10 Extension Topic – Organic Chemistry Alkanes

GUIDING QUESTIONS

- Why are alkanes generally unreactive, particularly towards polar reagents?
- Which class of reagents do alkanes react with and why?
- What type of reactions do alkanes undergo and why?
- How do alkanes react with halogens?
- What are the environmental concerns arising from the use of hydrocarbons?

LEARNING OUTCOMES

At the end of the chapter, you should be able to:

11.3 (a) explain the general unreactivity of alkanes, including towards polar reagents

11.3 (b) describe the chemistry of alkanes as exemplified by the following reactions of ethane:
  - **(i)** combustion
  - **(ii)** free-radical substitution by chlorine and by bromine

11.3 (c) describe the mechanism of free-radical substitution with particular reference to the initiation, propagation and termination reactions

11.3 (n) recognise the environmental consequences of:
  - **(i)** carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine and of their catalytic removal
  - **(ii)** gases that contribute to the enhanced greenhouse effect

11.3 (o) recognise that petroleum, a chemical feedstock, is a finite resource and the importance of recycling

REFERENCES

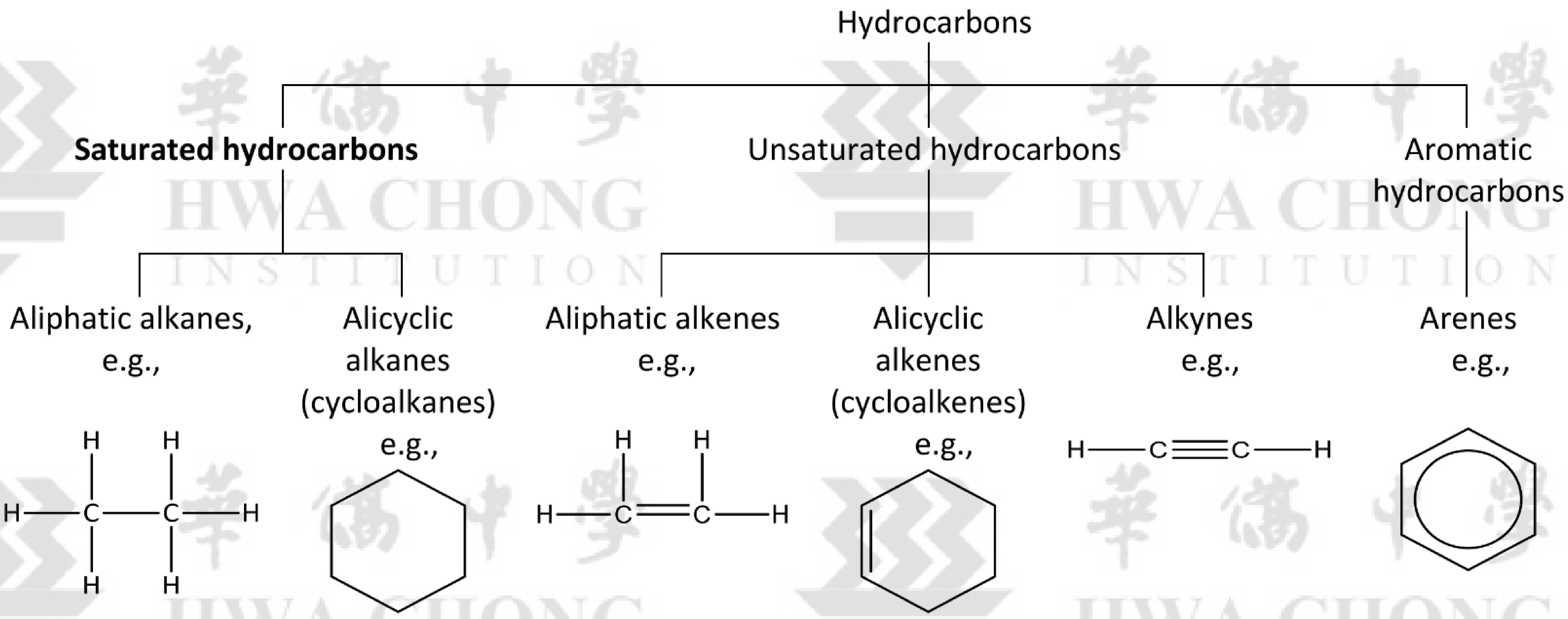
1. Peter Cann and Peter Hughes, *Cambridge International AS and A level Chemistry*, Hodder Education, Chapter 13.
2. John McMurry, *Organic Chemistry*, 6th ed., Thomson/Brooks/Cole, Chapters 3, 5 and 10.
3. Jonathan Clayden, Nick Greeves and Stuart Warren, *Organic Chemistry*, 2nd Ed., Oxford University Press, Chapter 37.

1 INTRODUCTION

Alkanes are the simplest and least reactive of the homologous series found in organic chemistry. The only two types of bonds contained in alkanes, C–C and C–H, are strong and non-polar. The C–C and C–H bonds are essentially non-polar due to similarity in electronegativities and hence unreactive towards polar reagents.

- They are often described as saturated hydrocarbons:
  Hydrocarbon – contains only carbon and hydrogen
  Saturated – contains only single bonds (i.e. only C–C and C–H single bonds for alkanes), hence each carbon has four bonds.

The chart below describes different types of hydrocarbons and some examples of them.



- Alkanes contain only sp^3 hybridised carbon atoms.

- Aliphatic alkanes contain open chains of carbon atoms which may be straight–chain or branched.

  In straight–chain alkanes, the carbon atoms are connected in a continuous line, whereas in branched alkanes the carbon atoms may be connected to two or three other carbon atoms.

- Cycloalkanes contain closed rings of carbon atoms.

Self-Practice 1.1

(a) Write the general formula of aliphatic alkanes and cycloalkanes.

(b) Which class of compounds is isomeric with cycloalkanes?

2 NOMENCLATURE

2.1 Straight-chain alkanes

Straight–chain alkanes are named according to the number of carbon atoms in their chain with an –***ane*** suffix.

Examples

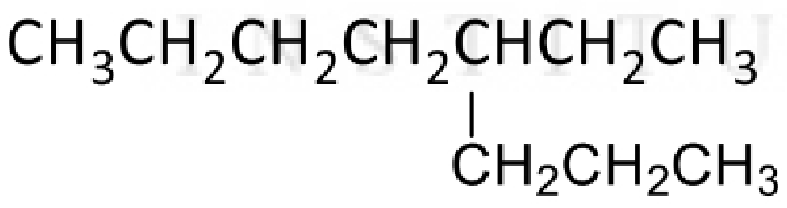
Number of carbons (*n*)	**Name**	**Formula (C_nH_{2n+2})**	**Number of carbons (*n*)**	**Name**	**Formula (C_nH_{2n+2})**
1	**Meth**ane	CH_4	6	**Hex**ane	C_6H_{14}
2	**Eth**ane	C_2H_6	7	**Hept**ane	C_7H_{16}
3	**Prop**ane	C_3H_8	8	**Oct**ane	C_8H_{18}
4	**But**ane	C_4H_{10}	9	**Non**ane	C_9H_{20}
5	**Pent**ane	C_5H_{12}	10	**Dec**ane	$C_{10}H_{22}$

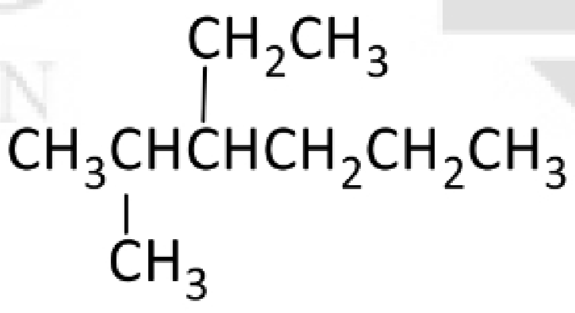
Table 1. Names of straight-chain alkanes

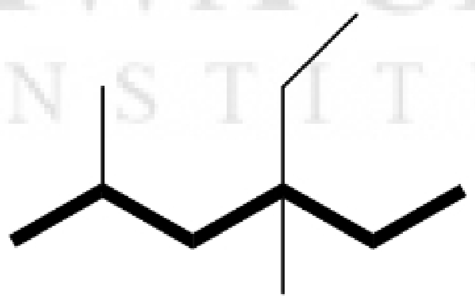
2.2 Branched (or substituted) alkanes

1. Locate the longest continuous chain of carbon atoms; this chain determines the parent name for the alkanes.
2. Number the longest chain beginning with the end of the chain nearer to the substituent, if any.
3. Use the numbers obtained by application of rule no. 2 to designate the location of the substituent group.
4. When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain. Cite them in alphabetical order. The number prefixes *di*-, *tri*-, *tetra*-, etc. are ignored in alphabetizing (refer to point 6).
5. When two substituents are present on the same carbon atom, use that number twice.
6. When two or more substituents are identical, indicate this by the use of the prefixes di-, tri-, tetra- and so on.

