

Class 12 Chemistry: Formulas and Named Reactions

All 10 NCERT chapters (Part I and Part II) · CBSE syllabus 2026-27 · NCERT textbook (Reprint 2026-27)

How to use this sheet. Every box covers the CBSE 2026-27 board-exam syllabus. Chapters 1 to 3 hold the numerical formulas. Chapters 4 to 10 list the key equations and every named reaction in the book. Surface Chemistry and Isolation of Elements are assessed only formatively in 2026-27, and they are not in this textbook, so they are not covered here. Constants: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$, $F = 96487 \text{ C mol}^{-1}$, $\frac{2.303RT}{F} = 0.059 \text{ V}$ at 298 K.

1. Solutions
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1 Solutions

CONCENTRATION TERMS

- Mass % = $\frac{\text{mass of component}}{\text{total mass of solution}} \times 100$
- ppm = $\frac{\text{parts of component}}{\text{total parts of solution}} \times 10^6$
- Mole fraction: $x_A = \frac{n_A}{n_A + n_B}$, $x_A + x_B = 1$
- Molarity $M = \frac{\text{moles of solute}}{\text{volume of solution in L}}$ (changes with temperature)
- Molality $m = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$ (independent of temperature)

HENRY'S LAW AND RAOULT'S LAW

- Henry's law (gas in liquid): $p = K_H x$; higher K_H means lower solubility
- Raoult's law: $p_1 = p_1^0 x_1$, $p_2 = p_2^0 x_2$
- $p_{\text{total}} = p_1^0 + (p_2^0 - p_1^0) x_2$
- Vapour composition: $y_1 = p_1 / p_{\text{total}}$

IDEAL AND NON-IDEAL SOLUTIONS

Type	Raoult's law	$\Delta_{\text{mix}} H$, $\Delta_{\text{mix}} V$	A-B vs A-A, B-B forces	Azeotrope / example
Ideal	obeyed	both 0	equal	n-hexane + n-heptane; bromoethane + chloroethane
Positive deviation	$p > \text{Raoult value}$	both > 0	weaker	Minimum boiling azeotrope; ethanol + water (95% ethanol)
Negative deviation	$p < \text{Raoult value}$	both < 0	stronger	Maximum boiling azeotrope; HNO_3 + water (68% HNO_3); chloroform + acetone

COLLIGATIVE PROPERTIES

- Relative lowering of vapour pressure: $\frac{p_1^0 - p_1}{p_1^0} = x_2$
- Elevation of boiling point: $\Delta T_b = K_b m$
- Depression of freezing point: $\Delta T_f = K_f m$
- Osmotic pressure: $\pi = CRT = \frac{n_2}{V} RT$
- K_b , K_f in K kg mol^{-1} depend only on the solvent.

MOLAR MASS OF SOLUTE (M_2)

- From ΔT_b : $M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1}$
- From ΔT_f : $M_2 = \frac{1000 \times w_2 \times K_f}{\Delta T_f \times w_1}$
- From π : $M_2 = \frac{w_2 RT}{\pi V}$ (best for polymers and proteins)
- w_1 , w_2 are masses (g) of solvent and solute.

VAN'T HOFF FACTOR AND ABNORMAL MOLAR MASS

- $i = \frac{\text{normal molar mass}}{\text{abnormal molar mass}} = \frac{\text{observed colligative property}}{\text{calculated colligative property}} = \frac{\text{total moles of particles after}}{\text{moles of particles before association/dissociation}}$
- Modified equations: $\Delta T_b = iK_b m$, $\Delta T_f = iK_f m$, $\pi = iCRT$, $\frac{p_1^0 - p_1}{p_1^0} = i \frac{n_2}{n_1}$
- Dissociation (e.g. KCl): $i > 1$. Association (e.g. ethanoic acid dimerising in benzene): $i < 1$.
- Isotonic solutions have equal π . Reverse osmosis applies pressure greater than π (desalination).

2 Electrochemistry

GALVANIC CELL

- Daniell cell: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$, $E^\circ = 1.1 \text{ V}$
- Notation: $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)}$ (anode left, cathode right)
- $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{cathode}} - E_{\text{anode}}$
- Standard hydrogen electrode: $E^\circ = 0$. Anode: oxidation. Cathode: reduction.

