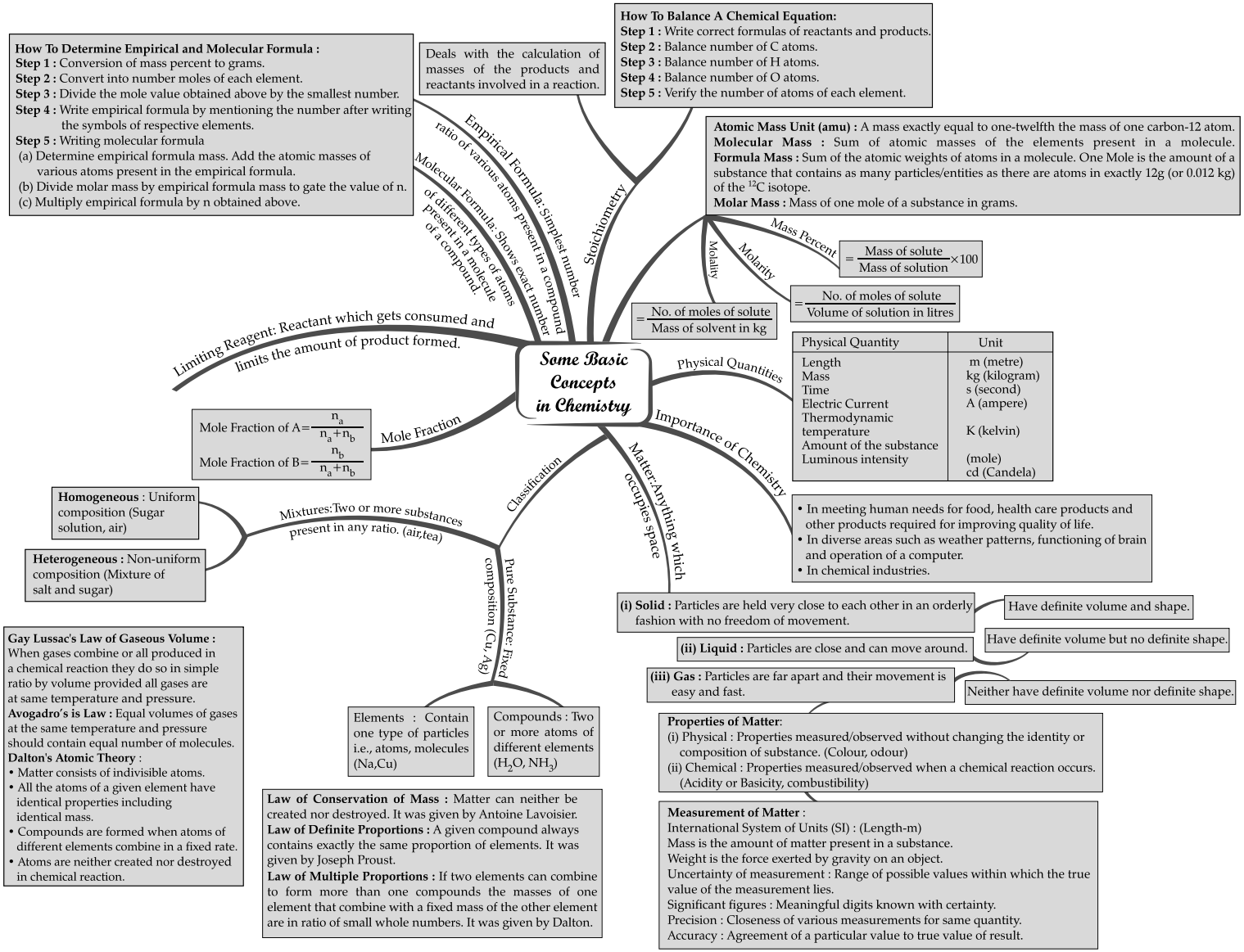
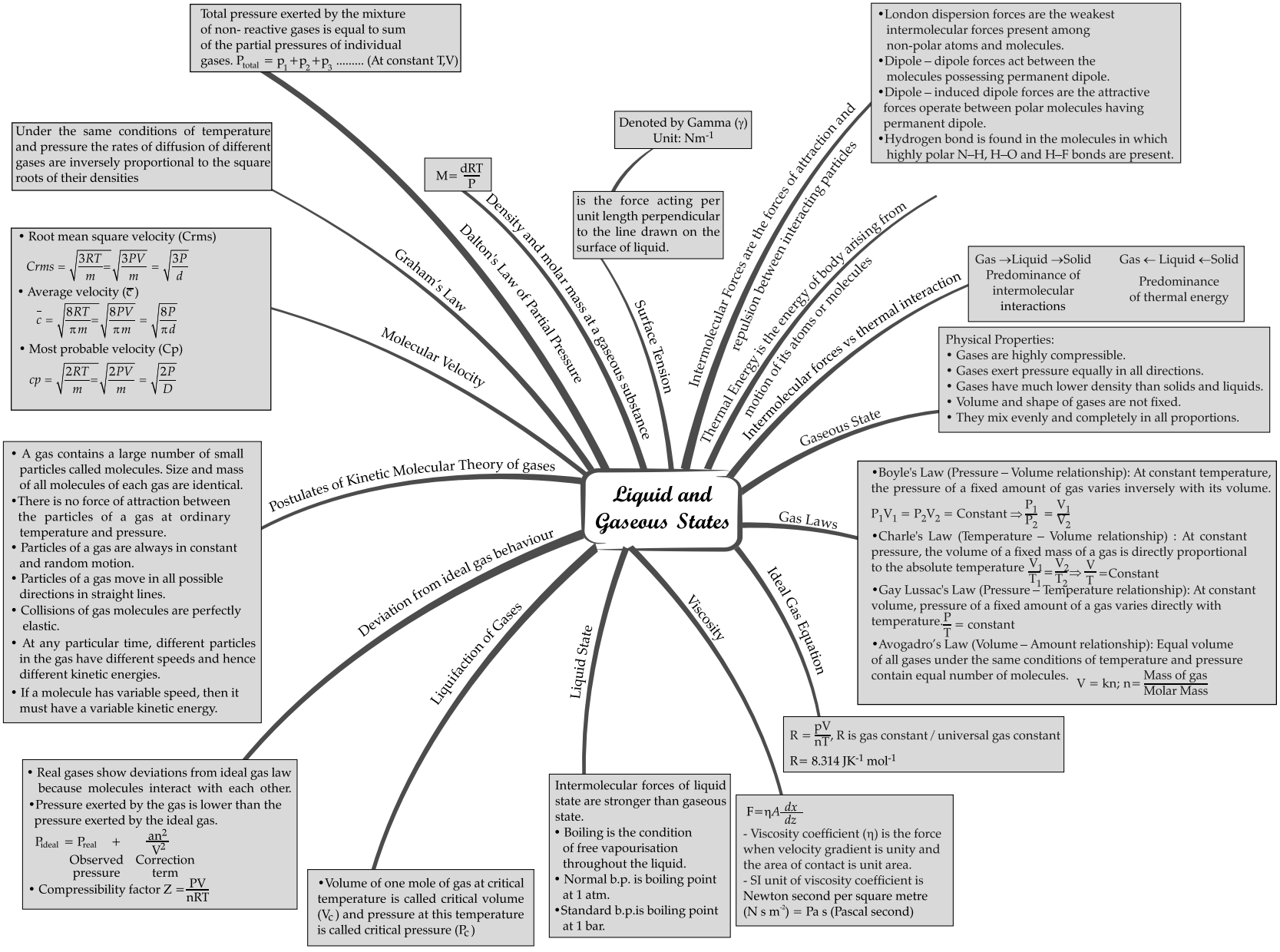
CHEMISTRY


Some Basic Concepts in Chemistry
Stoichiometry
Deals with the calculation of masses of the products and reactants involved in a reaction.
How To Balance A Chemical Equation:
Step 1 : Write correct formulas of reactants and products.
Step 2 : Balance number of C atoms.
Step 3 : Balance number of H atoms.
Step 4 : Balance number of O atoms.
Step 5 : Verify the number of atoms of each element.
How To Determine Empirical and Molecular Formula :
Step 1 : Conversion of mass percent to grams.
Step 2 : Convert into number moles of each element.
Step 3 : Divide the mole value obtained above by the smallest number.
Step 4 : Write empirical formula by mentioning the number after writing the symbols of respective elements.
Step 5 : Writing molecular formula
(a) Determine empirical formula mass. Add the atomic masses of various atoms present in the empirical formula.
(b) Divide molar mass by empirical formula mass to gate the value of n.
(c) Multiply empirical formula by n obtained above.
Empirical Formula: Simplest number ratio of various atoms present in a compound
Molecular Formula: Shows exact number of different types of atoms present in a molecule of a compound.
Atomic Mass Unit (amu) : A mass exactly equal to one-twelfth the mass of one carbon-12 atom.
Molecular Mass : Sum of atomic masses of the elements present in a molecule.
Formula Mass : Sum of the atomic weights of atoms in a molecule. One Mole is the amount of a substance that contains as many particles/entities as there are atoms in exactly 12g (or 0.012 kg) of the 12C isotope.
Molar Mass : Mass of one mole of a substance in grams.
Mass Percent = Mass of solute / Mass of solution ×100
Molarity = No. of moles of solute / Volume of solution in litres
Molality = No. of moles of solute / Mass of solvent in kg
Limiting Reagent: Reactant which gets consumed and limits the amount of product formed.
Physical Quantities
Physical Quantity | Unit
Length | m (metre)
Mass | kg (kilogram)
Time | s (second)
Electric Current | A (ampere)
Thermodynamic temperature | K (kelvin)
Amount of the substance | (mole)
Luminous intensity | cd (Candela)
Importance of Chemistry
• In meeting human needs for food, health care products and other products required for improving quality of life.
• In diverse areas such as weather patterns, functioning of brain and operation of a computer.
• In chemical industries.
Mole Fraction
Mole Fraction of A = na / (na + nb)
Mole Fraction of B = nb / (na + nb)
Classification
Mixtures: Two or more substances present in any ratio. (air, tea)
Homogeneous : Uniform composition (Sugar solution, air)
Heterogeneous : Non-uniform composition (Mixture of salt and sugar)
Pure Substance: Fixed composition (Cu, Ag)
Elements : Contain one type of particles i.e., atoms, molecules (Na, Cu)
Compounds : Two or more atoms of different elements (H2O, NH3)
Matter: Anything which occupies space
(i) Solid : Particles are held very close to each other in an orderly fashion with no freedom of movement.
Have definite volume and shape.
(ii) Liquid : Particles are close and can move around.
Have definite volume but no definite shape.
(iii) Gas : Particles are far apart and their movement is easy and fast.
Neither have definite volume nor definite shape.
Properties of Matter:
(i) Physical : Properties measured/observed without changing the identity or composition of substance. (Colour, odour)
(ii) Chemical : Properties measured/observed when a chemical reaction occurs. (Acidity or Basicity, combustibility)
Measurement of Matter :
International System of Units (SI) : (Length-m)
Mass is the amount of matter present in a substance.
Weight is the force exerted by gravity on an object.
Uncertainty of measurement : Range of possible values within which the true value of the measurement lies.
Significant figures : Meaningful digits known with certainty.
Precision : Closeness of various measurements for same quantity.
Accuracy : Agreement of a particular value to true value of result.
Gay Lussac's Law of Gaseous Volume : When gases combine or all produced in a chemical reaction they do so in simple ratio by volume provided all gases are at same temperature and pressure.
Avogadro's is Law : Equal volumes of gases at the same temperature and pressure should contain equal number of molecules.
Dalton's Atomic Theory :
• Matter consists of indivisible atoms.
• All the atoms of a given element have identical properties including identical mass.
• Compounds are formed when atoms of different elements combine in a fixed rate.
• Atoms are neither created nor destroyed in chemical reaction.
Law of Conservation of Mass : Matter can neither be created nor destroyed. It was given by Antoine Lavoisier.
Law of Definite Proportions : A given compound always contains exactly the same proportion of elements. It was given by Joseph Proust.
Law of Multiple Proportions : If two elements can combine to form more than one compounds the masses of one element that combine with a fixed mass of the other element are in ratio of small whole numbers. It was given by Dalton.


