CHM 101: GENERAL CHEMISTRY I

TOPICS: A. INTRODUCTION TO ELECTROCHEMISTRY
B. INTRODUCTION TO RADIOACTIVITY

PART A: INTRODUCTION TO ELECTROCHEMISTRY

Course Learning Objectives

By the end of this course, students should be able to:

1. Explain the basic principles of electrochemistry and radioactivity
2. Describe oxidation–reduction reactions and electrochemical cells
3. Explain electrode potentials and their applications

INTRODUCTION

Electrochemistry: The study of the relationship between electricity and chemical reactions

- A large number of metals, sodium hydroxide, chlorine, fluorine and many other chemicals are produced by electrochemical methods.
- Batteries and fuel cells convert chemical energy into electrical energy and are used on a large scale in various instruments and devices.
- The reactions carried out electrochemically can be energy efficient and less polluting. Therefore, study of electrochemistry is important for creating new technologies that are ecofriendly.

Electrochemical Cells

Electrochemical Cells: a devise that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction

- ➢ There are two types of electrochemical cells:
- Galvanic cells
- Electrolytic cells.
- A **galvanic (voltaic) cell** Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to *generate* electricity. This type of electrochemical cell is often called a *voltaic cell* after its inventor, the Italian

Electrochemical Cells contd.

- **Electrolytic cell** *consumes* electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$).
- Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system.
- The oxidation half-reaction occurs at one electrode (the **anode**), and the reduction half-reaction occurs at the other (the **cathode**).
- When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an ***electrolyte***, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby in **any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction.**
- **A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced.**

Electrochemical Cells contd.

- The reductant is the substance that loses electrons and is oxidized in the process; the oxidant is the species that gains electrons and is reduced in the process.
- The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.
- Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two half-reactions, one representing the oxidation process and one the reduction process.
- Some fundamental processes will be considered for more insight to the concept

ESSENTIALS AND FUNDAMENTAL ISSUES IN ELECTROCHEMISTRY

SETTING UP AN EQUILIBRIUM BETWEEN A METAL AND SOLUTION

A case study of insertion of zinc rod into solution containing zinc ions.

- There is a tendency for the zinc atoms on the surface of the rod to attracted into the solution as zinc ions.
- These zinc ions can be solvated by water molecules
- The electrons left behind when a zinc atoms is transformed into a positive ion remain on the rod
- Consequently, the region of the solution very close to the rod suffers an increase in positive charge (due to the extra zinc ions) while the zinc carries a layer of nnegative charge
- Other metals dipped into solutions of their ions undergo a similar but opposite change

SETTING UP AN EQUILBRIUM BETWEEN A METAL AND SOLUTION CONTD.

- In this case, some of the ions in solution cling on to the metal and attract electrons out of the rod.
- This leaves the rod with a positive charge
- Because the solution near to the rod loses positive ions, it becomes slightly negatively charged
- An electric double layer is set up which is known as Helmholtz double layer. Thus, for metal M and M^{n+}:

