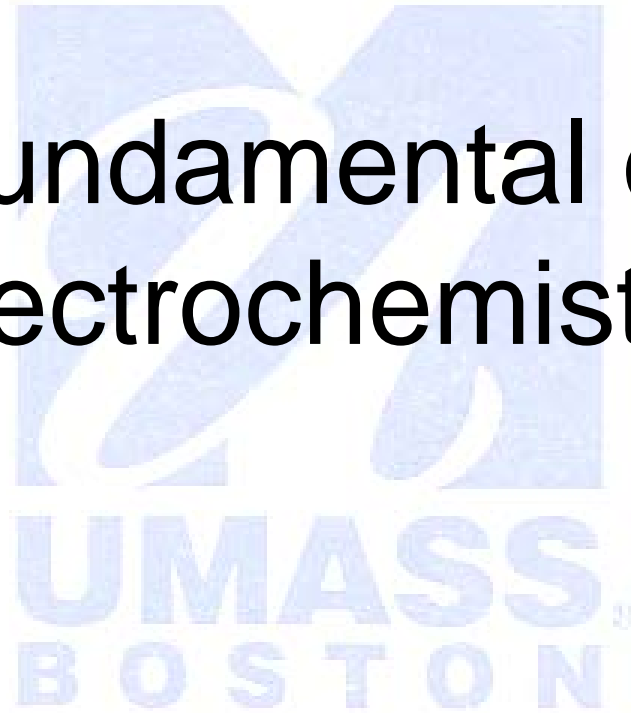


# Fundamental of Electrochemistry



# Redox reaction

- Redox = reduction and oxidation
  - The reaction involves electron transfer from one reactant to another – the oxidation state of the elements has to be changed.
- $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$ 
  - $\text{Cu}^{2+}$  gaining two electrons is oxidizing agent, being reduced.
  - Zn losing two electrons is reducing agent, being oxidized.
- Faraday constant:
  - The unit of electric charge is coulombs (C).
  - One electron has  $1.602 \times 10^{-19}$  C
  - One mole of electron has 96500 C of charge  
 $F=96500\text{C/mol}$

# Chemistry and electricity

- $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$ 
  - If  $\text{Cu}^{2+}$  is mixed with Zn, the electron will be transferred and chemical energy will become heat.  $\Delta G = \Delta H - T\Delta S < 0$ .