Examples

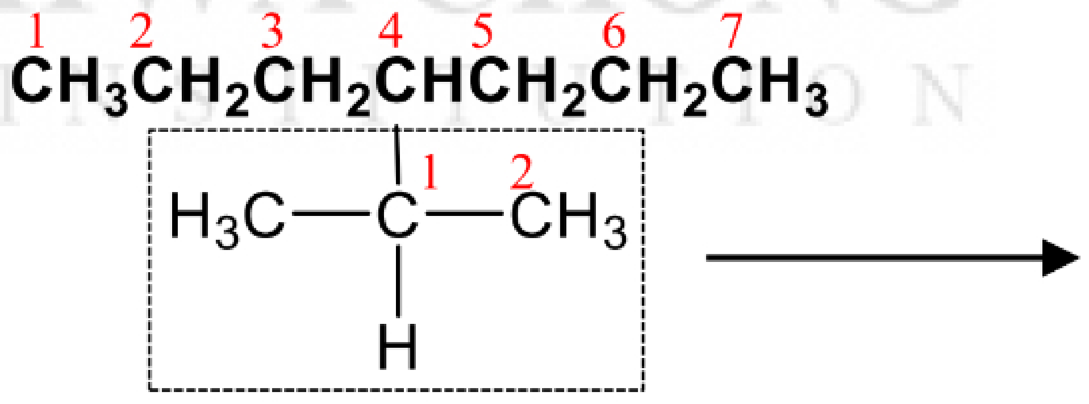

$CH_3CH_2CH_2CH_2\underset{\underset{\displaystyle CH_2CH_2CH_3}{|}}{C}HCH_2CH_3$


$CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}H\overset{\overset{\displaystyle CH_2CH_3}{|}}{C}HCH_2CH_2CH_3$



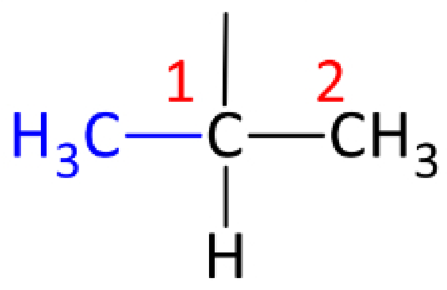
4–ethyloctane 3–ethyl–2–methylhexane 4–ethyl–2,4–dimethylhexane

In the case of a substituent also branching off, it is useful to treat the substituent separately.



4–(1–methylethyl)**heptane**

The substituent is named as it follows:



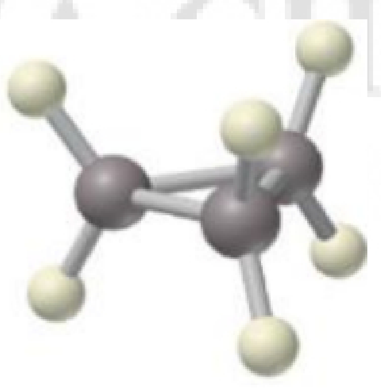
a (1–methylethyl) group

The carbon bonded to the parent chain is C1.

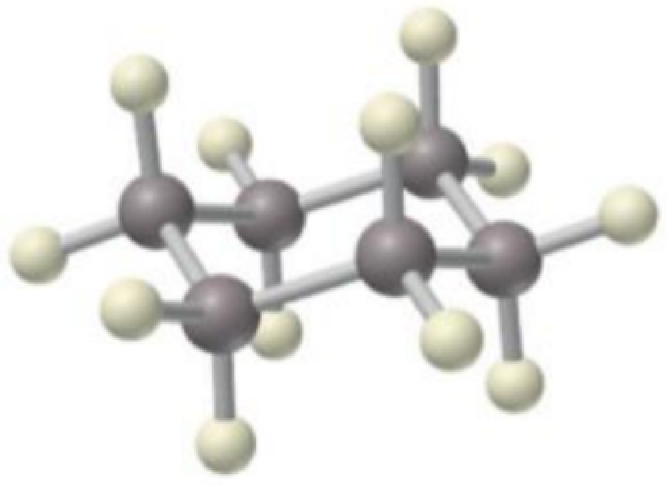
2.3 Cycloalkanes

To name a cycloalkane, add "*cyclo-*" as a prefix in front of the parent name of the corresponding alkane.

Examples



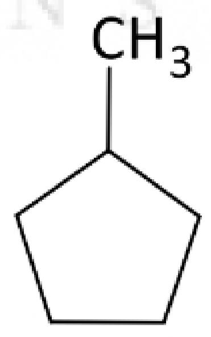
cyclopropane (C_3H_6)



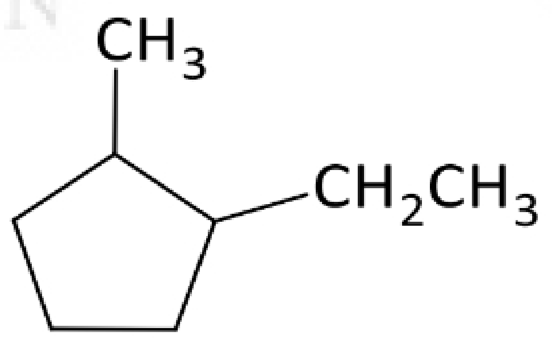
cyclohexane (C_6H_{12})

Substituted cycloalkanes are named by rules similar to those used for open–chain alkanes.

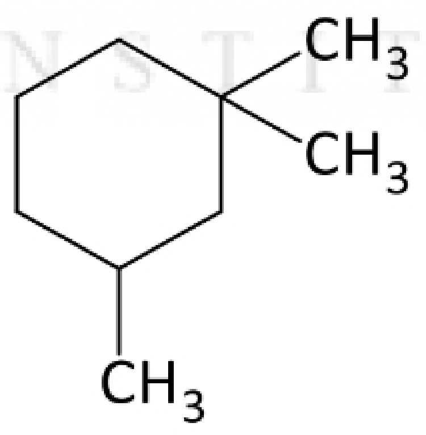
Examples



methylcyclopentane



1–ethyl–2–methylcyclopentane



1,1,3–trimethylcyclohexane

If there is just one substituent, no numbering is needed.

3 ISOMERISM

3.1 Constitutional (structural) Isomerism

Alkanes can exhibit constitutional isomerism.

The number of constitutional isomers increases dramatically as the number of carbon atoms increases. For example $C_{10}H_{22}$ has 75 and $C_{20}H_{42}$ has 366,319 constitutional isomers respectively.

Self-Practice 3.1

Draw the skeletal formulae of all the alkanes with the molecular formula of

(a) C_5H_{12}

(b) C_5H_{10}

3.2 Enantiomerism

Apart from exhibiting constitutional isomerism, some alkanes can also exhibit enantiomerism.

Self-Practice 3.2

Draw the structural formula of the alkane with the lowest M_r that can exhibit enantiomerism. Draw the mirror images of the enantiomers. *[J95/1/9(a) modified]*

4 PHYSICAL PROPERTIES

The electronegativity of carbon and hydrogen are 2.55 and 2.20 respectively. The C–H bond thus only has a very small dipole moment (considered as a non-polar bond). The molecules of alkanes are therefore non–polar and are held together mainly by weak dispersion forces.

4.1 Physical state

At room temperature and pressure, the lower alkanes, from methane to butane are gases.
The C_5–C_{17} straight–chain alkanes are liquids while those with 18 or more carbon atoms are solids.

Formula	Name	State (at r.t.p)	M_r	Melting point /°C	Boiling point /°C	Density /g cm^{-3}	Remarks (FYI only)
CH_4	methane	gas	16	–182	–162	–	major component of natural gas
C_2H_6	ethane	gas	30	–183	–89	–	component of natural gas
C_3H_8	propane	gas	44	–188	–42	–	component of liquefied petroleum gas (LPG), bottled gas
C_4H_{10}	butane	gas	58	–138	0	–	component of LPG, cigarette lighters
C_5H_{12}	pentane	liquid	72	–130	36	0.63	component of petrol
C_6H_{14}	hexane	liquid	86	–95	69	0.66	
C_7H_{16}	heptane	liquid	100	–91	98	0.68	
C_8H_{18}	octane	liquid	114	–57	126	0.70	major component of petrol

Table 2. Physical properties of some alkanes

4.2 Boiling point

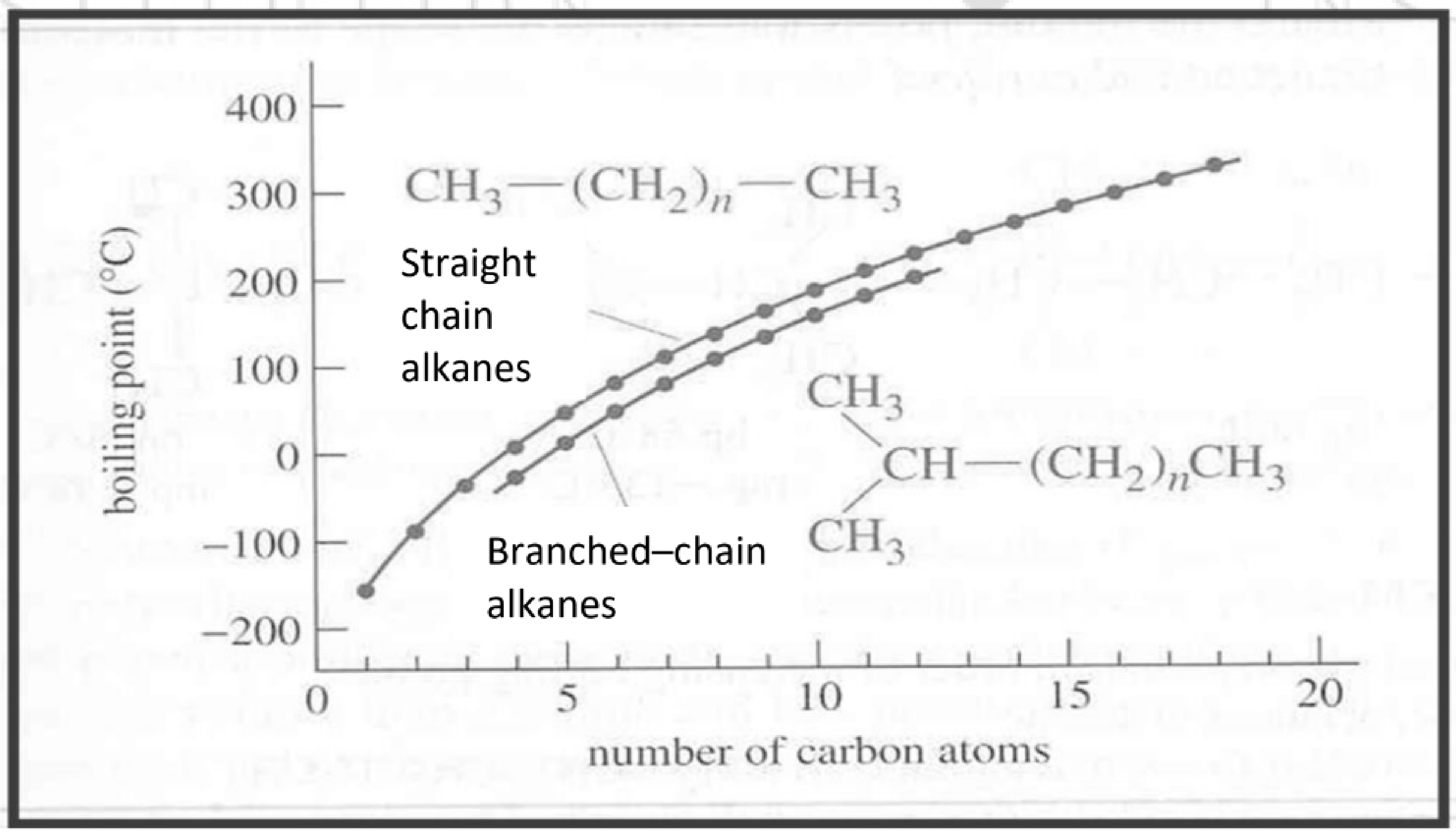
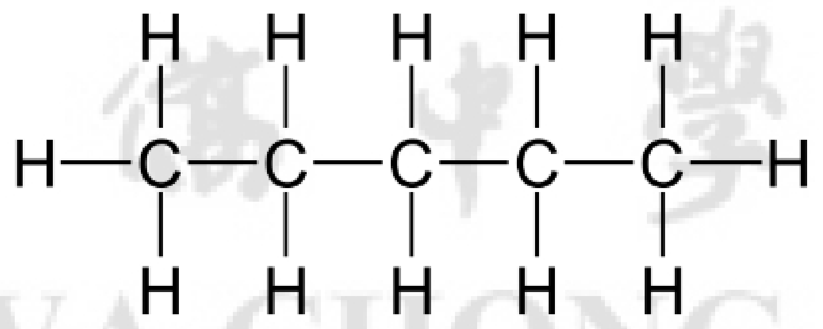


