

CH 2252 Instrumental Methods of Analysis

Unit – II

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Electro Analytical Chemistry

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Contents

- Electro analytical methods - basics

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Oxidation – Reduction Reactions

- Redox reactions are the foundation of electrochemical cells.
- "Redox" is short for "reduction and oxidation", two complimentary types of chemical reactions.
- The term **oxidation** originally referred to substances combining with oxygen, as happens when an iron bar rusts or a campfire log burns. We often refer to these two examples as corrosion and combustion.



- **Oxidation** is the *loss* of electrons or an *increase* in oxidation state by a molecule, atom, or ion.

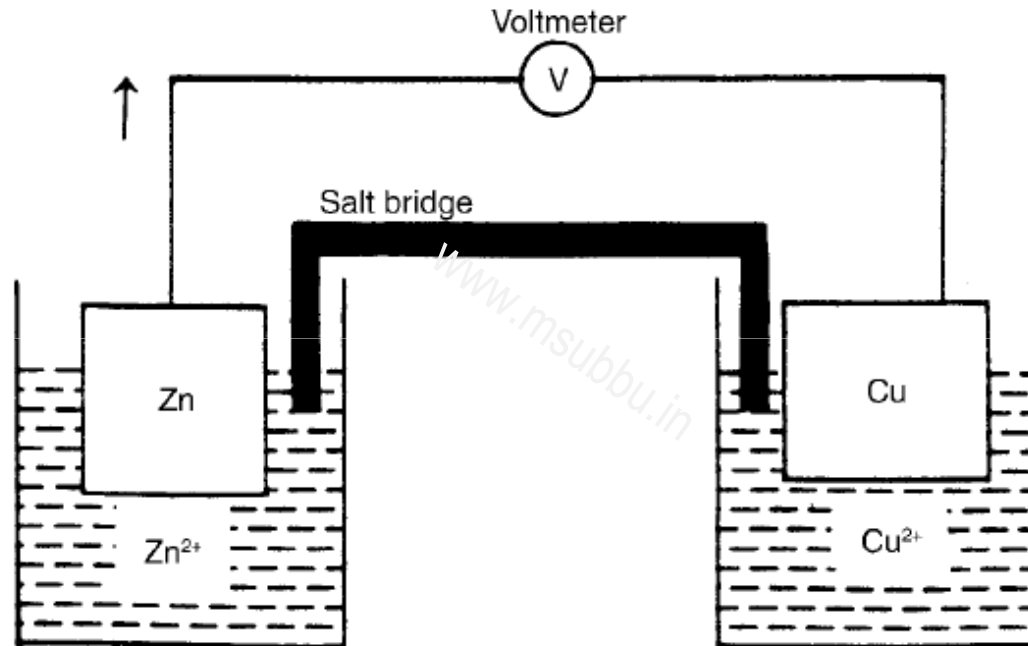


Reduction Reactions

- **Reduction** originally referred to the process of converting metal ores to pure metals, a process that is accompanied by a reduction in the mass of the ore.
- **Reduction** is the *gain* of electrons or a *decrease* in oxidation state by a molecule, atom, or ion.



Electrochemical Cell

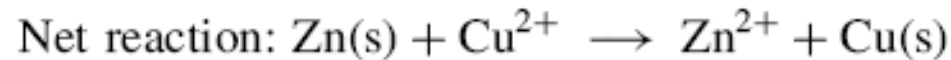
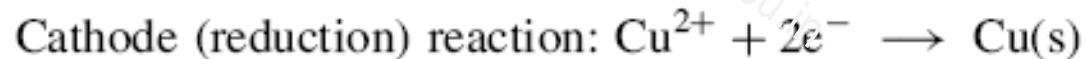


A complete Zn/Cu galvanic cell with a salt bridge separating the half-cells.

