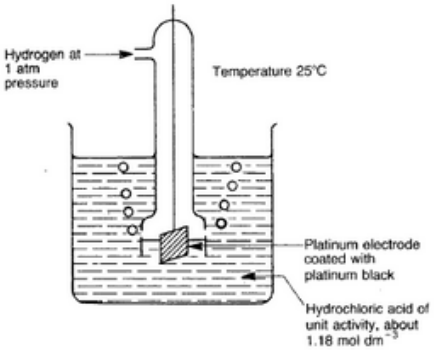
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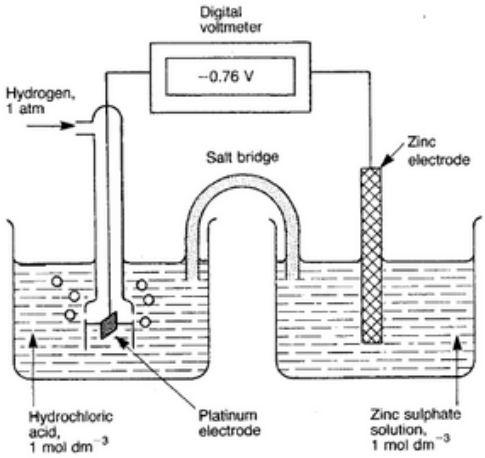
Pearson Edexcel

ELECTROCHEMISTRY

REDOX EQUILIBRIUM



A Standard hydrogen electrode (S.H.E)



Apparatus to measure the standard electrode potential

Since 2005
Chembase
School of Chemistry

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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.

$Fe^{2+} - e \longrightarrow Fe^{3+}$

Decrease in oxidation number is reduction.

$Cu^{2+} + e \longrightarrow Cu^{+}$

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

i. $Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+}$

ii. $C_2O_4^{2-} + MnO_4^{-} \longrightarrow Mn^{2+} + CO_2$

iii. $SO_2 + Br_2 \longrightarrow SO_4^{2-} + Br^{-}$

iv. $Cr_2O_7^{2-} + SO_3^{2-} \longrightarrow Cr^{3+} + SO_4^{2-}$

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.

$M - ne \longrightarrow M^{n+}$

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

$M^{n+} + ne \longrightarrow M_{(s)}$

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

$$M^{n+} + ne^- \rightleftharpoons M_{(s)}$$

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)

$M^{n+} + ne^- \rightleftharpoons M_{(s)}$

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 <u>electric potential</u> which is known as Absolute **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.

(The best instrument to use the potential difference is a potentiometer, as no electrons flow when it is used, as a result both half cells will be in equilibrium)

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

$Zn_{(s)} \longrightarrow Zn^{2+} + 2e$
$Cu^{2+} + 2e \longrightarrow Cu$

Zinc (more reactive) undergo oxidation hence acts as a negative terminal and copper as a positive terminal.

Zinc is the negative pole as electrons are lost. This terminal where oxidation occur 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. Theoretically, the salt bridge may contain any soluble salt, but neither ion of the salt should react with the ions of the electrolyte to produce a solid. KNO_3 is used as all K^+ & NO_3^- salts are soluble.

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. As Cu^{2+} is attracted from the solution to the electrode K^+ ions from the salt bridge replaces it. Also, the anion (SO_4^{2-}) from the same cell enters and travels through the salt bridge to the other half cell. Where excess cation (Zn^{2+}) from the solution enters the salt bridge and travels to the other cell whereas NO_3^- ions replaces the Zn^{2+} ions.

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

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

The maximum potential difference produced by an electrical cell with respect to given metals when no current flowing (no electrons flowing) is known as the electromotive force.

Eg: $Zn_{(s)} + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ E = 1.10V

$Cu + Zn^{2+} \longrightarrow Zn_{(s)} + Cu^{2+}$ E = -1.10V

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 H_2 gas bubbling over a platinum electrode immersed in 1 mol dm^{-3} dilute acid at standard conditions of H_2 gas at 100kPa (1 atm) pressure and 298K temperature. The platinum electrode is plated with finely divided platinum in order to make the adsorption of H_2 gas easier. H_2 gas is adsorbed by the inert platinum surface. Platinum acts as a catalyst to allow equilibrium between the H_2 gas and the H^+ in solution. The electrode should be <u>partially immersed</u> in the solution and the other half in the gas.