Liquid and Gaseous States
Dalton's Law of Partial Pressure
Total pressure exerted by the mixture of non- reactive gases is equal to sum of the partial pressures of individual gases. $P_{total} = p_1 + p_2 + p_3$ ..... (At constant T,V)
Density and molar mass at a gaseous substance
$M = \frac{dRT}{P}$
Surface Tension
Denoted by Gamma (γ) Unit: Nm^{-1}
is the force acting per unit length perpendicular to the line drawn on the surface of liquid.
Intermolecular Forces are the forces of attraction and repulsion between interacting particles
•London dispersion forces are the weakest intermolecular forces present among non-polar atoms and molecules.
•Dipole – dipole forces act between the molecules possessing permanent dipole.
•Dipole – induced dipole forces are the attractive forces operate between polar molecules having permanent dipole.
•Hydrogen bond is found in the molecules in which highly polar N–H, H–O and H–F bonds are present.
Thermal Energy is the energy of body arising from motion of its atoms or molecules
Intermolecular forces vs thermal interaction
Gas →Liquid →Solid
Predominance of intermolecular interactions
Gas ← Liquid ←Solid
Predominance of thermal energy
Gaseous State
Physical Properties:
• Gases are highly compressible.
• Gases exert pressure equally in all directions.
• Gases have much lower density than solids and liquids.
• Volume and shape of gases are not fixed.
• They mix evenly and completely in all proportions.
Gas Laws
•Boyle's Law (Pressure – Volume relationship): At constant temperature, the pressure of a fixed amount of gas varies inversely with its volume.
$P_1V_1 = P_2V_2 = \text{Constant} \Rightarrow \frac{P_1}{P_2} = \frac{V_1}{V_2}$
•Charle's Law (Temperature – Volume relationship) : At constant pressure, the volume of a fixed mass of a gas is directly proportional to the absolute temperature $\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow \frac{V}{T} = \text{Constant}$
•Gay Lussac's Law (Pressure – Temperature relationship): At constant volume, pressure of a fixed amount of a gas varies directly with temperature $\frac{P}{T} = \text{constant}$
•Avogadro's Law (Volume – Amount relationship): Equal volume of all gases under the same conditions of temperature and pressure contain equal number of molecules. $V = kn$; $n = \frac{\text{Mass of gas}}{\text{Molar Mass}}$
Ideal Gas Equation
$R = \frac{pV}{nT}$, R is gas constant / universal gas constant
$R = 8.314\ JK^{-1}\ mol^{-1}$
Viscosity
$F = \eta A \frac{dx}{dz}$
- Viscosity coefficient (η) is the force when velocity gradient is unity and the area of contact is unit area.
- SI unit of viscosity coefficient is Newton second per square metre ($N\ s\ m^{-2}$) = Pa s (Pascal second)
Liquid State
Intermolecular forces of liquid state are stronger than gaseous state.
• Boiling is the condition of free vapourisation throughout the liquid.
• Normal b.p. is boiling point at 1 atm.
•Standard b.p.is boiling point at 1 bar.
Liquifaction of Gases
•Volume of one mole of gas at critical temperature is called critical volume (V_c) and pressure at this temperature is called critical pressure (P_c)
Deviation from ideal gas behaviour
• Real gases show deviations from ideal gas law because molecules interact with each other.
•Pressure exerted by the gas is lower than the pressure exerted by the ideal gas.
$P_{ideal} = P_{real} + \frac{an^2}{V^2}$
Observed pressure
Correction term
• Compressibility factor $Z = \frac{PV}{nRT}$
Postulates of Kinetic Molecular Theory of gases
• A gas contains a large number of small particles called molecules. Size and mass of all molecules of each gas are identical.
•There is no force of attraction between the particles of a gas at ordinary temperature and pressure.
• Particles of a gas are always in constant and random motion.
• Particles of a gas move in all possible directions in straight lines.
• Collisions of gas molecules are perfectly elastic.
• At any particular time, different particles in the gas have different speeds and hence different kinetic energies.
• If a molecule has variable speed, then it must have a variable kinetic energy.
Molecular Velocity
• Root mean square velocity (Crms)
$Crms = \sqrt{\frac{3RT}{m}} = \sqrt{\frac{3PV}{m}} = \sqrt{\frac{3P}{d}}$
• Average velocity ($\bar{c}$)
$\bar{c} = \sqrt{\frac{8RT}{\pi m}} = \sqrt{\frac{8PV}{\pi m}} = \sqrt{\frac{8P}{\pi d}}$
• Most probable velocity (Cp)
$cp = \sqrt{\frac{2RT}{m}} = \sqrt{\frac{2PV}{m}} = \sqrt{\frac{2P}{D}}$
Graham's Law
Under the same conditions of temperature and pressure the rates of diffusion of different gases are inversely proportional to the square roots of their densities

Atomic Structure

- **Emission Spectra :** Spectrum of radiation emitted by a substance that has absorbed energy.
- **Absorption Spectra :** It is like photographic negative of an emission spectra.
- **Line / Atomic Spectra :** Emission spectra which do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelength with dark space between them.

$\bar{v} = 109677\,(\frac{1}{n_1^2} - \frac{1}{n_2^2})\ cm^{-1}$ where

n_1=1,2……n_2=n_1+1, n_1+2……

Series	n_1	n_2	Spectral Region
Lyman	1	2,3.....	Ultraviolet
Balmer	2	3,4.....	Visible
Paschen	3	4,5.....	Infrared
Brackett	4	5,6.....	Infrared
Pfund	5	6,7.....	Infrared

Types: — Atomic Spectra

Number of protons in nucleus of an atom or Number of electrons in a neutral atom — Atomic Number (Z)

Number of protons (Z) + number of neutrons (*n*) — Mass Number (A)

Atoms of same element having same atomic number but different mass number. (Isotopes of hydrogen: Protium ^1_1H, Deuterium ^2_1D and Tritium ^3_1T). — Isotopes

Atoms of different elements with different atomic number but same mass number. ($^{40}_{20}Ca$ and $^{40}_{18}Ar$) — Isobars

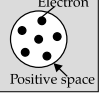
By J.J.Thomson Charge to mass ratio of electron
$= 1.758820 \times 10^{11}\ C\ kg^{-1}$
Charge electron $= 1.6022 \times 10^{-19} C$
Mass of electron $= 9.1094 \times 10^{-31} Kg$ — Discovery of Electron

By Ernest Rutherford
Charge on proton $= +1.6022 \times 10^{-19} C$
Mass of Proton $= 1.672 \times 10^{-27}$ Kg — Discovery of Proton

By James Chadwick
Charge on neutron = 0
Mass of neutron $= 1.675 \times 10^{-27}$ Kg — Discovery of Neutron

Thomson Model of Atom: (Watermelon Model)

Atom possesses a spherical shape in which the positive charge is uniformly distributed.



Rutherford's Nuclear Model of Atom

Postulates:
- Positive charge and most of the mass of atoms was densely concentrated in extremely small region i.e. nucleus.
- Nucleus is surrounded by electrons that move around the nucleus with high speed in circular path called orbits.
- Electrons and nucleus are held together by electrostatic forces of attraction.

Drawbacks:
- It cannot explain the stability of an atom.
- It does not say anything about the electronic structure of atoms.

Bohr's Model for Hydrogen Atom

Postulates:
- Electron in H atom can move around the nucleus in a circular path of fixed radius and energy called as orbits. These orbits are arranged concentrically around the nucleus.
- Each of these orbits has a definite energy known as energy levels or stationary states.
- When an electron jumps from a lower energy level to higher one, some energy is absorbed.
- $v = \frac{\Delta E}{n} = \frac{E_2 - E_1}{n}$ Bohr's frequency rule.

Angular momentum of electron: $m_e v_r = n\frac{h}{2\pi}$ n=1,2,3.....

Limitations:
- Unable to account for finer details of H atom. Spectrum observed by sophisticated spectroscopic techniques.
- Could not explain the ability of atoms to form molecules by chemical bonds.

Developments Leading To Bohr's Model of Atom

Photoelectric Effect: It was found By H.Hertz — It is the phenomenon of ejection of electrons from the surface of a metal when light of suitable frequency strikes on it.

KE of ejected electron $h\nu = h\nu_0 + 1/2\ m_e v^2$

Dual nature i.e. wave like and particle like of the electromagnetic radiation.
- Experimental results regarding atomic spectra.
- Wave nature of electromagnetic radiation.

It was given by James Maxwell.
Frequency (ν): Number of waves that pass a given point in one second. Unit – Hertz (Hz),
Velocity of light = Frequency × Wavelength
Wave number ($\bar{\nu}$): Number of wavelengths per unit length. Unit – m^{-1}
- **Particle nature of electromagnetic radiation:**
  Planck's quantum theory: E= hν
  Planck's constant (h) $= 6.626 \times 10^{-34}$ Js

Quantum Mechanical Model of Atom:

Schrodinger Equation
- Dual behaviour of atom i.e., particle and wavelike. De Broglie equation: $\lambda = \frac{h}{mv} = \frac{h}{p}$
- Heisenberg's Uncertainty Principle: It is impossible to determine simultaneously, the exact position and momentum of an electron.
  $\Delta x.\ \Delta p_x \geq = \frac{h}{4\pi}$
  $\Rightarrow \Delta v.\ \Delta x = \frac{h}{4\pi m}$

Fundamental Equation was developed by Schrodinger as $\hat{H}\psi = E = $ where $\hat{H}$ = Hamiltonian

Quantum Numbers

(i) Principal quantum number (n) :n = 1,2,3,4…….. Shell = K, L, M, N.....
(ii) Azimuthal quantum number (l) : For given value of n, l = 0 to n-1
(iii) Magnetic quantum number (m) : for subshell with l value $m_l = 2l+1$
(iv) Spin quantum Number (m_s): $+1/2$ (↑), $-1/2$ (↓)

Electronic Configuration of atoms

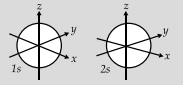
(i) $s^a p^b d^c$..... notation
(ii) Orbital diagram

Filling of electrons in orbitals

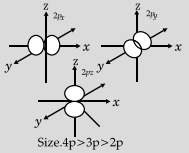
- **Aufbau Principle :** In the ground state of atoms, the orbitals are filled according to increasing energies.
- **Pauli Exclusion Principle :** No two electrons in an atom can have same set of four quantum numbers.
- **Hund's rule :** Pairing of electrons in the orbitals belonging to same subshell does not take place until each electron belonging to the subshell is singly occupied.

Shapes of orbitals

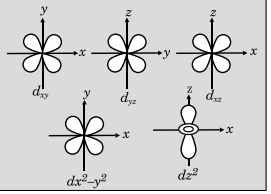
s Orbitals:
Spherically symmetric
Size increases with increase in size in n, ie, 4s>3s>2s>1s



p Orbitals:
Each p Orbital consists of two sections called lobes on either side of plane passing through the nucleus.



d Orbitals – "Clover leaf" distribution.
– Two angular nodes.



Energy of orbitals — Lower the value of $(n+l)$ for an orbital, lower is its energy.

Chemical Bonding

Types :
(i) Covalent Bond : A chemical bond formed between two atoms by mutual sharing of electrons between them to complete their octet.
(ii) Ionic Bond : A chemical bond formed by complete transfer of electrons from one atom to another acquire the stable nearest noble gas configuration.
(iii) Coordinate bond : A chemical bond formed by donation of two electrons from one atom to another to complete their octct.

Energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.

Postulates :
- Shape of molecule depends upon the number of valence shell electron pairs around central atom.
- Pairs of electrons in the valence shell repel one another.
- These pairs of electrons tend to occupy such positions in space that minimize repulsion.
- The valence shell is taken as a sphere with electron pairs localising on spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- When one or more resonance structures can represent a molecule, VSEPR model is applicable.
- **Decreasing order of repulsive interaction :** lp – lp > lp – bp > bp – bp

Valence Bond Theory : Given by L Pauling. It explains that a covalent bond is formed between two atoms by overlap of their half-filled valance orbitals, each of which contains one unpaired electron.
Orbital Overlap Concept : Formation of a covalent bond results by pairing of electrons in valence shell with opposite spins.
Types of Overlapping : (i) Sigma (σ) bond – end to end.
(ii) Pi (π) bond – axis remain parallel to each other.
Hybridisation : Process of intermixing of orbitals of different energies resulting in formation of new set of orbitals of equivalent energies and shape.
Types of Hybridisation –(i) sp (ii) sp^2 (iii) sp^3
Bonding Molecular Orbitals : Addition of atomic orbitals.
Antibonding Molecular Orbitals : Subtraction of atomic orbitals.

