

الكيمياء الكهربائية Electrochemistry SCIC 26241

Dr. Mahmoud A. Bedair

PROGRAM	بكالوريوس العلوم في الكيمياء الصناعية : Bachelor of Science in industrial Chemistry		البرنامج:
Course:	Electrochemistry - Electroplating		المقرر:
Course Code :	SCIC 26241		رمز المقرر:
Academic Year:	2023 - 2024		العام الجامعي:
Semester:	1 st .		الفصل الدراسي:

ELECTROCHEMISTRY

الكيمياء الكهربائية

SCIC 26241

Dr. Mahmoud A Bedair

Course Description وصف المقرر

<i>Course Title</i>	<i>Course Number</i>	<i>Contact Hours (CH)</i>		<i>Credit unit (CU)</i>	<i>Year</i>	<i>Level</i>	<i>Pre-requisite</i>
		<i>Lec.</i>	<i>Prac.</i>				
<i>Electrochemistry</i>	<i>SCIC 26241</i>	<i>2</i>	<i>0</i>	<i>2</i>	<i>2</i>	<i>4</i>	<i>none</i>

Course objectives: They are to identify the following.

- 1. Types of conductor*
- 2. Classification of electrolytic cells*
- 3. Measuring EMF*
- 4. Applications of electrochemistry*

Syllabus:

A-Theoretical contents

Electrolytic conductors, General electrochemistry concepts, Introduction to electrochemistry: electrode potentials, galvanic and electrolytic cells, Nernst equation, Corrosion and corrosion protection, Overview of applications of electrochemistry

CLOs		Aligned PLOs
1	Knowledge and Understanding: Upon completion of this course, student will be able to	
1.1	Demonstrate a broad understanding and critical view on principal of electrochemistry, Concepts and terminology of electrochemistry topics including; electrolyte solution theories, electrochemical (Galvanic) cell, origin of electrode potential theories, Faraday's law of electrolysis, ...etc (P)	K1
1.2	Describe correctly the different phenomena associated with electrochemistry i.e.; type of electrodes, cell presentation (notation), cell reactions, electromotive force (P)	K2
2	Skills : Upon completion of this course, student will be able to	
2.1	Demonstrate an ability in critical thinking, numeracy, statistical, analytical reasoning, use graphs, charts and to solving problems related to faraday's law and Nernst equation. (P)	S1
2.2	Perform experiments in electrochemistry, record, analyze, interpret the scientific data, and write reports. (P)	S2
2.3	Knows the proper procedures and regulations for safe handling and use of chemicals and can follow the proper procedures and regulations for safe handling when using chemicals. (P)	S3
2.4	Write a report/ poster on electrochemistry using communication and online technology in a good verbal and clear scientific language. (P)	S4
3	Values:	
3.1	Working a group leader in cooperation with other colleagues. (P)	V1

Course Content

No	List of Topics	Contact Hours
1	Electrolytic and Non-electrolytic conductors	4
2	Oxidation States & Redox Reactions	4
3	Galvanic (electrochemical) Cells	4
4	Cell Potential under Standard Conditions	3
5	Gibbs Energy and Redox Reactions	3
6	Cell Potential under Nonstandard Conditions and Nernst equation	3
7	Batteries & fuel cell	3
8	Corrosion	3
9	Electrolytic cell	3
Total		44

Code	Course Learning Outcomes	Teaching Strategies	Assessment Methods
1.0	Knowledge and Understanding Upon completion of this course, student will be able to		
1.1	Demonstrate a broad understanding and critical view on principal of electrochemistry, Concepts and terminology of electrochemistry topics including; electrolyte solution theories, electrochemical (Galvanic) cell, origin of electrode potential theories, Faraday's law of electrolysis, ...etc (P)	lecture / discussion Seminars /presentation	oral and written examinations laboratory reports
1.2	Describe correctly the different phenomena associated with electrochemistry i.e.; type of electrodes, cell presentation (notation), cell reactions, electromotive force (P)	lecture / discussion / Seminars /Individual presentation	oral and written examinations laboratory reports
2.0	Skills Upon completion of this course, student will be able to		
2.1	Demonstrate an ability in critical thinking, numeracy, statistical, analytical reasoning, use graphs, charts and to solving problems related to faraday's law and Nernst equation. (P)	lecture / discussion / Seminars /Individual presentation	oral and written examinations laboratory reports
2.2	Perform experiments in electrochemistry, record, analyze, interpret the scientific data, and write reports. (P)	Lab work, group work	lab report/ Lab notebook.
2.3	Knows the proper procedures and regulations for safe handling and use of chemicals and can follow the proper procedures and regulations for safe handling when using chemicals. (P)	lab demonstrations / hands-on student learning activities	Observation of practical skills / Safety exam / Practical assignments and laboratory reports
2.4	Write a report/ poster on electrochemistry using communication and online technology in a good verbal and clear scientific language. (P)	research activities / project-based learning / Technology-enabled learning	assignments and reports / project / seminar / report
3.0	Values Upon completion of this course, student will be able to		
3.1	Working a group leader in cooperation with other colleagues. (P)	lab demonstrations / whole group and small group discussion	group project reports / Practical assignments and laboratory reports /

Assessment Tasks for Students

#	Assessment task*		Week Due	Percentage of 'Total Assessment Score
1	Homework assignment		2	2 %
2	Lecture Quizzes		4	3 %
3	Mid-term exam		6	15 %
4	Homework assignment		8	0 %
5	Group work presentation		12	0
6	LAB	Quiz in Safety	5	0
7		LAB Sheet	15	10 %
8		Final practical exam	15	15 %
9		Lab report	15	5 %
10	Final Exam		16	50 %
			Total	100 %

Student Academic Counseling and Support

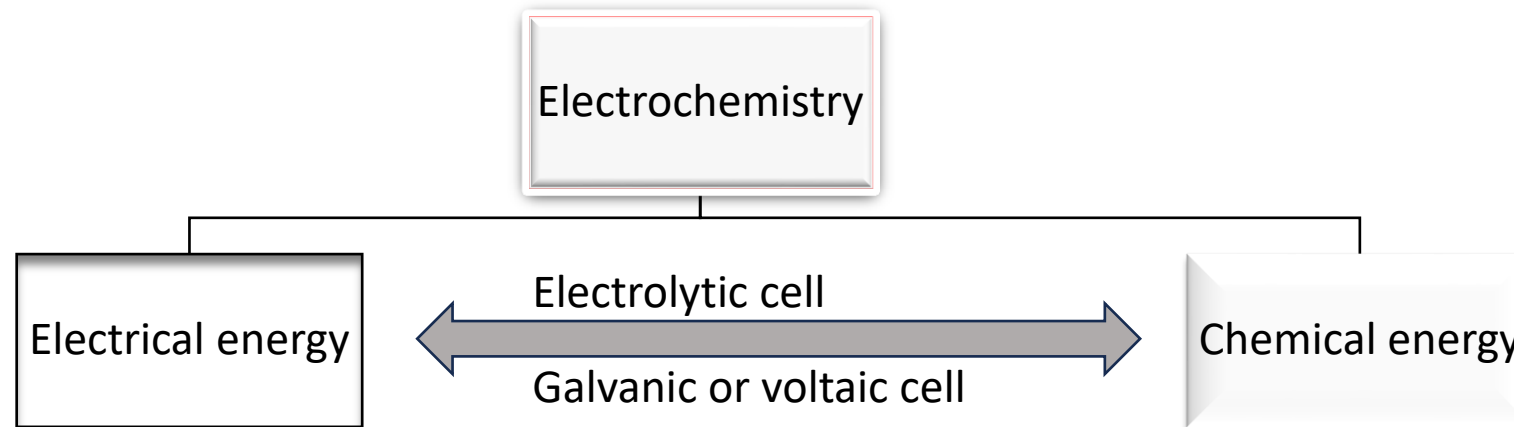
Arrangements for availability of faculty and teaching staff for individual student consultations and academic advice:

- Instructor will be available for academic counseling on daily basis for at **4h/day** during office hours.
- The office hours are listed in the instructor time table and delivered to students in the first lecturer in each semester.
- Instructor is available in a WhatsApp group with student.
- E-mail and Telephone number are delivered to student for any help during semesters.

Learning Resources

Required Textbooks	Handbook of Electrochemistry, 2007, Cynthia G. Zoski, Elsevier
Essential References Materials	• Electrochemistry, 2nd Edition, P.H. Rieger, Springer, 1993 ISBN: 0412043912, 9780412043918 • Electrochemistry and Corrosion Science, Nestor Perez, 2016, Springer International Publishing, ISBN: 978-3-319-24845-5, 978-3-319-24847-9
Electronic Materials	<i>Some course contents and materials are posted on Black board sites</i>
Other Learning Materials	• https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental Modules (Analytical Chemistry)/Electrochemistry • https://courses.lumenlearning.com/chemistryformajors/chapter/introduction-to-electrochemistry/ • https://pages.uoregon.edu/tgreenbo/electrolysis10.html • https://pages.uoregon.edu/tgreenbo/voltaicCellEMF.html

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Electrochemistry :

It is the branch of physical chemistry which study the **interaction electrical energy and chemical energy**.

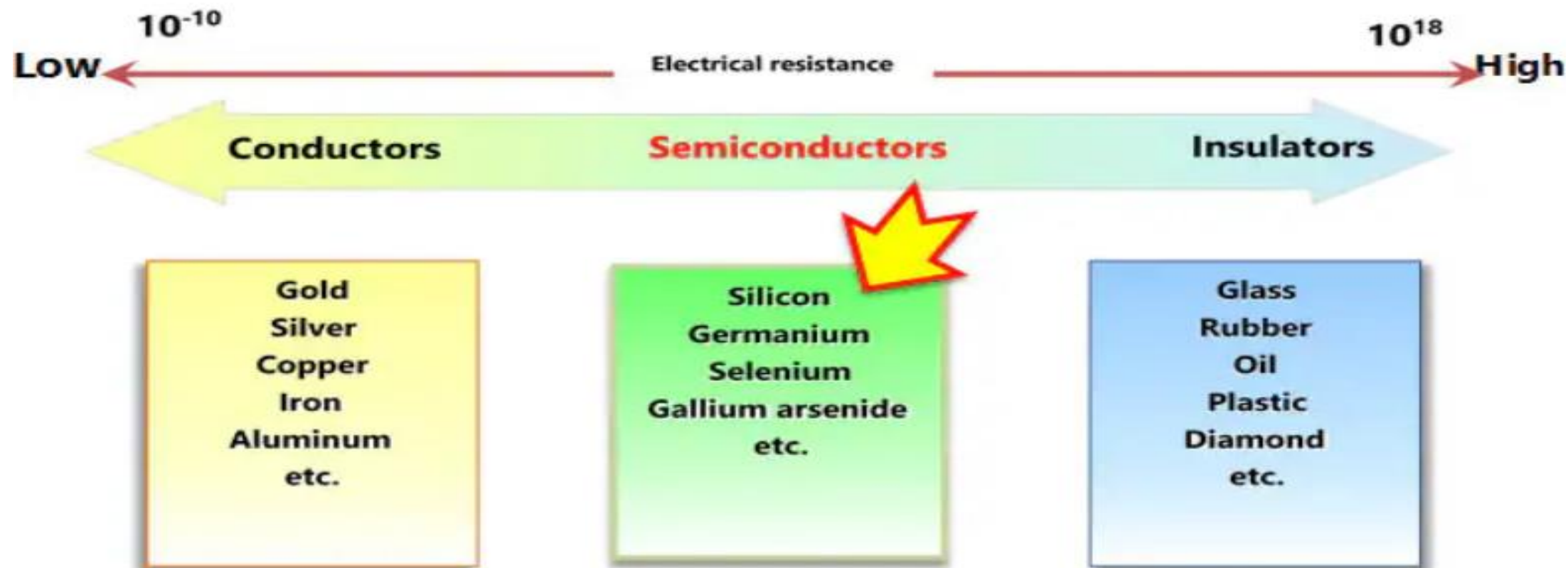
deals with the interactions of electrical energy with chemical species.

It is broadly divided into two categories, namely

- (i) production of **chemical change by electrical energy** (phenomenon of **electrolysis**) and*
- (ii) conversation of **chemical energy into electrical energy**, i.e., generation of electricity by spontaneous redox reactions.*

1. Electrolytic and Non-electrolytic conductors

Current: amount of electrical charges (electrons) moves through conductor

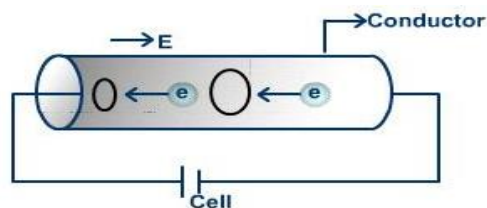


Electrical conductors or simply conductors:

Substance which has the **ability to transfer electrical charges from one position to another.**

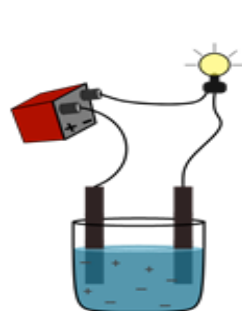
Substances which allow the passage of electric current through them

(i) Metallic or electronic conductors

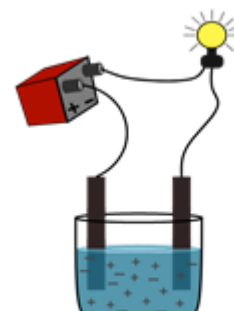


copper, silver, aluminum

(ii) Electrolytic conductors:



Weak Electrolyte



Strong Electrolyte

aqueous solutions of acids, bases and salts

non-electrolytes



Non Electrolyte

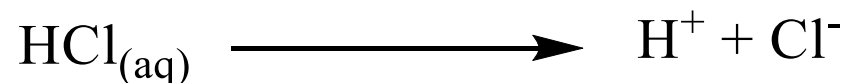
sugar, glycerine, alcohol

Distinction between metallic and electrolytic conduction

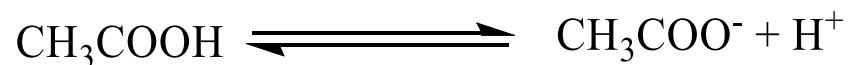
	Metallic	electrolytes
Definition	Any substance has less than four electrons in the outer shell orbit. e.g. Zn, Cu and Al	Any substance which molten or solution has the ability to conduct electricity. e. g. NaCl
Principle	Conduct electricity due to movement of electrons. It does not involve the transfer of any matter.	Conduct electricity due to movement of ions. It involves transfer of matter in the form of ions.
Effect of Temperature	Conductivity decreases by increasing temperature due to increasing of vibrational motion of electrons.	Conductivity increases by increasing temperature due to increasing of translational motion of ions.
Side reaction	Conductivity can't be associated with chemical change	Conductivity may be associated with chemical change Ions are oxidized or reduced at the electrodes.
Ohm's law	Ohm's law is followed.	Ohm's low is followed.
Faraday laws	Faraday laws is not followed.	Faraday laws is followed.

Electrolytes, weak-electrolyte and non-electrolyte

Strong electrolytes: Completely dissociated into ions in solution.



Weak electrolytes: Partially dissociated into ions in solution.



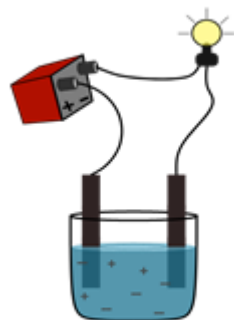
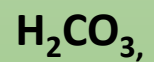
Non-electrolytes: Can't be dissociated into ions in solutions and so can't conduct electricity.

Non-electrolytes	Weak electrolytes	Strong electrolytes
Organic liquids or solutions	Weak acids and alkalis	Strong acids, alkalis and salt solutions
$\text{C}_2\text{H}_5\text{OH (l)}$	$\text{Ca(OH)}_2 \text{ (aq)}$	$\text{H}_2\text{SO}_4 \text{ (aq)}$
$\text{CCl}_4 \text{ (l)}$	$\text{NH}_3 \text{ (aq)}$	$\text{HNO}_3 \text{ (aq)}$
$\text{CHCl}_3 \text{ (l)}$	$\text{CH}_3\text{COOH (aq)}$	HCl (aq)
$\text{H}_2\text{O (l)}$	$\text{H}_2\text{SO}_3 \text{ (aq)}$	KOH (aq)
$\text{C}_{12}\text{H}_{22}\text{O}_{11} \text{ (aq)}$	$\text{H}_2\text{CO}_3 \text{ (aq)}$	NaOH (aq)

Types of Electrolytes

Weak electrolytes are only feebly ionized in the solution.

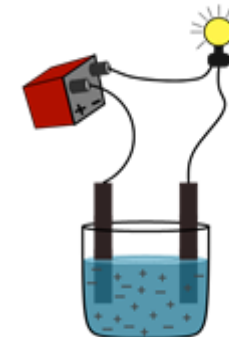
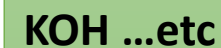
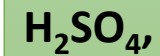
Examples are



Weak Electrolyte

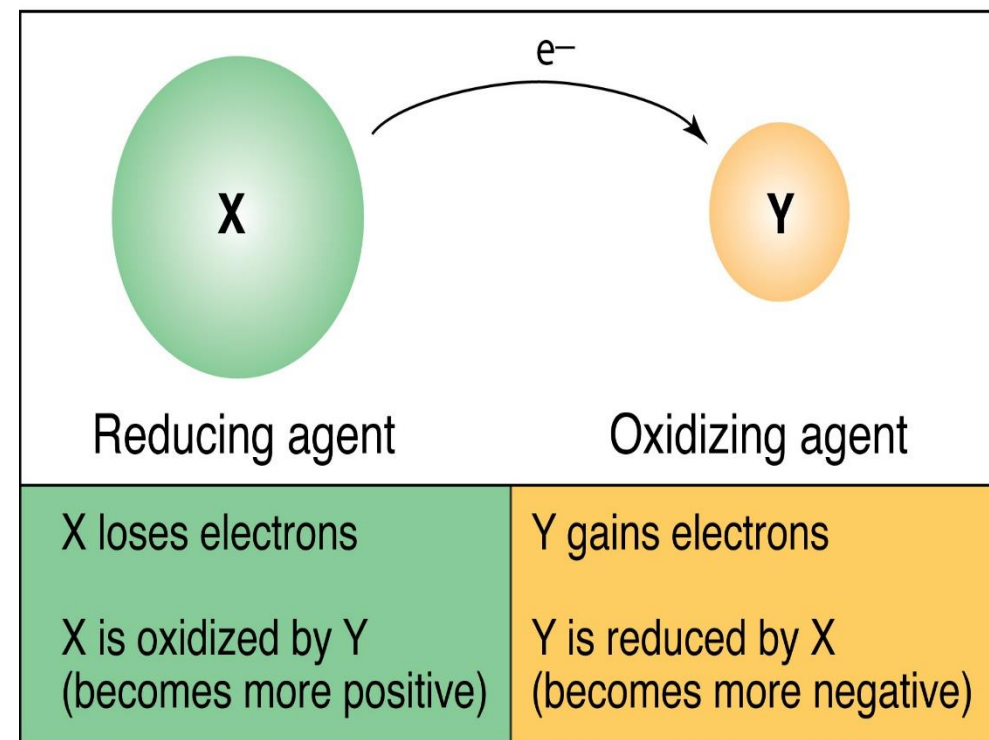
Strong electrolyte are highly ionized in the solution.