Zn electrode (anode) - immersed in Zinc sulfate, Cu electrode (cathode) - immersed in Copper sulfate

Components of an Electrochemical Cell

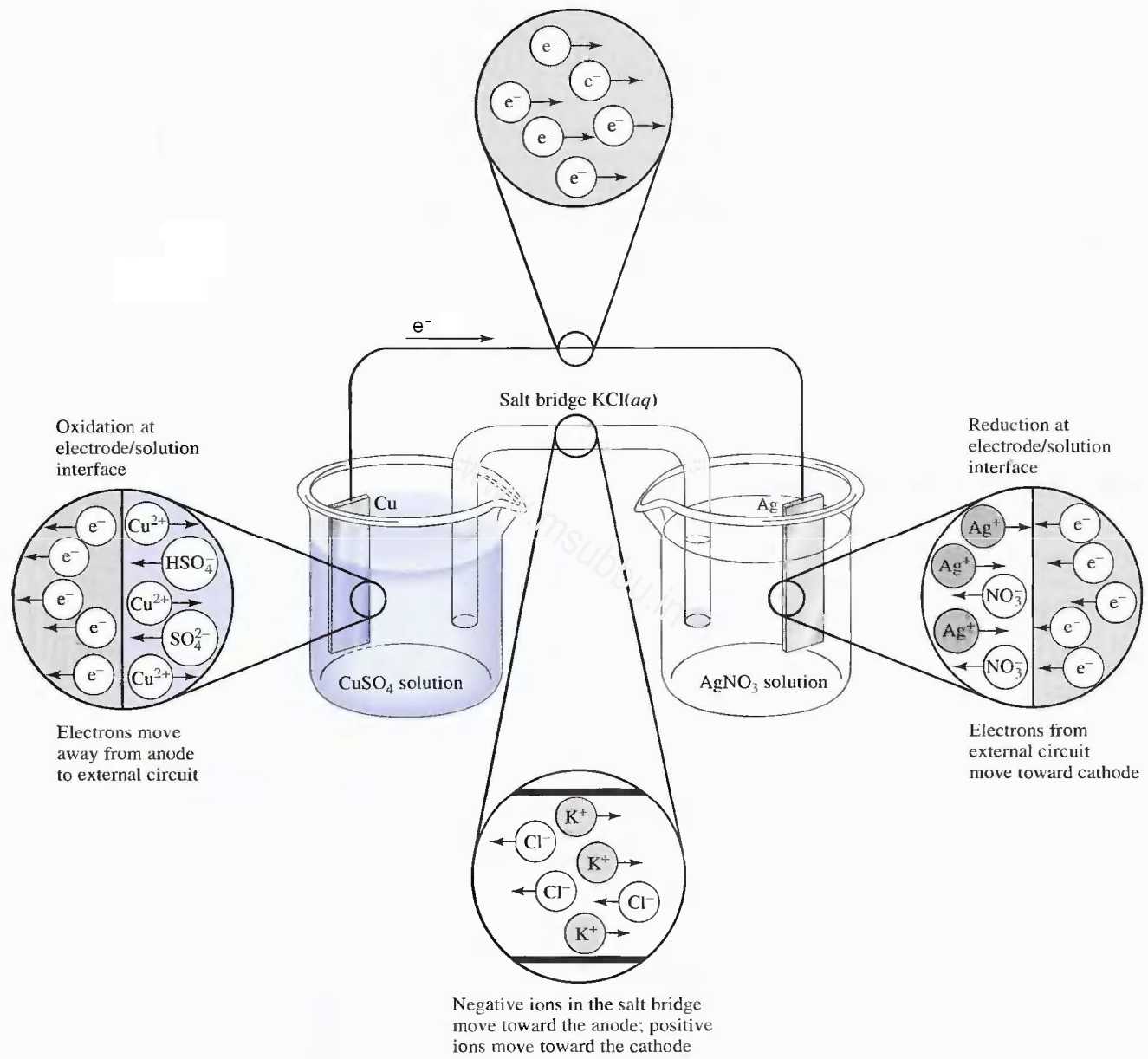
- Anode: oxidation occurs
- Cathode: reduction occurs



- In the electrolyte solution and the salt bridge the current flow is ionic (ion motion), and in the external circuit the current flow is electronic (electron motion)

