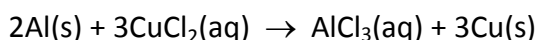


ELECTROCHEMISTRY

A. INTRODUCTION

1. Electrochemistry is the branch of chemistry which is concerned with the conversion of **chemical energy to electrical energy**, and vice versa.

- Electrochemical reactions involve the **transfer of electrons from one substance to another** (analogous to proton transfer in acids and bases).
- Consider the reaction



the net ionic equation is



- **Electrons are transferred from Al to Cu^{2+} .**
- We can re-write this equation as two **separate half-reactions**:

a) **OXIDATION HALF-REACTION**



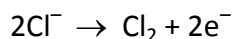
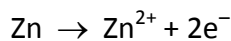
b) **REDUCTION HALF-REACTION**



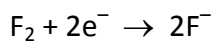
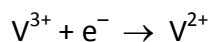
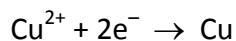
OXIDATION = loss of electrons

REDUCTION = gain of electrons

2. When a substance becomes **oxidized it becomes more positively charged** because it is losing electrons (negatively charged).



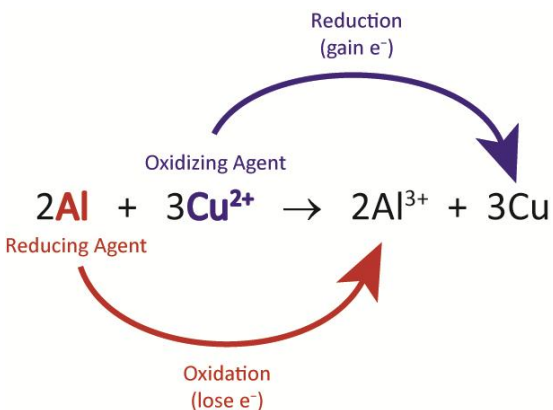
When a substance becomes **reduced it becomes more negatively charged** because it is gaining electrons.



3. Every reduction reaction must be accompanied by an oxidation reaction since the electrons must be transferred somewhere.

- These types of reactions are called **REDOX** reactions.

In the reaction



- Al is the **REDUCING AGENT** because it causes Cu^{2+} to become reduced,
- Cu^{2+} is the **OXIDIZING AGENT** because it causes Al to become oxidized.

The **OXIDIZING AGENT** is the reactant **reduced (gains e⁻)** during a reaction.

The **REDUCING AGENT** is the reactant **oxidized (loses e⁻)** during a reaction.

B. OXIDATION NUMBERS

1. Oxidation numbers can be used to determine whether an atom has been oxidized or reduced.

OXIDATION NUMBER = real or apparent charge an atom or ion has when all of the bonds are assumed to be ionic.

Determining oxidation number:

- a) Atoms in elemental form = **0**
- b) Simple ions = **the charge on ion**
 - i) Li^+ , Na^+ , K^+ , and all other **group 1** ions have oxidation number of **1+**.
 - ii) Ca^{2+} , Ba^{2+} , Mg^{2+} , and all other **group 2** ions have oxidation numbers of **2+**.
 - iii) F^- , Cl^- , Br^- , I^- (**halogens**) are usually **1-** however there are many exceptions especially in covalent compounds.
- c) Hydrogen = **1+** (except in metallic hydrides such as NaH or BaH_2 where it is 1-)
- d) Oxygen = **2-** (In peroxides, H_2O_2 , it is 1-)
- e) Oxidation numbers of other atoms are assigned so that the **sum of the oxidation numbers** (positive and negative) **equals the net charge on the molecule or ion.**

EXAMPLE 5.1 DETERMINING OXIDATION NUMBERS

Determine the oxidation numbers of each atom for the following:



$$\text{Cl} = 0$$

$$\text{Cl} = 1- \quad \text{C} = 4+$$

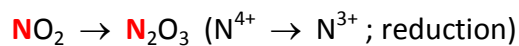
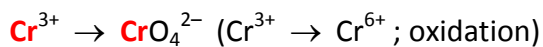
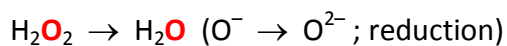
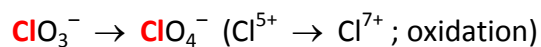
$$\text{O} = 2- \quad \text{N} = 4+$$

$$\text{O} = 2- \quad \text{P} = 5+$$

$$\text{K} = 1+ \quad \text{Cr} = 6+ \quad \text{O} = 2-$$

$$\text{C} = \frac{8}{3} \quad \text{H} = 1+$$

2. When an atom's oxidation number **increases it has become oxidized** and when an atom's oxidation number **decreases, it has become reduced**.



OXIDATION = loss of electrons = increase in oxidation number

REDUCTION = gain of electrons = decrease in oxidation number

EXAMPLE 5.2 REDOX REACTIONS

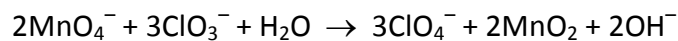
Which of the following reactions are redox reactions?

- A. $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$
- B. $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$
- C. $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$
- D. $\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$

(A) is the only redox reaction because it is the only reaction where atoms have a change in oxidation number.

EXAMPLE 5.3 OXIDATION NUMBERS

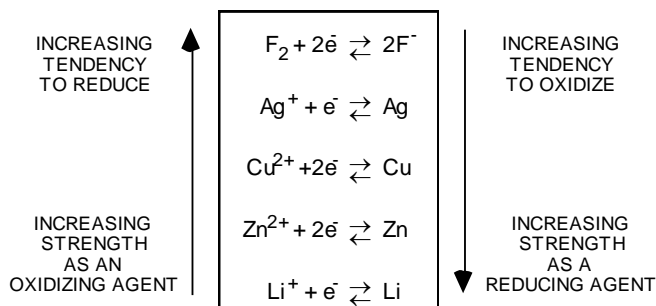
Identify the reducing agent in the following redox reaction:



ClO_3^- is the reducing agent

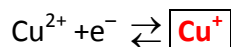
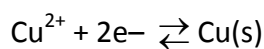
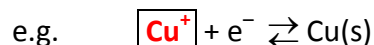
C. PREDICTING SPONTANEOUS REACTIONS

1. Excerpt from the [Table of Reduction Potentials](#):

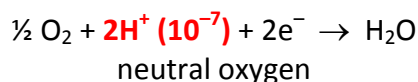
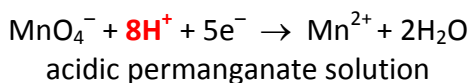


The following observation can be made from the Table of Reduction Potentials:

- i) In general, **metals** (exceptions Cu, Ag, Hg, and Au) are found in the **bottom right half** of the table (**reducing agents**).
- ii) In general, **halogens and oxyanions** (oxygen containing anions) are found in the **upper left half** of the table (**oxidizing agents**).
- iii) Some metals such as **Fe, Sn, Cr, Hg, and Cu** have more than one common oxidation number and thus have **more than one half-reaction**.
- iv) Some ions (**Cu⁺, Sn²⁺, Fe²⁺**) appear on both sides of the table and can **behave as oxidizing agents or reducing agents**.



- v) **H₂O₂** can be an oxidizing agent or a reducing agent.
- vi) Half reactions including H⁺ must be carried out in acidic solutions.



