



Studybeesofficial

Where Minds Pollinate

**Class 12
Chemistry**

Chapter 2
Electrochemistry
Handwritten Notes

Follow Our Socials

 **studybeesofficial**
 **studybeesofficialpak**
 **studybeesofficialpak**

ELECTROCHEMISTRY

momina_arshadd

Electrochemistry

Electrochemistry is concerned with conversion of electrical energy into chemical energy in electrolytic cell as well as the conversion of chemical energy into electrical energy in galvanic or voltaic cells. It involves redox reactions in which transfer of electrons between two or more substances takes place.

It deals with energy sources that are highly efficient, such as batteries and fuel cells. It involves transfer of electrons.

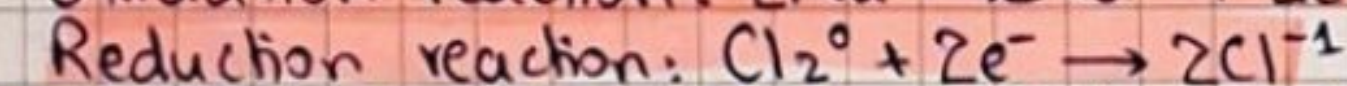
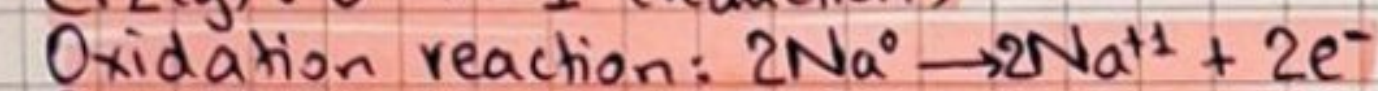
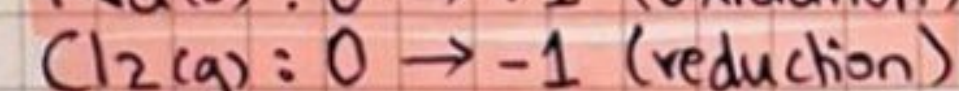
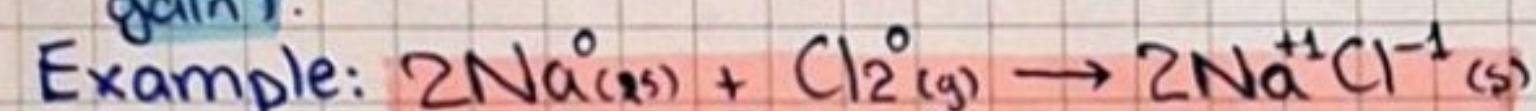
Oxidation-Reduction Concepts

- Oxidation: A reaction in which a substance loses an electron.

- Reduction: A reaction in which a substance gains an electron.

Together, they form redox reaction. Redox reactions involve change in oxidation state/numbers.

- Oxidation State or Number: The apparent charge on an atom of an element in a molecule or ion. It may be zero, positive or negative. Oxidation = Increase in oxidation no. (electron loss). Reduction = Decrease in oxidation no. (electron gain).



Disproportionation Reaction: A disproportionation reaction is a type of redox reaction where the same element is both oxidized and reduced simultaneously. Also called self-oxidation-reduction. In $2\text{H}_2\text{O}_2^0 \rightarrow 2\text{H}_2\text{O}^{-2} + \text{O}_2^0$, Oxygen in H_2O_2 is partially oxidized to O_2 (state = 0) and partially reduced to H_2O (oxidation state = -2).

Balancing Equations

- Redox Method (Oxidation Number Method): Based on the principle that total electrons lost = total electrons gained in the redox reaction. Used to balance redox reactions by comparing changes in oxidation numbers.

Steps: 1) Assign oxidation state to each element.

2) Identify the element changing oxidation state.

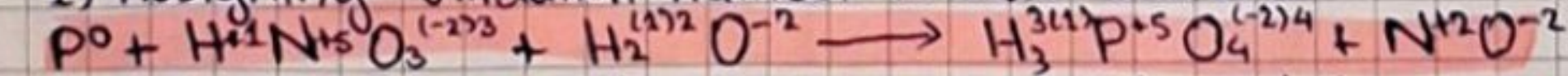
3) Draw bridge between elements and show electron loss or gain.

4) Multiply electron loss or gain by a number to get a common number.

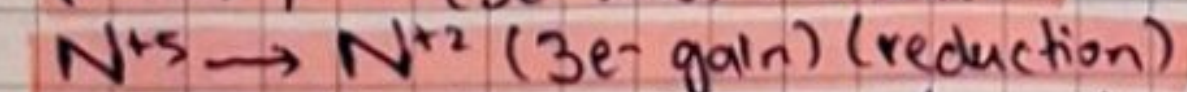
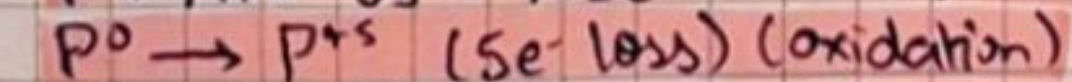
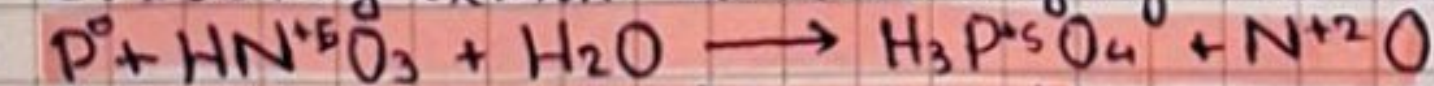
5) Inspection Method, Hydrogen and Oxygen.



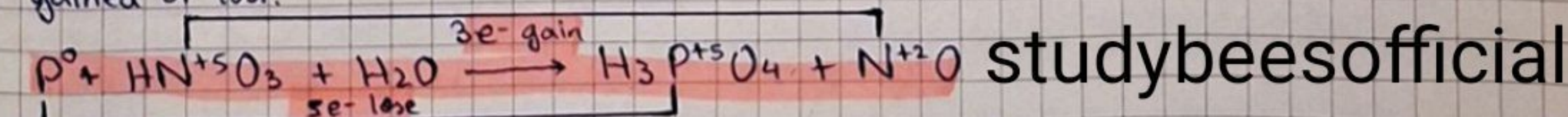
1) Assigning oxidation number to each element.



2) Identify element with changing oxidation state.



3) Draw bridge between atom whose oxidation state changed by the number of electron gained or lost.



4) Equalize number of electron loss and gain by multiply.

Electro → electricity/electrons
Chemistry → Redox Reactions
So, electrical energy ⇌ chemical energy.

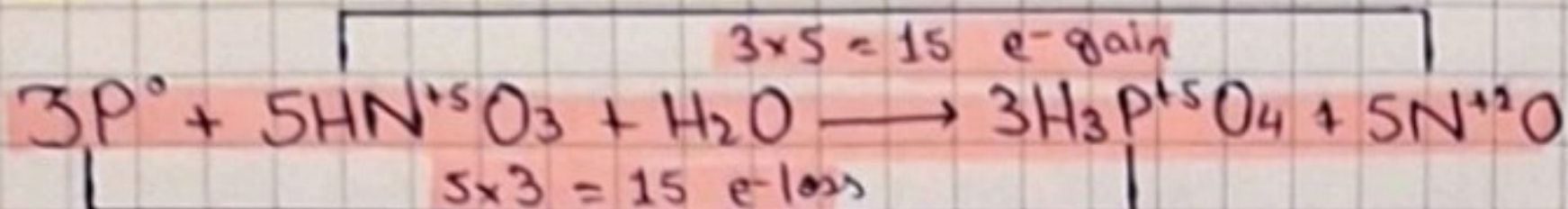
If Oxygen gain and Hydrogen is lost then its oxidation.
If Oxygen is lost and Hydrogen is gained then its reduction.

Rules for assigning oxidation state

- Element in its free state has an oxidation state of 0 (O_2 , H_2 , Fe)
- Ions, the oxidation state is equal to the ionic charge. ($\text{Fe}^{2+} = +2$)
- Hydrogen usually has an oxidation state +1. But in metal hydrides, hydrogen has state of -1.
- Oxygen generally has state of -2. Superoxide has -1/2 (O_2^-) Peroxide has -1 (O_2^{2-})
- The more electronegative element gets the negative oxidation state.
- Sum of oxidation state of neutral molecule is 0.
- Sum of oxidation state of all atoms in ion equals to overall charge of the ion.

+ sign comes when electrons are lost (oxidation)
- sign comes when electrons are gained (reduction).

Class

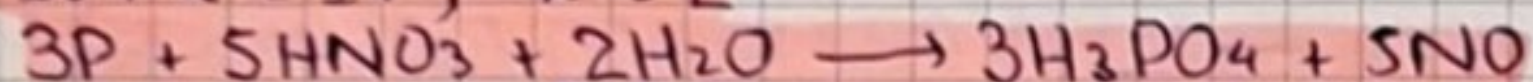


Coefficient 3 with P and H_3PO_4 and coefficient 5 with HNO_3 and NO.

5) Balance rest of equation by inspection method.

