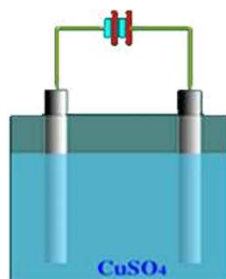


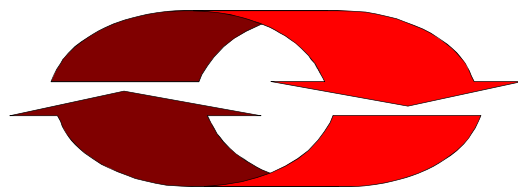
Chapter Two

ELECTROCHEMISTRY



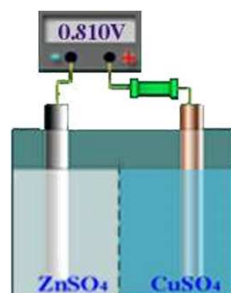
Electrolytic cell

Electric energy



Chemical energy

Galvanic cell



By Alebel N.B (PhD)

Electrochemistry

- A science studying the relationship between **chemical energy** and **electrical energy** and the rules of conversion of two energies
- It is the study of **solutions of electrolytes** and of phenomena occurring at electrodes immersed in these solutions
- It involves generating **electricity** by utilize *a spontaneous* chemical reaction (one with $K > 1$ and $G < 0$) **or**
- Using **electricity to force** a chemical reaction to occur (one that is *non-spontaneous*, $K < 1$ and $G > 0$)

Electrochemical cell

- It is a device which produces an EMF as a result of chemical reactions taking place at the electrodes i.e.,
- A cell in which chemical reaction is used to produce electric current or an electric current is used to produce a chemical reaction

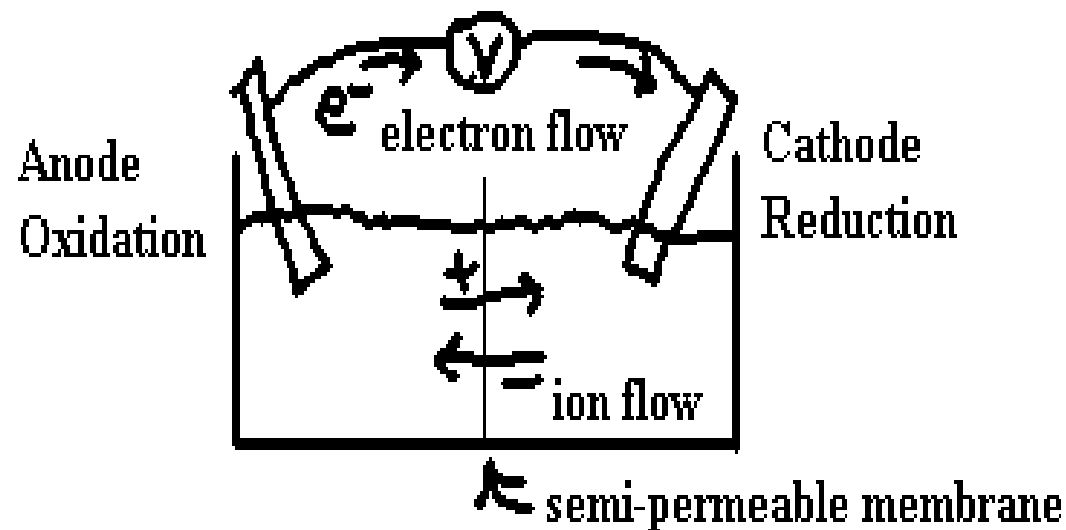
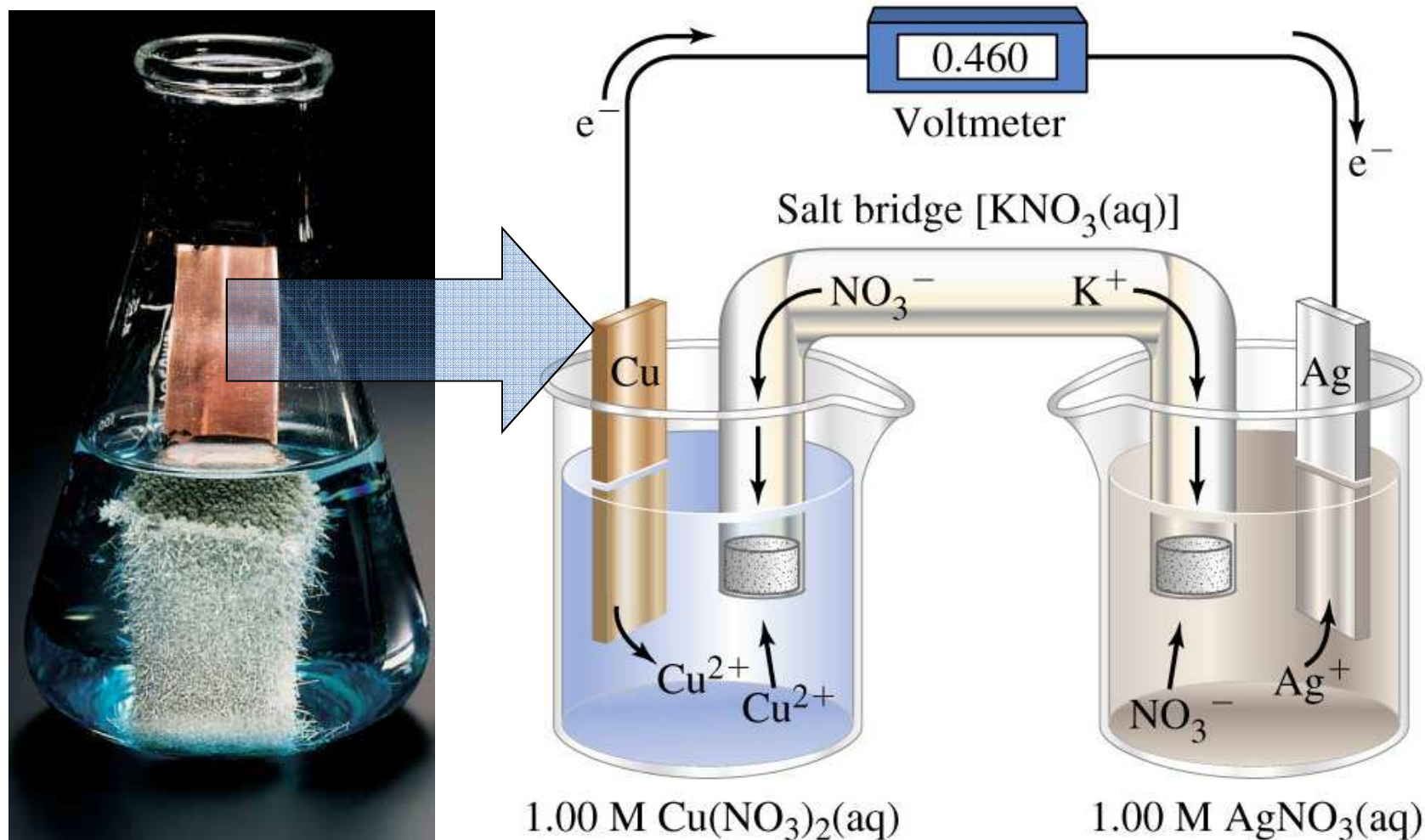


Figure 2.1 Scheme of electrochemical cell

Copper (Cu) in Ag^+ solution is spontaneous



Introduction A. Terms

Electrolysis: Electricity forces a chemical reaction to occur.

Example:



Redox Reactions - Chemical reactions which involve a transfer of electrons.

Electrochemical Cell - a system consisting of electrodes that dip into an electrolyte in which a reaction either generates or uses an electric current.

Cell 1: Battery or Voltaic Cell - An electrochemical cell in which a spontaneous reaction generates an electric current.



Cell 2: Electrolytic Cell - An electrochemical cell in which an electric current forces a reaction to occur.

Cell components:

- Anode and cathode: The cathode is the electrode at which the reduction occurs, while the anode is the electrode where the oxidation takes place.
- The salt bridge: it allows charge transfer through the solutions but prevents mixing of the solutions
- Liquid junctions: Cells with a liquid junction, such as that shown at the fritted porous disk are ordinarily employed to avoid direct reaction between the components of the two half-cells
- The platinum wires can be considered electrodes. Each will adopt an electrical potential that is determined by the tendency of the ions to give off or take on electrons, and this is called the electrode potential
- A Voltmeter : placed between the electrodes will indicate the difference in the potentials between the two electrodes.

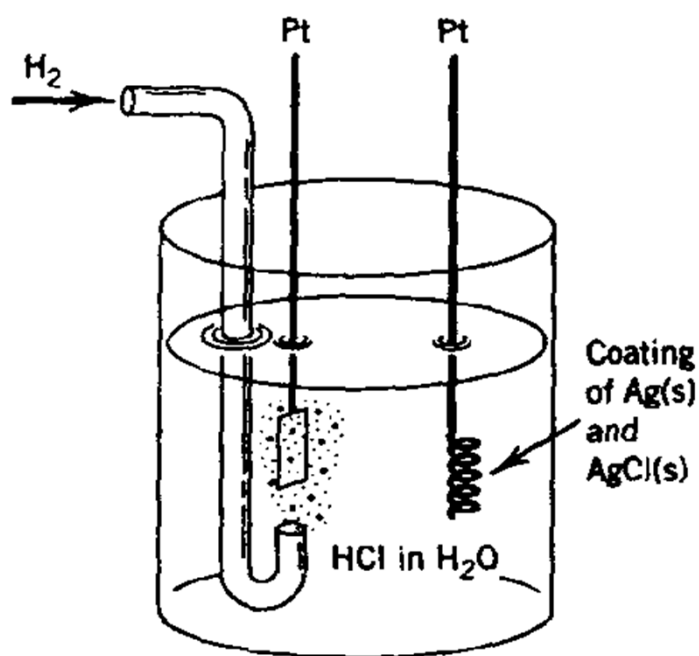
Liquid junction potential

- It occurs when two solutions of **different cons** are in contact with each other
- The more concentrated solns will have a tendency **to diffuse** into the comparatively less concentrated one.
- The rate of diffusion of each ion will be roughly proportional to its speed in an electric field
- If the anions diffuse more rapidly than the cations, they will diffuse ahead into **the dilute solution**, leaving the latter negatively charged and the concentrated solution positively charged

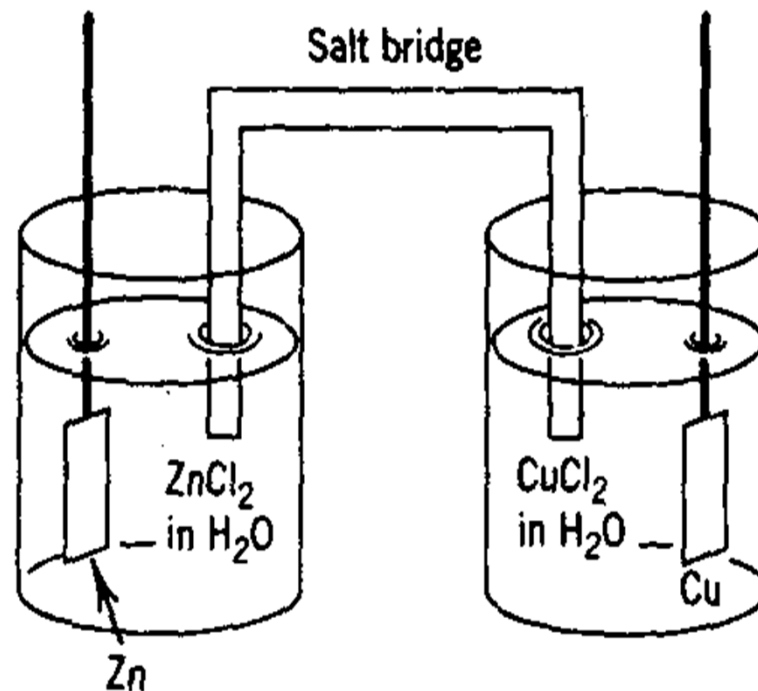
Liquid junction potential

- This will result in an **electrical double layer** of positive and negative charges at the junction of the two solutions
- Thus at the point of junction, a potential difference will develop because of the ionic transfer
- This potential is called **liquid junction potential** or **diffusion potential**
- The magnitude of the potential depends on the relative speeds of the **ions' movement**

In considering electrochemical cells it is important to make a clear distinction between cells without liquid junctions (Fig. a) and cells with liquid junctions (Fig. b)



(a)



(b)

Figure 2.2: Galvanic cell (a) without liquid junction (b) with liquid junction

Representing Cells Schematically

- Chemists frequently use a shorthand notation to describe electrochemical cells i.e.,



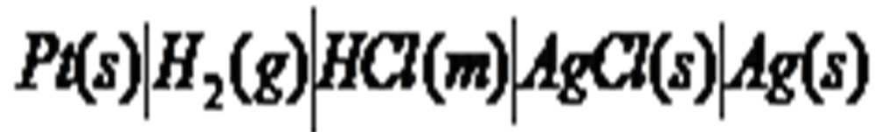
- single vertical line indicates a phase boundary, or interface, at which a potential develops.
- The double vertical line represents two phase boundaries, one at each end of the salt bridge. A liquid-junction potential develops at each of these interfaces.

Cont'd

- The **liquid junction potential** cannot be measured directly but calculated. EMF of a concentration cell with transference includes the liquid junction potential can be expressed as:
- $E_{\text{without transference}} = RT/F \ln(a_2/a_1)$
- $E_{\text{with transference}} = t_M RT/F \ln(a_2/a_1)$
- where a_2 and a_1 are activities of HCl solutions of right and left hand electrodes respectively and t_M be transport number of Cl^- and F is Faraday's Constant.
- **Liquid Junction potential** = $E_{\text{with transference}} - E_{\text{without transference}}$
$$= (t_M - 1) RT/F \ln(a_2/a_1)$$

Cont'd

1. **Cells without liquid junctions.** Examples are represented by:

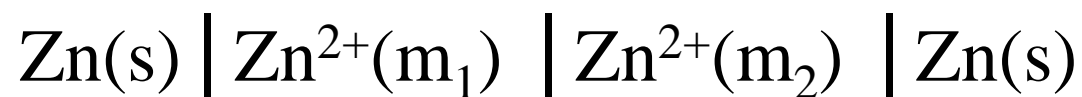


- The vertical lines represent phase boundaries. Hg-Na(x_{Na}) is a sodium amalgam with x_{Na} mole fraction sodium
- Cells of this type can be **held at equilibrium** independently, and therefore they can be given exact thermodynamic treatments
- The **emf** of the cell depends on the **electrodes** and **activity of the electrolyte solution**.