NERNST EQUATION

- Electrode $\text{M}^{n+} + n\text{e}^- \longrightarrow \text{M}$; $E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[\text{M}^{n+}]}$
- Cell at 298 K, $a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$



ENERGY AND EQUILIBRIUM

- $\Delta_r G = -nFE_{cell}$; $\Delta_r G^\circ = -nFE_{cell}^\circ$
- $\Delta_r G^\circ = -RT \ln K$
- At 298 K: $\log K_c = \frac{nE_{cell}^\circ}{0.059}$
- $E_{cell}^\circ > 0$ means $\Delta_r G^\circ < 0$: spontaneous.

VARIATION WITH CONCENTRATION

- κ decreases and Λ_m increases on dilution
- Strong electrolyte: $\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$
- Kohlrausch's law: $\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$
- Weak electrolyte: $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$, $K_a = \frac{c\alpha^2}{1-\alpha}$

BATTERIES, FUEL CELL, CORROSION

- Dry (Leclanché) cell: anode $Zn \rightarrow Zn^{2+} + 2e^-$; cathode $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$; about 1.5 V
- Mercury cell: $Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$; about 1.35 V, constant over its life
- Lead storage battery (discharge): $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
- H_2 - O_2 fuel cell: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
- Rusting: $2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$, $E_{cell}^\circ = 1.67$ V; rust is $Fe_2O_3 \cdot xH_2O$

CONDUCTANCE

- $R = \rho \frac{l}{A}$; conductivity $\kappa = \frac{1}{\rho}$ ($S\ m^{-1}$)
- Conductance $G = \frac{1}{R}$ (siemens, S)
- Cell constant $G^* = \frac{l}{A} = R\kappa$
- Molar conductivity: $\Lambda_m = \frac{\kappa}{c}$; with c in $mol\ L^{-1}$; Λ_m ($S\ cm^2\ mol^{-1}$) = $\frac{\kappa\ (S\ cm^{-1}) \times 1000}{c}$

ELECTROLYSIS (FARADAY'S LAWS)

- First law: $m = ZIt$, $Q = It$
- Second law: masses liberated by the same charge are in the ratio of their equivalent masses
- 1 F = 96487 C = charge on 1 mol of electrons
- Brine: $NaCl(aq) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$

3 Chemical Kinetics**RATE OF REACTION**

- Average rate = $-\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$
- For $aA + bB \rightarrow cC + dD$: rate = $-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$
- Rate law: rate = $k[A]^x[B]^y$; order = $x + y$ (found by experiment)
- Molecularity: number of species in an elementary step (never 0 or fractional)

UNITS OF k

Order	Unit of k
0	$mol\ L^{-1}\ s^{-1}$
1	s^{-1}
2	$L\ mol^{-1}\ s^{-1}$
n	$(mol\ L^{-1})^{1-n}\ s^{-1}$

ZERO ORDER

- $[R] = [R]_0 - kt$; $k = \frac{[R]_0 - [R]}{t}$
- Half-life: $t_{1/2} = \frac{[R]_0}{2k}$ ($\propto [R]_0$)
- Graph: $[R]$ vs t is a straight line with slope $-k$
- Examples: $2NH_3 \rightarrow N_2 + 3H_2$ on hot Pt; $2HI \rightarrow H_2 + I_2$ on gold.

FIRST ORDER

- $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$
- $[R] = [R]_0 e^{-kt}$
- Half-life: $t_{1/2} = \frac{0.693}{k}$ (independent of $[R]_0$)
- Gas phase $A(g) \rightarrow B(g) + C(g)$: $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$
- Graph: $\ln[R]$ vs t is a straight line with slope $-k$

PSEUDO FIRST ORDER

- One reactant in large excess, so its concentration hardly changes
- $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$
- Inversion of cane sugar: $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6$ (glucose) + $C_6H_{12}O_6$ (fructose)

TEMPERATURE AND COLLISION THEORY

- Arrhenius: $k = A e^{-E_a/RT}$; $\ln k = \ln A - \frac{E_a}{RT}$
- $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$
- A 10 K rise roughly doubles the rate constant
- Collision theory: rate = $P Z_{AB} e^{-E_a/RT}$ (P = probability or steric factor)
- A catalyst lowers E_a ; it does not change ΔG or the equilibrium constant



4 The d- and f-Block Elements

ELECTRONIC CONFIGURATION

- d-block: $(n-1)d^{1-10}ns^{1-2}$; exceptions Cr $3d^54s^1$, Cu $3d^{10}4s^1$
- Lanthanoids: $[Xe] 4f^{1-14}5d^{0-1}6s^2$
- Actinoids: $[Rn] 5f^{1-14}6d^{0-1}7s^2$
- Zn, Cd, Hg (d^{10} in ground state and common ions) are not regarded as transition metals.