Figure 1. Boiling points of straight-chain and branched-chain alkanes

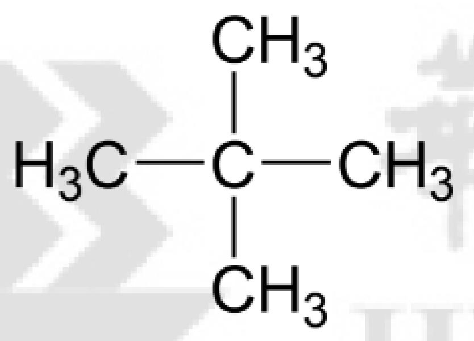
The boiling point of alkanes <u>increases regularly</u> with increasing number of carbon atoms in the chain.

As the number of carbon atoms increases, the **number of electrons in the molecule increases**, hence **size of the electron cloud increases** leading to **stronger dispersion forces** between the molecules. Thus, **more energy is required to overcome** the stronger dispersion forces between the molecules. <u>Branched–chain alkanes have lower boiling points than the straight–chain alkanes</u> with the same number of carbon atoms. Recall what you have learned in Topic 2 Chemical Bonding that explains this observation.



pentane

b.p. = 36 °C



2,2–dimethylpropane

b.p. = 9.5 °C

4.3 Melting point

The increase in melting point of alkanes is not as regular as that observed for their boiling points; this is because the dispersion forces between the molecules in a crystal depend not only on the size of the molecules but also on the arrangement of molecules in a crystal lattice. The table below illustrates the effect of structure on the melting point of four different C_6H_{14} isomers.

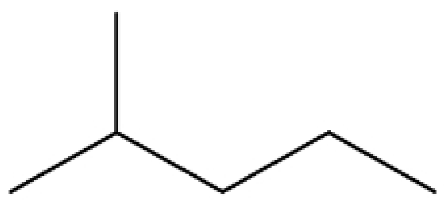
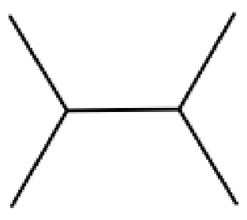
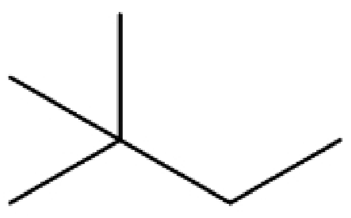
IUPAC Name	Structure	Boiling point / °C	Melting point / °C
Hexane		69	–95
2-methylpentane		60	–154
2,3-dimethylbutane		58	–135
2,2-dimethylbutane		50	–98

Table 3. Boiling and melting points of C_6H_{14} isomers

4.4 Solubility

In order for dissolution to occur, the solute molecules and the solvent molecules should have favourable intermolecular forces of attraction.

Alkanes can form favourable dispersion forces with non-polar solvents such as benzene and tetrachloromethane. Hence they are soluble in non-polar solvents.

Alkanes can only form permanent dipole-induced dipole intermolecular forces with water, which are much weaker than the hydrogen bonding between water molecules themselves (as well as the dispersion forces between alkane molecules). Hence they are insoluble in water.

4.5 Density

Liquid alkanes are less dense than water and form an immiscible layer above water.

Their densities increase slightly with increasing number of carbon atoms present. This is because the increase in the strength of dispersion forces causes the alkane molecules to attract more closely together, resulting in a slightly smaller volume of the liquid. Since ρ = m/V, with a larger relative molecular mass, the density of the liquid increases.

4.6 Viscosity

Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. The viscosity of liquid alkanes increases with increasing number of carbon atoms present as the dispersion forces between the molecules increases. In addition, longer-chain alkanes have higher viscosity as the long molecules tend to “tangle up” with one another.

Self-Practice 4.1

The following are boiling points of various alkanes given in ^{o}C and at atmospheric pressure.

Butane	Pentane	Hexane
0.5 ^{o}C	36 ^{o}C	69 ^{o}C

(a) Explain why the boiling point of butane is lower than that of pentane?

(b) Draw the structure of 2,2-dimethylbutane and predict whether it would have a higher or lower boiling point than hexane.

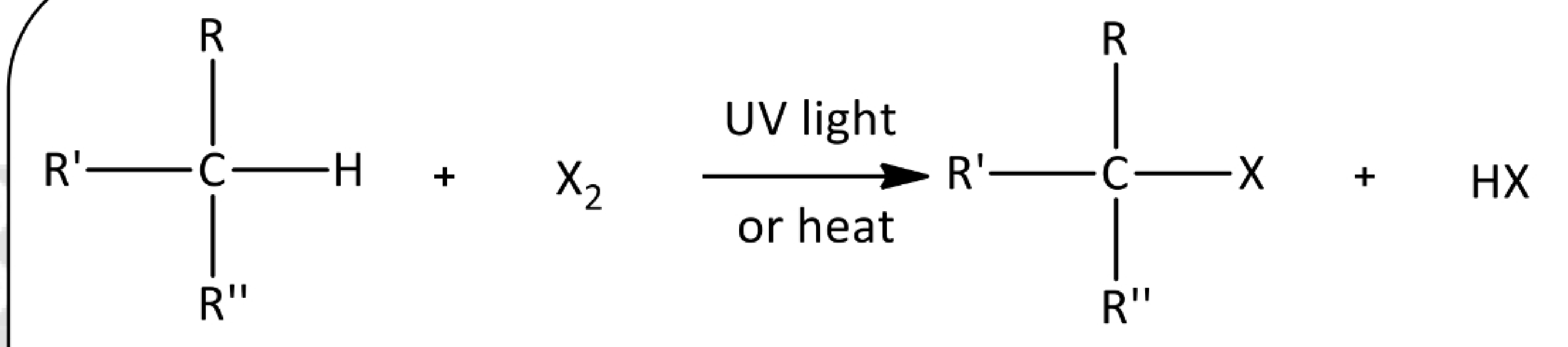
5 CHEMICAL PROPERTIES

5.1 Free radical substitution

Alkanes react with halogens (Cl_2 and Br_2) in the presence of ultraviolet light or heat to form halogenoalkanes (or alkyl halides). This type of reaction is known as free radical substitution, an example of non-polar reactions.

When initiated (started off) by the absorption of UV light or sunlight, the reaction is called a photochemical reaction. Although, remember that the free radical substitution can also be initiated if sufficient heat is supplied.

In the reaction, one or more of the hydrogen atoms in the alkane can be substituted by the halogen atom(s).



R, R', R'' = H, alkyl or aryl groups
X = Cl or Br

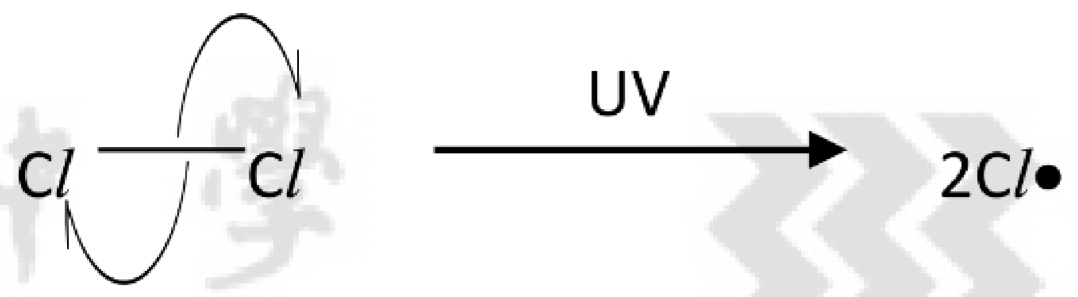
Reagent and conditions: Cl_2(g) or Br_2(*l*); UV light or heat

Observations: Greenish–yellow Cl_2 decolourised slowly
or Reddish–brown Br_2 decolourised slowly

5.1.1 Mechanism of the free radical substitution of methane by chlorine

Step 1. Initiation

The Cl–Cl bond is **homolytically** broken to give chlorine free radicals (Cl•). The energy required comes from the light absorbed or the heat supplied.



