Chapter 29

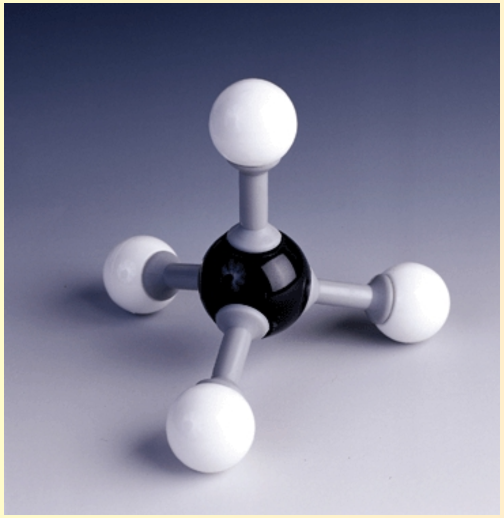
Alkanes

29.1 Introduction (SB p.102)

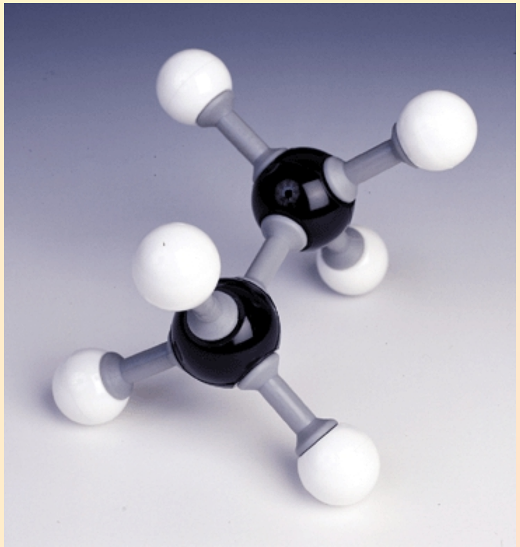
- Hydrocarbons
  - Aliphatic
    - Acyclic — Straight-chain or branched-chain alkanes, alkenes, alkynes
    - Alicyclic — Cycloalkanes, cycloalkenes
  - Aromatic
    - Benzene
    - Alkylbenzenes
    - Other cyclic compounds with (4n + 2) π electrons

Ball-and-stick models:

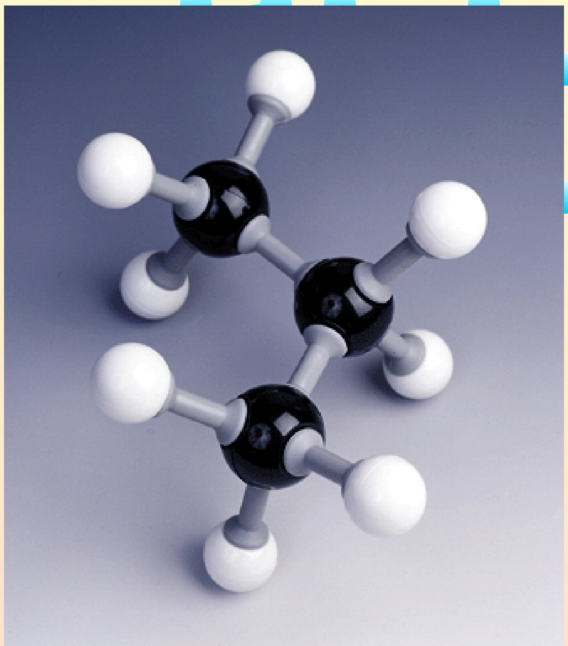
methane



ethane

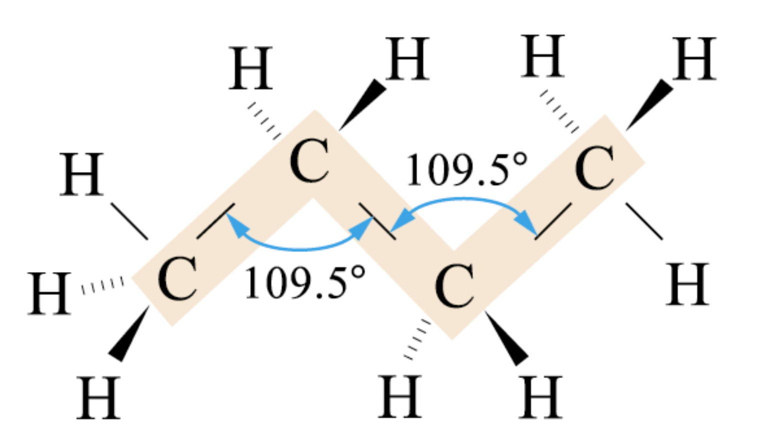


propane



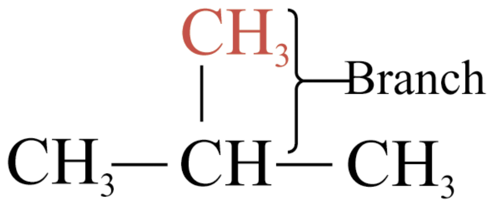
- All carbon atoms are ***sp*^3^-hybridized**
- All bond angles are **109.5°**

- The term "straight chain" is somehow misleading
- The carbon chain is actually **zigzag** in shape

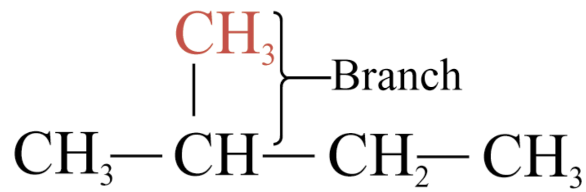


Branched-chain alkane is the molecule with carbon atoms present in **more than one continuous carbon chain**

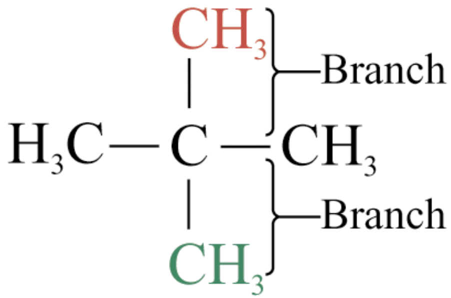
e.g.



Methylpropane



2-Methylbutane



Dimethylpropane

Straight-Chain Alkanes

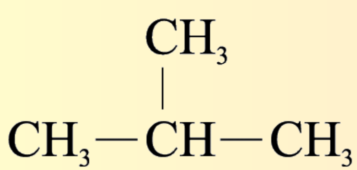
Name	Number of carbon atoms	Structure
Methane	1	CH_4
Ethane	2	CH_3CH_3
Propane	3	$CH_3CH_2CH_3$
Butane	4	$CH_3(CH_2)_2CH_3$
Pentane	5	$CH_3(CH_2)_3CH_3$
Hexane	6	$CH_3(CH_2)_4CH_3$
Heptane	7	$CH_3(CH_2)_5CH_3$
Octane	8	$CH_3(CH_2)_6CH_3$
Nonane	9	$CH_3(CH_2)_7CH_3$
Decane	10	$CH_3(CH_2)_8CH_3$

Branched-Chain Alkanes

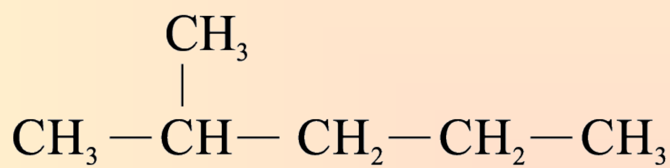
1. Select the longest possible straight chain; this gives the parent name for the alkane
2. Number the parent chain beginning with the end of the chain nearer the branched chain
3. Use the number obtained by application of rule 2 to designate the position of the branched chain
4. When two or more branched chains are present, give each branched chain a number corresponding to its position on the parent chain

5. When two or more branched chains are identical, indicate this by the use of the prefixes 'di-', 'tri-', 'tetra-', and so on.