(i) Bond Length : Equilibrium distance between the nuclei of two bonded atoms in molecule.
(ii) Bond Angle : Angle between the orbitals containing bonding electron pairs around central atom in a molecule complex ion.
(iii) Bond Enthalpy : Amount of energy required to break one mole of bonds of particular type between two atoms.
(iv) Bond Order : Number of bonds between the two atoms of a molecule.
(v) Resonance Structures : A set of two or more Lewis structures that collectively describe the electronic bonding a single polyatomic species.
(vi) Dipole Moment : Product of the magnitude of the charge and distance between centres of positive and negative charge. $\mu = Q \times r$

Postulates :
- Electrons in a molecule are present in various molecular orbitals as electrons are present in atomic orbitals.
- Atomic orbitals of comparable energies and proper symmetry combine.
- Atomic orbitals is monocentric while a molecular orbital is polycentric.
- Number of molecular orbitals formed is equal to number of combining atomic orbitals.
- Bonding molecular orbitals has low energy and high stability.

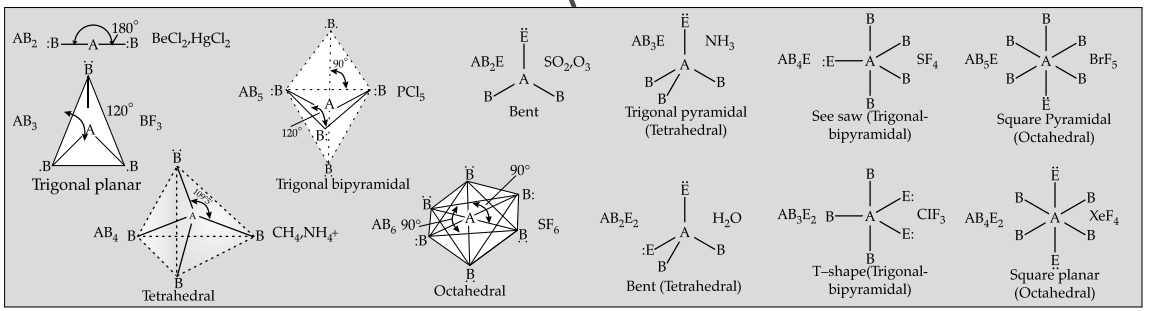
Types of MO : σ(Sigma), ⊼ (Pi), δ (Delta)

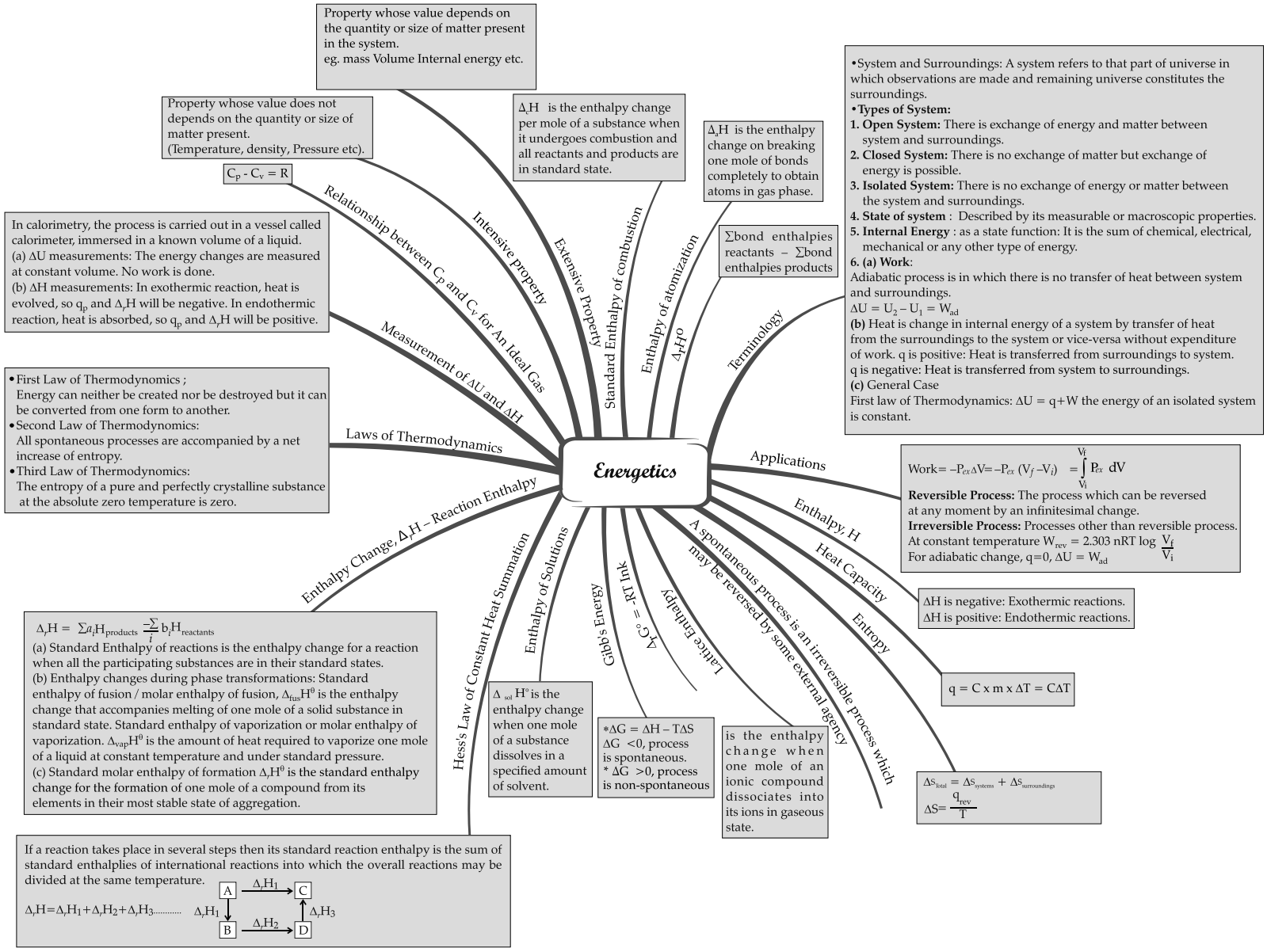
Kossel Lewis approach to chemical bonding :
* Lewis pictured the atom as a positively charged 'kernel' and the outer shell accommodates a maximum of eight electrons.
- Lewis postulated that atoms achieve the stable octet when linked by chemical bonds.
- Kossel gave following facts:
* In the periodic table, highly electronegative halogens and highly electropositive alkali separated by noble gases.
* Formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with gain and loss of electron by respective atoms.
* Negative and positive ions formed attain noble gas electronic configuration.
- Negative and positive ions are stabilized by electrostatic attraction.

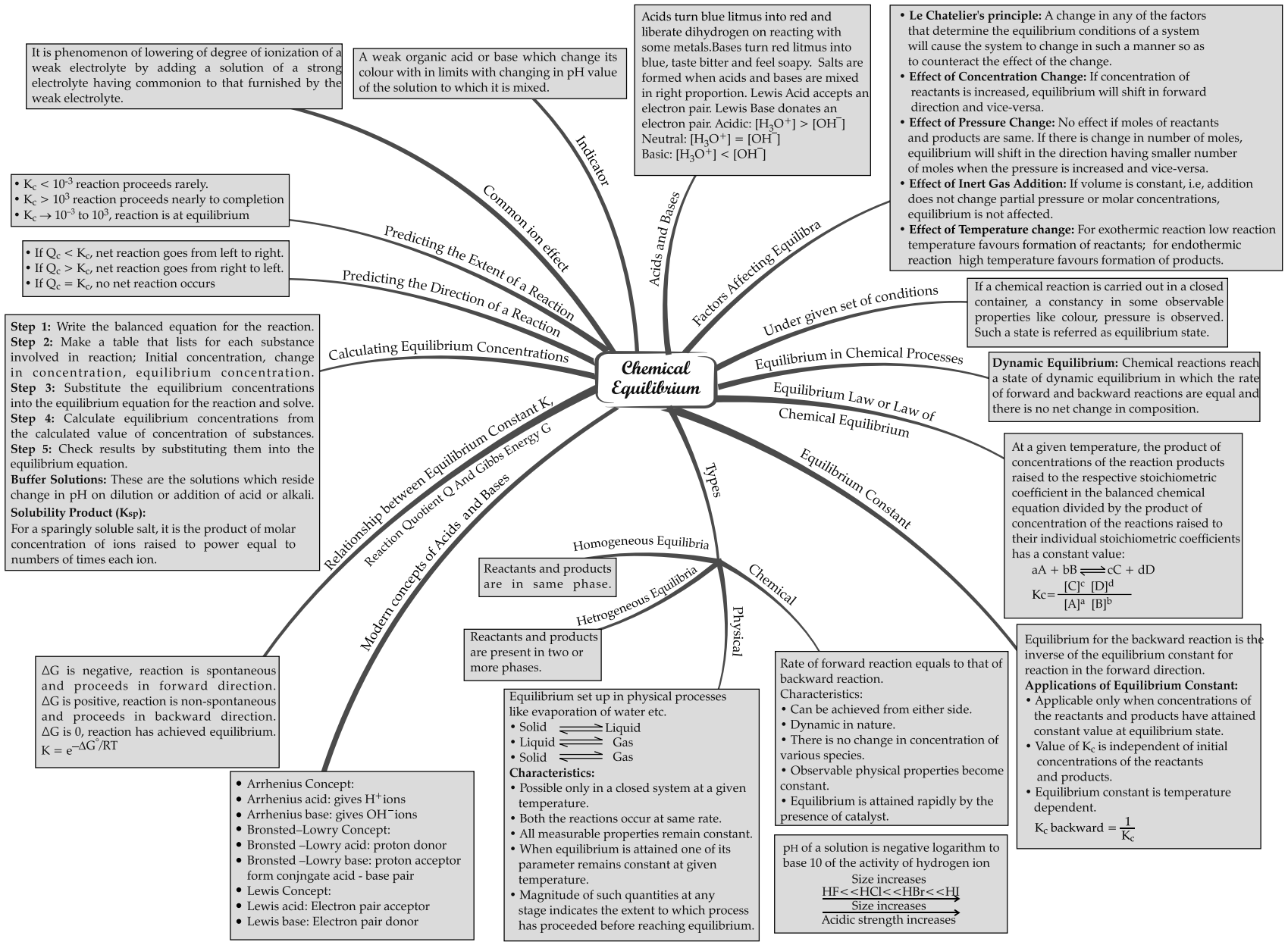
Octet Rule : Atoms can combine either by transfer of valence electrons from one atom to another or by sharing of valence electrons to complete octet in their valence shells.
Lewis dot Structure provides a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule.
How To Write A Lewis Dot Structure:
Step 1 : Add the valence electrons of the combining atoms to obtain total number of electrons.
Step 2 : For anions, each negative charge means addition of one electron. For cations, each positive charge means subtraction of one electron from total number of valence electrons.
Step 3 : Write chemical symbols of combining atoms.
Step 4 : Least electronegative atom occupies central position.
Step 5 : After accounting for shared pairs of electrons, remaining are either utilized for multiple bonding or remain as lone pairs.
Formal Charge= (Total number of valence electrons in free atom) – [(Total number of non-bonding electrons) + 1/2(Total number of bonding electrons)]
Limitations Of Octet Rule :
- Shows three types of exceptions i.e. incomplete octet of central atom, odd-electron molecules and expanded octet.
- Does not account for the shape of molecules.
- Fails to explain stability of molecules.