Examples are

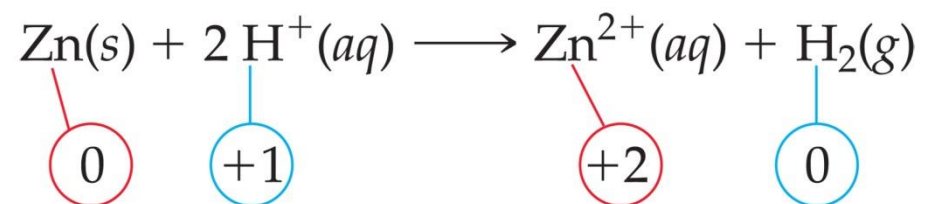


Strong Electrolyte

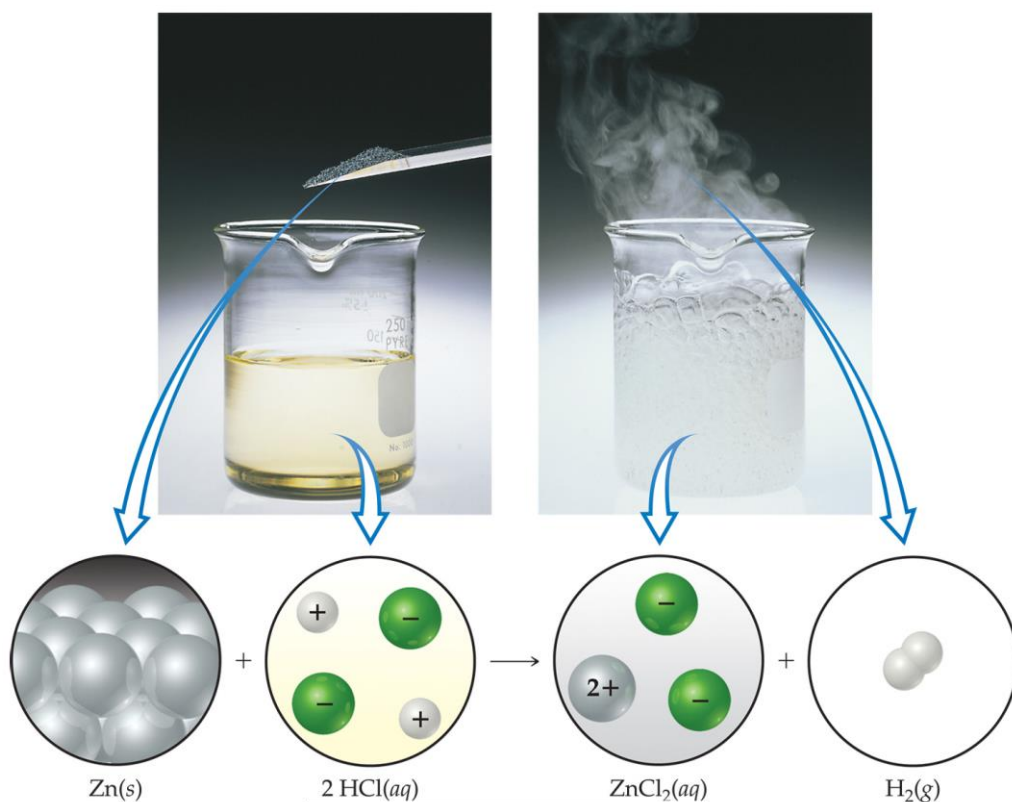
- Oxidation state is a useful tool for keeping track of electron transfers.
- It is most commonly used in dealing with metals and especially with transition metals.
- Oxidation signifies a **loss** of electrons and reduction signifies a **gain** of electrons.
- **Balancing redox reactions is an important step that changes in neutral, basic, and acidic solutions.**

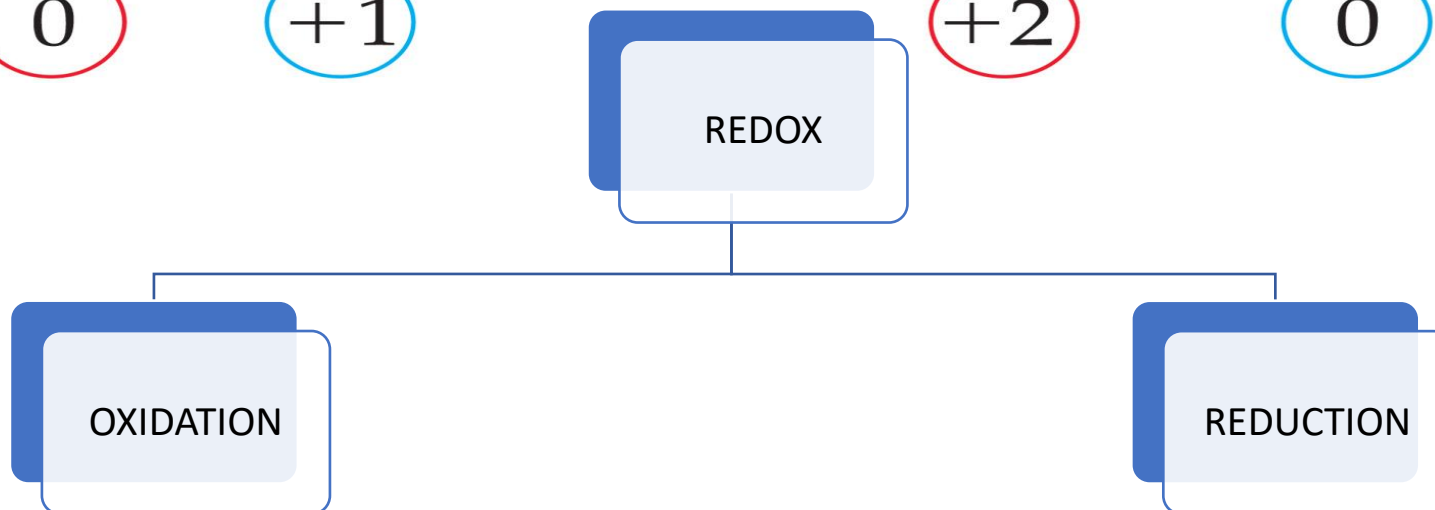
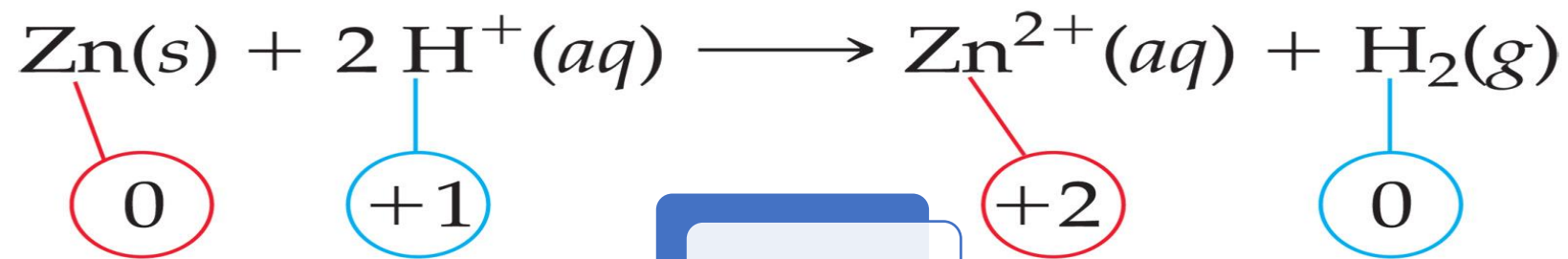


In redox reactions, electrons are transferred from one species to another.



In order to keep track of what loses electrons and what gains them, we assign **oxidation numbers**.





- A species is **oxidized** when it loses electrons.
- Here, zinc loses two electrons to go from neutral zinc metal to the Zn^{2+} ion.
- A species is **reduced** when it gains electrons.
- Here, each of the H^+ gains an electron and they combine to form H_2 .



0

+1

+2

0

REAGENTS

Oxidizing
reagent

Reducing Reagent

- What is reduced is the **oxidizing agent**.
- H^+ oxidizes Zn by taking electrons from it.

- What is oxidized is the **reducing agent**.
- Zn reduces H^+ by giving it electrons.

Redox reaction: Chemical reaction involves transfer of electrons between reacting species and so change in oxidation number occurs.



Oxidation: loss of electrons and so increase in oxidation number.



Reduction: gain of electrons and so decrease in oxidation number.

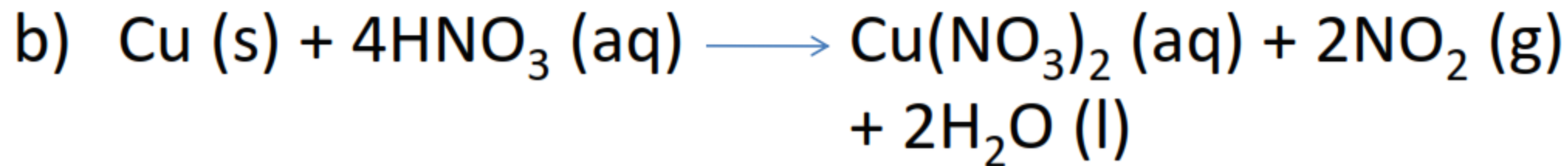
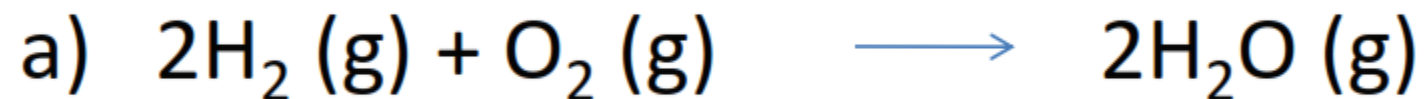


Oxidizing agent: Substance which oxidizes others and itself get reduced by gaining electrons.

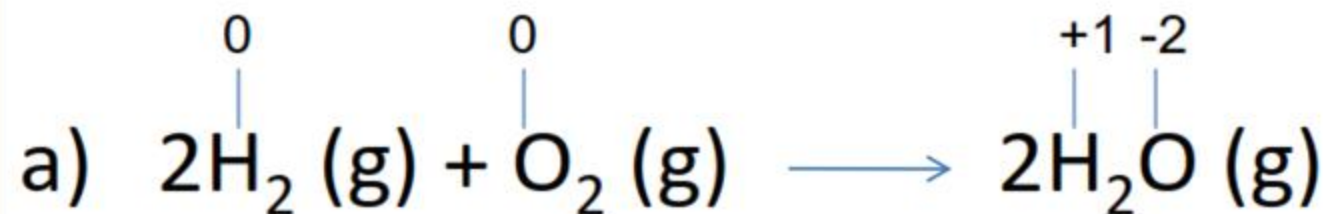
Reducing agent: Substance which reduces others and itself get oxidized by losing electrons.

Oxidation number: number of electrons that can be lost or gained or shared by element during chemical reaction.

- 2 • Identify the oxidizing agent and reducing agent in each of the following:

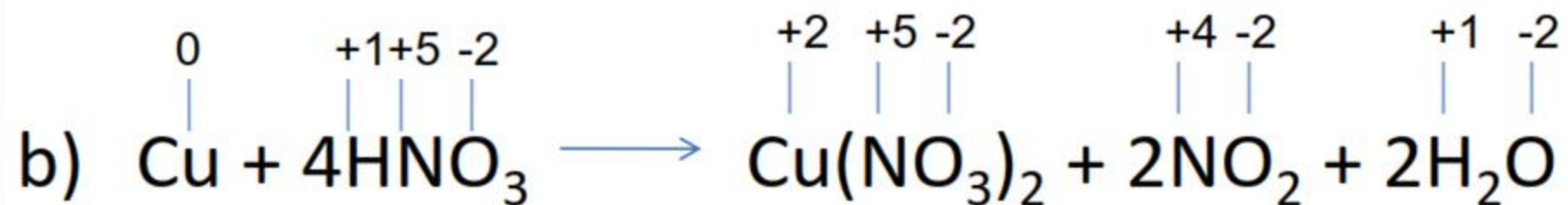


Answer



- O_2 was reduced (O.N. of O: $0 \rightarrow -2$); O_2 is the oxidizing agent

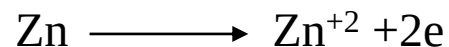
- H_2 was oxidized (O.N. of H: $0 \rightarrow +1$); H_2 is the reducing agent



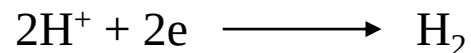
- Cu was oxidized (O.N. of Cu: $0 \rightarrow +2$); Cu is the reducing agent

- HNO_3 was reduced (O.N. of N: $+5 \rightarrow +4$); HNO_3 is the oxidizing agent

Show the oxidation and reduction half reactions then write oxidizing and reducing agent.



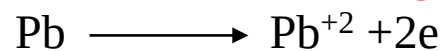
Oxidation (loss of electrons)



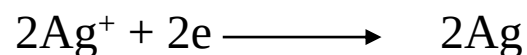
Reduction (gain of electrons)

Zn reducing agent

H^+ oxidizing agent



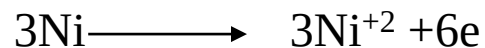
Oxidation (loss of electrons)



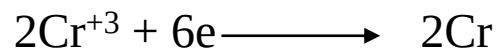
Reduction (gain of electrons)

Pb reducing agent

Ag^+ oxidizing agent



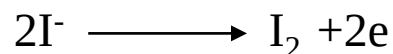
Oxidation (loss of electrons)



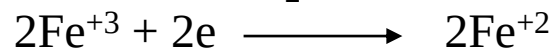
Reduction (gain of electrons)

Ni reducing agent

Cr^{+3} oxidizing agent



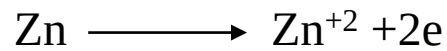
Oxidation (loss of electrons)



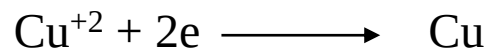
Reduction (gain of electrons)

I^- reducing agent

Fe^{+3} oxidizing agent



Oxidation (loss of electrons)



Reduction (gain of electrons)

Zn reducing agent

Cu^{+2} oxidizing agent

Oxidation number

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.



Oxidation numbers of all the elements in HCO_3^- ?



$$\text{O} = -2 \quad \text{H} = +1$$

$$3 \times (-2) + 1 + ? = -1$$

$$\text{C} = +4$$

Rules for oxidation numbers:

❑ Oxidation number for pure substances either atom or molecule equal zero.

Atom/molecule	S ₈	O ₂	Cl ₂	H ₂	Cu	Ag	Na
Oxidation number	zero	zero	zero	zero	zero	zero	zero

❑ Oxidation number of hydrogen ion always +1 (H⁺) except for metal hydrides, it has -1 oxidation number (H⁻) for example: NaH or CaH₂.

❑ Oxidation number for oxygen ion always -2 (O⁻²) except the following:

❑ Peroxides, it has -1 oxidation number (O⁻¹) e.g. Hydrogen peroxide H₂O₂ and sodium peroxide Na₂O₂.

❑ Super oxides, it has -1/2 oxidation number (O^{-1/2}) e.g. Potassium super oxide (KO₂).

❑ If it attached to high electronegative atom, it has +2 oxidation number (O⁺²) e.g. OF₂.

❑ Oxidation number for metallic ions (elements of groups 1A, 2A and 3 A in the periodic table), equal to group number with positive sign. e.g. Na⁺ (group 1A), Mg⁺² (group 2A) and Al⁺³ (group 3A).

❑ Oxidation number for group 7 in the periodic table (halogens) equal -1. e.g. F^- , Cl^- , Br^- and I^- except:

❑ If it attached to high electronegative atom, it has a positive oxidation number

e.g. Cl_2O (Cl^{+1}), HClO_3 (Cl^{+5}).

❑ Oxidation number for mono atomic ions, equal to its charge.

Ion	Cl^-	Na^+	Ca^{+2}	Al^{+3}	S^{-2}	O^{-2}
Oxidation number	-1	+1	+2	+3	-2	-2

❑ Summation of oxidation numbers of all atoms in neutral molecules equal to zero:

Neutral molecule:	NH_3	H_2O	NO_2	NaBrO_3	H_2SO_4
Oxidation number:	Zero	Zero	Zero	Zero	Zero

❑ Summation of oxidation numbers of all atoms in poly atomic ions equal to the charge of the ion:

ion:	NO_3^{-1}	NH_4^+	PO_4^{-3}	SO_4^{-2}
Oxidation number:	-1	+1	-3	-2



Oxidation numbers of all the elements in the following ?



$$\text{F} = -1$$

$$7x(-1) + ? = 0$$

$$\text{I} = +7$$



$$\text{Na} = +1 \quad \text{O} = -2$$

$$3x(-2) + (+1) + ? = 0$$

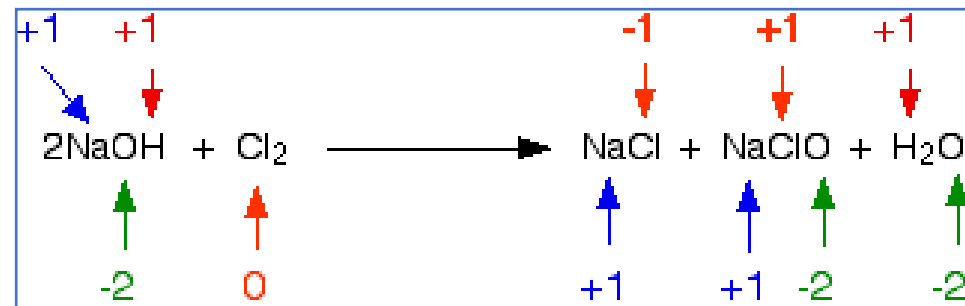
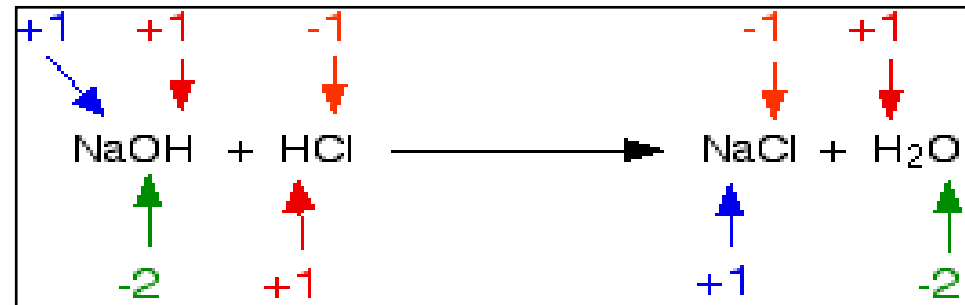
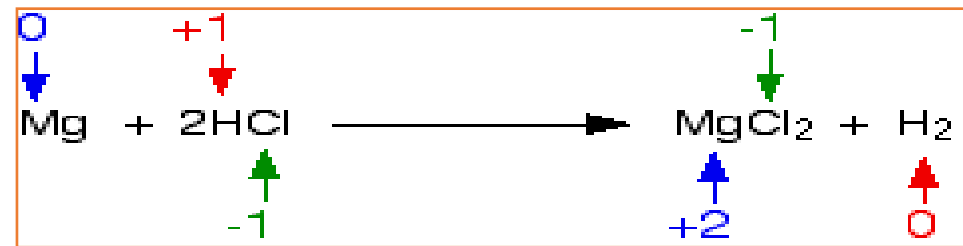
$$\text{I} = +5$$



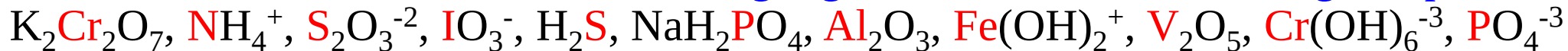
$$\text{O} = -2 \quad \text{K} = +1$$

$$7x(-2) + 2x(+1) + 2x(?) = 0$$

$$\text{Cr} = +6$$



❖ Calculate the oxidation number for the highlighted atoms in the following compounds:



$$\square \text{K}_2\text{Cr}_2\text{O}_7 = \text{zero}, \quad (2 \times +1) + 2 \text{Cr} + (7 \times -2) = \text{zero}$$

$$+2 + 2\text{Cr} - 14 = \text{zero}, \quad 2\text{Cr} - 12 = \text{zero}, \quad 2\text{Cr} = +12, \quad \text{Cr} = +6$$

$$\square \text{NH}_4 = +1, \quad \text{N} + (4 \times +1) = +1, \quad \text{N} + 4 = +1, \quad \text{N} = +1 - 4, \quad \text{N} = -3$$

$$\square \text{S}_2\text{O}_3 = -2, \quad 2\text{S} + (3 \times -2) = -2, \quad 2\text{S} - 6 = -2, \quad 2\text{S} = -2 + 6, \quad 2\text{S} = +4, \quad \text{S} = +2$$

$$\square \text{IO}_3 = -1, \quad \text{I} + (3 \times -2) = -1, \quad \text{I} - 6 = -1, \quad \text{I} = -1 + 6, \quad \text{I} = +5$$

$$\square \text{H}_2\text{S} = \text{zero}, \quad (2 \times +1) + \text{S} = \text{zero}, \quad +2 + \text{S} = \text{zero}, \quad \text{S} = -2$$

$$\square \text{NaH}_2\text{PO}_4 = \text{zero}, \quad +1 + (2 \times +1) + \text{P} + (4 \times -2) = \text{zero}$$

$$+1 + 2 + \text{P} - 8 = \text{zero}, \quad \text{P} - 5 = \text{zero}, \quad \text{P} = +5$$

$$\square \text{Al}_2\text{O}_3 = \text{zero}, \quad 2\text{Al} + (3 \times -2) = \text{zero}, \quad 2\text{Al} - 6 = \text{zero}, \quad 2\text{Al} = +6, \quad \text{Al} = +3$$

$$\square \text{Fe}(\text{OH})_2 = +1, \quad \text{Fe} + (2 \times (-2 + 1)) = +1, \quad \text{Fe} - 2 = +1, \quad \text{Fe} = +1 + 2, \quad \text{Fe} = +3$$

$$\square \text{V}_2\text{O}_5 = \text{zero}, \quad 2\text{V} + (5 \times -2) = \text{zero}, \quad 2\text{V} - 10 = \text{zero}, \quad 2\text{V} = +10, \quad \text{V} = +5$$

$$\square \text{Cr}(\text{OH})_6 = -3, \quad \text{Cr} + (6 \times -1) = -3, \quad \text{Cr} - 6 = -3, \quad \text{Cr} = -3 + 6, \quad \text{Cr} = +3$$

$$\square \text{PO}_4 = -3, \quad \text{P} + (4 \times -2) = -3, \quad \text{P} - 8 = -3, \quad \text{P} = -3 + 8, \quad \text{P} = +5$$

❖ Calculate the oxidation number for the Mn ion in the following compounds:

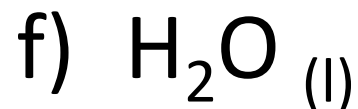
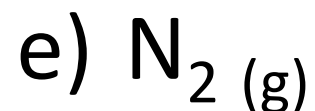


$$\square \text{MnO}_4^- = -1, \quad \text{Mn} + (4 \times -2) = -1, \quad \text{Mn} - 8 = -1, \quad \text{Mn} = -1 + 8 = +7$$

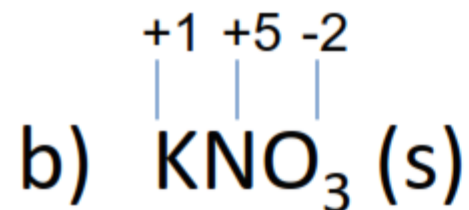
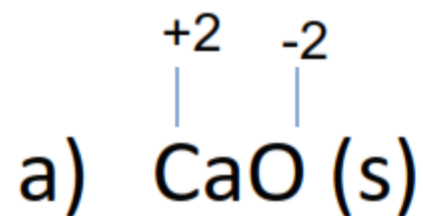
$$\square \text{MnO}_2 = \text{zero}, \quad \text{Mn} + (2 \times -2) = \text{zero}, \quad \text{Mn} - 4 = \text{zero}, \quad \text{Mn} = +4$$

$$\square \text{MnCl}_3 = \text{zero}, \quad \text{Mn} + (3 \times -1) = \text{zero}, \quad \text{Mn} - 3 = \text{zero}, \quad \text{Mn} = +3$$

