquad E^{\circ} = -0.42V$$

As the cation of an inactive metal, Ag^{+} is a better oxidizing agent than H_2O, so **Ag(*s*) forms at the cathode**.

NO_3^{-} cannot be oxidized, because N is already in its highest (+5) oxidation state. Thus **$O_2(g)$ forms at the anode:**

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

Solution (Cont'd):

(c) $MgSO_4$ $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ $E° = -2.37$ V

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E° = -0.42$V

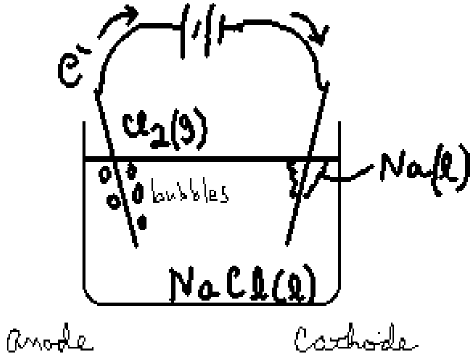
Mg^{2+} is a much weaker oxidizing agent than H_2O, so **$H_2(g)$ forms at the cathode**.

SO_4^{2-} cannot be oxidized, because S is already in its highest (+6) oxidation state.

Thus **$O_2(g)$ forms at the anode:**

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

Principles of Electrolysis



Molten Electrolyte:

- Consider the following electrolytic cell. Use a non-aqueous system such as molten NaCl as the medium and non-reactive (inactive) electrodes like platinum to successfully separate out pure Na.
- This is a very important method of producing sodium metal.
  - At the anode, Cl2 is evolved in the reaction:

$$2Cl^{-} = Cl_2(g) + 2e^{-}$$

  - At the Cathode, the molten sodium ions are converted to sodium metal (liquid at these temperatures) in the reaction

$$Na^{+} + e^{-} = Na(l)$$

- Alkali earth metals which are also highly reactive can be prepared using electrolysis of molten chloride salts as in the reaction:

$$MgCl(l) = Mg(l) + Cl_2(g)$$

Principles of Electrolysis

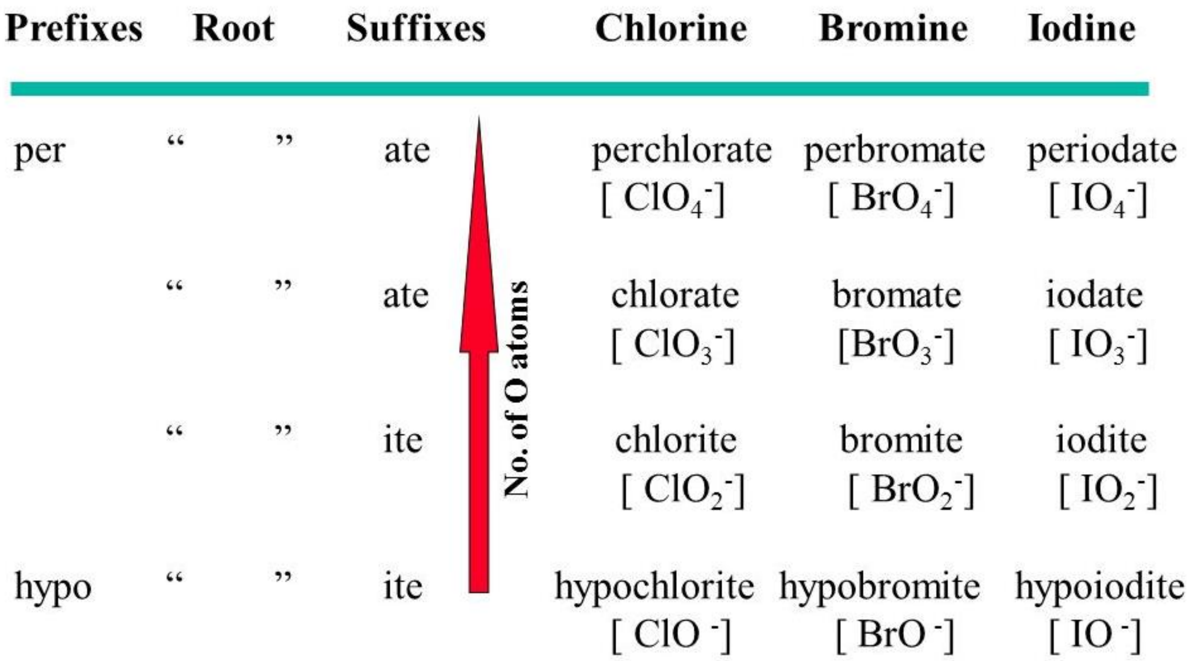
- Complication: Cl– we have seen to be more easily oxidized than water even though it has an oxidation potential (negative of the reduction potential for Cl2) which is more negative than that for water. This is due to *kinetics.*

- The water reaction is quite slow and requires a large voltage to force it to proceed with any speed. The Cl– oxidizes to Cl2 much more rapidly and the **overvoltage** we apply in an attempt to force the water to oxidize is sufficient to produce Cl2 which occurs faster.

	Reaction involves:	**Anode**	**Cathode**
1	Electrolyte	Anions oxidized	Cations reduced
2	Solvent	Solvent oxidized	Solvent reduced
3	Electrode	Electrode oxidized	Electrode reduced

Summary of the Electrolysis of Aqueous Salt Solutions

1. Cations of less active metals (Au, Ag, Cu, Cr, Pt, Cd) are reduced to the metal.
2. Cations of more active metals are <u>not</u> reduced. H_2O is reduced instead.
3. Anions that are oxidized, because of overvoltage from O_2 formation, include the halides, except for F^-.
4. Anions that are <u>not</u> oxidized include F^- and common oxoanions. H_2O is oxidized instead.



Prefixes	Root	Suffixes	Chlorine	Bromine	Iodine
per	“ ”	ate	perchlorate $[ClO_4^-]$	perbromate $[BrO_4^-]$	periodate $[IO_4^-]$
	“ ”	ate	chlorate $[ClO_3^-]$	bromate $[BrO_3^-]$	iodate $[IO_3^-]$
	“ ”	ite	chlorite $[ClO_2^-]$	bromite $[BrO_2^-]$	iodite $[IO_2^-]$
hypo	“ ”	ite	hypochlorite $[ClO^-]$	hypobromite $[BrO^-]$	hypoiodite $[IO^-]$

CHAPTER (2)

Review of Electrochemical Process Fundamentals

Part-2

Dynamics of Electroactive Ions

- Electroactive ions are transferred from the bulk of solution to the electrode surface by the following three mechanisms of mass transfer:
-

1. Electrical migration, which occurs under the influence of the electrical field (Revisit conductivity, ion mobility and transport numbers in electrochemistry).

2. Molecular Diffusion, where the driving force for diffusion is the concentration gradient between bulk solution and electrode-solution interface.
   - The rate of diffusion is given by Fick's law:

$$\mathbf{N = D.\ dC/dx}$$

Dynamics of Electroactive Ions

Where:

N = flux of electroactive ion discharged at electrode, mol/cm2.s;

D = diffusivity of ion, cm2/s ; C = concentration of ion, mol/cm3 ;

x = distance traveled by the diffusing electroactive ion , cm (0 < x < δ).