Electrochemical Cells

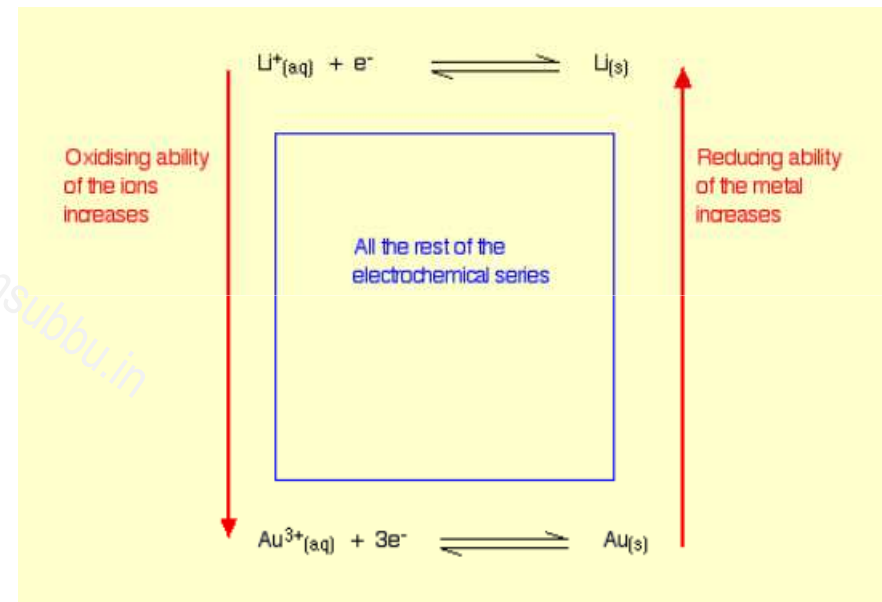
- A cell that uses a spontaneous redox reaction to generate electricity is called a **galvanic cell**. Batteries are examples of galvanic cells.
- A cell set up to cause a non-spontaneous reaction to occur by putting electricity into the cell is called an **electrolytic cell**.
- For the galvanic cell shown earlier, Zn is the anode and Cu is the cathode. In contrast, where this same cell is operated as an electrolytic cell, Cu would be the anode and Zn would be cathode.



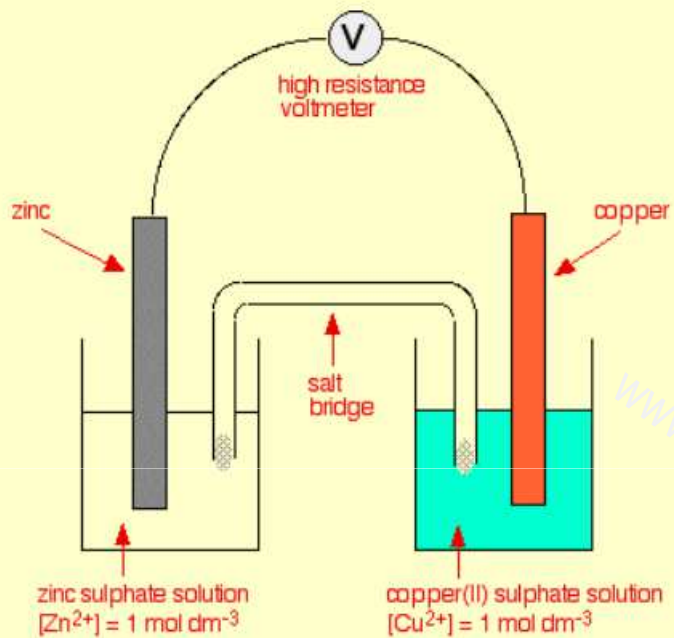
Electrochemical Series

The electrochemical series

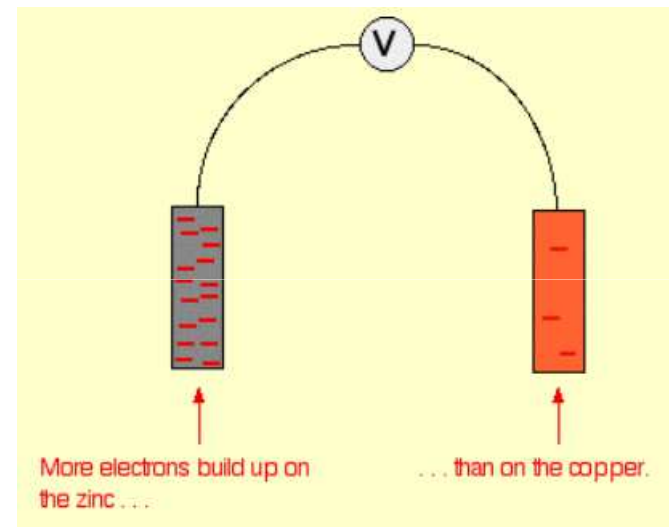
equilibrium	E° (volts)
$\text{Li}^+_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Li}_{(\text{s})}$	-3.03
$\text{K}^+_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{K}_{(\text{s})}$	-2.92
$\text{Ca}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Ca}_{(\text{s})}$	-2.87
$\text{Na}^+_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Na}_{(\text{s})}$	-2.71
$\text{Mg}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Mg}_{(\text{s})}$	-2.37
$\text{Al}^{3+}_{(\text{aq})} + 3\text{e}^- \rightleftharpoons \text{Al}_{(\text{s})}$	-1.66
$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Zn}_{(\text{s})}$	-0.76
$\text{Fe}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Fe}_{(\text{s})}$	-0.44
$\text{Pb}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Pb}_{(\text{s})}$	-0.13
$2\text{H}^+_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{H}_{2(\text{g})}$	0
$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})}$	+0.34
$\text{Ag}^+_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Ag}_{(\text{s})}$	+0.80
$\text{Au}^{3+}_{(\text{aq})} + 3\text{e}^- \rightleftharpoons \text{Au}_{(\text{s})}$	+1.50