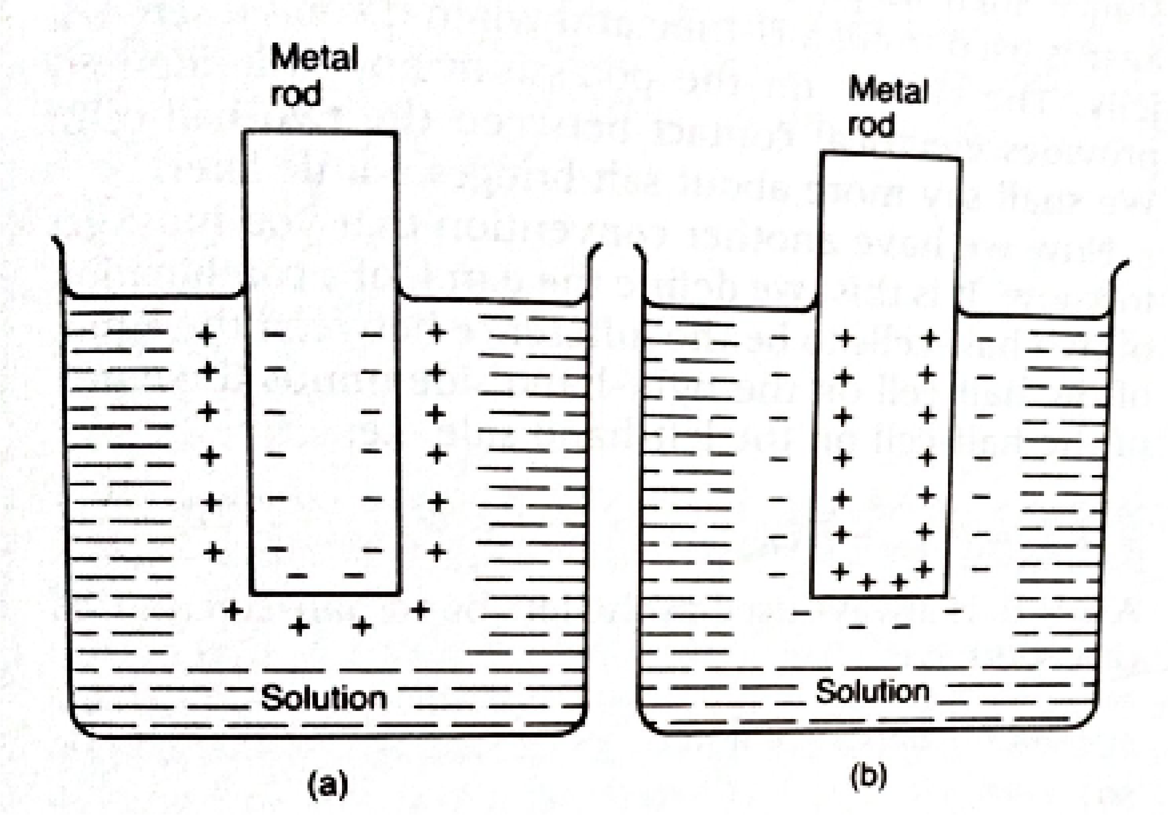


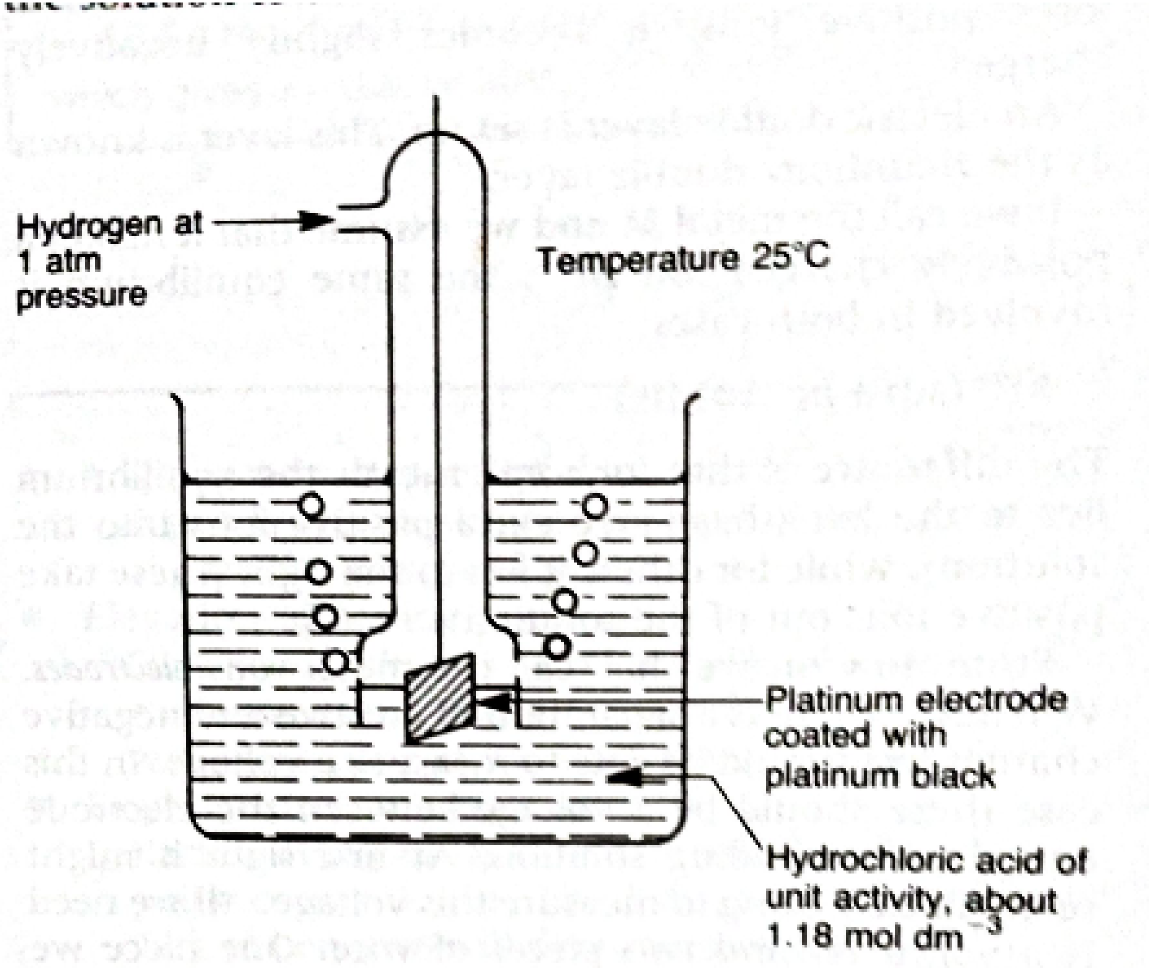
Fig. 1: (a) Zinc rod in contact with zinc solution
(b): Other metals dipped into solutions of their ions

