Calculations using combustion data:

Using formula: 
\[ \text{CxHy} + (x + y/4)\text{O}_2 \rightarrow x\text{CO}_2 + (y/2)\text{H}_2\text{O} \]

Percentage yield:

Percentage yield = (Actual mass of product formed / Theoretical mass) x 100%

Calculations using volume of gas:

<table>
<thead>
<tr>
<th>Condition</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Molar volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>s.t.p. (standard temperature and pressure)</td>
<td>273K</td>
<td>1 atm</td>
<td>22.4 dm(^3)</td>
</tr>
<tr>
<td>r.t.p. (room temperature and pressure)</td>
<td>298K</td>
<td>1 atm</td>
<td>24 dm(^3)</td>
</tr>
</tbody>
</table>

Note: For a gas, volume ratio = mole ratio

Titration and Back Titration:

Steps for back titration –
1. Determine amount of C required in titration
2. Using stoichiometry, find amount of A that reacted with C in the titration
3. Hence, amount of A that reacted with B = total amount of A (in excess) – amount that reacted with C
4. Thus determine amount of A that reacted with B, and thus amount of B

Summary: \( \eta_A = \eta_A \text{ that reacted with B} + \eta_A \text{ that reacted with C} \)

Double indicators:
Sometimes double indicators are used for the titration of dibasic acids
### Assumptions of ideal gas:
1. Gas particles behave as rigid spheres
2. Gas particles have negligible volumes compared to volume of the container
3. Intermolecular forces of attraction and repulsion between gas particles are negligible
4. Collision between gas particles and walls of container are perfectly elastic
5. Average KE of gas particles is directly proportional to absolute temperature
   - **Note:** Assumption 2 and 3 are most important, can bring up 4 if needed

### Boltzmann distribution curve:

![Boltzmann distribution curve](image)

**Things to note:**
- Peak of each curve represents most probably speed
- As temperatures increase, curve shifts right and particle cases in height

### Real gas and deviation from ideal behavior:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 K</td>
<td>N₂, CH₄, H₂</td>
</tr>
<tr>
<td>500 K</td>
<td>N₂, CH₄, H₂</td>
</tr>
<tr>
<td>1000 K</td>
<td>N₂, CH₄, H₂</td>
</tr>
</tbody>
</table>

Hence, deviation is minimal when
1. High temperatures
2. Low pressure
Chapter 5: Intro to Organic Chemistry

Definitions:

**Homologous series:** series of organic compounds where each successive member increases by the unit \(-\text{CH}_2\)

**Distinguishing test:** chemical test that aims to confirm presence of a particular compound, or differentiate between organic compounds

**Types of formulae:**
Structural formula is the most often used formula in organic chemistry

1. Displayed formula / full structural formula
   \[
   \begin{align*}
   &\text{C} \\
   &\text{O}
   \end{align*}
   \]

2. Condensed structural formula \([\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}]\)

3. Skeletal formula

4. Stereochemical formula

Overview of functional groups:
Chapter 6: Alkanes

Naming of Alkanes:

Straight Chain alkanes
They are named according to the number of carbon atoms

<table>
<thead>
<tr>
<th>Number of carbons (n)</th>
<th>Name</th>
<th>Formula (C\textsubscript{n}H\textsubscript{2n+2})</th>
<th>Number of carbons (n)</th>
<th>Name</th>
<th>Formula (C\textsubscript{n}H\textsubscript{2n+2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methane</td>
<td>CH\textsubscript{4}</td>
<td>6</td>
<td>Hexane</td>
<td>C\textsubscript{6}H\textsubscript{14}</td>
</tr>
<tr>
<td>2</td>
<td>Ethane</td>
<td>C\textsubscript{2}H\textsubscript{6}</td>
<td>7</td>
<td>Heptane</td>
<td>C\textsubscript{7}H\textsubscript{16}</td>
</tr>
<tr>
<td>3</td>
<td>Propane</td>
<td>C\textsubscript{3}H\textsubscript{8}</td>
<td>8</td>
<td>Octane</td>
<td>C\textsubscript{8}H\textsubscript{18}</td>
</tr>
<tr>
<td>4</td>
<td>Butane</td>
<td>C\textsubscript{4}H\textsubscript{10}</td>
<td>9</td>
<td>Nonane</td>
<td>C\textsubscript{9}H\textsubscript{20}</td>
</tr>
<tr>
<td>5</td>
<td>Pentane</td>
<td>C\textsubscript{5}H\textsubscript{12}</td>
<td>10</td>
<td>Decane</td>
<td>C\textsubscript{10}H\textsubscript{22}</td>
</tr>
</tbody>
</table>