E° – std electrode potential



The two equilibria which are set up in the half cells are:

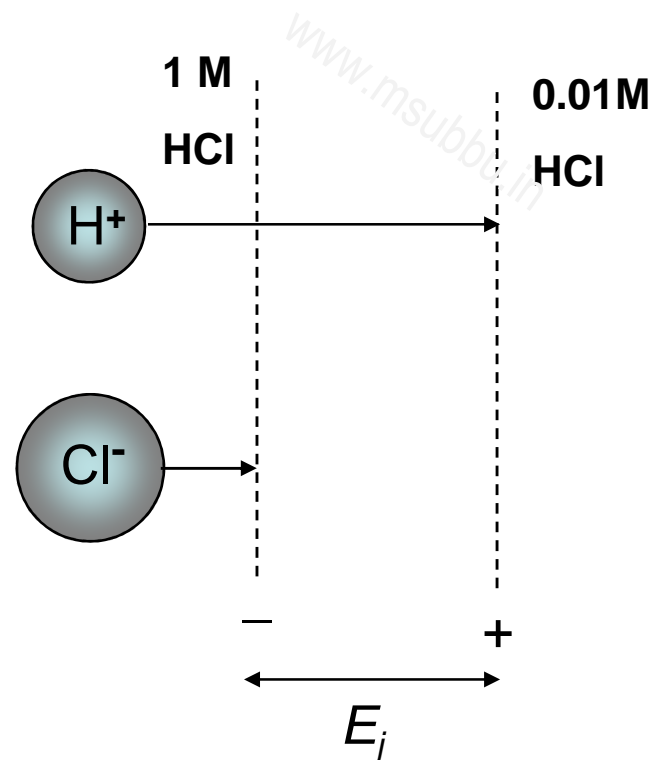


Liquid Junctions

- The interface between two solutions containing different electrolytes or different concentrations of the same electrolyte is called a **liquid junction**
- Often, electrochemical cells contain one or more liquid junctions
- For example, the cell shown on the previous slide contains two junctions: one between the anodic solution and the salt bridge, another between cathodic solution and the salt bridge
- Liquid junctions are important in electrochemical measurements because a small **junction potential** develops at these interfaces that influences the magnitude of the overall measured cell potentials