- If the reaction is separated in two **Half Reactions**

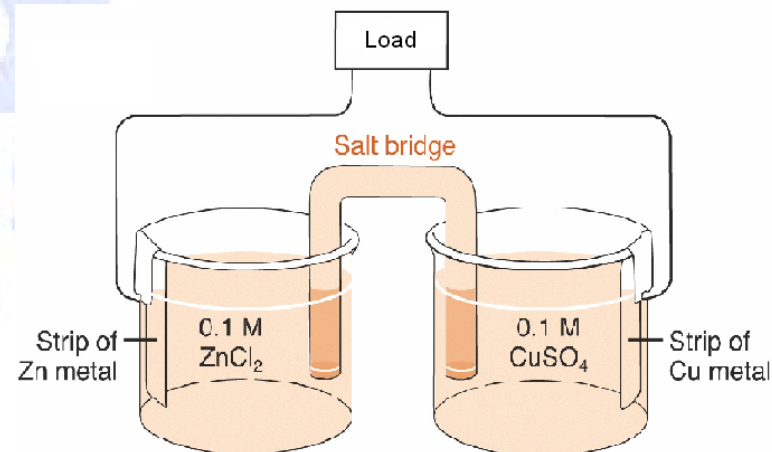


electrons flow from Zn  
electrode to Cu electrode

Current (?) flows from Cu to Zn

Cu is positive electrode

Zn is negative electrode



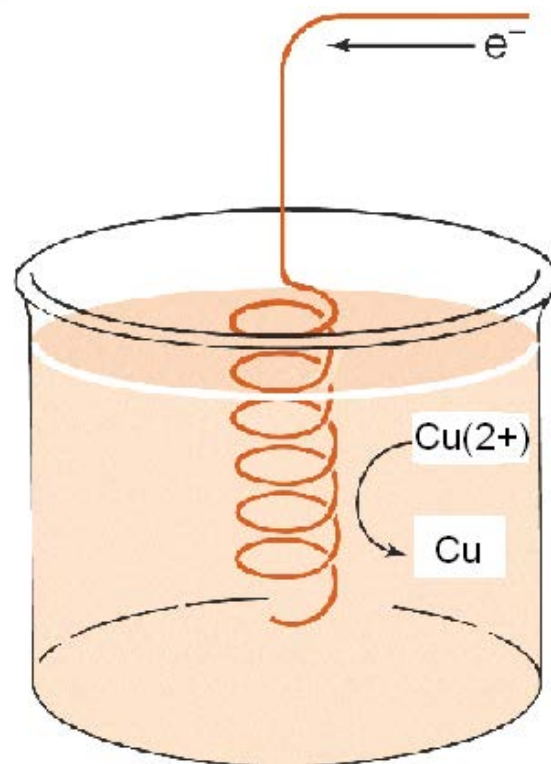
# The driving force of electron flow

- Second Law of thermodynamic: For spontaneous reaction,  $\Delta G < 0$ .
- $\text{Cu}^{2+} + 2\text{e} \rightarrow \text{Cu} \quad \Delta G_1$   
 $\text{Zn}^{2+} + 2\text{e} \rightarrow \text{Zn} \quad \Delta G_2$   
 $\Delta G = \Delta G_1 - \Delta G_2 < 0$
- $\Delta G = -\text{work}$   
so the electron flow from Zn to Cu through the load e.g. a radio to do the work, instead of generating heat.

# Redox reactions

- Redox reaction always happen in couple of oxidation and reduction and can not happen alone.
- For example the reaction can not happen

Electrons can not be created



# Electric current

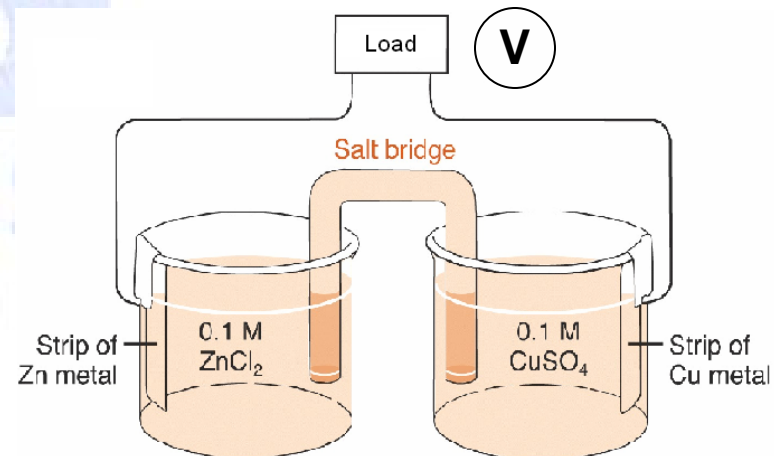
- Current is resulted from the movement of the charged species e.g. electron or ions in the solution.
- The direction of electric current is the direction of the movement of positive charges.
- Current flows from high potential to low potential, while electron flow from low potential to high potential.
- The unit of current is Ampere (A): the quantity of charge flowing each second through a circuit.  
 $1 \text{ A} = 1 \text{ C/s}$