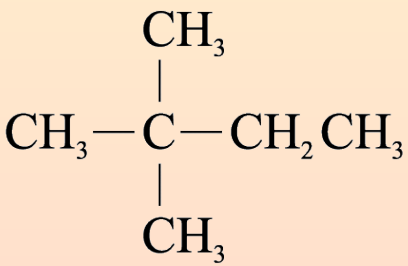
e.g.



Methylpropane



2-Methylpentane



2, 2-Dimethylbutane

Example 29-1

Draw the structure of the following compound. Is the name

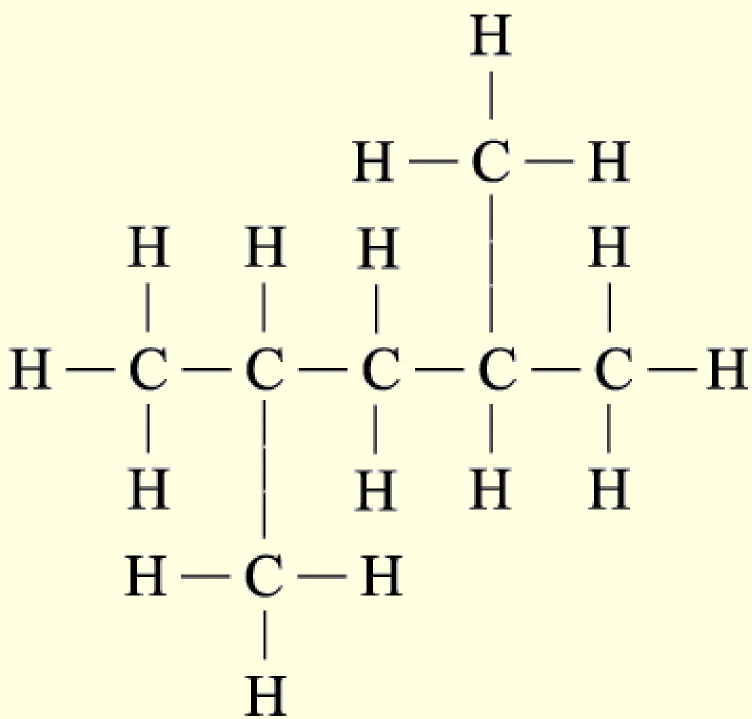
pr

na

(a

Solution:

(a)



The name is correct.

Example 29-1

Draw the structure of the following compound. Is the name

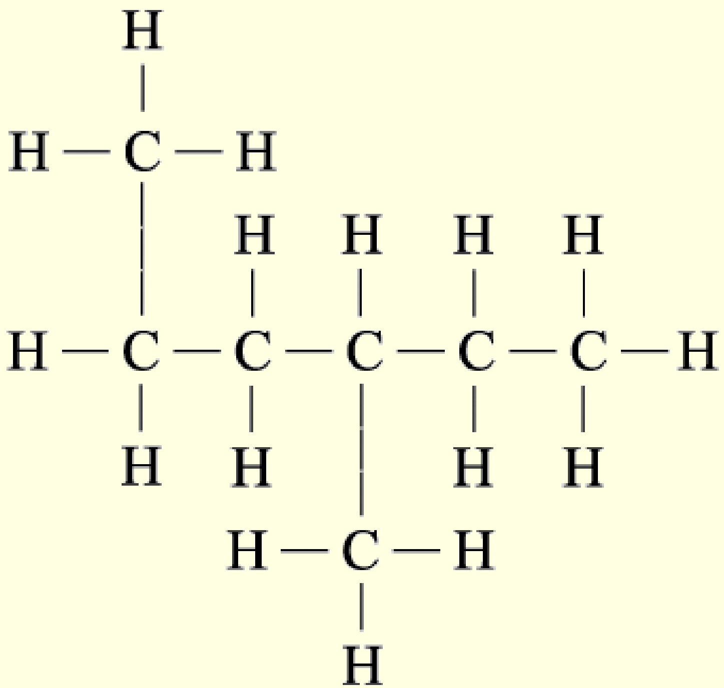
p

n

(

Solution:

(b)



The name is incorrect.

The correct name is

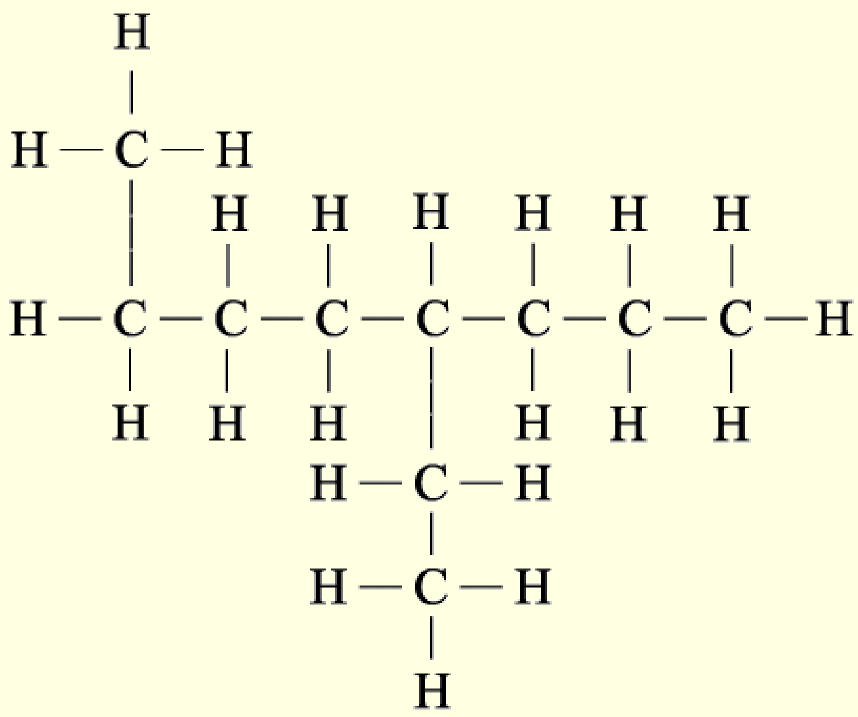
3-methylhexane.

Example 29-1

Draw the structure of the following compound. Is the name
p
n
(c

Solution:

(c)



The name is incorrect.

