ATTACKING REAGENTS

Electrophiles	Nucleophiles	Ambiphiles
They are positively charged or neutral molecules having electron deficient atom, seeking a site of high electron density to attack. Electrophiles have incomplete outer shells and are also called *Lewis acids* (electron-pair acceptors). Charged : H_3O^+, X^+ (where X = Cl, Br, I), NO_2^+, NO^+, NH_4^+, $\overset{+}{S}O_3H$, $C_6H_5\overset{+}{N}_2$, R^+, RCO^+. Neutral : BF_3, $AlCl_3$, $FeCl_3$, $SiCl_4$, $BeCl_2$, $ZnCl_2$, SO_3, CO_2, CS_2, CX_4, $RCOCl$, $>C{=}O$, $:CCl_2$.	They are negatively charged or neutral molecules having electron-rich atom with unshared electron pair, seeking electron deficient site to attack. They are also called *Lewis bases* (electron-pair donors). Charged : H^-, OH^-, X^-, CN^-, N_3^-, RO^-, R^-, RS^-, SH^-, HSO_3^-, NO_2^-, NH_2^-, $RCOO^-$, $HC{\equiv}C^-$. Neutral : $\ddot{N}H_3$, $H_2\ddot{O}$, $R\ddot{O}H$, $R\ddot{O}R$, $R\ddot{S}H$, $RMgX$, $Ph_3\ddot{P}$, RLi, $LiAlH_4$, etc.	They behave both like electrophiles and nucleophiles hence, have dual nature. $R\ddot{O}H$, $H\ddot{O}H$ and $R\ddot{P}H_2$

ELECTRON DISPLACEMENT EFFECTS IN COVALENT BONDS

Types of Electronic Displacement Effects

Inductive effect

Displacement of σ electrons along a saturated carbon chain when an electron donating (+*I* effect) or electron withdrawing (–*I* effect) group is attached at the end of the carbon chain.

- *Decreasing order of –I effect* :
  $-NO_2 > -CN > -COOH > -F > -Cl > -Br > -I > -H$
- *Decreasing order of +I effect* :
  $(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > CH_3- > D- > H-$

Electromeric effect

It involves the complete transfer of π electrons of a multiple bond to one of the bonded atoms in presence of an attacking reagent.

- *+E effect* : When electron transfer takes place to the atom to which the attacking reagent gets finally attached.
- *–E effect* : When electron transfer takes place away from the atom to which the attacking reagent gets finally attached.

Resonance or Mesomeric effect

It is defined as the polarity produced in the molecule by the interaction of two π bonds or between a π bond and a lone pair of electrons present on adjacent atom.

- *+R or +M effect* : $-OH$, $-OR$, $-SH$, $-SR$, $-NH_2$, $-NHR$, $-NR_2$, $-Cl$, $-Br$, $-I$, etc.
- *–R or –M effect* : $>C{=}O$, $-CHO$, $-COOR$, $-CN$, $-NO_2$, etc.
- In case of the elements of the second period in the periodic table, such resonance structures which violate octet rule should not be considered. *e.g.*,

$$\underset{\text{I}}{CH_2{=}CH-\overset{+}{N}H_3} \;\not\leftrightarrow\; \underset{\text{II}}{\overset{+}{C}H_2-CH{=}NH_3}$$

Hyperconjugation

It involves delocalisation of σ electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared *p*-orbital. For an alkyl group attached to unsaturated system it decreases with decrease in number of α-hydrogens. Thus, the order of hyperconjugation effect decreases in the order :

$CH_3- > CH_3CH_2- > (CH_3)_2CH- > (CH_3)_3C-$

Methods of Purification of Organic Compounds

Methods

Distillation under reduced pressure : It is used to purify liquids
- having very high boiling points.
- which decompose at or below their boiling points.

  e.g., Glycerol is separated from spent-lye in soap industry.

Steam distillation : This method is used to separate substances which are steam volatile, insoluble in water, possess a vapour pressure of 10-15 mm Hg and contain non-volatile impurities.
- Aniline is separated from aniline-water mixture.
- Essential oils, *o*-nitrophenol, bromobenzene, nitrobenzene, etc. can be purified.

Differential extraction : This method involves the shaking of an aqueous solution of an organic compound with an organic solvent in which the organic compound is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they can form two distinct layers which can be separated by using separating funnel.
- Benzoic acid can be extracted from its water-benzoic acid mixture using benzene.

Chromatography : It involves differential movement of individual components of a mixture through a stationary phase under the influence of a mobile phase.
- Widely used for separation, purification, identification and characterisation of the components of a mixture, whether coloured or colourless.