Lecture Exercise 5.1

Why are the C–H bonds in CH_4 unaffected during the initiation step? (Hint: bond energies)

Step 2. Propagation

The highly reactive chlorine radical collides with a methane molecule and abstracts a hydrogen atom to produce HCl and a methyl radical (•CH_3).

$$Cl\bullet + CH_4 \rightarrow HCl + \bullet CH_3 \qquad (1)$$

(Note: $\Delta H_{(1)}$ = B.E.$_{(C–H)}$ – B.E.$_{(HCl)}$ = 413 – 431 = **–18 kJmol^{-1}** which explains why it is the HCl and •CH_3 being formed and not the C–Cl and •H)

This methyl radical then reacts further with another molecule of Cl_2 in a second propagation step to yield the product chloromethane and **regenerate** a new chlorine radical.

$$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet \qquad (2)$$

The chlorine radical formed can again react with another methane molecule as in step (1) and so on, making the radical a homogeneous catalyst. Thus, once the reaction has been initiated, it becomes a self–sustaining cycle of repeating steps (1) and (2), making the overall process a **chain reaction**.

Lecture Exercise 5.2

(a) Why is the free radical reaction known as a chain reaction?

(b) Explain why the reaction of alkanes with halogens requires only a flash of ultraviolet light rather than prolonged radiation. *[J88/II/2(c) modified]*

Step 3. Termination

Two radicals collide and combine to form a stable product in this stage. The possible products are:

$$Cl\bullet + Cl\bullet \rightarrow Cl_2$$
$$Cl\bullet + \bullet CH_3 \rightarrow CH_3Cl$$
$$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$$

When these reactions occur, radicals needed for the propagation steps are consumed. The reaction cycle is broken and the chain reaction is terminated.

Lecture Exercise 5.3

(a) State the conditions used for the reaction between ethane and bromine.

$$C_2H_6 + Br_2 \rightarrow C_2H_5Br + HBr$$

(b) Why is this described as a *free–radical substitution* reaction?

(c) Write equations to show the mechanism for the above reaction.

[N2006/III/6(a) modified]

5.1.2 Formation of by–products

Halogenation of alkanes via free radical substitution may seem like a good method of obtaining halogenoalkanes at first, but in reality, the extent and the position of substitution is difficult to control.

A free radical is highly reactive and can react with almost any C–H bond present in the reaction mixture. In the presence of **excess halogen**, further substitutions of the product may occur resulting in a mixture of multi–substituted halogenoalkanes.

For example, chloromethane formed may further react with the chlorine radical to form dichloromethane:

$$CH_3Cl + Cl\bullet \rightarrow \bullet CH_2Cl + HCl$$

$$\bullet CH_2Cl + Cl_2 \rightarrow \underset{\text{dichloromethane}}{CH_2Cl_2} + Cl\bullet$$

Similarly, CH_2Cl_2 can undergo further chlorination to give $CHCl_3$ and CCl_4.

$$CH_4 \xrightarrow[UV]{Cl_2} CH_3Cl \xrightarrow[UV]{Cl_2} CH_2Cl_2 \xrightarrow[UV]{Cl_2} CHCl_3 \xrightarrow[UV]{Cl_2} CCl_4$$

Lecture Exercise 5.4

Suggest suitable reaction conditions for the substitution of methane by chlorine in UV light, so as to favour the production of

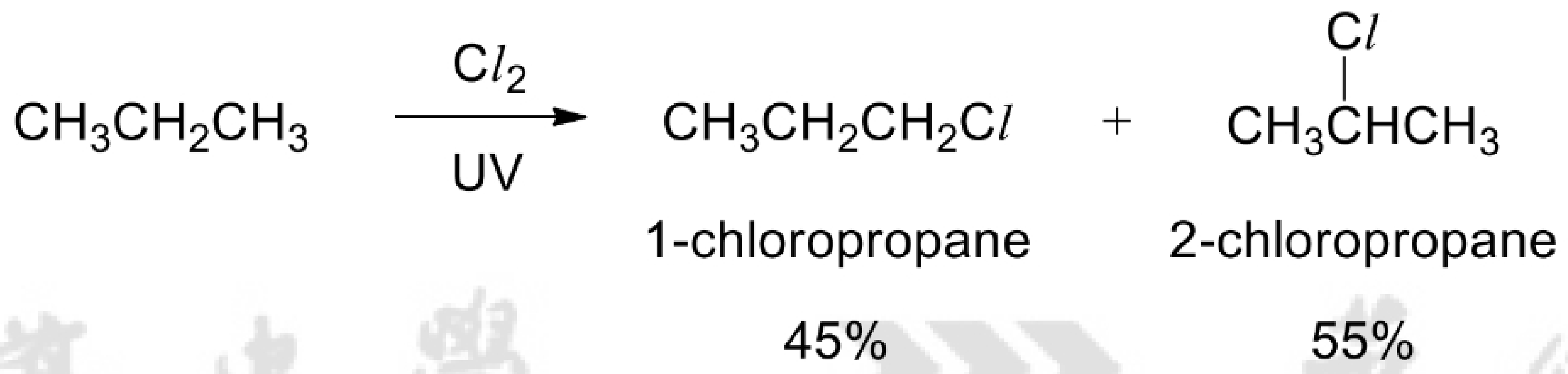
(a) chloromethane,

(b) tetrachloromethane.

5.1.3 Ratios of products formed when an alkane has non-equivalent hydrogen atoms

As all hydrogen atoms are susceptible to substitution, when an alkane contains 3 or more carbon atoms, isomeric products are formed depending on which H atom is substituted. The proportion of the isomers depends on the probability of the intermediates formed and the relative stability of the intermediates.

Let’s look at the chlorination of propane: two monochlorinated products are possible and their experimental yields are shown in the equation below. How can we explain their ratios?



$$CH_3CH_2CH_3 \xrightarrow[UV]{Cl_2} CH_3CH_2CH_2Cl + CH_3\overset{Cl}{C}HCH_3$$

1-chloropropane 45%

2-chloropropane 55%

Before we examine their ratios, let’s look at the classification of hydrogen atoms in alkanes and the stability of alkyl radicals.

Classification of carbon and hydrogen atoms

Carbon atoms are classified depending on the number of other carbon atoms attached to it. Hydrogen atom is classified according to the carbon atom to which it is attached. For example, a hydrogen atom attached to a primary carbon atom is called a primary hydrogen (*Table 4*).

In the following organic chemistry topics, we will use the same classification for radicals, carbocations, alcohols, amines, and so on.

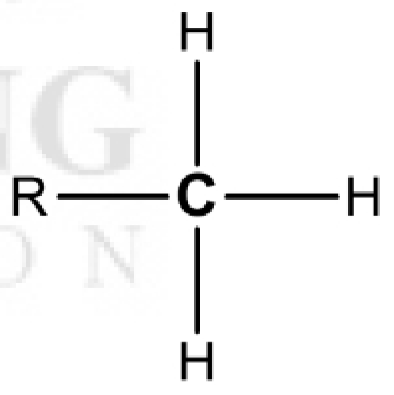
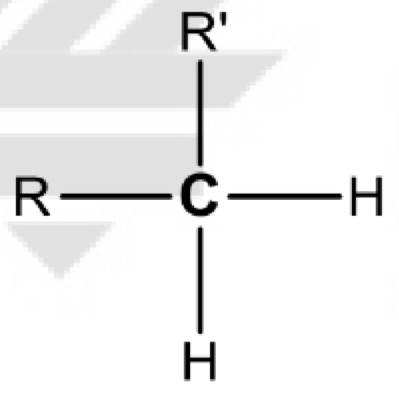
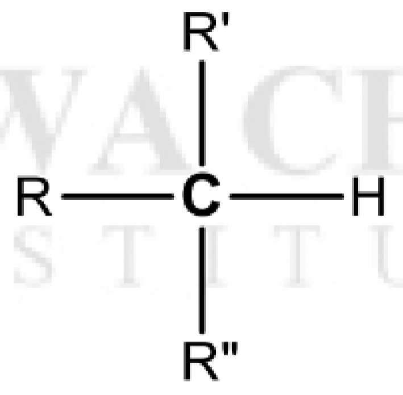
			
No. of alkyl groups attached	1	2	3
Type of carbon atom	Primary (1°)	Secondary (2°)	Tertiary (3°)
Type of hydrogen atom	Primary (1°)	Secondary (2°)	Tertiary (3°)

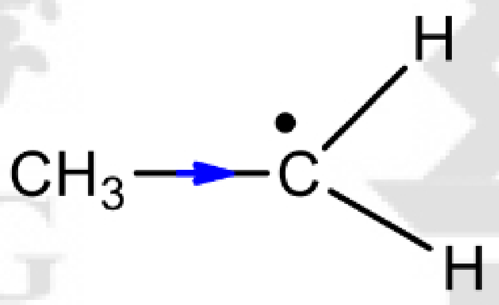
Table 4. Classification of carbon and hydrogen atoms

Stability of alkyl radicals

The alkyl groups attached to the carbon radical play a role in the stability of that carbon radical. **The more alkyl groups attached to the carbon radical – the more stable the radical** is and hence more easily it will be formed.

Stability : 3^o radical > 2^o radical > 1^o radical > methyl radical

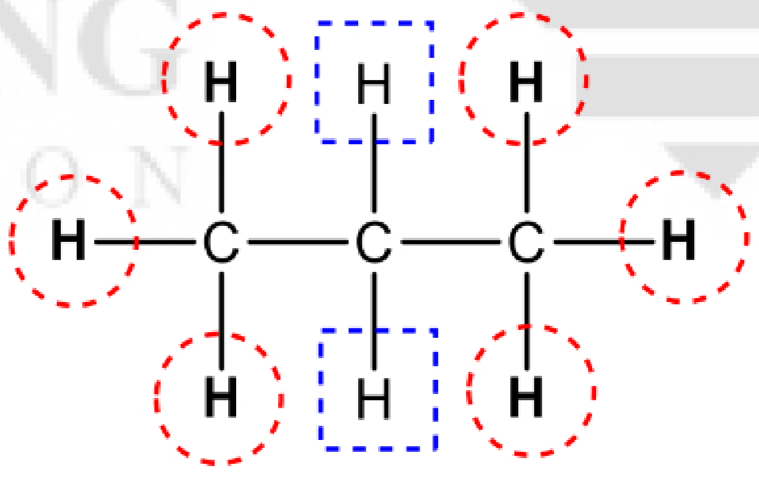
Reason: The inductive effect is the electron–donating or electron-withdrawing effect via sigma bonds. Non-polar C–C bonds can act as an electron “reservoir” which can compensate for the electron deficiency experienced by carbon radicals (or carbocations, see *Alkenes*).



