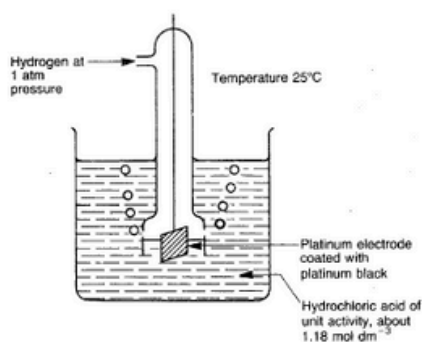


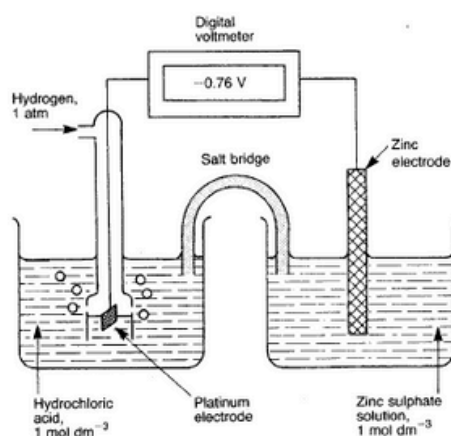
ELECTROCHEMISTRY

REDOX

EQUILIBRIA



A Standard hydrogen electrode (S.H.E)



Apparatus to measure the standard electrode poten-



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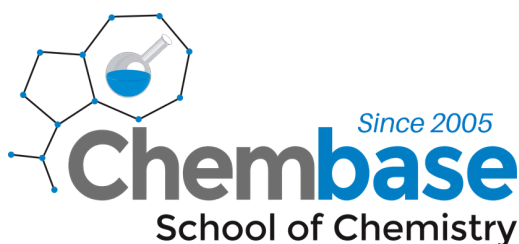
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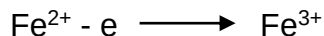
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1. Define the term Oxidation number

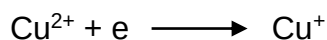
Oxidation number is the combining power of an atom, of an element or compound.

2. Define oxidation & reduction in terms of oxidation number

Increase in oxidation number is oxidation.



Decrease in oxidation number is reduction.

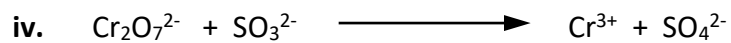
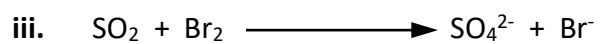
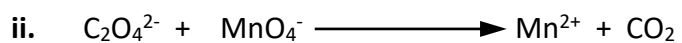
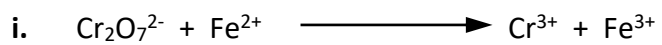


3. State the rules for balancing redox equations using the electron transfer method

- i) Write the oxidation half equation and balance it with respect to elements and charges. Electrons are usually put on the right-hand side of the oxidation half equation.
- ii) Similarly write a half equation for reduction and balance it with respect to elements and charges. Electrons are usually put on the left-hand side of the reduction half equation.
- iii) When balancing equations in an acidic medium, H^{+} is added to the side where oxygen is present and H_2O is added to the opposite side to balance it.
- iv) Equalize the number of electrons in both half equations.
- v) Add the equations so that electrons cancel off each other.

Eg:-

4. Balance the following equations by the electron transfer method



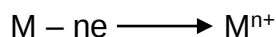
5. **Define the term redox equilibrium & explain how this is achieved when a metal is immersed in an aqueous solution of its salt.**

Redox equilibrium is a balanced position where the oxidant is reduced by accepting electrons while the reductant loses electrons and gets oxidized under the same conditions.

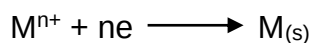
Eg: oxidant + e $\rightleftharpoons$ reductant

This can be demonstrated when a metal is immersed in an aqueous solution of its salt.

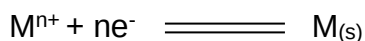
The metal gets oxidized by losing electrons and releasing M^{n+} ions to the solution.



Also, the aqueous M^{n+} ions can get reduced by accepting electrons and deposit as metal atoms on the metal.

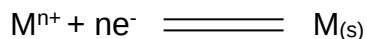


When the rate of both, oxidation and reduction become equal, then the system will achieve redox equilibrium, at constant temperature, pressure and concentration.



6. **Define the term electrode potential hence explain how this potential is formed when a metal is immersed in an aqueous solution.**

The power or potential of an aqueous species to oxidize or reduce is called the electrode potential (redox potential or reduction potential)



The forward reaction indicates the tendency (potential) of metal ions to get reduced and the backward reaction indicates the tendency (potential) to get oxidized.

As the metal ion loses electrons and cations, the electrons released will be acting as a layer of electrons on the surface of the metal. Similarly, the metal cations formed, surround the electrons (electric double layer). This results in an electric potential known as Electrode Potential at the metal surface.