As in the left side we have $15 + x$ oxygen, and right side has $12 + 5 = 17$ oxygen. So, to balance we need,

$$15 + x = 17, x = 2$$



- Construction of Redox Equations (Ion Electron Method): Any redox reaction consists of two half-reactions. (Oxidation half reaction and Reduction half reaction). Each half reaction is balanced separately.

Steps: 1) Balance atoms (except H and O).

2) Balance oxygen atoms using H_2O (for acidic/neutral material)

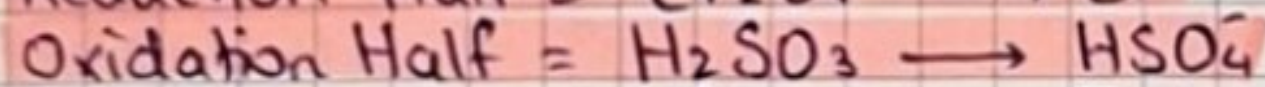
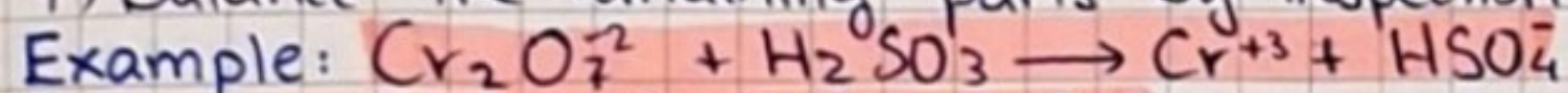
3) Balance hydrogen atoms using H^+

4) Balance charge using electrons (e^-)

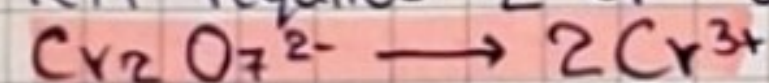
5) Equalise the number of electrons lost and gained in both half-reactions.

6) Add the half-reactions to get the overall balanced redox equation.

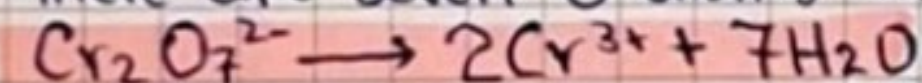
7) Balance the remaining parts by inspection method if needed.



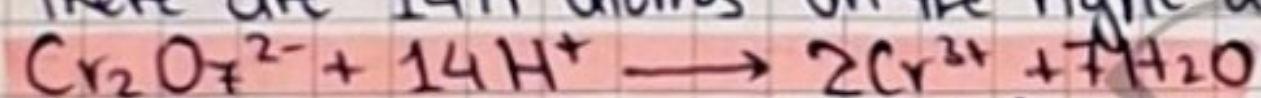
1) Balance each half-reaction. First, consider reduction half-reaction. Two Cr atoms on the left requires 2 Cr^{+3} on right.



There are seven O atoms on the left and none on the right. We will add $7H_2O$ on right.

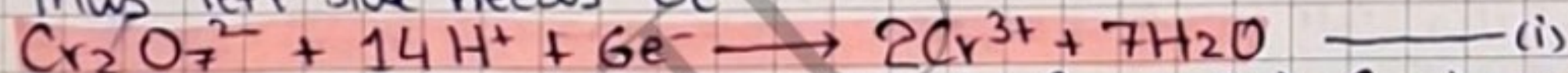


There are 14H atoms on the right and none on the left, so we add $14H^+$ on left.



Now balance charges. The left side has one di-negative and 14 mono-positive charges, $-2 + 14 = +12$. The right side has two tri-positive charges corresponding to $+3 \times 2 = +6$.

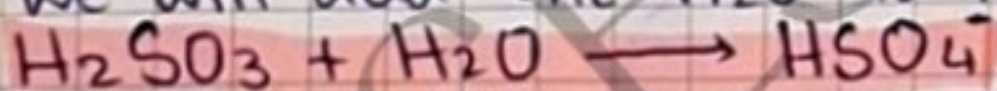
Thus left side needs $6e^-$



In other half reaction (oxidation half-reaction), S atoms are already balanced.



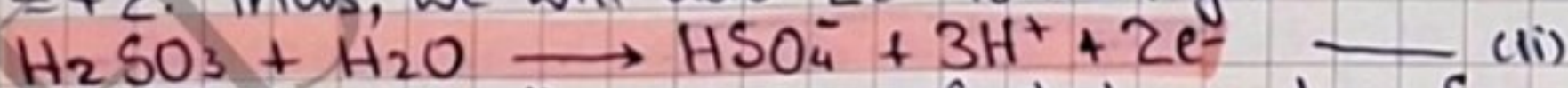
Balance O atoms. As there are three O atoms on the left and four on the right, we will add one H_2O to the left.



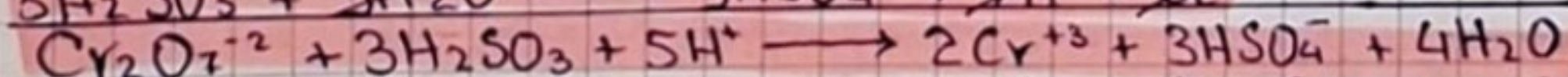
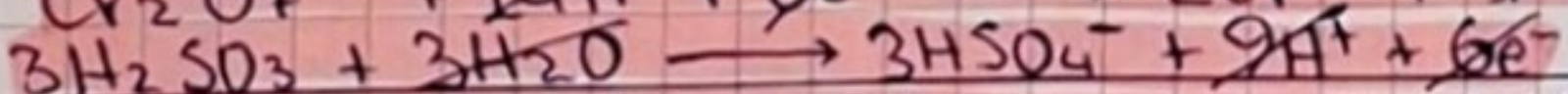
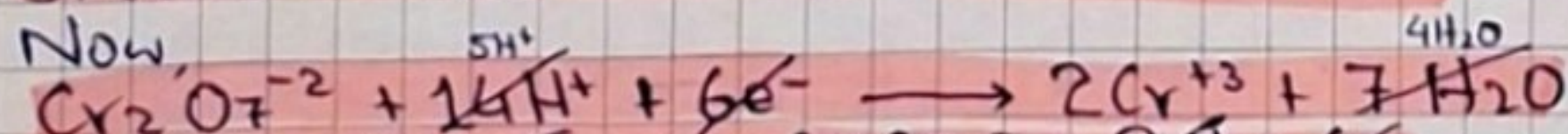
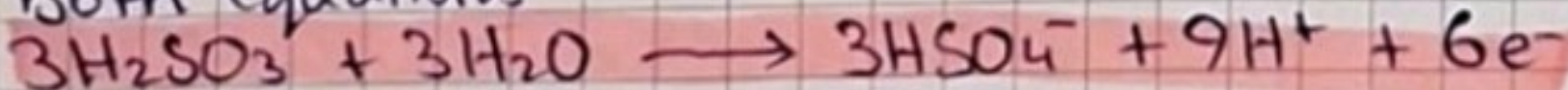
There are four H atoms on the left and one on the right. We will add $3H^+$ to right.



For charge, the left side is neutral but the right side has a net charge of $(-1) + (+3) = +2$. Thus, we will add $2e^-$ to the right.



Step 2) Equalize the number of electrons transferred in the two half-reactions and add half-reactions. And multiplying equation (ii) by three to balance electrons in both equations



Since charges are equal on both sides, therefore equation is balance.

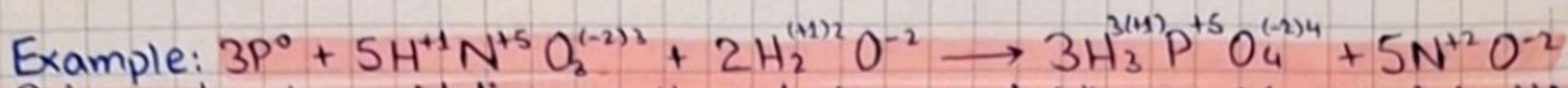
Oxidizing and Reducing Agents

- Oxidizing Agent: A substance which oxidizes other substance. It accepts electrons. The substance itself reduces. Oxidation state decreases.

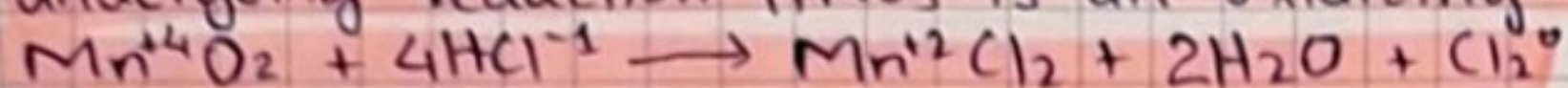
- Reducing Agent: A substance which reduces other substance. It releases electrons. The substance itself is oxidized. Oxidation state increases.

For basic material oxygen is balanced using OH^-

Oil Rig
- Oxidizing is loss
- Reduction is gain



P is undergoing oxidation, so its reducing agent. Whereas N present in HNO_3 is undergoing reduction HNO_3 is an oxidizing agent.



Mn present in MnO_2 is undergoing reduction, therefore MnO_2 is oxidizing agent. Cl of HCl is oxidised, so HCl is a reducing agent.