We can now use the abovementioned concepts to explain the **experimentally observed** ratio of the two monochlorination products formed from propane. There are two factors which affect the proportion of products formed:

1. Ratio of different types of hydrogen atoms present in the alkane

In the case of propane, the ratio of primary (H) hydrogens to secondary (H) hydrogens is 6:2. Therefore, based on probability only, there should be two types of monochlorinated products formed, 1–chloropropane and 2–chloropropane, and their ratio should be 6:2, or 3:1.



2. Stability of each type of carbon radical intermediate present

Propyl radical (•$CH_2CH_2CH_3$), formed by the abstraction of a primary hydrogen atom, is however a primary radical and less stable than the secondary isopropyl radical $CH_3\underset{\bullet}{C}HCH_3$, and hence it is less likely to form. So, formation of 1-chloropropane is less favoured.

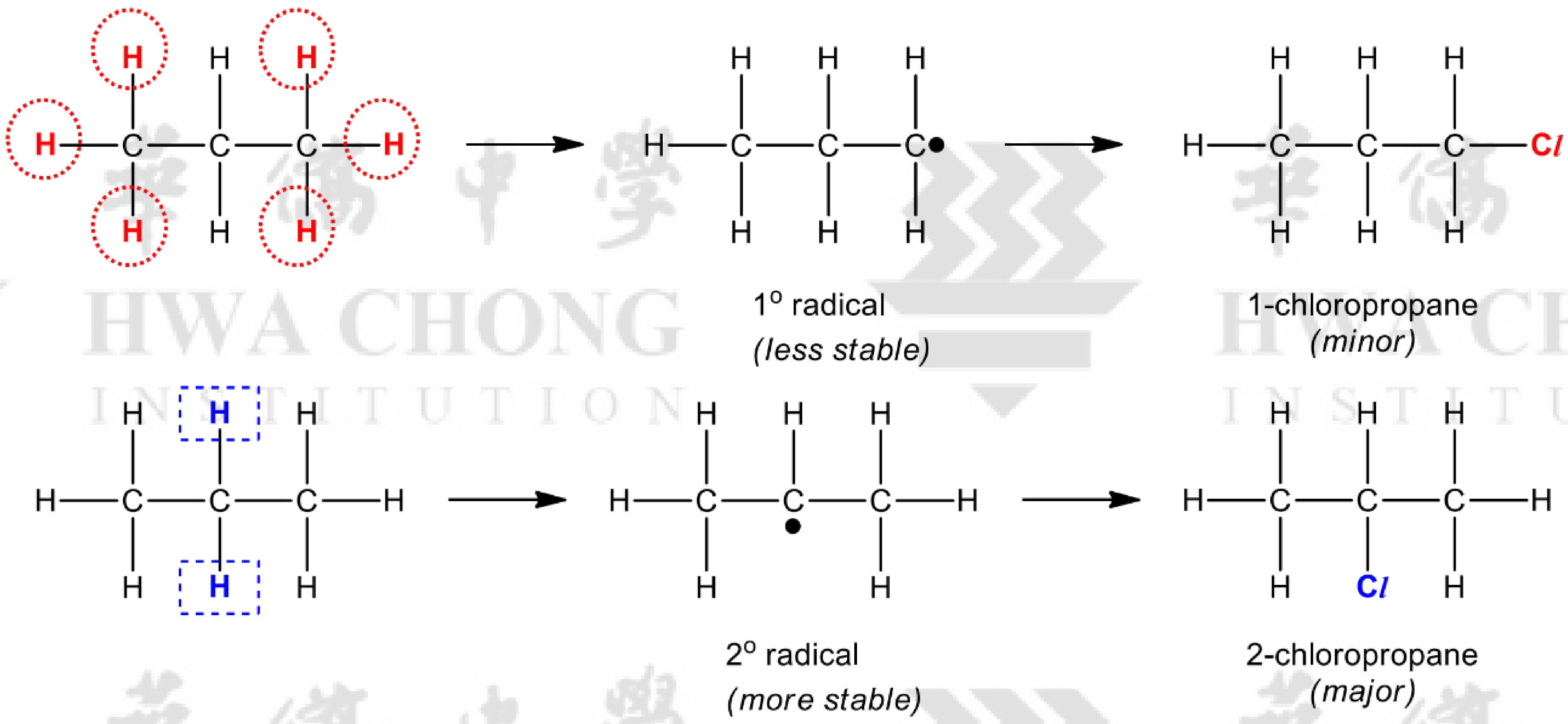


Figure 2. The formation of carbon radical intermediate and its subsequent chlorination

Hence, the <u>actual ratio</u> of 1–chloropropane:2–chloropropane cannot be 6:2. In fact, it is found to be 45:55 (or **nearly 1:1)**, which is due to both factors playing a role in the mechanism of the reaction. (Note to students: you will not be required to predict this ratio as it is experimentally determined; instead you should be able to explain the factors leading to it.)

Lecture Exercise 5.5

Pentane was reacted with limited chlorine in the presence of *uv* light. Assuming that only mono-chlorination takes place and the reaction occurs **at the same rate** at all carbon atoms, predict the ratio of the products obtained. *[HCI Prelim 2008/I/20]*

	1-chloropentane	:	2-chloropentane	:	3-chloropentane
A	3	:	2	:	1
B	1	:	2	:	3
C	1	:	3	:	2
D	3	:	1	:	2

2-methylbutane, $CH_3CH_2CH(CH_3)_2$, undergoes free radical substitution with Cl_2 to give 4 mono-substituted products **A**, **B**, **C**, and **D**.

Type of Hydrogen	Relative Reactivity
Primary, 1°	1
Secondary, 2°	3.5
Tertiary, 3°	5

The following information will allow you to determine the structures of **A**, **B**, **C** and **D**.

- The ratio of the four products formed can be found by multiplying the relative reactivity of the hydrogen responsible for the formation of the product to the number of hydrogen atoms in the compound that can form that product.
- There is twice as much of **C** as compared to **A** in the product mixture.
- **B** and **C** are both optically active.

Draw the structures of the 4 monochlorinated products and label each structure (**A**, **B**, **C** or **D**). Explain your answer.

[HCI Promo 2014/II/5]

Structure		Explanation

5.1.4 Reactivity of halogens with alkanes

The reactivity of alkanes towards halogenation decreases in the following order: $F_2 > Cl_2 > Br_2 > I_2$

Reaction of methane with halogens

Fluorine gas	Reacts vigorously, even in the dark and at room temperature. Dangerously exothermic because of the low F–F bond energy and the high C–F bond energy.
Chlorine gas	Requires UV light or heat. Reaction is exothermic.
Bromine liquid	Requires UV light or heat. Reaction is slower than with chlorine.
Iodine solid	No reaction.

The ΔH of the reactions of methane with the halogens are shown below:

$$CH_4 + X_2 \rightarrow CH_3X + HX \qquad \Delta H_r$$

Halogen (X)	ΔH_r / kJ mol^{-1}	H–X bond energy / kJ mol^{-1}	C–X bond energy / kJ mol^{-1}	X–X bond energy / kJ mol^{-1}
F	–478	562	484	158
Cl	–117	431	340	244
Br	–43	366	280	193
I	+22	299	240	151

Table 5. Bond energies for calculation of ΔH_r

From the table, the trend in reactivity matches the trend in ΔH_r, which is calculated as the overall enthalpy change for both propagation steps. Recall Topic 5 Chemical Energetics for the calculation of ΔH_r by the use of bond energies of the bonds broken and formed.

The C–H bond is broken in the first propagation step (Step 1), whereas H–X is formed. The X–X bond is broken in the second propagation step (Step 2) and C–X bond is formed.

Step 1:	$CH_3–H + X\bullet \rightarrow \bullet CH_3 + H–X$	$\Delta H_1 = BE(C–H) - \mathbf{BE(H–X)}$
Step 2:	$\bullet CH_3 + X–X \rightarrow CH_3–X + X\bullet$	$\Delta H_2 = BE(X–X) - \mathbf{BE(C–X)}$
Overall reaction:	$CH_4 + X_2 \rightarrow CH_3X + HX$	$\Delta H_r = \Delta H_1 + \Delta H_2$

Lecture Exercise 5.6

Chloroalkanes and bromoalkanes can be made by the reaction of the corresponding halogen with alkanes, for example:

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

Suggest why it is **not** possible to make iodoalkanes by this method. *[N2010/III/1(c)]*

5.2 Combustion of alkanes

Alkanes react with excess oxygen (complete combustion) to give carbon dioxide and water. The reaction is a highly exothermic process.

General equation $C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

Example $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H_c = -890\ \text{kJ mol}^{-1}$

$C_{20}H_{42}(s) + 30\tfrac{1}{2}\ O_2(g) \rightarrow 20CO_2(g) + 21H_2O(l)$ $\Delta H_c = -13368\ \text{kJ mol}^{-1}$

Although the combustion of alkanes is highly exothermic, it also has a high activation energy. For example, a mixture of methane and oxygen is stable unless ignited by a spark. The reaction, once started, accelerates explosively due to large amount of heat liberated.

Alkanes only burn in the gaseous state. Liquid and solid alkanes must be vapourised before they will burn.

