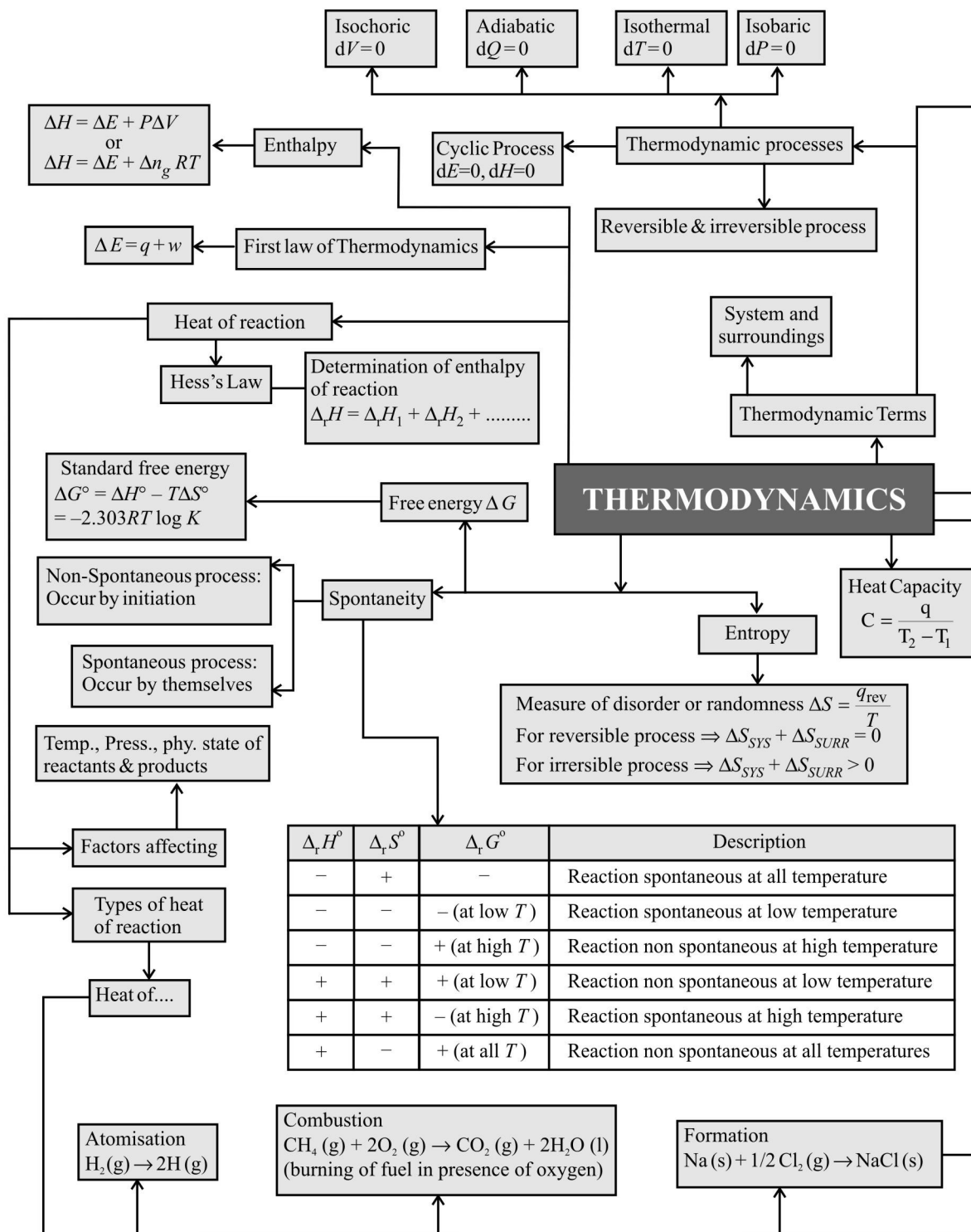
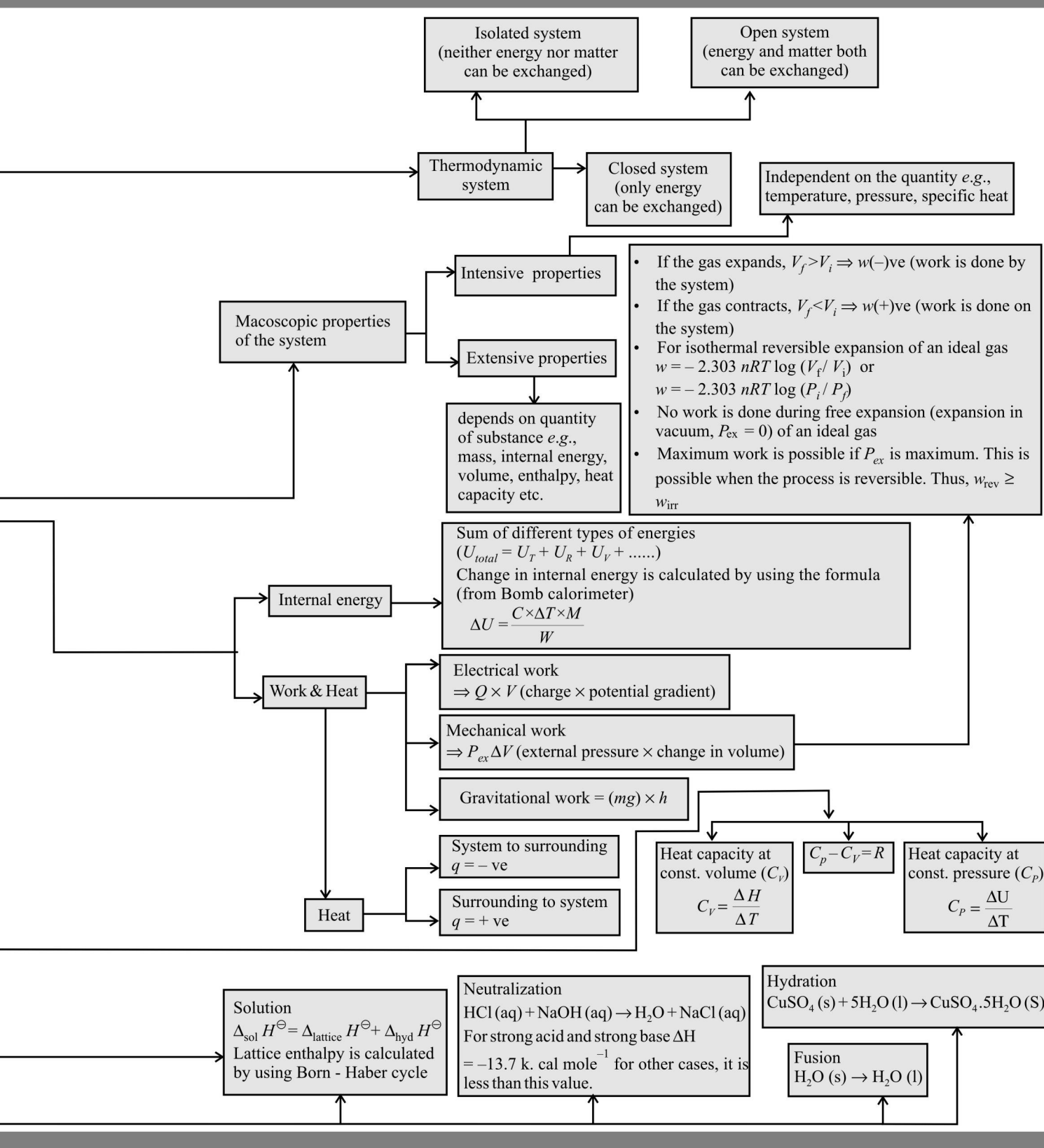


CHAPTER AT A GLANCE





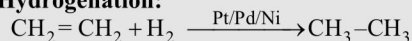
CHAPTER AT A GLANCE

- General formula: C_nH_{2n+2}

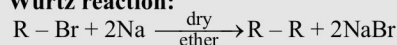
- C atom is in sp^3 hybridised state.

Preparation

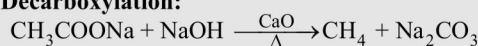
- Hydrogenation:**



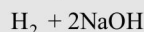
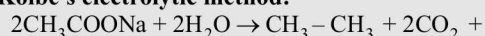
- Wurtz reaction:**



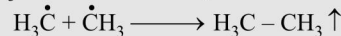
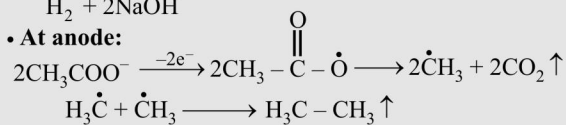
- Decarboxylation:**



- Kolbe's electrolytic method:**



- At anode:**



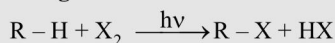
- At cathode:**



Properties

- Boiling points decreases with increase in branching
- Melting point with even no of C-atom > with odd no. of C-atoms

- Halogenation :**

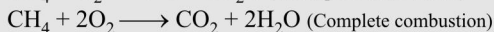
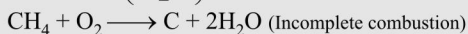
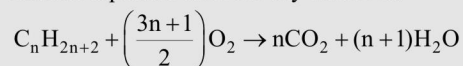


Reactivity order of halogen $\Rightarrow F_2 > Cl_2 > Br_2 > I_2$

Reaction proceeds via free radical chain mechanism

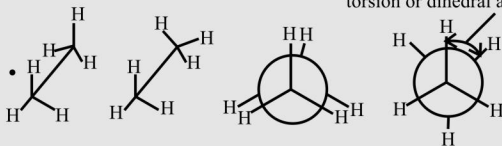
- Combustion:**

General equation used for any alkane is:



Conformation of ethane:

Angle of rotation or angle of torsion or dihedral angle

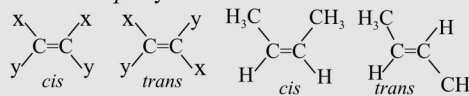


Eclipsed Staggered Eclipsed Staggered
Sawhorse projections of ethane Newman's projections of ethane

The order of stability of different conformations of ethane is Staggered > Skew or gauche > Eclipsed.

- General formula: C_nH_{2n}

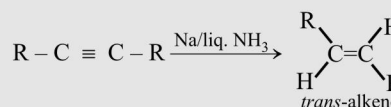
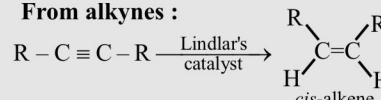
- C-atom is in sp^2 hybridised state.



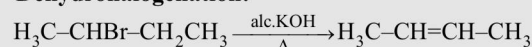
Geometrical isomers

Preparation

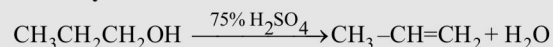
- From alkynes :**



- Dehydrohalogenation:**



- Dehydration of alcohol :**

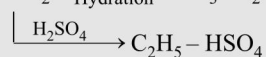
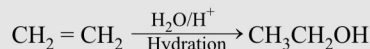
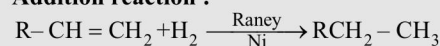


- From vicinal dihalides:**



Properties

- Addition reaction :**



- Markovnikov reaction**

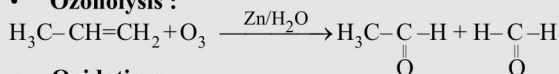


Reactivity: $HI > HBr > HCl > HF$

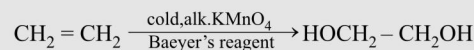
- Anti-Markovnikov reaction (Kharash effect) :**



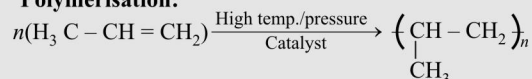
- Ozonolysis :**

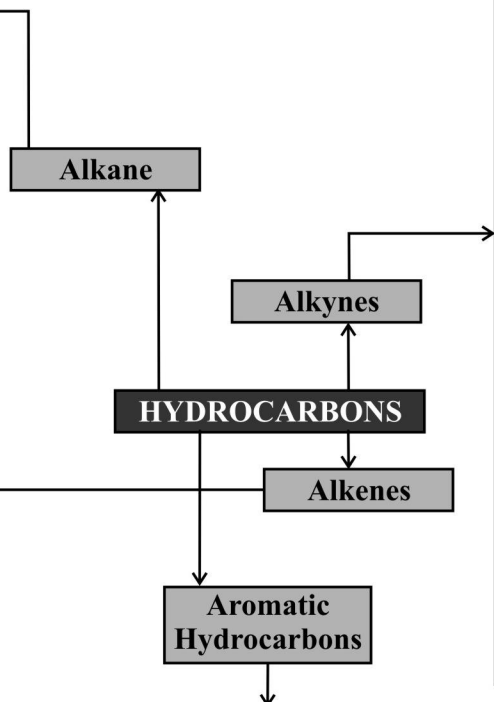


- Oxidation:**



- Polymerisation:**





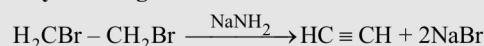
- General formula: C_nH_{2n-2}

- C-atom is in sp hybridised state.

Preparation

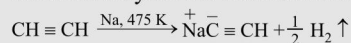


- **Dehydrohalogenation:**

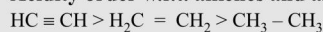


Properties

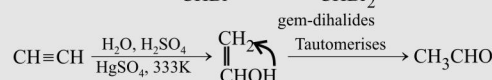
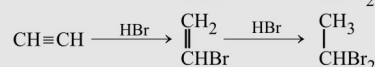
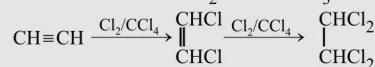
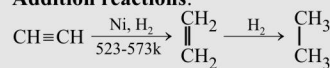
- Terminal alkynes are acidic in nature.



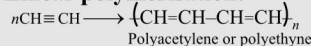
Acidity order w.r.t. alkenes and alkanes are



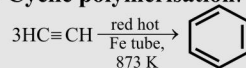
Addition reactions:



- **Linear polymerisation:**



- **Cyclic polymerisation:**

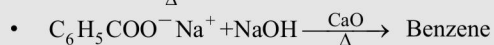
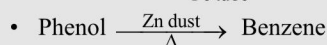
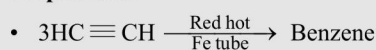


- It contains at least one unsaturated ring.

Aromaticity :

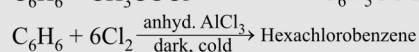
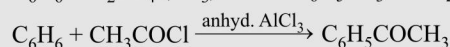
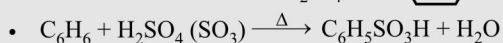
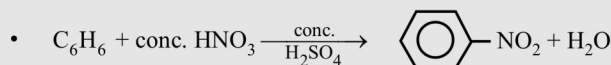
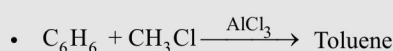
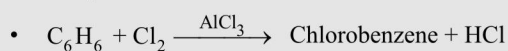
- Aromatic compound must have planar structure
- must contains $(4n+2)$ π electrons
- must have cyclic clouds of delocalised πe^- s

Preparation

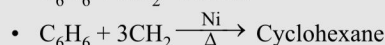
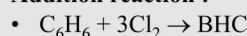


Properties

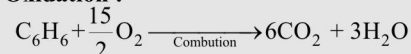
Electrophilic substitution:



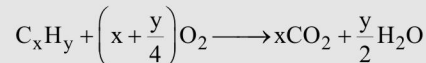
Addition reaction :



Oxidation :



General combustion reaction for any hydrocarbon is



***o* - and *p*- directing group :**

- $-NH_2$, $-NHR$, $-NHCOCH_3$
- $-OCH_3$, $-CH_3$, $-C_2H_5$, $-OH$ etc.

***m* - directing group :**

- $-NO_2$, $-CN$, $-CHO$, $-COR$, $-COOH$, etc.
- **Carcinogenicity** (Cancer producing properties)
Polynuclear hydrocarbons containing more than two benzene rings having cancer producing property. They are formed by in complete combustion of organic materials.

For example, 1, 2-Benzanthracene,
1, 2- benzpyrene etc.

CHAPTER AT A GLANCE

In corrosion, a metal is oxidised by loss of electrons to oxygen and forms metal oxide. Corrosion of iron (which is commonly known as rusting) occurs in presence of water and oxygen (air).

Rusting of Iron : According to electrochemical theory, rusting can be represented as :

Oxidation at Anode: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$; $E_{\text{oxi}}^{\circ} = -0.44 \text{ V}$

Reduction at Cathode: $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HCO}_3^-$
 $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}$
 $2\text{H} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

$$2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{H}_2\text{O}; E_{\text{red}}^{\circ} = 1.23 \text{ V}$$

Overall reaction of corrosion cell :

$\text{Fe} + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}; E_{\text{cell}}^{\circ} = 1.67 \text{ V}$

The ferrous ions so formed move through water and come at the surface of iron object where these are further oxidised to ferric state by atmospheric oxygen and constitute rust which is hydrated iron (III) oxide.

$$2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 4\text{H}^+$$

$$\text{Fe}_2\text{O}_3 + x\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$$

Rust

Prevention of Corrosion

- The metal surface is coated with paint which keeps it out of contact with air, moisture etc.
- By applying film of oil and grease on the surface of the iron tools and machinery.
- The iron surface is coated with non-corroding metals such as nickel, chromium, aluminium, etc.

Faraday's First Law: When an electric current is passed through an electrolyte, the amount of substance deposited or liberated at an electrode is proportional to the quantity of electric charge passed through the electrolyte.

If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation.

$$W \propto Q$$

A coulomb is the quantity of charge when a current of one ampere is passed for one second.

$$Q = \text{current in amperes} \times \text{time in seconds} = I \times t$$

$$W \propto I \times t$$

$$W = Z \times I \times t$$

where Z is a constant, known as electro-chemical equivalent, and is characteristic of the substance deposited.

Electro-chemical equivalent (Z) =

$$\frac{\text{equivalent wt. of element}}{96500}$$

Faraday's Second Law: It states that when same quantity of electricity is passed through different electrolytes, then the quantity of deposit is directly proportional to respective equivalent weight. (Equivalent wt. of electrolytes).

$$W \propto E$$

$$\frac{W_A}{E_A} = \frac{W_B}{E_B} = \frac{W_C}{E_C}$$

Regardless whether a cell is a voltaic or an electrolytic cell,

- The anode is the electrode at which oxidation occurs
- The cathode is the electrode at which reduction occurs

	Voltaic cell	Electrolytic-cell
Anode	Oxidation, Negative (–) terminal	Oxidation positive (+) terminal
Cathode	Reduction Positive (+) terminal	Reduction negative (–) terminal

• **Electrode potential**

$$E_{\text{cell}} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ}$$

For SHE, $E_{\text{cell}}^{\circ} = 0$

• **Nernst equation :**

For reaction, $\text{M}^{n+} + \text{ne}^- \rightarrow \text{M}(\text{s})$

$$E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[\text{M}^{n+}]}$$

• **For reaction :**

$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

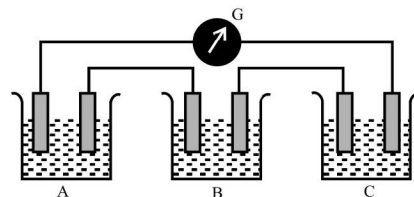
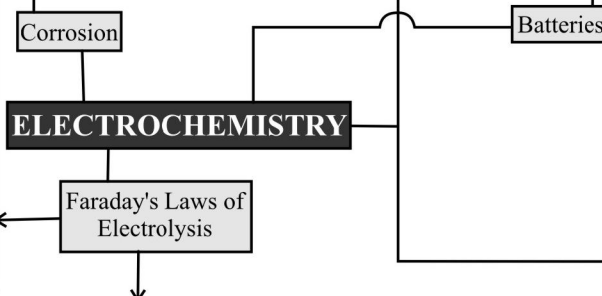
At equilibrium $E_{\text{cell}} = 0$

$$E_{\text{cell}}^{\circ} = \frac{2.303RT}{nF} \log K_c$$

$$\Delta_r G = -nFE_{\text{cell}} \text{ or } \Delta_r G = -nF E_{\text{cell}}^{\circ}$$

$$\text{or } \Delta_r G^{\circ} = -RT \ln K = -2.303 RT \log K$$

• **Electrochemical series:** Arrangement of elements in order of increasing value of E_{red}° . Reducing nature decreases from top to bottom in the series.





Name of cell/Battery	Anode (-)	Cathode (+)	Electrolyte	Reactions at electrodes	E _{cell}
• Dry cell (primary cell)	Zn container	Graphite rod	Powdered MnO ₂ +C + Paste of NH ₄ Cl+ ZnCl ₂	Anode: Zn(s) → Zn ²⁺ (aq) + 2e ⁻ Cathode: NH ₃ forms complex with Zn ²⁺ to give [Zn(NH ₃) ₄] ²⁺ MnO ₂ + 2NH ₄ ⁺ + e ⁻ → MnO(OH) + NH ₃ . NH ₃ Forms Complex with Zn ²⁺ to give [Zn(NH ₃) ₄] ²⁺	1.25 to 1.5 V
• Mercury cell (primary cell)	Zn-Hg amalgam	Paste of HgO and C	Paste of KOH + ZnO	Anode: Zn(Hg) + 2OH ⁻ → ZnO + H ₂ O + 2e ⁻ Cathode: HgO + H ₂ O + 2e ⁻ → Hg(l) + 2OH ⁻	1.35 V
• Lead storage Battery (secondary cell)	Pb	Pb + PbO ₂	38% by mass H ₂ SO ₄ (d=1.30 g cm ⁻³)	Anode: Pb(s) + SO ₄ ²⁻ (aq) → PbSO ₄ (s) + 2e ⁻ Cathode: PbO ₂ (s) + SO ₄ ²⁻ (aq) + 4H ⁺ (aq) + 2e ⁻ → PbSO ₄ (s) + 2H ₂ O(l) On applying a potential slightly greater than the potential of battery, battery can be recharged.	12 V consists of 6 cell each producing 2 V
• Ni-Cd Secondary cell Or Ni-Cd cell (Rechargeable)	Cd	NiO ₂	Moist KOH	Anode: Cd(s) + 2OH ⁻ (aq) → Cd(OH) ₂ (s) + 2e ⁻ Cathode: NiO ₂ (s) + 2H ₂ O + 2e ⁻ → Ni(OH) ₂ (s) + 2OH ⁻ (aq)	1.4 V
• Fuel cell (H ₂ -O ₂)	Porous carbon containing catalyst (finely divided Pt and Pd)	Porous carbon containing catalyst (finely divided Pt and Pd)	Concentrated NaOH solution	Anode: 2H ₂ (g) + 4OH ⁻ (aq) → 4H ₂ O(l) + 4e ⁻ Cathode: O ₂ (g) + 2H ₂ O(l) + 4e ⁻ → 4OH ⁻ (aq)	0.09 V

Conductance of Electrolytic Solutions:

• Conductance (G) = $\frac{1}{\text{Resistance}}$

Unit : ohm⁻¹ or Siemens

• Specific conductivity (κ) = $G \frac{l}{a}$ ($\frac{l}{a}$ = cell constant)

Unit = ohm⁻¹ cm⁻¹ or S cm⁻¹

• Molar conductance (Λ_m) = $\frac{1000 \times \kappa}{M}$

Unit = S cm² mol⁻¹

• Equivalent conductance (Λ_{eq}) = $\frac{1000 \times \kappa}{N}$

Unit = cm² ohm⁻¹ g-eq⁻¹

Conductance (G), molar conductivity (Λ_m) and equivalent conductivity (Λ_{eq}) increase with dilution where as specific conductivity (κ) decrease with dilution

Effect of concentration on Λ_m:

• For strong electrolytes, Λ_m increases slowly with dilution and can be represented by the equation : $\Lambda_m = \Lambda_m^\circ - AC^{1/2}$

(Debye-Huckel Onsager equation)

Plot of Λ_m against C^{1/2} is a straight line with intercept equal to Λ_m⁰ and slope equal to '-A.'

Thus, Λ_m decreases linearly with √C, when C = 0, Λ_m = Λ_m⁰ and Λ_m⁰ can be determined experimentally.

• For weak electrolytes, Λ_m increases as C decreases but does not reach a constant value even at infinite dilution. Hence, Λ_m⁰ cannot be determined experimentally.

• Kohlrausch's Law :

$$\Lambda_m = v_+ \lambda_+^\circ + v_- \lambda_-^\circ$$

Where λ₊⁰ is the limiting molar conductivity

of the cation and λ₋⁰ is the limiting molar conductivity of the anion at infinite dilutions.

v₊ and v₋ are number of cations and anions in one formula unit of electrolyte.

Applications of Kohlrausch's Law:

• Calculation of Molar Conductivity at Infinite Dilution for Weak Electrolytes :

In order to calculate Λ_m[∞] or Λ_m[∞] of a weak electrolyte say CH₃COOH, we determine Λ_m⁰ values of the strong electrolytes.

$$\Lambda_m^\infty(\text{CH}_3\text{COOH}) = \lambda_{\text{CH}_3\text{COO}^-}^\circ + \lambda_{\text{H}^+}^\circ \quad \dots\dots(i)$$

for strong electrolytes :

$$\Lambda_m^\infty(\text{CH}_3\text{COOK}) = \lambda_{\text{CH}_3\text{COO}^-}^\circ + \lambda_{\text{K}^+}^\circ \quad \dots\dots(ii)$$

$$\Lambda_m^\infty(\text{HCl}) = \lambda_{\text{H}^+}^\circ + \lambda_{\text{Cl}^-}^\circ \quad \dots\dots(iii)$$

$$\Lambda_m^\infty(\text{KCl}) = \lambda_{\text{K}^+}^\circ + \lambda_{\text{Cl}^-}^\circ \quad \dots\dots(iv)$$

$$\therefore \text{eqn (ii)} + \text{eqn. (iii)} - \text{eqn (iv)} = \text{eqn (i)}$$

$$\text{i.e., } \Lambda_m^\infty(\text{CH}_3\text{COOK}) + \Lambda_m^\infty(\text{HCl}) - \Lambda_m^\infty(\text{KCl}) = \Lambda_m^\infty(\text{CH}_3\text{COOH})$$

• Calculation of the Degree of Dissociation :

Λ_m^c is the molar conductivity of a solution at any concentration C and Λ_m⁰ the molar conductivity at infinite dilution (i.e., zero concentration), we will have

$$\alpha = \frac{\text{no. of dissociations}}{\text{no. of total ions present}}$$

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m^c}{\Lambda_m^\circ}$$

• Calculation of Dissociation Constant of a Weak Electrolyte :

$$K_c = \frac{C\alpha^2}{1-\alpha}$$

CHAPTER AT A GLANCE

Some important terms:

Denticity: The number of ligating (linking) atoms present in ligand is called denticity.

* **Unidentate ligands:** Only one donor atom is bonded to metal atom. Ex: H_2O , NH_3 , CO , CN^-

* **Bidentate ligands:** Two donor atoms or ions through which they are bonded to the metal ion.

Ex: Ethylene diamine $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$.

* **Polydentate ligand:** When several donor atoms are present in a single ligand.

Ex: EDTA^{4-} is an important hexadentate ligand.

* **Chelate:** In which there is a close ring of atoms caused by attachment of a ligand to a metal atom at two or more points *e.g.*, $[\text{Cu}(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_2]^{2+}$.

* **Ambidentate ligand:** Unidentate Ligands which can linked through two different atoms present in it are called ambidentate ligand.

Ex: NO_2^- can link through N as well as O.

Coordination number: CN of a metal ion is the number of ligand donor atoms to which the metal is directly bonded.

Coordination sphere: The metal ion and the ligands attached to it are enclosed in square bracket and collectively known as coordination sphere.

Counter ions: The ionisable groups are written outside the bracket and are called counter ions.

Homoleptic complexes: Complexes with only one kind of ligands, *e.g.*, $[\text{Co}(\text{NH}_3)_6]^{3+}$.

Heteroleptic complexes: With more than one kind of ligands, *e.g.* $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

Werner's coordination theory:

* Metal shows two different kinds of valences: primary valence and secondary valence.

• Primary valence

* This valence is normally ionisable and non-directional

* It is equal to positive charge on central metal atom.

* These valences are satisfied by negatively charged ions.

• Secondary valence

* This valence is non-ionisable and directional.

* The secondary valence equals the number of ligand atoms coordinated to the metal. It is fixed for a metal *e.g.*, for Fe^{2+} , it is 6; for Cu^{2+} is 4 and 6

* It is also called coordination number of the metal.

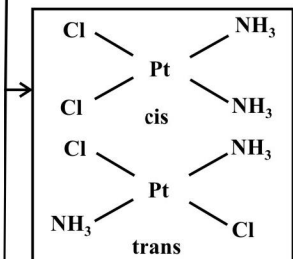
* It is commonly satisfied by neutral and negatively charged, sometimes by positively charged ligands.

COORDINATION COMPOUNDS

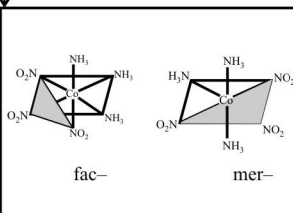
Isomerism

Stereoisomerism

Geometrical



Optical



Structural isomerism

• Linkage isomerism:

$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$,
 $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$
Nitrite ion bound through either oxygen or nitrogen.

• Coordination isomerism:

$[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$,
 $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
Interchange of ligands between cationic and anionic entities.

• Ionisation isomerism:

$[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$,
 $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$
These give different ion in solution

• Solvate isomerism:

$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
 $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$

Naming of coordination compounds: The following rules are used for naming coordination compounds:

- The cation is named first in both positively and negatively charged coordination entities.
- The ligands are named in an alphabetical order before the name of the central atom/ion.
- Names of the anionic ligands end in -ido, those of neutral and cationic ligands are the same except aqua for H_2O , ammine for NH_3 , carbonyl for CO and nitrosyl for NO .
- Prefixes mono, di, tri, *etc.*, are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bis, tris, tetrakis are used, the ligand to which they refer being placed in parentheses *e.g.*, $[\text{NiCl}_2(\text{PPh}_3)_2]$ is named dichloridobis(triphenylphosphine)nickel(II).
- Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.
- If the complex ion is a cation, the metal is named same as the element. *e.g.*, Co in a complex cation is called cobalt. If the complex ion is an anion, the name of the metal ends with the suffix -ate. *e.g.*, Co will be cobaltate.
- The neutral complex molecule is named similar to that of the complex cation.

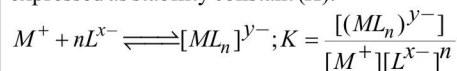


Colour in coordination compounds: The crystal field theory attributes the colour of the coordination compounds to $d-d$ transition of the electron, *i.e.*, electron jump from t_{2g} level to higher e_g level.
In the absence of ligands, crystal field splitting does not occur and hence the substance is colourless. *e.g.*,
[Ti(H₂O)₆]³⁺ - Violet in colour
[Cu(H₂O)₄]²⁺ - Blue in colour, *etc.*

Metal carbonyls: Metal carbonyls are homoleptic complexes in which carbon monoxide (CO) acts as the ligand *e.g.*, [Ni(CO)₄]

- The metal-carbon bond in metal carbonyls possess both σ - and π - character.
- **The M-C σ bond** is formed by the donation of lone pair of electrons from the carbonyl carbon into a vacant orbital of the metal.
- **The M-C π bond** is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π orbital of carbon monoxide.
- The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

Stability of coordination compounds: The stability of complex in solution refers to the degree of association between the two species involved in the state of equilibrium. It is expressed as stability constant (K).



- The factors on which stability of the complex depends :

* **Charge on the central metal atom:** As the magnitude of charge on metal atom increases, stability of the complex increases.

* **Nature of metal ion:** The stability order is $3d < 4d < 5d$ series.

* **Basic nature of ligands:** Strong field ligands form stable complex.

Valence bond theory

The salient features of the theory are :

- The central metal ion uses a number of empty orbitals for accommodating electrons donated by the ligands. The number of empty orbitals is equal to the coordination number of the metal ion for the particular complex.
- The atomic orbitals (s , p or d) of the metal ion hybridize to form hybrid orbitals with definite directional properties. These hybrid orbitals now overlap with the ligand orbitals to form strong chemical bonds.

Number of orbitals and types of hybridisation :

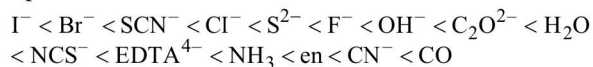
Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

- The d -orbitals involved in the hybridization may be either inner ($(n-1)$ d orbitals) or outer nd -orbitals. The complexes formed in these two ways are referred to as low spin and high spin complexes, respectively.
- If the complex contains unpaired electrons, it is paramagnetic in nature, while if it does not contain unpaired electron, it is diamagnetic in nature.

Crystal field theory (CFT): In this theory, ligands are treated as point charges in case of anions and dipoles in case of neutral molecules.

- The five d -orbitals are classified as
- * Three d -orbitals *i.e.*, d_{xy} , d_{yz} and d_{zx} are oriented in between the coordinate axes and are called t_{2g} -orbitals.
- * The other two d -orbitals, *i.e.*, $d_{x^2-y^2}$ and d_{z^2} oriented along the x , y axes are called e_g -orbitals.

- A series in which ligands are arranged in order of increasing magnitude of crystal field splitting, is called **spectrochemical series**.

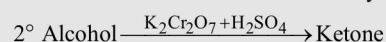
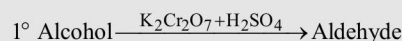


- In case of octahedral complexes, Energy of e_g set of orbitals > energy of t_{2g} set of orbitals.
- The energy of e_g orbitals will increase by $(3/5)\Delta_0$ and t_{2g} will decrease by $(2/5)\Delta_0$.
- Ligands for which $\Delta_0 < P$ are known as weak field ligands and form high spin complexes.
- If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital which produce this effect are known as strong field ligands and form low spin complexes.
- In tetrahedral complexes, Energy of t_{2g} set of orbitals > Energy of e_g set of orbitals.
- Pairing of electrons is not possible in tetrahedral complexes, so these are high spin complexes.
- $\Delta_t = (4/9)\Delta_0$

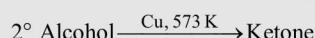
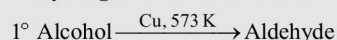
CHAPTER AT A GLANCE

Preparation of aldehydes and ketones:

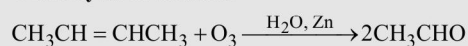
• Oxidation of alcohols:



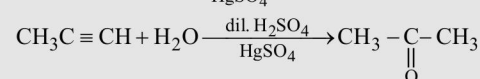
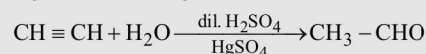
• Dehydrogenation of alcohols:



• Ozonolysis of alkenes:

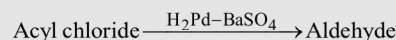


• Hydration of alkynes:



• Preparation of aldehydes only:

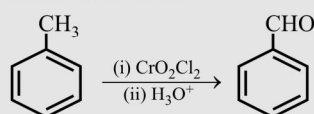
* Rosenmund reduction:



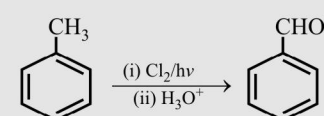
* Stephen reaction:



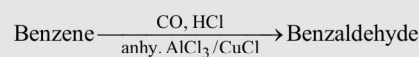
* Etard Reaction:



* Side chain chlorination:

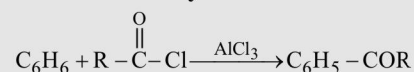


* Gatterman-Koch reaction:

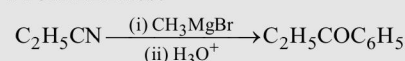


• Preparation of Ketones only:

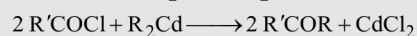
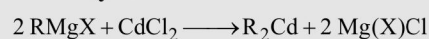
* Friedel crafts acylation:



* From nitriles:

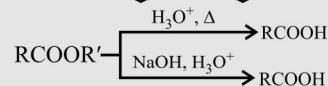
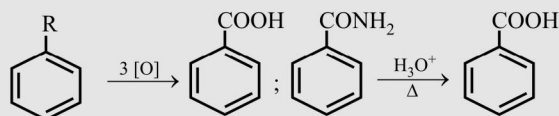
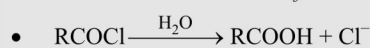
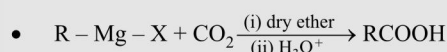
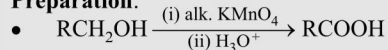


* From acyl chloride:



Carboxylic acids

Preparation:



Properties:

• Physical State :

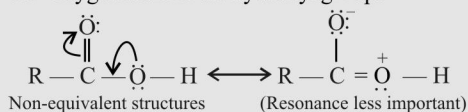
C₁ to C₃ = Colourless pungent smelling liquids.

C₄ to C₉ = Oily liquids having goat's butter like smell.

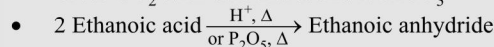
C₁₀ + = Colourless and odourless waxy solids.

These are polar substances and can form H-bonds with each other to form dimer structures.

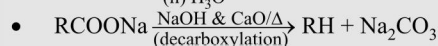
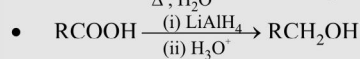
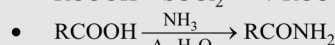
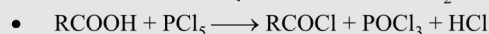
• Acidity of Carboxylic Acids : The acidic character of carboxylic acids is due to resonance in the acidic group which imparts electron deficiency (positive charge) on the oxygen atom of the hydroxyl group.



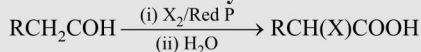
• Gives CO₂ with carbonates and NaHCO₃



• Esterification :



• Hell-Volhard Zelinsky reaction:





ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

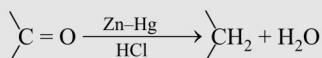
Aldehydes and Ketones

• Reduction to alcohols:

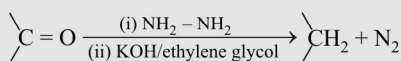
Aldehydes or Ketones $\xrightarrow{\text{Reagents}}$ 1° or 2° alcohols
Reagents : LiAlH_4 , NaBH_4 and $\text{H}_2/\text{Pd/Pt/Ni}$

• Reduction to hydrocarbons:

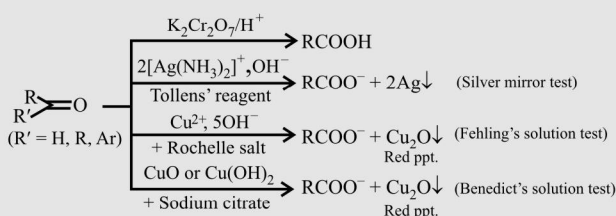
* *Clemmensen reduction:*



* *Wolff-kishner reduction:*



• Oxidation:



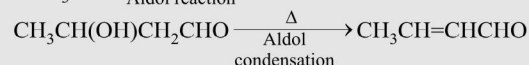
• Aldehydes give positive test with Tollen's reagent Benedict's reagent and Fehling solution while ketones do not give such test.

• Haloform reaction:



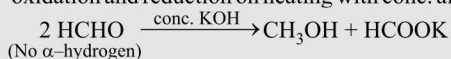
• Aldol condensation:

Condensation of aldehydes and ketones having atleast one α -H atom undergo a reaction with dil. alkali to form aldol or ketol.

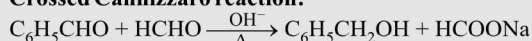


• Cannizzaro reaction:

Aldehydes with no α -hydrogen atom, undergoes self oxidation and reduction on heating with conc. alkali.



• Crossed Cannizzaro reaction:



Properties of aldehydes and ketones:

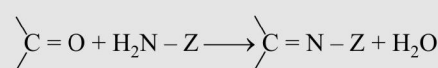
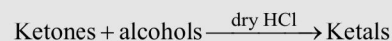
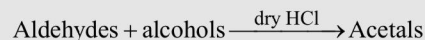
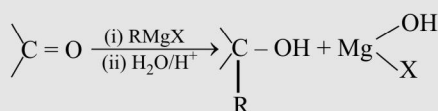
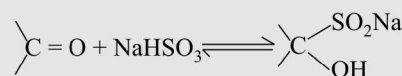
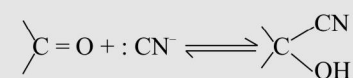
- **Physical state:** Formaldehyde (methanal) is a gas. All other aldehydes and ketones upto C_{11} are colourless volatile liquids. Higher members are solids at room temperature.
- **Odour:** Lower aldehydes have an unpleasant odour. Higher aldehydes and ketones have a pleasant odour.
- **Solubility:** Lower carbonyl compounds are soluble in water due to the formation of hydrogen bonds between the solute and water molecules but solubility decreases with increase in molecular weight due to the hydrophobic nature of the bigger alkyl groups in the higher members.
- **Boiling point:** Boiling point and Melting point \propto Molecular weight \propto 1/ Branching
Boiling points of carbonyl compounds are less than the corresponding alcohols of comparable molecular weight but are higher than corresponding alkanes. The relative boiling points of the carbonyl compounds with the same number of carbon atoms follow the order,
Amides > Carboxylic acids >> Esters \approx Acyl chlorides \approx Ketones \approx Aldehydes
- **Reactivity:** Reactivity depends on the nature of alkyl group attached to it. Smaller the alkyl group, the more reactive is the compound.

Reactivity \propto Magnitude of (+)ve charge on carbon atom of the carbonyl group.

- 40% aqueous solution of HCHO is called formalin. It is used as a disinfectant and antiseptic. It is also used for preserving biological specimen.
- $\text{HCHO} + \text{Lactose} = \text{Formamint}$ used for throat infection.

• Chemical Reaction:

Aldehydes are more reactive than ketones in nucleophilic addition reactions **due to electric and electronic resonance**. These reactions are following:



(Z = Alkyl, aryl, $-\text{NH}_2$, $-\text{OH}$, $-\text{NH}-\text{C}_6\text{H}_5$, $-\text{NHCONH}_2$ etc.)