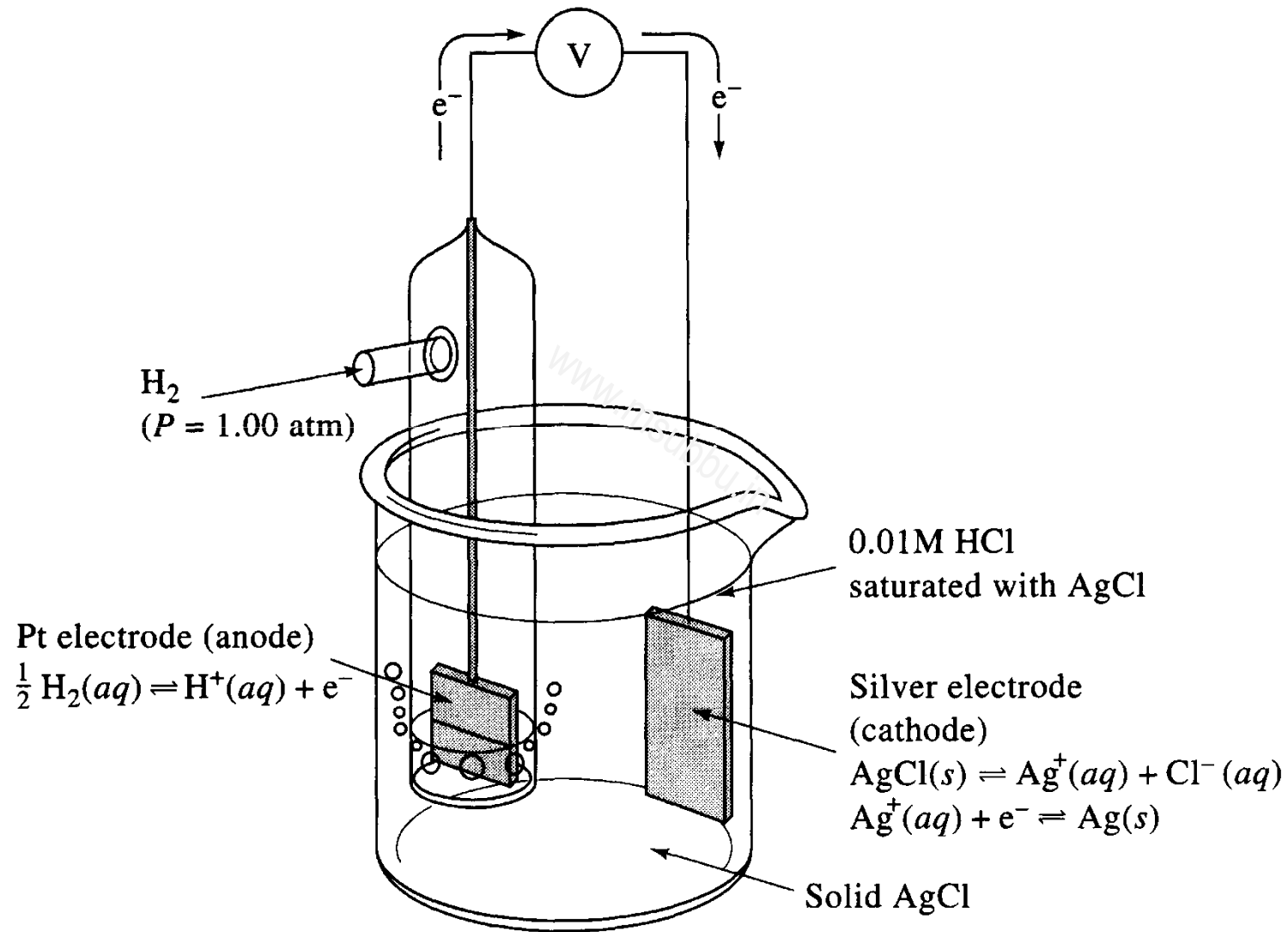
Liquid Junction Potential

- When two electrolyte solutions of different concentrations are brought into contact, a potential develops across the interface. This junction potential arises from the unequal distribution of cations and anions across the boundary due to differences in the rates at which these species diffuse



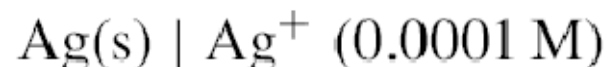
Junction potential resulting from this charge separation is about 30 mV

Cell with No liquid junction



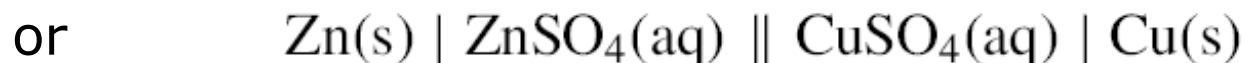
Schematic Representation of a Cell

- For example, the half-cell composed of a silver electrode and aqueous 0.0001 M Ag^+ ion (from dissolution of silver nitrate in water) is written in line notation as



The vertical stroke or line between Ag and Ag^+ indicates a phase boundary

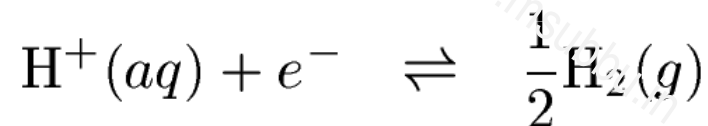
- The complete cell can be represented as