- **The thickness (δ) of the Nernst diffusion boundary layer is the region near the electrode surface where the concentration of the electroactive ion decreases from Cb to Ci.**

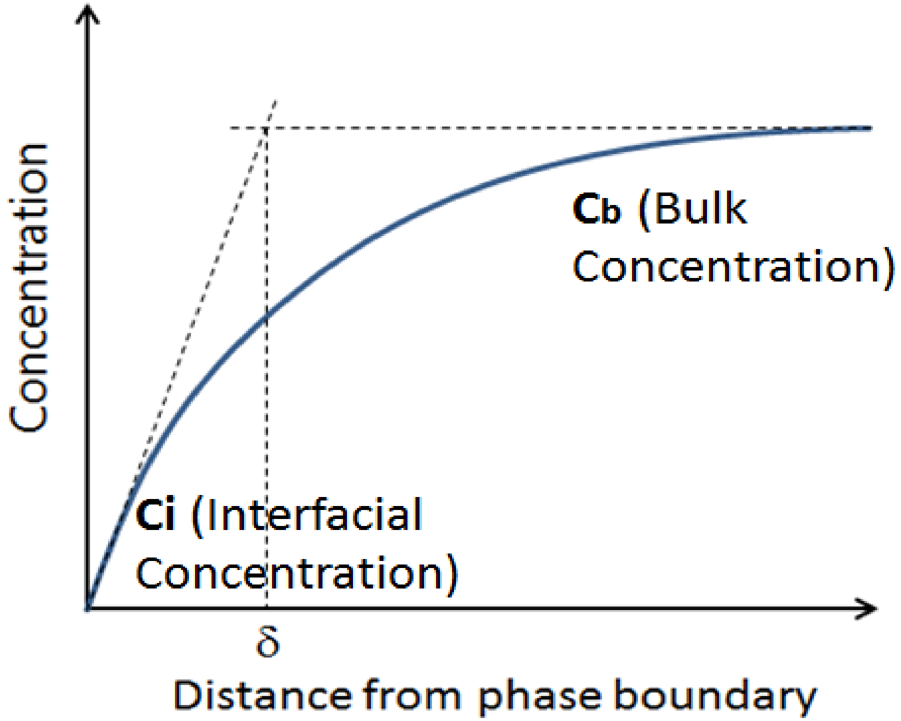


Figure (2.1):

Convective and Diffusive mass transfer of electroactive ion from bulk solution to electrode surface

Dynamics of Electroactive Ions

3. Natural convection:

This type of mass transfer arises from the density difference of solution between bulk and electrode surface.

Since the density of solution is proportional to its concentration, it follows that the density at the interface, ρi (corresponding to Ci) is lower than the bulk density, ρb (corresponding to Cb).

This density difference would cause an upflow of solution at the electrode surface resulting in replacing the dilute solution at the electrode surface with a fresh solution from the bulk of the cell.

4. Forced convection:

This type is prevailing when the electrolyte is mechanically mixed or circulated by pumping action. Fluid flow and velocity are important parameters to consider.

The processes occurring at the electrolyte-electrode surface are shown in **Figure (2-2).**

Dynamics of Electroactive Ions

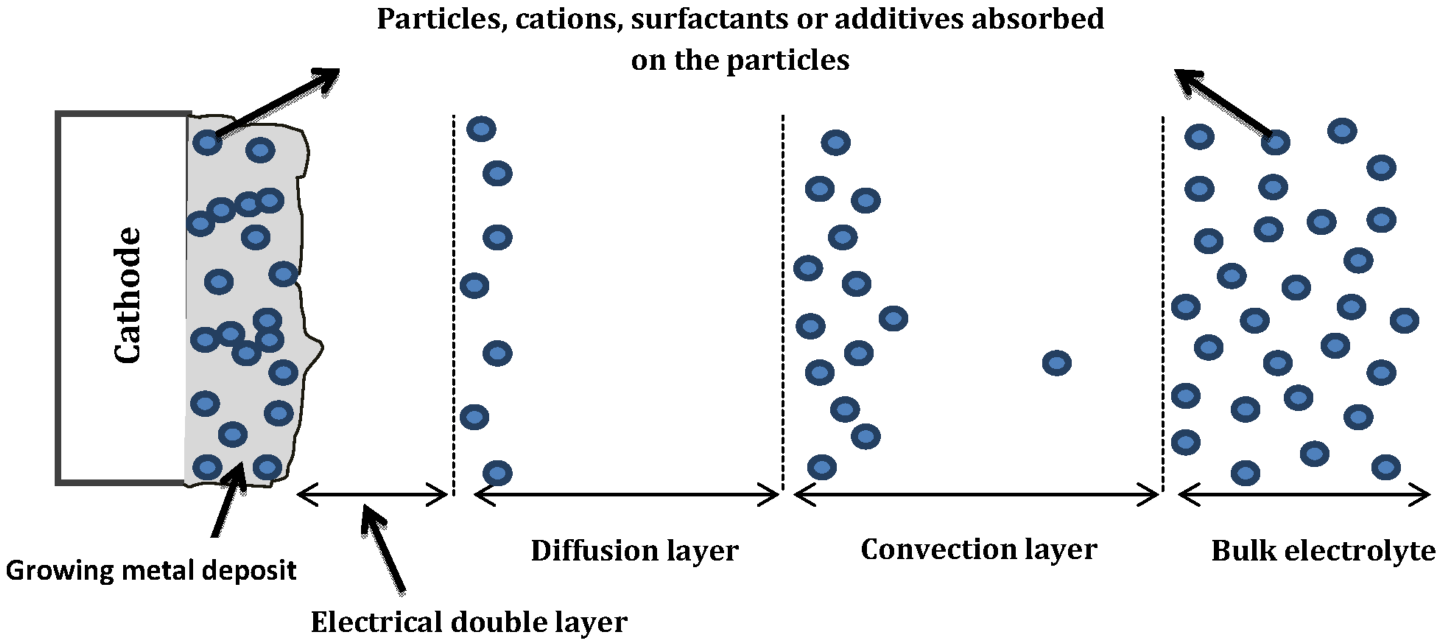
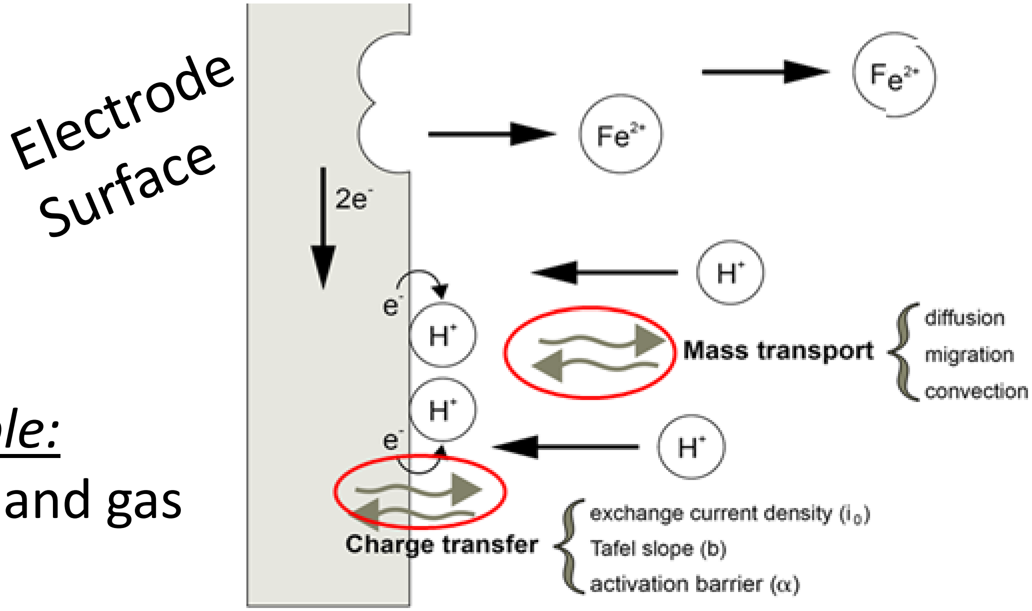