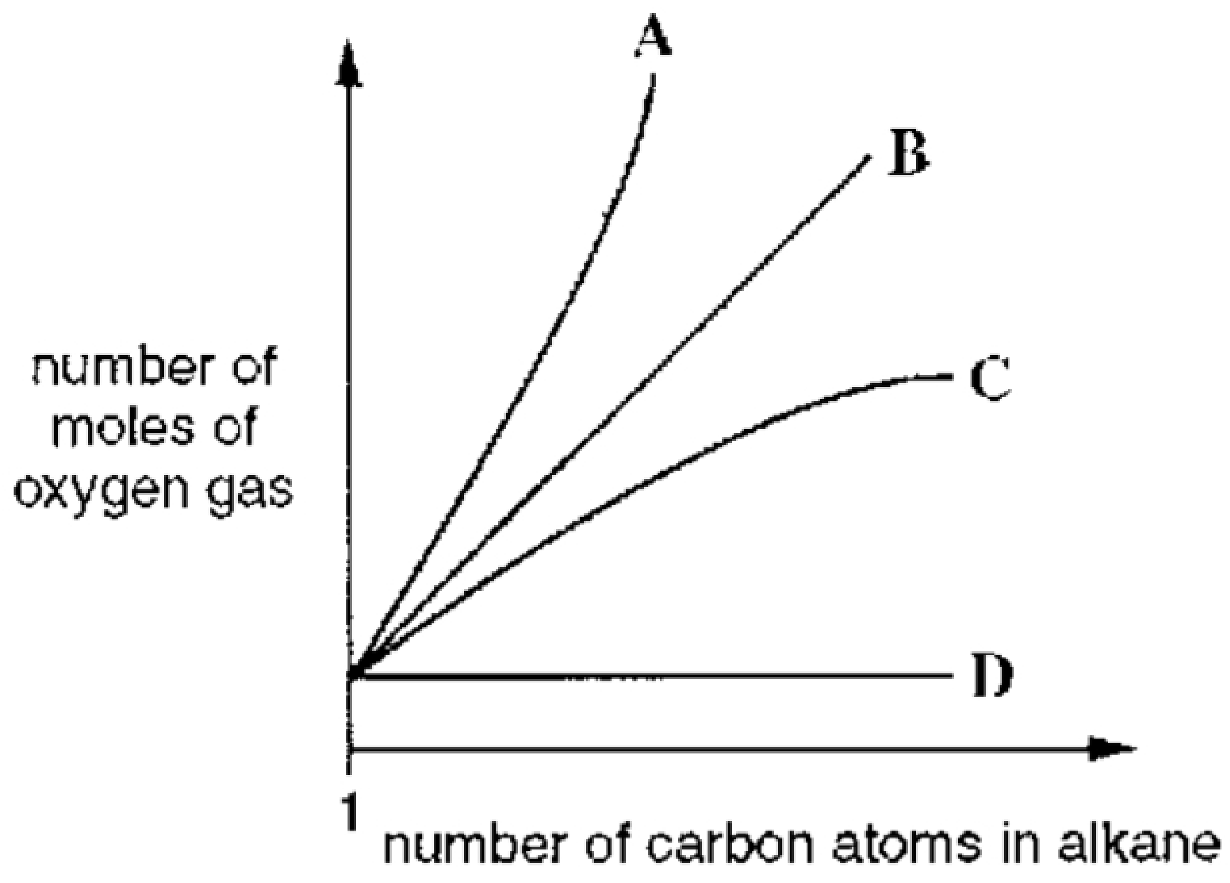
When they are burnt in a limited supply of oxygen (incomplete combustion), carbon (soot) and carbon monoxide are also formed and these have adverse environmental consequences.

Example $2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$

$CH_4 + O_2 \rightarrow C + 2H_2O$

Self-Practice 5.1

The complete combustion of alkanes to produce carbon dioxide and water is an important exothermic reaction. Which line on the graph shows the relationship between the number of carbon atoms in the alkane and the number of moles of oxygen gas needed for complete combustion of the alkane. *[J2003/I/23]*



6 ALKANES AS FUELS

Alkanes are found in crude oil and their main use is as fuels. A huge fraction of the energy we use comes from the combustion of alkanes. The gas in cookers, the petrol in cars, aviation fuel and diesel oil for powering ships and electric generators are all mixtures of alkanes.

6.1 Processing of crude oil

Fractional distillation

- Crude oil is a mixture of many hundreds of hydrocarbons. It also contains some compounds containing sulfur and nitrogen. It is an important source of aliphatic and aromatic hydrocarbons.
- The first stage in the processing of crude oil is fractional distillation, carried out at atmospheric pressure.