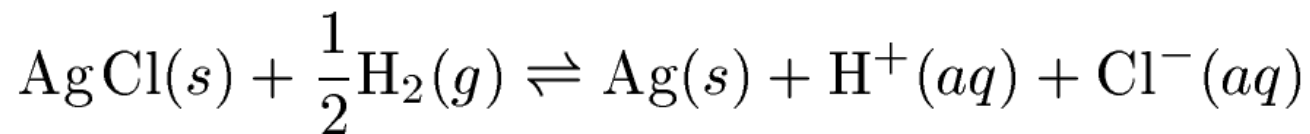
- The double vertical stroke after Zn^{2+} indicates a membrane junction or salt bridge. The double stroke shows the termination of one half-cell and the beginning of the second
- It is conventional to write the electrode that serves as the anode on the left in an electrochemical cell. The other components in the cell are listed as they would be encountered moving from the anode to the cathode

Electrode Potential

- It is useful to think of the cell reaction of an electrochemical cell as being made up of two half-cell reactions, each which has a characteristic electrode potential associated with it.
- Half reactions are return as reduction reactions



- To get the cell reaction, the second half reactions subtracted from the first (cell reaction = cathode reaction – anode reaction).



- Cell potential = cathode potential – anode potential

Standard Hydrogen Electrode

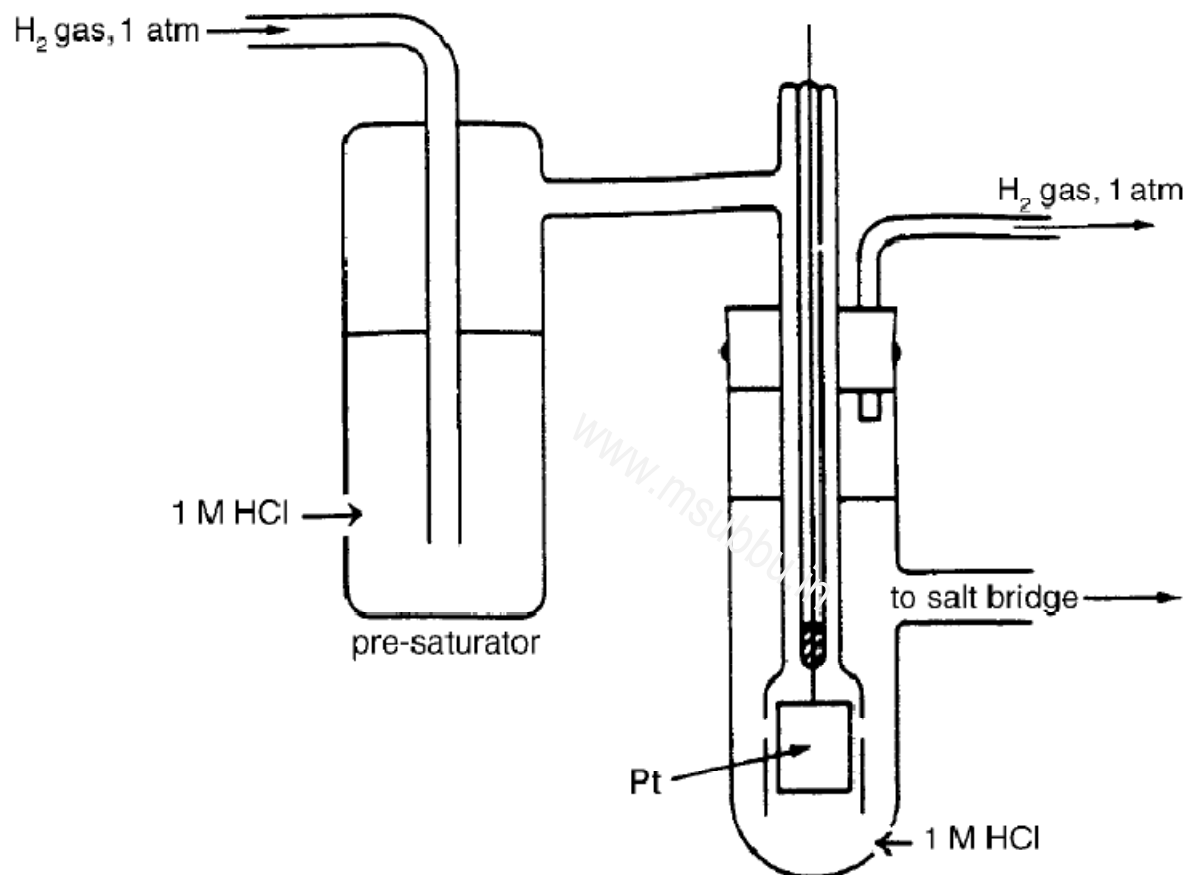
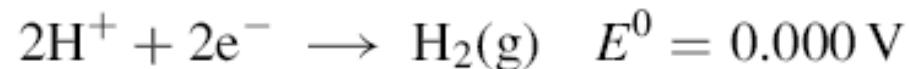


Figure 15.4 The standard hydrogen electrode (SHE). This design is shown with a presaturator containing the same 1 M HCl solution as in the electrode to prevent concentration changes by evaporation. (Aikens et al., by permission, Waveland Press Inc., Long Grove, IL, 1984. All rights reserved.)