7. State & explain the factors which effects the electrode potential

- i) **The nature of the metal**: Reactive metals will show higher electrode potential than less reactive metals because the ionization is faster when the metal is reactive.
- ii) **Temperature**: For exothermic redox half equations an increased temperature drives the equilibrium to the left thus makes the value of the electrode potential less positive (or more negative) & vice versa for endothermic half equations.
- iii) **Concentration & Pressure**: Increase in concentration & pressure of the aqueous solution will decrease the ionization of metal to metal ions. Therefore, the electrode potential will decrease with increased concentration & pressure

If the concentration of the species of the left side increases in the equilibrium reaction the equilibrium will shift to right causing increased electrode potential. Likewise, if the concentration of the species of right side is increased the equilibrium will shift to left causing the value of the electrode potential to be lower.

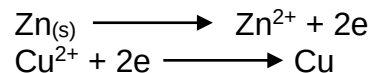
8. Explain how the electrode potential can be measured

At constant temperature, concentration & pressure then the variation of electrode potential depends only on the nature of the metal. However, it is not possible to measure the electric potential of a single electrode. There is no instrument available to measure single electric potential, but there are instruments to measure the potential difference

9. Describe an experiment to show the evidence for the existence of an electric potential when a metal is dipped in a solution of its salt

When two metals with different reactivity is immersed in aqueous solutions of their salts & connected by a salt bridge, and when the two metals are connected to a **high resistance voltmeter** as shown below, the high resistance voltmeter will show a reading indicating a potential difference between the two electric potentials. The high resistance of the voltmeter is deliberately designed to stop any current flow in the circuit. This means it draws very little current from the circuit and the voltage you are trying to measure doesn't drop.

Zinc dissolves from the zinc rod and copper is deposited on the copper rod.



Zinc acts as a negative terminal and copper as a positive terminal.

Zinc is the negative pole as electrons are lost. This terminal where oxidation occurs is referred to as the Anode and the positive terminal where reduction occurs (gaining of electrons) is referred to as the Cathode.

The salt bridge is a filter paper dipped in a salt of KNO_3

The purpose of the salt bridge is to complete the circuit by allowing the ions to move from one cell to the other. It also provides cations and anions to replace those consumed at the electrodes and balance the charges.

This system is called an electric cell and the two redox equilibrium systems are called electrical half cells.

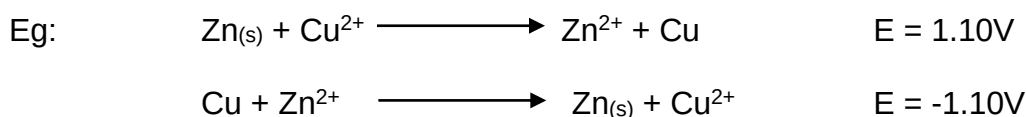
The convention is to write the anode reaction (oxidation reaction) on the left followed by two parallel short lines (||) to represent the salt bridge (also called as the solution junction) followed by the cathode reaction (Reduction reaction) (Reduction occurs at the cathode - RED CAT) on the right side of the salt bridge. (Reduction – Right). The physical state symbols, Standard temperature, concentration should be indicated. (if gaseous system pressure should be written instead of the concentration).



The above representation is also referred to as the cell diagram.

10. Define the term electromotive force (e.m.f)

The maximum potential difference produced by an electrical cell with respect to given metals is known as the electromotive force.



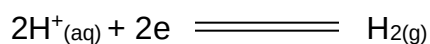
11. Describe the standard Hydrogen electrode & its importance

The electromotive force can only be measured in a complete circuit with two electrodes and is impossible to obtain the electrode potential for a single half cell, in other words only differences in potential are measurable. This can be done by arbitrarily assigning an electrode potential of zero to one particular half cell and comparing other half cells with this standard.

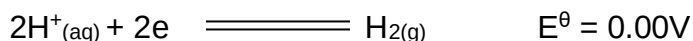
The standard chosen is not a metal, but hydrogen. Therefore, it is called a standard hydrogen electrode (S.H.E) [or standard hydrogen half cell]

The S.H.E consists of H₂ gas bubbling over a platinum electrode immersed in 1 mol dm⁻³ dilute acid at standard conditions of H₂ gas at 1 atm (101kPa) pressure and 25⁰C temperature. The platinum electrode is plated with finely divided platinum in order to make the absorption of H₂ gas easier. H₂ gas is absorbed by the inert platinum surface. Platinum acts as a catalyst to allow equilibrium between the H₂ gas and the H⁺ in solution. The electrode should be partially immersed in the solution and the other half in the gas.

The reaction that takes place in the S.H.E is



Under the standard conditions the e.m.f of the S.H.E is defined to be zero volts. The standard electrode potential is given the symbol E^θ The superscript 'θ' indicates standard conditions.



The Cell Diagram:

12. State the functions of 'Pt' electrode in the S.H.E

- 'Pt' does not ionize itself, therefore it acts as an inert metal connection to the H_2/H^+ system.
- 'Pt' allows H_2 gas to be absorbed on to its surface
- Finely divided 'Pt' increases the surface area so that the equilibrium between H_2 & H^+ is established rapidly.

13. Define the term Standard electrode potential (Standard reduction potential)

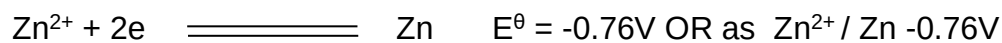
Standard electrode potential, E^θ , of an electrode is its potential (e.m.f) measured relative to the standard hydrogen where the concentrations of all solutions are 1 mol dm^{-3} & the pressure of all gases are 1 atm & the temperature is 298K.