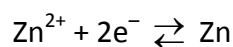
OXIDIZING AGENTS gain electrons, tend to be **CATIONS (+) OR NONMETALS**

REDUCING AGENTS lose electrons, tend to be **ANIONS (-) OR METALS**

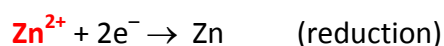
2. **Stronger oxidizing agents** are located on the **upper left** have a greater tendency to gain electrons (reduce)

Stronger reducing agents are located on the **lower right** have a greater tendency to lose electrons (oxidize).

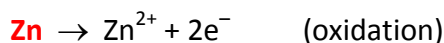
Consider the half-reaction for Zn and Zn^{2+}



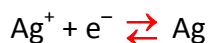
Zn^{2+} is an oxidizing agent and will be gain electrons:



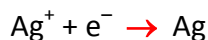
Zn is a reducing agent and will be lose electrons:



Note: When referring to an isolated half-reaction, use equilibrium arrows to show that the reaction can go forward or backward.



If the half-reaction is made to undergo either reduction or oxidation as a result of being part of a redox reaction, the use a one-way arrow.



3. Spontaneous reactions will occur when there is:

an oxidizing agent (reduction) and a reducing agent (oxidation)
and
the oxidizing agent must be above the reducing agent in the table.

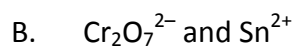
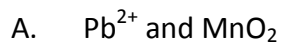
EXAMPLE 5.4 SPONTANEOUS REDOX REACTIONS

Which of the following metals Al, Pb, Cu, Fe and Ag can be oxidized by Cr^{3+} ?

Only Al and Fe can be oxidized by Cr^{3+} .

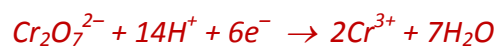
EXAMPLE 5.5 PREDICTING PRODUCTS OF REDOX REACTIONS

Predict whether a spontaneous reaction is expected and the products that would be formed.



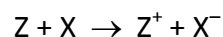
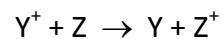
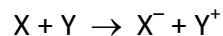
Reaction A is non-spontaneous and so will not occur.

Reaction B is spontaneous,



EXAMPLE 5.6 STRENGTHS OF OXIDIZING AGENTS

Consider the following spontaneous redox reactions:



What is the relative strengths of oxidizing agents (strongest to weakest)?

Oxidizing agents are reduced (gain e^-)



Order of oxidizing agents is $X > Y^+ > Z^+$

(Note if asked for reducing agents, order is $Z > Y > X^-$)

EXAMPLE 5.7 STRENGTHS OF REDUCING AGENTS

A solution containing Pd^{2+} reacts spontaneously with Ga to produce Pd and Ga^{3+} . However, a solution containing Pd^{2+} does not react with Pt. What are the reducing agent in order of increasing strengths?

Reducing agents are oxidized (lose e^-)



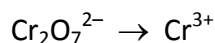
Order of reducing agents is $Pt < Pd < Ga$

D. BALANCING HALF REACTIONS

1. A half-reaction must be balanced for mass and charge. When balancing half-reactions it is very important to remember the charges of the ions. Steps to balancing a half-reaction are as follows:
- Balance all major **atoms other than oxygen and hydrogen**.
 - Balance **OXYGENS** by adding water (H₂O) molecules.
 - Assume that solutions are acidic and balance **HYDROGENS** by adding H⁺.
 - Balance the **CHARGE** by adding electrons (e⁻).

EXAMPLE 5.8 BALANCING HALF-REACTIONS IN ACIDIC SOLUTION

Balance the following half-reaction:



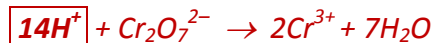
*Step 1: Balance **ATOMS**.*



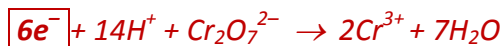
*Step 2: Balance **OXYGEN**.*



*Step 3: Balance **HYDROGEN**.*



*Step 4: Balance **CHARGE**.*

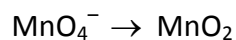


Note: *Electrons are negatively charged, add them to the side that has the greater charge.*

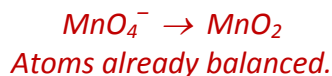
2. In **BASIC** solutions balance the equation as if it were acidic, then convert the equation to basic by **adding equal numbers of hydroxides ions (OH^-) to both sides of the equation and cancelling out the H^+ as water.**

EXAMPLE 5.9 BALANCING HALF-REACTIONS IN BASIC SOLUTION

Balance the following half-reaction:



*Step 1: Balance **ATOMS**.*



*Step 2: Balance **OXYGEN**.*



*Step 3: Balance **HYDROGEN**.*



*Step 4: Balance **CHARGE**.*



Step 5: Add OH^- and cancel out H_2O .

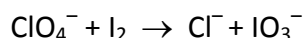


E. BALANCING REDOX EQUATIONS USING HALF-REACTIONS

- An overall redox equation can be obtained by breaking an equation into **separate reduction and oxidation half-reactions**, balancing each half and adding the two half-reactions back together once the number of electrons lost in oxidation are balanced by the electrons gained by reduction.

EXAMPLE 5.10 BALANCING A REDOX REACTION BY THE HALF-REACTION METHOD

Balance the following redox reaction:



Step 1: Break equation into two half-reactions.



Step 2: Balance each half-reaction.



Step 3: Lowest common multiple between electrons.

In this case LCM is 40, multiply reduction by 5 and oxidation by 4.

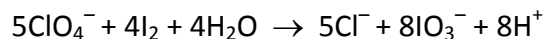


Step 4: Add two half-reactions, cancelling out electrons and common particles.

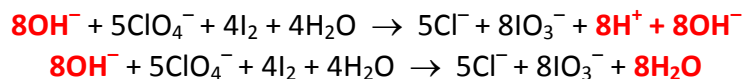


Balanced redox equations **DO NOT SHOW ELECTRONS** and the **NUMBER OF ATOMS AND THE TOTAL CHARGE** are balanced on both sides of the equation.

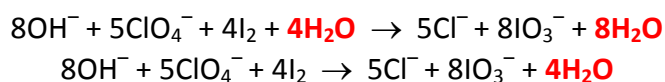
2. In basic solutions the **final equation** can be converted by adding equal numbers of hydroxide ions to both sides of the equation and cancelling out water molecules.



For basic solution, add 8OH^- to both sides of equation:



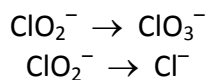
Cancel out water:



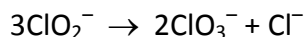
3. In some redox reactions, it is possible for the same chemical to undergo oxidation and reduction. Such a reaction is called a **DISPROPORTIONATION**.



The two half-reactions are:



Balanced redox equation is:

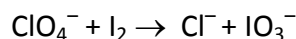


F. BALANCING REDOX EQUATIONS USING OXIDATION NUMBERS

1. Redox reactions can also be balanced using oxidation numbers:
 - i. Calculate the **changes in oxidation numbers** for the elements that undergo oxidation and reduction.
 - ii. **Balance increase and decrease** in oxidation number change.
 - iii. Balance **oxygen with H₂O** and **hydrogen with H⁺**.

EXAMPLE 5.11 BALANCING A REDOX REACTION BY OXIDATION NUMBERS

Balance the following redox reaction:



Step 1: Assign oxidation numbers to atoms and temporarily balance atoms that have a change in oxidation number.



Step 2: Balance change in oxidation number.

In this case LCM is 40, multiply decrease by 5 and increase by 4.