Electrode, Electrode Potential and Electrochemical Series

- **Galvanic Cell (Daniel Cell):** A galvanic cell is an electrochemical cell in which natural (spontaneous) redox reaction produces electric current. It uses chemicals to make electricity.

- Zinc rod
- Copper rod
- Zinc Sulphate (ZnSO_4) solution
- Copper(II) Sulphate (CuSO_4) solution
- Copper wire (to connect both metals)
- Salt bridge filled with electrolyte like KCl, KNO_3 or Na_2SO_4 .
- Two separate containers
- Voltmeter

Procedure: Put the zinc rod into zinc sulphate solution in one container. Put the copper rod into copper sulphate solution in the other container. Connect the zinc and copper rods with a wire. Connect the two solutions using a salt bridge. Now, the chemical reaction starts, and electric current flows through the external wire. Without a salt bridge, no current flows because charges would build up and stop the reaction.

Role of Salt Bridge: Allows ions to move between the two solutions without mixing them. Keeps both sides electrically neutral. Prevents charge buildup. Allows the reaction (and electricity flow) to continue.

Oxidation Half cell: Also called anode half-cell. Half cell in which oxidation occurs. The reaction taking place in oxidation half-cell is called the oxidation half reaction. Happens at electrode called anode. Reaction: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

Reduction Half cell: Also called cathode half-cell. Half cell in which reduction occurs. The reaction taking place in the reduction half-cell is called the reduction half reaction.

Happens at electrode called cathode. Reaction: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$

Flow of electrons: Zinc loses electrons more easily than copper. So the flow is zinc electrode $\rightarrow$ through wire $\rightarrow$ Copper electrode.

Overall reaction: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

- **Cell Potential:** The potential of the cell to do work on its surroundings by driving an electric current through a wire. The voltage produced by a galvanic cell under standard conditions. Also called electromotive force (emf), the force with which electrons are pushed to flow through the wire from anode to cathode. Measured in volts using voltmeter. Depends on the difference between standard electrode potentials of two half-cells. $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

Under Standard Conditions: Temperature 25°C (298K). Solution concentration: 1mol/dm^3 . Gas pressure 1 atm. The electrode with a more negative E° value acts as anode (oxidation). The electrode with a more positive E° value acts as cathode (reduction).

A positive E°_{cell} indicates a spontaneous redox reaction. Standard Hydrogen Electrode (SHE) is used as reference electrode. Its potential is 0.00V.

- **Standard Hydrogen Electrode:** SHE is the reference electrode used to measure electrode potential of other half-cells. Its structure is:

- Platinum electrode coated with platinum black
- Hydrogen gas at 1atm bubbled into 1M HCl.
- Operated at 298K.

Oxidizing agents:

$2\text{H} \rightarrow \text{H}_2\text{SO}_4$, HNO_3
 $2\text{K} \rightarrow \text{KMnO}_4$, $\text{K}_2\text{Cr}_2\text{O}_7$
 $\text{FSC} \rightarrow \text{FeCl}_3$, SO_3 , CO_2
 Halogens $\rightarrow \text{F}_2$, Cl_2 , Br_2 , I_2
 H_2O_2 , MnO_2 , CrO_3 , CaO
 High electronegativity = good oxidizing agent.
 Small size = good agent

Reducing agents:

Metals $\rightarrow$ group 1 and 2
 Electropositivity should be more = good agent (electronegativity low)
 Size big = good agent
 Hydrides $\rightarrow \text{LiH}$, NaH
 $\text{H} + \text{Halogen} \rightarrow \text{HI}$, HBr ...
 Pure C, P, H, S
 H_2S , Cu_2O , SnCl_2 , FeCl_2

Electrode:

- Solid conductor (usually metal) placed in contact with an electrolyte solution.
- Allows transfer of electron

Electrode Potential:

- Measure of tendency of an electrode to gain or lose electrons when it is in contact with its ions in solution.
- Measured in volts.

Standard Electrode Potential:

- The standard electrode potential (E°) is the potential of a half-cell under standard conditions (1M conc., 1 atm pressure, 25°C)

Its electrode potential is arbitrarily chosen as zero at all temperatures. Assigned a standard potential of 0.00 V. Can act as:

Cathode (Reduction): $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

$$E^\circ_{\text{H}^+(\text{aq})/\text{H}_2(\text{g})} = 0.00\text{V}$$

Anode (Oxidation): $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$

$$E^\circ_{\text{H}_2(\text{g})/\text{H}^+(\text{aq})} = 0.00\text{V}$$

Can act as both anode and cathode depending up the nature of the electrode with which it is connected.

- **Method to measure the electrode potentials:** SHE is the primary reference electrode used to measure the standard electrode potentials of other half-cells, such as copper and zinc.

If above H then its oxidized (anode) and below H then its reduction (cathode).

Determination of Standard Electrode Potential of Zn^{2+}/Zn Electrode:

Zinc rod in 1M ZnSO_4 . Connected to SHE via salt bridge. Electrons flow from zinc to hydrogen electrode. Zinc is anode, SHE is cathode. Cell potential (E°_{cell}) = 0.76V

$$E^\circ_{\text{cell}} = E^\circ_{\text{anode}} + E^\circ_{\text{cathode}}$$

$$0.76 = E^\circ_{\text{anode}} + 0$$

$$E^\circ_{\text{anode}} = +0.76 \text{ (oxidation)}$$

$$\text{So, } E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76\text{V (reduction)}$$

Determination of Standard Electrode Potential of Cu^{2+}/Cu Electrode: Copper rod in 1M CuSO_4 . Connected to SHE via salt bridge. Electrons flow from hydrogen to copper electrode. SHE is anode, Cu is cathode. Cell potential (E°_{cell}) = 0.34V.

$$E^\circ_{\text{cell}} = E^\circ_{\text{anode}} + E^\circ_{\text{cathode}}$$

$$0.34 = 0 + E^\circ_{\text{cathode}}$$

$$E^\circ_{\text{cathode}} = +0.34\text{V}$$

$$\text{So, } E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34\text{V (reduction)}$$

and -0.34V is oxidation.

- **Determination of Cell Potential:** Each redox reaction consists of two half-reactions.

The more positive reduction potential is used as cathode (reduction). The less positive (or more negative) reduction potential is reversed and used as anode (oxidation). Overall cell reaction is the sum of the two half-reactions. $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.

- **Feasibility of a Reaction:** The sign of the sum of E° values of the two half-cells reactions. If this value is positive, a reaction occurs spontaneously or will be feasible. The negative value indicates that the reaction is not feasible.

• If $E^\circ_{\text{cell}} > 0$, its spontaneous

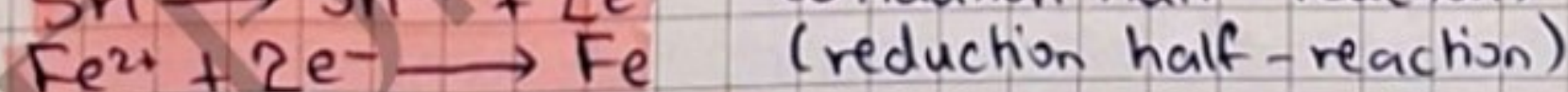
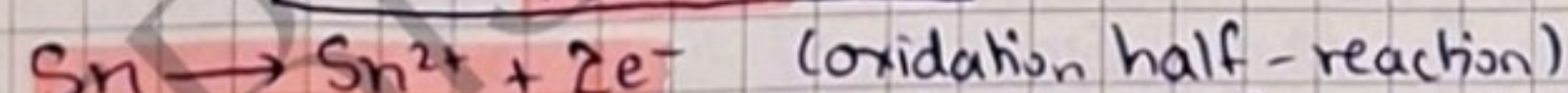
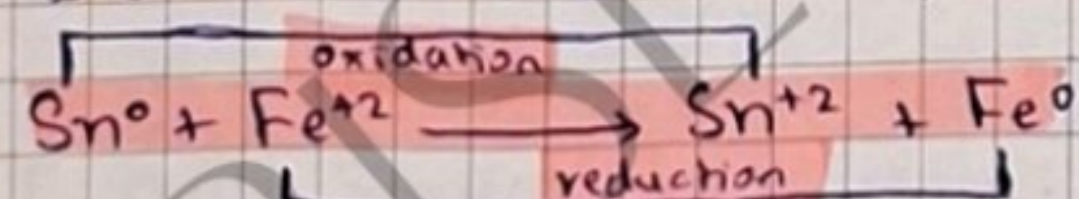
• If $E^\circ_{\text{cell}} < 0$, its non-spontaneous

Example: $\text{Sn} + \text{Fe}^{2+} \rightarrow \text{Sn}^{2+} + \text{Fe}$

The standard reduction potential values are:

$$E^\circ_{\text{Fe}} = -0.14\text{V, (cathode, reduction)}$$

$$E^\circ_{\text{Sn}} = -0.44\text{V (anode, oxidation)}$$



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ_{\text{cell}} = -0.44 - (-0.14)$$

$$E^\circ_{\text{cell}} = -0.30\text{V}$$

As, its negative, therefore the given reaction is not feasible. However reverse reaction can be feasible.