14. Describe how standard electrode potentials are measured

The E^θ can be measured by connecting the metal electrode which is immersed in its metal ions (concentration of 1 mol dm^{-3}) to the S.H.E & measure the voltage between the two. Both half cells should be connected by a salt bridge at a temperature of 298K & pressure of 1atm.

Eg:- below is an apparatus setup to measure the standard electrode potential of Zinc.

The standard electrode potential of a piece of zinc dipped into a solution of 1mol dm^{-3} Zn^{2+} ions, can be written either as:-



The oxidized form (one with the higher oxidation number) is written on the left, followed by a slash and then the reduced form on the right. (Reduction - Right)

If the standard electrode potential of a gas has to be measured, the metal electrode compartment has to be replaced with a platinum plate dipped into a 1mol dm^{-3} solution of anion of the gas.

Eg:- Cl_2 gas at 1atm bubbling over platinum which is dipped in 1mol dm^{-3} NaCl solution.

15. Describe and explain the below 3 main types of half cells used in the calculation of standard electrode potentials.

- metal – metal ion half cell
- non metal – non metal ion half cell
- ion – ion half cell.

Metal – metal ion half cell:

The apparatus setup to measure the standard electrode potential of Zinc mentioned earlier is an example for a metal – metal ion half-cell. The zinc is the negative terminal as it is oxidized to give out electrons. And Hydrogen is the positive terminal as it is reduced.



Always oxidation takes place at the negative terminal (Anode) & Reduction takes place at the positive terminal (cathode)

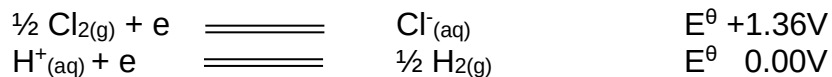
NOTE: The more positive reduction potential (where reduction occur) is the positive terminal & the less positive / more negative reduction potential is the negative terminal.

Non metal – Non metal ion half cell:

In half cells where metals are not present the electrical contact with the solution is achieved using an inert platinum wire or platinum foil. The redox equilibrium is achieved at the surface of

the platinum electrode. The electrode should be partially immersed in the solution and the other half in the gas.

Eg: measuring the standard electrode potential of Cl_2/Cl^- half cell.



The Cl_2/Cl^- half cell forms the positive terminal (reduction as more positive) & the S.H.E is the negative terminal. As a result H_2 molecules will lose electrons to the $\text{Cl}_2 / \text{Cl}^-$ half cell.

The Cell Diagram:

Ion – Ion half cell:

When half-cell consists of ions of the same element in different oxidation states (eg: $\text{Fe}^{2+}, \text{Fe}^{3+}$ system and $\text{MnO}_4^-, \text{H}^+, \text{Mn}^{2+}$ system) an inert electrode such as platinum is used. The concentration of each ion should be 1M.

The Cell Diagram:

16. **Table of Standard Electrode Potentials.**
(REFER LAST PAGE FOR DETAILED DATA BOOKLET VALES)

REDUCTION HALF-EQUATION		E°/V
OXIDISED FORM + ne ⁻ ⇌	REDUCED FORM	
Li ⁺ (aq) + e ⁻	⇌ Li(s)	-3.03
Rb ⁺ (aq) + e ⁻	⇌ Rb(s)	-2.93
K ⁺ (aq) + e ⁻	⇌ K(s)	-2.92
Ca ²⁺ (aq) + 2e ⁻	⇌ Ca(s)	-2.87
Na ⁺ (aq) + e ⁻	⇌ Na(s)	-2.71
Mg ²⁺ (aq) + 2e ⁻	⇌ Mg(s)	-2.37
Al ³⁺ (aq) + 3e ⁻	⇌ Al(s)	-1.66
Zn ²⁺ (aq) + 2e ⁻	⇌ Zn(s)	-0.76
Fe ²⁺ (aq) + 2e ⁻	⇌ Fe(s)	-0.44
PbSO ₄ (s) + 2e ⁻	⇌ Pb(s) + SO ₄ ²⁻ (aq)	-0.36
V ³⁺ (aq) + e ⁻	⇌ V ²⁺ (aq)	-0.26
Ni ²⁺ (aq) + 2e ⁻	⇌ Ni(s)	-0.25
Pb ²⁺ (aq) + 2e ⁻	⇌ Pb(s)	-0.13
2H ⁺ (aq) + 2e ⁻	⇌ H ₂ (g)	0.00
S ₄ O ₆ ²⁻ (aq) + 2e ⁻	⇌ 2S ₂ O ₃ ²⁻ (aq)	+0.09
SO ₄ ²⁻ (aq) + 4H ⁺ (aq) + 2e ⁻	⇌ H ₂ SO ₃ (aq) + H ₂ O(l)	+0.17
Cu ²⁺ (aq) + 2e ⁻	⇌ Cu(s)	+0.34
VO ²⁺ (aq) + 2H ⁺ (aq) + e ⁻	⇌ V ³⁺ (aq) + H ₂ O(l)	+0.34
IO ⁻ (aq) + H ₂ O(l) + 2e ⁻	⇌ I ⁻ (aq) + 2OH ⁻ (aq)	+0.49
I ₂ (aq) + 2e ⁻	⇌ 2I ⁻ (aq)	+0.54
Fe ³⁺ (aq) + e ⁻	⇌ Fe ²⁺ (aq)	+0.77
Ag ⁺ (aq) + e ⁻	⇌ Ag(s)	+0.80
ClO ⁻ (aq) + H ₂ O(l) + 2e ⁻	⇌ Cl ⁻ (aq) + 2OH ⁻ (aq)	+0.89
NO ₃ ⁻ (aq) + 3H ⁺ (aq) + 2e ⁻	⇌ HNO ₂ (aq) + H ₂ O(l)	+0.94
VO ₂ ⁺ (aq) + 2H ⁺ (aq) + e ⁻	⇌ VO ²⁺ (aq) + H ₂ O(l)	+1.00
Br ₂ (aq) + 2e ⁻	⇌ 2Br ⁻ (aq)	+1.09
MnO ₂ (s) + 4H ⁺ (aq) + 2e ⁻	⇌ Mn ²⁺ (aq) + 2H ₂ O(l)	+1.23
Cr ₂ O ₇ ²⁻ (aq) + 14H ⁺ (aq) + 6e ⁻	⇌ 2Cr ³⁺ (aq) + 7H ₂ O(l)	+1.33
Cl ₂ (aq) + 2e ⁻	⇌ 2Cl ⁻ (aq)	+1.36
Mn ³⁺ (aq) + e ⁻	⇌ Mn ²⁺ (aq)	+1.51
MnO ₄ ⁻ (aq) + 8H ⁺ (aq) + 5e ⁻	⇌ Mn ²⁺ (aq) + 4H ₂ O(l)	+1.51
MnO ₄ ⁻ (aq) + 4H ⁺ (aq) + 3e ⁻	⇌ MnO ₂ (s) + 2H ₂ O(l)	+1.70
F ₂ (g) + 2e ⁻	⇌ 2F ⁻ (aq)	+2.87
F ₂ (g) + 2H ⁺ (aq) + 2e ⁻	⇌ 2HF(aq)	+3.06