Adsorption chromatography (stationary phase is solid)
- **Column chromatography :** It involves separation of a mixture over a column of adsorbent packed in a glass tube.

  Mixture of naphthalene and benzophenone can be separated by this.
- **Thin layer chromatography :** It involves the separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate.

  Amino acids can be detected by spraying the plate with ninhydrin solution.

Partition chromatography : It is a liquid/liquid chromatography in which both the mobile phase and the stationary phase are liquids and used for the separation of sugars and amino acids.
- **Paper chromatography:** A special quality paper known as chromatographic paper is used. It contains water trapped in it, which acts as the stationary phase.

Crystallisation : Differential solubilities of a given organic compound and its impurities in the same solvent.
- Crystallisation of sugar (containing an impurity of common salt) is achieved by shaking the impure solid with hot ethanol at 348 K (sugar dissolves whereas common salt remains insoluble).

Sublimation : Some solid substances change from a solid to a vapour state without passing through the liquid state. Sublimable compounds get separated from non-sublimable impurities.
- Iodine from sodium chloride (as iodine sublimes readily leaving behind sodium chloride).
- Camphor, naphthalene, anthracene, benzoic acid, etc. are purified.

Distillation : It is used to separate
- volatile liquids from non-volatile impurities.
- liquids having sufficient difference in their boiling points.
- Hexane (b.p. 342 K) and toluene (b.p. 384 K)
- Chloroform (b.p. 334 K) and aniline (b.p. 457 K)

Fractional distillation : If the difference in boiling points of two liquids is not much, this method is used.
- Crude oil in petroleum industry is separated into various useful fractions such as gasoline, kerosene oil, diesel oil, lubricating oil, etc.

QUALITATIVE ANALYSIS

Detection of Elements and their Confirmatory Tests

Carbon (Copper oxide test)

$2CuO + C \xrightarrow{\Delta} 2Cu + CO_2\uparrow$

Confirmatory test

$\underset{\text{Lime water}}{CO_2\uparrow + Ca(OH)_2} \longrightarrow \underset{\text{Milkiness}}{CaCO_3\downarrow} + H_2O$

Hydrogen (Copper oxide test)

$CuO + 2H \xrightarrow{\Delta} Cu + H_2O$

Confirmatory test

$\underset{\text{White}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4 \cdot 5H_2O}$

Nitrogen

$Na + C + N \xrightarrow{\Delta} \underset{\text{(Lassaigne's extract)}}{NaCN}$

Confirmatory test

$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$

$Fe(OH)_2 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$

$3Na_4[Fe(CN)_6] + 4FeCl_3 \rightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$

Sulphur

$2Na + S \xrightarrow{\Delta} \underset{\text{(Lassaigne's extract)}}{Na_2S}$

Confirmatory test

$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} \rightarrow \underset{\text{Deep violet}}{Na_4[Fe(CN)_5NOS]}$

$Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH} \underset{\text{Black ppt.}}{PbS\downarrow} + 2CH_3COONa$

Halogens

$Na + X \xrightarrow{\Delta} \underset{\text{(Lassaigne's extract)}}{NaX}$

(X = Cl, Br or I)

Confirmatory test

$NaX + AgNO_3 \xrightarrow{HNO_3} \underset{\text{ppt.}}{AgX\downarrow}$

— White ppt. soluble in aqueous NH_3 (or NH_4OH) confirms Cl.

$\underset{\text{White ppt.}}{AgCl\downarrow} + 2NH_{3(aq.)} \longrightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]Cl}$

— Yellow ppt. partially soluble in aqueous NH_3 (or NH_4OH) confirms Br.

— Yellow ppt. insoluble in aqueous NH_3 (or NH_4OH) confirms I.

Nitrogen and sulphur

$Na + C + N + S \xrightarrow{\Delta} NaSCN$

(Lassaigne's extract)
Sodium thiocyanate

Confirmatory test

$3NaSCN + FeCl_3 \longrightarrow \underset{\text{Blood red colour}}{[Fe(SCN)_3]} + 3NaCl$

Phosphorus

$P \xrightarrow[\Delta]{Na_2O_2,\ boil} Na_3PO_4$

Confirmatory test

$Na_3PO_4 + 3HNO_3 \xrightarrow{\Delta} H_3PO_4 + 3NaNO_3$

$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \xrightarrow{\Delta} (NH_4)_3PO_4 \cdot 12MoO_3\downarrow + 21NH_4NO_3 + 12H_2O$

Ammonium phosphomolybdate
(Yellow ppt.)