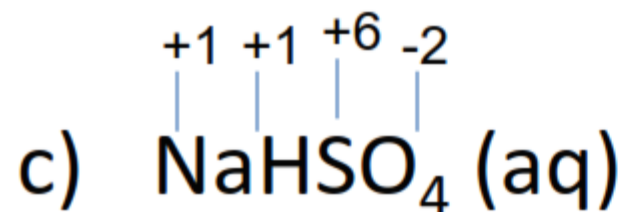
Q: Determine the oxidation number (O.N.) of each element in these compounds:



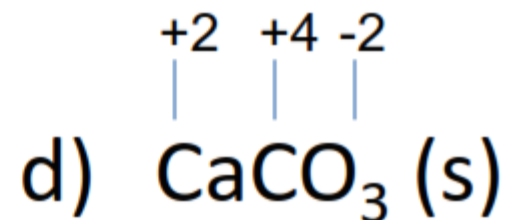
Answer



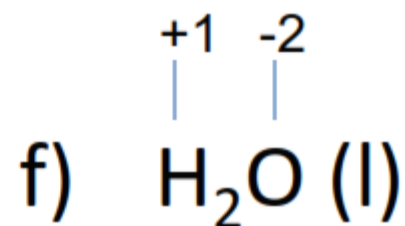
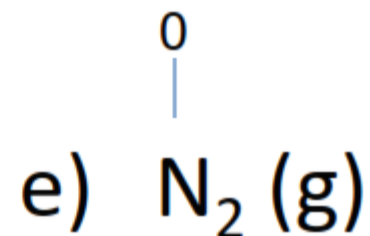
$$\text{N} = 0 - (+1) - 3(-2) = +5$$



$$\text{S} = 0 - (+1) - (+1) - 4(-2) = +6$$

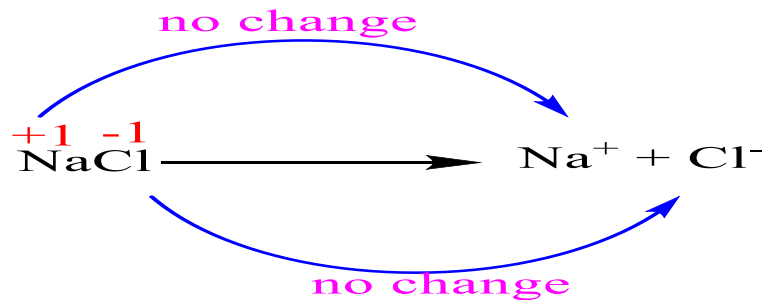
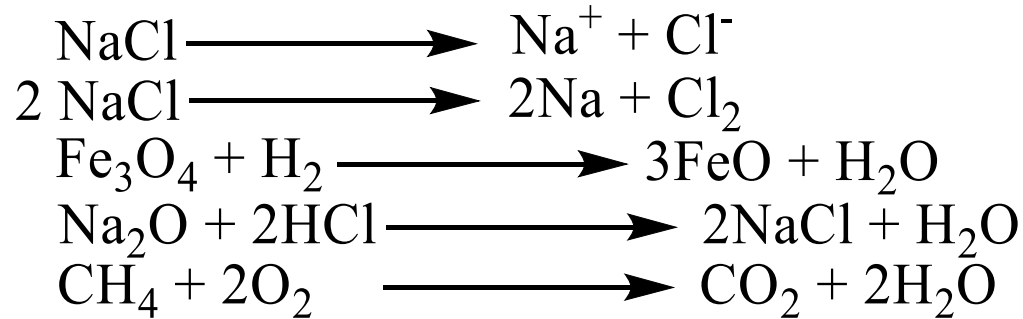


$$\text{C} = 0 - (+2) - 3(-2) = +4$$

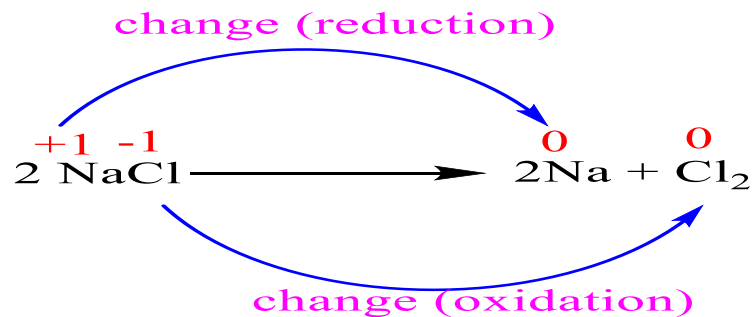


❖ Redox reaction should involve change in oxidation number between reactants and products.

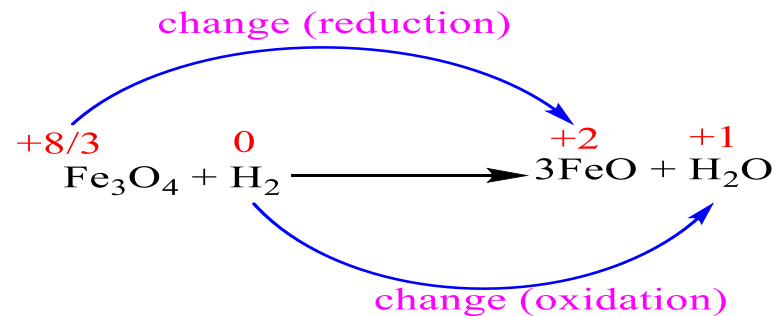
❑ Which of the following is a redox reaction:



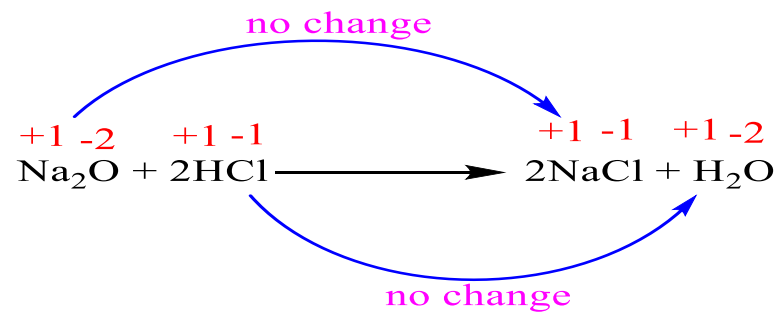
not a redox reaction



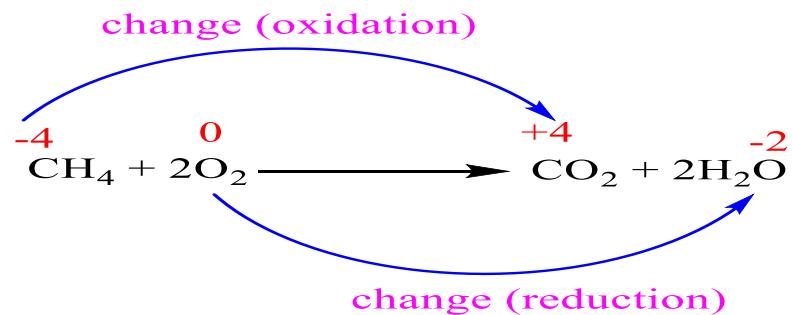
redox reaction



redox reaction



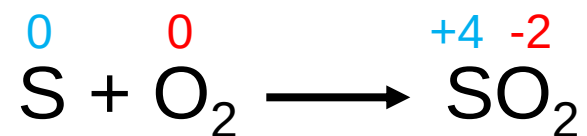
not a redox reaction



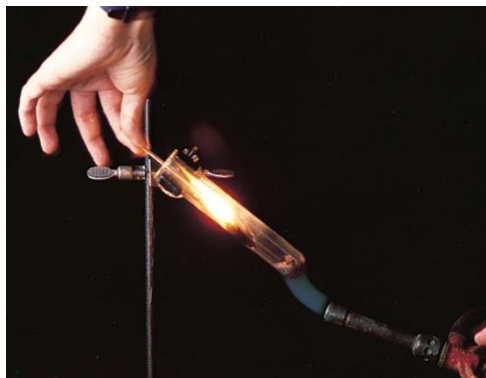
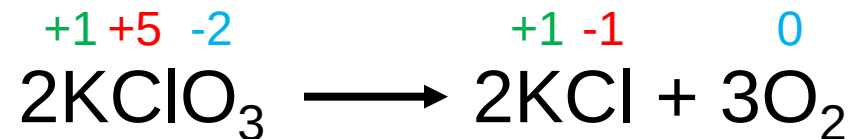
redox reaction

Types of Oxidation-Reduction Reactions

Combination Reaction

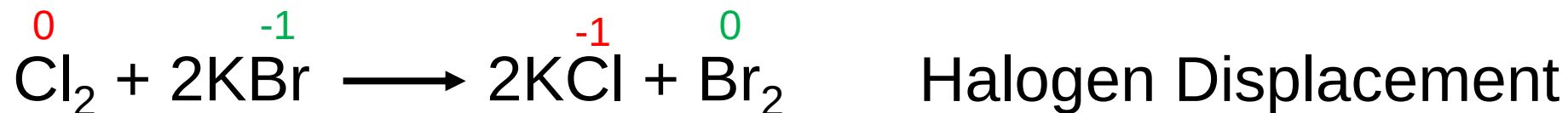
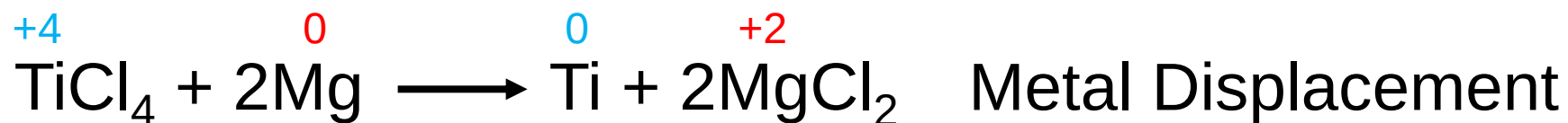
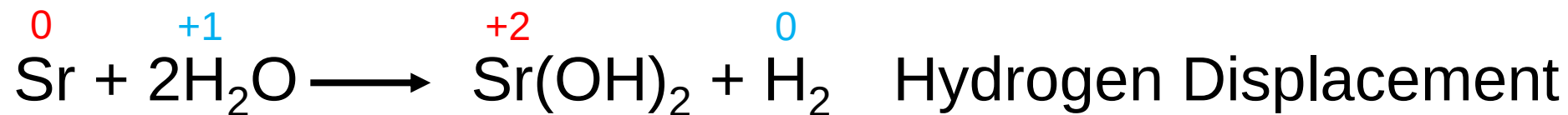


Decomposition Reaction



Types of Oxidation-Reduction Reactions

Displacement Reaction



Balancing redox equation.

❖ A- Ion – electron (half reaction method):

- 1) Split the reaction into two halves.
- 2) Balance atoms in the half reactions except oxygen and hydrogen atoms.
- 3) Balance oxygen by adding one water molecule for each missed oxygen atom.
- 4) Balance hydrogen atoms by the following methods:
 - a) In acid medium , add proton for each missed hydrogen atom.
 - b) In basic medium, add H_2O for each missed hydrogen atom and add OH^- ion in the other side.
- 5) Balance the charge by adding electrons.
- 6) Multiply by any factor to get the same number of electrons in the two half reactions.
- 7) Add the two half reactions to get the balanced equation.

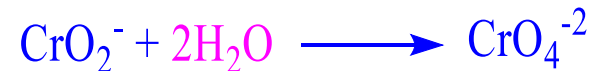
❖ Balance the following redox reaction in acid medium:



1. Split the reaction into two halves.



2. Balance atoms in the half reactions except oxygen and hydrogen atoms. (It is already balanced).
3. Balance oxygen by adding one water molecule for each missed oxygen atom.



4. Balance hydrogen atoms by (In acid medium) , adding proton for each missed hydrogen atom.



5. Balance the charge by adding electrons.



6. Multiply by any factor to get the same number of electrons.



7. Add the two half reactions to get the balanced equation.



❖ Balance the following redox reaction in basic medium:



1. Split the reaction into two halves.



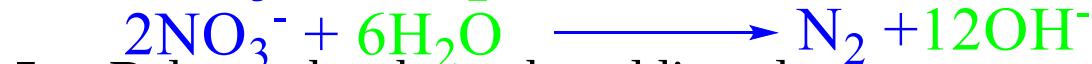
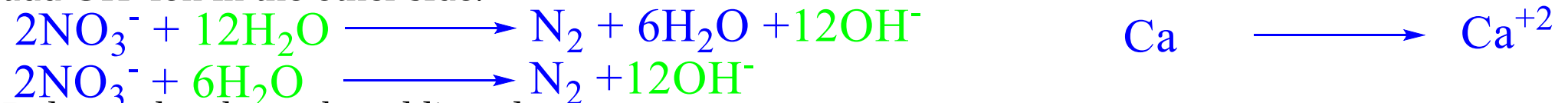
2. Balance atoms in the half reactions except oxygen and hydrogen atoms.



3. Balance oxygen by adding one water molecule for each missed oxygen atom.



4. Balance hydrogen atoms by (In basic medium) adding H_2O for each missed hydrogen atom and add OH^- ion in the other side.



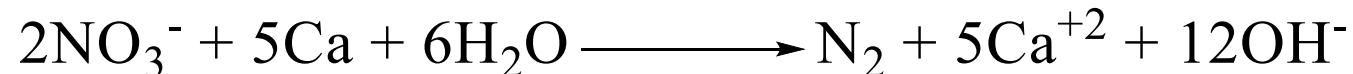
5. Balance the charge by adding electrons.



6. Multiply by any factor to get the same number of electrons.



7. Add the two half reactions to get the balanced equation.



Home work.

❖ Balance the following redox reactions in basic medium (ion- electron method):



❖ Balance the following redox reactions in acidic medium (ion- electron method):



Balancing redox equation.

❖ B- Oxidation number method:

- 1) Determine oxidation number for all atoms in the equation.
- 2) Balance atoms that participate in the oxidation and the reduction processes.
- 3) Draw a line to connect the reactant atom that participates in the oxidation process with its product and write the number of lost electrons on the line. Repeat this step for atom participates in the reduction process.
- 4) Multiply by any factor to get the same number of electrons.
- 5) Balance oxygen by adding one water molecule for each missed oxygen atom.
- 6) Balance hydrogen atoms by the following methods:
 - a) In acid medium , add proton for each missed hydrogen atom.
 - b) In basic medium, add H_2O for each missed hydrogen atom and add OH^- ion in the other side.

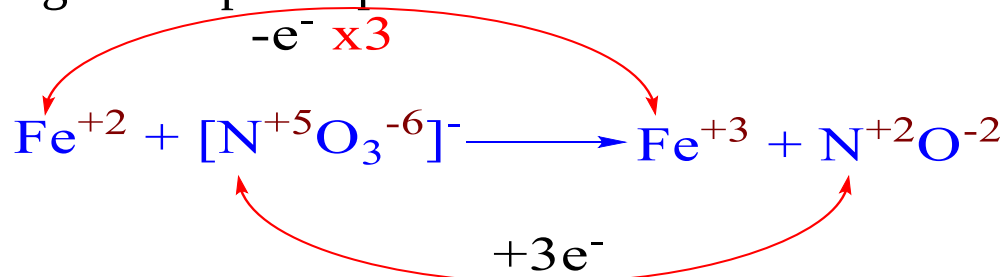
❖ Balance the following redox reaction in acid medium by oxidation number method:



1. Determine oxidation number for all atoms in the equation.



2. Balance atoms except oxygen and hydrogen atoms. (It is already balanced).
3. Draw a line to connecting atoms participate in the oxidation and reduction processes.



4. Multiply by any factor to get the same number of electrons.



5. Balance oxygen by adding one water molecule for each missed oxygen atom.



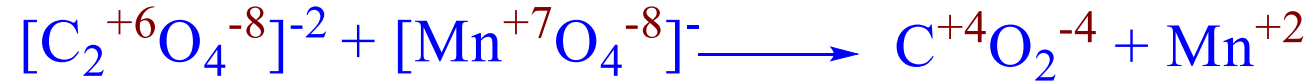
6. Balance hydrogen atoms by (In acid medium), adding proton for each missed hydrogen atom.



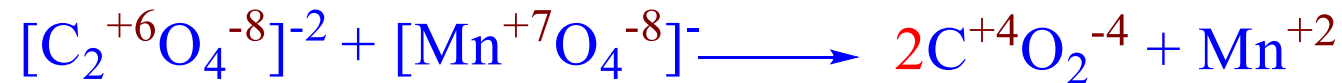
❖ Balance the following redox reaction in acid medium by oxidation number method:



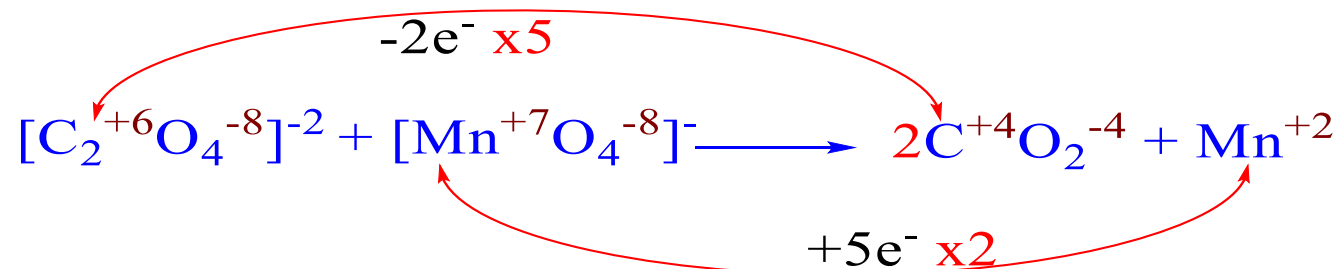
1. Determine oxidation number for all atoms in the equation.



2. Balance atoms except oxygen and hydrogen atoms.



3. Draw a line to connecting atoms participate in the oxidation and reduction processes.



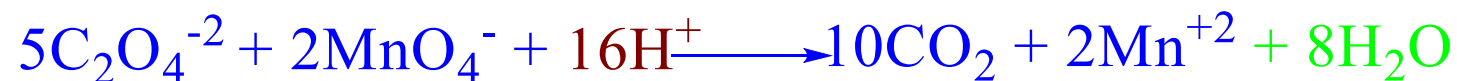
4. Multiply by any factor to get the same number of electrons.