OXIDISED FORM IS A POOR OXIDISING AGENT

OXIDISED FORM

OXIDISING POWER OF

OXIDISED FORM IS A STRONG OXIDISING AGENT

REDUCED FORM IS A STRONG REDUCING AGENT

REDUCED FORM

REDUCING POWER OF

REDUCED FORM IS A POOR REDUCING AGENT

17. Explain how to compare the relative strengths of oxidizing & reducing agents based on the standard electrode potentials

Standard electrode potentials give a direct measure of the relative oxidizing & reducing power of species. The half equations are written as reductions.

The half equation with the most positive (largest) reduction will be the most powerful oxidizing agent. The species with smallest (most negative) reduction potential will be the least powerful oxidizing agent.

The half equation with the most negative (smallest) reduction potential will be the most powerful reducing agent & vice versa.

- ❖ The table of electrode potential is arranged so that the strongest oxidizing agent (F_2) which has the most positive value for E^θ at the bottom & the weakest oxidizing agent Li^+ which has the most negative value at the top.

18. Describe the use of standard electrode potentials to predict the oxidizing & reducing half equations in a redox reaction.

As half equations are written as reductions in the electrode potential table, one equation has to be reversed as to oxidation & reductions to occur simultaneously.

The half equations with the most negative E^θ value is the reducing agent hence undergo oxidation. As oxidation is losing electrons this should be reversed.

Eg:- The reaction between 'Zn' & 'Cu' ions. Will 'Zn' metal reduce Cu^{2+} ions or 'Cu' metal will reduce 'Zn' ions

As Zn^{2+} has the highest negative value this should be oxidized. (lose electrons)

The half equation is reversed to provide electrons & form the more positive system (the oxidized form) the Cu^{2+} takes up the electrons.

By combining both half equations,

- ❖ When a half equation is reversed, the sign of $E^\ominus$ is changed. If the reduced form is negative $E^\ominus$ then the reversed form will have the positive of the same value. If the reduced form is positive, then the reversed will be negative.
- ❖ If the equation is doubled or halved the $E^\ominus$ value is not altered but remains the same.
- ❖ The use of $E^\ominus$ values relate only to standard conditions. Changes in temperature, pressure or concentration will affect the $E^\ominus$ value.

19. Explain how to predict the reactivity of metals & non- metals from the reduction potential data.

The half equations are written as reduction, if the reduction potential has a lesser positive value (more negative) for metals, then such metal will get oxidized easily. Meaning the backward reaction which is metal turning to metal ion is more feasible. Such metal where oxidation occur easily is more reactive than metals with greater positive / less negative electrode potential.

As for non-metals, if the reduction potential is more positive / less negative such nonmetal will be more reactive as non-metals undergo reduction unlike metals which undergo oxidation.

20. Describe how the standard electrode potentials can be used to predict the feasibility of a reaction. Hence define **Standard Cell Potential.**

The standard electrode potentials indicate the relative strengths of oxidizing and reducing agents. The overall potential / cell potential is found by adding the reduction / oxidation half equations.