SHE

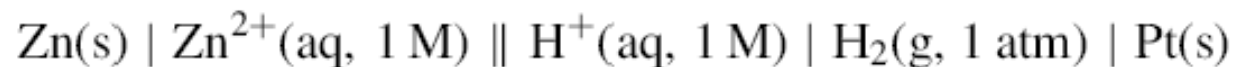
- Standard hydrogen electrode (SHE) has an assigned electrode potential of exactly zero volts at all temperatures
- The SHE, shown in previous slide, consists of a platinum electrode with a surface coating of finely divided platinum (called a platinized Pt electrode) immersed in a solution of 1 M hydrochloric acid, which dissociates to give H⁺. Hydrogen gas, H₂, is bubbled into the acid solution over the Pt electrode. The finely divided platinum on the electrode surface provides a large surface area for the reaction



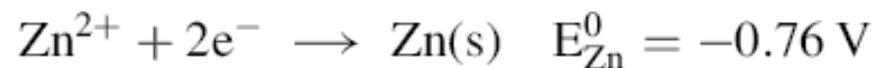
- Under standard state conditions, that is, when the H₂ pressure equals 1 atm and the ideal concentration of the HCl is 1 M, and the system is at 25°C, the reduction potential for the reaction given above is exactly 0 V.

Standard Reduction Potential

- The term standard reduction potential means that the ideal concentrations of all solutes are 1 M and all gases are at 1 atm; other solids or liquids present are pure (e.g., pure Pt solid); temperature is 25°C
- By connecting the SHE half-cell with any other standard half-cell and measuring the voltage difference developed, we can determine the standard reduction potential developed by the second half-cell.



$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$



$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

when half-reactions written as reductions

Can't measure potential on each electrode independently - only differences

Standard reference electrode is usually standard hydrogen electrode (SHE)

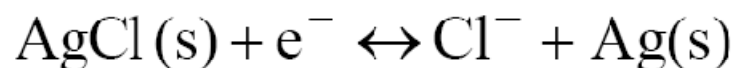


Practical Reference Electrodes

Although the standard hydrogen electrode is of great fundamental importance, the difficulty in preparing the electrode surface and controlling the activities of the reactants make it impractical enough so that it is seldom used for routine measurements. Instead, simple, easy to prepare, rugged reference electrodes are preferred.

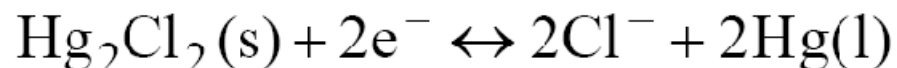
Alternative **reference electrodes**:

- **Ag/AgCl electrode**



$$E_{\text{cell}} = +0.20 \text{ V vs. SHE}$$

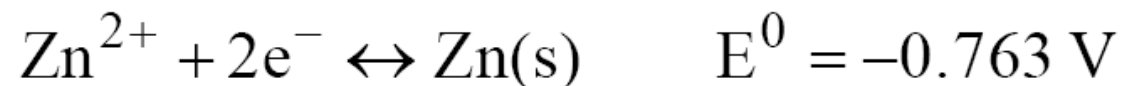
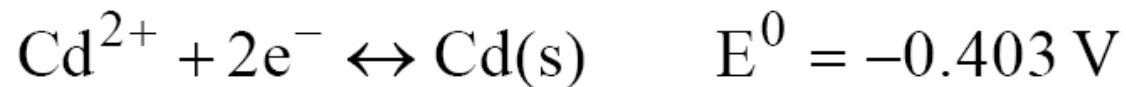
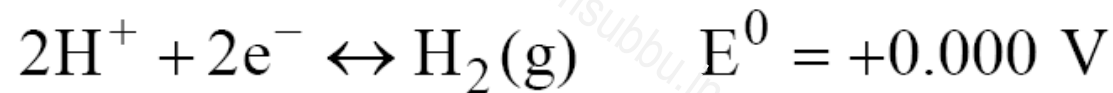
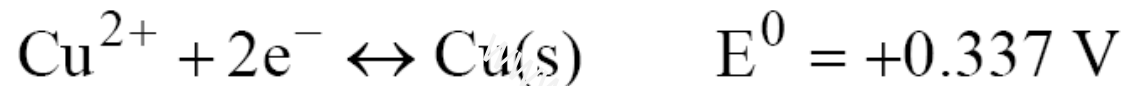
- **Calomel electrode**