Figure 2.2

The processes occurring at an electrochemical interface (*Example:* metal dissolution from electrode and gas evolution at metal surface)



Deviations from Faraday's Laws

I. Current Inefficiency

II. Polarization (Overpotential):

A) Concentration Polarization:
B) Activation Polarization

I. Current Inefficiency

- In many electrochemical reactions, the actual amount of product is less than the theoretical amount calculated according to Faraday’s laws.
- The percentage ratio between the actually produced and the theoretically calculated amounts is known as “current efficiency”.
- This can be also defined as the fraction of the total current which is used in producing the main product.

<u>The major causes of current inefficiency are:</u>

a- **Occurrence of secondary reactions along with the main reaction:**

For example, in the deposition of zinc, hydrogen gas evolves simultaneously with zinc deposition:

$$\mathrm{Zn2+ + 2e- \rightarrow Zn} \qquad \text{(main)}$$

$$\mathrm{2\ H+ + 2e- \rightarrow H2} \qquad \text{(secondary)}$$

I. Current Inefficiency

b-Mixing of cathodic products with anodic products:

- In electrolysis of brine to produce NaOH and Cl_2 using graphite electrodes (for example), chlorine gas which is an anodic product dissolve in water and diffuse to the cathode where it reacts with the formed NaOH.
- Thus, undesirable products are obtained resulting in a loss in the yield of Cl_2 and NaOH:

$$NaCl \rightarrow Na^+ + Cl^- \qquad H_2O \rightarrow OH^- + H^+$$

$$2C1^- \rightarrow Cl_2 + 2e^- \qquad 2H^+ + 2e^- \rightarrow H_2$$

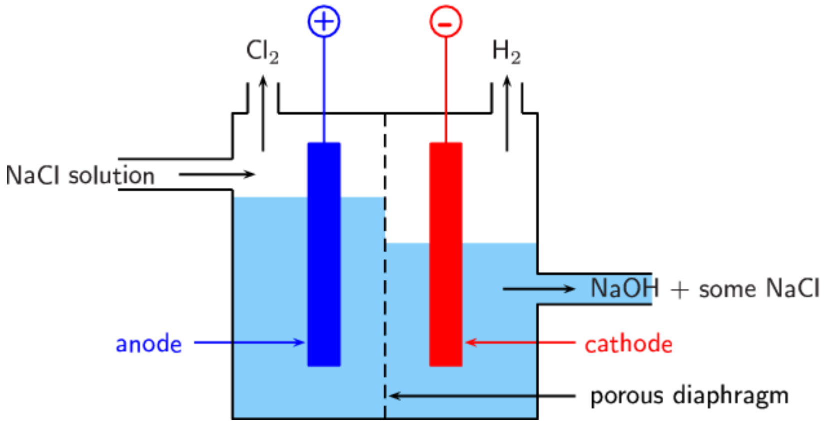
$$Na^+ + OH^- \rightarrow NaOH$$

- The desired products of NaOH and Cl_2 are lost by the reaction:

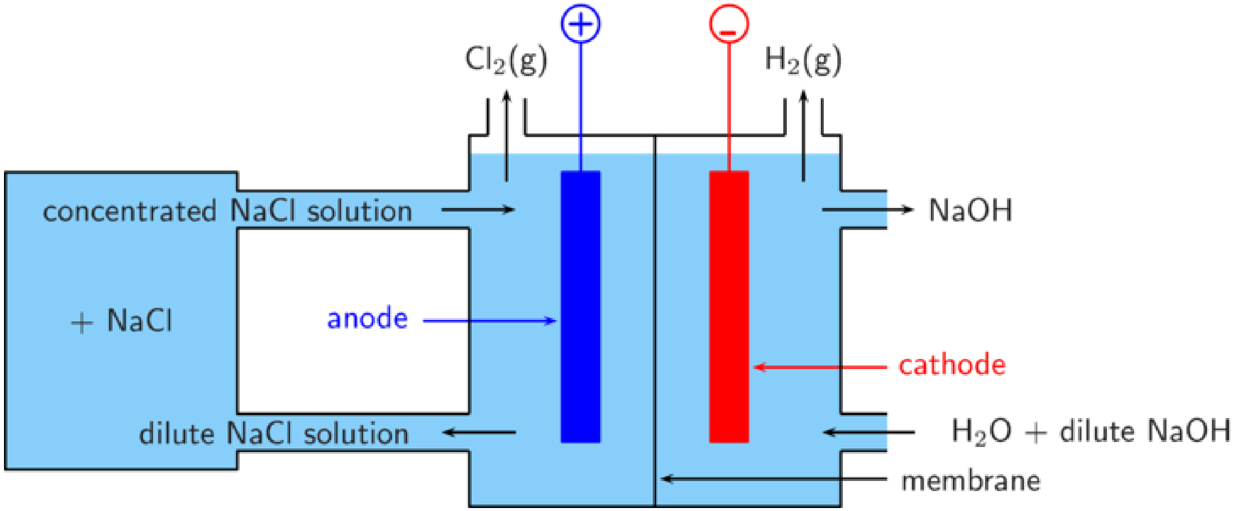
$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$$

I. Current Inefficiency

- To prevent the mixing of NaOH and chlorine, a porous diaphragm or membrane is used to divide the cell into separated anode and cathode compartments (see Figure 2.3 a & b).



a



b

I. Current Inefficiency

Current efficiency (η)

Feed is electrical charge

$$\eta = \frac{Q_{theoretical}}{Q_{effective}}$$

Product is mass produced

$$\eta = \frac{m_{effective}}{m_{theoretical}}$$

(effective here mean actual)

II- Polarization (Overpotential):

- This is the difference between the actual potential and the theoretical (*reversible*) potential required to complete an electrolysis process.
- It can also be defined as the extra voltage that should be added to the theoretical potential in order to complete an electrolysis process.
- The main types of polarization are the concentration polarization and the activation (or chemical) polarization. A third type id the voltage losses due to Ohmic resistance in the cell.