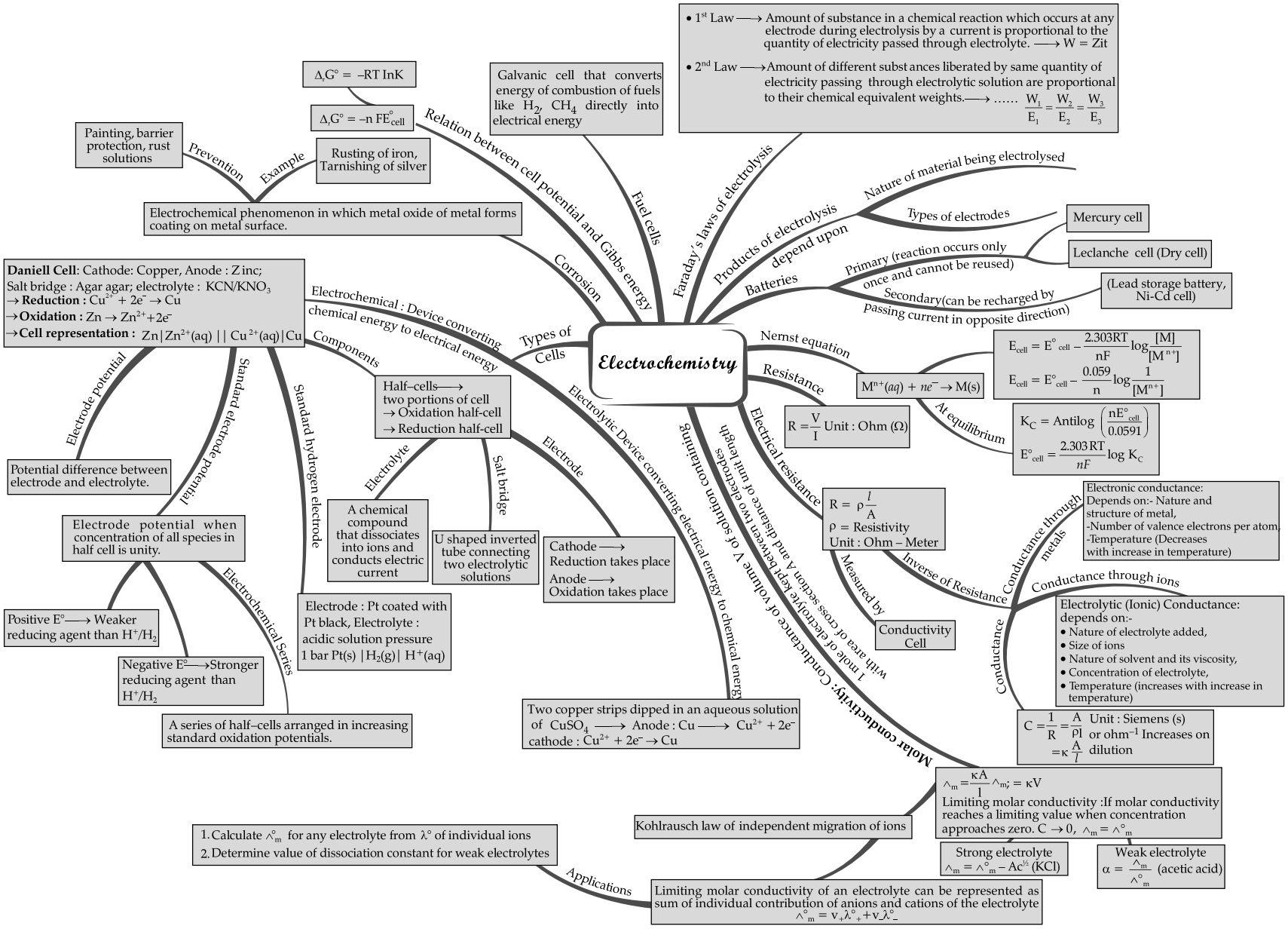
Hydrogen Bond: Formed when the negative end of one molecule attracts the positive end of other.
Types:
(i) Intermolecular : Between two different molecules of same or different substances.
(ii) Intramolecular : Between two highly electronegative atoms in the same molecule.

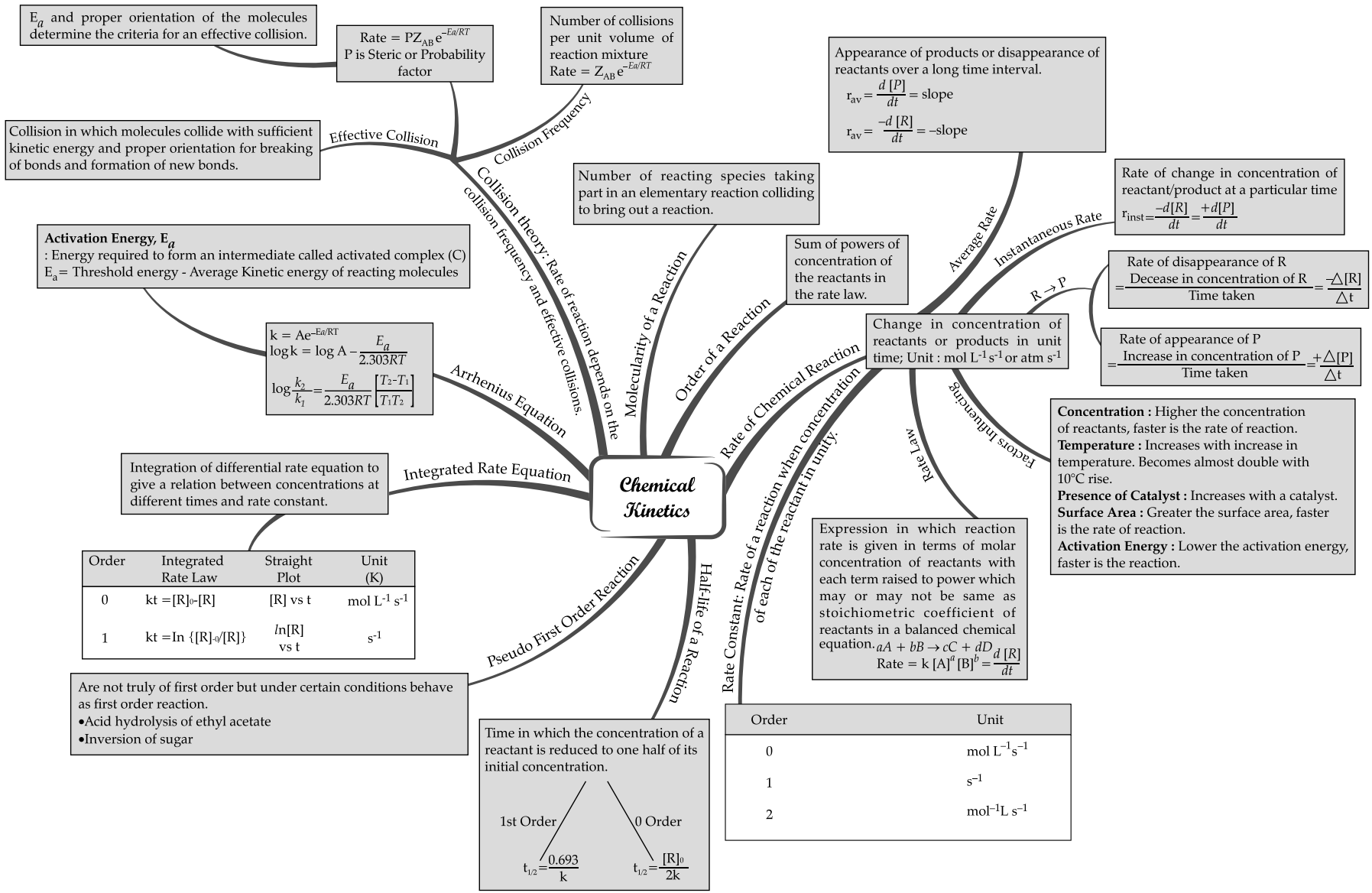
Chemical Bond:Attractive forces which hold the various chemical constituents together in different chemical species.
Lattice Enthalpy
Valence Shell Electron Pair Repulsion (VSEPR)
Bond Parameters
Molecular orbital theory
Hybridization
Chemical Bonding