5. Balance oxygen by adding one water molecule for each missed oxygen atom.



6. Balance hydrogen atoms by (In acid medium) , adding proton for each missed hydrogen atom.



Redox reaction and electrochemical cell

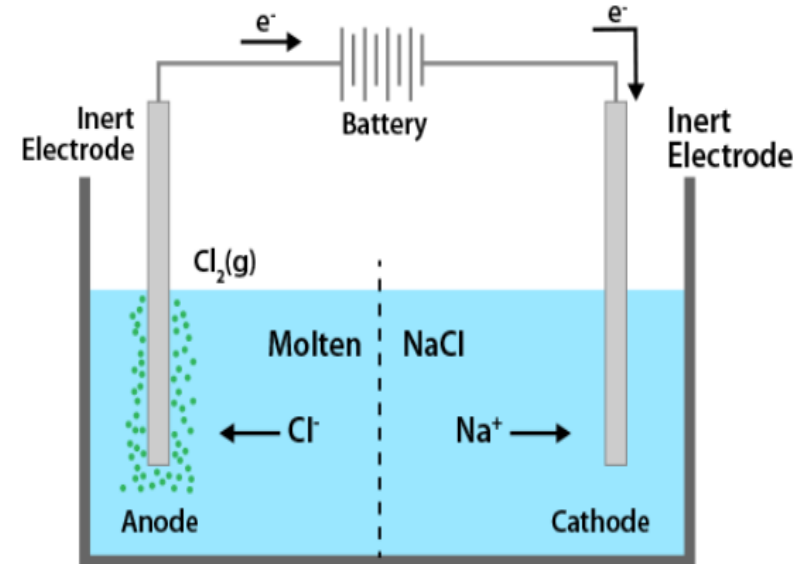
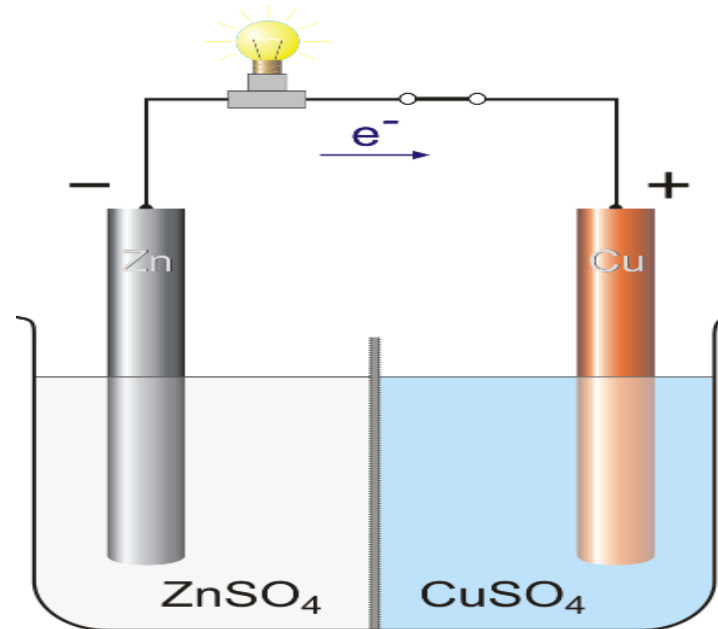
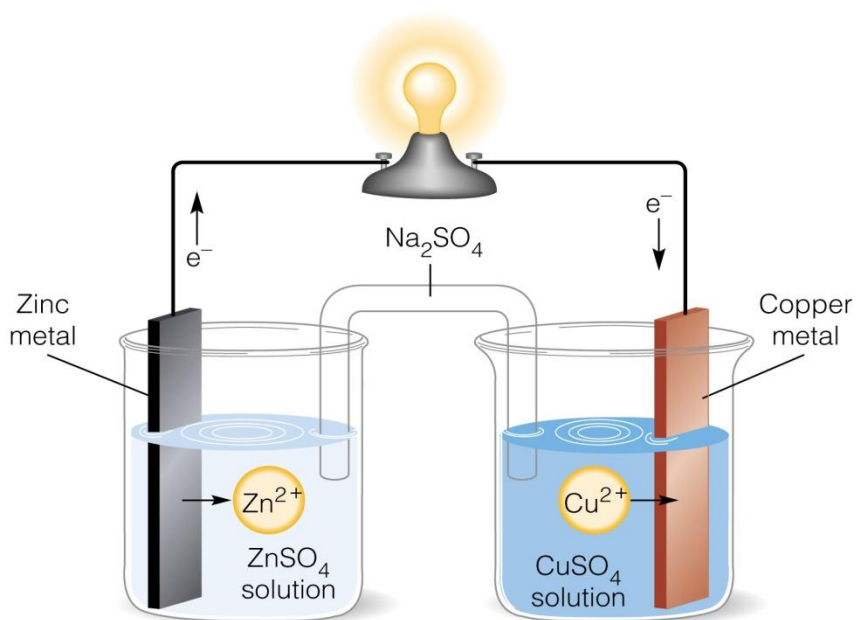
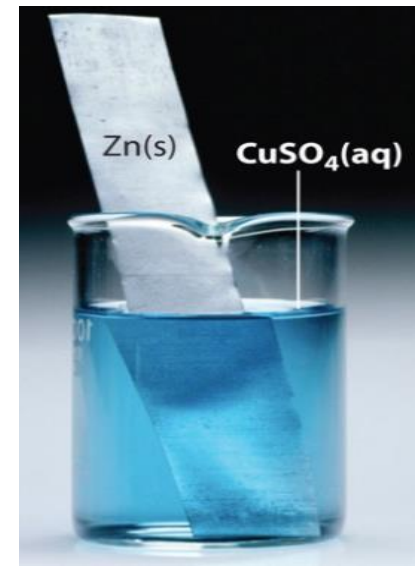
- When Zn metal immersed in a CuSO_4 solution, a redox reaction occurred where the movement of ions and electrons occurred at the interface between metal and solution:



- We need to separate the movement of electrons outside the solution to separate the electrical and chemical energy.
- So, we immersed Zn metal in its own ions, Cu metal in CuSO_4 ions and connect them by metallic and electrolytic conductors.

Electrochemical cell is an apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction.

i.e. device used to convert electrical energy to chemical energy and vice versa.



Electrochemical cell consists of:

1. Electrodes (anode and cathode) that dip into
2. Electrolytes and connected by
3. Metallic and electrolytic conductors.

Anode is the electrode at which oxidation occurs, while the **Cathode** is the electrode at which reduction occurs.

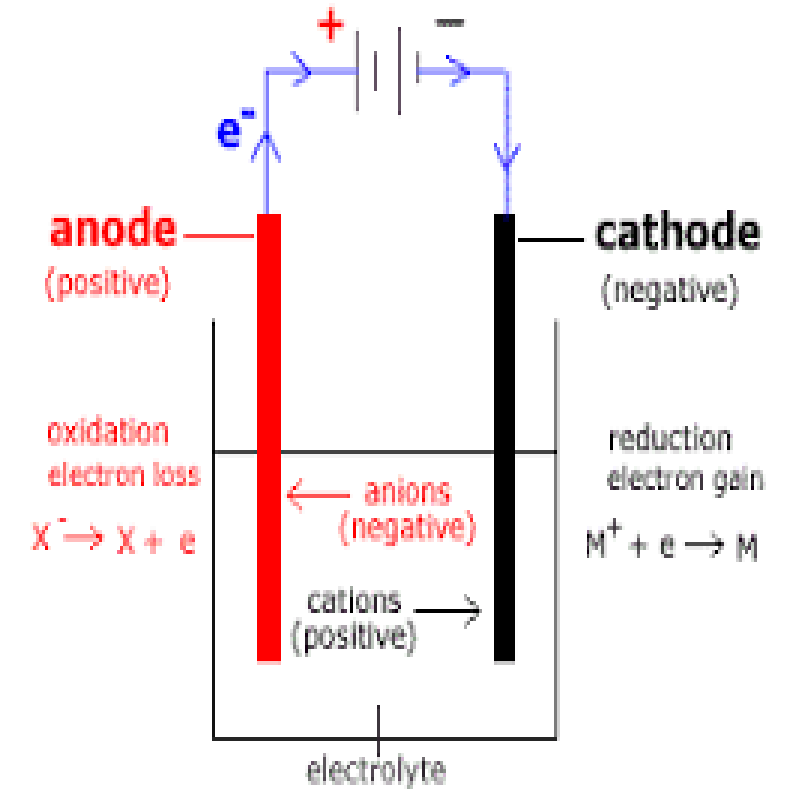
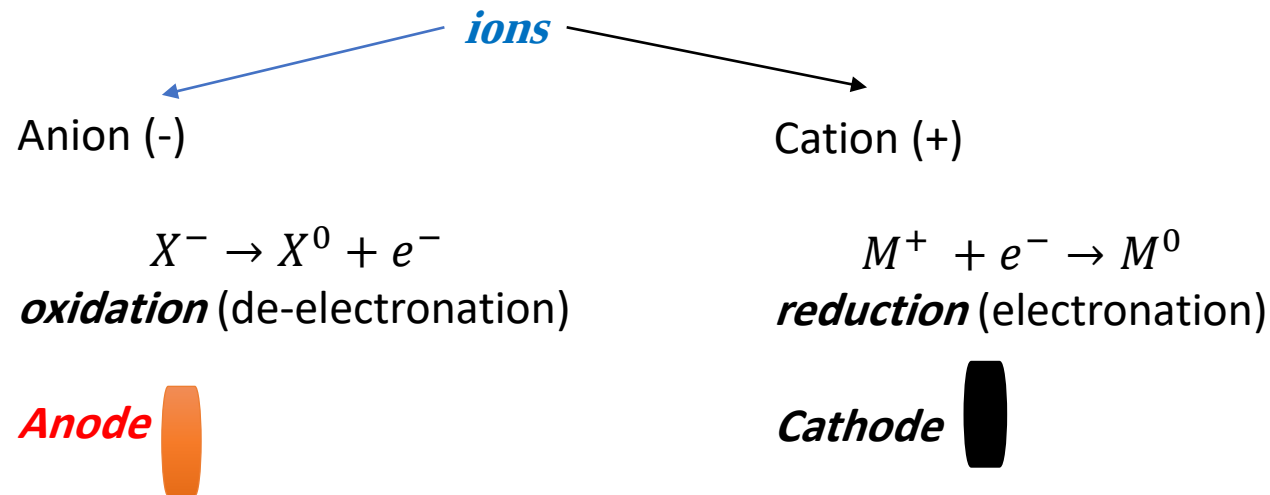
Half cell is one electrode either anode or cathode dipped in its electrolyte.

Electrolysis is the process in which electrical current is used to produce a chemical reaction.

Electromotive force (EMF) is the potential difference between two electrodes of a cell which causes the flow of electrons from one electrode to another.

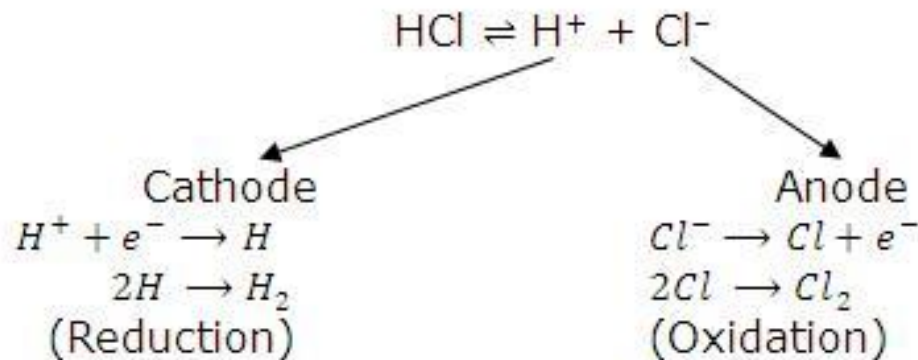
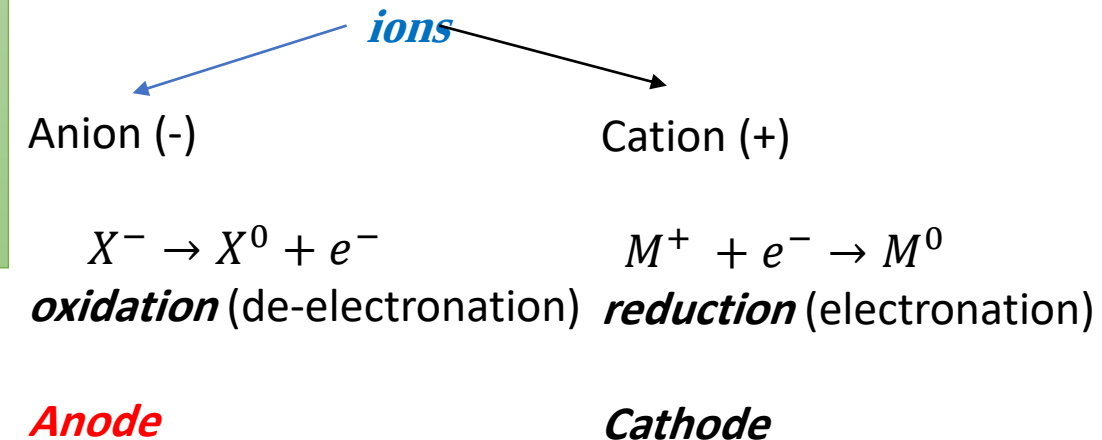
Passing current I

- An electrolytic conductor (aqueous solution or fused electrolyte),
- Two rods or plates (**electrodes**) (metallic conductors)
- Battery.
- The electrolytic solution conducts electricity by the movement of charged particles called **ions** towards the respective oppositely charged electrodes



Chemical decomposition of an electrolyte

- Molecules of an electrolyte when dissolved in water split up into ions, i.e., into **cations** and **anions**.
- On passing current, these ions move towards oppositely charged electrodes.
- On reaching the electrodes the ions lose their charge either by accepting electrons or losing electrons and thereby deposited at the respective electrodes or undergo a secondary change



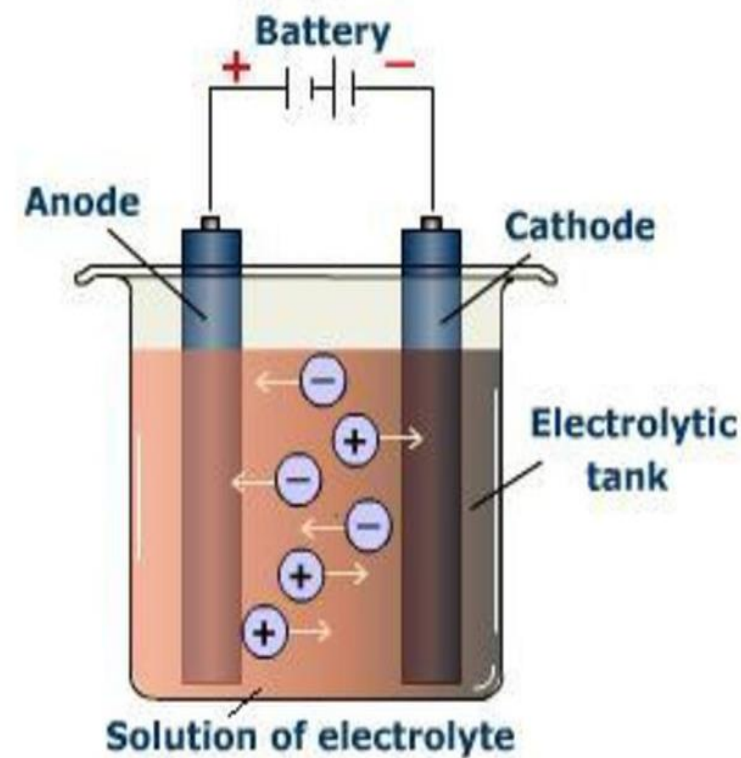
The device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity.

The device in which conversion of electrical energy into chemical change is done .

An electrolytic cell consists of

- A vessel for the electrolytic solution or fused electrolyte
- Two metallic electrodes (**Inert** electrodes)
- A source of electric current.

Electrolytic Cells



Preferential Discharge Theory

If more than one type of ions is attracted towards a particular electrode, then the one discharged is the ion which requires **least energy**.

The potential at which the ion is discharged is called **discharge or deposition potential**.

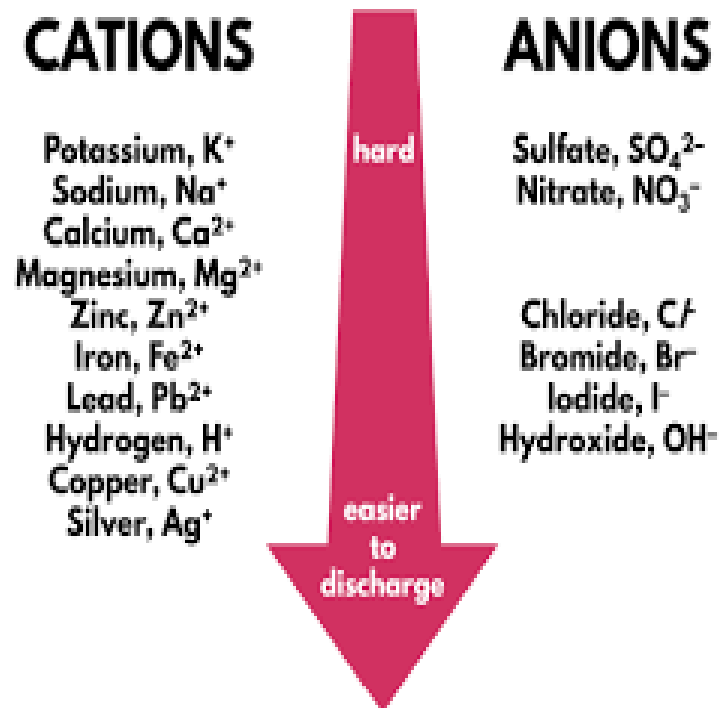
The values of discharge potential are different for different ions

the electrolysis of a solution of NaCl yields

H_2 at the cathode and

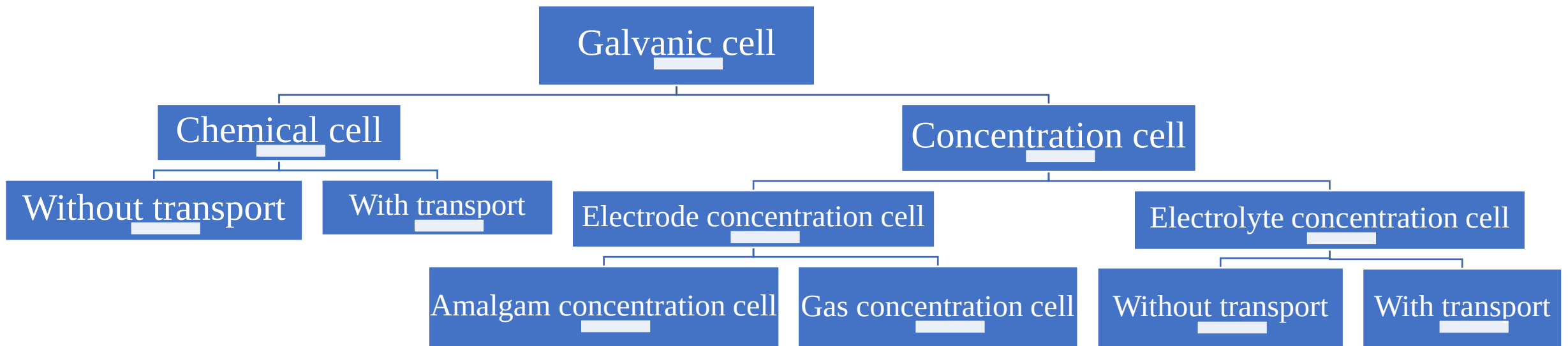
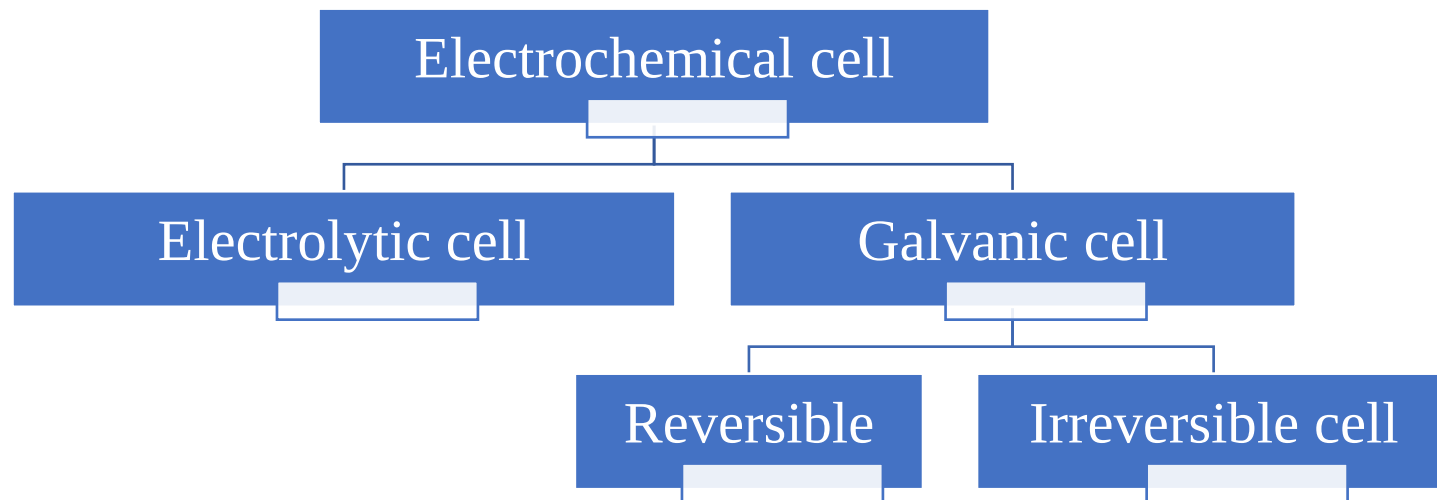
Cl_2 at the anode

less preferred" ions Na^+ and OH^- form the base NaOH



Comparison between galvanic and electrolytic cell

	Galvanic cell (Voltaic)	Electrolytic cell
Principle	Convert chemical energy to electrical energy.	Convert electrical energy to chemical energy.
External emf	Not present.	Present.
Electrodes	Active (participate in the redox reaction)	Usually inert (don't participate in the redox reaction).
Anode	Oxidation, negative	Oxidation, positive
Cathode	Reduction, positive	Reduction, negative
Salt bridge	May be present.	Not present.
Cations	From dissolution of anode.	Moves to cathode.
Anions	Remained after deposition at cathode.	Moves to anode.
Chemical reaction	Spontaneous.	Non spontaneous.



Reversible and Irreversible Cells

A cell is said to be reversible if it fulfills the following conditions:

- (a) Suppose the EMF of the cell is E_{cell} . If an external EMF of the same magnitude is applied to balance the EMF of the cell no current should flow to and from the cell.
- (b) If the external EMF is decreased by an infinitesimal amount ΔE_{cell} , a small current should flow from the cell and a chemical reaction, proportional to the quantity of electricity passing, should take place in the cell.
- (c) If the external EMF is increased by an infinitesimal amount ΔE_{cell} , the current should flow in the opposite direction, proportional to the quantity of electricity passing and the cell reaction should be reversed.

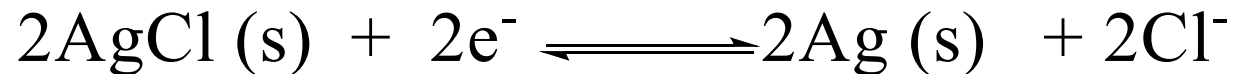
If the cell does not satisfy these conditions, it is said to be *irreversible*.