KEY PROPERTIES

- Spin-only magnetic moment:

$$\mu = \sqrt{n(n+2)} \text{ BM}$$
 $(n = \text{unpaired electrons})$
- Coloured ions: d-d transitions (partly filled d orbitals)
- Variable oxidation states; Mn shows the most (+2 to +7)
- Form complexes, interstitial compounds, alloys; act as catalysts

POTASSIUM DICHROMATE

- $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \longrightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$
- $2\text{Na}_2\text{CrO}_4 + 2\text{H}^+ \longrightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Na}^+ + \text{H}_2\text{O}$
- $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \longrightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$
- pH: $2\text{CrO}_4^{2-} + 2\text{H}^+ \longrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$;
 $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$
- Oxidant (acid): $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

POTASSIUM PERMANGANATE

- $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \longrightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$
- $3\text{MnO}_4^{2-} + 4\text{H}^+ \longrightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$
- Acidic: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- Neutral or faintly alkaline:
 $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \longrightarrow \text{MnO}_2 + 4\text{OH}^-$

LANTHANIDS AND ACTINIDS

- Lanthanoid contraction: steady fall in atomic and ionic radii from La to Lu (poor shielding by 4f electrons). So Zr and Hf have almost identical radii.
- Lanthanoids: mainly +3 (Ce^{4+} oxidant, Eu^{2+} reductant). Actinoids: wider range of oxidation states, all radioactive.
- Mischmetall: about 95% lanthanoid metal + 5% iron.

5 Coordination Compounds

KEY TERMS

- Coordination number: number of ligand donor atoms bonded to the metal
- Ligands: unidentate (Cl^- , NH_3), didentate (en, $\text{C}_2\text{O}_4^{2-}$), polydentate (EDTA^{4-} , hexadentate)
- Ambidentate: $\text{NO}_2^-/\text{ONO}^-$, $\text{SCN}^-/\text{NCS}^-$
- Werner: primary valence = oxidation state (ionisable); secondary valence = coordination number

IUPAC NAMING RULES

- Cation named before anion; ligands in alphabetical order before the metal
- Anionic ligands end in -o (chlorido, cyanido); aqua, ammine, carbonyl
- Prefixes di-, tri-, bis-, tris- for complex ligand names
- Oxidation state in Roman numerals; anionic complex ends in -ate (ferrate, cuprate)
- $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$: pentaamminechloridocobalt(III) chloride

ISOMERISM

- Geometrical: cis/trans in square planar $[\text{MX}_2\text{L}_2]$ and octahedral $[\text{MX}_2\text{L}_4]$; fac/mer in $[\text{MA}_3\text{B}_3]$
- Optical: non-superimposable mirror images, e.g. $[\text{Co}(\text{en})_3]^{3+}$
- Linkage: $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ vs $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$
- Coordination, ionisation and solvate (hydrate) isomerism

VALENCE BOND THEORY

CN	Hybridisation	Shape	Example
4	sp^3	tetrahedral	$[\text{NiCl}_4]^{2-}$ (paramagnetic)
4	dsp^2	square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ (diamagnetic)
6	d^2sp^3 (inner)	octahedral	$[\text{Co}(\text{NH}_3)_6]^{3+}$ (diamagnetic)
6	sp^3d^2 (outer)	octahedral	$[\text{CoF}_6]^{3-}$ (paramagnetic)

CRYSTAL FIELD THEORY

- Octahedral: e_g above, t_{2g} below, split by Δ_o . Tetrahedral: $\Delta_t = \frac{4}{9}\Delta_o$ (always high spin).
- $\Delta_o > P$ (pairing energy): strong field, low spin. $\Delta_o < P$: weak field, high spin.
- Spectrochemical series: $\text{I}^- < \text{Br}^- < \text{SCN}^- < \text{Cl}^- < \text{S}^{2-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{edta}^{4-} < \text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$
- Colour: light absorbed for d-d transition; the complementary colour is seen
- Metal carbonyls: synergic bonding (σ donation from CO, π back-donation from metal)



