CHEMISTRY

FOR TTCs

YEAR TWO

STUDENT'S BOOK

SCIENCE AND MATHEMATICS EDUCATION OPTION

FOREWORD

Dear Student, Rwanda Basic Education Board is honoured to present to you this Chemistry Book for Year two which serves as a guide to competence-based teaching and learning to ensure consistency and coherence in the learning of chemistry subject. The Rwandan educational philosophy is to ensure that you achieve full potential at every level of education which will prepare you to be well integrated in society and exploit employment opportunities.

The government of Rwanda emphasizes the importance of aligning teaching and learning materials with the syllabus to facilitate your learning process. Many factors influence what you learn, how well you learn and the competences you acquire. Those factors include the instructional materials available among others. Special attention was paid to the activities that facilitate the learning process in which you can develop your ideas and make new discoveries during concrete activities carried out individually or with peers.

In competence-based curriculum, learning is considered as a process of active building and developing knowledge and meanings by the learner where concepts are mainly introduced by an activity, a situation or a scenario that helps the learner to construct knowledge, develop skills and acquire positive attitudes and values. For effective use of this textbook, your role is to:

- Work on given activities which lead to the development of skills
- Share relevant information with other learners through presentations, discussions, group work and other active learning techniques such as role play, case studies, investigation and research in the library, from the internet or from your community;
- Participate and take responsibility for your own learning;
- Draw conclusions based on the findings from the learning activities. I wish to sincerely extend my appreciation to the people who contributed towards the development of this book, particularly REB staff who organized the whole process since its inception. Special gratitude goes to the University of Rwanda which provided experts in design and layout services, illustrations and image antiplagiarism, lecturers and teachers who diligently worked to successful completion of this book. Any comment or contribution would be welcome for the improvement of this textbook for the next edition.

Dr. MBARUSHIMANA Nelson

Director General, REB

ACKNOWLEDGEMENT

I wish to express my appreciation to all the people who played a major role in development of this Chemistry textbook for year two . It would not have been successful without active participation of different education stakeholders.

I owe gratitude to different Universities and schools in Rwanda that allowed their staff to work with REB in the in-house textbooks production project. I wish to extend my sincere gratitude to lecturers, teachers and all other individuals whose efforts in one way or the other contributed to the success of writing of this textbook.

Special acknowledgement goes to the University of Rwanda which provided experts in design and layout services, illustrations and image anti-plagiarism.

Finally, my word of gratitude goes to the Rwanda Basic Education Board staff particularly those from the department of curriculum who were involved in the whole process of in-house textbook writing.

Joan MURUNGI,

Head of Curriculum, Teaching and Learning Resources Department

TABLE OF CONTENT

UNIT 1

TRENDS OF CHEMICAL PROPERTIES OF GROUP 13 ELEMENTS AND THEIR COMPOUNDS

Key unit competence: **Compare and contrast the chemical properties of the Group 13 elements and their compounds in relation to their position in the Periodic Table**

1.1. Physical properties of Group 13 elements (physical state, metallic character, physical appearance and density).

ACTIVITY 1.1

Observe the picture A and B below and answer the questions that follow

A B

(i) Identify the pictures above A and B and suggest an element from which the pictures are made of.

(ii) What is the appearance of these pictures?

(iii) In which group of the periodic table does this element belong?

(iv) Iron is metal that is used to make bars for windows and door frames. How does the density of iron compare with this element you mentioned in (i) above?

(v) What physical property of this element that allows them to be used to make the materials A and B

With the exception of boron, group 13 elements are metals. Boron is a non-metal element with high melting point and low density.

Aluminium is a metal element and has a low density, it is a good conductor of heat and electricity, shiny, malleable, ductile and it has higher melting point than groups 1and 2 metals due to strong metallic bond resulting from 3 valency electrons involved in making metallic bonding in aluminium metal.

In small atoms electrons are held tightly and are difficult to remove, while in large ones they are less tightly held since they are far away from the nucleus and are easy to remove so that the ionization energy decreases down the group as the atomic radius increases.

The greater the forces of attraction and hence the boiling point and melting point decrease down the group as the atomic radius increases.

Table1.1. Physical properties of Group 13 elements

Element	Atomic Number	Nature/ metallic character	Physical state	Melting points (°C)	Atomic radius (pm)	Appearance
B	3	Non-metal	solid	2075	98	Non-shiny
Al	13	Metal	solid	660	143	Shiny
Ga	31	Metal	solid	30	141	Shiny
In	49	Metal	solid	156	166	Shiny
Tl	81	Metal	solid	303	171	Shiny

As you can see in this table, there is a general increase of atomic radius down the group. This is due to increase in atomic size which increases the shielding of screening effect.

Melting points decrease and then increase the abnormal behavior of boron is due to diagonal relationship with silicon in group which form a giant atomic structure and metalloid. Gallium has the lowest melting point due to an unusual structure. Each atom has one closest neighbor at a distance of 2.43 Å. This remarkable structure tends towards discrete diatomic molecules rather than a metallic structure. This accounts for the incredibly low melting point of gallium at 30 °C.

APPLICATION ACTIVITY 1.1

1. How do you expect the electrical conductivity to vary down the group 13 elements? Justify your answer.

2. How do you compare the atomic radius, and melting points of group13 to those of group 2 elements?

1.2. Reactions of group 13 elements with oxygen, water, halogens, dilute acids and sodium hydroxide.

ACTIVITY 1.2

1. (a) In terms of s,p,d,f orbitals give the electronic structure of aluminium (Z=13)

(b) How many valency electrons does aluminium possess? Explain how you reached this conclusion.

(c) Give the formula of the compound formed between aluminium and chlorine(Z=17)

d) Explain why the compound AlCl is not formed.

2. How do the S- block elements react with:

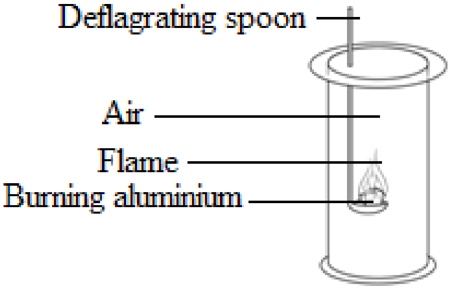
(i) oxygen, (ii) dilute acids (iii) water (iv) halogens . Give one reaction example in each case.

3. What type of oxides do these elements form when they react with oxygen?

4. Do you expect the elements in group 13 to react in a similar way like S- block elements? Discuss.

(a) Reflaction with oxygen

Experiment 1.2(a): burning an aluminium metal in air/oxygen and amphoteric properties of Al_2O_3



Apparatuses: deflagrating spoon, Bunsen burner, glass beaker.

Chemicals: aluminum sheet, hydrochloric acid and sodium hydroxide solutions(2M)

Other requirements: match box and petroleum gas

Procedure :

(a) Cut a small piece of aluminium

(b) Place it on a deflagrating spoon and heat it in a non-luminous flame

(c) When combustion is complete, divide the solid residue into two portions and place each portion in two different glass test tubes

(d) Add 10ml of hydrochloric acid to the first test tube and 10ml of sodium hydroxide to the second test tube. Record your observations

Study questions

i) Write the equations of the reaction that takes place when aluminium metal is burnt in air

ii) Name the product that is formed.

iii) Write the equations of reaction between the product in (ii) with HCl and with NaOH.

Aluminium burns in oxygen to form aluminium oxide

- In its compounds, Aluminum occurs exclusively in the +3 oxidation state. It rapidly reacts with oxygen in air to give water an insoluble coating of Al_2O_3. This oxide layer protects the metal beneath from further corrosion.

$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$$

-All other Group 13 elements also produce compounds of the formula M_2O_3:

$$4M(s)+3O_2(g) \longrightarrow 2M_2O_3(s)$$ where M represents Al, Ga, In, or Tl

Aluminium, gallium, and indium have +3 as the most stable oxidation state, whereas thallium has +1 oxidation state as the most stable.

- The most common oxide of boron, B_2O_3 or boron trioxide, is produced by heating boric acid:

$$2H_3BO_3 \longrightarrow B_2O_3+3H_2O$$

(b) Reactions with acids

(i) Reaction with HCl

Aluminium reacts when warmed with moderately concentrated hydrochloric acid forming aluminium chloride and hydrogen gas:

$$2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$$

Hydrogen is tested using a burning splint. A pop sound is heard during the test.

(ii) Reaction with H_2SO_4

Aluminium does not react with dilute sulphuric acid but reacts with concentrated sulphuric acid forming aluminium sulphate, sulphur dioxide and water:

$$2Al(s) + 6H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3SO_2(g) + 6\,H_2O(g)$$

Sulphur dioxide gas is tested using a violet solution of potassium manganate (VII) that decolorizes to give colorless $Mn^{2+}(aq)$ ion

$$SO_2(g) + MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + H_2O(l)$$

Note: Aluminium does not react with HNO_3 because of the insoluble layer of Al_2O_3 formed which prevents further reaction.

(c) Reaction with alkali

Experiment 1.2(b): to investigate the reaction of aluminium with concentrated sodium hydroxide solution

Learners perform experiments to investigate the reaction of aluminium with NaOH solution

Apparatuses: thermometer, pyrex/ borosilicate beaker, stirrer

Chemicals: aluminium powder,40% sodium hydroxide solution

Procedure

a) Prepare 40% of sodium hydroxide by mixing 100cm^3 of water with 40g of sodium hydroxide
b) Take 0.5 g of aluminium powder into a Pyrex beaker.
c) Pour the solution of sodium hydroxide in the Pyrex beaker containing aluminium powder and allow the reaction to proceed for about 5 minutes.
d) Use thermometer to record the temperature during the process.

What did you observe as aluminium powder was added into sodium hydroxide

Study questions

(i)Write equations to show how aluminium reacts with concentrated sodium hydroxide.

(ii) Use equation to justify your observations.

Aluminium reacts vigorously with sodium hydroxide solution forming sodium aluminate and hydrogen gas.

$$2Al(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow 2NaAl(OH)_4(aq) + 3H_2(g)$$

(d) Reaction with halogens

- Aluminium fluoride is made by direct combination of the metal with fluorine.

$$2Al(s) + 3F_2(g) \longrightarrow 2AlF_3(s)$$

- Aluminium chloride is made by passing chlorine gas over heated aluminium metal

$$2Al(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s)$$

Al, Ga, In and Tl react with halogens to give binary halides of formula EX_3. In this case, all 3 valence electrons are used in the reaction. All trihalides of group 13 elements are known except Tl(III) iodide ,because iodine is a weak oxidizing agent.

$2E + 3X_2 \longrightarrow 2EX_3$, E:is a group 13 element, TlI_3 doesn't exist.

Fluorides are ionic and have high melting points due to the small size of fluoride ion.

APPLICATION ACTIVITY 1.2

1. Aluminium does not react with water whether hot or cold. Suggest where this property is applied in daily life.
2. Write equations to show how concentrated hydrochloric acid, sulphuric acid, nitric acid and concentrated potassium hydroxide solution react with aluminium powder.
3. Write equations to show how the elements of group 13 form halides when they react with chlorine.

1.3. Amphoteric character of aluminium and gallium oxides and hydroxides.

ACTIVITY 1.3

Experiment to investigate acid-base character of group 2 and 13 oxides.

Materials/ apparatus : aluminium oxide, test tubes, distilled water, 1M hydrochloric acid, universal indicator, 1M sodium hydroxide (Magnesium oxide, 1M nitric acid)

Procedure 1

a. - Put about 0.5 g of Al_2O_3solid in a test tube and then add water. Record your observations

- Remove water and devide the solid into 2 portions and help them in 2 test-tubes

b. Pour 3 ml of 1 mol/litre HCl solution in the **third** test tube and add 2 drops of universal indicator.

c. Pour 3 ml of 1 mol/litre NaOH solution in the **fourth** test tube and add 2 drops of universal indicator.

d. Put the first portion of Al_2O_3 solid in the test tube containing HCl solution and shake gently.

e. Put the second portion of Al_2O_3 solid in the test tube containing NaOH solution and shake gently.

f. Note the observable changes in both tests.

Study questions

1. (i) Explain your observations in procedure (a), (b) and (c)

(ii) Write equation for the reaction that takes place in procedure (d) and (e)

(iii) Comment on reactions that occur in (d) and (e)

2. a. Put about 0.1 g of MgO in a test tube.

b. Add 2ml of water to the MgO solid in the test tube and shake the mixture.

c. Put 2 drops of phenolphthalein indicator in MgO solution.

d. Add 5ml of 1 mol/litre HNO_3 to the solution containing MgO solution.

e. Note the observable changes.

f. Interpret the acid –base character of the solutions of CaO and Al_2O_3

It dissolves in mineral acids to form aluminium salts: in this case it acts as a base.

$Al_2O_3(aq) + 6\,HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2O(l)$ **(Basic nature)**

Or $Al_2O_3(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2O(l)$

It dissolves in caustic alkali to form aluminate: in this case it acts as an acid.

$Al_2O_3(s) + 2NaOH(aq) \longrightarrow Na_2Al_2O_3 + H_2O$ **(Acidic nature)**

Or $Al_2O_3(aq) + 2OH^-(aq) + 3H_2O(l) \longrightarrow 2[Al(OH)_4]^-(aq)$

Similarly, Aluminium hydroxide also shows amphoteric properties.

$$3HCl(aq) + Al(OH)_3(s) \longrightarrow AlCl_3(aq) + 3H_2O(l)$$

$$Al(OH)_3(s) + NaOH\ (aq) \longrightarrow Na[Al(OH)_4]$$

Amphoteric oxides exhibit both basic and acidic properties. When they react with an acid, they produce salts and water, showing basic properties. While reacting with alkalis, they form salts and water showing acidic properties.

APPLICATION ACTIVITY 1.3

1. (a) Aluminium oxide is said to be amphoteric, whereas calcium oxide is said to be basic, yet the two oxides are metal oxides? Explain the origin of that difference.

b) Explain the concept of amphoteric using aluminium hydroxide

(c) What type of oxides do S- block elements form? Acidic, basic, or neutral. Explain.

(d) Do you expect the group 13 elements to form similar oxides? Give a reason for your answer.

2. Suggest other oxides of metals that behave similarly like aluminium oxide and write equations for the reactions.

1.4. Anomalous properties of boron and its compounds

ACTIVITY 1.4

1. The first members of elements in their groups behave differently from other members. With reference to beryllium explain the cause of this exceptional behavior.

Boron – the first member of group 13 shows anomalous behavior due to the small size and high nuclear charge/size ratio, high electronegativity. This makes boron typically non-metal whereas the other members of the group are metals.

The melting point and boiling points of boron are much higher than those of other elements of group 13.

Boron forms only covalent compounds whereas aluminum and other elements of group 13 form even some ionic compounds. The oxide of boron is acidic in nature whereas those of others are amphoteric and basic.

$$B_2O_3(s)+NaOH\ (aq) \longrightarrow NaBO_2(aq)+H_2O(l)$$

The trihalides of boron (BX_3) exist as monomers. The reason being that due to its small size, it cannot accommodate 4 large sized halogens atoms around it.

The hydrides of boron i.e. boranes are quite stable and are formed by many molecules such as diborane (B_2H_6) ,triboranes (B_3H_8) while those of aluminum are unstable.

Dilute acids have no action on boron; other group 13 elements are dissolved in acids to liberate H_2.Borates are more stable than aluminates. Boron does not decompose steam water while other members do so.

Boron combines with metals to give borides e.g. Mg_3B_2. Other members form simply alloys.

Concentrated nitric acid oxidizes boron to boric acid but no such action is noticed with other group members.

$$B(s) + 3HNO_3(l) \longrightarrow H_3BO_3(aq)+ 3NO_2(g)$$

APPLICATION ACTIVITY 1.4

(a) What is the cause of abnormal behavior of boron

b) State any anomalous properties of boron compared to those of aluminium

1.5. Identification of Al^{3+} ion in aqueous solution and uses of group 13 elements and their compounds.

1.5.1. Identification of Al^{3+} ions

ACTIVITY 1.5

Experiment to identify and test for the presence of Al^{3+} in solution

Apparatuses: beaker, test tubes, droppers, test tube rack

Chemicals: aluminum salt solution, sodium hydroxide, ammonia solution

Procedure:

a) Pour about $2cm^3$ of a solution of aluminium salt into 2 different test tubes

b) To $2cm^3$ of solution of aluminium salt in the first test tube add drop by drop a solution of sodium hydroxide until excess. Then observe what happens.

c) In a second test tube, to a $2cm^3$ of aluminium salt add drop by drop a solution of ammonia until excess and observe.

Study question

(i) Write ionic equation to show aluminium ions reacts with a few drops of solution of sodium hydroxide and then in excess to justify your observations

(ii) Write an ionic equation to justify your observation when ammonia solution is added in excess to a solution of aluminium ions

Aqueous solution of aluminium salt when reacted with a solution of sodium hydroxide, a white precipitate of $Al(OH)_3$ is formed. $Al(OH)_3$ precipitate dissolves in excess of sodium hydroxide as soluble $Al(OH)_4^-$ complex ion:

$$Al^{3+}(aq) + 3NaOH(aq) \longrightarrow \underset{\text{White precipitate}}{Al(OH)_3(s)} + 3Na^+(aq)$$

$$Al(OH)_3(s) + OH^-(aq) \longrightarrow \underset{\text{Colourless solution}}{Al(OH)_4^-(aq)}$$

When reacted with a solution of ammonia, aluminium ion Al^{3+} produces a white precipitate of $Al(OH)_3$ insoluble in excess ammonia solution

$$Al^{3+}(aq) + 3NH_4OH(aq) \longrightarrow Al(OH)_3(s) + 3NH_4^+(aq)$$

$$Al(OH)_3(s) + \text{excess ammonia} \longrightarrow \text{no observable change}$$

1.5.2. Uses of group 13 elements

Aluminium

Aluminium is abundant in the Earth's crust and its applications are many varied; hereafter some of those applications and uses; it is used in:

- making cooking utensils: this is because of its bright appearance and lightness, resistance to corrosion, and its thermal conductivity
- window frames or doors in buildings and houses
- Overhead high tension cables for distribution of electricity: this is because of its low density and very good electrical conductivity.
- Alloys (e.g. Al and Mg) for the construction of airplanes and small boats due to its lightness, malleability and higher tensile strength in the alloy.
- Being completely resistant to corrosion it is ideal for packaging food.
- The insulating property of aluminium arises from its ability to reflect radiant heat; this property is used in firefighters' wear to reflect the heat from the fire and keep them cool.
- The polished surface of aluminium is used in the reflectors of car headlights.
- Aluminium is a component of clay (ibumba), mainly hydrous sulphate of aluminium, used in the traditional manufacture of clay pots (ibibindi/ inkono).
- Clay is also one of the basic raw materials in the production of cement

Boron

Applications of boron are found in:

- control rods to keep nuclear reactions in balance and avoid explosion; boron absorbs excess neutrons preventing them from bombarding too many uranium atoms which may result into explosion (fuel of nuclear reactors)
- the manufacture of hard boron steel
- as an additive to semiconductors silicon and germanium
- the manufacture of borosilicate glass used in vacuum flasks and test tubes

Gallium

Gallium is used as a semiconductor, e.g: with phosphorus and arsenic in light emitting diodes.

Note that sodium tetrahydridoborate(III), $NaBH_4$, and lithium tetrahydroxoaluminate(III), $LiAlH_4$, are used as reducing agents in organic chemistry.

APPLICATION ACTIVITY 1.5

1. Explain using an ionic equation why aluminium ions form a white precipitate with a solution of sodium hydroxide which dissolves in excess to form a colourless solution again and precipitate persists when a solution of ammonia is used.
2. You are provided with aluminium oxide and hydrochloric acid. Describe an experiment you can carry out to identify the aluminium ions in aluminium oxide indicating all the apparatus you will need to successfully carry out the experiment.

SKILLS LAB 1

With reference to Boron and aluminium, carry out the research to find out how the oxides of these metals are prepared in the laboratory .Your research should include:

(i)Materials/ apparatus needed

(ii) The experimental setup

(iii) Procedure used to prepare the oxides.

END UNIT ASSESSMENT 1

1. (a) Explain the following statements.

   (i) Aluminium alloys are used to make aircraft body.

   (ii) A mixture of dilute sodium hydroxide and aluminium pieces are used to open drain.

   (iii) Concentrated nitric acid can be transported in aluminium container.

   (iv) Aluminium wire is used to make transmission cables.

2. Water is suspected to contain calcium and aluminium ions. State a chemical test that should be used to confirm the presence of the suspected ions. State the reagent, observations and related chemical equation if any.

3. If you need to prepare aluminium hydroxide, why is it better to add a solution of ammonia to a solution of aluminium salt, rather than to add a solution of sodium hydroxide?

4. (a)How does gallium react with:

   (i) Hydrochloric acid? (ii) Sodium hydroxide?

   (b) With reference to aluminium oxide, explain the term amphoteric oxide. Write equations to illustrate.

5. Explain why aluminium is suitable for the following uses:

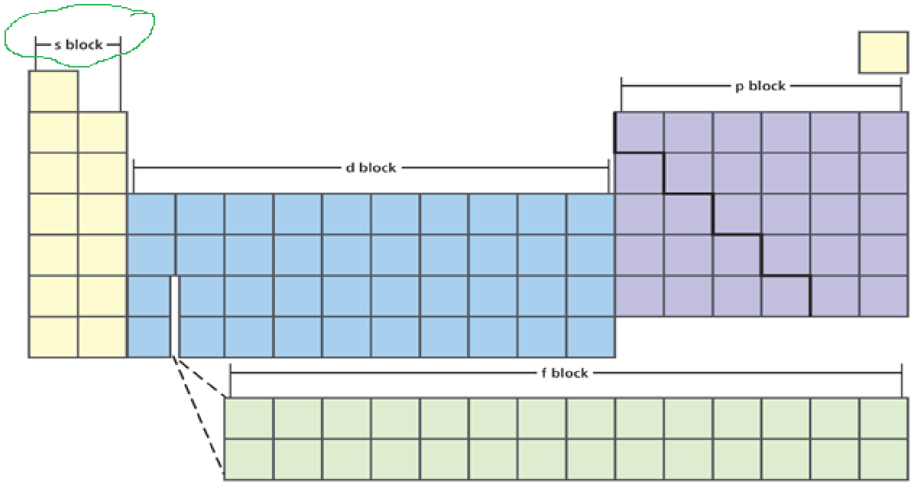
(a) Manufacture of window frames (b)Electrical wiring (c)Packaging food (d)Suits for firefighters

UNIT 2

CHEMICAL PROPERTIES OF S- BLOCK ELEMENTS

Key unit competence: **Describe the trends in chemical properties of s bloc elements and their compounds.**

INTRODUCTORY ACTIVITY



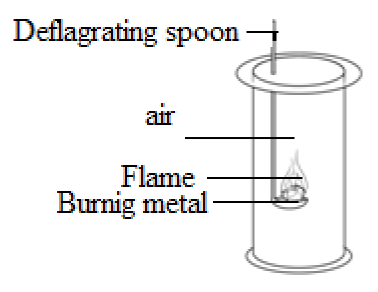
(i) Look at the periodic table chart above and name some of the elements found in s-block.

(ii) To which group does an s-block element belong? Give reasons to justify your answer.

2.1. Reactivity of Group 1 and 2 elements with: oxygen, water and halogens.

ACTIVITY 2.1

1. Group 1 elements are stored in paraffin/oil/ why?
2. It is not advisable to add calcium metal into a concentrated solution of hydrochloric acid? Explain the statement.
3. Sodium is shiny but when exposed to air it tarnishes and forms a white layer on its surface after a short time. Explain.
4. When a piece of sodium metal is dropped into water a vigorous reaction occurs and some flames of fire are seen on the surface of water with a hissing sound. Explain the source of fire and hissing sound.
5. When a stream of chlorine gas is passed through burning sodium, white fumes are formed. Suggest the name of the white fumes.
6. **Experiment to investigate how alkali and alkaline earth metals react with oxygen**



Apparatuses: deflagrating spoon, Bunsen burner, glass beaker, filter paper,

Chemicals: lithium, sodium calcium, magnesium, potassium, water, and red litmus paper

Other requirements: knife, match box and petroleum gas

Procedure:

(i). Cut a small piece of lithium and wrap it in piece of filter paper to remove the oil.

(ii). Place it on to a deflagrating spoon and heat it in a non-luminous flame.

(iii). Observe what happens.

(iv). When combustion is complete, dip the deflagrating spoon into a beaker of 100 ml filled up to 50 ml of water.

(v). Stir the water with the spoon and then drop a piece of litmus paper into the solution in the beaker. Observe.

(vi). Repeat the experiment with sodium , calcium, magnesium and barium.

Study questions :

a) Write the equations of reactions that take place when each metal is burnt in air.

b) Name the product that was formed in each case.

c) What are the color changes when the aqueous solutions above are tested with litmus paper? Explain why?

d) Write the equations of reaction between each product in (b) with water

Group 1 elements reacts by losing one electron in the outer shell whereas Group 2 metals react by losing 2 electrons; the latter is less reactive than the corresponding former metals.

They mainly form ionic compounds.

(a) Reactions of Group 1 elements (the alkali metals)

(i) Reaction with oxygen.

Lithium burns with a carmine-red flame to give white lithium oxide:

$$4Li\ (s) + O_2\ (g) \longrightarrow 2Li_2O\ (s)$$

Sodium burns with a yellow flame to give pale yellow sodium peroxide. Some sodium oxide is formed as well.

$$2Na(s) + O_2(g) \longrightarrow Na_2O_2(s)$$

Potassium burns with a lilac flame to give yellow potassium superoxide:

$$K(s) + O_2(g) \longrightarrow KO_2(s)$$

Rubidium and caesium react similarly to potassium to give superoxides; RbO_2 (orange), CsO_2 (red).

(ii) Reactions of the alkali metals with water.

All of the metals react in a similar way. Lithium reacts slowly, melting and rushing about the surface of the water. Sodium reacts vigorously, and may catch fire; potassium reacts violently and always inflames. Rubidium and caesium react extremely violently, and would sink but for the fact they don't survive for long enough.

$$2Li(s) + 2H_2O(l) \longrightarrow 2LiOH(aq) + H_2(g)$$

(b) Reactions of Group 2elements (the alkaline earth metals)

(i)Reaction with oxygen.

All of the group 2 metals react in a similar way, though barium also forms substantial amounts of barium peroxide BaO_2. Magnesium burns vigorously with a brilliant white flame - the only element in the *s*-block which does not show its flame test colour (none) when burning. Calcium burns with a brick-red or orange-red flame, strontium with a crimson flame, barium with a pale apple green flame. All of the oxides are white, ionic, basic solids.

$$2Mg (s) + O_2(g) \longrightarrow 2MgO(s)$$

(ii) Reactions of the alkaline earth metals with chlorine.

All of the metals react similarly to give white, ionic chlorides.

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$

(iii) Reactions of the alkaline earth metals with water.

Magnesium reacts very slowly with cold water, but rapidly with steam:

$$Mg(s) + H_2O(g) \longrightarrow MgO(s) + H_2(g)$$

Calcium reacts quite quickly with cold water to give a milky suspension of calcium hydroxide, some of which dissolves. Strontium and barium react similarly, the reaction of barium being vigorous and giving a colourless solution of barium hydroxide – the most soluble of the group 2 hydroxides.

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

(c) Reactions of group 1 and 2 elements with halogens:

They react with halogens to form metal halides. They all react vigorously with chlorine to produce ionic chlorides of formula MCl and MCl_2 respectively except that $BeCl_2$ is covalent when anhydrous, (where M represents an element of group 1 or 2 respectively)

$M(s) + 1/2Cl_2(g) \longrightarrow MCl(s)$ Or $M(s)+Cl_2(g) \longrightarrow MCl_2(s)$

$2K(s) + Cl_2(g) \longrightarrow 2KCl(s)$ Or $Ca(s) + Cl_2(g) \longrightarrow CaCl_2(s)$

APPLICATION ACTIVITY 2.1

1. (a)State what happens when the following elements are dropped in water

   (i)sodium (ii) calcium (iii) magnesium (iv) potassium (v) barium

   (b)compare the reactivity of:

   (i) calcium and barium with water

   (ii) Sodium and rubidium with water.

Write equations to show how sodium and calcium react with each of the following :

(i)Dilute hydrochloric acid (ii) Dilute sulphuric acid
(iii) Dilute nitric acid

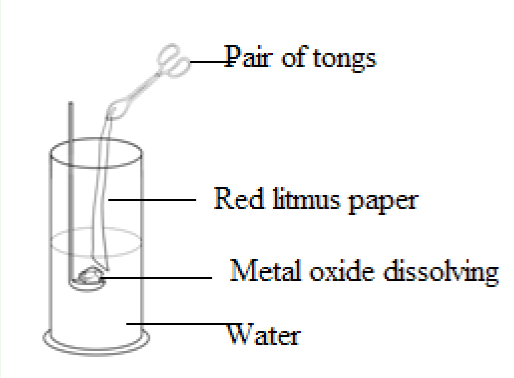
2.2. Properties of Group 1 and 2 oxides and hydroxides.

ACTIVITY 2.2

1. When calcium is burned in air it burns with a red flame forming white ash. Give the name of the white ash. When the white ash is dropped in water, it turns milky. The milky solution turns a red litmus paper blue. Explain using relevant equations giving the name of the milky solution. When this milky solution is solidified it used in agriculture. Suggest a reason why it is used in agriculture.
2. **Apparatuses:** deflagrating spoon, Bunsen burner, glass beaker, filter paper,

   Chemicals: lithium, sodium, potassium, water, and red litmus paper

Other requirements: knife, match box and petroleum gas



Procedure:

a) Cut a small piece of lithium and wrap it in piece of filter paper to remove the oil.

b) Place it on to a deflagrating spoon and heat it in a non-luminous flame.

c) Observe what happens

d) When combustion is complete, dip the deflagrating spoon into a beaker of 100 ml filled up to 50 ml of water.

e) Stir the water with the spoon and then drop a piece of litmus papers into the solution in the beaker. Observe

f) Repeat the experiment with sodium , calcium and magnesium and barium

Study questions :

i) Write the equations of reactions that take place when each metal is burnt in air

ii) Name the product that was formed in each case.

iii) What are the color changes when the aqueous solutions above are tested with litmus paper? Explain why?

(a)Reactions of group 1 and group 2 oxides with cold water.

All of the oxides react to give the hydroxide; peroxides and superoxides give other products as well. Group 1 hydroxides are water-soluble, group 2 oxides are sparingly soluble apart from barium hydroxide which is fairly soluble.

Group 1: $Li_2O(s) + H_2O(l) \longrightarrow 2LiOH(aq)$

$Na_2O_2(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2O_2(aq)$

$2KO_2(s) + H_2O(l) \longrightarrow 2KOH(aq) + H_2O_2(aq) + O_2(g)$

Group 2:$MgO(s) + H_2O(l) \longrightarrow Mg(OH)_2(aq)$

All the group 2 oxides react similarly; the hydroxides are sparingly soluble and give white suspensions except for barium hydroxide. Calcium oxide reacts very exothermically.

(b)Reactions of group 1 and group 2 oxides with dilute acids.

All the reactions are shown as ionic equations with $H^+(aq)$ ions.

Group 1: $Li_2O(s) + 2H^+(aq) \longrightarrow 2Li^+(aq) + H_2O(l)$

$Na_2O_2(s) + 2H^+(aq) \longrightarrow 2Na^+(aq) + H_2O_2(aq)$

$2KO_2(s) + 2H^+(aq) \longrightarrow 2K^+(aq) + H_2O_2(aq) + O_2(g)$

Group 2: $MgO(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2O(l)$

All the group 2 oxides react similarly except with sulphuric acid. In this case magnesium oxide reacts as given, but the sulphates of Calcium and Barium are insoluble. The oxide therefore reacts superficially but reaction then ceases.

APPLICATION ACTIVITY 2.2

1. Using molecular balanced equation show how potassium, strontium, barium, rubidium and cesium reacts with:

   (a) oxygen (b) sulphuric acid (c) dilute nitric acid (d) ethanoic acid(acetic acid) (d) water

2.3. Effect of heat on Group 1 and 2 carbonates and nitrates.

ACTIVITY 2.3

Experiment: effect of heat on nitrates and carbonates

Apparatus: glass test tubes, pair of tongs, wooden splint/match stick, Bunsen burner/heat source and spatula.

Chemicals: Lithium nitrate, potassium nitrate and magnesium carbonate

Other requirements: match box

Procedure 1

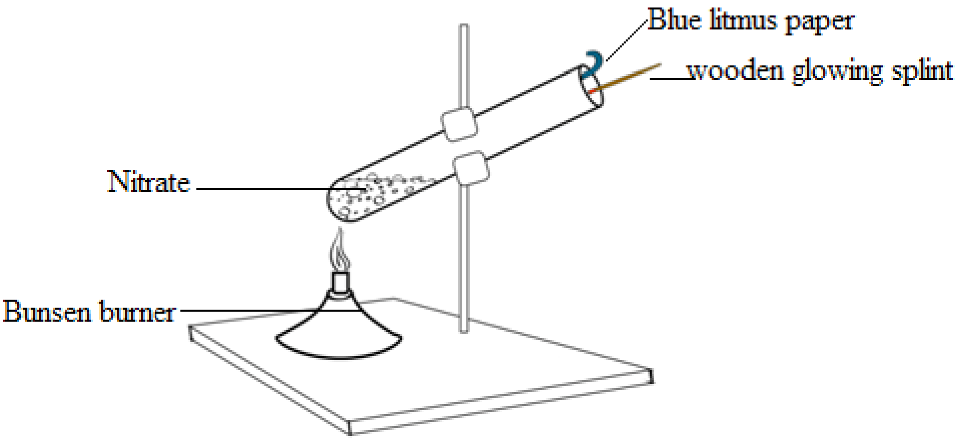
1.Take two spatula end full of lithium nitrate into a test tube and heat it strongly until there is no further change.

2. Test the gases evolved with a damp blue litmus paper and a glowing splint.

3. Observe and make conclusions on your observations.

Repeat the procedure but using potassium nitrate/sodium nitrate

Laboratory apparatus setting for thermal decomposition of a salt



Procedure 2

1. Put 2g of calcium nitrate in a Pyrex test tube
2. Heat strongly
3. Use a wet blue litmus paper to test the gas given off
4. Note your observations
5. Replace calcium nitrate with calcium carbonate, and sodium carbonate

Questions:

i) Write balanced equations for reactions in the above activities.

Caution: avoid the use of barium nitrate and strontium nitrate which can explode.

ii) How do you expect other nitrates of other metals in the s block decompose on heating

iii) Indicate the different between the nitrates of group1 and 2.

iv) Write equations to show how calcium carbonates and sodium carbonates decompose when heated.

Group 1 compounds are more resistant to heat than the corresponding compounds in Group 2. Lithium compounds often behave similarly to Group 2 compounds, but the rest of Group 1 act differently in various ways.

(a) **Heating the nitrates**

Most nitrates tend to decompose on heating to the metal oxide, brown fumes of nitrogen dioxide, and oxygen. For example, a typical Group 2 nitrate like magnesium nitrate decomposes this way:

$$2Mg(NO_3)_2(s) \longrightarrow 2MgO(s)+4NO_2(g)+O_2(g)$$

In Group 1, lithium nitrate behaves in the same way, producing lithium oxide, nitrogen dioxide, and oxygen as shown:

$$4LiNO_3(s) \longrightarrow 2Li_2O(s)+4NO_2(g)+O_2(g)$$

The other Group 1 nitrates, however, do not decompose completely at regular laboratory temperatures. They produce the metal nitrite and oxygen, but no nitrogen dioxide:

$$2XNO_3(s) \longrightarrow 2XNO_2(s)+O_2(g)$$

Each of the nitrates from sodium to cesium decomposes in this way; the only difference is in the temperature required for the reaction to proceed. For larger metals, the decomposition is more difficult and requires higher temperatures.

(b)Heating the carbonates

Most carbonates decompose on heating to the metal oxide and carbon dioxide. For example, a typical Group 2 carbonate like calcium carbonate decomposes like this:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

In Group 1, lithium carbonate behaves in the same way, producing lithium oxide and carbon dioxide:

$$Li_2CO_3(s) \longrightarrow Li_2O(s) + CO_2(g)$$

The rest of the Group 1 carbonates do not decompose at laboratory temperatures, although at higher temperatures this becomes possible. The decomposition temperatures again increase down the Group.

(i)Explaining thermal stability of nitrates and carbonates

There are two ways of explaining the increase in thermal stability down the Group.

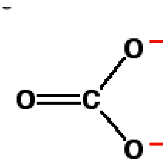
- In terms of the energetics of the process.
- In terms of the polarizing ability of the positive ions.

(ii)Explaining the trend in terms of the polarizing ability of the positive ion

A small positive ion has a large amount of charge packed into a small volume of space; this is especially true if it has a charge greater than +1. An ion with a high charge density has a marked distorting effect on any negative ions which happen to be nearby. A larger positive ion has the same charge spread over a larger volume of space. Its charge density is therefore lower, and it causes less distortion to nearby negative ions.

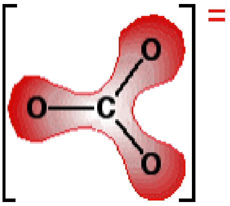
The structure of the carbonate ion

The molecular structure of carbonate is given below:



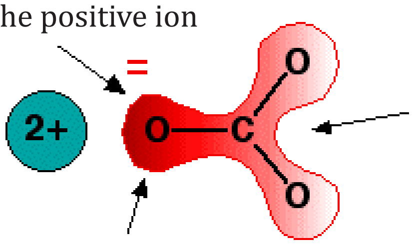
This figure shows two carbon-oxygen single bonds and one double bond, with two oxygen atoms each carrying a negative charge. However, experimental data shows that all the carbonate bonds are identical, with the charge spread out over the whole ion (concentrated on the oxygen atoms). In other words, the charges are delocalized.

This is a more complicated version of the bonding in benzene or in ions like ethanoate. The next diagram shows the delocalized electrons. The shading shows electron density, implying a greater chance of finding electrons around the oxygen atoms than near the carbon.



Polarizing the carbonate ion

Imagine that this ion is placed next to a positive ion. The positive ion attracts the delocalized electrons in the carbonate ion towards itself. The carbonate ion becomes polarized. The diagram shows what happens with an ion from Group 2, carrying two positive charges:



The decolourised electrons are pulled towards the positive ion

This end of the ion is its way to breaking away and beconing carbon dioxide

This oxygen atom is well on the way to becoming an oxide ion

If this system is heated, the carbon dioxide breaks free, leaving a metal oxide. The amount of heat required depends on how polarized the ion was. If it is highly polarized, less heat is required than if it is only slightly polarized. If the positive ion only has one positive charge, the polarizing effect is lessened. This is why the Group 1 compounds are more thermally stable than those in Group 2. The Group 1 compound must be heated more because the carbonate ion is less polarized by a singly-charged positive ion.

The smaller the positive ion, the higher the charge density, and the greater the effect on the carbonate ion. As the positive ions get bigger down the group, they have less effect on the carbonate ions near them. To compensate, the compound must be heated more in order to force the carbon dioxide to break off and leave the metal oxide.

The polarization argument is exactly the same for these compounds. The small positive ions at the top of the Group polarize the nitrate or hydrogen carbonate ions to a greater extent than the larger positive ions at the bottom. Again, the Group 1 compounds need more heat than those in Group 2 because the Group 1 ions are less polarizing.

APPLICATION ACTIVITY 2.3

1. (a)Compare the thermal stability of magnesium carbonate and calcium carbonate giving the equations of the reactions that occur.

   (b) Explain the variation in thermal stability in carbonates down group 2 elements.

   (c) Compare the thermal stability of sodium carbonate magnesium carbonate.

2. When magnesium carbonate is heated strongly a white substance is fo rmed.

   (i) What is the name of the white substance?

   (ii) Write the equation for the reaction that occur

3. Heating magnesium nitrate strongly, a white solid is formed with evolution of a reddish brown gas

   (i) What is the name of the white substance?

   (ii) Write equation for the reaction that occurs.

   (iii) What is the name of a brown gas?

4. Heating sodium nitrate strongly forms a colourless solution with evolution of colourless gas which rekindles a glowing splint. Give the name of the colourless solution and the colourless gas.

2.4. Solubility of Group 1 and 2 compounds, uses of their elements and their compounds.

a) Solubility of group 1 and 2 compounds

ACTIVITY 2.4

1. (a)You are provided with 10 test tubes.

(i)Put a half spatula end of each of the following compounds in a labeled test tube containing 10ml of water.

N°1= Magnesium carbonate ; N°2= sodium carbonate ; N°3= Calcium hydroxide, N°4= sodium hydroxide; N°5= barium hydroxide; N°6 = magnesium hydroxide; N°7= Barium carbonate; N°8= potassium carbonate, N°9 calcium nitrate, N°10 sodium nitrate

(ii)Shake the test tubes and try to make a solution. Write down your observations and related comments.

(b) (i)Pour 50 ml of paraffin in a beaker

(ii) Put 1g of calcium hydroxide and try to make a solution.

(iii) put 1g of sodium hydroxide and try to make a solution

Repeat procedure (i) to (ii) using 50 ml of water in another beaker

Write down your observations and comments.

Repeat procedures (i)-(iii) using any oxide of group 1 and group2 for instance sodium oxide and calcium oxide.

Write down your observations and comments.

All group 1 salts and hydroxides are soluble in water.

However lithium carbonate, lithium hydroxide are less soluble of group 1 compounds due to their high covalent properties.

Carbonates

The carbonates of Group 1 metals are all very soluble - increasing to an astonishing 261.5 g per 100 g of water at 20°C temperature for cesium carbonate.

The least soluble Group 1 carbonate is lithium carbonate. A saturated solution of lithium carbonate has a concentration of about 1.3 g per 100 g of water at 20°C. Solubility of the carbonates increases as you go down the group.

The solubility of Group 2 carbonates decreases down the group since the crystal lattices are hard to break(the lattice of dissociation is highly endothermic) and again much energy is released when the ions are hydrated (the enthalpy of hydration is highly exothermic). The decrease in solubility of the carbonates down the group is due the decrease in hydration enthalpy.

(b) Uses of group 1 and 2 elements and their compounds

Sodium

- Caustic soda, sodium hydroxide, and soda ash, sodium carbonate are the most important alkali used in industry. Both find applications in paper making, alumina, soap, and rayon. Sodium carbonate (soda ash) is used in water treatment.
- NaOCl is used as bleaching agent and disinfectant
- NaCl is used in seasoning food, preparing hydrogen chloride gas, in soap production, manufacture of sodium, chlorine, sodium hydroxide and sodium carbonate.
- Molten sodium is used as a coolant in nuclear reactor. Its high thermal conductivity and low melting temperature and the fact that its boiling temperature is much higher than that of water make sodium suitable for this purpose.
- Sodium wire is used in electrical circuits for special applications. It is very flexible and has a high electrical conductivity. The wire is coated with plastics to exclude moisture.
- Sodium vapor lamps are used for street lighting; the yellow light is characteristic of sodium emission.

Magnesium

- Chlorophyll, the pigment that absorbs light in plants, is a complex of magnesium and is necessary for photosynthesis.
- Magnesium hydroxide is used as Anti-acid medicine
- Magnesium is used in making Grignard reagents, the organic magnesium compounds.
- Magnesium is used as sacrificial anode to prevent iron sheet from rusting.
- Salts of magnesium and calcium are used in chemistry laboratory as drying agents.

Calcium

- Calcium is the major component of Limestone, raw material for manufacturing cement and slaked lime.
- One of the important materials involving calcium is plaster of Paris, which gets its name because a major ingredient (gypsum), $CaSO_4.nH_2O$, was mined near Paris. Plaster of Paris is used in making casts for broken bones, but it is also used for sculptures and plasterboard walls. Gypsum is used in the manufacture of cement.
- Calcium carbonate is used in the extraction of iron, manufacture of tiles, plates, laboratory mortar and pestle, in agriculture to reduce the acidity of soil.

APPLICATION ACTIVITY 2.4

1. (a) (i)Group 1 elements form ionic compounds. Explain the statement.

   (ii)State the properties of ionic compounds

   (b) Explain why lithium forms compounds with a covalent character contrarily to other component of the same group. State the properties of covalent compounds

2. Write equations to show the thermal stability of group 1 and 2 nitrates and carbonates using relevant examples and give the difference between their thermal stabilities.

3. State what would be observed if both nitrates mentioned above in (2) were separately heated.

4. Indicate how you would test for gaseous products in both reactions in (2) above. Giving the observations expected and reagents used.

5. Explain the trend in solubility of group 1 and 2 compounds down the group.

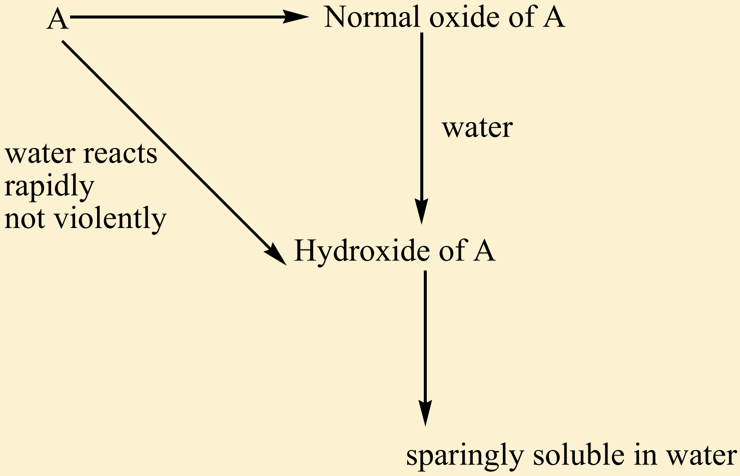
SKILLS LAB 2

Learners in their groups design experiments to investigate the solubility, thermal stability of group 2 carbonates. Indicating the apparatus, procedures and the setup of the experiments. You will be required to make by a writing a clear report.

END UNIT ASSESSMENT 2

1. When water is added to compound (A) of calcium, solution of compound (B) is formed. When carbon dioxide is passed into the solution, it turns milky due to the formation of compound (C). If excess of carbon dioxide is passed into the solution milkiness disappears due to the formation of compound (D). Identify the compounds A, B, C and D. Explain why the milkiness disappears in the last step.