Measurement of voltage difference between two double layers (Helmholtz double layer).

The standard hydrogen electrode potential

$2H^+_{(aq)} + 2e^- \leftrightarrow H_{2\,(g)}$

- ✓ $E^{\Theta}{}_{SHE} = 0.000\ V$
- ✓ Better still:
- ✓ $E^{\Theta}\ H^+/H_2 = 0.000\ V$



Standard Electrode Potential

- With the achievement of SHE , METAL can be connected to the SHE and measure the voltage between the two
- A convention has been established which expressed the EMF of a combination of two half-cells to be thje difference between the EMF of the half-cell on RHS minus the EMF of the half-cell on the LHS
- Thus: E^{Θ} cell = E^{Θ} right – E^{Θ} left
- **E^{Θ} cell = E^{Θ} Zn^{2+}/Zn – E^{Θ} H^{+}/H_2**

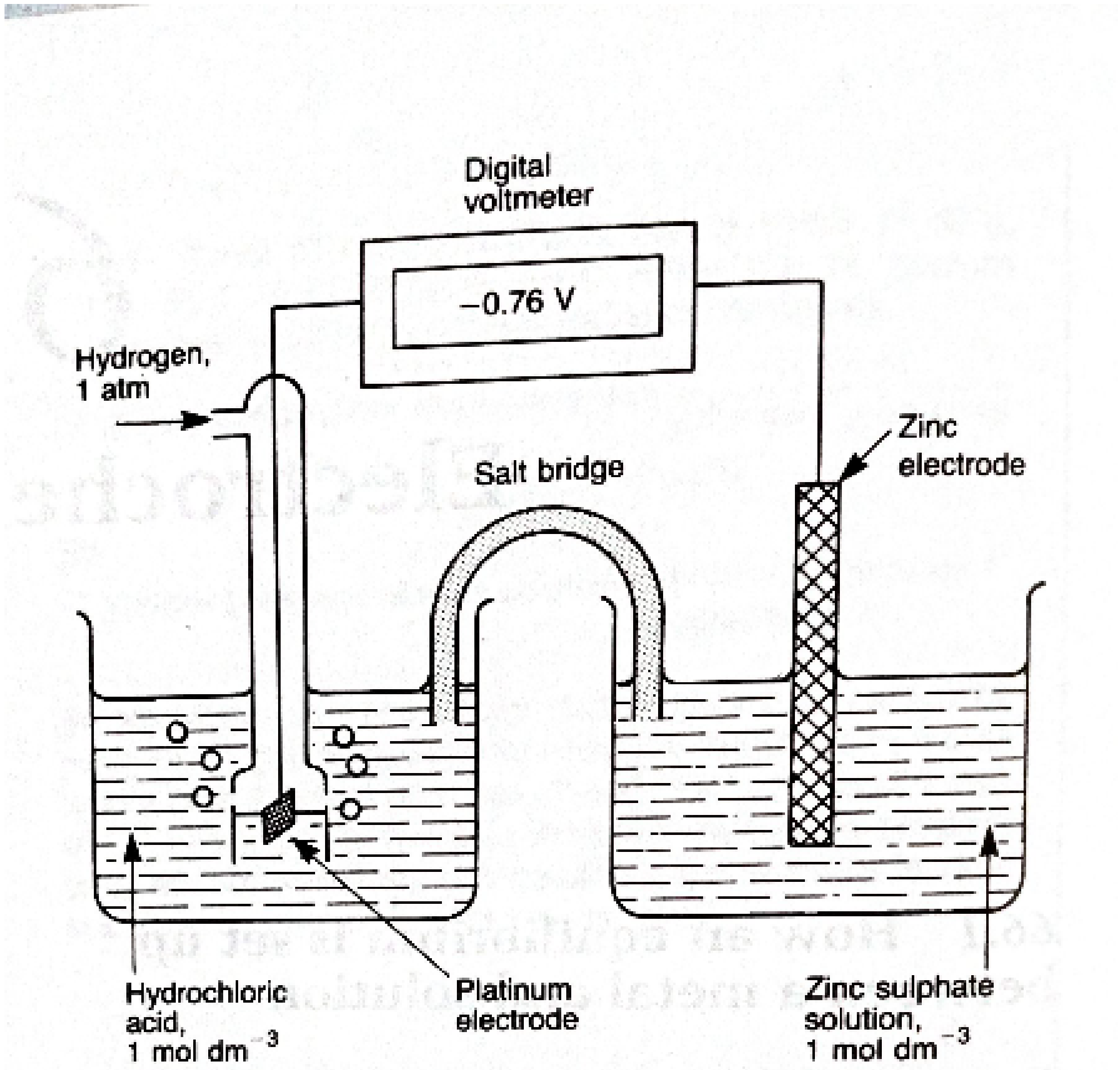
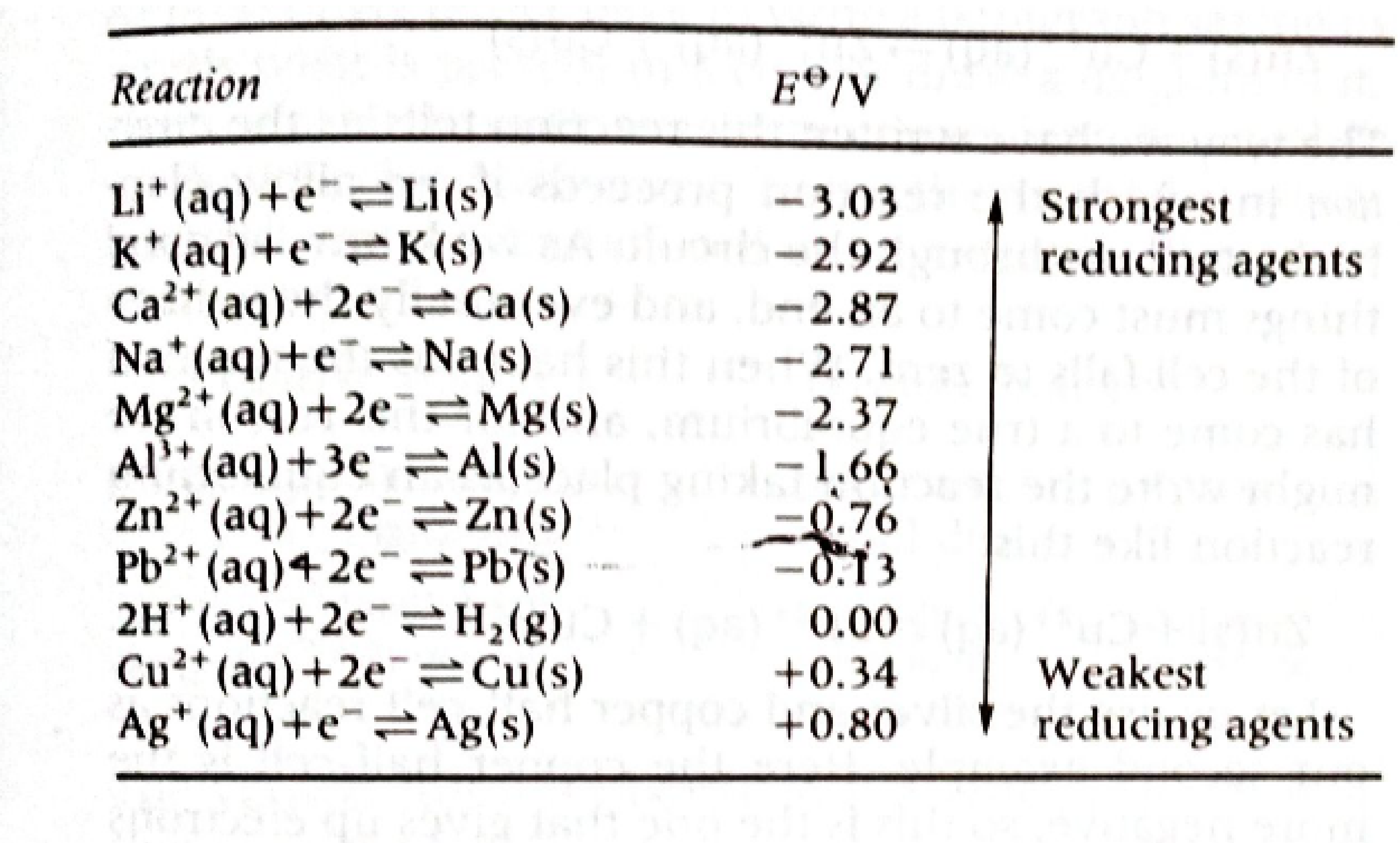