6 Haloalkanes and Haloarenes

PREPARATION

- From alcohols: $\text{ROH} + \text{HX} \xrightarrow{\text{ZnCl}_2} \text{RX} + \text{H}_2\text{O}$;
 $3\text{ROH} + \text{PX}_3 \longrightarrow 3\text{RX} + \text{H}_3\text{PO}_3$;
 $\text{ROH} + \text{SOCl}_2 \longrightarrow \text{RCl} + \text{SO}_2 \uparrow + \text{HCl} \uparrow$
- Alkene + HX: Markovnikov's rule (H goes to the carbon with more H)
- Arenes: $\text{C}_6\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{Fe, dark}} \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$ (o- and p-products with toluene)

SUBSTITUTION: SN1 AND SN2

- SN2: one step, inversion of configuration; $\text{CH}_3\text{X} > 1^\circ > 2^\circ > 3^\circ$
- SN1: carbocation, racemisation; $3^\circ > 2^\circ > 1^\circ$
- Reactivity of halides: $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$
- KCN gives cyanide (R-CN); AgCN gives isocyanide (R-NC). KNO_2 gives R-ONO; AgNO_2 gives R-NO₂

WURTZ, WURTZ-FITTIG, FITTIG

- Wurtz: $2\text{RX} + 2\text{Na} \xrightarrow{\text{dry ether}} \text{R-R} + 2\text{NaX}$
- Wurtz-Fittig: $\text{ArX} + \text{RX} + 2\text{Na} \xrightarrow{\text{ether}} \text{Ar-R} + 2\text{NaX}$
- Fittig: $2\text{ArX} + 2\text{Na} \xrightarrow{\text{ether}} \text{Ar-Ar} + 2\text{NaX}$

HALOGEN EXCHANGE

- Finkelstein: $\text{R-X} + \text{NaI} \xrightarrow{\text{dry acetone}} \text{R-I} + \text{NaX}$ (X = Cl, Br)
- Swarts: $\text{H}_3\text{C-Br} + \text{AgF} \longrightarrow \text{H}_3\text{C-F} + \text{AgBr}$ (also Hg_2F_2 , CoF_2 , SbF_3)
- Sandmeyer: $\text{ArN}_2^+\text{X}^- \xrightarrow{\text{Cu}_2\text{X}_2} \text{ArX} + \text{N}_2$ (X = Cl, Br)

ELIMINATION AND GRIGNARD

- Dehydrohalogenation with alcoholic KOH. Zaitsev (Saytzeff) rule: the more substituted alkene is the major product
- $\text{R-X} + \text{Mg} \xrightarrow{\text{dry ether}} \text{R-MgX}$
- $\text{R-MgX} + \text{H}_2\text{O} \longrightarrow \text{R-H} + \text{Mg(OH)X}$

HALOARENES

- Less reactive to nucleophiles (resonance, sp^2 carbon); $-\text{NO}_2$ at o/p raises reactivity
- $\text{C}_6\text{H}_5\text{Cl} \xrightarrow[\text{(ii) H}^+]{\text{(i) NaOH, 623 K, 300 atm}} \text{C}_6\text{H}_5\text{OH}$
- Electrophilic substitution goes o- and p- (halogen is deactivating but o/p-directing)
- Friedel-Crafts: chlorobenzene + CH_3Cl or CH_3COCl with anhyd. AlCl_3

7 Alcohols, Phenols and Ethers

PREPARING ALCOHOLS

- Acid-catalysed hydration: $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{OH}$ (Markovnikov)
- Hydroboration-oxidation:
 $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow[\text{(ii) H}_2\text{O}_2/\text{OH}^-]{\text{(i) B}_2\text{H}_6} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (anti-Markovnikov product)
- Reduction: $\text{RCHO} \xrightarrow{\text{H}_2, \text{Pd} / \text{NaBH}_4} \text{RCH}_2\text{OH}$;
 $\text{RCOOH} \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) LiAlH}_4} \text{RCH}_2\text{OH}$
- Grignard: HCHO gives 1° , other aldehydes give 2° , ketones give 3° alcohols