Nernst Equation

The electrode potential between ~~concent~~ is influenced by the concentration of the ions involved in the redox reaction. Nernst equation shows relationship between standard electrode potential (E°) to the actual electrode potential (E) under non-standard conditions.

Mathematically: $E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{oxidized species}]}{[\text{reduced species}]}$

• n = no. of electrons transferred from reduced species to oxidized species.

• R = the universal gas constant (8.314Jmol^{-1})

• T = Kelvin temperature $298\text{K}/25^\circ\text{C}$

• F = Charge of a mol of electron and charge of 1mol of electron is $9.648 \times 10^4\text{Cmol}^{-1}$

• $[\text{oxidized species}]$ = Conc. of species with higher oxidation state.

Class

• [reduced species] = Conc. of species with lower oxidation state.

• $\ln = 2.303 \log$

$$E = E^\circ + \frac{2.303RT}{nF} \log \frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

$$E = \frac{2.303RT}{F} = \frac{2.303 \times 8.314 \times 298}{9.648 \times 10^4} = 0.059 \text{ J C}^{-1} = 0.059 \text{ V}$$

$$E = E^\circ + 0.059/n \log [\text{oxidized species}]/[\text{reduced species}]$$

- **Electrode potentials and concentration:** The electrode potential depends on the concentration of ions in the solution. For example, the standard electrode potential of copper is +0.34V when Cu^{2+} concentration is 1M. If the Cu^{2+} concentration is decreased (for example, by adding water), the equilibrium shifts to produce more Cu^{2+} ions, making reduction harder because fewer ions are available to accept electrons. This lowers electrode potential, so it is no longer standard value. Increasing ion concentration makes reduction easier because more ions are available to gain and increases the electrode potential. The Nernst equation can be used to calculate how changes in ion concentration affects the electrode potential.

Example: The standard electrode potential of Cu^{2+}/Cu system is +0.34V. What is the electrode potential of a solution containing 0.5M Cu^{2+} ions.

$$E = E^\circ + 0.059/n \log [\text{oxidized species}]/[\text{reduced species}]$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} + 0.059/n \log [\text{oxidized species}]/[\text{reduced species}]$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.34 + 0.059/2 \log 0.5/1 \quad \because \text{Cu}^{2+} = 0.5 \text{ and Cu} = 1$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.34 + 0.0295 \times (-0.301)$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.331 \text{ V}$$

Electrochemical Series

The electrochemical series is a list of elements (particularly metals) arranged in the order of their electrode standard potentials, measured under standard conditions. (1M ion conc, 25°C, 1 atm) with reference to the standard hydrogen electrode (SHE). The International Union of Pure and Applied Chemistry (IUPAC) recommends expressing half-cell reactions as reduction reactions, so their E° values are known as standard reduction potential. To obtain oxidation potential of an electrode, simply reverse the sign of reduction potential. Any change in standard conditions will alter the electrode potential values.

- **Activity Series of Metals:** A displacement/replacement reaction occurs when a more reactive element displaces a less reactive element from its compound. $A + XY \rightarrow X + AY$

Example: When Zn metal is added to CuSO_4 solution, Zn is oxidized to Zn^{2+} and Cu^{2+} is reduced to Cu metal. $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$.

When Cu metal is placed in ZnSO_4 solution, no reaction occurs because Cu is less reactive than Zn. Cu^{2+} has a higher reduction potential than Zn^{2+} .

Metals like Mg and Al can also displace Cu^{2+} , but Ag cannot. Reactive Metals like Na and K can displace H_2 from water. Less reactive metals like Cu and Ag cannot.

Activity Series: Ranks metals (and hydrogen) based on their ease of oxidation.

Metals are arranged in decreasing order of activity. A metal higher in the series can donate electrons to ions of metal lower in the series.

Key observations: Metals higher in the activity series can displace metals lower in the series from their compounds. The greater the gap between two elements in the series, the more vigorous the displacement reaction.

Example: $\text{Ba(s)} + \text{PbO(s)} \rightarrow \text{BaO(s)} + \text{Pb}$
Ba is more reactive, so it gets oxidized and displaces Pb.

$\text{Fe} + \text{MgCl}_2 \rightarrow \text{No Reaction}$

Fe is less reactive than Mg, so it can not displace Mg^{2+} .

The Relative Reactivity of Species as Oxidizing or Reducing Agents

Electrode potential values (also called reduction potentials) help compare the reactivity of elements, compounds, and ions as oxidizing or reducing agents.

Another equation:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{molar conc. product}]}{[\text{molar conc. reactants}]}$$

$$1 \text{ J C}^{-1} = 1 \text{ V}$$

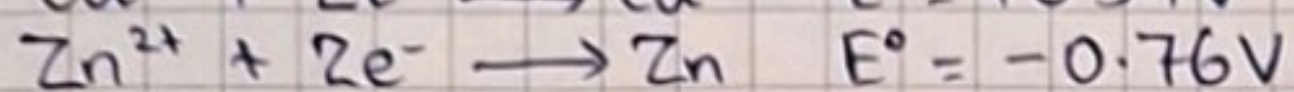
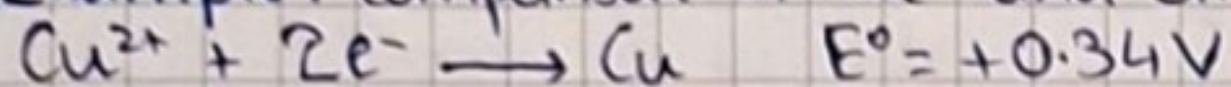
Cu, Ag, Hg
Moderately noble metals, no reaction with water or HCl.
React with oxidizing acids (HNO_3)
Pt, Au very noble metals. React only with aqua regia

Li, K, Ba, Sr, Ca, Na very active. React with cold water. (K and Na react violently). Also react violently with acids.
Mg, Al, Mn, Zn, Cr, Fe, Cd Intermediate activity. React slowly with HCl, do not react with water, but steam.
Co, Ni, Sn, Pb moderate, react slow with HCl and not with water.
 H_2

Class

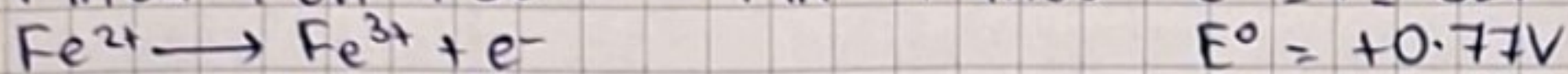
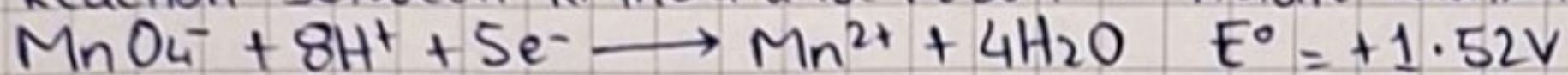
- Higher reduction potential: Indicates a stronger oxidizing agent. The species has a greater tendency to gain electrons. (be reduced).
- Lower reduction potential: Indicates a stronger reducing agent. The species has a greater tendency to lose electrons. (be oxidized).

Example: Comparison of Cu^{2+} and Zn^{2+}



Cu^{2+} has a higher reduction potential than Zn^{2+} . Therefore, Cu^{2+} is a stronger oxidizing agent than Zn^{2+} .

Reaction between KMnO_4 and FeSO_4 in Acidic Solution.



MnO_4^- has a higher reduction potential than Fe^{2+} . Therefore MnO_4^- acts as a strong oxidizing agent. Fe^{2+} acts as a strong reducing agent.

Types of Electro-chemical cells

Devices that convert electrical energy into chemical energy and vice versa are electrochemical cells. There are two types: Electrolytic cells and Galvanic (Voltaic) cells.

- **Electrolytic Cells:** Cell which uses electricity to continue the chemical reaction. Non-spontaneous in nature. Example, Down Cell, Nelson's Cell. The process is called electrolysis. Electrolysis is a process in which a chemical reaction occurs by means of an electric current in a molten state or in an aqueous state.

Working of Electrolytic Cells: Oxidation occurs at the anode (positive electrode) where electrons are lost. Reduction occurs at the cathode (negative electrode) where electrons are gained. The battery pushes electrons to start the reaction, making the reaction non-spontaneous.

Apparatus: An electrolytic cell containing an electrolyte (molten or aqueous). Two electrodes dipped into the solution. A battery connected to the electrodes. Electrons move through wires by metallic conduction, and through the solution by ions (cations and anions). The electrodes are the point where conduction changes from metal $\rightarrow$ electrolyte and back. At one electrode, ions gain electrons, at the other lose electrons. Then electrons then return to the battery through the wire. Hence, a redox reaction happens at the electrodes.