Cont'd

- For two electrode system electrochemical cells without liquid junction, there are only two junctions formed
- As a result for cells equilibrium is established and hence thermodynamic treatment is possible

2. Cells with liquid junctions. Examples are represented by:



- The symbol \mid represents a junction between two liquids, and \parallel represents salt bridge made up of a concentrated solution of KCl or NH_4NO_3 , in which the anion and the cation have nearly equal mobilities

Cont'd

- Cell with liquid junctions are **never** completely at equilibrium
- Because diffusion always occurs **at the liquid junction** and contributes an unknown potential (**emf**)
- However, these contributions are often **small** compared with experimental errors, as a result **Td treatment** of cells with junction is impossible
- To obtain the r/n s/p b/n the EMF for a cell and the chemical potentials or activities of the reactants and products, we will consider the following cell **without a liquid junction**:



Cont'd

- Where **m** is the molality and **cathode** half-cells are placed at the **right** and **anode** half-cells drawn **at the left**
- So in the given cell: **Pt_L/H₂(g)/HCL(m)** is anodic half-cell
- anodic reaction involves oxidation of H₂(g) on the Pt rod

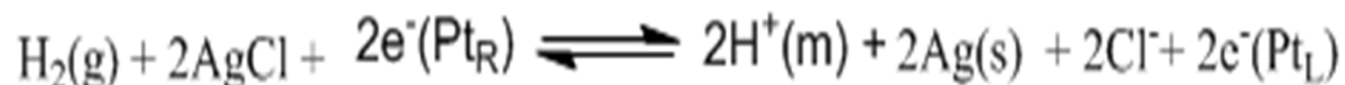


These two ens go to **Pt electrode** and enter into the external **circuit**

- Ag⁺/Ag(s)/Pt_R** is cathode half-cell and involves reduction of Ag⁺ i.e.,

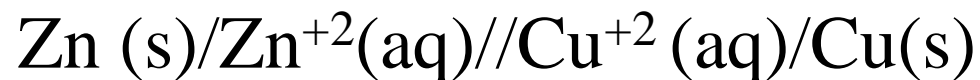
$$2\text{AgCl} + 2\text{e}^- \rightleftharpoons 2\text{Ag} + 2\text{Cl}^-$$

- The (net) sum of these electrode reactions is the cell reaction and referred to as **an electrochemical reaction**



Summary

- ◆ Symbolic notation: **Anode // Cathode** => the cell is with junction
- ◆ Symbolic notation; **Anode — cathode** => the cell is without junction and (“—” stands for HCl)



- ✓ Thus , $\text{Zn}/\text{Zn}^{+2}(\text{aq})$ represents $\text{Zn(s)} \rightarrow \text{Zn}^{+2} + 2\text{e}^{-}$
- ✓ Thus , $\text{Cu}^{+2}(\text{aq})/\text{Cu(s)}$ represents $\text{Cu}^{+2} + 2\text{e}^{-} \rightarrow \text{Cu(s)}$

🌱 The difference in electrical potential between **two electrodes** is called **voltage or cell potential or emf**

🌱 Since emf results from **flow of electrons**, such a reaction must necessarily be one involving **oxidation and reduction**

1. A silver-lithium battery is a voltaic cell with a silver cathode and a lithium anode. What is the voltage of this voltaic cell?

➤ $E^0_{\text{cell}} = E^0_{\text{red}}(\text{cathode}) - E^0_{\text{red}}(\text{anode})$

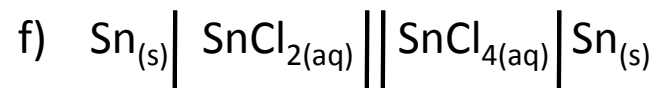
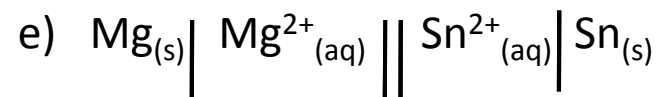
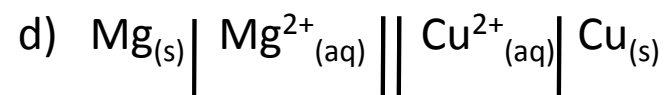
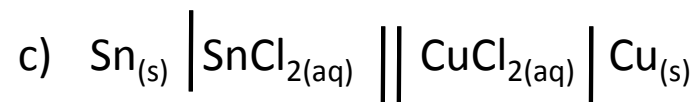
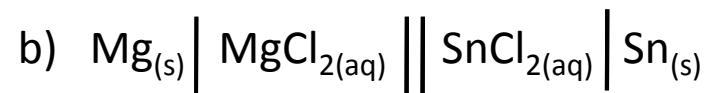
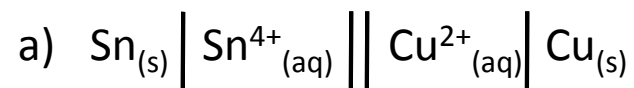
➤ $E^0_{\text{cell}} = 0.8\text{V} - (-3.05\text{V}) = \underline{\underline{\mathbf{3.85\ Volts}}}$

2. What will happen if a science project on batteries suggests that a cathode be made out of Zinc and the anode of Copper?

✓ $E^0_{\text{cell}} = E^0_{\text{red}}(\text{cathode}) - E^0_{\text{red}}(\text{anode})$

✓ $E^0_{\text{cell}} = -0.76\text{V} - (0.34\text{V}) = \mathbf{-1.10\ Volts}$

Match the cell notation to the descriptions



1. Copper placed in a solution of copper(II) chloride and tin metal placed in a solution of tin(II) ions
2. A copper-magnesium cell
3. Magnesium in a solution of magnesium chloride and tin in a solution of tin(II) chloride
4. A tin(II) ion solution containing tin and a solution of magnesium ions containing magnesium
5. Two tin electrodes in solution of tin(II) chloride and tin (IV) chloride respectively
6. Copper place in a copper(II) solution and tin place in a tin(IV) solution

Answer 1c. 2d. 3b. 4e.5f. 6a

Voltaic Cell Notation

Additional Examples

$\text{Pt} \mid \text{H}_2 \mid \text{H}^+ \parallel$ (Half Cell)
 Hydrogen electrode as **anode** (electrode on left)
 $\text{H}_2 \text{ -----} 2\text{H}^+ + 2\text{e}^-$
 Three phases: Pt solid, H_2 gas, H^+ solution

$\parallel \text{Fe}^{3+}, \text{Fe}^{2+} \mid \text{Pt}$ **Cathode** Reaction (electrode on right)
 $\text{Fe}^{3+} + \text{e}^- \text{ -----} \text{Fe}^{2+}$

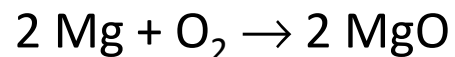
$\parallel \text{Cd}^{2+} \mid \text{Cd}$ **Cathode** Reaction (electrode on right)
 $\text{Cd}^{2+} + 2\text{e}^- \text{ -----} \text{Cd}$

$\text{Ti} \mid \text{Ti}^+ \parallel \text{Sn}^{2+} \mid \text{Sn}$
 $2\text{Ti} + \text{Sn}^{2+} \text{ -----} 2\text{Ti}^+ + \text{Sn}$
 $2\text{Ti} \text{ ----} 2\text{Ti}^+ + 2\text{e}^-$ (**anode**)
 $\text{Sn}^{2+} + 2\text{e}^- \text{ ---} \text{Sn}$ (**cathode**)

Oxidation and Reduction

Oxidation is...

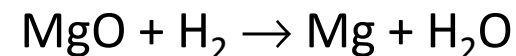
- the **loss** of electrons
- an increase in oxidation state
- the addition of oxygen
- the loss of hydrogen



notice the magnesium is losing electrons

Reduction is...

- the **gain** of electrons
- a decrease in oxidation state
- the loss of oxygen
- the addition of hydrogen



notice the Mg^{2+} in MgO is gaining electrons

Types of Half Cells

● Half cells are sometimes known as **redox electrodes** or **redox couples**

● The **three** most common types of half cell are:

1. Metal-metal half cell is a type of half cell which is formed by a metal and solution containing the metal ion

E.g. Zn/ZnCl₂ cell, Cu/CuSO₄ cell, etc.

➤ The equilibrium is established b/n the metal and its ion such as, $\text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2\text{e}^-$

2. Non-metal ion half cell is contains non-metal electrode into the solution containing the ion of the same non-metal

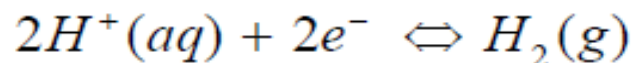
➤ The **hydrogen electrode** (strictly the hydrogen half cell) is a good example of this

Cont'd

- The **electrode** consists of **platinum foil** coated with platinum black
- The electrode is inert although it allows the hydrogen to absorb on its surface
- The following equilibrium is established b/n the absorbed layer of hydrogen molecules and the oxonium ions:



Or more simply:



In a cell diagram hydrogen electrode is represented as

$Pt|H_2(g)|H^+(aq)$ if platinum is the anode, or

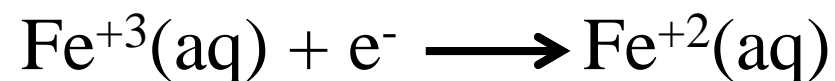
$H^+(aq)|H_2(aq)|Pt$ if platinum is the cathode.

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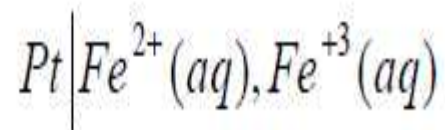
3) The ion-ion half-cell: is type of half-cell consists of an inert electrode (Pt) dipping into a solution containing ions of the **same metal** in two **different oxidation state**

■ Example **iron(III) and iron(II)** half-cell

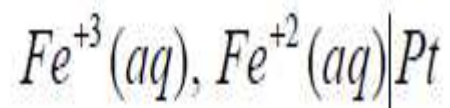
■ In this the following equilibrium is established:



In a cell diagram this half-cell is represented as

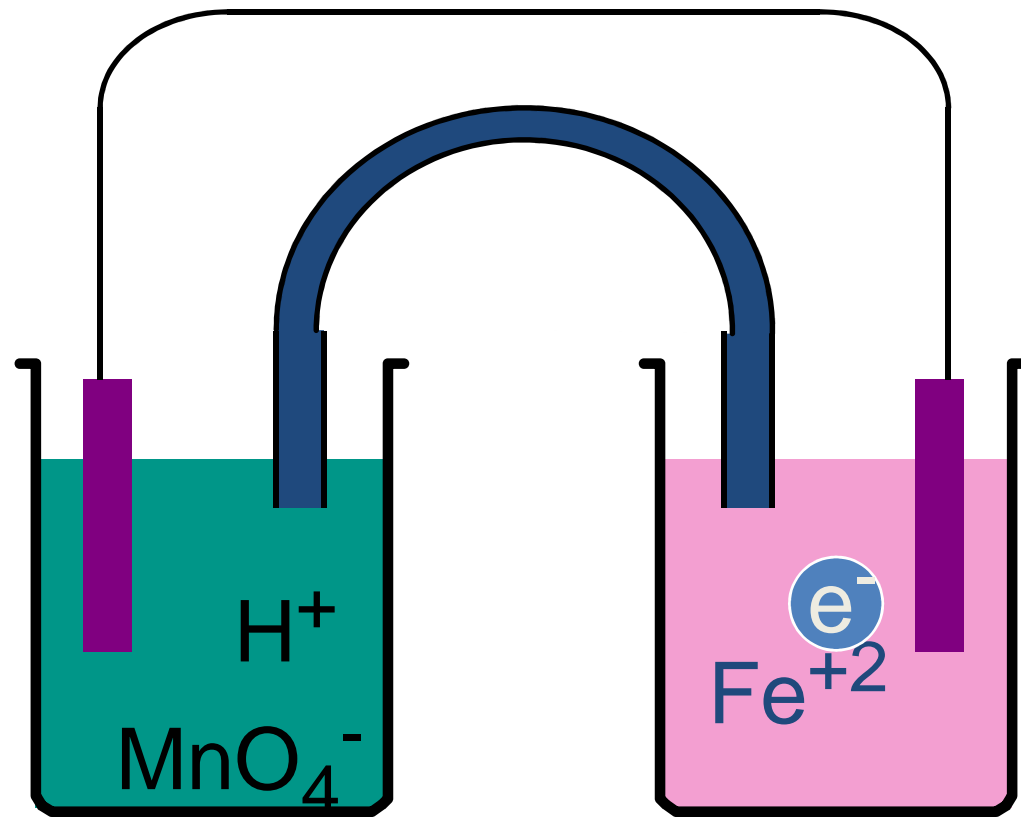


if platinum is the anode, or



if platinum is the cathode.

- | Electricity travels in a complete circuit



Determination of Oxidizing and Reducing Agents

- I. Determine oxidation # for all atoms in both the reactants and products.
 - II. Look at same atom in reactants and products and see if oxidation # increased or decreased
 - If oxidation # decreased; substance **reduced**
 - If oxidation # increased; substance **oxidized**
- **Oxidizing Agent**: Substance that oxidizes the other substance by accepting electrons. It is **reduced** in reaction.
 - **Reducing Agent**: Substance that reduces the other substance by donating electrons. It is **oxidized** in reaction.

Oxidation Numbers (ON)

- The charge that an atom (group of atoms) would have if it were ionic
- The charge the atom would have in a molecule (or anionic compound) if electrons were completely transferred.

☐ Usefulness:

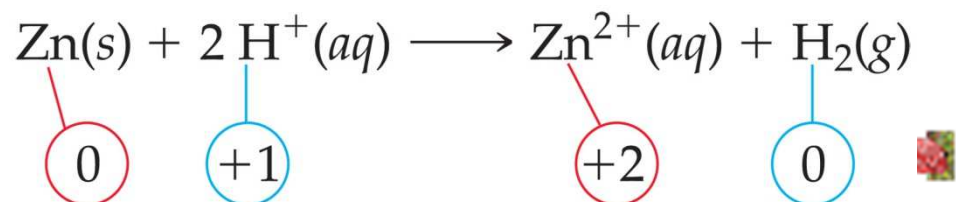
1) Naming variably charged compounds.

Example: FeCl_3 = Iron(III)chloride

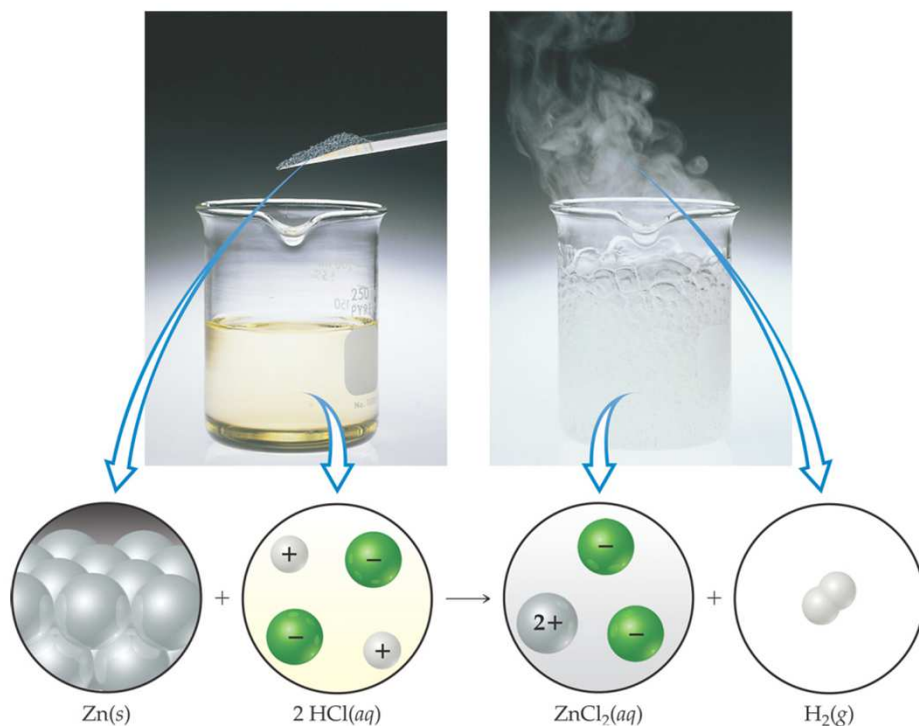
2) Determining if a reaction is redox.

3) Balancing a redox reaction.

Oxidation Numbers



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



Oxidation Numbers of

[illegible]

Assigning Oxidation States

- Each atom in a pure element has an oxidation state of “0”.
e.g. F_2 O_3 K N_2 Fe
- For mono-atomic ions, the oxidation state is equal to the charge on the ion.
e.g. F^- Al^{3+} Fe^{2+} O^{2-}
- The oxidation state of oxygen in a compound (e.g. CH_3OH) is almost always “-2”. But In H_2O_2 and O_2^{2-} it is -1
- The oxidation state of hydrogen in a compound (e.g. CH_3OH) is almost always “+1”.
- The sum of the oxidation states in a neutral compound must equal “0”.
- The sum of the oxidation states in a complex ion must equal the charge on the complex ion.