The correct name is

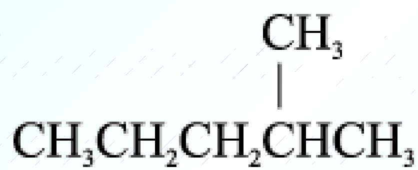
4-ethyloctane.

Check Point

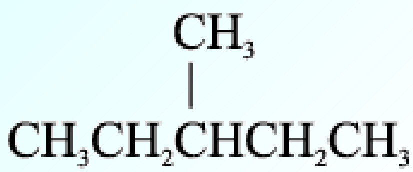
Draw ... ive
the I...

$CH_3CH_2CH_2CH_2CH_2CH_3$

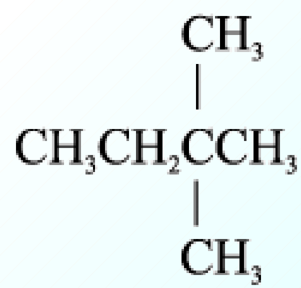
Hexane



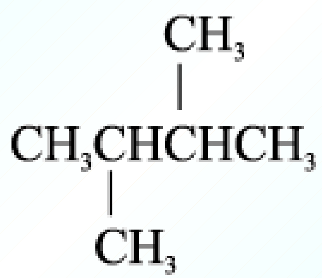
2-Methylpentane



3-Methylpentane



2,2-Dimethylbutane

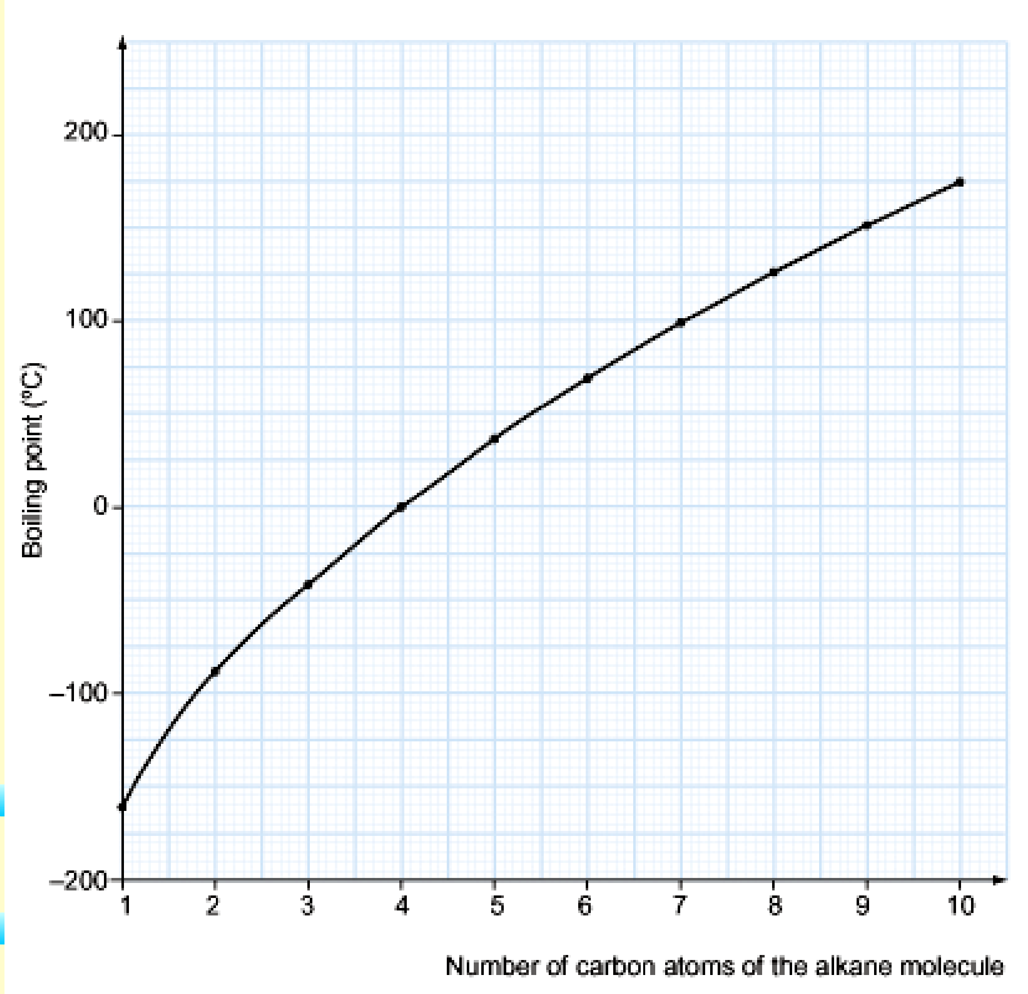


2,3-Dimethylbutane

Number of carbon atom(s)	Straight-chain alkane	Boiling point (°C)	Melting point (°C)	Density at 20°C (g cm^{-3})
1	Methane	–161	–183	—
2	Ethane	–89	–172	—
3	Propane	–42	–188	—
4	Butane	0	–135	—
5	Pentane	36	–130	0.626
6	Hexane	69	–95	0.657
7	Heptane	98	–91	0.684
8	Octane	126	–57	0.703
9	Nonane	151	–54	0.718
10	Decane	174	–30	0.730

- At R.T., $C_1 – C_4$: gases ; $C_5 – C_{17}$: liquids ; > C_{18}: waxy solid

Boiling Point

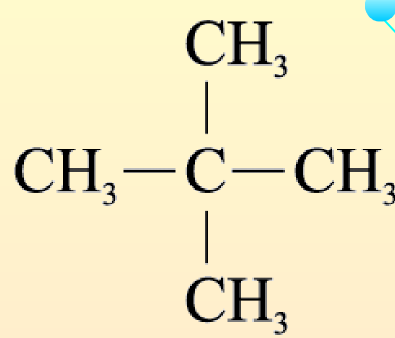


- Higher members have higher boiling points

Reason:

- **Increase in molecular mass**
- **Increase in intermolecular force**

$CH_3CH_2CH_2CH_2CH_3$

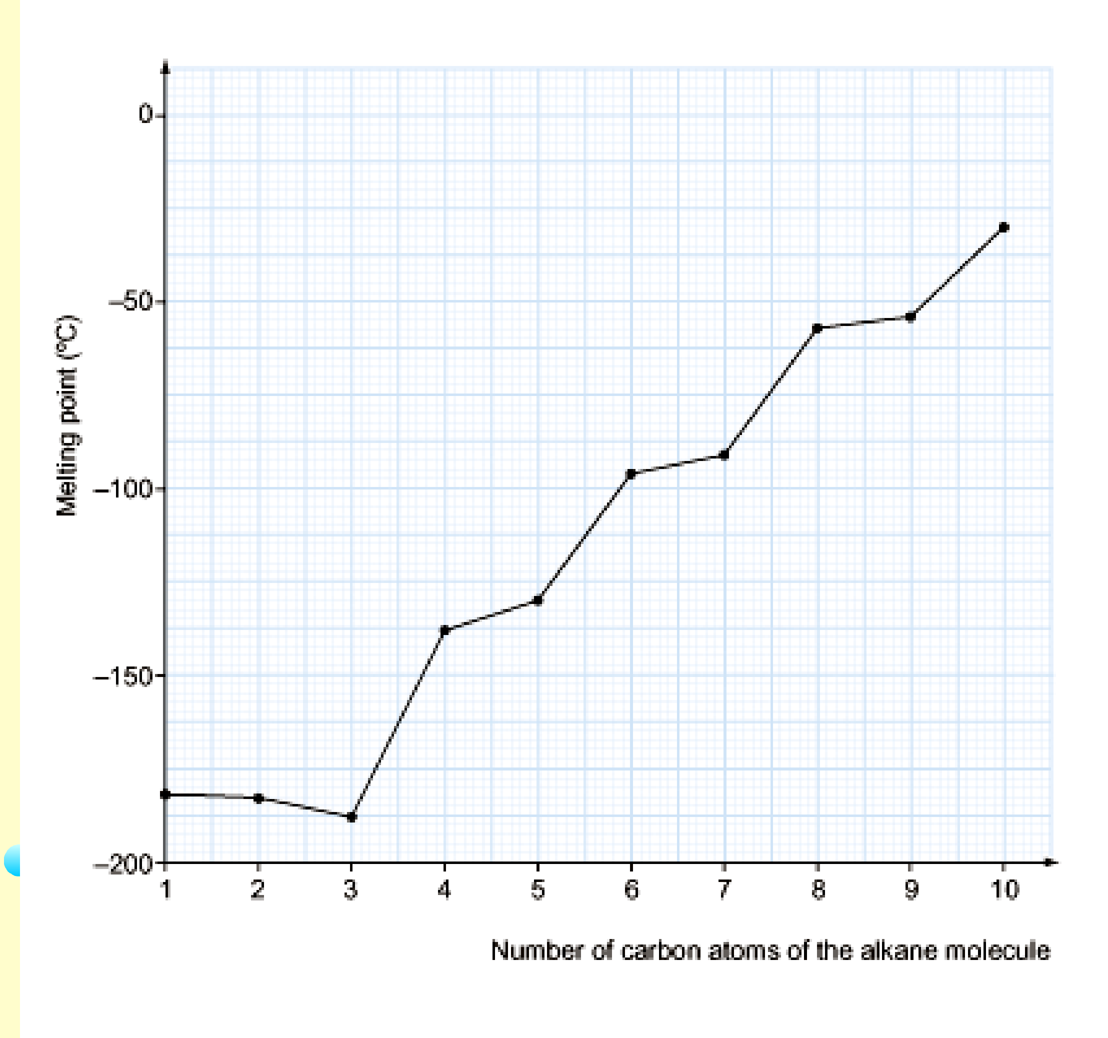


Pentane	Dimethylpropane
b.p. = 36°C	b.p. = 9.5°C
m.p. = −130°C	m.p. = −15.9°C

Branched-chain alkanes have lower boiling points than straight-chain alkanes

∵ molecule is more compact ⇒ surface area ↓
⇒ van der Waals' force ↓ ⇒ boiling point ↓

Melting Point



- Higher members have higher melting points

Reason:

- **Increase in molecular mass**
- **Increase in intermolecular force**

Density

All alkanes and cycloalkanes have densities **less than 1 g cm^{-3}** at 20°C.

⇒ Petroleum floats on water surface

Solubility

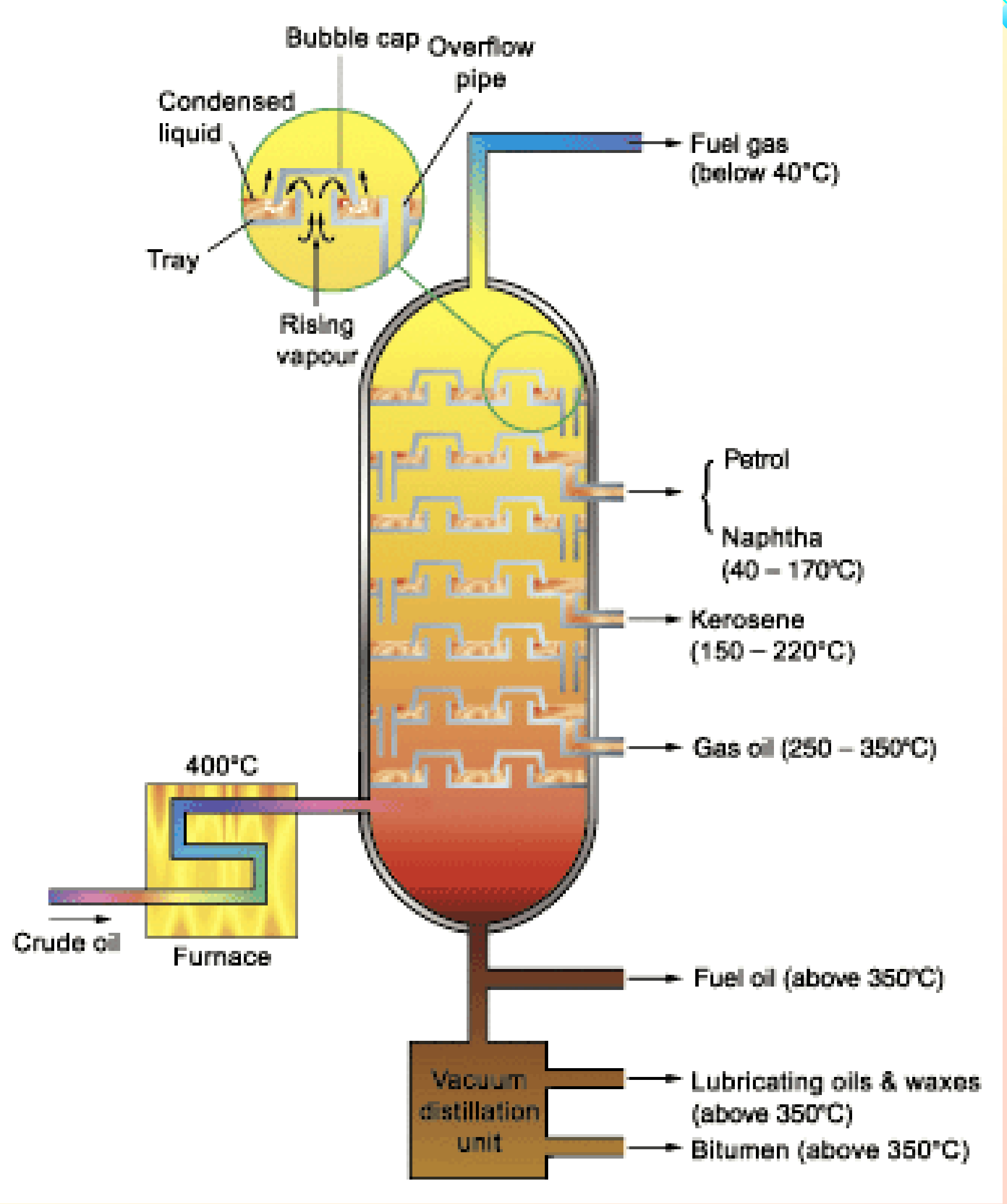
Alkanes:

- **non-polar** compounds
- insoluble in water and highly polar solvents
- **soluble in non-polar solvents** like benzene, 1,1,1-trichloroethane

Petroleum Refining

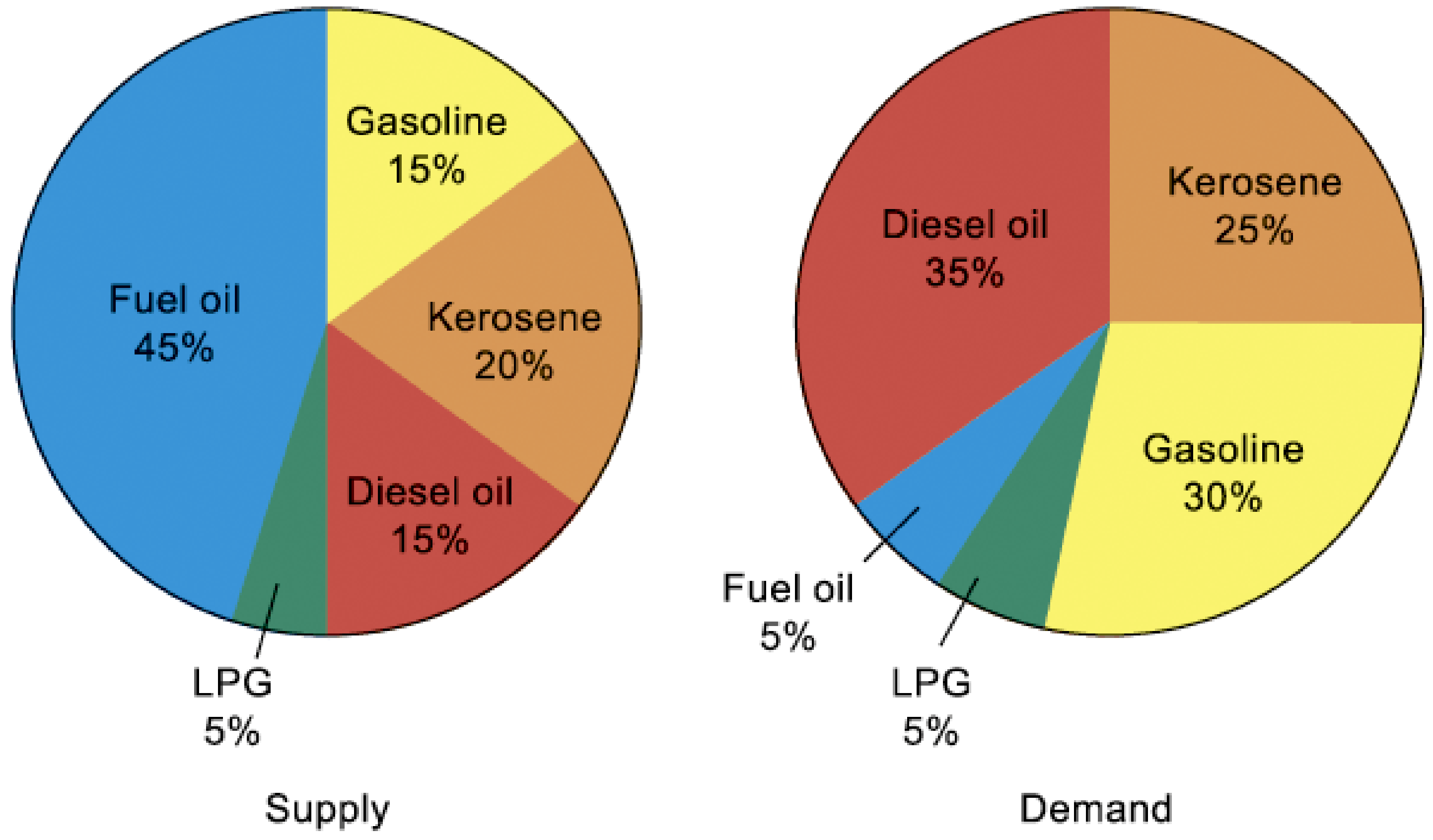
- 1st step: **fractional distillation**
- Petroleum is **separated into different fractions in the fractionating tower**
- Each fraction is a **simple mixture** and has **specific uses**

Simplified diagram of fractionating tower:



Fraction	Boiling point range (°C)	Number of carbon atoms that the molecules contain	Major uses
Fuel gas	< 40	1 – 4	As gaseous fuel, raw materials for manufacture of chemicals
Petrol	40 – 150	5 – 10	Fuel for motor vehicles
Naphtha			Fuel for manufacture of town gas
Kerosene	150 – 220	10 – 14	Fuel for aeroplanes, domestic liquid fuel
Gas oil	220 – 350	14 – 25	Fuel for trucks, lorries and locomotives
Fuel oil	> 350	> 25	Fuel for cargo ships and to generate electricity in power stations
Lubricating oil	> 350	> 25	Lubricating oil for moving parts of machinery
Bitumen	> 350	> 25	For surfacing roads and roofs

Cracking of Petroleum



Cracking is the process of **breaking down of large alkane molecules** in the heavier fractions of petroleum into lighter fractions of smaller molecules in the **absence of air**

e.g. $C_{11}H_{24} \longrightarrow C_9H_{20} + CH_2 = CH_2$

$C_{14}H_{30} \longrightarrow C_8H_{18} + 2CH_2 = CH_2 + 2C + 2H_2$

Catalytic cracking :