# Terminologies

- **Redox** ( short for Oxidation/Reduction) reactions:
- electrons,  $ne^-$ , are transferred between reactants
- A substance which loses electrons is **oxidized**, the substance is **reductant**. A reductant (reducing agent) is a substance causing **reduction**.
- A substance which gains electrons is **reduced**, the substance is **oxidant**, An oxidant (oxidizing agent) is a substance causing **oxidation**.
- Reactions involving oxidation of A to B and reduction of C to D:
  - $aA + cC \leftrightarrow bB + dD$
  - Separated into two **half-reactions** with equal but opposite e-transfer:
    - $aA + ne^- \rightarrow bB$  (**cathode**)
    - and  $cC - ne^- \rightarrow dD$  (**anode**)

# Chemistry and electricity

- $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$ 
  - If  $\text{Cu}^{2+}$  is mixed with Zn, the electron will be transferred and chemical energy will become heat.  $\Delta G = \Delta H - T\Delta S < 0$ .
  - If the reaction is separated in two **Half Reactions**
    - $\text{Cu}^{2+} + 2e \rightarrow \text{Cu}$
    - $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e$electrons flow from Zn electrode to Cu electrode  
Current flows from Cu to Zn  
Cu is positive electrode  
Zn is negative electrode





# Electrochemical Potential

- Electrode potentials express the driving force for oxidation or reduction
  - A negative electrode potential describes a material easier to oxidize compared to chemical species with a more positive potential
  - A positive electrode potential describes a material easier to reduce.
- This is given by electromotive force or potential, “E” with units of volts
- Electrochemical potential express the possibility of the redox reaction, but does not express the kinetic of the reaction!

# Electrode potential

- Redox reaction energy creates measurable electrochemical potential determined by the thermodynamics & related equilibria of the reaction
- Requires complete circuit to compare the voltage between electrodes.
- Can not measure the voltage of half a cell, requires 2 electrodes
- placed in an electrolytic medium. For ex., voltmeter reads 0.46 V in:  
 $\text{Cu} \mid \text{CuSO}_4(0.1 \text{ M}) \mid \text{AgSO}_4(0.1 \text{ M}) \mid \text{Ag}$

# Electric potential

- Moving charges from one potential to another needs to do work:

$$\text{Work} = \text{Potential difference} \times \text{charge}$$

- $\Delta G = -\text{work} = -\text{Potential difference} \times \text{charge}$

Relationship between free energy and potential difference.

- Units: potential (E): Volt (V)  
work (W): Joule = one coulomb of charge moves between the points of 1 Volt

$$= -nFE$$

$$\Delta G = -nFE$$

# Terminologies

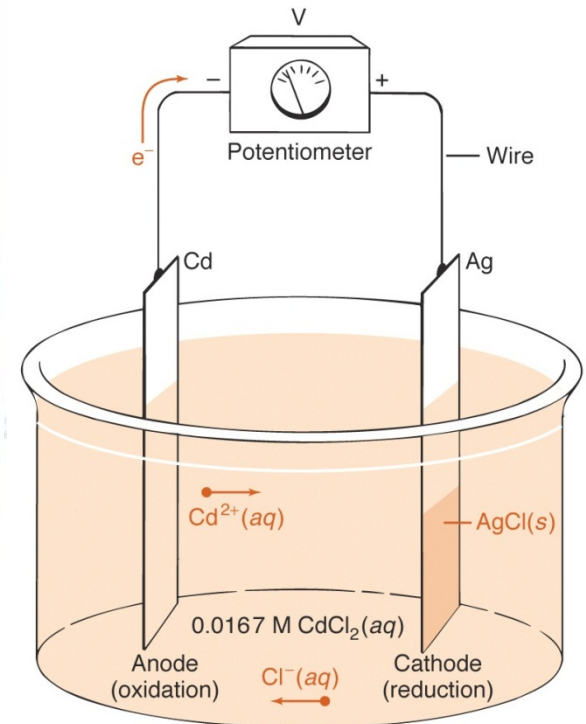
- Resistance:
  - Ohm's law:  $R=E/I$
- Power: work done in the unit time
  - $P=\text{work}/s=Eq/s=E \times q/s$
  - $P=E \times I$
  - Unit Watt (W)