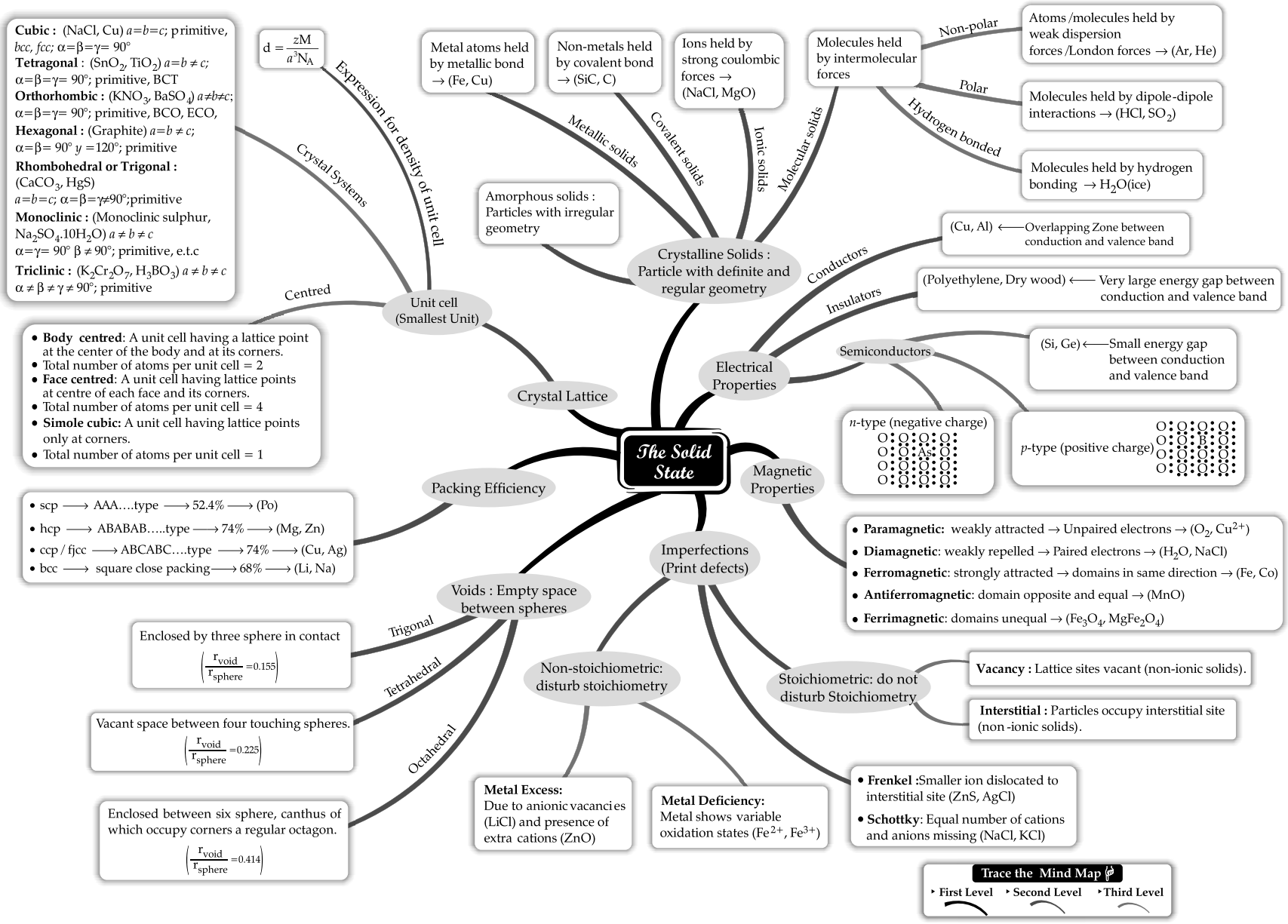


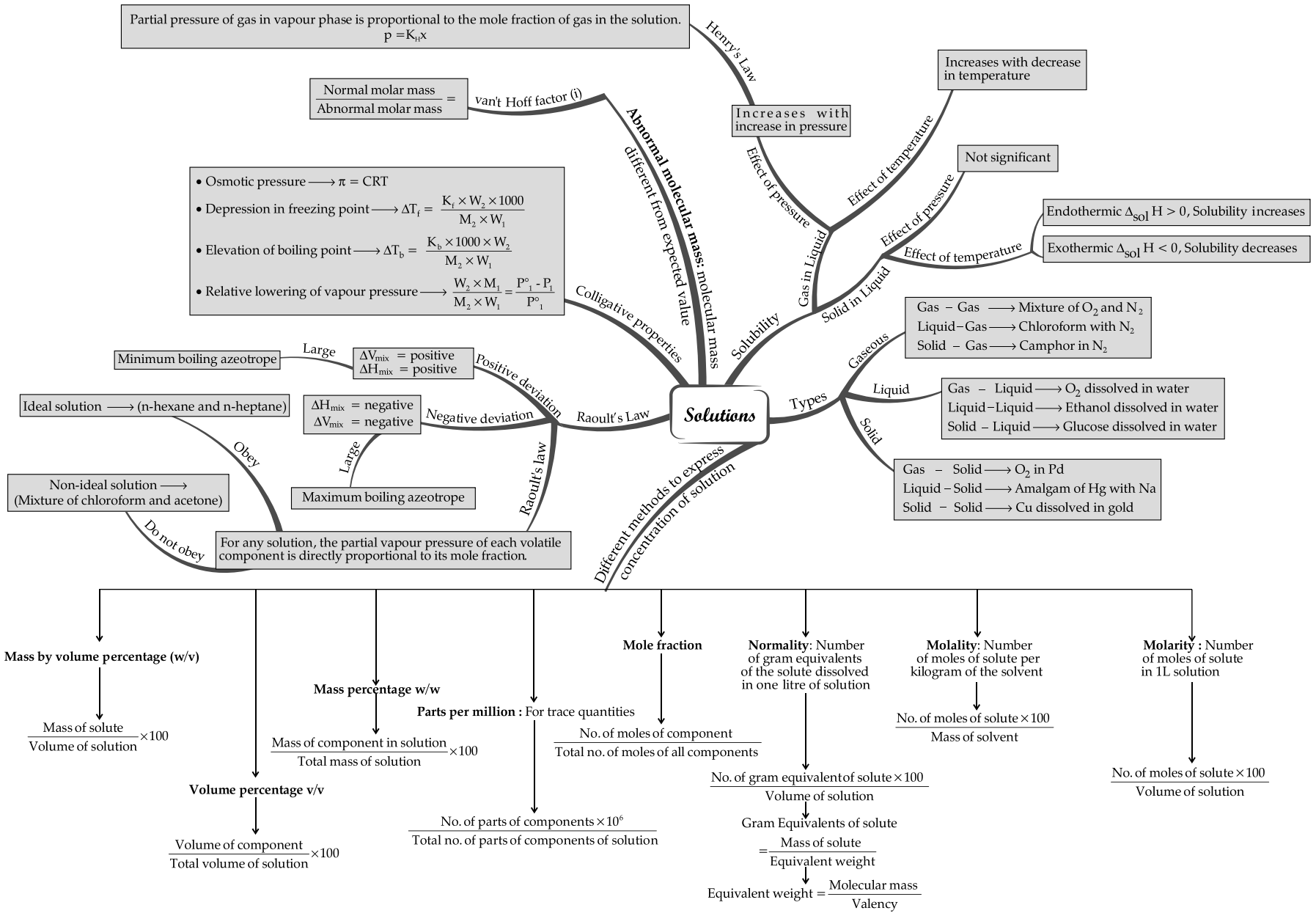

Energetics
Intensive property
Property whose value depends on the quantity or size of matter present in the system. eg. mass Volume Internal energy etc.
Extensive Property
Property whose value does not depends on the quantity or size of matter present. (Temperature, density, Pressure etc).
Relationship between C_p and C_v for An Ideal Gas
$C_P - C_v = R$
Measurement of ΔU and ΔH
In calorimetry, the process is carried out in a vessel called calorimeter, immersed in a known volume of a liquid.
(a) ΔU measurements: The energy changes are measured at constant volume. No work is done.
(b) ΔH measurements: In exothermic reaction, heat is evolved, so q_p and $\Delta_r H$ will be negative. In endothermic reaction, heat is absorbed, so q_p and $\Delta_r H$ will be positive.
Laws of Thermodynamics
• First Law of Thermodynamics ; Energy can neither be created nor be destroyed but it can be converted from one form to another.
• Second Law of Thermodynomics: All spontaneous processes are accompanied by a net increase of entropy.
• Third Law of Thermodynomics: The entropy of a pure and perfectly crystalline substance at the absolute zero temperature is zero.
Enthalpy Change, $\Delta_r H$ – Reaction Enthalpy
$\Delta_r H = \sum a_i H_{products} - \sum b_i H_{reactants}$
(a) Standard Enthalpy of reactions is the enthalpy change for a reaction when all the participating substances are in their standard states.
(b) Enthalpy changes during phase transformations: Standard enthalpy of fusion / molar enthalpy of fusion, $\Delta_{fus}H^0$ is the enthalpy change that accompanies melting of one mole of a solid substance in standard state. Standard enthalpy of vaporization or molar enthalpy of vaporization. $\Delta_{vap}H^0$ is the amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure.
(c) Standard molar enthalpy of formation $\Delta_f H^0$ is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable state of aggregation.
Hess's Law of Constant Heat Summation
If a reaction takes place in several steps then its standard reaction enthalpy is the sum of standard enthalplies of international reactions into which the overall reactions may be divided at the same temperature.
$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$.....
A → C ($\Delta_r H_1$), A → B ($\Delta_r H_1$), B → D ($\Delta_r H_2$), C → D ($\Delta_r H_3$)
Enthalpy of Solutions
$\Delta_{sol} H^\circ$ is the enthalpy change when one mole of a substance dissolves in a specified amount of solvent.
Gibbs Energy
$\Delta G^\circ = -RT \ln K$
*ΔG = ΔH – TΔS
ΔG <0, process is spontaneous.
* ΔG >0, process is non-spontaneous
Lattice Enthalpy
is the enthalpy change when one mole of an ionic compound dissociates into its ions in gaseous state.
A spontaneous process is an irreversible process which may be reversed by some external agency
Entropy
$\Delta S_{total} = \Delta S_{systems} + \Delta S_{surroundings}$
$\Delta S = \frac{q_{rev}}{T}$
Heat Capacity
q = C x m x ΔT = CΔT
Enthalpy, H
ΔH is negative: Exothermic reactions.
ΔH is positive: Endothermic reactions.
Applications
Work= $-P_{ex}\Delta V = -P_{ex}(V_f - V_i) = \int_{V_i}^{V_f} P_{ex}\, dV$
Reversible Process: The process which can be reversed at any moment by an infinitesimal change.
Irreversible Process: Processes other than reversible process.
At constant temperature $W_{rev} = 2.303\ nRT \log \frac{V_f}{V_i}$
For adiabatic change, q=0, $\Delta U = W_{ad}$
Terminology
• System and Surroundings: A system refers to that part of universe in which observations are made and remaining universe constitutes the surroundings.
• Types of System:
1. Open System: There is exchange of energy and matter between system and surroundings.
2. Closed System: There is no exchange of matter but exchange of energy is possible.
3. Isolated System: There is no exchange of energy or matter between the system and surroundings.
4. State of system : Described by its measurable or macroscopic properties.
5. Internal Energy : as a state function: It is the sum of chemical, electrical, mechanical or any other type of energy.
6. (a) Work:
Adiabatic process is in which there is no transfer of heat between system and surroundings.
$\Delta U = U_2 - U_1 = W_{ad}$
(b) Heat is change in internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. q is positive: Heat is transferred from surroundings to system. q is negative: Heat is transferred from system to surroundings.
(c) General Case
First law of Thermodynamics: ΔU = q+W the energy of an isolated system is constant.
$\Delta_r H^o$
Enthalpy of atomization
$\Delta_a H$ is the enthalpy change on breaking one mole of bonds completely to obtain atoms in gas phase.
Standard Enthalpy of combustion
$\Delta_c H$ is the enthalpy change per mole of a substance when it undergoes combustion and all reactants and products are in standard state.
∑bond enthalpies reactants – ∑bond enthalpies products