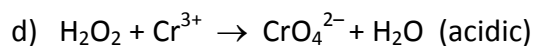
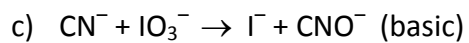
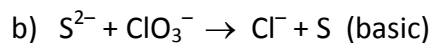
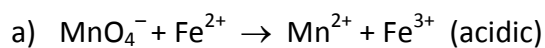
*Step 3: Balance **OXYGENS** by adding **H₂O** and **HYDROGENS** by adding **H⁺**. **DO NOT ADD ELECTRONS.***



Remember, **DO NOT ADD ELECTRONS** in the oxidation number method since electrons are balanced by balancing change in oxidation number.

SAMPLE PROBLEM 5F.1 BALANCING A REDOX REACTION BY OXIDATION NUMBERS

Balance the following redox reactions by the oxidation number method:



G. REDOX TITRATIONS

1. Acid–base titrations are useful for determining the concentration of an unknown sample of acid or base. In a similar manner, redox reactions can be used to determine the concentration of an unknown oxidizing or reducing agent by a **REDOX TITRATION**.

2. OXIDIZING AGENTS

- One of the most common oxidizing agents used in redox titrations is **acidic KMnO_4** .



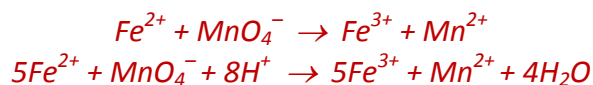
- The K^+ in KMnO_4 is left out because it is a **spectator ion**.
- In permanganate titrations, **the MnO_4^- , acts as its own indicator**.
- The permanganate ion, **MnO_4^- , is purple** while **Mn^{2+} is colourless**. When **MnO_4^- (purple)** is added to a reducing agent, it is converted to Mn^{2+} (colourless). Once all the reducing agent has been oxidized by MnO_4^- , any additional MnO_4^- will remain purple.

The endpoint of a redox titration involving MnO_4^- as an oxidizing agent is indicated by a colour change from colourless to purple.

EXAMPLE 5.12 REDOX TITRATION INVOLVING THE PERMANGANATE ION

A 100.0 mL sample containing FeCl_2 is titrated with 0.100 M KMnO_4 solution. If 27.45 mL of KMnO_4 solution were required to reach the end-point, what was the $[\text{FeCl}_2]$?

First we need the balanced redox equation.



The remainder of the calculation is similar to acid-base titration calculations.

Calculate **MOLES** of MnO_4^-

$$0.100 \text{ M MnO}_4^- \times \frac{27.45 \text{ mL}}{1000 \text{ mL}} = 0.002745 \text{ mol MnO}_4^-$$

Use **MOLE RATIO** from balance equation.

$$0.002745 \text{ mol MnO}_4^- \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4^-} = 0.0137 \text{ mol Fe}^{2+}$$

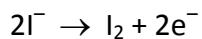
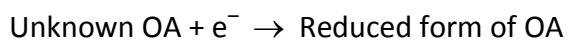
Determine **CONCENTRATION**.

$$\frac{0.0137 \text{ mol Fe}^{2+}}{0.100 \text{ L}} = \mathbf{0.137 \text{ M Fe}^{2+}}$$

and since Fe^{2+} and FeCl_2 are in a 1:1 ratio, $[\text{FeCl}_2] = 0.137 \text{ M}$.

3. REDUCING AGENTS

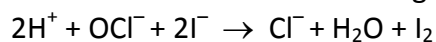
- Commonly used reducing agent is **NaI or KI**. A large number of substances can oxidize I^- to I_2 according to the half-reaction:



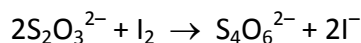
- Titrations involving I^- are indirect and involve two consecutive steps:
 - a) I^- is oxidized to I_2 by the unknown oxidizing agent, and
 - b) The I_2 produced in the first step is titrated with a reducing agent of known concentration, such as thiosulphate ion, $\text{S}_2\text{O}_3^{2-}$.
- The concentration of the I^- can be determined from the $[\text{I}_2]$ and this is used to determine the concentration of the unknown oxidizing agent.
- **Starch is used as an indicator for the I_2 titration.** Starch- I_2 produces a dark blue solution (like Iodine Clock reaction). When I_2 is titrated, the dark blue complex disappears. The end point of the titration is indicated by the complete disappearance of the blue colour.

EXAMPLE 5.13 REDOX TITRATION INVOLVING THE IODIDE ION

A 25.00 mL sample of bleach is reacted with excess KI according to the equation:

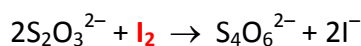
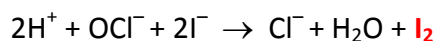


The I_2 produced requires exactly 46.84 mL of 0.7500 M $\text{Na}_2\text{S}_2\text{O}_3$ to bring the titration to the endpoint according to the equation:



using starch solution as an indicator. What is the $[\text{OCl}^-]$ in the bleach?

Note: The **TWO** reactions are linked together. The I_2 produced in the first reaction is used up in the second



Use titration data to calculate the moles of $\text{S}_2\text{O}_3^{2-}$

$$\text{moles } \text{S}_2\text{O}_3^{2-} = 0.7500 \text{ M} \times \frac{46.84 \text{ mL}}{1000 \text{ mL/L}} = 0.03513 \text{ mol } \text{S}_2\text{O}_3^{2-}$$

Next, calculate the moles of I_2

$$\text{moles } \text{I}_2 = 0.03513 \text{ mol } \text{S}_2\text{O}_3^{2-} \times \frac{\text{I}_2}{2 \text{ S}_2\text{O}_3^{2-}} = 0.01757 \text{ mol } \text{I}_2$$

Now moles of OCl^- can be calculated

$$\text{moles } \text{OCl}^- = 0.01757 \text{ mol } \text{I}_2 \times \frac{\text{OCl}^-}{\text{I}_2} = 0.01757 \text{ mol } \text{OCl}^-$$

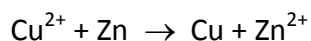
Finally, the $[\text{OCl}^-]$ can be calculated

$$[\text{OCl}^-] = \frac{0.01757 \text{ mol}}{0.02500 \text{ L}} = \mathbf{0.7026 \text{ M}}$$