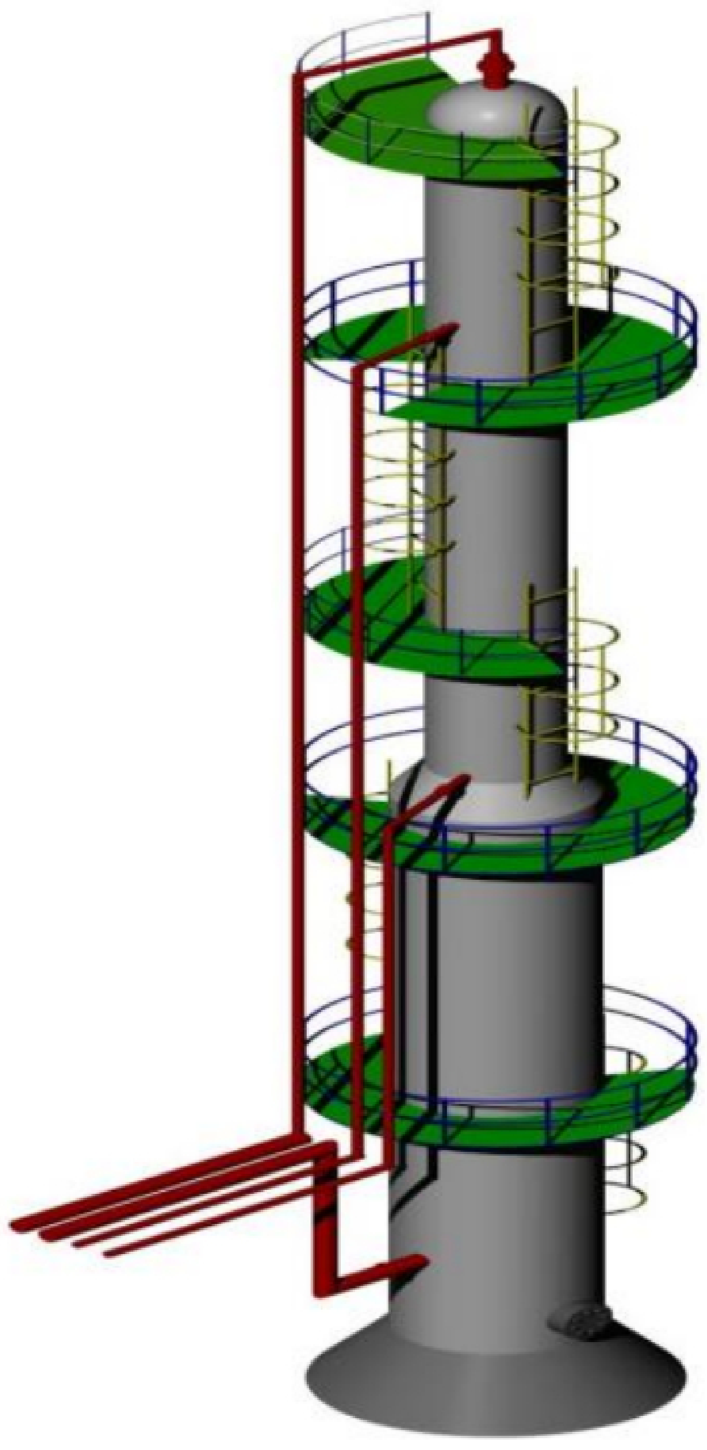


Figure 3. Model of a fractional distillation tower

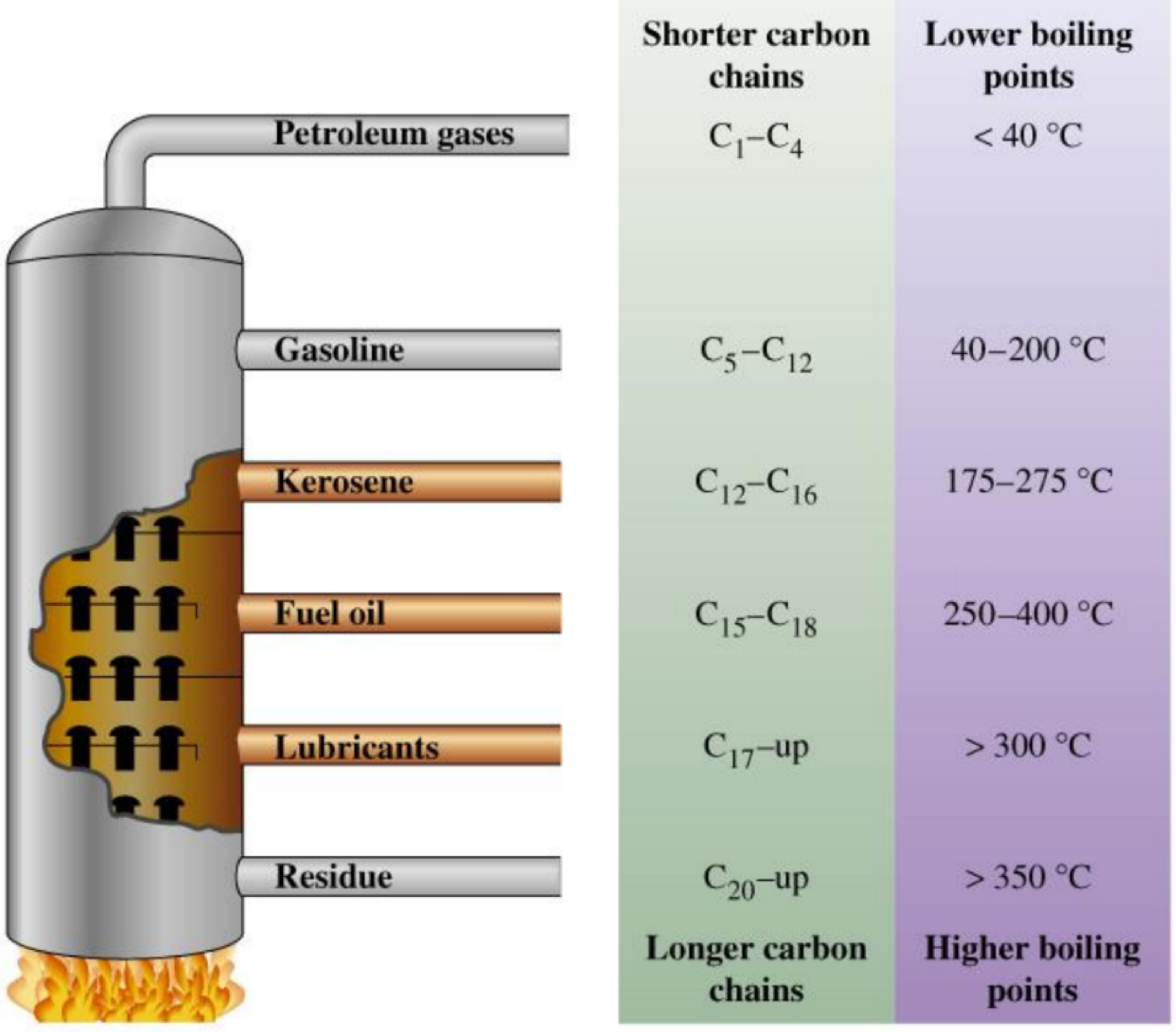


Figure 4. Fractional distillation of crude oil

Fraction	No. of C atoms	Boiling point range / °C	% in crude oil	Uses
Petroleum gas	1 – 4	< 40	2	Fuel, petrochemical feedstock
Gasoline	5 – 12	40 – 200	20	Fuel for petrol engines, petrochemical feedstock
Kerosene	12 – 16	175 – 275	13	Airplane fuel, can be cracked to give more gasoline
Gas oil	15 – 18	250 – 400	20	Fuel for diesel engines, can be cracked to give more gasoline
Residue	> 20	> 350	45	Lubricating oil, power station fuel, bitumen for roads, can be cracked to give more gasoline

Table 6. Fractions of crude oil and their uses

Petroleum is an important energy source. However, it is a finite resource (a resource that does not renew itself at a sufficient rate for sustainable economic extraction in meaningful human time-frames). The world has a limited supply of petroleum, and current estimations tell us that within the next few decades mankind will have completely depleted this valuable natural resource.

6.2 Environmental consequences of the use of hydrocarbons

6.2.1 Carbon monoxides and unburnt hydrocarbons

Carbon monoxide and unburnt hydrocarbons arise due to incomplete combustion of the fuel, which may be caused by various factors such as short reaction time in the internal combustion engine, poor maintenance of the engine and a lack of oxygen supply in the engine.

Carbon monoxide is a dangerous pollutant as it binds irreversibly with hemoglobin in blood by forming a stable complex and reduces the capacity of hemoglobin to transport oxygen. This causes drowsiness, headaches and is fatal above 2000 ppm. Being odorless, it gives no warning of its presence.

Unburnt hydrocarbons by themselves cause little damage, but in the presence of sunlight, they react with oxygen, ozone and oxides of nitrogen to form ***photochemical smog*** (read Section 6.2.2 below).

6.2.2 Oxides of nitrogen

NO and NO_2, collectively known as NO_x, are formed inside the combustion chambers of motor vehicles. At the high temperature of combustion, atmospheric nitrogen and oxygen combine to form NO which is further oxidized to NO_2.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Oxides of nitrogen irritate lungs, cause bronchitis and pneumonia and lower resistance to respiratory infections. They often result in the formation of ***photochemical smog*** where the strong sunlight interacts with pollutant gas causing a complex series of photochemical reactions which produce a choking mixture of ozone, NO_x and other gases. Photochemical smog has a harmful effect on plants. It may also result in chest pains and breathing difficulties in children.
NO_2 dissolves in water to give a mixture of nitrous (HNO_2) and nitric (HNO_3) acids:

$$2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$$

NO_2 also catalyses the formation of SO_3 from SO_2. SO_3 then dissolves in water to form H_2SO_4.

$$SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$$

HNO_3 and H_2SO_4 are strongly acidic. When they are present in rainwater, they produce ***acid rain***. Acid rain renders farm land unsuitable for cultivation (due to the acidity of the soil), causes corrosion of buildings and other man–made structures, and adversely affects marine lives (due to increased acidity of water). In addition, NO_2 can be easily regenerated by atmospheric oxygen:

$$NO(g) + \tfrac{1}{2} O_2(g) \rightarrow NO_2(g)$$

6.2.3 Enhanced greenhouse effect

The "greenhouse effect" is the heating of the Earth due to the presence of greenhouse gases. It is named this way because of a similar effect produced by the glass panes of a greenhouse. Increase in the amount of greenhouse gases in the Earth's atmosphere enhances the greenhouse effect.

As concentration of greenhouse gases increases, there will be a greater proportion of radiation trapped in the atmosphere, resulting in an increase in global temperatures.

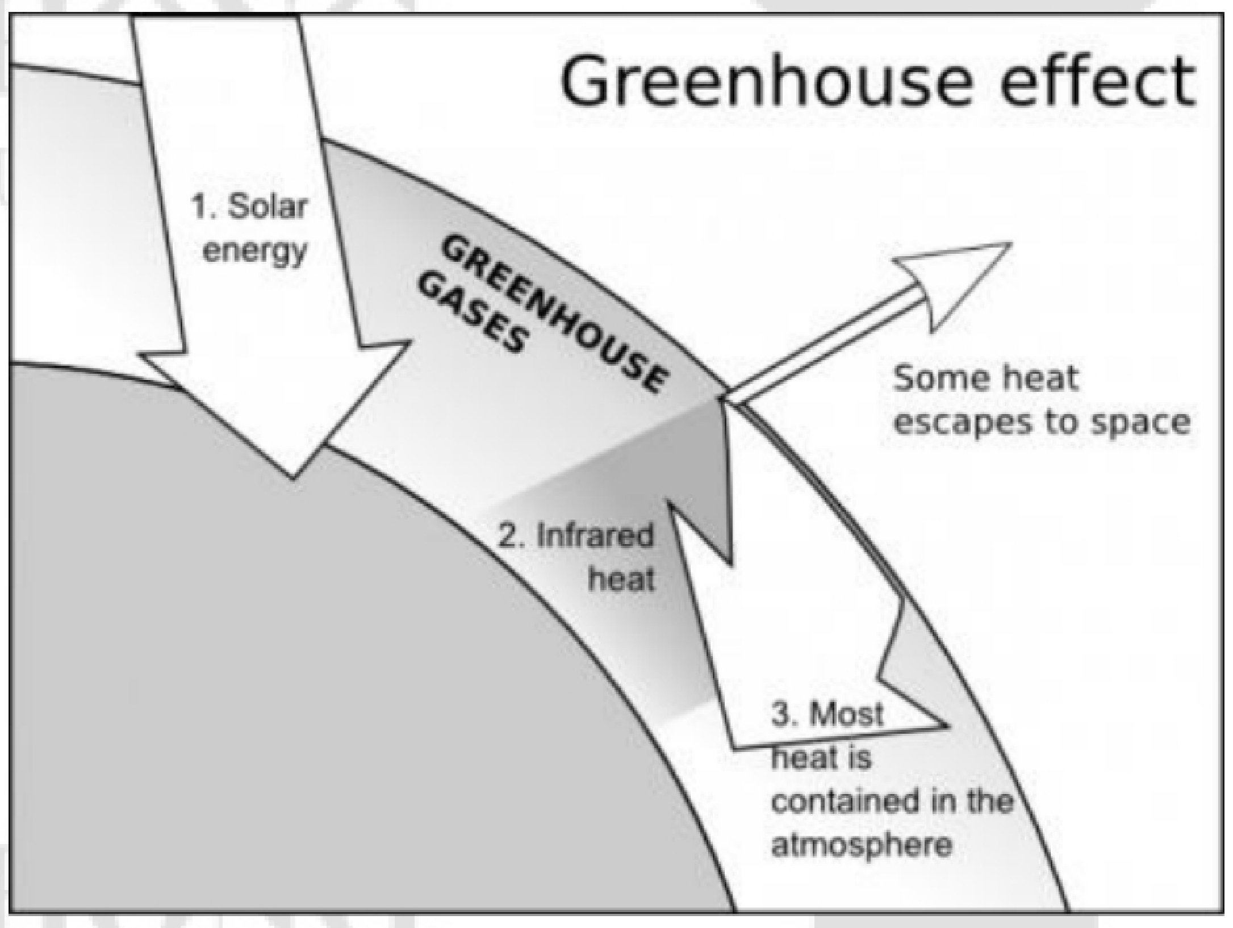


Figure 5. Illustration of greenhouse effect

What are greenhouse gases? http://www.ncdc.noaa.gov/oa/climate/gases.html

Many chemical compounds present in Earth's atmosphere behave as 'greenhouse gases'. These are gases which allow direct sunlight (relative shortwave energy) to reach the Earth's surface unobstructed. As the shortwave energy (that is in the visible and ultraviolet portion of the spectra) heats the surface, longer–wave (infrared) energy (heat) is re–radiated to the atmosphere. Greenhouse gases absorb this energy, thereby allowing less heat to escape back to space, and 'trapping' it in the lower atmosphere.

Many greenhouse gases occur naturally in the atmosphere, such as **carbon dioxide**, methane, water vapour, and nitrous oxide, while others are synthetic. Those that are man–made include the chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs), as well as sulfur hexafluoride (SF_6). Atmospheric concentrations of both the natural and man–made gases have been rising over the last few centuries due to the industrial revolution. As the global population has increased and our reliance on fossil fuels (such as coal, oil and natural gas) has been firmly solidified, so emissions of these gases have risen. While gases such as carbon dioxide occur naturally in the atmosphere, through our interference with the carbon cycle (through burning forest lands, or mining and burning coal), we artificially move carbon from solid storage to its gaseous state, thereby increasing atmospheric concentrations, making carbon dioxide a major greenhouse gas.