Example for reversible cell

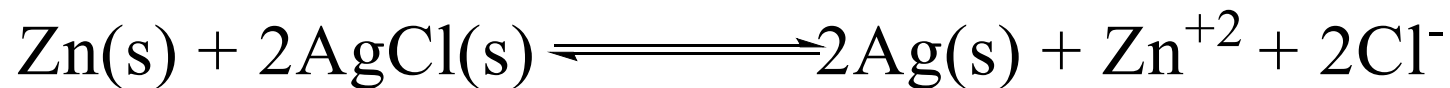
- ❑ Consider a cell composed of a zinc and a silver-silver chloride electrode, both dipping into a solution of zinc chloride.
- ❑ When the two electrodes are connected externally through a conductor, electrons flow through the outer circuit from the zinc to the silver-silver chloride.
- ❑ During this passage of current zinc dissolves at one electrode (anode) to form zinc ions,



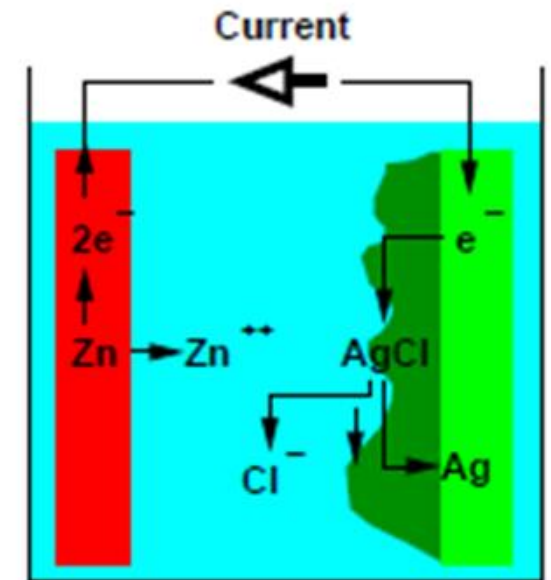
while at the other electrode (cathode) the reaction takes place.



- ❑ The net reaction for the cell is, therefore,



This process continues as long as the external opposing potential is infinitesimally smaller than that of the cell.

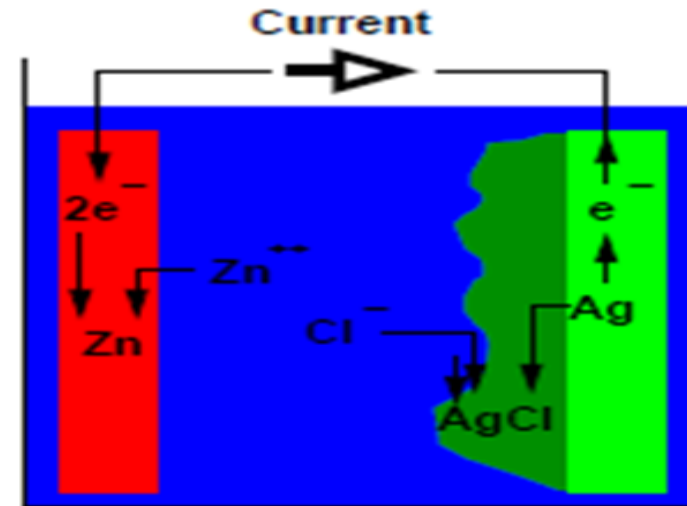
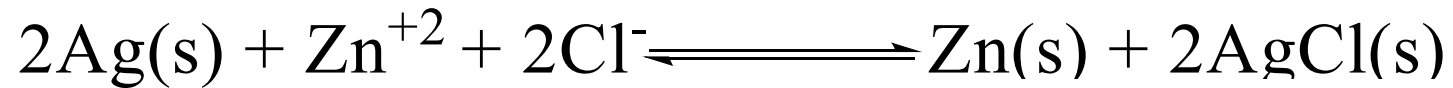


If external opposing potential becomes slightly larger than that of the cell, the direction of current flow is reversed, and so is the cell reaction. Now zinc ions go to form zinc at one electrode, silver chloride is formed from silver and chloride ions at the other, and the over-all cell reactions becomes:

At anode: $\text{Zn}^{+2} + 2\text{e}^{-} \rightleftharpoons \text{Zn}$

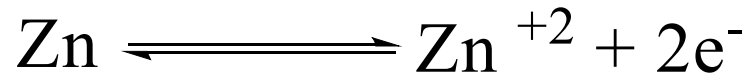
At Cathode: $2\text{Ag}(\text{s}) + 2\text{Cl}^{-} \rightleftharpoons 2\text{AgCl}(\text{s}) + 2\text{e}^{-}$

The overall cell reaction:

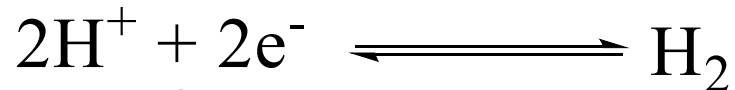


Example for irreversible cell

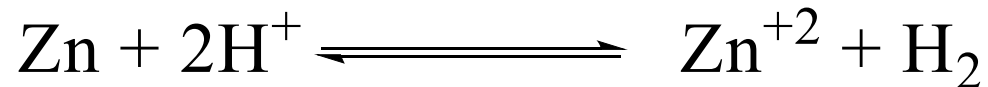
- ❑ Consider a cell composed of a zinc and a Cu electrode, both dipping into a solution of H_2SO_4 .
- ❑ When the two electrodes are connected externally through a conductor, electrons flow through the outer circuit from the zinc to the H_2SO_4 .
- ❑ During this passage of current zinc dissolves at one electrode (anode) to form zinc ions,



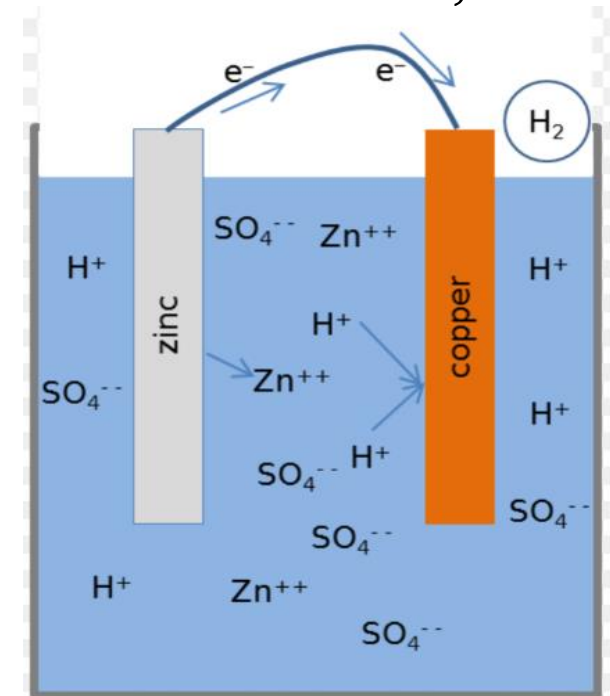
while at the other electrode (cathode) the reaction takes place.



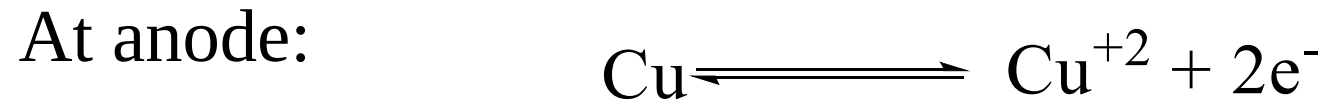
- ❑ The net reaction for the cell is, therefore,



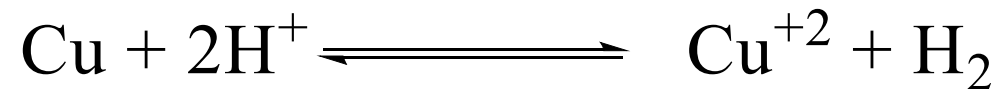
This process continues as long as the external opposing potential is infinitesimally smaller than that of the cell.



If external opposing potential becomes slightly larger than that of the cell, the direction of current flow is reversed, and a new cell reaction produced. Now Cu metal is oxidized to Cu^{+2} at one electrode, the H^{+} ions reduced to H_2 gas, and the over-all cell reactions becomes:



The overall cell reaction:

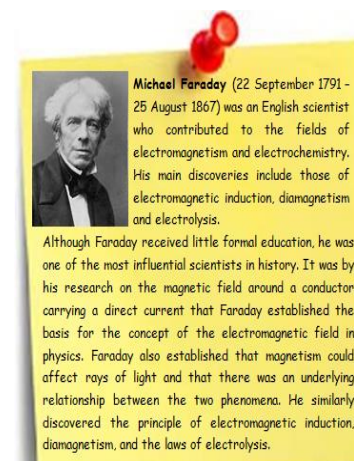


Quantitative Considerations

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred

For example	
$1Ag_{(aq)}^+ + 1e^- \rightarrow Ag_{(s)}$	$1Cu_{(aq)}^{2+} + 2e^- \rightarrow Cu_{(s)}$
1 mol of electrons reduces 1 mol of	1 mol of electrons reduces only 0.5 mol of
$Ag^+ \rightarrow Ag$ metal	$Cu_{(aq)}^{2+} \rightarrow Cu_{(s)}$ metal

Recall that the charge on 1 mol of electrons is 1 faraday (1 F), which is equal to 96,486 C.



Faraday's Laws of Electrolysis:

Faraday's laws are the **two laws** given by Michael Faraday in 1834 which describes and defines the quantitative relationship between **electricity** and **ions deposited** at electrodes. The two laws of Faraday's Laws of Electrolysis are:

Faraday's First Law of Electrolysis

The mass of ions or substances liberated, deposited or dissolved at an electrode during electrolysis is directly proportional to the quantity of electricity transferred to the electrode.

$Q = \text{current in amperes} \times \text{time in seconds}$

$$Q = i \times t$$

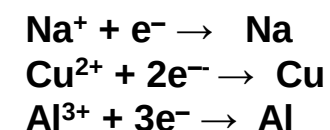
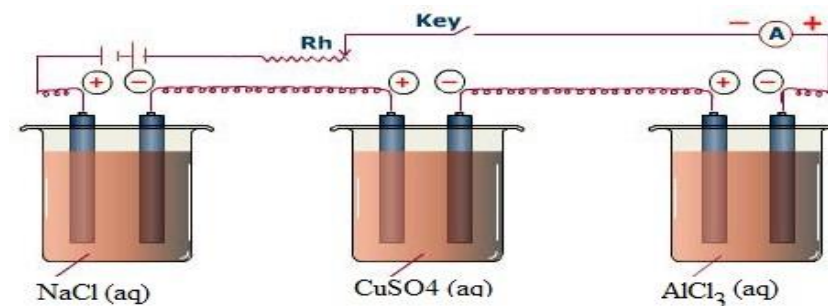
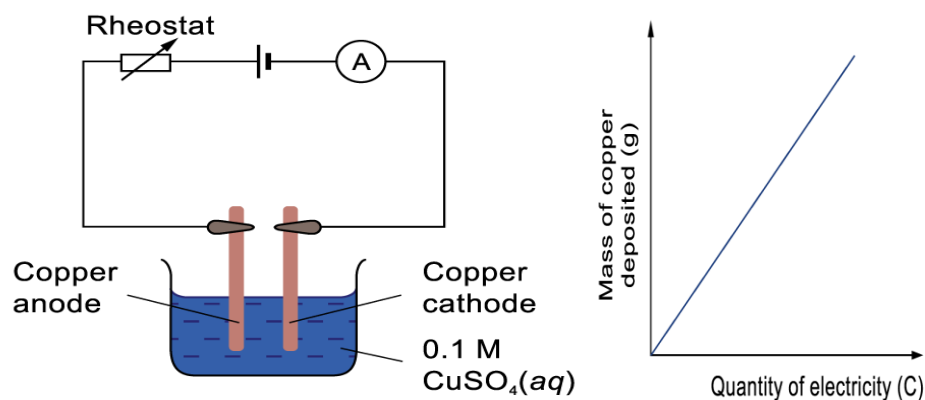
$$W \approx i \times t$$

Faraday's laws of electrolysis

Faraday's second Law of Electrolysis

If same amount of electricity is passed through different electrolytes then the mass of substances deposited in the electrodes are proportional to their respective equivalent weight or chemical equivalent.

$$W \approx \text{equivalent weight}$$



Faraday Constant

Element	Electrolyte	No. of coulombs to liberates 1 mole of metal atom
Iron	$\text{Fe}_2(\text{SO}_4)_3(\text{aq})$	289 500
Copper	$\text{CuSO}_4(\text{aq})$	193 000
Iron	$\text{Fe}(\text{NO}_3)_2(\text{aq})$	193 000
Zinc	$\text{ZnCl}_2(\text{aq})$	193 000
Silver	$\text{AgNO}_3(\text{aq})$	96 500

Charge of 1 mole of electrons
 = 1 Faraday
 = 96 500 coulombs

Number of moles of product formed = $\frac{It}{zF}$

$$\text{Moles of Electrons} = \frac{Q (C)}{F (C \text{ mol}^{-1})} = \frac{It}{F}$$

$$W = \frac{At \cdot wt}{n}$$

$$W = \frac{I t At \cdot wt}{F z}$$

Units and Equations

1 Volt = 1 Joule per Coulomb = 1 J C

Coulomb: The S.I. unit of charge.

Current: Measured in **Amperes, A**

Current = charge / time (**IN SECONDS**)

units = C s⁻¹ = A

or

Coulombs = Amperes x time

$$Q = I \times t$$

Q = Charge in Coulombs,

I = current in Amperes

t = time in Seconds

e.g. if 1.50 A flows for 5.00 min then the charge

$$Q = (1.50 \text{ A})(5.00 \times 60 \text{ sec}) = 450 \text{ C}$$

From the 1st and 2nd law of faraday:

$$W \approx \text{eq. wt} \times Q$$
$$W \approx \text{eq. wt} \times i \times t$$

$$W = \frac{\text{eq. wt} \times i \times t}{F}$$

$$W = \frac{\text{At. wt} \times i \times t}{z \times F}$$

Where W = The mass of ions or substances liberated, deposited or dissolved at an electrode (gm)

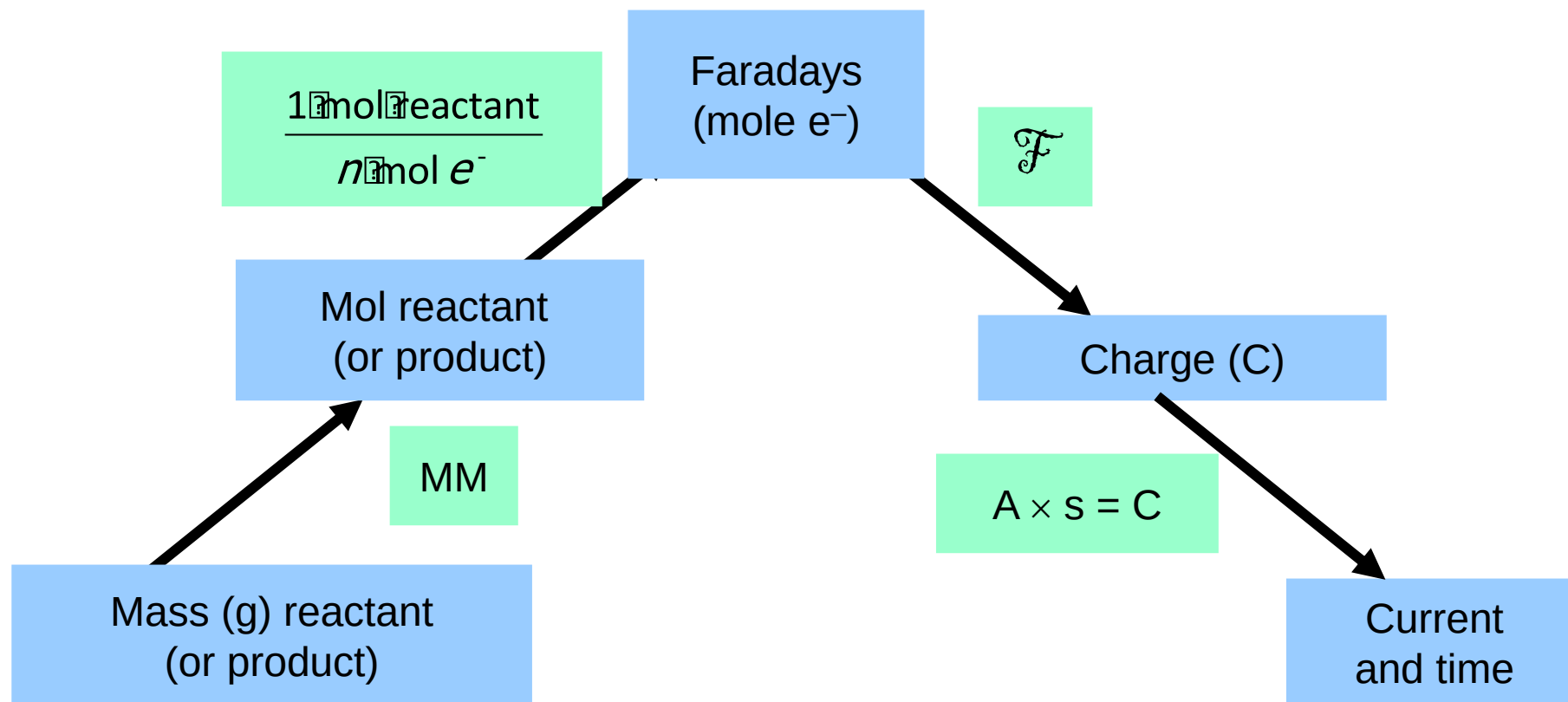
i = current (A)

t = time (s)

F= faraday constant (96500 c)

Q= amount of electrical charge (c)

Z = amount of electron transferred during oxidation or reduction reaction.



How many grams of Al(s) and Cl₂(g) are produced if a cell of molten AlCl₃ is electrolyzed with 0.452 amps for 1.5 hours?

Solution

$$I = 0.452 \text{ A}$$

$$t = 1.5 \times 60 \times 60 = 5400 \text{ s}$$

$$F = 96500 \text{ c}$$

$$\text{At.wt (Cl}_2\text{)} = 2 \times 35.5 = 71$$

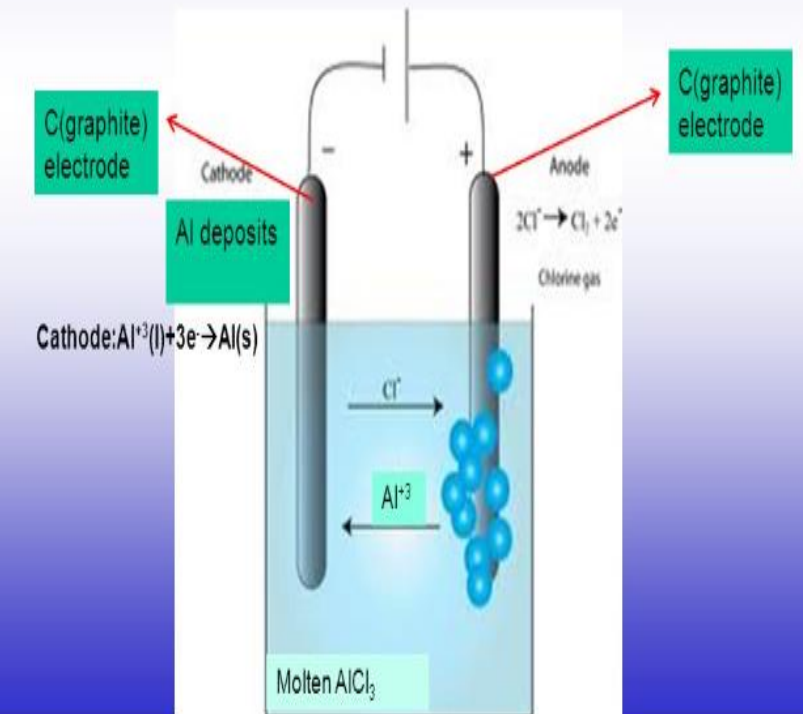
$$\text{At.wt (Al)} = 27$$



$$W = \frac{I t \text{ At. wt}}{F z}$$

Al	Cl ₂
$W = \frac{0.452 \times (1.5 \times 60 \times 60) \times 27}{96485 \times 3} = 0.228 \text{ g}$	$W = \frac{0.452 \times (1.5 \times 60 \times 60) \times 70.9}{96485 \times 2} = 0.896 \text{ g}$

Overall electrolytic cell rxn: $\text{AlCl}_{3(l)} \rightarrow \text{Al(s)} + 3/2\text{Cl}_{2(g)}$



How many seconds required for deposition of 20 g of Cu from CuSO_4 using a current with a value of 15 A (At.wt of Cu = 63.54, $F = 96500$ c)

Solution

$$I = 15 \text{ A}$$

$$W = 20 \text{ g}$$

$$F = 96500 \text{ c}$$

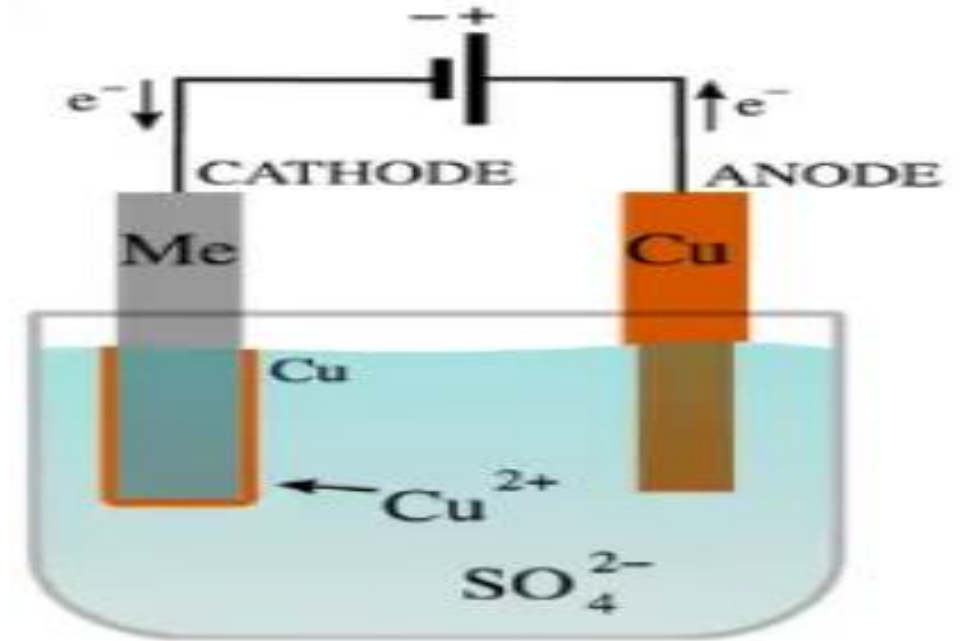
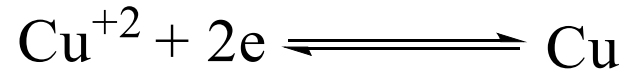
$$\text{At.wt (Cu)} = 63.54$$

$$t = \text{????}$$

$$W = \frac{I t \text{ At.wt}}{F z}$$

$$t = \frac{W z F}{I \text{ At.wt}}$$

$$t = \frac{20 \times 2 \times 96500}{15 \times 63.54} = 4050 \text{ s} = 67.5 \text{ min} = 1.125 \text{ h}$$



Calculate the amount of electrical charges (Q) required for deposition of 0.15 g of Zn from ZnSO₄ solution

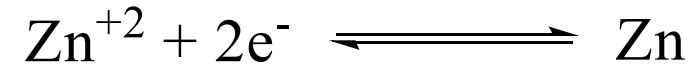
Solution

$$W = 0.15 \text{ g}$$

$$F = 96500 \text{ c}$$

$$\text{At.wt (Zn)} = 65.73$$

$$Q = \text{????}$$



$$W = \frac{Q \text{ At. wt}}{F z}$$

$$Q = \frac{W z F}{\text{At. wt}}$$

$$Q = \frac{0.15 \times 2 \times 96500}{65.37} = 442.86 \text{ c}$$

What are the weights (g) of both Au and Cl₂ produced by passing of 1000 c through AuCl₃ solution?