H. ELECTROCHEMICAL CELLS

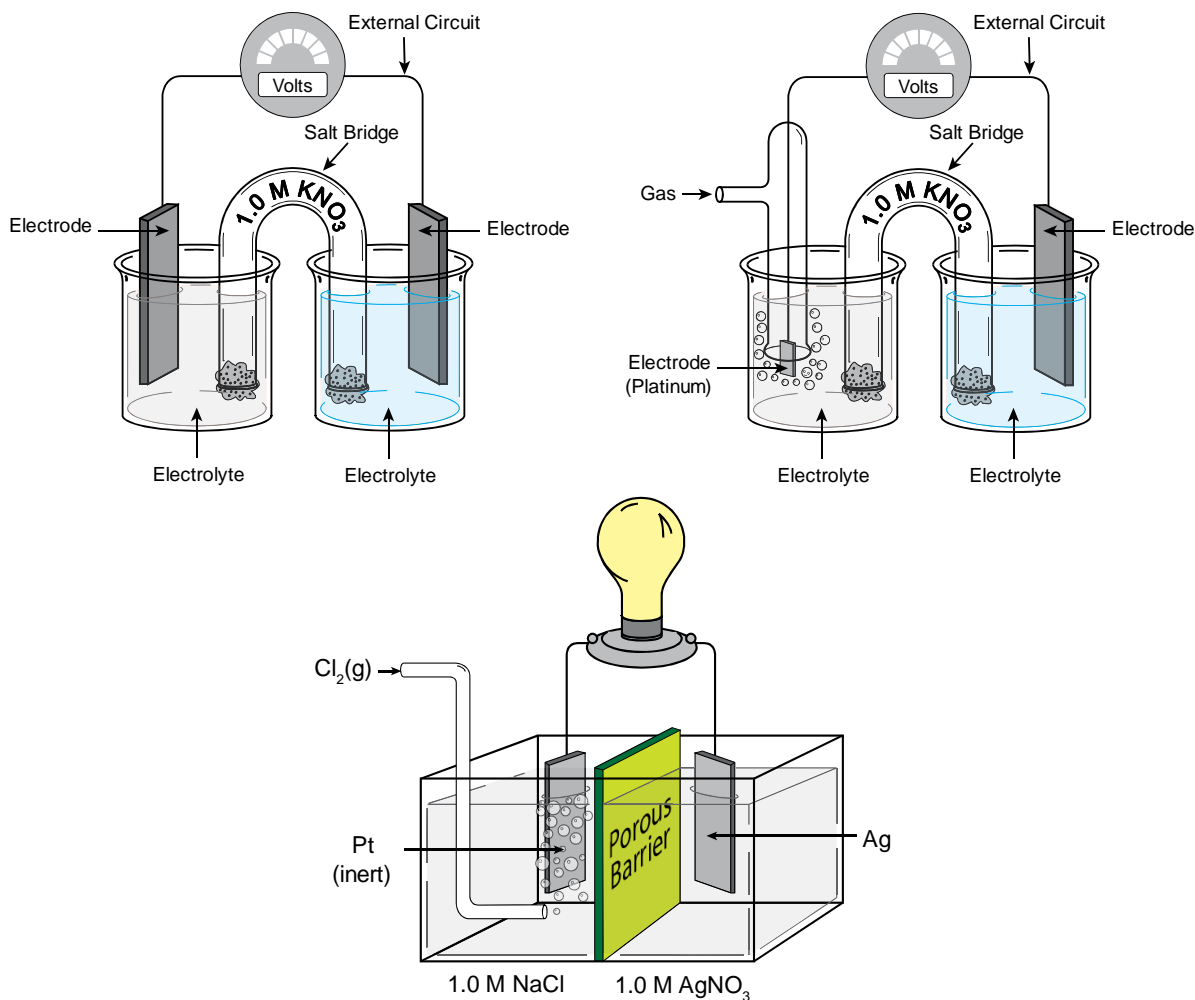
1. An **ELECTROCHEMICAL CELL (galvanic or voltaic cell)** is a chemical system in which a **SPONTANEOUS redox reaction can produce useful electrical work.**

Consider the reaction

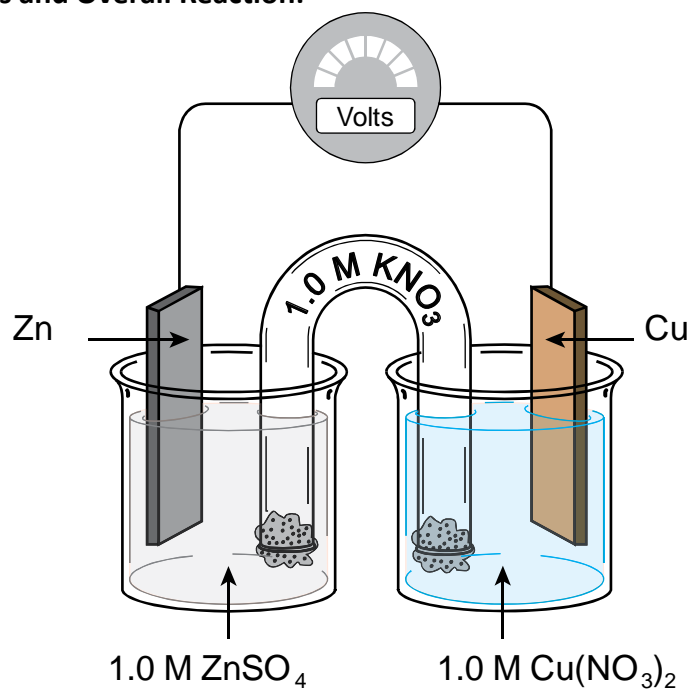


- A spontaneous reaction will occur when zinc metal is placed into a solution of CuSO_4 ; however, no usable energy is produced because the energy is lost as heat.
- Can be **used to produce electricity** if the two half reactions are made to occur in **separate containers or CELLS.**

2. Electrochemical cells:



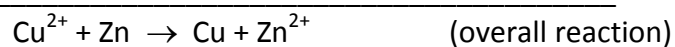
a) Half Reactions and Overall Reaction:



- In the electrochemical cell above, we have Zn(s), ZnSO₄(aq), Cu(s), and Cu(NO₃)₂(aq). The half-reactions are:



- Cu²⁺ is reduced to Cu and Zn is oxidized to Zn²⁺.**
- The reduction and oxidation half-reactions that occur will be:

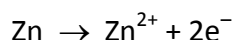


b) **Electrodes**

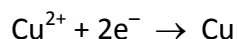
ANODE is the electrode where **OXIDATION** occurs.

CATHODE is the electrode where **REDUCTION** occurs.

- Zinc metal loses electrons and becomes **oxidized** to zinc ions, Zn^{2+} , at the **ANODE**, so it decreases in mass.



- Copper ions, Cu^{2+} , gain electrons and are **reduced** to copper metal at **CATHODE**, so it increases in mass.

c) **External Circuit**

- Electrons produced at the zinc electrode flow through the wire to the copper electrode where they reduce copper ions. The electrons will continue to flow through the wire until the redox reaction reaches equilibrium.

Electrons flow through the wire from the anode to the cathode.

d) **Connecting Cells**

- A **SALT BRIDGE** composed of a concentrated solution of a **strong electrolyte**, usually KNO_3 or KCl , or a porous membrane connects the two cells to complete the circuit.

The salt bridge keeps the two compartments **electrically neutral by allowing ions to migrate between the cells.**

Positive Zn^{2+} and Cu^{2+} ions (**cations**) are attracted to the **cathode**.

Negative NO_3^{-} and SO_4^{2-} ions (**anions**) are attracted to the **anode**.

EXAMPLE 5.14 DRAWING AN ELECTROCHEMICAL CELL

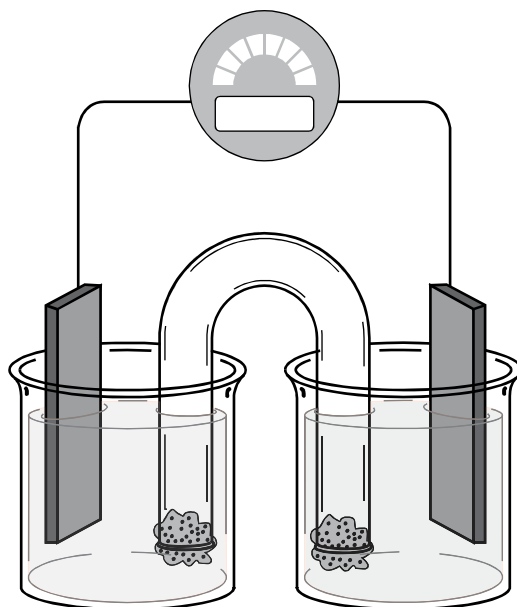
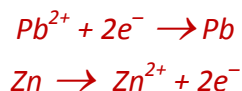
Assume two half-cells consisting of Pb(s) in a Pb(NO₃)₂ solution and Zn(s) in a ZnCl₂ solution are connected to make an electrochemical cell. Draw and label the parts of the cell, write the equations for the individual half-reactions and overall reaction, and indicate the directions in which the ions and electrons move.