2. The element **A** is a member of group1 or 2. Some reactions of A are shown below.



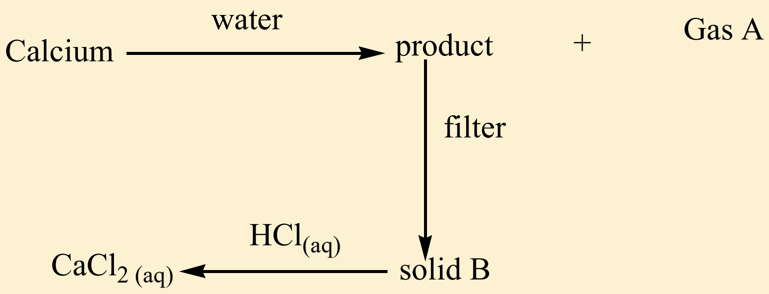
(a) On the basis of this information, what can you deduce about the identity of **A**?

(b) Write equations for the reactions of **A** with oxygen, hydrochloric acid and water

(c) Write equation for the reaction of oxide of **A** with water and dilute sulphuric acid.

3. (a)A common method for making metal chlorides is to react the metal with the appropriate acid . State why it is undesirable to attempt to make a solution of calcium chloride by reacting calcium metal with concentrated hydrochloric acid.

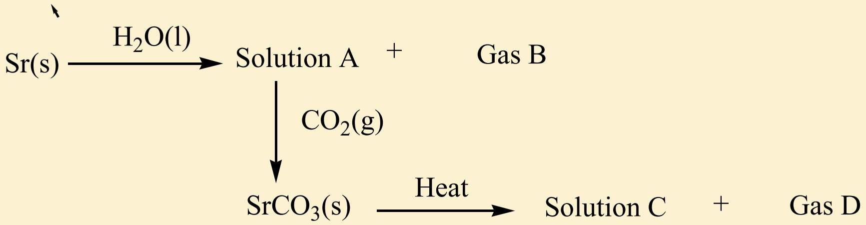
(b) a scheme for making an aqueous solution of calcium chloride is shown below.



(i) Identify gas A and the solid product B and give a balanced equation for the reaction of calcium with water.

(ii) Give the balanced equation for the reaction of solid B with dilute hydrochloric and state how you would obtain crystals of hydrated calcium chloride from the resulting solution.

4. The reactions of strontium are typical of group 2 element. Identify, by formula, substance **A-D** in the flow chart.



UNIT
3

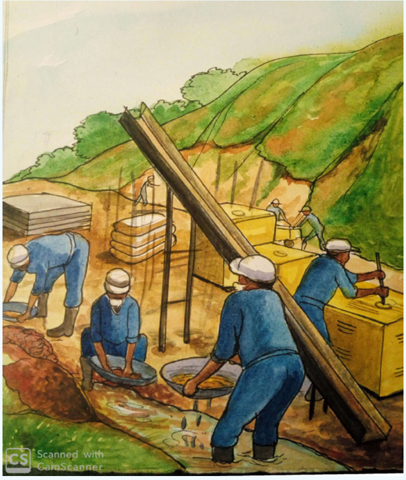
TRENDS IN CHEMICAL PROPERTIES OF GROUP 14 ELEMENTS AND THEIR COMPOUNDS

Key unit competence: Compare the chemical properties of the Group 14 elements and their compounds in relation to their position in the periodic table.

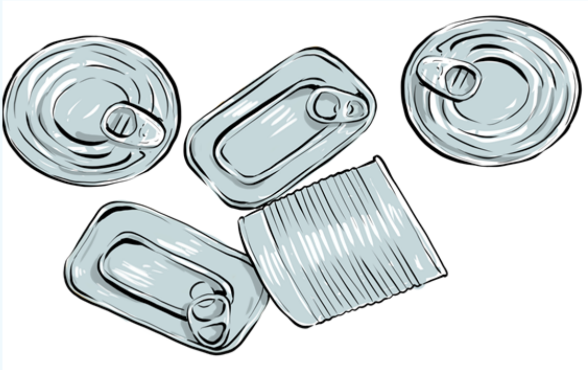
INTRODUCTORY ACTIVITY

Observe carefully the pictures below and answer the questions that follow

X



Y



Z

(i) Suggest the name of activity above in Y?(farming or mining) Give a reason for your answer.

(ii) Can you mention any mineral mined in your area? Suggest the importance of that mineral to the community and dangers associated with mining to the environment and how they can be solved.

(iii) Suggest the mineral being mined in Y. Give a reason basing on X and Z.

3.1. Comparative study of physical properties of the Group 14 elements.

ACTIVITY 3.1

1.With reference to group 13 elements discuss the variation of the following physical properties of group 14 elements

(i) metallic character

(ii) physical state and

(iii) electrical conductivity

2. Carbon (graphite) is a non-metal in group 14 but is a good conductor of electricity whereas carbon (diamond) is a poor conductor. Explain in terms of structure and bonding.

Group 14 elements are carbon ($_6C$), silicon ($_{14}Si$), germanium ($_{32}Ge$), tin ($_{50}Sn$) and lead ($_{82}Pb$). The elements of group 14 have one important feature in common; **each of them has four valence electrons.** They are characterized by the electronic configuration of 4 electrons in the outermost shell (ns^2np^2). The group is also called carbon family.

Group 14 elements show the clearest trend from **non-metal** to **metal character** down the group from **carbon** to **lead**.

In group 14 of the periodic table, there is a considerably greater change in physical properties from top to bottom in the group than there is for example, in the alkali metals of group 1 on the left and the halogens of group 17 on the right.

Carbon is a **typical non-metal** element, silicon and germanium are **semi-metals** or **metalloids** tin and lead are **metals**. However, the elements of group 14 have one important feature in common, namely each of them has four valence electrons.

In the compounds of carbon, it almost invariably completes the valence shell by forming four covalent bonds. When it forms 4 simple covalent bonds, they have a tetrahedral arrangement around the carbon atom.

Silicon and germanium also usually form four simple covalent bonds with a tetrahedral arrangement.

Tin and lead, which are larger in volume, have smaller ionization energies than carbon and silicon, and they often lose just two of their valence electrons to form the Sn^{2+} and Pb^{2+} ions.

APPLICATION ACTIVITY 3.1

Compare the metallic, physical state and electrical conductivity with reference to S-block, group 13 and group 14 elements.

3.2. Reactions of C, Sn, Pb, Si with oxygen, hydrogen, chlorine, dilute acids/concentrated acids and hydroxides.

ACTIVITY 3.2

1. Write equations to show how group 13 elements react with :

   (i)oxygen (ii) hydrogen (iii) halogens (iv) dilute acids(sulphuric acid and hydrochloric acid)

2. (i) What is meant by the term “amphoteric” ?

   (ii)Describe why the oxide of aluminium is said to be amphoteric.

   (iii)Write equations to show how aluminium reacts with sodium hydroxide solution.

   (iv)Containers made of aluminium are not supposed to keep a solution of sodium hydroxide. Explain.

(a) Reaction of group 14 elements with chlorine:

The group 14 elements mainly form tetrachlorides in the form MCl_4 but lead doesn't directly react with Chlorine.

$Si + 2Cl_2 \longrightarrow SiCl_4$, $Sn + 2Cl_2 \longrightarrow SnCl_4$

$PbCl_4$ is unstable molecule and is prepared from PbO_2. It decomposes to make stable $PbCl_2$

(b) Reaction of group 14 elements with hydrogen:

Carbon graphite reacts with hydrogen gas at 30 ^{0}C to 95^{0}C to produce a mixture of methane (CH_4), ethane (C_2H_6) and propane (C_3H_8). The primary product is methane and the other products are produced due to free radical reaction of the methane.

$C(s) + 2H_2(g) \longrightarrow CH_4(g)$

Apart from carbon, other elements of group 14 do not react with hydrogen directly.

(c) Reaction of group 14 elements with acids and bases:

Experiment to investigate the effect of concentrated nitric and sulphuric acid

Materials needed: concentrated nitric and sulphuric acid, source of heat, test tube holder, spatula, charcoal, boiling test tube.

Procedure

1. Get a piece of charcoal and burn it. Observe and write the chemical equation that represents the change that takes place when the charcoal burns.

2. (a) Put about 1 gram of carbon charcoal powder in a boiling tube.

   b) Add 1 ml of concentrated nitric acid.

   c) Heat strongly on a Bunsen burner flame using a test tube holder.

   d) Observe and note the changes during heating.

   e) Deduce the chemical changes that have occurred.

3. Repeat procedure (b), (c), (d) using concentrated sulphuric acid

Study questions:

i) Write equations to show how charcoal reacts with concentrated sulphuric acid, nitric acid

ii) Describe the behavior of the acid in the this reaction.

Carbon does not react with dilute acids but reacts with hot, concentrated acids:

$$C(s) + 4HNO_3(aq) \longrightarrow CO_2(g) + 4NO_2(g) + 2H_2O(l)$$

$$C(s) + 2H_2SO_4(aq) \longrightarrow CO_2(g) + 2SO_2(g) + 2H_2O(l)$$

Silicon reacts with concentrated HNO_3:

$$Si + 4HNO_3 \longrightarrow SiO_2 + 4NO_2 + 2H_2O$$

Silicon reacts with concentrated sodium hydroxide (base)

$$Si(s) + 2OH^-(aq) + H_2O(l) \longrightarrow SiO_3(aq)^{2-} + 2H_2(g)$$

Tin reacts with concentrated nitric acid to form tin dioxide and nitrogen dioxide:

$$Sn(s) + 4HNO_3(aq) \longrightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$$

Cold dilute nitric acid reacts with tin to form a mixture of tin II nitrate and ammonium nitrate solution.

$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Tin is sufficiently metallic to form various mixtures of $Sn(SO_4)_2$ and hydrated SnO_2 and sulphur dioxide when it reacts with hot, concentrated sulphuric acid.

$$Sn + 4H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2SO_2 + 4H_2O$$

$$Sn + 2H_2SO_4 \longrightarrow SnO_2 + 2SO_2 + 2H_2O$$

Tin reacts with strongly non-oxidising acids in solution to form tin(II) salts and hydrogen gas:

$$Sn + 2HCl \longrightarrow SnCl_2 + H_2$$

Tin reacts with concentrated or molten sodium hydroxide base to form a stannate ion SnO_2^{2-} and hydrogen gas:

$$Sn + 2OH^- \longrightarrow SnO_2^{2-} + H_2$$

Lead reacts with hot concentrated sulphuric acid according to the following equation to form lead(II) sulphate and sulphur dioxide:

$$Pb + 2H_2SO_4 \longrightarrow PbSO_4 + SO_2 + 2H_2O$$

The reaction of lead with concentrated nitric acid forms lead(II) nitrate and nitrogen dioxide as shown in the equation:

$$Pb + 4HNO_3 \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$$

The reaction of lead with dilute nitric acid forms lead(II) nitrate and nitrogen monoxide as shown in the equation:

$$3Pb + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

The reaction of lead with boiling, concentrated hydrochloric acid forms lead(II) chloride and hydrogen gas following the equation:

$$Pb + 2HCl \longrightarrow PbCl_2 + H_2$$

Lead which is amphoteric; reacts with **hot, concentrated sodium hydroxide** to form trihydroxoplumbate (II) and hydrogen gas as shown by the equation:

$$Pb(s) + 2OH^-(aq) + H_2O(l) \longrightarrow PbO_3^{2-}(aq) + H_2(g)$$

APPLICATION ACTIVITY 3.2

1. Write the molecular structure of carbon dioxide, carbonate ion and carbon monoxide.
2. Describe how CO_2 gas dissolves in water and state the nature of the solution formed.
3. Describe 2 chemical properties of amphoteric substances using Al_2O_3 as an example.
4. Write equation to show how Carbon, silicon and tin react with the following :
   (i) concentrated sulphuric acid
   (ii) concentrated nitric acid
   (iii) concentrated sodium hydroxide
   (iv) A stream of chlorine gas.

3.3. Reaction of oxides, chlorides of group 14 elements with water, acids and strong alkaline solutions.

ACTIVITY 3.3

1. Describe how the oxides of group 13 elements with reference to aluminium react with

   (i) Water (ii) dilute hydrochloric acid (iii) concentrated sodium hydroxide solution.

2. Write equations to show how the aluminium chloride is acidic when dissolved in water.
3. Do you expect group 14 oxides and chlorides behave in a similar way or differently?

Reaction of CO_2 with water:

Carbon dioxide reacts with water to form carbonic acid.

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

The reaction is reversible, but H_2CO_3 dissociates to produce H^+ and HCO_3 ; the dissociation of carbonic acid is also reversible since carbonic acid is a weak acid.

Carbon dioxide is an acidic oxide, so H_2CO_3 does not react with acids.

Experiment to investigate the effect of carbondioxide in water

Materials needed: plastic straw, beaker/plastic bottle and phenolphthalein indicator

Procedure:

- Put about 50ml of water in a plastic container or beaker
- Add a few drops of phenolphthalein into the container of water
- Blow the air into the water using a plastic straw as shown below.

Record your observations

Study questions:

(i) What is the purpose of the indicator in this experiment.

(ii) Why did the indicator change colour?

(ii) Suggest the reaction that has occurred in this experiment.

(iii)During the experiment to investigate the effect of carbondioxide and water the indicator changes colour. Why?

(ii)Reaction of CO_2 with sodium hydroxide:

Experiment to investigate the effect of carbondioxide on sodium hydroxide.

Materials needed: a beaker/plastic bottle, a solution of 50ml concentrated sodium hydroxide, plastic straw and phenolphthalein indicator

Procedure:

Put about 50ml of concentrated sodium hydroxide in a beaker

Add a few drops of phenolphthalein indicator

Blow the air into the beaker or plastic bottle for some time until the colour of the indicator turn colourless as show below

Record your observations

Observe and make conclusion

Study questions: (i) what is the purpose of the indicator in this experiment.

(ii) Why did the indicator change colour?

(ii) Suggest the reaction that has occurred in this experiment.

Carbon dioxide reacts with sodium hydroxide, NaOH, to form sodium carbonate salt.

$$CO_2(g) + 2NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l)$$

Reactions of CCl_4 with water, acids and bases:

Carbon tetrachloride does not react with water, acids, and alkaline solutions.

Reaction of SiO_2 with water: Silicon dioxide does not react with water.

Reaction of SiO_2 with acids: Silicon dioxide reacts with HF acid **only**:

$$SiO_2(s) + 4HF(aq) \longrightarrow SiF_4(aq) + 2H_2O(l)$$

This reaction is the one used to write on the glass, for example on the windscreen of vehicle.

Reaction of SiO_2 with bases: Silicon dioxide reacts with hot concentrated NaOH solution.

$$SiO_2(s) + 2OH^-(aq) \longrightarrow SiO_3^{2-}(aq) + H_2O(l)$$

Reaction of $SiCl_4$ with water:

Silicon dioxide undergoes hydrolysis in water, this is due to the fact that silicon atom possesses vacant d-orbitals that can partially accommodate an oxygen atom during the reaction unlike in the case of CCl_4.

$$SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4H^+(aq) + 4Cl^-(aq)$$

Reaction of $SiCl_4$ with acids, bases and water: $SiCl_{4(l)}$ does not react with acids, bases and water.

Reaction of SnO_2 with water: SnO_2 does not react with water.

Reaction of SnO and SnO_2 with acids:

SnO_2 does not dissolve in dilute acids but it reacts with hot concentrated sulphuric acid, H_2SO_4

$$SnO_2(S) + 2H_2SO_4(conc) \quad + (heat) \longrightarrow Sn(SO_4)_2(aq) + 2H_2O(l)$$

SnO_2 also reacts with hot concentrated HCl acid.

$$SnO_2(s) + 4HCl(conc.) \ + (heat) \longrightarrow SnCl_4(aq) + 2H_2O(l)$$

SnO also reacts with concentrated HCl acid.

$$SnO(s) + 2HCl(aq) \longrightarrow SnCl_2(aq) + H_2O(l)$$

Reaction of SnO_2 and SnO with bases

SnO_2 reacts with concentrated NaOH to produce a stannate (IV) ion:

$$SnO_2(s) + 2OH^-(conc) \longrightarrow SnO_3^{2-}(aq) + H_2O(l)$$

SnO reacts with dilute NaOH to produce a hydrogen stannate (II) ion:

$$2SnO(s) + 2OH^-(aq) \longrightarrow 2HSnO_2^-(aq)$$

Reaction of SnO with concentrated alkali such as NaOH, disproportionation occurs in which one ion of tin in SnO gains electrons to be reduced and another ion of tin loses electrons to be oxidised.

$$2SnO(s) \longrightarrow Sn(s) + SnO_2(s)$$

SnO is more basic than SnO_2 due to its lower oxidation state and ionic character.

d) Reaction of lead oxides and chlorides

Reaction of $SnCl_4$ with water

$SnCl_4$ hydrolyses in water to produce hydrogen chloride fumes.

$$SnCl_4(l) + 2H_2O(l) \longrightarrow SnO_2(s) + 4HCl(aq)$$

The tetrachlorides of group 14 elements are colourless liquids apart from $PbCl_4$ which is a yellow liquid. $SnCl_4$ is unstable and it decomposes to $SnCl_2$ and Cl_2.

Reaction of PbO_2 and PbO with water:

Figure 3.1(a) : lead (IV) oxide (PbO_2) Solid

Figure 3.1(b): lead (II) oxide (PbO) Solid

PbO_2 and PbO are amphoteric, insoluble in water but react with acids and bases. PbO is more stable than PbO_2.

Reaction of PbO_2 and PbO with acids:

Because most lead salts are insoluble, the nature of the acid used is important, we use an acid that does not possess anions that form an insoluble salt with lead ions. So dilute HNO_3 is used:

PbO_2 and PbO react with HNO_3, HCl and H_2SO_4 acids according to the following equations:

$$PbO(s) + 2HNO_3(cold, dilute) \longrightarrow Pb(NO_3)_2(aq) + H_2O(l)$$

$$PbO(s) + 2HCl(hot, dilute) \longrightarrow PbCl_2(aq) + H_2O(l)$$

$$PbO(s) + H_2SO_4(hot, conc) \longrightarrow PbSO_4(s) + H_2O(l)$$

PbO_2 reacts with concentrated HCl at room temperature to produce $PbCl_2$, Cl_2 and H_2O. it is a strong oxidizing agent.

$$PbO_2(s) + 4HCl(aq) \longrightarrow PbCl_2(s) + 2H_2O(l) + Cl_2(g)$$

$PbCl_2$ formed is sparingly soluble in the cold aqueous solution but is soluble in hot water.

At 0^0C, the reaction produces $PbCl_4$ and water:

$$PbO_2(s) + 4HCl(aq) \longrightarrow PbCl_4(aq) + 2H_2O(l)$$

PbO_2 reacts with hot, concentrated H_2SO_4 to produce $PbSO_4$, oxygen and water:

$$2PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l) + O_2(g)$$

Reaction of PbO_2 and PbO with alkaline solutions:

Plumbates are formed on reaction with OH^-:

$$PbO(s) + 2OH^-(aq) \longrightarrow PbO_2^{2-}(aq) + H_2O(l)$$

$$PbO_2(s) + 2OH^-(aq) \longrightarrow PbO_3^{2-}(aq) + H_2O(l)$$

Thus PbO and PbO_2 are amphoteric oxides.

Reaction of $PbCl_4$ and $PbCl_2$ with water and HCl:

$PbCl_4(l) + 2H_2O(l) \longrightarrow PbO_2(s) + 4HCl(aq)$, the reaction is rapid (hydrolysis)

$PbCl_2$ dissolves in concentrated HCl due to the formation of a soluble complex

$PbCl_4^{2-}$

$$PbCl_2(s) + 2Cl^-(aq) \longrightarrow [PbCl_4]^{2-}(aq)$$

APPLICATION ACTIVITY 3.3

1. Discuss the reactions of chlorides of group 14 with water giving expected observations and reactions that occur.

2. The chloride of carbon does not react with water but other chlorides do. Gives reasons to justify the statement.

3.4 Thermal stability of oxides, halides and hydroxides.

ACTIVITY 3.4

1. Briefly discuss the thermal stability of carbonates of group 2 elements
2. Do you expect the thermal stability of oxides, chlorides and hydroxides of group 14 elements follow similar trend as carbonates of group 2. Justify your answer.

The thermal stability of dioxides and tetrachlorides of group 14 decreases down the group from carbon to lead due to the increase in size of the group 14 atoms. Hydroxides of group 14 follow a similar trend like those of halides and oxides.

The increase in size of group 14 atoms down the group results **in weaker bonds.** Thus $PbCl_4$ is the least stable of the chlorides of group 14 elements.

a)Stability of oxides of group 14 elements

The thermal stability of **XO** increases downward the group from carbon to lead.

X represents: C, Si, Sn and Pb. The stability of **XO** increases in the order:

$CO < SiO < SnO < PbO$

Silicon monoxide is obtained by heating SiO_2 and Si under special conditions.

$$SiO_2(s) + Si(s) \longrightarrow 2SiO(s)$$

The main valency of oxides of tin, is +4, in other words SnO_2 is the most stable tin oxide; the valency of +2, SnO, is subsidiary.

On exposure to air at room temperature, SnO_2 is formed.

$$2Sn(s) + O_2(g) \longrightarrow 2SnO_2(s)$$

The main valency of oxides of lead, is +2, in other words, PbO is the most stable lead oxide; the valency of +4 is subsidiary. PbO is the most stable oxide of group 14 elements. PbO_2 cannot be prepared from lead monoxide because it decomposes at 300^0C.

b) Thermal stability of halides of group 14 elements

CCl_4, $SiCl_4$ and $GeCl_4$ are very stable and they do not decompose even at high temperatures.

$SnCl_4$ decomposes only when it is heated to form $SnCl_2$ and Cl_2, so $SnCl_4$ is more stable.

$PbCl_4$ decomposes readily without heating to form $PbCl_2$ and Cl_2.

Thermal stability of tetrahalides of group 14 halides decreases down the group from carbon to lead because the bonds in Group 14 halides become longer and weaker down the group.

Thermal stability of tetrahalides of group 14 also decreases from fluorides to iodides.

All the tetrahalides are volatile covalent compounds except SnF_4 and PbF_4 which have some ionic character.

$PbBr_4$ and PbI_4 do not exist since iodine and bromine are not strong oxidizing agents enough to remove all 4 valence electrons.

c) Thermal stability of hydroxides of group 14 elements

Lead (II) hydroxide $Pb(OH)_2$ decomposes at temperatures ranging between 100^0C and 145^0C to produce PbO and H_2O .

Tin (II) hydroxide $Sn(OH)_2$ decomposes easily between 60^0C and 120^0C to produce SnO and H_2O.

Carbon and silicon are non-metals, so they don't form hydroxides.

APPLICATION ACTIVITY 3.4

1. Explain the following statements

   (i) Carbondioxide is a gas whereas silicon dioxide is a solid at room temperature.

   (ii) Lead (II) chloride is ionic whereas lead(IV) chloride is covalent.

   (iii) Describe the thermal stability of chlorides of group 14 elements

   (iv) Carbon tetrachloride/chloromethane does not react with water whereas other chlorides react with water.

2. Lead (IV) chloride decomposes to form lead(II) chloride and chlorine whereas lead(iv) oxide decomposes to form lead(II) oxide and oxygen. Explain

www.s-cool.co.uk/a-level/chemistry/group-ii-and-group-iv/revise-it/group-iv-tetrahalides

3.5. Trends in stability of oxidation states: +2 and +4 as a result of inert pair effect and Uses of Group 14 elements and their compounds

a)Stability of oxidation states as a result of inert pair effect

ACTIVITY 3.5

(i) Write the valence electronic configuration of carbon, silicon and germanium using s, p, d and f notation.

(ii) Predict the general formula for the elements used to represent the elements mentioned in (i) explain how you arrived at your answer.

(iii) In relation to the physical properties of elements and compounds suggest where these elements are used in daily life.

All the elements of Group 14 form four single bonds such as in tetrahalides of formula CCl_4, $SiCl_4$, $GeCl_4$, $SnCl_4$ with the exception of $PbBr_4$ and PbI_4 that do not exist because bromine and iodine are not sufficiently strong oxidizing agents to convert Pb to Pb^{4+}. Germanium, tin and lead can ionize to form Ge^{2+}, Sn^{2+} and Pb^{2+} and also are capable of forming Ge^{4+}, Sn^{4+}, Pb^{4+} respectively.

Germanium dioxide GeO_2 is more stable than germanium monoxide GeO. The oxide of tin in +4 oxidationstate is slightly more stable than that in +2 state. Silicon oxide predominantly exists as SiO_2. SiO is too unstable to exist at room temperature and pressure but may exist at about 2000 ^{0}C. Carbon oxides are stable in +4 state. Thus CO which is unstable reacts exothermically to form the stable compound of CO_2. In lead compounds, the +2 state is more stable than +4 state. PbO_2 is unstable and is a very strong oxidizing agent.

$$PbO_2(s) + 4HCl(aq) \longrightarrow PbCl_2(s) + Cl_2(g) + 2H_2O(l).$$

The stability of compounds with the oxidation state of **+2** in group 14 elements generally increases on moving down the group from carbon to lead.

The stability of compounds with the oxidation state of **+4** in group 14 elements increases on moving upward the group from lead to carbon. The bonding in tetravalent compounds is predominantly covalent.

Inert pair effect: Inert pair effect refers to the inability of the outermost **s**-electrons to participate in chemical bonding in Ge, Sn and Pb elements of group 14 and hence only 2 electrons of the outermost **p** orbital are involved.

The outermost **s** sub-energy level electrons are much more tightly attracted to the nucleus than the outermost **p** orbital. As we move down the group, the difference in energy level between **s** and **p** orbitals becomes wider.

So if we use weak oxidizing agents, only 2 electrons in **p** orbitals are removed. If we use a strong oxidizing agent, 2 electrons in **s** orbital and 2 electrons in **p** orbital are all removed from the shell.

b)Uses of elements of group 14 and their compounds

Group 14 elements are used in numerous applications. The wide applications are due to the fact that some of the elements in the group are non-metals, metals and metalloids.

Carbon uses:

- As a component of fuel for combustion as charcoal or coal.
- As the main component of crude oil and its derivatives used in our everyday life such: fuel, plastics, etc…
- As good chemical reducing agent used in extraction of metals (metallurgy).
- As a lubricant in moving parts of machines, to make electrodes, in lead pencils when mixed with clay.
- Carbon isotope, C-14 isotope is used in archaeological dating.

- Diamond is used to make glass cutters, drilling devices and as abrasive for smoothing hard materials as precious gemstone in jewelry and ornamental objects; it is also a precious stone appreciated in jewelry.

Silicon uses:

- Silicon is used as a semi-conductor in transistors in electrical gadgets such as radios, computers, amplifiers etc..
- Silicon in form of silicates is used in ceramics and in glass production.
- Silicon is also used in medicine to make silicone implants.
- Many rocks that we use for building our houses and other buildings are Silicates.
- Ferrosilicon alloy is used as a deoxidizer in steel manufacture.
- Silicon dioxide can be used to produce toothpastes and in semiconductors; silicon dioxide is the main component of sand, a raw material in the manufacture of glass.

Germanium uses:

- Germanium being a metalloid, is used in transistors in electrical gadgets such radios, computers, amplifiers etc..

Tin uses:

- Tin is used in plating steel sheets to resist corrosion; it is used for example to make canned tins to avoid the corrosion of the materials which are in contact with an acid medium.

Figure 3.2(a) Tinned cans

Lead uses:

- Lead is used in making linings of vessels which are used in industrial production of sulphuric acid.

Figure 3.3(b): Lead bricks

- Lead bricks alloyed with 4% antimony is used in radiation shielding
- Lead is used in accumulator plates of the batteries and as shielding materials against dangerous radiations such as X-rays, gamma rays etc.

Figure 3.4(c)

APPLICATION ACTIVITY 3.5

1. Explain using examples what is meant by the term “inert pair effect” as applied in group14 elements.
2. Explain using examples, the variation of +2 and +4 oxidation states in group 14 elements.
3. Give two uses of carbon diamond and carbon graphite in relation to their physical properties.

SKILLS LAB 3

Make a field visit to find out how tin ore (cassiterite) is mined and make a report. In you report you will include the following:

Materials needed: books, pens and probably a camera or smart phone to take some pictures

What to do! Make a report

Probable Areas to visit in Rwanda: Rutongo in Rulindo

Musha in Rwamagana

Rwinkwavu in Kayonza and some other areas.

END UNIT ASSESSMENT 3

1. State 2 uses of carbon in daily life.

2. Diamond is considered to be very hard, predict its application.

3. Carbon forms hydrocarbons such as methane when combined with hydrogen. State where methane is found in Rwanda and indicate its uses.

4. Silicon is a semi-conductor. Predict its uses in electric gadgets.

5. Tin resists corrosion. Based on this property discuss the applications of tin in daily life.

6. Describe how diamond is used on a large scale.

7. Describe the materials that are manufactured using lead, tin and silicon as the main component.

8. Give 3 compounds which contain:

   i) Silicon ii) Lead.

9. With the help of equations describe an experiment that can be carried out to test for the presence of lead (ii) ions in a solution. Indicate the expected observations and reagent(s) used in this experiment.

10. Carbon dioxide is a gas at room temperature whereas silicon dioxide is a solid of high melting point. Explain.

11. Give the general formula to represent group 14 elements and write the electronic configuration of silicon, germanium and tin (for atomic numbers, refer to the periodic table.)

12. For each reaction, explain why the given products form.

    $Pb(s) + Cl_2(g) \rightarrow PbCl_2(s)$

    $Mg_2Si(s) + 4H_2O(l) \rightarrow SiH_4(g) + 2Mg(OH)_2(s)$

    $GeO_2(s) + 4OH^-(aq) \rightarrow GeO_4^{4-}(aq) + 2H_2O(l)$

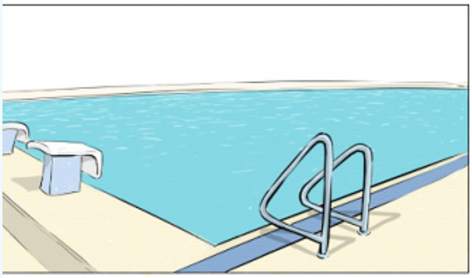
UNIT 4

TRENDS IN CHEMICAL PROPERTIES OF GROUP 17 ELEMENTS AND THEIR COMPOUNDS

Key unit competence: **Explain the chemical properties of group 17 and their compounds.**

INTRODUCTORY ACTIVITY

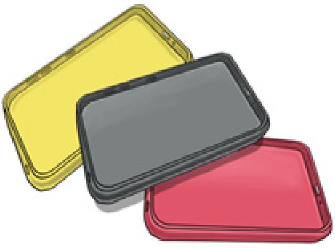
Look at the pictures below carefully and answer the questions that follow.



A

B

C



D

E

(i) Identify the pictures A, B, C, D and E.

(ii) Identify the substance that makes water look green in picture A.

(iii) Suggest substances/materials or chemicals that make it easy for activity in picture B to be carried out?

(iv) Suggest the element that is common in all pictures A to E.

4.1 Reactions with oxygen, water, sodium hydroxide (both dilute and cold or hot concentrated).

ACTIVITY 4.1

(i) Using the picture A of the introductory activity, suggest the chemical reaction that took place for water to turn green.

(ii) What is the main component of bleaching agents?

(iii) The reactivity of halogens decreases down the group whereas group 1 and 2 elements reactivity increases down the group. Explain

(iv) Write equations to show how group 1 and 2 react with halogens.

Due to their valence electronic structure of $\mathbf{ns^2\ np^5}$ halogens gain easily one electron to complete the octet structure, that is why they exhibit an oxidation state (-1) in most of their compounds. They are generally considered as good oxidizing agents.

All the halogens are highly reactive; they are the most reactive group of non-metals in the periodic table. They react with metals and non-metals to form halides. But in Group 17 elements (halogens), the reactivity of halogens decreases down the group in the order: $F_2 > Cl_2 > Br_2 > I_2$. Hence each halogen displaces those below it from their salts.

(a)Reactions of halogens with water

Fluorine exhibits anomalous behavior in many properties. The anomalous behavior of fluorine is caused by its small size and very high electronegativity.

Fluorine reacts vigorously with water to produce oxygen O_2 and hydrofluoric acid HF.

$$2F_2(g) + 2\,H_2O(l) \longrightarrow O_2(g) + 4HF(aq)$$

Chlorine dissolves slightly in water at room temperature (25°C). At 80°C and above, Cl_2 gas is insoluble in water. Chlorine reacts with water to produce hydrochloric acid, HCl and Hypochlorous acid, HClO:

$$Cl_2\,(g) + H_2O\,(l) \longrightarrow HCl\,(aq) + HClO\,(aq)$$

Hypochlorous acid is a bleaching agent.

Bromine dissolves in water; it reacts with water slowly to form hydrogen bromide HBr and hypobromous acid, HBrO:

$$Br_2(g) + H_2O(l) \longrightarrow HBr(aq) + HBrO(aq)$$

Solubility of iodine in water is very low. Iodine does not react with water.

Table 12.2 compares the oxidizing power of halogens when a given halogen is mixed with an aqueous solution of another halide.

(b) Reaction of halogens with hydroxide:

Chlorine reacts with excess cold dilute OH^- and the reaction equation is:

$$Cl_2(g) + 2OH^-(aq) \longrightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$$

or $Cl_2 + NaOH \longrightarrow NaCl + NaClO + H_2O$

With hot concentrated OH^-, chlorate ClO_3^-, is formed:

$$Cl_2(g) + 6OH\text{-}(conc) \longrightarrow Cl^-(aq) + ClO_3^-(aq) + 2H_2O(l)$$

or $3Cl_2 + 6NaOH \longrightarrow 5\ NaCl + NaClO_3 + 3H_2O$

The same reactions occur for Br_2 and I_2.

Fluorin**e** unlike other halogens, does not form oxosalts with alkalis and it does not form oxoacids as shown in the following reactions:

$$2OH^-(dil) + 2F_2O \longrightarrow F_2 + 2F^- + H_2O$$

$$4OH^-(conc) + 2F_2 \longrightarrow 4F^- + O_2 + 2H_2O$$

APPLICATION ACTIVITY 4.1

1. Bleaching agents contain sodium hypochlorite (NaClO) as the one the main components. Write balanced equations to show sodium hypochlorite can be prepared from sodium metal indicate the conditions for the reactions that occur.

2. Sodium chlorate is one of the main products of the reaction between sodium hydroxide and chlorine.

   (i) State the condition for the reaction and write a balanced equation for the reaction.

   (ii) With help of an equation show how sodium chlorate can be used to prepare oxygen.

   (iii)Indicate the conditions under which alkalis react with halogens. Use bromine to show those reactions and their conditions.

   (iv)How does fluorine differ from other halogens in reference to reaction with alkalis?

4.2. Trends in oxidizing power down the group (displacement reactions).

ACTIVITY 4.1

(i) Write equation to show a solution of copper (ii) sulphate reacts with zinc metal. Use this reaction to explain that a solution of zinc sulphate does not react with copper .

(ii) Use the reaction in (i) to explain the term oxidation, reduction, oxidizing and reducing agents.

(iii) Explain why a solution of potassium chloride does not react with bromine but a solution of potassium iodide reacts with chlorine.

The table below shows how the halogens react with their solutions in displacement reactions to show the variation in reactivity down the group.

Table 4.1: halogens react with their solutions in displacement reactions

Halogen	$F^-(aq)$	$Cl^-(aq)$	$Br^-(aq)$	$I^-(aq)$
$F_2(g)$	No change	Greenish solution = $Cl_2(aq)$/ displacement of Cl^-	Red solution = $Br_2(aq)$/ displacement of Br^-	Red solution = $I_2(aq)$/ displacement of I^-
$Cl_2(g)$	No change	No change	Red solution (as above)	Red solution (as above)
Br_2 (l,aq)	No change	No change	No change	Red solution (as above)
I_2(s,aq)	No change	No change	No change	No change

APPLICATION ACTIVITY 4.2

1. (a)Copy and complete the following reactions below:

(i)$KCl(aq) + Br_2(l) \longrightarrow$
(ii)$NaBr(aq) + I_2(s) \longrightarrow$
(iii)$KCl(aq) + I_2(s) \longrightarrow$
(iv)$KI(aq) + Br_2(l) \longrightarrow$
(v) $KI(aq) + I_2(aq) \longrightarrow$

(b)Explain why the reactions occur and others do not occur.

4.3 Reaction with metals and non-metals.

ACTIVITY 4.3

1. When a stream of chlorine gas is passed through burning sodium, white fumes are formed. Suggest the name of the white fumes.

2. A similar reaction occurs when magnesium, calcium and phosphorous react with chlorine. Suggest the products formed and write equations for the reaction that occur.

3. Which product do you expect to form when a stream of chlorine is passed through heated iron metal? Justify your answer

(a)Reaction with metals:

Halogens react with metals to form salts, metal halides. Example: bromine reacts with magnesium to form magnesium bromide

$$Mg(s) + Br_2(l) \longrightarrow MgBr_2(s)$$

The preparation of certain anhydrous metal halides is carried out using this method of reacting a halogen and a metal. Examples: **$MgCl_2$** (white solid), **$AlCl_3$** (white solid), **$FeCl_3$** (brown solid), **$FeBr_3$** (dark red solid) etc… are halides that can be prepared in this way.

Generally metal halides are ionic, the most ionic being the ones where the metal has low oxidation states (+1, +2).

For the same metal in the same oxidation state, the ionic character of the metal halides decreases down the group:

$MF > MCl > MBr > MI$; whereby M is a monovalent metal.

If a metal exhibits more than one oxidation state, the halide in a higher oxidation state will be more covalent than the one with a lower oxidation state.

Example: **$SnCl_4$** and **$PbCl_4$** are more covalent than **$SnCl_2$** and **$PbCl_2$** respectively.

(b) Reaction with non-metals

- Halogens react with hydrogen gas to form hydrogen halides but the affinity for hydrogen decreases from fluorine to iodine.

$$Cl_2(g) + H_2(g) \longrightarrow 2HCl(g)$$

- The halogens do not react directly with oxygen. However, Fluorine forms two oxides with oxygen which are F_2O and F_2O_2.

$$O_2(g)+F_2(g) \longrightarrow F_2O_2(g)$$

Halogens form many oxides such as, Cl_2O, Cl_2O_6, etc.. In those oxides, except for fluorine, halogens have positive oxidation states due to the high electronegativity of oxygen; this makes them unstable and very reactive.

Fluorine forms compounds with oxygen where it has a negative charge; they are rather oxygen fluoride; e.g. OF_2

- With phosphorus, all halogens react with phosphorus to form phosphorus (III) halides of the form **PX_3.** The reaction equation of phosphorus with bromine is represented in a general equation as:

$$2P(s) + 3Br_2(g) \longrightarrow 2PBr_3(l)$$

In excess chlorine or bromine, phosphorus reacts to form phosphorus (V) chloride or bromide:

$$2P(s) + 5Cl_2(g) \longrightarrow 2PCl_5(s)$$

The reaction between phosphorus (III) chloride and chlorine to form phosphorus (V) chloride is reversible:

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5$$

APPLICATION ACTIVITY 4.3

1. With help of equations show how chlorine reacts with the following compounds.

   (i) Water (ii) phosphorous (iii) sodium hydroxide solution

   (iv) sodium and magnesium

2. Descibe the bleaching action of chlorine and state where in industry this reactions is applied

4.4 Preparation and behavior of hydrides of halogens with regard to: acid strength, volatility and their reducing power.

ACTIVITY 4.4

1. (a)What is an acid?

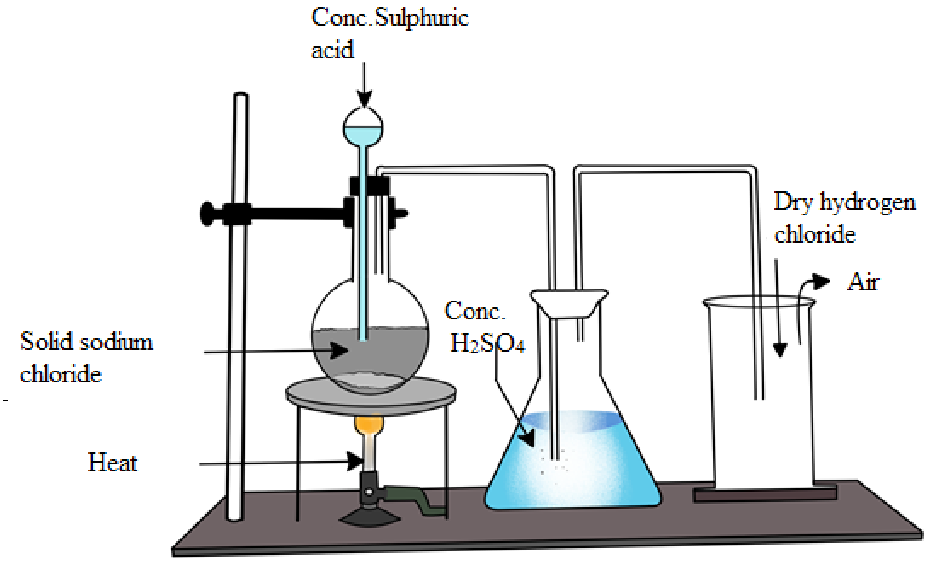
   (b) Acids are classified as strong or weak. Explain this statement using specific examples.

   (c) Discuss the factors which determine the strength of acids.

   (d) Ethanol boils at 78^{0}C whereas water boils at 100^{0}C yet both exist as liquids at room temperature. Explain

   (e) What does the oxidizing and reducing power depend on?

Preparation of hydrogen chloride



Fgure 4.1: Preparation of hydrogen chloride

Equation for reaction: NaCl (s) + H_2SO_4 (aq) $\longrightarrow$ $NaHSO_4$ (aq) + HCl(g)

Hydrogen chloride gas is prepared by reacting a concentrated solution of sulphuric on chlorides of group 1 elements. The gas is passed through concentrated solution of sulphuric acid to dry it and collected by downward delivery. Other hydrides cannot be prepared this way because Cconcentrated H_2SO_4 oxidizes Br^- and I^- to form Br_2 and I_2 elements respectively.

Concentrated H_2SO_4 cannot oxidize F^- and Cl^- ions.

$$2HBr(g) + H_2SO_4(conc) \longrightarrow Br_2(l) + SO_2(g) + 2H_2O(l)$$

$$6HI(g) + H_2SO_4(conc) \longrightarrow 3I_2(s) + S(s) + 4H_2O(l)$$

(c)Acid strength of acid hydrides

The acid strength is a measure of how an acid dissociates in water into its ions. Strong acids dissociate completely into their ions, whereas a weak acid dissociates partially into its ions.

Examples:

- Hydrochloric acid is a strong acid:

$HCl(aq) + H_2O(l) \longrightarrow H^+(aq) + Cl^-(aq)$ complete dissociation.

- Hydrofluoric acid is a weak acid:

$HF(aq) + H_2O(l) \rightleftharpoons H^+(aq) + F^-(aq)$ partial dissociation

The acid strength of hydrogen halides (HX) increases down the group from HF to HI:

HF < HCl < HCl < HBr < HI

Because of the very electronegativity and small size of F, it forms very strong H-F bond. In water, it is slightly dissociated to give few H^+ ions in solution; therefore it is a weak acid.

This is due to the strong bond H-F; in other words, the bond strength HX decreases down the group.

(d)Volatility of hydrogen halides

Volatility is the state of having a low boiling point to evaporate easily.

The boiling points of hydrogen halides generally increase down the group. This is because the van der Waals' forces increases with size (the forces increase with increase of the surface of contact between molecules).

The high electronegativity of fluorine atom is the root cause of the strong hydrogen bonds. It is liquid at room temperature while other hydrogen halides are gases.

The trend in volatility: HF> HCl < HBr < HI

Table 4.4: Variation of boiling points of hydrogen halides

Hydrogen halide	Boiling points/°C
HF	19.9
HCl	-85
HBr	-66.7
HI	-35.4

HF is an exception to the general trend (it has a high boiling point of 19.9 ^{0}C). It is almost liquid at room temperature while the rest are gases because there are strong hydrogen bonds between HF molecules. For the other Hydrogen halides, the boiling point increases with increasing molecular mass.

(d)Reducing power

The reducing power of hydrogen halides is dependent on the ability of their anions (halide ions) to liberate electrons.

It becomes easier to oxidize the hydrogen halides as we go down the group because the electron on the halide ion becomes less attracted to the nucleus as we move down the group.

Hence the order of reducing power is: $I^- > Br^- > Cl^- > F^-$

Given that halogens are the best oxidizing agents since they tend to capture electrons from other elements to achieve the octet electronic configuration, the halide ions are not expected to be good reducing agents.

However, an iodide ion, due to its big size, can easily liberate an electron and therefore act as a mild reducing agent.

Hence HI is the strongest reducing agent of all hydrogen halides.

HI can reduce Cl_2, Br_2, O_2, Fe^{3+} salts, etc... to produce molecular iodine, I_2:

$$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$$

$$O_2(g) + 4HI(aq) \longrightarrow 2H_2O(l) + 2I_2(aq)$$

That is why when a colourless aqueous solution of HI is exposed to air, it turns brown because of the presence of I_2.

APPLICATION ACTIVITY 4.4

1. Hydrogen chloride is prepared by reacting a concentrated solution of sulphuric acid with solid sodium chloride.

   (a)Write a balanced equation for the reaction that occurs.

   (b) Other hydrogen halides (HBr and HI) cannot be prepared by the same method as hydrogen Chloride. Using equations explain.

   (c) (i)write equation for the reaction of concentrated phosphoric acid (H_3PO_4) with NaBr (s)

   (ii) Why does the concentrated solution of phosphoric acid cause HBr to be evolved during the reaction?

2. You have two unknown sample solutions A and B. You are told that one is a solution of NaCl(aq), the other is a solution of NaI(aq). You are asked to identify them. When you add a solution of Fe^{3+}(aq) which has a yellow colour, to both sample solutions, you get the following results: (a) Adding Fe^{3+}(aq) to A gives a yellow solution; (b) Adding Fe^{3+}(aq) to B gives a solution with a complicated mixture of colours between green and violet.