# Critical Relationships

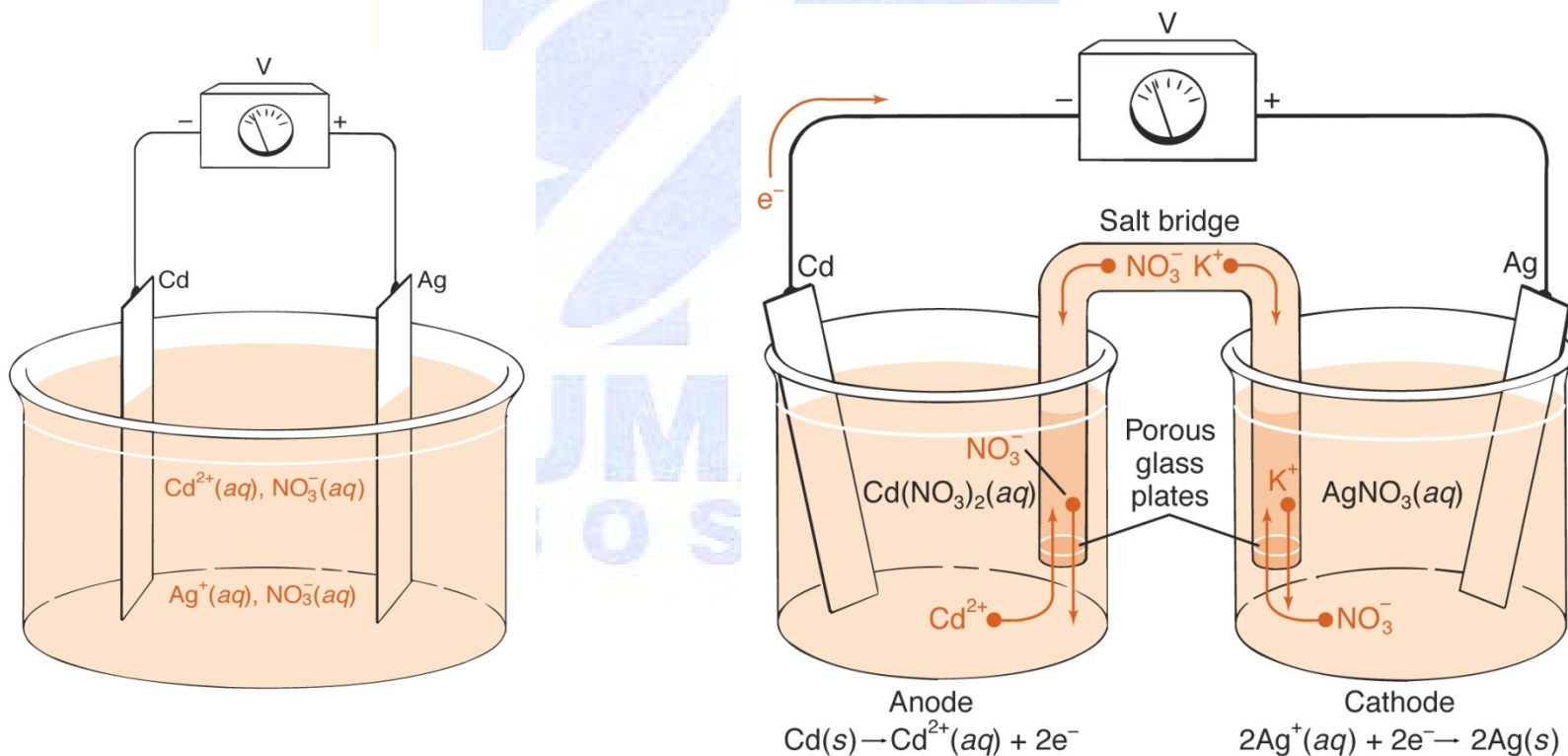
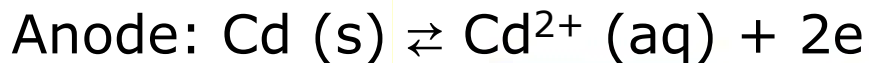
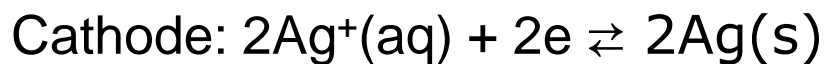
- Charge and moles
  - $Q \text{ (C)} = n \text{ (moles)} \times F \text{ (Faraday constant } 96500)$
- Work and voltage
  - $\text{Work (J)} = E \text{ (V)} \times Q \text{ (C)}$
- Free energy and potential
  - $\Delta G \text{ (J)} = -n(\text{mole}) \times F \text{ (96500C/mol)} \times E \text{ (V)}$
- Ohm's law
  - $I \text{ (A)} = E \text{ (V)} / R \text{ (ohm)}$
- Power
  - $P \text{ (watt)} = \text{work (J)} / S = E \text{ (V)} \times I \text{ (A)}$