REACTIONS OF ALCOHOLS

- Lucas test (conc. $\text{HCl} + \text{ZnCl}_2$): 3° turbid at once, 1° no turbidity at room temperature, 2° in between
- Dehydration: $\text{C}_2\text{H}_5\text{OH} \xrightarrow[\text{443 K}]{\text{conc. H}_2\text{SO}_4} \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$
- Oxidation: 1° to aldehyde (PCC) or acid (KMnO_4); 2° to ketone (CrO_3); 3° resist
- Heated Cu at 573 K: 1° gives aldehyde, 2° gives ketone, 3° gives alkene
- Esterification: $\text{ROH} + \text{R'COOH} \xrightleftharpoons{\text{H}^+} \text{R'COOR} + \text{H}_2\text{O}$

PREPARING PHENOL

- From chlorobenzene: NaOH at 623 K and 300 atm, then acidify
- From benzenesulphonic acid: fuse with NaOH, then acidify
- From diazonium salt:
 $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{H}_2\text{O} \xrightarrow{\text{warm}} \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{HCl}$
- Cumene process: cumene $\xrightarrow{\text{O}_2}$ cumene hydroperoxide $\xrightarrow{\text{H}^+, \text{H}_2\text{O}}$ phenol + acetone

REACTIONS OF PHENOL

- Acidity: phenol > water > alcohols; $-\text{NO}_2$ raises acidity, $-\text{CH}_3$ lowers it
- Bromine water: 2,4,6-tribromophenol (white ppt)
- Kolbe: sodium phenoxide + CO_2 , then H^+ , gives salicylic acid
- Reimer-Tiemann: CHCl_3 + aq. NaOH, then H^+ , gives salicylaldehyde
- Dilute HNO_3 : o- and p-nitrophenol; conc. HNO_3 : picric acid

ETHERS

- Williamson synthesis: $\text{R-X} + \text{R'-ONa} \longrightarrow \text{R-O-R'} + \text{NaX}$ (use a 1° halide; 3° halides give alkenes)
- From alcohols: $2\text{C}_2\text{H}_5\text{OH} \xrightarrow[\text{413 K}]{\text{H}_2\text{SO}_4} \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{H}_2\text{O}$
- Cleavage by HI: $\text{R-O-R} + \text{HX} \longrightarrow \text{RX} + \text{R-OH}$; anisole gives phenol + CH_3I
- Anisole undergoes o/p substitution (Friedel-Crafts, nitration, bromination)



8 Aldehydes, Ketones and Carboxylic Acids

PREPARING ALDEHYDES AND KETONES

- Rosenmund: $\text{RCOCl} \xrightarrow{\text{H}_2, \text{Pd}-\text{BaSO}_4} \text{RCHO}$
- Stephen: $\text{RCN} \xrightarrow{\text{SnCl}_2+\text{HCl}} \text{RCH}=\text{NH} \xrightarrow{\text{H}_3\text{O}^+} \text{RCHO}$
- Etard: toluene $\xrightarrow{\text{CrO}_2\text{Cl}_2, \text{CS}_2}$ chromium complex $\xrightarrow{\text{H}_3\text{O}^+}$ benzaldehyde
- Gatterman-Koch: benzene $\xrightarrow[\text{anhyd. AlCl}_3/\text{CuCl}]{\text{CO, HCl}}$ benzaldehyde
- Ketones: $2\text{R}'_2\text{Cd} + 2\text{RCOCl} \longrightarrow 2\text{RCOR}' + \text{CdCl}_2$; nitrile + Grignard, then hydrolysis

NUCLEOPHILIC ADDITION

- HCN gives cyanohydrin; NaHSO_3 gives bisulphite adduct
- Ammonia derivatives $\text{H}_2\text{N}-\text{Z}$: oxime (NH_2OH), hydrazone, 2,4-DNP derivative, semicarbazone
- Alcohols: hemiacetal and acetal (aldehydes); ketal with ethylene glycol (ketones)
- Reactivity: $\text{HCHO} > \text{other aldehydes} > \text{ketones}$

TESTS THAT TELL ALDEHYDES FROM KETONES

- Tollens' (silver mirror):
 $\text{RCHO} + 2[\text{Ag}(\text{NH}_3)_2]^+ + 3\text{OH}^- \longrightarrow \text{RCOO}^- + 2\text{Ag} + 2\text{H}_2\text{O} + 4\text{NH}_3$
- Fehling's (red-brown ppt):
 $\text{RCHO} + 2\text{Cu}^{2+} + 5\text{OH}^- \longrightarrow \text{RCOO}^- + \text{Cu}_2\text{O} + 3\text{H}_2\text{O}$. Aromatic aldehydes do not respond.
- Iodoform (CH_3CO^- or $\text{CH}_3\text{CH}(\text{OH})^-$): NaOI gives yellow CHI_3