$$E_{\text{cell}} = +0.24 \text{ V vs. SHE}$$

electrode potential varies with activity of ion

If $a=1.00$ M, the electrode potential, E , becomes *standard* electrode potential, E^0



The most positive E or E^0 spontaneously **forward** forming **cathode**

Thermodynamics of Cell Potentials

- The relationship between the potential of an electrochemical cell and the concentration of reactants and products in a general redox reaction



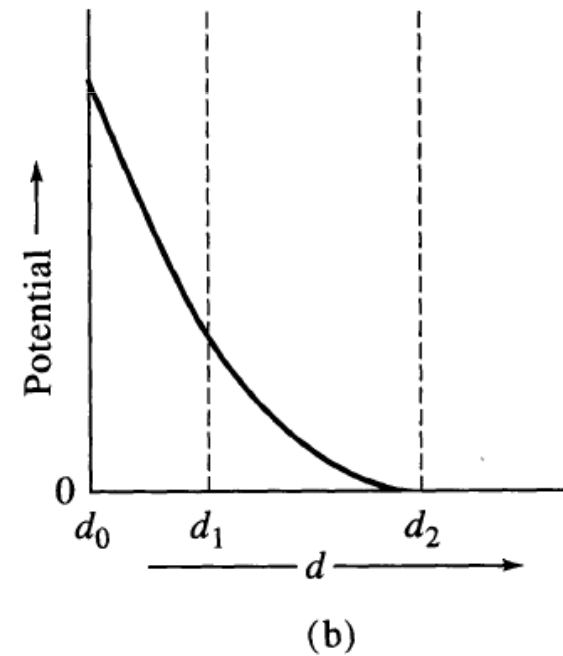
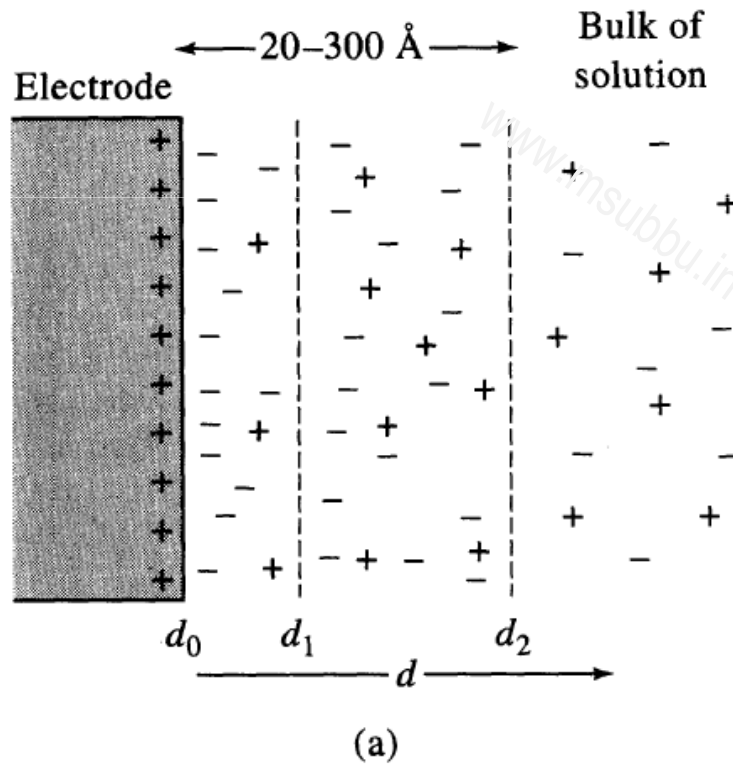
is given by the Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where n is the moles of electrons associated with the oxidation/reduction process; F is Faraday constant

Electrical Double Layer

- (i) Tightly bound inner layer
- (ii) Loosely bound outer layer



Faradaic currents:

proportional to species concentration
due to redox reaction

Non-faradaic currents:

charging of double layer (capacitance)
not due to redox reactions