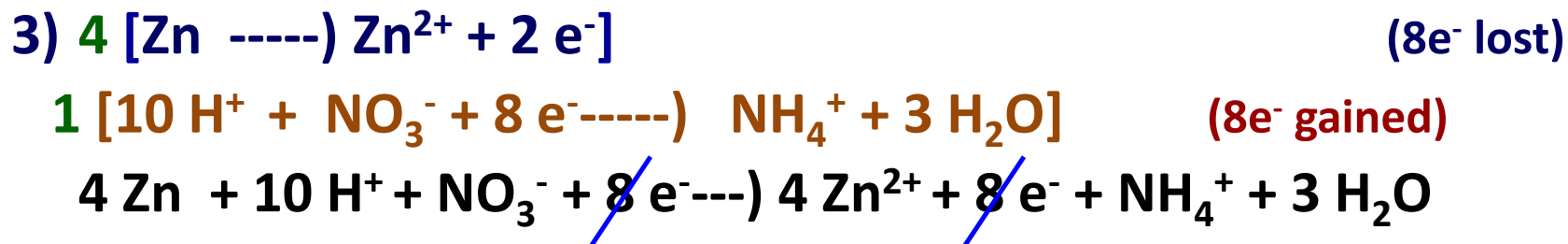
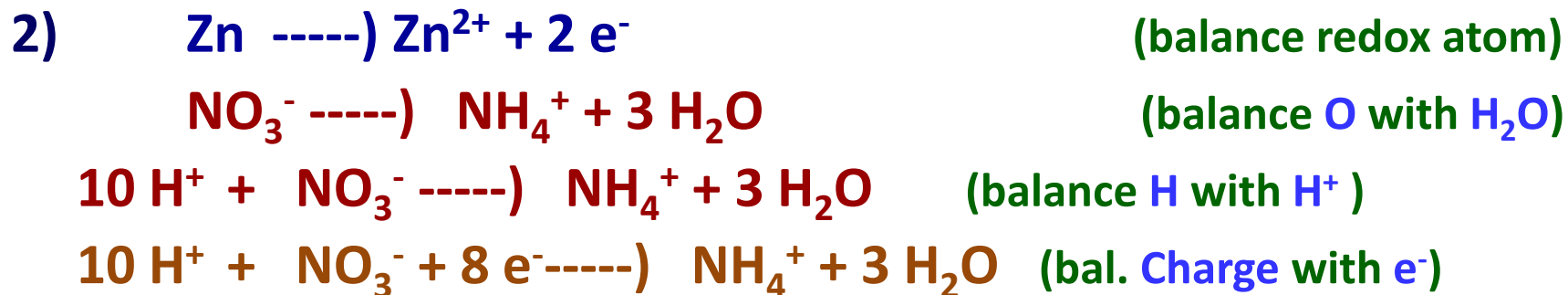
Balancing Redox Rxns A. acidic media

- Many are difficult and require a systematic method: Note that you must first determine if the reaction occurs in **acid** or **base**.
- **Steps: 1-3 for acidic media & Steps 4-6 for basic media**
 - 1. Assign ON's & split into two half reactions**
 - 2. Complete & balance each half reaction:**
 - a. balance atom undergoing redox**
 - b. balance O by adding H₂O's**
 - c. balance H by adding H⁺'s**
 - d. balance ionic charge by adding e⁻'s**
 - 3. Combine half reactions and finish (if in acidic media):**
 - a. 1st - multiply half reactions by integers to cancel e⁻'s.**
 - b. 2nd - add 1/2 Rxns & cancel same species on both sides.**

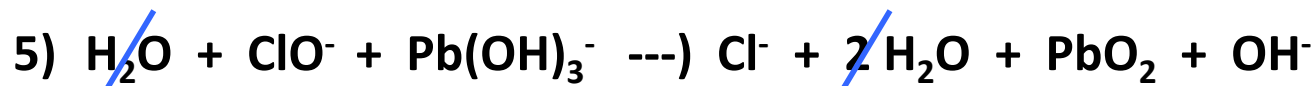
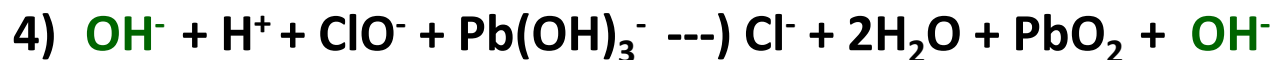
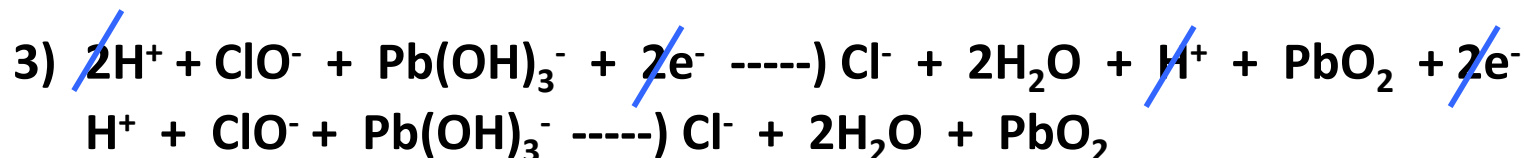
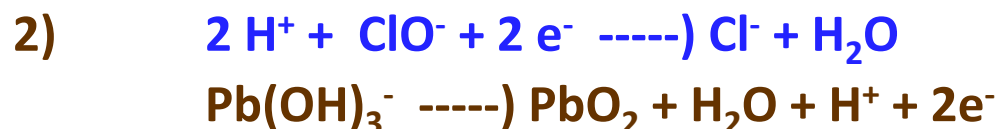
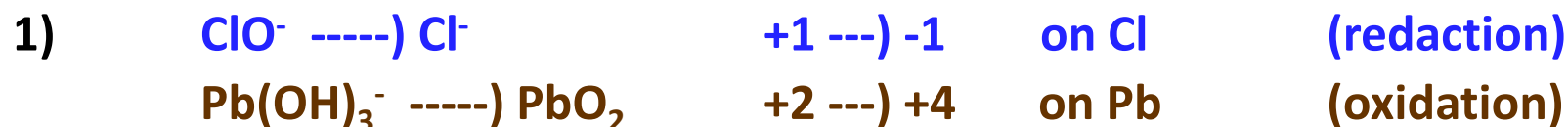
Balancing Redox Rxns B. Basic media

4. If in basic media add OH^- equal to # H^+ to both sides.
5. Convert H^+ & OH^- on same side to H_2O & simplify by canceling H_2O if needed.
6. Check result by noting if following are both balanced: elements & charge.

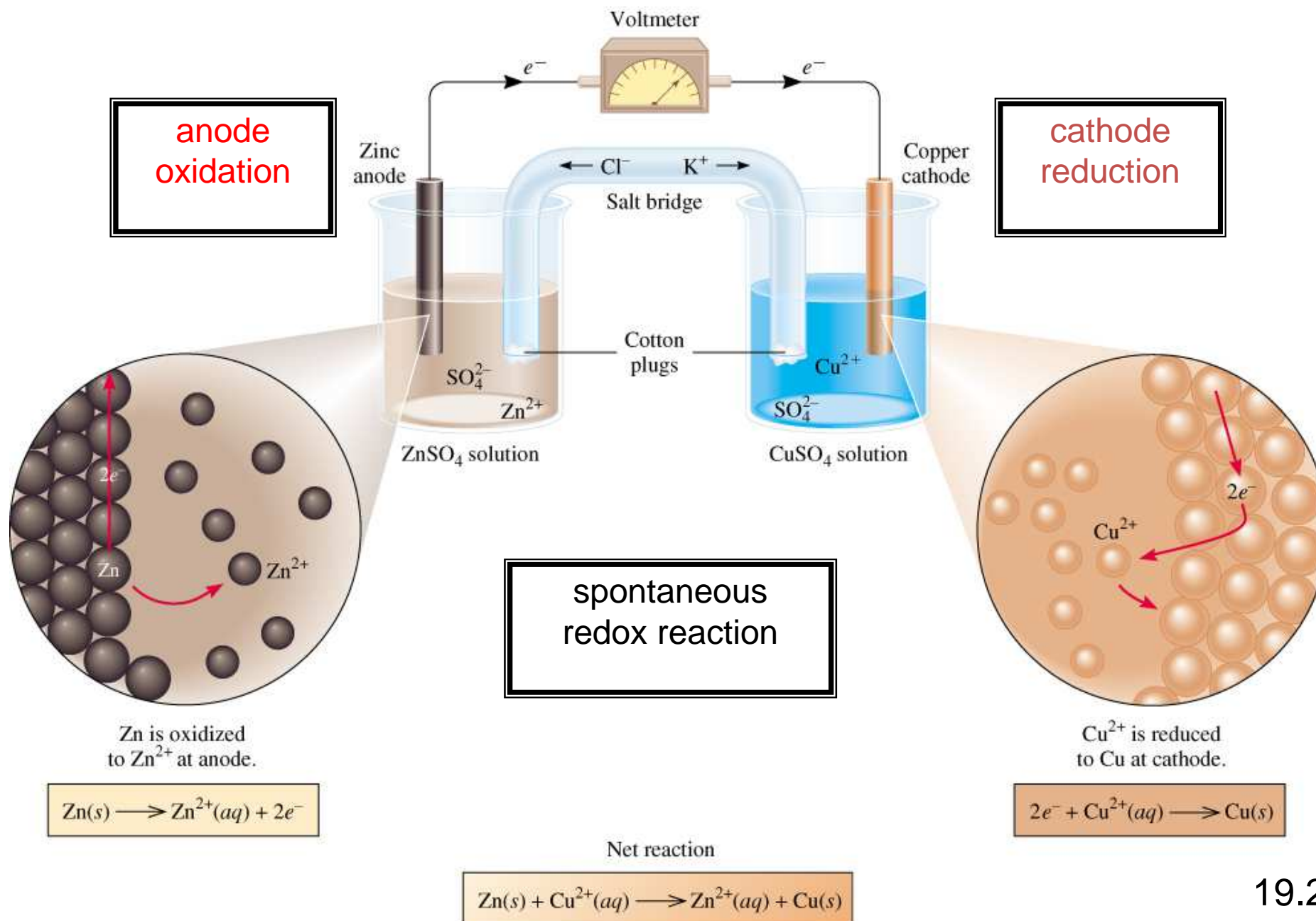
Balancing Redox Rxns C. Example 1 in acid



Balancing Redox Rxns C. Example 2 (basic)



Galvanic Cells

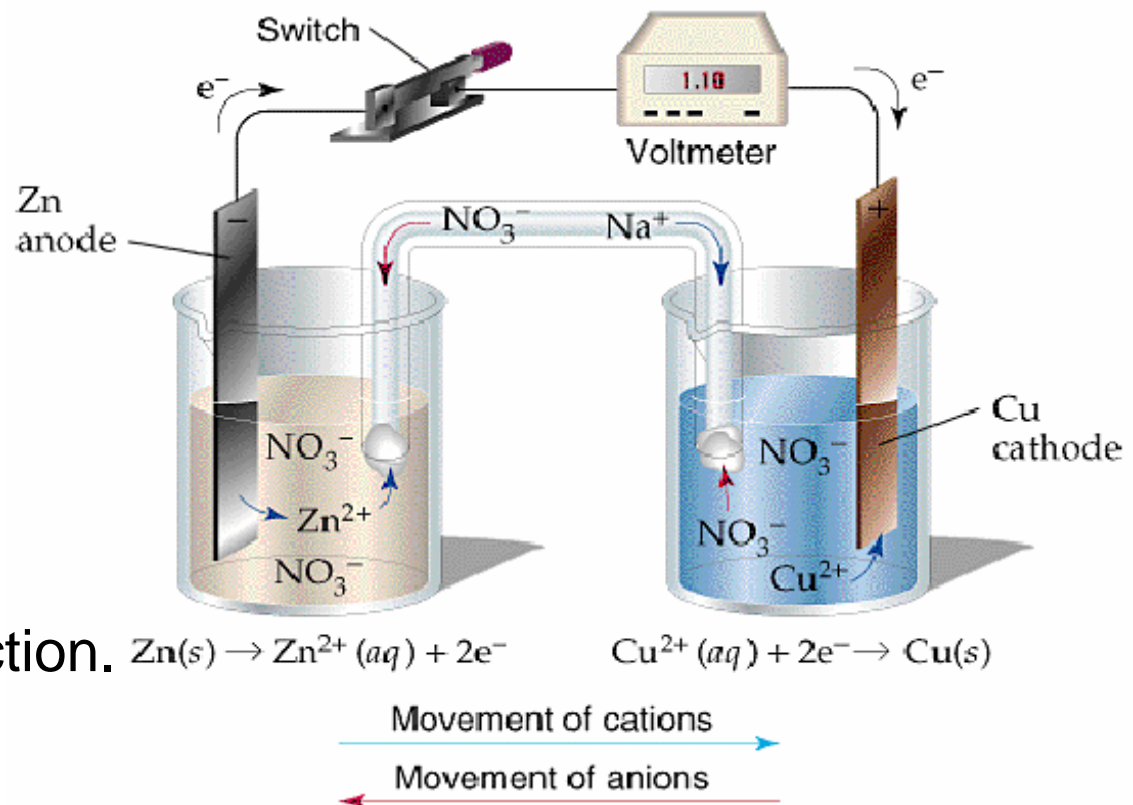


- **Galvanic cells consist of**

- **Anode:** $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
- **Cathode:** $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$
- **Salt bridge** (used to complete the electrical circuit): cations move from anode to cathode, anions move from cathode to anode.

- The two solid metals are the **electrodes** (cathode and anode).

- As oxidation occurs, Zn is converted to Zn^{2+} and 2e^- . The electrons flow towards the anode where they are used in the reduction reaction.



The ANODE...	The CATHODE...
Supplies electrons to external circuit (wire)	Accepts electrons from external circuit (wire)
Is negative pole of battery	Is positive pole of battery
Is site of OXIDATION	Is site of REDUCTION
Is written on left- hand side if convention is followed	Is written on right-hand side if convention is followed
Is half-cell with lowest electrode potential	Is half-cell with highest electrode potential

Cell Potential (E_{cell}) or Electromotive force (emf)

- Force with which electrons flow from - electrode (anode on left) to + electrode (cathode on right) through external wire
 - Due to PE difference of electrons before/after transfer
 - In electrochemical cell, electric potential created between two dissimilar metals
 - Greater tendency or potential of two half-reactions to occur spontaneously, greater emf of cell
- Measured in **volts (V)**-why called cell voltage)
 - **1 V = 1 J/coulomb** (of charge transferred)
 - Measured with voltmeter which draws current through known resistance (heat is produced)

Electromotive Force (emf)

- The potential difference between the anode and cathode in a cell is called the **electromotive force (emf)**.
- It is also called the **cell potential**, and is designated E_{cell} (in Volts).
- Electromotive force (emf) is the force required to push electrons through the external circuit.
- For 1M solutions at 25 °C (standard conditions), the standard emf (standard cell potential) is called E°_{cell} .
- **Standard Reduction Potentials**
- Convenient tabulation (arrangement) of electrochemical data.
- Standard reduction potentials, E°_{red} are measured relative to the standard hydrogen electrode (SHE).