Branched (or substituted alkanes)
They are named according to the IUPAC rules:

1. Locate longest continuous chain of carbon atoms
2. Number the longest chain beginning with the end closer to the substituents
3. Use the number allocated to determine the position of the substituents
4. When 2 or more substituents are present, give them a number corresponding to their location
5. When 2 substituents are present on the same carbon, use that number twice
6. When 2 or more substituents are identical, indicate by using a prefix of di-, tri-, tetra-

Examples

- 4-ethyl-octane
- 3-ethyl-2-methylhexane
- 4-ethyl-2,4-dimethylhexane

Physical properties of alkanes:
The molecules of alkanes are non-polar due to the C-H bonds and are held together mainly by weak dispersion forces

Boiling point – Increase with number of carbon atoms due to increasing size of electron cloud and thus stronger dispersion forces between molecules

- Branched-chain alkanes have lower boiling point than straight chains due to smaller surface area of contact between molecules
- Thus dispersion forces between branched-chain alkanes are weaker
Catalytic Reforming
Reforming straight-chain alkanes is done by changing straight-chain alkanes into branched-chain alkanes and cyclic hydrocarbons without loss of any carbon atoms

Done by passing vaporized alkane mixture over platinum-coated aluminum oxide catalyst at 500°C and moderately high pressure

Environmental consequences of burning fuel:

<table>
<thead>
<tr>
<th>Carbon monoxides and unburnt hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>They arise primarily due to incomplete combustion of fuel</td>
</tr>
<tr>
<td>Carbon monoxide: binds irreversibly to haemoglobin in blood and forms a stable complex, thus reducing capacity of haemoglobin to transport oxygen</td>
</tr>
<tr>
<td>Unburnt hydrocarbons: in the presence of sunlight, they react with oxygen, ozone and oxides of nitrogen to form photochemical smog</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxides of nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOₓ are formed inside the combustion chambers of motor vehicles. At high temperatures of combustion, atmospheric oxygen and nitrogen combine to form NO and later oxidized to NO₂</td>
</tr>
</tbody>
</table>
| \[
\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO} \\
2\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{NO}_2
\] |
| They irritate lungs, cause pneumonia and lower resistance to respiratory infections. They also result in the formation of photochemical smog which has a harmful effect on plants |
| Formation of nitrous and nitric acid: \(2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3\) |
| Formation of sulfuric acid: \(2\text{SO}_2 + \text{NO}_2 \rightarrow 2\text{SO}_3 + \text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2\) |
| HNO₃ and H₂SO₄ are strongly acidic and form acid rain which causes corrosion of buildings and man made structures, and also harms marine life and agriculture |
### Greenhouse effect

It is the heating of the earth due to the presence of greenhouse gases, which causes radiation to be trapped in the atmosphere and increase in global temperature.

Greenhouse gases:
- **Natural**: Carbon dioxide, Methane, Water vapor and Nitrous oxides
- **Manmade**: Chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs)

### Catalytic converters

It removes pollutant gases from the exhaust by oxidizing or reducing them, where the gases passes through a converter containing an alloy of platinum or rhodium (heterogeneous catalyst):

\[
2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2 \\
2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 
\]

However, catalytic converters only work with unleaded petrol as lead poisons the catalyst by binding permanently to it.