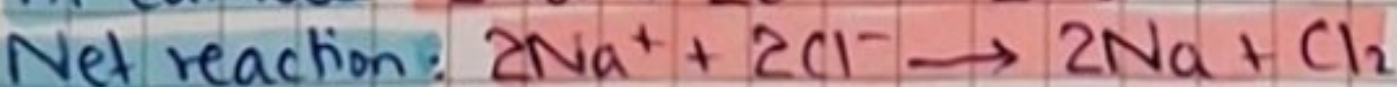
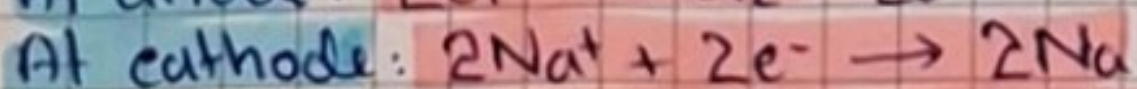
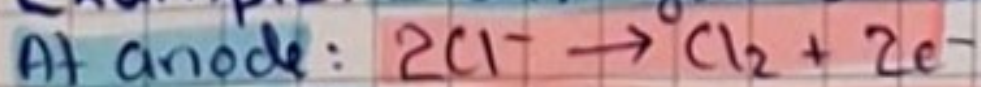
Units used in Electrolysis: The SI unit of charge is the coulomb (C), which equals the charge on 6.25×10^{18} electrons. A more convenient unit in chemistry is the Faraday (F), which is the charge carried by 1 mole of electrons, equal to 96487 C. The unit of current is ampere (A), which is equal to 1 coulomb per second.

Factors affecting the Products of Electrolysis

Electrolysis drives a non-spontaneous redox reaction. The products released depend on:

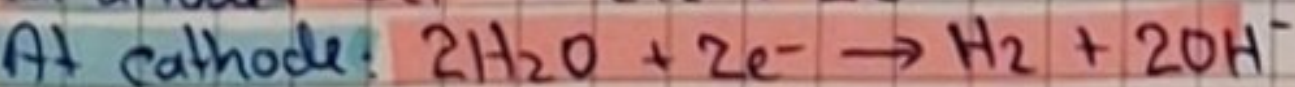
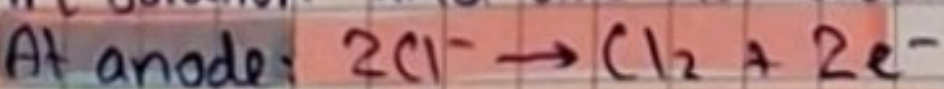
- **State of the Electrolyte:** For molten electrolyte, its own ions are discharged. And for aqueous electrolyte, contains water ions too, so water may produce H_2 at the cathode.
- **Position in the Electrochemical Series:** Ions higher in the series are more easily reduced, lower ones are oxidized. In aqueous solutions, cations less reactive than hydrogen (eg. Cu^{2+}) are discharged at the cathode. More reactive cations (Na^+ , Mg^{2+}) are not discharged, instead water is reduced to hydrogen gas.
- **Concentration of Electrolyte:** High ion concentration makes it easier for those ions to be discharged. If an ion is in low concentration, water may discharge instead.

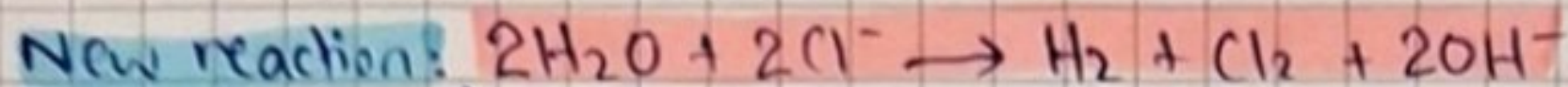
Example: Electrolysis of fused NaCl



Electrolysis of concentrated aqueous NaCl (brine)

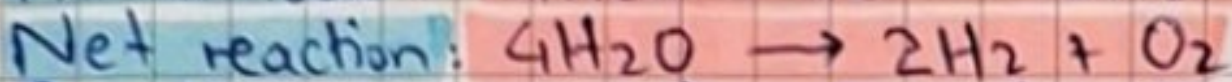
Since the solution contains a higher concentration of Cl^- ions. So they are discharged at the anode instead of OH^- ions. Na^+ ions being more reactive than hydrogen remain in solution and are not discharged, instead water molecules are discharged at cathode.





Electrolysis of dilute aqueous NaCl

In dilute aqueous NaCl solution, Cl^- ions have lower concentration. So, chloride ions are not discharged at the anode. Instead, OH^- ions are discharged at anode. Na^+ ions being more reactive than hydrogen remain in the solution and water molecules are discharged at cathode.



Relation between the Faraday Constant, Avogadro Constant, the Charge on Electron

The amount of substance produced at an electrode during electrolysis depends on the period of time for which a constant current is passed and the quantity of charge in coulombs that passes through the electrolyte. The relation between current and time is:

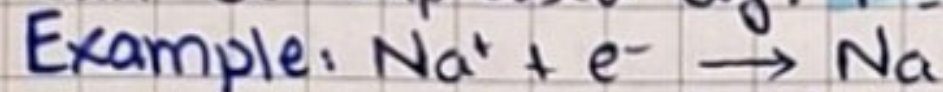
$Q = I \times t$, where Q is quantity of charge in coulombs, I is current in ampere and t is time in seconds. The quantity of electricity can be expressed by Faraday constant (F). One faraday is the amount of electric charge carried by one mole of electrons.

Charge on one electron = $1.60217662 \times 10^{-19}\text{C}$

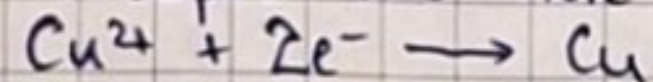
Charge on one mole of electrons = $1.60217662 \times 10^{-19}\text{C} \times 6.022 \times 10^{23}$ per mol

Charge on one mole of electrons = $96485.332\text{Cmol}^{-1}$

This quantity of charge is referred to as one Faraday. Thus, the quantity of charge in electrolysis can be determined from the number of Faraday's of charge, which passes. For most calculations, the value of the Faraday will be taken as 96500C . The relationship between the Faraday constant, avogadro constant and charge on electron can be expressed by: $F = N_A \cdot e$



To deposit one mole of Na, the amount of electricity needed is $1F$ (96500C)



But to deposit one mole of Cu, 2 mole of electrons are required. So, the amount of electricity needed is $2F$.

SHORT QUESTIONS

The oxidation potential of Zn is +0.76V and its reduction potential is -0.76V.

The standard oxidation potential of zinc is +0.76V because zinc is a highly reactive metal and has a strong tendency to lose electrons to form Zn^{2+} ions. Therefore the oxidation reaction: $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ is spontaneous, giving a positive oxidation potential. The reduction potential of zinc is -0.76V because Zn^{2+} ions do not readily gain electrons to form zinc metal. Since reduction is the reverse process, it is non-spontaneous, therefore the reduction potential is negative.

A salt bridge maintain the electrical neutrality in the cell.

A salt bridge maintains electrical neutrality in a galvanic cell by allowing the migration of ions between the two half-cells. During the cell reaction, positive ions accumulate in the cathode compartment, while negative ions accumulate in the anode compartment, which would stop the flow of electrons if not balanced. The salt bridge contains an inert electrolyte such as KCl or KNO_3 , whose ions move to neutralize charges. Anions migrate toward the anode and cations towards cathode, preventing charge build up. This maintains electrical neutrality and allows cell to continue functioning, ensuring a continuous current. Na and K can displace hydrogen from acids but Cu and Pt cannot.

Sodium (Na) and Potassium (K) can displace hydrogen from acids because they are highly reactive metals, placed above hydrogen in the electrochemical (activity) series. They have a strong tendency to lose electrons, forming positive ions and therefore readily replace hydrogen from acids to produce hydrogen gas. On the other hand, Copper (Cu), and Platinum (Pt) cannot displace hydrogen from acids because they are less reactive metals and lie below hydrogen in the activity series. They do not lose electrons easily and thus cannot reduce hydrogen ions of the acids to hydrogen gas.

Define oxidation in terms of oxidation electron transfer.

Oxidation is a chemical process in which an atom, ion, or molecule loses electrons. In terms of electrons transfers, oxidation involves the removal of one or more electrons, resulting in an increase in oxidation state. For example: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$. Here zinc is oxidized because it loses electrons.

What is the oxidation number of oxygen in H_2O_2 ?

In hydrogen peroxide (H_2O_2), the oxidation number of oxygen is -1. This is because oxygen is bonded to another oxygen atom, and in peroxides, oxygen does not exhibit its usual oxidation state of -2. The O-O single bond reduces its ability to attract electrons completely, so each oxygen in H_2O_2 has an oxidation number of -1 instead of -2. Therefore, H_2O_2 is classified as a peroxide because the oxidation state of oxygen is -1.

Identify the reducing agent in the reaction $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$

The reducing agent in this reaction is Zn. This is because zinc loses electrons and gets oxidized to Zn^{2+} . By losing electrons, zinc provides electrons to Cu^{2+} , causing copper ions to gain electrons and get reduced to metallic copper. Therefore, the substance that loses electrons and causes reduction of the other is the reducing agent, which in this reaction is zinc.

Explain what happens at the anode during the electrolysis of aqueous sodium chloride.

