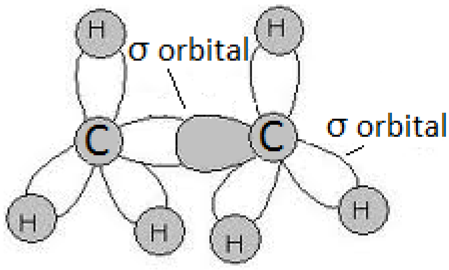
Chapter 16a (AS-Level)

Hydrocarbons: Alkanes

The physical properties of alkanes

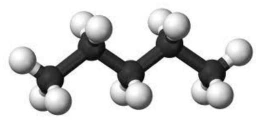
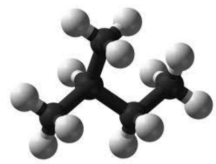
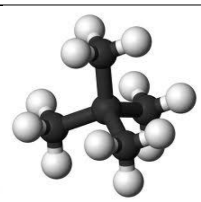
The homologous series of the alkanes have the following properties:

- They have a general formula of C_NH_{2N+2}
- They are non-polar molecules with only C-H and C-C bonds
- All the C-C bonds are single bonds so the alkanes are described as saturated hydrocarbons
- The atoms in the alkanes are held together by σ orbitals, which forms the axis between the 2 carbon nuclei and is formed by the overlap of 2 atomic σ-orbitals
- The 2 electrons in the σ (sigma) orbital attract both nuclei, binding them together in a σ-bond
- The σ bond lies between the carbon atoms and either a hydrogen and carbon atoms. All the bond angles are 109.5°
- The atoms in the molecule can rotate freely about each C-C bond. This freedom to rotate gives great flexibility to the alkane chains.



- The physical states of the alkanes at room temperature and pressure changes form gases to liquids to solids as the number of carbon atoms in the molecule increases.
  The volatility of the alkanes decreases as the number of the carbon atoms increases.

The below table shows the boiling points for pentane and isomers of pentane:

Alkane	Structural formula	Boiling point (°K)	Space filling model
Pentane	$CH_3CH_2CH_2CH_2CH_3$	309	
2-methylbutane	CH_3 (on C-2) $CH_3CHCH_2CH_3$	301	
2,2-dimethylpropane	CH_3 CH_3CCH_3 CH_3	283	

As the number of branches in the chain increases, the boiling point decreases. All the isomers have the same number of atoms, so the trend cannot be explained using the number of electrons.

As the isomers become more branched, the overall shape of the molecule becomes from the long balloon shape of pentane to the spherical shape of 2,2-dimethylpropane. The long balloon shape of pentane allows it to get closer to other pentane molecules than 2,2-dimethylpropane.

The intermolecular forces increase when the molecules can approach each other and this is the case with pentane, which is way it has a higher boiling point than the other isomers as they cannot approach each other enough.

Chemical properties of alkanes

Combustion in air

Alkanes make excellent fuels. Complete combustion in air produces carbon dioxide and water. For example, the combustion of butane:

$$C_4H_{10}\ (g) + 6\tfrac{1}{2}\ O_2\ (g) \rightarrow 4\ CO_2\ (g) + 5\ H_2O\ (g)$$

The incomplete combustion of butane in an insufficient amount of oxygen produces carbon monoxide and water instead of carbon dioxide:

$$C_4H_{10}\ (g) + 4\tfrac{1}{2}\ O_2\ (g) \rightarrow 4\ CO\ (g) + 5\ H_2O\ (g)$$

Carbon monoxide is a toxic gas as it has no smell and colour and readily bonds to the iron groups of haemoglobin in the blood. This causes the haemoglobin to become unable to carry oxygen which may cause death in serious cases.

The substitution reaction of alkanes

Alkanes are inert compounds as they are non-polar. The carbon and hydrogen in the alkanes have very similar electronegativities and so they are non-polar.

This also means that they are not attacked by common chemical reagents like acids, alkalis, water, etc. which are highly polar, and initiate the reaction by their attraction to the polar groups. These polar reagents don't react with the alkanes.

Some non-polar reagents will react with the alkanes. These include the group IV elements chlorine, bromine, etc. that will react with alkanes under ultraviolet light, which will substitute the hydrogen atoms in the alkane with halogen atoms.

For example, when chlorine is mixed with methane under UV light, chloromethane is formed and hydrogen chloride gas is evolved:

$$CH_4\ (g) + Cl_2\ (g) \rightarrow CH_3Cl\ (g) + HCl\ (g)$$

This is a photochemical reaction as it requires UV light to begin.

Further substitution is possible, in turn producing dichloromethane, trichloromethane and tetrachloromethane.

The substitution mechanism

The sequence of the stages in a reaction is called the reaction mechanism. In this reaction, energy from ultraviolet light has to be absorbed to break the Cl-Cl bond. This is called photodissociation. Homolytic fission occurs and 2 free radicals of chlorine form. As homolytic fission of chlorine has to occur first, so it is the initiation step.

$$Cl\text{-}Cl\ (g) \rightarrow Cl^{\cdot}\ (g) + Cl^{\cdot}\ (g)$$

The reaction of a chlorine free radical with a methane molecule produces hydrogen chloride and a methyl free radical.

$$Cl^{\cdot}(g) + H\text{-}CH_3\ (g) \rightarrow Cl\text{-}H\ (g) + CH_3^{\cdot}\ (g)$$

A methyl radical can react with a chlorine molecule to make chloromethane and new chlorine radical.

$$CH_3^{\cdot}(g) + Cl\text{-}Cl\ (g) \rightarrow CH_3Cl\ (g) + Cl^{\cdot}\ (g)$$

These 2 steps enable the reaction to continue. In the first step, a chlorine radical is used up. The second step releases a new chlorine free radical allowing the repetition of the first step. The reaction will continue as long as there is a supply of methane molecules and chlorine free radicals. These two steps make up a chain reaction and are known as the propagation steps of the reaction.

When the reagents are used up, no more chloromethane and hydrogen chloride are formed. The reaction can end in two ways:

- Either that the chlorine free radicals recombine to make chlorine molecules,

$$Cl^{\cdot}\ (g) + Cl^{\cdot}\ (g) \rightarrow Cl\text{-}Cl\ (g)$$

Or;

- The methyl free radicals recombine to make an ethane molecule

$$CH_3^{\cdot}\ (g) + CH_3^{\cdot}\ (g) \rightarrow CH_3CH_3\ (g)$$

These termination steps will remove the free radicals and disrupt the propagation steps and stopping the chain reaction. The following steps make up the reaction mechanism:

- Initiation,
- 2 propagation steps,
- And one of the termination steps

As the reaction is a substitution reaction involving free radicals, it is called a free-radical substitution.

END OF LESSON