# Galvanic Cells

- Converting chemical energy into electric energy by using spontaneous chemical reaction.
- Reduction - cathode:  
 $2\text{AgCl (s)} + 2\text{e}^- \rightleftharpoons 2\text{Ag (s)} + 2\text{Cl}^- \text{ (aq)}$
- Oxidation - Anode:  
 $\text{Cd (s)} \rightleftharpoons \text{Cd}^{2+} \text{ (aq)} + 2\text{e}^-$
- Total reaction:  
 $\text{Cd (s)} + 2\text{AgCl} \rightleftharpoons \text{Cd}^{2+} \text{ (aq)} + 2\text{Ag (s)} + 2\text{Cl}^- \text{ (aq)}$



# Separation of Redox Reactions



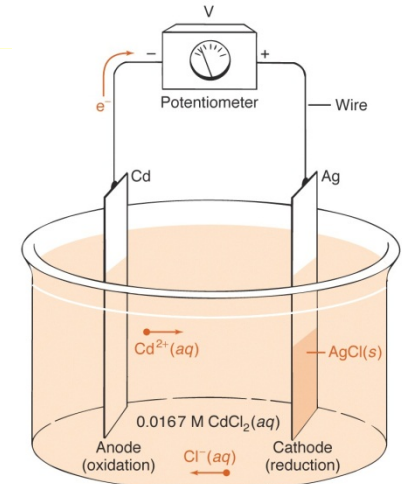
# Salt Bridge

- Electronic conductivity Vs ionic conductivity
  - Electronic conductivity: movement of electrons
  - Ionic conductivity: movement of ions
  - Both are under potential difference or in the electric field.
- Salt bridge: connecting two half reactions with ionic conductive salt

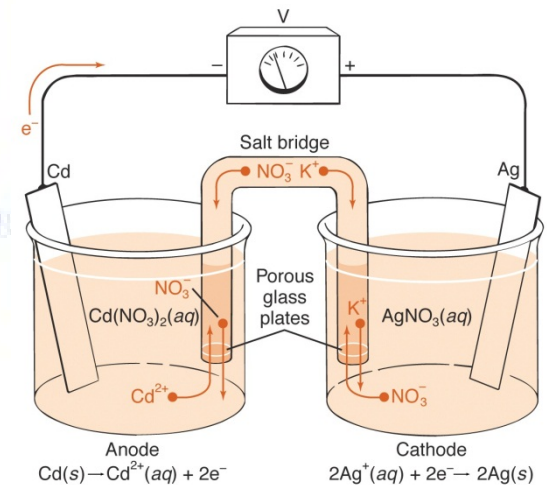


# Notation of electrochemical reactions

- | phase boundary; || salt bridge (two phases)
- $\text{Cd (s)}|\text{CdCl}_2(\text{aq})|\text{AgCl (s)}|\text{Ag(s)}$



- $\text{Cd(s)}|\text{Cd(NO}_3)_2(\text{aq})||\text{AgNO}_3(\text{aq})|\text{Ag(s)}$   
How about without salt bridge?