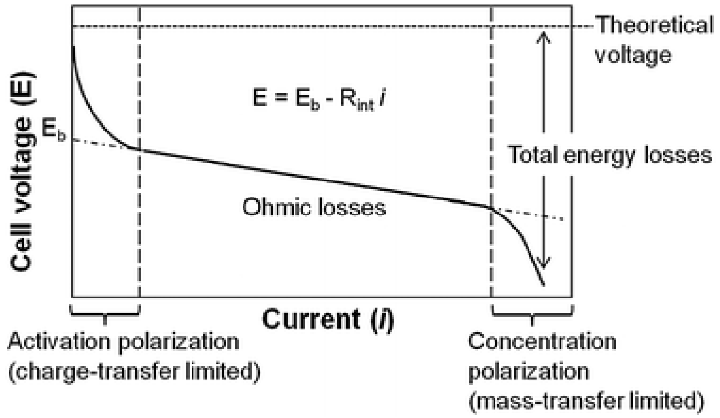
A) Concentration Polarization:

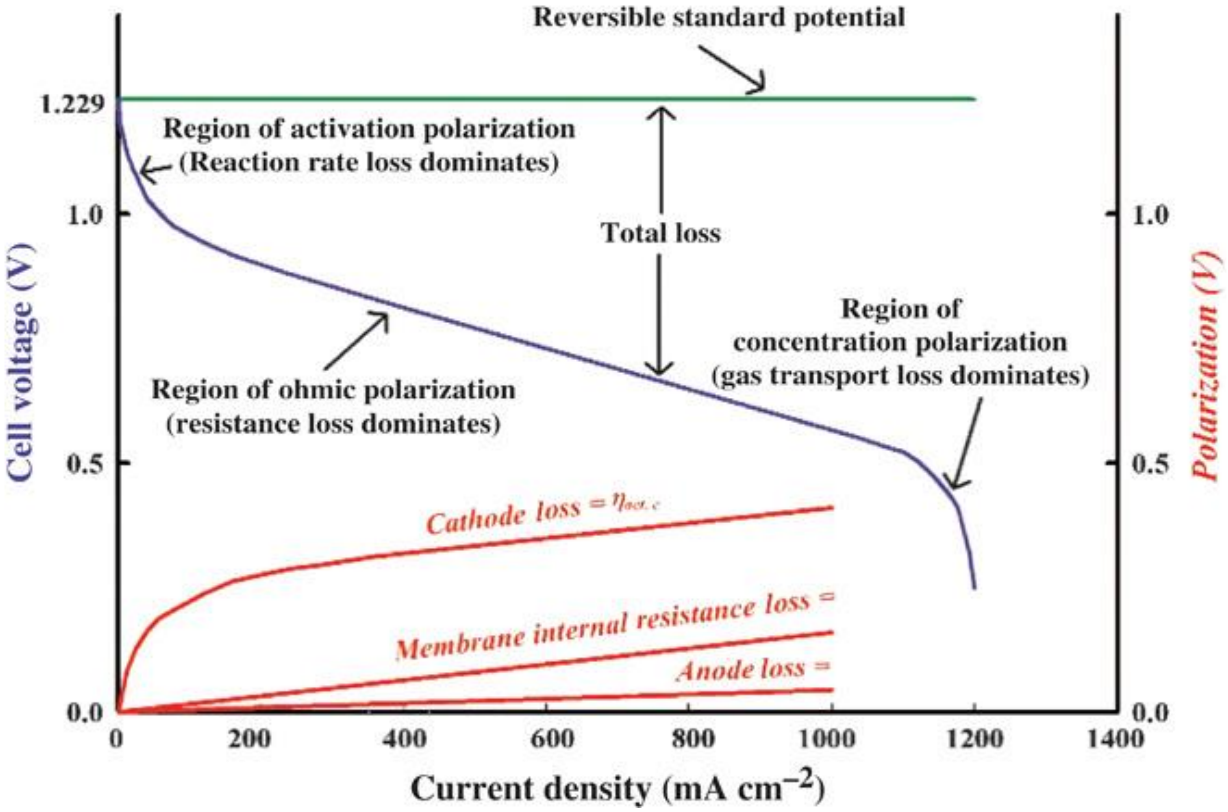
- To illustrate what is meant by concentration polarization (overpotential), consider the deposition of a metal (e.g. copper) from its electrolytic solution (e.g. $CuSO_4$) of concentration C_b.

II- Polarization (Overpotential):

- Concentration Polarization (ήc)
- Activation Overpotential (ήa)
- Ohmic voltage drop (I.R)

ή = ήc + ήa + I.R





A) Concentration Polarization:

- The equilibrium potential needed to deposit the metal at the cathode is given by the reversible value which is calculated from Nernst equation:

$$e_1 = e° - (RT/zF) \ln C_b$$

- After deposition, the metal ion concentration drops from Cb in the bulk of solution to Ci at the electrode surface.
- Accordingly, the new potential which is needed to deposit the metal is given by:

$$e2 = e° - (RT/zF) \ln Ci$$

- The difference between e2 and el is known as the "concentration polarization or overpotential" and is given by:

$$ή c = e2 - e1 = (RT/zF) \ln (Cb/Ci)$$

This is illustrated in Figure (2.4) in which the current "I" is plotted against the voltage or potential “e”.

A) Concentration Polarization:

- Concentration polarization arises owing to the slowness (delay) of the rate of mass transfer of the electroactive ion from the bulk of solution to the electrode surface.
- If the rate of mass transfer of the electroactive ion is fast enough to compensate for the decrease in metal ion concentration at the electrode surface, there should be concentration overpotential.

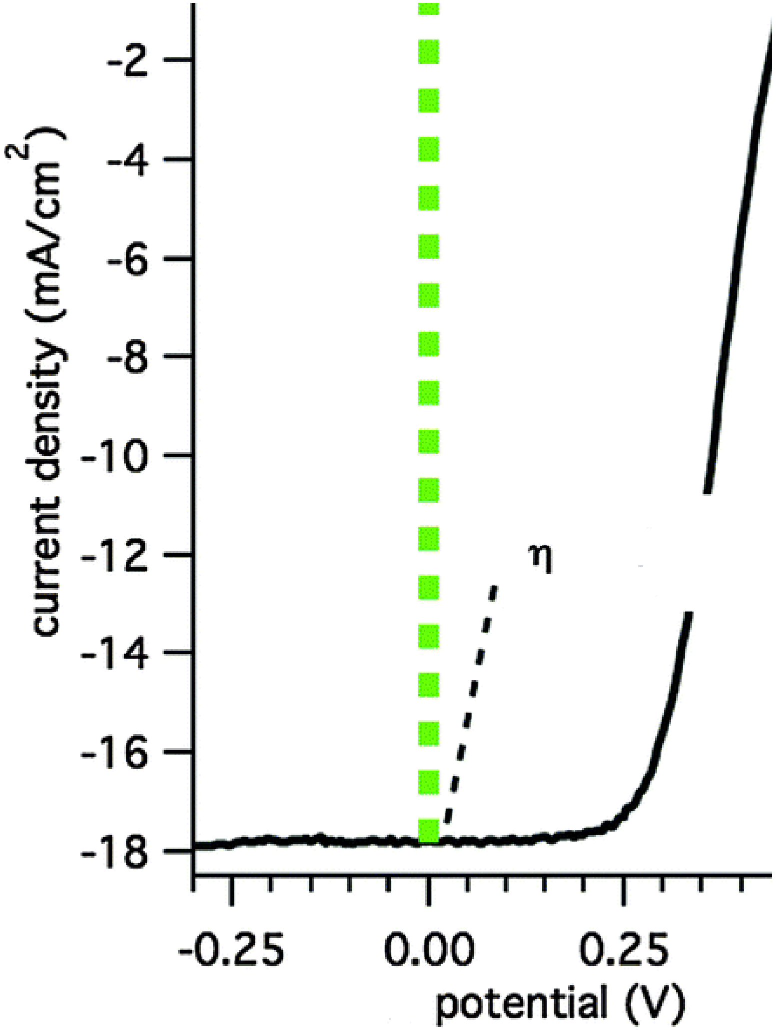


Figure (2.4): i *versus* e *plot*

A) Concentration Polarization:

The Limiting Current Concept:

- This is the maximum possible current at which a given electrochemical process can be conducted.
- It is reached when the interfacial concentration of the electroactive ion (Ci) becomes zero, that is, when the mass transfer is maximum.
- The limiting current, denoted as I_L, is industrially an important parameter because it corresponds to the maximum rate of production according to Faraday’s laws:

$$\mathbf{m_{max} = M.I_L.t/zF}$$

- If the current is increased beyond the limiting value, I_L, a new reaction starts, e.g. evolution of hydrogen gas in the process of metal deposition from aqueous solutions.