in the presence of catalyst, smaller and highly branched hydrocarbons formed

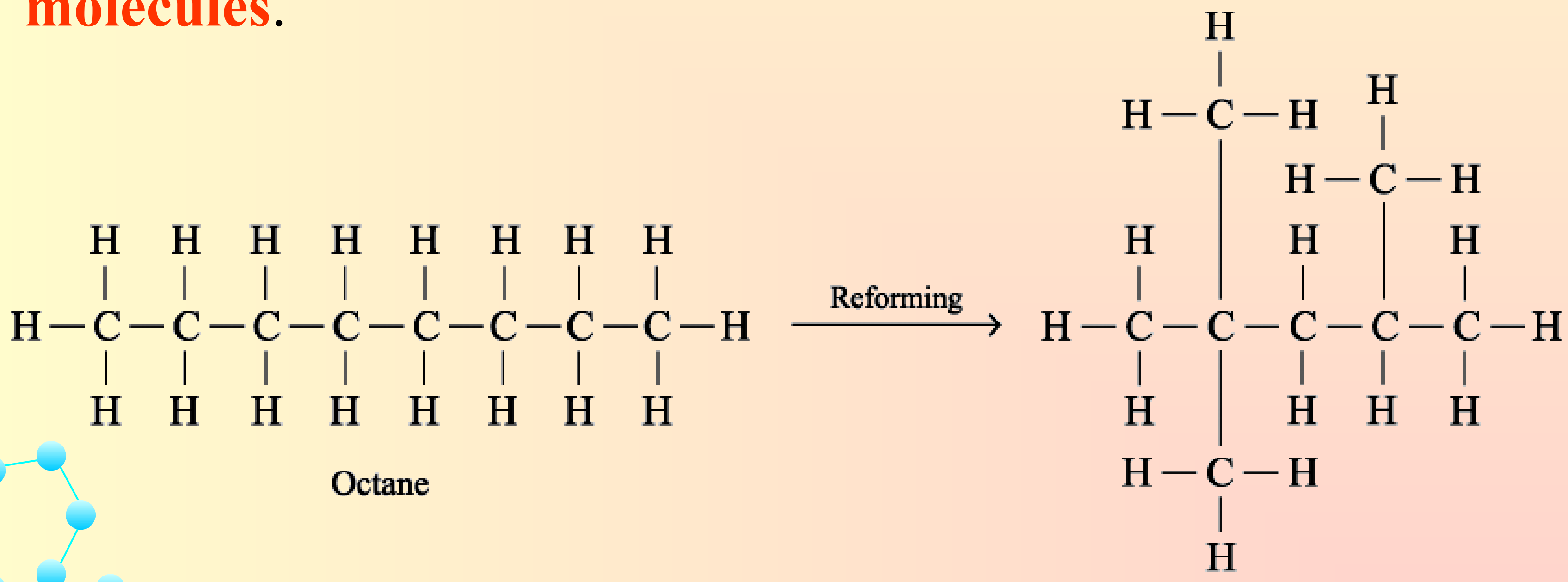
Thermal cracking :

in the absence of catalyst, unbranched chains formed

Cracking tower

Reforming

Reforming is a process in which **straight-chain alkanes** are heated under pressure in the presence of a platinum catalyst. The chains **break up and reform to give branched-chain molecules**.



Octane

2,2,4-Trimethylpentane

Example 29-2

Solution:

(a) Catalytic cracking is the process in which a mixture of alkanes from the heavier fractions is heated at very high temperatures, in the presence of catalysts and the absence of air, to form smaller, highly branched hydrocarbons.
For example,

$$C_8H_{18} \longrightarrow C_5H_{12} + C_3H_6$$

(b) Thermal cracking is the breakdown of large alkane molecules in the heavier fractions to lighter fractions of smaller molecules in the absence of catalysts and air. Straight-chain alkanes are usually formed in this process.
For example,

$$C_{14}H_{30} \longrightarrow C_8H_{18} + 2CH_2 = CH_2 + 2C + 2H_2$$

Solution:

(c) Reforming is a process in which straight-chain alkanes are heated under pressure in the presence of a platinum catalyst. The chains break up and reform to give branched-chain molecules.

For example,

$$CH_3(CH_2)_6CH_3 \xrightarrow{\text{reforming}} CH_3C(CH_3)_2CH_2\underset{}{\overset{\overset{CH_3}{|}}{C}}HCH_3$$

Combustion

Complete combustion :

Alkanes react with **sufficient oxygen** to give carbon dioxide and water through a complex series of reaction with the **release of a large amount of energy**.

General formula:

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

Methane: main component of natural gas and domestic gas

Butane: component of bottle gas

Combustion reaction: **free radical reaction**

The energy released during combustion dominates a large part of world's **transport**, **industry** and **domestic heating**

In the **limited supply of oxygen**, alkanes burn to give **CO(g)** and **carbon particles**

$$C_4H_{10}(g) + \left(\frac{7}{2}\right)O_2(g) \longrightarrow 2CO(g) + 2C(s) + 5H_2O(l)$$

Chlorination

- Methane reacts with chlorine **under diffuse sunlight** or **heating** but not in dark

- A **mixture of products** (CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4) is formed with the **replacement of hydrogen by one or more chlorine atom**

$$CH_4(g) + Cl_2(g) \xrightarrow{\text{UV light}} CH_3Cl(g) + HCl(g)$$

$$CH_3Cl(g) + Cl_2(g) \xrightarrow{\text{UV light}} CH_2Cl_2(g) + HCl(g)$$

$$CH_2Cl_2(g) + Cl_2(g) \xrightarrow{\text{UV light}} CHCl_3(g) + HCl(g)$$

$$CHCl_3(g) + Cl_2(g) \xrightarrow{\text{UV light}} CCl_4(g) + HCl(g)$$

- **If methane is in excess, CH_3Cl is major product**

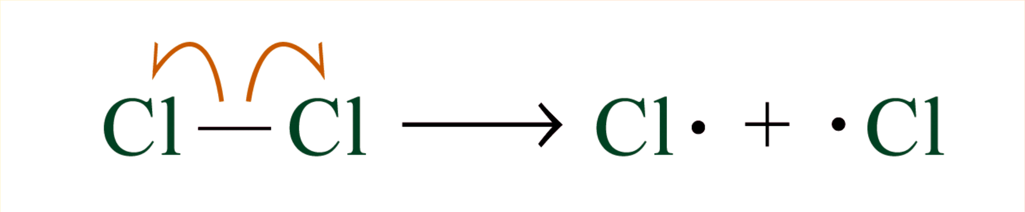
- **If chlorine is in excess, CCl_4 is major product**

Reaction Mechanism: Free Radical Substitution Reaction

Mechanism of reaction :

1. *Chain initiation*

- homolytic fission of chlorine molecules by heat or light into two chlorine radicals
  Step 1:



2. *Chain propagation*

Step 2:

$$H_3C—H + \cdot Cl \longrightarrow H_3C\cdot + H—Cl$$

Methyl radical

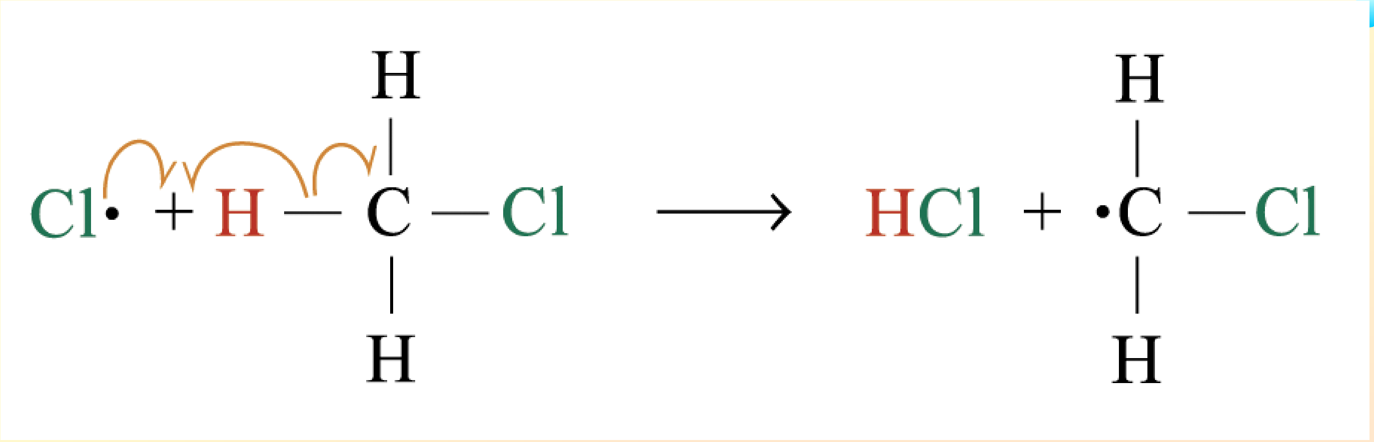
Step 3:

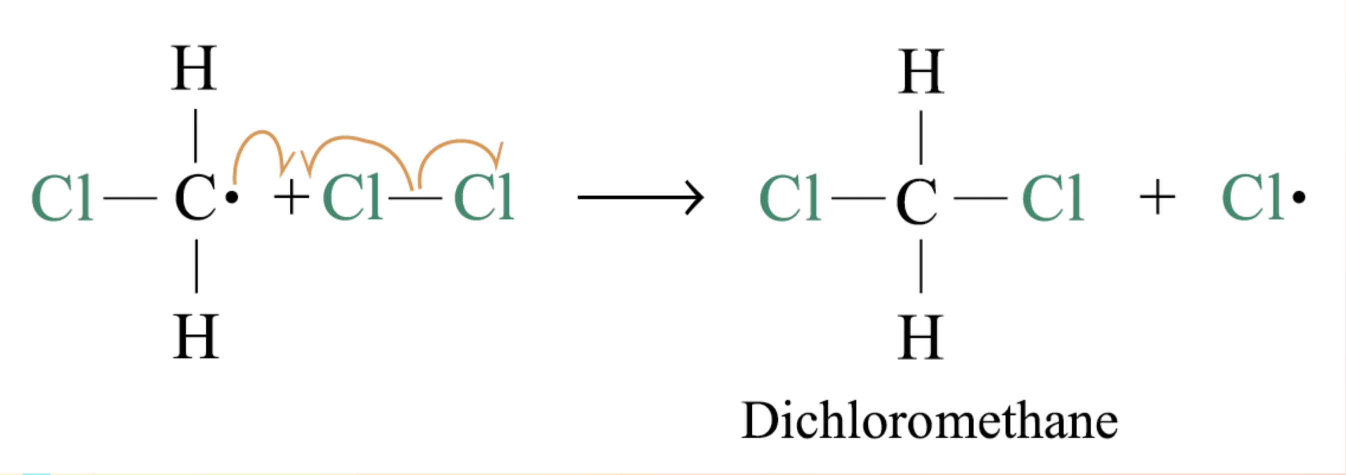
$$Cl—Cl + \cdot CH_3 \longrightarrow CH_3—Cl + \cdot Cl$$

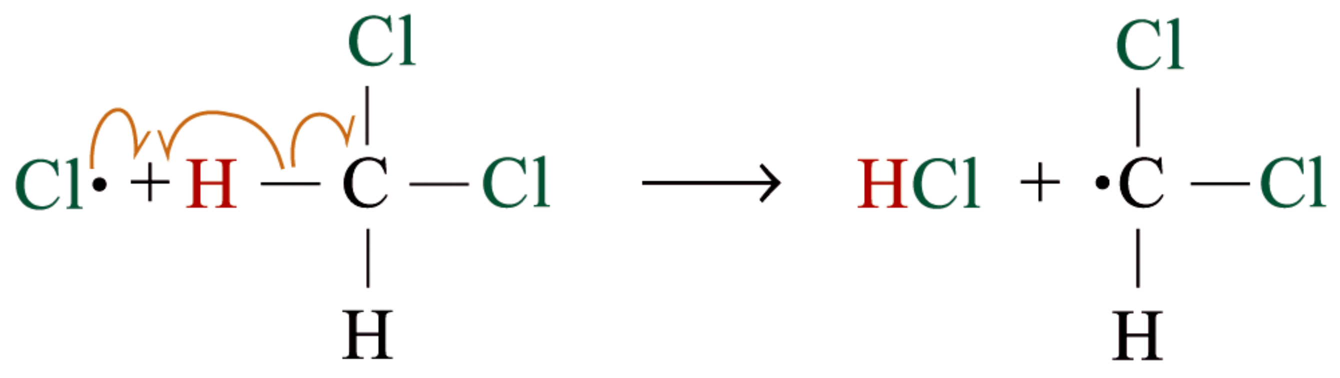
Chloromethane

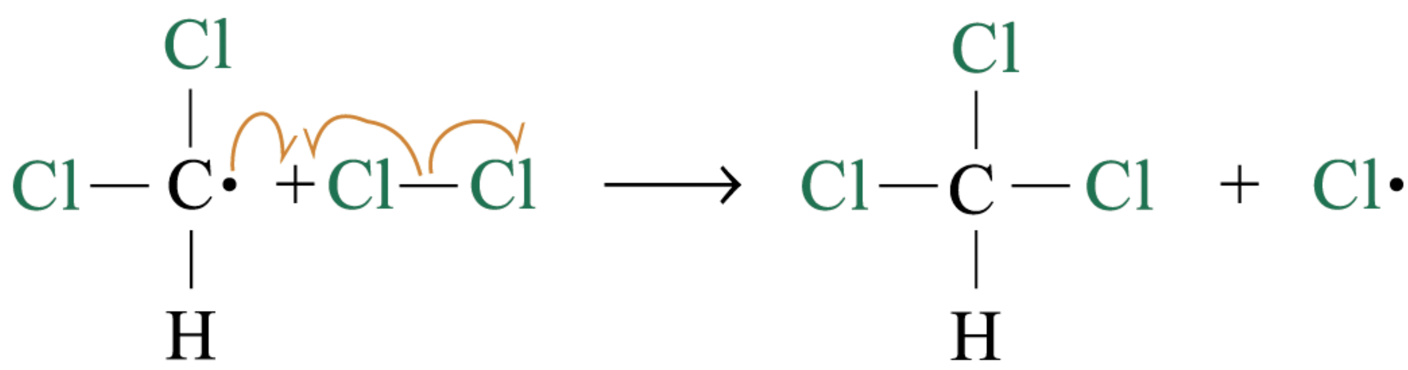
- steps 2 and 3 repeat hundreds or thousands of time due to formation of the **reactive intermediate** in each step
  $\Rightarrow$ **chain reaction**

Further substitution occurs:

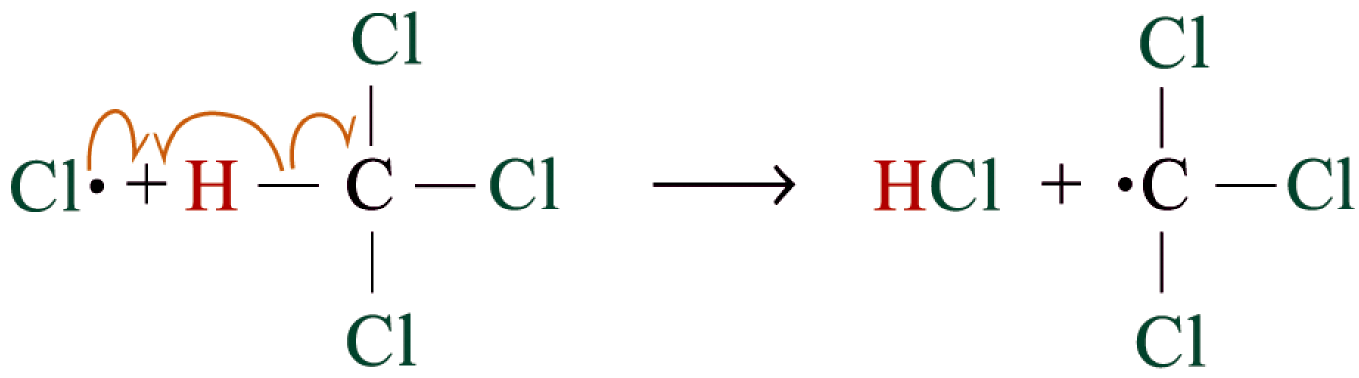


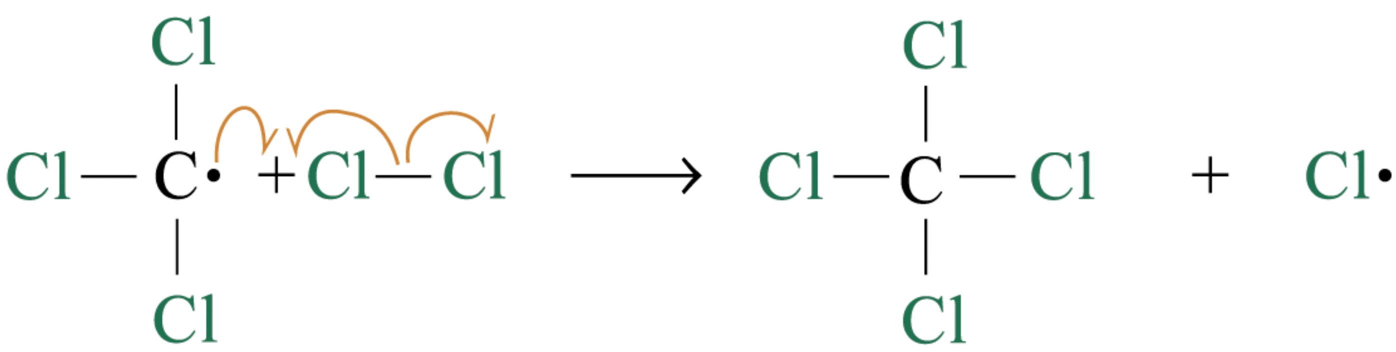






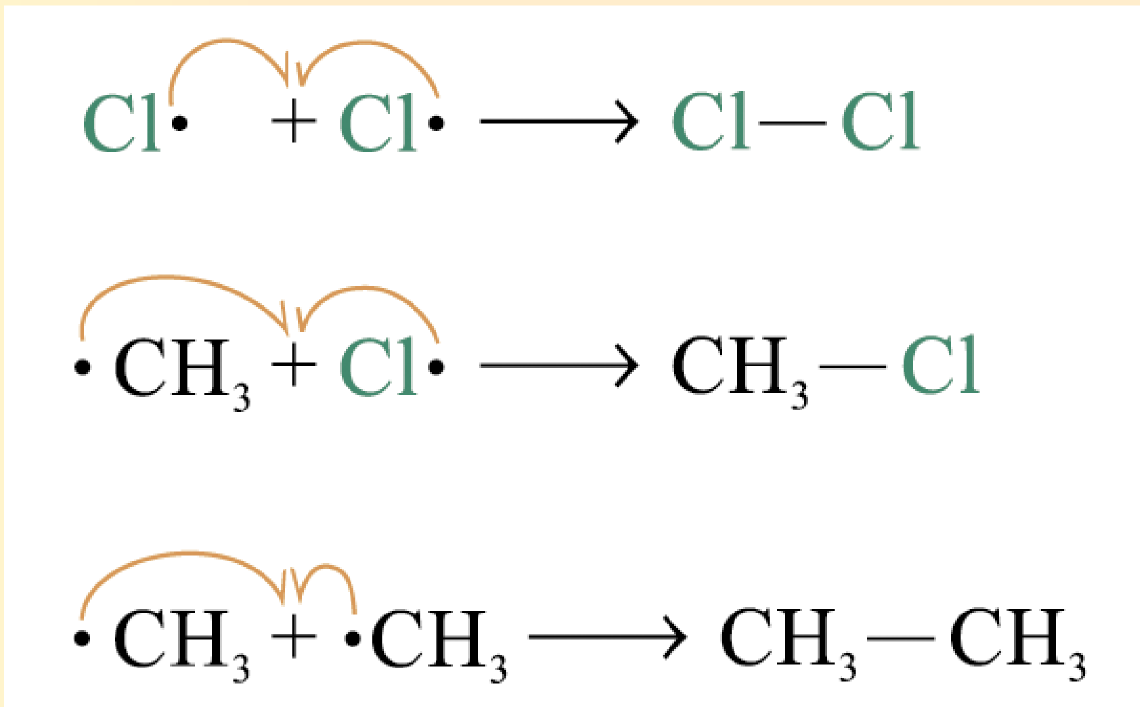
Trichloromethane


Cl• + H — CCl3 → HCl + •CCl3


Cl3C• + Cl — Cl → CCl4 + Cl•
Tetrachloromethane

3. *Chain termination*

- **two free radicals combine** to form a **neutral molecule**
- the chain reaction is terminated



Solution:

The reaction mechanism is shown as follows:

1. Chain initiation

$$Cl{-}Cl \longrightarrow Cl\bullet + \bullet Cl$$

2. Chain propagation

$$Cl\bullet + H{-}CH_2CH_3 \longrightarrow HCl + \bullet CH_2CH_3$$

$$CH_3CH_2\bullet + Cl{-}Cl \longrightarrow CH_3CH_2Cl + Cl\bullet$$

Solution:

3. Chain termination

$$Cl\cdot + Cl\cdot \longrightarrow Cl - Cl$$

$$CH_3CH_2\cdot + Cl\cdot \longrightarrow CH_3CH_2 - Cl$$

$$CH_3CH_2\cdot + CH_3CH_2\cdot \longrightarrow CH_3CH_2 - CH_2CH_3$$

(a) Cracking must be carried out in the absence of air because combustion occurs instead of cracking in the presence of air.

(b) Let the molecular formula of the alkane be C_nH_{2n+2}.

$$\text{Relative molecular mass of the alkane} = 72$$

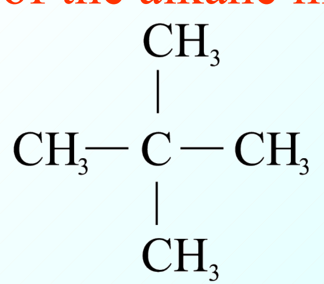
$$12.0 \times n + 1.0 \times (2n + 2) = 72$$

$$n = 5$$

∴ The alkane has the molecular formula of C_5H_{12}.

As the alkane produces one product only on monochlorination, all hydrogen atoms of the alkane molecule must be equivalent.

∴ It must be



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