~ END ~
Chemical properties of Alkenes:
Alkenes are more reactive than alkanes due to the electron rich C=C where the \( \pi \) bond (electron cloud) attracts electrophiles

During a reaction, the weaker \( \pi \) bond is broken instead in the C=C bond, forming two strong bonds in the product. This reaction is known as **electrophilic addition**

\[ \text{unsaturated alkene} + \text{electrophile} \rightarrow \text{saturated product} \]

Electrophilic addition of hydrogen halides (H–X):

**Step 1:** Rate determining step
Polar HBr approaches the \( \pi \) electron cloud. The high electron density of \( \pi \) electron cloud “attacks” electron deficient H atom on HBr

**Step 2:**
Bromide anion acts as nucleophile and attacks unstable carbocation
More than one product forms too, however 3 products can actually form instead of 2.

However, nitration of trifluoromethylbenzene results in only 1 product.

This can be explained through the resonance and inductive effect.

**Effects on reactivity of benzene ring:**

*Activating groups*: Electron-donating substituents increase electron density of benzene ring and thus increase reactivity

*Deactivating groups*: Electron-withdrawing substituents decrease electron density

There are 2 ways which electrons can be donated or withdrawn from the benzene ring –

1. Through the sigma bond → inductive effect
2. Through the pi bond → resonance effect

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Inductive effect</th>
<th>Resonance effect</th>
<th>Overall effect on reactivity</th>
<th>Overall effect on position of incoming group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl groups</td>
<td>Electron donating</td>
<td>-</td>
<td>Activating</td>
<td>2,4-directing</td>
</tr>
<tr>
<td>-OH, -NH₂, -OCH₃</td>
<td>Electron withdrawing</td>
<td>Electron donating</td>
<td>Activating</td>
<td>2,4-directing</td>
</tr>
<tr>
<td>-F, -Cl, -Br, -I</td>
<td>Electron withdrawing</td>
<td>Electron donating</td>
<td>Weakly Deactivating</td>
<td>2,4-directing</td>
</tr>
<tr>
<td>-CHO, -NO₂, -CO₂H, -CN</td>
<td>Electron withdrawing</td>
<td>Electron withdrawing</td>
<td>Deactivating</td>
<td>3-directing</td>
</tr>
</tbody>
</table>
Uses of halogenoalkanes:

Chlorofluorocarbons (CFCs) are used as refrigerants, aerosol propellants and fire extinguishers and have some useful properties
1. They are inert and non-flammable
2. They are non-toxic
3. They are compounds that liquefy under pressure and thus vaporize readily when pressure is released
4. They are odorless

Effect of CFCs on ozone:

Normally, ozone is formed when oxygen atoms are produced as O₂ absorbs UV light
\[ O_2 + O \rightarrow O_3 \]

However, CFCs deplete this ozone layer when they drift upwards to the atmosphere
\[ CF_3Cl + uv \rightarrow Cl\cdot + •CF_3 \]

The chlorine radical then acts to destroy the ozone by removing O₃ and O from the atmosphere
\[ Cl\cdot + O_3 \rightarrow ClO\cdot + O_2 \]
\[ ClO\cdot + O \rightarrow Cl\cdot + O_2 \]

Measures to protect the ozone layer:
1. Reduce the usage of CFCs
2. Use substitutes such as hydrocarbons, hydrofluorocarbons or fluorocarbons
4. Oxidative cleavage of alkenes

\[
\begin{align*}
\text{CH}_3\text{C} & \equiv \text{CH}_3 \\
& + 4[O] \xrightarrow{\text{KMnO}_4, \text{dilute H}_2\text{SO}_4, \text{heat under reflux}} 2\text{CH}_3\text{C} \equiv \text{O} \\
\end{align*}
\]

Reagents and conditions: KMnO₄, dilute H₂SO₄, heat under reflux
Observations: Orange solution (Cr³⁺) turns green (Cr²⁺)
Purple solution (MnO₄⁻) decolourises (Mn²⁺)