# Standard Electrode Potentials

- Standard electrode potential, “ $E^\circ$ ”, when each of the chemical species participating in a redox process are at standard state and unit activity
  - No absolute point of reference about for an electrode potential scale
  - One half-cell has been arbitrarily defined as  $E \equiv 0.0000$  volt. Reference is a hydrogen-platinum half-cell containing unit activities, called the "**Standard Hydrogen Electrode**"
  - All other electrode or rest potentials are reported compared to SHE

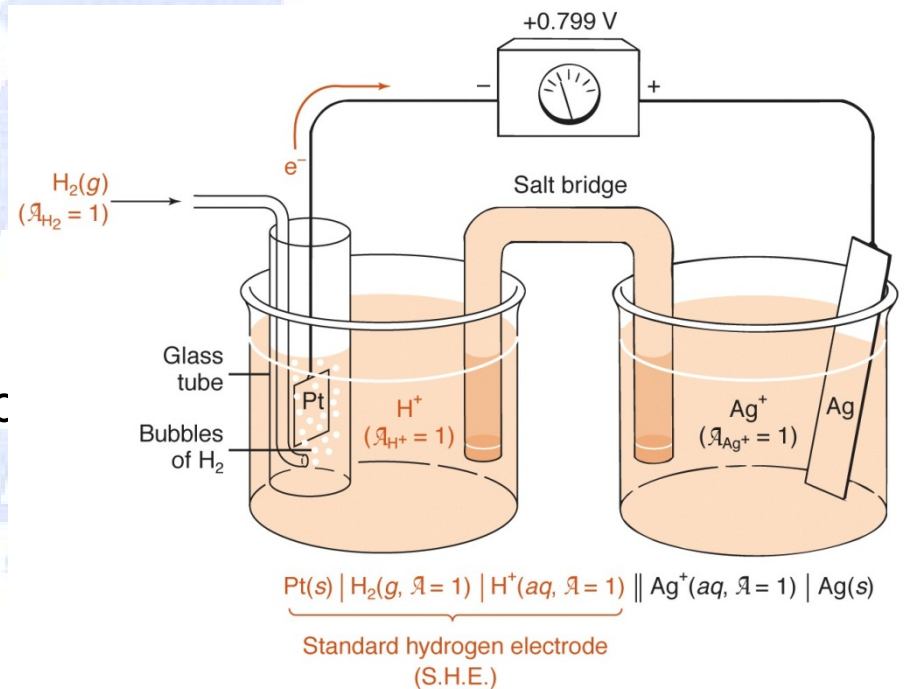
# Standard Potential

- "Standard Hydrogen Electrode" :  
 $\text{Pt}, \text{H}_2(\text{pressure} = 1 \text{ atm}) \mid$   
 $\text{H}^+(\text{activity} = 1)$  (the "SHE" or  
Normal Hydrogen Potential  
"NHE") SHE describes:  
 $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{gas})$   
 $E^\circ = 0 \text{ V}$
- All other electrode or rest potentials are reported compared to SHE

e.g.



$$E^\circ = 0.799 \text{ V}$$



# Oxidation/reduction power

**Table 14-1** Ordered redox potentials

	Oxidizing agent	Reducing agent	$E^\circ$ (V)
↑ Oxidizing power increases	$\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-$		2.890
	$\text{O}_3(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{O}_2(\text{g}) + \text{H}_2\text{O}$		2.075
	⋮		
	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$		1.507
	⋮		
	$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$		0.799
	⋮		
	$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$		0.339
	⋮		
	$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$		0.000
	⋮		
	$\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}(\text{s})$		-0.402
	⋮		
	$\text{K}^+ + \text{e}^- \rightleftharpoons \text{K}(\text{s})$		-2.936
	$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}(\text{s})$		-3.040

Reducing power increases ↓