The two half-reactions are:



Since Pb²⁺ is the stronger oxidizing reagent, it will become reduced and Zn(s) will become oxidized.

The two half-reactions are:



I. STANDARD REDUCTION POTENTIALS

1. The tendency of electrons to flow in an electrochemical cell is called the **VOLTAGE**, or **ELECTRICAL POTENTIAL** to do work.

VOLTAGE is the WORK DONE PER ELECTRON TRANSFERRED

- Since electrons cannot flow in an isolated half-cell, an individual half-cell voltage cannot be determined. However, the **difference in electrical potentials between two half-cells can be measured**.
- A **ZERO-POINT** is **ARBITRARILY** defined on the voltage scale. The voltage for the **HYDROGEN HALF-CELL** is defined to be

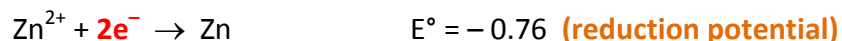


- Where E° is the **STANDARD REDUCTION POTENTIAL**, in volts and the “°” in E° means **STANDARD STATE**.
 - An electrochemical cell is said to be at **STANDARD STATE** if
 - a) it is at **25 °C**, and
 - b) all gases are at **101.3 kPa (1 atm)**, and
 - c) all elements are in their standard states (**normal phases at 25 °C**), and
 - d) all solutions involved in the cell have a **concentration of 1.0 M**.
2. All voltages listed in the table of **STANDARD REDUCTION POTENTIALS** are determined at **standard state** and are measured as the tendency to undergo reduction **relative to the hydrogen half-cell**.

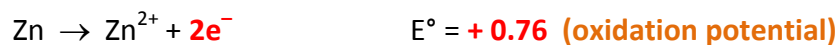


- Positive reduction potentials indicate that the half reaction has a **greater tendency to be reduced** than the hydrogen half cell.
- Negative reduction potentials indicate that the half reaction has a **lower tendency to be reduced** than the hydrogen half cell. The oxidation reaction will occur when these half reactions are connected to a hydrogen half cell.

- Since the voltage is a measure of the work done, reversing a **reduction** reaction such as

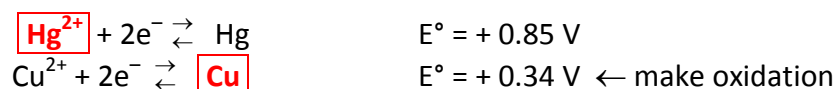


produces an **oxidation** reaction with a changed sign for E°

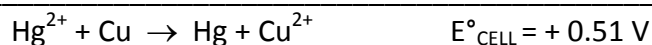
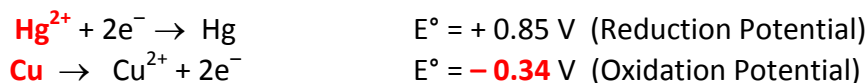


The value of an oxidation potential is the negative of the reduction potential (opposite signs).

3. When two half-reactions are combined, the voltage for the overall reaction is found to be the difference between the voltages of the individual half-cells.



- The voltage for the overall reaction is

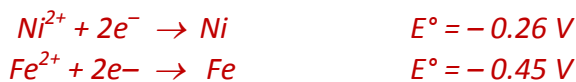


The electrochemical cell potential is determined by **adding the half-cell voltages for the reduction potential and oxidation potential.**

EXAMPLE 5.15 CALCULATING CELL POTENTIALS

Calculate the potential of the cell: $\text{Ni}^{2+} + \text{Fe} \rightarrow \text{Ni} + \text{Fe}^{2+}$.

The half-reactions involved are:



The voltage for the overall reaction is:



Note: This reaction is **SPONTANEOUS** since Ni^{2+} is higher than Fe and the reaction has a **POSITIVE VOLTAGE**.

EXAMPLE 5.16 CALCULATING CELL POTENTIALS

Calculate the potential of the cell: $\text{Ni} + \text{Fe}^{2+} \rightarrow \text{Ni}^{2+} + \text{Fe}$.

The half-reactions involved are:



The voltage for the overall reaction is:



Note: This reaction is **NOT SPONTANEOUS** since Fe^{2+} is lower than Ni and the reaction has a **NEGATIVE VOLTAGE**.

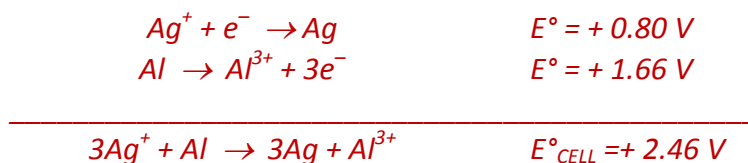
EXAMPLE 5.17 CALCULATING CELL POTENTIALS

Calculate the potential of the cell: $3\text{Ag}^+ + \text{Al} \rightarrow 3\text{Ag} + \text{Al}^{3+}$.

The half-reactions involved are:



The voltage for the overall reaction is



Note: Although the Ag^+/Ag half-reaction is multiplied by 3 to balance the electrons, the voltage is **NOT** multiplied by 3.

If E° is **POSITIVE** for a redox reaction, the reaction is expected to be **SPONTANEOUS**.

If E° is **NEGATIVE** for a redox reaction, the reaction is **NON-SPONTANEOUS**.

4. The **SURFACE AREA of an electrode does not affect the voltage of the cell**. This is because the **CONCENTRATION OF A SOLID IS CONSTANT**.
- Increasing the surface area of a solid electrode has **no effect on the concentration of the solid**.
 - No equilibrium shift** and no change in half-cell potential.
 - Increasing the surface area of an electrode increases the **AMPERAGE (Rate of electron flow)** of the cell but not the voltage.
 - Increasing the surface area of the electrode, also **increases the length of time that the cell can operate**.

5. When a half-reaction is **NOT** at standard state, it is governed by Le Châtelier's principle like any other equilibrium.

- Consider the following half-reaction



- If the $[\text{Cu}^{2+}]$ is greater than 1.0 M the equilibrium shifts right and the reduction potential increases.

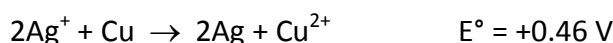


- If the $[\text{Cu}^{2+}]$ is less than 1.0 M the equilibrium shifts left and the reduction potential decreases.

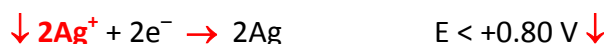


- Notice that the "°" is omitted from the E° symbol since it is not at standard state.