Solution

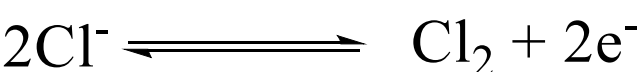
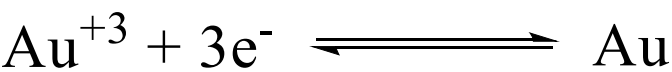
$$W = \text{????? g}$$

$$F = 96500 \text{ c}$$

$$\text{At.wt (Au)} = 197$$

$$Q = 1000 \text{ c}$$

$$\text{At.wt (Cl}_2\text{)} = 2 \times 35.5 = 71$$



$$W = \frac{Q \text{ At.wt}}{F z}$$

Au	Cl ₂
$W = \frac{1000 \times 197}{96485 \times 3} = 0.68 \text{ g}$	$W = \frac{1000 \times 70.9}{96485 \times 2} = 0.367 \text{ g}$

Aluminum metal (Al) can be produced from electrolysis of Aluminum oxide (Al₂O₃). Calculate the time required for deposition of 454 g of Al metal using current of 11.2 A?

Solution

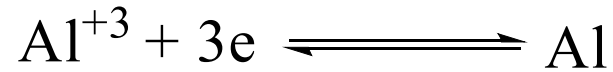
$$W = 454 \text{ g}$$

$$F = 96500 \text{ c}$$

$$\text{At.wt (Al)} = 27$$

$$I = 11.2 \text{ A}$$

$$t = \text{????}$$



$$W = \frac{I t \text{ At.wt}}{F z}$$

$$t = \frac{W z F}{I \text{ At.wt}}$$

$$t = \frac{454 \times 3 \times 96500}{11.2 \times 27} = 434632.9 \text{ s} = 7243 \text{ min} = 120.73 \text{ h}$$

In the electrolysis of KI, I₂ formed at anode while H₂ formed at cathode. If current with 5.2 A passed for 46 min, calculate the weight of both I₂ and H₂.

Solution

$W = \text{????? g}$

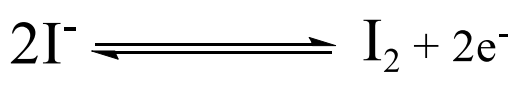
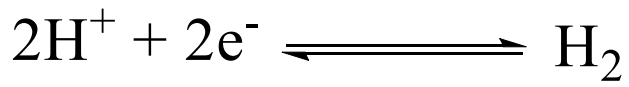
$F = 96500 \text{ c}$

$\text{At.wt (I}_2\text{)} = 2 \times 127 = 254$

$I = 5.2 \text{ A}$

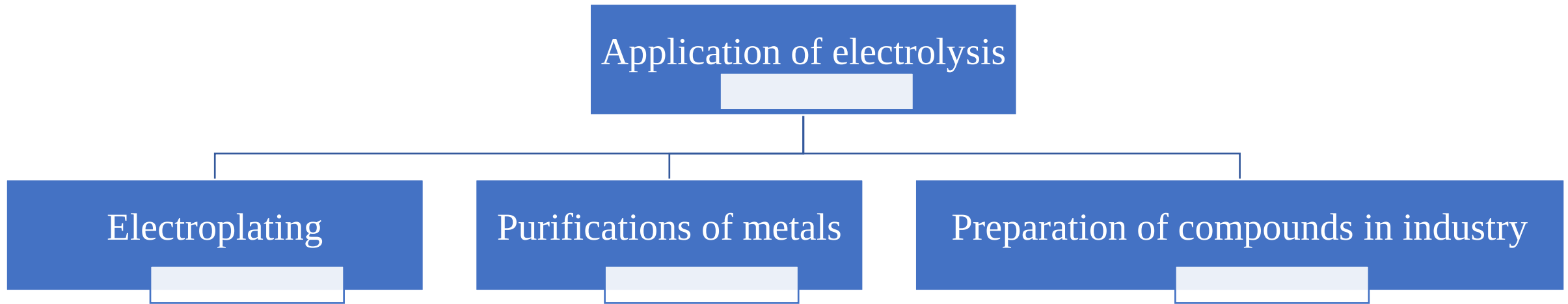
$\text{At.wt (H}_2\text{)} = 2 \times 1 = 2$

$t = 46 \times 60 = 2760 \text{ s}$



$$W = \frac{I \ t \ \text{At. wt}}{F \ z}$$

I ₂	H ₂
$W = \frac{5.2 \times 2760 \times 254}{96485 \times 2} = 18.888 \text{ g}$	$W = \frac{5.2 \times 2760 \times 2}{96485 \times 2} = 0.148 \text{ g}$



Electroplating

is the process of deposition a layer of any desired metal on another metal by means of electricity.

is the process of plating a metal onto the other by hydrolysis mostly to prevent corrosion of metal or for decorative purposes.

Advantages

- Shiny appearance and decoration.
- protection against corrosion

Theory of Electroplating:

The metal salt aqueous solution i.e. electrolytic solution undergoes ionization forming ions. When a potential difference is applied to this salt solution by dipping two electrodes in the solution, the metal ions migrate from the solution and get deposited on the cathode (the article to be electroplated). Now there are two cases:

❖ When anode is made of the coating metal,

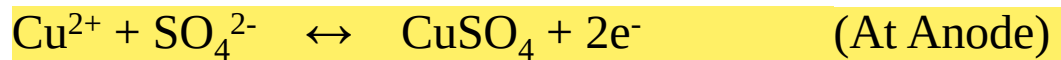
The concentration of the plating bath solution will not alter during electrolysis because metal ions deposited on the cathode from the bath are continuously replenished by the reaction of free anions with the anode metal. For Example, If CuSO_4 solution is used as an electrolyte and anode is of pure copper then,



On passing current, Cu^{2+} ions migrate to cathode and get deposited there.



The free sulphate ions present in bath migrate to the copper anode and dissolve an equivalent amount of copper from the anode to form copper sulphate.



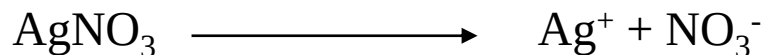
Copper sulphate thus formed, dissolves in the electrolyte and thus there is a continuous replenishment of electrolyte salt during electrolysis

❖ When the anode is made up of some inert material like graphite

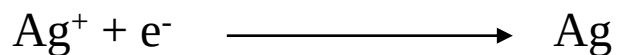
The electrolyte salt is continuously added to the electrolytic bath in order to maintain proper concentration of the coating metal ions. In such cases, the process of electroplating is continuous because anode is not consumed and hence its replenishment is not required.

Electroplating of spoon with silver

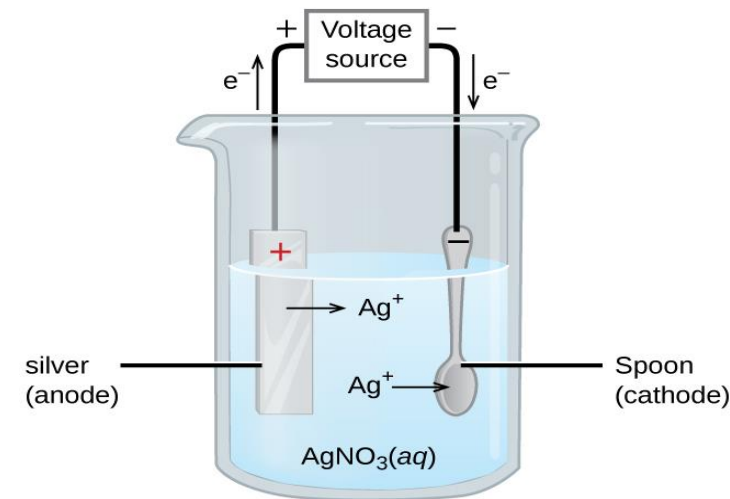
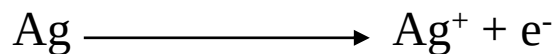
1. The surface of spoon should be cleaned and then connected to negative terminal to act as cathode .
2. sheet of pure silver metal should be connected to positive terminal to act as anode.
3. Both electrodes immersed in one electrolyte containing silver ions e.g. AgNO_3 .



4. At cathode silver ion from solution reduced on spoon Surface as a layer of silver metal



5. At anode the Ag^+ consumed from solution generated again from oxidation of silver metal connected to positive terminal of battery .



We should note that

- ❑ Amount of silver deposited on spoon depends on amount of current according to Faraday laws
- ❑ The redox reaction of electroplating occurred due to the presence of battery. So its- non spontaneous reaction.
- ❑ In Electroplating - Electrical energy has been converted to chemical energy.

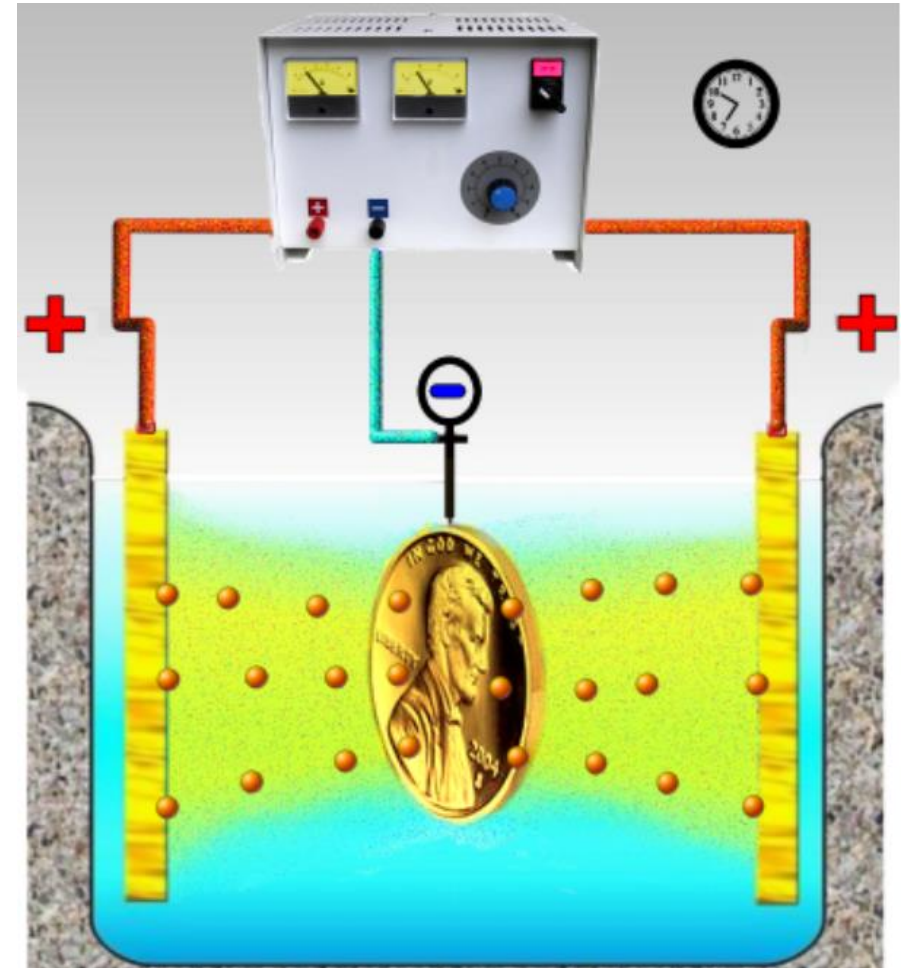
Preparation of Basis Material:

Before a metal or non-metal is electroplated, the surface must be physically, chemically and mechanically clean.

- ❑ Physical cleaning: means freedom from Oils, greases, superficial dirt associated with polishing, buffing operations and atmospheric dust.
- ❑ Chemical cleaning: means freedom from oxides or other surface formed compounds of the basis metal,
- ❑ Mechanical cleaning: means freedom from surface skin of damaged material e.g. loose fragments, scratches & strains produced by mechanical operation.

Electroplating involves a series of operations, each of which is vital in determining the quality of final product. Following are the minimum number of steps involved in succession:

1. Pickling (Removal of scales)
2. Mechanical preparation of surface
3. Cleaning for physical cleanliness
4. Rinsing
5. Acid dipping for chemical cleanliness
6. Rinsing
7. Electroplating
8. Rinsing
9. Drying



Pickling: This involves the removal of relatively heavy scales of oxides formed from hot rolling, casting and heat treatment and also involves removal of rust or tarnish due to exposure to atmosphere. This operation usually precedes polishing & buffing Pickling consists of immersing the article in dil. HCl or dil. H₂SO₄. For cleaning copper, nickel & brass metal in the pickling bath consists of a dilute solution of HNO₃ or a mixture of dil. HNO₃ & dil. H₂SO₄.

Mechanical Preparation: This is done to achieve better appearance and better surface protection from corrosion and superior engineering properties. The rough surfaces are made smooth by mechanical methods such as grinding with the help of grinding stone or grinding wheel and scratch rubbing either with the help of wire brush or abrasive paper of cloth.

Physical Cleanliness: This involves the removal of oil, grease, atmospheric dust or polishing and buffing compounds. It is done by using organic solvent such as trichloroethylene or perchloroethylene. This is followed by cleaning with aqueous cleaning agents such as sodium carbonate, sodium hydroxide and sodium silicate.

Rinsing: Rinsing the article with clean running water is important between different steps in electroplating. Rinsing is done either by dipping the metal in clean running water &/or by spray rinsing or both depending upon the shape and drag out characteristics of the article being plated.

Acid dipping for chemical cleanliness: This is done by dipping the metal in 10-30% by volume of dil. HCl or dil. H₂SO₄. This operation removes any tarnish film produced during cleaning process and also neutralizes any alkaline film formed which cannot be completely removed by rinsing. This is essential to ensure that the pH of the plating bath is not affected. Subsequent to the acid dip and the rinse following it, neutralization by dipping the metal in dilute cyanide solution may be desirable to prevent rusting. produced by depositing a continuous coating of Cu or Ag by chemical reduction or metal spraying produced by depositing a continuous coating of Cu or Ag by chemical reduction or metal spraying.

There are major factors that influence the last plating. These include:

- ☐ The voltage level of current.
- ☐ The temperature and chemical composition of the bath.
- ☐ The current length of time.
- ☐ The distance between the cathode and the anode.

Uses of Electroplating

The major application is to:

- 1) optimize a material's resistance towards corrosion. The plated layer often serves as a sacrificial coating which reveals that it dissolves before the base substance.
- 2) Improving wear resistance.
- 3) Improving the thickness of the metal surface.
- 4) Enhancing the electrical conductivity like plating a copper layer on an electrical component.
- 5) Minimizing Friction.
- 6) Improving surface uniformity.

There are two ways in which concentration of metal ions in electrolyte is maintained :

1. Addition of electrolyte externally followed by analysis. In this case inert anode such as graphite is used. Ex. Electroplating of Chromium & Rhodium.
2. By using continuously dissolving anode of the metal ion to be coated. Ex. Electroplating of Silver, zinc, Nickel & Copper.

Although the later type of process would appear to maintain a balanced concentration of metal ion in solution because the same amount of current flows from anode to cathode. But, however, in practice there are several factors which upset this balanced concentration of metal ion in solution.

These factors are:

1. Difference in anodic and cathodic current efficiencies.
2. Passivation of anode by the formation of obstructive film e.g. oxide, chloride, sulphide etc.

When anodic current efficiency is lower than cathodic current efficiency and when the anode passivates a balance concentration of metal ion cannot be maintained.

Important characteristics of Electroplating:

- ❑ If electroplating is done for decoration, thin film is deposited but if the electroplating is done for protection, thick coating is desired. In actual practice for protection against corrosion multiple coatings are given on metal surface.
- ❑ The coating must adhere strongly to the surface otherwise the film may get removed by peeling off. Maximum adhesion can be achieved by the removal of dust, dirt, extraneous matter such as oil, grease, surface formed compounds e.g. oxides etc from the base metal surface.
- ❑ If protection from abrasion is desired, the coating must be hard. The hardness is measured in Brinels. For lead coating hardness is 5 Brinels and for Cr coating it is 1000 Brinels
- ❑ **Brightness:** The coating must be bright. The brightness of the film depends upon the smoothness of the surface and natural reflectance of the coated metal.

- ❑ **Current Density:** Current density is defined as the current required for coating per unit area of the object and it is expressed in A/cm^2 or mA/cm^2 . The current density used in electroplating should be of proper strength. If the current density is too high it will result in loose and brittle film while if it is too low the rate of deposition will be very low. Hence the optimum current densities should be used. However the upper limit of current density in electroplating can be raised by keeping the electrolytic bath at elevated temperature and also by agitating the bath.
- ❑ **Metal ion Concentration:** The electrolyte concentration should be low to prevent high electrolytic resistance. The low metal ion concentration does not mean that dilute solutions are to be used. Those electrolyte solutions which undergo slow ionization or whose ionization is suppressed by the addition of another salt having common ion or which produces metal ion not by primary ionization but by secondary ionization are to be used.
- ❑ **Throwing Power:** Throwing power means the ability of electrolytic bath to give a deposit of uniform thickness over the entire irregularly shaped cathode area. Maximum throwing power is shown by such a cell system in which all cathodes no matter how irregularly shaped receive a uniform coating. While electrolytic bath with Poor throwing power produces an article which is virtually uncoated in crevices and corners.

Factors affecting throwing Power:

- 1. Optimum displacement of electrodes:** In case of irregularly shaped object throwing power can be improved by optimum displacement of anodes together with the use of auxiliary anodes.
- 2. High conductance of electrolytic solution:** High conductance of electrolytic solution causes uniform distribution of current over even a complex surface. In other words high conductance of solution causes uniform rate of deposition over the entire cathode.
- 3. Additives:** Throwing power is usually enhanced in presence of additives such as complexing agents and levelers. The function of Levelers is to produce a level deposit by getting itself adsorbed at regions where rapid diffusion of ions takes place i.e the adsorbed leveler decreases the electron transfer rate at such regions. Ex. For Nickel plating, Sodium allyl sulphate is employed as leveler.
- 4. Hydrogen evolution:** When electrode reactions are competed simultaneously by hydrogen evolution, the metal deposition takes place at high overpotential. This in turn causes reduction in the overpotential at these points, thereby resulting in more uniform deposits.

Nickel electroplating

Nickel electroplating is a technique of [electroplating](#) a thin layer of [nickel](#) onto a [metal](#) object. The nickel layer can be decorative, provide [corrosion](#) resistance, [wear](#) resistance, or used to build up worn or undersized parts for salvage purposes.

Watts baths

A ***Watts bath***, named for its inventor [Oliver Patterson Watts](#), is an aqueous electrolyte solution for plating nickel from a nickel anode. It can deposit both bright and semi-bright nickel. Bright nickel is typically used for decorative purposes and corrosion protection. Semi-bright deposits are used for engineering applications where high corrosion resistance, ductility or electrical conductivity is important, and a high luster is not required

Bath composition

Chemical Name	Formula	Bright		Semi-bright	
		Metric	US	Metric	US
Nickel sulfate	NiSO ₄ ·6H ₂ O	150–300 g/L	20–40 oz/gal	225–300 g/L	30–40 oz/gal
Nickel chloride	NiCl ₂ ·6H ₂ O	60–150 g/L	8–20 oz/gal	30–45 g/L	4–6 oz/gal
Boric acid	H ₃ BO ₃	37–52 g/L	5–7 oz/gal	37–52 g/L	5–7 oz/gal

Typical Recipe and Conditions *Watts Nickel*

Component	Concentration/g L ⁻¹
Nickel sulphate	330
Nickel chloride	45
Boric acid	40
Additives	various
Temperature	60 °C
pH	4
Current density	2-10 A dm ⁻²

Operating conditions

- Temperature: 40-65 ° C
- Cathode current density: 2-10 A/dm²
- pH: 4.7-5.1

Applications

- Decorative coating
- Engineering applications

What is the Job of the Bath?