Reactions with an overall positive $E^\ominus_{\text{cell}}$ are energetically feasible where as those with an overall negative $E^\ominus_{\text{cell}}$ are not feasible in the given direction but feasible in the opposite direction.

21. Write half-equations for the below reactions hence calculate the standard electrode potentials.

I. Ag^+ / Ag half cell where silver rod is +ve terminal & the E^θ is 0.80V (w.r.t. S.H.E)

II. $\text{Cl}_2 / \text{Cl}^-$ half cell where Cl_2 half cell is +ve terminal & the E^θ is 1.36V (w.r.t. S.H.E)

III. $\text{Fe}^{2+} / \text{Fe}$ half cell where iron rod is -ve terminal & the E^θ is 0.44V (w.r.t. S.H.E)

IV. $\text{Cr}^{2+} / \text{Cr}$ half cell where 'Cr' rod is -ve terminal & the E^θ is 0.91V (w.r.t. S.H.E)

22. Explain the different methods used to measure the standard cell potential in order to determine the feasibility of a reaction.

□ **Method I**

Write the half equations and reverse the less positive / more negative half equation as to represent oxidation thus add the two half equations. The more positive / less negative one should be written as reduction. When the equation is reversed then the sign of the reduction potential also will reverse.

□ **Method II**

The cell voltage / potential also can be found by subtracting the less positive E^θ value (more negative) from the more positive E^θ value (less negative).

□ **Method III**

With the help of the below equations;

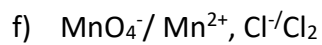
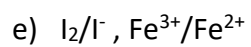
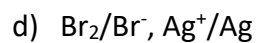
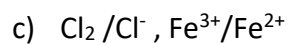
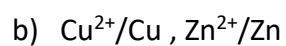
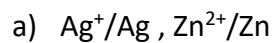
$$E^\theta_{\text{cell}} = E^\theta_{\text{RHS}} - E^\theta_{\text{LHS}}$$

RHS = Right Hand Side (Reduction half equation)
LHS = Left Hand Side (Oxidation half equation)

OR

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

23. Calculate the Standard cell potential of the below electrochemical cells by writing the relevant half equations.



24. Predict whether a reaction will occur between following species, indicating the half equations & standard cell potential values

i. Cl_2 & I^-

ii. F_2 & Na

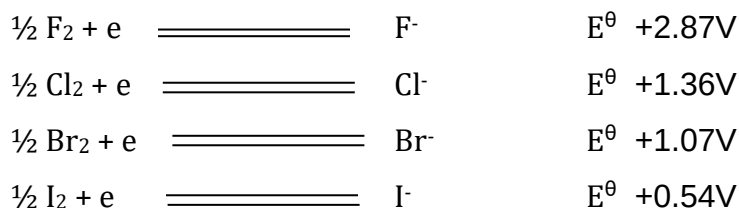
iii. F^- & Na^+

iv. I_2 & Br^-

v. F_2 & Na^+

25. Explain with the help of E^θ values why halogen higher in group 17 displaces a lower halogen from a solution of its halide ion.

By analyzing the below electrode potential values of the halogen it can be said that down group 17 the reducing ability decreases due to decrease in the positive value of E^θ and the ability of the halide ion to act as reducing agents increases.



The halogen with greater positive E^θ value (more reactive) can displace a halogen with less positive E^θ value (less reactive) from an aqueous solution of its salt. Which means the halogen with the less positive E^θ value will undergo oxidation as the halide ion is converted to halogen thus act as a reducing agent while the other acts as an oxidizing agent.

26. With the help of the above E^θ values of the halogens construct redox equations to show the why Cl_2 is more reactive than Br_2 and why Br_2 is more reactive than I_2 .

27. Explain how to predict the direction of the electron flow using E^θ values.

The direction of the electron flow can be predicted by comparing the E^θ values of the two half cells. The electron flow will be from oxidation half-cell to the reduction half-cell. Meaning from the more negative (or less positive) half-cell to the more positive (or less positive) half-cell.

In Chemistry always think in terms of electron flow not current flow. The electrons flow via the external circuit and not through the electrolyte. Only ions travel through the electrolyte.

In an electrochemical cell electrons flow from the negative pole to the positive pole thus the more positive pole attracts electrons.

28. Describe how a feasible reaction will not take place in practice.

- **Non-standard conditions :**

The standard cell potentials are calculated by using the standard reduction potentials given in the data tables. A feasible reaction under standard conditions may not be feasible under non-standard conditions.

- **Higher activation energy :**

Feasible reactions with respect to the cell potential may not take place in reality due to high activation energy.

Eg:

- i. Reaction between hydrogen & oxygen gas is feasible under standard conditions as the E_{cell} is positive but the reaction does not occur unless ignited.
- ii. Reaction between hydrogen gas and CuSO_4 should result a precipitate of Cu as the E_{cell} is positive. But such is never observed as the H-H bond has higher activation energy.

NOTE: However, if the E^θ values differ by more than 0.30V, predictions based on E values are usually correct.

29. Redox Titrations

- **Potassium manganate (VII) titrations: -**

KMnO_4 can be used as a self indicator due to the intense purple colour and gives a pink colour even in very dilute solution. In titrations involving KMnO_4 it is usually held in the burette, so the pink solution can be easily observed at the end point.