6. Operating electrochemical cells are **not at equilibrium**. Consider the cell:



THE REDUCTION REACTION:



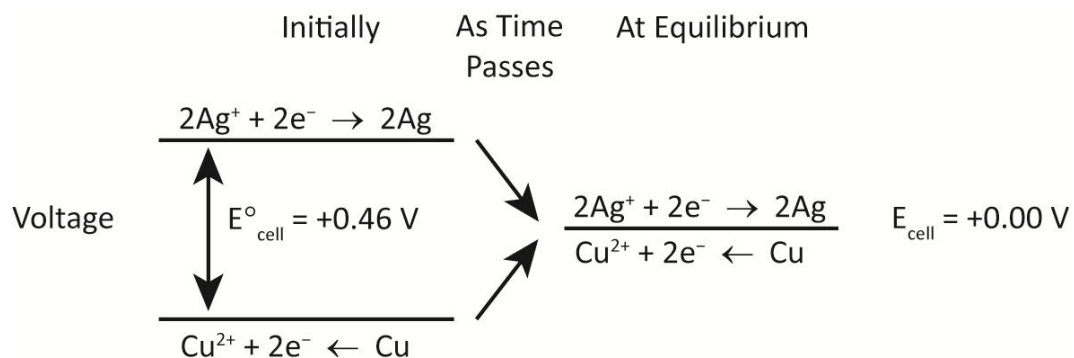
- The $[\text{Ag}^{+}]$ decreases as the reaction occurs and so the reduction potential decreases.

THE OXIDATION REACTION:



- As the $[\text{Cu}^{2+}]$ increases, the reduction potential of $\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$ increases. The tendency for reduction increases as the cell operates.

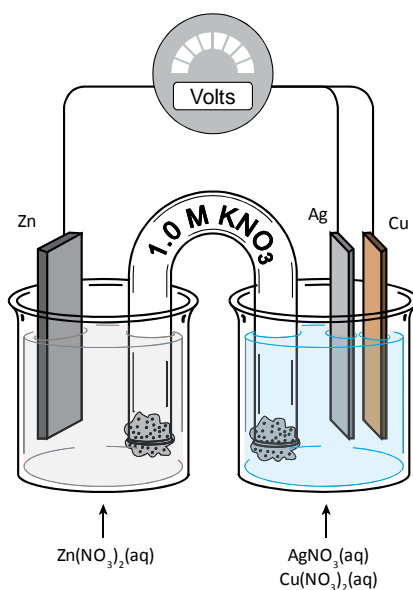
- Overall, the following occurs as the cell continues to operate until it reaches equilibrium.



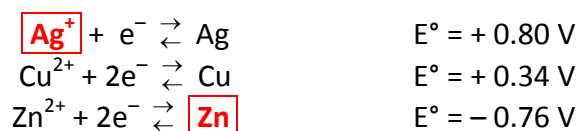
When an electrochemical cell reaches **EQUILIBRIUM**,
the **VOLTAGE OF THE CELL IS 0.00 V**.

J. SELECTING PREFERRED REACTIONS

1. When a cell contains a mixture of substances, several reactions may appear to be possible. Consider the following cell:



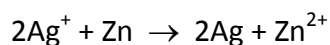
- The possible half-reactions are:



STRONGEST OXIDIZING AGENT will become reduced.

STRONGEST REDUCING AGENT will become oxidized.

- Therefore, the **Ag⁺ will reduce** and form Ag(s) and the **Zn(s) will oxidize** to form Zn²⁺.



2. Determining the preferred half-reactions:

- First, list the species present, breaking up all **ionic compounds into ions**.
- The chemical highest on the left undergoes reduction (**strongest oxidizing agent**).
- The chemical lowest on the right undergoes oxidation (**strongest reducing agent**).

EXAMPLE 5.18 SELECTING PREFERRED REACTIONS

An iron strip is placed in a mixture of $\text{Br}_2(\text{aq})$ and $\text{I}_2(\text{aq})$. What is the preferred reaction which occurs?

The species present are Fe, Br_2 and I_2 . The possible reactions are:



The preferred reduction involves Br_2 and the only oxidation possible involves Fe. The overall reaction is



Note: Any ion capable of being reduced will be a **SPECTATOR ION** if there is **another ion in the same solution which has a greater tendency to be reduced**. Similarly, any ion capable of being oxidized will be a spectator ion if there is another ion in the same solution which has a greater tendency to be oxidized.

The following ions are generally considered to be spectator ions:

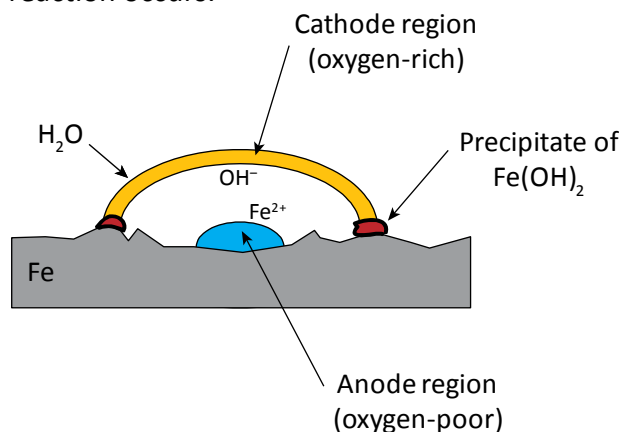


K. CORROSION OF METALS

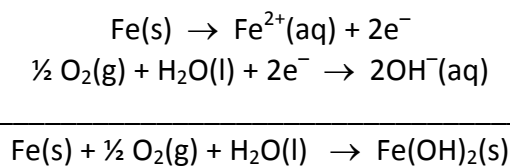
- Rusting is a common electrochemical reaction resulting from the oxidation of iron metal (Fe) by oxygen (O₂) in the air.

CORROSION = oxidation of a metal

- When iron is exposed to the atmosphere in the presence of water, the following spontaneous reaction occurs.



- Iron (Fe) is oxidized at the oxygen-poor region** in the centre of the drop, while **O₂ is reduced at the oxygen-rich region** at the outer surface. When the Fe²⁺ meets the OH⁻, it precipitates as Fe(OH)₂.



- The Fe(OH)₂ is oxidized to a complex mixture of Fe₂O₃ and H₂O by the O₂ in the air. **“Rust” is just Fe₂O₃•xH₂O**, where “x” is variable.
 - The variability of “x” explains the different colours rust can have (red, brown, yellow, black) since differing numbers of water molecules attached to the Fe₂O₃ will change the colour of the component.
- The rate of corrosion changes when iron is in contact with different metals.
 - When the metal is a **stronger reducing agent** than Fe (more readily oxidized) it is **preferentially oxidized**.
 - If the metal is a **weaker reducing agent** than Fe, such as Cu, it acts as a conductor of electrons and **speeds up the rate of Fe oxidation**.

PREVENTING CORROSION**a) Isolating The Metal From The Environment**

- i) **Apply a protective layer** to the metal such as paint, plastic, or grease. If oxygen and water cannot reach the metal, it will not corrode.
- ii) **Apply a metal which is corrosion-resistant** to the surface of the original metal. Tin can be applied to the surface of steel cans. The tin is quickly oxidized to produce a thin layer of tin oxide which protects the underlying metal from further corrosion.

b) Electrochemical Methods**i) Cathodic Protection**

We can prevent the corrosion of iron by providing an alternative source of electrons to oxygen.

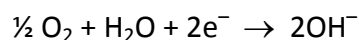
CATHODIC PROTECTION = protecting a substance from unwanted oxidation by connecting it to a stronger reducing agent.

Magnesium and zinc are stronger reducing agents than iron. When attached to iron, they will become oxidized first, leaving the iron metal intact. The attached metal is purposely oxidized and is referred to as a **SACRIFICIAL ANODE**, the Fe acts as a **CATHODE** and remains in its reduced form.