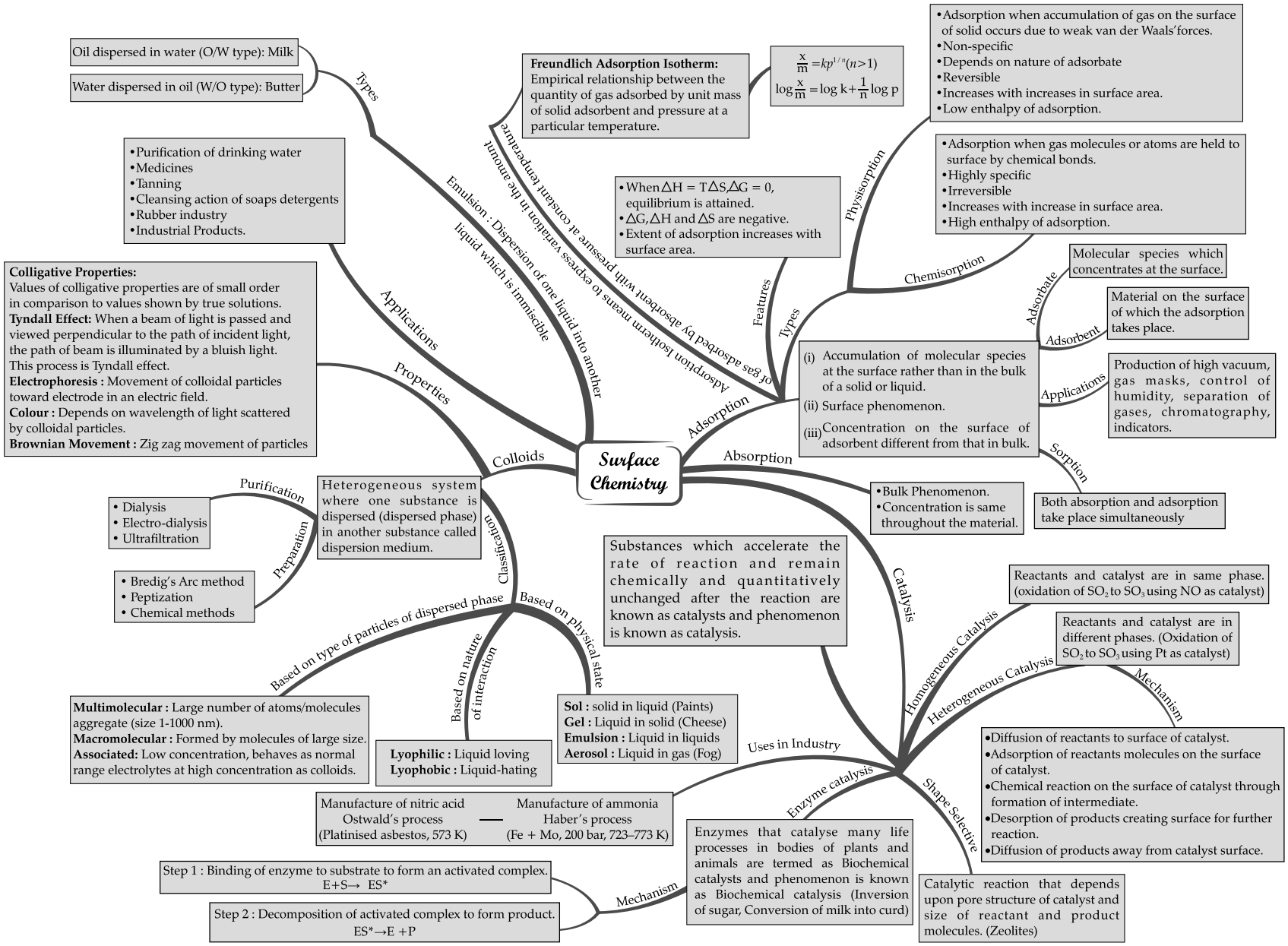

Chemical Equilibrium
Common ion effect
It is phenomenon of lowering of degree of ionization of a weak electrolyte by adding a solution of a strong electrolyte having commonion to that furnished by the weak electrolyte.
Indicator
A weak organic acid or base which change its colour with in limits with changing in pH value of the solution to which it is mixed.
Acids and Bases
Acids turn blue litmus into red and liberate dihydrogen on reacting with some metals.Bases turn red litmus into blue, taste bitter and feel soapy. Salts are formed when acids and bases are mixed in right proportion. Lewis Acid accepts an electron pair. Lewis Base donates an electron pair. Acidic: [H3O+] > [OH−]
Neutral: [H3O+] = [OH−]
Basic: [H3O+] < [OH−]
Factors Affecting Equilibra
• Le Chatelier's principle: A change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to counteract the effect of the change.
• Effect of Concentration Change: If concentration of reactants is increased, equilibrium will shift in forward direction and vice-versa.
• Effect of Pressure Change: No effect if moles of reactants and products are same. If there is change in number of moles, equilibrium will shift in the direction having smaller number of moles when the pressure is increased and vice-versa.
• Effect of Inert Gas Addition: If volume is constant, i.e, addition does not change partial pressure or molar concentrations, equilibrium is not affected.
• Effect of Temperature change: For exothermic reaction low reaction temperature favours formation of reactants; for endothermic reaction high temperature favours formation of products.
Predicting the Extent of a Reaction
• Kc < 10−3 reaction proceeds rarely.
• Kc > 103 reaction proceeds nearly to completion
• Kc → 10−3 to 103, reaction is at equilibrium
Predicting the Direction of a Reaction
• If Qc < Kc, net reaction goes from left to right.
• If Qc > Kc, net reaction goes from right to left.
• If Qc = Kc, no net reaction occurs
Under given set of conditions
If a chemical reaction is carried out in a closed container, a constancy in some observable properties like colour, pressure is observed. Such a state is referred as equilibrium state.
Equilibrium in Chemical Processes
Dynamic Equilibrium: Chemical reactions reach a state of dynamic equilibrium in which the rate of forward and backward reactions are equal and there is no net change in composition.
Equilibrium Law or Law of Chemical Equilibrium
At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentration of the reactions raised to their individual stoichiometric coefficients has a constant value:
aA + bB ⇌ cC + dD
Kc = [C]c [D]d / [A]a [B]b
Equilibrium Constant
Equilibrium for the backward reaction is the inverse of the equilibrium constant for reaction in the forward direction.
Applications of Equilibrium Constant:
• Applicable only when concentrations of the reactants and products have attained constant value at equilibrium state.
• Value of Kc is independent of initial concentrations of the reactants and products.
• Equilibrium constant is temperature dependent.
Kc backward = 1/Kc
Types
Chemical
Rate of forward reaction equals to that of backward reaction.
Characteristics:
• Can be achieved from either side.
• Dynamic in nature.
• There is no change in concentration of various species.
• Observable physical properties become constant.
• Equilibrium is attained rapidly by the presence of catalyst.
Homogeneous Equilibria
Reactants and products are in same phase.
Hetrogeneous Equilibria
Reactants and products are present in two or more phases.
Physical
Equilibrium set up in physical processes like evaporation of water etc.
• Solid ⇌ Liquid
• Liquid ⇌ Gas
• Solid ⇌ Gas
Characteristics:
• Possible only in a closed system at a given temperature.
• Both the reactions occur at same rate.
• All measurable properties remain constant.
• When equilibrium is attained one of its parameter remains constant at given temperature.
• Magnitude of such quantities at any stage indicates the extent to which process has proceeded before reaching equilibrium.
Calculating Equilibrium Concentrations
Step 1: Write the balanced equation for the reaction.
Step 2: Make a table that lists for each substance involved in reaction; Initial concentration, change in concentration, equilibrium concentration.
Step 3: Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve.
Step 4: Calculate equilibrium concentrations from the calculated value of concentration of substances.
Step 5: Check results by substituting them into the equilibrium equation.
Buffer Solutions: These are the solutions which reside change in pH on dilution or addition of acid or alkali.
Solubility Product (Ksp):
For a sparingly soluble salt, it is the product of molar concentration of ions raised to power equal to numbers of times each ion.
Relationship between Equilibrium Constant K, Reaction Quotient Q And Gibbs Energy G
ΔG is negative, reaction is spontaneous and proceeds in forward direction.
ΔG is positive, reaction is non-spontaneous and proceeds in backward direction.
ΔG is 0, reaction has achieved equilibrium.
K = e−ΔG°/RT
Modern concepts of Acids and Bases
• Arrhenius Concept:
• Arrhenius acid: gives H+ ions
• Arrhenius base: gives OH− ions
• Bronsted–Lowry Concept:
• Bronsted –Lowry acid: proton donor
• Bronsted –Lowry base: proton acceptor form conjngate acid - base pair
• Lewis Concept:
• Lewis acid: Electron pair acceptor
• Lewis base: Electron pair donor
pH of a solution is negative logarithm to base 10 of the activity of hydrogen ion
Size increases
HF << HCl << HBr << HI
Size increases
Acidic strength increases

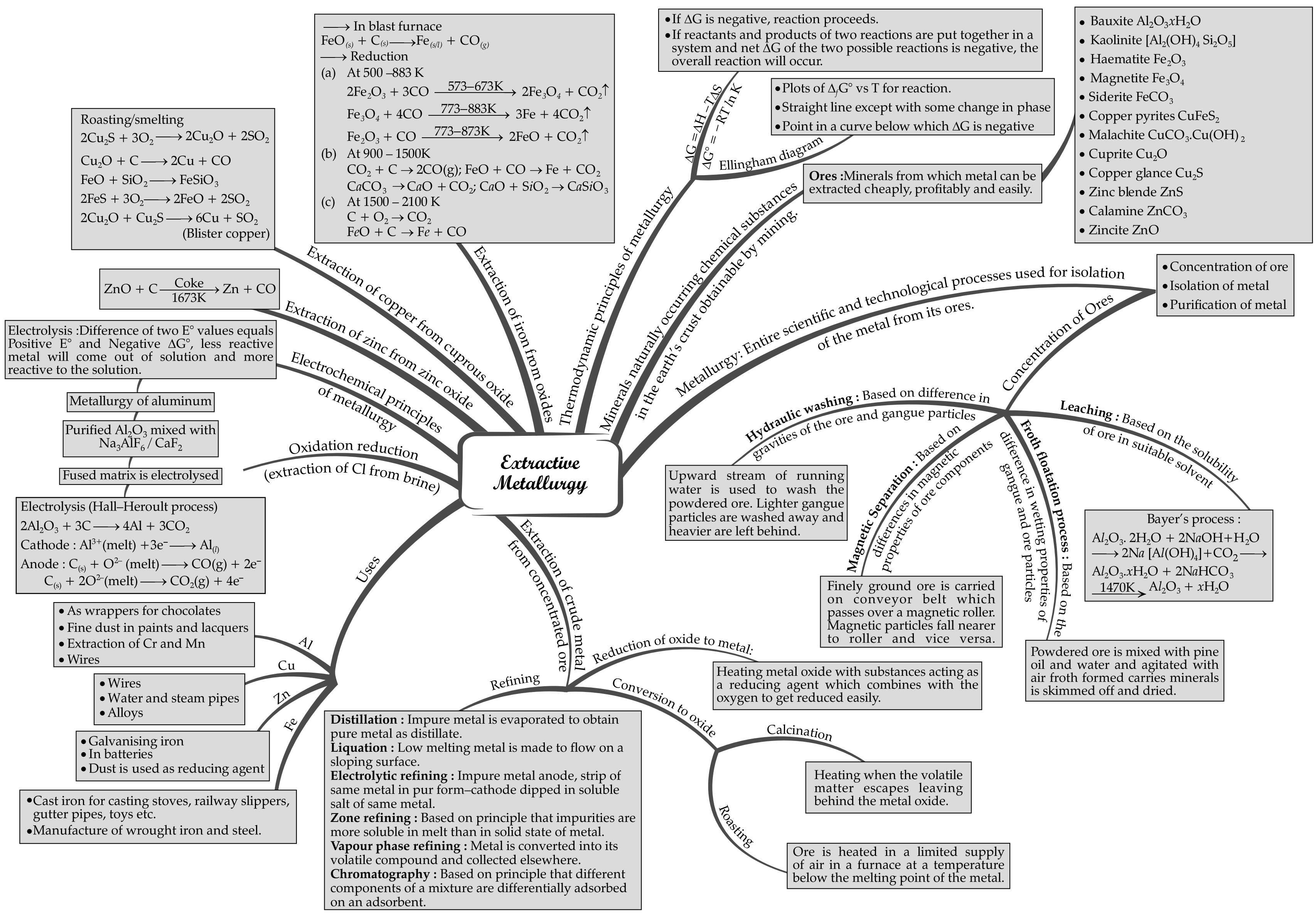

Electrochemistry
Faraday's laws of electrolysis
• 1st Law ⟶ Amount of substance in a chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through electrolyte. ⟶ W = Zit
• 2nd Law ⟶ Amount of different substances liberated by same quantity of electricity passing through electrolytic solution are proportional to their chemical equivalent weights. ⟶ ..... W1/E1 = W2/E2 = W3/E3
Products of electrolysis depend upon
Nature of material being electrolysed
Types of electrodes
Mercury cell
Batteries
Primary (reaction occurs only once and cannot be reused)
Leclanche cell (Dry cell)
Secondary(can be recharged by passing current in opposite direction)
(Lead storage battery, Ni-Cd cell)
Fuel cells
Galvanic cell that converts energy of combustion of fuels like H2, CH4 directly into electrical energy
Relation between cell potential and Gibbs energy
ΔrG° = –RT InK
ΔrG° = –n FE°cell
Corrosion
Example
Rusting of iron, Tarnishing of silver
Prevention
Painting, barrier protection, rust solutions
Electrochemical phenomenon in which metal oxide of metal forms coating on metal surface.
Types of Cells
Electrochemical : Device converting chemical energy to electrical energy
Daniell Cell: Cathode: Copper, Anode : Zinc; Salt bridge : Agar agar; electrolyte : KCN/KNO3
→ Reduction : Cu2+ + 2e– → Cu
→ Oxidation : Zn → Zn2+ + 2e–
→ Cell representation : Zn|Zn2+(aq) || Cu2+(aq)|Cu
Components
Half–cells ⟶ two portions of cell
→ Oxidation half-cell
→ Reduction half-cell
Electrode
Cathode ⟶ Reduction takes place
Anode ⟶ Oxidation takes place
Salt bridge
U shaped inverted tube connecting two electrolytic solutions
Electrolyte
A chemical compound that dissociates into ions and conducts electric current
Electrolytic Device converting electrical energy to chemical energy
Two copper strips dipped in an aqueous solution of CuSO4 ⟶ Anode : Cu ⟶ Cu2+ + 2e–
cathode : Cu2+ + 2e– → Cu
Electrode potential
Potential difference between electrode and electrolyte.
Standard electrode potential
Electrode potential when concentration of all species in half cell is unity.
Positive E° ⟶ Weaker reducing agent than H+/H2
Negative E° ⟶ Stronger reducing agent than H+/H2
Standard hydrogen electrode
Electrode : Pt coated with Pt black, Electrolyte : acidic solution pressure 1 bar Pt(s) |H2(g)| H+(aq)
Electrochemical Series
A series of half–cells arranged in increasing standard oxidation potentials.
Nernst equation
Ecell = E°cell – (2.303RT/nF) log [M]/[M n+]
Ecell = E°cell – (0.059/n) log 1/[Mn+]
Mn+(aq) + ne– → M(s)
Resistance
R = V/I Unit : Ohm (Ω)
At equilibrium
KC = Antilog (nE°cell/0.0591)
E°cell = (2.303RT/nF) log KC
Electrical resistance
R = ρ l/A
ρ = Resistivity
Unit : Ohm – Meter
Inverse of Resistance
Measured by
Conductivity Cell
Molar conductivity: Conductance of volume V of solution containing 1 mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length
Conductance through metals
Electronic conductance: Depends on:- Nature and structure of metal, -Number of valence electrons per atom, -Temperature (Decreases with increase in temperature)
Conductance through ions
Electrolytic (Ionic) Conductance: depends on:-
• Nature of electrolyte added,
• Size of ions
• Nature of solvent and its viscosity,
• Concentration of electrolyte,
• Temperature (increases with increase in temperature)
Conductance
C = 1/R = A/ρl = κ A/l Unit : Siemens (S) or ohm–1 Increases on dilution
∧m = κA/l ∧m; = κV
Limiting molar conductivity :If molar conductivity reaches a limiting value when concentration approaches zero. C → 0, ∧m = ∧°m
Kohlrausch law of independent migration of ions
Strong electrolyte ∧m = ∧°m – Ac½ (KCl)
Weak electrolyte α = ∧m/∧°m (acetic acid)
Applications
1. Calculate ∧°m for any electrolyte from λ° of individual ions
2. Determine value of dissociation constant for weak electrolytes
Limiting molar conductivity of an electrolyte can be represented as sum of individual contribution of anions and cations of the electrolyte
∧°m = ν+λ°+ + ν–λ°–


