

Introduction of fundamental concepts of chemistry

Moles

1 mole = 6.022×10^{23} atoms, molecules, protons, etc.

Number of Moles = $\frac{\text{Mass (g)}}{\text{Molar mass (g/m)}}$

Number of molecules = $n \times \text{Avogadro's number}$

1amu = 1.661×10^{-27} kg or 10^{-24} g

1 litre = $1\text{dm}^3 = 1000\text{cm}^3 = 1000\text{ml}$

1cm³ = 1ml

1m³ = 1000litre = 1000dm³ = 106ml = 106cm³

Monoisotopic atoms or atoms having no isotopes are Four, Gold(Au), Arsenic(Ar), Fluorine(F), Iodine(I)

Relative atomic mass of an element = $\frac{(\text{mass of atom A} \times \% \text{abundance of A}) + (\text{mass of Isotope B} \times \% \text{abundance of B})}{100}$

At STP 0°C(273K) 22.414volume

At room temp 25°C(298K) 24volume

At 50°C 26Volume

For ionic only empirical formula

For molecules Molecular and empirical formula

Molecular formula = $n \times \text{empirical formula}$

Where $n = \frac{\text{molar mass molecular formula}}{\text{molar mass of empirical formula}}$

Empirical formula:

i) calculate the %age of each element in compound

ii) divide %age by atomic mass of each element to get no of moles

iii) divide all values with least mole no..

iv) if result is in fractions then multiply with suitable no to get whole number

Combustion analysis:

The %age of C, H, O...

Mass of C / mass of whole compound $\times 100\%$

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Stoichiometry:

All reactants must be converted to product

No side reaction occurs

Law of conservation of mass and law of definite proportion obeyed

Applicable to only irreversible reactions

Percentage composition:

$\%w/w = \frac{\text{w of solute}}{\text{weight of solution}} \times 100$

$\%w/v = \frac{\text{weight of solute}}{\text{volume of solution}} \times 100$

$\%v/w = \frac{\text{volume of solute}}{\text{weight of solution}} \times 100$

$\%v/v = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100$

$\% \text{Yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$

Theoretical yield is always **greater than** the actual yield.

Molarity: Number of moles of solute in 1 dm³ or 1 liter of solution

$M = \frac{m}{\text{molar mass}} \times \frac{1}{1000 \text{ cm}^3}$

$M = \frac{\text{moles of solute}}{\text{volume of solution in litre or dm}^3}$

$M = \frac{m}{\text{molar mass}} \times \frac{1000}{\text{given volume}}$

Note: one molar liquid is more concentrated than one molal liquid

And molarity is affected by temperature

Molality isn't affected by temperature

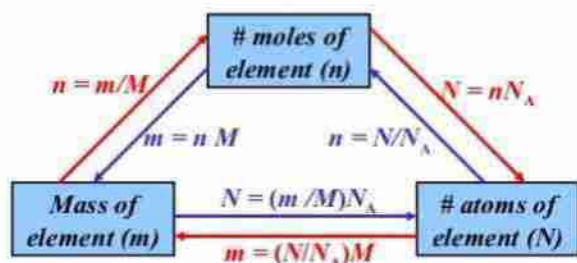
Mole fraction:

$X_a = \frac{n_a}{n_{\text{total}}}$

It has no units, its value is always less than one.

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Relationships between Mass, Mole, and Avogadro's Number



n : number of moles

m : mass

M : molar mass

N : number of atoms

N_A : Avogadro's number, 6.022×10^{23}

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Atomic Structure

Electron(cathode rays)

Experiment by william crook

Glass=>green glow

Alumina=>Red glow

Sn (stone)=>Yellow

Glass discharge tube:

0.01torr

5000-10000volts

Negatively charged

Charge on $e = 1.6022 \times 10^{-19} \text{C}$

$e/m = 1.7588 \times 10^{11} \text{CKg}^{-1}$

Mass of electron = $9.1 \times 10^{-31} \text{kg}$

Note mass of electron is negligible

Cathode rays are independent of the nature of gas used because they are electrons..

Proton(Canal rays)

Eugen golstein 1886

Note protons are not the anode rays

Red glow on glass

Depend upon the nature of gas used because cations of atoms contain different no of protons thus depends upon nature of gas

Charge on p= $1.6022 \times 10^{-19} \text{C}$

Mass= $1.6726 \times 10^{-27} \text{kg}$ or 10^{-24}g

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Neutrons:

J.chadwick 1932

1Neutron=1positron+1electrino+1neutrino

Positron and electron has same charge and positron has 1 mass while electrino mass is negligible... Neutrino is chargeless and massless particle

Fast neutron are not effective and slow ionizable because of high penetrating lower

Fast neutron energy= 1.2Mev

Fast neutron produce alpha particles

Slow neutron= 1ev

Are ionisable because of less penetrating power

Slow neutron produce beta and gamma rays

Shapes of orbitals:

Energy of subshells: $f > d > p > s$

Penetration of subshells: $s > p > d > f$

Quantum numbers

Principal Quantum number: $n=1,2,3,4...$

Distance and energy of electrons

Tells about Shells

Azimuthal Quantum number(l): $(l=n-1)$

$n=1, l=0=s$ subshell

$n=2, l=0(s), 1(p)=p$ subshell

$n=3, l=0(s), 1(p), 2(d), =$

Tells about shapes of orbitals

$S \Rightarrow$ spherical

$P \Rightarrow$ dumbbell shaped

$d \Rightarrow$ double dumbbell

d_{z^2} has a collar..
Electron density is max at nodal plane collar shaped...
 $f \Rightarrow$ quadruple dumbbell complicated..

Magnetic Quantum:(m)

$m = -l$ to $+l$

Mean if l is 0 then $m = 0$ mean in s there is only one orbital

If l is 1 then $m = -1, 0, +1$ mean in p there are 3 orbitals

If l is 2 then $m = -2, -1, 0, +1, +2 = d$ and there are five orbitals....

It tells about orbitals or orientation of orbitals in space

Spin Quantum number:(s)

Tells spin of electron in orbitals

$+1/2, -1/2$

Electronic configuration: distribution of e in subshell and orbitals..

Auf-bau principle;

Electron filling is in increasing order..

$(n+1)$ rule

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Pauli's exclusion:

No two electrons in an atom can have same set of 4 quantum number mean spin s opposite of two e in an orbital

Hund's rule:

In degenerate (having same energy) orbitals, electron will be placed with same spin first in different orbitals and then filled completely with opposite spin...

Short trick for electronic configuration Ss,psps,dps,dps.fdpd,fdps

Chemical Bonding

$\Delta E > 1.7$

Ionic bonds are Non directional bond that's why ionic compounds don't show the phenomenon of isomerism

Ionic bond is formed favorably b/w low Ionization energy (metal) and High Electron affinity (of non metal)

This is also called electrovalent bond

Properties of ionic compounds:

Solid state, soluble in polar solvents

Fast reactions,

High melting and Boiling point than covalent bond

Note: Covalent compounds have greater Boiling and melting point

But B.P and melting point is high for ionic as bond comparison

Conductors in molten and solution forms

Don't show isomerism

VSEPR Theory:

Explains shapes of molecules

Electron pairs, lone pairs, bond pairs,

Shape of molecule is due to repulsion of electron pairs

Repulsion, L.P, L.P > L.P, B.P > B.P, B.P...

Note in VSEPR theory Double and triple bonds are shown by single line

Note: if lone pair is not calculated in shape still it is gonna affect the Shape

Shapes of molecules:

There must be at least two bond pairs

AB₂ type: both are bond pairs

Linear geometry

180° bond angle

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AB₃ type: three bond pairs

Trigonal planar, 120° bond angle

If two bond pairs 1 lone pair

Bent angular not V shaped

Less than 120° angle

AB₄ type:

Four bond pairs, Tetrahedral

If 3 bond pairs 1 lone pair

Pyramidal, less than 109.5 angle

Example: PH₃, NH₃, H₃O⁺

If 2 lone pair 2 bond pairs

Bent or V-shaped

Less than 109.5° Example H₂O, H₂S

Valence Bond theory (VBT):

Explain shapes of molecules, atomic orbitals are half filled which combine to form a bond

extent of overlapping increase bond strength

Linear overlapping produce sigma bonds

Sideway overlapping produce pi bonds

VBT, VSEPR=tells about shapes of molecules
But MOT don't

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Hybridization:

mixing of orbitals of same orbit having different shapes and energies to form equal number of hybrid orbitals of same shapes and energies

$sp \Rightarrow$ Linear

$sp^2 \Rightarrow$ trigonal planar, $sp^3 \Rightarrow$ tetrahedral

$dsp^2 \Rightarrow$ square planar

$dsp^3 \Rightarrow$ trigonal bipyramidal

$d^2sp^3 \Rightarrow$ octahedral

Hybridization calculation:

NH_2^-

Calculate steric No=no of sigma bond+lone pair(-ve charge) if positive charge then don't add or subtract anything

In NH_2^-

Steric no=2 sigma +1 lone pair+1 -ve charge

Steric no=4= $\Rightarrow sp^3$..