- e.g.
- i. Zinc blocks bolted to iron-hulled ships to prevent them from rusting.
 - ii. Low voltage electric current from an electrical generator (electron pump).
 - iii. Galvanized iron nails.
 - iv. Buried gas and oil tanks made from steel have thick braided wire connecting to them to posts made of magnesium or zinc.

ii) Change the Condition of the Surroundings

We can prevent corrosion by altering the reduction reaction that causes Fe to become oxidized:



- If **oxygen is removed** from the solution, the reduction potential decreases.
- **Increase [OH⁻] ions** also causes the reduction potential to decrease.

L. ELECTROLYSIS

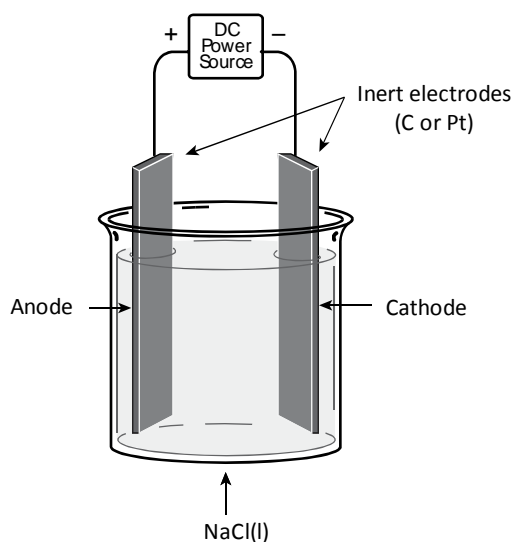
1. **ELECTROLYSIS** is the process of supplying electrical energy to a molten ionic compound or a solution containing ions so as to produce a chemical change.

ELECTROLYTIC CELLS involve **NONSPONTANEOUS** redox reactions that require energy to occur (**ENDOTHERMIC**).

ELECTROCHEMICAL CELLS involve **SPONTANEOUS** redox reactions that release energy (**EXOTHERMIC**).

2. ELECTROLYSIS OF MOLTEN BINARY SALTS

- **Binary salts** are made up of **only two different elements**, e.g. NaCl, KBr, MgI_2 , AlF_3 , etc.
- Molten binary salts, such as NaCl, **contain only two kinds of ions**. (Molten NaCl is NaCl(l), only Na^+ and Cl^- ions present. NaCl(aq) which is a solution and contains Na^+ , Cl^- , and H_2O).



- No need for a salt bridge to keep the reactants separated since no spontaneous reaction will occur. Although, a **barrier can be used to prevent products from mixing**.

EXAMPLE 5.19 ELECTROLYSIS OF MOLTEN BINARY SALTS

What products are formed at the anode and cathode and what is the overall reaction when molten NaCl(l) is electrolyzed using inert electrodes? Determine the minimum voltage required.

NaCl(l) only contains Na^+ , and Cl^- so the only possible reactions are:

OXIDATION



REDUCTION



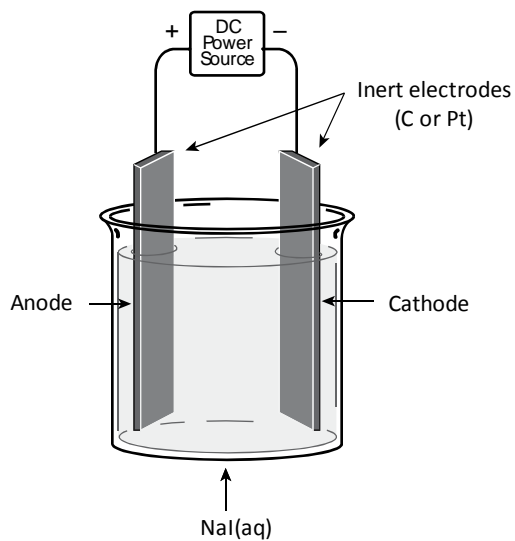
The half-reactions that occur are:



$\text{Cl}_2(\text{g})$ is produced at the anode, $\text{Na}(\text{s})$ is produced at the cathode and a voltage of at least 4.07 V must be applied for the reaction to occur.

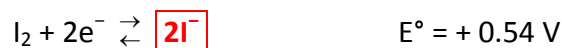
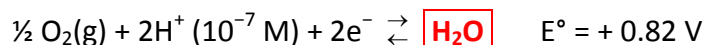
3. ELECTROLYSIS OF AQUEOUS SOLUTIONS

- In addition to the ions from the salt, aqueous solutions introduce the complication of **water which may behave as an oxidizing or reducing agent.**
- Consider the electrolysis of aqueous sodium iodide, NaI(aq) :

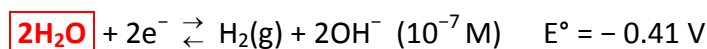


Electrolysis of aqueous solutions must consider the possibility
 H_2O may be oxidized and/or reduced.

- Two possible oxidations (RA):



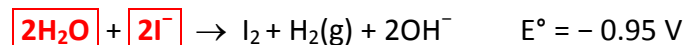
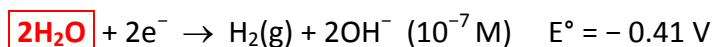
- Two possible reductions (OA):



STRONGEST OXIDIZING AGENT becomes reduced

STRONGEST REDUCING AGENT become oxidized

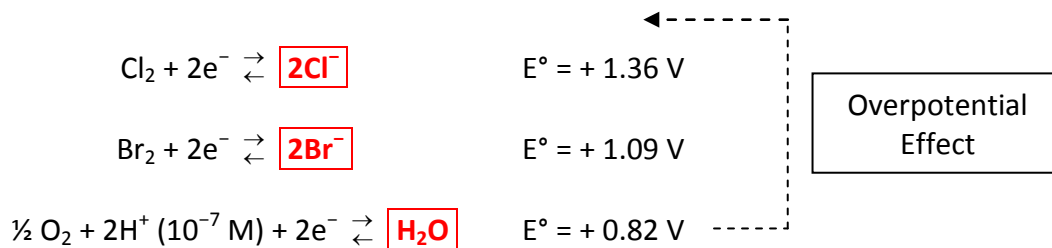
- The half-reactions and the overall reaction involving the electrolysis of $\text{NaI}(\text{aq})$ are:



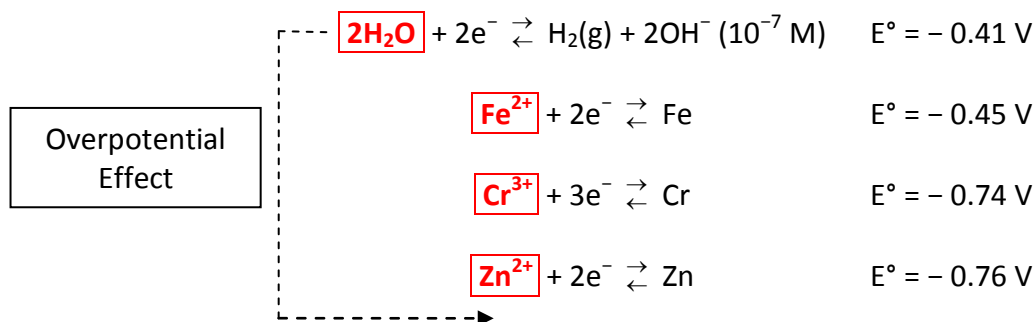
so at least + 0.95 V must be applied to the cell.