REACTIONS OF CARBOXYLIC ACIDS

- Acidity: $\text{F}_3\text{C}-\text{COOH} > \text{Cl}_3\text{C}-\text{COOH} > \text{Cl}_2\text{CHCOOH} > \text{NO}_2\text{CH}_2\text{COOH} > \text{NC}-\text{CH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{HCOOH} > \text{ClCH}_2\text{CH}_2\text{COOH} > \text{C}_6\text{H}_5\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{CH}_3\text{CH}_2\text{COOH}$; electron-withdrawing groups raise acidity
- With NaHCO_3 : CO_2 effervescence (test for $-\text{COOH}$). With $\text{PCl}_5/\text{SOCl}_2$: acid chloride. With NH_3 , then heat: amide.
- Reduction: $\text{RCOOH} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) LiAlH}_4/\text{ether or B}_2\text{H}_6} \text{RCH}_2\text{OH}$
- Decarboxylation: $\text{RCOONa} \xrightarrow[\text{NaOH}+\text{CaO, heat}]{\text{NaOH}+\text{CaO, heat}} \text{RH} + \text{Na}_2\text{CO}_3$
- Hell-Volhard-Zelinsky: $\text{R}-\text{CH}_2-\text{COOH} \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) X}_2/\text{red P}} \text{R}-\text{CHX}-\text{COOH}$ (α -halogenation)
- Ring substitution: $-\text{COOH}$ is deactivating and meta-directing (no Friedel-Crafts)

REDUCTION OF THE CARBONYL GROUP

- To alcohols: NaBH_4 or LiAlH_4
- Clemmensen: $>\text{C}=\text{O} \xrightarrow{\text{Zn-Hg, conc. HCl}} >\text{CH}_2$
- Wolff-Kishner:
 $>\text{C}=\text{O} \xrightarrow{\text{NH}_2\text{NH}_2} >\text{C}=\text{NNH}_2 \xrightarrow{\text{KOH/ethylene glycol, heat}} >\text{CH}_2$

ALDOL AND CANNIZZARO

- Aldol (has α -H, dil. NaOH):
 $2\text{CH}_3\text{CHO} \longrightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO} \xrightarrow{\text{heat}} \text{CH}_3\text{CH}=\text{CHCHO}$
- Cross aldol: two different carbonyl compounds give a mixture of four products
- Cannizzaro (no α -H, conc. alkali):
 $2\text{HCHO} + \text{KOH} \longrightarrow \text{CH}_3\text{OH} + \text{HCOOK}$

PREPARING CARBOXYLIC ACIDS

- 1° alcohols/aldehydes $\xrightarrow{\text{KMnO}_4 \text{ or } \text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+}$ acids
- Alkylbenzene $\xrightarrow[\text{H}_3\text{O}^+]{\text{KMnO}_4-\text{KOH, heat}}$ benzoic acid (whole side chain goes to $-\text{COOH}$)
- Nitriles and amides $\xrightarrow{\text{H}_3\text{O}^+}$ acids; Grignard $\xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) CO}_2}$ RCOOH
- Acyl halides, anhydrides and esters hydrolyse to acids

9 Amines

PREPARATION

- Nitro reduction: $\text{ArNO}_2 \xrightarrow{\text{Fe/HCl or Sn/HCl or H}_2/\text{Pd}} \text{ArNH}_2$
- Ammonolysis: $\text{RX} + \text{NH}_3 \longrightarrow \text{RNH}_2$, giving a mixture of 1°, 2°, 3° amines and quaternary salt
- Nitriles: $\text{RCN} \xrightarrow{\text{H}_2/\text{Ni or LiAlH}_4} \text{RCH}_2\text{NH}_2$ (one carbon more)
- Amides: $\text{RCONH}_2 \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) LiAlH}_4} \text{RCH}_2\text{NH}_2$

BASICITY

- Gas phase: $3^\circ > 2^\circ > 1^\circ > \text{NH}_3$
- Aqueous (methyl): $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$
- Aqueous (ethyl): $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$
- Aniline is weaker than NH_3 (lone pair delocalised into the ring); lower pK_b means stronger base