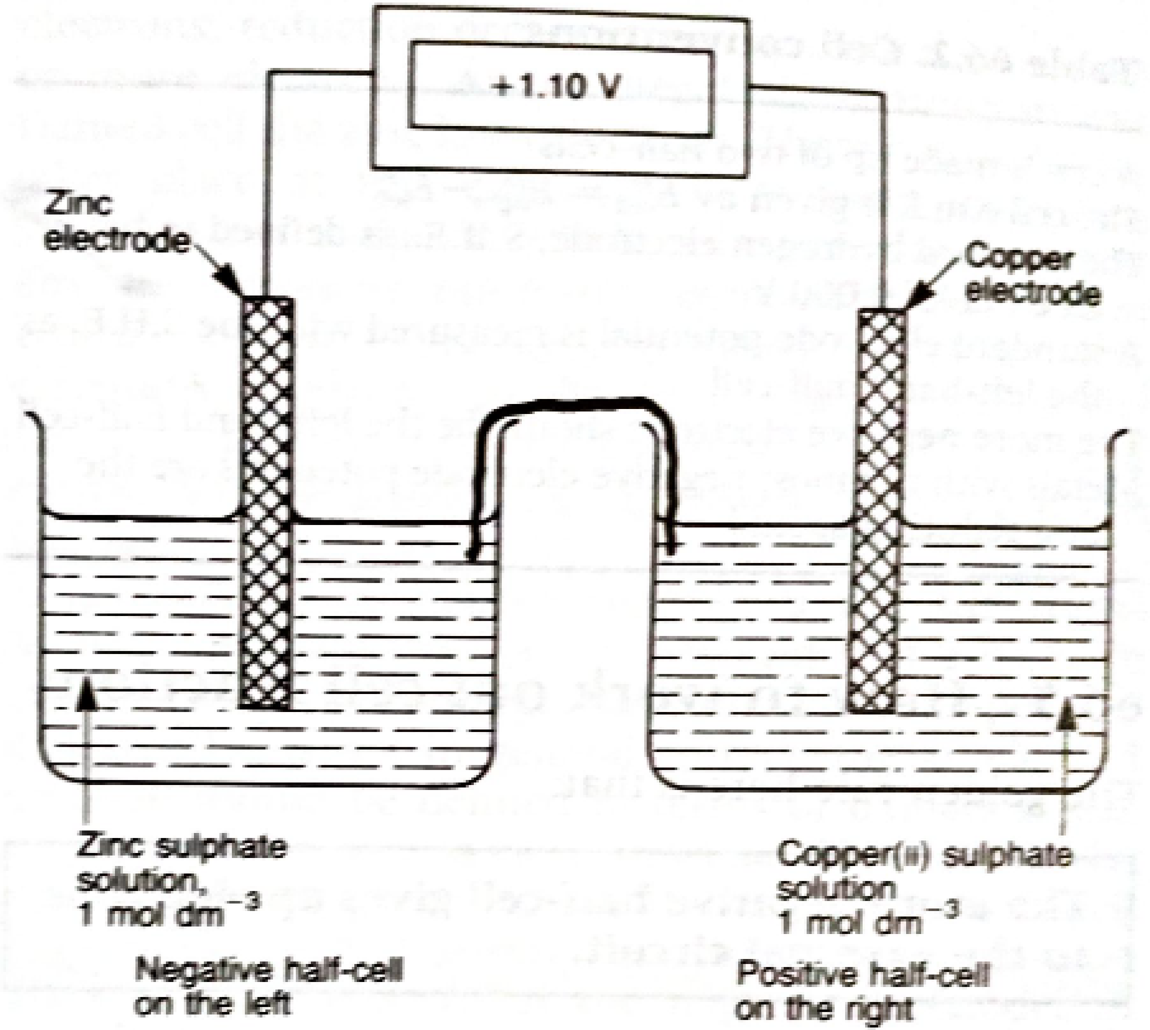
Table of Standard Electrode Potential at 25^{O}C