The half reaction of KMnO_4 in acidic solution is given as:-

KMnO_4 oxidizes organic compounds as it is a strong oxidizing agent. KMnO_4 cannot be obtained in a state of high purity. Therefore, solutions of KMnO_4 should be standardized to know its accurate concentrations. Usually $\text{Na}_2\text{C}_2\text{O}_4$ (Sodium ethanedioate) is commonly used as a standard to standardize KMnO_4 solution.

The reaction after the oxidation of ethanedioate ion is

Therefore, the overall reaction:

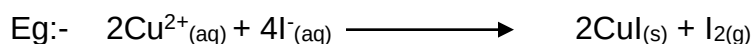
The reaction initially is quite slow. The product Mn^{2+} catalyses the reaction hence makes it much faster. A reaction where the product catalyses the reaction is called an autocatalytic.

□ **Sodium thiosulphate titrations:-**

The thiosulphate ions are oxidized to tetrathionate ions ($\text{S}_4\text{O}_6^{2-}$) at the presence of the oxidizing agent I_2 , where I_2 reduces itself to I^- ions. The yellow brown colour of I_2 gradually disappears as the reaction proceeds.

Titration of I_2 with $\text{S}_2\text{O}_3^{2-}$ the solution turns from yellow brown to colourless at the end point. As the colour difference is difficult to observe, freshly prepared starch solution is added to the conical flask at closer to the end point. When starch is added the solution turns deep blue due to the formation of starch iodine complex which turns colourless at the end point.

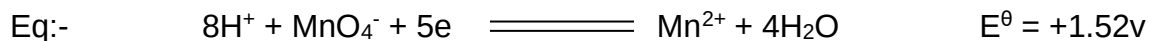
The above titration can be used to determine the amount of copper present in brass, or the number of water molecules of water of crystallization in hydrated CuSO_4



In the above reaction I^- ions are oxidized to I_2 therefore the liberated I_2 can be titrated against sodium thiosulphate solution to find the amount of I_2 , thus the amount of Cu^{2+} can be found.

30. Predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ions.

Increasing the concentration of the reactants of the redox half equation will shift the position of the equilibrium towards products as to the Le Chatelier's principle & therefore will increase the electrode potential value. Under this nonstandard condition symbol E is used without the superscript θ . As a result, E becomes more positive or less negative. Likewise, when the concentration of the products is increased the equilibrium will shift towards reactant resulting E value to be less positive or more negative and vice versa when the concentration is decreased (less than 1M).



Increasing the H^+ ion concentration or MnO_4^- concentration will increase the E value.

If the concentration of the both oxidized and reduced form was decreased by the same amount, it will make no difference to the electrode potential. Any tendencies for the equilibrium position to move will cancel out resulting no overall change. In such cases E will be equal to $E^\ominus$ value. (Explained further under Nernst equation)

31. Explain how feasibility of a reaction can be predicted under non-standard conditions.

If the difference of $E^\ominus$ values of the two half cells is over 0.30V, then the reaction predicted under standard conditions will occur. Therefore, a reaction may occur under non-standard conditions if the difference is much greater than 0.30V. But if it is less than 0.30V such reaction will not be feasible.

THE NERNST EQUATION

Nernst equation is helpful to calculate the electrode potential under non-standard conditions. It is used to deduce the value of the electrode potential as the concentration of aqueous species changes from standard (1M) to non-standard conditions.

There are different versions of the Nernst equation, the below is helpful to find the electrode potential due to the change in concentration of ions where as other form is helpful deduce the effect of temperature which is not relevant at this level.

$$E = E^\ominus + (0.059 / Z) \log_{10} \frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

Where,

E is the electrode potential under non-standard conditions,

$E^\ominus$ is the standard electrode potential,

Z is the number of electrons transferred in the reaction,

[oxidized species] refers to the concentration of the oxidized form (higher oxidation state),

[reduced species] refers to the concentration of the reduced form (lower oxidation state).

- **Discuss the factors to be considered when applying the Nernst equation to the below systems, Cu/Cu^{2+} , $\text{Fe}^{3+}/\text{Fe}^{2+}$, Cl_2/Cl^-**

- **$\text{Fe}^{3+}/\text{Fe}^{2+}$ system;**

Oxidized species is the one in the higher oxidation state – which is Fe^{3+} ions.
The reduced species is the one in the lower oxidation state – which is Fe^{2+} ions.

The square brackets indicate concentrations in mol dm^{-3} .

If the concentration of both $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions increase / decrease from the standard condition to the same extent then $\log 1$ will be equal to zero hence $E = E^\theta$

- **Cu/Cu^{2+} system;**

The oxidized species is Cu^{2+} ; whereas reduced species is Cu. The concentration of the solid metal copper is taken as 1M as in equilibrium due to their activity is 1.

As two electrons are transferred the value of Z will be 2.

- **Cl_2/Cl^- system;**

The oxidized species will be Cl_2 , and the reduced species is Cl^- . Again, the concentration of Cl_2 gas is taken as 1M.

As Cl_2 gives 2Cl^- the concentration of Cl in the Nernst equation should be squared as in equilibrium. And the Z will be 2 as two electrons are transferred.