Reduction potential

□ More negative E°

- more easily electron is added
- More easily reduced
- Better oxidizing agent

□ More positive E°

- more easily electron is lost
- More easily oxidized
- Better reducing agent

Standard Reduction Potentials at 25°C*

Half-Reaction	$E^0(\text{V})$
$\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}^-(\text{aq})$	+2.87
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2\text{O}$	+2.07
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Co}^{2+}(\text{aq})$	+1.82
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+1.77
$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \longrightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$	+1.70
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \longrightarrow \text{Ce}^{3+}(\text{aq})$	+1.61
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$	+1.51
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Au}(\text{s})$	+1.50
$\text{Cl}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$	+1.33
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	+1.23
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Br}_2(\text{l}) + 2\text{e}^- \longrightarrow 2\text{Br}^-(\text{aq})$	+1.07
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \longrightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}$	+0.96
$2\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Hg}_2^{2+}(\text{aq})$	+0.92
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Hg}(\text{l})$	+0.85
$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	+0.68
$\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O} + 3\text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$	+0.59
$\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{I}^-(\text{aq})$	+0.53
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-(\text{aq})$	+0.40
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$	+0.34
$\text{AgCl}(\text{s}) + \text{e}^- \longrightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22
$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}$	+0.20
$\text{Cu}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Cu}(\text{s})$	+0.15
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	+0.13
$2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$	0.00
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ni}(\text{s})$	-0.25
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Co}(\text{s})$	-0.28
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \longrightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.31
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cd}(\text{s})$	-0.40
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{3+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Al}(\text{s})$	-1.66
$\text{Be}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Be}(\text{s})$	-1.85
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ca}(\text{s})$	-2.87
$\text{Sr}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sr}(\text{s})$	-2.89
$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ba}(\text{s})$	-2.90
$\text{K}^+(\text{aq}) + \text{e}^- \longrightarrow \text{K}(\text{s})$	-2.93
$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.05

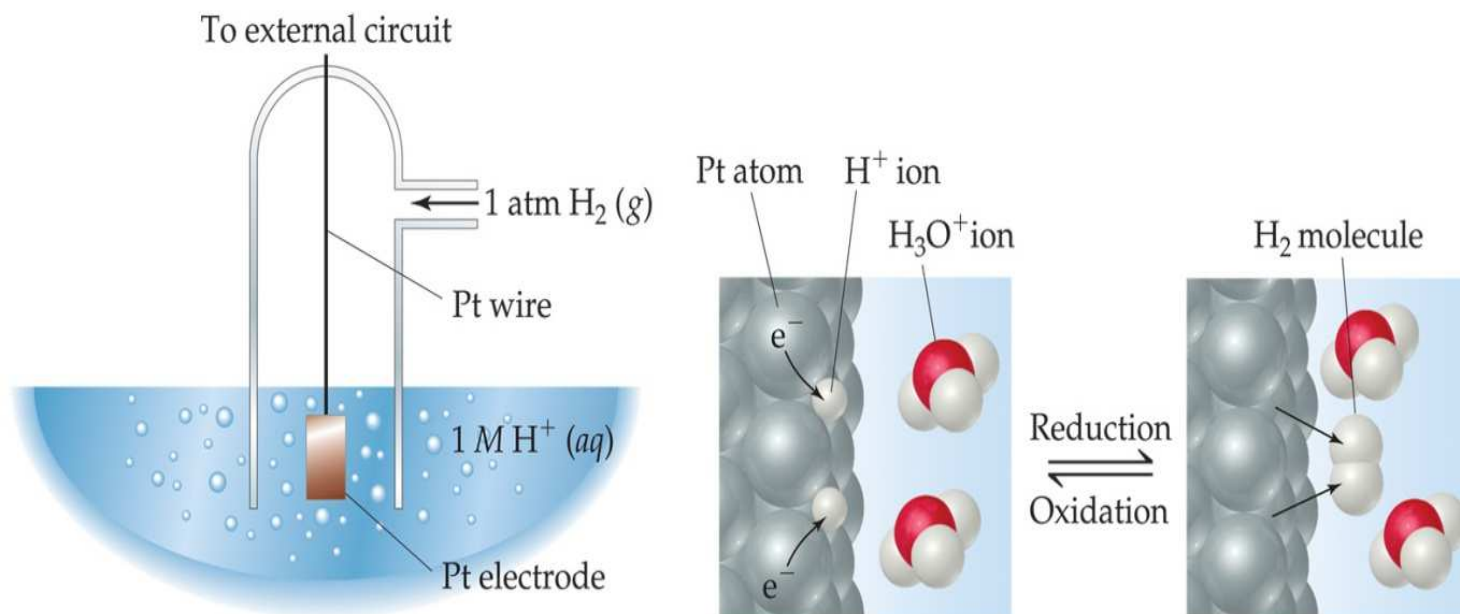
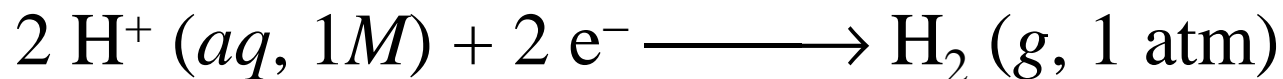
Increasing strength as oxidizing agent

Increasing strength as reducing agent

- E^0 is for the reaction as written
- The more positive E^0 the greater the tendency for the substance to be reduced
- The half-cell reactions are reversible
- The sign of E^0 changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction *does not* change the value of E^0

Standard Hydrogen Electrode (SHE).

- Their values are referenced to a standard hydrogen electrode (SHE)
- By definition, the reduction potential for hydrogen is 0.0 V



- In SHE; HCl or H_2SO_4 act as electrolyte
Pt- acting as inert electrode (supporting electrolyte)
 H_2 - acting as electrode

The Standard Hydrogen Electrode (SHE)



25°C

1.00 M H^+

1.00 atm H_2

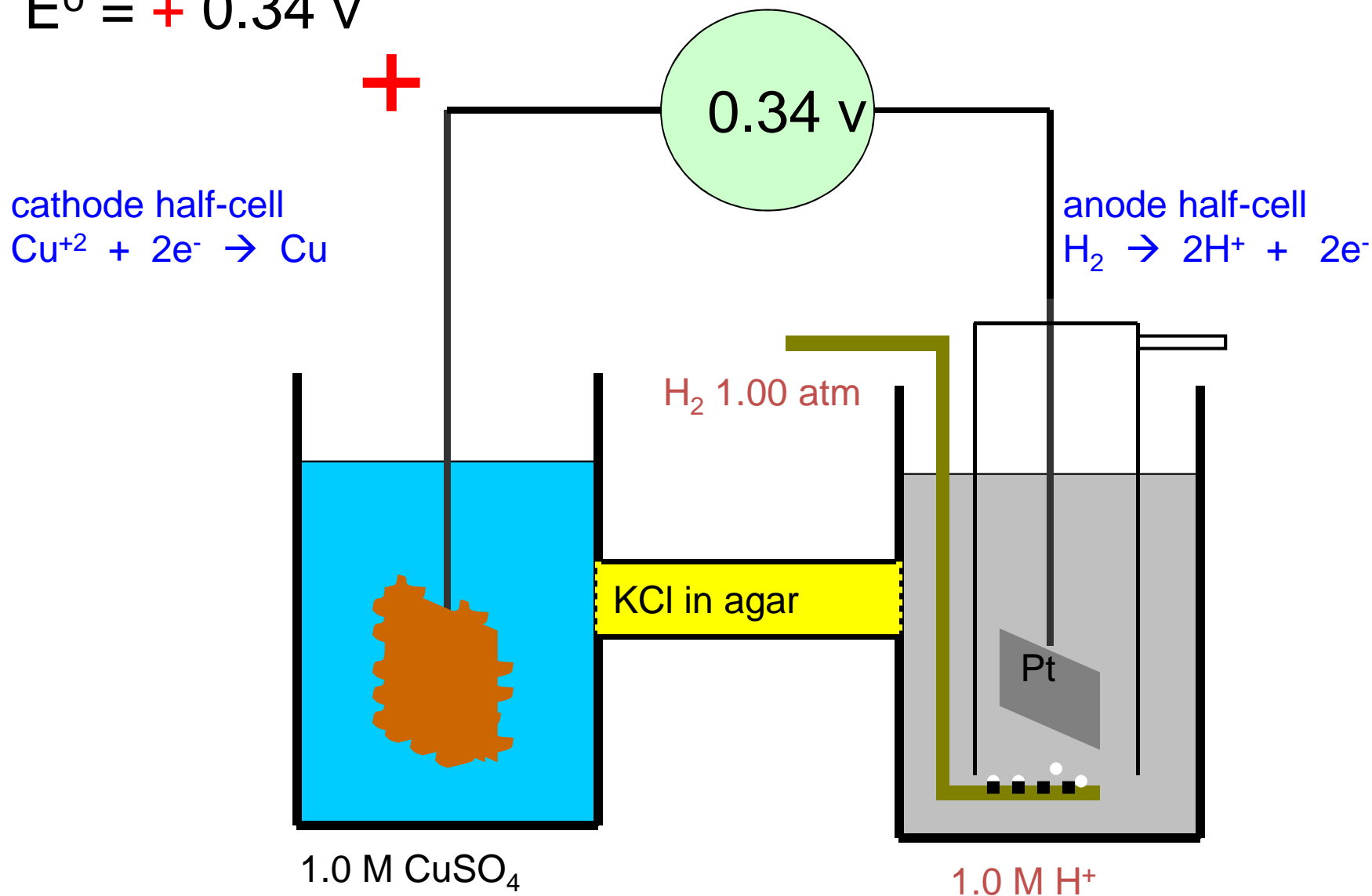
Half-cell



$$E^\circ_{\text{SHE}} = 0.0 \text{ volts}$$

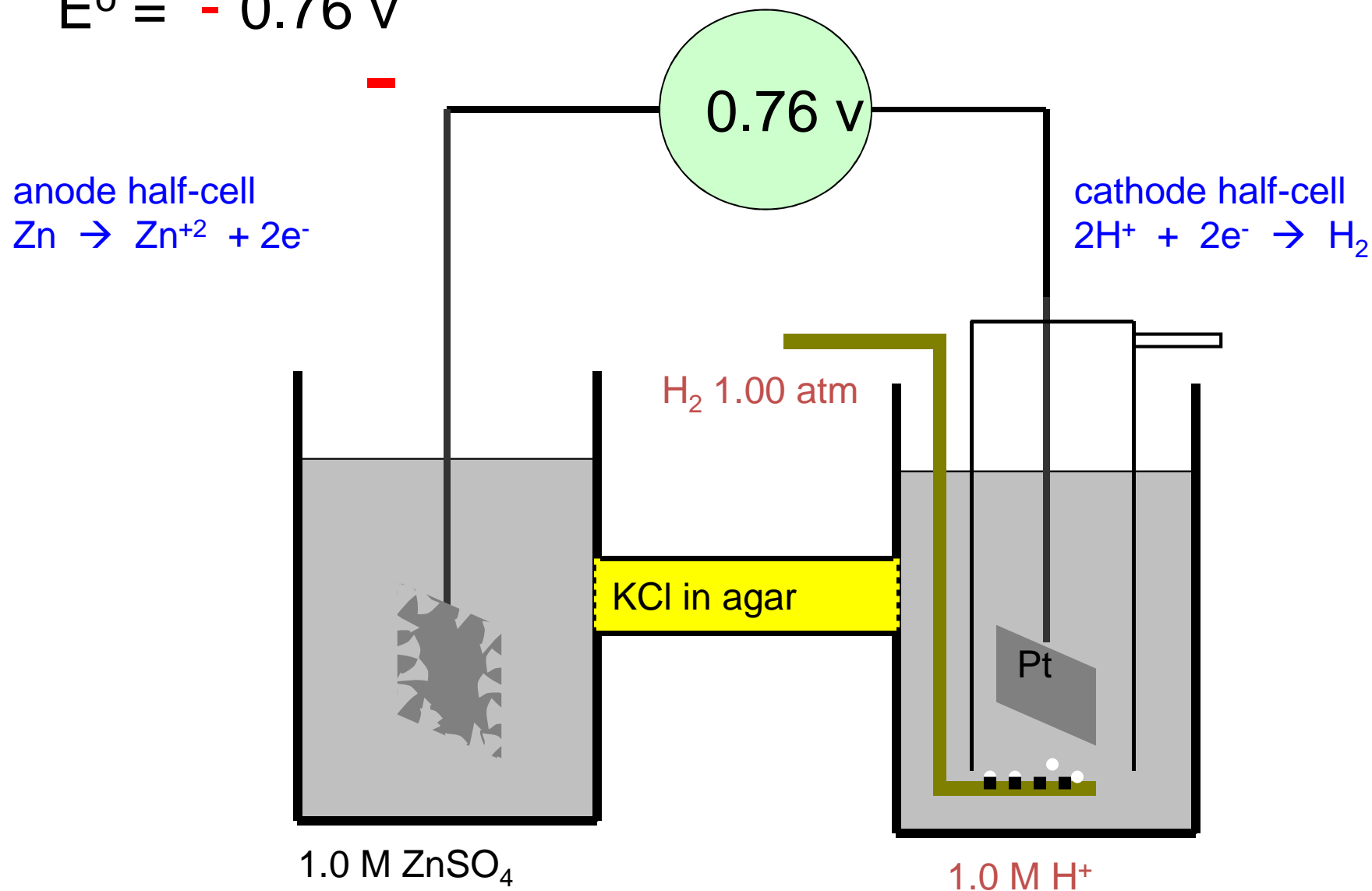
Now let's combine the copper half-cell with the SHE

$$E^{\circ} = + 0.34 \text{ v}$$



Now let's combine the zinc half-cell with the SHE

$$E^\circ = -0.76 \text{ v}$$



Standard Cell Potentials

- The cell potential at standard conditions can be found through this equation:

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} (\text{cathode}) - E_{\text{red}}^{\circ} (\text{anode})$$

- Because cell potential is based on the potential energy per unit of charge, it is an intensive property

Zn/Cu For the oxidation in this cell,

$$E_{\text{red}}^{\circ} = -0.76 \text{ V}$$

For the reduction,

$$E_{\text{red}}^{\circ} = +0.34 \text{ V}$$

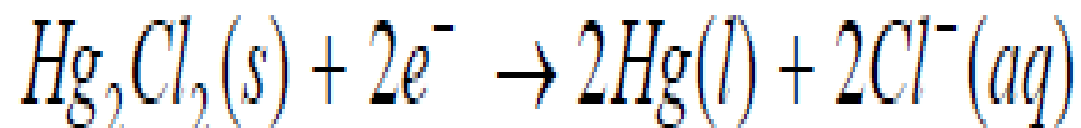
Cell Potentials

$$\begin{aligned}E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ} (\text{cathode}) - E_{\text{red}}^{\circ} (\text{anode}) \\&= +0.34 \text{ V} - (-0.76 \text{ V}) \\&= +1.10 \text{ V}\end{aligned}$$

- Under standard conditions, voltage of cell is same as total voltage of redox reaction
Standard emf of cell potential (E_{cell}°)
- Under nonstandard conditions, cell voltage computed by using Nernst equation

2. The Calomel Electrode

- The H_2 electrode is relatively difficult to set up and operate under standard conditions
- It is far easier to use the calomel electrode as a secondary reference electrode to calibrate other electrodes
- Calomel is mercury (I) chloride, Hg_2Cl_2 . The half reaction for the electrode is:



- A saturated solution of KCl is frequently used for the calomel electrode

Cont'd

- If the **calomel electrode** is **anode**, the symbolic notation is $\text{Hg (l)} / \text{Hg}_2\text{Cl}_2(\text{S}) / \text{sat. KCl (aq)}$
- The half cell reaction is $\text{Hg (l)} \rightarrow \text{Hg}^+ + \text{e}^-$
- If the **calomel electrode** acts as **cathode**, the SN is $\text{Sat. KCl (aq)} / \text{Hg}_2\text{Cl}_2(\text{S}) / \text{Hg (l)}$
- The half cell reaction is $\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-(\text{aq})$
- The electrode potential of the calomel electrode is known accurately over a range of **concentrations** and **temperatures**
- When the concentration of the KCl solution 1M, the electrode potential is +0.2415 V at 298 K.