5. Hydrolysis of esters

\[
\begin{align*}
\text{R} \text{`O\text{O} – \text{R'}} & + \text{H}_2\text{O} \xrightarrow{\text{dilute H}_2\text{SO}_4, \text{heat under reflux}} \text{R\text{`O\text{O} – \text{H}} + \text{R’\text{`OH}} \\
\end{align*}
\]

Reagents and conditions: dilute H₂SO₄, heat under reflux
Remarks: Esters can also be hydrolysed by bases like dilute NaOH, heat under reflux followed by acidification with dilute H₂SO₄ at room temperature and pressure.

Chemical reactions of carboxylic acids:
The C=O and O–H group are so close in proximity that carboxylic acids do not behave like aldehydes, ketones or alcohols.

Carboxylic acids are stronger acids than alcohols and they do not undergo nucleophilic addition like aldehydes and ketones
- The flow of electrons from the O–H group makes the carboxyl carbon less electron deficient

There are 3 main types of reactions that carboxylic acids can undergo:
1. Acid-metal/Acid-base reaction
2. Nucleophilic acyl substitution reaction
3. Reduction of the CO₂H group
Acid hydrolysis of esters:

\[
\begin{align*}
R-CR'OR' + H_2O & \xrightarrow{\text{dilute } H_2SO_4, \text{ Heat under reflux}} R-COOH + R'OH \\
\end{align*}
\]

Reagents and conditions: dilute H$_2$SO$_4$, heat under reflux
Remarks: The reaction is reversible. A large excess of water (dilute acid) is used to ensure equilibrium lies to the right. Notice that this is the reverse reaction of esterification.

Base hydrolysis of esters:

\[
\begin{align*}
R-CR'OR' + H_2O & \xrightarrow{\text{dilute NaOH, Heat under reflux}} R-COOH + R'OH \\
\end{align*}
\]

Reagents and conditions: dilute NaOH, heat under reflux followed by acidification with dilute H$_2$SO$_4$ at room temperature and pressure
Remarks: The reaction is rapid and irreversible. Resonance-stabilised RCO$_2$H is a acid that has little tendency to react with alcohol, thus the reaction goes to completion. To obtain the carboxylic acid, aqueous NaOH is added to the mixture at the end of the reaction.

Commercial uses of esters:
Esters are prepared industrially mainly for use as essence, perfumes or artificial flavoring. Esters are also widely used as organic solvents.

~ END ~
Chapter 12: Carbonyl Compounds

Introduction:
A carbonyl (–C=O) functional group is probably the most important functional group in organic and biological chemistry.

The two simplest types of carbonyl compounds are aldehydes and ketones.

Carbonyl compounds are named the following manner –
1. For **aldehydes**, find the longest parent chain containing the –CHO group and number the carbonyl carbon.
2. Aldehydes with the –CHO attached directly to a ring system are named by adding the suffix -carbaldehyde.
3. For **ketones**, parent chain is the longest one containing the ketone group and numbering begins at the end nearer the carbonyl carbon.
4. Aldehydes end with a –al and ketones end with –one.

Isomerism:
Saturated aliphatic aldehydes and ketones have the general formula C\textsubscript{n}H\textsubscript{2n}O and thus they are structural isomers if they have the same number of carbon atoms in the compound.

Physical properties of aldehydes and ketones:

- **Nature of carbonyl carbon** – it is sp\textsuperscript{2} hybridized and hence covalent with other atoms, and are thus planar.
  - C=O bonds are polarized as O is more electronegative than C.
  - Hence carbon has partial +ve charge and oxygen has partial –ve charge.
- **Boiling points** – they have higher boiling points than non-polar hydrocarbons of similar relative Mr but lower than alcohols and carboxylic acids.
  - Alkanes are non-polar, only have weak dispersion forces, but carbonyl group is polar and hence pd-pd interactions between molecules.
  - However alcohols and carboxylic acids can form H-bonds between molecules.
- **Solubility in water** – they have polar and non-polar regions, able to act as a solvent for both.
  - Lower aliphatic aldehydes and ketones are soluble in water due large to their ability to form hydrogen bonds with water molecules.
Nucleophilic addition and condensation reactions of aldehydes and ketones:

The C=O bond is similar to the C=C bond as both react to saturate the double bond by addition
- However in C=O, O is much more electronegative and withdraws electron density to itself
- Thus the carbonyl carbon has a partial +ve charge and can be attacked by nucleophiles, resulting in nucleophilic addition or condensation reactions

Nucleophilic addition:

Reaction with Hydrogen Cyanide, HCN

\[
\text{C}=\text{O} \quad + \quad \text{H-CN} \quad \xrightarrow{\text{trace KCN(aq)}} \quad \text{NC-C}=\text{O} \quad \xrightarrow{\text{cold}} \quad \text{CN-C}=\text{OH} \quad \text{cyanohydrin}
\]

| Reagents and conditions: | HCN with trace KCN(aq), cold (10-20°C) |
| Comments: | KCN is used as a catalyst; CN⁻ ion is regenerated at the end of the reaction. |

Note: HCN is a toxic gas and is generated in situ through the following reaction
- \(2\text{KCN} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{HCN}\)

**Step 1:** Carbonyl carbon attack by nucleophile CN⁻

- CN⁻ ion acts as nucleophile and attacks electron-deficient carbonyl carbon and leads to formation of stable tetrahedral intermediate anion (alkoxide)

**Step 2:** Protonation of intermediate to give a cyanohydrin

- The CN⁻ ion is regenerated
**Functional groups** | Ability to be reduced by
---|---|---|---
| H₂ / Ni | LiAlH₄ in dry ether | NaBH₄ in methanol |
| Alkenes | + | - | - |
| Carboxylic Acids | - | + | - |
| Esters | - | + | - |
| Nitriles | + | + | - |
| Aldehydes | + | + | + |
| Ketones | + | + | + |

**Oxidation:**

With acidified potassium dichromate (VI)

Only for aldehydes as they contain a hydrogen attached directly to the carbonyl carbon

\[
\text{R-C} = \text{H} + [\text{O}] + \text{K₂Cr₂O₇ / dilute H₂SO₄ or KMnO₄ / dilute H₂SO₄, heat under reflux} \rightarrow \text{R-C} = \text{O} \rightarrow \text{R-C} = \text{H}
\]

Reagents and conditions: K₂Cr₂O₇ / dilute H₂SO₄ or KMnO₄ / dilute H₂SO₄, heat under reflux

Comments: Orange solution (Cr₂O₇²⁻) turns green (Cr³⁺)

Purple solution (MnO₄⁻) turns colourless

Note: This can be used as a test to distinguish between aldehydes and ketones

With Tollens’ Reagent (Silver Mirror Test)

All aldehydes reduce Ag⁺ in Tollens’ reagent to silver metal and deposit on the walls

\[
\text{R-C} = \text{H} + 2[\text{Ag(NH₃)₂}]^+ + 3\text{OH}^- \rightarrow \text{R-C} = \text{O}^- + 2\text{Ag} + 4\text{NH}_3 + 2\text{H}_2\text{O}
\]

Reagents and conditions: Tollens’ reagent, heat

Observations: Silver mirror formed

Comments: A useful distinguishing test for the presence of an aldehyde functional group.

Ketones do not reduce Tollens’ reagent thus no silver mirror will form.