During the electrolysis of aqueous sodium chloride (brine), chloride ions (Cl^-) are oxidized at the anode because the anode is the positive electrode where oxidation takes place. Chloride ions lose electrons to form chlorine gas. $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$. Although OH^- ions are present, Cl^- ions are discharged in preference due to their lower discharge potential. As a result, chlorine gas is released at the anode, confirming that oxidation of chloride ions occurs during this process.

What does a positive standard electrode potential indicate about a substance's tendency to gain electrons?

A positive standard electrode potential indicates that a substance has a strong tendency to gain electrons and undergo reduction. The more positive the electrode potential, the more readily the substance accepts electrons. A positive value means the reduction process

is spontaneous, and the substance acts as a good oxidizing agent, as it easily gains electrons during a chemical reaction.

Calculate the oxidation number of chromium in $K_2Cr_2O_7$.

In potassium dichromate ($K_2Cr_2O_7$), let the oxidation number of chromium be x . We know, Oxidation number of $K = +1$ and $O = -2$. The compound is neutral so the sum of oxidation numbers = 0:

$$2(+1) + 2(x) + 7(-2) = 0 \Rightarrow x = +6$$

Therefore, the oxidation number of chromium in $K_2Cr_2O_7$ is +6.

Describe the role of the standard hydrogen electrode in electrochemistry.

The Standard Hydrogen Electrode (SHE) serve as the reference electrode in electrochemistry. It is assigned a fixed potential of 0.00V and is used to measure and compare the electrode potentials of other electrodes. It consists of platinum metal dipped in 1M H^+ solution with hydrogen gas bubbling over it at 1 atm pressure. By connecting SHE with another half-cell, the standard electrode potential of that cell can be determined. Therefore, SHE provides a universal standard for comparing oxidation and reduction tendencies of different substances.

What is the significance of activity series of metals?

The activity series of metals is a list of metals arranged in order of their reactivity, from most reactive to least reactive. It is significant because it helps predict chemical reactions, such as which metal can displace another metal from its salt solution and which metals can displace hydrogen from acids. It also indicates the ease of oxidation, as metals higher in the series lose electrons more readily, while those lower resist oxidation. Therefore, the activity series is important for understanding displacement reactions, extraction of metals, corrosion and electrochemical processes.

How can you deduce the feasibility of a redox reaction using electrode potentials?

The feasibility of a redox reaction can be determined by calculating the cell potential (E°_{cell}) using standard electrode potentials. The reduction potential of the cathode is subtracted from the oxidation potential of the anode: $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$. If E°_{cell} is positive, the redox reaction is feasible and spontaneous. If E°_{cell} is negative, the reaction is not spontaneous and therefore not feasible under standard conditions.

Bauxite ore is used for the commercial preparation of Al. For this purpose, bauxite ore is first purified to produce pure alumina, Al_2O_3 . Alumina is electrolyzed. The following reaction occurs: $2Al_2O_3(s) \rightarrow 4Al(s) + 3O_2(g)$. Calculate the mass of Al, that collects at cathode and the volume of oxygen that collects at anode when Al_2O_3 is electrolyzed for 10 hours with a 15 ampere current at 1 atm and 25°C.

$$\text{Current (I)} = 15 \text{ A}, \quad t = 10 \text{ h} = 36000 \text{ s}$$

$$\text{Total charge } Q = It = 15 \times 36000 = 540000 \text{ C}$$

$$\text{Number of moles of electrons: } n(e^-) = Q/F = 540000/96485 = 5.597 \text{ mol}$$

For the half-reaction, 3 mol e^- produce 1 mol Al ($Al^{3+} + 3e^- \rightarrow Al$)

$$n(Al) = n(e^-)/3 = 5.597/3 = 1.8656 \text{ mole}$$

$$\text{Mass of aluminum: } n(Al) \times M_{Al} = 1.8656 \times 26.98 = 50.3 \text{ g}$$

From the overall reaction $2Al_2O_3 \rightarrow 4Al + 3O_2$, 12 e^- produce 3 mol O_2 , so 1 mol e^- produces $1/4$ mol O_2 .

$$n(O_2) = 1/4 n(e^-) = 0.25 \times 5.597 = 1.3992 \text{ mol}$$

Using $PV = nRT$

$$V = nRT = 1.3992 \times 0.08206 \times 298.15 = 34.2 \text{ dm}^3$$

Which of the following compounds will give more mass of metal, when 15 ampere current is passed through a molten mass of these salts for 1hr.

a) NaCl b) $CaCl_2$

To determine which compound gives more mass of metal, we compare the number of electrons needed to deposit one mole of each metal. For NaCl, $Na^+ + e^- \rightarrow Na$. Sodium requires 1 electron to deposit 1 mole of Na. For $CaCl_2$, $Ca^{2+} + 2e^- \rightarrow Ca$. Calcium requires 2 electrons to deposit 1 mole of Ca. With the same current and same time, the same number of electrons is supplied, so the metal requiring fewer electrons (Na) will deposit more moles of metals. Therefore, sodium (from NaCl) will give more mass of metal than calcium from $CaCl_2$, because Na^+ needs only one electron, while Ca^{2+} requires two electrons to form metal.

Class

How many hours would electroplating have to be continued at the rate of 5 ampere if 75g of copper is to be deposited from CuSO_4 solution?

Current $I = 5 \text{ A}$

Mass of copper to deposit $m = 75 \text{ g}$

Molar mass of $\text{Cu} = 63.5 \text{ g/mol}$

Copper ion: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

First calculate moles of Cu : $n = m/M = 75/63.5 = 1.18 \text{ mol}$

Since 2 moles of electrons deposit 1 mole Cu : $n(\text{e}^-) = 2 \times 1.18 = 2.36 \text{ mol}$

Charge required: $Q = n(\text{e}^-) \times F = 2.36 \times 96485 = 227720 \text{ C}$

Now, using $Q = It$: $t = Q/I = 227720/5 = 45544 \text{ s}$

Convert into hours: $45544/3600 = 12.65 \text{ hours}$

Electroplating must be continued for approximately 12 hours and 40 minutes

Differentiate between the following:

a) galvanic and electrolytic cell

Galvanic Cell

Converts chemical energy into electrical energy.

Spontaneous reaction (E°_{cell} is positive)

Anode is negative and Cathode is positive

Used to produce electricity

b) oxidation half-reaction and reduction half-reaction

Oxidation Half-reaction

It involves loss of electrons

Oxidation number of element increases

Occurs at anode

Example: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

An electroplating apparatus is used to coat jewellery with gold. What mass of gold can be deposited from a solution that contains $[\text{Au}(\text{CN})_4]^-$ ion if a current of 5.0 amperes flows for 30 minutes? The following half-reaction occurs: $[\text{Au}(\text{CN})_4]^- (\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s}) + 4\text{CN}^- (\text{aq})$

Current $I = 5.0 \text{ A}$

Time $t = 30 \text{ min} = 30 \times 60 = 1800 \text{ s}$

Half reaction: $[\text{Au}(\text{CN})_4]^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{CN}^-$

This shows 3 electrons deposit 1 mole of gold

Calculate charge passed: $Q = It = 5 \times 1800 = 9000 \text{ C}$

Calculate moles of electrons: $n(\text{e}^-) = Q/F = 9000/96485 = 0.0933 \text{ mol}$

Moles of Gold deposited: Since 3 mol electrons deposit 1 mol gold $n(\text{Au}) = 0.0933/3 = 0.0311$

Mass of Gold deposited: Atomic mass of gold 197 g/mol , $n \times M = 0.0311 \times 197 = 6.13 \text{ g}$

Approximately 6.1 grams of gold are deposited when a 5 ampere current flows for 30 minutes.

Construct redox equations using the following half reactions

a) $\text{SO}_2 \rightarrow \text{HSO}_4^-$ $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$

Balance the oxidation half-reaction:

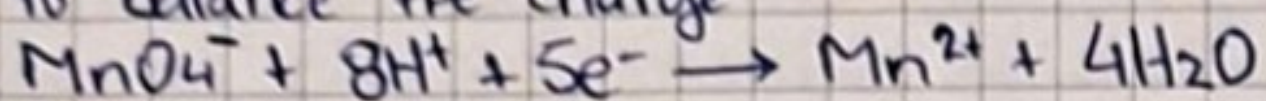
The sulfur is oxidized from +4 in SO_2 to +6 in HSO_4^- . The half reaction is balanced by adding water to balance oxygen, hydrogen ions to balance hydrogen, and electrons to balance the charge

$\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{HSO}_4^- + 3\text{H}^+ + 2\text{e}^-$

Balance the reduction half-reaction:

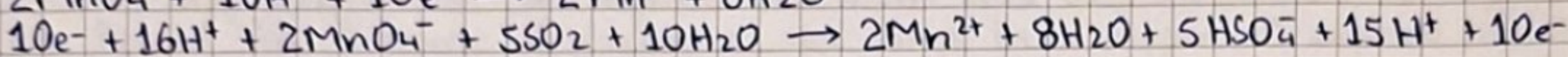
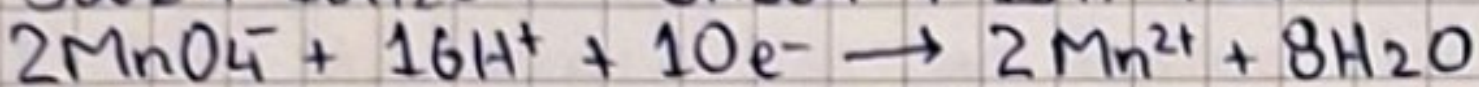
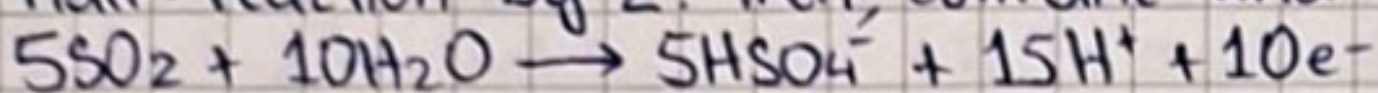
Class

The manganese is reduced from +7 in MnO_4^- to +2 in Mn^{2+} . The half-reaction is balanced by adding water to balance oxygen, hydrogen ions to balance hydrogen, and electrons to balance the charge.