3. Silver-Silverchloride electrode

- In this electrode; - $\text{Ag}/\text{AgCl(s)}$ – used as electrode
- HCl – used as electrolyte
- If $\text{Ag}/\text{AgCl(s)}$ electrode is **anode**, the symbolic notation is $\text{Ag(s)} / \text{AgCl(s)} / \text{HCl(aq)}$
- If $\text{Ag}/\text{AgCl(s)}$ electrode is **cathode**, the symbolic notation is $\text{HCl(aq)} / \text{AgCl(s)} / \text{Ag(s)}$
- The cathodic half-cell reaction $\text{AgCl(s)} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-(\text{aq})$
- Calomel and $\text{Ag}/\text{AgCl(s)}$ electrodes can be prepared in the laboratory but, $\text{Ag}/\text{AgCl(s)}$ electrodes are easy to prepare than calomel due to
- ✚ The chemicals are not dangerous as Hg to handle
- ✚ The material supply is sufficient (inexpensive as Hg)

Free Energy

- ΔG for a redox reaction can be found by using the equation

$$\Delta G = -nFE$$

where n is the number of moles of electrons transferred,
and F is a constant, the Faraday

$$1 F = 96,485 \text{ C/mol} = 96,485 \text{ J/V-mol}$$

- Under standard conditions,

$$\Delta G^\circ = -nFE^\circ$$

Nernst Equation

- Remember that

$$\Delta G = \Delta G^\circ + RT \ln Q$$

- This means

$$-nFE = -nFE^\circ + RT \ln Q$$

➤ Dividing both sides by $-nF$,

➤ we get:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

or, using base-10 logarithms,

$$E = E^\circ - \frac{2.303 RT}{nF} \log Q$$

Nernst Equation

❖ At room temperature (298 K),

$$\frac{2.303 RT}{F} = 0.0592 \text{ V}$$

➤ Thus the equation becomes

$$E = E^{\circ} - \frac{0.0592}{n} \log Q$$

Extensive vs intensive

- Free energy is **extensive** property so need to multiply by no of moles involved

$$\Delta G = -nFE$$

- But to convert to E we need to divide by no of electrons involved

$$E^{\circ} = -\Delta G^{\circ} / nF$$

- E is an **intensive** property

The Nernst equation

➤ Working in nonstandard conditions

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$-nFE = -nFE^{\circ} + RT \ln Q$$

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

$$E = E^{\circ} - \frac{0.0592}{n} \log Q$$

Electrode potentials and pH

- For the cell reaction



- The Nernst equation

$$E_{H_2 \rightarrow 2H^+} = E_{H_2 \rightarrow 2H^+}^{\circ} - \frac{0.06V}{n} \left(\log \frac{[H^+]^2}{p_{H_2}} \right)$$

$$E_{H_2 \rightarrow 2H^+} = - \frac{0.06V}{n} \left(\log [H^+]^2 \right)$$

- Half-cell potential is proportional to pH**

The pH meter is an electrochemical cell

- Overall cell potential is proportional to pH

$$E_{cell} = (0.06V)(pH) + E_{ref}$$

$$pH = \frac{E_{cell} - E_{ref}}{0.06V}$$

- In practice, a hydrogen electrode is impractical

Cell potentials and equilibrium

$$\Delta G^{\circ} = -nFE^{\circ}$$

- Lest we remember...

$$\Delta G^{\circ} = -RT \ln K$$

- So then

$$nFE^{\circ} = -RT \ln K$$

- and

$$E^{\circ} = \frac{RT}{nF} \ln K = \frac{2.303RT}{nF} \log_{10} K$$

Many pathways to one ending

- Measurement of **K** from different experiments

- Concentration data

$$\frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- Thermochemical data

$$\Delta G^\circ = -RT \ln K$$

- Electrochemical data

$$nFE^\circ = -RT \ln K$$

Summery

- Can measure the [cell voltage or potential or electromotive force (EMF)] using a voltmeter; and can calculate theoretical voltages from equations & tables.
- The voltage (E) developed by a cell is the reduction minus oxidation potentials:
- $E_{\text{cell}} = E_{\text{reduction}} - E_{\text{oxidation}}$ or
- **Note:** can't separate the two half reactions in the lab; so, how calculate $E_r \& o$?
- By setting an arbitrary standard and comparing all other half cell reactions to this standard
- Arbitrary Standard is the hydrogen half cell reduction under standard conditions (1 M, 1 atm, 25°C) ; a value of 0.00 V was assigned.

Spontaneity of Redox Reactions



Relationships Among ΔG° , K , and E°_{cell}

ΔG°	K	E°_{cell}	Reaction Under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	$=1$	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

$$\Delta G^\circ = -RT \ln K = -nFE^\circ_{\text{cell}}$$

The Battery

- It is a cell or connected group of cells that converts chemical energy into electrical energy which involve the transfer of electrons from one species to the another
- It is an electro chemical cell (also called storage cell)
- Several factors influence the choice of materials such as Voltage, Weight, Capacity, Current density, and Rechargeability

Types of Batteries

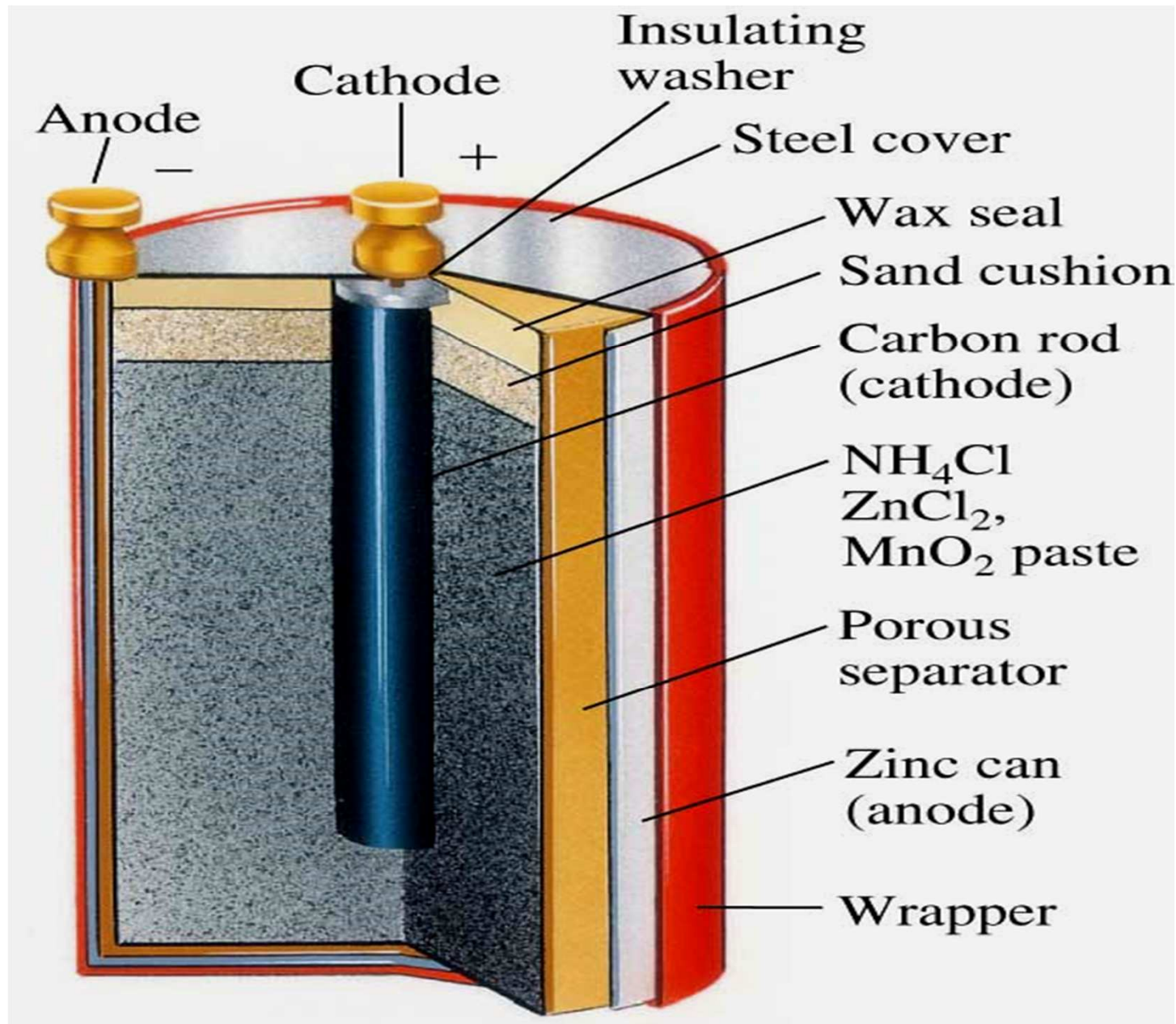
1. The *primary battery* converts chemical energy to electrical energy *directly*, using the chemical materials within the cell to start the action.
 2. The *secondary battery* must first be *charged* with electrical energy before it can convert chemical energy to electrical energy.
- The *secondary battery* is frequently called a *storage battery*, since it stores the energy that is supplied to it.

Primary cells

- The chemical reaction which produces energy is **irreversible**, which means the battery can be used once then discarded (useless) i.e.,
- Cannot be recharged
- Chemical process not reversible
- Zinc carbon (1.5v) and alkaline (1.5v) are good example



The zinc-carbon (Leclanche) dry cell



The zinc-carbon (Leclanche) dry cell

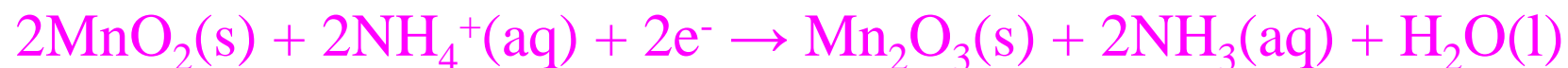
- One example of a dry cell is flashlight and radio batteries
- The cell's container is made of zinc which acts as an electrode.
- A graphite rod (C) is in the center of the cell which acts as the other electrode.
- The space between the electrodes is filled with a mixture of:
 1. ammonium chloride, NH_4Cl
 2. manganese (IV) oxide, MnO_2
 3. zinc chloride, ZnCl_2
 4. porous inactive solid

The zinc-carbon dry cell

- ☀ **At the anode (-)** oxidation of the zinc case produces electrons:



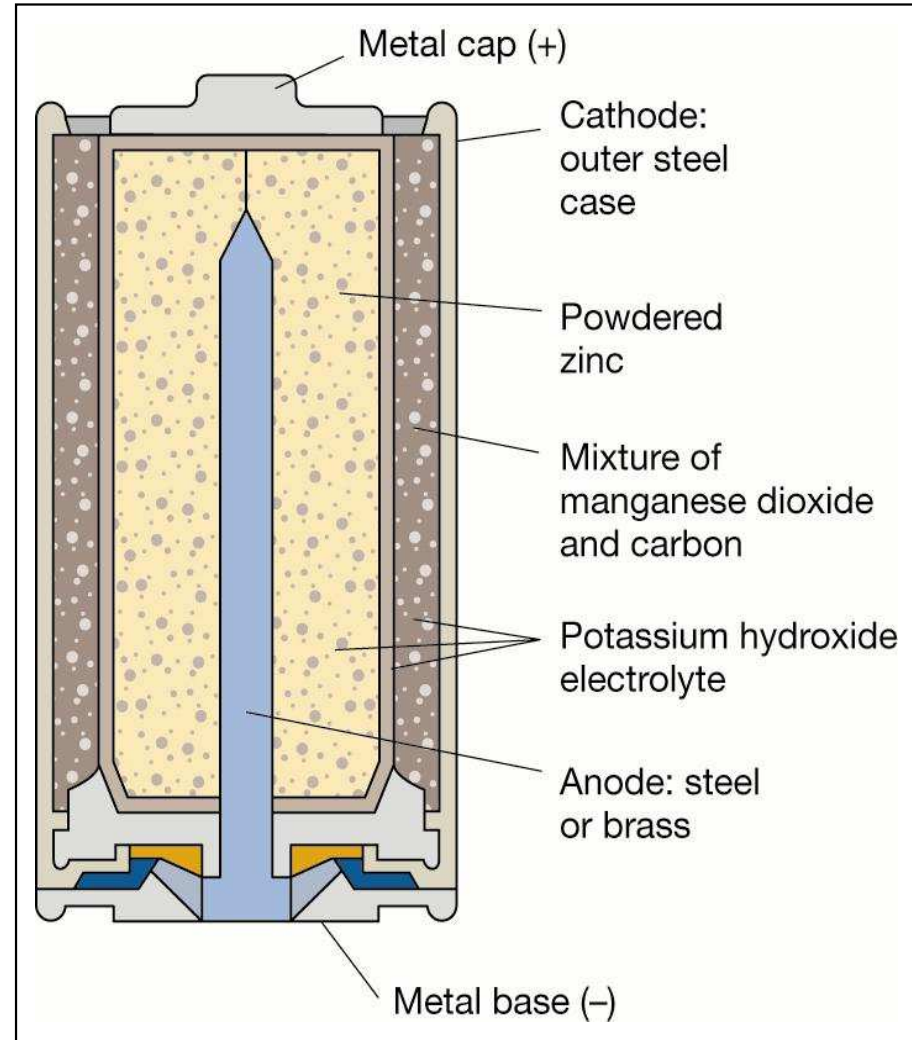
- ☀ **At the cathode (+)** Manganese dioxide is reduced in a complicated reaction that is thought to be: $E^\circ_{\text{red}} = 0.75 \text{ V}$



- ◆ A new cell produces about **1.5 volts**, but this diminishes significantly during use
- ◆ To maintain a net forward reaction, the soluble reaction products must migrate away from the electrodes.
- ◆ But, during use the build up of products around the electrodes slows and can even stop the forward reaction. This is known as **polarisation**
- ◆ If the cell is allowed to rest, the products migrate away from the electrodes and the cell can recover.

Alkaline cells

- In this cell the NH_4Cl (aq) is replaced by KOH (aq)
- This provides more useable voltage and greater capacity than the typical dry cell
- It is optimised for performance and long life

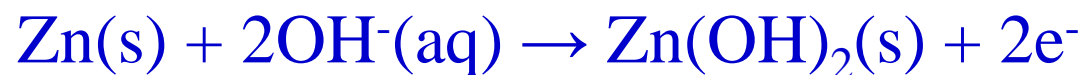


Alkaline cells

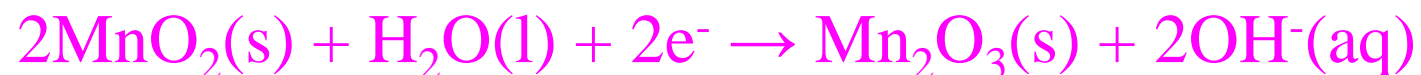
- ✚ At the anode **Zinc powder** around the central metal rod is oxidised:



- ✚ Once formed, **Zn²⁺** reacts immediately with **OH⁻** ions in the electrolyte to form **zinc hydroxide**. The overall reaction at the anode is therefore written as:



- ✚ At the **cathode** Manganese dioxide is reduced:



- ✚ They have about 5 times the life of a zinc-carbon dry cell
- ✚ There is no build up of electrolyte so no '**rest**' **time** is needed
- ✚ They are slightly more expensive but offer better value for money

Car Batteries

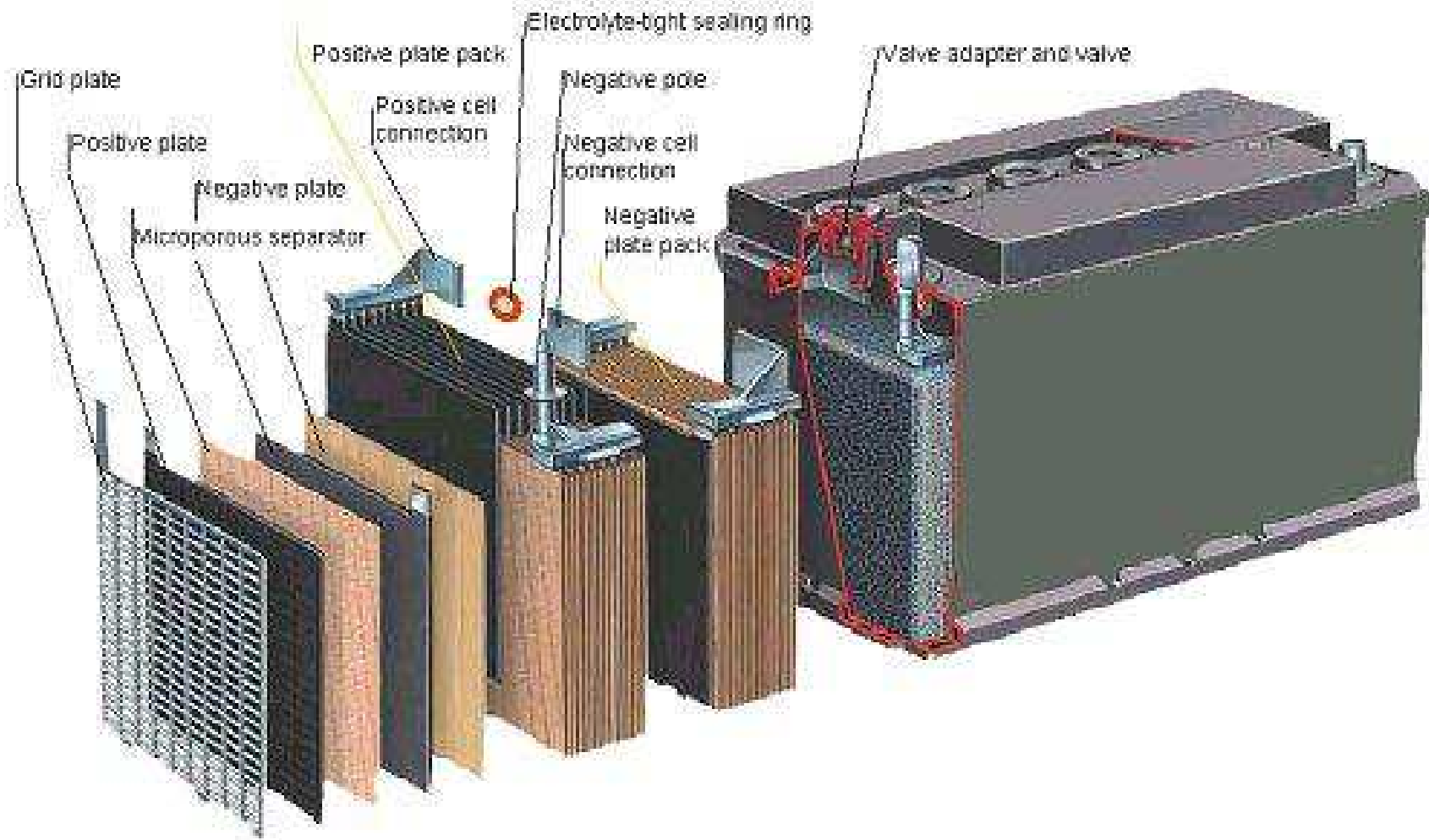
- These are used to start a car's engine and operate the car's electrical accessories when the engine is not running
- Lead-acid batteries are the most widely used type of secondary cell
- They are relatively cheap and reliable, provide high currents, and have a long lifetime
- An alternator (a dynamo) provides electrical energy when the car is running.