- **Calculate the electrode potentials of below half systems at 298K;**

I. Cu^{2+}/Cu where the concentration of aqueous ions is 0.01M

II. $\text{Cl}_2 / \text{Cl}^-$ where the concentration of aqueous ions is 1.5M

III. $\text{Fe}^{3+}/\text{Fe}^{2+}$ where the concentration of ions are 0.1M & 0.02M respectively

32. Describe the application of electrode potentials in the construction of simple storage cells.

Cells generate an electric current by a chemical action. A cell is made by opposing any two electrode systems of different electrode potential. The electrode with more negative electrode potential provides (negative pole) & the electrode with more positive electrode potential accepts electrons (positive pole)

Redox reaction occurs in a cell. Oxidation & reduction occur in separate half cells & the electrons pass through the external wire under the voltage difference of the two half cells, generating an electric current.

A simple illustration of an electrical cell could be shown as below. These cells are called primary cells. The redox reactions occur until the concentration of the reactants decrease and the voltage of the cell drop. The function of the cell stops thus no longer can be used.

33. State the relationship between standard cell potential E_{cell} , Gibbs Free Energy & Faradays constant.

The Gibbs Free Energy is directly proportional to the overall cell potential. The relationship between Gibbs Free energy & cell potential can be represented by the following equation.

$$\begin{aligned} G &= \text{Gibbs Free Energy} \\ n &= \text{number of electrons involved in the cell reaction} \\ F &= \text{Faradays constant (96,500C)} \\ &\quad \text{(charge of one mole of electrons)} \\ E_{\text{cell}} &= \text{Overall Cell Potential} \end{aligned}$$

By combining the above equation with the equation $\Delta G = -T \Delta S^{\theta}_{\text{total}}$ the below relationship can be derived;

ELECTROLYSIS

1) A. What is meant by the term “Electrolysis”?

B. Define the below terms;

i. Electrodes :

ii. Electrolytic cell (Voltameter) :

2) Explain how electrolysis occurs?

3) A. Show what happens during electrolysis of **molten** NaCl using a detail labelled diagram.

B. Write the half reactions (cathode & anode reactions) & overall reaction of the above electrolysis of molten NaCl, indicate the oxidation & reduction.

Cathode reaction :

Anode reaction :

Overall reaction :

- 4) Write the observations of the electrolysis of molten lead (II) bromide.

Hence write the ionic equations representing the reactions at each electrode.

- 5) A. What are the additional ions present in an aqueous solution than in the molten solution?

B. Write all the ions available in the solutions of $\text{NaCl}_{(\text{aq})}$, dilute H_2SO_4 , $\text{CuSO}_{4(\text{aq})}$

C. Write the ionic half equations for the hydrolysis of H_2O

D. Describe the term '**selective discharge of ions**'

E. What are the factors that affect the selective discharge of ions?

F. Below shown is the table of electrochemical series* of cations & anions in order of their ease of discharge.

Poor oxidizing agent ↓ Strong oxidizing agent	Positive ions	Negative ions	Ease of discharge of ions increases downwards ↓
	Potassium (K^+)	Sulphate (SO_4^{2-})	
	Calcium (Ca^{2+})	Nitrate (NO_3^-)	
	Sodium (Na^+)	Hydroxide (OH^-)	
	Magnesium(Mg^{2+})	Chloride (Cl^-)	
	Aluminium (Al^{3+})	Bromide (Br^-)	
	Zinc (Zn^{2+})	Iodide (I^-)	
	Iron (II)(Fe^{2+})		
	Lead (II) (Pb^{2+})		
	Hydrogen (H^+)		
	Copper (II) (Cu^{2+})		
	Silver (Ag^+)		

*Electrochemical series is another way to compare reactivities. Each metal is placed in a circuit with a standard electrode called the hydrogen electrode. The voltages produce gives the above order of the electrochemical series. The metal ions in this series are closely parallel to the reactivity series.

- 7)** Explain the effect of the position of the group in the electrochemical series in selective discharge of ions

The cation which has the highest $E^\ominus$ value (more positive/ less negative) is most easily reduced at the cathode thus discharged as a solid or gas.

Similarly, the ease of discharge of the anion at the anode depends on the ease of oxidation. Least positive / more negative ion is selected for discharge as it undergoes oxidation.

NOTE : the above prediction is based on the standard conditions, if the concentration / temperature are non-standard, if the difference in electrode potentials are greater than 0.30V the reaction may occur as predicted.

- 8)** Explain the effect of the concentration of ions in selective discharge of ions

9) Similarly, explain the effect of the Nature of the electrode in selection discharge of ions

10) write the half equations, Overall equations & Observations in below Electrolysis;

Electrolysis of aqueous NaCl with carbon electrodes:

Cathode Reaction :

Anode Reaction :

Overall Reaction :

What is formed in the Solution :

What you can SEE (observations) :

What is the problem with collecting chlorine gas over water?