1. Provides an electrolyte
2. Provides a source of the metal to be plated
3. Allows the anode reaction to take place
4. Wets the cathode work-piece
5. Helps to stabilise temperature

Parameters that may influence the quality of electrodeposits

1. Current density (low to high current)
2. The nature of anions/cations in the solution
3. Bath composition, temperature, fluid flow
4. Type of current waveform
5. the presence of impurities
6. physical and chemical nature of the substrate surface

Current efficiency

Is the ratio between the actual amount of metal deposit, M_a to that calculated theoretically from Faradays Law, M_t .

$$\text{Current efficiency} = \frac{M_a}{M_t} \times 100$$

Example:

Nickel is plated from a Watts bath at a current density of 3 A dm⁻². The current efficiency is 96%. The molar mass of nickel is 58.71 g mol⁻¹. The density of nickel is 8.90 g cm⁻³. The Faraday constant is 96 485 C mol⁻¹. What will be the averaged plating thickness in 1 hour?

Solution

Assume that the reaction is:



So, two electrons are involved for every Ni atom, and $z = 2$

The current density used in plating nickel is 96% of the total current, i.e., 0.96 x 3 A dm⁻².

The average deposit thickness is given by:

$$x = \frac{\text{M.I.t}}{\rho.A.z.F}$$

$$x = \frac{(58.71 \text{ g mol}^{-1})(0.96 \times 3 \text{ A})(3600\text{s})}{(8.90 \text{ g cm}^{-3})(100 \text{ cm}^2)(2)(96485 \text{ C mol}^{-1})}$$

$$x = 3.54 \times 10^{-3} \text{ cm} = 35.4 \times 10^{-4} \text{ cm} = 35 \text{ }\mu\text{m}$$

Electrolytic Refining of Metals

Definition: The process of electrolytic refining of metals is used to extract impurities from crude metals.

Here in this process, a block of crude metal is used as anode, a diluted salt of that metal is used as electrolyte and plates of that pure metal is used as cathode.

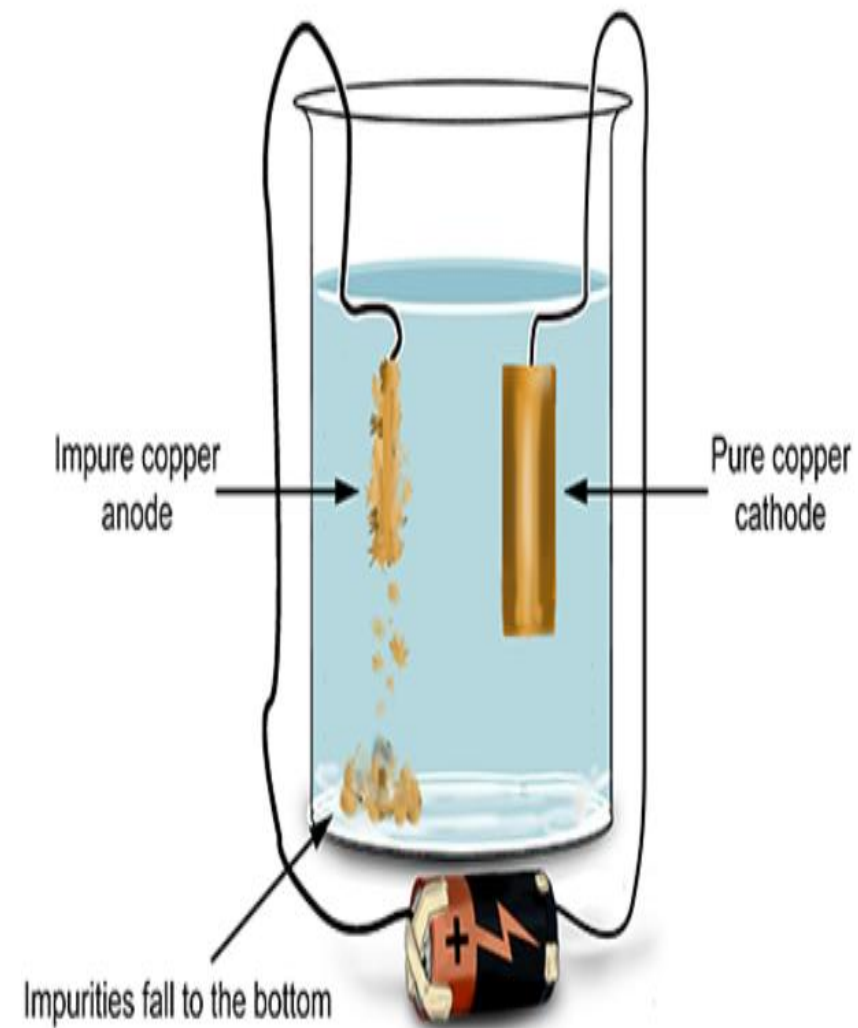
Electrolytic Refining of Copper

For understanding the process of electrolytic refining of metals, we will discuss about an example of electrolytic refining of copper. Copper extracted from its ore, known as blister copper, is 98 to 99 % pure but it can easily be made up to 99.95% pure for electrical application by the process of electrorefining.

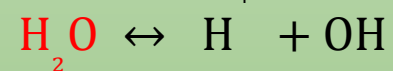
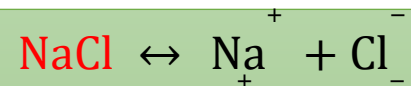
In this process of electrolysis, we use a block of impure copper as anode or positive electrode, copper sulfate acidified with sulfuric acid, electrolyte and pure copper plates coated with graphite, as cathode or negative electrode.

The copper sulfate splits into positive copper ion (Cu^{++}) and negative sulfate ion (SO_4^{--}). The positive copper ion (Cu^{++}) or cations will move towards negative electrode made of pure copper where it takes electrons from cathode, becomes Cu atom and is deposited on the graphite surface of the cathode.

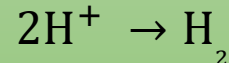
On the other hand, the SO_4^{--} will move towards positive electrode or anode where it will receive electrons from anode and become radical SO_4 but as radical SO_4 can not exist alone, it will attack copper of anode and form CuSO_4 . This CuSO_4 will then dissolve and split in the solution as positive copper ion (Cu^{++}) and negative sulfate ion (SO_4^{--}). These positive copper ions (Cu^{++}) will then move towards negative electrode where it takes electrons from cathode, become Cu atoms and are deposited on the graphite surface of the cathode. In this way, the copper of impure crude will be transferred and deposited on the graphite surface of the cathode. The metallic impurities of anode are also merged with SO_4 , form metallic sulfate and dissolve in the electrolyte solution. The impurities like silver and gold, which are not effected by sulfuric acid-copper sulfate solution, will settle down as the anode sludge or mud. At a regular interval of electrolytic refining of copper, the deposited copper is stripped out from the cathode and anode is replaced by a new block of crude copper.



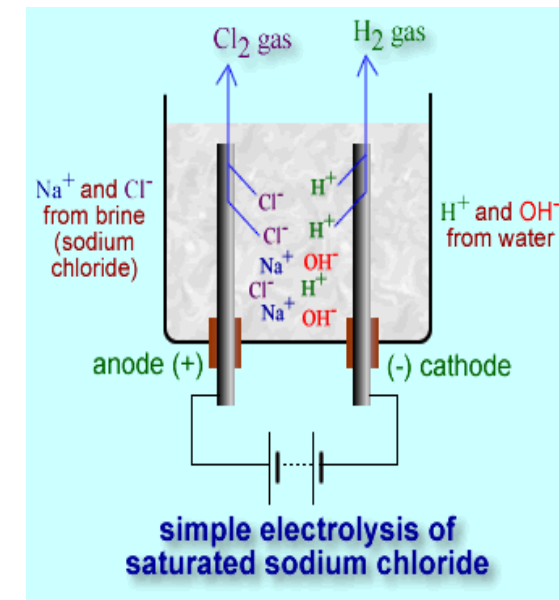
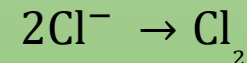
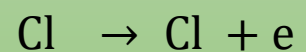
Electrolysis of sodium chloride *NaCl* solution



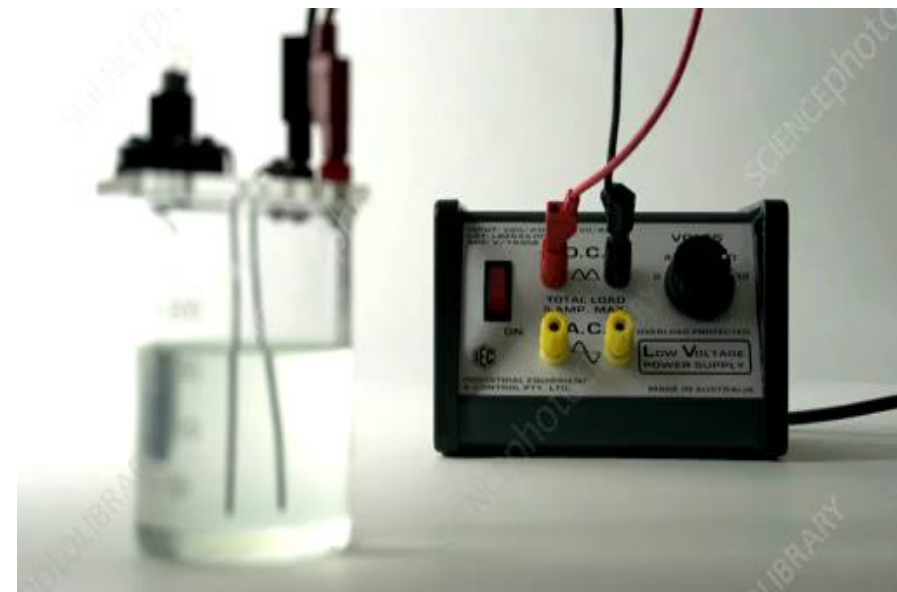
At cathode



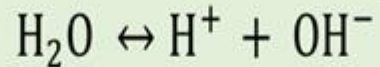
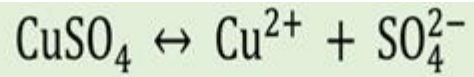
At Anode



- Discharge potential of H⁺ ions are lower than Na⁺ ions.
- Cl⁻ ions are discharged in preference to OH⁻ ions.
- Na⁺ and OH⁻ ions remain in solution and the solution when evaporated yields crystals of sodium hydroxide.

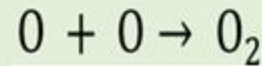
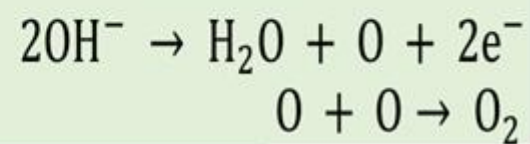
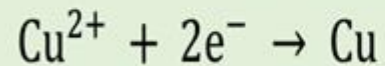


(ii) Electrolysis of CuSO_4 solution using platinum electrodes:

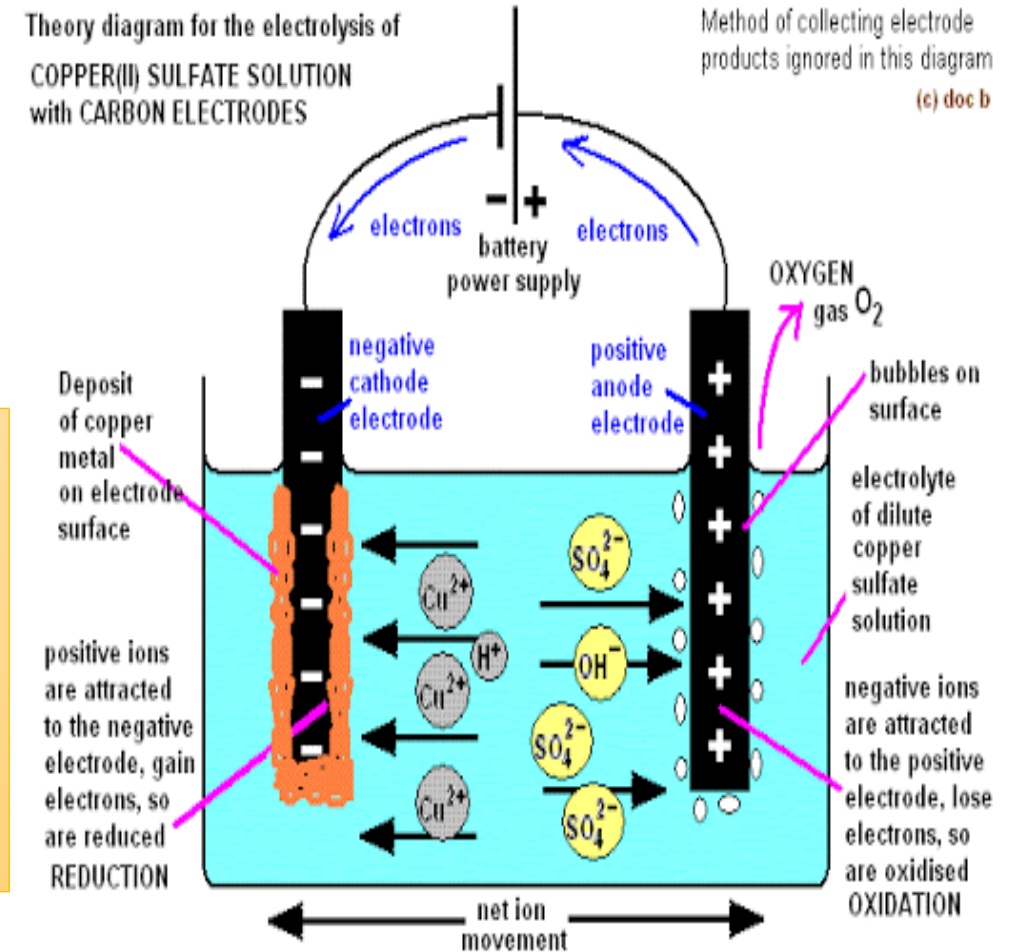


At cathode

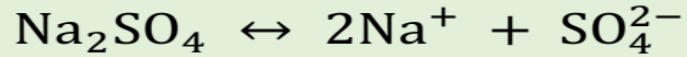
At Anode



- Cu^{2+} ions have **lower** discharge potential than H^+ ions.
- OH^- ions are discharged at anode as these have **lower** discharge potential than SO_4^{2-} ions.
- Thus, copper is deposited at cathode and oxygen gas is evolved at anode.
- The "less preferred" ions H^+ (from H_2O) and SO_4^{2-} (from CuSO_4) form sulfuric acid H_2SO_4

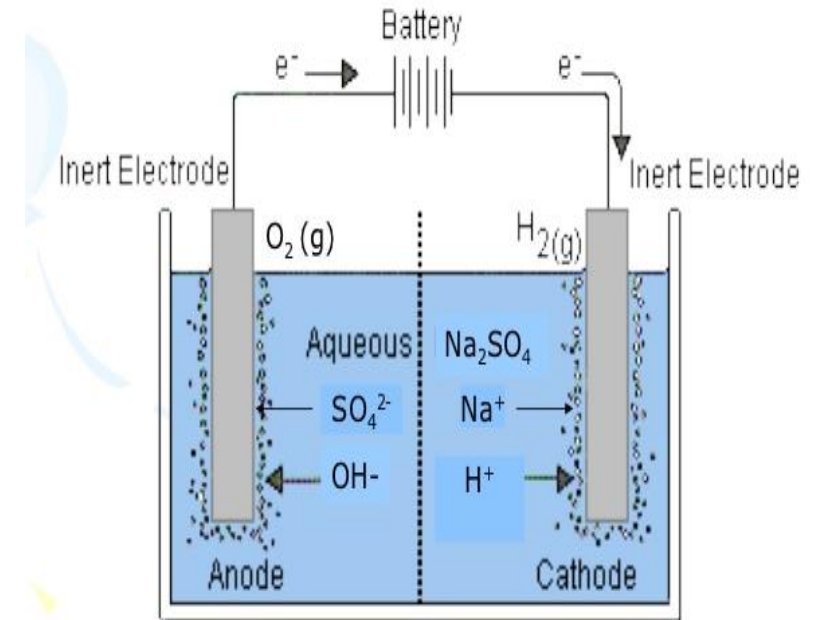
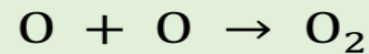
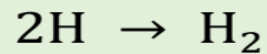
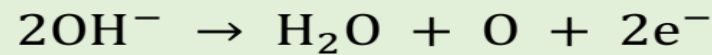
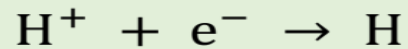


Electrolysis of Na_2SO_4 solution using inert electrodes



At cathode

At Anode



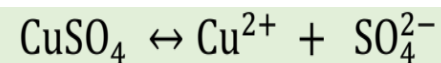
- H^+ is discharged at cathode as H^+ ions have lower discharge potential than Na^+ ions.
- OH^- ions are discharged at anode as these have lower discharge potential than SO_4^{2-} ions.
- Thus, hydrogen is evolved at cathode and oxygen is evolved at anode, i.e., the net reaction describes the electrolysis of water. The ions of Na_2SO_4 conduct the current through the solution and take no part in the overall chemical reaction.

The decreasing order of discharge potential or the increasing order of deposition of some of the ions is given below:

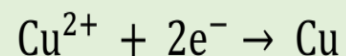
For cations: K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Zn^{2+} , H^+ , Cu^{2+} , Hg^{2+} , Ag^+

For anions: SO_4^{2-} , NO_3^- , OH^- , Cl^- , Br^- , I^-

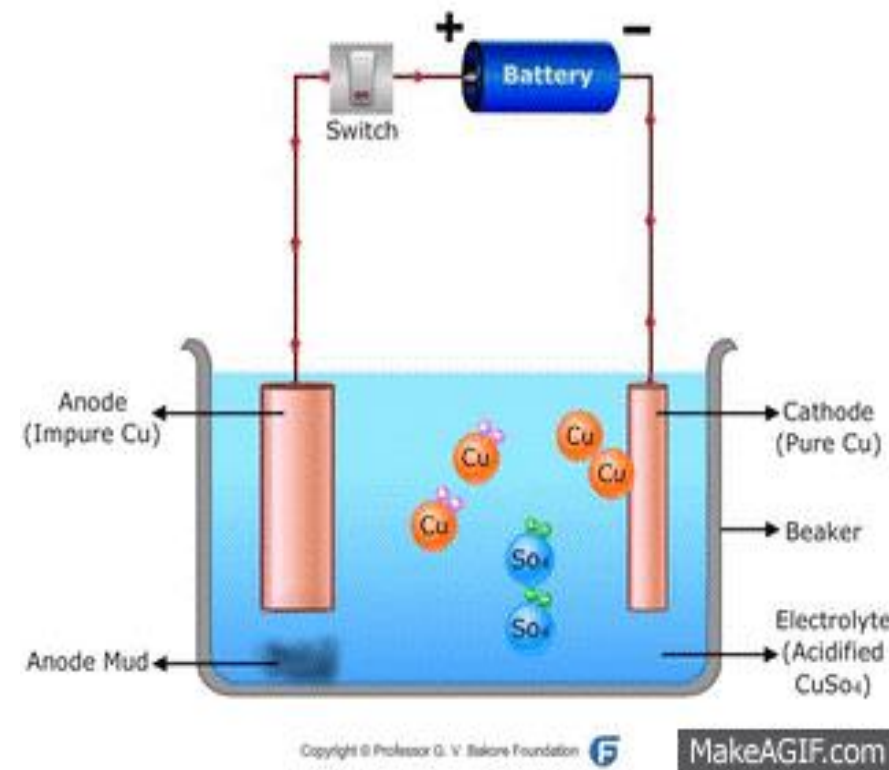
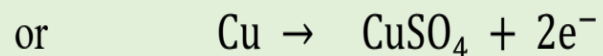
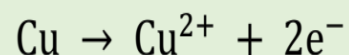
Electrolysis of copper sulphate solution using copper electrodes



At cathode, copper is deposited.

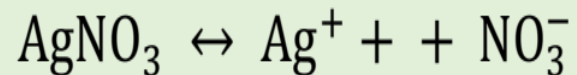


At anode, the copper of the electrode is oxidised to Cu^{2+} ions or ions solution dissolve equivalent amount of copper of the anode.

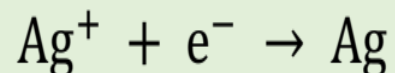


Thus, during electrolysis, copper is transferred from anode to cathode

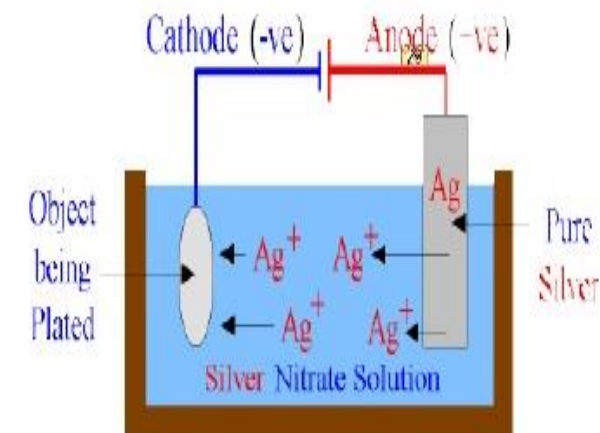
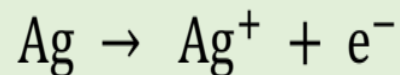
Electrolysis of silver nitrate solution using silver electrodes



At cathode, silver is deposited.