A) Concentration Polarization:

Relating Concentration Polarization and Operating Current:

- At steady state, which is the usual mode of industrial operation, the amount of electroactive ions transferred to the electrode surface is equal to the amount deposited at the electrode.
- A mass balance for one mole of metal to be deposited on a unit area of electrode surface yields:

$$\mathbf{N = I/(zF) = (I.t+/(zF) - D(dC/dx)}$$

Where: I = current density (defined as the total current per unit area of electrode surface), A/cm2.

t+ = transport number of electroactive ion (taken as a cation).

- Note that the flux N has mol/cm2.s units and thus I.t/zF (t = time). appeared as I/zF (t = 1 second).
- The first term in the right hand side of the equation is the amount of electroactive ion transferred by electrical migration while the second term is that due to diffusion.

n = I t/zF

A) Concentration Polarization:

- The effect of convection is negligible at the electrode surface. Rearranging the above equation:

$$(I/zF)(1 - t_+) = -D\,(dC/dx)$$

$$(I/zF)(t_-) = -D\,(dC/dx)$$

$$(I.t_-)/(zF)\int_0^{\delta} dx = -D\int_{C_b}^{C_i} dC$$

$$\{(I.t_-)/(zF)\}(\delta - 0) = D\,(C_b - C_i)$$

- Collecting a group of parameters in one (K) to simplify the equation:

$$I = K\,(C_b - C_i)$$

where: $K = (DzF) / (t_-.\,\delta)$

- Since $D/\delta = k$, the mass transfer coefficient (cm/s), then:

$$K = (zFk) / (t_-)$$

Solving for C_i: $C_i = C_b - (I/K)$

A) Concentration Polarization:

- By increasing the current density gradually, a state is reached where C_i becomes zero and the current density remains constant at the limiting value, I_L.
- The limiting current density is given by:

$$I_L = K \, . \, C_b \qquad \text{and} \qquad C_b = I_L / K$$

- Eliminating C_b: $\quad C_i = (I_L / K) – (I / K)$
- Since, $\quad ή_c = (RT/zF) \ln (C_b/C_i)$

- Substituting for the two concentrations:

$$ή_c = (RT/zF) \ln [(I_L / K)/\{(I_L/K) - I/K\}]$$

$$ή_c = (RT/zF) \ln [I_L / (I_L - I)]$$

Where $\quad I$ = operating current density, A/cm2

and $\quad I_L$ = limiting current density.

A) Concentration Polarization:

Maximization of Operating Current and Mass Transfer Rate:

- Concentration polarization is undesirable in industrial electrochemical processes because it increases their energy consumption.
- At the same time, it is desirable in practical applications to increase the limiting value of the operating current in order to increase the rate of production.
- Both goals can be achieved through increasing the rate of mass transfer of the electroactive ions.
- To find methods for increasing the rate of mass transfer in electrochemical processes, consider the following equation:

A) Concentration Polarization:

This equation shows that the rate of mass transfer can be increased by the following methods:

1. **Increasing the bulk concentration (Cb),** which leads to an increase in the rate of diffusion with a consequent decrease in concentration overpotential and an increase in the limiting current. This method has a limited effect due to the fact that Cb cannot be increased beyond the solubility of the salt.
2. **Increasing the diffusivity (or diffusion coefficient), D,** of the electroactive ion. This can be achieved by heating the solution to decrease its viscosity. This will facilitate the movements of ions in the solution. Diffusivity is related to the absolute temperature and viscosity by Stokes-Einstein equation which indicates that:

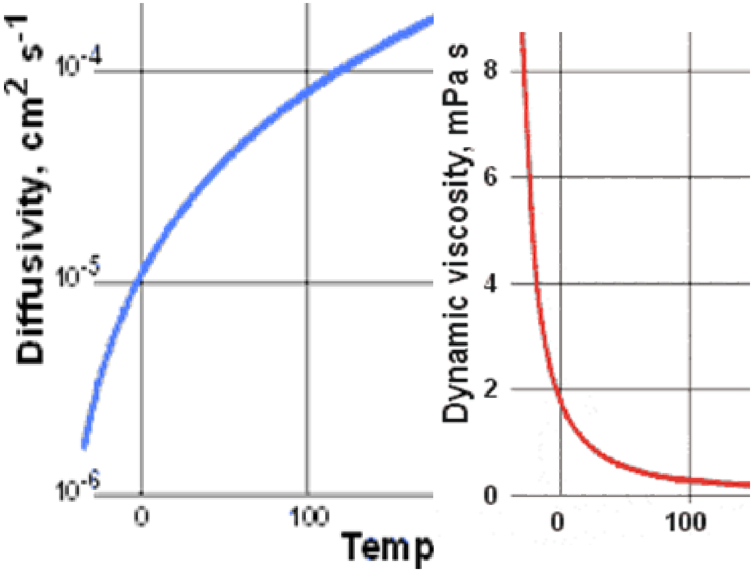
   D.T/π = Constant (See next slide)
3. **The best method to increase the rate of mass transfer is to reduce the thickness of the diffusion layer (δ),** because this layer represents the resistance to mass transfer in the cell. This can be achieved by the following ways:
   - Circulating the solution in the cell using a centrifugal pump or by gas stirring (injecting gas bubbles into the cell).
   - Movement of the electrode such as rotation or vibration.

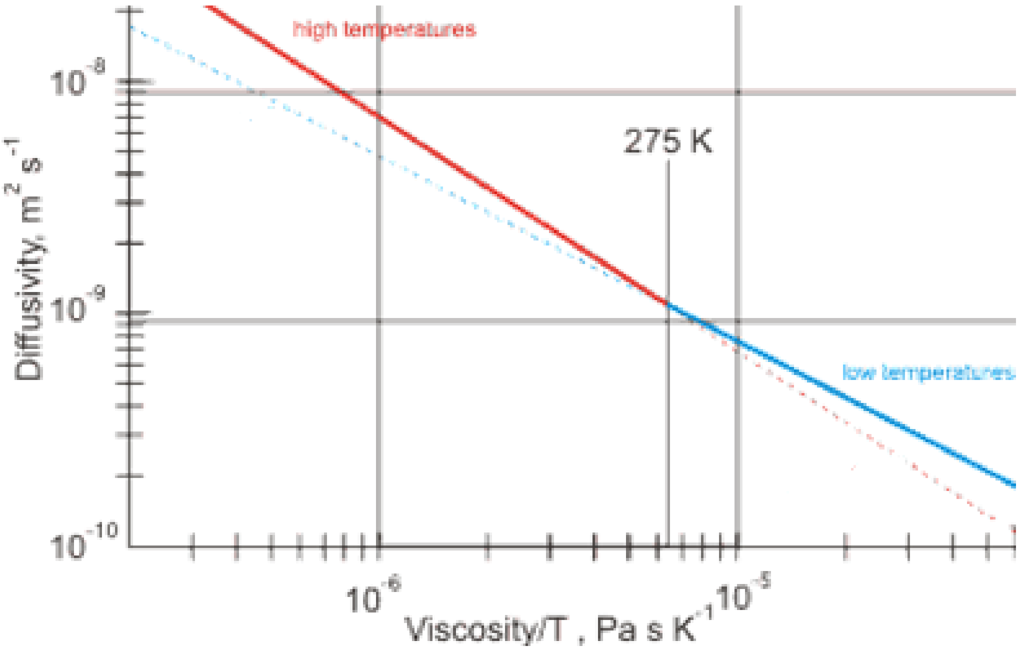
More on Stokes-Einstein equation

- For particles or large molecules in a viscous fluid (usually a liquid solution), the Stokes-Einstein equation can be applied:

$$D = k_B.T/(6\pi.\mu.r)$$

- Here, k_B is the Boltzmann constant, μ is the solvent viscosity and r is the radius of the diffusing particle (ion or molecule).





A) Concentration Polarization:

Experimental Determination of Concentration Polarization (ή$_c$) and Limiting Current (I_L):

- The concentration polarization is experimentally measured at a specified current density by measuring the potential difference between the cathode and a reference electrode placed in the cup of the Luggin tube which is filled with the same solution as that in the cell (Figure 2.5).
- The tip of the Luggin tube is placed close to the cathode surface.
- The potential difference between the cathode and the reference electrode is measured by a potentiometer according to the compensation method. The same apparatus shown in Figure (2.5) is also used in the experimental determination of the limiting current.
- A current- potential curve is constructed by increasing the cell current stepwise and measuring the corresponding cathode potential.
- The limiting current is obtained at the plateau shown in the indicated “I” versus “e” curve (Figure 2.6).

Experimental Determination of Concentration Polarization and Limiting Current

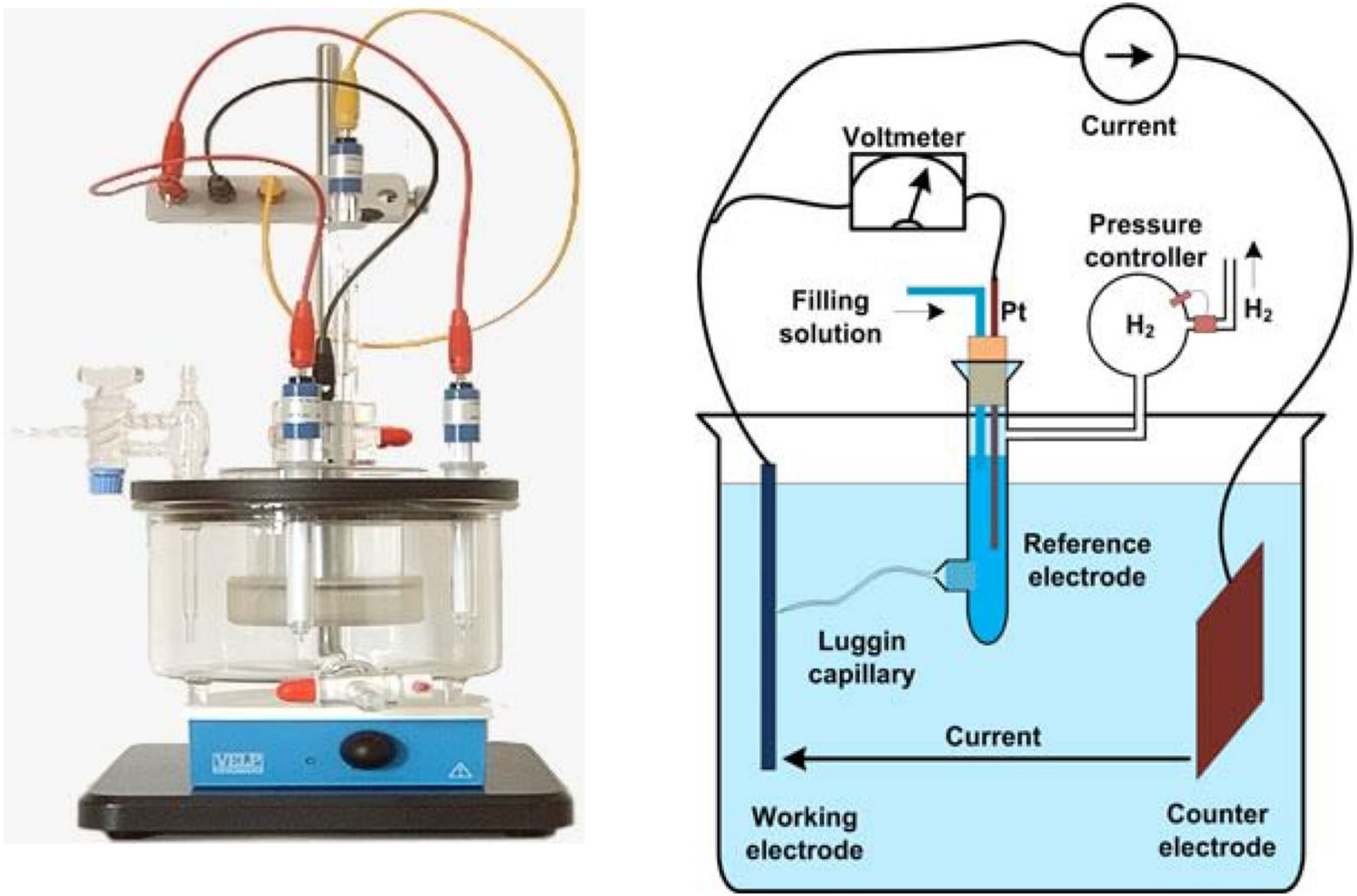


Figure (2.5): Cell apparatus for concentration polarization measurement

A) Concentration Polarization:

- A current- potential curve is constructed by increasing the cell current stepwise and measuring the corresponding cathode potential.

- The limiting current is obtained at the plateau shown in the indicated "I" versus "e" curve (Figure 2.6).