Chemical Kinetics
Collision theory: Rate of reaction depends on the collision frequency and effective collisions.
Effective Collision
Collision in which molecules collide with sufficient kinetic energy and proper orientation for breaking of bonds and formation of new bonds.
E_a and proper orientation of the molecules determine the criteria for an effective collision.
Rate = $PZ_{AB}e^{-Ea/RT}$
P is Steric or Probability factor
Collision Frequency
Number of collisions per unit volume of reaction mixture
Rate = $Z_{AB}e^{-Ea/RT}$
Activation Energy, E_a
: Energy required to form an intermediate called activated complex (C)
E_a = Threshold energy - Average Kinetic energy of reacting molecules
Arrhenius Equation
$k = Ae^{-Ea/RT}$
$\log k = \log A - \frac{E_a}{2.303RT}$
$\log \frac{k_2}{k_1} = \frac{E_a}{2.303RT}\left[\frac{T_2 - T_1}{T_1T_2}\right]$
Molecularity of a Reaction
Number of reacting species taking part in an elementary reaction colliding to bring out a reaction.
Order of a Reaction
Sum of powers of concentration of the reactants in the rate law.
Integrated Rate Equation
Integration of differential rate equation to give a relation between concentrations at different times and rate constant.
Order | Integrated Rate Law | Straight Plot | Unit (K)
0 | $kt = [R]_0 - [R]$ | [R] vs t | mol L^{-1} s^{-1}
1 | $kt = \ln\{[R]_0/[R]\}$ | ln[R] vs t | s^{-1}
Pseudo First Order Reaction
Are not truly of first order but under certain conditions behave as first order reaction.
•Acid hydrolysis of ethyl acetate
•Inversion of sugar
Half-life of a Reaction
Time in which the concentration of a reactant is reduced to one half of its initial concentration.
1st Order: $t_{1/2} = \frac{0.693}{k}$
0 Order: $t_{1/2} = \frac{[R]_0}{2k}$
Rate of Chemical Reaction
Change in concentration of reactants or products in unit time; Unit : mol L^{-1} s^{-1} or atm s^{-1}
Average Rate
Appearance of products or disappearance of reactants over a long time interval.
$r_{av} = \frac{d[P]}{dt}$ = slope
$r_{av} = \frac{-d[R]}{dt}$ = –slope
Instantaneous Rate
Rate of change in concentration of reactant/product at a particular time
$r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$
R → P
Rate of disappearance of R
$= \frac{\text{Decease in concentration of R}}{\text{Time taken}} = \frac{-\triangle[R]}{\triangle t}$
Rate of appearance of P
$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = \frac{+\triangle[P]}{\triangle t}$
Factors Influencing
Concentration : Higher the concentration of reactants, faster is the rate of reaction.
Temperature : Increases with increase in temperature. Becomes almost double with 10°C rise.
Presence of Catalyst : Increases with a catalyst.
Surface Area : Greater the surface area, faster is the rate of reaction.
Activation Energy : Lower the activation energy, faster is the reaction.
Rate Law
Expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to power which may or may not be same as stoichiometric coefficient of reactants in a balanced chemical equation.
$aA + bB \rightarrow cC + dD$
$\text{Rate} = k[A]^a[B]^b = \frac{d[R]}{dt}$
Rate Constant: Rate of a reaction when concentration of each of the reactant in unity.
Order | Unit
0 | mol $L^{-1}s^{-1}$
1 | s^{-1}
2 | $mol^{-1}L\ s^{-1}$


The Solid State
Crystal Lattice
Unit cell (Smallest Unit)
Crystal Systems
Cubic : (NaCl, Cu) a=b=c; primitive, bcc, fcc; α=β=γ= 90°
Tetragonal : (SnO_2, TiO_2) a=b ≠ c; α=β=γ= 90°; primitive, BCT
Orthorhombic : (KNO_3, $BaSO_4$) a≠b≠c; α=β=γ= 90°; primitive, BCO, ECO,
Hexagonal : (Graphite) a=b ≠ c; α=β= 90° y =120°; primitive
Rhombohedral or Trigonal : ($CaCO_3$, HgS) a=b=c; α=β=γ≠90°;primitive
Monoclinic : (Monoclinic sulphur, $Na_2SO_4.10H_2O$) a ≠ b ≠ c α=γ= 90° β ≠ 90°; primitive, e.t.c
Triclinic : ($K_2Cr_2O_7$, H_3BO_3) a ≠ b ≠ c α ≠ β ≠ γ ≠ 90°; primitive
Expression for density of unit cell
$d = \frac{zM}{a^3 N_A}$
Centred
Body centred: A unit cell having a lattice point at the center of the body and at its corners.
Total number of atoms per unit cell = 2
Face centred: A unit cell having lattice points at centre of each face and its corners.
Total number of atoms per unit cell = 4
Simole cubic: A unit cell having lattice points only at corners.
Total number of atoms per unit cell = 1
Crystalline Solids : Particle with definite and regular geometry
Amorphous solids : Particles with irregular geometry
Metallic solids
Metal atoms held by metallic bond → (Fe, Cu)
Covalent solids
Non-metals held by covalent bond → (SiC, C)
Ionic solids
Ions held by strong coulombic forces → (NaCl, MgO)
Molecular solids
Molecules held by intermolecular forces
Non-polar
Atoms /molecules held by weak dispersion forces /London forces → (Ar, He)
Polar
Molecules held by dipole-dipole interactions → (HCl, SO_2)
Hydrogen bonded
Molecules held by hydrogen bonding → H_2O(ice)
Electrical Properties
Conductors
(Cu, Al) ⟵ Overlapping Zone between conduction and valence band
Insulators
(Polyethylene, Dry wood) ⟵ Very large energy gap between conduction and valence band
Semiconductors
(Si, Ge) ⟵ Small energy gap between conduction and valence band
n-type (negative charge)
p-type (positive charge)
Magnetic Properties
Paramagnetic: weakly attracted → Unpaired electrons → (O_2, Cu^{2+})
Diamagnetic: weakly repelled → Paired electrons → (H_2O, NaCl)
Ferromagnetic: strongly attracted → domains in same direction → (Fe, Co)
Antiferromagnetic: domain opposite and equal → (MnO)
Ferrimagnetic: domains unequal → (Fe_3O_4, $MgFe_2O_4$)
Packing Efficiency
scp ⟶ AAA….type ⟶ 52.4% ⟶ (Po)
hcp ⟶ ABABAB…..type ⟶ 74% ⟶ (Mg, Zn)
ccp / fjcc ⟶ ABCABC….type ⟶ 74% ⟶ (Cu, Ag)
bcc ⟶ square close packing⟶ 68% ⟶ (Li, Na)
Imperfections (Print defects)
Voids : Empty space between spheres
Trigonal
Enclosed by three sphere in contact $\left(\frac{r_{void}}{r_{sphere}} = 0.155\right)$
Tetrahedral
Vacant space between four touching spheres. $\left(\frac{r_{void}}{r_{sphere}} = 0.225\right)$
Octahedral
Enclosed between six sphere, canthus of which occupy corners a regular octagon. $\left(\frac{r_{void}}{r_{sphere}} = 0.414\right)$
Non-stoichiometric: disturb stoichiometry
Metal Excess: Due to anionic vacancies (LiCl) and presence of extra cations (ZnO)
Metal Deficiency: Metal shows variable oxidation states (Fe^{2+}, Fe^{3+})
Stoichiometric: do not disturb Stoichiometry
Vacancy : Lattice sites vacant (non-ionic solids).
Interstitial : Particles occupy interstitial site (non -ionic solids).
Frenkel :Smaller ion dislocated to interstitial site (ZnS, AgCl)
Schottky: Equal number of cations and anions missing (NaCl, KCl)
Trace the Mind Map
First Level
Second Level
Third Level


Solutions
Types
Gaseous
Gas – Gas ⟶ Mixture of O_2 and N_2
Liquid–Gas ⟶ Chloroform with N_2
Solid – Gas ⟶ Camphor in N_2
Liquid
Gas – Liquid ⟶ O_2 dissolved in water
Liquid–Liquid ⟶ Ethanol dissolved in water
Solid – Liquid ⟶ Glucose dissolved in water
Solid
Gas – Solid ⟶ O_2 in Pd
Liquid – Solid ⟶ Amalgam of Hg with Na
Solid – Solid ⟶ Cu dissolved in gold
Solubility
Gas in Liquid
Henry's Law
Partial pressure of gas in vapour phase is proportional to the mole fraction of gas in the solution.
$p = K_H x$
Increases with increase in pressure
Effect of pressure
Effect of temperature
Increases with decrease in temperature
Solid in Liquid
Effect of pressure
Not significant
Effect of temperature
Endothermic $\Delta_{sol} H > 0$, Solubility increases
Exothermic $\Delta_{sol} H < 0$, Solubility decreases
Colligative properties
• Osmotic pressure ⟶ $\pi = CRT$
• Depression in freezing point ⟶ $\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$
• Elevation of boiling point ⟶ $\Delta T_b = \frac{K_b \times 1000 \times W_2}{M_2 \times W_1}$
• Relative lowering of vapour pressure ⟶ $\frac{W_2 \times M_1}{M_2 \times W_1} = \frac{P^\circ_1 - P_1}{P^\circ_1}$
Abnormal molecular mass: molecular mass different from expected value
$\frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$ = van't Hoff factor (i)
Raoult's Law
Positive deviation
ΔV_{mix} = positive
ΔH_{mix} = positive
Large
Minimum boiling azeotrope
Negative deviation
ΔH_{mix} = negative
ΔV_{mix} = negative
Large
Maximum boiling azeotrope
Raoult's law
Ideal solution ⟶ (n-hexane and n-heptane)
Obey
Non-ideal solution ⟶ (Mixture of chloroform and acetone)
Do not obey
For any solution, the partial vapour pressure of each volatile component is directly proportional to its mole fraction.
Different methods to express concentration of solution
Mass by volume percentage (w/v)
$\frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$
Volume percentage v/v
$\frac{\text{Volume of component}}{\text{Total volume of solution}} \times 100$
Mass percentage w/w
$\frac{\text{Mass of component in solution}}{\text{Total mass of solution}} \times 100$
Parts per million : For trace quantities
$\frac{\text{No. of parts of components} \times 10^6}{\text{Total no. of parts of components of solution}}$
Mole fraction
$\frac{\text{No. of moles of component}}{\text{Total no. of moles of all components}}$
Normality: Number of gram equivalents of the solute dissolved in one litre of solution
$\frac{\text{No. of gram equivalent of solute} \times 100}{\text{Volume of solution}}$
Gram Equivalents of solute $= \frac{\text{Mass of solute}}{\text{Equivalent weight}}$
Equivalent weight $= \frac{\text{Molecular mass}}{\text{Valency}}$
Molality: Number of moles of solute per kilogram of the solvent
$\frac{\text{No. of moles of solute} \times 100}{\text{Mass of solvent}}$
Molarity : Number of moles of solute in 1L solution
$\frac{\text{No. of moles of solute} \times 100}{\text{Volume of solution}}$