4. In practice, it is found that a **higher potential than calculated must be supplied to cause electrolysis.**

- Causes include the **nature of the electrodes, temperature, current, and time.**
- Difference between actual potentials required for electrolysis and the calculated potential is termed **HALF-CELL OVERPOTENTIAL.**
- Overpotentials vary for each half-cell but the difference in potentials is **very large for oxidation and reduction of neutral water.**

OXIDATION:

- We would **expect that O_2 will be produced**. In practice however, we find that **Cl_2 or Br_2 are actually produced**.

REDUCTION:

- In addition when dilute solutions of Fe^{2+} , Cr^{3+} or Zn^{2+} are electrolyzed, we would **expect that H_2 is produced** but in practice, **Fe , Cr , or Zn will be produced**.

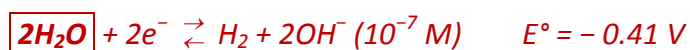
Electrolysis of aqueous solutions containing Cl^- or Br^-
will produce Cl_2 or Br_2 at the anode.

Electrolysis of aqueous solutions containing Fe^{2+} , Cr^{3+} , or Zn^{2+}
will produce Fe , Cr , or Zn at the cathode.

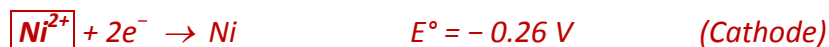
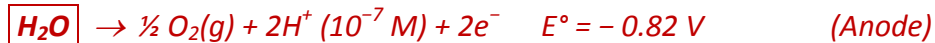
EXAMPLE 5.20 ELECTROLYSIS OF AQUEOUS SOLUTIONS

What products are formed at the anode and cathode and what is the overall reaction when a solution containing $\text{NiSO}_4(\text{aq})$ is electrolyzed using inert electrodes? Determine the minimum voltage required.

First, the species present Ni^{2+} , SO_4^{2-} , H_2O (neutral) and the possible reactions are:

OXIDATION**REDUCTION**

*The SO_4^{2-} reaction is **NOT** possible since the solution is neutral, so the half-reactions that occur are:*



$\text{O}_2(\text{g})$ is produced at the anode, $\text{Ni}(\text{s})$ is produced at the cathode and a voltage of at least 1.08 V must be applied for the reaction to occur.

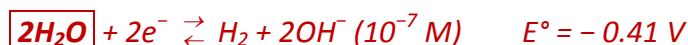
EXAMPLE 5.21 ELECTROLYSIS AQUEOUS SOLUTIONS

What is the overall reaction which occurs when a 1 M solution of HCl(aq) is electrolyzed using carbon electrodes?

First, the species present H^+ , Cl^- , H_2O (acidic) and the possible reactions are:

OXIDATION

Overpotential Effect

REDUCTION

Due to the high overpotential of H_2O , the Cl^- is oxidized so the two half reactions are



$Cl_2(g)$ is produced at the anode, $H_2(g)$ is produced at the cathode and a voltage of at least 1.36 V must be applied for the reaction to occur.

SAMPLE 5L.1 ELECTROLYSIS REACTIONS

Determine the products and overall reaction when the following solutions are electrolyzed using inert electrodes? Determine the minimum voltage required.

**5. ELECTROPLATING**

ELECTROPLATING = electrolytic process in which a metal is reduced or “plated out” onto an object connected to the cathode.

- The **CATHODE** is made out of the material which will receive the metal plating.
- The **ELECTROPLATING SOLUTION** contains ions of the metal which is to be “plated” onto the cathode.
- The **ANODE** may be made of the same metal which is to be “plated out” onto the cathode. (This is normal but an inert electrode can also be used.)

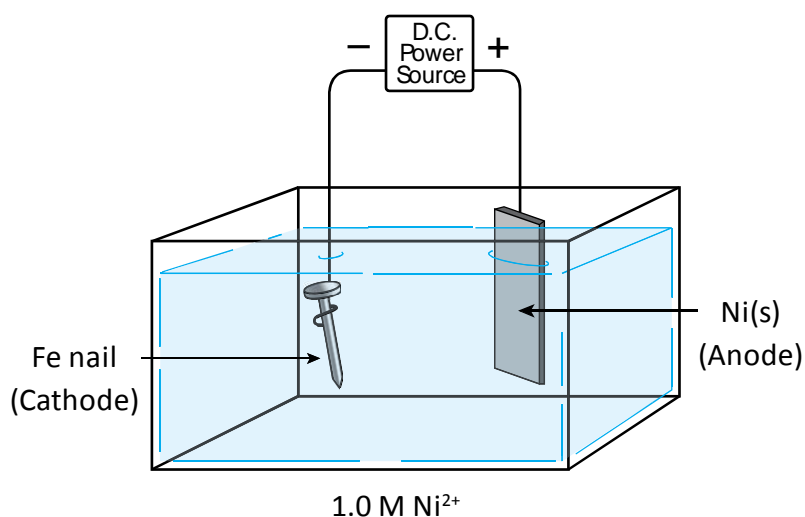
EXAMPLE 5.21 ELECTROPLATING CELLS

Design a cell to electroplate an iron nail with nickel metal. Include in the design: the ions present in the solution, the direction of ion flow, the substance used for the anode and cathode, and the direction of electron flow when the cell is connected to a DC power source.

Since nickel metal must be produced, the reduction reaction is:



The cell is setup as follows:



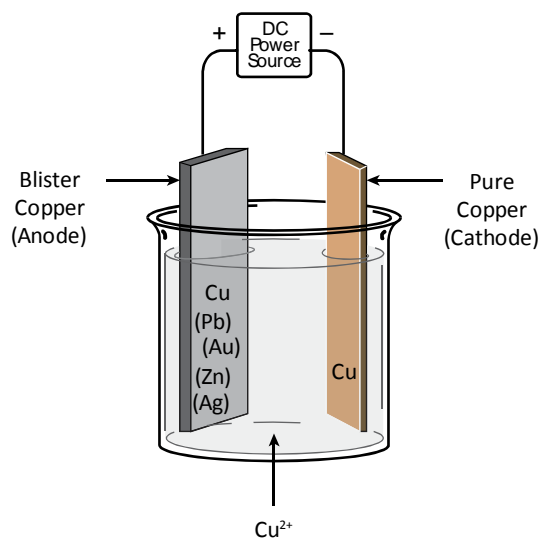
- The iron nail must have the Ni(s) plated onto it, so it must be the **CATHODE**.
- Make the **ANODE** out of Ni(s) so that the oxidation reaction

$$\text{Ni(s)} \rightarrow \text{Ni}^{2+} + 2\text{e}^{-}$$
 will ensure a continuous supply of Ni^{2+} ions in the solution.
- Since electrons always flow from "**ANODE TO CATHODE**", connect DC power in such a way as to supply electrons to the cathode.
- The ions needed in solution will Ni^{2+} and some anion that does **NOT** form a precipitate with Ni^{2+} . The NO_3^{-} is always a good choice since all nitrates are soluble.
- As with spontaneous reactions, **CATIONS (Ni^{2+})** migrate to cathode and **ANIONS (NO_3^{-})** migrate towards the anode.

6. ELECTROREFINING

ELECTROREFINING = process of purifying a metal by electrolysis.

Involves “plating out” a metal from an impure anode onto a pure cathode.



- Voltage is controlled so that **only Zn, Pb and Cu are oxidized** to Zn²⁺, Pb²⁺ and Cu²⁺ at the anode while other impurities such as **Au and Ag remain**.
- Copper ion, **Cu²⁺ are preferentially reduced** at cathode because they are stronger oxidizing agents than Zn²⁺ and Pb²⁺.
- Other metals in the blister copper can be selectively purified by adjusting the voltage.