INFO SHOTS

Gas Chromatography(GC) – Sensor Can 'Smell' Prostate Cancer!

A Research team from the University of Liverpool has reached an important milestone towards creating a urine diagnostic test for prostate cancer. The use of a gas chromatography (GC) – sensor system combined with advanced statistical methods towards the diagnosis of urological malignancies', which describes a diagnostic test using a special tool to 'smell' the cancer in men's urine. The GC sensor system is able to successfully identify different patterns of volatile compounds that allow classification of urine samples from patients with urological cancers. The research team used a gas chromatography sensor system called Odoreader that was developed by a team led by Professor Probert and Professor Norman Ratcliffe at UWE Bristol. The test involves inserting urine samples into the Odoreader that are then measured using algorithms developed by the research team at the University of Liverpool and UWE Bristol. "The Odoreader has a 30 metre column that enables the compounds in the urine to travel through at different rates thus breaking the sample into a readable format. This is then translated into an algorithm enabling detection of cancer by reading the patterns presented. The positioning of the prostate gland which is very close to the bladder gives the urine profile a different algorithm if the man has cancer."

QUANTITATIVE ANALYSIS

Methods of Analysis

Estimation of carbon and hydrogen

Liebig's combustion method :

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \xrightarrow{\Delta} xCO_2 + \frac{y}{2}H_2O$$

$$\% \text{ of C} = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of compound taken}} \times 100,$$

$$\% \text{ of H} = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{\text{Mass of compound taken}} \times 100$$

Estimation of halogen

Carius method :

$$X \xrightarrow[AgNO_3]{HNO_3, \Delta} AgX\downarrow$$

$$\% \text{ of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of compound taken}} \times 100$$

$$\% \text{ of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of compound taken}} \times 100$$

$$\% \text{ of I} = \frac{127}{235} \times \frac{\text{Mass of AgI formed}}{\text{Mass of compound taken}} \times 100$$

Estimation of sulphur

Carius method :

$$S \xrightarrow[\text{(ii) } BaCl_2]{\text{(i) } HNO_3, \Delta} \underset{\text{White ppt.}}{BaSO_4\downarrow}$$

$$\% \text{ of S} = \frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \text{ formed}}{\text{Mass of compound taken}} \times 100$$

Estimation of carbon, hydrogen and nitrogen

The elements carbon, hydrogen and nitrogen present in a compound can be determined by an apparatus known as CHN elemental analyser. It requires only 1-3 mg of the compound and displays the values of the element on the screen. The results are accurate within ±0.03% error.

Estimation of nitrogen

Dumas method :

$$C_xH_yN_z + \left(2x + \frac{y}{2}\right)CuO \xrightarrow{\Delta}$$

$$xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x + \frac{y}{2}\right)Cu$$

$$\% \text{ of N} = \frac{28}{22400} \times \frac{\text{Vol. of } N_2 \text{ at STP}}{\text{Mass of compound taken}} \times 100,$$

$$\text{Vol. of } N_2 \text{ at STP} = \frac{P_1V_1 \times 273}{760 \times T_1}$$

Kjeldahl's method :

$$\text{Organic compound} + H_2SO_{4\,(conc.)} \xrightarrow{\Delta}$$

$$(NH_4)_2SO_4 \xrightarrow[\Delta]{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$\% \text{ of N} = \frac{1.4 \times \text{Molarity of acid} \times \text{Vol. of acid used} \times \text{Basicity of acid}}{\text{Mass of compound taken}},$$

$$\% \text{ of N} = \frac{1.4 \times \text{Normality of acid} \times \text{Vol. of acid used}}{\text{Mass of compound taken}}$$

(for monobasic acid)

Estimation of phosphorus

Ignition method :

$$P \xrightarrow[\text{Heat}]{HNO_3} H_3PO_4$$

$$H_3PO_4 + Mg^{2+} + NH_4Cl \xrightarrow{\Delta} \underset{\text{Magnesium ammonium phosphate (white ppt.)}}{MgNH_4PO_4} + HCl$$

$$2MgNH_4PO_4 \xrightarrow{\Delta} \underset{\text{Magnesium pyrophosphate}}{Mg_2P_2O_7} + 2NH_3 + H_2O$$

$$\% \text{ of P} = \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7 \text{ formed}}{\text{Mass of compound taken}} \times 100$$

Estimation of oxygen

% of oxygen in a compound = 100 – (Sum of the % of all other elements present in the compound).