If it is NH_2^+

Steric no=2 sigma bond+1 lone pair

Steric no=3= sp^2

S character is directly proportional to ionic character and directly proportional to Stability and directly proportional to E.N

Note: sigma bond is stronger than pi bond because of extent of overlapping and

There are 3 orbitals in p one make sigma bond p_x to p_x and p_y, p_z will make pi bonds

Note: p_x to p_x sigma bond is more stronger than s to s sigma bond because of extent of overlapping(more overlapping)

1)Bond angle $\propto 1/\text{No. of lone pairs}$

2)Bond angle \propto %age of S-character

3)Bond angle $\propto 1/E.N$ of side atom

4)Resonance energy \propto Stability

5)Resonance energy \propto No. of Resonating structures

6)Resonance energy $\propto 1/\text{unstability}$

7)Resonance Energy $\propto 1/\text{reactivity}$

8)%age of S-Character \propto Strength of bond

9)%age of S-character \propto Electronegativity

10)Bond energy \propto Strength of bond

11)Bond energy \propto %age S-character

12)Bond energy \propto Multiplicity

- 13) Bond energy \propto E.N difference
- 14) Bond energy \propto 1/size of atom
- 15) Bond energy \propto 1/Bond length
- 16) Bond length \propto 1/strength of bond
- 17) Bond length \propto 1/polarity
- 18) Bond length \propto 1/E.N difference
- 19) Bond length \propto 1/ %age of S-character
- 20) Bond length \propto 1/ Bond order
- 21) Bond length \propto 1/ Multiplicity
- 22) Bond length \propto Size of atom
- 23) Dipole moment \propto polarity
- 24) Bond order \propto Stability
- 25) Bond order \propto Energy
- 26) Bond order \propto strength of bond
- 27) Bond order \propto 1/ Bond length

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Bond energy \propto No of bonds

Triple bonds > double bonds > single bond

Maximum bond energy

H-H, N-N, F-F, O-O

H-H has max bond energy because of small radio and having less no of electron repulsion

H-H > N-N > O-O > F-F

Vander waals force:

1) Dipole-Dipole forces: b/w polar molecules

H-Cl, H-Br, CHCl₃ etc

2) Debye forces: b/w polar and non-polar molecules

H₂O + Ne, H₂O + Cl₂

3) London dispersion forces: b/w two non-polar molecules, b/w Noble gases, Halogens

Hydrocarbons

Hydrogen Bonding:

Strongest physical bond

B/w lone pair of Partial positive H atom

F, O, N

Because it's a physical bond thus not gonna affect chemical properties can affect physical

properties...

Note: Hydrogen bonding is max in H₂O

H-F vs H₂O hydrogen bond

H-F > H₂O

But H-F vs H₂O hydrogen Bonding
Hydrogen Bonding is the phenomenon not a bond thus H₂O > HF

Gases

Space b/w gases molecules is 300times greater as compared to their diameter

Joule thomson effect:

process of liquifying by sudden expansion after compression

All gases are compressed except Helium and Hydrogen because of low force of interaction and small size

Gases expand by temperature

Intermolecular forces b/w gases are weak.

Boyle's Law: T, n constant (B-T)

$$V \propto 1/p$$

$$V \propto K/p$$

$$Pv = k(\text{constant})$$

$$P_1V_1 = P_2V_2 = P_3V_3 = \text{constant}$$

P vs V graph is rectangular hyperbola

But p vs 1/v graph is straight line

Pv vs => straight at PV line because pv = constant...

These graphs are isotherm graphs

According to Boyle's pressure of gases is because of exerting force of gases molecules to the wall of container

Charles law: P, n constant (P-C)

$$V \propto T,$$

$$V/T = K(\text{constant})$$

$$V_1/T_1 = V_2/T_2 = \text{Constant}$$

The Kelvin scale was introduced by Charles law....

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Absolute zero of temperature:

$$-273.16^\circ\text{C} = -459^\circ\text{F} = \text{Zero Kelvin}$$

$$K = ^\circ\text{C} + 273$$

$$F = 9/5^\circ\text{C} + 32$$

$$V_t = V^\circ(1 + T/273)$$

V_t = volume at any temp

V[°] = Volume of gas at 0[°]C = 546cm³

T = temperature on Centigrade scale

Convert that temp in Kelvin..

Note volume of gas at 0[°]C is 546cm³

Note: for 1°C rise or fall, the volume of gas change is 2cm^3

General Gas equation:

$$PV=nRT$$

R is ideal gas constant:

$$R=0.0821\text{dm}^3\text{atmk}^{-1}\text{mol}^{-1}$$

$$8.314\text{Jmol}^{-1}\text{K}^{-1}$$

$$\approx 2 \text{ Calorie}$$

$$V=T/P$$

Liquids

Melting point is smaller than room temp

Boiling point is greater than room temp

Intermolecular forces are stronger than gases but weaker than solids

Evaporate and diffuse little than gases

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Evaporation:

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Spontaneous conversion of liquid into vapour, gaseous, phase

Evaporation is a spontaneous and an endothermic process

Depends upon surface area, temperature, intermolecular forces

Vapour Pressure: the pressure exerted by the vapours of same liquid in equilibrium with the liquid at a given temp

Vapour pressure $\propto 1/\text{Boiling point}$

Vapour pressure depends upon:

- Intermolecular forces
- Nature of liquid
- Size of molecule
- Temperature

Vapour pressure doesn't depend upon:

- Surface area
- Volume of the container
- Amount of the liquid in container

$$\text{Vapour pressure} = P = P_a + \Delta H$$

$P_a \rightarrow$ atmospheric pressure

ΔH height difference in mercury level

Vapour pressure is measured by Manometer

Vapor Pressure:

$H_2O \Rightarrow 100^\circ C$

C_2H_5OH (ethyl alcohol) $\Rightarrow 78.5^\circ C$

Acetone $\Rightarrow 56^\circ C$

$HF \Rightarrow 19.5^\circ C$

Water has lowest vapour pressure as

Vapor pressure $\propto 1/B.P$

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Boiling point:

Temperature point at which vapour pressure of liquid becomes equal to external atmospheric pressure

$B.P \propto \text{External pressure}$

$B.P \propto 1/\text{Vapour pressure}$

Cramming points:

B.P of water is $120^\circ C$ at 1489 torr pressure

B.P of water is $29^\circ C$ at 23.7 torr pressure

B.P of water is $98^\circ C$ at 700 torr pressure at the top on murree

B.P of water is $69^\circ C$ at 323 torr pressure

Hydrogen Bonding:

Electrostatic force of attraction b/w a highly E.N atom (F,O,N) of one polar molecule and partially

positive charged H-atom of another molecule

\Rightarrow Strongest physical bond

\Rightarrow HF has strongest H-Bond

\Rightarrow H_2O has strongest H-Bonding

\Rightarrow It can affect only physical properties

Hydrogen bonding is also present in Sugar molecules, Nucleic Acids, Paints and dyes

Solids

Note; melting and boiling point of Covalent solid is high than Ionic solid than Molecular solid as in molecular solid there are just van der waals force of attraction

Structure of ICE:

Molecular solid,

Density is 9 times less than water

As volume is 9 times more than water

9% increase in volume due to empty spaces

Tetrahedral geometry of molecules

Diamond like structure

Hexagonal packing

6 atoms per unit cell

12 coordination number

O-atom in ice is attached with four H-atoms by two chemical bonds and two physical (H-Bonds) bonds

Water start freezing at 4°C

H₂O has Maximum density at 4°C because of decreasing in volume and then volume increases 4 to 0°C .

Giant ionic structure: **JOIN MDCAT ASPIRANTS GROUP**
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Sodium Chloride:

Face centered Cube

Number of formula is 4 per unit cell

Na⁺ is surrounded by six 6 Cl⁻ ions and

1 Cl⁻ is surrounded by 6 Na⁺ ions

Coordination no is 6

High M.P and B.P

Non conductor in solid form

NaCl molecule present only in Vapour phase

Simple molecular Solid:

Solid Iodine:

Face centered Cube

Low M.P and B.P as non polar and van der waals force of attraction

As non polar thus london dispersion forces are present

In gaseous state

Coordination number is 12

4 atoms per unit cell

Bond length in gaseous state of I₂=266.6pm

Bond length of I₂ in crystal lattice = 271.5 pm

Non conductors

Soluble in non polar solvent CCl₄

Greyish black in colour

Giant Covalent Solid:

Diamond: transparent

It absorbs invisible radiations and re-emits radiation of visible wavelength that's why glow in dark

sp³ hybridised

Tetrahedral geometry

Face centered cube

Non conductor

Very high Melting point: 3550°C

Highest refractive index

5 allotropes of carbon

Bucky ball

Diamond

Coal

Graphite

Ozone

Only graphite is conductor

Packing of points in solids:

Hexagonal close packing

12 12 12

AB AB AB

12 34 5 6

1,3,5 layers have same arrangement

2,4,6 layers have same arrangement

Coordination number is 12

6 atoms per unit cell

Cubic close packing:

123 123 123

ABC ABC ABC

123 456. 789

1,4,7 layers are same

2,5,8 are same

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3,6,9 are same
Coordination no is 12
4 atoms per unit cell

Chemical equilibrium

Reversible reactions:

Reaction which takes place both direction

It never completes

Equilibrium is ultimate goal

Only carried out in closed container

Macroscopic properties

We study dynamic equilibrium reactions

Can be initiated at either side

Catalyst can't change the equilibrium position just lowers activation energy

Homogeneous equilibrium=both product and reactants are in same phase

Heterogeneous equilibrium: both reactants and products are in different phases

Note:At equilibrium only rate of forward reaction is equal to rate of backward reaction

But no of moles and concentration of products and reactants are equal isn't necessary

Equilibrium constant doesn't depend upon initial concentration of reactants but depends upon equilibrium concentration.