Tollens’ reagent contains [Ag(NH₃)₂]⁺ ions and is highly unstable, thus it should be freshly prepared using the following method

- 1 drop of dilute NaOH to about 3cm³ of AgNO₃ to produce brown ppt of Ag₂O
- Dilute NH₃ then added drop wise until brown ppt first formed dissolves – contains [Ag(NH₃)₂]⁺
Reaction with haloalkanes (as a nucleophile)
Primary, secondary and tertiary amines can react with haloalkanes to form secondary amines, tertiary amines and quaternary ammonium salts

\[
\begin{align*}
R-\text{NH}_2 & \quad + \quad R'-\text{X} & \quad \text{heat} & \quad R-\text{NHR'} + \quad R'-\text{X} \\
\text{primary amine} & \quad & \quad & \quad \text{secondary amine} \\
R-\text{NHR'} & \quad + \quad R'-\text{X} & \quad \text{heat} & \quad R-\text{NR}_2' + \quad R'-\text{X} \\
\text{secondary amine} & \quad & \quad & \quad \text{tertiary amine} \\
R-\text{NR}_2' & \quad + \quad R'-\text{X} & \quad \text{heat} & \quad R-\text{NR}_3' + \quad X \\
\text{tertiary amine} & \quad & \quad & \quad \text{quaternary ammonium salt}
\end{align*}
\]

Reagents & conditions: Halogenoalkane, heated in sealed tube
Comment: To prevent multiple substitutions, excess amine is used.

Reaction with acyl chlorides (as a nucleophile)
They can react with acid chlorides to form amides

\[
\begin{align*}
\text{H-} \quad R & \quad \text{N} \quad \text{H} & \quad + \quad \text{R}'-\text{C} \quad \text{Cl} & \quad \rightarrow \quad \text{R}'-\text{C} \quad \text{NHR} \quad \text{HCl} \\
\text{H-} \quad R & \quad \text{N} \quad \text{R'} & \quad + \quad \text{R}''-\text{C} \quad \text{Cl} & \quad \rightarrow \quad \text{R}''-\text{C} \quad \text{NHR} \quad \text{HCl}
\end{align*}
\]

Reagents & conditions: Acid chlorides, room temperature
Comment: Tertiary amines do not contain a replaceable H atom on the nitrogen; are incapable of forming amides.

Reaction with bromine
Only for phenylamines due via an electrophilic substitution mechanism to form a white ppt

\[
\text{NH}_2 + 3\text{Br}_2(aq) \rightarrow \text{Br} + 3\text{HBr} + \text{NH}_2\text{Br}
\]

Reagents & Conditions: Aqueous bromine, room temperature
Observations: Yellow-orange solution decolourise; white ppt formed
Comments: No Lewis acid catalyst (halogen carrier) is required for this reaction, unlike bromination of benzene (which requires A/Cl\textsubscript{3} or FeCl\textsubscript{3}). –NH\textsubscript{2} group is 2, 4-directing.
Explanation: Like phenol, the lone pair of electrons on the nitrogen atom is delocalised into the benzene ring, the electron density in the ring is greatly increased, making it much more susceptible to electrophilic attack than benzene. Hence, the presence of the –NH\textsubscript{2} group highly activates the benzene ring towards electrophilic substitution and no catalyst is required.
Physical properties of amino acids:
Formation of zwitterions gives amino acids some unusual properties
• Amino acids are crystalline solids with high melting points due to strong electrostatic forces of attraction between dipolar zwitterions in solid lattice structure
• They are more soluble in water than organic solvents due to strong ion-dipole interaction

Peptide bond formation:
Amide linkage between amino acids is called a peptide bond and is formed from the condensation reaction between −CO₂H and −NH₂

Features of polypeptide chain:
• Backbone is the main chain of polypeptide which includes everything but the side chains that are the R-groups of each amino acid residue
• Amino acid residues are amino acids condensed together in a polypeptide chain
• Peptide bonds which arise from the condensation reaction between adjacent amino acids
• N- and C- termini where there is an uncondensed amino group and one uncondensed carboxylic aid group
• Polypeptide chains are always written from the N-terminus to the C-terminus

PROTEINS
They are formed when a large number of amino acids are condensed together to form a long polypeptide chain

Hydrolysis of proteins:
Proteins can be hydrolyzed into their constituent amino acids by an enzyme or heating in the presence of dilute acid or alkali for several hours

![Diagram of peptide bond formation and hydrolysis]