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

$$2H^+_{(aq)} + 2e \quad \rightleftharpoons \quad H_{2(g)}$$

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.

$$2H^+_{(aq)} + 2e \quad \rightleftharpoons \quad H_{2(g)} \qquad E^\theta = 0.00V$$

The Cell Diagram:

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

- 'Pt' does not ionize itself, therefore its acts as an inert metal connection to the H_2/H^+ system.
- 'Pt' allows H_2 gas to be adsorbed 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 $moldm^{-3}$ & the pressure of all gases are 100kPa (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 $1moldm^{-3}$) 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 1moldm^{-3} Zn ions, can be written either as:-

$Zn^{2+} + 2e \quad \rightleftharpoons \quad Zn \qquad E^{\theta} = -0.76V$ OR as Zn^{2+} / Zn -0.76V

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 1moldm^{-3} solution of anion of the gas.

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

15. Explain the convention to draw the cell diagram.

Instead of drawing a cell diagram it's much convenient to write it. Following rules are applied when writing a cell diagram;

The solid single vertical line (I) represents the phase boundary. Equilibrium between two different phases (aqueous I solid)

$Zn^{2+}(aq)$ I Zn (s) $\qquad E^{\theta} = -0.76$ V

It the equilibrium lies within two solutions of the same phase, Platinum electrode should be used with a vertical line and a comma to separate the same phase ions. (not a line)

Pt(s) I $Fe^{3+}(aq)$, $Fe^{2+}(aq)$ $\quad E^{\theta} = +0.77$ V

The S.H.E can be represented as;

Pt(s) I ½ $H_2(g)$ I $H^+(aq)$

The convention is to write the anode reaction (oxidation reaction) on the left followed by two parallel dotted short lines (ll) to represent the salt bridge (also called as the solution junction) followed by the cathode reaction (Reduction reaction) (Reduction occur at the cathode - RED CAT) on the right side of the salt bridge. (Reduction – Right). In short the positive electrode should be on the right side.

The physical state symbols, Standard temperature, concentration should be indicated. (if gaseous system pressure should be written instead of the concentration. The complete cell diagram for the previous equilibrium would be:

Eg: Zn(s) I $Zn^{2+}(aq)$ (1M,298K) ll $Cu^{2+}(aq)$ (1M,298K) I Cu(s)

The two reduced forms (Zn & Cu) should face either ends of the cell diagram.

16. 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.

$Zn \longrightarrow Zn^{2+} + 2e$ (Oxidation Anode)
$H^+ + e \longrightarrow \frac{1}{2} H_2$ (**R**eduction **C**athode-**RED CAT**)

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.

Cell Diagram: $Zn^{2+}(aq)\ I\ Zn(s)\ II\ Pt(s)\ I\ H^+(aq)\ I\ \frac{1}{2} H_2(g)$

Note : The standard electrode potential is always written on the left side when its represented with respect to S.H.E (even if it's positive or negative)

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.

$\frac{1}{2} Cl_{2(g)} + e \rightleftharpoons Cl^-_{(aq)}$ E^θ +1.36V
$H^+_{(aq)} + e \rightleftharpoons \frac{1}{2} H_{2(g)}$ E^θ 0.00V

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 Cl_2 / Cl^- half cell.

$Pt(s)\ I\ \frac{1}{2} H_2(g)\ I\ H^+(aq)\ II\ \frac{1}{2} Cl_{2(g)}\ I\ Cl^-_{(aq)}$

The Cell Diagram:

Ion – Ion half cell:

When half-cell consists of ions of the same element in different oxidation states (eg: Fe^{2+}, Fe^{3+} system and MnO_4^-, H^+, Mn^{2+} system) an inert electrode such as platinum is used. The concentration of each ion should be 1M.

Pt(s) I Fe^{3+}(aq), Fe^{2+}(aq) E^θ = +0.77 V

The Cell Diagram:

- Standard electrode potential reactive metals & non metals such as K, Na, Li, Ca, F cannot be determined experimentally as they react with water and they do not establish an equilibrium with water. The E^θ values of such elements are calculated from thermochemical data.

Standard electrode potentials

$E^{\ominus}$ Standard electrode potential of aqueous system at 298 K, that is, standard emf of electrochemical cell in the hydrogen half-cell forms the left-hand side electrode system.

	Right-hand electrode system	$E^{\ominus}/V$
1	$Na^+ + e^- \rightleftharpoons Na$	−2.71
2	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.37
3	$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.66
4	$V^{2+} + 2e^- \rightleftharpoons V$	−1.18
5	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76
6	$Cr^{3+} + 3e^- \rightleftharpoons Cr$	−0.74
7	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44
8	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	−0.41
9	$V^{3+} + e^- \rightleftharpoons V^{2+}$	−0.26
10	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.25
11	$H^+ + e^- \rightleftharpoons \frac{1}{2}H_2$	0.00
12	$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.09
13	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.15
14	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
15	$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
16	$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
17	$S_2O_3^{2-} + 6H^+ + 4e^- \rightleftharpoons 2S + 3H_2O$	+0.47
18	$Cu^+ + e^- \rightleftharpoons Cu$	+0.52
19	$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
20	$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.68
21	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
22	$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
23	$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2 + H_2O$	+0.80
24	$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	+0.89
25	$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
26	$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.09
27	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
28	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
29	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
30	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.51
31	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77

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.
- Also, the negative sign indicates that the metal electrode is negative with respect to S.H.E, whereas positive sign indicates positive electrode with respect to S.H.E

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 equation 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,

- The sign of the electrode potential indicates the polarity of the half-cell when it is connected to the S.H.E. Therefore, the sign should not change just because one reverses the half equation.

- As an alternative method of calculation, when a half equation is reversed, the sign of E^{θ} is changed. If the reduced form is negative E^{θ} then the reversed form will have the positive of the same value. If the reduced form is positive, then the reversed will be negative. (This is not based on correct science even though one gets the correct answer)

- If the equation is doubled or halved the E^{θ} value is not <u>altered</u> but remains the same.

- The use of E^{θ} values relate only to standard conditions. Changes in temperature, pressure or concentration will affect the E^{θ} 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^{θ}_{cell} are energetically feasible where as those with an overall negative E^{θ}_{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. Cl_2 / Cl^- half cell where Cl_2 half-cell is +ve terminal & the E^θ is 1.36V (w.r.t. S.H.E)

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

IV. Cr^{2+} / 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 inorder to determine the feasibility of a reaction.

- **Method I (Alternative method based on incorrect science)**

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;

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

RHS = Right Hand Side (Reduction half equation)

LHS = Left Hand Side (Oxidation half equation)

OR

$$E^\theta_{cell} = E^\theta_{cathode} - E^\theta_{anode}$$

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

a) Ag^{+}/Ag , Zn^{2+}/Zn

b) Cu^{2+}/Cu , Zn^{2+}/Zn

c) Cl_2 /Cl^{-} , Fe^{3+}/Fe^{2+}

d) Br_2/Br^{-}, Ag^{+}/Ag

e) I_2/I^{-} , Fe^{3+}/Fe^{2+}

f) MnO_4^{-}/ Mn^{2+}, $Cl^{-/}Cl_2$

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

a. Cl_2 & I^-

b. F_2 & Na

c. F^- & Na^+

d. I_2 & Br^-

e. F_2 & Na^+

25. State the relationship between standard cell potential E_{cell}, total entropy change & equilibrium constant.

The total entropy change is directly proportional to the electrode potential. The relationship between total entropy & electrode potential is given by the following equation.

n = number of electrons involved in the cell reaction

F= Faraday's constant (96,500C)
(Charge of one mole of electrons)

T= Temperature

By combining the above equation with the equation $\triangle S^{\theta}_{total} = R \ln K$ the below relationship can be derived;

As n,F & R are constants at a given temperature T, lnK is proportional to E^{θ}_{cell}

26. 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.

$\frac{1}{2} F_2 + e$	═══	F^-	E^{θ} +2.87V
$\frac{1}{2} Cl_2 + e$	═══	Cl^-	E^{θ} +1.36V
$\frac{1}{2} Br_2 + e$	═══	Br^-	E^{θ} +1.07V
$\frac{1}{2} I_2 + e$	═══	I^-	E^{θ} +0.54V

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.

27. 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.

28. 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 form the more negative (or less positive) half-cell to the more positive (or less negative) 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.

29. 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 as electrode potentials change with conditions. (Temperature, pressure & concentration)

- **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.

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).

Eq:- $8H^+ + MnO_4^- + 5e \rightleftharpoons Mn^{2+} + 4H_2O$ $E^\theta = +1.52v$

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^θ value.

31. Define disproportionation using oxidation number

Disproportionation is the simultaneous increase (oxidation) & decrease (reduction) in the oxidation number of the same species in the same reaction.

Eg:

32. Use appropriate electrode potentials & write ionic equations to predict whether disproportionation will occur in the following, under standard conditions.

a. $2Cu^+ \longrightarrow Cu_{(s)} + Cu^{2+}$

b. $3Fe^{2+} \longrightarrow 2Fe^{3+} + Fe_{(s)}$

c. VO^{2+} ⟶ $VO_2^{+} + V^{3+}$

d. $MnO_{2(s)}$ ⟶ $MnO_4^{-} + Mn^{2+}$

e. Sn^{2+} ⟶ $Sn_{(s)} + Sn^{4+}$

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:

Acid is important to ensure the reduction to Mn^{2+} ion. In alkali medium $KMnO_4$ yields Manganese (IV) oxide (MnO_2) as a brown precipitate which will interfere with the end point. Dilute sulfuric acid which is used should be boiled inorder to remove the dissolved O_2, if not the dissolved oxygen will oxidize some of the reducing agent.

$KMnO_4$ 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 $Na_2C_2O_4$ (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

I. Iron tablets are composed of hydrated Iron (II) sulfate, 6.25g of powdered Iron tablets were dissolved in water & the solution was made up to 250cm^3. 25 cm^3 of this solution was pipetted out & transferred into a conical flask, Hence 25cm^3 of dilute sulfuric acid was added to this. The mixture was then titrated with 0.02M solution of $KMnO_4$. The mean titre was 24.30cm^3. Calculate the percentage of Iron in the tablets.

- **<u>Sodium thiosulfate titrations</u>:-**

The thiosulfate ions are oxidized to tetrathionate ions ($S_4O_6^{2-}$) 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 $S_2O_3^{2-}$ 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. (Starch is not added at the beginning as the starch I_2 complex is an insoluble complex, as concentration of I_2 is high initially the insoluble complex will not allow thiosulfate to react)

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 $CuSO_4$

Eg:- $2Cu^{2+}_{(aq)} + 4I^-_{(aq)} \longrightarrow 2CuI_{(s)} + I_{2(g)}$

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.

2. Brass is an alloy of copper & zinc, the proportions of which are varied to create a range of brasses with different properties. The percentage of copper in a small brass screw was determined as follows:

a. The screw was weighed. Its mass was found to be 2.19g.
b. Some concentrated nitric acid was added to the screw. This was carried out in a fume cupboard. The copper & the zinc both reacted to form soluble nitrates, nitrogen dioxide & water.
c. The solution was neutralized. It, & the washings, was transferred to a 250cm^3 standard flask & the volume made up to 250 cm^3 with distilled water.
d. 25 cm^3 samples were measured by pipette into conical flasks & excess solid potassium iodide was added.
e. The zinc ions did not react. Copper ions reacted according to the equation;
f.

$$2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$$

g. The liberated iodine was then titrated against a 0.106 mol dm^{-3} solution of sodium thiosulfate, adding starch as the indicator near the end point.

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

The mean titre was 23.75cm^3.
Calculate the percentage of copper in the brass screw.

33. Discuss the uncertainty of measurement and their effect on the final results.

Percentage uncertainty depends on the value which is measured (how big / small) and the uncertainty/ error of the apparatus. Also depends on the number of recordings taken each time.

- **How to fond the error / uncertainty of an instrument?**

This is done by dividing the smallest reading on the apparatus by 2.

Eg: Burette which reads to minimum 0.01ml, the error would be +/- 0.005ml, Thermometer reads to 1^0C error would be +/- 0.5 ^{0}C

- **How to calculate the total uncertainty / error?**

This depends on number of readings taken each time. If two readings taken error should be multiplied by 2 inorder to obtain the total error.

Eg. of apparatus where error is multiplied by 2 : **Digital scale, burette, thermometer**

Eg. of apparatus where error is not multiplied by 2 : **Pipette, measuring cylinder, Volumetric flask**

- **How to calculate the percentage error / percentage uncertinity ?**

$$\% \text{ error} = \frac{\text{Total error}}{\text{measured value}} \times 100$$

% error can be minimized by taking larger measured values.

Accuracy of pipettes, burettes depend on its quality, temperature & viscosity of the solutions being used. For Burettes of error +/- 0.05cm^3 for each reading will give a maximum error of 0.1cm^3.

Inorder to minimize the percentage error the concentration of the standard solution is chosen so that the titre is between 20cm^3-30cm^3. Percentage error increases if the titre volume is less and vice versa.

The overall error is found by adding together all individual errors of each apparatus. Such as burette, pipette, volumetric flask, weighing scale ect.

34. Calculate the percentage error due to weighing and titration in the above example of iron contents in the iron tablets. Hence state the total uncertainty of the iron content.

35. A sample of mass 1.30g of a d-block metal sulfate, $M_2(SO_4)_3$ was dissolved in water. Excess potassium iodide was added and the iodine liberated was titrated against standard sodium thiosulfate solution. The titre showed that 0.00325 mol of the transition metal sulfate was present in the 1.30g.

a. Calculate the molar mass of the $M_2(SO_4)_3$.
b. Hence calculate the atomic mass of the element M. Suggest its identity.
c. Assume that the error in each weighing is +/-0.01g, calculate the percentage error in the mass of $M_2(SO_4)_3$ taken.
d. Assuming that there are no other significant errors, calculate the maximum & minimum values of the molar mass & hence of the atomic mass of the element M.
e. What does this indicate about the reliability of the identification of M?

FUEL CELLS

1. 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.

2. Discuss the possible advantages of developing other types of cells such as fuel cell.

- **Hydrogen – Oxygen Fuel Cell:**

Fuel cell converts chemical energy into electrical energy. It generates electricity from Hydrogen & Oxygen gas using Pt/Ni electrodes & a solution of an ACID or ALKALI. H_2 & O_2 travels thought the porous 'Pt' electrode. 'Pt' catalyzes the reactions taking place at the electrodes.

- In the presence of an acid electrolyte below reactions takes place:

Anode (negative electrode) : $H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e$

Cathode (positive electrode) : $\frac{1}{2} O_{2(g)} + 2H^+_{(aq)} + 2e \longrightarrow H_2O_{(l)}$

Overall Reaction : $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)}$

The hydrogen ions from the anode goes through the porous membrane which is in between the two electrodes towards the cathode which the reacts with O_2 to produce water.

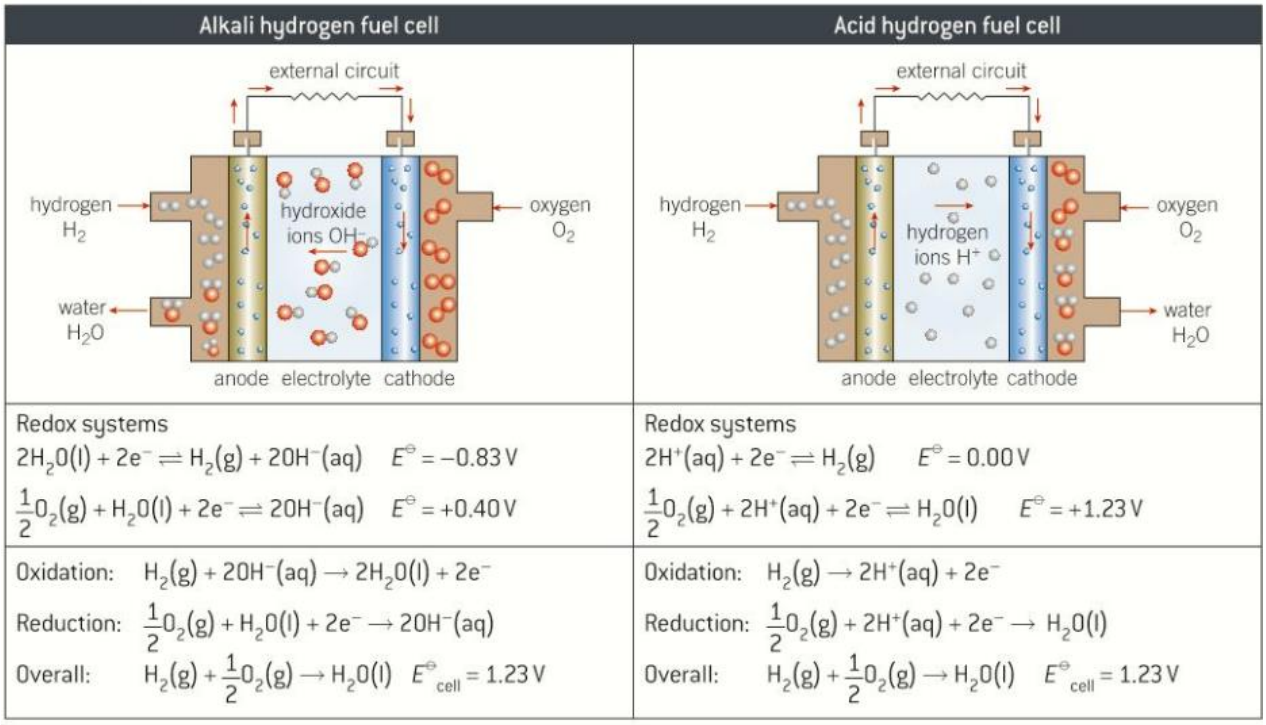
- In the presence of an alkali electrolyte below reactions takes place:

Anode (negative electrode) : $H_{2(g)} + 2OH^-_{(aq)} \longrightarrow 2H_2O_{(l)} + 2e$

Cathode (positive electrode) : $\frac{1}{2} O_{2(g)} + 2H_2O_{(l)} + 2e \longrightarrow 2OH^-_{(aq)}$

Overall Reaction : $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)}$

The electrons travel via the external circuit from the negative pole to the positive pole. This helps to drive an electric motor.



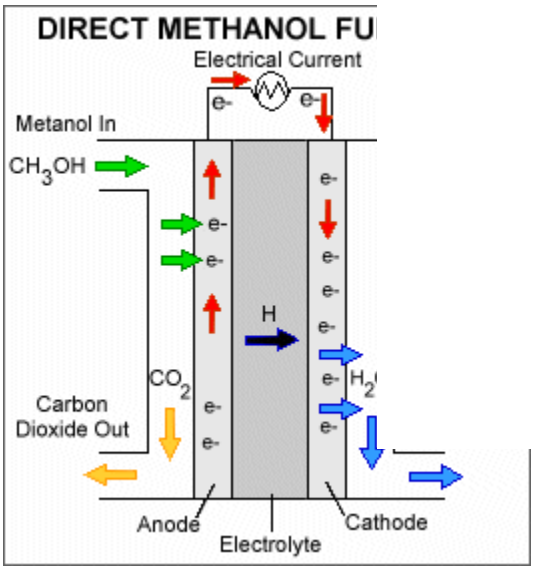
✓ **<u>Advantages :</u>**

No toxic gases evolved only H_2O is produced as a bi-product. Produce more energy per gram compared to hydrocarbon fuel. Lighter & very efficient as energy is directly transferred to the motor. Good alternative to the use of finite fossil fuel.

✓ **<u>Disadvantages / Limitations:</u>**

Materials used to make the membrane involves high costs, Manufacturing the cell releases toxic waste, difficult to store H_2 gas as high-pressure tanks required, H_2 is made from finite nonrenewable fossil fuels as it's the cheapest. Thus produces CO_2 during production. Fuel cell freezes at low temperature during winter. As a safety measure H_2 gas can be absorbed in to a suitable material

- **Alcohol fuel cells (Methanol /Ethanol)**



Ethanol could be made from sugarcane. Methanol is highly flammable, poisonous liquid made from either fossil fuel or agricultural waste. The use of methanol is advantageous because it is much easier to store than hydrogen gas, as it does not require high pressure/ low temperature.

Methanol fuel cell operates at a temperature between 90 ^{0}C – 120 ^{0}C. Methanol is oxidized to carbon dioxide. Electrons are transported via the external circuit from anode to the cathode.

- In the presence of an acid electrolyte below reactions takes place:

Anode (negative electrode) : $CH_3OH + H_2O \longrightarrow 6H^+ + 6e + CO_2$

Cathode (positive electrode) : $3/2\ O_{2(g)} + 6H^+_{(aq)} + 6e \longrightarrow 3H_2O_{(l)}$

Overall Reaction : $CH_3OH + 3/2\ O_{2(g)} \longrightarrow 2H_2O + CO_2$

- In the presence of an alkali electrolyte below reactions takes place:

Anode (negative electrode) : $CH_3OH + 6OH^- \longrightarrow 5H_2O + 6e + CO_2$

Cathode (positive electrode) : $3/2\ O_2 + 3H_2O + 6e \longrightarrow 6OH^-$

Overall Reaction : $CH_3OH + 3/2\ O_{2(g)} \longrightarrow 2H_2O + CO_2$

Methanol can be made by the reaction of carbon monoxide with hydrogen. CO is obtained from hydrocarbon fuel thus has a significant carbon foot print. Alcohol fuel cells produce limited amount of power therefore cannot power vehicles.

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