GABRIEL AND HOFFMANN

- Gabriel phthalimide: phthalimide $\xrightarrow{\text{KOH}} \text{RX} \xrightarrow{\text{NaOH(aq)}} \text{RNH}_2$ (1° aliphatic amines only)
- Hoffmann bromamide:
 $\text{RCONH}_2 + \text{Br}_2 + 4\text{NaOH} \longrightarrow \text{RNH}_2 + \text{Na}_2\text{CO}_3 + 2\text{NaBr} + 2\text{H}_2\text{O}$ (one carbon fewer)

TESTS FOR AMINES

- Carbylamine (1° only):
 $\text{R}-\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\text{heat}} \text{R}-\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$ (foul smell)
- Hinsberg (benzenesulphonyl chloride): 1° gives a product soluble in alkali; 2° gives an insoluble product; 3° does not react
- Nitrous acid: 1° aliphatic gives N_2 gas; aromatic 1° gives diazonium salt (273-278 K)



ANILINE: RING REACTIONS

- Bromine water: 2,4,6-tribromoaniline (white ppt)
- Monosubstitution: protect first by acetylation (acetanilide)
- Nitration gives some m-product (anilinium ion is meta-directing)
- Sulphonation gives sulphanilic acid; no Friedel-Crafts ($-\text{NH}_2$ binds AlCl_3)

DIAZONIUM SALTS

- Diazotisation:

$$\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + 2\text{HCl} \xrightarrow{273-278\text{ K}} \text{C}_6\text{H}_5\text{N}_2^+ \text{Cl}^- + \text{NaCl} + 2\text{H}_2\text{O}$$
- Sandmeyer: $\text{Cu}_2\text{Cl}_2/\text{HCl}$, $\text{Cu}_2\text{Br}_2/\text{HBr}$ or CuCN/KCN gives ArCl , ArBr , ArCN
- Gattermann: Cu/HCl or Cu/HBr gives ArCl , ArBr
- KI gives ArI ; HBF_4 then heat gives ArF ; H_3PO_2 or $\text{CH}_3\text{CH}_2\text{OH}$ gives ArH ; warm water gives ArOH
- Coupling: with phenol (alkaline) gives orange p-hydroxyazobenzene; with aniline (acidic) gives yellow p-aminoazobenzene

10 Biomolecules**GLUCOSE: PROOF OF STRUCTURE**

- HI , heat: n-hexane (straight 6-C chain)
- NH_2OH : oxime; HCN : cyanohydrin (carbonyl group present)
- Bromine water: gluconic acid ($-\text{CHO}$ present)
- Acetic anhydride: pentaacetate (five $-\text{OH}$ groups)
- HNO_3 : saccharic acid (a 1° alcohol group present)
- Glucose gives no 2,4-DNP or Schiff's test and no bisulphite adduct, which led to its cyclic structure.

CARBOHYDRATES

- Sucrose = α -D-glucose + β -D-fructose (C1-C2 link, non-reducing)
- Hydrolysis changes rotation from dextro to laevo: invert sugar
- Maltose = 2 α -D-glucose (C1-C4); lactose = β -D-galactose + β -D-glucose
- Starch = amylose (15-20%, water soluble) + amylopectin (80-85%); cellulose = β -D-glucose chains
- Anomers (α , β) differ only at C1

PROTEINS AND ENZYMES

- Peptide bond: $-\text{CO}-\text{NH}-$ between α -amino acids
- Amino acids exist as zwitterions
- Structure: primary (sequence), secondary (α -helix, β -pleated sheet), tertiary, quaternary
- Denaturation: loss of 2° and 3° structure; the primary structure stays
- Enzymes: biocatalysts that lower activation energy

NUCLEIC ACIDS, VITAMINS, HORMONES

- Nucleoside = base + sugar; nucleotide = nucleoside + phosphate
- DNA: deoxyribose; A, G, C, T; double helix (A pairs with T, G with C). RNA: ribose; A, G, C, U
- Fat-soluble vitamins: A, D, E, K (stored). Water-soluble: B group, C
- Hormones: steroids (estrogens, androgens), polypeptides (insulin, endorphins), amino acid derivatives (epinephrine). Insulin and glucagon regulate blood glucose.

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