Secondary cells

- ◆ The chemical action of these batteries can be reversed
- ◆ Which means they can be discharged and recharged many times depending on the application, power and features
- ◆ Nicad and nickel metal hydride fall into this category i.e.,
- ◆ Lead acid (2.0V)
- ◆ Nickel - cadmium (1.2V)
- ◆ Nickel - metal hydride (1.2V)
- ◆ Lithium - ion (3.3V)



Battery cross section



Composition of a battery

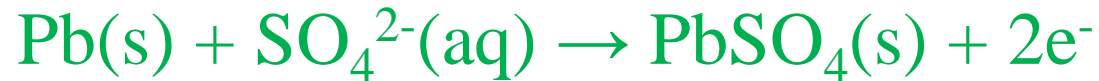
- The Lead Acid battery is made up of separator plates, lead plates, and lead oxide plates
- various other elements are used to change density, hardness, porosity, etc.) with a 35% sulphuric acid and 65% water solution (is called electrolyte which causes a chemical reaction that produce electrons)
- When a battery discharges the electrolyte dilutes and the sulphur deposits on the lead plates (Pb).
- When the battery is recharged the process reverses and the sulphur dissolves into the electrolyte.

Lead-acid batteries

- Comprised of **six separate cells** connected together in series giving a total potential difference of about **12 volts**
- In a typical car battery each cell contains **three positive** electrodes sandwiched between **four negative** electrodes
- Contact between the electrodes is prevented by the presence of a **porous separator**
- In this cell usually; **Pb(s)** - used as anode
 - **PbO₂(s)** – used as cathode
- A solution of **H₂SO₄ (aq)** (about 4M) acts as the electrolyte.

Lead-acid batteries

■ At the anodes (-)



- These ions combine with sulfate ions from the electrolyte to form a coating of lead(II) sulphate on the electrodes

■ At the cathodes (+)



- This reaction forms a coating of lead(II) sulfate on the electrodes

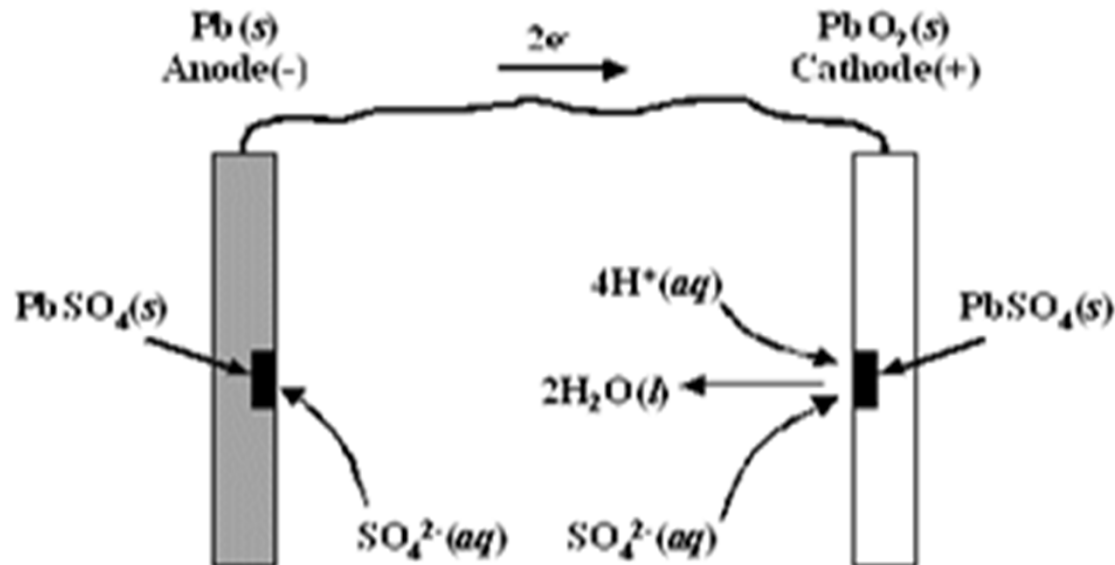
■ Sulfuric acid provides the protons and sulfate ions:



■ Overall redox reaction: $\text{PbO}_2(\text{s}) + \text{Pb(s)} + 4\text{H}^+(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$

Lead-acid batteries

- The product of both electrode reactions, $\text{PbSO}_4(\text{s})$ forms as a solid on the surface of the electrodes
- This enables the battery to be recharged i.e.,
- Thus, ions do not diffuse from one half-cell to the other. Therefore, the two electrodes can be placed in the same container of acid.



Cont'd

- The EMF **per "cell"** under standard conditions is:

$$\begin{aligned} E^0_{\text{cell}} &= E^0_{\text{red}}(\text{cathode}) - E^0_{\text{red}}(\text{anode}) \\ &= (+1.685 \text{ V}) - (-0.356 \text{ V}) = \underline{\underline{2.041 \text{ V}}} \end{aligned}$$

- But **6 cells** can be combined end-to-end (i.e. in *series*) to produce about **12 V**
- This is a reversible reaction. If electrical current is applied in the opposite direction (this is the job of a generator or alternator in your car) the electrodes are regenerated, i.e.,



Nickel Cadmium (Nicad, or Cadnica cell)

- **Anode:** $\text{Cd(s)} + 2\text{OH}^-(aq) \rightarrow \text{Cd(OH)}_2(s) + 2e^-$
- **Cathode:** $\text{NiO}_2(s) + 2\text{H}_2\text{O(l)} + 2e^- \rightarrow \text{Ni(OH)}_2(s) + 2\text{OH}^-(aq)$
- Net rxn: $\text{Cd(s)} + \text{NiO}_2(s) + 2\text{H}_2\text{O(l)} \rightarrow \text{Cd(OH)}_2(s) + \text{Ni(OH)}_2(s)$
- This type of cell uses **KOH (aq)** as **electrolyte**
- The solid products of the respective electrode reactions adhere to the electrodes and do not diffuse throughout the cell
- Thus, the redox reaction is reversible (i.e. like the lead acid cell, the nickel cadmium cell is reversible)
- No gases are produced, so the cell can be sealed (conserved)

Fuel Cells

✚ How does fuel cell differ from a battery?

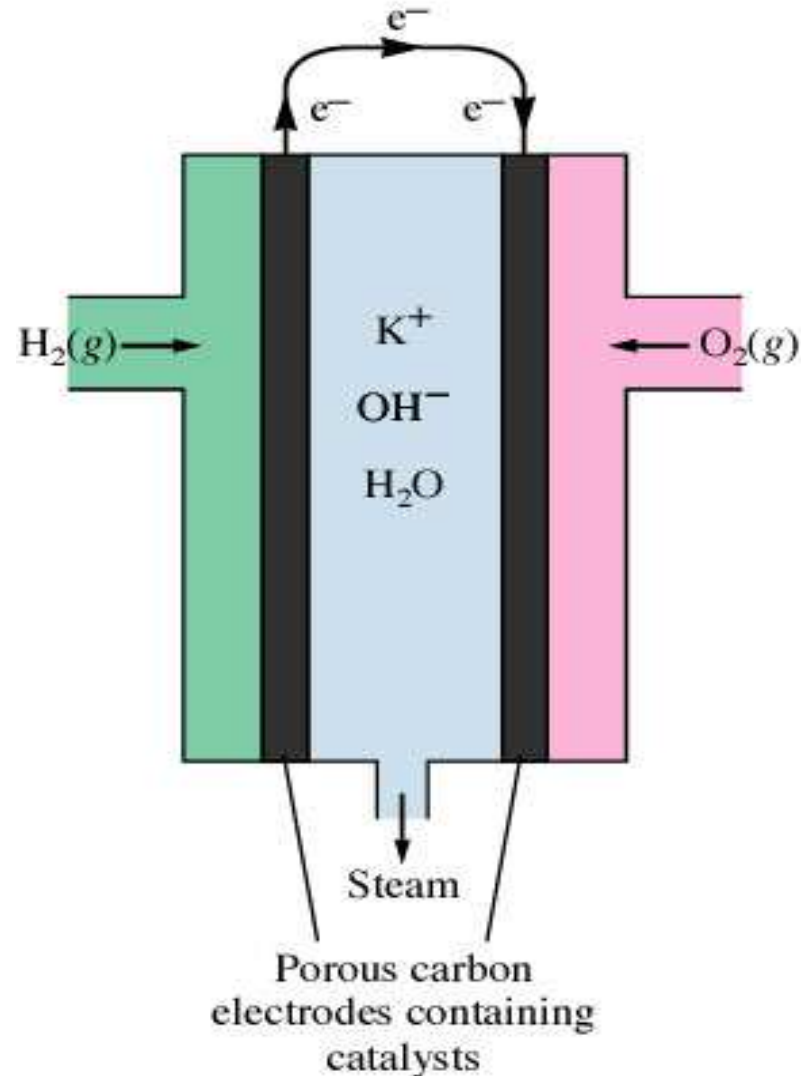
- In fuel cell raw materials are continuously fed into the cell when it is operating
- while in galvanic cells the sources are electrodes and electrolytes which are installed during the fabrication of the cell.
- When the reaction reaches equilibrium, they must either be recharged or discarded.
- Cells can be constructed in which the reactants are supplied continuously, allowing constant production of electrical energy.
- These devices are called fuel cells

Fuel cells

- They transform **chemical energy** directly into **electrical energy**
- This enables efficient use to be made of the energy released by **spontaneous** redox reactions
- Energy losses such as those that occur in **a coal-fired** power station are avoided.
- They are up to 100-80% efficient compared with **30-40%** for thermal power stations. the rest is "**wasted**" as heat
- In addition modern designs for fuel cells employ the waste heat that they produce to make **steam**.
- **This steam** can be used for heating or to operate a turbine.

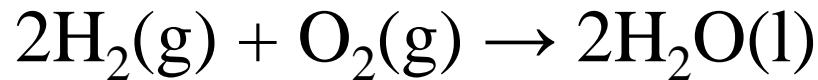
Fuel cells

- voltaic cells where the reactants are continuously supplied
- The fuel cell used in the Apollo program used pure **oxygen** and **hydrogen** gas as reactants.
- **Potassium hydroxide** solution was used as the electrolyte and the cell operated at about 250°C .
- This is commonly referred to as an alkaline fuel cell.



Alkaline fuel cells

- At the anode (-): $2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \rightarrow 4\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$
- At the cathode (+): $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$
- The overall equation is:



- Each cell produces about **one volt**.
- Higher voltages are obtained by connecting a number of fuel cells in series to form a battery
- The only by-products are **water and heat**

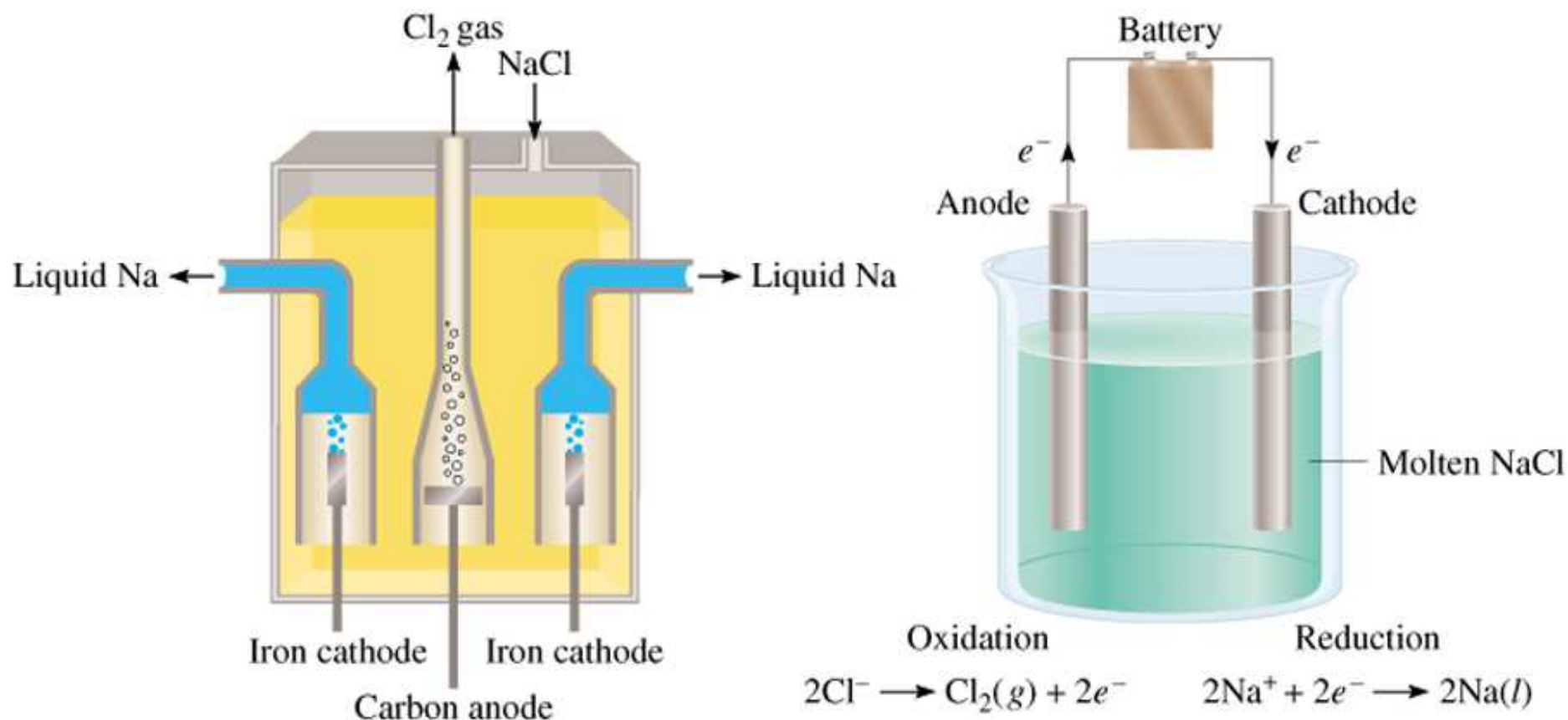
4. Photovoltaic cells, PVs

- PVs are cells which convert **sun light** directly into **electricity**
- The working principle of PV cells involves absorption of light by photoactive material

Electrolytic Cells

- An **electrolytic cell** is an electrochemical cell in which an electric current drives an otherwise nonspontaneous reaction.
 - ◆ The process of producing a chemical change in an electrolytic cell is called **electrolysis**.
 - ◆ Many important substances, such as aluminum metal and chlorine gas are produced commercially by electrolysis.

Electrolysis is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.