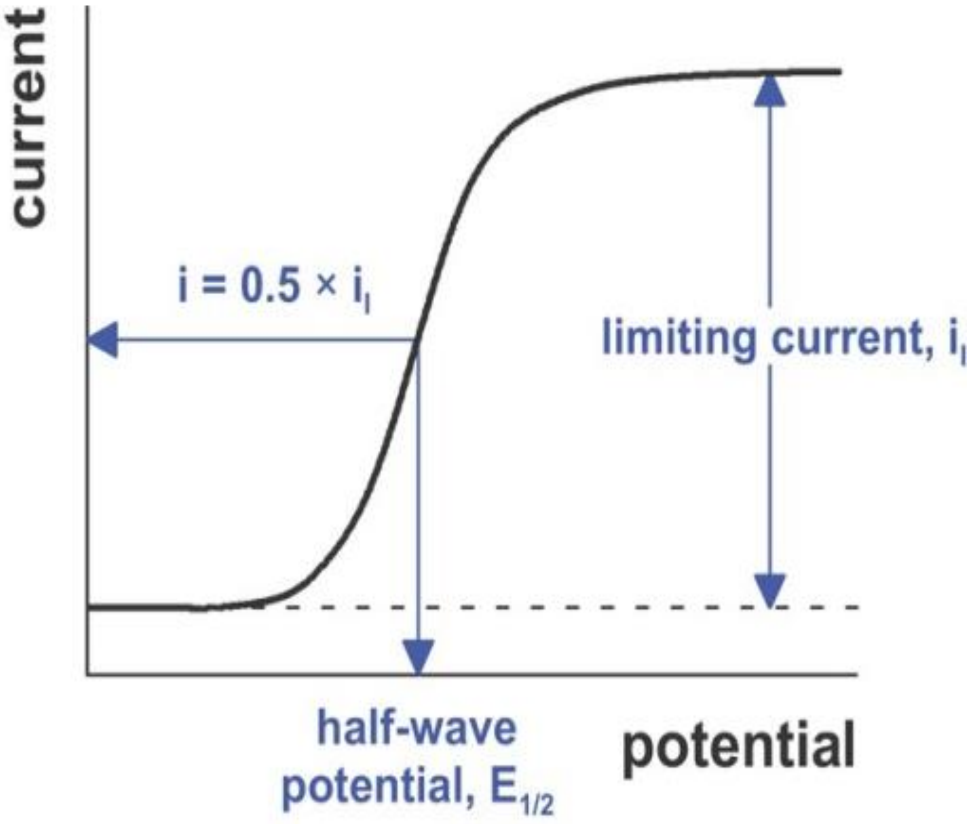


Figure (2.6):

Limiting current in the "I" versus "e" curve

II- Polarization (Overpotential):

B) Activation Polarization:

- This is the extra voltage which should be added to the theoretical potential in order to start the electrochemical reaction or the change in potential that is required just to make the reaction go faster.
- This type of polarization arises due to the slowness in the charge transfer step, that is, the charge transfer step needs more energy than the theoretical value (ΔG) to take place.
- A reaction for which activation polarization dominates is referred to as **activation controlled**.
- Activation polarization is exhibited with the discharge of gases, e.g. H2, O2 and Cl2.
- Most metals deposit with a *negligible* activation overpotential except Co, Ni and Fe.

B) Activation Polarization:

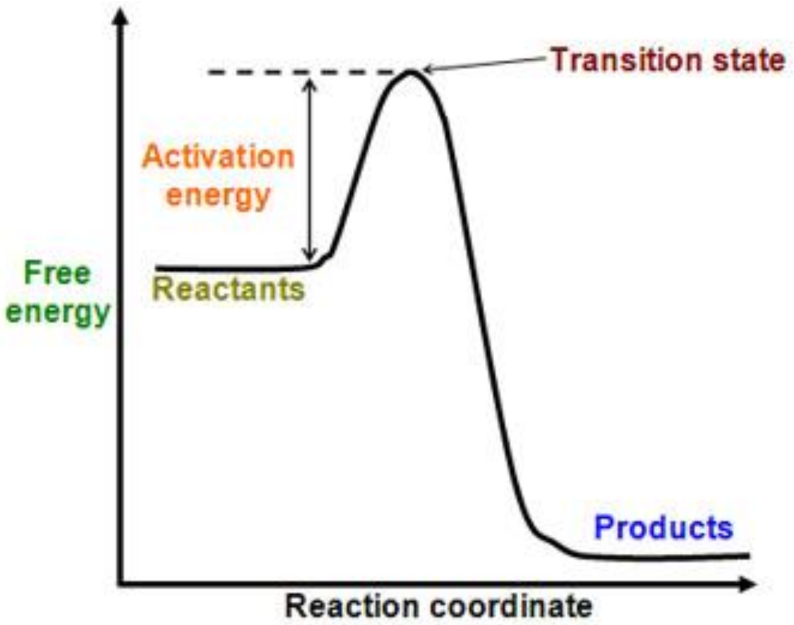
- Since the hydrogen discharge reaction is common in electrolysis of aqueous solutions, it is taken as an example for illustrating the activation overpotential. Theories of H_2 overpotential are:

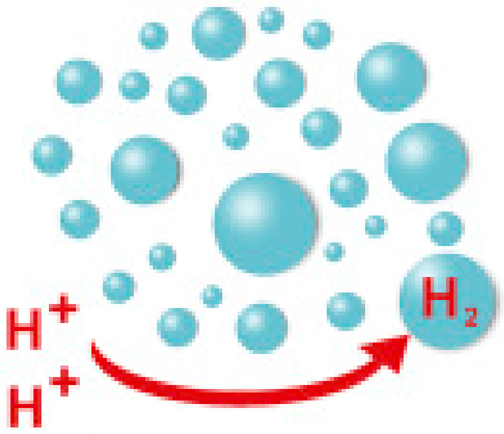
a) The slow discharge theory:

$H^+ + e^- \rightarrow H$ (Slow)
$H + H \rightarrow H_2$ (Fast)

b) The slow combination theory:

$H^+ + e^- \rightarrow H$ (Fast)
$H + H \rightarrow H_2$ (Slow)





B) Activation Polarization:

Factors Affecting Activation Polarization:

1) The current density: It is found that activation polarization increases with the current density according to Tafel's equation:

$$\acute{\eta}_a = a + b \log i$$

Where: (a) and (b) are constants depending on electrode material, temperature and the electrode surface roughness.

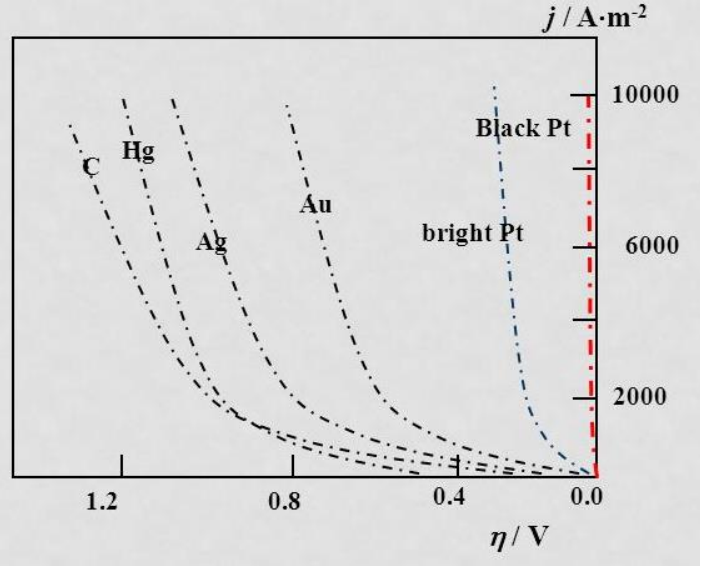
2) Electrode material:

- Hydrogen overpotential is high on metals such as Hg, Zn and Pb. It has the lowest value on Pt. The effect of the electrode material may be attributed to the fact that some metals such as Pt, Fe, Co and Ni act as good *catalysts* for hydrogen discharge reaction.
- Other metals such as Hg, Zn and Pb are not good catalysts for the discharge reaction and accordingly, a higher amount of energy is needed to carry out the reaction **(Figure 2.7)**.