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Irreversible reactions:

Reactions which takes place in one direction

It gets completed, no equilibrium state, can occur in both closed and open container

$$R_f = k_f[A][B]$$

$$R_r = k_r[C][D]$$

$$K_c = K_f / K_r [C][D] / [A][B]$$

K_c => equilibrium constant

Equilibrium constant (K_c):

It may or may not have units

Independent of initial concentration

=>Kc values change only by changing temperature

=>Kc position changes by changing temperature, pressure, volume , concentration

=>Note Catalyst doesn't effect the equilibrium value and position just lowers activation energy

Equilibrium constant in other terms

Kc,Kp,Kx,Kn

$K_p = K_c(RT)^{\Delta n}$

$\Delta n = \text{product} - \text{reactant}$

$\Delta n = 0 \Rightarrow K_p = K_c$

$\Delta n > 0 \Rightarrow K_p > K_c$

$\Delta n < 0 \Rightarrow K_p < K_c$

Le-Chatliers principle:

If we remove products the Reaction will proceed in the forward direction..

If we increase pressure the equilibrium shift towards the other side

If we decrease pressure the Pressure at any side equilibrium will shift at that side where we decreasing the pressure

Temperature:

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Endothermic reactions:

In endothermic reaction temp is in reactants side thus if we are increasing temp mean we are increasing reactants thus equilibrium shift to product aide

Exothermic reactions:

In exothermic reactions temp is in product side if we are increasing temp mean we are increasing product thus equilibrium shift to reactant direction

Haber's process:formation of ammonia

$N_2 + 3H_2 = 2NH_3 \Rightarrow -46.11 \text{ kJ/mol}$

200-300atm pressure

400C

Fe=>catalyst

+Al₂O₃/MgO/SiO₂=>promoter (catalyst of catalyst)

Note if question is asked that what if we increase temp in haber process

Ans:haber process is an exothermic reaction thus if we increase the temp upto 400c the equilibrium will shift backward and less no of products will be formed

If we want more product we need to decrease temp upto a limit, by removing products, by increasing pressure at reactant sides,....

Contact process:

formation of So₃:

$2SO_2 + O_2 = 2SO_3 \Rightarrow -979 \text{ KJ/mol}$

1atm, 400-500°C

V₂O₅ but earlier we use platinized asbestos

Bronsted lowry theory:

Acid=proton donor

Base:proton acceptor

Acid+Base \rightleftharpoons (acid will convert into conjugate base and Base will convert into conjugate Acid)

Note:Strong acid and bases conjugate will be weak

While weak acid and bases conjugates will be strong

Ionic product of water:

H₂O \rightleftharpoons H⁺ +OH⁻

K_c=[H⁺][OH⁻]/[H₂O]

K_c[H₂O]=[H⁺][OH⁻]

1.8x10⁻¹⁶x55.5=1.01x10⁻¹⁴=[H⁺][OH⁻]=K_w

K_w=1x10⁻¹⁴

K_w=[H⁺][OH⁻]

K_w=1x10⁻¹⁴ at 25°C

K_w value increases 75 times by increasing temperature 0°C to 100°C

For neutral solutions:[H⁺]=[OH⁻]

For acidic solutions:[H⁺] > [OH⁻]

For Basic solutions:[H⁺] < [OH⁻]

PH=less than 7 acidic

PH=greater than 7 basic

PH=-log[H⁺]

PoH=-log[OH⁻]

Pkw=PH+POH

14=PH+POH

Pkw=14

K_a ∝ H⁺ ∝ Acidic strength ∝ 1/PH ∝ 1/Pka

K_b ∝ OH⁻ ∝ Basic strength ∝ 1/POH ∝ 1/Pkb

Buffer solution:

Acidic Buffer:weak acid+salt of that acid with strong base

Basic Buffer:weak base+salt of that base with strong acid

PH=Pka+log[salt]/[Acid]

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$$PH = PKa - \log[Acid]/[salt]$$

$$POH = Pkb + \log[salt]/[Base]$$

$$POH = PKb - \log[Base]/[salt]$$

$$Then = PH + POH = 14$$

A best buffer is than where concentration of the and their base or acid ratio is same

Thus by formula

$$PoH = pkb$$

$$Ph = pka$$

Solubility: Ksp constant

$$Ksp = \text{Products/reactant}$$

$$Ksp = [A^+][B^-][s][s]$$

We ignore reactant because of sparingly soluble

$$Ksp = \text{ionic product} = \text{Saturated solution}$$

$$Ksp > \text{ionic product} = \text{unsaturated solution}$$

$$Ksp < \text{ionic product} = \text{supersaturated solution}$$

Ionic product is the(ions) products of sparingly soluble salt

Solubility of CaF_2 is 2×10^{-4} find Ksp

$$[Ca^{+}] = 2 \times 10^{-4}$$

$$[2F^{-}]^2 = 2 \times 2 \times 10^{-4} \times 2 \times 2 \times 10^{-4}$$

$$Ksp = [2 \times 10^{-4}][16 \times 10^{-8}]$$

$$Ksp = [32 \times 10^{-12}]$$

$$Ksp = 3.2 \times 10^{-11}$$

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Short cut

$$[Ca] = s$$

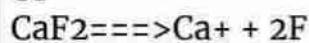
$$[2F]^2 = 4s^2$$

$$[s][4s^2] = 4s^3 = 4 \times 2 \times 2 \times 10^{-4} \times 10^{-4} \times 10^{-4}$$

$$= 32 \times 10^{-12}$$

$$\text{Solubility} = s^3 = Ksp/4$$

Or



$$Ksp = [s][2s]^2$$

$$Ksp = [s][2s]^2 = 4s^3$$

$$s^3 = Ksp/4 \Rightarrow \text{you can also find Solubility "s"}$$

Common ions effect:

It is application of Le Charlie's principle

It is always the reverse direction

In common ion effect the term electrolyte is used instead of acid base or salt

With the help of common ion effect we can suppress ionisation of other electrolyte

It is study of increasing concentration of product in term of common ions

Reaction kinetics

Rate of reaction:

$$\Delta C / \Delta t$$

$$\text{Units} = \text{mol/dm}^3\text{s}$$

As reaction proceeds rate of reaction decreases

$$\text{At start: } R_{\text{instantaneous}} > R_{\text{average}}$$

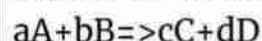
$$\text{At } T=0: R_{\text{instantaneous}} = R_{\text{average}}$$

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Rate law: according to guldberg and wages rate of a balanced chemical reaction is directly proportional to the products of their reactants

$$\text{Rate} \propto \text{Reactants}$$



$$\text{Rate} = K[A]^a[B]^b$$

Specific rate constant or Velocity constant:

When concentration of reactants is unity then rate of reaction is equals rate constant

Note: specific rate constant only changes by changing temperature

Order of Reaction:

The Order of Reaction refers to the power dependence of the rate on the concentration of each reactant. Thus, for a first-order reaction, the rate is dependent on the concentration of a single species. A second-order reaction refers to one whose rate is dependent on the square of the concentration of a single reactant

$$\text{Rate} = K[A]^3[B]^2$$

$$\text{Then order of Reaction} = 3 + 2 = 5$$

Order of Reaction is an experimental value

Indicating by performing kinetic studies

May be fraction

May be zero

Maximum value is 3 i.e 3rd order reaction

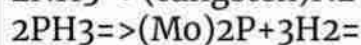
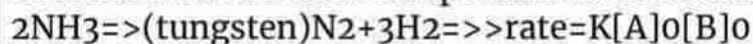
Molecularity=total no of moles taking part in chemical reaction

It can be more than 3

It can't be in fraction just in whole numbers

Zero order reaction:

Reaction whose rate is independent of concentration of reactants



graph of first order reaction is a straight line along concentration because independent of concentration.

$$[\text{A}]_t = [\text{A}]^\circ - Kt$$

$$K = \frac{[\text{A}]^\circ - [\text{A}]_t}{t}$$

$[\text{A}]^\circ$ initial concentration

$[\text{A}]_t$ concentration at any time

K = rate constant

t = time

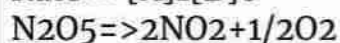
Half life for Zero order reaction

$$T_{1/2} = \frac{[\text{A}]^\circ}{2K}$$

$[\text{A}]^\circ$ initial concentration of reactants

1st order reaction:

$$\text{Rate} \propto [\text{A}]^1[\text{B}]^0$$



$$\ln A_t = \ln A^\circ - Kt$$

$$K = \frac{1}{2t} \ln \frac{A^\circ}{A_t}$$

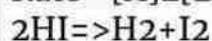
$$K = \frac{2.303}{t} \log \frac{A^\circ}{A_t}$$

$$A_t = A^\circ e^{-kt}$$

$$T_{1/2} = \frac{0.693}{K}$$

2nd order reaction:

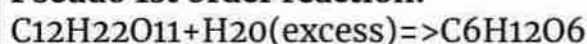
$$\text{Rate} \propto [\text{A}]^2[\text{B}]^0, \text{ or } [\text{A}]^1[\text{B}]^1$$



$$\text{Rate} = k[\text{HI}]^2$$

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Pseudo 1st order reaction:

Note H_2O is in excess thus not included in reaction thus $\text{rate} \propto [\text{C}_{12}\text{H}_{22}\text{O}_{11}]^1$

Note: if any reactant is in excess then don't include that reactant in rate law...

Half life:

Time required to convert half of reactants into product

1st order: $T_{1/2} = 0.693 / K_a$

Half life of first order reaction doesn't depend upon initial concentration of reactants

Zero, 2nd, 3rd orders depend upon initial concentration

Rate Constant: K :

Units of rate constant depend upon order of reaction

$$\text{Rate} = K[A][B]$$

$$K = \text{Rate} / [A][B]$$

$$K = \text{mol/dm}^3 \text{ s}$$

For zero order reaction K units = $\text{mol/dm}^3 \text{ s}$

For first order reaction K units = s^{-1}

For 2nd order reaction k units = $\text{dm}^3/\text{mol s}$

3rd order reaction units = $\text{dm}^6/\text{mol}^2 \text{ s}$

Rate units Trick:

$$K = (M)^{1-n} / \text{time}$$

M = molarity or concentration

$$M = \text{mol/dm}^3$$

n = order of reaction

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Energy of activation:

Minimum amount of energy required to convert reactants into products

E_a = derived from collision theory of reaction rate

Both exo and endothermic reaction need to cross activation energy

In endothermic reactions energy of reactant is less than products

$$\text{Endotherm} = \text{Reactants} + \text{Energy} \rightarrow \text{Products}$$

\Rightarrow Products energy is more and energy is inversely proportional to Stability

$$\Delta H = +ve$$

$$\Delta H = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

Exothermic reactions energy of reactants is more than products

$$\text{Exothermic} \Rightarrow \text{Reactant} - \text{Energy} = \text{Products}$$

$$\Delta H = -ve$$

Arrhenius equation:

$$K = Ae^{-E_a/RT}$$

$$K \propto -E_a \Rightarrow K \propto 1/E_a$$

$$K \propto -1/T \Rightarrow K \propto T$$

Note by increasing temperature activation energy doesn't change

Mean temperature doesn't affect the Activation Energy...

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Catalyst=

Increase rate of reaction

Lowers the activation energy

Can't start a reaction

Homocatalyst: reactants of Catalyst are in same phases

Heterocatalyst: reactants+catalyst are in different phases

Autocatalyst: they produce at the time of reaction and function as catalyst

Characteristics of catalyst:

Specific in nature

Can't start but speeds up the reaction

Equilibrium position not affected by catalyst

Finesse increase the reactivity of Catalyst

Promoters:

Hydrogenation of oil(Ni,(Cu/Te)), \Rightarrow veg ghee

Ni is catalyst while Cu/Te are catalyst of catalyst (promoter)

Enzymes biological catalyst;

Essentially proteins

More efficient than inorganic catalyst

Increase rate of reaction 10^6 – 10^{12} times
Highly specific in nature
Temperature and PH sensitive

Thermo-chemistry

1joule= 10^{-7} ergs=0.239cal

1cal=4.18j

Pure water molarity:55.6M

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Exothermic reactions:

$\Delta H = -ve$

$H_r > H_p$

After releasing heat from products they convert from unstable to stable compounds

$C + O_2 \Rightarrow CO_2 \Rightarrow \Delta H = -393.7 \text{ kJ/mol}$

Endothermic reactions:

$\Delta H = +ve$

$H_r < H_p$

After absorbing energy endothermic products become more energetic and energy is inversely proportional to Stability thus product become less stable

$2H_2O \Rightarrow 2H_2 + O_2 \Rightarrow \Delta H = +285.5 \text{ kJ/mol}$

System: Any matter under study

Surrounding: Environment other than system

Boundary: Real or imaginary surface separating system and surrounding

\Rightarrow Like a flask is boundary

State Function:

Macroscopic property, depends upon initial and final state and not the path followed

For closed path state Function value is zero

Examples

UHSg

U=>internal energy

H=>enthalpy

S=>entropy

G=>gibbs free energy

We don't calculate absolute value of state function we Calculate change of state function, $\Delta U, \Delta H, \Delta S, \Delta G$

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Path function:

Microscopic property depends upon path followed and not by initial and final position

And in closed path value isn't zero

q=heat, work done,...

Standard state in thermochemistry:

Concentration: 1M

Pressure: 1 atm

Temperature: 25°C, 298K

If an exothermic reaction takes place rapidly in the air, the temperature of surrounding increase and for endothermic vice versa

Enthalpy of reaction: ΔH_r

Amount of heat energy absorbed or evolved

It may be +ve or -ve

Enthalpy of formation: ΔH_f

Amount of heat energy absorbed or evolved when 1 mole of compound formed from its elements

It may be +ve or -ve

Enthalpy of Atomisation: ΔH_a

Amount of energy required to form atom from its element

It is always required (Always endothermic)

Thus Always +ve

Enthalpy of Neutralization: ΔH_n

Amount of heat energy evolved by reaction of acid and base and 1 mole of water is formed

Strong acid+Strong base=> $\Delta H_n = -57.4\text{ kJ}$ per mole of water formed

For two moles of water $\Delta H_n = 2 \times -57.4\text{ kJ}$

If any of weak +strong or weak partner

Reacts still they evolve heat but

Value of ΔH_n is less than -57.4

Enthalpy of combustion: ΔH_c

Amount of energy evolved by burning hydrocarbons in excess supply of oxygen

Combustion is always exothermic

Always -ve

Enthalpy change of solution: ΔH_s

Amount of energy absorbed or released

When one mole of solute is dissolved in solvent

It may be +ve, -ve

Ionisation energy is always endothermic always required always +ve

Always endothermic reaction, $\Delta H = +ve$

Heat of Atomisation

Ionisation energy

Always exothermic reaction, $\Delta H = -ve$

Enthalpy of Neutralization

Enthalpy of Combustion

ΔH may be both +ve, -ve

Enthalpy of reaction

Enthalpy of formation

Enthalpy of solution

Note these All enthalpies are for one mole

And standard conditions

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Bond energy: lattice energy

Amount of Energy required to break all bonds present in one mole of substance is Bond

Energy

Lattice energy:

Amount of energy released when bonds in one mole of a substance of lattice formed

Bond energy = lattice energy

Bond energy \propto to bond order (No of Bonds)

Bond energy = Ethyne > ethene > ethane

Bond energy $\propto 1/\text{Bond length}$

Bond Energy \propto s character

B.E = $sp > sp^2 > sp^3$

B.E \propto lone pair

Enthalpy:

:Total heat content of system:total energy

It is a state function

It is an extensive property

Which depends upon amount of material

Enthalpy of reaction depends upon:

- Physical state of reactants and products
- Process at constant pressure, or at constant volume
- Quantities of reactants
- Temperature

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First Law of thermodynamics:

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$$q = \Delta E \pm w$$

Work done by the system = -ve

Work Done on the system = +ve

First law of thermodynamics is based on law of conservation of energy

Energy of universe remains constant

At constant volume:

$$q_v = \Delta E \pm P\Delta V. \text{ As } \Delta v = 0$$

$$q_v = \Delta E + 0$$

$$q_v = \Delta E$$

At constant volume: $\Delta H = \Delta E$

At constant pressure:

$$q_p = \Delta E \pm w. q_p = \Delta H$$

$$q_p > q_v \implies \Delta H > \Delta E$$

Hess law of Constant heat summation:

=> ΔH° can be measured experimentally by calorimeter

=> And can be mathematically by Hess' law

Glass calorimeter: used to measure the enthalpy of Neutralization, ΔH_n

Bomb Calorimeter: used to measure the enthalpy of combustion.

$$q = mc\Delta T$$

=> Calorimeter used for single step Reaction

Hess' Law:

Enthalpy change of a system depends only on its initial and final states, it is independent of path

$\Sigma \Delta H = \text{in cycle} = 0$

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Hess' law can be applied for one step Reaction or for more than one step Reaction

Born Haber's Cycle

For ionic compounds, But same law of Hess' $\Delta H_{\text{lattice}} = \Delta H_f - H_x$

Lattice energy:

Amount of energy released when one mole of ionic crystal is formed from its gaseous ions

$\text{Na} + \text{Cl} \rightarrow -787 \text{ kJ/mol}$

$\text{NaF} > \text{NaCl} > \text{NaBr} > \text{NaI}$

====> **Lattice energy useful points:** <=====

Structure of ionic compounds

Properties of ionic compounds

Strength of bonding of ionic compounds

Electrochemistry

Oxidation Number method:

$\text{Br}_2 + \text{NaOH} \Rightarrow \text{NaBr} + \text{NaBrO}_3 + \text{H}_2\text{O}$

Write oxidation state on each element

Then separate both Br₂ Br Br then check difference in Oxidation state and cross multiply both oxidation no of Br

Then balance atoms thus it is balanced now

Ion-Electron method: JOIN MDCAT ASPIRANTS GROUP

In Acidic medium;

Separate oxidation half and reduction half **03040639627**

Balance electrons

O-atoms by H₂O molecules

H-atoms by H⁺ ions

In Basic medium;

Separate oxidation and reduction Half

Balance electrons
O-atoms by OH⁻ ions
H atoms by H₂O molecules

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Electrode potential:

Electrode of any element in contact with solution of its own ions develops a potential called Electrode potential

Standard Hydrogen Electrode: SHE, NHE

electrode potential of SHE/NHE is arbitrary taken as zero

SHE => standard conditions: 25°C, 1atm, 1M HCl solution

Platinum, pt, foil coated with finely divided pt-Black

Hydrogen gas is bubbled and came in contact with its own ions

E_{oxidation} = 0

E_{reduction} = 0

Coupling of each element with SHE generates the potential of each element

Standard oxidation potential: Element release electron

Standard reduction potential: gain of electron

$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{anode}} + \text{AND } E^{\circ}_{\text{cathode}}$

$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidation}} + E^{\circ}_{\text{reduction}}$

$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{oxidation}} - E^{\circ}_{\text{oxidation}}$

$E^{\circ}_{\text{oxidation}} = -E^{\circ}_{\text{reduction}}$

Modern Batteries:

Portable or Leclanche's cell

Spontaneous chemical change Produce current

Primary cell, batteries: cells not rechargeable

2ndary cell, batteries: cells are rechargeable

Fuel cells(Rechargeable):

Electrodes: porous compressed carbon and platinum impregnated

Platinum functions as a catalyst

Electrolyte: KOH

Fuel: H₂, N₂H₄, CH₃OH, NH₃

Efficiency: 60% efficiency

Convert 75% bind energy of fuel

Oxygen functional as Cathode

Uses of fuel cells;

Used during space flight produce electricity and pure water

Are more efficient

Do not cause pollution

Fuel cell can supply electricity continuously

So long the fuel are filled in it

Jab tak fuel khatam nahi hota kaam karta rahega fuel khatam hone ke baad dobara daal lena fuel

No drop in potential or voltage with time

Disadvantage;

High cost of catalyst used in fuel(Pt)

Difficulty in handling the gaseous fuel

Highly corrosive nature of Electrolyte KOH

S and p block elements**Orders****Increasing or Decreasing Order**

01. Melting point=

$\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$

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02. Colour of the flame=

Li-Red,

Na-Golden

K-Violet

Rb-Red

Cs-Blue

Ca-Brick red

Sr-Blood red

Ba-Apple green

03. Stability of hydrides =

$\text{LiH} > \text{NaH} > \text{KH} > \text{RbH} > \text{CsH}$

04. Basic nature of hydroxides=

$\text{LiOH} < \text{NaOH} < \text{KOH} < \text{RbOH} < \text{CsOH}$

05. Hydration energy=

$\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$

06.) Reducing character=

$\text{Li} > \text{Cs} > \text{Rb} > \text{K} > \text{Na}$

07. Stability of +3 oxidation state=

$\text{B} > \text{Al} > \text{Ga} > \text{In} > \text{Tl}$

08. Stability of +1 oxidation state=

$\text{Ga} < \text{In} < \text{Tl}$

09. Basic nature of the oxides and hydroxides=

$\text{B} < \text{Al} < \text{Ga} < \text{In} < \text{Tl}$

10. Relative strength of Lewis acid=

$\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$

11. Ionisation energy=

$\text{B} > \text{Al} < \text{Ga} > \text{In} < \text{Tl}$

12. Reactivity=

$\text{C} < \text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$

13. Metallic character=

$\text{C} < \text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$

14. Acidic character of the oxides=

$\text{Co}_2 > \text{SiO}_2 > \text{GeO}_2 > \text{SnO}_2 > \text{PbO}_2$

15. Reducing nature of hydrides=

$\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4 < \text{PbH}_4$

16. Thermal stability of tetrahalides=

$\text{CCl}_4 > \text{SiCl}_4 > \text{GeCl}_4 > \text{SnCl}_4 > \text{PbCl}_4$

17. Oxidising character of M^{+4} species=

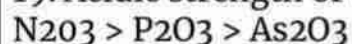
$\text{GeCl}_4 < \text{SnCl}_4 < \text{PbCl}_4$

18. Ease of hydrolysis of tetrahalides=

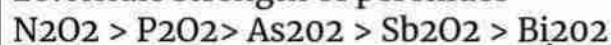
$\text{SiCl}_4 < \text{GeCl}_4 < \text{SnCl}_4 < \text{PbCl}_4$

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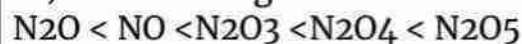
19. Acidic strength of trioxides=



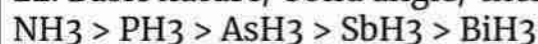
20. Acidic strength of peroxides=



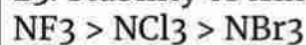
21) Acidic strength of oxides of nitrogen=



22. Basic nature/ bond angle/ thermal stability and dipole moment of hydrides=



23. Stability of trihalides of nitrogen=



24. Lewis base strength=



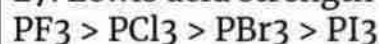
25. Ease of hydrolysis of trichlorides=



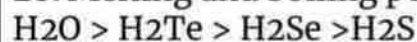
26. Lewis acid strength of trihalides of P, As, and Sb=



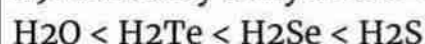
27. Lewis acid strength among phosphorus trihalides



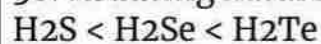
28. Melting and boiling point of hydrides=



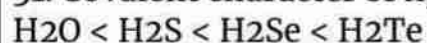
29. Volatility of hydrides=



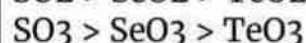
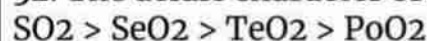
30. Reducing nature of hydrides=



31. Covalent character of hydrides=



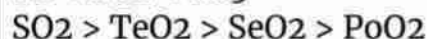
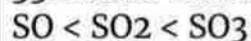
32. The acidic character of oxides (elements in the same oxidation state)=



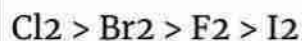
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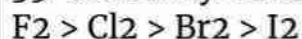
33. Acidic character of oxide of a particular element (e.g. S)=



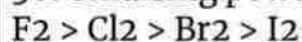
34. Bond energy of halogens=



35. Solubility of halogen in water =



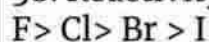
36. Oxidising power=



37. Enthalpy of hydration of X ion=



38. Reactivity of halogens:=



39. Ionic character of M-X bond in halides



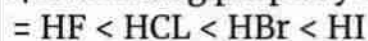
40. Reducing character of X ion:=



41. Acidic strength of halogen acids=



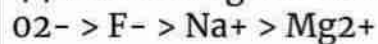
42 Reducing property of hydrogen halides



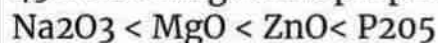
43. Oxidising power of oxides of chlorine



44. Decreasing ionic size=



45 Increasing acidic property=



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46 Increasing bond length=

$N_2 < O_2 < F_2 < Cl_2$

47 Increasing size=

$Ca^{2+} < Cl^- < S^{2-}$

48 Increasing acid strength=

$HClO < HClO_2 < HClO_3 < HClO_4$

49 Increasing oxidation number of iodine=

$HI < I_2 < ICl < HIO_4$

50. Increasing thermal stability=

$HOCl < HOClO < HOClO_2 < HOClO_3$

2nd groups s can have only two electrons

Group:1= $ns^1 = M+1$ (Li Na K Rb Cs Fr)

Group:2= $ns^2 = M+2$ (Be Mg Ca Sr Ba Ra)

Be is not counted in alkaline earth metals it is rare

In S groups down group size increase

Left to right size decrease

Be is smallest in size in S group

Down the group in S blocks ionisation enthalpy decreases and Cs has least Ionization enthalpy in periodic table

Hydration energy decrease down the group

Size is inversely proportional to Hydration energy

Flame coloration

Li=>Red

Na=>golden yellow

K=>lilac, pink

Rb=>red (reddish violet)

Cs=>Blue

Fr=>radioactive

Be=>No colour

Mg=>No colour

Ca=>orange red

Sr=>red

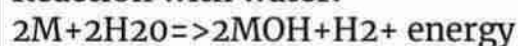
Ba=>pale green

Cu=>blue green

Pb=>greyish white

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Reaction with water:

Down the group reactivity **increase**

Melting and Boiling point decreases down the group => s group

Mg has lowest melting and boiling point

Due to its loose hexagonal arrangement



Melting and Boiling point increase from left to right up to IV-A group then Decreases in period

due to first increasing and then decreasing the no of unpaired electrons...

In group IA to IV-A decreases down the group

In group V to VIII-A decrease down group

Mg has the lowest melting and boiling point...

Silicon (Si) has highest melting and boiling point increment in its group

Down the group conductivity increases as size increase and metallic character increase

Effective nuclear charge left to right increases that's why size decreases and top to bottom decreases and size increases

And atomic radii decreases left to right and increases down the group as shell and shielding effect increases

Note: No variation in atomic radii

Continuous decreasing or increasing

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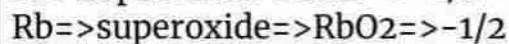
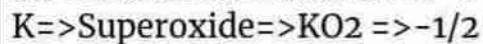
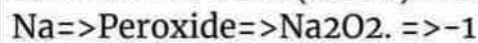
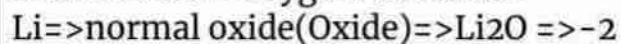
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Ionic radii

Cation < neutral atom < Anion

Effective nuclear charge is attraction of proton, nucleus felt by last, valence electrons

Reaction with Oxygen. Oxidation



Fr radioactive

Size => normal oxide < peroxide < superoxide

Be, Mg, Ca form oxides (normal oxide)

Sr, Ba form Peroxides

Mg(OH)₂ milk of magnesia
Controls acidity

Reaction with Halogens

Reactivity:metals=>Li>Na>K>Rb>Cs

Halogens=>F>Cl>Br>I

Li highest polarising power in it's group because of small in size

(Be)Beryllium and Aluminum (Al) oxide,Hydroxide are amphoteric

Zinc (Zn) also form amphoteric oxides

Beryllium is hard metal form covalent compounds

Beryllium is hard that it can scratch a glass Form covalent bonds Max covalent character

Don't react with water even in red hot conditions

Alkaline earth metals nitrites when they are hydrolyzed, reaction with water,they produce ammonia

F=>pale yellow gas

Cl=>greenish yellow gas

Br=>orange red liquid

I=>greenish black solid

Oxidizing power=>F,Cl,,Br,I

E.N same

E.A=>Cl,F,Br,I

Bond energy Cl,Br,F,I

Fluorine can replace all halogens

I can't replace another halogen

Permanent bleaching=> nascent oxygen[O]

Temporary bleaching=>nascent hydrogen

Freons=>Chlorofluorocarbons are refrigerants ,coolants

Teflons[CF₂-CF₂]=>quality plastic ,stable in acid and bases , non stick utensils

Halothane=>F₃-C-C-Cl-Br is an anesthesia

Chloroform anesthesia

Pyrene CCl₄ non polar solvent.

AgBr photography fungicide

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Ionisation energy is always required, always endothermic, always +Ve

2nd Ionization energy is always greater than its 1st Ionization energy

Penetration effect:s>p>d>f

Ionization energy increases from left to right but due to complete,half filled orbitals are stable

and show variations are group IIA,IVA...

Top to bottom ionisation energy decreases

Ionisation energy trend in period

IA<IIIA<IIA<IVA<VIA<VA<VII<VIII

Some groups are showing variations due to their complete and half filled orbital stability
Orbital stability

Complete filled>half filled>partially filled

Group showing completely filled orbitals are IIA ns² and VIIIA ns²,np⁶

Group showing half filled IA ns¹, IV A ns²,np³

For comparison of Ionization energy check the filling of orbitals either half,completely or Partially..

E.N increases left to right and decreases top to bottom

It is a molecular property having no units

$\Delta E.N=0-0.5$ =non polar

$\Delta E.N=0.5-1.6$ =polar covalent

$\Delta E.N=1.7$ (50%covalent and 50%Ionic)

$\Delta E.N=1.8$ ionic

Note:in Bond b/w H-F having difference of E.N 1.9 still it is a highly polar covalent bond not an ionic

Fluorine has highest E.N 4.0

And Cesium has the lowest E.N=0.7

E.N is zero for noble gases

Fluorine is the single element by bonding with oxygen, oxygen shows positive oxidation state and have -ve oxidation state by forming bond with other atoms

$E.N>F>O>N$

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Electron affinity

1st E.A may be +ve or -ve but 2nd ,3rd... are always gonna be endothermic +ve for an atom

E.A increases left to right and Decreases top to bottom

But some variations are there due to half and complete filled orbitals group IA has higher affinity

than IIA and for same group IV has higher E.A than VA

So II<I<III<V<IV<VI<VII

$E.A=Cl>Br>F>I$

Conductance:

Left to right Decreases top to bottom increases

Depends upon:

Metallic character, no of free electrons , packing of ions

Conductivity trend= $\text{Ag(silver)} > \text{Cu} > \text{Au(gold)} > \text{Al} > \text{Na}$

Coal= \Rightarrow sp^3 hybridization \Rightarrow no conductivity no free electrons and tetrahedral structure

Diamond= \Rightarrow sp^3 hybridization no conductance cubical packing(tetrahedral)

Graphite= \Rightarrow sp^2 hybridization= \Rightarrow hexagonal packing and conductor

Ozone.

Oxidation state;

Increases left to right

Variations in groups due to d and f subshell

Usually group no is max oxidation number

The Fluorine is the only atom having single oxidation state -1 (Only -ve because no atom has more E.N than Fluorine)

Noble gases also shows oxidation state of $+ -2, 4, 6, 8$

Oxidation state is directly proportional to Covalent character and Acidic strength

Hydration energy:

Is directly proportional to charge density and inversely proportional to size

Note Aluminum with Iodine forms Covalent bond

Amphoteric oxides:

Be, Al, Zn forms amphoteric oxides

Ionic oxides are Basic

Covalent oxides are Acidic

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Transition elements

All transition elements are metals

3d series= \Rightarrow 4th period Sc21 to Zn30

Each series has 10 element as d has only 5 orbitals

4d series Y39 to Cd48 5th period

5d series La Hg80

6d series Ac89 to Cn112.

D block elements are called outer transition elements

F block elements are also called inner transition elements has 14 elements in one series 7 Orbital

Lanthanides Ce58 to Lu71

Actinides Th90 to Lr103

Sc=>iiiB to Mn viiB Fe,Co,Ni ViiiB Cu=>iB Zn=>iiB

Group iB(Cu,Ag,Au) are coinage metals have highest conductivity

Group iiB(Zn,Cd,Hg) are pseudo transition metals or non typical transition metals

Group iiB and iiiB are non typical transition elements

ViB=>Cr,Mo,W has highest melting and boiling point

W has the highest Mp and Bp among three...

Radii=>1st decreases from iiiB to viA then constant viiB,viiiB(Mn,Fe,Co,Ni) and then increases iB,iiB

Chromium has the highest heat of atomisation in the periodic table

D series general electronic configuration

$(n-1)d^{1-10}, ns^{1-2}$

Note electrons will be added in d at last and will be released from S orbital...

Cr,Mo,W,Cu,Au,Ag show abnormal electronic configuration

Oxidation state:

Variable oxidation state except Zn(which shows only +2 oxidation state)

Common oxidation state in transition elements is +2 (which is common in all)

Oxidation state which is commonly found in transition elements is +6

Oxidation in transition elements periods 1st increase then decrease

Higher oxidation state is directly proportional to Covalent character and acidic strength

Low oxidation state is directly proportional to ionic character and basic strength

Transition elements used as catalyst having vacant d orbitals and surface for adsorption and showing variable Oxidation state

Eg=> $TiCl_4 + (C_2H_5)_3$ Ziegler natta catalyst

$V_2O_5, Ni, Cu, Fe, Pt, \dots$

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Fundamental principles of organic chemistry

Cracking/Pyrolysis

Higher to lower hydrocarbons

Thermal cracking; under high temp, lower unsaturated hydrocarbon obtained (petrochemicals)

Steam cracking; at 900°C and rapid cooling, lower unsaturated hydro chemicals (petrochemicals)

Catalytic cracking; by using catalyst $\text{SiO}_2 + \text{Al}_2\text{O}_3 + 500^{\circ}\text{C} + 2\text{atm}$
To increase quantity and also quality of gasoline

Nucleophile \Rightarrow directly proportional to size of molecule, and inversely proportional to E.N and

Basic character

Alkene, alkyne, benzene NH_3 , are also nucleophile

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Free radical; bearing an unpaired or odd e^- specie
Are result of homolytic cleavage

Electrically neutral and paramagnetic in nature (attracted by magnet)
Stability $\Rightarrow 3^{\circ} > 2^{\circ} > 1^{\circ}$
Short Lived (intermediate in reactions)

Carbanion \Rightarrow stability $1^{\circ} > 2^{\circ} > 3^{\circ}$

Carbocation \Rightarrow stability $3^{\circ} > 2^{\circ} > 1^{\circ}$

Carbanion and cation are formed result of heterolytic cleavage of bond
Are short lived...

Alkane shows only chain isomerism
And also conformational isomerism

Functional isomers
Aldehyde and ketone
Alcohol and ether
Carboxylic acids and esters

Metamerism

Distribution of carbon chain either side of functional group

Tautomerism, (dynamic isomerism, phototropism, keto-enol isomerism, karyo tropism:) is due to shifting of H b)w atom...

Geometric isomerism, Configurational

Alkane, alkyne don't show geometric isomerism

Only alkene shows geometric isomerism

Cis-form

Polar molecules thus have strong Intermolecular forces and that's why have High B.p

Dipole is not zero

Strong Intermolecular force

High B.P

Low M.P

Loose packing, Unsymmetrical

B.P depends upon IMF and M.P depends upon intermolecular forces

Trans-form

Dipole moment is zero

And non polar thus weaker intermolecular forces

High M.P

Low B.P

Compact packing, symmetrical

Optical isomerism

Shown by chiral carbon

-ve lactic acid => dextro form rotates light right side and found in sour milk

+Ve lactic acid => leavo form, rotates light left side

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Mirror images are called **enantiomers**

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Lactic acid IUPAC name; 2 hydroxy propionic acid, propanoic acid

In amino acids all are optically active except the glycine because having similar group of H..thus no chiral carbon(having different group on four sides)

=> Halothane formula: 2 bromo, 2 chloro, 1,1,1 trifluoroethane

Hydrocarbons

Alkanes

C_nH_{2n+2} general formula

Are paraffin, least reactive and sp^3 hybridized, 25% s character which is directly proportional to

ionic character and E.N

Are nonpolar and weak intermolecular forces

Low melting and boiling point

C1-C4 gases

C5-C17 liquid

C18- solids..

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Stability order:

Alkane > Benzene > Alkyne > Alkene

Combustion:

$CH_4 + 2O_2$ (excess oxygen) $\Rightarrow CO_2 + 2H_2O$

$\Delta H = -892 \text{ kJ/mol}$

Note for balance equation

No of carbon dioxide molecule = no of C

And No of H_2O are $= 1/2$ half of H atom

If there is no excess of oxygen

There will be no production of CO_2

$CH_4 \Rightarrow CO, C, H_2O, \dots$

By oxidation of methane we get CO_2 and H_2O but **catalytic oxidation** of all other alkanes we get **carboxylic acids**..

Alkane \Rightarrow alcohol \Rightarrow aldehyde/ketone \Rightarrow carboxylic acid

Catalyst are $Cu + 400^\circ C + 200 \text{ atm}$

$K_2Cr_2O_7 + H_2SO_4$

$KMnO_4 + H_2SO_4$ are catalysts that produce nascent oxygen....

Free radical substitution to alkane by replacement of H...

Neither electrophilic nor nucleophilic substitution...because alkane are nonpolar...

Reactivity = $F > Cl > Br > I$

Alkenes; olefins

Most reactive hydrocarbons having double bond

Show Beta elimination reaction mechanism (Hydrogen eliminated at Beta Carbon alpha attached to halogens)

There must be Beta hydrogen for example neopentyl chloride having no beta hydrogen thus not gonna show reaction

For Beta elimination reaction mechanism Alcoholic base \Rightarrow Alkene

\Rightarrow $\text{HBr} + \text{H}_2\text{O}_2 \Rightarrow$ Antimarkovnikov's rule

(Note if medium is Aqueous than \Rightarrow Alcohols are formed)

Alkene formation by dehydration of alcohols

Also beta elimination reaction mechanism

Al_2O_3 $340-450^\circ\text{C}$

Alkene formation by partial reduction of Alkynes

$\text{Pd}(\text{BaSO}_4)$ quinoline \Rightarrow Lindlars catalyst Cis alkene \Rightarrow alkynes partial reduction

$\text{Na} + \text{Liquid ammonia} \Rightarrow$ Birch synthesis Trans alkene by partial reduction of alkyne

Reactivity = Alkene > Alkyne > Benzene > Alkane

By hydrogenation Vegetable ghee formation

Alkene \Rightarrow Pd/Pt Ni $250^\circ\text{C} \Rightarrow$ alkane

In sabatier senderens reaction Raney nickel is used 100°C 3atm ...

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Baeyer's Test:

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1% Cold alkaline KMnO_4 by reaction with alkene adds two OH group adjacent carbon by breakage of double bond

By reaction with alkyne it only adds Oxygen to two adjacent carbon where is triple bond

Baeyer's test used to check unsaturation of Alkene, Alkyne...

Hot KMnO_4 is used for formation of carboxylic acids, ketone, according to type of alkene

Ozonolysis used to locate the position of double bond

By Alkene aldehyde and ketone are formed

Polythene or polyethylene

$-\text{[Ch=Ch]}-$ ziegler natta catalyst is used $\text{AlCl}_3 + \text{TiCl}_4$ 400°C 100atm

Benzene

Highest ratio of C/H
Lowest ratio of H/C
C-C = 1.397Å C-H 1.09Å
Bond angle is 120
Sp² hybridized, one unhybridized orbital p_z orbital
Regular hexagonal planar structure

Heat of hydrogenation for Benzene

Is -208 kJ/mol as there are 3 π bonds

For 1 π bond heat of hydrogenation is -120 kJ/mol for 3 is 358.5 kJ/mol but for benzene 3 π bonds it is 208 kJ/mol so benzene resonating energy is 150.5 kJ/mol

Benzene doesn't show polymerization and elimination reactions..

Hydrogenation of benzene

Benzene + 3H₂ (Ni + 200°C, pt h₃o+) => cyclohexane

Note 3 molecules of hydrogen

And 6 hydrogen atom for hydrogenation of benzene is used

Benzene ring is oxidized by very strong oxidizing agent V₂O₅

For side chain reaction in benzene one carbon atom is oxidized by 3[O]

For methyl 3[O]

For ethyl 6[O]

Ortho para (2,4) directing groups are ring activating groups, except halogens still they are deactivating but they are ortho para directing groups due to strong inductive effect, they increase electron density at ortho and para position

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Meta directing groups are deactivating groups which decreases electron density at Meta position (3,5)

Alkyl halides

Haloethane => an anesthesia, optically active compound (beta carbon is chiral carbon)

Name: 2-bromo, 2-chloro, 1,1,1-trifluoroethane

Freons: (CF₂Cl₂)

Aerosols propellants, are refrigerants

Ozone depletion

Chloroform:(CHCl₃)

Polar solvent, anesthetics, specimens preservation

Carbon tetrachloride (CCl₄):

Non polar solvent, produce freons

Fire extinguisher

Teflons-(CF₂-CF₂)-:

Tetrafluoroethylene

Corrosion free machines, covering wires

Non stick pan, utensils quality plastic Electrical neutral

Alkyl halides reactions;

Are highly reactive , show substitution and elimination Reactions and don't show addition

Reactions Are saturated

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Reactivity:

R-I>R-Br>R-Cl>R-F

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Nucleophilic substitution reaction:

Stronger nucleophile substitute weaker nucleophile

SN₂:

- In primary alkyl halides
- Non polar solvent
- Rate is directly proportional to nucleophile and substrate
- Bimolecular Reactions
- Follow 2nd order kinetics
- Nucleophile attacks backside of leaving group
- 100%Inversion
- No Carbocation intermediate....
- Need a strong nucleophile..
- Ease of SN₂ reaction;
- 1°>2°>3° alkyl halides

SN₁:

- In tertiary alkyl halides

- Polar solvent
- 2 step mechanism
- 1st step is slow and rate determining step
- 2nd step is fast
- Rate is directly proportional to only substrate
- Unimolecular reaction
- 1st order kinetics
- Nucleophile can attack both side
- 50%inversion and 50%retention
- Racemic mixture formation
- Reaction occurs either strong or weak nucleophile

Ease of SN1 reaction:

$3^\circ > 2^\circ > 1^\circ$

Note:SN1 is faster than SN2 instead of having two steps

And SN2 reaction needs strong nucleophile

But SN1 Reactions doesn't depends upon strength of nucleophile

SN1 and E1 rate is affected by nature of leaving group

Nucleophilic substitution (SN) reaction occurs in presence of a strong nucleophile

Elimination reaction occurs in presence of a strong Base

Elimination reactions in alcoholic medium presence of a strong base

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E1:
Unimolecular, strong base, complete in two step, 1st step is just like SN1 reaction

Ease of reaction $3^\circ > 2^\circ > 1^\circ$

In result alkene are formed from alkyl halide

E2:
Bimolecular, strong base, complete in one step
Ease of reaction $1^\circ > 2^\circ > 3^\circ$

Note:There must be a beta Hydrogen for elimination reaction if no beta H no elimination

Alcohols and phenols

$C_nH_{2n+2}O..$

Preparation of methyl alcohol/ carbinol, zerone

$Co + 2H_2 (ZnO + Cr_2O_3 + 450^\circ C + 200 atm) \Rightarrow CH_3OH$

Ethanol/grain alcohol

Ethene + H_2SO_4 ethyl hydrogen sulphate + H_2O $100^\circ C \Rightarrow$ ethyl alcohol

Preparation of alcohol by fermentation

From molasses 60% sucrose solution

Sucrose \Rightarrow (yeast, invertase) glucose + sucrose

Glucose + fructose \Rightarrow (yeast, zymase) ethanol + CO_2

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Alcohol From starch:

Starch \Rightarrow (yeast, diastase) maltose

Maltose \Rightarrow (yeast, maltase) \Rightarrow 2 Glucose

Glucose \Rightarrow (yeast, zymase) ethanol CO_2

By industrial we get upto 12-14% alcohol

By redistillation \Rightarrow we get 95% ethyl alcohol

And by lime distillation we get 100% ethyl alcohol

100% alcohol is absolute alcohol

For avoiding drinking purpose of alcohol we mix it with some denaturation

Like methyl, pyridine, acetone 10%

90% ethyl alcohol \Rightarrow then it is called denatured alcohol

Lower alcohols are colourless and toxic liquid sweet smell and burning taste

Solubility \Rightarrow readily soluble in water due to H bond but in higher alcohols it decreases

Reaction of alcohols $R-OH$ ($R-O$ bond breakage)

$R-OH + PCl_5 \Rightarrow POCl_3 + HCl + R-Cl$

$R-OH + PCl_3 \Rightarrow H_3PO_3 + R-Cl$

$R-OH + SOCl_2 \Rightarrow HCl + SO_2 + R-Cl$

Note HCl and SO_2 are gases thus purest **Alkyl halide** is formed

Reactivity;

Tertiary alcohols $>$ secondary $>$ primary

Reaction of alcohols ($ROH \Rightarrow O-H$ bond breakage)

$R-OH + 2Na \Rightarrow RONa + H_2$

$\text{Roh} + \text{Naoh} \Rightarrow \text{RONa} + \text{H}_2\text{O}$

$\text{Roh} + \text{RCOOH} \Rightarrow \text{ester}$

Note H^+ from alcohol and OH^- from carboxylic acid

Oxidation reaction

Primary alcohols ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$) \Rightarrow Aldehydes

Secondary Alcohols ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$) \Rightarrow Ketones

Tertiary alcohols ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$) \Rightarrow don't show reaction and show beta Elimination reaction and form Alkene

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Note tertiary alcohols by oxidation form Alkenes (by beta elimination reaction)

Dehydration of Alcohols

Ethyl alcohols (Conc H_2SO_4) $180^\circ \Rightarrow$ ethene + H_2O

Ethyl alcohol (Conc H_2SO_4) $140^\circ \Rightarrow$ ether is formed

Note by decreasing temp from two molecule one Water molecule is removed but in 180°C from one molecule of alcohol one water is removed

And in same reaction if aluminum oxide Al_2O_3 is used then only Alkene are formed by alcohols

What is the temp..

Doesn't matter if there is tertiary 2ndry or primary alcohols..

Lucas test;

Distinguish between $1^\circ 2^\circ 3^\circ$ Alcohols

Lucas reagent is $\text{ZnCl}_2 + \text{HCl}$

Alcohol + lucas reagent \Rightarrow Alkyl halide + H_2O

An oily layer is formed after reaction

Primary alcohols Don't show lucas test

No oily layer is formed (but gives by heating)

Secondary alcohols show lucas test oily layer is formed after 5-10 minutes

Tertiary alcohols show the Lucas test oily layer is immediately formed....

Iodoform test:

Distinguish between methanol and ethanol

In primary alcohols only ethanol gives an iodoform test.....

Phenols; benzene + one or more OH groups

Carbolic acid is the simplest phenol

Benzene+OH \Rightarrow carbolic acid, benzinol or simplest phenol

Phenol preparation by dows process
Chlorobenzene+base(NaOH) \Rightarrow phenoxide

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Phenoxide+HCl \Rightarrow phenol

Phenol is acidic in nature that's why it only reacts with strong bases

Phenol +Zn dust \Rightarrow Benzene

Nitration \Rightarrow phenol+dilute HNO₃ (nitric acid)

Ortho , para nitrophenol mixture

Phenol+Dilute nitric acid \Rightarrow 2,4,6 nitrophenol

2,4,6 nitrophenol \Rightarrow Picric acid

Sulphonation \Rightarrow phenol+H₂SO₄ \Rightarrow ortho, or para mixture is produced

Halogenation \Rightarrow phenol+bromine water \Rightarrow 2,4,6 bromophenol

Hydrogenation of phenol +3H₂ \Rightarrow Cyclohexanol is formed

Backelite formation;Synthetic rubber

Formaldehyde (methanal +phenol) \Rightarrow ortho hydroxy, para hydroxy benzyl alcohol

Aldehydes and ketones

C_nH_{2n}O

both aldehyde and ketone general formula

Carbonyl group

C=O is planar C ,O both are Sp² hybridized

Pi electron is attracted by O towards itself and partial negative charge on O

Aldehydes are more reactive than ketones because having less steric hindrance and less electron donating alkyl group thus more electrophilic carbon

Aldehydes with smaller chains are more reactive than longer...

Aldehydes and ketones show Nucleophilic addition reaction...as there is unsaturation having pi bond

Aldehydes preparation;

Methanol + O₂ {FeO Mo₂O₃ 500°C} => methanal + H₂O

Methanol + O₂ (Pt/asbestos 300°) => methanal + H₂O

Ethene + O₂ (PdCl₂ + CuCl₂ (promoter)) => ethanal

Ethanol + [O] (Na₂Cr₂O₇) => ethanal + H₂O

Primary alcohols on oxidation => Aldehydes

Secondary Alcohols => Ketone

Tertiary alcohols => no reaction beta elimination and form Alkene

Ketone preparation

2° Alcohols (K₂Cr₂O₇) => Ketone

Aldehydes and ketones give Nucleophilic addition reaction

Base catalyst generates strong Nucleophile

+C=O => OH- => -O-C-OH

Acid catalyst generates strong electrophile

+C=O => H+ => +C-OH

In both acid and base catalysed reactions are Nucleophilic addition reactions, same product also and product are same in both aldehyde and ketone..

Aldehyde and ketone + HCN cyanohydrin group is attached to both H+ to O- and CN- to C+

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Other base catalysed reaction

Addition of NaHSO₃ => all R-CHO and only methyl ketones... give this reaction

Aldol condensation => dil NaOH + alpha hydrogen => aldol => both aldehyde and ketone group present

Cannizzaro's reaction => 50% NaOH + no alpha hydrogen disproportionate reaction...

Haloform reaction => acetyl group or methyl ketonic group

Acid catalysed reaction (addition reaction (adduct))

DNPH (di-nitro-phenyl hydrazine)

X + 2,4-DNPH => X-2,4-DNPH + H₂O

Note: X can be any aldehyde and ketone group and in product it will be same as reactant

And in reactant it is Hydrazine

And in product it is Hydrazone + H₂O

Aldehyde by reaction with 2,4-DNPH gives Yellow colouration

And Ketone gives Red colour

Reaction with NaBH₄/LiAlH₄

Partial reduction

Aldehydes to primary Alcohols

Ketones to secondary Alcohols by partial reduction

Note: $\text{NaBH}_4/\text{LiAlH}_4$ don't reduce Alkyne and alkenes because These NaBH_4 , LiAlH_4 generates H^- and in alkene there must be an electrophile and H^- is a Nucleophile..

NaBH_4 and LiAlH_4 don't do partial reduction of double bonds or triple bonds...

Note: NaBH_4 Don't do partial reduction of Carboxylic acid to alcohols

But LiAlH_4 does partial reduction of Carboxylic acid to their relevant Alcohols...

Differentiation reaction Aldehyde and Ketone

Aldehyde reacts with mild oxidizing agents

And ketone don't react

For ketone strong oxidizing agent is required

Tollens Test: Silver mirror test

($\text{AgNO}_3 + \text{NH}_4\text{OH}$) Aldehyde aromatic aliphatic both give this reaction

Aldehydes are reducing agent

It's a redox reaction

Ketone don't give this reaction

Fehling's solution test:

($\text{CuSO}_4 + \text{NaOH} + \text{Tartaric acid}$)

Brick red ppt of Cu_2O by only Aliphatic Aldehydes, Ketone don't give this reaction

Benedict's solution test:

($\text{CuSO}_4 + \text{NaOH} + \text{Citric acid}$)

Just like Fehling's test...

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Sodium nitroprusside test ($\text{Na}[\text{Fe}(\text{CN})\text{NO}]$)

Ketone give this reaction

Aldehyde don't give this reaction

Iodoform test;

Compounds containing methyl ketonic group show this test yellow ppt of CHI_3 is formed

$\text{Acetaldehyde} + 3\text{I} + \text{NaOH} \Rightarrow \text{CHI}_3 + \text{HCOOH} + 3\text{NaI} + 3\text{H}_2\text{O}$

In primary Alcohols only ethyl alcohol give this reaction

In secondary alcohols 2-Ol give this reaction

In aldehydes only acetaldehyde gives this reaction..

In Ketones all methyl ketone show this reaction..

Aldol condensation:

Aldehydes and ketones having alpha Hydrogen give this reaction

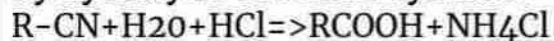
Cannizzros Reaction:

Aldehydes and ketones having no alpha hydrogen gives this reaction

Carboxylic acids

Preparation by oxidation of aldehyde and ketone (two chain of carboxylic acid) using $K_2Cr_2O_7 + H_2SO_4$...

By hydrolysis of alkane cyanide..



Carboxylic acids form 8 membered ring in non polar solvent..having 2 physical (H bond) and 8

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chemical bonds..

C1-C3 pungent smell

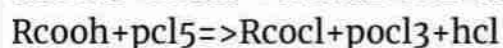
C4-C6 unpleasant smell

Alkyl chain is inversely proportional to H bond and Solubility...

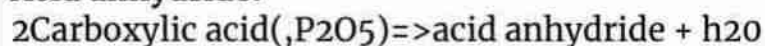
Note:acidic strength and Reactivity are Inversely proportional to Chain length...

Esterification is a Nucleophilic substitution Reaction mechanism.....

Acid Halides

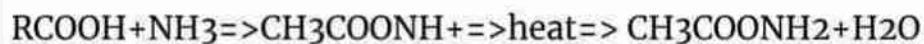


Acid anhydride:



Amide formation;

Note it is two step process not formed directly

**Reactivity order:**

Acid halides > carboxylic acids > acid anhydride > Esters > Acid amides

Acidic strength;

Electron withdrawing groups **increase** acidity

Electron donating groups decrease acidity

Closer the electron withdrawing group stronger will be the acid

Fluoro carboxylic acid > chloro > bromo > iodo

Trichloro carboxylic acid > di > mono > carboxylic

Note: Dichloro carboxylic acid > fluoro acid

And dibromo, iodocarboxylic acid, > Fluoro acid

1chlorocarboxylic acid > 2chloro > 3chloro..

Acidic strength;

Carboxylic acids > Phenols > water > Alcohols

Exception; only Methylalcohol is more acidic than Water...

Mineral acids are stronger than organic acids.....

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