Reaction	$E^{\ominus}$/V	
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.03	↑ Strongest reducing agents
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.92	
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87	
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71	
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37	
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66	
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76	
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13	
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00	
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34	Weakest reducing agents ↓
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80	

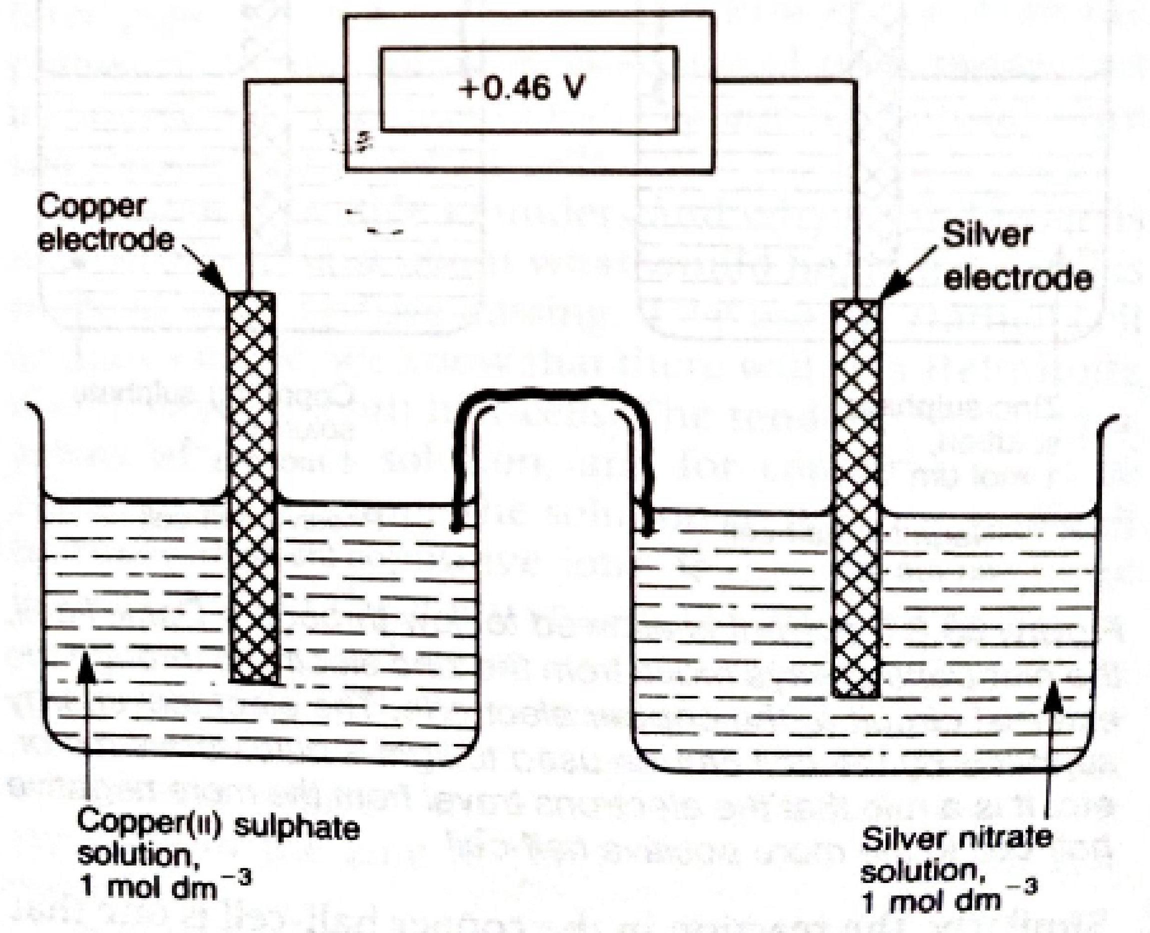
Combining half-cells

- A Daniel cell can be made by combining Zn and Cu half-cells
- E^{θ} cell = E^{θ} right – E^{θ} left
- **E^{θ} cell = E^{θ} Cu^{2+}/Cu – E^{θ} Zn^{2+}/Zn**
- **E^{θ} cell = 0.34V- (- 0.76V) = 1.1 V**



Combining half-cells contd.