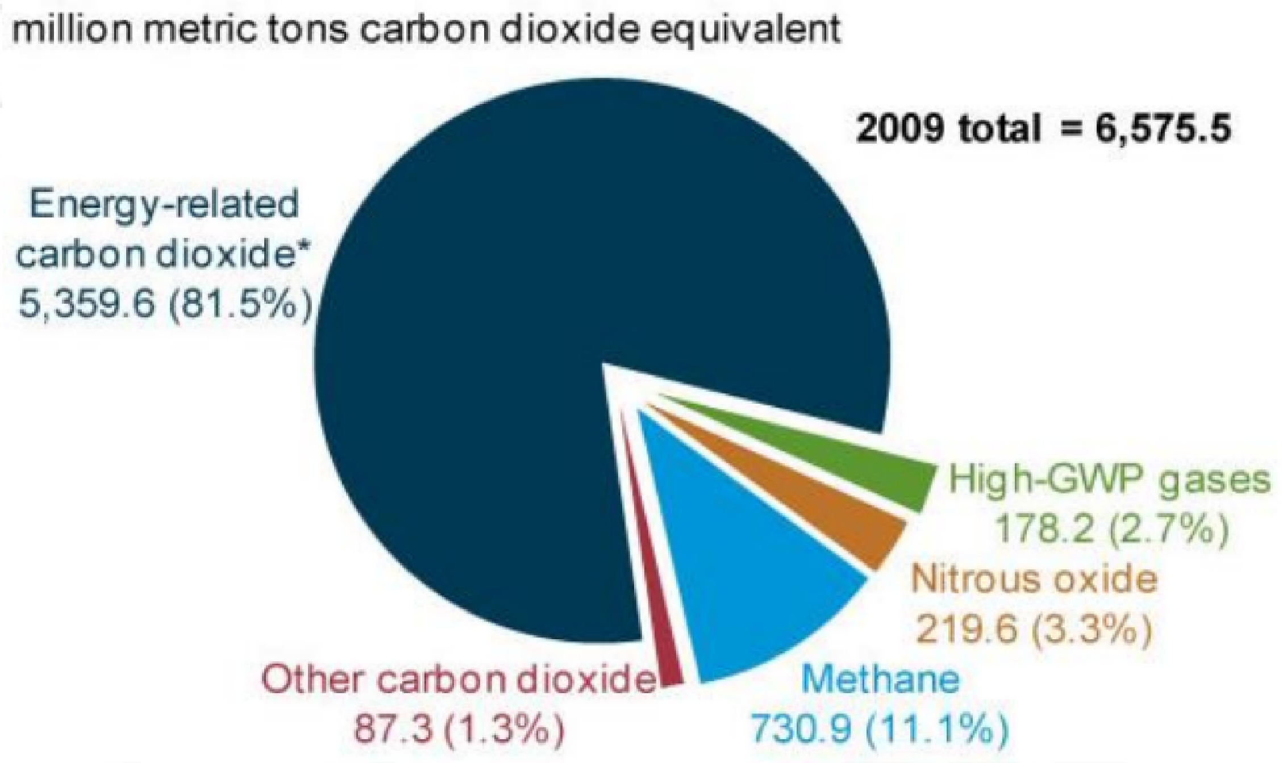


Figure 6. U.S. greenhouse gas emissions by gas, 2009

6.2.4 Impact of Methane on the Environment

Methane is one of literally millions of compounds in the carbon cycle, but one of the most abundant. It is formed when carbon-containing compounds decompose in the absence of air (anaerobic conditions). The organisms that bring this about are called methanogens. Each year an estimated 5×10^{14} g of biologically produced methane is released into the atmosphere. This vast amounts of methane produced in the biosphere have been touted as a renewable, carbon neutral energy source. However, this also carries particular significance to the global climate because methane is a highly potent greenhouse gas, with a greenhouse factor ~30. Although present at much lower concentrations in the atmosphere than CO_2, methane currently accounts for ~20% of the radiactive forcing of all greenhouse gases.

6.3 Catalytic converter

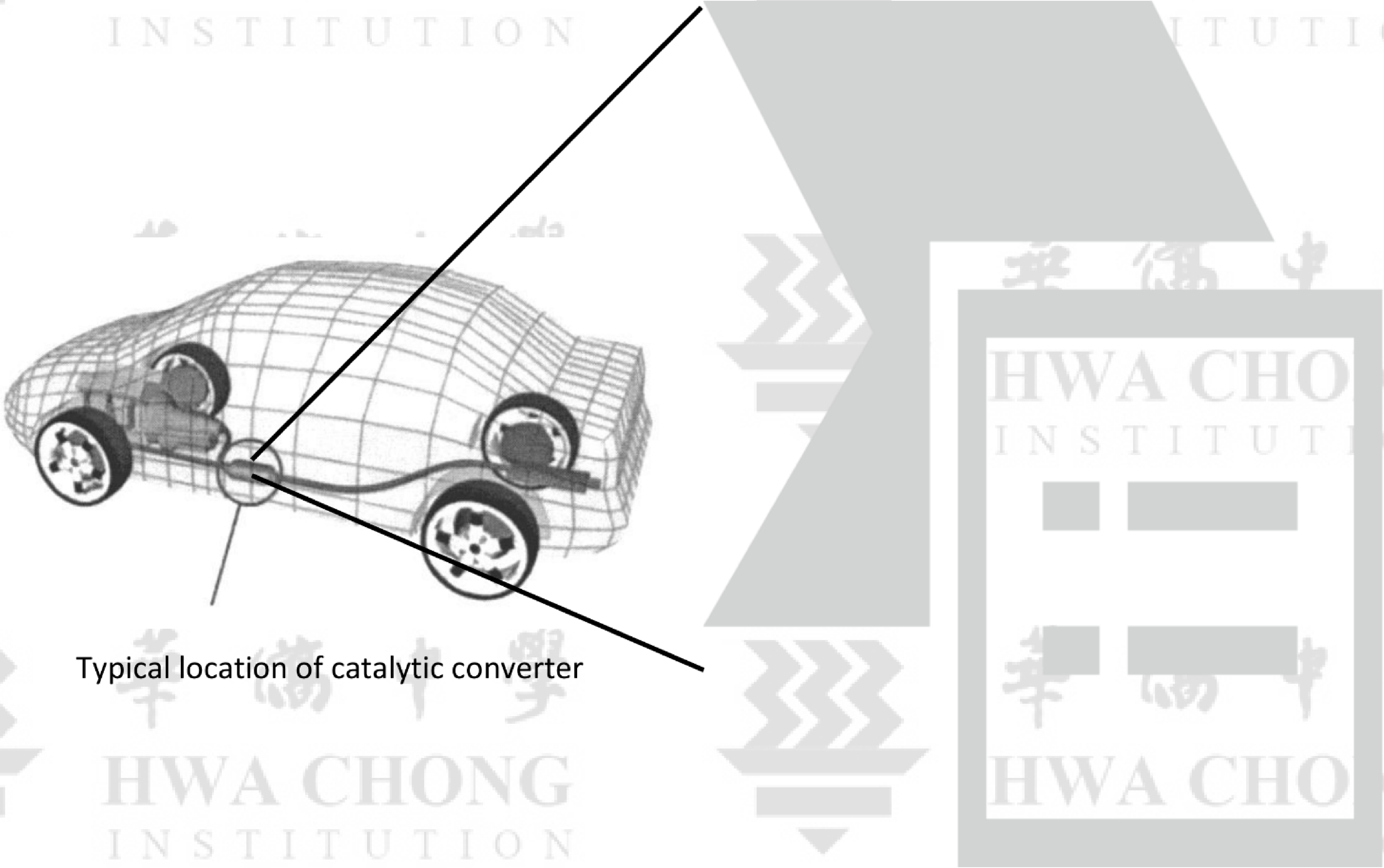


Figure 7. Expanded view of a catalytic converter

A catalytic converter removes pollutant gases from the exhaust by oxidizing or reducing them. The exhaust gases pass through a converter containing an alloy of platinum or rhodium. The mechanism of the reaction is that of a heterogeneous catalyst reaction (recall Topic 6 Reaction Kinetics for the mechanism). The harmful gases are adsorbed onto the surface on the metals, go through a reaction and then the harmless gas products desorb from the surface.

Three main pollutants (CO, NO_x and unburnt hydrocarbons) are removed from exhaust gases by the catalytic converter. According to the following equations, these harmful gases are converted into less harmful CO_2, N_2 and water vapour.

$$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$$

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

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

However, catalytic converters only work with unleaded petrol because lead ‘poisons’ the catalyst in the converter (i.e. destroy their catalytic action).

Self-Practice 6.1

How are oxides of nitrogen formed in a car engine?

A oxidation of nitrogen by ethanol in petrol

B reaction of nitrogen with oxygen

C oxidation of nitrogen by carbon dioxide

D reaction of nitrogen compounds in petrol with oxygen *[N2001/III/19]*

The three-way catalytic systems which are fitted to the exhaust systems of cars remove nitrogen oxides, carbon monoxide and unburnt hydrocarbons. Oxidation and reduction are both involved.

(a) State whether the catalysis is homogeneous or heterogeneous.

(b) What reaction or reactions are catalysed by the reduction catalyst?

(c) What reaction or reactions are catalysed by the oxidation catalyst?

(d) Name a substance which poisons the catalyst and suggest a remedy for this poisoning.

6.4 Importance of recycling

Recycling is a process to convert waste materials into new products to prevent waste of potentially useful materials, reduce the consumption of fresh raw materials, reduce energy usage, reduce air pollution (from incineration) and water pollution (from landfilling) by reducing the need for "conventional" waste disposal and lower greenhouse gas emissions as compared to plastic production. Recycling is a key component of modern waste reduction and is the third component of the "Reduce, Reuse and Recycle" waste hierarchy.

Recycling is very important as waste has a huge negative impact on the natural environment.

- Harmful chemicals and greenhouse gases are released from rubbish in landfill sites. Recycling helps to reduce the pollution caused by waste.
- Habitat destruction and global warming are some the effects caused by deforestation. Recycling reduces the need for raw materials so that the rainforests can be preserved.
- Huge amounts of energy are used when making products from raw materials. Recycling helps to preserve natural resources.

Recycling is essential to cities around the world and to the people living in them.

- No space for waste. Landfill sites are filling up fast.
- Reduce financial expenditure in the economy. Making products from raw materials costs much more than if they were made from recycled products.
- Preserve natural resources for future generations. Recycling reduces the need for raw materials; therefore preserving natural resources for the future.