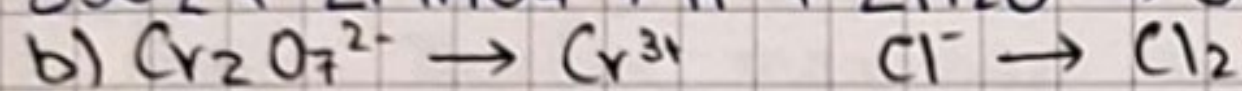
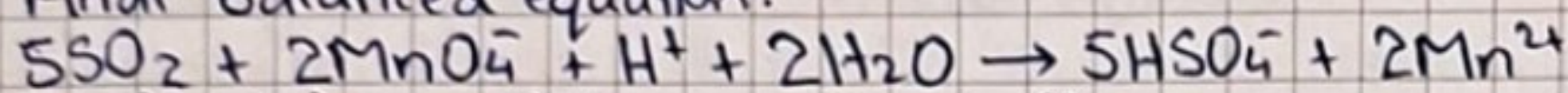


Combine half-reactions:

To equalize the electron transfer, multiply the oxidation half reaction by 5 and the reduction half-reaction by 2. Then, combine and cancel common species.

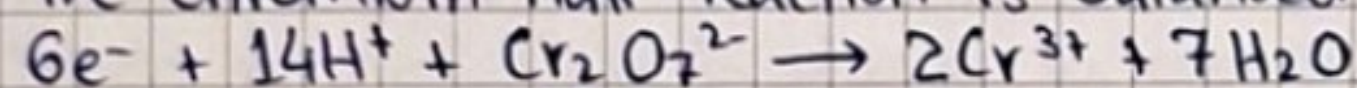


Final balanced equation:

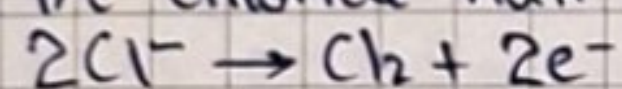


Balance the half reactions:

The chromium half-reaction is balanced for mass and charge in acidic solution.

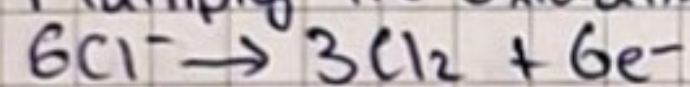


The chloride half-reaction is balanced for mass and charge.

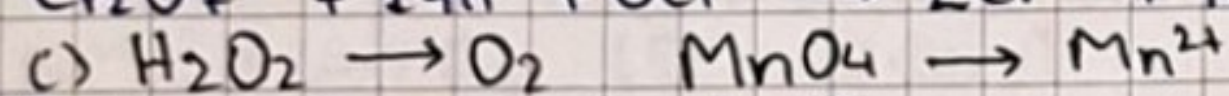
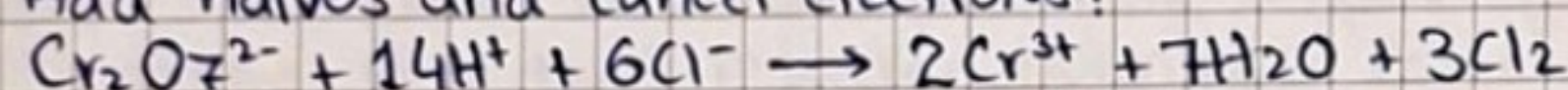


Equalize:

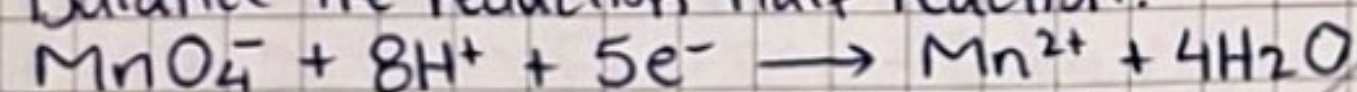
Multiply the oxidation half by 3



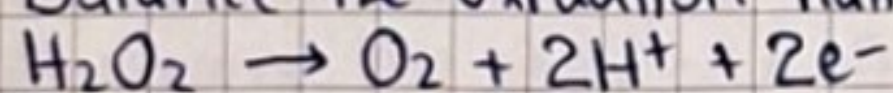
Add halves and cancel electrons:



Balance the reduction half reaction:

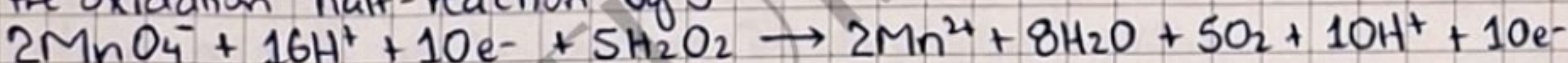


Balance the oxidation half reaction:

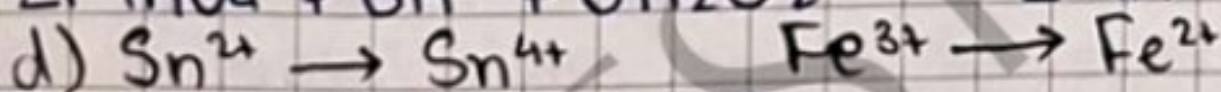
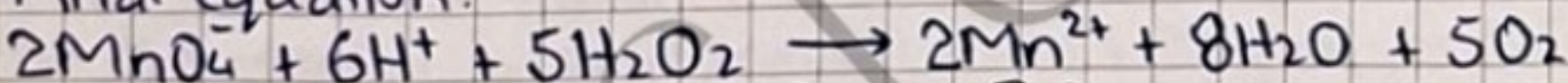


Combine Half Reactions and Simplify:

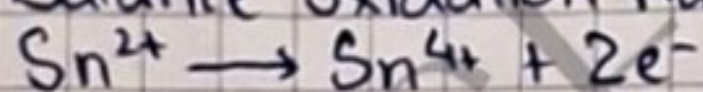
To balance the electrons transferred, the reduction half-reaction is multiplied by 2, and the oxidation half-reaction by 5



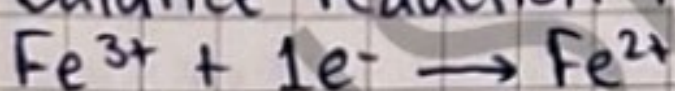
Final equation:



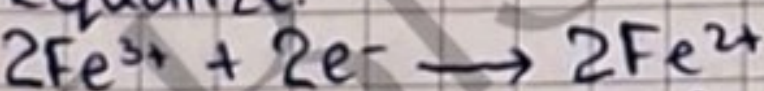
Balance oxidation half:



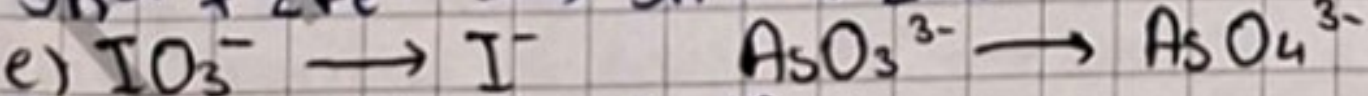
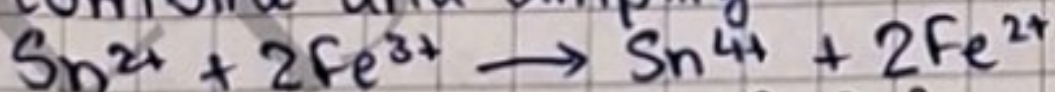
Balance reduction half:



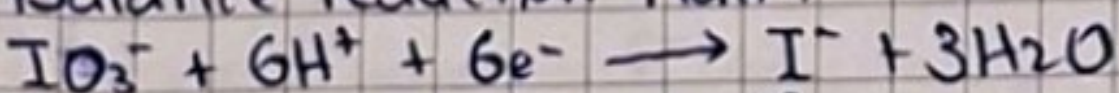
Equalize:



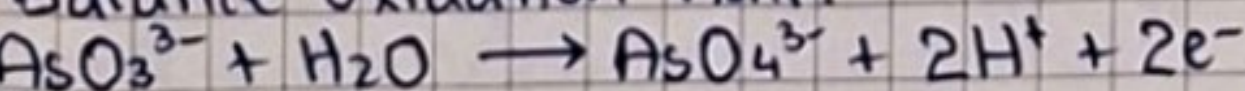
Combine and Simplify:



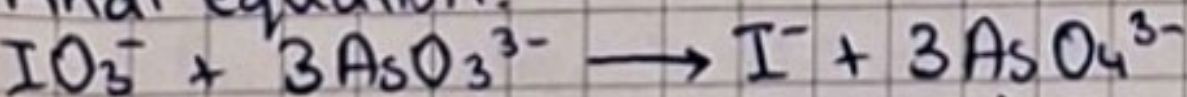
Balance reduction half:



Balance oxidation half:



Final equation:



In the reaction between potassium permanganate and iron (II) sulphate in an acidic solution $\text{MnO}_4^- + \text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + \text{Fe}^{3+}$

a) Identify the oxidation states of manganese and iron before and after the reaction

Manganese in $\text{MnO}_4^- \rightarrow +7$ and in $\text{Mn}^{2+} \rightarrow +2$

Iron in $\text{Fe}^{2+} \rightarrow +2$ and in $\text{Fe}^{3+} \rightarrow +3$

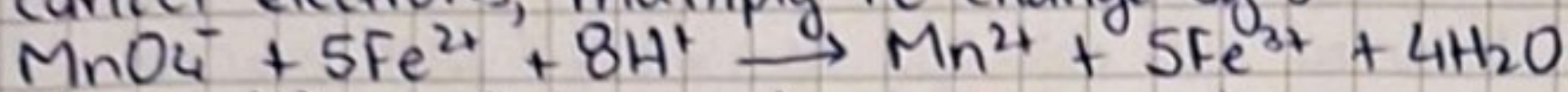
b) Explain which species is oxidized and which is reduced

$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ is oxidized (loss of 1e^-).

$\text{Mn}^{7+} \rightarrow \text{Mn}^{2+}$ is reduced (gain of $5e^-$)

c) Balance the redox reaction using changes in oxidation number.

Change in oxidation number: $\text{Mn} +7 \rightarrow +2$ (gain $5e^-$). $\text{Fe} +2 \rightarrow +3$ (loss $1e^-$). To cancel electrons, multiply Fe change by 5



d) Identify oxidizing and reducing agents.

Oxidizing agent is MnO_4^- (it is reduced, so it oxidizes Fe^{2+})

Reducing agent is Fe^{2+} (it is oxidized, so it reduces MnO_4^-)

Explain why magnesium can displace zinc from zinc sulphate solution but copper can not. Predict the outcome of placing a zinc strip in a copper (II) sulphate solution, including the balanced chemical equation.

Magnesium is more reactive than zinc and is placed above zinc in the activity series of metals. Therefore, magnesium has a greater tendency to lose electrons from Mg^{2+} ions.

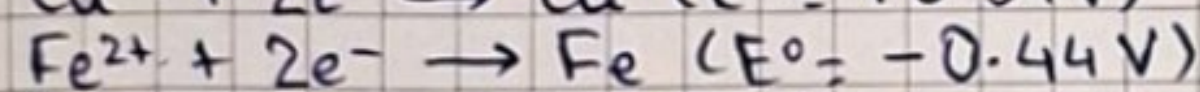
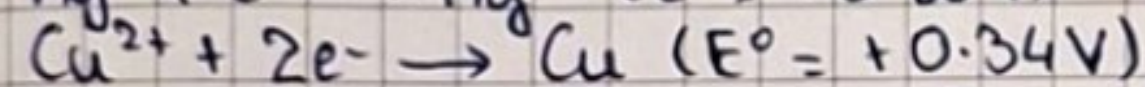
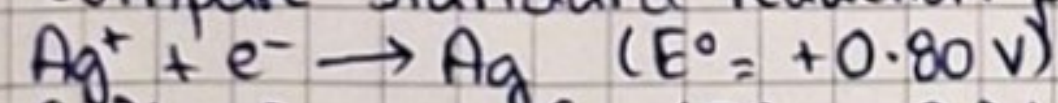
Due to this higher reactivity, magnesium can displace zinc from zinc sulphate solution.

However, copper is less reactive than zinc, so it cannot displace zinc from its compound.

When a zinc strip is placed in copper (II) sulfate solution, zinc being more reactive displaces copper from the solution. Zinc becomes Zn^{2+} by losing electrons, while Cu^{2+} gains electrons and forms copper metal. $\text{Zn(s)} + \text{CuSO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{Cu(s)}$. This shows that zinc is oxidized and copper ions are reduced, resulting in deposition of copper on the zinc strip.

Predict the outcome of mixing aqueous solutions of FeSO_4 and AgNO_3 with Cu based on their standard electrode potentials. Explain your reasoning.

Compare standard reduction potentials (E°):



A species with higher (more positive) reduction potential has a greater tendency to gain electrons (be reduced). A metal will be oxidized if its corresponding reduction potential is lower than that of the ion it is placed with.

Copper placed in AgNO_3 (Ag^+) solution:

Ag^+ has a higher reduction potential (+0.80 V) than Cu^{2+} (+0.34 V), so Ag^+ will be reduced and Cu will be oxidized. The cell potential is positive:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80 - 0.34 = +0.46 \text{ V}$$

So the reaction is spontaneous: $\text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)}$

Silver metal plates out on the copper strip. Oxidizing Agent Ag^+ . Reducing agent Cu

Copper placed in FeSO_4 (Fe^{2+}) solution:

Fe^{2+} has a much lower reduction potential (-0.44 V) than Cu^{2+} (+0.34 V). That means Fe^{2+} is less likely to be reduced than Cu^{2+} , copper metal is less reactive than iron metal in this sense, so copper will not be oxidized by Fe^{2+} . The cell potential would be negative:

$$E^\circ_{\text{cell}} = E^\circ_{\text{Fe}^{2+}/\text{Fe}} - E^\circ_{\text{Cu}^{2+}/\text{Cu}} = -0.44 - 0.34 = -0.78$$

So the reaction is non-spontaneous and no displacement occurs.

No reaction, the copper strip remains unchanged and iron stays as Fe^{2+} in solution

Using the Nernst equation, calculate the cell potential of a galvanic cell with the following half-reactions of $\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$ ($E^\circ = -0.76 \text{ V}$) and $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ ($E^\circ = +0.34 \text{ V}$)

if the concentration of Zn^{2+} is 0.1 M and Cu^{2+} is 1.0 M.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

Cathode = Cu^{2+}/Cu (because of higher E°)

Anode = Zn^{2+}/Zn

$$E^\circ_{\text{cell}} = 0.34 - (-0.76) = 1.10 \text{ V}$$

Now, for a reaction involving 2 electrons ($n=2$)

$$E = E^\circ - 0.0592/n \log \text{Product/Reactant}$$

$$\therefore Q = \text{Zn}^{2+}/\text{Cu}^{2+} = 0.1/1.0 = 0.10$$

$$E = 1.10 - 0.0592/2 \log (0.10)$$

$$E = 1.10 - 0.592/2 (-1)$$

$$E = 1.13 \text{ V (approximately)}$$

A voltaic cell is constructed using a copper electrode in a 1M solution of copper (II) sulphate and a zinc electrode in a 1M zinc sulphate solution.

a) Calculate the cell potential under standard conditions using the given

Class

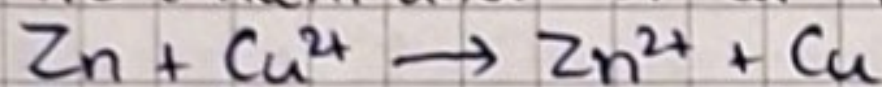
Standard reduction potentials: $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34\text{V}$ and $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76$

Cathode: Cu^{2+}/Cu

Anode: Zn^{2+}/Zn

$$E_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.34 - (-0.76) = 1.10\text{V}$$

b) Discuss how the Nernst equation can be used to predict the effect of changing the concentration of Cu^{2+} ions on the cell potential.



The Nernst equation (at 25°C , $n=2$) is:

$$E = E^\circ - 0.0592/n \log Q = 1.10 - 0.0592/2 \log ([\text{Zn}^{2+}]/[\text{Cu}^{2+}])$$

So, when $[\text{Cu}^{2+}]$ increases, the reaction quotient $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}]$ decreases (smaller $Q \Rightarrow \log Q$ more negative), making the subtraction term negative and increasing E . Conversely, decreasing $[\text{Cu}^{2+}]$ increases Q , lowers E .

Short numeric illustration with $\text{Zn}^{2+} = 1.0\text{M}$:

$$\text{If } [\text{Cu}^{2+}] = 1.0\text{M } E = 1.10\text{V}$$

$$\text{If } [\text{Cu}^{2+}] = 0.1\text{M, using Nernst equation, } Q = 10, E = 1.0704\text{V (decreases)}$$

$$\text{If } [\text{Cu}^{2+}] = 2.0\text{M, using Nernst equation, } Q = 0.5, E = 1.109\text{V (increases)}$$