- A Daniel cell can also be made by combining Ag and Cu half-cells
- E^{Θ} cell = E^{Θ} right – E^{Θ} left
- **E^{Θ} cell = Ag^{+}/Ag – E^{Θ} Cu^{2+}/Cu**
- **E^{Θ} cell = 0.80V- 0.0.34V = 0.46 V**

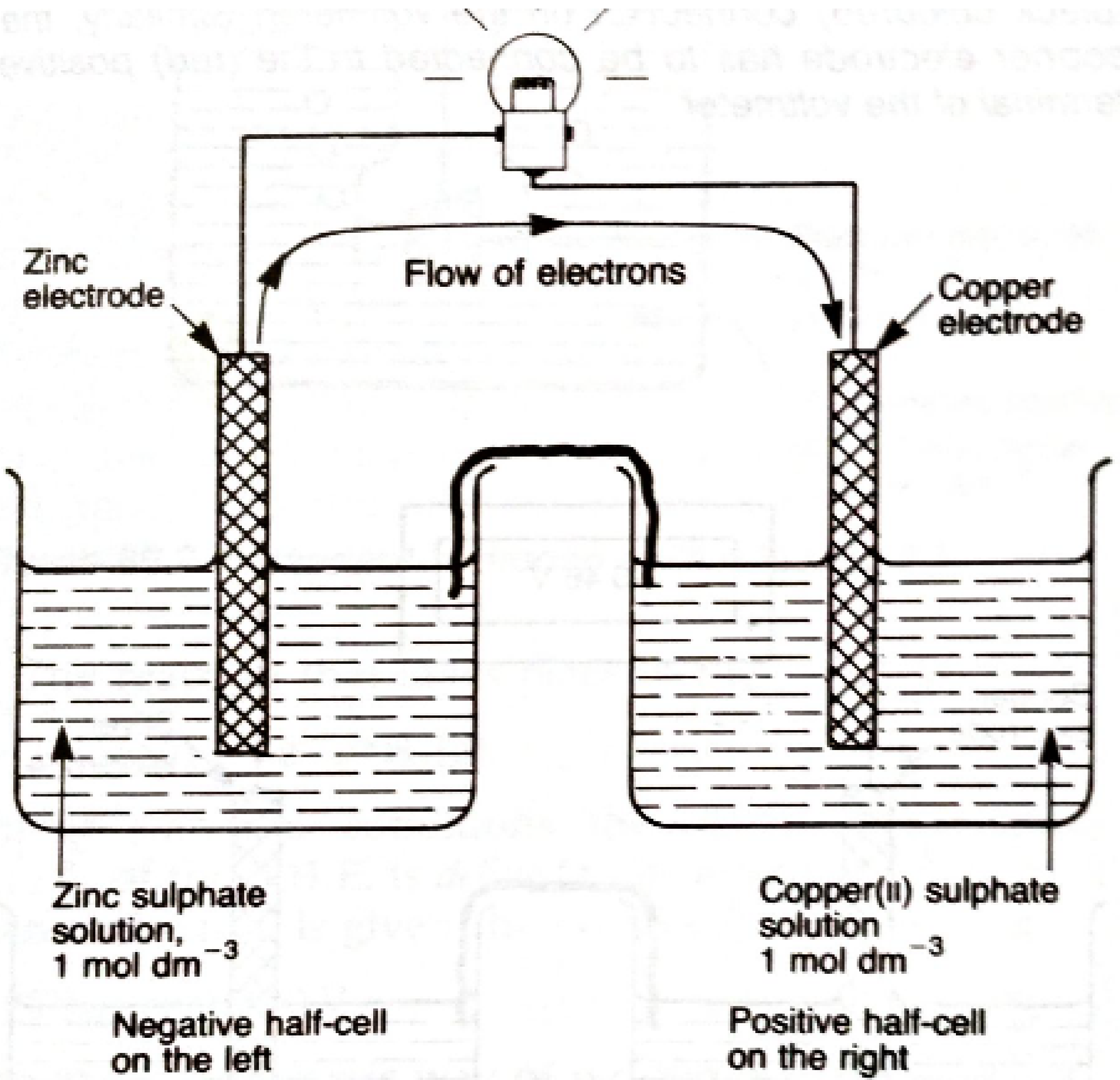


CONCEPT OF WORKING OUT CELL REACTIONS

A) **For Copper and Zinc cells**

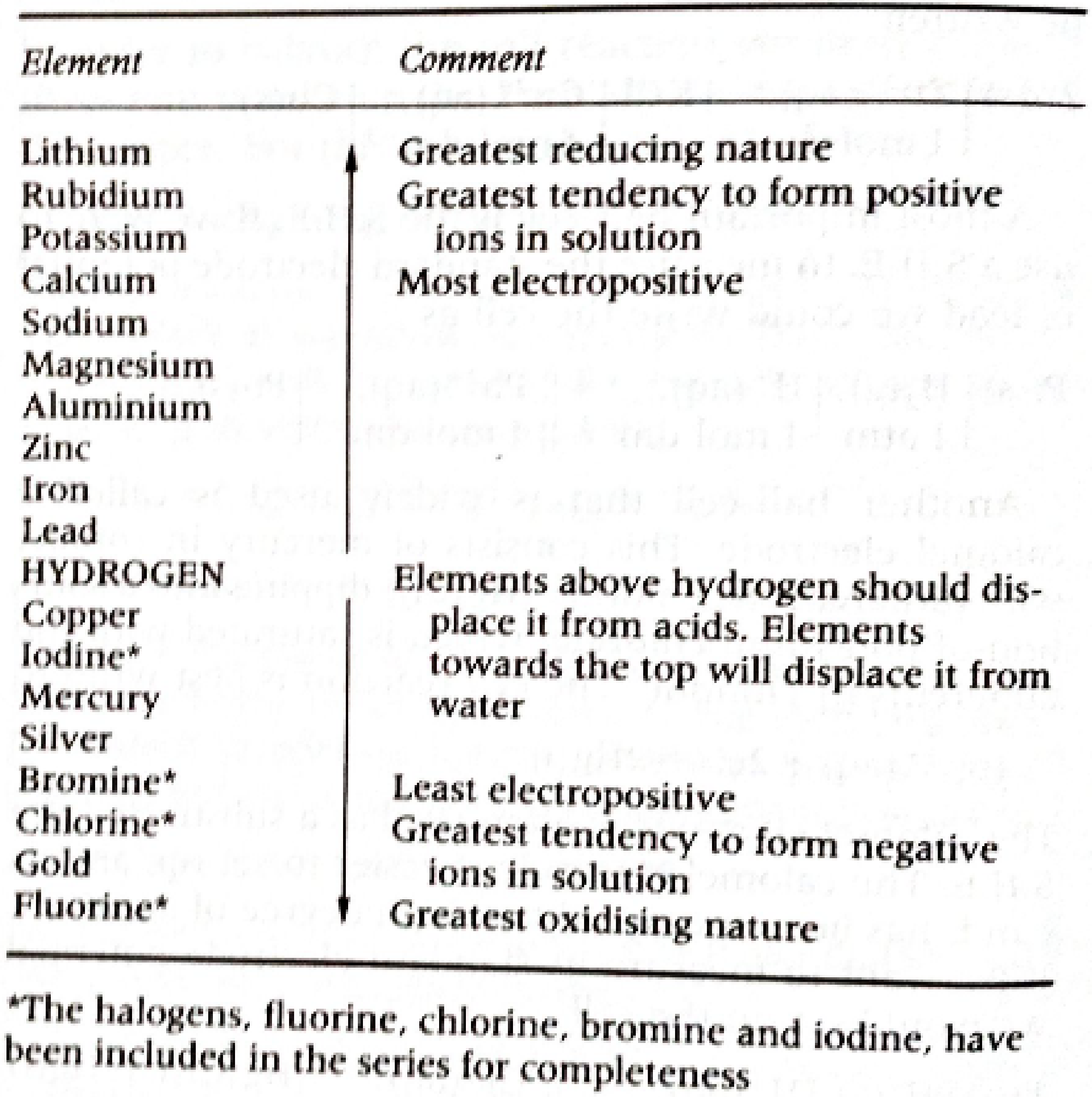
- E^{θ} cell = E^{θ} Cu^{2+}/Cu – E^{θ} Zn^{2+}/Zn
- $Zn(s) \rightarrow Zn^{2+} + 2e^{`-}$
- $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$
- Combine the two half-cells
- $Zn(s) + Cu^{2+}(aq) \leftrightarrow Zn^{2+} + Cu(s)$

- B) For Silver and Copper half-cells



ELECTROCHEMICAL SERIES

- The series was made to arrange elements in order of reactivities



Element	*Comment*
Lithium	Greatest reducing nature
Rubidium	Greatest tendency to form positive ions in solution
Potassium	
Calcium	Most electropositive
Sodium	
Magnesium	
Aluminium	
Zinc	
Iron	
Lead	
HYDROGEN	Elements above hydrogen should displace it from acids. Elements towards the top will displace it from water
Copper	
Iodine*	
Mercury	
Silver	
Bromine*	Least electropositive
Chlorine*	Greatest tendency to form negative ions in solution
Gold	
Fluorine*	Greatest oxidising nature

*The halogens, fluorine, chlorine, bromine and iodine, have been included in the series for completeness

ASSIGNMENT