B) Activation Polarization:

Figure (2.7):

Hydrogen evolution overpotential over various metal surfaces



- In the electrolytic production of hydrogen it is uneconomic to use metals such as Hg and Pb as cathodic materials to produce hydrogen.
- Otherwise, the amount of energy consumed will be high due to the high value of activation overpotential.

3) Temperature:

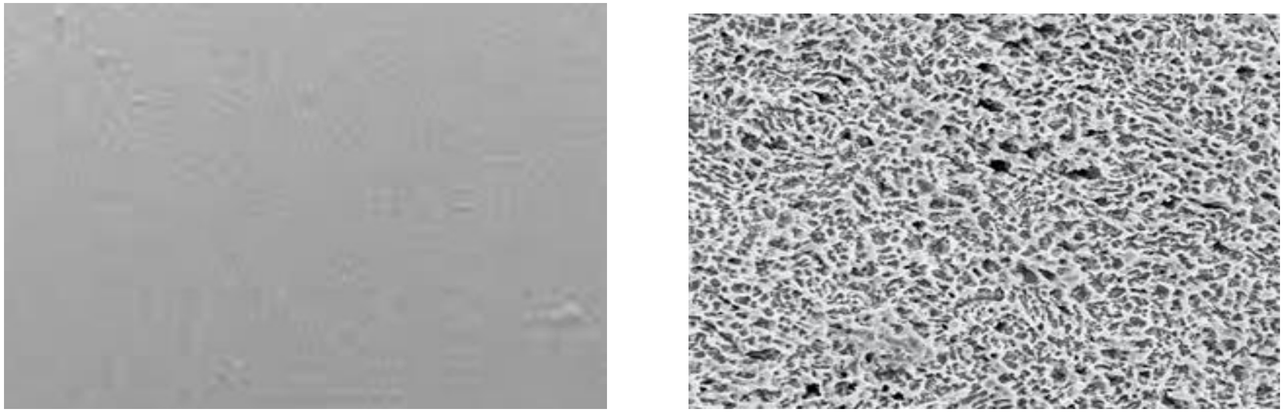
Increase of temperature leads to a decrease in the value of hydrogen overvoltage. This is because heating activates the hydrogen discharge reaction and consequently the reaction needs *less electrical energy* to occur.

B) Activation Polarization:

4) Surface roughness of the electrode:

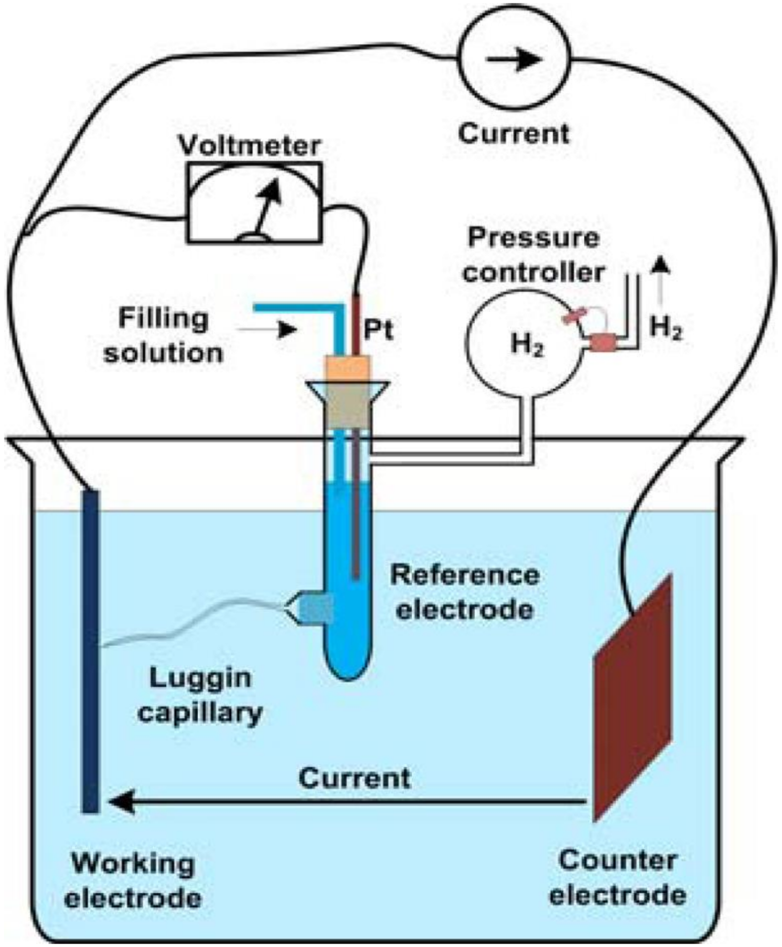
- Hydrogen overpotential decreases with increasing the degree of surface roughness.
- This is because increasing surface roughness results in *increasing the true area* of the electrode. This is followed by a *decrease in the effective current density*.
- According to Tafel's equation, a decrease in the current density should lead to a decrease in hydrogen overpotential.

$$\acute{\eta}a = a + b \log i$$



B) Activation Polarization:

- Activation polarization
- is measured by the same method used for measuring concentration polarization except for the fact that the cell should be fitted with a stirrer.
- The function of the stirrer is to eliminate concentration polarization which may be present.



B) Activation Polarization:

SUMMARY:

- Any electrochemical reaction involves two steps:
    1. Mass transfer of the electroactive ion from the bulk of the solution to the electrode surface.
    2. Charge transfer from the electrode surface to the electroactive ion: $Mn+ + ne- \rightarrow M$

1. Slowness in any of the two steps results in overpotential at the electrode surface.
2. If the first step (mass transfer) is slow, concentration polarization will be produced. If the second step (charge transfer) is slow, activation polarization will be produced.
3. If the two steps are slow, both concentration and activation polarizations will be produced: $\acute{\eta} = \acute{\eta}c + \acute{\eta}a$
4. If resistance in cell (e.g. due to a barrier) is significant, then:

$$\acute{\eta} = \acute{\eta}c + \acute{\eta}a + I.R$$

Voltage and Energy Efficiencies

Voltage efficiency (ζ voltage) is defined as the ratio between the theoretical voltage calculated and the actual voltage required to carry out the electrochemical reaction:

$$\zeta\ \text{voltage} = E\ \text{theo} / E\ \text{actu}$$

$$E\ \text{theo} = E\ \text{theo, anode} + E\ \text{theo, cathode}$$

$$E\ \text{actu} = E\ \text{theo} + \acute{\eta}\text{, anode} + \acute{\eta}\text{, cathode} + IR$$

$$\acute{\eta}\text{, anode} = (\acute{\eta}c + \acute{\eta}a)\ \text{anode}$$

$$\acute{\eta}\text{, cathode} = (\acute{\eta}c + \acute{\eta}a)\ \text{cathode}$$

It should be noted that the signs are important in calculating the individual electrode potentials but not the total cell voltage.

Since energy is given by: $q\ (\text{Joule}) = E\ (\text{Volt}).Q\ (\text{Coul}) = E\ (\text{Volt}).I\ (\text{Amp}).t\ (\text{sec})$

Therefore, the power: $q/t\ (\text{W}) = E\ (\text{Volt}).I\ (\text{Ampere})$

Power efficiency depends on both voltage and current efficiencies:

$$\zeta\ \text{power} = \zeta\ \text{voltage} \,.\, \zeta\ \text{current}$$

where $\zeta\ \text{current} = I\ \text{theo} / I\ \text{actu}$