At anode, the silver of the electrode is oxidised to Ag^+ ions which go into the solution or ions dissolve equivalent amount of silver of the electrode.



Some more examples of electrolysis

Electrolyte	Electrode	Cathodic reaction	Anodic reaction
Aqueous acidified CuCl_2 solution	Pt	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
Molten PbBr_2	Pt	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	$2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$
Sodium chloride solution	Hg	$2\text{Na}^+ + 2\text{e}^- \rightarrow 2\text{Na}$	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
Silver nitrate solution	Pt	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	$2\text{OH}^- \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^-$
Sodium nitrate solution	Pt	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	$2\text{OH}^- \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^-$

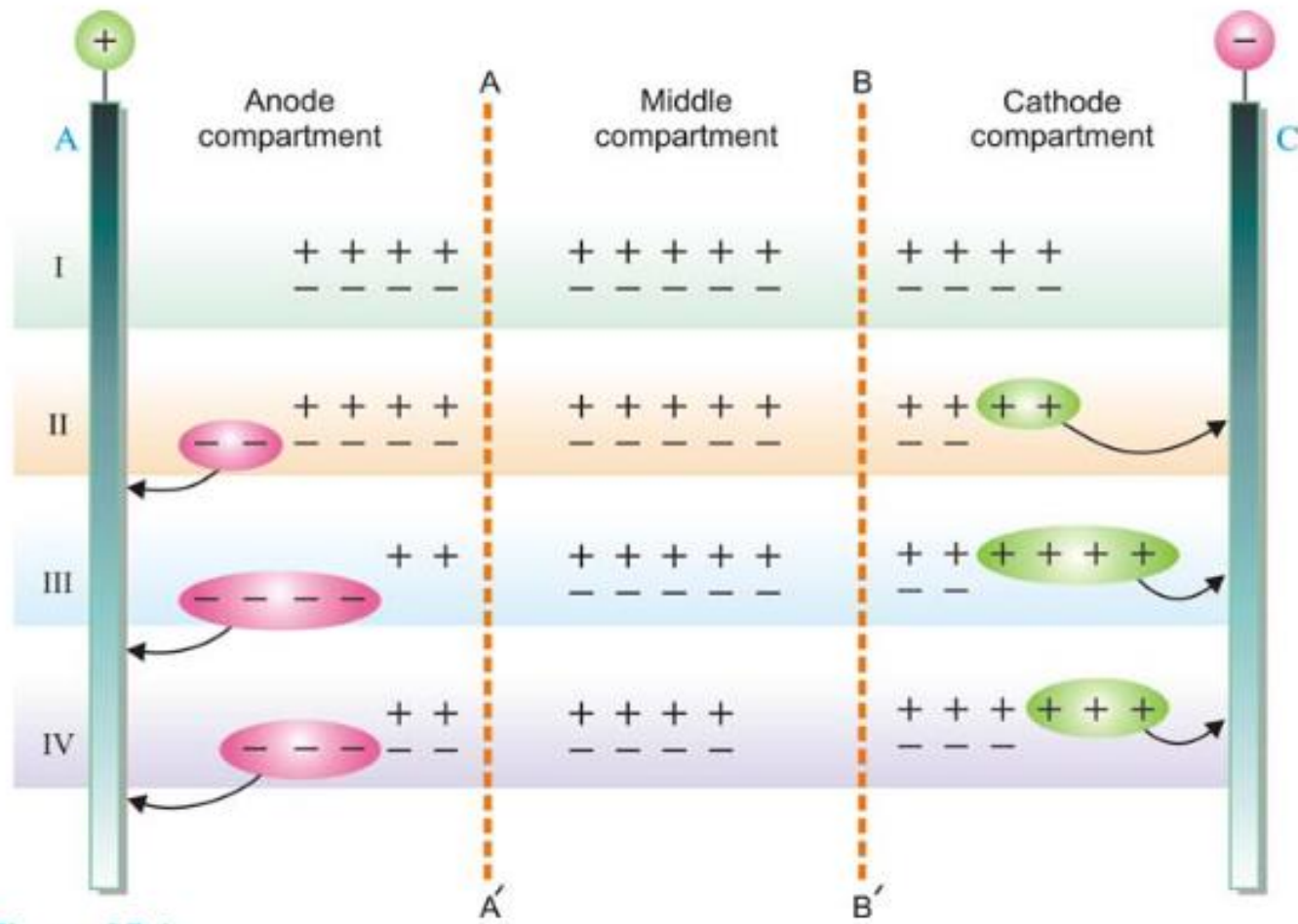
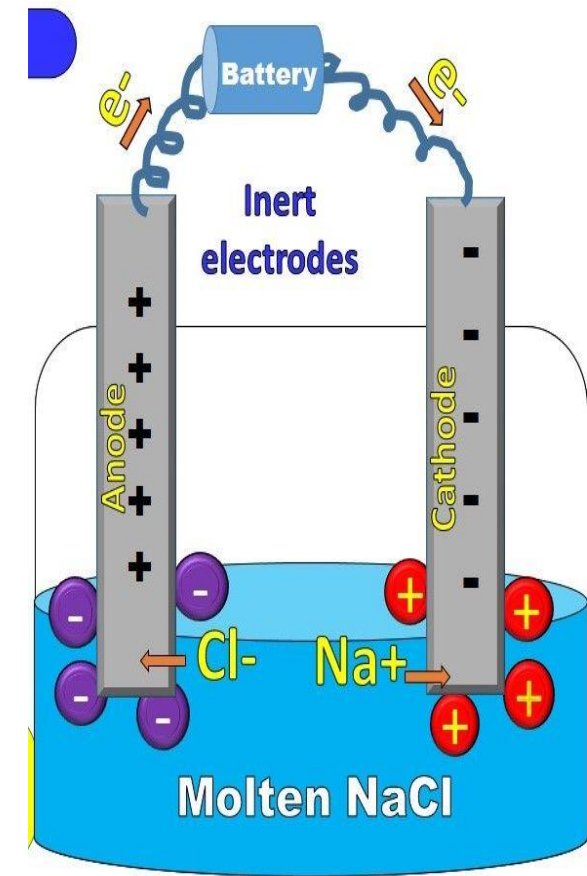
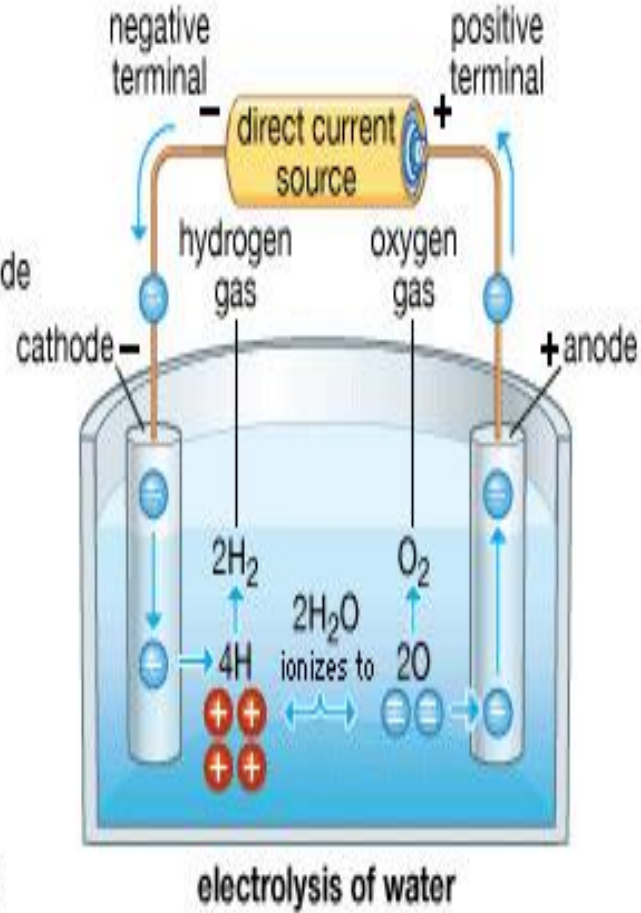
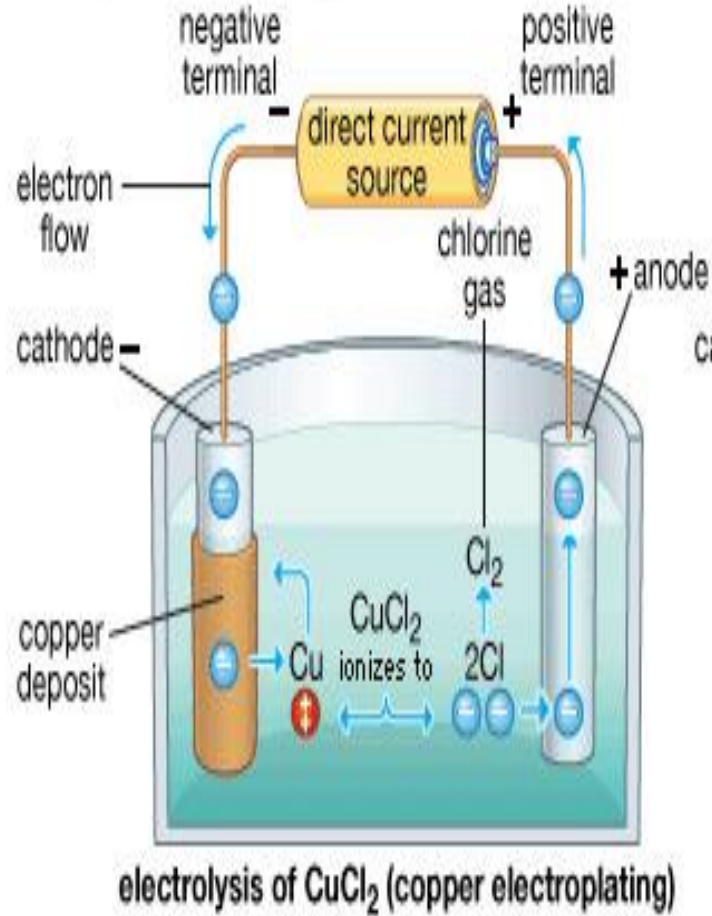


Figure 25.4

Examples of electrolytic cells



1- Write all the ions present in the aqueous solutions of the following:

- Caustic potash
- Acetic acid
- Formic acid
- Ammonium chloride solution
- Phosphoric acid
- Magnesium sulphate

2. State the reactions occurring at the **anode** during the electrolysis of :

1. Copper sulphate solution, using copper electrodes.
2. Copper sulphate solution, using platinum electrodes.
3. Aluminium oxide, dissolved in cryolite using carbon electrodes

2. State the reactions occurring at the anode during the electrolysis of :

(i) Copper sulphate solution, using copper electrodes.

(i) Copper sulphate solution, using platinum electrodes.

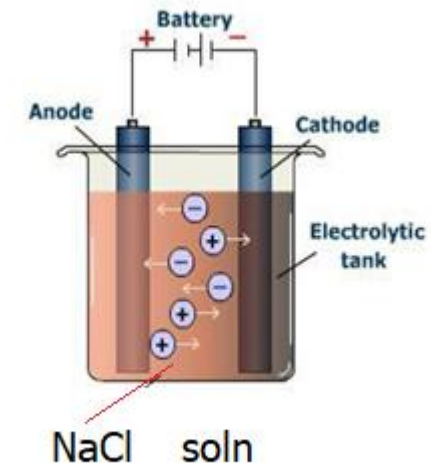
(ii) Aluminium oxide, dissolved in cryolite using carbon electrodes

I/ Choose the correct answer

1. Electrolysis of acidified CuCl_2 on Pt electrodes give ($\text{Cu} - \text{H}_2 - \text{O}_2 - \text{Cl}_2$) at cathode.
2. Electrolysis of acidified CuCl_2 on Pt electrodes give ($\text{Cu} - \text{H}_2 - \text{O}_2 - \text{Cl}_2$) at Anode.
3. The reaction done at cathode when acidified CuCl_2 is electrolysis
 - a) $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
 - b) $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
 - c) $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
 - d) $2\text{OH}^- \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^-$

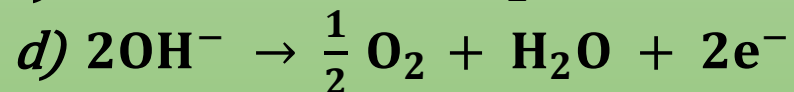
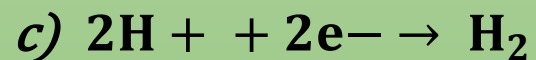
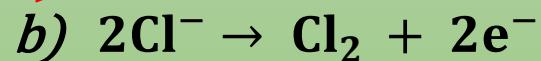
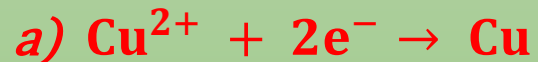
II/ Use the following Figure, Complete the following

1. The cell is called cell.
2. **Positive** ions in the electrolytic tank are and
3. **Negative** ions in the electrolytic tank are and
4. At Anode is evolved .
5. At Cathode is evolved.



I/ Choose the correct answer

1. Electrolysis of acidified CuCl_2 on Pt electrodes give (**Cu** – H_2 – O_2 – Cl_2) at cathode.
2. Electrolysis of acidified CuCl_2 on Pt electrodes give (Cu – H_2 – O_2 – **Cl_2**) at Anode.
3. The reaction done at cathode when acidified CuCl_2 is electrolysis

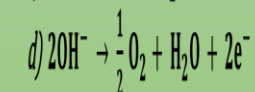
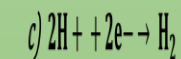
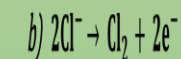
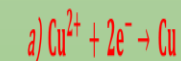


II/ Use the following Figure, Complete the following

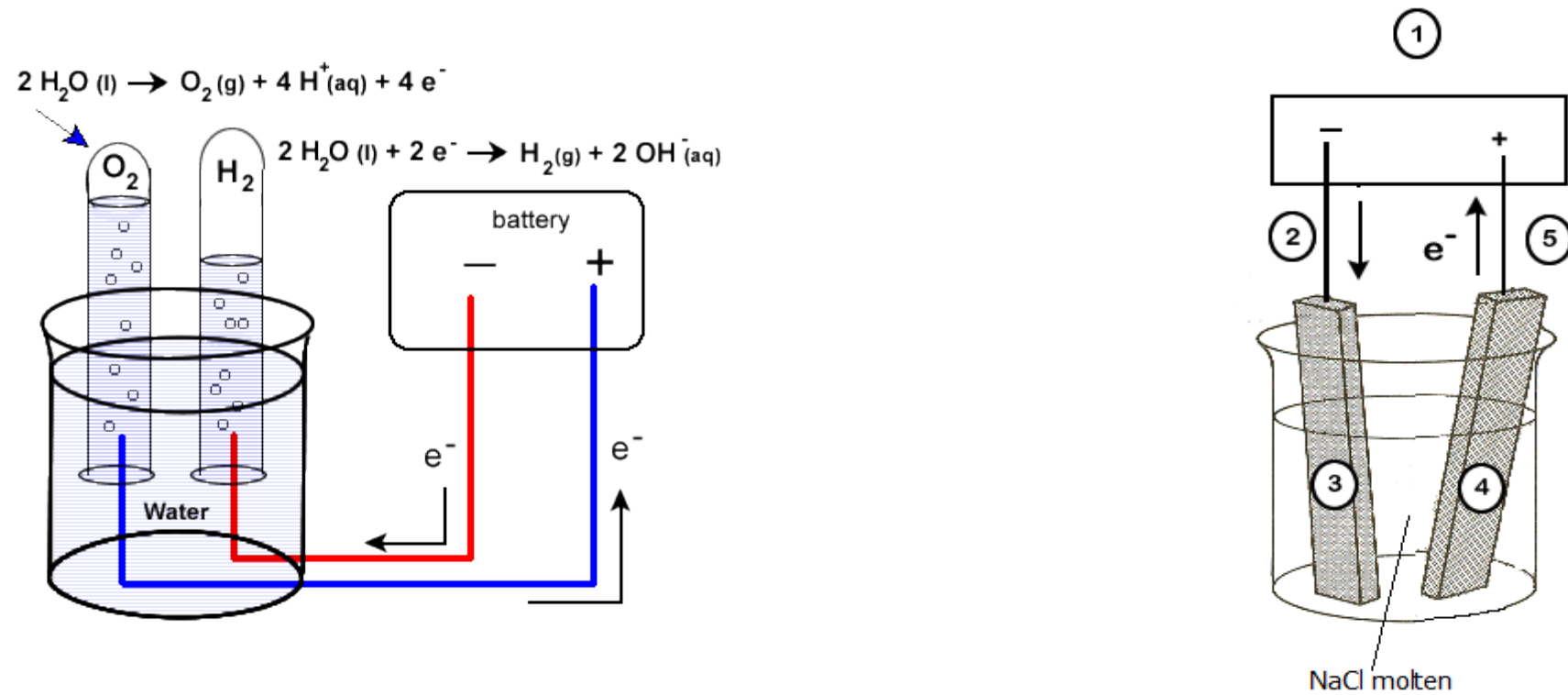
1. the cell is called **electrolytic** cell.
2. Positive ions in the electrolytic tank are **Na^+** and **H^+** .
3. Negative ions in the electrolytic tank are **OH^-** and **Cl^-** .
4. At Anode **Cl_2** is evolved .
5. At Cathode **H_2** is evolved.

I/ Choose the correct answer

1. Electrolysis of acidified CuCl_2 on Pt electrodes give (**Cu** – H_2 – O_2 – Cl_2) at cathode.
2. Electrolysis of acidified CuCl_2 on Pt electrodes give (Cu – H_2 – O_2 – **Cl_2**) at Anode.
3. The reaction done at cathode when acidified CuCl_2 is electrolysis



Carefully study the diagram of our set-up, taking special care to trace the path of the electrons.



- Complete

1. Electrochemical cells are composed of an and in two separate solutions.
2. An electric current consists of a flow of
3. The electrode where oxidation occurs is called the and the electrode where reduction occurs is called the
4. In electroplating, the object to be plated is made the

- Complete

1. Electrochemical cells are composed of an **anode** and **cathode** in two separate solutions.
2. An electric current consists of a flow of **charged particles (ions)**.
3. The electrode where oxidation occurs is called the **anode** and the electrode where reduction occurs is called the **cathode**.
4. In electroplating, the object to be plated is made the **cathode**.

Which of the following is **not a strong** electrolyte?

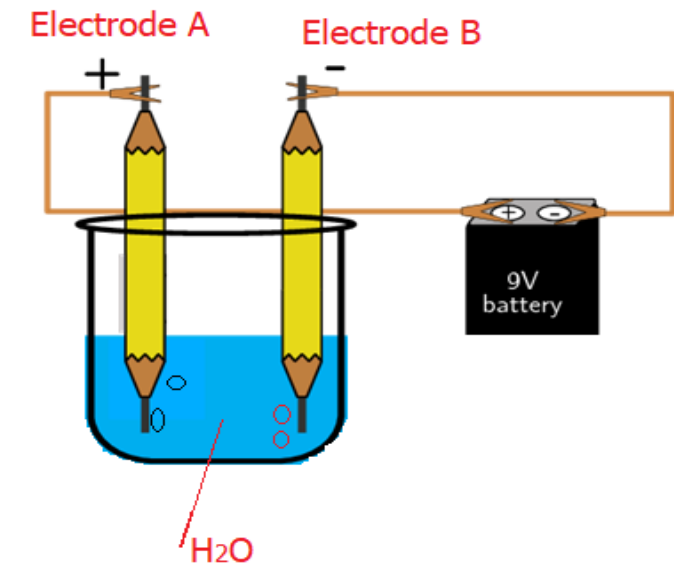
- a) CH_3COOH
- b) NaClO_4
- c) KNO_3
- d) KCl

Complete:

1. The electronic conductance depends on , ... , .
2. The conductivity of electrolytic solution depends upon , ...

In the Figure

1. Electrode A is called Where electrode B is called
2. H_2O is electrolyzed to and
3. At electrode A , the reaction Take place.
4. At electrode B , the reaction Take place.
5. Oxidation occur at electrode Where reduction occur at electrode





Products of electrolysis :

Electrolyte	Products		Reactions involved	
	At cathode	At anode	At cathode	At anode
Molten NaCl	Na metal	Cl ₂ gas	$\text{Na}_{(l)}^{+} + e^{-} \longrightarrow \text{Na}_{(l)}$	$\text{Cl}_{(l)}^{-} \longrightarrow \frac{1}{2} \text{Cl}_{2(g)} + e^{-}$
Aqueous NaCl	H ₂ gas	Cl ₂ gas	$\text{H}_2\text{O}_{(l)} + e^{-} \longrightarrow \frac{1}{2} \text{H}_{2(g)} + \text{OH}_{(aq)}^{-}$	$\text{Cl}_{(aq)}^{-} \longrightarrow \frac{1}{2} \text{Cl}_{2(g)} + e^{-}$
Dil. H ₂ SO ₄	H ₂ gas	O ₂ gas	$\text{H}_{(aq)}^{+} + e^{-} \longrightarrow \frac{1}{2} \text{H}_{2(g)}$	$2\text{H}_2\text{O}_{(l)} \longrightarrow \text{O}_{2(g)} + 4\text{H}_{(aq)}^{+} + 4e^{-}$
Conc. H ₂ SO ₄	H ₂ gas	S ₂ O ₈ ²⁻	$\text{H}_{(aq)}^{+} + e^{-} \longrightarrow \frac{1}{2} \text{H}_{2(g)}$	$2\text{SO}_{4(aq)}^{2-} \longrightarrow \text{S}_2\text{O}_{8(aq)}^{2-} + 2e^{-}$