Electrolysis of aqueous H₂SO₄ with Carbon or Platinum electrodes:

Cathode Reaction :

Anode Reaction :

Overall Reaction :

What is formed in the Solution :

What you can SEE (observations) :

Electrolysis of aqueous CuSO₄ with Carbon or Platinum electrodes:

Cathode Reaction :

Anode Reaction :

Overall Reaction :

What is formed in the Solution :

What you can SEE :

Electrolysis of aqueous AgNO_3 with carbon electrodes:

Cathode Reaction :

Anode Reaction :

Overall Reaction :

What is formed in the Solution :

What you can SEE :

Electrolysis of aqueous CuSO_4 with Copper electrodes:

Cathode Reaction :

Anode Reaction :

Overall Reaction :

What is formed in the Solution :

What you can SEE :

- 12.** Describe what happens when CuSO_4 is electrolyzed by using Copper electrodes

ELECTROLYSIS CALCULATIONS

01.

- i. The mass of a substrate deposited in an electrode depends on what?
- ii. What is the unit where electric charge is measured?
- iii. What is the unit electric current is measured?

02.

- i. Define one Coulomb of charge
- ii. Write an equation to show the quantity of electricity (Q) when 'I' amps flow for 't' seconds

03. State the Faradays first law of electrolysis

04.

- i. Define the term 'Faraday'
- ii. One mole of electrons (faraday) is equal to how many Coulombs?
- iii. Therefore 1 faraday is equal to how many Coulombs?
- iv. State the relationship between Faraday constant, the Avogadro constant & the charge on the electron.

05.

- a) Calculate the value of Avogadro constant, given that Faraday constant 96500C & electronic charge $1.60 \times 10^{-19} \text{ C}$

- b) Describe the experiment to determine the value of Avogadro constant by the electrolytic method.

The value of the Avogadro's constant can be found by calculating the charge associated with one mole of electrons.

$$\text{Avogadro's constant (L)} = \frac{\text{charge of 1 mole of electrons}}{\text{charge of an electron}}$$

The charge of 1 mole of electrons can be found by the below simple electrolysis of CuSO_4 solution using copper electrodes.

The Experimental Procedure is as follows:

- Record the mass of the electrodes.
- Attach the electrode to a DC power supply, ammeter and a variable resistor (variable resistor is used in order to ensure constant flow of current) dip the electrodes in a solution of CuSO_4 .
- Pass a constant electric current for a given time period.
- Remove the electrodes and record the dry mass after washing with distilled water and propanone.
- Reweigh the cathode and anode.

The mass of the cathode increases as copper is deposited and the mass of the anode decrease as the Cu^{2+} ions from the anode moves into the cathode. It is preferable to measure the decrease in mass of the anode to know the mass deposited as not all the copper is stuck to the cathode well as some may leave the cathode during the washing process.

The calculation steps are as follows:

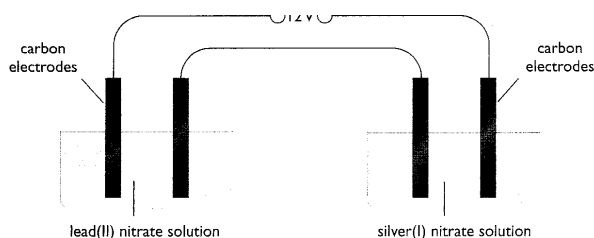
- Calculate the electrical charge ($Q=I.t$)
- If the above charge is required to deposit the mass at the cathode which was found calculate the charge required to deposit 1 mole of copper (which is 63.5g)
- As to the cathode equation 2 mole of electrons needed to deposit 1 mole of copper. Thus, the above answer of the charge is for 2 mole hence dividing the above charge by 2 we get the charge of 1 mole of electrons.
- If the charge of 1 electron is $1.6 \times 10^{-19}\text{C}$, dividing the charge of 1 mole of electrons by charge of an electron the value of the Avogadro's constant can be found

- 06.** Write the number of Faradays of electrical charge needed to reduce below ions to atoms
- 1 mole of Ag^{2+} to Ag
 - 1 mole of Al^{3+} to Al
 - 2 moles of Cu^{2+} to Cu
- 07.** Calculate the total charge in coulombs in below examples
- A current of 5A was passed through the electrolyte for 20 seconds
 - A current of 12A was passed through the electrolyte for 20 minutes
 - A current of 9A was passed through the electrolyte for 1 hour
- 08.** Write an equation to calculate the mass of ions deposited in electrolysis, hence define its symbols

- 09.** Calculate the mass of metal deposited at cathode in grams of below situations.
- When a current of 2.5A passes through a solution of Copper (II) Sulphate for 12 minutes
 - When a current of 5A passes through a solution of silver nitrate for 120 seconds
- 10.** Calculate the volumes of hydrogen & oxygen gas produced (at r.t.p) when a solution of dilute sulphuric acid is electrolysed using platinum electrodes, if a current of 10 amps flows for 15 minutes.
- 11.** How long would it take to deposit 10g of silver on the cathode during the electrolysis of silver (II) nitrate solution using a current of 5 amps?

12. During the electrolysis of lead (II) nitrate solution, lead is deposited at the cathode, & oxygen is released from the anode, if a current of 0.350 amp flows for 1000 seconds, Calculate
- The mass of lead deposited,
 - The volume of oxygen produced (at r.t.p)

13. Two solutions are connected as shown below in order to carry out electrolysis.



At the end of the electrolysis, it was found that 2.07 g of lead had been deposited on the cathode in the left beaker. Calculate

- The quantity of electricity that passed during the experiment
- The mass of silver deposited at the cathode