Surface Chemistry
Colloids
Properties
Applications
Types
Oil dispersed in water (O/W type): Milk
Water dispersed in oil (W/O type): Butter
Emulsion : Dispersion of one liquid into another liquid which is immiscible
•Purification of drinking water
•Medicines
•Tanning
•Cleansing action of soaps detergents
•Rubber industry
•Industrial Products.
Colligative Properties:
Values of colligative properties are of small order in comparison to values shown by true solutions.
Tyndall Effect: When a beam of light is passed and viewed perpendicular to the path of incident light, the path of beam is illuminated by a bluish light. This process is Tyndall effect.
Electrophoresis : Movement of colloidal particles toward electrode in an electric field.
Colour : Depends on wavelength of light scattered by colloidal particles.
Brownian Movement : Zig zag movement of particles
Heterogeneous system where one substance is dispersed (dispersed phase) in another substance called dispersion medium.
Classification
Purification
• Dialysis
• Electro-dialysis
• Ultrafiltration
Preparation
• Bredig's Arc method
• Peptization
• Chemical methods
Based on type of particles of dispersed phase
Based on physical state
Based on nature of interaction
Multimolecular : Large number of atoms/molecules aggregate (size 1-1000 nm).
Macromolecular : Formed by molecules of large size.
Associated: Low concentration, behaves as normal range electrolytes at high concentration as colloids.
Lyophilic : Liquid loving
Lyophobic : Liquid-hating
Sol : solid in liquid (Paints)
Gel : Liquid in solid (Cheese)
Emulsion : Liquid in liquids
Aerosol : Liquid in gas (Fog)
Adsorption
Adsorption Isotherm means to express variation in the amount of gas adsorbed by absorbent with pressure at constant temperature
Freundlich Adsorption Isotherm: Empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.
$\frac{x}{m} = kp^{1/n} (n>1)$
$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$
Features
• When ΔH = TΔS, ΔG = 0, equilibrium is attained.
• ΔG, ΔH and ΔS are negative.
• Extent of adsorption increases with surface area.
Types
Physisorption
•Adsorption when accumulation of gas on the surface of solid occurs due to weak van der Waals' forces.
•Non-specific
•Depends on nature of adsorbate
•Reversible
•Increases with increases in surface area.
•Low enthalpy of adsorption.
Chemisorption
•Adsorption when gas molecules or atoms are held to surface by chemical bonds.
•Highly specific
•Irreversible
•Increases with increase in surface area.
•High enthalpy of adsorption.
(i) Accumulation of molecular species at the surface rather than in the bulk of a solid or liquid.
(ii) Surface phenomenon.
(iii) Concentration on the surface of adsorbent different from that in bulk.
Adsorbate
Molecular species which concentrates at the surface.
Adsorbent
Material on the surface of which the adsorption takes place.
Applications
Production of high vacuum, gas masks, control of humidity, separation of gases, chromatography, indicators.
Sorption
Both absorption and adsorption take place simultaneously
Absorption
•Bulk Phenomenon.
•Concentration is same throughout the material.
Catalysis
Substances which accelerate the rate of reaction and remain chemically and quantitatively unchanged after the reaction are known as catalysts and phenomenon is known as catalysis.
Homogeneous Catalysis
Reactants and catalyst are in same phase. (oxidation of SO_2 to SO_3 using NO as catalyst)
Heterogeneous Catalysis
Reactants and catalyst are in different phases. (Oxidation of SO_2 to SO_3 using Pt as catalyst)
Mechanism
•Diffusion of reactants to surface of catalyst.
•Adsorption of reactants molecules on the surface of catalyst.
•Chemical reaction on the surface of catalyst through formation of intermediate.
•Desorption of products creating surface for further reaction.
•Diffusion of products away from catalyst surface.
Uses in Industry
Manufacture of nitric acid
Ostwald's process
(Platinised asbestos, 573 K)
—
Manufacture of ammonia
Haber's process
(Fe + Mo, 200 bar, 723–773 K)
Enzyme catalysis
Enzymes that catalyse many life processes in bodies of plants and animals are termed as Biochemical catalysts and phenomenon is known as Biochemical catalysis (Inversion of sugar, Conversion of milk into curd)
Mechanism
Step 1 : Binding of enzyme to substrate to form an activated complex.
E+S→ ES*
Step 2 : Decomposition of activated complex to form product.
ES*→E +P
Shape Selective
Catalytic reaction that depends upon pore structure of catalyst and size of reactant and product molecules. (Zeolites)


Extractive Metallurgy
Metallurgy: Entire scientific and technological processes used for isolation of the metal from its ores.
• Concentration of ore
• Isolation of metal
• Purification of metal
Minerals naturally occurring chemical substances in the earth's crust obtainable by mining.
Ores : Minerals from which metal can be extracted cheaply, profitably and easily.
• Bauxite $Al_2O_3xH_2O$
• Kaolinite $[Al_2(OH)_4 Si_2O_5]$
• Haematite Fe_2O_3
• Magnetite Fe_3O_4
• Siderite $FeCO_3$
• Copper pyrites $CuFeS_2$
• Malachite $CuCO_3.Cu(OH)_2$
• Cuprite Cu_2O
• Copper glance Cu_2S
• Zinc blende ZnS
• Calamine $ZnCO_3$
• Zincite ZnO
Thermodynamic principles of metallurgy
$\Delta G = \Delta H - T\Delta S$
$\Delta G° = -RT \ln K$
• If ΔG is negative, reaction proceeds.
• If reactants and products of two reactions are put together in a system and net ΔG of the two possible reactions is negative, the overall reaction will occur.
Ellingham diagram
• Plots of $\Delta_f G°$ vs T for reaction.
• Straight line except with some change in phase
• Point in a curve below which ΔG is negative
Extraction of iron from oxides
⟶ In blast furnace
$FeO_{(s)} + C_{(s)} \longrightarrow Fe_{(s/l)} + CO_{(g)}$
⟶ Reduction
(a) At 500 – 883 K
$2Fe_2O_3 + 3CO \xrightarrow{573-673K} 2Fe_3O_4 + CO_2\uparrow$
$Fe_3O_4 + 4CO \xrightarrow{773-883K} 3Fe + 4CO_2\uparrow$
$Fe_2O_3 + CO \xrightarrow{773-873K} 2FeO + CO_2\uparrow$
(b) At 900 – 1500K
$CO_2 + C \rightarrow 2CO(g)$; $FeO + CO \rightarrow Fe + CO_2$
$CaCO_3 \rightarrow CaO + CO_2$; $CaO + SiO_2 \rightarrow CaSiO_3$
(c) At 1500 – 2100 K
$C + O_2 \rightarrow CO_2$
$FeO + C \rightarrow Fe + CO$
Extraction of copper from cuprous oxide
Roasting/smelting
$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$
$Cu_2O + C \longrightarrow 2Cu + CO$
$FeO + SiO_2 \longrightarrow FeSiO_3$
$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$
$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$
(Blister copper)
Extraction of zinc from zinc oxide
$ZnO + C \xrightarrow[1673K]{Coke} Zn + CO$
Electrochemical principles of metallurgy
Electrolysis : Difference of two E° values equals Positive E° and Negative ΔG°, less reactive metal will come out of solution and more reactive to the solution.
Metallurgy of aluminum
Purified Al_2O_3 mixed with Na_3AlF_6 / CaF_2
Fused matrix is electrolysed
Electrolysis (Hall–Heroult process)
$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$
Cathode : $Al^{3+}(melt) + 3e^- \longrightarrow Al_{(l)}$
Anode : $C_{(s)} + O^{2-}(melt) \longrightarrow CO(g) + 2e^-$
$C_{(s)} + 2O^{2-}(melt) \longrightarrow CO_2(g) + 4e^-$
Oxidation reduction (extraction of Cl from brine)
Uses
Al
• As wrappers for chocolates
• Fine dust in paints and lacquers
• Extraction of Cr and Mn
• Wires
Cu
• Wires
• Water and steam pipes
• Alloys
Zn
• Galvanising iron
• In batteries
• Dust is used as reducing agent
Fe
• Cast iron for casting stoves, railway slippers, gutter pipes, toys etc.
• Manufacture of wrought iron and steel.
Extraction of crude metal from concentrated ore
Refining
Distillation : Impure metal is evaporated to obtain pure metal as distillate.
Liquation : Low melting metal is made to flow on a sloping surface.
Electrolytic refining : Impure metal anode, strip of same metal in pur form–cathode dipped in soluble salt of same metal.
Zone refining : Based on principle that impurities are more soluble in melt than in solid state of metal.
Vapour phase refining : Metal is converted into its volatile compound and collected elsewhere.
Chromatography : Based on principle that different components of a mixture are differentially adsorbed on an adsorbent.
Reduction of oxide to metal:
Heating metal oxide with substances acting as a reducing agent which combines with the oxygen to get reduced easily.
Conversion to oxide
Calcination
Heating when the volatile matter escapes leaving behind the metal oxide.
Roasting
Ore is heated in a limited supply of air in a furnace at a temperature below the melting point of the metal.
Concentration of Ores
Hydraulic washing : Based on difference in gravities of the ore and gangue particles
Upward stream of running water is used to wash the powdered ore. Lighter gangue particles are washed away and heavier are left behind.
Magnetic Separation : Based on differences in magnetic properties of ore components
Finely ground ore is carried on conveyor belt which passes over a magnetic roller. Magnetic particles fall nearer to roller and vice versa.
Froth floatation process : Based on the difference in wetting properties of gangue and ore particles
Powdered ore is mixed with pine oil and water and agitated with air froth formed carries minerals is skimmed off and dried.
Leaching : Based on the solubility of ore in suitable solvent
Bayer's process :
$Al_2O_3 . 2H_2O + 2NaOH + H_2O \longrightarrow 2Na[Al(OH)_4] + CO_2 \longrightarrow$
$Al_2O_3.xH_2O + 2NaHCO_3$
$\xrightarrow{1470K} Al_2O_3 + xH_2O$

Preparation and Properties of Compounds

Periodic Trends in Properties of Elements

Properties	Group	Period
(a) Atomic Radius : Distance from the centre of the nucleus to the outermost shell containing electrons.	Increases	Decreases
(b) Electron Gain Enthalpy : Energy released when a neutral isolated gaseous atom accepts an electron from anion.	Becomes less negative	Becomes more negative
(c) Ionization Energy: The minimum amount of energy required to remove an electron from the outermost orbit of an isolated atom in gaseous state.	Decreases	Increases
(d) Electronegativity : Tendency of an atom to attract the shared pair of electrons towards itself.	Decreases	Increases
(e) Electron Affinity	Decreases	Increases
(f) Valency: Number of univalent atoms which combine with an atom of given element.	No Change	Increases from 1 to 4 and then decreases from 4 to 0.
(g) Metallic Character	Increases	Decreases
(h) Non–Metallic Character	Decreases	Increases

Purpose

To ease out difficulty in studying individually the chemistry of all the elements and their compounds.

Genesis of Periodic Classification

- Law of Triads: Johann Dobereiner (1829)
- Law of Octaves: John Alexander Newlands (1865)
- Periodic Law: Dimitri Mendeleev and Lothar Meyer. It states that the physical and chemistry properties of the elements are periodic function of their atomic weights.
- Modern Periodic Law: Henry Moseley (1913) It states that the physical and chemical properties of the elements are periodic functions of their atomic numbers.

Horizontal rows – Periods (Numbered from 1 to 7)
Vertical columns – Groups (Numbered from 1 to 18)

IUPAC Nomenclature of Elements with Atomic number > 100

Derived from the atomic number of element using numerical roots for 0 and numbers 1-9 and "ium" is added at the end.

Diagonal relationship

It exists between certain pairs of diagonally adjacent elements in the 2nd and 3rd periods

eg: Li ↘↙ Be ↘↙ B ↘↙ C ↘↙ N ↘↙ O ↘↙ F
Ne ↘↙ Mg ↘↙ Al ↘↙ Si ↘↙ P ↘↙ S ↘↙ Cl

Properties of Elements based on Electronic Configuration

- Electronic Configuration is the distribution of electrons into orbitals of an atom.
- In periods: Number of elements in each period is twice the number ofatomic orbitals available in the energy level that is being filled.
- Group wise: Elements in same group have similar valence shell electronic configurations, same number of electrons in outer orbitals and similar properties. These are classified into four blocks i.e., s-block, p-block, d-block and f-block.

Periodic Table Classification based on Types of Elements

f -Block Elements

- Also called as Inner Transition Elements.
- Contain of Lanthanoids and Actinoids.
- Outer elatronic configuration is $(n-2)\ f^{1-14}\ (n-1)\ d^{1-10} ns^{0-2}$
- All are metals.
- Actinoids are radioactive.

d- Block Elements

- Group 3-12
- Outer elatronic configuration is $(n-1)\ d^{1-10}\ ns^{1-2}$
- Forms coloured ions.
- Exhibit variable valencies, paramagnetism.
- Also called as Transition elements.
- Some are used as catalysts.

P- Block elements

- Group 13 to 18.
- Also called as representatives or main group elements
- Outermost configuration varies from $ns^2\ np^1$ to $ns^2\ np^6$
- At the end of period are low reactive noble gases.
- Halogens and Chalcogens have high negative electron gain enthalpies.
- Metallic character increases down the group.

s-Block Elements

- Group 1 (alkali metals) and Group 2 (alkaline earth metals)
- Outermost configuration is ns^1 or ns^2
- Reactive with low IE.
- Metallic character and reactivity increases down the group.