   Question: Which solution is A, which solution is B? Justify

4.5. Uses and hazards of halogens and their compounds.

ACTIVITY 4.5

Observe the pictures in figure 4.2 , A, B, C, D and E below and answer the following questions

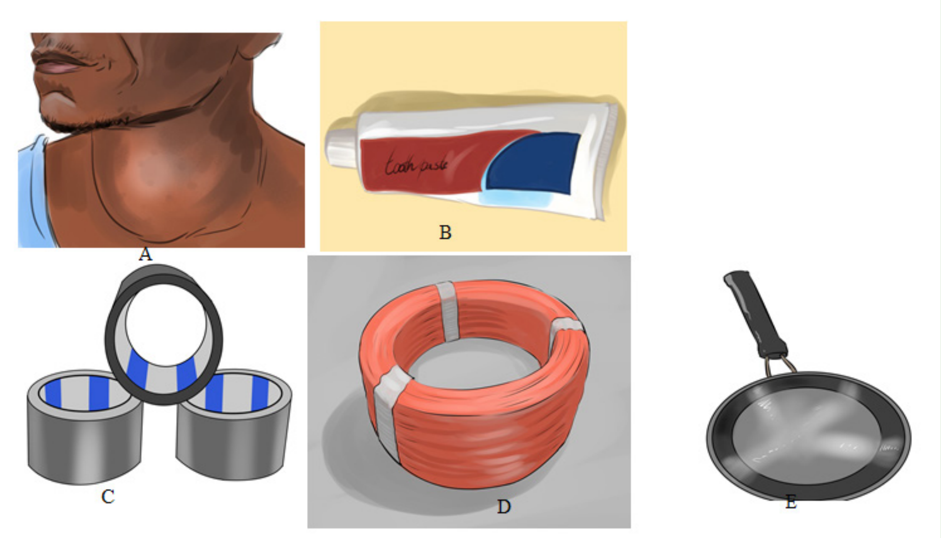


Figure 4.2

(a) Identify the pictures A-E

(i) What is name of this condition that caused the swelling in picture above. What is its cause? How can we prevent it?

(ii) How often do you use substance B and for what reason? Can you identify some components in B? Why is added in the tooth paste?

(b) (i)Identify the similarity between pictures C, D and E.

(ii)Suggest some elements that are used to make materials C, D and E

(c) Suggest the dangers caused by these materials to the environment.

a) Uses of halogens /group 17 elements and their compounds

Halogens and their compounds have many applications and uses in different domains:

- Fluorine is used in production of synthetic fibres. It is also used as an ingredient in toothpastes as well as in the manufacture of HF.
- NaCl is the main food seasoning table and kitchen salt; it is also used in many industrial processes such as: NaOH production, soap manufacturing, etc…
- Chlorine is used to synthesize products for bleaching clothes, papers, etc. It is used as an antiseptic and as fungicide.
- Chlorine is used in water treatment as well as in the manufacture of plastics such as Polychloroethene (polyvinyl chloride: PVC).
- Chlorine is used to make DDT (Dichlorodiphenyltrichloroethane: a banned chemical), and other chlorinated aromatic compounds used as pesticides.
- A Chlorine compound, HCl is important in the human stomach for digestion.
- Halogen elements are used to manufacture polymers.
- Bromine is used in photographic industry (film manufacture).
- Iodine is used in food in the form of iodised salt and in drugs to fight against goitre and to kill bacteria in wounds, etc.

b) Hazards caused by group 17 elements

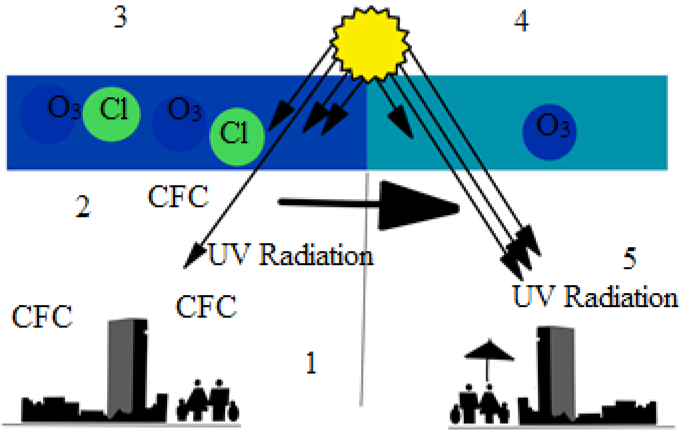
CFCs: **Chlorofluorocarbons**

Chlorofluorocarbons are hydrocarbons where some or all of the hydrogen atoms have been replaced by chlorine and fluorine atoms. Most of those compounds are stable and unreactive at high temperature. That is why they were used as aerosol propellants, refrigerants, and solvents.

One example of CFC is Freon 12 (CCl_2F_2) that was used in refrigerators.

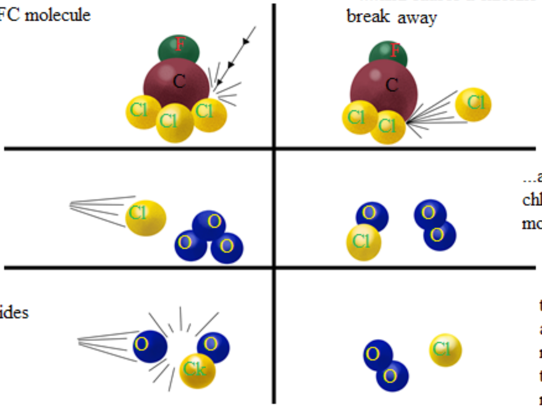
Because of their chemical inertness, CFCs can diffuse unchanged into the upper atmosphere up to the ozone layer (10-15 km). There, photochemical reactions cause them to break down into radicals, $^{\cdot}Cl$. Radicals, being very active chemical species, react with ozone to form ordinary oxygen, hence destruction of ozone layer. For this reason, their use has been banned all over the World.

Ozone layer depletion process



1. CFCs released
2. CFCs rise into ozone layer
3. UV released chlorine from CFCs
4. Chlorine destroys ozone
5. Depleted ozone by more UV
6. More UV, more skin cancer

Figure 4.4.3.(a) depletion of ozone layer



Ultra violet radiation strikesa CFC molecule

....and causes a chlorine atom to break away

The chlorine atom collides with an ozone molecule

...and steals an oxygen atom to form a chlorinemonoxide and leave a molecule of ordinary oxygen

when a free atom of oxygen collides with the molecule of chlorine monoxide

the two oxygen atoms form a molecule of oxygen. the clorine atom is released and free to destroy more ozone

Figure 4.3 (b) depletion of ozone layer

APPLICATION ACTIVITY 4.5

1. Carbon compounds containing chlorine and fluorine are highly volatile and were used in in refrigerators, aerosol propellants and solvent. However, because of that low boiling point they easily escape into atmosphere and cause air pollution. In the atmosphere they destroy ozone layer which protects us from dangerous ultraviolet rays from the sun.

   Using equations describe how the ozone layer is destroyed by these chlorofluorocarbons.

2. Suggest the effects of ultraviolet rays to plants and animals.

SKILLS LAB 4

Carry out a research to find the main components of bleaching agents and substances that can be bleached apart from clothes.

Explain how bleaches are used as disinfectants and discuss any effect of using bleaches.

END UNIT ASSESSMENT 4

1. State different hydrogen halides that can be formed.

2. What is the difference between hydrogen halides and hydrohalic acids?

3. Describe the anomalous behaviour of fluorine in the group (explain at least 3 differences from the rest of the halogens).

4. Write the equation of the reaction that takes place between: a) Solid chloride with concentrated sulphuric acid. b)Bromine and hot concentrated sodium hydroxide solution.

5. Briefly explain the trend in volatility of hydrogen halides as you move down the group.

6. Explain why the hydrogen halides acidity increases in the order: $HF < HCl < HBr < HI$

7. Explain the trend in solubility of halogens in water as you move down the group.

8. You have two test tubes; one contains water, the other contains a solution of chlorine in water, and you are asked to identify them. What test are you going to do in order to identify the content of the two test tubes?

9. Write equations to show how bromine reacts with the following.

   (a) water (b)hot and concentrated sodium hydroxide solution

   (c) heated Iron metal (d) potassium iodide. e) cold and dilute sodium hydroxide

UNIT 5

TRENDS IN CHEMICAL PROPERTIES OF PERIOD 3 ELEMENTS AND THEIR COMPOUNDS.

Key unit competence: **Explain the variation of Period 3 elements and their compounds in relation to their positions in the Periodic Table.**

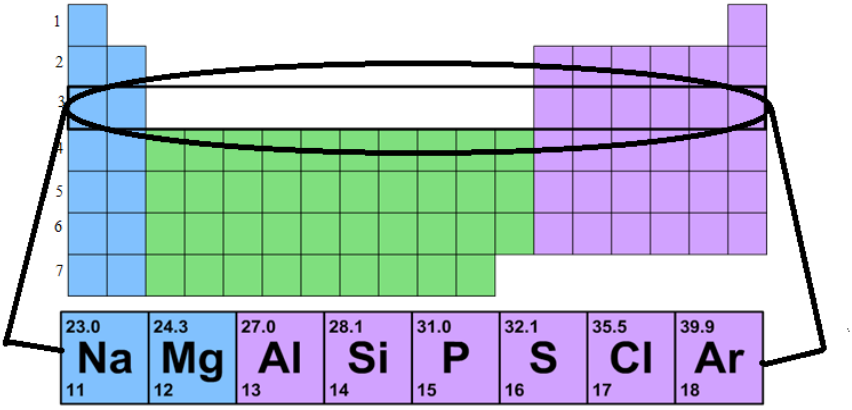
INTRODUCTORY ACTIVITY

1. Look at the elements enclosed in a circle below in the periodic table;

   (i) What do these elements have in common?

   (ii) Give a reason to support your answer in (i) above.

   (iii) Write the electronic configuration of all members indicated in the picture below in terms of s, p , d and f notation.



5.1. Physical properties of period III elements:

ACTIVITY 5.1

1. Consider the elements Li, Be, B, N, F and Ne

   (a) Which elements exist as diatomic molecules in the gaseous state at room temperature?

   (b) Which element has the highest boiling point?

   (c)Which element forms a chloride of the form XCl_3?

   (d) Which element has the largest first ionization energy?

   (e) Which element has the smallest second ionization energy?

2. (a)Which element has high electronegativity?

   (b)Are these metals or non-metals? Explain.

   (c) Do you expect them to conduct electricity? Explain.

(a) Variation of First ionization energies (IE) of Period 3 elements

First ionization energy generally increases across Period 3 from left to right. However, it drops at aluminium and Sulphur (table 5.1 and Fig.5.1). This can be explained in term of more stable electronic structures of the two elements after losing 1 electron:

Al : $[3s^2 3p^1] \longrightarrow Al^+[3s^2] + e^-$; the electronic structure of Al^+ with a full $3s^2$ orbital is more stable than the one of Al with incomplete $3p^1$ orbital.

In the same way:

S: $[3s^2 3px^2 py^1 pz^1] \longrightarrow S^+[3s^2 3px^1 py^1 pz^1] + e^-$; the electronic structure of S^+, with a half-full $3p^3$ orbital is more stable than the $3p^4$ orbital of sulphur.

Table 5.1 (a): Variation of first ionization energies of period 3

Element	Proton number	Symbol	1st ionization energy (kJ/mol)
Sodium	11	Na	496
Magnesium	12	Mg	738
Aluminium	13	Al	578
Silicon	14	Si	789
Phosphorus	15	P	1012

Sulphur	16	S	1000
Chlorine	17	Cl	1251
Argon	18	Ar	1521

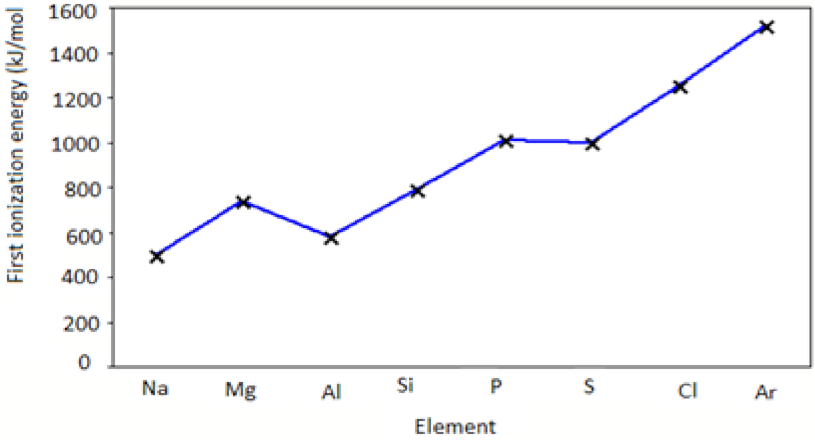


Figure5.1 (a) : Graph of first ionization energies of period 3 elements

Going across Period 3, there are more protons in each nucleus so the nuclear charge in each element increases. Therefore the force of attraction between the nucleus and outer electron is increased, and there is a negligible increase in shielding because each successive electron enters the same energy level. So apart from the two exceptions mentioned above, the first ionization energy increases from left to right in the period (figure 5.1).

(b) Variation of atomic radius of Period 3 elements

Table 5.2 (b): Variation of atomic radius of period 3 elements

Element	Proton number	Symbol	Atomic radius (nm)
Sodium	11	Na	0.191
Magnesium	12	Mg	0.160
Aluminium	13	Al	0.130
Silicon	14	Si	0.118
Phosphorus	15	P	0.110
Sulphur	16	S	0.102
Chlorine	17	Cl	0.099
Argon	18	Ar	0.095

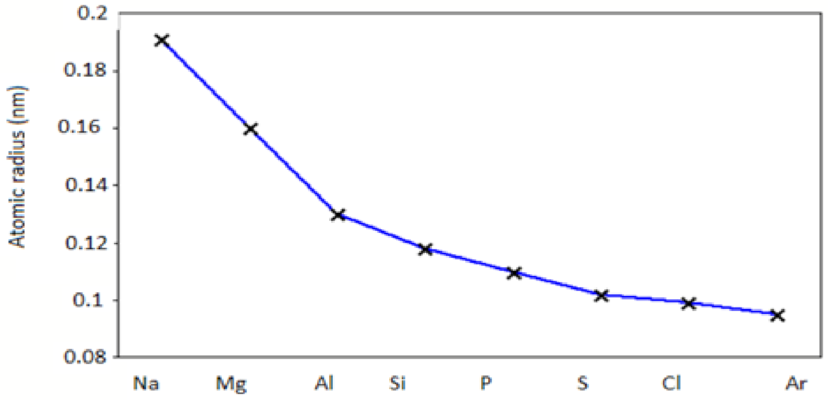


Figure 5.2(b): Graph showing the variation of atomic radius of period 3 elements

Going across Period 3 from left to right, the number of protons in the nucleus increases so, the nuclear charge increases. There are more electrons, but the increase in shielding is negligible because each extra electron enters the same principal energy level. Therefore, the force of attraction between the nucleus and the electrons increases. So the atomic radius decreases as indicated in the Figure 5.2 and table 5.2.

(c) Variation of electronegativity of Period 3 elements

Table 5.3 (c): Variation of electronegativity of period 3 elements

Element	Proton number	Symbol	Electronegativity (scale 0 to 4)
Sodium	11	Na	0.9
Magnesium	12	Mg	1.2
aluminium	13	Al	1.5
Silicon	14	Si	1.8
Phosphorus	15	P	2.1
Sulphur	16	S	2.5
Chlorine	17	Cl	3.0

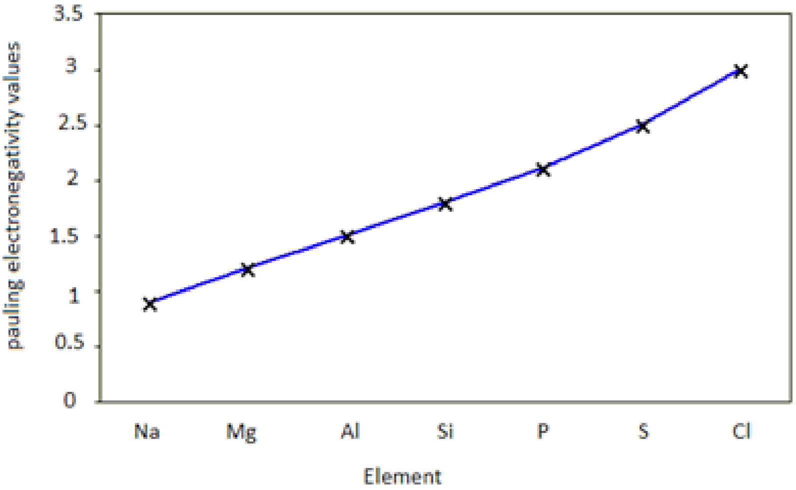


Figure 5.3 (c): Graph showing the variation of electronegativity of period 3 elements

Going across Period 3 from left to right electronegativity increases almost linearly due to the nuclear charge increase as atomic radius decreases. There are more electrons, but the increase in shielding is negligible because each extra electron enters the same principal energy level so electrons will be more strongly attracted to the nucleus.

You might expect argon (with 18 electrons) to be the most electronegative element in Period 3, but its outer energy levels are full. Therefore, it does not form covalent bonds with other atoms, so it is given an electronegativity value of zero.

(d) Variation of melting and boiling points in Period 3

Melting and boiling points generally increase going from sodium to silicon, then decrease going to argon with a "jump" at Sulphur (Fig and Table 5.4).

Table 5.4(d): Variation of melting and boiling points of period 3 elements

Element	Proton number	Symbol	Melting point (K)	Boiling point (K)
Sodium	11	Na	371	1156
Magnesium	12	Mg	922	1380
Aluminium	13	Al	933	2740
Silicon	14	Si	1683	2628
Phosphorus	15	P	317	553
Sulphur	16	S	392	718
Chlorine	17	Cl	172	238
Argon	18	Ar	84	87

Sodium, magnesium and aluminium are all metals. They have metallic bonding, in which positive metal ions are attracted to delocalized electrons. Going from sodium to aluminium, the charge on the metal ions increases from +1 to +3 through magnesium at +2, the number of delocalized electrons increases, so the strength of the metallic bonding increases and the melting points and boiling points increase.

Silicon has giant covalent bonding structure. It has a giant lattice structure similar to that of diamond, in which each silicon atom is covalently-bonded to four other silicon atoms in a tetrahedral arrangement. This extends in three dimensions to form a giant macromolecule and this explains the very high melting point and boiling point.

Phosphorus, sulphur, chlorine and argon, are all non-metals, and they exist as small, separate molecules. Phosphorus, sulphur and chlorine exist as simple molecules. Argon exists as separate atoms (monatomic). When these elements melt or boil, it is the van der Waals' forces between the molecules which are broken; being weak they need little energy to overcome them.This explains why their melting and boiling points are low. However, Sulphur has a higher melting point and boiling point than the other three because phosphorus exists as P_4 molecules, Sulphur exists as S_8 molecules, chlorine exists as Cl_2 molecules, and argon exists as individual Ar atoms.

The strength of the van der Waals' forces decreases as the size of the molecule decreases, so the melting points and boiling points decrease in the order S_8> P_4> Cl_2>Ar

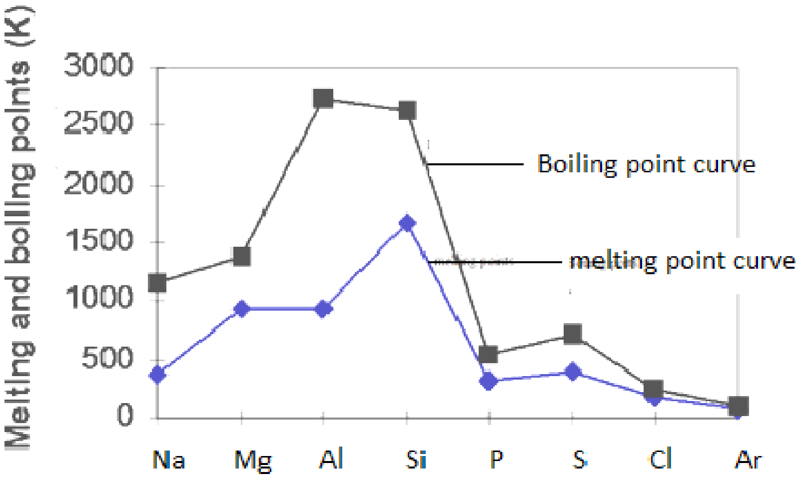


Figure 5.4(d): The graph showing the variation of melting and boiling points across period 3 elements

(e) Variation of electrical conductivity of Period 3 elements

Electrical conductivity increases going across Period 3, left to right, from sodium to aluminium, then decreases sharply to silicon as indicated by the graph 5.5 below.

Table 5.5 (e):Variation of relative electrical conductivity of period 3 elements

Element	Proton number	Symbol	Relative electrical conductivity (Al as reference = 1)
Sodium	11	Na	0.26
Magnesium	12	Mg	0.42
Aluminium	13	Al	1.00
Silicon	14	Si	0.10
Phosphorus	15	P	0
Sulphur	16	S	0
Chlorine	17	Cl	0
Argon	18	Ar	0

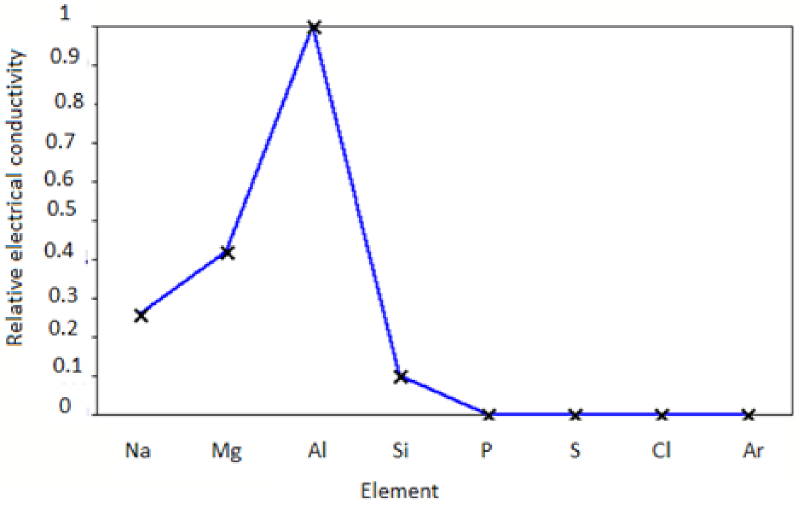


Figure 5.5 (e): Graph showing the variation of relative electrical conductivity of period 3 elements

The delocalized electrons are free to move and carry charge. Going from sodium to aluminium, the number of delocalized electrons increases, there are more electrons which can move and carry charge so the electrical conductivity increases.

Silicon is called a semi-conductor because at higher temperatures more electrons are promoted to the higher energy levels so there are more delocalized electrons to move and carry charge.

Phosphorus, sulphur and chlorine, the outer electrons are not free to move and carry charge because they are held strongly in covalent bonds. In argon (mono atomic) the outer electrons are not free to move and carry charge because they are held strongly in a stable third energy level and this explains their zero electrical conductivity.

(f) Variation of metallic character of period 3 elements

Metallic character decreases as you move across a period 3 in the periodic table from left to right. This occurs as atoms more readily accept electrons to fill the valence shell than lose them. Note that as the metallic character decreases across the period, the reducing power decreases whereas oxidizing power increases.

(g)Variation of electron affinity across period 3 elements

The **electron affinity** [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

$$X(g) + e^- \longrightarrow X^-(g) \qquad \text{EA1}$$

As we might predict, it becomes easier to add an electron to an atom across the period from left to right as the effective nuclear charge of the atoms increases. As we go from left to right across period 3, electron affinity values tend to become more negative, i.e. ability to acquire electrons increases.

The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups.

Magnesium and phosphorous have anomalous electron affinity, Magnesium has a positive EA while phosphorous is less negative. This is due to their electron arrangement, where in magnesium the electron should be added to 2p orbital which is a less stable structure compared to the electronic structure of the atom $[Ne]3s^2$. Similarly in phosphorous the electron should be added to 3p orbital which is half filled and thermodynamically stable.

Table 5.6. Showing Variation of electron affinity across period 3 elements

Element	Na	Mg	AL	Si	P	S	Cl
Electron affinity	-20	+67	-30	-135	-60	-200	-365

APPLICATION ACTIVITY 5.1

1. (i) Explain the variation of the ionization energy and electronegativity in period 3 elements.

(ii) Explain the anomalous behavior indicated by magnesium and phosphorous in figure 5.1 above .

2. The table below shows the melting points of the period 3 elements except for silicon:

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Mp/K	371	923	933	-	317	392	172	84

(a) Explain in terms of bonding why the melting point of magnesium is higher than that of sodium.

(b) Predict the approximate melting point of silicon.

(c) Explain why chlorine has a lower melting point than sulphur.

3. (d) Explain the variation of metallic character, atomic radii, melting and boiling points, electron affinity and electrical conductivity across the period.

4. Use the information in the following table to explain the statements below.

	Na	Mg	Al	Si	P	S	Cl
Atomic radius/nm	0.156	0.136	0.125	0.117	0.110	0.104	0.090
Ionic radii/ nm	0.095	0.065	0.050			0.184	0.181
1st Ionization energy/ kjmol^{-1}	425	743	579	791	1060	1003	1254

(a) Atomic radius decreases across the period

(b) First ionization energy increases across the period

5.2 .Chemical properties: reaction with hydrogen, trends in oxidizing/reducing power across the period.

ACTIVITY 5.2

1. Write the formula of the hydrides of group14 elements .

2.How do you expect these hydrides to react with water (group 14 and 13)

3. Describe the nature of bonding in these hydrides of group 14 and 13.

4.Describe the oxidizing and reducing power of group 17 elements.

5. How do you think these two properties in (4) vary across the period 3 elements? Give reasons for your answer.

(a) Reaction with Hydrogen

Sodium and magnesium react with hydrogen to form ionic hydrides.

$$2Na(s) + H_2\ (g) \longrightarrow 2NaH\ (s)$$

$$Mg(s) + H_2\ (g) \longrightarrow MgH_2(s)$$

Chlorine reacts with hydrogen to form covalent hydrogen chloride gas

$$Cl_2 (g) + H_2 (g) \longrightarrow 2HCl(g)$$

(b) Reducing and oxidizing power

Elements on the left of the period three are metals.They react by losing their valance electrons; hence they are good reducing agents.Their reducing power decreases from Na to Al.

The elements on the right of the period three are non-metals. They react by gaining or sharing their valance electrons; they are good oxidising agents.Their oxidising power increases from Si to Cl.

In general the oxidizing power increases from left to right and the reducing power decreases from left to right across period 3 due to decrease of atomic size that affects the ionization energy and electronegativity.

APPLICATION ACTIVITY 5.2

1. Explain why the reducing power decreases while the oxidizing power increases across period 3 elements.

2. Describe the behavior of hydrides of period 3 elements in terms of:

   (i) bonding (ii) structure (iii) melting and boiling points (iv) reaction with water.

5.3. Properties of Period 3 compounds:

(a) Nature of oxides (Alkalinity and acidity of oxides).

ACTIVITY 5.3

1. Experiment to investigate the nature of oxides of period 3 elements

Materials needed: sodium oxide, calcium oxide, aluminium oxide, water, litmus paper (red & blue), boiling test tube

Procedure:

(i) Add a spatula full of sodium oxide in a boiling test tube followed by water. Shake to mix.

(ii)Insert a pice of a blue and red litmus paper separately

(iii) Observe the effect of the solution on both litmus papers.

(iv)Repeat procedure (i) to (iii) using calcium oxide

(v) Make observations and comment on them.

Study question

Write equations to show what takes place when the oxides react with water.

Table 5.7. Formula of oxides of period 3 elements

Sodium	Magnesium	Aluminium	Silicon	Phosphorous	Sulphur	Chlorine
Na	Mg	Al	Si	P	S	Cl
Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2	Cl_2O_7
				P_4O_6	SO_3	Cl_2O
Basic		Amphoteric	Acidic			

The metallic oxides on the left of the period table basic, aluminium is amphoteric, silicon dioxide is slightly acidic while other oxides are acidic.

5.4 Ionic and covalent character of compounds (chlorides, hydrides and oxides).

ACTIVITY 5.4

1. The ionic character of hydrides of group 1 elements increases in the order LiH<NaH <KH<RbH<CsH . Explain

2. How do we determine which compounds have greater ionic character?

3. The table below gives some data about the chlorides of period 3 elements.

Formula	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	S_2Cl_2	Cl_2
Boiling point/^{0}C	1465	1418	423	57	76	136	-34
pH of aqueous solution	7	6	2	2	2	1	1

(a) Explain why the boiling point of NaCl is higher than that of $MgCl_2$.

(b) Explain why the pH of NaCl is 7 and that of $AlCl_3$ is 2.

(c) A solution of aluminium chloride turns a blue litmus paper red whereas a solution of sodium chloride has no effect on litmus paper. Explain.

The chlorides of interest are given in the table below:

Table 5.8 (a): Formula of chlorides of period 3 elements

Sodium	Magnesium	Aluminium	Silicon	Phosphorous	Sulphur
NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5	S_2Cl_2
				PCl_3	

Sulphur forms three chlorides: SCl_2 SCl_4, and S_2Cl_2 . The last one is the most common. Aluminum chloride may be found, under certain conditions, as a dimmer, Al_2Cl_6. Phosphorous forms two chlorides, PCl_3 and PCl_5.

The nature and structure: Sodium chloride and magnesium chloride are ionic and consist of giant ionic lattices at room temperature.

Aluminum chloride exhibits covalency characters. Aluminium ion has high charge density; due to this, the electron cloud of the chloride is distorted toward the aliminium ion, Al^{3+}, impacting an appreciable covalent property to the bond. The other chlorides are simple covalent molecules.

Hydrides are commonly named after binary compounds that hydrogen forms with other elements of the periodic table. Hydride compounds in general form with almost any element, except a few noble gases. The common hydrides of period 3 elements are shown in the table below.

Table 5.9(b): Showing the nature of bonding of hydrides period and chlorides 3

Element	Na	Mg	Al	Si	P	**S**	**Cl**
Formula of hydride	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	HCl
Nature of bonding and structure	Ionic	Partially Ionic	Partially ionic	Covalent small covalent gaseous molecule	Covalent small covalent gaseous molecule	Covalent small covalent gaseous molecule	Covalent small covalent gaseous molecule

As we can see the hydrides of period 3 vary from ionic hydride such as NaH at the left side to polar covalent hydride such as HCl at the right side of the period.

APPLICATION ACTIVITY 5.4

1. Consider the following oxides:

CaO, Al_2O_3 , Na_2O , MgO , P_2O_5 , SO_2 SiO_2

(a) State which of the oxides are:

(i) Basic (ii) acidic (iii) neutral (iv)Amphoteric

(b)Describe briefly how you could test to see whether a solid oxide is basic , acidic , neutral or amphoteric

2. (a)In each of the following species state whether the metal oxide is ionic or covalent and explain why : Na_2O , Al_2O_3

(b) An unknown inorganic oxide is a white solid of melting temperature 1710°C and has no action towards water. State and explain whether or not this is sufficient information to deduce whether the bonding is ionic or covalent.

3. The behavior of hydrides of the elements Na-Cl in water is summarized below

NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	HCl
Reacts forming hydrogen gas and alkaline solution			No reaction	Reacts to form a slightly alkaline solution	Reacts to form a slightly acidic solution	Reacts to form an acidic solution

(a) Write equations to summarize the reactions of NaH and MgH_2 with water.

(b) Suggest a reason why SiH_4 has no reaction with water.

(c) Write an equation to account for the formation of a slightly alkaline solution when PH_3 reacts with water.

(d) Write an equation to account for the formation of an acidic solution when HCl reacts with water.

(e) Explain the trends and differences in the reactions of these hydrides with water in terms of their structure and bonding

SKILLS LAB 5

Project: identification of substances found in banana peelings

Materials needed: fresh banana peelings, paraffin, match box with match sticks.

Procedure:

1. Collect fresh banana peeling and dry them on a clean place. This may take a week or more (do not place them directly on the sun).
2. Put the dry banana peelings in container and burn them completely until you obtain black ash.
3. Using a sieve , filter to obtain a clean powder.
4. Keep the powder safely until you back to school.
5. Dissolve the powder in a plastic beaker and insert a blue litmus paper. Observe and make conclusion.
6. Repeat the procedure 1-5 for other plant materials such as leaves or stems and find whether they are acidic, basic or neutral.

END UNIT ASSESSMENT 5

1.The table below gives some data about the chlorides of elements of period 3

Formula	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	S_2Cl_2	Cl_2
Boling point/^0C	1465	1418	423	57	76	136	-34
pH of aqueous solution	7	6	2	2	2	1	1

(a) Explain why the boiling point of NaCl is higher than that of $MgCl_2$.

(b) Make a research and explain why the pH of NaCl is 7 and that of $AlCl_3$ is 2.

2. (a) Distinguish between dissolving and hydrolysis.

(b) Name one chloride that dissolves in water, and one chloride that undergo hydrolysis.

(c) State how the bonding in the chlorides changes on crossing the second and third periods from left to right

(d) Suggest two ways how you would know that a reaction has taken place when a few drops of water is added to silicon (iv) chloride.

3. (a)Write an equation that shows that a solution of beryllium chloride in water is acidic.

(b) Predict the shape of PCl_3 molecule and suggest a likely bond angle.

(c)Iron (III) chloride, $FeCl_3$, forms dimmers in the gas phase similar to those of aluminium chloride. Draw the likely structure of these two dimers.

4. Carbon and silicon are in the same group of the periodic table and form both tetrachloride,CCl_4 and $SiCl_4$ respectively. However, CCl_4 does not undergo hydrolysis whereas $SiCl_4$ hydrolyses in water to form white fumes.

(a) Identify the white fumes.

(b) Write equation for the reaction to show how silicon (IV) chloride hydrolyses in water.

(c) Explain why silicon (IV) chloride hydrolyses whereas carbon tetrachloride does not.

UNIT
6

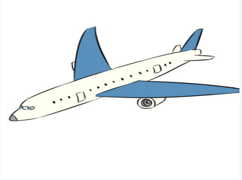
PROPERTIES AND USES OF TRANSITION METALS

Key unit competence: **Explain the properties and uses of transition metals.**

INTRODUCTORY ACTIVITY

Look at these pictures below carefully and answer the following questions.

A



B

C

D

E

F

G

H

(i) Identify the pictures from A to H

(ii) Suggest the elements from which the materials/objects are made of.

(iii) Give reasons why the elements you suggested are used to make such materials.

6.1. Definition and Electronic configuration of transition metals (1^{st} series).

ACTIVITY 6.1

1. Write the electron configuration of the following atoms and ions:

   (a) Ca (Z=11) (b) Ca^{2+}, Na(Z=11), and Na^+

2. Referring to the portion of periodic table below

   (a) Write the electron configuration of the elements from Sc to Zn.

   (b) Point out any difference between the electron configuration of the above elements and that of other elements in s and p blocks.

   (c) From the differences indicated between their electronic configurations, define the term transition element/metal.

3. State some of the physical properties of elements in the S-block.

According to IUPAC system, a transition metal is "***an element whose atom has a partially filled d sub-shell, or which can give rise to cations with an incomplete d sub-shell***".

The elements are also called **d-block elements** because their valence electrons are in d-orbitals.

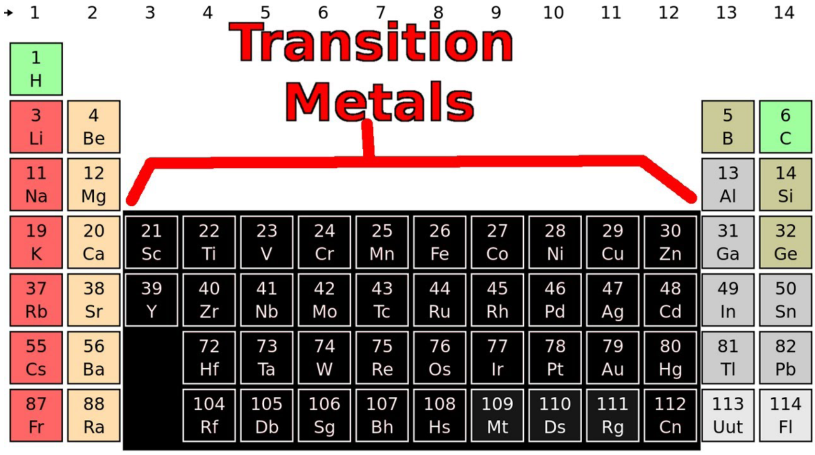


Figure 6.1. (a) Portion of periodic table with transition metals in the middle

The properties of transition elements are between the highly reactive metallic elements of the s-block which generally form ionic compounds and the less reactive elements of the p-block which form covalent compounds. Transition metals form ionic compounds as well as covalent compounds.

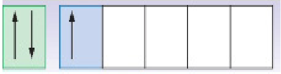
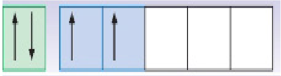
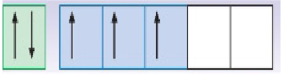
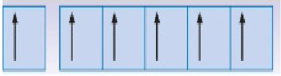
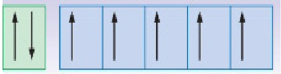
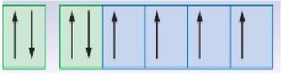
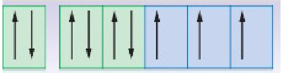
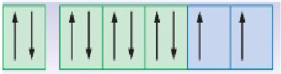
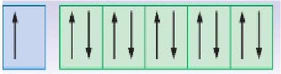
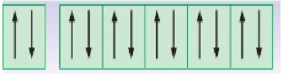
The first 3 rows, i.e. period 4, period 5 and period 6, are called **first transition series**, **second transition series** and **third transition series** respectively.

The metals of the first series are all hard and dense, good conductors of heat and electricity.

This block is known as the transition metals because some of their properties show a gradual change between the active metals in s-block and p-block where non-metals are found.

Electron configuration is the arrangement of electrons in orbitals around the nucleus. The electronic structure of the first transition series is shown in the table below:

Table 6.1 Electronic configuration of the first transition series

Element	Atomic number	Electronic configuration	Noble gas configuration	Electron in box diagram
Scandium (Sc)	21	$1s^22s^22p^63s^23p^64s^23d^1$	$[Ar]4s^23d^1$	
Titanium (Ti)	22	$1s^22s^22p^63s^23p^64s^23d^2$	$[Ar]4s^23d^2$	
Vanadium (V)	23	$1s^22s^22p^63s^23p^64s^23d^3$	$[Ar]4s^23d^3$	
Chromium (Cr)	24	$1s^22s^22p^63s^23p^64s^13d^5$	$[Ar]4s^13d^5$	
Manganese (Mn)	25	$1s^22s^22p^63s^23p^64s^23d^5$	$[Ar]4s^23d^5$	
Iron (Fe)	26	$1s^22s^22p^63s^23p^64s^23d^6$	$[Ar]4s^23d^6$	
Cobalt (Co)	27	$1s^22s^22p^63s^23p^64s^23d^7$	$[Ar]4s^23d^7$	
Nickel (Ni)	28	$1s^22s^22p^63s^23p^64s^23d^8$	$[Ar]4s^23d^8$	
Copper (Cu)	29	$1s^22s^22p^63s^23p^64s^13d^{10}$	$[Ar]4s^13d^{10}$	
Zinc (Zn)	30	$1s^22s^22p^63s^23p^64s^23d^{10}$	$[Ar]4s^23d^{10}$	

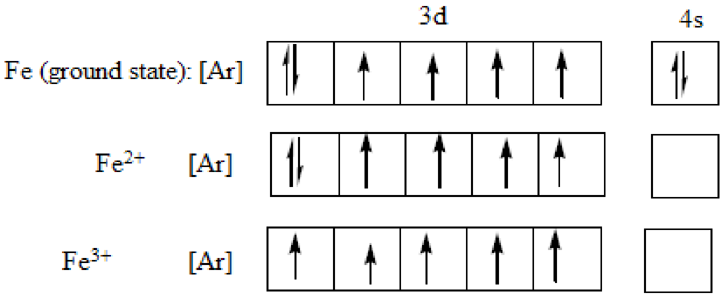
When building electronic structure of transition metals, 4s orbital is filled before 3d orbitals.

The transition elements are stable when their d-orbitals are filled (d^{10}) or half filled (d^5).This explains the electronic structure of copper, [Ar] $4s^13d^{10}$ instead of [Ar] $4s^23d^9$. The same applies for Cr: [Ar] $4s^13d^5$ and not [Ar] $4s^23d^4$.

In order to attain that stability an electron can jump from 4s orbital to 3d orbital because those two orbitals are close in energy.

This also explains why Fe^{2+} with $3d^6$ is *easily oxidized* to Fe^{3+} with $3d^5$ and Mn^{2+} with $3d^5$ is *resistant to oxidation* to Mn^{3+} with $3d^4$.

Transition metals form ions by losing electrons first from the 4s sub-shell rather than the 3d sub-shell. Hence electronic configuration of Fe, Fe^{2+} and Fe^{3+} are the following:



The 4s electrons are removed before 3d electrons. This is because the 3d electrons are inner while the 4s electrons are outer therefore the outer electrons (4s) have to be removed before the inner electrons.

APPLICATION ACTIVITY 6.1

1. How do the electron structures of transition elements differ from those of the elements in the main groups of the periodic table?
2. Describe the electronic structure of chromium. How are the important oxidation states determined by this structure?
3. Using [Ar] to represent argon core, give the electronic configuration of the following.

   (i) chromium metal (ii) copper (ii) ions (iii) vanadium (ii) ions (iv) copper (i) ions (v)titanium (iii) ions

4. Explain why it is difficult to oxidize Mn^{2+} (aq) to Mn^{3+} (aq).

6.2. Physical and special Properties of the transition metals.

(a)Melting and boiling points

ACTIVITY 6.2(a)

1. Given sodium, magnesium and aluminum. Explain the variation of melting and boiling points.

The melting points and the molar enthalpies of fusion of the transition metals are both high in comparison to main group elements. Most of the transition metals have melting points above 1000 ^oC; mercury is liquid at room temperature.

This is due to the high number of valence electrons that increases the electrostatic attraction force between those electrons and the metallic cations, hence increasing the strength of the metallic bond and the melting point.

Table 6.2 : Melting and boiling points of the 1st series of Transition Metals

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
MP/^0C	1400	1677	1917	1903	1244	1539	1495	1455	1083	420
BP/^0C	2477	3277	3377	2642	2041	2887	2877	2837	2582	908

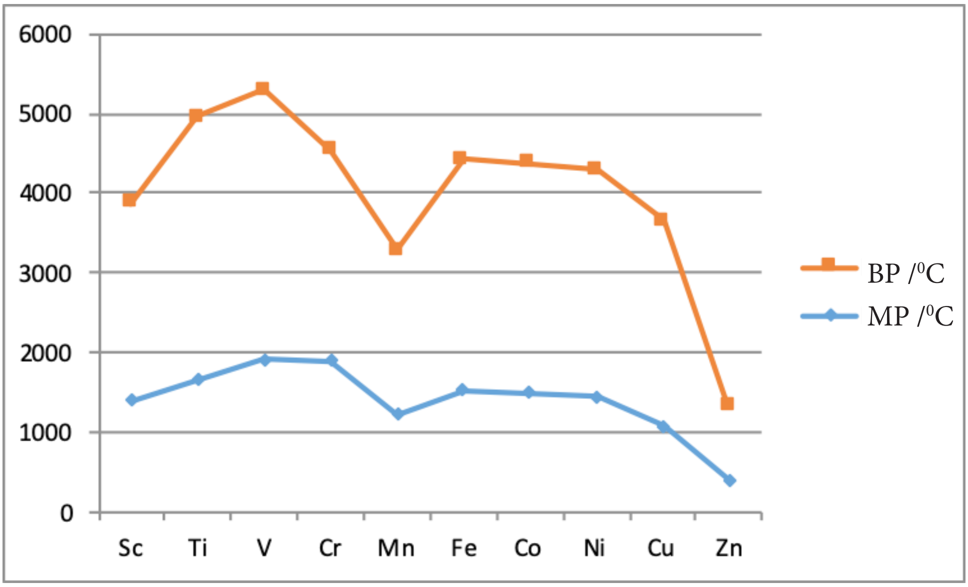


Figure 6.2; Variation of melting and boiling points of transition metals

(b) Densities and atomic/metallic radii

ACTIVITY 6.2(b)

1. Compare the metallic character and densities of period 3 elements.
2. How do you expect these elements to compare with those of transition elements? (research)

The transition elements are much denser than the s-block elements and show in general a gradual increase in density from left to right in a period as you can see below from scandium to copper. This trend in density can be explained by a decrease in metallic radii coupled with the relative increase in atomic mass.

Table 6.3 : Density/g cm $^{-3}$of the first transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

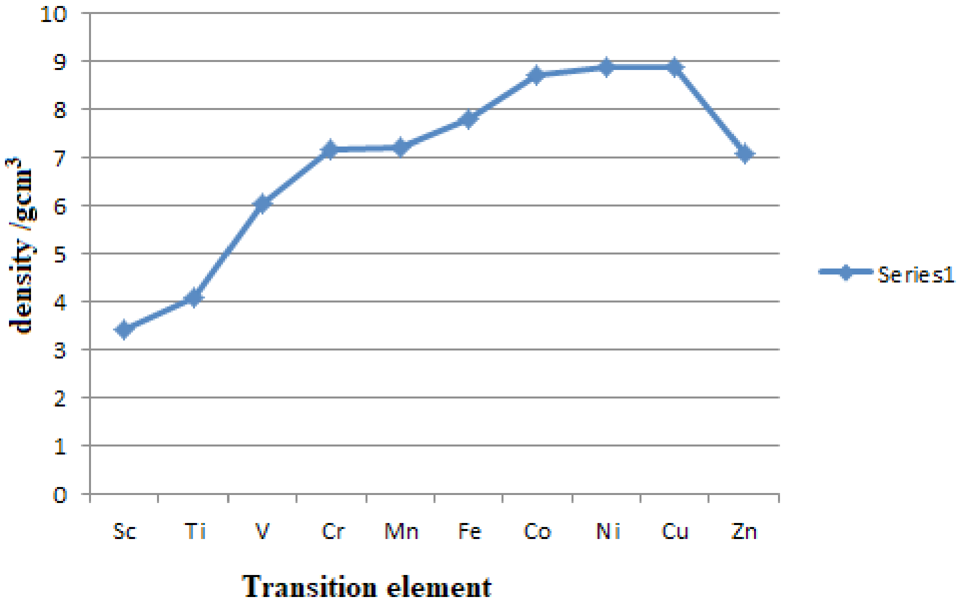


Figure 6.3: Variation of density of first series transition elements

Table 6.4: Metallic radii of the first transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
164	147	135	129	137	126	125	125	128	137

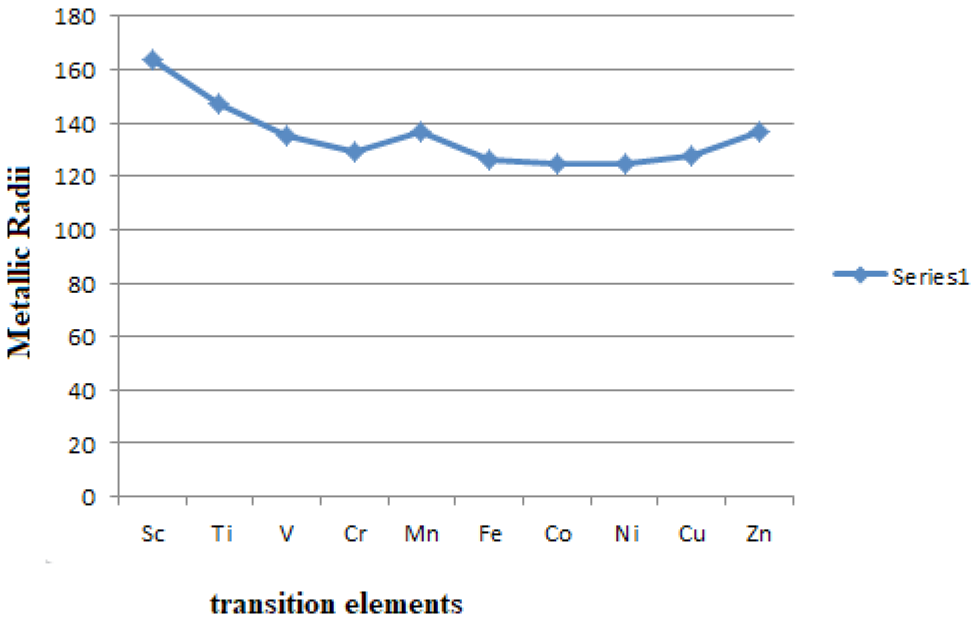


Figure 6.4. Variation of atomic radii of first transition elements

(c) Ionization energies

ACTIVITY 6.2(c)

(i) Use period 3 elements to explain the variation in ionization energies.

(ii) Write equations to show the ionization energies of magnesium and aluminium. Explain the variation in ionization energy between magnesium and aluminium.

The ionization energy of transition metals is related to the energies of its d -orbitals, its ease of oxidation, and its basicity. In simplest terms, the greater a metal's ionization energy, the harder it is to pull an electron from it.

As the number of protons increases across a period (or row) from left to right of the periodic table, the first ionization energies of the transition-metal elements are relatively the same, while that for the main-group elements increases.

In moving across the series of metals from scandium to zinc, a small change in the values of the first and second ionization energies is observed. This is due to the build-up of electrons in the immediately underlying d-sub-shells that efficiently shields the 4s electrons from the nucleus and minimizing the increase in **effective nuclear charge** from element to element.

Table 6.5: First, second and third ionization energies of 1st Series Transition metals /kJ mol^{-1}

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1st I.E	631	656	650	653	717	762	758	736	745	906
2nd I.E	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
3rd I.E	2393	2657	2833	2990	3260	2962	3243	3402	3556	3829

Figure 6.5 below provides the first ionisation energies for transition metals of 1st, 2nd and 3rd rows (series).

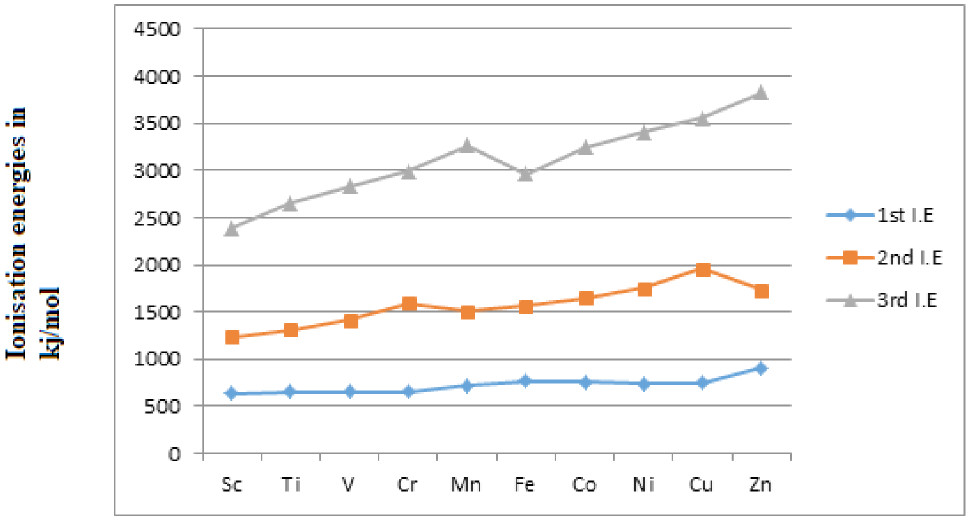


Figure: First 6.5 Ionization Energies of the transition elements.

In general, ionization energy increases as we move from left to right across the period. Notable dips occur at row 1, group 10 (Ni) and row 3, group 7 (Re).

(d)Transition elements have variable oxidation states

ACTIVITY 6.2(d)

(1) (a) What is meant by term oxidation state/number?

(b) Calculate the oxidation state of the following underlined elements

(i) $\underline{Mn}O_2$ (ii) $\underline{Fe}_2O_3$ (iii) $\underline{Mn}O_4^-$ (iv) $\underline{Fe}O$ (v) $\underline{V}_2O_5$ (vi) $\underline{V}_2O_3$

(2) Write the formula of ions formed by sodium, magnesium and calcium and aluminium

(3) Explain why these ions have the charges indicated

(4) The charges indicated (oxidation number) on those ions correspond to what? Period number or group number?

Oxidation state is a number assigned to an element in chemical combination which represents the number of electrons lost or gained. The transition elements from titanium to copper all form ions with two or more oxidation states. In most cases, this is the result of losing the two electrons from the 4s orbital. The 4s electrons are lost first because they are in the highest energy level. However, because the 3d and 4s energy level are so close in energy, the 3d electrons can also be lost when an atom forms a stable ion. The common oxidation states shown by the first transition series are shown in the following table:

Table 6.6. The oxidation states shown by the transition metals (series)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2	+2	+2	**+2**	+2	**+2**	**+2**	+1	+2
	+3	+3	+3	+3	**+3**	**+3**	+3	**+2**	
	+4	+4	+4	**+4**	+4	+4	+4		
		+5	+5	+5	+6				
			+6	+6					
				+7					

- The common stable oxidation states for those transition metals with variable oxidation states are bolded and underlined.

- The oxidation state corresponding to a full or half-filled d-orbital is energetically stable. For example, Fe^{3+} is more stable than $Fe^{2+}$and Mn^{2+} is more stable than Mn^{3+}.
- However, in most compounds and solutions, copper exist as Cu^{2+} ion rather than Cu^{+} ion. Meaning that the former is more stable than the latter. The explanation of this is beyond this level.

(e) Most transition metals and their compounds have high ability of being catalysts

ACTIVITY 6.2(e)

1. Ammonia is manufactured on large scale by Haber process. In this process hydrogen gas reacts with nitrogen gas in the ratio of 3:1 respectively. This process requires a catalyst

   (i)What is a catalyst?

   (ii) Name the catalyst used in this process

2. Many chemical processes in our bodies require catalyst/enzymes. Give one chemical process in our body and mention the catalyst used.

A catalyst is a substance that can speed up or that can slow down the rate of reaction. A catalyst that speeds up the reaction provides another pathway with lower activation energy.

During the catalytic activity, transition metal ions undergo changes in their oxidation states but are regenerated at the end of the reaction.

The reasons for transition metals to work as catalysts:

- Presence of empty d orbitals which enable transition metal ions (or atoms) to form temporary bonds with reactant molecules at the surface of a catalyst and weakens the bond in the reactant molecules.
- Variable oxidation states which allow them to work as catalysts in the reactions involving the transfer of electrons.

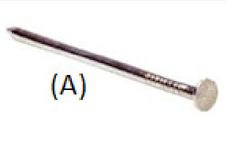
Table 6.7. Reactions catalyzed by transition metals

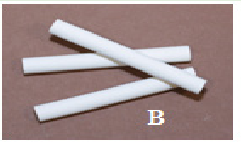
Transition elements	Substance use as a catalyst	Reaction catalyzed
Ti	$TiCl_3/Al_2(C_2H_5)_6$	Polymerization of ethene into polythene
V	V_2O_5 or vanadate (VO_3^-)	$2SO_2 + O_2 \rightleftharpoons 2\ SO_3$
Fe	Fe or Fe_2O_3	$N_2 + 3H_2 \rightleftharpoons 2NH_3$ Haber process
Ni	Ni	$RCH{=}CH_2 + H_2 \rightarrow RCH_2CH_3$ Hardening of vegetable oil (E.g.: Manufacture of margarine)
Cu	Cu or CuO	$CH_3CH_2OH + ½O_2 \rightarrow CH_3CHO + H_2O$ Oxidation of ethanol to ethanal
Pt	Pt	$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3$ Contact process
Pt	Pt	$4NH_3 + 5\ O_2 \rightarrow 4NO + 6\ H_20$ Manufacture of nitric acid from ammonia

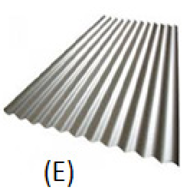
(f) Most transition metal ions are paramagnetic

ACTIVITY 6.2(f)

Given the following materials:







1. Using a magnet, classify the above materials into two groups as shown in the table below.

Objects attracted by a magnet	Objects not attracted by a magnet

2. Some metals attract magnets while others do not. Suggest reasons

Paramagnetism is a property of substances to be attracted in a magnetic field. Substances which are not attracted (i.e. slightly repelled) in a magnetic field are said to be diamagnetic. Transition metal ions show paramagnetism because of the presence of unpaired electrons in their 3d sub-shells.

The greater the number of unpaired electrons, the stronger the paramagnetism; that is the reason why:

- Fe^{3+} is more paramagnetic than Fe^{2+} because Fe^{3+} has five unpaired electrons while Fe^{2+} has four unpaired.
- Sc^{3+} and Zn^{2+} have no paramagnetic effect because they do not have unpaired electrons.

Other examples of paramagnetic substances are: Cr, Mn, $CuSO_4$, Fe, Co, Ni, Pt.

Examples of diamagnetic substances are: Zn, Cu^+, Au^+, TiO_2.

(g) Formation of alloys

ACTIVITY 6.2(g)

(i) Look at the objects indicated and suggest the elements from which they are made of.

(ii) Why do you think these elements are selected to make these objects?

An alloy is a mixture (solid solution) made by combining two or more elements where at least one is a metal.

Importance of alloying:

- Increase of the strength of a metal,
- Resistance to corrosion,
- Gives to the metal a good appearance

Generally, alloys are harder than the separate metals and have lower melting points. For example, *brass* (alloy of zinc and copper) is much stronger than either pure copper or pure zinc. The table below gives the properties and uses of alloys formed by transition metals (first series):

Table 6.8. Properties and uses of some common alloys formed by transition metals (first Series)

Alloy	Colour	Composition	Properties	Uses
Bronze	Chocolate brown	90 % copper 10 % tin	Hard and strong Does not corrode easily Has shiny surface	To build statues and monuments In the making of medals, swords and artistic materials.
Brass	Yellow	70 % copper 30 % zinc	Harder than copper	In the making of musical instruments and kitchenware.
Steel	Blue, grey, etc	99 % iron 1 % carbon	Hard and strong	In the construction of building and bridges. In the building of the body of cars and railway tracks.
Stainless steel	Ranges of colors, including blue, black, bronze, gold, green, red/ violet	74 % iron 8 % carbon 18 % chromium	Shiny Strong Does not rust	To make cutlery and surgical instruments.

Duralumin	Metallic colour	93 % aluminium 3 % copper 3 % magnesium 1 % manganese	Light Strong	To make the body of airplanes and bullet trains.
Pewter	Grey	96 % tin 3 % copper 1 % antimony	Luster Shiny Strong	In the making of souvenirs.

(h) Formation of complex ions

ACTIVITY 6.2(h)

(a) Aluminum ions hydrolyze in water to $[Al(H_2O)_6]^{3+}$. Give the name of these compounds.

(b) Why does aluminium hydrolyze in water whereas sodium ions do not?

A complex or coordination compound is a chemical species made of a central metal (cation or neutral) bonded to other chemical species called ligands by coordination or dative bonds. A complex may be neutral, positively or negatively charged.

Transition metal form complexes because of:

- Their small and highly charged ions,
- The presence of vacant (empty) d-orbitals which can accommodate lone pair of electrons donated by other groups (ligands)

The general formula of a complex is the following: $\mathbf{[ML_n]^y}$

Where:

- M-metal ion or atom
- L-Ligand
- n-the number of ligands surrounding the metal
- y-the charge of the complex; $\mathbf{[ML_n]}$ indicates a neutral complex.

- **Coordination number of a complex**: is the number of coordinate bonds on the central metal in a complex.

- **Ligand:** It is a species (anion or a molecule) that is bonded to a central metal ion or atom in a complex. A ligand should have at least one lone pair of electrons to form a coordinate bond.

Ligands are classified depending on the number of sites at which one molecule of a ligand is coordinated to the central metallic atom; the ligands are classified as *monodentate* (or undented) and *polydentate* (or multidentate) ligands.

(i)Many transition metal ions and their compounds are coloured

1. Experiment 1: Observation of the colors of transition elements

Apparatus: Test tubes, droppers, spatula, test tube holders.

Chemicals: NaCl, $CaCl_2$, $FeSO_4$, $Fe_2(SO_4)_3$, $KMnO_4$, $K_2Cr_2O_7$ distilled water, $Cr_2(SO_4)_3$.

(a) What are the colors of the compounds above?

(c) Determine the oxidation states of each metal in the above compounds?

(d) (i)Take an endful spatula of each product given above and put each in a test tube.

(ii)Put 10 mL of distilled water in each test tube.

(iii)Write down the colors of solutions formed and conclude.

2. Experiment 2: Investigation of ligand exchange reactions involving copper (II) ions, Cu^{2+}

Apparatus: Test tubes, droppers, spatula, test tube holders.

Chemicals: Copper (II) sulphate, concentrated hydrochloric acid, concentrated ammonia solution and distilled water.

Procedure:

(i) Use a spatula to place a small amount of anhydrous copper (II) sulphate in a test tube.

(ii) Add 10 drops of distilled water to the anhydrous copper (II) sulphate and shake

(iii) To the test tube in step 2, add concentrated ammonia solution drop by drop while shaking the test tube until there is no further change. Record all observations.

(iv) Repeat steps 1 and 2

(v) To the test tube from step 4, add concentrated hydrochloric acid drop by drop while shaking until there is no further change. Record all observations.

Study questions :

(a) What happens when anhydrous copper (II) sulphate is dissolved in water?

(b) Describe what is observed when concentrated ammonia is added drop wise to an aqueous solution of copper (II) sulphate. Write balanced equations for each observation if possible

(c) Describe what happens when concentrated hydrochloric acid is added to an aqueous solution of copper (II) sulphate. Write balanced equation(s) for the observation(s) made.

(d) State any other possible observation(s) for this experiment.

3. Experiment 3. Effect of sodium hydroxide and ammonia solution of transition metal cations

Materials/apparatus: 1M NH_3 (aq) , 1M NaOH (aq) , enough test tubes , enough droppers, test tube rack, test tube holder, Ni^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Cr^{3+}, Co^{2+}, Cu^{2+}

Procedure:

(i) Add about 1cm^3 of each of solutions of the cations indicated in a test tube

(ii) Add a few drops of sodium hydroxide solution drop wise until in excess

(iii) Repeat procedure (i) and (ii) above using ammonia solution

(iv) Make observations in each case for sodium hydroxide and ammonia solution

(v) Record your observations in a suitable form.

(vi) Write ionic equations for the reactions that occur in each case.

Formation of colored ions by transition elements is associated with presence of incompletely filled 3d orbitals.

Table : 6.9. colour of different transition metal ions

Ion (aq)	Colour	Outer 3d electrons
Sc^{3+}	Colourless	$3d^0$
Ti^{3+}	Purple	$3d^1$
V^{3+}	Green	$3d^2$
Cr^{3+}	Green	$3d^3$
Mn^{2+}	Pink	$3d^5$
Fe^{2+}	Green	$3d^6$
Co^{2+}	Pink	$3d^7$
Ni^{2+}	Green	$3d^8$
Cu^{2+}	Blue	$3d^9$
Zn^{2+}	Colourless	$3d^{10}$

This property has its origin in the excitation of d electrons from lower energy d-orbitals to higher energy. In fact, when the central metal is surrounded by ligands, these cause d orbitals to be split into groups of higher and lower energy orbitals. When electrons fill d-orbitals, they fill first of all the lower energy orbitals; if there is free space in higher energy d-orbitals, an electron can be excited from lower energy d-orbitals to higher energy d-orbitals by absorbing a portion of light corresponding to a given colour, the remaining color light is the white light minus the absorbed colour.

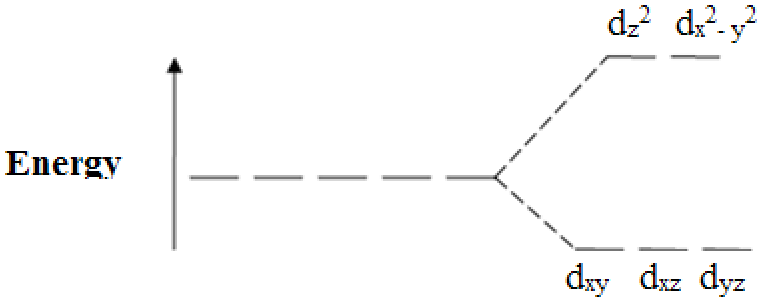


Figure 6.6: d-orbital split into two groups of different energies

When a coloured object is hit by white light, the object absorbs some colour and the colour transmitted or reflected by the object is the colour which has not been absorbed. The observed colour is called **complementary colour.**

When a metal cation has full d-orbitals, such as Cu^+ or Zn^{2+}or no electron in d orbital, such as Sc^{3+},it is colorless because there is no electron to be excited from lower d orbitals to higher d orbitals.

Table 6.10: Complementarities of colors observed and absorbed when light is emitted

Observed/transmitted colour	Absorbed/complementary colour
White	No absorption of light
Black	Total absorption of light
Greenish yellow	Violet
Yellow	Blue
Red	Blue-green
Violet	Yellow-green
Dark blue	Yellow
Blue	Orange
Green	Red

The colour of a particular transition metal ion depends upon two factors:

The nature of the ligand

Example: The color of hydrated copper (II) ion $[Cu(H_2O)_4]^{2+}$, is pale blue but on addition of sufficient amount of ammonia added turns to deep blue.

$$[Cu(H_2O)_4]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) \quad 4H_2O(aq)$$

Pale blue **Deep blue**

Also on the addition of sufficient concentrated hydrochloric acid the pale blue solution turns to yellowish brown.

$$[Cu(H_2O)_4]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 4H_2O(aq)$$

Pale blue **Yellow brown**

The oxidation state of the metal ion

Example: $Cr^{2+}(aq)$ is blue but $Cr^{3+}(aq)$ is green

The principle of ligand exchange

Completing reactions involve competitions between different ligands for central metal. A more powerful ligand displaces a less powerful ligand from a complex. During the process there is a change in colour.

Here below is a list of some ligands in increasing order of strength.

$O_2^{2-} < I^- < Br^- < S^{2-} < \underline{SCN}^{=}$ (S–bonded) $< Cl^- < N_3^- < F^- < NCO^- < OH^- < \underline{C_2O_4}^{2=} \approx H_2O < NCS^{=}$ (N–bonded) $< CH_3CN < NH_3 <$ en (ethylenediammine) $< NO_2^- < PPh_3 < CN^- < CO$

The stability of a complex ion is measured by its stability constant. The higher the stability constant of a complex, the more stable is the complex.

(j) Anomalous properties of Zinc and scandium.

On the basis of the properties of transition metals, scandium and zinc are not considered as typical transition metals even though they are members of the d-block.

Table 6.2(j): differences between scandium and zinc.

Zinc	Scandium
It has a complete d-orbital.	Has one oxidation state,+3 Its compounds are diamagnetic
Zinc forms only the colourless Zn^{2+} ion, isoelectronic with the Ga^{3+}ion, with 10 electrons in the 3d subshell.	Sc forms only the colourless Sc^{3+}ion, isoelectronic with the Ca^{2+} ion, with no electrons in the 3d subshell.
Zinc and its compounds are not paramagnetic	It forms compounds containing ions with a completely empty 3d subshell.

ACTIVITY 6.2(j)

1. (a) The first ionization energy of cobalt is only slightly larger than the first ionization energy of iron. Explain.

   (b) The third ionization energy of iron is much lower than the 3rd ionization energy of Mn. Explain.

2. Which gaseous ion is more stable, Mn^{2+} or Mn^{3+}? Explain why.

3. You are provided with substance D which contains one cation and one anion. You are required to identify the cation and anion in D. Carry out the following tests and record your observations and deductions in the table below. Identify any gas evolved.

1) Note appearance of D	Green solid	………………………
2) Put one spatula end-full of D in a test tube and heat it strongly until there is no further change	……………………… ……………………… ……………………… …………………………	• hydrated salt present. • Gas is SO_2 probably SO_3^{2-} or SO_4^{2-} salt present. • D is a transition compound probably containing Cr^{3+} or Ni^{2+}
3) Dissolve one spatula of D in about $10cm^3$ of water and divide the resultant solution into five parts.	D dissolves to give green solution.	……………………… ………………………
a) To the 1st part is added sodium hydroxide solution drop wise until in excess	A green precipitate which slightly dissolves to give a violet solution.	……………………… …………………………

b) To the second part is added dilute sodium hydroxide solution drop-wise until in excess followed by 1cm^3 of 10% hydrogen peroxide solution and the resultant mixture boiled and later cooled. The resultant solution is then divided into three portions	A green precipitate soluble in excess NaOH to form a green solution. On boiling with H_2O_2 a yellow solution is formed with evolution of a colourless gas which relights a glowing splint.	…………………………
i) To the 1st portion is added silver nitrate solution drop-wise until no further change takes place.	A brick red precipitate. Silver chromate is formed. Hence CrO_4^{2-} compound formed.	
ii) To the second portion is added a drop of barium chloride solution	…………………………… ……………………………	Barium chromate formed. Hence CrO_4^{2-} compound formed
iii) To the 3rd portion is added a few drops of hydrochloric acid.	……………………………	
c) To the third part of the solution is added a few drops of butanol followed by 3 drops of dilute H_2SO_4	A deep blue lake is formed.	……………………

d) To the fourth part was added a few drops of lead nitrate solution.	A white precipitate is formed	………………………………
e) To the last part was carried a test of one's own choice. Test: To the last portion is added a few drops of barium nitrate followed by 1 cm^3 of dilute nitric acid.	…………………………	Presence of SO_4^{2-} confirmed.

- The cation in D is **Cr^{3+}.**
- The anion in D is **SO_4^{2-}.**

SKILLS LAB 6

THEORY: Copper is a transition element and has wide range of uses including electroplating materials with copper(coating other substances with copper metal using electrolysis)

Carry out the research to investigate how electroplating a key can be carried out.

You are required to design an experimental setup for this experiment and propose the procedure and make conclusion.

END UNIT ASSESSMENT 6

1. Compare and comment on the melting points of transition metals and those of s-block metals.

2. Using [Ar] to represent the argon core, give the electronic configurations of the following

   (a)Cu   (b)Co^{2+} (c)Ti^{3+}

3. Briefly explain the following

   (a) the second ionization energy of copper is higher than the second ionization energy of Zinc.

   (b) it is difficult to oxidize Mn^{2+}(aq) to Mn^{3+} (aq)

   (c) On passing from scandium to titanium, the increase in the third ionization energy is much larger than the increase in the first ionization energy.

   (d) the metallic radius of vanadium is smaller than that of titanium.

4. (a) Why is iron a stronger metal than magnesium?

   (b) Why does iron form two ions whereas sodium forms only one?

   (c) Iron (iii) ion is non-paramagnetic whereas iron (ii) is paramagnetic. Explain.

5. Aqueous sodium hydroxide is added separately to solutions of transition metals, A, B, and C. Identify A, B and C from the following observations.

   A: The white precipitate which appears is soluble in an excess of aqueous sodium hydroxide and also in ammonia solution.

   B: The blue precipitate which appears is insoluble in excess of sodium hydroxide but dissolves in aqueous ammonia to form a deep blue solution.

   C: The green precipitate which appears is insoluble in an excess of aqueous sodium hydroxide and also in ammonia solution.

UNIT 7

INTRODUCTION TO ORGANIC COMPOUNDS AND ISOMERISM IN ORGANIC COMPOUNDS

Key Unit competence: **Apply IUPAC rules to name organic compounds and explain their types of isomers**

INTRODUCTORY ACTIVITY

1. The human being uses energy in different forms and from different sources. Give the names of the compounds which are used as fuels.

2. Have you ever observed petroleum, alcohol, and vinegar mixed with water?

   If yes, how each of them behaves when mixed with water?

   If no, now take a small quantity of petroleum, alcohol, and vinegar and pour each of it differently in a half-filled flask of water. Explain your observations and why those substances behave differently in water.

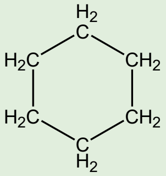
7.1. Classification of organic compounds

ACTIVITY 7.1

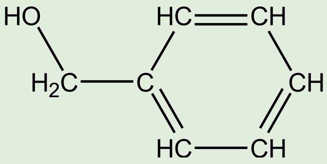
Observe the following compounds and based on the structure of the chain of each compound, attempt to classify them.

1. $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ 2. $CH_3\text{-}CH_2\text{-}C{\equiv}CCH_2CH_3$ 3. $CH_3CH_2CH_2OH$

4.

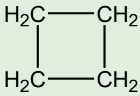


5.

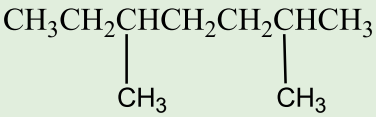


6. $CH_3\text{-}CH_2\text{-}CH{=}CH_2$

7.

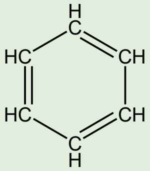


8.

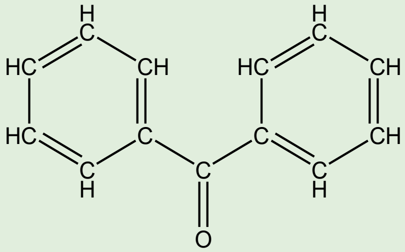


$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$$

9.



10.



Organic chemistry is the chemistry of carbon compounds. Carbon forms a vast number of compounds because it can form strong covalent bonds with itself. This enables it to form long chains (up to 5000 in length) of carbon atoms, and hence an almost infinite variety of carbon compounds are known.

All organic compounds contain carbon. Most contain hydrogen. Carbon always forms four covalent bonds and hydrogen one.

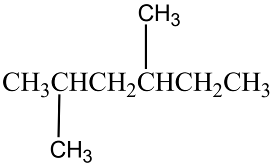
7.1.1 Aliphatic compounds

Aliphatic compounds are the large class of organic molecules consisting essentially of straight or branched chains of carbon atoms. Aliphatic compounds include the alkanes, alkenes, and alkynes and their derivatives.

Examples of aliphatic compounds

$CH_3CH_2CH_2CH_2CH_2CH_3$

Hexane



$CH_3CH(CH_3)CH_2CH(CH_3)CH_2CH_3$

2,4-dimethylhexane

$H_2C{=}CHCH_2CH_3$

But-1-ene

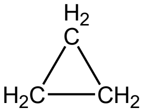
$HC{\equiv}CH$

Acethylene

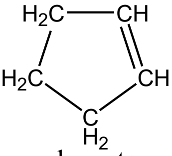
7.1.2. Alicyclic compounds

Alicyclic or cyclic aliphatic compounds are organic compounds that contain one or more carbon rings that may be saturated (joined by single bonds) or unsaturated (joined with double or triple bond).

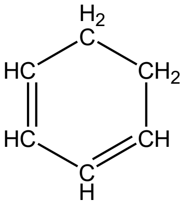
Examples of alicyclic compounds



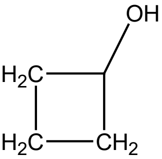
cyclopropane



cyclopentene



cyclohexadiene

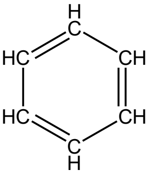


cyclobutane

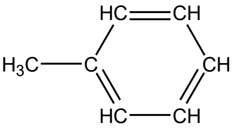
7.1.3. Aromatic compounds

Aromatic compounds are large class of unsaturated chemical compounds characterized by one or more planar rings of atoms joined by covalent bonds of two different kinds. Benzene (C_6H_6) is the best-known aromatic compound and the parent to which numerous other aromatic compounds is related.

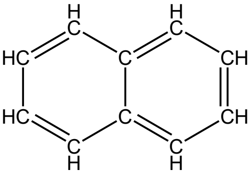
Examples of aromatic compounds



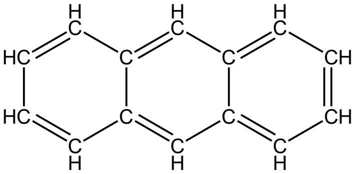
benzene



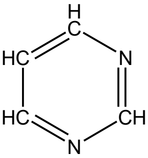
toluene



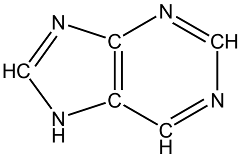
naphtalene



anthracene



pyrimidine

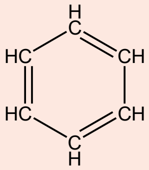


purine

APPLICATION ACTIVITY 7.1

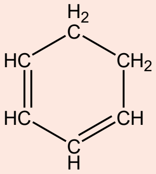
Classify each of the following organic compounds as aliphatic, aromatic or alicyclic.

A



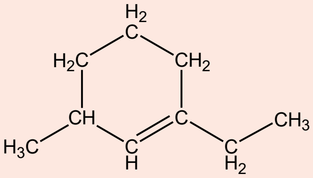
cyclohexatriene

B



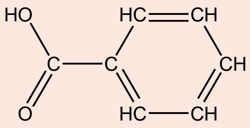
cyclohexadiene

C



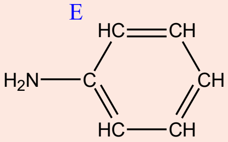
1-Ethyl-3-methylcyclohexene

D



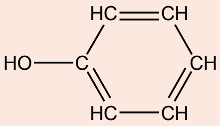
Benzoic acid

E



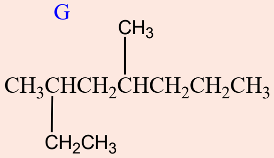
Aniline

F



Phenol

G



$CH_3\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}CH_2\overset{\displaystyle CH_3}{\overset{|}{CH}}CH_2CH_2CH_3$

2-Ethyl-4-methylheptane

H

$CH_3CH_2CH{=}CHCH_2$

Pent-2-ene

J

$HC{\equiv}CCH_2CH_3$

But-1-yne

K

$CH_3CH_2CH_2COOH$

Butanoic acid

7.2. Types of formulae for organic compounds

ACTIVITY 7.2

Match the compound in column A with its corresponding compound in column B in terms of similarities and ratio of atoms

Column A	Column B
1. C_2H_5	A. $C_6H_{12}O_6$
2. CH_2O	B. C_6H_6
3. CH	C. C_6H_{12}
4. C_2H_4	D. C_2H_{10}
	E. C_3H_8

7.2.1. Empirical formula

An **empirical formula** is the simplest whole number ratio of the atoms in a compound as found by experiment i.e. chemical analysis. It gives no structural information and may or may not be the same as the molecular formula e.g. CH_4 is both the empirical formula and the molecular formula of methane. However, the molecular formula of the butane molecule is C_4H_{10} but its empirical formula is C_2H_5. The molecular formula of a glucose sugar molecule is $C_6H_{12}O_6$ but its empirical formula is only CH_2O.

Empirical formula is calculated from the percentage composition.

The steps are :

(i) The percentage of each element is divided by its atomic weight.

(ii) The result in (i). above is then divided by the smallest one among them to give the atomic ratio.

(iii) If the atomic ratios obtained in ii. are not the whole number, they should be multiplied by a suitable common factor to convert each of them to the whole numbers (or approximately equal to the whole numbers). Minor fractions are ignored by rounding up or down (ex: 7.95 = 8).

Example

A certain organic compound has 39.13% by mass carbon, 52.23% oxygen and the rest of hydrogen. Calculate the empirical formula of the compound.

Answer:

Elements	**C**	**H**	**O**
% composition	39.13	8.64	52.23
Relative Ratio of atoms,molecules	$\frac{39.13}{12} = 3.26$	$\frac{8.64}{1} = 8.64$	$\frac{52.23}{16} = 3.26$
Smallest ratio	$\frac{3.26}{3.26} = 1$	$\frac{8.64}{3.26} = 2.65$	$\frac{3.26}{3.26} = 1$
Whole number ratio and Empirical formula $C_3H_8O_3$	3	7.95=8	3

Note: 2.65 can not be corrected to 3 so we multiply those atomic ratios with 3. We get 7.95 which is rounded to 8.

7.2.2 Molecular formula

The **molecular formula** represents a summary of all the atoms in the molecule and a **general formula** sums up the formulae of a series of compounds e.g. a homologous series of chemically similar compounds.

e.g. if **n = 5** for the number of carbon atoms in the molecular formula you get

- alkanes of molecular formula $\mathbf{C_5H_{12}}$
- alkenes/cycloalkanes of formula $\mathbf{C_5H_{10}}$
- alcohols/ethers of formula $\mathbf{C_5H_{12}O}$ and amines of formula $\mathbf{C_5H_{13}N}$

This is a formula expressing the true number of atoms of various elements present in a molecule .

Molecular formula = Empirical formula × n ,where $n = \frac{\text{Molecular weight}}{\text{Empirical weight}}$

when n=1, then the molecular formula is the same as the empirical formulae

Examples

1. An organic compound that contains 31.9% by mass carbon, 6.8% hydrogen and 18.51% nitrogen the rest being oxygen has a vapour density of 37.5. Calculate the molecular formula of the compound.

Answer

Elements	**C**	**H**	**O**	**N**
% composition	31.9	6.8	42.79	18.51
Relative Ratio of atoms, molecules	$\frac{3.26}{3.26}=1$	$\frac{6.8}{1}=6.8$	$\frac{42.79}{16}=2.674$	$\frac{18.51}{14}=1.322$
Atomic ratio	$\frac{2.658}{1.322}=2.01=2$	$\frac{6.8}{1.322}=5.14=5$	$\frac{6.674}{1.322}=2.02=2$	$\frac{1.322}{1.322}=1$

Empirical formula , $C_2H_5NO_2$

Vapour density =½ molecular weight

Therefore, molecular weight = 2× vapour density= 2×37.5= 75gr/mol

$$n=\frac{\text{Molecular weight}}{\text{Empirical weight}}=\frac{75}{75}=1$$

Hence molecular formule = empirical formula = $C_2H_5NO_2$

2. 0.45g of organic acid on combustion gave 0.44g of carbon dioxide and 0.09g of water. If the molecular weight of the acid is 90, deduce the molecular formula.

Answer

Percentage of carbon in the sample : $\frac{12}{44} \text{x} \frac{0.44}{0.45} \text{x}100=26.66\%$

Percentage of hydrogen in the sample : $\frac{2}{18} \text{x} \frac{0.09}{0.45} \text{x}100=2.22\%$

Percentage of oxygen in the sample = 100-26.66-2.22=71.12%

Elements	**C**	**H**	**O**
% composition	26.66	2.22	71.12
Atomic Ratio	$\frac{26.66}{12}=2.22$	$\frac{2.22}{1}=1$	$\frac{71.12}{16}=4.44$
Smallest ratio	$\frac{2.22}{2.22}=1$	$\frac{2.22}{2.22}=1$	$\frac{4.44}{2.22}=2$
Empirical formula	CHO_2		
Molecular formula	n= 90/45=2	$C_2H_2O_4$	Oxalic acid

Note: From the above calculation, we can extend our generalized expression:

$$\% \text{ of carbon in the sample} = \frac{12}{44} \times \frac{m_{co_2}}{m_{sample}} \times 100$$

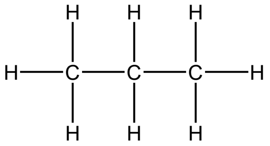
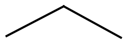
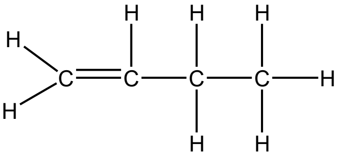
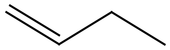
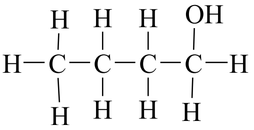
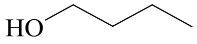
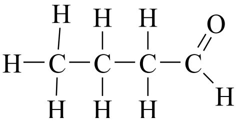
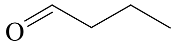
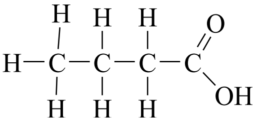
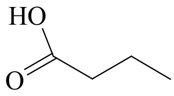
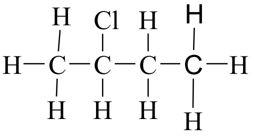
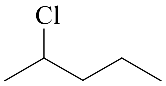
$$\% \text{ of hydrogen in the sample} = \frac{2}{18} \times \frac{m_{H_2O}}{m_{sample}} \times 100$$

% of Oxygen in the sample = 100 - (% of H_2 + % of carbon)

7.2.3. Structural formula

There are three types of structural formulas: displayed, condensed and skeletal (stick) formulas. Structural formula shows how the different atoms in a molecule are bonded (i.e. linked or connected).

Table 7.1. Types of formula of organic compounds

Molecular formula	Condensed structural formula	Displayed structural formula	Stick / skeletal/line formula
C_3H_8	$CH_3CH_2CH_3$		
C_4H_8	$CH_2{=}CH\text{-}CH_2CH_3$		
$C_4H_{10}O$	$CH_3CH_2CH_2CH_2OH$		
C_4H_8O	$CH_3CH_2CH_2CHO$		
$C_4H_8O_2$	$CH_3CH_2CH_2COOH$		
C_4H_8Cl	 $CH_3\overset{\overset{Cl}{\vert}}{C}HCH_2CH_3$		

Note: -Stick/line formula is also considered as structural formula.

- Only carbon and hydrogen atoms are not shown in line formula

APPLICATION ACTIVITY 7.2

1. An organic compound M contains, C (80%), H (6.7%) and the remaining being oxygen.

   a) Determine the empirical fomula of M.

   b) Deduce its molecular formula if the molecular mass of M is 120 g

2. A complete combustion of 7.5 g of an organic compound M containing carbon, hydrogen and oxygen gave 17.8 g of CO_2 and 9.27 g of water.

   a) Determine the empirical formula of M and deduce its molecular formula if the molecular mass of M is 74 g.

   b) Suggest a possible structural (displayed, condensed and skeletal) formula for the compound M.

7.3. Functional groups and homologous series

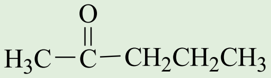
7.3.1. Functional groups

ACTIVITY 7.3

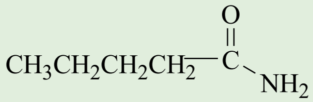
Observe the structure of the following compounds and CIRCLE the features that distinguish each from others.

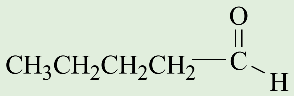
1 $H_2C{=}CHCH_2CH_2CH_3$

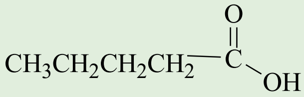
2 $HC{\equiv}CCH_2CH_2CH_3$

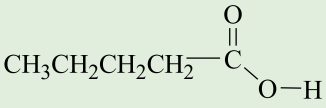
3

$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2CH_3$

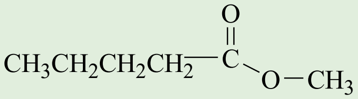
4 $CH_3CH_2CH_2CH_2-NH_2$

5

$CH_3CH_2CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$

6

$CH_3CH_2CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$

7

$CH_3CH_2CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

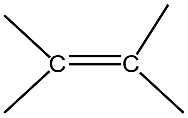
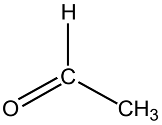
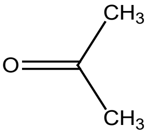
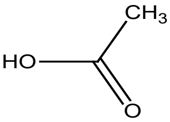
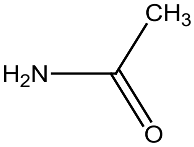
8

$CH_3CH_2CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$

9

$CH_3CH_2CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3$

What name assigned to the encircled features?

A **functional group** is an atom or group of atoms in a molecule which determines the characteristic properties of that molecule. Examples of some common functional groups are indicated in the Table 7.2.

Table 7.2: The common functional groups

Functional group	Family/ homologous series	Prefix/ suffix	Example	Systematic name
C = C	Alkenes	-ene		Ethene
C ≡ C	Alkynes	-yne	$-C\equiv C-$	Ethyne
R-X	Haloalkanes	Halo-	H_3C-Cl	Chloromethane
R-OH	Alcohols/ Alkanols	-ol	H_3C-OH	Methanol
R-O-R	Ether	-ether	CH_3-O-CH_3	Dimethylether
R-CO-H	Aldehydes/ Alkanals	-al		Ethanal
R-CO-R	Ketones/ Alkanones	-one		Propanone
R-COOH	Carboxylic acids	-oic acid		Ethanoic acid
R-C ≡ N	Nitriles	-nitrile	$CH_3-CH_2-C\equiv N$	Propanenitrile
R-NH_2	Amines	-amine	CH_3-CH_2-NH_2	Ethnamine
R-CO-NH_2	Amide	-amide		Ethanamide
R-COO-R	Ester	-oate	$CH_3COOCH_2CH_3$	Ethyl ethanoate

APPLICATION ACTIVITY 7.3.1

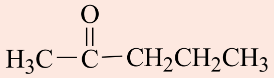
1. Give a precise definition of functional group.

2. Indicate the name of functional group in the following compounds:

a $H_2C=CHCH_2CH_2CH_3$

b $HC\equiv CCH_2CH_2CH_3$

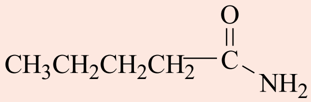
c



$H_3C-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$

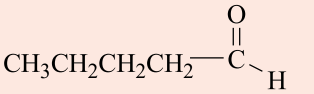
d $CH_3CH_2CH_2CH_2-NH_2$

e



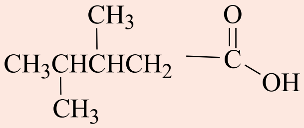
$CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-NH_2$

f



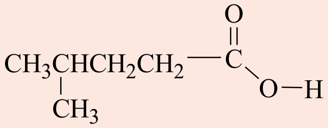
$CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-H$

g



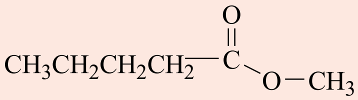
$CH_3\underset{CH_3}{\underset{|}{CH}}\overset{CH_3}{\overset{|}{CH}}CH_2-\overset{O}{\overset{\|}{C}}-OH$

h



$CH_3\underset{CH_3}{\underset{|}{CH}}CH_2CH_2-\overset{O}{\overset{\|}{C}}-O-H$

j



$CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3$

7.3.2. Homologous series

ACTIVITY 7.3.2

Observe the structure of the following compounds and point out their similarities and differences

1 $HCOOH$ methanoic acic

2 CH_3COOH ethanoic acid

3 CH_3CH_2COOH propanoic acid

4 $CH_3CH_2CH_2COOH$ butanoic acid

5 $CH_3CH_2CH_2CH_2COOH$ pentanoic acid

6 $CH_3CH_2CH_2CH_2CH_2COOH$ hexanoic acid

7 $CH_3CH_2CH_2CH_2CH_2CH_2COOH$ heptanoic acid

8 $CH_3CH_2CH_2COOCH_2CH_3$ ethyl butanoate

When members of a class of compounds having similar structures are arranged in order of increasing molecular mass, they are said to constitute a **homologous series**. Each member of such a series is referred to as a "homologous" of its immediate neighbors.

For example, the following sequence of straight chain of alcohols forms a homologous series.

CH_3-OH: Methyl alcohol

CH_3-CH_2-OH: Ethyl alcohol

CH_3-CH_2- CH_2-OH: Propyl alcohol

CH_3-CH_2-CH_2-CH_2-OH: Butyl alcohol

Characteristics of a homologous series

1. Any member of the series differs from the next by the unit – CH_2 – (methylene group)

2. The series may be represented by a general formula of alcohols which is $C_nH_{2n+1}OH$

   where n =1,2,3, etc.

3. The chemical properties of the members of a homologous series are similar, though in some series the first members show different behaviour.

4. The physical properties such as density, melting point and boiling point generally increase with increasing molecular mass.

APPLICATION ACTIVITY 7.3.2

1. How are butane and isobutane related? How do they differ?

2. Give **one word or phrase** for each of the following descriptions:

   a. The name of the homologous series to which 2-methylpropene belongs.

   b. The name of the functional group that gives alcohols their properties.

   c. The group of organic compounds that have acidic properties.

3. The table below gives the boiling point of ten organic compounds.

	Compound	Molecular formula	Boiling point (°C)
1	Methane	CH_4	-162
2	Ethane	C_2H_6	- 89
3	Propane	C_3H_8	- 42
4	Butane	C_4H_{10}	0
5	Pentane	C_5H_{12}	36
6	Methanol	CH_4O	64.7
7	Ethanol	C_2H_6O	78.4
8	Propan-1-ol	C_3H_8O	97
9	Propane-1,2-diol	$C_3H_8O_2$	188
10	Propane-1,2,3-triol	$C_3H_8O_3$	290

The following questions refer to the compounds shown in the above table.

a. To which homologous series do the following compounds belong?

i. Compounds 1 - 5

ii. Compounds 6 - 10

b. Which of the above compounds are gases at room temperature?

c. What is the reason for the trend of increasing boiling points seen in compounds 1 to 5?

d. Despite the fact that the length of the carbon chain in compounds 8, 9 and 10 is the same, the boiling point of propan-1,2, 3-triol is much higher than the boiling point of propan-1-ol. What is responsible for this large difference in boiling point?

7.4. Isomerism in organic compounds

ACTIVITY 7.4

Consider the following set of compounds and use them for activity 7.4.1 and activity 7.4.2

a. $CH_3CH_2CH_2CH_2CH_2CH_3$

b. $CH_3CH(OH)CH_2CH_2CH_3$

c. $CH_3CH_2CH_2CHO$

d. $CH_3CH{=}CHCH_2CH_3$

e. $CH_3CH{=}CHCH_3$

f. $CH_3CH_2CH_2CH_2CH_2COOH$

g. $CH_3CH_2CH_2CH_2CH_2OH$

h. $CH_3COCH_2CH_3$

i. $CH_3CH_2CH_2COOCH_2CH_3$

j. $CH_3CH_2CH_2OCH_2CH_3$

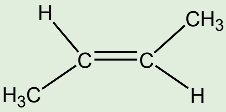
k. $CH_2{=}CHCH_2CH_2OH$

l. $CH_3CH_2CH_2CH(OH)CH_3$

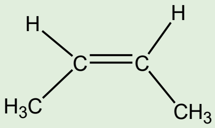
m. $CH_3CH(CH_3)CH_2CH_2CH_3$

n. $CH_3CH(CH_3)CH(CH_3)CH_3$

o.



p.



7.4.1. Structural isomers

ACTIVITY 7.4.1

Analyze the structure of the compounds listed above and point out:

1. Compounds with the same structural formula
2. Compounds with the same molecular formula
3. Are there any compounds having the same molecular formula but different by their structures?
4. Explain the main differences displayed by them? Name the relationship between them?

Isomerism is the existence of compounds that have the same molecular formula but different arrangements of atoms; these compounds are called "**isomers**".

Structural isomers are compounds with the same molecular formula but with different structural formulae. They are subdivided into position isomers, chain isomers, and functional isomers.

a. Position isomerism

Position isomers are compounds with the same molecular formula but different positions of the functional group or substituent(s).

Examples: $CH_3CH_2CH_2CH_2OH$ and $CH_3CH_2CH(OH)CH_3$

b. Chain isomerism

Chain isomers are compounds with the same molecular formula, belonging to the same homologous series, with chain of carbon atoms of different length.

Examples: $CH_3CH_2CH_2CH_2CH_3$, $CH_3CH(CH_3)CH_2CH_3$ and $CH_3C(CH_3)_2CH_3$

c. Functional isomerism

Functional (group) isomers are compounds which have the same molecular formula but different functional groups.

Examples:

C_2H_6O: CH_3OCH_3 and CH_3CH_2OH

$C_4H_8O_2$: $CH_3CH_2CH_2COOH$ and $CH_3CH_2COOCH_3$

APPLICATION ACTIVITY 7.4.1

For each of the given molecular formula, write out their corresponding possible position isomers and functional isomers

a) $C_4H_{10}O$ b) $C_5H_{10}O_2$ c) $C_5H_{10}O$

7.4.2 Stereoisomerism

ACTIVITY 7.4.2 (a)

1. What is the relationship between compounds o) and p) in the activity 7.4 ?
2. Suggest examples of other organic compounds which have a similar relationship.

Stereoisomers are compounds that have the same structural formula in terms of order of attachment, but differ in arrangements of the atoms in space.

a. Geometrical isomerism

Geometrical isomers or cis-trans isomers are compounds with the same molecular formula, same arrangement of atoms but differ by spatial arrangements.

This type of isomers is mainly found in alkenes due to the restricted rotation around the carbon-carbon double bond.

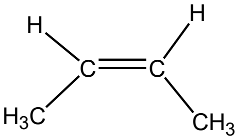
The necessary condition for an alkene to exhibit geometrical isomerism is that each carbon doubly bonded has two different groups attached to it.

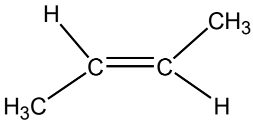
The isomer in which the two $-CH_3$ group lie on the same side of the molecule is called the cis isomer (Latin *cis*, meaning "on this side") and is named cis-2-butene.

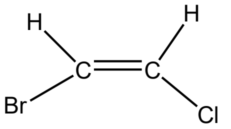
The isomer with the two $-CH_3$ group on opposite sides of the molecule is the trans isomer (Latin *trans*, meaning "across") and is named *trans*-2-butene.

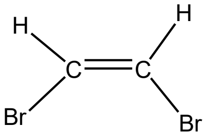
These two compounds are cis-trans isomers (or geometric isomers), compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule

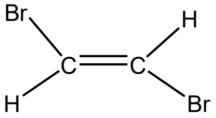
Examples

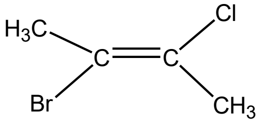

cis-2-butene


trans-2-butene


cis-1-bromo-2-chloroethene


cis-1,2-dibromoethene


trans-1,2-dibromoethene


trans-2-bromo-3-chlorobut-2-ene

b. Optical isomers

ACTIVITY 7.4.2(b)

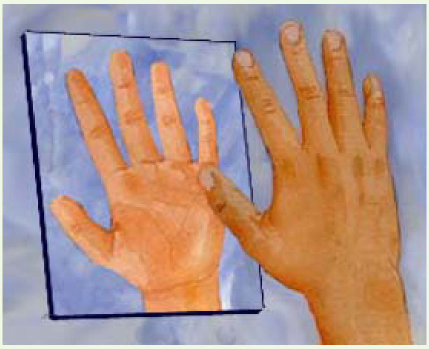


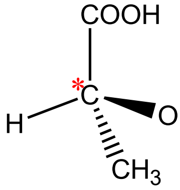
Figure 7.1: Mirror image

1. Look at your two hands or the figure 7.1 and discuss the relationship between them?
2. What are the necessary conditions for a pair of organic compounds to exhibit a similar relationship?
3. What name is given to such compounds?

Optical isomers are compounds with the same molecular formula and arrangements of atoms but have different effect on the plane polarized light.

A compound that rotates the plane polarized light is said to have an **optical activity.**

This type of isomerism occurs in compounds containing an asymmetric (asymmetrical) carbon atom or ***chiral centre*** or **Stereogenic Centers: the Stereogenic Carbon Atom**



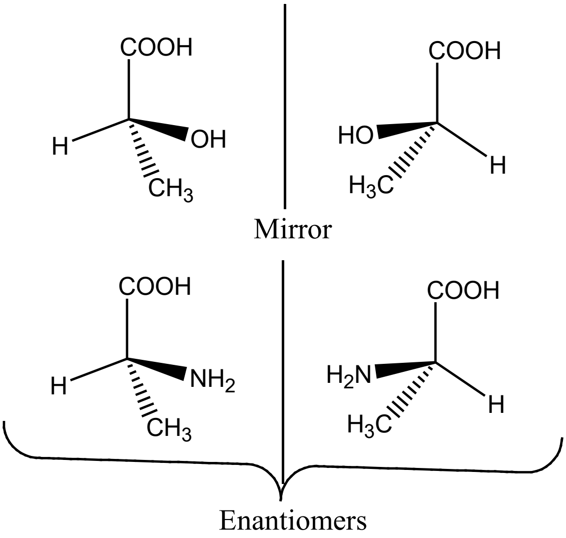
Carbon atoms with four different groups attached to them are called Stereogenic carbon atoms (also called chiral carbon or asymmetric carbon (*)

When a molecule has chiral centre, there are two non- superimposable isomers that are mirror images of each other.

Such compounds are called **enantiomers.**

In a mirror, the left hand is the image of the right hand and they are non-superimposable, i.e. they are enantiomers. An achiral object is the same as its mirror image, they are superimposable.

Examples



2-Hydroxpropanoic acid

2-Aminopropanoic acid

APPLICATION ACTIVITY 7.4.2

1. What is meant by “isomers”
2. Using examples, distinguish structural isomers and stereoisomers. Describe the sub-classes of each type of isomers.
3. Explain how the nature of the C=C bond gives rise to cis-trans isomerism.
4. Identify which of the isomers of hexene exhibit geometrical isomerism.
5. Which of the following compounds can exist as optical isomers? Justify your answer

    a. $CH_3CH_2CH_2CH_2CH_3$

    b. $CH_3CH(Cl)CH_3$

    c. $CH_3CH_2CH(NH_2)CH_3$

    d. $CH_3\ CH_2CH_2CH(CH_3)_2$

7.5. General rules of nomenclature of organic compounds according to IUPAC

ACTIVITY 7.5

The list of names of compounds is given below.

Acetylene, ethanol, aniline, formic acid, Paracetamol, 2-methylpentane, formalin, acetaldehyde, ethanol, methanoic acid, acetone, propanone, 2,4-dimethylhexane, but-2-ene.

Select, from the list above the following:

(1) the actual IUPAC names

(2) the common names

The organic compounds are named by applying the rules set by the International Union of Pure and Applied Chemistry (IUPAC). The purpose of the IUPAC system of nomenclature is to establish an international standard of naming compounds to facilitate the common understanding.

In general, an IUPAC name has three parts:

(i) A **prefix** that indicates the type and the position of the substituents on the main chain.

(ii) The **base** or **root** that indicates a major chain or ring of carbon atoms found in the molecule's structure. e.g. **Meth-** for one carbon atom, **eth-** for 2 carbon atoms, **prop-** for 3 carbon atoms, **pent-** for five carbon atoms, **hex-** for six carbon atoms, **hept-, oct-, non-, dec-**, etc.

(iii) The suffix designates the functional group.

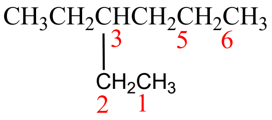
Example **-ane** for alkanes, **-ene** for alkenes, **-ol** for alcohols, **-oic acid** for carboxylic acids, **-al** for aldehydes, **-one** for ketones and so on.

Steps followed for naming organic compounds:

1. Identify the parent hydrocarbon:

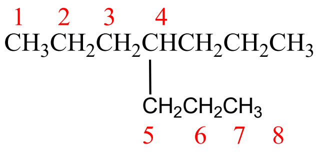
It should have the maximum length, or the longest chain

Example



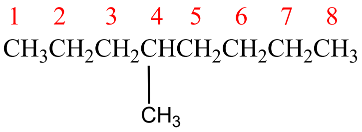
$CH_3CH_2CH(CH_2CH_3)CH_2CH_2CH_3$

3-Ethylhexane



$CH_3CH_2CH_2CH(CH_2CH_2CH_3)CH_2CH_2CH_3$

4-Propyloctane

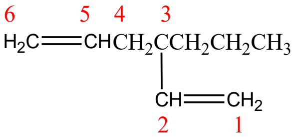


$CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_3$

4-methyloctane

It should have the maximum number of multiple bonds

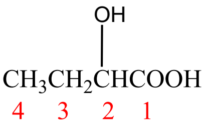
Example



$H_2C{=}CHCH_2C(CH{=}CH_2)HCH_2CH_2CH_3$

3-propylhexa-1,5-diene

2. Identify the parent functional group, if any, with the highest order of priority

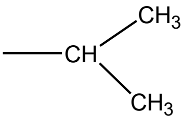
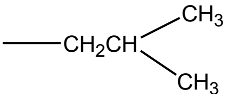
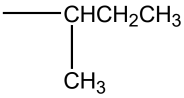
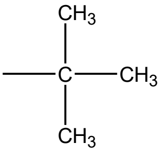

$CH_3CH_2\overset{OH}{\overset{|}{C}}HCOOH$

2-Hydroxybutanoic acid

3. Identification of the side chains.

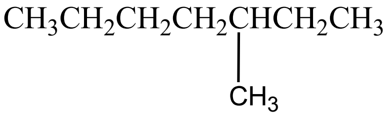
Side chains are usually alkyl groups. An **alkyl group** is a group obtained by a removal of one hydrogen atom from an alkane. The name of alkyl group is obtained by replacing **-ane** of the corresponding alkane by **–yl (Table 7.3)**.

Table 7.3: Nomenclature of useful alkyl groups

Formula of alkyl group	Name of alkyl group	Corresponding alkane
—R	Alkyl	Alkane
—CH_3	Methyl (Me)	Methane
—CH_2CH_3	Ethyl (Et)	Ethane
—$CH_2CH_2CH_3$	Propyl (Pr)	Propane
	isopropyl(^{i}Pr)	propane
—$CH_2CH_2CH_2CH_3$	Butyl (Bu)	Butane
	isobutyl(^{i}Bu)	Butane
 $-\underset{CH_3}{\underset{\vert}{C}}HCH_2CH_3$	*sec*-butyl(^{s}Bu)	Butane
 $-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-CH_3$	*tert*-butyl(^{t}Bu)	Butane

A side chain must be identified by the smallest possible numbers.

Example

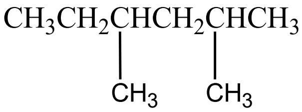


$CH_3CH_2CH_2CH_2\underset{CH_3}{CH}CH_2CH_3$

3-Methylheptane not 5-Methylheptane

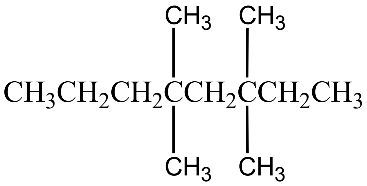
4. If the same substituent occurs two or more times, the prefix di-, tri-, tetra- , ... is attached to substituent's name.

Examples



$CH_3CH_2\underset{CH_3}{CH}CH_2\underset{CH_3}{CH}CH_3$

2,4-dimethylhexane

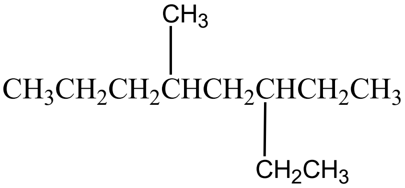


$CH_3CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_3$

3,3,5,5-tetramethyloctane

5. Identify the remaining functional groups, if any, and name them. Different side chains and functional groups will be listed in alphabetical order.

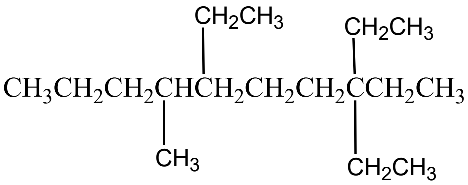
Examples



$CH_3CH_2CH_2\overset{CH_3}{CH}CH_2\underset{CH_2CH_3}{CH}CH_2CH_3$

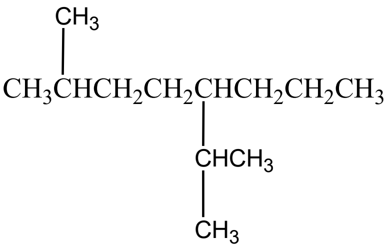
3-Ethyl-5-methyloctane not 5-Methyl-3-ethyloctane

The prefixes ***di, tri, tetra***...are not taken into consideration when grouping alphabetically. But prefixes such iso-, neo- are taken into account



$CH_3CH_2CH_2\underset{CH_3}{CH}\overset{CH_2CH_3}{CH}CH_2CH_2CH_2\overset{CH_2CH_3}{\underset{CH_2CH_3}{C}}CH_2CH_3$

3,3,6-triethyl-7-methyldecane



$CH_3\overset{CH_3}{CH}CH_2CH_2\underset{\underset{CH_3}{CHCH_3}}{CH}CH_2CH_2CH_3$

5-isopropyl-2-methyloctane

Identify the position of the double/triple bond.

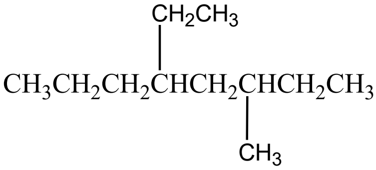
Example:

$CH_3CH_2CH{=}CHCH_2CH_2CH_3$: hept-3-ene (3-heptene)

Number the chain (left to right or right to left).

The sum of the numbers which show the location of the substituents is the x smallest possible.

Example

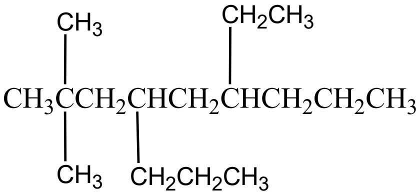


$$CH_3CH_2CH_2\overset{\overset{\displaystyle CH_2CH_3}{|}}{C}HCH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$$

5-Ethyl-3-methyloctane not 4-Ethyl-6-methyloctane

The correct name will be the one which shows the substituents attached to the third and fifth carbon, respectively and not to the fourth and the fifth carbon atom.

Numbers are separated by commas. Hyphens are added between numbers and words. Successive words are merged in one word.



$$CH_3\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_2\underset{\underset{\displaystyle CH_2CH_2CH_3}{|}}{C}HCH_2\overset{\overset{\displaystyle CH_2CH_3}{|}}{C}HCH_2CH_2CH_3$$

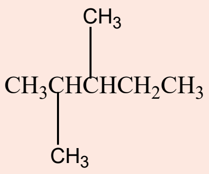
6-Ethyl-2,2-dimethyl-4-propylnonane

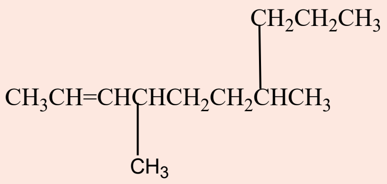
APPLICATION ACTIVITY 7.5

1. Complete the sentence; the systematic nomenclature of organic compounds follows rules established by the ....

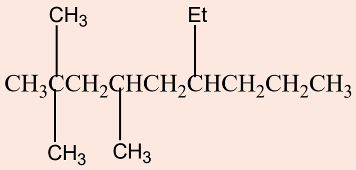
2. What are the main parts which made up the name of an organic compound?

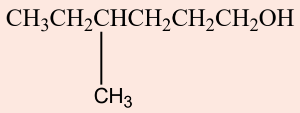
3. Name each of the following compounds using the IUPAC system.

a) 
$CH_3\underset{CH_3}{C}H\overset{CH_3}{C}HCH_2CH_3$

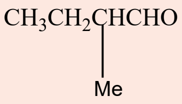
e) 
$CH_3CH{=}CH\underset{CH_3}{C}HCH_2CH_2\overset{CH_2CH_2CH_3}{C}HCH_3$

b) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

c) 
$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{CH_3}{C}HCH_2\overset{Et}{C}HCH_2CH_2CH_3$

f) 
$CH_3CH_2\underset{CH_3}{C}HCH_2CH_2CH_2OH$

g) $CH_3CH_2CH_2CH_2CH_2COOH$

d) 
$CH_3CH_2\underset{Me}{C}HCHO$

SKILLS LAB 7

Homemaking Shoe Polish

You are provided with the following

Materials

- 100 g banana peelings
- 2 g black dye coloring powder
- 1teaspoon rock salt

Tools

- Mortar and pestle,
- Stirring rod,
- Plastic spoon,
- Plastic cup,
- Steel fork

Operational Procedure

1. Scrape the white part of the banana peel with the use of steel fork.

2. Mash the peeling with mortar and pestle.

3. Pour in the salt and mix it with the peelings.

4. Pour in the black dye powder and mix it with the peeling-salt mixture.

5. Put the finished product in its packaging.

Note: Before applying the shoe polish made with this method, clean your shoes with a damp cloth to remove any loose dirt.

Question: What improvements would you apply to make this shoe polish more effective?

END UNIT ASSESSMENT 7

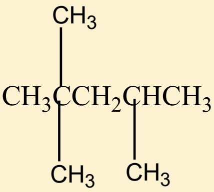
1. a. An atom or group of atoms which dictates the characteristic properties of an organic compound is………………………………………… ……………………………………………………..

   b. A set of compounds that have the same functional group is referred as ……………………………

2. Chain isomers belong to the same class. True/False

3. Organic compounds belonging to the same class have similar physical properties. Tue/False

4. What is the name of the following compound?



$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{CH_3}{C}HCH_3$

   A. 1,1-butyl-2- methylpropane

   B. 2,2,4-trimethylpentane

   C. 2,2,4-methylpentane

   D. 2,4,4-trimethylpentane

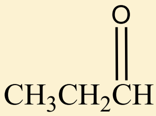
   E. none of the above

5. The compounds that follow belong to which class of organic compounds/?

   (i) $HC{\equiv}CCH_2CH_3$

   A. alcohols B. alkenes C. alkynes D. aromatic

   (ii)



$CH_3CH_2\overset{O}{\overset{\|}{C}}H$

   A. ethers B. aldehydes C. ketones D. alcohols

7. Write the structural formula of:

   a. 4-ethyl-3-methylheptane

b. 3-ethyl hexane

c. 3,3,5-trimethyloctane

d. 4-ethyl-2,2-dimethylnonane

8. Consider the following compound. $CH_3CH_2CH_2CH_2OH$

a. Determine the percentage composition of each element present in the compound.

b. Determine the empirical formula of the above molecule

c. From the results from a) calculate the molecular formula of the compound

d. Write all possible structural formulae of isomers of the compound.

e. Name the isomers in d) according to the IUPAC system.

f. From the results in d)

(i) Classify the isomers as chain, position, functional and optical isomers.

(ii) Show the compound that can exhibit optical isomerism.

9. Which compounds can exist as cis-trans (geometric) isomers? Draw them.

a) $CHCl{=}CHBr$

b) $CH_2{=}CBrCH_3$

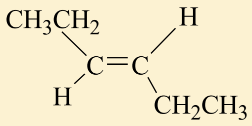
c) $(CH_3)_2C{=}CHCH_2CH_3$

d) $CH_3CH{=}CHCH_2CH_3$

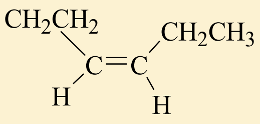
10. What are cis-trans (geometric) isomers? What two types of compounds can exhibit cis-trans isomerism?

11. Classify each compound as a cis isomer, a trans isomer, or neither.

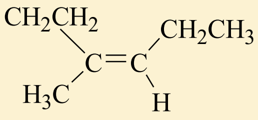
a)



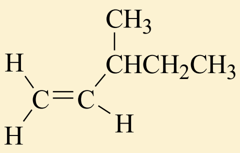
b)



c)



d)



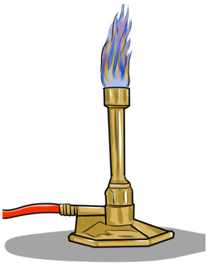
UNIT 8

ALKANES

Key unit competence: **Relate the chemical properties of alkanes to their reactivity and uses and explain their physical properties.**

INTRODUCTORY ACTIVITY

Observe the following pictures and answer the questions below:

			
(A): Kivu watt power station	**(B)**	**(C)**	**(D)**

1. In Rwanda, natural gas has been discovered in Lake Kivu and the government is under its exploitation. Suggest the name and formula of the gas extracted in Kivu watt power station?
2. Suggest the names and structures of the chemical compounds used to produce energy in the picture C.
3. What is the source of the fumes produced as shown by the picture D?
4. Analyse the environmental problems caused by the fumes observed in the picture D and suggest different ways to solve it.
5. The cosmetic in picture B is made of which chemicals and what is the main source of these chemicals?
6. Outline all possible uses of the chemical compound extracted in Kivu watt power station.

8.1. Nomenclature of straight chain hydrocarbon alkanes (up to carbon 20) and branched hydrocarbons using IUPAC system.

ACTIVITY 8.1

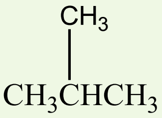
Given the following organic compounds, suggest the answers of the questions below:

(A) CH_4

(B) $CH_3CH_2CH_3$

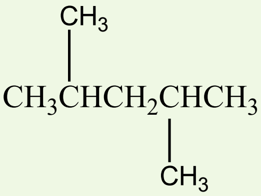
(C) $CH_3CH_2CH_2CH_3$

(D)



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_3$

(E)



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2\underset{\underset{CH_3}{|}}{C}HCH_3$

Questions:

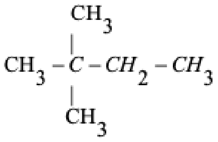
1. All the five compounds given above are made of only two elements. Identify these two elements and find out other characteristics all the five compounds have in common.
2. Identify the particular similarity between compound (D) and (E).
3. Explain how compounds (D) and (E) differ from (B) and (C).
4. Suggest the names of the above five organic compounds.

Alkanes are the simplest class of organic compounds. They are made of carbon and hydrogen atoms only and contain two types of bonds, carbon-hydrogen (C-H) and carbon-carbon (C-C) single covalent bonds. They do not have functional groups.

Alkanes form a homologous series with the general formula $\mathbf{C_nH_{2n+2}}$ where n is the number of carbon atoms in the molecule. The first member of the family has the molecular formula $\mathbf{CH_4}$ (n=1) and is commonly known as methane and the second member with molecular formula is $\mathbf{C_2H_6}$ (n=2) is called ethane.

The alkanes are **saturated hydrocarbons.** “Saturated” means that they contain the maximum content of hydrogen possible, with no double or triple bonds between carbon atoms. It is possible to have alkanes with straight or with branched chains, for example:

$CH_3CH_2CH_2CH_2CH_3$ **straight chain**



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-CH_3$$

branched chain

Alkanes are the simplest compounds to name. All alkanes end their names with the suffix **–ane.**

When naming a molecule from its structure, you just need to follow some simple steps:

a) Find and name the longest unbranched chain in the molecule.

b) Identify and name groups attached to this chain.

c) Number the chain consecutively, starting at the end nearest a substituent group.

d) Designate the location of each substituent group by an appropriate number and name.

e) Assemble the name, listing groups in alphabetical order.

The first four members are known by their common names, from C_5 and above the Roman prefixes indicating the number of carbon atoms is written followed by the ending “**ane**” of the alkanes.

Note: Alkyl groups are obtained when one hydrogen atom is removed from alkanes; therefore their names are deduced from the corresponding alkanes by replacing “**ane**” ending with “**yl**”.

Table 8.1. Examples of naming alkanes

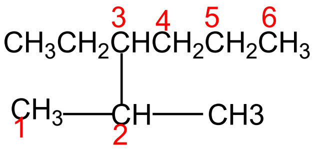
n	Formula of Alkanes	Name of alkanes	Alkyl group formulae	Name of alkyl groups
1	CH_4	methane	CH_3-	methyl
2	CH_3CH_3	ethane	CH_3CH_2-	ethyl
3	$CH_3CH_2CH_3$	propane	$CH_3CH_2CH_2$-	propyl
4	$CH_3(CH_2)_2CH_3$	butane	$CH_3(CH_2)_2CH_2$-	butyl
5	$CH_3(CH_2)_3CH_3$	pentane	$CH_3(CH_2)_3CH_2$-	pentyl
6	$CH_3(CH_2)_4CH_3$	hexane	$CH_3(CH_2)_4CH_2$-	hexyl
7	$CH_3(CH_2)_5CH_3$	Heptane	$CH_3(CH_2)_5CH_2$-	Heptyl
8	$CH_3(CH_2)_6CH_3$	Octane	$CH_3(CH_2)_6CH_2$-	Octyl
9	$CH_3(CH_2)_7CH_3$	Nonane	$CH_3(CH_2)_7CH_2$-	Nonyl
10	$CH_3(CH_2)_8CH_3$	Decane	$CH_3(CH_2)_8CH_2$-	Decyl
11	$CH_3(CH_2)_9CH_3$	Undecane	$CH_3(CH_2)_9CH_2$-	Undecyl
12	$CH_3(CH_2)_{10}CH_3$	Dodecane	$CH_3(CH_2)_{10}CH_2$-	Dodecyl
13	$CH_3(CH_2)_{11}CH_3$	Tridecane	$CH_3(CH_2)_{11}CH_2$-	Tridecyl
14	$CH_3(CH_2)_{12}CH_3$	Tetradecane	$CH_3(CH_2)_{12}CH_2$-	Tetradecyl
15	$CH_3(CH_2)_{13}CH_3$	Pentadecane	$CH_3(CH_2)_{13}CH_2$-	Pentadecyl
16	$CH_3(CH_2)_{14}CH_3$	Hexadecane	$CH_3(CH_2)_{14}CH_2$-	Hexadecyl
17	$CH_3(CH_2)_{15}CH_3$	Heptadecane	$CH_3(CH_2)_{15}CH_2$-	Heptadecyl
18	$CH_3(CH_2)_{16}CH_3$	Octadecane	$CH_3(CH_2)_{16}CH_2$-	Octadecyl
19	$CH_3(CH_2)_{17}CH_3$	Nonadecane	$CH_3(CH_2)_{17}CH_2$-	Nonadecyl
20	$CH_3(CH_2)_{18}CH_3$	Icosane	$CH_3(CH_2)_{18}CH_2$-	Icosyl

Note: n is the number of carbon atoms

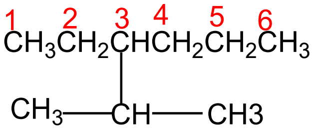
Prefixes **di, tri, tetra, sec, tert**, are not considered when alphabetizing.

f) In case of chains of the same length, the priority is given for part where many branched of alkyl groups appear.

Examples:



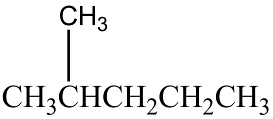
3-ethyl-2-methylhexane
(two substituents)



not
3-isopropylhexane
(one substituent)

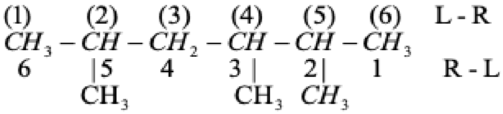
The prefix "**iso**" is used when all carbons, except one, form a continuous chain. This one carbon is part of an **iso group** at the end of the chain.

Example:



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3$ Isopentane

g) If there are more than one substituent, the numbering is done so that the sum of the numbers used to locate the locants is minimum. This is the lowest sum rule.



$$\begin{array}{cccccccccccc} (1) & & (2) & & (3) & & (4) & & (5) & & (6) & L-R \\ CH_3 & - & CH & - & CH_2 & - & CH & - & CH & - & CH_3 & \\ 6 & & |5 & & 4 & & 3| & & 2| & & 1 & R-L \\ & & CH_3 & & & & CH_3 & & CH_3 & & & \end{array}$$

The longest chain has 6 carbons, it is a hexane chain. The sum of locants:

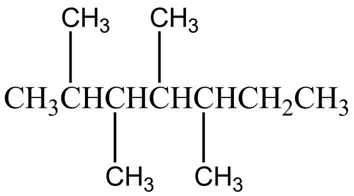
i) L-R = 2+4+5 = 11

ii) R-L = 2+3+5 = 10

Since the sum of the locants for R-L numbering is minimum, then it is preferred.

The name of alkane is given by the numbers of the locants (2,3,5-) followed by the prefixed substituent (trimethyl), followed by the name of the long chain (hexane): 2,3,5-trimethylhexane.

Example:



$$CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{CH_3}{|}}{C}H\overset{\overset{CH_3}{|}}{C}H\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$$

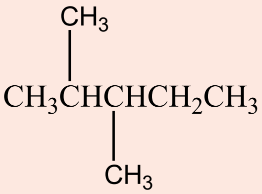
2,3,4,5-tetramethylheptane
not 3,4,4,6-tetramethylheptane

The system of nomenclature described above is called the IUPAC system (IUPAC stands for International Union of Pure and Applied Chemistry).

APPLICATION ACTIVITY 8.1

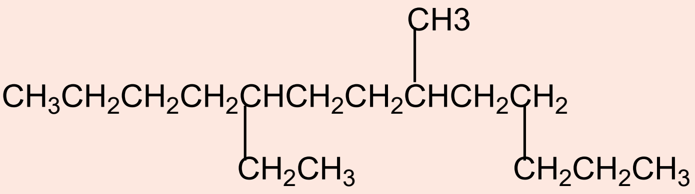
1. Name each of the following alkanes according to the IUPAC system:

a)



$$CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$$

b)



$$CH_3CH_2CH_2CH_2\underset{\underset{CH_2CH_3}{|}}{C}HCH_2CH_2\overset{\overset{CH3}{|}}{C}HCH_2\underset{\underset{CH_2CH_2CH_3}{|}}{C}H_2$$

2. Draw the structure of the following compounds:

(a) 3-ethyl-4-propyloctane

(b) 4-ethyl-2-methylhexane

(c) 2,2-dimethylpentane

8.2. Definition of homologous series and homologous series of alkanes.

ACTIVITY 8.2

Given the following organic compounds:

A: CH_3-CH_2-CH_2-CH_3

B: CH_3-CH_2-CH_2-CH_2-CH_3

C: CH_3-CH_2-CH_2-CH_2-CH_2-CH_3

D: CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3

a) Identify the similarities between compound A, B, C and D.

b) Identify the difference between compound A and B.

c) Identify the difference between compound C and B.

d) What is the relationship between organic compounds A, B, C and D.

A **homologous series is a** series in which members have similar chemical properties and each differs from the preceding by a methylene group –CH_2-.

A homologous series is a family of compounds with the same functional group and with similar chemical properties.

When members of a class of compounds having similar structures are arranged in order of increasing molecular mass, they are said to constitute a **homologous series**. Each member of such a series is referred to as a “homologous” of its immediate neighbours. For example, the following sequence of straight chain of alkanes forms a homologous series.

CH_4: Methane

CH_3-CH_3: Ethane

CH_3-CH_2- CH_3: Propane

CH_3-CH_2-CH_2-CH_3: Butane

etc.

APPLICATION ACTIVITY 8.2

Write the structural formulae of first five members of the homologous series of alkanes.

8.3. Physical properties of straight and branched alkanes

ACTIVITY 8.3

Observe the following pictures and answer the questions below:

Gas containers

Gasoline

Candle waves

1) (a) Nowadays, the gas is used in cooking in some of rwandan homes. The gas used is a mixture of some alkanes.

   i) Suggest the alkanes in that mixture.

   ii) The mixture is in which physical state at room temperature.

   (b) The commonly used fuel (gasoline) in vehicles is an alkane. Suggest one alkane which can be used as fuel in vehicles and state the physical state of this fuel at room temperature.

   (c) Candle wax is made using alkanes. Suggest the alkane used to make it and indicate its physical state at room temperature.

2) Between candle wax and gasoline, which one can be easily converted into vapours? Suggest a reason to your answer.

3) When you mix gasoline and water what do you observe? Explain your observations.

The values of melting, boiling points, density and physical state of some alkanes are summarized in the table below.

Table 8.2: Physical parameters of alkanes

Alkanes	Melting Point ^{0}C	Boiling Point ^{0}C	Density	Physical state
CH_4	-182.6	-162.0	0.4240	gas
C_2H_6	-172.0	-89.0	0.5463	
C_3H_8	-157.1	-44.0	0.5824	
C_4H_{10}	-135.0	-0,5	0.5933	
C_5H_{12}	-129.7	36.2	0.6264	Liquid
C_6H_{14}	-94.5	69.0	0.6594	
C_7H_{16}	-90.5	98.4	0.6837	
C_8H_{18}	-57.0	125.6	0.7028	
C_9H_{20}	-53.7	150.7	0.7179	
$C_{10}H_{22}$	-29.7	174.0	0.7298	
....	....	....	....	
....	....	....	....	
$C_{17}H_{36}$	16.0	300.0	0.769	
$C_{18}H_{38}$	28.0	309.0	0.7767	Solid and elsewhere as n increase

The above table shows that the boiling and melting points of homologue alkanes increase with the number of carbon i.e. molecular mass.

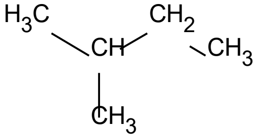
The boiling and melting points depend on the magnitude of the Van Der Waal's forces that exist between the molecules. These forces increase in magnitude with molecular mass.

Note: Branched chain isomers have lower boiling and melting points than their straight chain isomers, because straight chain isomers are closer packed than the branched chain isomers.

Examples: n-pentane: CH_3-CH_2-CH_2-CH_2-CH_3 Boiling point is 36 °C

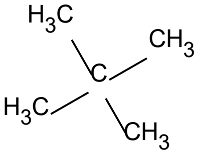
Isopentane:

(2-methylbutane)



Boiling Boiling point is 28 °C

Neopentane:



Boiling point is 9.5°C

(2,2-dimethylpropane)

Boiling points decrease with increase in branching because increased branching gives the molecule a more nearly spherical shape and this reduces the extent of contact between neighbouring molecules. In other words, the branched isomers are less packed than straight chain isomers, and hence the attractive force between the molecules are reduced hence decrease in the boiling points.

Alkanes are not soluble in water, because of their low polarity and also because of their inability to form hydrogen bonds. They are, however soluble in non-polar solvents, like CCl_4, CS_2, benzene, and are miscible with one another.

APPLICATION ACTIVITY 8.3

1. (a) Put 5 ml of hexane in a test tube; add 5ml of water and shake. Record your observations.

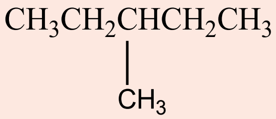
   (b) Repeat the above procedure using heptane instead of hexane.

   (c) Repeat the steps (a) and (b) using carbon tetrachloride instead of water and record your observations.

   Question: interpret all your observations.

2. Predict which one of the following compounds has higher boiling point (which one is less volatile) and explain why.

A)



$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$

B) CH_3-CH_2-CH_2-CH_2-CH_2-CH_3

8.4. Laboratory preparation of alkanes by decarboxylation and other general methods.

ACTIVITY 8.4

Laboratory preparation of an alkane

Requirements:

1) Stand and accessories

2) Delivery tube

3) Sodium hydroxide solid (NaOH)

4) Sodium acetate solid (CH_3COONa)

5) Calcium oxide solid (CaO)

Procedure:

Set up the apparatus as shown on the diagram below

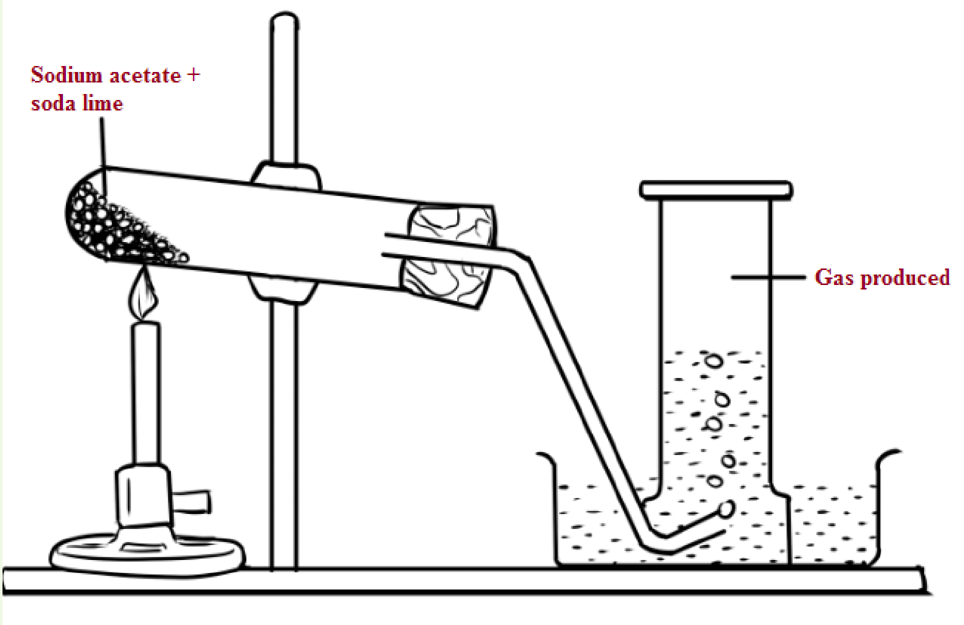


Figure 8.1 Laboratory preparation of an alkane

(a) Prepare a mixture of the reagents in ratio 1:1. Weigh about 3 grams of sodium acetate and the same quantity as soda lime. Mix them thoroughly in a beaker.

(b) Place about 4 grams of the mixture into a boiling tube. Seal the boiling tube with a stopper with a gas-delivery tube. The gas-delivery tube should look upwards.

(c) Fix the boiling tube on a stand.

(d) Heat the test-tube gently. After a while the gas starts liberating.

(e) Prepare an empty test-tube or measuring cylinder. Collect some gas keeping this test-tube on top of the gas delivery tube.

Question: Suggest the name and formula of the gas produced.

Methane can be prepared by the reaction between sodium acetate and sodium hydroxide solid according to the equation:

$$CH_3COONa(s) + NaOH(s) \xrightarrow[heat]{CaO(s)} CH_4(g) + Na_2CO_3(s)$$

Other gaseous alkanes can be prepared in the same way according to the general equation.

$$RCOONa(s) + NaOH(s) \xrightarrow[heat]{CaO(s)} RH(g) + Na_2CO_3(s)$$

Note: The reaction is practically used to reduce by one carbon the length of carbon chain. It is referred as **decarboxylation** of sodium carboxylates.

Other reactions used for the preparation of alkanes are the following:

1) **Addition reaction of hydrogen** to alkenes and alkynes in the presence of catalyst like Nickel, Palladium or platinum produces alkanes. This reaction is called hydrogenation reaction of alkenes and alkynes; it is also called a reduction reaction of alkenes and alkynes.

$$\underset{\text{alkene}}{R\text{-}CH{=}CH\text{-}R'} + H_2 \xrightarrow[150^{0C}]{Ni} \underset{\text{Alkane}}{R\text{-}CH_2\text{-}CH_2\text{-}R'}$$

Example:

$$\underset{\text{But-1-ene}}{CH_3CH_2\text{-}CH{=}CH_2} + H_2 \xrightarrow[150^0\mathbf{C}]{Ni} \underset{\text{Butane}}{CH_3CH_2\text{-}CH_2\text{-}CH_3}$$

2) From halogenoalkanes or Alkyl halides

a) $2\,RX + Zn \xrightarrow{H^+} 2RH + Zn^{2+} + 2X^-$

Example:

$$2CH_3CH_2CHBrCH_3 + Zn \xrightarrow{H^+} 2CH_3CH_2CH_2CH_3 + 2Br^-$$

b) $R - X + H_2 \xrightarrow{Pd} RH + HX$

Example:

$$CH_3-Cl+H_2\xrightarrow{Pd}CH_4+HCl$$

c) $RX+Mg\xrightarrow{Ether/sec}RMgX\xrightarrow{H_2O/NH_3/CH_3OH}RH+\begin{Bmatrix}MgXOH\\MgNH_2X\\Mg(CH_3O)X\end{Bmatrix}$

Example:

$$CH_3Br+Mg\rightarrow CH_3MgBr\xrightarrow{CH_3Br}CH_3-CH_3+MgBr_2$$

d) Alkyl halides when heated with sodium metal in ether solution give higher alkanes (alkanes with more carbon atoms) (**Wurtz reaction**).

Example: $2CH_3CH_2Br+2Na\xrightarrow{ether/heat}CH_3-CH_2-CH_2-CH_3+2NaBr$

Note: This reaction is practically useful in organic synthesis to increase the length of carbon chain.

e) When Alkyl halides are treated with Zn-Cu couple, in the presence of ethanol, alkanes are formed.

Note: Zn-Cu couple is obtained by adding Zinc granules in aqueous copper (II) sulphate solution where copper is deposited on the Zn pieces.

Example:

$$CH_3CH_2Cl\xrightarrow{\text{Ethanol/Zn-Cu}}CH_3CH_3$$

3) From carbonyl compounds (aldehydes or ketones)

Reduction of carbonyl compounds, with amalgamated Zinc (alloy made of zinc and mercury) and HCl. This is the Clemmensen reduction).

Example: $CH_3CH_2COCH_3\xrightarrow{Zn(Hg)/HClconc}CH_3-CH_2-CH_2-CH_3+H_2O$

APPLICATION ACTIVITY 8.4

Complete the following reactions:

a) $CH_3CH_2COONa(s) + NaOH(s) \xrightarrow[\text{heat}]{CaO(s)}$

b) $CH_3CH_2Br + H_2 \xrightarrow{Pd}$

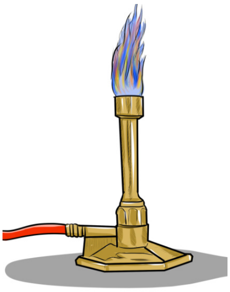
c) $CH_3CH{=}CHCH_2CH_3 + H_2 \xrightarrow[150^0C]{Ni}$

d) $CH_3CH_2CH_2Cl \xrightarrow{\text{Ethanol/Zn-Cu}}$

8.5. Uses and chemical properties of alkanes

ACTIVITY 8.5.1

Observe the following pictures and outline some of the uses of alkanes

			
A	B	C	D

8.5.1. Uses of alkanes

(1) Methane (CH_4)

Methane finds many uses:

- It is used as a **fuel** at homes, ovens, water heaters, kilns and automobiles as it combusts with oxygen to produce heat.
- Highly refined liquid methane is used as **rocket fuel**.
- Methane is used as fuel for electricity generation.

- It is used as a vehicle fuel in the form of liquefied natural gas (LNG).
- Methane can be used as raw material in the production of urea, a fertilizer.

In general, methane is more environmental friendly than gasoline/petrol and diesel.

(2) Butane (C_4H_{10})

- Butane is a key ingredient of synthetic rubber.
- It is used as fuel in cigarette lighters.
- When blended with propane and other hydrocarbons, it may be referred to commercially as LPG, for liquefied petroleum gas.
- Butane gas cylinders are used in cooking.
- Also used in aerosol spray cans.

(3) Propane (C_3H_8)

- Propane is used as a **propellant** for aerosol sprays such as shaving creams and air fresheners.
- Propane is also used as fuel for home heat and back up electrical generation in sparsely populated areas that do not have natural gas pipelines.
- Propane is commonly used in movies for explosions.

(4) Ethane (C_2H_6)

- Ethane is used in the preparation of ethene and certain heavier hydrocarbons.
- Ethane can be used as a refrigerant in cryogenic refrigeration systems.

(5) Pentane (C_5H_{12})

- Pentane is used in the production of polystyrene **foams** and other foams.
- Used in laboratories as **solvents**.
- It is also an active ingredients of **pesticides**.
- Used as solvent in **liquid chromatography.**

(6) Hexane (C_6H_{14})

- It is used in the formulation of glues for shoes, leather products, and roofing.
- It is also used to extract cooking oils such as canola oil or soy oil from seeds.

- Hexane is used in extraction of pyrethrine from pyrethrum; e.g. Horizon SOPYRWA (a pyrethrum factory in Musanze District).
- Also for cleansing and degreasing a variety of items, and in textile manufacturing.

(7) Heptane (C_7H_{16})

- Heptane is used as solvent in paints and coatings.
- Pure n-heptane is used for research, development and pharmaceutical manufacturing.
- Also as a minor component of **gasoline.**
- It is used in laboratories as a **non-polar solvent**.

8.5.2. Chemical properties of alkanes

ACTIVITY 8.5.2

Observe the following pictures and answer the questions below:

	
A	B

Question: Suggest the name of the reaction that takes place in the above two pictures and the possible equations.

Generally, alkanes are quite inert towards common reagents because:

- The C-C bond and C-H bonds are strong and do not break easily.
- Carbon and hydrogen have nearly the same electronegativity value hence C-H bond is slightly polarized; generally C-H bond is considered as covalent.

They, however, undergo the following reactions:

1) Reaction with oxygen

Alkanes react with oxygen to produce carbon dioxide and water (if oxygen is enough to burn all quantity of hydrocarbons). If oxygen is insufficient, carbon monoxide and water or carbon and water are produced. This reaction is called "**combustion**".

$$C_nH_{2n+2} + \frac{(3n+1)}{2} O_2(g) \longrightarrow nCO_2(g) + (n+1)\ H_2O\ (g) + \text{heat}$$

$$C_nH_{2n+2} + \frac{(2n+1)}{2} O_2(g) \longrightarrow nCO\ (g) + (n+1)\ H_2O\ (g) + \text{heat}$$

$$C_nH_{2n+2} + \frac{(n+1)}{2} O_2(g) \longrightarrow nC\ (g) + (n+1)\ H_2O\ (g) + \text{heat}$$

Examples:

a) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

b) $C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$

2) Reaction with halogens (halogenation)

$R\text{-}H + X_2 \rightarrow RX + HX$ where X = Cl, Br, I

Example: Reaction of methane with bromine

$$CH_4 + Br_2 \rightarrow CH_3Br + HBr$$

Mechanism of the reaction:

A **mechanism of a reaction** is a description of the course of the reaction which shows steps of the reaction and the chemical species involved in each step.

The mechanism for the reaction between methane and bromine is the following.

i. Phase 1: Initiation (radical formation)

$$B_2 \xrightarrow{h\nu} 2B\ \bullet$$

i. Phase 2: Propagation

$$CH_4 + Br\bullet \rightarrow \bullet CH_3 + HBr$$

$$\bullet CH_3 + Br_2 \rightarrow CH_3Br + Br\bullet$$

iii. Phase 3: Termination steps (Radicals combination and end of the formation of radicals)

$$CH_3\bullet + CH_3\bullet \rightarrow CH_3 - CH_3$$

$$CH_3\bullet + Br\bullet \rightarrow CH_3Br$$

$$Br\bullet + \bullet Br \rightarrow Br_2$$

Notice:

(i) Br_2 reacts as Cl_2 but slowly while iodine reacts hardly or does not. Fluorine, the most electronegative element of the periodic table reacts with alkanes to give coke, i.e. a decomposition reaction:

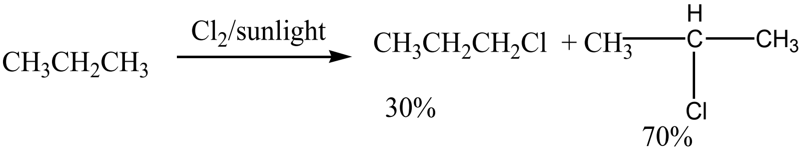
$$C_nH_{2n+2} + (n+1)F_2 \xrightarrow{\text{Light(hv)}} nC_{(S)} + (2n+2)\ HF$$

Example:

$$CH_4 + 2F_2 \xrightarrow{\text{light}} C + 4HF$$

(ii) Due to radical formation involved, the main product of reaction is the one from the most stable radical, starting with tertiary, secondary, primary and methyl in decreasing order of stability.

A tertiary free radical is better stabilized by the electron donating methyl groups than the secondary, primary and methyl ones where the carbon atom is attached to more hydrogen atoms.



$$CH_3CH_2CH_3 \xrightarrow{Cl_2/\text{sunlight}} \underset{30\%}{CH_3CH_2CH_2Cl} + \underset{70\%}{CH_3-\overset{H}{\underset{Cl}{C}}-CH_3}$$

3) **Dehydrogenation of alkanes** gives alkenes under heat and a catalyst like V_2O_5.

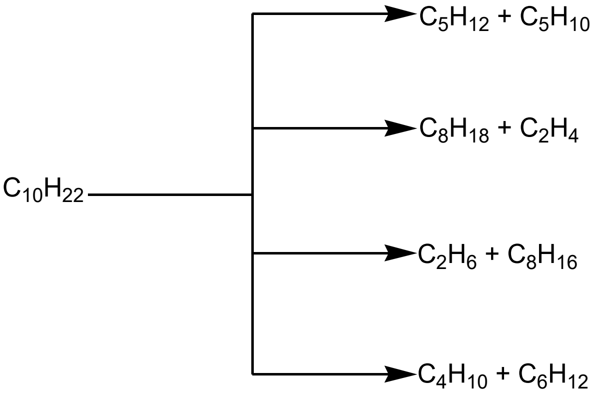
Example:

$$CH_3CH_2CH_2CH_3 \xrightarrow[500^oC]{V_2O_5} CH_3CH_2CH{=}CH_2 + H_2$$

4) Cracking

On heating or in the presence of a catalyst, large molecules of alkanes are decomposed into smaller alkanes and alkenes. If the cracking is performed on heating, it is referred as **thermocracking**.

If the cracking is performed using a catalyst; it is referred as **catalytic cracking** and many products result from one reactant as shown below.



APPLICATION ACTIVITY 8.5

1. In Rwanda, gas methane has been discovered in Lake kivu and the government is under its exploitation. Outline all possible uses of methane gas.

2. The hydrocarbon C_5H_{12} burns to form carbon dioxide and water. Write the balanced equation for the reaction.

3. Name the environmental problem that is caused by the formation of carbon dioxide during the combustion of hydrocarbon.

SKILLS LAB 8

Preparation of Beeswax Candles

Beeswax is the major component of honeycomb and it consists of at least 284 different compounds, mainly a variety of long-chain alkanes such as hentriacontane ($CH_3(CH_2)_{29}CH_3$).

Beeswax is the natural, non-toxic waxy substance secreted by bees after they consume honey. Bees use this wax to construct their honeycombs, and when cleaned and filtered, it can be used for beautiful and beneficial candles.

Beeswax candles are reputed to have several health benefits, including:

- **Light**
- **Lower Toxicity**
- **Neutralizing Pollutants**
- **Relaxation**

Describe how you can make beeswax candles and collect all the requirements to make them.

END UNIT ASSESSMENT 8

1. Answer by **True** or **False**

   a) 2,2-dimethylbutane is an isomer of hexane

   b) Boiling point of alkanes increases with increasing the length of the chain.

   c) Alkanes are polar molecules.

2. Draw the structures of the following formulas:

   a) Octane

   b) 2,3,5-trimethyl-4-propylheptane

   c) 2,2-dimethylpropane

   d) Isobutane

   e) 4-ethyl-2,3-dimethyloctane

3. a) What do you understand by the term hydrocarbon?

   b) What is the relationship between the number of carbon atoms in a hydrocarbon and its boiling point?

4. Consider the alkane with the formula $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

   a) Write down the balanced chemical equation of combustion of the compound,

   b) Name the environmental problem that is caused by the performance of the reaction in a) and suggest different ways to solve that environmental problem.

5. Show how each of the following conversions can be accomplished with a good yield

a) CH_3-Br to $CH_3-CH_2-CH_3$

b) $CH_3-CH=CH-CH_3$ to $CH_3-CH_2-CH_2-CH_3$

c) $CH_3-Br + CH_3-CH_2-Br + 2Na \longrightarrow CH_3-CH_2-CH_3 + NaBr$

d) $CH_3-CH=CH-CH_3 + H_2 \xrightarrow{Pd} CH_3-CH_2-CH_2-CH_3$

UNIT
9

ALKENES AND ALKYNES

Key unit competence: **Relate the chemical properties of alkenes and alkynes to their reactivity and uses and explain their physical properties**

INTRODUCTORY ACTIVITY

Observe the following pictures and answer the questions below after making a research:

	
(A): Plastics	**(B): Yellow banana**

Questions:

1. The plastic materials are manufactured from which organic compounds?
2. Give some examples of chemical reactions which are used to produce plastics.
3. Suggest the name and structure of a plant hormone involved in the ripening of fruits.
4. The items which appear in the picture A above are very useful in our daily life but they also present some disadvantages. Describe these advantages and suggest solutions to these disadvantages.
5. What will happen to the above plastics when heated?

9.1. Definition of alkenes, homologous series, nomenclature and structure of alkenes

ACTIVITY 9.1

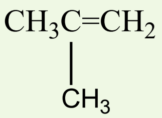
Suggest the IUPAC names of the following compounds:

A: CH_3CH_3

B: $CH_2{=}CH_2$

C: $CH_3CH{=}CH_2$

D:



$$\begin{array}{l} CH_3C{=}CH_2 \\ \quad\;\; | \\ \quad\; CH_3 \end{array}$$

Alkenes are a homologous series of hydrocarbons which contain at least one carbon-carbon double bond. Since their skeleton can add more hydrogen atoms, they are referred as unsaturated hydrocarbons.

The general formula of alkenes is C_nH_{2n}.

Example: Ethene (C_2H_4)

The double bond in alkenes is made of one sigma bond and one pi bond. This gives rise to the impossibility of rotation around the double bond. The hybridization state in alkenes is sp^2 and the structure around each carbon doubly bonded is trigonal planar with a bond angle value of 120^o.

IUPAC names of alkenes are based on the longest chain of carbon atoms that contains the double bond.

The name given to the chain is obtained from the name of the corresponding alkane by changing the suffix from **–ane** to **–ene**.

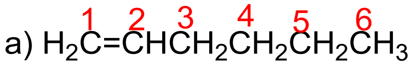
If the double bond is equidistant from each end, number the first substituent that has the lowest number. If there is more than one double bond in an alkene, all of the bonds should be numbered in the name of the molecule, even terminal double bonds. The numbers should go from lowest to highest, and be separated from one another by a comma.

The chain is always numbered from the end that gives the smallest number for the location of the double bond.

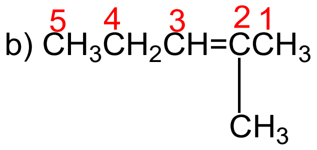
If a compound contains two or more double bonds, its location is identified by a prefix number. The ending is modified to show the number of double bonds:

- **a diene** for two double bonds,
- **a triene** for two three bonds,
- **a tetraene** for four double bonds.

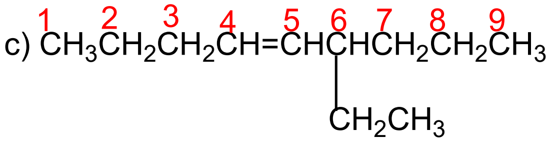
Examples:

a) 

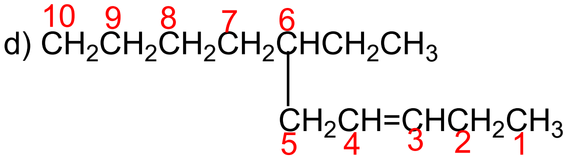
$H_2C{=}CHCH_2CH_2CH_2CH_3$ hex-1-ene

b) 

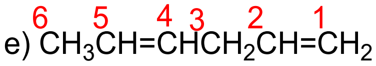
$CH_3CH_2CH{=}C(CH_3)CH_3$ 2-methylpent-2-ene

c) 

$CH_3CH_2CH_2CH{=}CHCH(CH_2CH_3)CH_2CH_2CH_3$ 6-ethylnon-4-ene

d) 

$CH_2CH_2CH_2CH_2CH(CH_2CH{=}CHCH_2CH_3)CH_2CH_3$ 6-ethyldec-3-ene

e) 

$CH_3CH{=}CHCH_2CH{=}CH_2$ 1,4-hexadiene or hexa-1,4-diene

APPLICATION ACTIVITY 9.1

1) Write the structural formula of:

   a) 4-ethylhept-3-ene

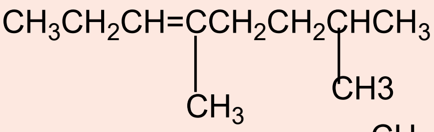
   b) 3-ethyl-2,4,6-trimethyloct-2-ene

   c) Buta-1,2-diene

2) Name each of the following compounds according to the IUPAC system.

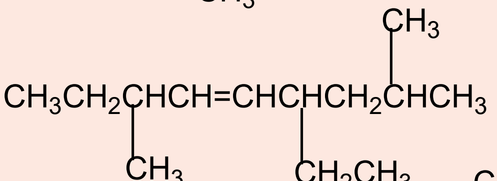
   a) $CH_3HC{=}CHCH_2CH_2CH_2CH_3$

   b)



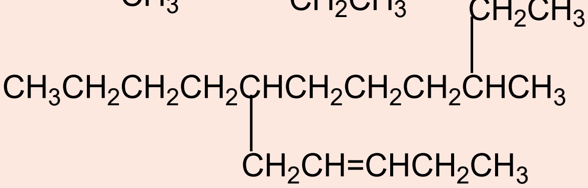
$CH_3CH_2CH{=}\underset{CH_3}{C}CH_2CH_2\underset{CH3}{CH}CH_3$

   c)



$CH_3CH_2\underset{CH_3}{CH}CH{=}CH\underset{CH_2CH_3}{CH}CH_2\overset{CH_3}{CH}CH_3$

   d)



$CH_3CH_2CH_2CH_2\underset{CH_2CH{=}CHCH_2CH_3}{CH}CH_2CH_2CH_2\overset{CH_2CH_3}{CH}CH_3$

9.2. Structural and geometrical isomerism in alkenes.

ACTIVITY 9.2

Using C_4H_8 as molecular formula of butene, draw its three displayed formulae and identify the differences between these three molecules drawn.

Alkenes exhibit two types of isomerism: structural isomerism and stereoisomerism.

1) Structural isomerism

Alkenes show as well position isomerism and chain isomerism.

- In position isomerism, the position of the double bond changes but the length of the chain remains the same.

Example:

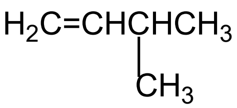
CH_2=$CHCH_2CH_2CH_3$ and CH_3CH=$CHCH_2CH_3$

Pent-1-ene pent-2-ene

- The chain isomerism arises due to difference in the length of the chains.

Example:

H_2C=$CHCH_2CH_2CH_3$ and



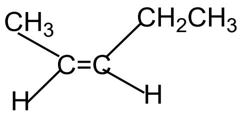
$$\underset{\displaystyle CH_3}{H_2C\text{=}CH\underset{|}{C}HCH_3}$$

pent-1-ene 3-methylbut-1-ene

2) Stereoisomerism

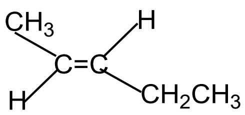
Due to the impossibility of rotation around the double bond, alkenes give rise to **cis-trans** (geometrical) isomerism.

Examples:



cis pent-2-ene

and



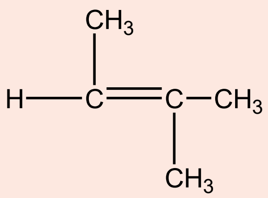
trans pent-2-ene

APPLICATION ACTIVITY 9.2

1. Write four structural isomers of C_6H_{12} and suggest their names.

2. Which of the following alkenes can exhibit a cis-trans isomerism? Explain your answer.

A)



$$H-\overset{\displaystyle CH_3}{\overset{|}{C}}=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$$

B) $CH_3CH_2CH(CH_3)CH$=$CH(CH_3)$

9.3. Preparation methods of alkenes and chemical test for ethene.

ACTIVITY 9.3

Preparation of an alkene

Set up the apparatus as shown in the figure below (Figure 9.1) and follow the instructions to perform the experiment on the preparation of ethene.

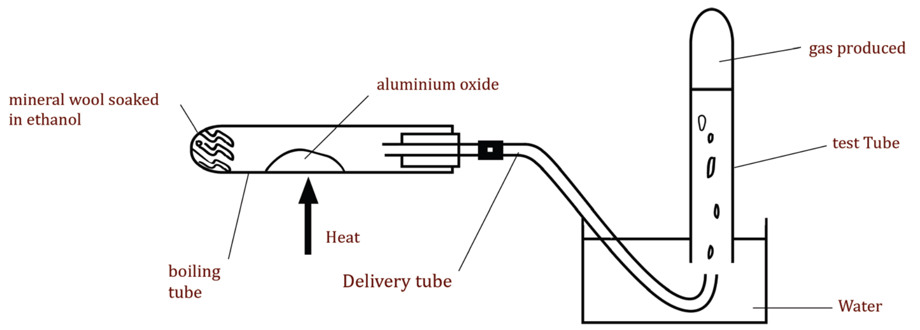


Figure 9.1 Preparation of ethene

Laboratory preparation of an alkene

Requirements:

Chemicals: Ethanol, aluminium oxide, lime water, mineral wool.

Apparatus: Boiling tube, Rubber stopper with hole, Delivery tube, Test-tube rack, test tubes, Spatula, Bunsen burner, Glass rod, Matches.

Procedure and setting:

- Pour some ethanol into the boiling tube to a 3 cm depth
- Add some glass wool to soak up the ethanol, using a glass rod to push the wool down the tube.
- Clamp the boiling tube in a horizontal position using a retort stand.
- Put a small amount of aluminium oxide about half way along the boiling tube.

- Complete the setup of the apparatus as shown in the diagram above.
- Light the Bunsen burner, adjust it to a blue flame and heat the aluminium oxide. (Make sure the test tube is filled with water when you start to collect the gas produced.)
- As the aluminium oxide gets hot the heat reaches the ethanol at the end of the tube. The ethanol then changes to vapour, passes over the hot aluminium oxide and is dehydrated to produce alkene gas.
- Collect the gas and close the test tube with a stopper.

Questions:

1) Name the gas produced during this experiment.

2) Test the gas produced in the above experiment using bromine or potassium permanganate and interpret your observations.

Different methods are used for the preparation of alkenes. Most of them are elimination reactions.

1) Dehydration of alcohols

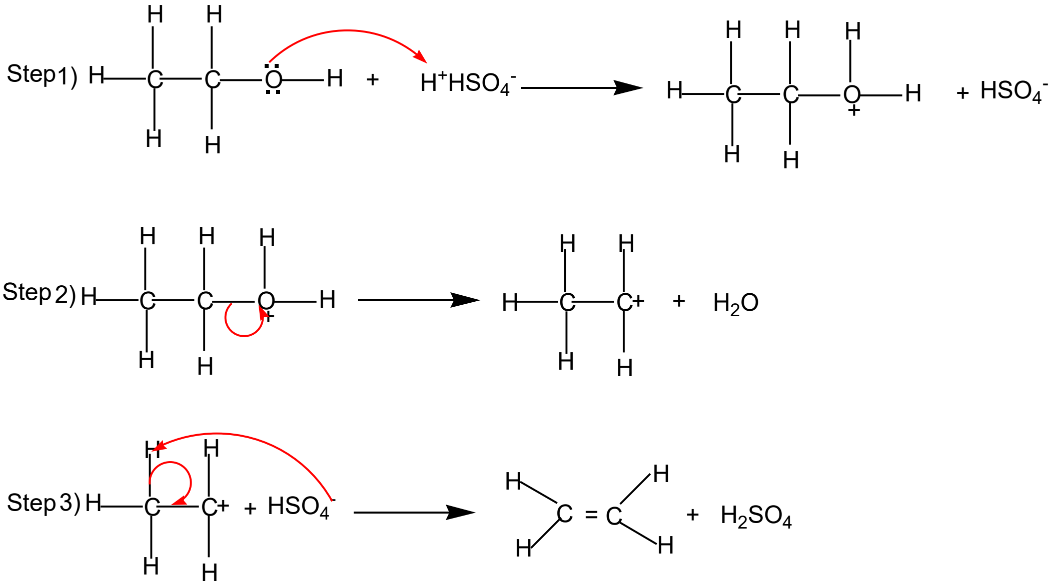
An alkene may be obtained by dehydration of an alcohol. The reaction involves the loss of H and OH (water) from adjacent carbons of an alcohol to form an alkene. The dehydrogenation is carried out by heating an alcohol with concentrated sulphuric acid or 85% phosphoric acid.

$$CH_3CH_2OH \xrightarrow[180^oC]{\text{conc. } H_2SO_4} H_2C{=}CH_2 + H_2O \qquad \text{or}$$

$$CH_3CH_2OH \xrightarrow[100^oC]{85\%\ H_3PO_4} H_2C{=}CH_2 + H_2O$$

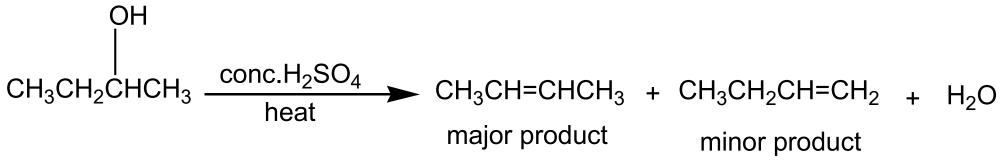
Mechanism of the reaction

The dehydration of alcohols giving alkenes occurs in three steps.

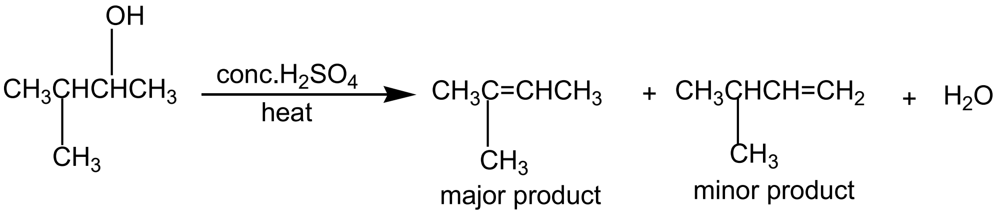


If two or more alkenes may be obtained, the one having more substituents on the double bond generally predominates. This is the **Zaitsev’s rule.**

Example:



$$CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[\text{heat}]{\text{conc.}H_2SO_4} \underset{\text{major product}}{CH_3CH{=}CHCH_3} + \underset{\text{minor product}}{CH_3CH_2CH{=}CH_2} + H_2O$$



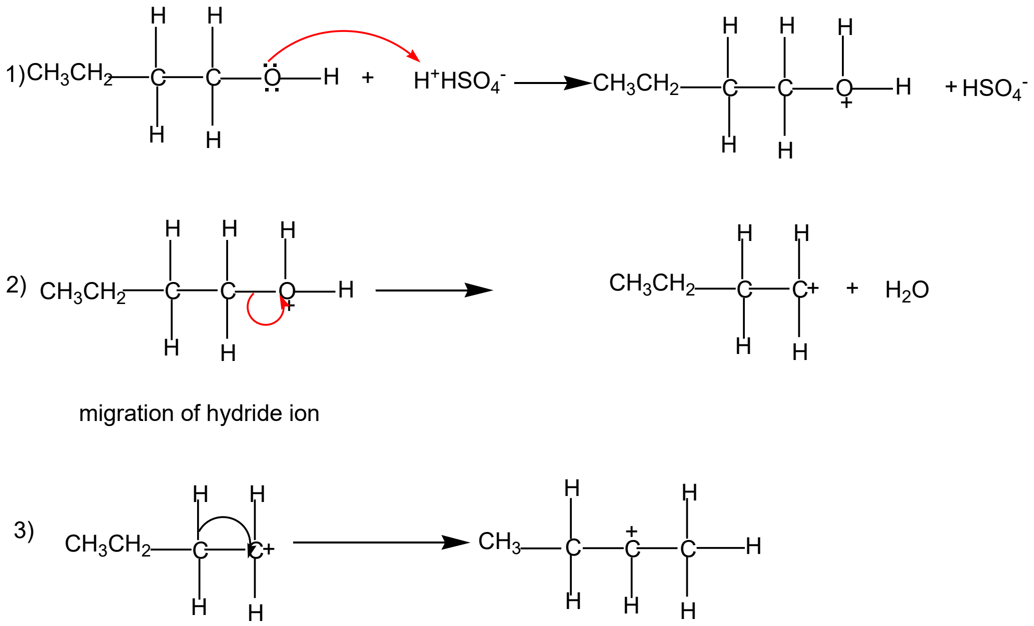
$$CH_3\underset{\underset{CH_3}{|}}{C}H\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[\text{heat}]{\text{conc.}H_2SO_4} \underset{\text{major product}}{CH_3\underset{\underset{CH_3}{|}}{C}{=}CHCH_3} + \underset{\text{minor product}}{CH_3\underset{\underset{CH_3}{|}}{C}HCH{=}CH_2} + H_2O$$

This is due to the stability of the intermediate carbocation. The carbocation produced in step 2 may undergo a transposition (rearrangement) of a hydride ion or a methyl group giving a more stable carbocation and therefore a more stable alkene.

Example 1:

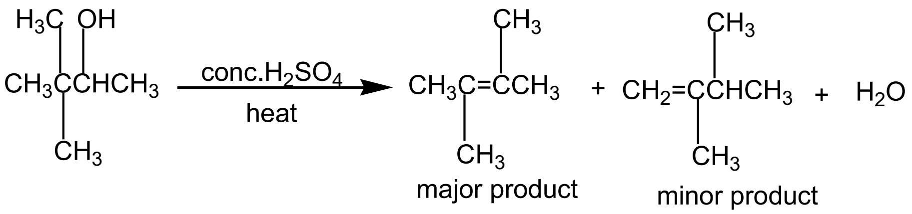
$$CH_3CH_2CH_2CH_2OH \xrightarrow[heat]{conc.H_2SO_4} \underset{\text{major product}}{CH_3CH{=}CHCH_3} + \underset{\text{minor product}}{CH_3CH_2CH{=}CH_2} + H_2O$$

Mechanism:



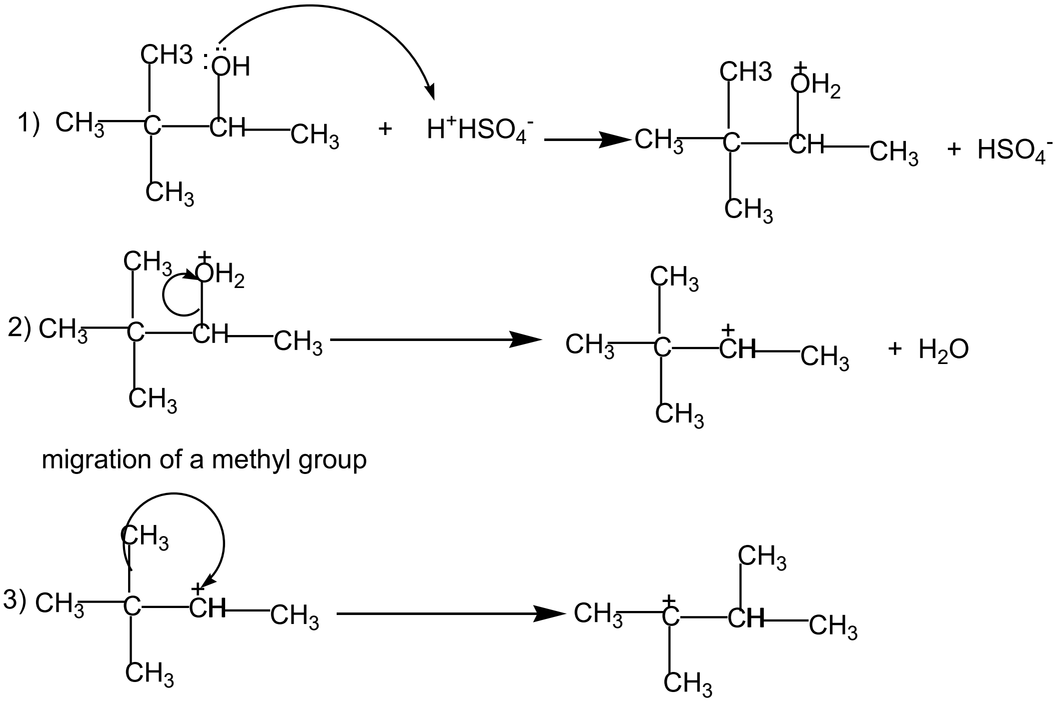
From the secondary carbocation, two products can be obtained and the reaction follows the **Zaitsev’s rule.**

Example 2:



$$CH_3\overset{H_3C}{\underset{CH_3}{C}}\overset{OH}{C}HCH_3 \xrightarrow[heat]{conc.H_2SO_4} \underset{\text{major product}}{CH_3\underset{CH_3}{C}{=}\overset{CH_3}{C}CH_3} + \underset{\text{minor product}}{CH_2{=}\underset{CH_3}{C}\overset{CH_3}{C}HCH_3} + H_2O$$

Mechanism:



migration of a methyl group

From the tertiary carbocation, two products can be obtained and the reaction follows the Zaitsev's rule.

The dehydration of alcohols leading to alkenes may also be effected by heating alcohols in the presence of alumina.

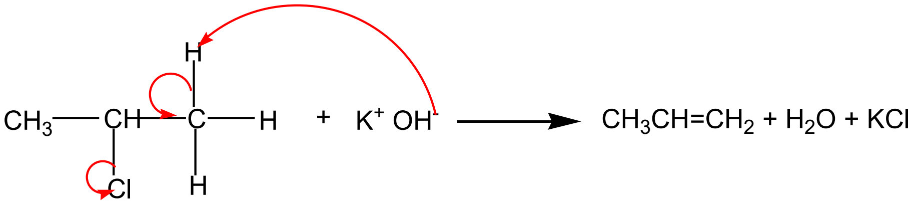
Example:

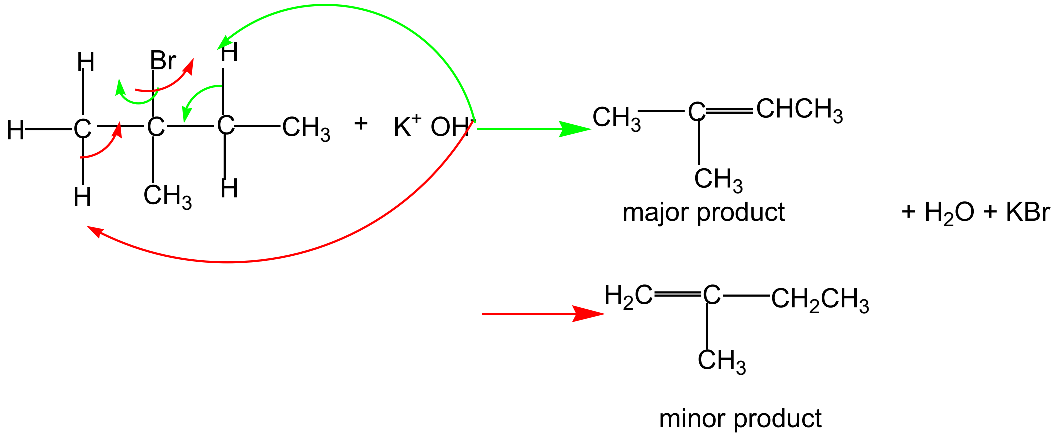
$$CH_3CH_2OH \xrightarrow[\text{heat}]{Al_2O_3} H_2C{=}CH_2 + H_2O$$

2) Dehydrohalogenation of halogenoalkanes

Halogenoalkanes react with hydroxide ions in ethanolic solution to yield alkenes. The reaction follows the Zaitsev's rule.

Example:





3) Dehalogenation of dihalogenoalkanes

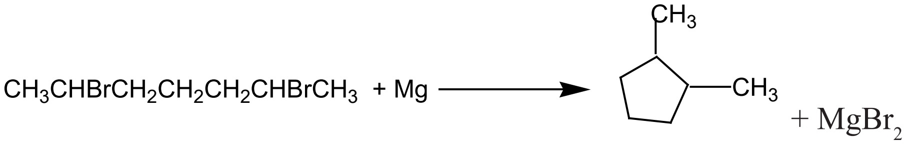
When a compound containing two halogen atoms on the adjacent carbon atoms is treated with magnesium or zinc it transforms to an alkene.

Example:

$$(CH_3)_3CCH_2CHBrCH_2Br + Zn \longrightarrow (CH_3)_3CCH_2CH{=}CH_2 + ZnBr_2$$

When the two halogen atoms are attached to non-adjacent carbon atoms, a cyclic alkane is formed.

Example:



4) Laboratory preparation and chemical test for ethene

When ethanol is heated in the presence of aluminium oxide, a gas is produced. This gas does not react with lime water. This means that the produced gas is not carbon dioxide, this gas is ethene. The equation of the reaction is:

$$CH_3CH_2OH \xrightarrow[\text{heat}]{Al_2O_3} H_2C{=}CH_2 + H_2O$$

The gas decolourises bromine water. Bromine water is used to identify the presence of a carbon-carbon double bond or triple bond. The bromine adds across the double bond and a dibromoalkane is formed. The reaction between athene and bromine water is shown below:

$$H_2C{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$$

If you shake an alkene with bromine water (or bubble a gaseous alkene through bromine water), the solution becomes colourless. Alkenes decolourise bromine water.

When ethene reacts with acidified potassium manganate (VII), the purple colour of the permanganate solution turned to colourless or light pink indicating the presence of the carbon – carbon double bond. The reaction is the following:

$$5H_2C{=}CH_2 + 2MnO_4^- + 6H^+ \rightarrow 5CH_2OHCH_2OH + 2Mn^{2+}$$

The ethene gas burns with a smoky flame producing carbon dioxide and heat energy. The carbon dioxide produced turns into milky lime water.

$$H_2C{=}CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O + \text{heat}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

APPLICATION ACTIVITY 9.3

1) Refer to the IUPAC system and name the alkenes formed when the following alcohols are dehydrated in the presence of sulphuric acid.

   a) 2-methylpropan-1-ol

   b) 2,3-dimethylbutan-2-ol

   c) 2-methylbutan-2-ol

2) What are the products of the dehydrohalogenation of the following compounds? Show the major product.

   a) 1-bromo-2-methylpropane

   b) 2-bromo-3-methylpentane

   c) 3-chloro-3-ethylpentane

3) Establish the formula of the compounds formed when each of the following dihalogenoalkanes react with magnesium.

a) $(CH_3)_2CHCHClCHClCH_3$

b) $CH_3CH_2C(Br)(CH_3)CH(Br)CH_2CH_3$

4) Describe the chemical test used to identify the presence of a carbon-carbon double bond in an organic compound.

9.4. Physical properties of alkenes

ACTIVITY 9.4

1. Put in a test tube 5ml of cyclohexene, add 5ml of water and mix. Record your observations and interpret them.

2. Put in a test tube 5ml of cyclohexene, add 5ml of tetrachloromethane and mix. Record your observations and interpret them.

3. An alkene containing 25 atoms of carbon and 50 atoms of hydrogen is found in the nature. Predict its physical state at room temperature.

- Alkenes which have less than 5 carbon atoms are gaseous at ordinary temperature, the other are liquid up to 18 while others are solids as the number of carbon atoms increases.
- Boiling points and melting points of alkenes are less than those of alkanes but also increase as the molecular weight increase.
- Alkenes are insoluble in water but soluble in most organic solvents.
- Cis-alkenes have a slightly higher boiling point than the trans-isomers because the dipole moments in trans structures cancel each others.

APPLICATION ACTIVITY 9.4

1) Propene and butene are in the same homologous series of alkenes, which one has higher boiling point? Explain.

2) Pentane which is an alkane is insoluble in water; predict what will happen when pentene, which is an alkene, is mixed with water.

9.5. Chemical properties of alkenes

ACTIVITY 9.5

1) To the test tube containing ethene add about 1ml of bromine. Interpret your observations and suggest the balanced reaction that takes place.

2) To the test tube containing again ethene, add about 1ml of very dilute potassium permanganate solution and shake the tube a few times. For this one also interpret your observations and suggest the balanced reaction that takes place.

3) Into another closed test tube containing ethene remove the stopper and apply a light to the mouth of the test tube using a lighted splint. Allow the gas to burn and when it has stopped burning add a small amount of lime water to the test tube, stopper it and shake the tube a few times. Interpret your observations and suggest the balanced reaction that takes place

a) Addition reactions

Alkenes are far more reactive than alkanes due to the carbon-carbon double bond. These compounds are unsaturated and they can easily undergo addition reactions to yield saturated products.

The double bond in alkenes is a region of high density of electrons. Therefore, this region is readily attacked by electrophiles. An **electrophile** is an atom, a molecule or an ion which is electron-deficient; i.e. it is a Lewis acid or an electron pair acceptor.

- **Addition of hydrogen halides**

Hydrogen halides (HCl, HBr, HI) react with alkenes to yield halogenoalkanes. The reaction is carried out either with reagents in the gaseous state or in inert solvent such as tetrachloromathane.

Example:

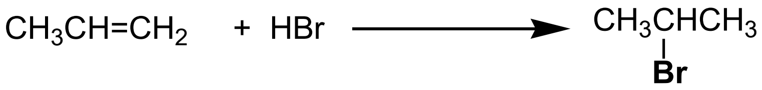
$$CH_2{=}CH_2 + HCl \longrightarrow CH_3CH_2Cl$$

When hydrogen halides add to unsymmetrical alkenes, the reaction leads to the formation of two products in two steps. The first step leads to the formation of two different carbocations with the major product formed from the more stable carbocation. This is the **Markownikov's rule.** That is "*The electrophilic addition of an unsymmetric reagent to an unsymmetric double bond proceeds by involving the most stable carbocation.*

The order of stability of the carbocations is:

$$\xrightarrow[\text{Increasing order of stability}]{\text{Methyl} < \text{Primary carbocation} < \text{Secondary carbocation} < \text{Tertiary carbocation}}$$

Example: Reaction of propene with hydrogen bromide



$$CH_3CH{=}CH_2 + HBr \longrightarrow CH_3\underset{\underset{\mathbf{Br}}{|}}{C}HCH_3$$

In the presence of peroxide, the reaction follows a free radical mechanism and it does not follow the Markonikov's rule.

Example:

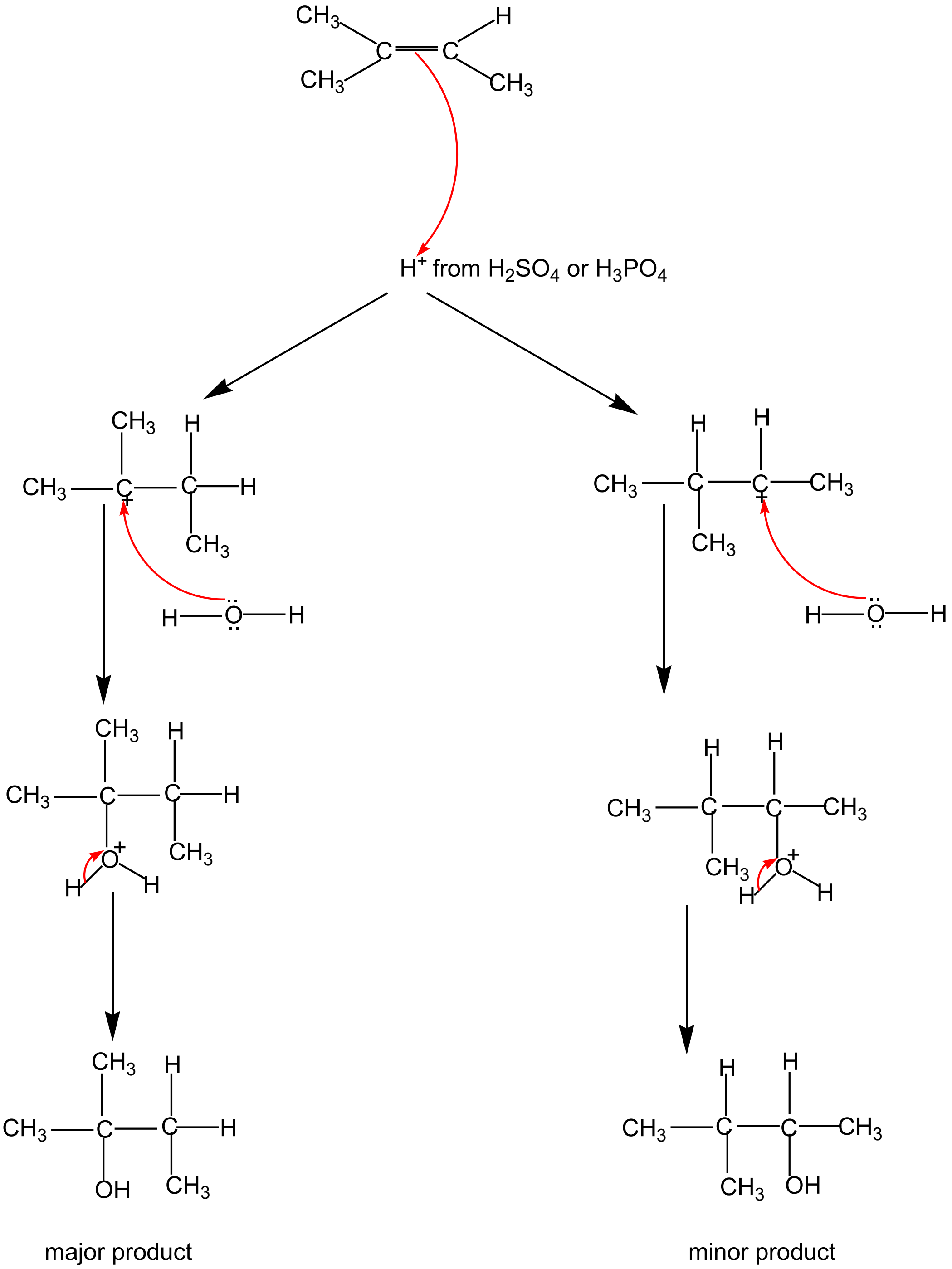
$$CH_3CH{=}CH_2 + HBr \xrightarrow{\text{peroxides}} CH_3CH_2CH_2\mathbf{Br}$$

- **Addition of water**

The hydration of alkenes catalysed by an acid is an electrophilic addition. Ethene can be transformed into ethanol. The first step consists of adding concentrated sulphuric acid. The second step consists of the hydrolysis of the product of the first step.

In industry the reaction is carried out at approximately 300 °C in the presence of phosphoric acid as a catalyst.

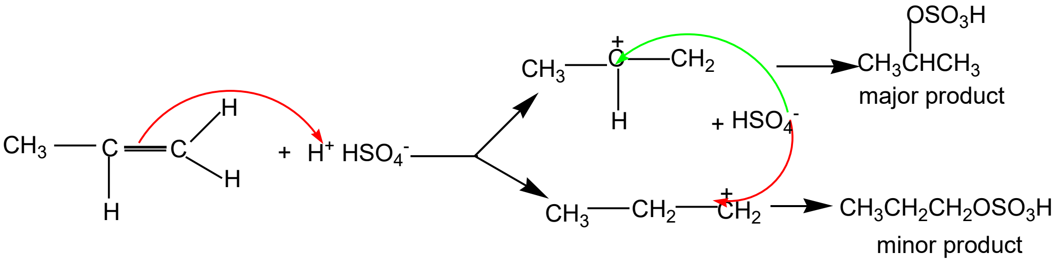
Example: Hydration of 2-methylbut-2-ene

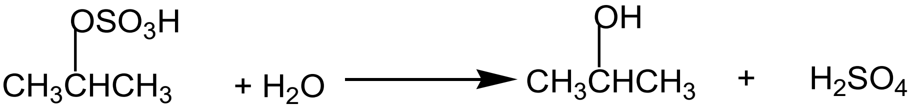


- **Addition of cold concentrated sulphuric acid**

When cold concentrated sulphuric acid reacts with alkene, an alkyl hydrogen sulphate is obtained. If the starting alkene is unsymmetrical, two different alkyl hydrogen sulphates are obtained. If the alkyl hydrogen sulphate is warmed in the presence of water, an alcohol is obtained.

Example: Reaction of propene with H_2SO_4





$$\underset{\displaystyle CH_3CHCH_3}{OSO_3H} + H_2O \longrightarrow \underset{\displaystyle CH_3CHCH_3}{OH} + H_2SO_4$$

- **Addition of halogens**

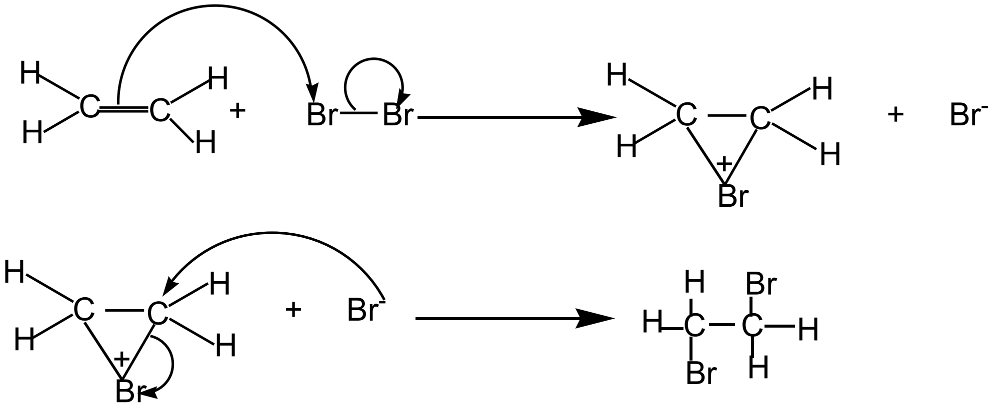
The addition of halogens (halogenation) on alkenes yields vicinal dihalogenoalkanes. The reaction takes place with pure reagents or by mixing reagents in an inert organic solvent.

When a chlorine or bromine molecule approaches an alkene, the pi electrons cloud interact with the halogen molecule causing its polarisation.

Example: Reaction of ethene with bromine in an inert organic solvent gives:

$$H_2C{=}CH_2 + Br_2 \rightarrow CH_2Br\text{-}CH_2Br$$

The reaction follows the mechanism below:



The reaction with bromine is a useful test for alkenes. The brown red colour of bromine is discharged in alkenes.

- **Hydrogenation**

In the presence of a catalyst (Pt, Ni, Pd), alkenes react with hydrogen to give alkanes.

Example:

$$CH_3CH_2CH{=}CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_2CH_3$$

This reaction is very useful when transforming vegetable oils into fats such as margarine by hydrogenation. The process is referred as **hardening**.

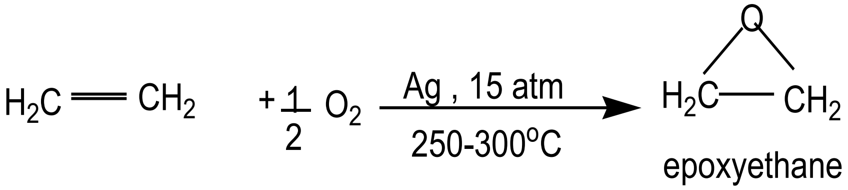
b) Oxidation reactions

Alkenes are readily oxidised due to the presence of the double bond.

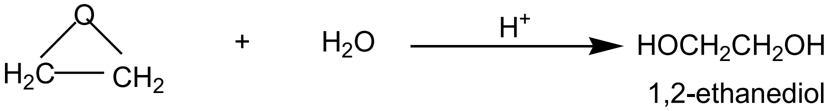
(i) Reaction with oxygen

- **Transformation to epoxides**

Ethene react with oxygen in the presence of silver as a catalyst to yield epoxyethane.



Epoxyethane is a very reactive substance. It reacts with water to give 1,2-ethanediol which is used in the making of polyesters, detergents, and so on.



- **Combustion**

Alkenes burn in oxygen to give carbon dioxide, water and energy.

$$C_nH_{2n} + 3n/2\ O_2 \longrightarrow nCO_2 + nH_2O$$

Example:

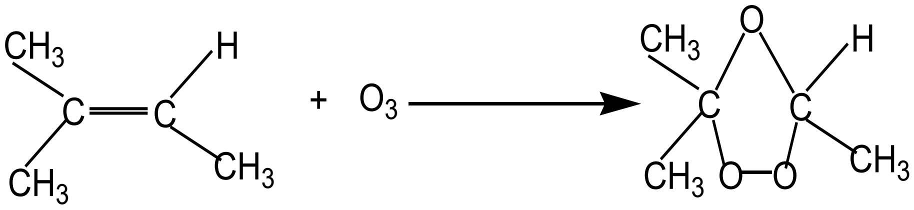
$$CH_3CH{=}CHCH_2CH_3 + \frac{15}{2}O_2 \longrightarrow 5CO_2 + 5H_2O + \text{Energy}$$

(ii) Reaction with ozone

An alkene reacts with ozone to give an ozonide.

The reaction is carried out at low temperature (below 20°C) in non-aqueous medium.

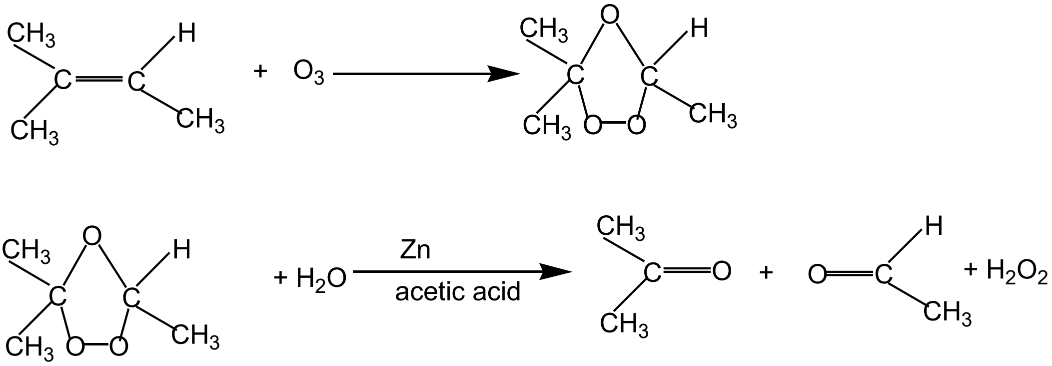
Example:



ozonide

On hydrolysis, the ozonide splits into two carbonyl compounds. The reaction which is an oxidative cleavage is referred to as **ozonolysis**.

Since the by-product is hydrogen peroxide, the hydrolysis is carried out in the presence of a reducing agent.



The interest of the ozonolysis reaction is that it can help to identify the location of the double bond in an alkene.

(iii) Reaction with potassium permanganate

Alkenes react with dilute potassium permanganate solution to give diols. The reaction takes place in the cold condition. The colour change depends on the medium of the reaction.

Example:

$$5H_2C{=}CH_2 + 2MnO_4^- + 6H^+ \rightarrow 5CH_2OHCH_2OH + 2Mn^{2+}$$

very pale pink (almost colourless)

$$H_2C{=}CH_2 + 2MnO_4^- + 2OH^- \rightarrow CH_2OHCH_2OH + 2MnO_4^{2-}$$

dark green solution

$$3H_2C{=}CH_2 + 2MnO_4^- + 4H_2O \rightarrow CH_2OHCH_2OH + 2OH^- + 2MnO_2$$

dark brown precipitate

This reaction also is used to test for the presence a double bond.

Note: An alkane does not react with $KMnO_4$ but an alkene reacts with $KMnO_4$ producing a dark brown precipitate of MnO_2.

c) Hydroformylation

The hydroformylation is a process by which alkenes react with carbon monoxide and hydrogen in the presence of rhodium catalyst to give aldehydes.

Example:

$$CH_3CH{=}CH_2 + CO + H_2 \longrightarrow CH_3CH_2CH_2CHO$$

d) Addition polymerization

Alkenes undergo addition polymerisation reaction to form long chain polymers .i.e a polymer is a large molecule containing a repeating unit derived from small unit called monomers. A polymerisation reaction involves joining together a large number of small molecules to form a large molecule.

Many different addition polymers can be made from substituted ethene compounds.

Each polymer has its physical properties and therefore many polymers have wide range of uses.

Summary of most alkene polymers obtained from alkenes as monomers and their uses (Table 9.1)

Table 9.1: Polymers of alkenes

Polymers	Monomers	Uses
Polyethylene(PE) $-(CH_2-CH_2-)_n-$	$CH_2=CH_2$	Films, bags, pipe, insulating gloves, bottle stoppers, lids and plastic wraps
Polypropylene (PP) $-(CH_3-CH-CH_2)_n-$	$CH_3-CH=CH_2$	Household items, plastic wraps, automobile parts,batteries, garden furniture, syringes, bottle appliance.
Polystyrene (PS) $(C_6H_5-CH-CH_2)_n$	$C_6H_5-CH=CH_2$	plastic wraps, kitchen utensils, furniture covers, thermal insulation, toys and office supplies, disposal razors.
Polyvinyl chloride $-(CH_2-CHCl)_n-$	$CH_2=CHCl$	Household items, electrical wire insulation, water pipes, floor, coverings, window and door covers, items for chemicals and industry sports.
Polytetrafluoro Ethylene(PTFE) $-(CF_2-CF_2)_n-$	$CF_2=CF_2$	Orthopedic and prosthetic appliances, Hearing aids, corrosion resistant and mechanical parts, upholstery, joints, flying pan coatings, electric insulation.

APPLICATION ACTIVITY 9.5

1) Write the equations of the reaction between 3-methylpent-2-ene with:

   a) Oxygen in the presence of silver catalyst.

   b) Cold dilute potassium permanganate solution

2) Describe the observations when butane and but-2-ene react separately with potassium manganate (VII) solution.

9.6. Definition alkynes and homologous series, structure and nomenclature of straight and branched alkynes

ACTIVITY 9.6

1) Write the names and structural formulae of the first three members of the homologous series of alkenes.

2) Suggest the names and structural formulae of the first three members of the homologous series of alkynes.

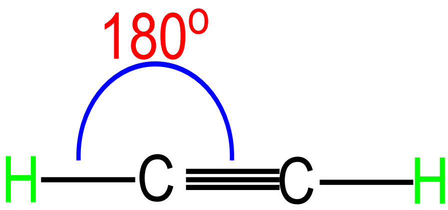
Alkynes are aliphatic hydrocarbons with at least one carbon-carbon triple bond. A triple bond consists of one sigma bond and two pi bonds.

The general formula of this homologous series is C_nH_{2n-2}. Some members of this homologous series are:

$HC\equiv CH$	Ethylene or acetylene
$CH_3C\equiv CH$	Propyne
$CH_3CH_2C\equiv CH$	But-1-yne
$CH_3C\equiv CCH_3$	But-2-yne

According to the VSEPR model, the molecular geometry in alkynes include bond angle of 180° around each carbon triply bonded. Thus, the shape around the triple bond is linear.

Example: structure of ethyne.



There are two types of alkynes: terminal alkynes and non-terminal (internal) alkynes

A terminal alkyne has a triple bond at the end of the chain e.g.: $R\text{-}C\equiv C\text{-}H$

A non-terminal alkyne has a triple bond in the middle of the chain: $R\text{-}C\equiv C\text{-}R'$

Examples:

$HC\equiv CHCH_2CH_2CH_3$, a terminal alkyne

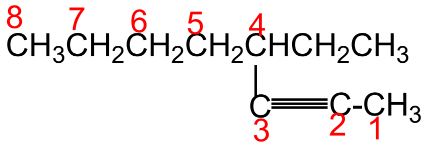
$CH_3C\equiv CCH_2CH_3$, a non-terminal alkyne

Alkynes are named by identifying the longest chain containing the triple bond and changing the ending **–ane** from the corresponding alkane to **–yne**.

Examples:

$H\text{-}C\equiv C\text{-}H$: ethyne

$HC\equiv C\text{-}CH_2CH_2CH_3$: pent-1-yne



$CH_3CH_2CH_2CH_2\underset{C\equiv C\text{-}CH_3}{\underset{|}{C}}HCH_2CH_3$, 4-ethyloct-2-yne

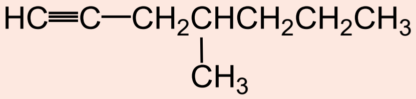
Alkynes with four or more carbon atoms have structural isomers.

Example:

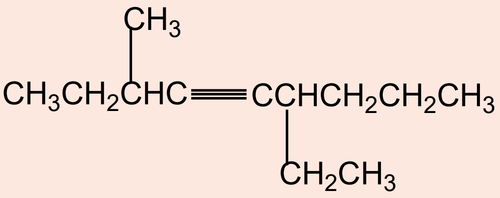
$HC\equiv CCH_2CH_2CH_3$ and $CH_3C\equiv CCH_2CH_3$ are isomers of C_5H_8

APPLICATION ACTIVITY 9.6

1. Name according to the IUPAC system, each of the following compounds.

a) 

$HC\equiv C-CH_2\underset{\substack{|\\ CH_3}}{C}HCH_2CH_2CH_3$

b) 

$CH_3CH_2\overset{\substack{CH_3\\ |}}{C}HC\equiv C\underset{\substack{|\\ CH_2CH_3}}{C}HCH_2CH_2CH_3$

2. Write structural formula for:

a) 2,5-dimethylhex-3-yne

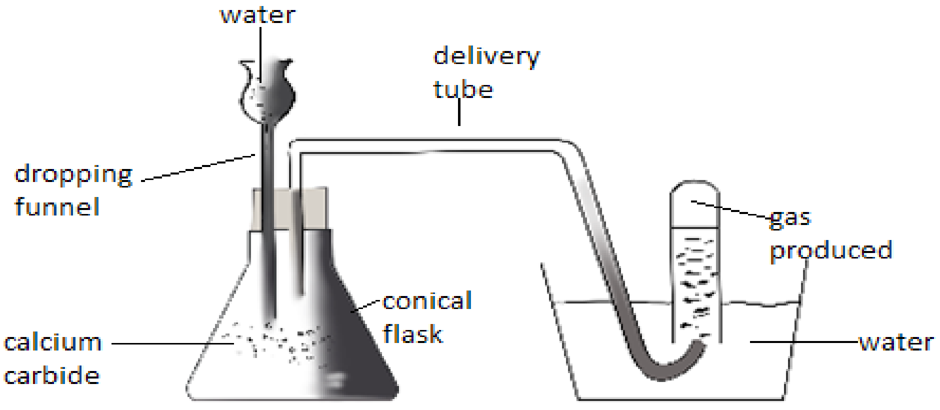
b) 4- ethyl-5-methyloct-1-yne

9.7. Physical properties and industrial preparation method of alkynes.

ACTIVITY 9.7

Preparation of an alkyne

Set up the apparatus as shown in the diagram below.



Laboratory preparation of an alkyne

Procedure:

- Place 2g of calcium carbide in a conical flask
- Using the dropping funnel, add water dropwise.
- Collect the gas produced in the test tube.
- Remove the first tube and connect a second test tube.

Questions:

1) To the first test tube add two drops of bromine water. Record your observations and interpret them.

2) To the second test tube add two drops of potassium manganate (VII). Record your observations and interpret them.

3) Suggest the name and formula of the alkyne produced during this experiment.

4) is the gas produced soluble in water or not? Explain your answer.

a) Physical properties of alkynes.

Alkynes are non-polar compounds with physical properties similar to those of alkenes with the same number of carbon atoms. Their linear structure gives them greater intermolecular forces than alkenes.

Examples: table 9.2: boiling and melting points

Compound	Melting point/^oC	Boiling point/^oC
Propene	-185	-47
Propyne	-101	-23
Pent-1-ene	-138	30
Pent-1-yne	-90	40

Alkynes are water insoluble but they dissolve in each other and in non-polar solvents.

b) Preparation of alkynes

- **Preparation of ethyne**

Ethyne (acetylene) can be prepared from calcium carbide which is obtained by reduction of calcium oxide by coke at high temperature.

$$2CaO(s) + 5C\,(s) \xrightarrow{2000^{0}C} 2CaC_2(s) + CO_2\,(g)$$

$$CaC_2(s) + 2H_2O(l) \longrightarrow HC{\equiv}CH + Ca(OH)_2\,(aq)$$

A more quick industrial production consists of heating methane alone at high temperature for 0.01-0.05second.

$$2CH_4(g) \xrightarrow[\text{electric discharge}]{1773K} C_2H_2(g) + 3H_2(g)$$

- **Alkylation of acetylene**

The hydrogen atom of ethyne as that of other terminal alkynes is slightly acidic and therefore it can be removed by a strong base like $NaNH_2$ or KNH_2.The products of the reaction are acetylides. Acetylides react with halogenoalkanes to yield higher alkynes.

Example:

$$HC{\equiv}CH + NaNH_2\ \text{liq.} \longrightarrow HC{\equiv}C^-Na^+ + NH_3$$

$$HC{\equiv}C^-Na^+ + CH_3CH_2CH_2\text{-}Cl \rightarrow HC{\equiv}CHCH_2CH_2CH_3 + NaCl$$

$$CH_3CH_2CH_2C{\equiv}CH + NaNH_2\ \text{liq.} \longrightarrow CH_3CH_2CH_2C{\equiv}\,C^-Na^+ + NH_3$$

$$CH_3CH_2CH_2C{\equiv}\,C^-Na^+ + CH_3CH_2\text{-}Cl \rightarrow CH_3CH_2CH_2C{\equiv}CCH_2CH_3 + NaCl$$

- **Dehydrohalogenation**

The dehydrohalogenation of vicinal or germinal dihalogenoalkanes yields alkynes

$RCHXCH_2X$ (or RCH_2CHX_2) + $2KNH_2$ (or 2KOH) $\rightarrow RC{\equiv}CH + 2NH_3 + 2KX$ (or $2H_2O$)

Examples:

$$CH_3CH_2CHBrCH_2Br + 2KNH_2 \rightarrow CH_3CH_2C{\equiv}CH + 2KBr + 2NH_3$$

$$CH_3CHBrCH_2Br + 2KOH \rightarrow CH_3C{\equiv}CH + 2KBr + 2H_2O$$

- **Dehalogenation**

The dehalogenation of a tetrahalogenoalkane yield an alkyne.

Example:

$$CH_3CH_2CCl_2CHCl_2 + 2Zn \rightarrow CH_3CH_2C{\equiv}CH + 2ZnCl_2$$

APPLICATION ACTIVITY 9.7

1) Which of 3, 4,4-trimethylpent-1-yne and oct-3-yne has a high volatility? Explain

2) Table salt (NaCl) is water soluble but hex-2-yne is not. Explain why.

3) By which reactions higher members of the alkynes family are prepared?

4) Suggest a synthesis for each of the following compounds using acetylene as the starting organic material.

   a) Propyne

   b) 2-butyne

   c) 3-hexyne

9.8. Chemical properties of alkynes

ACTIVITY 9.8

1) To the test tube containing ethyne add about two drops of bromine. Interpret your observations and suggest the balanced equation of the reaction that takes place.

2) To the test tube containing again ethyne, add about two drops of very dilute potassium permanganate solution.

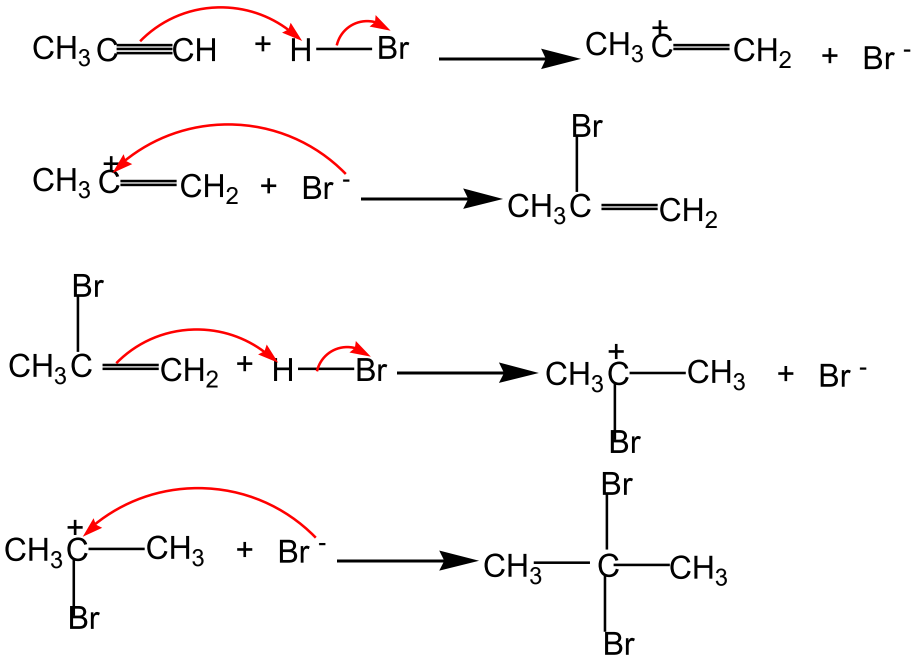
As unsaturated hydrocarbons, alkynes are very reactive. Because they are unsaturated hydrocarbons, alkynes undergo addition reactions. Alkynes can add two moles of reagents.

Even though they have a higher electron density than alkenes, they are in general less reactive because the triple bond is shorter and therefore the electron cloud is less accessible.

a) Addition of hydrogen halides

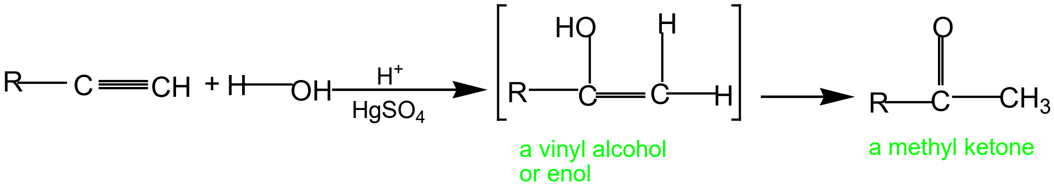
Alkynes react with hydrogen halides to yield dihalogenoalkanes; the reaction follows the Markovnikov's rule. The reaction takes place in four steps.

Example:

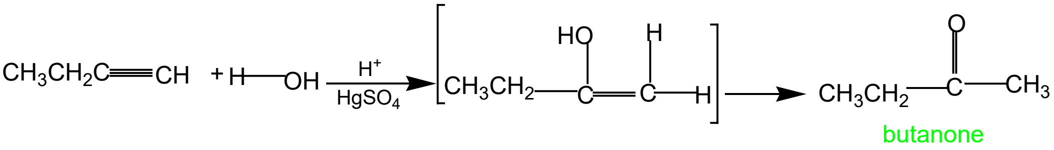


b) Addition of water

Alkynes react with water in the presence of sulphuric acid and mercury sulphate at 60°C to give carbonyl compounds.



Example:



c) Hydrogenation

The hydrogenation of alkynes in the presence of palladium catalyst gives alkanes

The reaction requires two moles of hydrogen for a complete saturation.

Example:

$CH_3CH_2C\equiv CH + 2H_2 \rightarrow CH_3CH_2CH_2CH_3$

In the presence of Lindlar catalyst, the alkynes are partially hydrogenated giving alkenes

Example:

$$CH_3CH_2C\equiv CH + H_2 \xrightarrow{\text{Lindlar catalyst}} CH_3CH_2CH{=}CH_2$$

A Lindlar catalyst is a heterogeneous catalyst that consists of palladium deposited on calcium carbonate and poisoned with different lead derivatives such as lead oxide or lead acetate. A heterogeneous catalyst is the one which is in the phase different from that of the reactants.

d) Reaction with metals

Terminal alkynes react with active metals to yield alkynides and hydrogen gas. Internal alkynes do not react as they do not have an acidic hydrogen atom.

Example:

$$CH_3CH_2C\equiv CH + Na \rightarrow CH_3CH_2C\equiv C^-Na^+ + \frac{1}{2}H_2$$

e) Reaction with metal salts

When a terminal alkyne is passed through a solution of ammoniacal silver nitrate, a white precipitate of silver carbide is formed.

$CH_3C\equiv CH\ (g) + 2AgNO_3\ (aq) + 2NH_3\ (aq) \rightarrow CH_3C\equiv C^-Ag^+(s) + NH_4NO_3\ (aq)$

When a terminal alkyne is passed through a solution of ammoniacal copper (I) chloride, a red precipitate of copper (I) carbide is formed.

$2CH_3CH_2C\equiv CH\ (g) + 2CuCl\ (aq) + 2NH_3\ (aq) \rightarrow 2CH_3C\equiv C^-Cu^+(s) + 2NH_4Cl\ (aq)$

The reactions above are used to:

- Differentiate between terminal and non-terminal alkynes.
- Differentiate ethene and ethyne

The reaction shows that hydrogen atoms of ethyne are slightly acidic, unlike those of ethene.

APPLICATION ACTIVITY 9.8

1) Write the formula(s) and the name (s) of the products of the reaction of pent-1-yne with :

   a) water

   b) hydrogen chloride

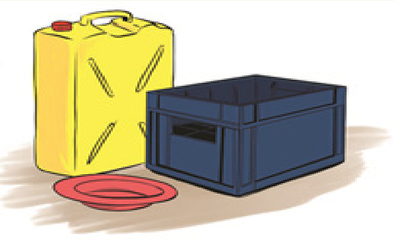
   c) sodium metal

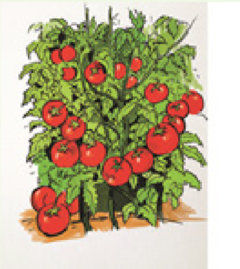
2) Outline the mechanism of the reaction between but-2-yne with hydrogen bromide

9.9. Uses of alkenes and alkynes

ACTIVITY 9.9

Look at the pictures below and suggest the importance of alkenes and alkynes.





Synthetic flowers

- Alkenes are extremely important in the manufacture of plastics which have many applications such as: packaging, wrapping, clothing, making clothes, artificial flowers, pipes, cups, windows,...
- Ethene is a plant hormone involved in the ripening of fruits, seed germination, bud opening; etc
- Ethene derivatives are also used in the making of polymers such as polyvinylchloride (PVC), Teflon...
- Alkenes are used as raw materials in industry for the manufacture of alcohols, aldehydes, etc.
- Alkynes are used in the preparation of many other compounds. For example ethyne is used in the making of ethanal, ethanoic acid, vinyl chloride, trichloroethane, ...
- Ethyne (acetylene) is used as a fuel in welding and cutting metals.
- Propyne is used as substitute for acetylene as fuel for welding.

APPLICATION ACTIVITY 9.9

Alkenes, alkynes and their derivatives have many applications in our daily life.

a) Explain this statement by giving examples.

b) The plastics produced from alkenes, alkynes and their derivatives are very useful but they have some disadvantages. Describe these disadvantages and outline different ways of solving this problem.

SKILLS LAB 9

Project work: Although plastics have many uses, the majority of them are non-biodegradable reason why they have side effects and therefore some of them are being replaced by more eco-friendly plastics (biodegradable plastics).

1) Design a project of making plastics which are biodegradable.

2) Design a project of recycling plastics especially non-biodegradable.

END UNIT ASSESSMENT 9

I. Multiple choice questions. Choose the best answer in the following by noting the corresponding letter.

1) Which of the following is given off during ripening of fruits and vegetables?

   a) Ethane

   b) Ethene

   c) Ethyne

   d) Methane

2) Loss of hydrogen halide is called:

   a) Halogenation

   b) Dehydration

   c) Dehydrohalogenation

   d) Hydrogenation

3) Alkenes can be oxidized using which powerful oxidizing agent in acidified medium?

   a) Potassium manganate (VII)

   b) Sodium manganate (VI)

   c) Calcium manganate (VI)

   d) All of them

4) The molecular formula of-------- fit the general formula (C_nH_{2n-2}).

   a) Alkanes

   b) Alkynes

   c) Alcohols

   d) Alkenes

5) Acetylene is also called:

a) Ethyne

b) Ethene

c) Ethane

d) Methane

II. Open questions

6) Give five possible isomers of C_5H_{10}.

7) Show how the following conversion may be accomplished

CH_3-$CH=CH_2$ to Propyne

8) Two hydrocarbons **D** and **E**, all have the molecular formula C_6H_{12}. **D** decolourises an aqueous solution of bromine and shows geometric isomerism. **E** also decolourises an aqueous solution of bromine but does not show geometric isomerism. Draw possible structures of **D** and **E**.

10) a) Alkenes such as ethene and propene have been described as the building blocks of the organic chemical industry. Discuss this statement, giving examples.

b) What particular features of the chemistry of alkenes make them suitable for this role and why are alkanes less suitable.

UNIT 10

HALOGENOALKANES (ALKYL HALIDES)

Key unit competence: Relate the physical and chemical properties of halogenoalkanes to their reactivity and uses.

INTRODUCTORY ACTIVITY

Observe the following pictures then make a research and suggest the answers to the questions asked below:

A: Anesthesia

B: Insecticide

(1) Give at least one example of chemical substance which can be used as anaesthetic drug containing carbon and chlorine.

(2) Suggest the name and structural formula of an organic compound containing carbons and halogen atoms which can be used as insecticide.

3) The compounds which are suggested in (1) and (2) above belong to the same homologous series. These compounds can be obtained from the reaction between alkanes and halogens. What homologous series do these componds belong to?

4) Outline others uses of these compounds produced from alkanes and halogens.

5) The chemicals produced from alkanes and halogens or alkenes and halogens are very useful but, they have bad effects to the environment. Describe these bad effects and suggest the solutions.

10.1. Definition of halogenoalkanes, homologous series and nomenclature

ACTIVITY 10.1

Given the following organic compounds:

A: CH_3CH_3 B: $CH_3CH{=}CH_2$ C: CH_3CH_2Cl D: $CH_3CH_2CH_2Cl$

E: $CH_3CH_2CH_2CH_2Cl$

Write their IUPAC names and identify the ones which are in the same homologous series.

Halogenoalkanes are compounds in which a halogen atom has replaced at least one of the hydrogen atoms in an alkane chain.

When the halogen atom is attached to a hydrocarbon chain the compound is called a **halogenoalkane** or **haloalkane** or an **alkyl halide**.

The homologous series called **halogenoalkanes** has the functional group –C-X

Where X=F, Cl, Br or I. some members of the series are listed below:

CH_3Cl: Chloromethane

CH_3CH_2Cl: Chloroethane

$CH_3CH_2CH_2Cl$: Chloropropane

$CH_3CH_2CH_2CH_2Cl$: Chlorobutane

The halogenoalkanes contain only single bonds, and their names are based on the alkane homologous series. They are named using the prefixes **fluoro-, chloro-, bromo-** and **iodo-**.

Numbers are used if necessary to indicate the position of the halogen atom in the molecule.

Examples:

CH_3CH_2Cl: Chloroethane; here it is not necessary to indicate the number 1.

$CH_3CHBrCH_3$: 2-bromopropane.

If the molecule contains more than one halogen atom of the same kind, the prefixes **di-, tri-, tetra-**, etc... are used.

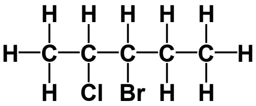
Examples:

CH_2ClCH_2Cl: 1,2-dichloroethane

$CHCl_2CHClCH_3$:1,1,2-trichloropropane.

If there is more than one halogen atom in the compound, they are listed alphabetically.

Example:



3-bromo-2-chloropentane

APPLICATION ACTIVITY 10.1

1. Name the following halogenoalkanes and draw their full displayed formulae:

   a) $CH_3CH_2CH_2CHICH_3$

   b) $CH_3CH_2CHCl_2$

   c) CCl_4

   d) $CHCl_3$

   e) $(CH_3)_3CBr$

2. Write the structural formulae for the following compounds:

   a) 1,2-dibromo-3-chloropropane

   b) 1,1,2-trichloro-1,2,2-trifluoroethane

10.2. Classification, isomerism and physical properties of halogenoalkanes

ACTIVITY 10.2

(1) a) Draw four structural isomers of C_4H_9Cl

b) Classify the above isomers as primary, secondary or tertiary halogenoalkanes.

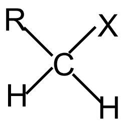
c) Identify the positional and chain isomers of C_4H_9Cl.

(2) Comparing one of the isomers of C_4H_9Cl and 1-bromobutane, indicate the one which has higher boiling point and explain your reasoning.

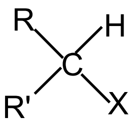
a) Classification of halogenoalkanes

There are three types of halogenoalkanes:

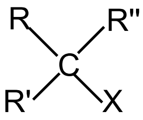
Primary



Secondary



Tertiary



A primary halogenoalkane has a halogen atom attached to the ended carbon atom of the chain. A secondary halogenoalkane has a halogen atom attached to a carbon bonded to two other carbon atoms while a tertiary halogenoalkane has a halogen atom attached to a carbon bonded to three other carbon atoms.

b) Isomerism

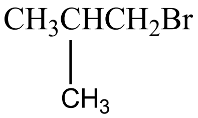
Halogenoalkanes exhibit both chain and position isomerism.

Example: Molecular formula: C_4H_9Br

i) Chain isomerism: This arises due to arrangement of carbon atoms in chains of different size.

The chain isomers are:

$CH_3CH_2CH_2$-CH_2-Br: 1-bromobutane



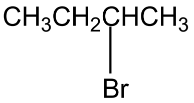
$$\underset{\displaystyle CH_3}{CH_3CH}CH_2Br$$ 2-methyl-1-bromopropane

ii) Position isomerism: This arises due to the different positions taken by the halogen atom on the same carbon chain.

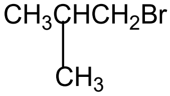
The following compounds are position isomers: $CH_3CH_2CH_2CH_2$-Br and $CH_3CH_2CHBrCH_3$; because the atoms of bromine are on different positions of the chain.

Hence, all isomers of the compound with molecular formula C_4H_9Br are the following:

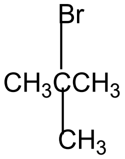
$CH_3CH_2CH_2CH_2Br$



$$CH_3CH_2\underset{\displaystyle Br}{CH}CH_3$$



$$CH_3\underset{\displaystyle CH_3}{CH}CH_2Br$$



$$CH_3\overset{\displaystyle Br}{\underset{\displaystyle CH_3}{C}}CH_3$$

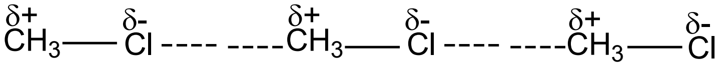
c) Physical properties of halogenoalkanes

i) Volatility

Volatility is a property that shows if a substance transforms easily or not into vapour or gaseous form. This property depends on the nature of the bonds that make up the molecule of the substance. Generally covalent compounds and substances are more volatile than polar compounds. We know that halogens when bonded to other atoms form polar bonds because they possess high electronegativities: F = 4.0, Cl = 3.0, Br = 2.8, I = 2.5, and C = 2.5.

The more the difference of electronegativities of the atoms that form the bond, the more polar is the bond. This explains the high polarity of C-F bond with an electronegativity difference of 1.5, and the low polarity of C-Cl and C-Br bonds where the electronegativity differences are 0.5 and 0.3 respectively.

The presence of polarity or charge distribution results into more attraction between polar molecules called dipole-dipole attraction forces, one type of Van der Waals forces, as shown below:



$$\overset{\delta+}{CH_3}-\overset{\delta-}{Cl}\;\text{----}\;\text{----}\overset{\delta+}{CH_3}-\overset{\delta-}{Cl}\;\text{----}\;\text{----}\overset{\delta+}{CH_3}-\overset{\delta-}{Cl}$$

The dashed line represents the attraction forces between the polar molecules or dipoles.

Therefore, more energy must be supplied to separate polar molecules and this explains why melting and boiling temperatures of fluoroalkanes and chloroalkanes are higher than those of alkanes of similar molecular mass.

As we have already learnt, molecules of organic halogen compounds are generally polar. Due to the greater polarity as well as higher molecular mass as compared to the parent hydrocarbons, the intermolecular forces of attraction (dipole-dipole and van der Waals) are stronger in the halogen derivatives. That is why the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.

Table 10.1: Comparison of boiling points of some halogenoalkanes

Boling points of haloakanes(^{0}C)					
R X=	H	F	Cl	Br	I
CH_3	-161.7	-78.4	-24.2	3.6	42.4
CH_3CH_2	-88.6	-37.7	12.3	38.4	72.3
$CH_3(CH_2)_2$	-42.1	-2.5	46.6	71.0	102.5
$CH_3(CH_2)_3$	-0.5	32.5	78.4	101.6	130.5
$CH_3(CH_2)_4$	36.1	62.8	107.8	129.6	157.0
$CH_3(CH_2)_7$	125.7	142.0	182.0	200.3	225.5

Chloromethane, bromomethane, chloroethane and some chlorofluoromethanes are gases at room temperature. Higher members are liquids or solids.

The attractions get stronger as the molecules get bigger in size. For the same alkyl group, the boiling points of alkyl halides increase in the order: RF <RCl < RBr, < RI, this is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

ii) Solubility

The solubility is the capacity of a substance to dissolve in a given solvent; in chemistry the most common solvent we refer to is water. It is a result of the interaction between the molecules of the substance, a solute, and the molecules of the solvent.

Polar molecules can interact with water molecules, but the attractive forces set up between water molecules and molecules concerned are not as strong as the hydrogen bonds present in water. Halogenoalkanes therefore, although they dissolve more than alkanes, are only slightly soluble in water.

iii) State

The state of matter is the physical appearance of that matter: solid, liquid and gaseous.

Chloromethane, bromomethane, chloroethane and chloroethene are colourless gases at room temperature and pressure. The higher members are colourless liquids with a sweet pleasant smell.

iv) Density

The density is a measure of the quantity of matter by volume unit. Cotton wool is less dense than sand because if you compare the quantity of matter cotton wool and sand contained in for instance 1m^3, you find that there more matter in sand than in cotton wool.

The density of halogenoalkanes increases in the order RCl < RBr < RI, since the atomic weight of halogens increases in order Cl < Br < I. Iodo, bromo and polychloro derivatives are denser than water but chloro derivatives are less dense than water.

APPLICATION ACTIVITY 10.2

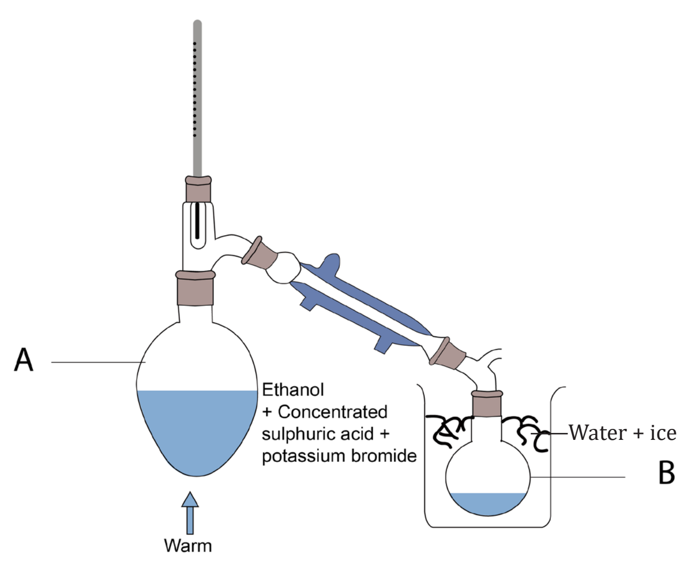
1. Draw three positional isomers of chlorobromopropane, C_3H_6BrCl
2. Arrange each set of compounds below in order of increasing boiling points and explain why.
   (a) Bromomethane, tribromomethane, chloromethane, dibromomethane.
   (b) 1-chloropropane, 2-chloro-2-methylpropane, 1-chlorobutane.
3. Explain the origin of the difference between the boiling temperatures of the following compounds:

Compound	Molar mass/gmol^{-1}	Boiling temperature/°c
C_5H_{12}	72	36
C_3H_7Cl	79	46
C_3H_8	44	-42

10.3. Preparation of halogenoalkanes.

ACTIVITY 10.3

Use the following set up for preparation of halogenoalkanes



Preparation of halogenoalkanes

Procedure:

(a) Add concentrated sulphuric acid to ethanol slowly with lots of shaking and cooling in flask A.

Note: Care has to be taken because a great deal of heat is produced when the two are mixed, and there is a real risk of the ethanol boiling and spraying concentrated sulphuric acid around.

(b) Add solid potassium bromide to the mixture in (a) and connect the flask to a condenser so that the halogenoalkane formed can be distilled off.

(c) Warm (or heat gently) until no more droplets of halogenoalkane collect.

(d) The halogenoalkane produced has a low boiling point but is denser than water and almost insoluble in it. To prevent it from evaporating, collect it under water in a flask surrounded by ice.

Questions:

(1) What is the role of concentrated sulphuric acid in this process?

(2) Write the equations of the reactions that take place during this process.

(2) Suggest the name and the formula of the halogenoalkane produced during this experiment.

1) From alkenes and alkynes

Halogenoalkanes can be prepared by a reaction of alkenes or alkynes with:

(i) hydrogen halides

Addition of hydrogen halide to alkenes, gives alkyl halides as the products. The orientation in the addition reaction is described by Markovnikov's rule (see alkenes).

Examples:

$$CH_3CH_2CH_2CH{=}CH_2 + HCl \longrightarrow \underset{\text{Major product}}{CH_3CH_2CH_2CHClCH_3} + \underset{\text{minor product}}{CH_3CH_2CH_2CH_2CH_2Cl}$$

□□□□□ □ □

$$CH_3C{\equiv}CH + 2HBr \longrightarrow CH_3CBr_2CH_3$$

(ii) Halogens

Examples:

$$CH_3CH{=}CHCH_3 + Br_2 \rightarrow CH_3CHBrCHBrCH_3$$

$$CH_3C{\equiv}CH + 2Cl_2 \rightarrow CH_3CCl_2CHCl_2$$

2) From alcohols

When ethanol reacts with potassium bromide in the presence of concentrated sulphuric acid, bromoethane is formed. The reactions that took place in flask A are the following:

$$KBr + H_2SO_4 \longrightarrow HBr + KHSO_4$$

$$CH_3CH_2OH(l) + HBr(aq) \longrightarrow CH_3CH_2Br(aq) + H_2O(l)$$

In this reaction the hydroxyl group –OH is replaced with a bromine atom.

Halogenoalkanes are also obtained from alcohols using other reagents such as phosphorus halides (PCl_3, PCl_5, PBr_3, PI_3) and thionyl chloride ($SOCl_2$)

Examples:

$3CH_3CH_2CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2CH_2Cl + 3H_3PO_3$

$CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2OH + POCl_3 + HCl$

$CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$

3) From alkanes

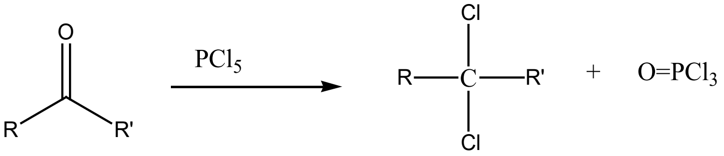
Direct halogenation of alkanes in the presence of ultraviolet light gives alkyl halides and a hydrogen halide.

$$R\text{-}H + X_2 \xrightarrow{UV} R\text{-}X + HX$$

Example:

$$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$$

4) From aldehydes or ketones



Example:

$$CH_3CH_2COCH_3 + PCl_5 \rightarrow CH_3CH_2CCl_2CH_3 + POCl_3$$

APPLICATION ACTIVITY 10.3

1. Complete the following chemical reactions:

   a. $CH_2=CH_2 + HCl \rightarrow$

   b. $CH_3CH_3 + Cl_2 \rightarrow$

   c. $CH_3CH_2\text{-}OH + HBr \rightarrow$

   d. $CH_3\text{-}CH_2CH_2OH + PCl_5 \rightarrow$

   e. $CH_3CH_2\text{-}OH + SOCl_2 \rightarrow$

   f. $3CH_3CH_2CH_2\text{-}OH + PCl_3 \rightarrow$

2. Give the reagent and conditions needed to make 1-bromopropane from propan-1-ol.

10.4. Chemical reactions of halogenoalkanes

ACTIVITY 10.4

To investigate some reactions of halogenoalkanes

(a) To 5cm^3 of dilute sodium hydroxide solution in a test tube, add 5 drops of 1-bromobutane and gently warm the mixture.

Note: Carefully smell the product.

(b) Neutralize the solution with dilute nitric acid by adding 5 drops of nitric acid.

(c) Then add 5 drops of silver nitrate and observe. Write down your observations.

Question:

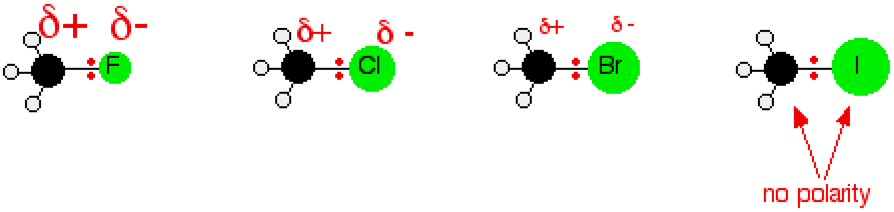
Write equations of the reactions that take place.

In order for any reagent to react with the halogenoalkanes, the carbon-halogen bond has to be broken. Because that gets easier as you go from fluoride to chloride, to bromide, to iodide, the compounds get more reactive in that order. Iodoalkanes are the most reactive and fluoroalkanes are the least.

Influence of bond polarity:

Considering the four halogens, fluorine is the most electronegative and iodine the least. That means that the electron pair in the carbon-fluorine bond will be dragged most towards the halogen end.

Looking at the methyl halides as simple examples:



In the case of methyl iodide, The electronegativities of carbon and iodine are equal and so there will be no separation of charge on the bond.

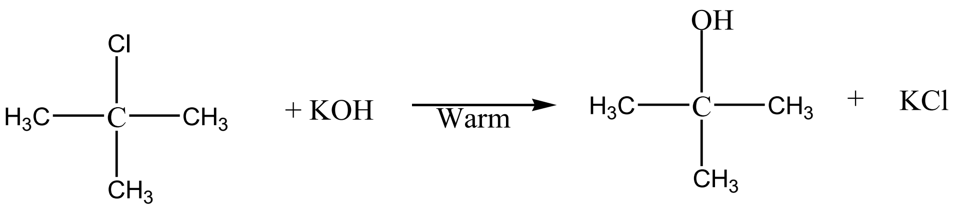
1) Nucleophilic substitution reaction

Because the carbon atom attached to the halogen atom is deprived of its electron, it carries a partial positive charge $-C^{\partial+}-X^{\partial-}$. Thus when electron rich substrates called nucleophiles, approach the carbon atom, the halogen atom leaves as a halide ion. Hence alkyl halides undergo nucleophilic substitution reaction.

(a) Reaction with aqueous alkali: when alkyl halides are refluxed with aqueous alkali, alcohols are produced through substitution of the halogen by hydroxide ion. This reaction is also called "**hydrolysis**".

$$CH_3-CHBr-CH_2-CH_3+OH^- \xrightarrow[\text{Dilute KOH}]{} CH_3-CHOH-CH_2-CH_3+Br^-$$

Examples: $CH_3-CH_2Br+KOH \xrightarrow{warm} CH_3CH_2OH+KBr$



$$(CH_3)_3CCl + KOH \xrightarrow{\text{Warm}} (CH_3)_3COH + KCl$$

The hydrolysis can also take place when water alone is added to tertiary alkyl halides. In this case water molecules act as nucleophiles.

$$(CH_3)_3CBr + H_2O \longrightarrow (CH_3)_3COH + HBr$$

(b) Reaction with sodium alkoxides

Treatment of alkyl halides with sodium alkoxides produces ethers (Wiliamson synthesis)

$$R-X+R-O-Na \xrightarrow{heat} R-O-R+NaX$$

$$CH_3CH_2-Br+CH_3-CH_2-O-Na^+ \xrightarrow{heat} CH_3-CH_2-O-CH_2-CH_3+NaBr$$

(c) Reactions with silver salt of carboxylic acid

When alkyl halides are refluxed with silver salt of carboxylic acid, esters are formed:

$$R-X+R'COO^-Ag^+ \xrightarrow{heat} R-O-CO-R'+AgX$$

$$\text{e.g}: CH_3CH_2Cl+\underset{\text{Silver propanoate}}{CH_3CH_2COO^-Ag^+} \xrightarrow{heat} \underset{\text{ethyl propanoate}}{CH_3CH_2O-CO-CH_2CH_3}$$

(d) Reaction with potassium cyanide

When alkylhalides are refluxed with KCN, in presence of an alcohol, alkyl nitriles are produced

$$R-X+KCN \xrightarrow{heat/alcohol} R-CN+KX$$

$$\text{e.g}: CH_3-CH_2-CH_2-Cl+KCN \xrightarrow{Heat\ alcohol} \underset{\text{butanonitrile}}{CH_3-CH_2-CH_2-CN}+KCl$$

Note: This reaction is of practical importance in organic synthesis because it is used to increase the length of a carbon chain.

(e) Reaction with silver nitrite

When alkyl halides are refluxed with silver nitrite, a mixture of a nitro alkane and alkyl nitrite are obtained as the products. The difference between the two products is in the bonds between the nitrite and the alkyl: C-NO_2 in nitro alkane and C-ONO in alkyl nitrite.

The two products can be separated by fractional distillation.

$$CH_3-Br + AgNO_2 \xrightarrow{heat} \begin{cases} CH_3-O-N=O \text{ methyl nitrite} \\ \\ CH_3NO_2 \text{ nitromethane} \end{cases}$$

(f) Reaction with ammonia and amines

Reaction of alkyl halide with concentrated ammonia produces a mixture of amines.

$R\text{-}CH_2\text{-}I + NH_3 \rightarrow R\text{-}CH_2\text{-}NH_2 + HI$

The alkyl amine produced can then react with a molecule of alkyl iodide to produce a series of substituted amines as shown in the reactions below:

$$CH_3-CH_2-I + CH_3-CH_2NH_2 \longrightarrow \underset{\text{Diethyl amine}}{(CH_3-CH_2)_2NH} + HI$$

$$(CH_3-CH_2)_2NH + CH_3-CH_2-I \longrightarrow \underset{\text{Triethyl amine}}{(CH_3-CH_2)_3N} + HI$$

$$(CH_3-CH_2)_3N + CH_3-CH_2-I \longrightarrow \underset{\text{Tetra ethyl ammonium iodide}}{(CH_3-CH_2)_4N^+I^-}$$

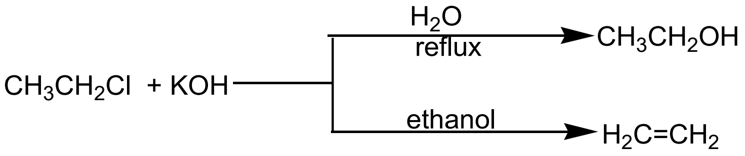
2) Elimination reactions

An elimination reaction is where a saturated organic compound loses an atom or group of atoms to form an unsaturated organic compound. Elimination is the opposite of addition reaction.

Alkyl halides when boiled with alcoholic potassium hydroxide form alkenes by elimination reaction. Hence the alkyl halide loses a molecule of the hydrogen halide.

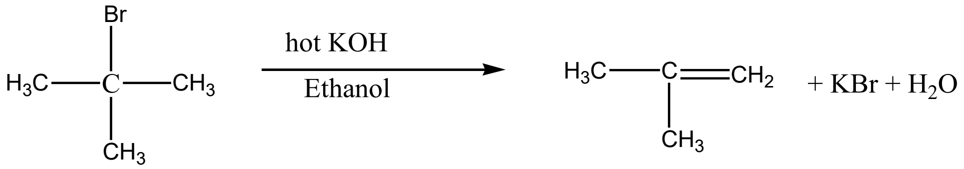
Example : $CH_3\text{-}CHCl\text{-}CH_3 + KOH \xrightarrow{Alcohol} CH_3-CH=CH_2 + KCl + H_2O$

Note: Elimination reaction usually occurs in competition with substitution reaction. So when chloroethane is treated with a solution of potassium hydroxide two organic products are formed depending on the conditions of the reaction.



Ethene is formed by elimination reaction while diethyl ether is formed by substitution reaction.

Elimination is favoured by use of high temperature and a strong base (for example alcohol) instead of water.



3) Wurtz reaction

Alkyl halides react with sodium metal to give alkanes.

$$2CH_3CH_2Br+2Na\xrightarrow{ether/heat}CH_3-CH_2-CH_2-CH_3+2NaBr$$

4) Reaction of polyhalides

These are compounds in which more than one halogen atom is present. There are two types of polyhalides.

- **Gem dihalides**: this is where two halogen atoms are attached to the same carbon atom.

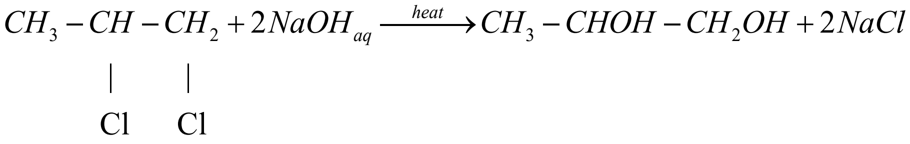
Examples:

$$CH_3-CH_2-CHCl_2\xrightarrow{excess\ \text{hot /alcolic KOH}}CH_3-C\equiv CH$$

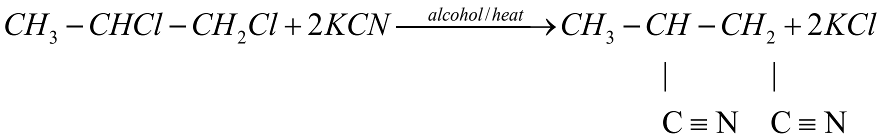
$$CH_3-CCl_2-CH_3\xrightarrow{excess\ \text{hot /alcolic KOH}}CH_3-C\equiv CH$$

- **Vicinal dihalides**: Here the two halogen atoms are on adjacent carbon atoms.

Examples:



$$CH_3-\underset{\substack{|\\ \mathrm{Cl}}}{CH}-\underset{\substack{|\\ \mathrm{Cl}}}{CH_2}+2NaOH_{aq}\xrightarrow{heat}CH_3-CHOH-CH_2OH+2NaCl$$



$$CH_3-CHCl-CH_2Cl+2KCN\xrightarrow{alcohol/heat}CH_3-\underset{\substack{|\\ \mathrm{C\equiv N}}}{CH}-\underset{\substack{|\\ \mathrm{C\equiv N}}}{CH_2}+2KCl$$

The reactions of dihalogenoalkanes are similar to those of monohalogenoalkanes but require more reagents.

APPLICATION ACTIVITY 10.4

1. Give the structural formula of the main product of each of the following reactions:

   a) $(CH_3)_2CH\text{-}CH_2Br$ + NaOH in ethanol, heat

   b) $CH_3CH_2CHBrCH_2CH_3$ + NaOH(aq)

2. Complete the following equations:

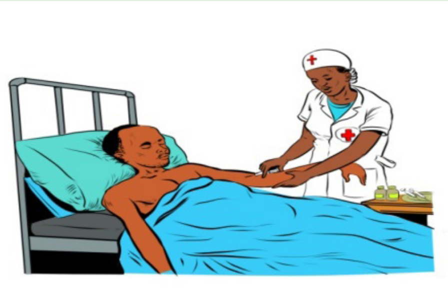
   a) $CH_3CH_2\text{-}CH_2\text{-}I + NH_3 \longrightarrow$

   b) $(CH_3)_3CCl + H_2O \longrightarrow$

10.5. Uses of halogenoalkanes and dangers associated with CFCs

ACTIVITY 10.5

Using the following pictures, outline the advantages and disadvantages of halogenoalkanes.



A

B

Halogenoalkanes have many uses in our everyday life such as in agriculture, at home, industry as solvents, medicine and in pharmacy.

Solvents:

CH_2Cl_2 in varnish and paints manufacturing

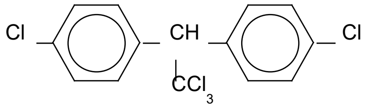
- CCl_4 is used as the most organic solvent for fats and oils and can be used as fire extinguisher
- CH_3CCl_3: is used in cleaning of most ink.
- $CHCl=CCl_2$: is used in dry cleaning and in caffeine extraction

Medicine:

- $CHCl_3$ (chloroform): is used in anesthesia

Agriculture:

- DDT: Dichloro diphenyl trichloroethane is used as insecticides DDT, colorless chemical pesticide, dichlorodiphenyltrichloroethane, used to eradicate disease-carrying and crop-eating insects. It was first isolated in Germany in 1874, but not until 1939 did the Swiss Nobel Prize-winning chemist Paul Müller recognize it as a potent nerve poison on insects. The product is banned in Rwanda. Below is the structure of DDT.



Home: Refrigeration perfumes, etc…

Halogenoalkanes which have boiling temperatures just below room temperature can easily be liquefied by a slight increase in pressure. Halogenoalkanes containing chlorine and fluorine and no hydrogen are Chlorofluorohydrocarbons. Examples are $CFCl_3$, CCl_2F_2 and $C_2Cl_2F_4$. They are usually called chlorofluorocarbons or CFCs. In addition to having low boiling temperatures, they are non-flammable, odourless, stable, non-toxic and solvents.

- **CFCs appeared to be ideal for use as fluids in refrigerators and as solvents in aerosol sprays.** They were developed in the 1920s as what appeared to be ideal replacements for liquid ammonia and liquid sulphur dioxide, which were formerly used as fluids in refrigerators and air-conditioning units. Being good solvents, they were also ideal as the solvents in aerosol sprays. Aerosols were used to dispense insecticides, hairsprays, perfumes and deodorants, window-cleaning, polishes, waxes and laundry products. As more and more uses were found for these remarkable compounds, CFCs became big business, with hundreds of thousands of tones being produced yearly. Now they are being phased out. These stable, non-toxic compounds are dangerous!
- **Their high stability has turned out to be a problem,** during all the time that the use of CFCs was increasing, no-one thought about what would happen to the gases in the atmosphere. Because of their lack of reactivity and insolubility in water, there is no natural process for removing CFCs. In fact they drift up into the stratosphere where

ultraviolet light causes photolysis, i.e. a reaction cause by light. The chlorine radicals formed in photolysis take part in a chain reaction which converts ozone into oxygen.

(a) $CFC \xrightarrow{UV} Cl.$

(b) $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$

(c) $ClO\bullet + O \rightarrow Cl\bullet + O_2$

(d) $ClO\bullet + O_3 \rightarrow ClO_2 + O_2$

As you can notice, the chain of reaction above results in the decomposition of ozone into ordinary oxygen, which does have the capacity to absorb, and stop dangerous UV from reaching the Earth. This can be avoided if and only if human activities send no CFCs in the atmosphere.

And what can be done?

- **Reduce the thickness of the ozone layer,** reactions (a) to (c) form a chain. This is why one chlorine radical from one CFC molecule can destroy thousands of ozone molecules.
- **Replacements for CFCs have been found,** because of concern over the decrease in the ozone layer, many nations have agreed to cut down the use of CFCs. Alternative compounds are already in production. Hydrohalocarbons contain at least one hydrogen atom per molecule. The C-H bond can be attacked by HO• radicals in the lower atmosphere and the compounds do not reach the upper atmosphere. Hydrohalocarbons include
    - Hydrochlorofluorocarbons, HCFCs, e.g. $CHCl_2CF_3$, used in blowing plastics foam and $CHClF_2$, used in air-conditioners
    - Hydrofluorocarbons, HFCs, e.g. CH_2FCF_3, used in air-conditioners and refrigerators. HCFs cause no damage to the ozone layer, although they are greenhouse gases.

APPLICATION ACTIVITY 10.5

Explain in detail why fluoroalkanes find special uses?

SKILLS LAB 10

Because of concern over the decrease in the ozone layer, many nations have agreed to cut down the use of CFCs. Make a research and synthesise the chemicals to replace these CFCs.

END UNIT ASSESSMENT 10

1. Which of the following is NOT a halogenoalkane compound:

   a. 3-iodohexane

   b. Pentane

   c. 2-chloro-3-methylpentane

   d. 2-bromopentane

2. Choose from a list of words and fill in the missing words in the text below“**halogenoalkanes, iodine, alkyl halide, haloarene, thyroxine”**

   …………………………..compounds are compounds in which the halogen atoms like chlorine, bromine, ………… or fluorine are attached to a hydrocarbon chain or an aromatic ring. When the halogen atom is attached to a hydrocarbon chain the compound is called an …………………… or ………………………..

3. Answer by **true** or **false**

   a. Chloroform is employed as a solvent or as a paint remover.

   b. Iodoform was used earlier as an antiseptic.

   c. Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are gases at room temperature.

   d. DDT: Dichloro diphenyl trichloroethane is used as anaesthesia.

   e. Halogenoalkanes therefore, although they dissolve more than alkanes, are only slightly soluble in water.

   f. Halogenoalkanes undergo nucleophilic substitution reactions in which the halogen atom is replaced by a nucleophile.

4. Name the following halides according to IUPAC system and classify them as primary, secondary or tertiary halogenoalkanes

   a) $(CH_3)_2CHCHClCH_3$

   b) $CH_3CH_2C(CH_3)_2CH_2I$

   c) $(CH_3)_3CCH_2Br$

   d) $CH_3CH(CH_3)CHBrCH_3$

5. Write the structures of the following organic halogenoalkanes.

   a) 2-chloro-3-methylpentane

   b) 2-chloro-2-methylpropane

   c) 2,3-dichlorobutane

6. Write the structure of the major organic product in each of the following reactions:

   a) $(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}$

   b) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{water}}$

   c) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

   d) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}}$

UNIT 11

ALCOHOLS AND ETHERS

Key unit competence: Compare the physical and chemical properties of alcohols and ethers and explain their preparation methods, reactivity and uses

INTRODUCTORY ACTIVITY

Observe each image carefully then make a research and answer the questions below.

Sorghum

Banana

Sorghum beer (Ikigage)

Banana wine (Urwagwa)

1. Describe how sorghum beer is prepared.

2. Describe how banana wine is prepared.

3. In both banana wine and sorghum beer there is an alcohol; suggest the name and chemical formula of this alcohol.

4. The alcohol prepared from banana or sorghum can be used to prepare other organic compounds; using chemical equations show how these other compounds can be produced from alcohol.

5. Outline other uses of alcohols.

11.1. Definition, homologous series, nomenclature, isomerism and classification of alcohols.

ACTIVITY 11.1

Observe the structural formula of the following organic compounds, and answer the questions below.

A: CH_3CH_3 B: $CH_3CH{=}CH_2$ C: CH_3CH_2Cl D: CH_3CH_2OH

E: $CH_3CH_2CH_2OH$

1) Write the IUPAC names of the above compounds.

2) Identify the ones which are in the same homologous series and suggest the name of this homologous series.

Alcohols are organic compounds that are derivatives of hydrocarbons where one or more hydrogen atoms is or are replaced by hydroxyl (-OH) group. They are represented by the general formula: $\mathbf{C_nH_{2n+1}OH}$ or **ROH** where R is a radical: alkyl group made by a chain of carbon atoms.

Alcohols are called monohydric if only one hydroxyl group is present (eg: CH_3CH_2-OH) Dihydric alcohols are those with two hydroxyl group (diol: vicinal and gem), trihydric (triols) and polyhydric are those with many – C-OH groups. The functional group attached is –OH group to any atom of carbon.

According to IUPAC system, alcohols are named by replacing the final "**e**" of the parent hydrocarbon with "**ol**", then specify the position of **-OH** group before ending by **ol**.

Examples:

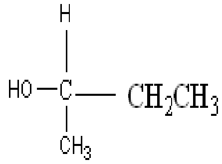
CH_3OH: Methanol

CH_3-CH_2-OH: ethanol

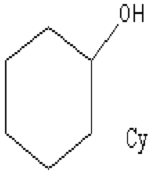
CH_3-CH_2-CH_2-OH: Propan-1-ol

CH_3-CHOH-CH_3: Propan-2-ol

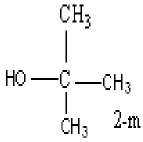
CH_3-CH_2-CH_2-CH_2OH: Butan-1-ol



butan-2-ol



Cyclohexanol



2-methyl propan-2-ol or tertiobutanol

When there are more than one hydroxyl group present, prefixes, **di, tri, tetra**, are used.

Examples:

$HOCH_2$-CH_2OH: Ethane-1, 2-diol (ethylene glycol)

$HOCH_2$-CHOH-CH_2OH: propane-1,2,3-triol (glycerin or glycerol)

Alcohols are classified as:

Primary alcohols: These have only one alkyl group attached to the carbon carrying the –OH.

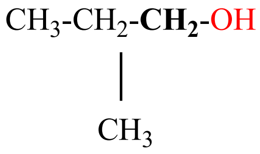
Examples:

CH_3-$\mathbf{CH_2}$-OH

ethanol

CH_3-CH_2-$\mathbf{CH_2}$-OH

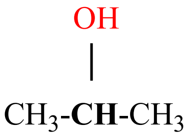
propan- 1-ol



$$\underset{\displaystyle CH_3}{CH_3\text{-}\underset{|}{CH_2}}\text{-}\mathbf{CH_2}\text{-}OH$$

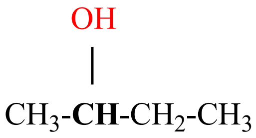
2-methylopropan-1-ol

Secondary alcohols: They are alcohols in which the OH group is attached to a carbon atom bonded to two other carbon atoms.



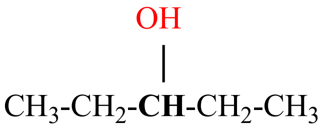
$$CH_3\text{-}\overset{\overset{\displaystyle OH}{|}}{\mathbf{CH}}\text{-}CH_3$$

propan-2-ol



$$CH_3\text{-}\overset{\overset{\displaystyle OH}{|}}{\mathbf{CH}}\text{-}CH_2\text{-}CH_3$$

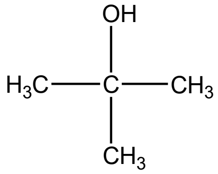
butan-2-ol



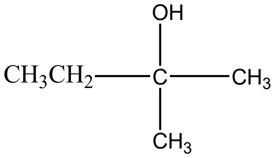
$$CH_3\text{-}CH_2\text{-}\overset{\overset{\displaystyle OH}{|}}{\mathbf{CH}}\text{-}CH_2\text{-}CH_3$$

pentan-3-ol

Tertiary alcohols: they are alcohols in which the OH group is attached to a carbon atom bonded to three other carbon atoms.



2-methylpropan-2-ol



2-methylbutan-2-ol

Alcohols containing at least three carbon atoms exhibit different types of isomerism:

- **Chain isomerism**:

  This is due to the difference in the size of the chain.

  Example: Butan-1-ol and 2-methyl propan-1-ol

- **Position isomerism**:

  This is due to different positions taken by the –OH in the same carbon chain.

  Examples:

  C_3H_8O: there exist propan-1-ol and propan-2-ol

  $C_4H_{10}O$ has 2 pairs of position isomers such as butan-1-ol, butan-2-ol and

  2-methyl propan-1-ol, 2-methyl propan-2-ol.

- **Functional isomers:** Except methanol which has one carbon, other alcohols are isomers with ethers another chemical function of general formula R-O-R' where R and R' are alkyl groups or aryl groups but not hydrogen.

Examples: C_2H_6O has 2 functional isomers:

CH_3-CH_2-OH (alcohol: ethanol) and CH_3-O-CH_3 (ether: methoxymethane or dimethyl ether).

C_3H_8O represents $CH_3CH_2CH_2OH$ or CH_3 -CHOH-CH_3 (both alcohols) and one ether: CH_3-CH_2-O-CH_3 (methoxyethane).

APPLICATION ACTIVITY 11.1

Write six condensed structural formulas of alcohols with the molecular formula C5H120 and suggest their names and their classes.

11.2. Physical properties of alcohols

ACTIVITY 11.2

Analyze the following data and answer the questions below:

Name	Boiling Point/K	Name	Boiling point/K
Methanol	337	Methane	111.3
Ethanol	351	Ethane	184.4
Propan-1-ol	371	Propane	231
Butan-1-ol	396	Butane	272.5

1) Explain the trends in the boiling point of the molecules given in the table above.

2) Compare and explain the differences in the boiling point of alkanes and alcohols.

a) Boiling points

The chart shows the boiling points of some simple primary alcohols and alkanes with up to 4 carbon atoms.

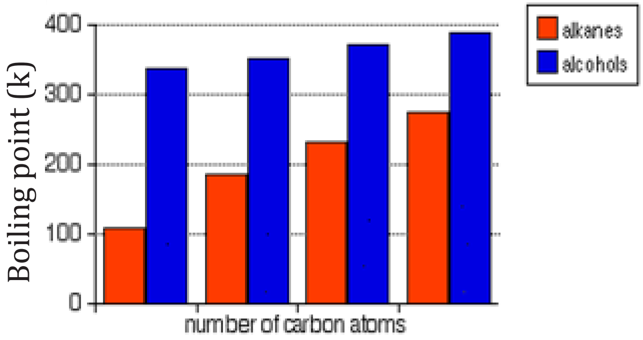


Figure 11.1: Boiling points of alcohols and alkanes

The boiling point of an alcohol is always much higher than that of the alkane with the same number of carbon atoms.

- The boiling points of the alcohols increase as the number of carbon atoms increases.
- The boiling point of alcohols with branches is lower than that of

unbranched alcohols with the same number of carbon atoms. This is because increased branching gives molecules a nearly spherical shape and the surface area of contact between molecules in the liquid decreases. This results in weakened intermolecular forces and therefore in lower boiling points.

- Tertiary alcohols exhibit the lowest boiling point than secondary and primary alcohols:

Primary alcohol > Secondary alcohol > Tertiary alcohol

Highest boiling point ↑ (Primary alcohol)

Lowest boiling point ↑ (Tertiary alcohol)

The patterns in boiling point reflect the patterns in intermolecular attractions. In the case of alcohols, there are hydrogen bonds set up between the slightly positive hydrogen atoms and lone pairs on oxygen in other molecules.

b) Solubility of alcohols in water

Alcohols are soluble in water. This is due to the hydroxyl group in the alcohol which is able to form hydrogen bonds with water molecules. Alcohols with a smaller hydrocarbon chain are very soluble. As the length of the hydrocarbon chain increases, the solubility in water decreases.

With four or more carbon atoms in the hydrocarbon chain, the decrease in solubility becomes visible as the mixture forms two immiscible layers of liquid. With increasing number of carbon atoms, the effect of the hydrocarbon group disrupts the mixed hydrogen bond between water and the alcohol molecules.

c) Volatility

Alcohols are volatile and the volatility decreases as the molecular mass increases. Compared to alkyl halides, alcohols are less volatile. Polyalcohols are viscous or solids. **Example:** propane-1, 2, 3-triol (glycerine). This is due to stronger intermolecular forces than those of monoalcohols.

APPLICATION ACTIVITY 11.2

1. Ethanol with a molecular mass of 46 and butane with a molecular mass of 58 have the boiling point of 78^{0}C and -0.5^{0}C, respectively. Explain these differences.

2. Explain why alcohols dissolve easily in water than alkanes

11.3. Preparations of alcohols

ACTIVITY 11.3

Complete the following chemical equations.

a) $CH_3CH_2CH_2CH_2Cl + KOH \xrightarrow{\text{water}}$

b) $CH_2{=}CH_2 + H_2O \xrightarrow{H_2SO_4}$

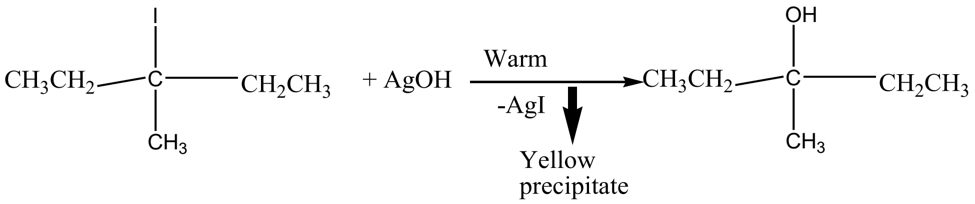
Alcohols are prepared with different methods:

a) From alkyl halides

Alkyl halides when refluxed with aqueous alkali (NaOH or KOH) or moist silver hydroxide (AgOH) produce alcohols. The hydrolysis occurs by a nucleophile substitution reaction.

$$R-X+KOH \xrightarrow{warm} R-OH+KX$$

$$CH_3CH_2CH_2Cl+KOH \rightarrow CH_3CH_2CH_2OH+KCl$$



b) From alkenes

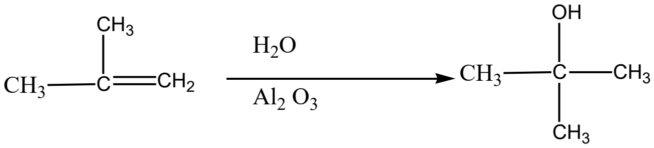
Alkenes react with water in the presence of concentrated sulphuric acid to yields alcohols.

$$R\text{-}CH{=}CH_2 \xrightarrow[H_2SO_4]{H_2O} R\text{-}CHOH\text{-}CH_3$$

$$CH_3CH{=}CH_2 \xrightarrow[H_2SO_4]{H_2O} CH_3CHOH\text{-}CH_3$$

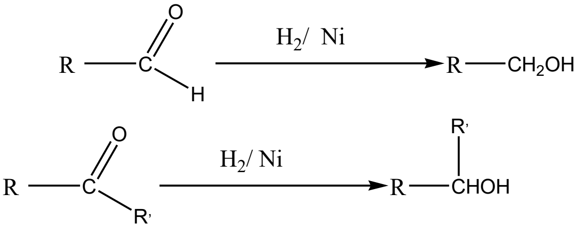
Notice: Alkenes in the presence of Aluminium oxide reacts with water to form alcohols in vapour phase then condense to give liquid alcohols.

Example:



c) From carbonyl compounds

When aldehydes and ketones are reduced by hydrogen in the presence of a suitable catalyst like Pt, Ni or Pd, they form primary and secondary alcohols respectively.



Examples:

$$CH_3CH_2CHO + H_2 \xrightarrow{Ni} CH_3CH_2CH_2OH$$

$$CH_3COCH_2CH_3 + H_2 \xrightarrow{Ni\ /\ Heat} CH_3CHOHCH_2CH_3$$

Note: Lithium tetrahydridoaluminate ($LiAlH_4$) can also be used as a reducing agent.

Examples:

$$CH_3CH_2CH_2CHO \xrightarrow[Ether]{LiAlH_4} CH_3CH_2CH_2CH_2OH$$

$$CH_3\text{-}CO\text{-}CH_3 \xrightarrow[Ether]{LiAlH_4} CH_3\text{-}CHOH\text{-}CH_3$$

Lithium tetrahydridoaluminate is not stronger enough as reducing agent to reduce a double bond unlike H_2 which can reduce both the double bond and the carbonyl group.

$$CH_3CH_2CH_2CHO \xrightarrow[\text{Ether}]{LiAlH_4} CH_3CH_2CH_2CH_2OH$$

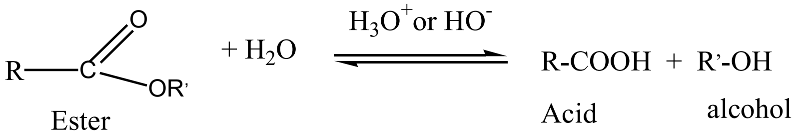
$$CH_3\text{-}CO\text{-}CH_3 \xrightarrow[\text{Ether}]{LiAlH_4} CH_3\text{-}CHOH\text{-}CH_3$$

$$CH_3CH{=}CH\text{-}CHO \xrightarrow{LiAlH_{4}/\text{Ether}} CH_3CH{=}CHCH_2OH$$

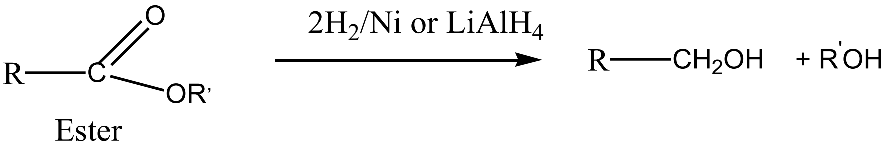
$$CH_3CH{=}CH\text{-}CHO \xrightarrow{H_2/Ni/\text{heat}} CH_3CH_2CH_2CH_2OH$$

d) From esters

Esters on hydrolysis in the presence of mineral acid or alkalis produce alcohols and carboxylic acids.



$$CH_3COOCH_2CH_3 + H_2O \underset{}{\overset{H_3O^+}{\rightleftharpoons}} CH_3COOH + CH_3CH_2OH$$

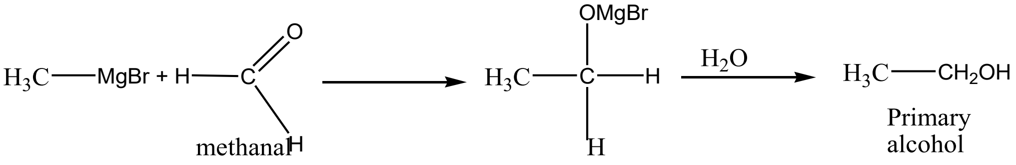


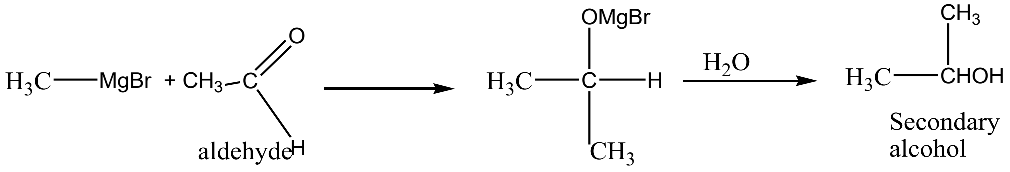
Note: In spite of $LiAlH_4$ we can also use $NaBH_4$, KBH_4 by H^- attack specifically on C=O group followed by hydrolysis.

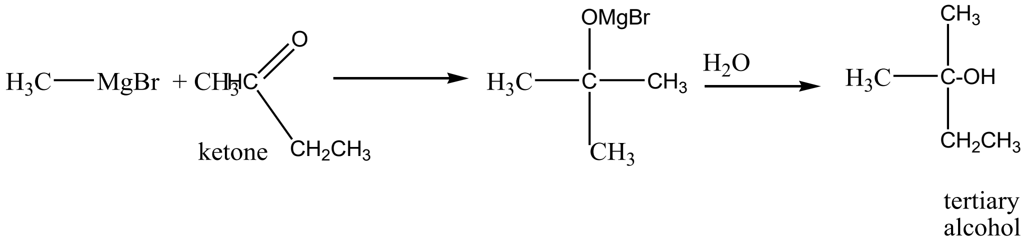
e) From Grignard reagents

The reaction between carbonyl compound and Grignard reagent (alkyl magnesium halides) produces an alcohol with more carbon atoms. The reaction is a nucleophilic addition on a carbonyl compound.

Examples:







f) From primary amine to give primary alcohol

Primary amines react with nitrous acid to produce primary alcohols.

$$R-NH_2 \xrightarrow{NaNO_2/HCl} R\text{-}OH + N_2 + H_2O + NaCl$$

Example:

$$CH_3CH_2CH_2NH_2 \xrightarrow{NaNO_2\ /\ HCl} CH_3CH_2CH_2OH + N_2 + H_2O + NaCl$$

APPLICATION ACTIVITY 11.3

1. Using chemical equations, explain how butan-2-ol could be prepared:
   a) from an alkene
   b) from a halogenoalkane
2. Complete the following reactions:
   a) $CH_3CH_2CH_2CH{=}CHCH_3 + H_2O \xrightarrow{H_2SO_4}$
   b) $(CH_3)_2C{=}CHCH_3 + HCl \longrightarrow A \xrightarrow{NaOH_{(aq)}} B$

11.4. Local preparation of ethanol by fermentation

ACTIVITY 11.4

Process of alcoholic fermentation

Analyse the pictures below and answer the following questions:

(1)

(2)

(3)

(4)

(5) **(6)**

1) Describe the process followed to produce alcohol using the above images.
2) What are the raw materials used in the process?
3) What is the main component of the final product?
4) Give the name of the process illustrated by the above pictures.
5) Suggest another process that can be used to yield the above alcohol.

This method is mainly used to prepare ethanol industrially. Ethanol is prepared from starch (e.g. maize, cassava, millet, sorghum) and sugar (e.g. banana juice, molasses) by fermentation process.

Fermentation can be defined as any of many anaerobic biochemical reactions in which enzymes produced by microorganisms catalyse the conversion of one substance into another.

Alcoholic fermentation is the process in which enzymes act on carbohydrates to give simpler compounds like ethanol (alcohol) and carbon dioxide (CO_2).

a) From starch: malt obtained either from maize grain, millet, or cassava contains an enzyme called diastase which catalyzes the hydrolysis of starch to maltose.

$$2(C_6H_{10}O_5)n + nH_2O \xrightarrow{\text{diastase}} nC_{12}H_{22}O_{11} \text{ (maltose)}$$

At room temperature, yeast is added and one of its enzymes called **maltase** catalyzes the hydrolysis of maltose to simple sugar called glucose.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{maltase}} \underset{\text{glucose}}{2\,C_6H_{12}O_6}$$

Finally another enzyme of yeast called **zymase** catalyzes the decomposition of glucose to ethanol.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2\ CH_3CH_2OH \quad + 2CO_2$$

b)From sugar

Molasses containing sugars are mixed with water and yeast and then allowed to ferment for several days after which ethanol is obtained during fermentation process.

One enzyme of the yeast called **sucrase** catalyzes the hydrolysis of sucrose present in the molasses to glucose and fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Sucrase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Thus, another enzyme of yeast called zymase catalyzes the decomposition of glucose to ethanol.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2\ CH_3CH_2OH \quad + 2CO_2$$

The ethanol obtained by fermentation process is only about 11%. This is made concentrated by distillation which converts it to about 95% ethanol.

This, on further distillation, yields a constant boiling mixture whose composition does not change (an azeotropic mixture). Therefore, 100% ethanol is obtained by either:

(i) Adding quick lime which removes water

(ii) Distilling with of benzene as a third component

Note: Methanol can be prepared industrially by the reaction of carbon monoxide and hydrogen at 300 ˚C and a pressure of 200 atmospheres.

$$CO + 2\ H_2 \xrightarrow{300\ ^0C \text{ under } 200 \text{ atm}} CH_3OH$$

Table 11.1: A comparison of fermentation with the direct hydration of ethylene

	Fermentation	Hydration of ethene

Type of process	A batch process. Everything is put into a container and then left until fermentation is complete. That batch is then cleared out and a new reaction set up. This is inefficient.	A continuous flow process. A stream of reactants is passed continuously over a catalyst. This is a more efficient way of doing things.
Rate of reaction	Very slow.	Very rapid.
Reaction conditions	Uses gentle temperatures and atmospheric pressure.	Uses high temperatures and pressures, needing lots of energy input.
Use of resources	Uses renewable resources based on plant material.	Uses non-renewable(finite) resources

APPLICATION ACTIVITY 11.4

Briefly, describe the preparation of ethanol by alcoholic fermentation.

11.5. Chemical properties of alcohols

ACTIVITY 11.5

To investigate the oxidation reaction of an alcohol.

Requirements: methanol, ethanol, 2M sulphuric acid, potassium dichromate solution, test tubes, burner, droppers, propan-2-ol and 2-methylpropan-2-ol.

Procedure:

- Put 5 drops of methanol in test tube
- Add 10 drops of dilute sulphuric acid followed by 5 drops of potassium dichromate solution.
- Warm the mixture gently
- Repeat the experiment with ethanol, propan-2-ol and 2-methylpropan-2-ol.

Questions:

1) What happens to the colour of the solution?

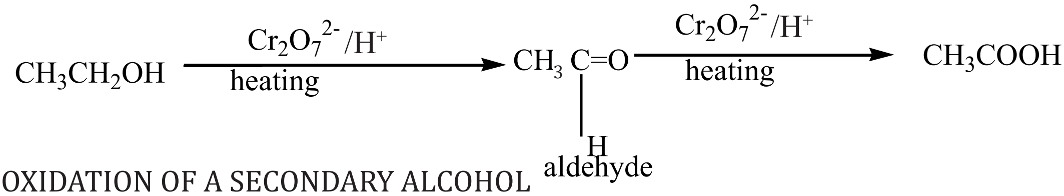
2) Explain the observations.

3) Write the equations for the reactions that take place.

(a)Oxidation

Primary and secondary alcohols are oxidized to aldehydes and ketones respectively by use of acidified $K_2Cr_2O_7$, CrO_3, acidified $KMnO_4$, nitric acid once concentrated.

Examples: OXIDATION OF A PRIMARY ALCOHOL



$$CH_3CH_2OH \xrightarrow[\text{heating}]{Cr_2O_7^{2-}/H^+} \underset{\text{aldehyde}}{\underset{H}{\underset{|}{CH_3C}}}{=}O \xrightarrow[\text{heating}]{Cr_2O_7^{2-}/H^+} CH_3COOH$$

OXIDATION OF A SECONDARY ALCOHOL

$$CH_3CHOHCH_3 \xrightarrow[\text{heating}]{Cr_2O_7^{2-}/H^+} \underset{\text{ketone}}{CH_3COCH_3}$$

Aldehydes formed by oxidation of primary alcohols tend to undergo further oxidation to carboxylic acids.

Ketones formed by oxidation of secondary alcohols are not further oxidised, unless if the oxidising agent is hot and concentrated in which case bonds around the –CO- group are broken and two smaller carboxylic acids are formed.

Example:

$$CH_3CH_2CH_2COCH_2CH_3 \xrightarrow{\text{conc. } KMnO_4/\text{Hot}} CH_3CH_2CH_2COOH + CH_3COOH$$

Tertiary alcohols resist oxidation because they have no hydrogen atom attached on the functional carbon atom.

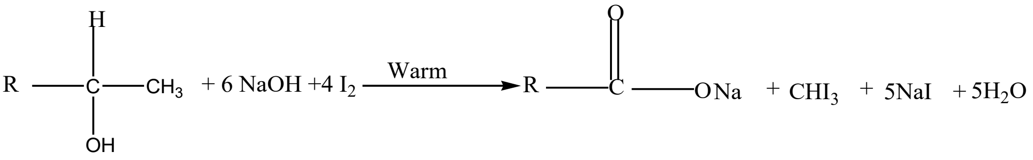
These reactions help to distinguish between primary, secondary and tertiary alcohols because primary and secondary alcohols decolourise the purple solution of $KMnO_4$.

An acidified potassium dichromate solution is turned from orange to green when it reacts with primary and secondary alcohols.

Oxidation also occurs when the alcohol is in gaseous phase by use of silver or copper catalyst under 500 ˚C and 300 ˚C respectively. In the first case, the vapour of the alcohol is passed with air (oxygen) over heated silver.

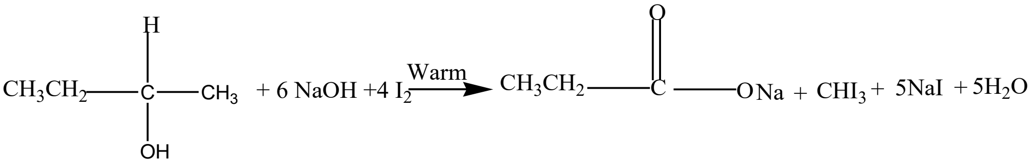
Secondary alcohols having the following structure R-CHOH-CH_3 only undergo oxidation, on treatment with iodine solution in the presence of sodium hydroxide to give a yellow precipitate of tri-iodomethane.

Note: This is a reaction which is characteristic of methyl ketones, CH_3-CO-R′; but iodine here acting as an oxidizing agent first oxidizes the CH_3-CHOH-R′to CH_3-CO-R′; then the methyl ketone formed then gives the yellow precipitate of CHI_3 (*Iodoform*). From the reaction involved we have the **Iodoform test**.



$$R\text{-}CH(OH)\text{-}CH_3 + 6\,NaOH + 4\,I_2 \xrightarrow{\text{Warm}} R\text{-}C(=O)\text{-}ONa + CHI_3 + 5NaI + 5H_2O$$

Example:

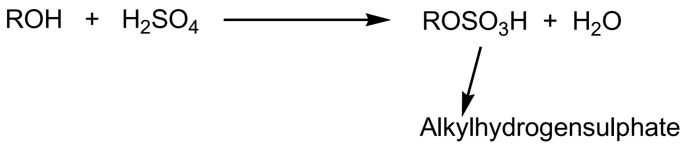


$$CH_3CH_2\text{-}CH(OH)\text{-}CH_3 + 6\,NaOH + 4\,I_2 \xrightarrow{\text{Warm}} CH_3CH_2\text{-}C(=O)\text{-}ONa + CHI_3 + 5NaI + 5H_2O$$

(b)Reaction with sulphuric acid

Alcohols react with concentrated sulphuric acid to give different products depending on the nature of the alcohol and conditions of reactions.

i) At about 0°C alcohols react with sulphuric acid to produce alkyl hydrogen sulphates.



$$ROH + H_2SO_4 \longrightarrow ROSO_3H + H_2O$$

This reaction is a substitution reaction where the OH group has been replaced by HSO_4^-

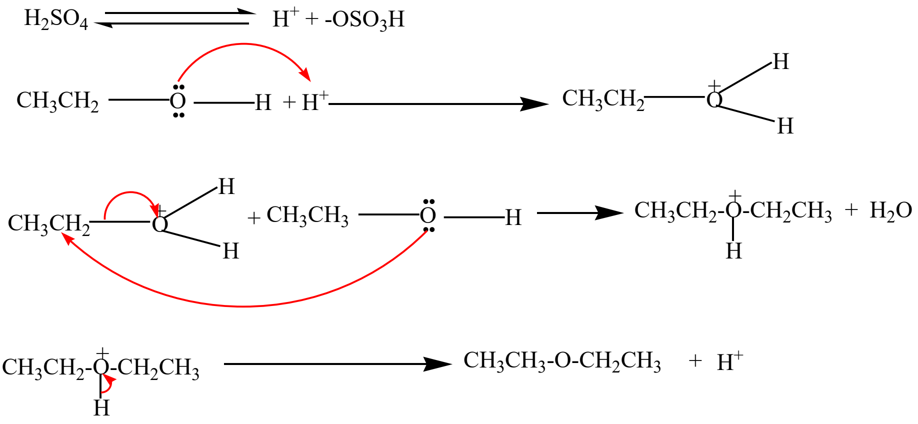
ii) At about 140°C in the presence of excess primary alcohol and concentrated sulphuric acid, ether is formed.

$$2R\text{-}CH_2OH \xrightarrow{H_2SO_4/140^\circ C} R\text{-}CH_2\text{-}O\text{-}CH_2\text{-}R + H_2O$$

Example:

$$2CH_3CH_2OH \xrightarrow{H_2SO_4\ /\ 140^oC} CH_3CH_2\text{-}O\text{-}CH_2CH_3 + H_2O$$

Mechanism:



$$2CH_3CH_2OH \xrightarrow{H_2SO_4\ /\ 140^oC} CH_3CH_2\text{-}O\text{-}CH_2CH_3 + H_2O$$

This reaction is an intermolecular dehydration.

(c) Elimination reaction

Alcohols are dehydrated by heating with concentrated sulphuric acid or phosphoric acid to alkenes. The ease of dehydration is in the order tertiary > secondary > primary. This reaction is the intramolecular dehydration of an alcohol.

Example

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow[170^0C]{H_2SO_4} CH_3\text{-}CH{=}CH_2 + H_2O$$

Notice: For primary alcohols any temperature between 170^0C-180^0C is sufficient and the acid should be sufficiently concentrated.

An alcohol may also be hydrated in the pressure of phosphoric acid at 160^0c or in the aluminum oxide at 300^0c.

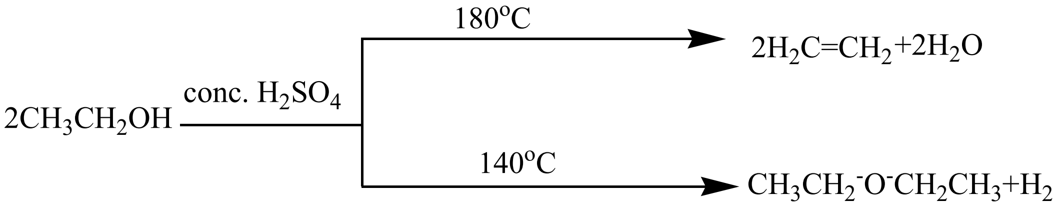
Example:

$$CH_3CH_2CHOHCH_3 \xrightarrow[160^oC]{H_3PO_4} CH_3CH{=}CHCH_3$$

$$CH_3CH_2OH_{(g)} \xrightarrow[300^0c]{Al_2O_3} H_2C = CH_2 + H_2O$$

This dehydration respects Zaïtsev's elimination law (see alkenes).

Elimination always competes with nucleophilic substitution reaction. Substitution leading to formation of ether is favoured by use of excess primary alcohols while higher temperatures favour elimination. Therefore, dehydration of ethanol may produce both alkenes by elimination and diethylether by substitution reaction. The relative proportion of two products depends on the condition of the reaction.



(d)Esterification

Alcohols react with organic acids in the presence of mineral acids such as sulphuric acid (catalyst) with elimination of water under 100°C to produce an ester that is given off with a perfume smell. This reaction is called "**esterification**".

$$R'OH + RCOOH \underset{reflux}{\overset{H_2SO_4}{\rightleftharpoons}} R'OOCR + H_2O$$

Example:

$$CH_3COOH+CH_3CH_2OH \overset{Conc\,H_2SO_4}{\rightleftharpoons} CH_3COOCH_2CH_3+H_2O$$

(e)Reaction with strong electropositive metals and metal hydroxides

Electropositive metals like Na, K, reacts with alcohols forming alkoxide with evolution of hydrogen gas.

$$2\ R\text{-}OH + 2\ Na \longrightarrow \underset{\text{Alcoxide}}{2\ R\text{-}O\text{-}Na} + H_{2(g)}$$

Example:

$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2ONa + H_2$

Note: Alcohols are not enough acidic to react with metal hydroxides such as sodium hydroxide or potassium hydroxide.

$$R\text{-}OH + NaOH \longrightarrow \text{No reaction}$$

(f)Action of hydrohalic acids (HX)

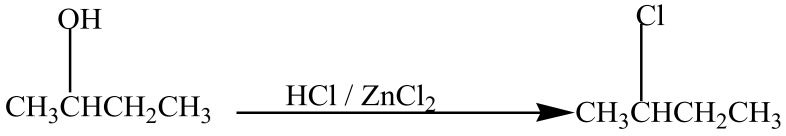
Alcohols react with hydrohalic acids to give alkyl halides.

Examples:

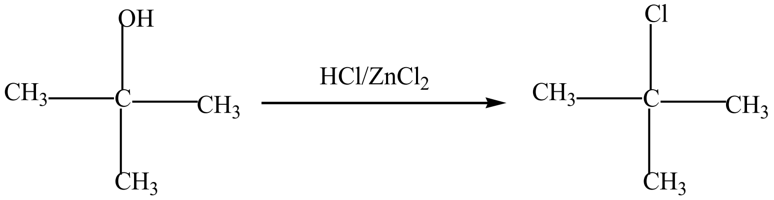
$$CH_3CH_2CH_2OH + HBr \rightarrow CH_3CH_2CH_2Br + H_2O$$

$$CH_3CH_2CH_2OH + HI \rightarrow CH_3CH_2CH_2I + H_2O$$

$$CH_3CH_2CH_2CH_2OH + HCl \xrightarrow{HCl\ /\ ZnCl_2} CH_3CH_2CH_2CH_2Cl + H_2O$$



$$CH_3\overset{OH}{C}HCH_2CH_3 \xrightarrow{HCl\ /\ ZnCl_2} CH_3\overset{Cl}{C}HCH_2CH_3$$



$$CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_3 \xrightarrow{HCl/ZnCl_2} CH_3-\overset{Cl}{\underset{CH_3}{C}}-CH_3$$

The reaction with concentrated hydrochloric acid is catalyzed by anhydrous zinc chloride. This reaction is called **LUCAS test** and is used to distinguish between simple primary, secondary or tertiary alcohols. In this reaction, the alcohol is shaken with a solution of zinc chloride in concentrated hydrochloric acid.

Observations: Immediate cloudiness indicates the presence of a tertiary alcohol. If the solution becomes cloudy within 5 minutes then the alcohol is a secondary one. Primary alcohol would show no cloudiness at room temperature since the reaction is very slow.

For example all alcohols which are isomers of $C_4H_{10}O$ can be distinguished by the Lucas test.

Alcohols are also transformed into halogenoalkanes using phosphorus halides and thionyl chloride

Examples:

$$3CH_3CH_2CH_2OH + PCl_3 \rightarrow 3CH_3CH_2CH_2Cl + H_3PO_3$$

$3CH_3CH_2CH_2OH + PBr_3 \rightarrow 3CH_3CH_2CH_2Brl + H_3PO_3$

$3CH_3CH_2CH_2OH + PI_3 \rightarrow 3CH_3CH_2CH_2I + H_3PO_3$

$CH_3CH_2CH_2OH + PCl_5 \rightarrow CH_3CH_2CH_2Cl + POCl_3 + HCl$

$CH_3CH_2CH_2OH + SOCl_2 \rightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$

APPLICATION ACTIVITY 11.5

1. Complete the following chemical reactions and name the products obtained:

   a) