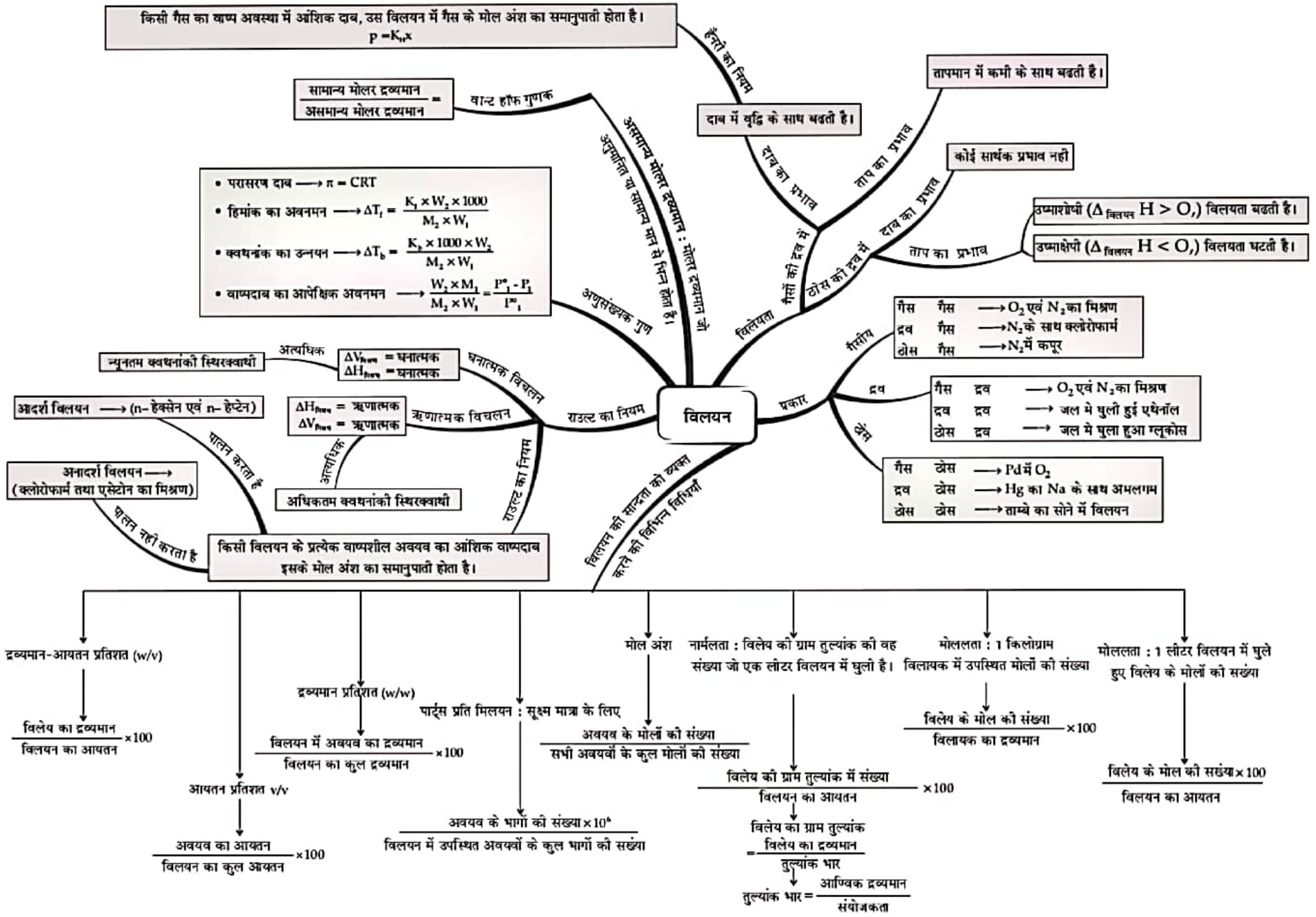
अध्याय 2 — विलयन



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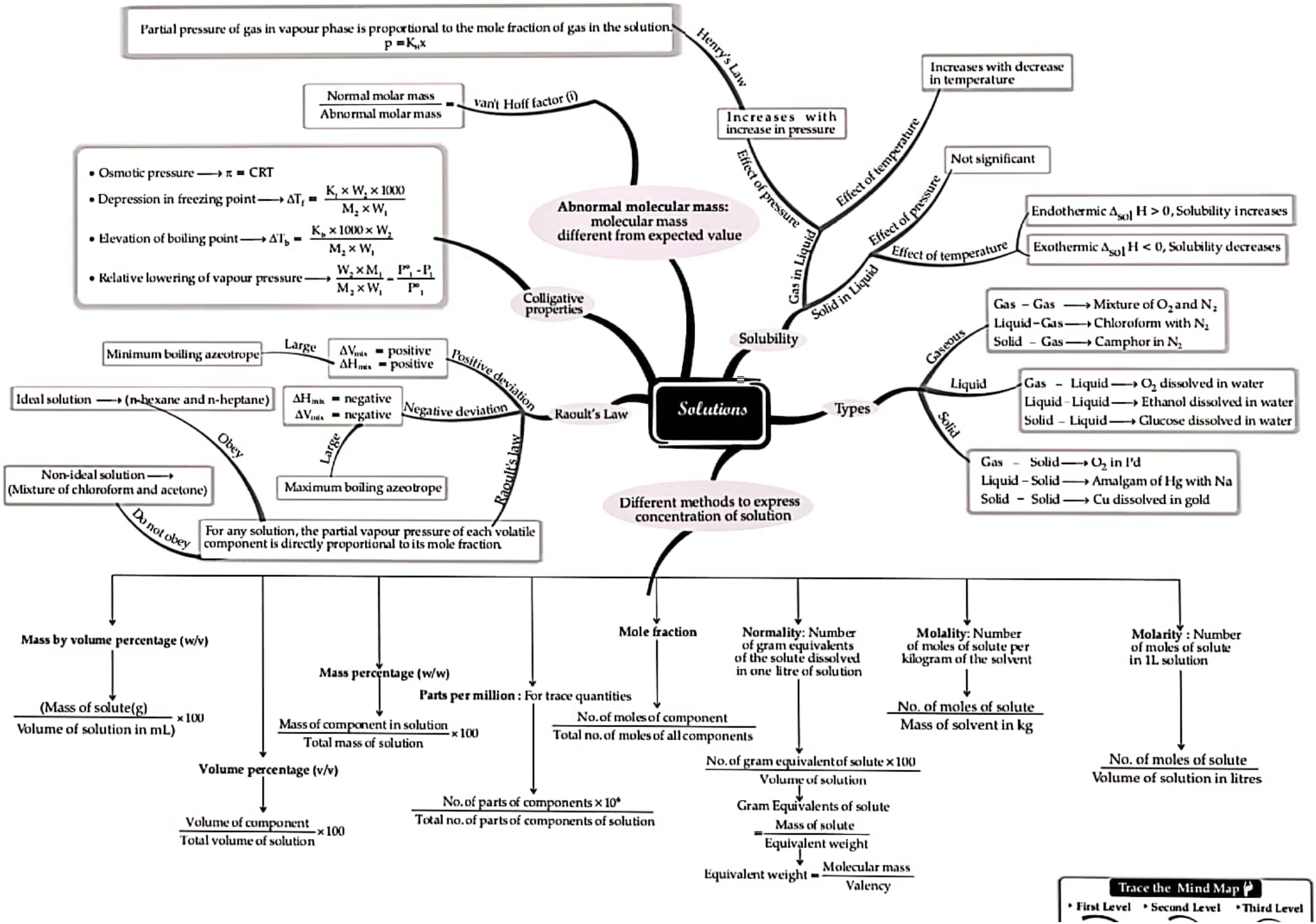

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Electrochemistry

- Relation between cell potential and Gibbs energy
  - $\Delta_r G^\circ = -RT \ln K$
  - $\Delta_r G^\circ = -n F E^\circ_{cell}$
- Fuel cells
  - Galvanic cell that converts energy of combustion of fuels like H_2, CH_4 directly into electrical energy
- 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 ⟶ ..... $\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3}$
- Products of electrolysis depends upon
  - Nature of material being electrolysed
  - Types of electrodes
- Corrosion
  - Electrochemical phenomenon in which metal oxide of metal forms coating on metal surface.
  - Example: Rusting of iron, tarnishing of silver
  - Prevention: Painting, barrier protection, rust solutions
- Types of Cells
  - Electrochemical : Device converting chemical energy to electrical energy
    - Components
      - Half-cell ⟶ two portions of cell
        - Electrolyte: A chemical compound that dissociates into ions and conducts electric current
        - Salt bridge: U shaped inverted tube connecting two electrolytic solution
        - Electrode
          - Cathode ⟶ Reduction takes place
          - Anode ⟶ Oxidation takes place
    - Daniell Cell: cathode: Copper, Anode : Zinc; Salt bridge : Agar agar; electrolyte : KCN/KNO_3
      - ⟶ Reduction : $Cu^{2+} + 2e^- \rightarrow Cu$; $Zn(s)$
      - ⟶ Oxidation : $Zn^{2+} + 2e^-$; $Zn|Zn^{2+}(C_1) \,||\, Cu^{2+}(C_2)|Cu$
    - 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^+/H_2
      - Negative E° ⟶ Stronger reducing agent than H^+/H_2
    - Standard hydrogen electrode
      - Electrode : Pt coated with Pt black, electrolyte : acidic solution pressure 1 bar $Pt(s)\,|H_2(g)|\,H^+(aq)$
    - Electrochemical Series
      - A series of half-cells arranged in increasing standard oxidation potentials.
  - Electrolytic : Device converting electrical energy to chemical energy
    - Two copper strips dipped in an aqueous solution of $CuSO_4$ ⟶ Anode : $Cu \longrightarrow Cu^{2+} + 2e^-$; cathode : $Cu^{2+} + 2e^- \rightarrow Cu$
- Nernst equation
  - $M^{n+}(aq) + ne^- \rightarrow M(s)$
  - $E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nT} \log \frac{[M]}{[M^{n+}]}$
  - $E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$
  - At equilibrium: $K_C = \text{Antilog}\left(\frac{nE^\circ_{cell}}{0.0591}\right)$; $E^\circ_{cell} = \frac{2.303RT}{nF} \log K_C$
- Resistance
  - $R = \frac{V}{I}$ Unit : Ohm (Ω)
- Electrical resistance
  - $R = \rho \frac{l}{A}$
  - ρ = Resistivity
  - Unit : Ohm – Meter
- Batteries
  - Primary (reaction occurs only once and cannot be reused)
    - Mercury cell
    - Leclanche cell (Dry cell)
  - Secondary (can be recharged by passing current in opposite direction)
    - (Lead storage battery, Ni-Cd 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
  - Measured by: Conductivity Cell
  - Inverse of Resistance
  - Conductance
    - 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 solvation
        - Nature of solvent and its viscosity,
        - Concentration of electrolyte,
        - Temperature (increases with increase in Temperature)
  - $C = \frac{1}{R} = \frac{A}{\rho l}$ or $= \kappa \frac{A}{l}$ Unit : Siemens (s) or ohm Increases on dilution
  - $\Lambda_m = \frac{\kappa A}{1}$; $\Lambda_m = \kappa V$
  - Limiting molar conductivity : If molar conductivity reaches a limiting value when concentration approaches zero. $C \rightarrow 0$, $\Lambda_m = \Lambda^\circ_m$
  - Kohlrausch law of independent migration of ions
    - Strong electrolyte $\Lambda_m = \Lambda^\circ_m - Ac^{th}$ (KCl)
    - Weak electrolyte $\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}$ (acetic acid)
    - Limiting molar conductivity of an electrolyte can be represented as sum of individual contribution of anions and cations of the electrolyte $\Lambda^\circ_m = \nu_+ \lambda^\circ_+ + \nu_- \lambda^\circ_-$
    - Applications
      1. Calculate Λ°_m for any electrolyte from λ° of individual ions
      2. Determine value of dissociation constant for weak electrolytes

Trace the Mind Map

• First Level • Second Level • Third Level

SPLANET CLASSES

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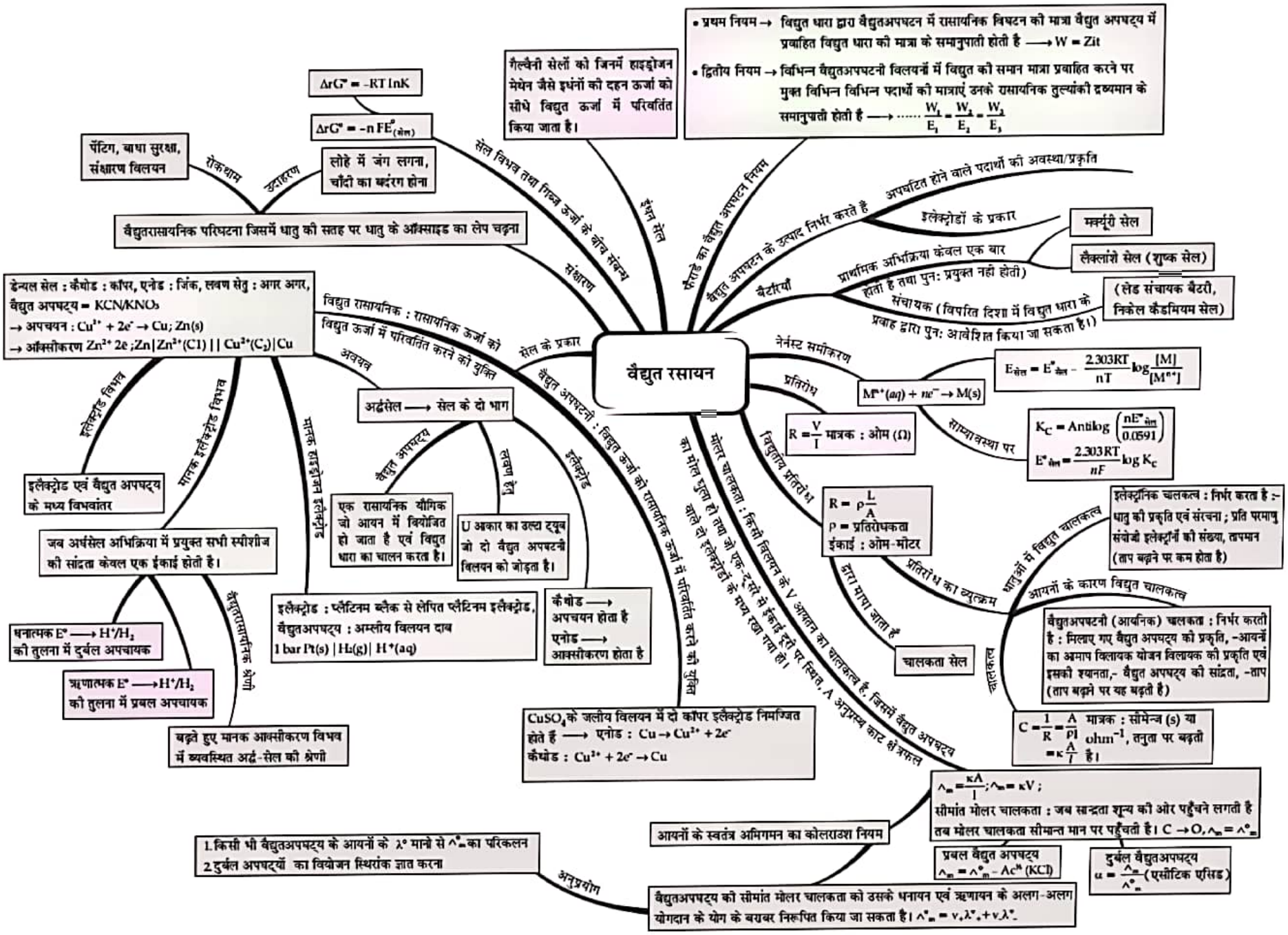
अध्याय 3 — वैद्युत रसायन



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Chemical Kinetics

Collision Theory: Rate of reaction depends on the collision frequency and effective collisions.

- 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
- Number of collisions per unit volume of reaction mixture
  Rate = $Z_{AB}e^{-Ea/RT}$
- Effective Collision
  - Collision in which molecules collide with sufficient kinetic energy and proper orientation for breaking of bonds and formation of new bonds.
- Collision Frequency

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

$$k = Ae^{-Ea/RT}$$
$$\log k = \log A - \frac{E_a}{2.303RT}$$
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303RT}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

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

Not truly of first order but under certain conditions behave, as first order reaction.
In such reaction, one reactants is in excess.
- 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.

- First Order: $t_{1/2} = \frac{0.693}{k}$
- Zero Order: $t_{1/2} = \frac{[R]_0}{2k}$

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.

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
    $= \frac{\text{Decease in concentration of R}}{\text{Time taken}} = \frac{-\Delta[R]}{\Delta t}$
  - Rate of appearance of P
    $= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = \frac{+\Delta[P]}{\Delta t}$

Rate Law

Expression in which reaction rate in 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.

$aA + bB \rightarrow cC + dD$

$$\text{Rate} = k[A]^a[B]^b = \frac{d[R]}{dt}$$
$$k = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

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	$mol^{-1}L\,s^{-1}$

Factors Influencing rate of reaction

- **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 is the surface area, faster is the rate of reaction.
- **Activation Energy :** Lower the activation energy, faster is the reaction.

Trace the Mind Map
First Level · Second Level · Third Level

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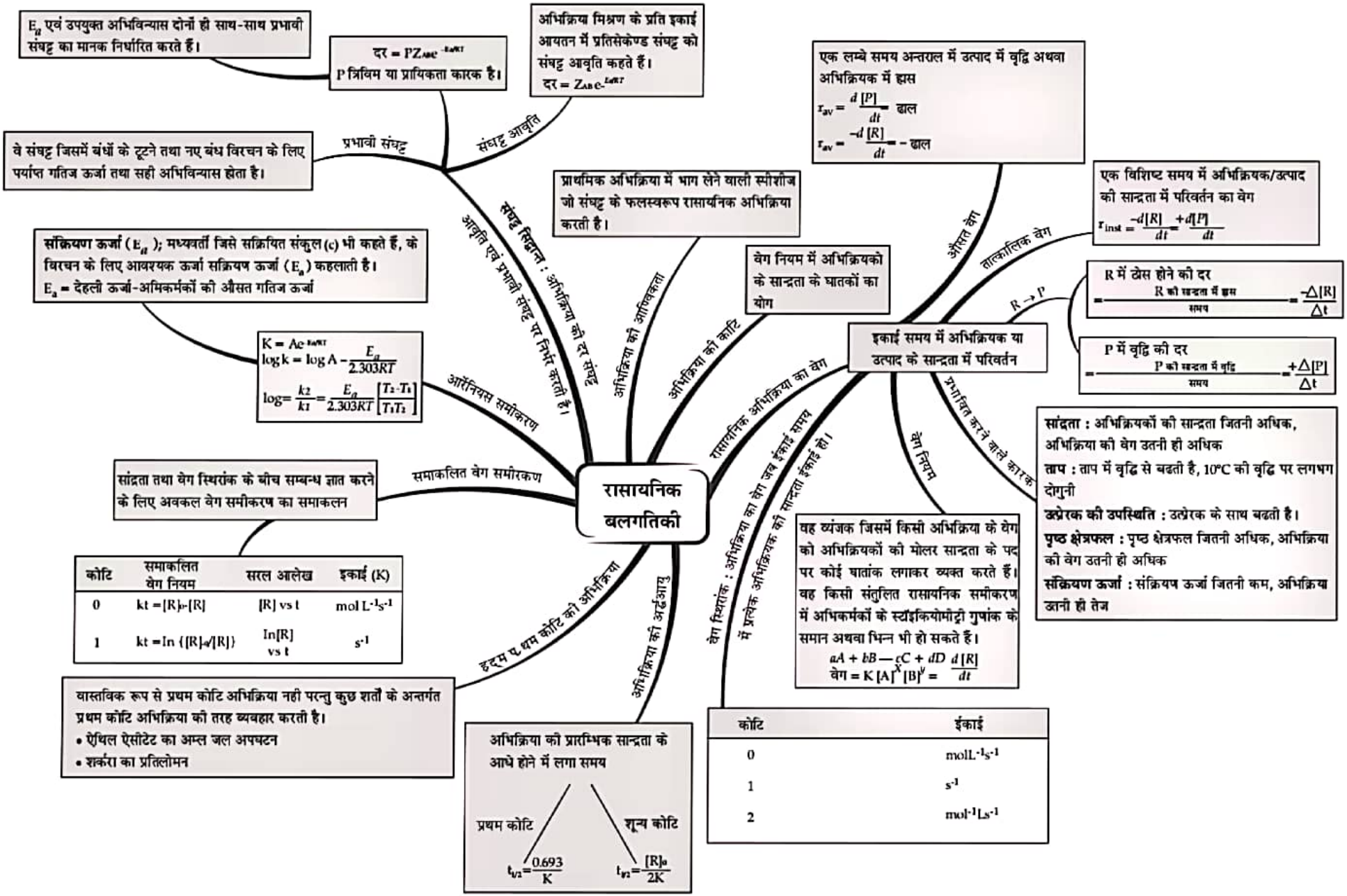
अध्याय 4 — रासायनिक बलगतिकी



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अध्याय 7 — P ब्लॉक के तत्व

P ब्लॉक के तत्व

वर्ग 18 के तत्व

- **उपलब्धता :** रेडॉन के अतिरिक्त सभी वायुमंडल में पायी जाती है
- **इलेक्ट्रॉनिक विन्यास :** He के अतिरिक्त $ns^2 np^6$
- **आयनन एन्थैल्पी :** उच्च
- **परमाणु त्रिज्या :** वर्ग में नीचे की ओर परमाणु त्रिज्या में वृद्धि
- **इलेक्ट्रॉन लब्धि एन्थैल्पी :** अधिक धनात्मक
- **भौतिक गुण :** एक परमाण्विक, रंगहीन, गंधहीन तथा स्वादहीन । जल में अल्प विलेय है।
- **गलनांक तथा क्वथनांक :** निम्न
- **रासायनिक गुण :** न्यूनतम अभिक्रियाशील ; जीनॉन-फ्लुओराइड XeF_2, XeF_4 and XeF_6.
- **जीनॉन आर्क्सीजन यौगिक :** XeO_3, $XeOF_2$, $XeOF_4$

वर्ग 16 के तत्व

- इलेक्ट्रॉनिक विन्यास : ns^2np^4
- परमाणु तथा आयनी त्रिज्या : वर्ग में नीचे जाने पर बढ़ती है।
- आयनन एन्थैल्पी : वर्ग में नीचे जाने पर घटती है।
- इलेक्ट्रॉन लब्धि एन्थैल्पी : O से कम S ऋणात्मक होता है।
- विद्युत ऋणात्मकता : परमाणु संख्या में वृद्धि के साथ कम होती है।
- भौतिक गुण : O तथा S अधातु है, Se तथा Te उपधातु है जबकि Po एक धातु है। सभी तत्व अपरूपता प्रदर्शित करते हैं।
- गलनांक एवं क्वथनांक : वर्ग में नीचे जाने पर बढ़ती है।
- रासायनिक गुण : परिवर्तनशील
  - ✓ हाइड्रोजन के साथ क्रियाशीलता : स्थायी हाइड्राइड
  - ✓ हैलोजन के साथ क्रियाशीलता $F^- > Cl^- > Br^- > I^-$
- S के आक्सोअम्ल :

- डायऑक्सीजन (O_2) :
  - विरचन : $2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$
  - गुण : रंगहीन एवं गंधहीन गैस
  - $2Ca + O_2 \longrightarrow 2CaO$; $4Al + 3O_2 \longrightarrow 2AlO_3$
  - $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$; $4HCl + O_2 \xrightarrow{CuCl} 2Cl + 2H_2O$

वर्ग 17 के तत्व

- **उपलब्धता :** F और Cl बहुलता से उपलब्ध जबकि Br एवं I कम मात्रा में
- **इलेक्ट्रॉनिक विन्यास :** ns^2np^5
- **परमाणु तथा आयनिक त्रिज्या :** अपने आवर्त में सबसे छोटी परन्तु F से I तक बढ़ती है।
- **आयनन एन्थैल्पी :** वर्ग में नीचे जाने पर घटती है।
- **इलेक्ट्रॉन लब्धि एन्थैल्पी :** वर्ग में नीचे जाने पर कम ऋणात्मक
- **विद्युत ऋणात्मकता :** उच्च, वर्ग में नीचे जाने पर घटती है।
- **भौतिक गुण :** F एवं Cl गैस है, Br द्रव है तथा I ठोस
- **गलनांक एवं क्वथनांक :** परमाणु क्रमांक के साथ बढ़ती है।
- **रासायनिक गुण :**

सभी -1 ऑक्सीकरण अवस्था प्रदर्शित करती है, Cl, Br तथा I +1, +3, +5 तथा +7 ऑक्सीकरण अवस्था प्रदर्शित करती है।
हाइड्रोजन के प्रति अभिक्रियाशीलता $H-F > H-Cl > H-Br > H-I$
ऑक्सीजन के प्रति अभिक्रियाशीलता F, OF_2 (स्थायी) तथा O_2F_2 बनाती है।
धातुओं के प्रति अभिक्रियाशीलता $MF > MCl > MBr > MI$
अन्य हैलोजनों के प्रति अभिक्रियाशीलता XX', XX'_3, XX'_5 एवं XX'_7 बनाता है।

- **क्लोरीन :**

विरचन : $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$
डेकॉन विधि : $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$
गुण : तीखी गन्ध वाली, दमघोंटू हरित-पीली गैस है। वायु से भारी है।

$2Al + 3Cl_2 \longrightarrow 2AlCl_3$
$H_2 + Cl_2 \longrightarrow 2HCl$
$H_2S + Cl_2 \longrightarrow 2HCl + S$
$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$
$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$
(ठंडा एवं तनु)
$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$
$CH_4 + Cl_2 \xrightarrow{uv} CH_3Cl + HCl$
$C_2H_4 + Cl_2 \xrightarrow{\text{कक्ष ताप}} C_2H_4Cl_2$
$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$
$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$
$Cl_2 + H_2O \longrightarrow 2HCl + 0$

'अन्तराहैलोजन यौगिक : XX' - sp^3 (रैखिक) XX'_3 sp^3d (T- आकार) XX'_5 sp^3d^2 (वर्ग पिरैमिडी), XX'_7 sp^3d^3 (पंचकोणीय द्विपिरैमिडी)

वर्ग 15 के तत्व

- **इलेक्ट्रॉनिक विन्यास :** ns^2np^3
- **तत्व :** $_7N$, $_{15}P$, $_{33}As$, $_{51}Sb$, $_{83}Bi$
- **परमाणु एवं आयनी त्रिज्या :** वर्ग में नीचे की ओर बढ़ती है।
- **आयनन एन्थैल्पी :** वर्ग में नीचे की ओर बढ़ने पर आयनन एन्थैल्पी परमाण्विक आकार में लगातार वृद्धि के कारण घटती है।
- **विद्युत ऋणात्मकता :** वर्ग में नीचे की ओर जाने पर परमाण्विक आकार में वृद्धि के कारण घटता है।
- **भौतिक गुण :** बहुपरमाणुक, वर्ग में नीचे की ओर जाने पर धात्विक गुण बढ़ता है। N व P अधातु है, As तथा Sb उपधातु है तथा Bi धातु है। क्वथनांक ऊपर से नीचे की ओर बढ़ता है एवं गलनांक, As तक बढ़ता है एवं उसके बाद Bi तक घटता है। N के अलावा सभी तत्व अपरूपता प्रदर्शित करते हैं।
- **रासायनिक गुण :** सामान्य आक्सीकरण अवस्था : -3, +3 एवं +5 नाइट्रोजन असमान्य गुण (व्यवहार) प्रदर्शित करता है।

डायनाइट्रोजन विरचन

- **प्रयोगशाला में :**
  $NH_4Cl + NaNO_2 \longrightarrow N_2 + 2H_2O + NaCl$
- **तापीय अपघटन :**
  $(NH_4)_2Cr_2O_7 \xrightarrow{\text{ताप}} N_2 + 4H_2O + Cr_2O_3$
  $Ba(N_3)_2 \longrightarrow Ba + 3N_2$
- **गुण :**
  रंगहीन, गंधहीन, स्वादहीन तथा अविषैली गैस
  $6Li + N_2 \xrightarrow{\Delta} 2Li_3N$
  $3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$
  $N_2 + 3H_2 \xrightarrow{773K} 2NH_3$, $\Delta_fH^\circ = 46.1\ KJ\ mol^{-1}$
  $N_2 + O_2 \xrightarrow{\Delta} 2NO$

अमोनिया विरचन

$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$
$N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta_fH^\circ = -46.1\ kJ\ mol^{-1}$
गुण :
तीखी गंध वाली रंगहीन गैस है। जल में घुलनशील है।
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)SO_4$
(श्वेत अवक्षेप)
$FeCl_3 + NH_4OH \longrightarrow Fe_2O_3.xH_2O + NH_4Cl$
(भूरा अवक्षेप)

नाइट्रोजन के ऑक्साइड

P- Block Elements

Group 18 Elements

- **Occurrence :** All except radon occur in atmosphere
- **Electronic configuration :** $ns^2 np^6$ except He
- **IE :** High
- **Atomic radii :** Increases down group
- **Electron gain enthalpy :** Largely positive
- **Physical properties :** Monoatmic, colourless, odorless and tasteless. Sparingly soluble in water.
- **M.P. and B.P. :** Low
- **Chemical properties :** Least reactive ; Xenon fluoride compounds : XeF_2, XeF_4 and XeF_6
- **Xenon oxygen compounds :** XeO_3, $XeOF_2$, $XeOF_4$

Group 16 Elements

- Electronic configuration : ns^2np^4
- Atomic and ionic radii : Increase down the group
- IE : Decreases down the group
- Electron Gain enthalpy : O hass less–ve than S.
- Electro-negativity : Decreases with increase in atomic number
- Physical properties : O and S are non metals, Se and Te metalloids whereas Po is a metal. All exhibit allotropy
- M.P. and B.P. : Increases down the group
- Chemical properties : variable
  - ✓ Reactivity with hydrogen : stable hydrides
  - ✓ Reactivity with halogens : $F^- > Cl^- > Br^- > I^-$
- Oxoacids of S :

- Dioxygen (O_2) :

Preparation : $2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$

Properties : Colourless and odourless gas

$2Ca + O_2 \longrightarrow 2CaO$; $4Al + 3O_2 \longrightarrow 2Al_2O_3$

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$; $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

Group 17 Elements

- **Occurrence :** F and Cl are fairly abundant while Br and I less so
- **Electronic configuration :** ns^2np^5
- **Atomic Ionic/radii :** Smallest in periods but increases from F to I
- **IE :** Decreases down the group
- **Electron gain enthalpy :** Less –ve down the group
- **Electro-negativity :** High, decreases down the group
- **Physical properties :** F and Cl are gases, Br is liquid and I is solid
- **M.P. and B.P. :** Increases with atomic number
- **Chemical properties :**
  - All exhibit –1 oxidation state Cl, Br and I exhibit + 1, + 3, + 5 and + 7.O.N
  - **Reactivity towards hydrogen :** $H-F > H-Cl > H-Br > H-I$
  - **Reactivity towards oxygen :** F form OF_2 (stable) and O_2F_2
  - **Reactivity towards metals :** $MF > MCl > MBr > MI$
  - **Reactivity towards other halogens :** Forms XX', XX'_3, XX'_5 and XX'_7.

Chlorine

Preparation : $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

Deacon's process : $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

Properties : Greenish yellow gas with pungent and suffocating odour. Heavier than air

$2Al + 3Cl_2 \longrightarrow 2AlCl_3$

$H_2 + Cl_2 \longrightarrow 2HCl$

$H_2S + Cl_2 \longrightarrow 2HCl + S$

$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$

$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$ (cold and dilute)

$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$

$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$

$C_2H_4 + Cl_2 \xrightarrow{RT} C_2H_4Cl_2$

$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$

$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$

$Cl_2 + H_2O \longrightarrow 2HCl + O$

Inter-halogen compounds: $XX' - sp^3$(linear), $XX'_3 sp^3d$ (T–shaped), $XX'_5\ sp^3d^2$ (square pyramidal), $XX'_7\ sp^3d^3$ (Pentagonal bipyramidal)

Group 15 Elements

- **Electronic configuration :** ns^2np^3
- **Elements :** $_7N$, $_{15}P$, $_{33}As$, $_{51}Sb$, $_{83}Bi$
- **Atomic and Ionic radii :** Increase in size down the group.
- **Ionization enthalpy :** Decreases down the group due to gradual increase in atomic size.
- **Electro-negativity :** Decreases down the group with increasing atomic size.
- **Physical properties :** Polyatomic, metallic character increases down the group. N and P are non-metals, As and Sb metalloids and Bi metal. B.P increases top to bottom and M.P increases upto As and then decreases upto Bi. Except Ni all show allotropy.
- **Chemical properties :** Common O.N : –3, +3 and +5. Nitrogen shows anomalous behaviour.

Dinitrogen preparation

- **In laboratory :**

$NH_4Cl + NaNO_2 \longrightarrow N_2 + 2H_2O + NaCl$

- **Thermal decomposition :**

$(NH_4)_2Cr_2O_7 \xrightarrow{Heat} N_2 + 4H_2O + Cr_2O_3$

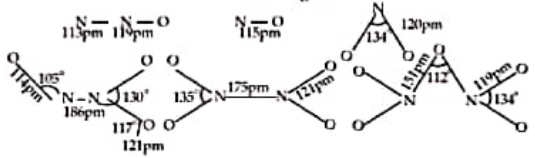
$Ba(N_3)_2 \longrightarrow Ba + 3N_2$

- **Properties :**

Colourless, odourless, tasteless and non-toxic gas

$6Li + N_2 \xrightarrow{\Delta} 2Li_3N$

$3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$



$N_2 + 3H_2 \xrightarrow{773K} 2NH_3, \Delta H^\circ = 46.1\ KJ\ mol^{-1}$

$N_2 + O_2 \xrightarrow{\Delta} 2NO$

Ammonia Preparation

$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\Delta H^\circ = -46.1\ kJ\ mol^{-1}$

Properties :

Colourless with pungent odour, soluble in water

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)_2SO_4$ (white ppt)

$FeCl_3 + NH_4OH \longrightarrow Fe_2O_3.xH_2O + NH_4Cl$ (Brown ppt)

Oxides of nitrogen

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d– and f–Block Elements

d–Block transition elements groups 3–12

- Position : Between *s*- and *p*–blocks.
- Electronic configuration : $(n-1)d^{1-10}ns^{1-2}$
- Physical properties : Show typical metallic properties, melting and boiling point are high; High enthalpies of atomization.
- Decrease in radius with increasing atomic number. 'Lanthanoid contraction is due to filling of 4f before 5d orbitals, hence 2nd, 3rd d-series exhibit similar radii. Also due to imperfect shielding of one e- by another in the same set of orbitals in same set of orbitals.'
- Ionisation enthalpies : Increases from left to right.
- Oxidation states : Variable; higher ON stable.
- Trends in M^{2+}/M E° : E° for Mn, Ni and Zn are more negative than expected.
- Trends in M^{3+}/M^{2+} E° : Variable.
- Chemical reactivity and E° values : Variable; Ti^{2+}, V^{2+} and Cr^{2+} are strong reducing agents.
- Magnetic properties : Diamagnetism and paramagnetism. Magnetic moment increases with increasing atomic number.
- Formation of coloured ions : Form coloured compounds due to d-d transitions.
- Formation of complex compounds : Form a large number of complex compounds.
- Catalytic properties : Due to variable oxidation states and ability to form complexes.
- Forms interstitial compounds : Non-stoichiometric and are neither ionic nor covalent.
- Alloy formation : Due to similar atomic sizes.

Uses

- Helps in production of iron and steels.
- TiO in pigment industry.
- MnO_2 in dry battery cells.
- As catalysts in industry.
- Ni complexes useful in the polymerization of alkynes and other organic compounds such as benzene.
- AgBr in photographic industry.

f– Block Transition Elements

Actinoids

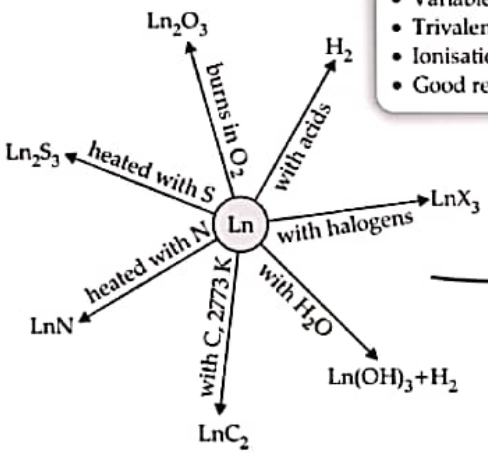
Lanthanoid contraction is progressive decrease in atomic/ionic radii from La^{3+} to Lu^{3+}

- Electronic configuration: $[Rn]5f^{1-14}\ 6d^{0-2}7s^2$
- Ionic sizes : Gradual decrease along the series.
- Oxidation states : Most common is +3. They show ON of +4, +5, +6 and +7.
- **General characteristics :**
  - –Silvery in appearance.
  - –Display variety of structures.
  - –Highly reactive metals.
  - –Irregularities in metallic radii, greater than in lanthanoids.
  - –Magnetic properties more complex than lanthanoids.

Lanthanoids

- Electronic configuration : $4f^{1-14}\ 5d^{0-1}\ 6s^2$
- Atomic and ionic sizes : Decrease from La to Lu
- Oxidation states : Most common is +3. Some elements exhibit +2 and +4.
- **General characteristics :**
  - Silvery white soft metals and tarnish rapidly in air.
  - Hardness increases with increasing atomic number.
  - Metallic structure and good conductors of heat and electricity.
- Variable density.
- Trivalent lanthanoid ions are coloured.
- Ionisation Enthalpies : Low third ionisation enthalpies.
- Good reducing agents.

Chemical Properties



Oxides and oxoanions of metals

- Potassium dichromate $K_2Cr_2O_7$

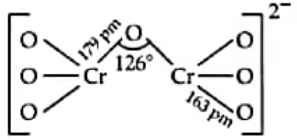
  Preparation : $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

  $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

  $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

  Properties : $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

  Oxidises iodides to iodine, H_2S to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^-



- Potassium permanganate $KMnO_4$

  Preparation : $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

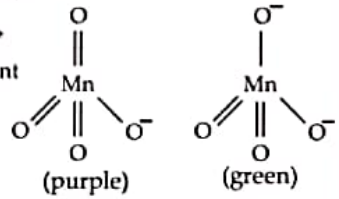
  $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

  $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

  Properties : Intense colour, weak temperature dependent paramagnetism

  $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

  Oxidizes I^- to I_2, Fe^{2+} to Fe^{3+}, $C_2O_4^{2-}$ to CO_2, S^{2-} to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^-



Trace the Mind Map

First Level · Second Level · Third Level

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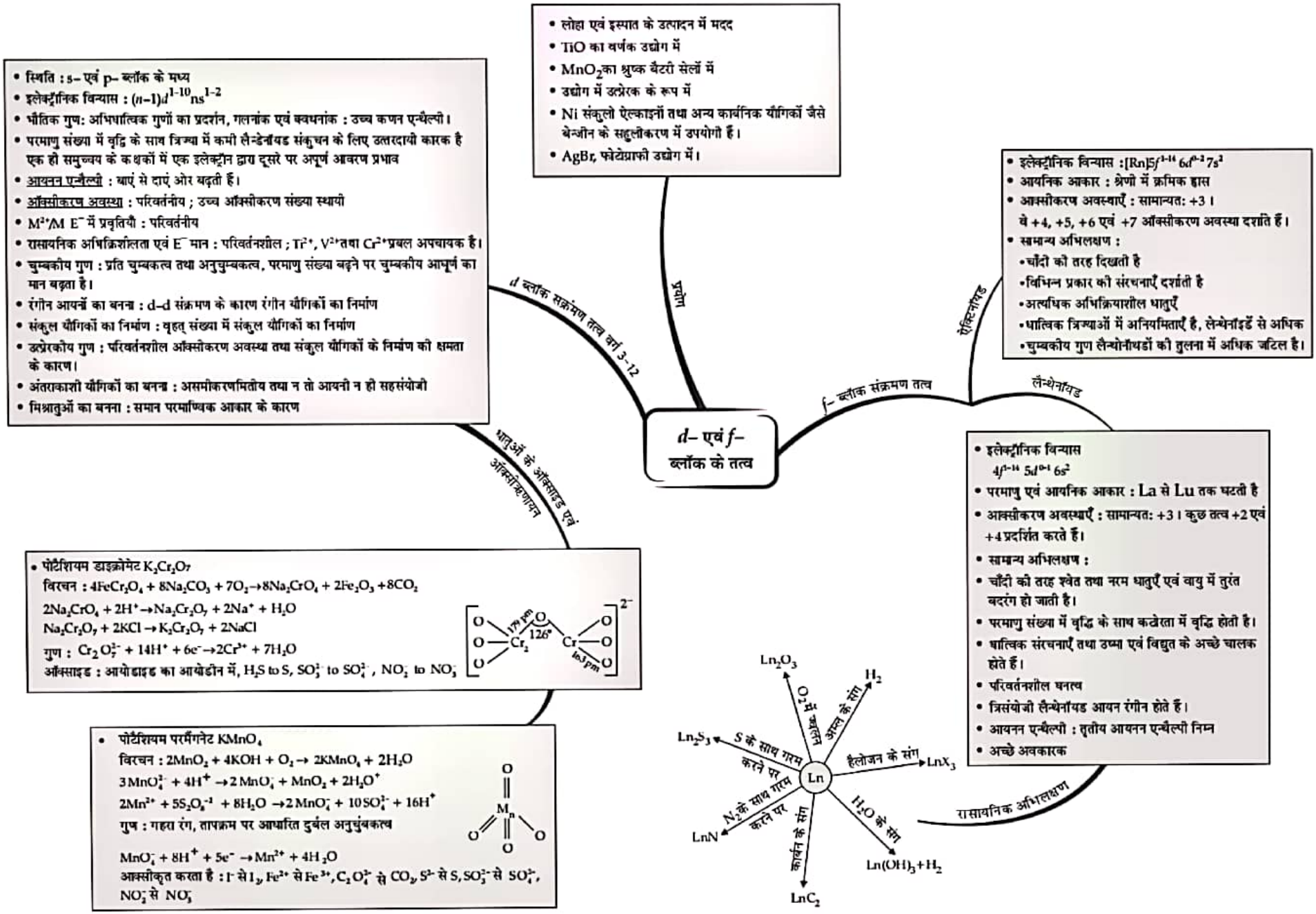
अध्याय 8 — d-एवं f-ब्लॉक के तत्व



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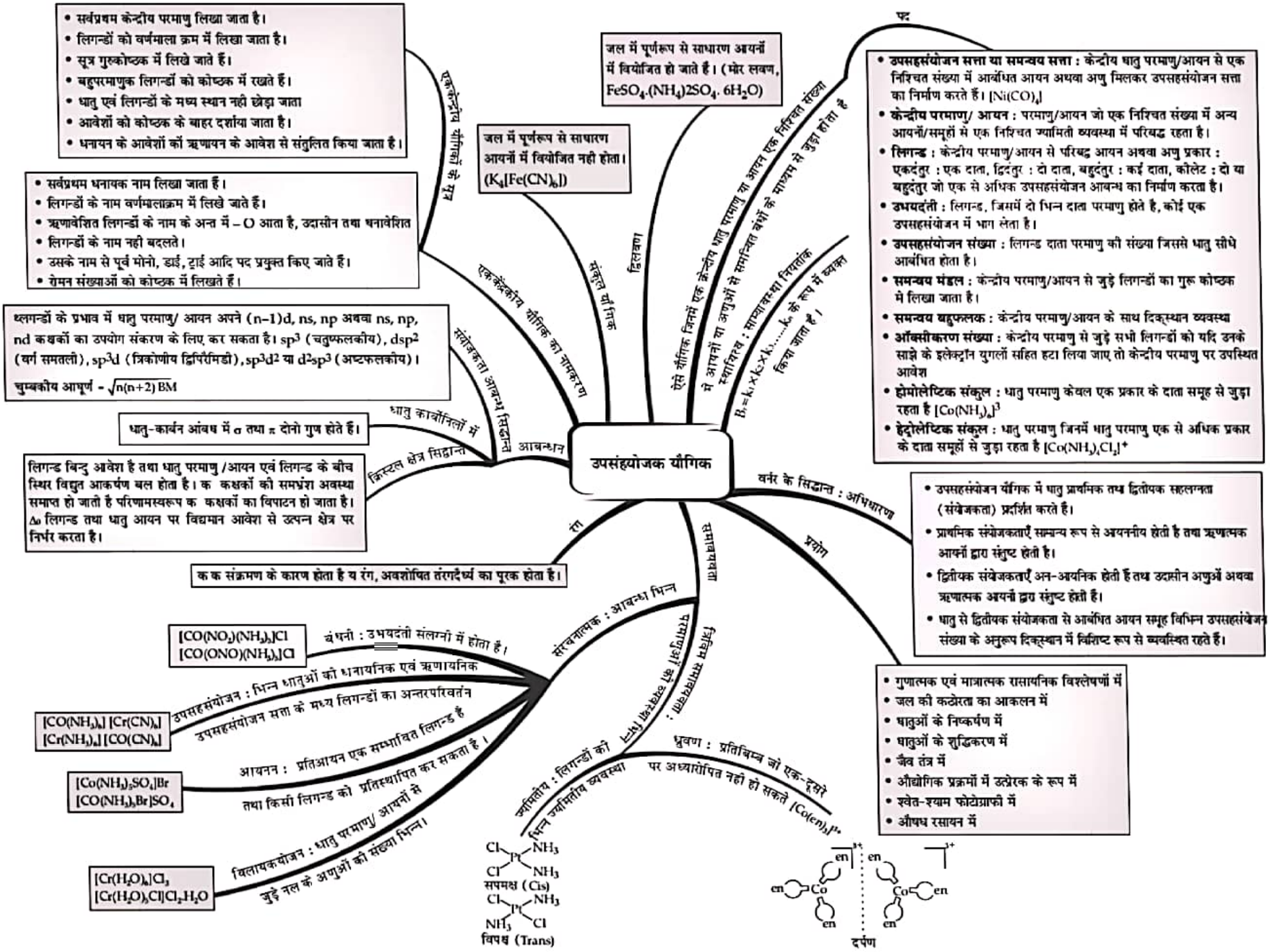
अध्याय 9 — उपसंहयोजक यौगिक



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Coordination Compounds

Complex compound
Do not dissociate into simple ions when dissolved in water. $K_4[Fe(CN)_6]$

Double salt
Dissociate completely into simple ions when dissolved in water. (Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$)

Compounds in which a central metal atom or ion is linked to a fixed number of ions or molecules through coordinate bonds.

Terms
- **Coordination entity :** A central metal atom/ion bonded to fixed number of ions or molecules. $[Ni(CO)_4]$
- **Central atom/ion :** Atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement.
- **Ligands :** Ions or molecules bound to central atom/ion types : Unidentate – single donor, Didentate – two donors, Polydentate – several donors, Chelating – Di-or polydentate which forms more than one coordinate bonds. Ambidentate : Can ligate through two different atoms.
- **Coordination number :** No. of ligand donor atoms to which metal is directly bonded.
- **Coordination sphere :** Central atom/ion and the ligands attached to it and enclosed in square bracket.
- **Coordination polyhedron :** Spatial arrangement of ligand atoms with central atom/ion.
- **Oxidation number :** Charge of central atom if all ligands are removed along with e– pairs shared with central atom.
- **Homoleptic complex :** Metal is bound to one type of donor groups. $[Co(NH_3)_6]^{3+}$
- **Heteroleptic complex :** Metal is bound to more than one type of donor groups $[Co(NH_3)_4Cl_2]^+$

Stability: Expressed by equilibrium constant
$B_r = k_1 \times k_2 \times k_3 ... k_n$

Werner's Theory: Postulates
- In coordination compounds metals show primary and secondary linkages valences
- Primary valences are ionisable and are satisfied by negative ions.
- Secondary valences are non-ionisable and are satisfied by neutral molecules or negative ions.
- Ions/groups bound by secondary linkages to metal have characteristic spatial arrangements corresponding to different coordination numbers.

Uses
- In qualitative and quantitative chemical analysis.
- Estimation of hardness of water.
- In extraction of metals.
- In purification of metals.
- In biological systems.
- As catalysts for industrial processes.
- In black and white photography.
- In medicinal chemistry.

Naming of mononuclear

Formulas of mononuclear
- Central atom is listed first.
- Ligands in alphabetical order.
- Formula is enclosed in square bracket.
- Polyatomic ligands in parenthesis.
- No space between ligand and metal.
- Charge is indicated outside brackets.
- Charge of cation(s) balanced by charge of anion(s).

Naming
- Cation is named first.
- Naming of ligands in alphabetical order.
- Anionic ligands end in -o, neutral and cationic are same.
- Prefixes mono, di, tri etc. are used.
- Followed by Roman numeral in parentheses.

Bonding

Valance bond theory
Metal atom/ion under the influence of ligands can use its (n–1)d, ns, np or ns, np, nd orbitals for hybridisation; sp^3(Tetrahedral), dsp^2(Square planar) sp^3d (Trigonal pyramidal), sp^3d^2 and d^2sp^3 (Octahedral); Magnetic moment $= \sqrt{n(n+2)}$ BM

In metal carbonyls
Metal–carbon bond possess both σ and π character

Crystal field theory
Ligands are point charges and there is electrostatic force of attraction between ligands and metal atom/ion. Degeneracy of d orbitals is lifted causing splitting of d orbitals. Δ depends upon the field produced by the ligand and charge on metal ion.

Colour
Caused by d-d transition; The colour is complementary to wavelength absorbed.

Isomerism

Structural: Different bonds
- Linkage: Occurs in ambidentate ligand — $[Co(NO_2)(NH_3)_5]Cl_2$, $[Co(ONO)(NH_3)_5]Cl_2$
- Coordination: Interchange of ligands between catonic and anionic entities of different metal ions — $[Co(NH_3)_6][Cr(CN)_6]$, $[Cr(NH_3)_6][Co(CN)_6]$
- Ionisation: Counter ion is a potential ligand and can displace a ligand — $[Co(NH_3)_5SO_4]Br$, $[Co(NH_3)_5Br]SO_4$
- Solvate-Differ in number of water molecules attached to metal atom/ion. — $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$

Stereoisomerism : Different spatial arrangements
- Geometrical : Different arrangement of the ligands

- Optical: Images which cannot be superimposed $[Co(en)_3]^{3+}$

Trace the Mind Map
- First Level
- Second Level
- Third Level

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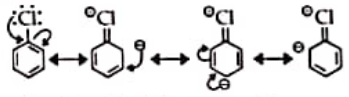
Haloalkanes and Haloarenes

Polyhalogen compounds

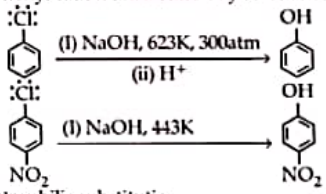
- Chloroform
  - Solvent for fats, alkaloids, I etc.
  - Production of freon.
  - Antiseptic: Iodoform
- Carbon tetrachloride
  - Manufacture of refrigerants and propellants.
  - Cleaning fluid.
- Freons
  - For aerosol propellants, refrigeration and air conditioning purposes.
- DDT
  - As insecticide
- Dichloromethane
  - Paint remover.
  - Propellant in aerosols.
  - Metal cleaning and finishing solvent.

Haloarenes

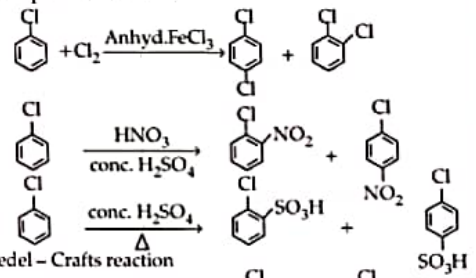
- Reactions :
  - (a) Nucleophilic substitution
    - (i) Resonance effect



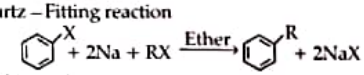
    - (ii) Hybridisation of C in C-X bond : Haloalkane –sp^3; Haloarence –sp^2
    - (iii) Phenyl cation unstabilised by resonance



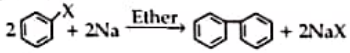
  - (b) Electrophilic substitution



  - (c) Reaction with metals
    - Wurtz – Fitting reaction

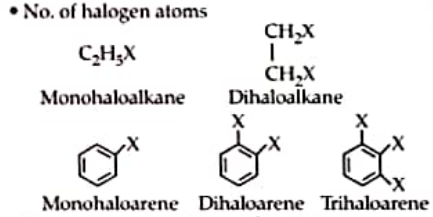


    - Fittig reaction

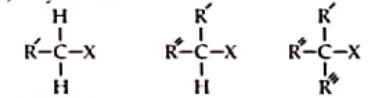


Classification

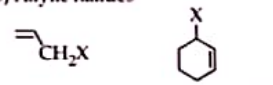
- No. of halogen atoms



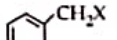
- Compounds containing sp^3 C–X bond
  - (a) Alkyl halides



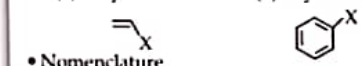
  - (b) Allylic halides



  - (c) Benzylic halides



- Compounds containing sp^2 C–X bond
  - (a) Vinylic halides
  - (b) Aryl halides



- Nomenclature
  - Common name : Alkyl group followed by halides. Dihalogen derivatives, prefixes o–, m–, p– are used.
  - IUPAC name : Numerals are used.
- Nature of C –X bond
  - : Carbon –halogen bond is polarized.

Racemisation S_N1

- Chiral : Objects which are non-superimposable.
- Achiral : Objects which are superimposable.

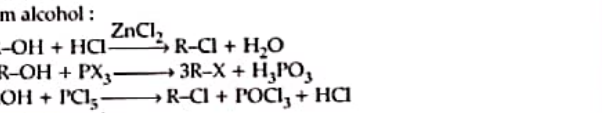
S_N2 Stereochemical inversion

- (a) Dextro (+/d)
- (b) Laevo (–/l)

Haloalkanes

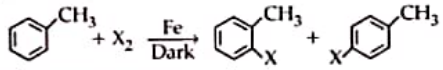
=>Preparation

- From alcohol :

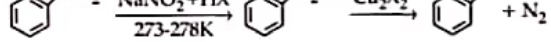


- From hydrocarbons :
  - (a) By free radical halogenation

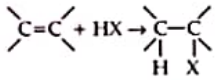
  - (b) By electrophilic substitution

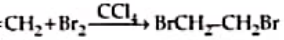


  - (c) Sandmeyer's reaction

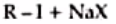


  - (d) From alkenes



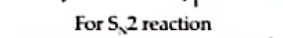


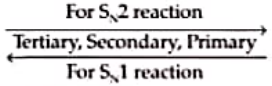
- Halogen exchange :



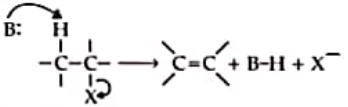
=>Properties

- Physical : Colourless, volatile, sweet smell.
  - Lower members are gases at room temperature while higher are solids.
  - B.P : RI > RBr > RCl > RF.
  - M.P : Para isomers have high m.p. than ortho and meta – isomers.
  - Density : Increases with increase in number of C/X atoms and atomic masses of the X atoms.
  - Solubility : Very slightly soluble in water.
- Chemical :
  - (a) Nucleophilic substitution

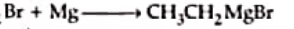




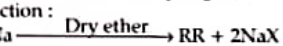
  - (b) Elimination reaction



  - B = Base; X = Leaving group
  - (c) Reaction with metals



  - Wurtz reaction :



Trace the Mind Map

- First Level
- Second Level
- Third Level

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अध्याय 10 — हैलोएल्केन तथा हैलोऐरीन

हैलोएल्केन तथा हैलोऐरीन

पॉलिहैलोजन यौगिक

- **क्लोरोफार्म**
  - I
  - फ्रेऑन के उत्पाद में
- **आयोडोफार्म**
- **D.D.T.**
- **डाइक्लोरोमेथेन**
  - पेन्ट अपचनक
  - ऐरोसॉल में प्रणोदक
  - धातु की सफाई एवं फिनिशिंग विलायक के रूप में
- प्रशीतक तथा प्रणोदक का उत्पादन
- साफ करने वाला द्रव

रेसिमीकरण S_N1

- काइरल : वस्तुएँ जो अपने दर्पण प्रतिबिम्ब पर अध्यारोपित नहीं होती।
- एकाइरल : वस्तुएँ जो अपने प्रतिबिम्ब पर अध्यारोपित हो जाती है।

S_N2 विविम समायनिक प्रतिलोमन

(a) दक्षिण ध्रुवण (+/d)
(b) वाम ध्रुवण (–/l)

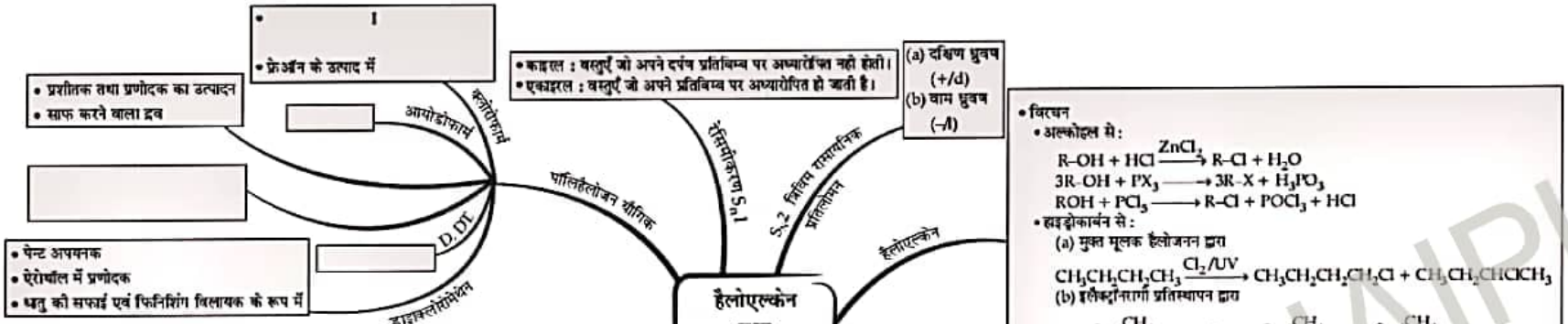
हैलोएल्केन

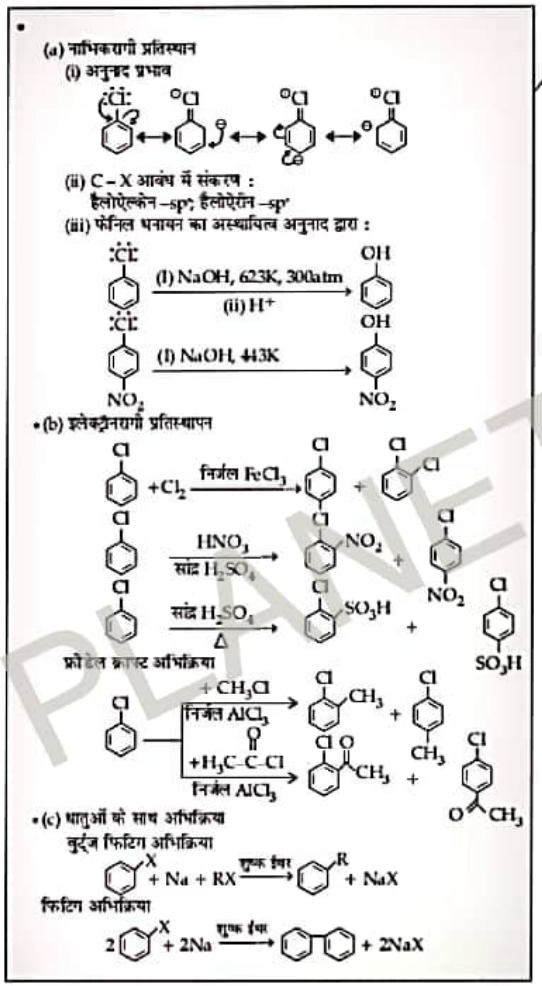
- विरचन
  - अल्कोहल से :

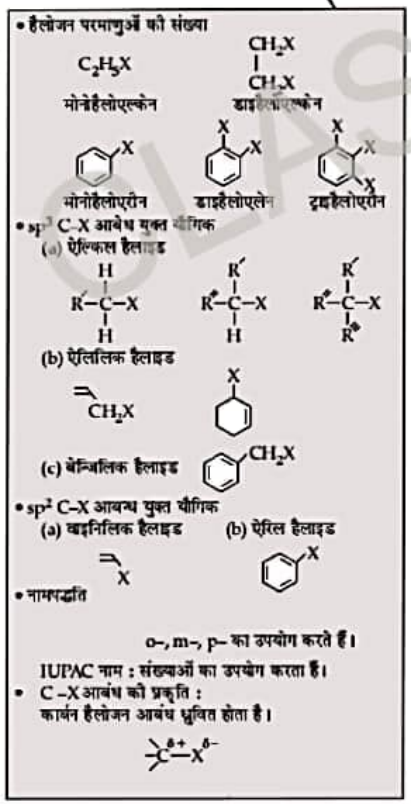
$$R\text{–}OH + HCl \xrightarrow{ZnCl_2} R\text{–}Cl + H_2O$$
$$3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3$$
$$ROH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$$

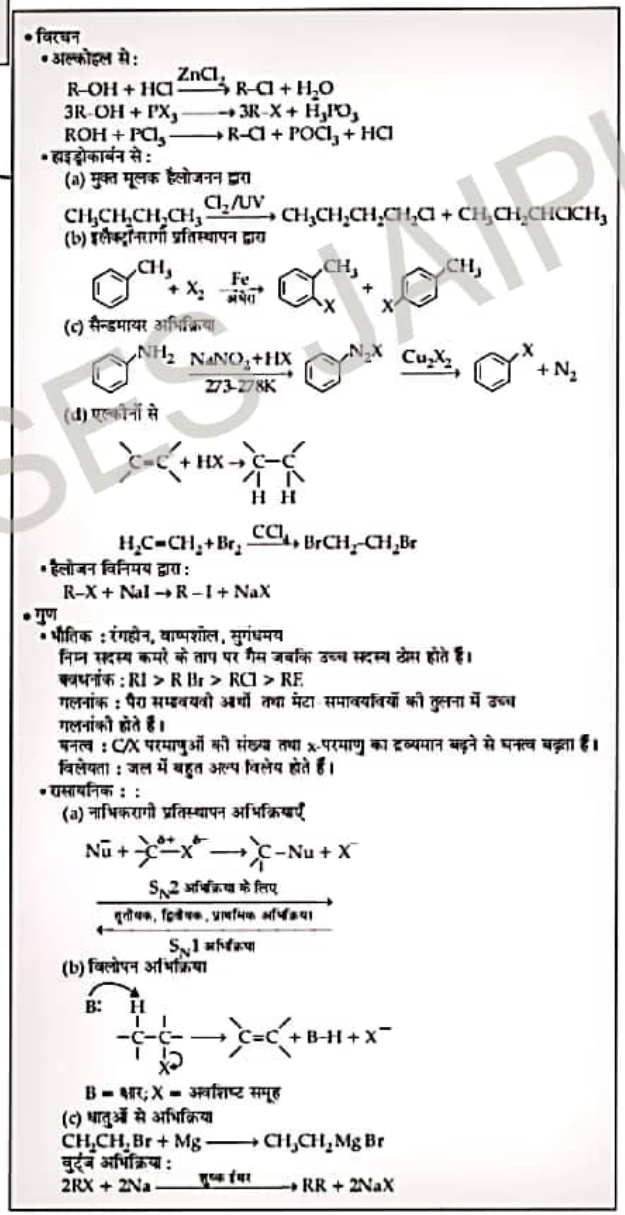
  - हाइड्रोकार्बन से :

(a) मुक्त मूलक हैलोजनन द्वारा









$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UV} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

(b) इलैक्ट्रॉनरागी प्रतिस्थापन द्वारा

(c) सैन्डमायर अभिक्रिया

(d) एल्कीनों से

$$H_2C{=}CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2\text{–}CH_2Br$$

  - हैलोजन विनिमय द्वारा :

$$R\text{–}X + NaI \rightarrow R\text{–}I + NaX$$

- गुण
  - भौतिक : रंगहीन, वाष्पशील, सुगंधमय
    निम्न सदस्य कमरे के ताप पर गैस जबकि उच्च सदस्य ठोस होते हैं।
    क्वथनांक : RI > R Br > RCl > RF.
    गलनांक : पैरा समावयवी आर्थो तथा मेटा समावयवियों की तुलना में उच्च गलनांकी होते हैं।
    घनत्व : C/X परमाणुओं की संख्या तथा x-परमाणु का द्रव्यमान बढ़ने से घनत्व बढ़ता है।
    विलेयता : जल में बहुत अल्प विलेय होते हैं।
  - रासायनिक : :

(a) नाभिकरागी प्रतिस्थापन अभिक्रियाएँ

$$\bar{Nu} + \overset{\delta+}{C}\text{–}\overset{\delta-}{X} \longrightarrow C\text{–}Nu + X^-$$

S_N2 अभिक्रिया के लिए →
तृतीयक, द्वितीयक, प्राथमिक अभिक्रिया
← S_N1 अभिक्रिया

(b) विलोपन अभिक्रिया

B = क्षार; X = अवशिष्ट समूह

(c) धातुओं से अभिक्रिया

$$CH_3CH_2Br + Mg \longrightarrow CH_3CH_2MgBr$$

वुर्ट्ज अभिक्रिया :

$$2RX + 2Na \xrightarrow{\text{शुष्क ईथर}} RR + 2NaX$$

वर्गीकरण

- हैलोजन परमाणुओं की संख्या

- sp^3 C–X आबंध युक्त यौगिक

(a) ऐल्किल हैलाइड

(b) ऐलिलिक हैलाइड

(c) बेन्जिलिक हैलाइड

- sp^2 C–X आबन्ध युक्त यौगिक

(a) वाइनिलिक हैलाइड (b) ऐरिल हैलाइड

- नामपद्धति

o–, m–, p– का उपयोग करते हैं।
IUPAC नाम : संख्याओं का उपयोग करता है।

- C–X आबंध की प्रकृति :
  कार्बन हैलोजन आबंध ध्रुवित होता है।

$$\overset{\delta+}{C}\text{–}\overset{\delta-}{X}$$

हैलोऐरीन

-

(a) नाभिकरागी प्रतिस्थान

(i) अनुनाद प्रभाव

(ii) C – X आबंध में संकरण :
हैलोऐल्केन –sp^3; हैलोऐरीन –sp^2

(iii) फेनिल धनायन का अस्थायित्व अनुनाद द्वारा :

- (b) इलेक्ट्रॉनरागी प्रतिस्थापन

फ्रीडेल क्राफ्ट अभिक्रिया

- (c) धातुओं के साथ अभिक्रिया

वुर्ट्ज फिटिग अभिक्रिया

फिटिग अभिक्रिया

GS PLANET CLASSES JAIPUR

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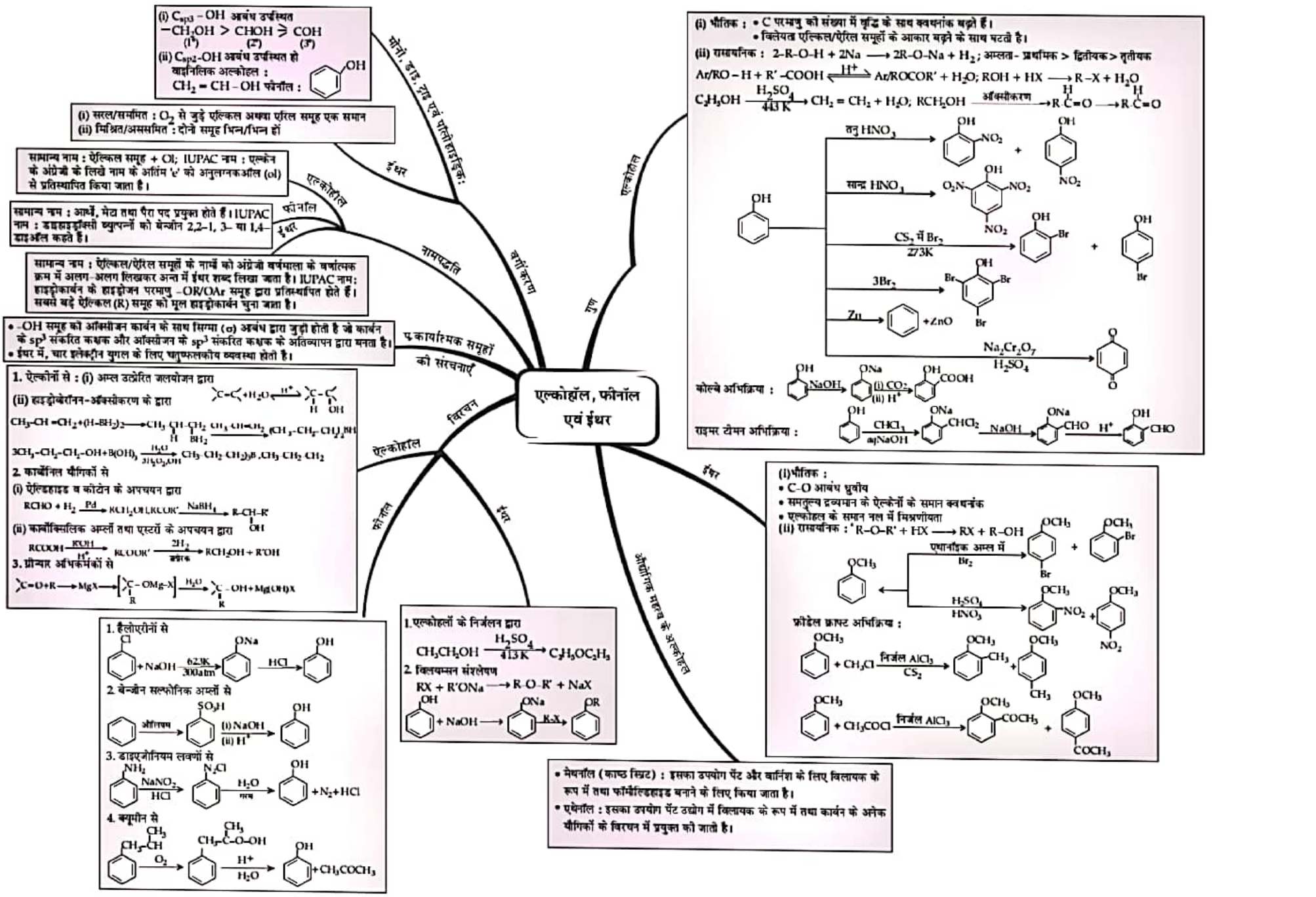
अध्याय 11 — एल्कोहॉल फीनॉल एवं ईथर



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Aldehydes, Ketones and Carboxylic Acids

Properties · Preparation · Nomenclature and uses

ALDEHYDES AND KETONES:

(i) Physical:
Boiling points are higher than hydrocarbons and ethers of comparable molecular masses.

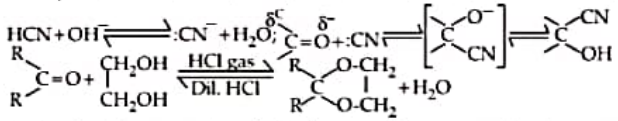
(ii)Chemical :Nucleophilic addition reactions :
Aldehydes are more reactive than ketones due to steric and electronic reasons.

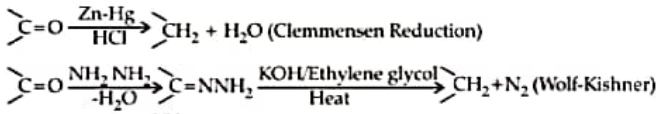
$HCN + OH^- \rightleftharpoons :CN^- + H_2O$; $\overset{\delta+}{C}=\overset{\delta-}{O} + :CN^- \rightleftharpoons$ [intermediate] $\rightleftharpoons C(CN)(OH)$

$R_2C=O + CH_2OH\text{–}CH_2OH \underset{\text{Dil. HCl}}{\overset{\text{HCl gas}}{\rightleftharpoons}} R_2C(O\text{–}CH_2)_2 + H_2O$

Reduction : (a) To alcohols – aldehydes and ketones reduce to primary and secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$.
(b) To hydrocarbons –

$>C=O \xrightarrow[\text{HCl}]{\text{Zn-Hg}} >CH_2 + H_2O$ (Clemmensen Reduction)





$>C=O \xrightarrow[-H_2O]{NH_2NH_2} >C=NNH_2 \xrightarrow[\text{Heat}]{\text{KOH/Ethylene glycol}} >CH_2 + N_2$ (Wolf-Kishner)

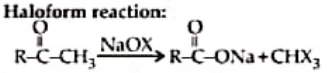
Oxidation: $RCHO \xrightarrow{[O]} R\text{–}COOH$

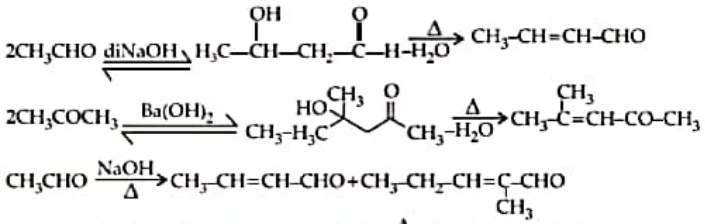
Tollen's test : $RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + 2Ag\downarrow + 2H_2O + 4NH_3$ (Silver mirror)

Fehling's test : $RCHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O\downarrow + 3H_2O$ (Red brown ppt)

Haloform reaction:
$R\text{–}CO\text{–}CH_3 \xrightarrow{NaOX} R\text{–}CO\text{–}ONa + CHX_3$

Reactions due to α - hydrogen:





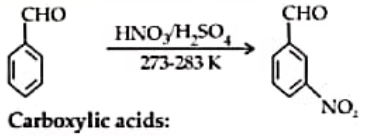
$2CH_3CHO \xrightarrow{\text{dil NaOH}} H_3C\text{–}CH(OH)\text{–}CH_2\text{–}CO\text{–}H \xrightarrow[-H_2O]{\Delta} CH_3\text{–}CH=CH\text{–}CHO$

$2CH_3COCH_3 \underset{}{\overset{Ba(OH)_2}{\rightleftharpoons}} CH_3\text{–}C(OH)(CH_3)\text{–}CH_2\text{–}CO\text{–}CH_3 \xrightarrow[-H_2O]{\Delta} CH_3\text{–}C(CH_3)=CH\text{–}CO\text{–}CH_3$

$CH_3CHO \xrightarrow[\Delta]{NaOH} CH_3\text{–}CH=CH\text{–}CHO + CH_3\text{–}CH_2\text{–}CH=C(CH_3)\text{–}CHO$

Cannizzaro reaction : $2HCHO + \text{conc } KOH \xrightarrow{\Delta} CH_3OH + HCOOK$

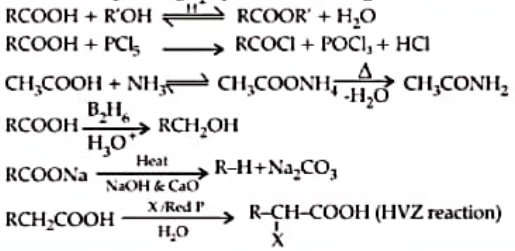
Electrophilic substitution reaction:



Carboxylic acids:

(i) Physical: Higher boiling points than aldehydes, ketones or alcohols. Solubility decreases with increasing number of C atoms

(ii)Chemical : $2RCOOH + 2Na \longrightarrow 2RCOONa + H_2$



Forms corresponding anhydride on heating with mineral acids

$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$

$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

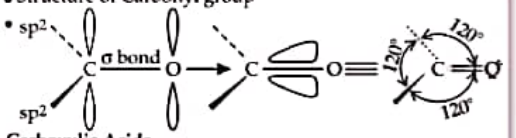
$CH_3COOH + NH_3 \rightleftharpoons CH_3COONH_4 \xrightarrow[-H_2O]{\Delta} CH_3CONH_2$

$RCOOH \xrightarrow[H_3O^+]{B_2H_6} RCH_2OH$

$RCOONa \xrightarrow[\text{NaOH \& CaO}]{\text{Heat}} R\text{–}H + Na_2CO_3$

$RCH_2COOH \xrightarrow[H_2O]{X_2/\text{Red P}} R\text{–}CH(X)\text{–}COOH$ (HVZ reaction)

Nomenclature and uses

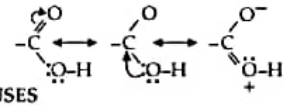


1. Aldehydes and Ketones

Common names :
- Replace corresponding carboxylic acids with aldehyde.
- Alkyl phenyl ketones by adding acyl group as prefix to phenone.

IUPAC names :
Replacing –e with –al and –one as required.
- Structure of Carbonyl group

2. Carboxylic Acids



Common names : end with –ic
- IUPAC names : replace –e in the corresponding alkane
- with –oic acid.

Structure of Carboxyl Group

3. USES

(a) Carboxylic acids
- Methanoic acid in rubber, textile, dyeing, leather industries.
- Ethanoic acid as solvent
- Higher fatty acids in manufacture of soaps and detergents.

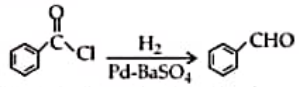
(b) Aldehydes of ketones
- As solvents.
- Starting materials and reagents for synthesis of products.

Preparation

ALDEHYDES:

1. From acyl chloride

2. From nitriles and esters : Stephen reaction



$RCN + SnCl_2 + HCl \longrightarrow RCH=NH \xrightarrow{H_3O^+} RCHO$

3. From hydrocarbons : Etard reaction

Gattermann – Koch reaction

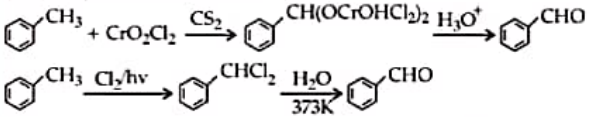
KETONES:

1.From acyl chloride

$2R\text{–}Mg\text{–}X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$

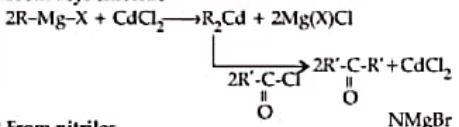
$R_2Cd + 2R'\text{–}CO\text{–}Cl \longrightarrow 2R'\text{–}CO\text{–}R + CdCl_2$

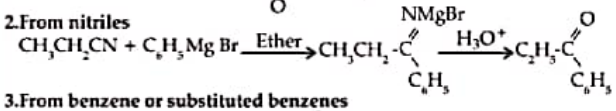
2.From nitriles



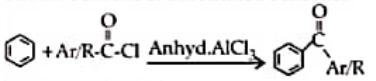
$CH_3CH_2CN + C_6H_5MgBr \xrightarrow{\text{Ether}} CH_3CH_2\text{–}C(=NMgBr)\text{–}C_6H_5 \xrightarrow{H_3O^+} C_2H_5\text{–}CO\text{–}C_6H_5$

3.From benzene or substituted benzenes





Carboxylic Acids:



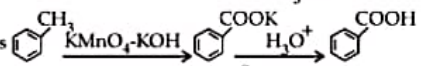
1.From primary alcohols and aldehydes $RCH_2OH \xrightarrow[H_3O^+]{\text{alk. } KMnO_4} RCOOH$

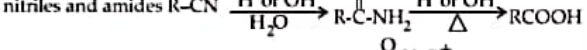
2.From alkylbenzenes

3.From nitriles and amides $R\text{–}CN \xrightarrow[H_2O]{H^+ \text{ or } OH^-} R\text{–}CO\text{–}NH_2 \xrightarrow[\Delta]{H^+ \text{ or } OH^-} RCOOH$

4.From Grignard reagents $R\text{–}Mg\text{–}X + CO_2 \longrightarrow R\text{–}C(=O)\text{–}OMgX \xrightarrow{H_3O^+} RCOOH$

5.From acyl halides and anhydrides

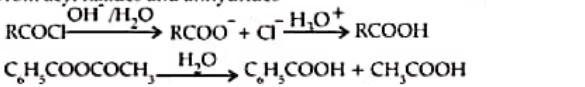


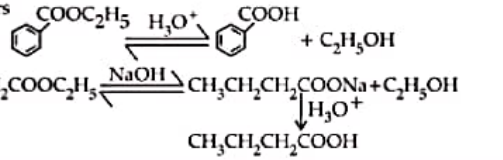


$RCOCl \xrightarrow{OH^-/H_2O} RCOO^- + Cl^- \xrightarrow{H_3O^+} RCOOH$

$C_6H_5COOCOCH_3 \xrightarrow{H_2O} C_6H_5COOH + CH_3COOH$

6.From esters





$CH_3CH_2CH_2COOC_2H_5 \underset{}{\overset{NaOH}{\rightleftharpoons}} CH_3CH_2CH_2COONa + C_2H_5OH \xrightarrow{H_3O^+} CH_3CH_2CH_2COOH$

Trace the Mind Map
- First Level
- Second Level
- Third Level

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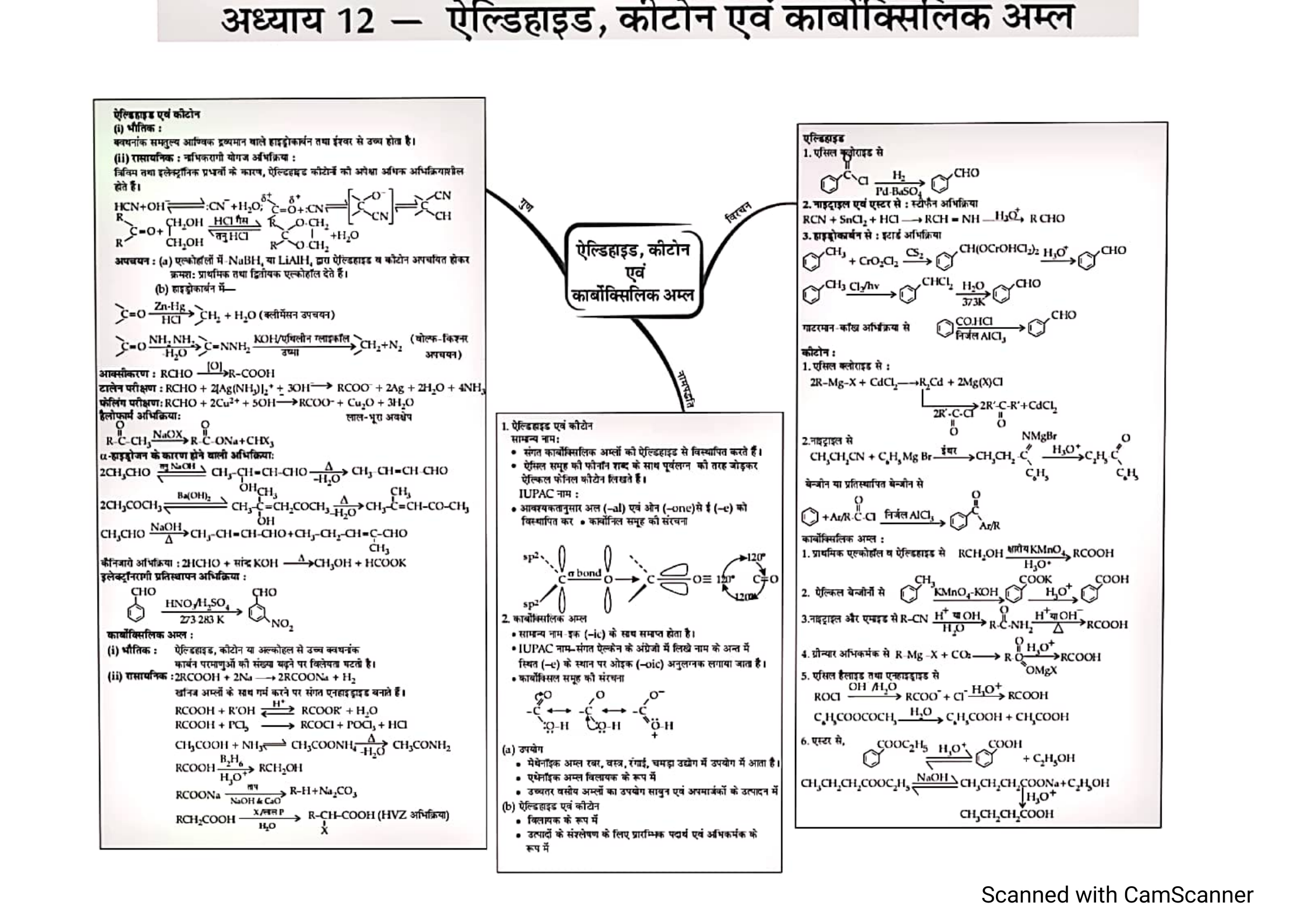
अध्याय 12 — ऐल्डिहाइड, कीटोन एवं कार्बोक्सिलिक अम्ल



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ऐमीन

रासायनिक अभिक्रियाएं

(i) एमीनो के क्षारीय गुण

- अम्लों से प्रतिक्रिया कर लवण बनाती है। $R{-}NH_2 + HX \rightleftharpoons R{-}NH_3X$ (लवण)
- क्षार से अभिक्रिया कर पितृ ऐमीन पुनर्जनित करती है।
  $RNH_3X + OH \longrightarrow RNH_2 + H_2O + X$
- स्थायित्व का क्रम : $1° > 2° > 3°$

(ii) $C_2H_5{-}NH(C_2H_5) + CH_3{-}CO{-}Cl \xrightarrow{\text{क्षार}} C_2H_5{-}N(C_2H_5){-}CO{-}CH_3 + HCl$

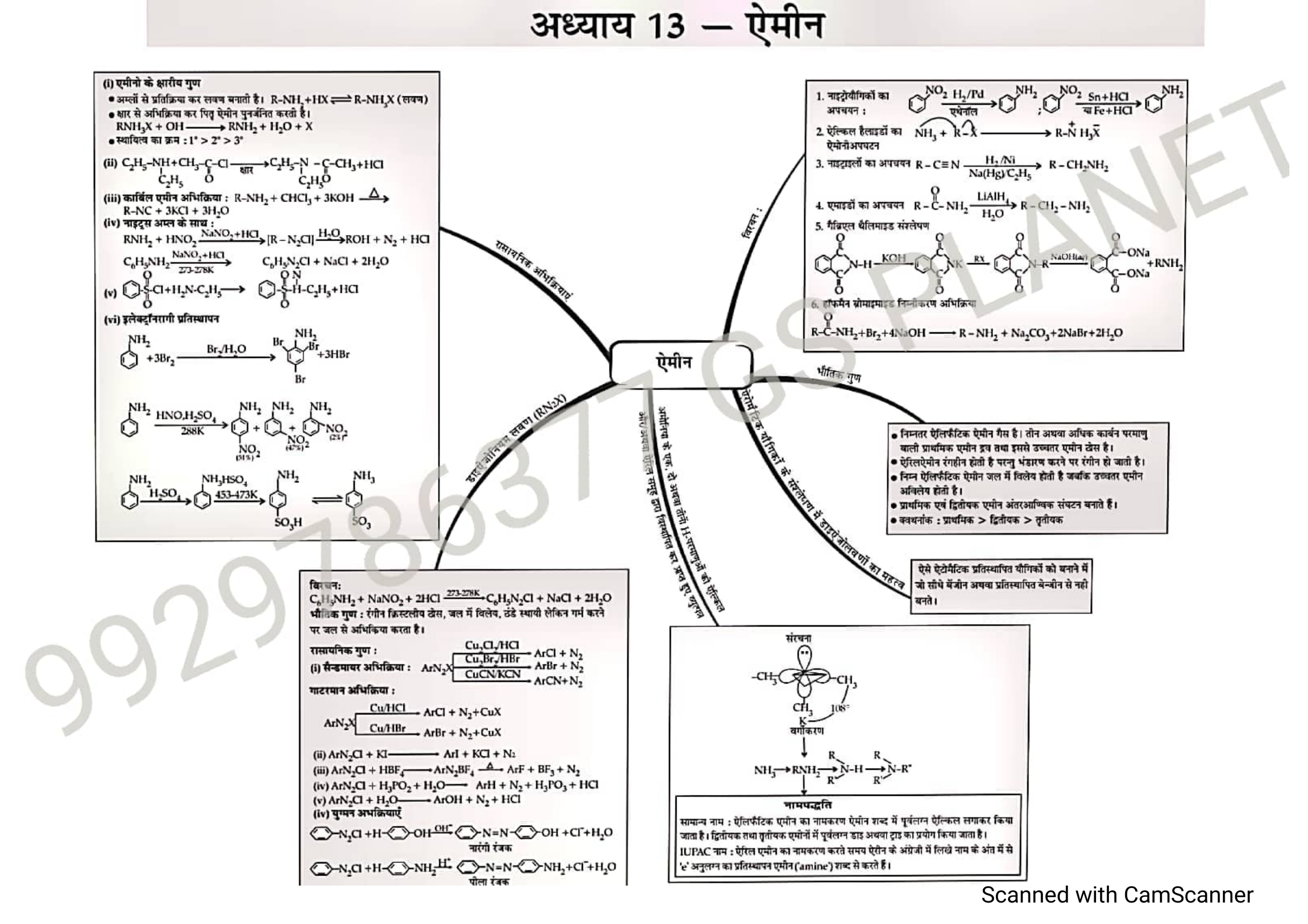
(iii) कार्बिल एमीन अभिक्रिया : $R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R{-}NC + 3KCl + 3H_2O$

(iv) नाइट्रस अम्ल के साथ :

$RNH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R-N_2Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$

$C_6H_5NH_2 \xrightarrow[273\text{-}278K]{NaNO_2 + HCl} C_6H_5N_2Cl + NaCl + 2H_2O$

(v)



(vi) इलेक्ट्रॉनरागी प्रतिस्थापन

डाइऐज़ोनियम लवण (RN_2X)

विरचन:

$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278K} C_6H_5N_2Cl + NaCl + 2H_2O$

भौतिक गुण : रंगीन क्रिस्टलीय ठोस, जल में विलेय, ठंडे स्थायी लेकिन गर्म करने पर जल से अभिक्रिया करता है।

रासायनिक गुण :

(i) सैन्डमायर अभिक्रिया :

$ArN_2X \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$

$ArN_2X \xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$

$ArN_2X \xrightarrow{CuCN/KCN} ArCN + N_2$

गाटरमान अभिक्रिया :

$ArN_2X \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$

$ArN_2X \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$

(ii) $ArN_2Cl + KI \longrightarrow ArI + KCl + N_2$

(iii) $ArN_2Cl + HBF_4 \longrightarrow ArN_2BF_4 \xrightarrow{\Delta} ArF + BF_3 + N_2$

(iv) $ArN_2Cl + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$

(v) $ArN_2Cl + H_2O \longrightarrow ArOH + N_2 + HCl$

(iv) युग्मन अभिक्रियाएं

विरचन :

1. नाइट्रोयौगिकों का अपचयन :

2. ऐल्किल हैलाइडों का ऐमोनीअपघटन $NH_3 + R{-}X \longrightarrow R{-}\overset{+}{N}H_3\overset{-}{X}$

3. नाइट्राइलों का अपचयन $R-C \equiv N \xrightarrow[Na(Hg)/C_2H_5]{H_2/Ni} R-CH_2NH_2$

4. एमाइडों का अपचयन $R-CO-NH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$

5. गैब्रिएल थैलिमाइड संश्लेषण

6. हॉफमैन ब्रोमाइमाइड निम्नीकरण अभिक्रिया

$R{-}CO{-}NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

भौतिक गुण

- निम्नतर ऐलिफैटिक ऐमीन गैस है। तीन अथवा अधिक कार्बन परमाणु वाली प्राथमिक एमीन द्रव तथा इससे उच्चतर एमीन ठोस है।
- ऐरिलऐमीन रंगहीन होती है परन्तु भंडारण करने पर रंगीन हो जाती है।
- निम्न ऐलिफैटिक ऐमीन जल में विलेय होती है जबकि उच्चतर एमीन अविलेय होती है।
- प्राथमिक एवं द्वितीयक एमीन अंतरआण्विक संघटन बनाते हैं।
- क्वथनांक : प्राथमिक > द्वितीयक > तृतीयक

ऐरोमैटिक यौगिकों के संश्लेषण में डाइएज़ोनियम लवणों का महत्व

ऐसे ऐरोमैटिक प्रतिस्थापित यौगिकों को बनाने में जो सीधे बेंजीन अथवा प्रतिस्थापित बेन्जीन से नहीं बनते।

अमोनिया के एक, दो अथवा तीनों H-परमाणुओं को ऐल्किल और/अथवा ऐरिल समूह द्वारा विस्थापित कर प्राप्त हुए व्युत्पन्न

संरचना

वर्गीकरण

$NH_3 \rightarrow RNH_2 \rightarrow R(R')N{-}H \rightarrow R(R')N{-}R''$

नामपद्धति

सामान्य नाम : ऐलिफैटिक एमीन का नामकरण ऐमीन शब्द में पूर्वलग्न ऐल्किल लगाकर किया जाता है। द्वितीयक तथा तृतीयक एमीनों में पूर्वलग्न डाइ अथवा ट्राइ का प्रयोग किया जाता है।

IUPAC नाम : ऐरिल एमीन का नामकरण करते समय ऐरीन के अंग्रेजी में लिखे नाम के अंत में से 'e' अनुलग्न का प्रतिस्थापन एमीन ('amine') शब्द से करते हैं।

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Amines

Chemical reactions

(i) Basic character of amines

- React with acids to form salts $R-NH_2 + HX \rightleftharpoons R-NH_3X$ (salt)
- React with base to regenerate parent amines
  $RN^+H_3X^- + OH^- \longrightarrow RNH_2 + H_2O + X$
- Order of stability of ions : 1° > 2° > 3°

(ii) $C_2H_5-NH(C_2H_5) + CH_3-C(=O)-Cl \xrightarrow{Base} C_2H_5-N(C_2H_5)-C(=O)-CH_3 + HCl$

(iii) Carbylamine reaction : $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$

(iv) With nitrous acid

$RNH_2 + HNO_2 \xrightarrow{NaNO_2+HCl} [R-N_2Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$

$C_6H_5NH_2 \xrightarrow[273\text{-}278K]{NaNO_2+HCl} C_6H_5N_2Cl + NaCl + 2H_2O$

(v)

(vi) Electrophilic substitution reactions

Preparation

1. Reduction of nitro compounds

2. Ammonolysis of alkyl halides $NH_3 + R-X \longrightarrow R-\overset{+}{N}H_3\overset{-}{X}$
3. Reduction of nitriles $R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2NH_2$
4. Reduction of amides $R-C(=O)-NH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$
5. Gabriel phthalimide synthesis

6. Hoffmann bromamide degradation reaction
   $R-C(=O)-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

Physical properties

- Lower aliphatic amines are gases. Primary amines with three or more C atoms are liquid and higher ones are solid.
- Arylamines are colourless but get coloured on storage.
- Lower aliphatic amines are soluble in water, while higher are insoluble.
- Primary and secondary amines form intermolecular association.
- Boiling point : primary > secondary > tertiary

Diazonium Salts (RN_2X)

Preparation :
$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$

Physical properties : Colourless crystalline solid, soluble in water, stable in cold but reacts with water on warming.

Chemical properties :

(i) Sandmeyer reaction: $ArN_2^+X^-$
- $\xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$
- $\xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$
- $\xrightarrow{CuCN/KCN} ArCN + N_2$

Gattermann reaction :
$ArN_2^+X^-$
- $\xrightarrow{Cu/HCl} ArCl + N_2 + CuX$
- $\xrightarrow{Cu/HBr} ArBr + N_2 + CuX$

(ii) $ArN_2^+Cl^- + KI \longrightarrow ArI + KCl + N_2$

(iii) $ArN_2^+Cl^- + HBF_4 \longrightarrow ArN_2^+BF_4^- \xrightarrow{\Delta} ArF + BF_3 + N_2$

(iv) $ArN_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$

(v) $ArN_2^+Cl^- + H_2O \longrightarrow ArOH + N_2 + HCl$

(vi) Coupling reaction :

Importance of diazonium salts in synthesis of aromatic compounds

In preparation of substituted aromatic compounds which cannot be prepared by direct substitution in benzene/ substituted benzene.

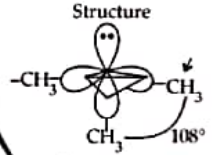
Derivatives of ammonia, obtained by replacement of one, two or all the three H- atoms by alkyl and/ or aryl groups

Structure

Classification

$NH_3 \rightarrow RNH_2 \rightarrow R_2NH \rightarrow R_2NR'$

Nomenclature



Common name : Aliphatic amine is named by prefixing alkyl group to amine. In secondary and tertiary amines prefix di or tri is put before name of alkyl group.
IUPAC name : replacement of 'e' of alkane by the word amine. Suffix 'e' of arene is replaced by amine.

Trace the Mind Map: First Level · Second Level · Third Level

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Biomolecules

Proteins

-(Polymers of amino acids)
-Amino acids contain $-NH_2$ and $-COOH$ group.

Classification :

- **On the basis of relative number of $-NH_2$ and $-COOH$ group:**
  - (i) Neutral : Equal number of $-NH_2$ and $-COOH$ group.
  - (ii) Basic : More number of $-NH_2$ than $-COOH$ group.
  - (iii) Acidic : More number of $-COOH$ than $-NH_2$ group.
- **On the basis of place of synthesis :**
  - (i) Essential – cannot be synthesized in the body.
  - (ii) Non-essential – synthesized in the body.
- **On the basis of shape :**
  - (I) Fibrous : Fibre-like structure
  - (ii) Globular : Spherical

Structure : H_2N-CH_2-[CO–NH]$-CH(CH_3)-COOH$ (Peptide linkage: CO–NH)

Denaturation of protein :
When a protein in its native form is subjected to physical change, globules unfold, helix get uncoiled and protein loses its biological activity.

Carbohydrates

Optically active polyhydroxy aldehydes or ketones or compounds which produce units with specific functional groups on hydrolysis.

- **Classification :**

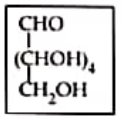
(I) **Monosaccharides :** (Aldehyde group – aldose, keto group –ketose)

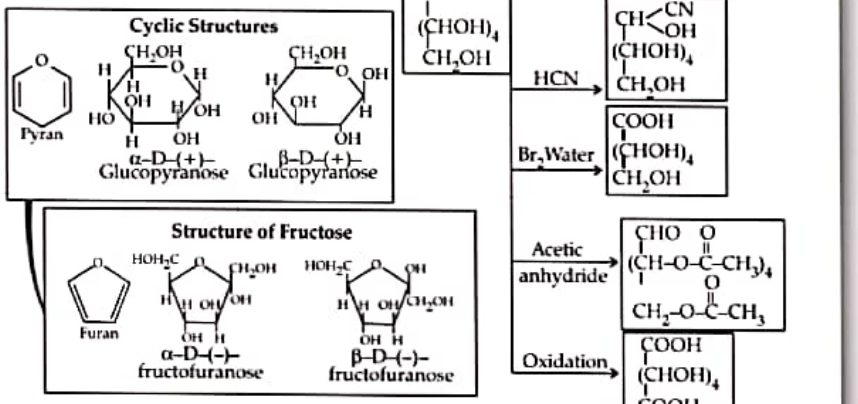
Glucose : Preparation :

(a) **From sucrose :** $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$ (Sucrose → Glucose + Fructose)

(b) **From starch :** $(C_6H_{10}O_5)_n + nH_2O \xrightarrow[393K;\ 2\text{-}3\ atm]{H^+} nC_6H_{12}O_6$

- **Structure :**





(II) **Disaccharides :** Linkage between 2 monosaccharides– Glycosidic linkage (Sucrose, maltose)
(III) **Polysaccharides :** Large number of monosaccharides units joined by glycosidic linkages. e.g.
(a) Starch : Polymer of α–glucose with two components amylose and amylopectin
(b) Cellulose
(c) Glycogen

Importance :
- Form a major portion of food.
- As storage molecules.
- Cellulose forms cell wall of bacteria and plants.
- Raw materials for industries like textiles, paper, lacquers and breweries.

Vitamins

Organic compounds required in diet in small amounts to perform specific biological functions for maintenance and growth.

Classification :
(i) **Fat soluble :** Soluble in fats and oils but insoluble in water. (Vitamins A,D,E and K)
(ii) **Water soluble :** B group and vitamin C are soluble in water.

Nucleic Acids

Chromosomes : Particles in nucleus responsible for heredity. Chromosomes are made up of proteins and nucleic acid.
Two types : Deoxyribonucleic acid (DNA), ribonucleic acid (RNA)
Composition : In DNA, sugar is β–D–2–deoxyribose whereas in RNA is β–D–ribose. DNA contains A,G,C,T whereas RNA has A,G,C,U.
Structure :
Nucleoside : Formed by attachment of a base to 1′ of sugar
Nucleotide : Formed by link to phosphoric acid at 5′ of sugar.

–Sugar(Base)–Phosphate–[Sugar(Base)–Phosphate]–Sugar(Base)–

Types of RNA : m–RNA, r–RNA, t–RNA

Biological Functions :
- Chemical basis of heredity.
- Responsible for identity of different species of organisms.
- Nucleic acids are responsible for protein synthesis in cell.

Enzymes

Globular proteins specific for particular reaction and for particular substrate. Mechanism : Reduces the magnitude of activation energy

DNA Fingerprinting : Unique sequence of bases on DNA

A sequence of bases on DNA is unique for a person and information regarding this is called DNA fingerprinting. It is same for every cell and cannot be altered by any known treatment. DNA fingerprinting is now used
(i) in forensic laboratories for identification of criminals.
(ii) to determine paternity of an individual.
(iii) to identify the dead bodies in any accident by comparing the DNA's of parents or children.
(iv) to identify racial groups to rewrite biological evolution.

Trace the Mind Map
- First Level
- Second Level
- Third Level

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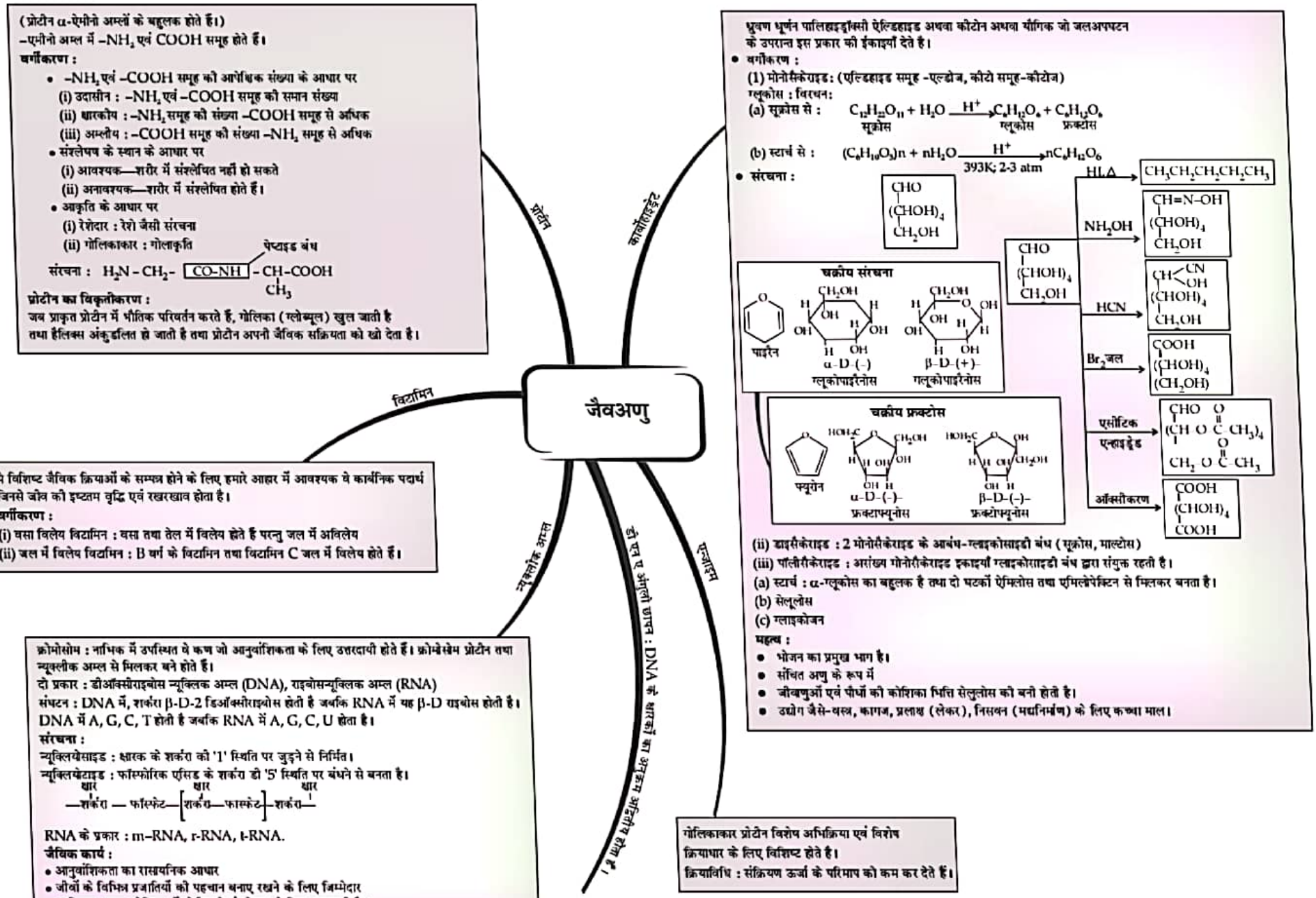
अध्याय 14 — जैवअणु



जैवअणु

प्रोटीन

(प्रोटीन α-ऐमीनो अम्लों के बहुलक होते हैं।)
–एमीनो अम्ल में $-NH_2$ एवं COOH समूह होते हैं।

वर्गीकरण :

- $-NH_2$ एवं –COOH समूह की आपेक्षिक संख्या के आधार पर
  - (i) उदासीन : $-NH_2$ एवं –COOH समूह की समान संख्या
  - (ii) क्षारकीय : $-NH_2$ समूह की संख्या –COOH समूह से अधिक
  - (iii) अम्लीय : –COOH समूह की संख्या $-NH_2$ समूह से अधिक
- संश्लेषण के स्थान के आधार पर
  - (i) आवश्यक—शरीर में संश्लेषित नहीं हो सकते
  - (ii) अनावश्यक—शरीर में संश्लेषित होते हैं।
- आकृति के आधार पर
  - (i) रेशेदार : रेशे जैसी संरचना
  - (ii) गोलिकाकार : गोलाकृति

संरचना : H_2N-CH_2- [CO-NH] $-CH(CH_3)-COOH$ (CO-NH : पेप्टाइड बंध)

प्रोटीन का विकृतीकरण :
जब प्राकृत प्रोटीन में भौतिक परिवर्तन करते हैं, गोलिका (ग्लोब्यूल) खुल जाती है तथा हैलिक्स अंकुडलित हो जाती है तथा प्रोटीन अपनी जैविक सक्रियता को खो देता है।

कार्बोहाइड्रेट

ध्रुवण घूर्णन पालिहाइड्रॉक्सी ऐल्डिहाइड अथवा कीटोन अथवा यौगिक जो जलअपघटन के उपरान्त इस प्रकार की ईकाइयाँ देते है।

- **वर्गीकरण :**

(1) मोनोसैकेराइड: (एल्डिहाइड समूह -एल्डोज, कीटो समूह-कीटोज)

ग्लूकोस : विरचन:

(a) सूक्रोस से : $\underset{\text{सूक्रोस}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{ग्लूकोस}}{C_6H_{12}O_6} + \underset{\text{फ्रक्टोस}}{C_6H_{12}O_6}$

(b) स्टार्च से : $(C_6H_{10}O_5)n + nH_2O \xrightarrow[393K;\ 2\text{-}3\ atm]{H^+} nC_6H_{12}O_6$

- **संरचना :**

(ii) डाइसैकेराइड : 2 मोनोसैकेराइड के आबंध-ग्लाइकोसाइडी बंध (सूक्रोस, माल्टोस)
(iii) पॉलीसैकेराइड : असंख्य मोनोसैकेराइड इकाइयाँ ग्लाइकोसाइडी बंध द्वारा संयुक्त रहती है।
(a) स्टार्च : α-ग्लूकोस का बहुलक है तथा दो घटकों ऐमिलोस तथा एमिलोपेक्टिन से मिलकर बनता है।
(b) सेलूलोस
(c) ग्लाइकोजन

महत्व :

- भोजन का प्रमुख भाग है।
- संचित अणु के रूप में
- जीवाणुओं एवं पौधों की कोशिका भित्ति सेलुलोस की बनी होती है।
- उद्योग जैसे-वस्त्र, कागज, प्रलाक्ष (लेकर), निसवन (मद्यनिर्माण) के लिए कच्चा माल।

विटामिन

ये विशिष्ट जैविक क्रियाओं के सम्पन्न होने के लिए हमारे आहार में आवश्यक वे कार्बनिक पदार्थ जिनसे जीव की इष्टतम वृद्धि एवं रखरखाव होता है।

वर्गीकरण :
(i) वसा विलेय विटामिन : वसा तथा तेल में विलेय होते हैं परन्तु जल में अविलेय
(ii) जल में विलेय विटामिन : B वर्ग के विटामिन तथा विटामिन C जल में विलेय होते हैं।

न्यूक्लीक अम्ल

क्रोमोसोम : नाभिक में उपस्थित वे कण जो आनुवांशिकता के लिए उत्तरदायी होते हैं। क्रोमोसोम प्रोटीन तथा न्यूक्लीक अम्ल से मिलकर बने होते हैं।
दो प्रकार : डीऑक्सीराइबोस न्यूक्लिक अम्ल (DNA), राइबोसन्यूक्लिक अम्ल (RNA)
संघटन : DNA में, शर्करा β-D-2 डिऑक्सीराइबोस होती है जबकि RNA में यह β-D राइबोस होती है। DNA में A, G, C, T होती है जबकि RNA में A, G, C, U होता है।

संरचना :
न्यूक्लियोसाइड : क्षारक के शर्करा की '1' स्थिति पर जुड़ने से निर्मित।
न्यूक्लियोटाइड : फॉस्फोरिक एसिड के शर्करा की '5' स्थिति पर बंधने से बनता है।

```
  क्षार             क्षार                क्षार
—शर्करा — फॉस्फेट—[शर्करा—फास्फेट]—शर्करा—
```

RNA के प्रकार : m–RNA, r-RNA, t-RNA.

जैविक कार्य :

- आनुवांशिकता का रासायनिक आधार
- जीवों के विभिन्न प्रजातियों की पहचान बनाए रखने के लिए जिम्मेदार
- न्यूक्लिक अम्ल कोशिका में प्रोटीन के संश्लेषण के लिए उत्तरदायी है।

डी एन ए अंगुली छापन : DNA के क्षारकों का अनुक्रम अद्वितीय होता है।

एन्ज़ाइम

गोलिकाकार प्रोटीन विशेष अभिक्रिया एवं विशेष क्रियाधार के लिए विशिष्ट होते है।
क्रियाविधि : संक्रियण ऊर्जा के परिमाप को कम कर देते हैं।

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