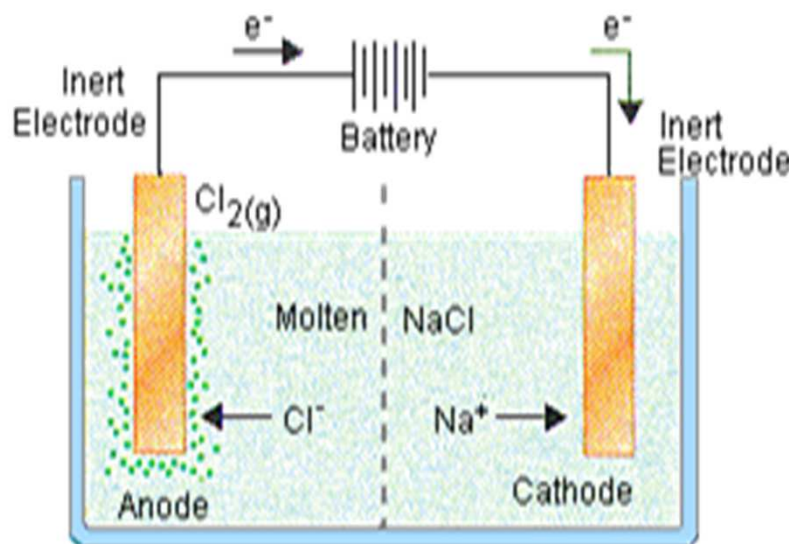
Electrolysis of Molten NaCl

Cathode (-): $2\text{Na}^+(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Na}(\text{l})$

Anode (+): $2\text{Cl}^-(\text{aq}) \longrightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

- $2\text{NaCl}(\text{l}) \xrightarrow{\text{electrolysis}} 2\text{Na}(\text{l}) + \text{Cl}_2(\text{g}) \quad E^\circ_{\text{cell}} = -4.07\text{ V}$

➤ The **dotted vertical** line in the center of the below figure represents a diaphragm that keeps the Cl_2 gas produced at the anode from coming into contact with the sodium metal generated at the cathode



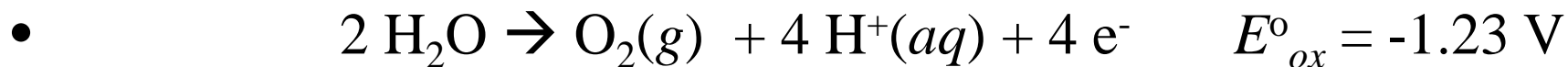
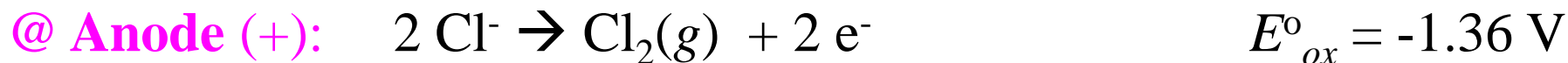
The Electrolysis of Aqueous NaCl



➤ Because it is much easier to reduce water than Na^+ ions, the only product formed at the cathode is hydrogen gas.

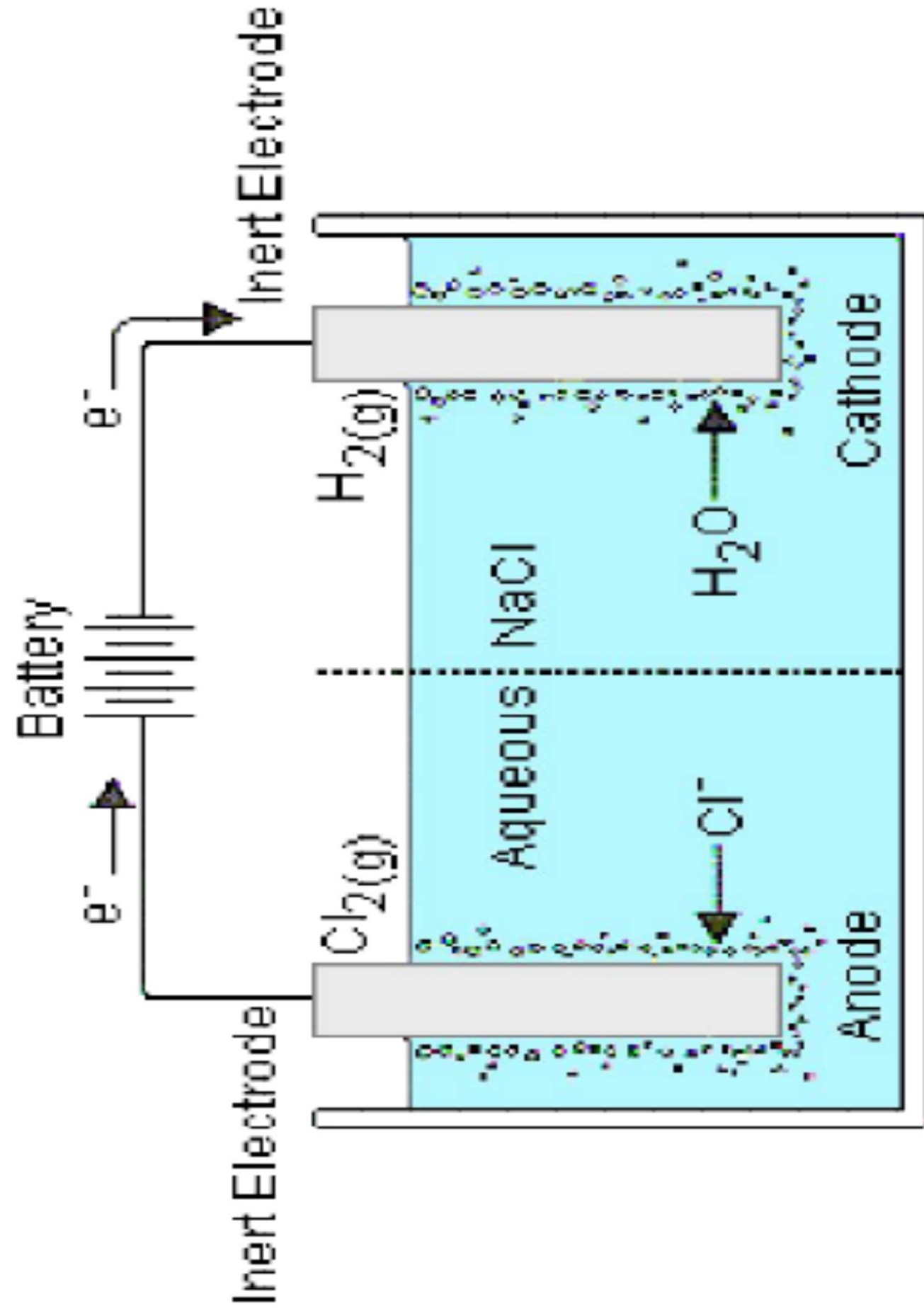


✓ There are also two substances that can be oxidized at the anode: Cl^- ions and water molecules.

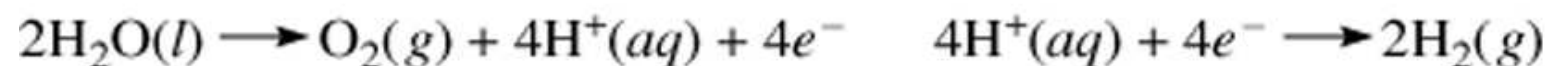
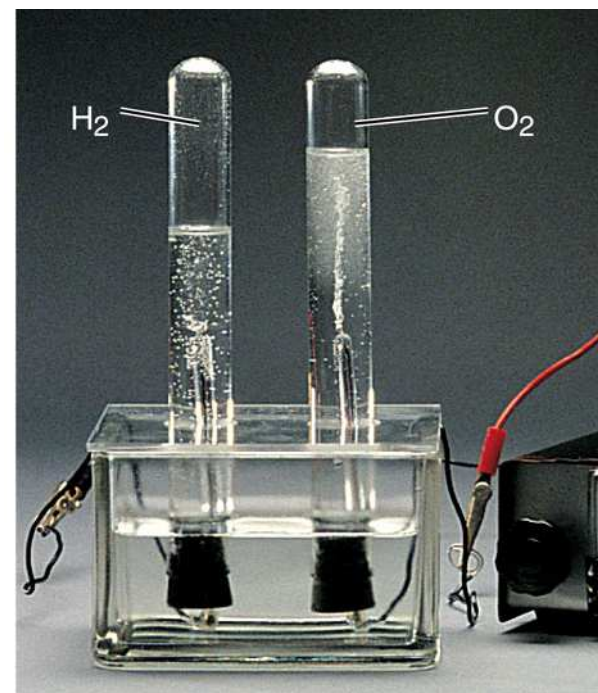
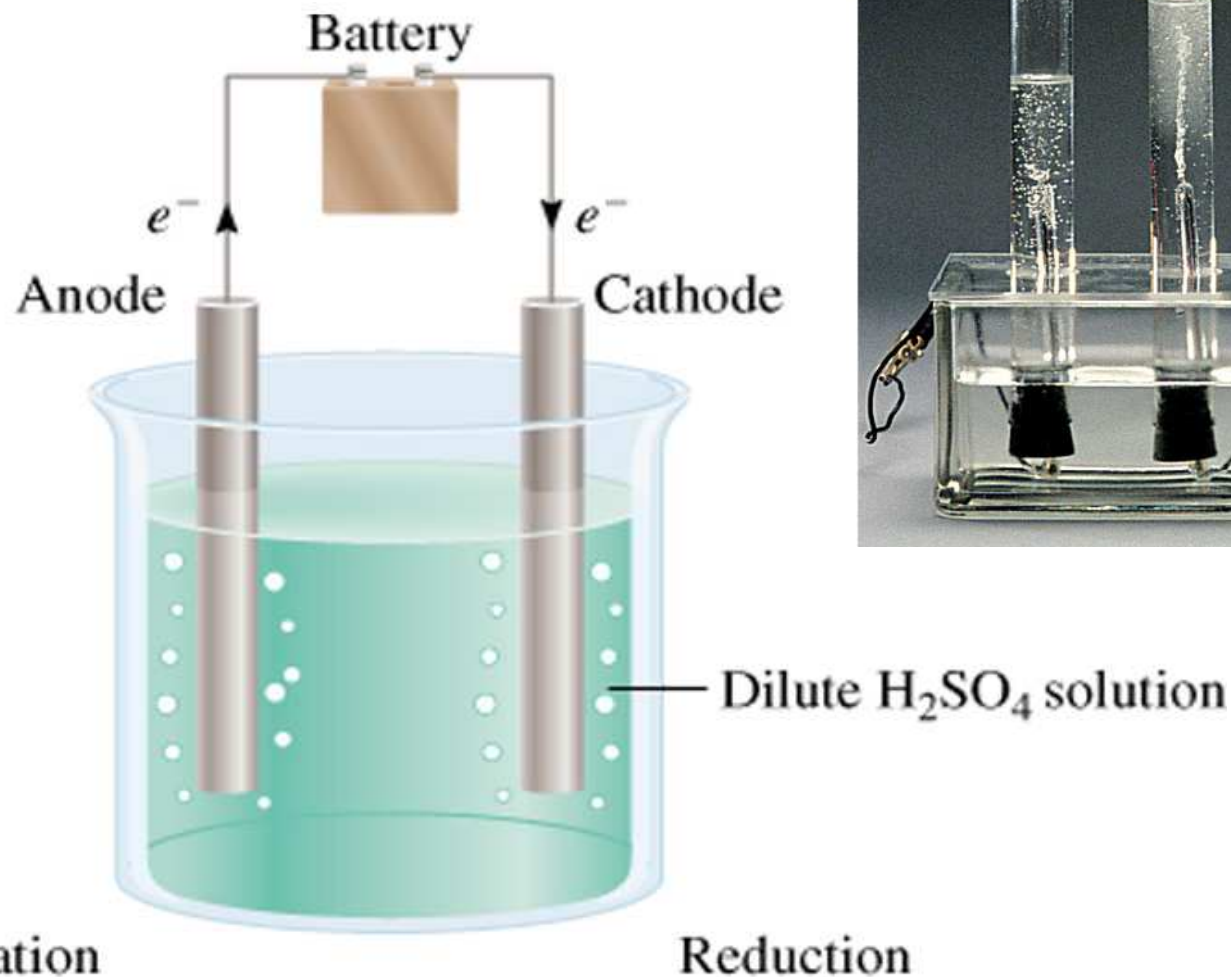


➤ The standard-state potentials for these half-reactions are so close to each other that we might expect to see a mixture of Cl_2 and O_2 gas collect at the anode. In practice, the only product of this reaction is Cl_2 .





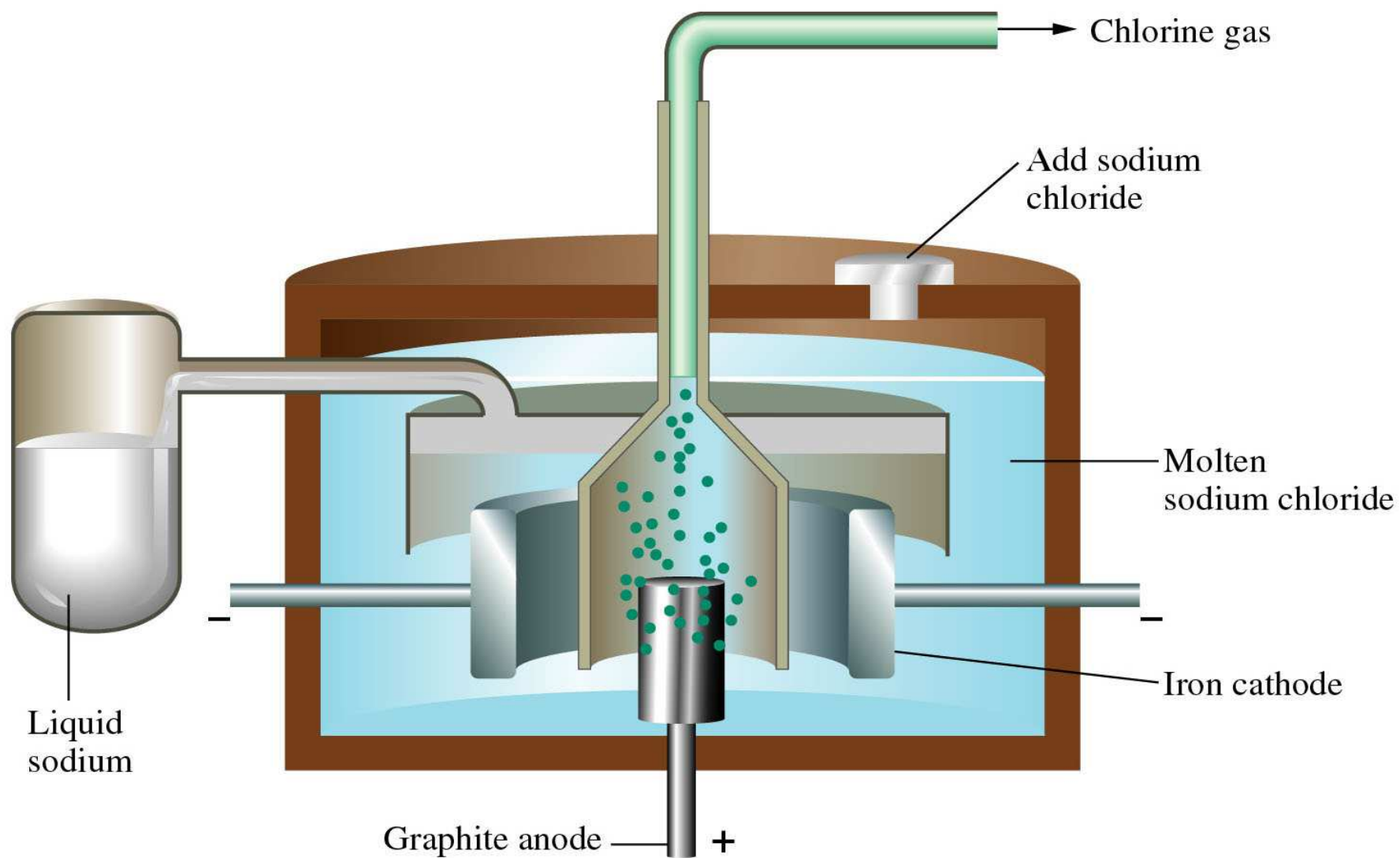
Electrolysis of Water

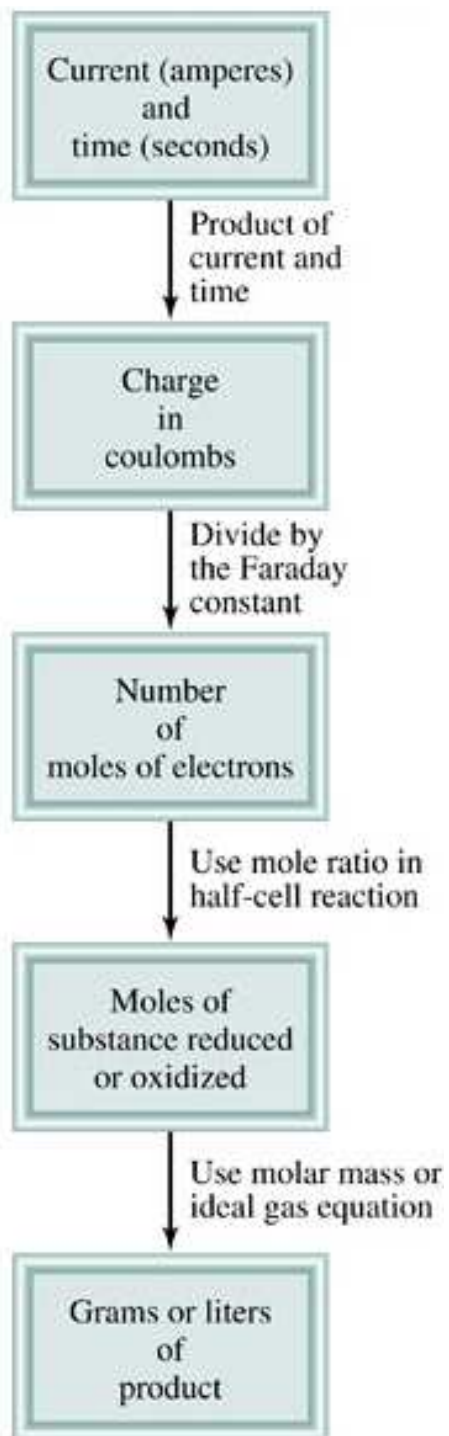


Electrolysis of Molten Salts

- A **Downs cell** is a commercial electrochemical cell used to obtain sodium metal by electrolysis of molten NaCl.
 - ◆ A number of other reactive metals are obtained by the electrolysis of a molten salt.
 - ◆ Lithium, magnesium, and calcium metals are all obtained by the electrolysis of the chlorides.

A Downs cell for the preparation of sodium metal.





Electrolysis and Mass Changes

$$\text{charge (C)} = \text{current (A)} \times \text{time (s)}$$

$$1 \text{ mole } e^- = 96,500 \text{ C}$$

Electrolysis

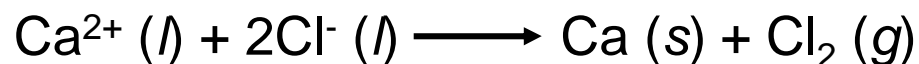
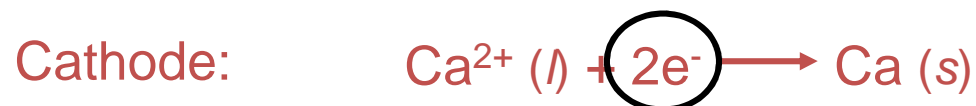
- **Faraday' s Equation**

- q = charge (coulombs, C) $q = It = n\mathcal{F}$
- I = current (Amperes, A, or C/s)
- t = time (s)
- n = moles of electrons transferred in process
- \mathcal{F} = Faraday' s constant (96,485 C/mol)

- Units tell us how these quantities are related
- Calculate moles of substance electrolyzed as

$$\text{moles} = \frac{I t}{n \mathcal{F}}$$

1. How much Ca will be produced in an electrolytic cell of molten CaCl_2 if a current of 0.452 A is passed through the cell for 1.5 hours?



2 mole e^- = 1 mole Ca

$$\text{mol Ca} = 0.452 \frac{\text{C}}{\text{s}} \times 1.5 \text{ hr} \times 3600$$

$$= 0.0126 \text{ mol Ca}$$

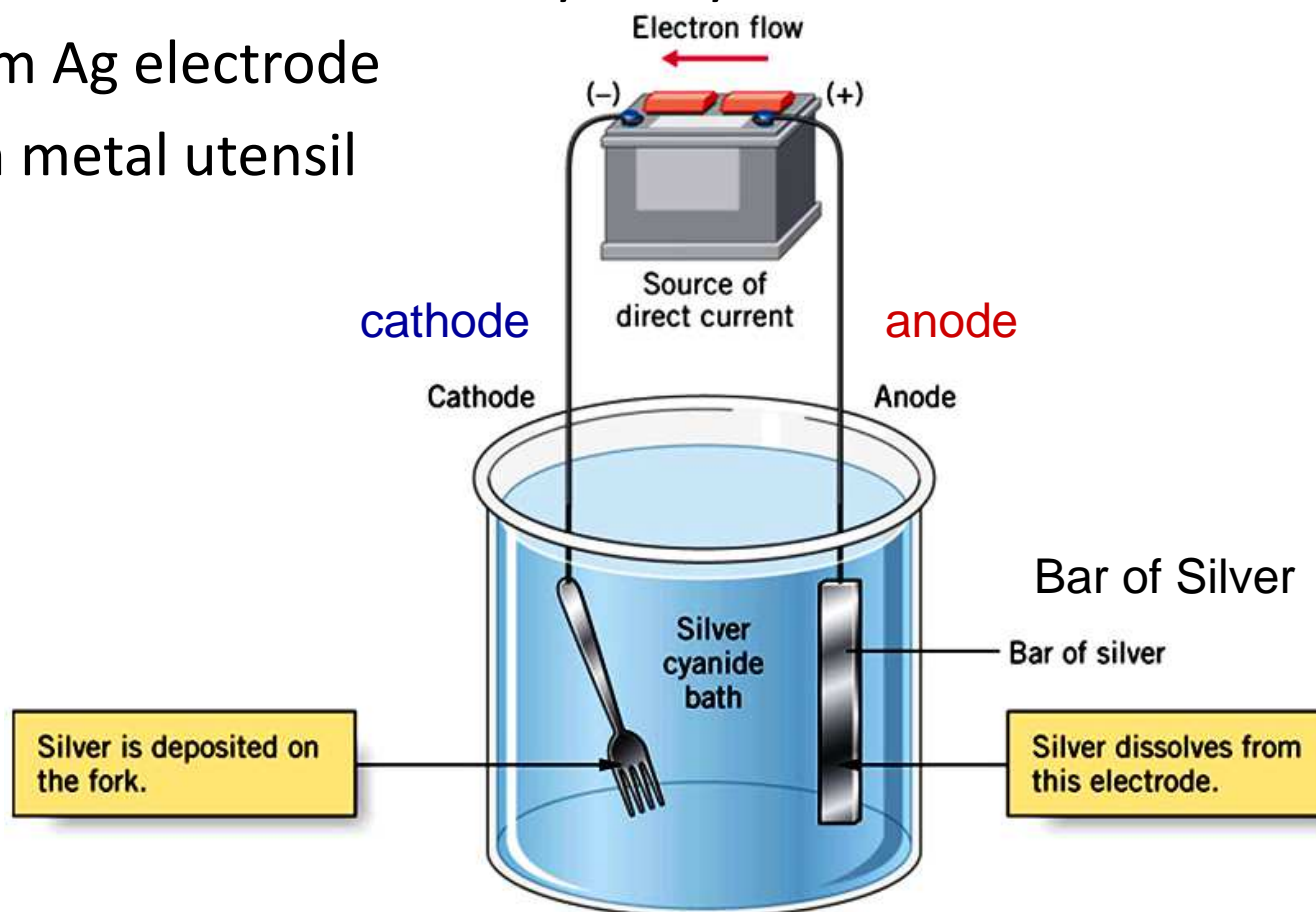
$$= 0.50 \text{ g Ca}$$

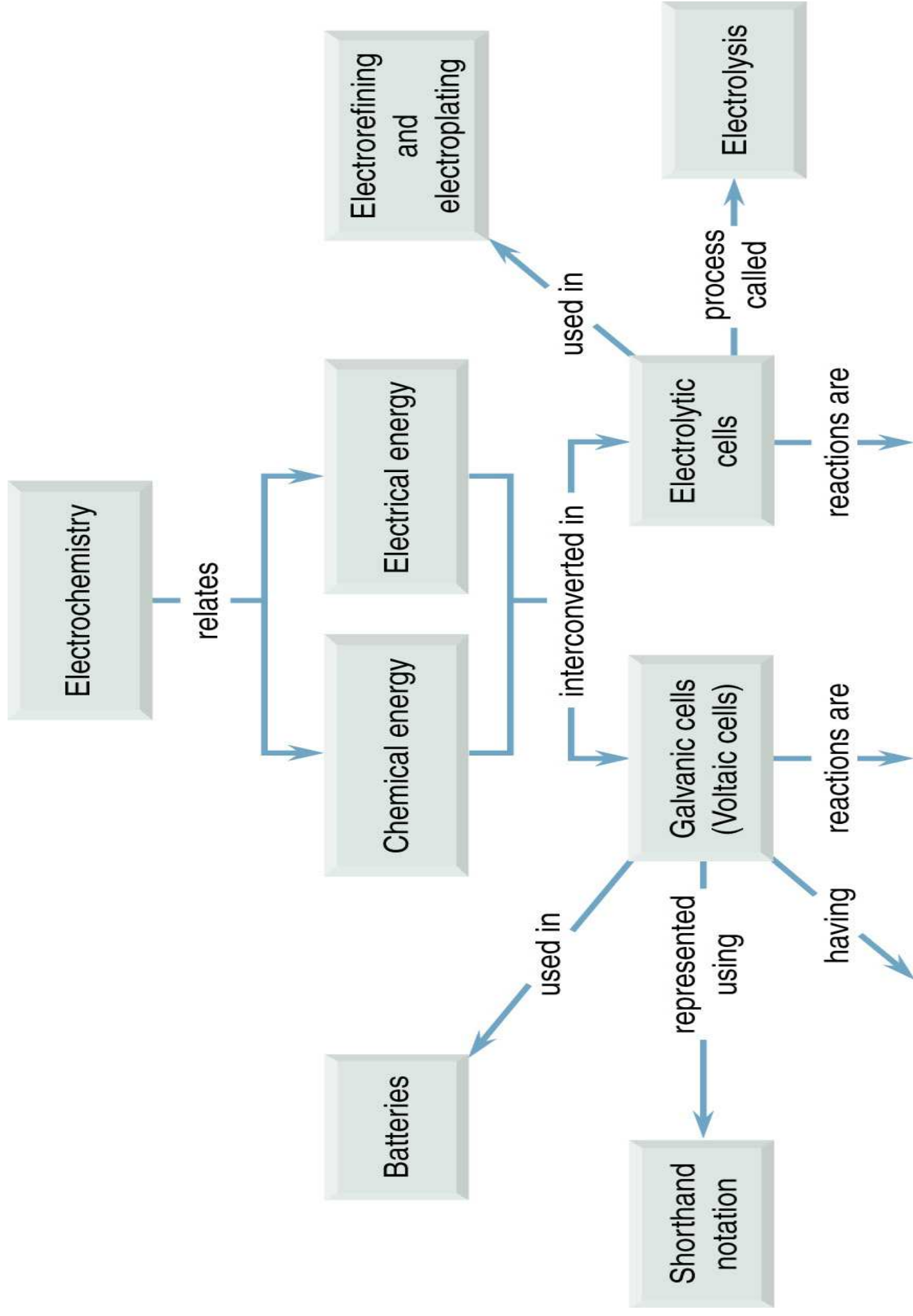
$$\frac{\text{s}}{\text{hr}} \times \frac{1 \text{ mol } e^-}{96,500 \text{ C}} \times \frac{1 \text{ mol Ca}}{2 \text{ mol } e^-}$$

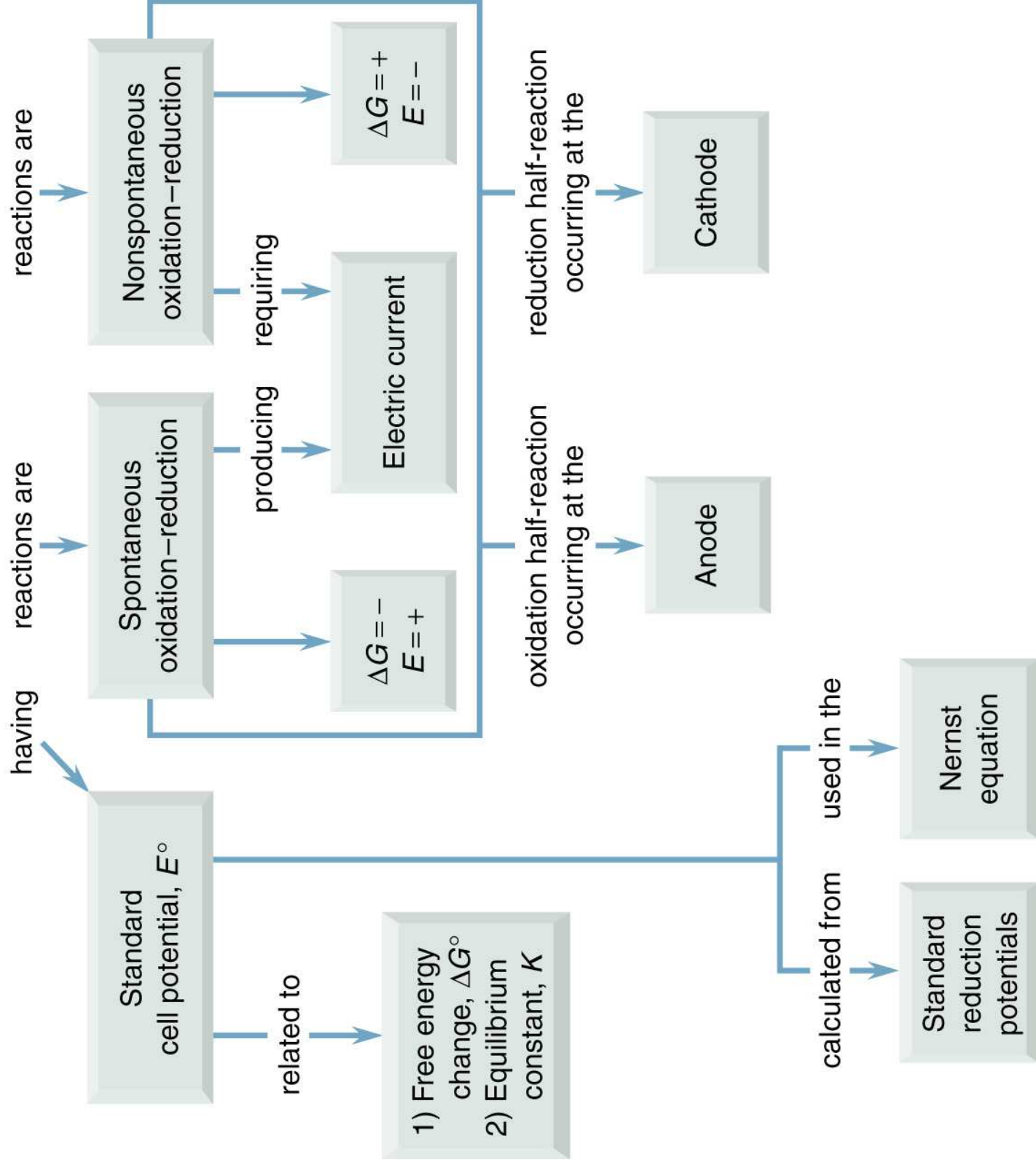
Application of Electrolysis

Electroplating

- Put fork and bar of silver in AgCN bath
- Set potential so that cell runs electrolytically
- Ag dissolves from Ag electrode
- Ag deposited on metal utensil







THE WORLD EXPECTS YOU MORE

THANK YOU !!!!!!!!!!!!!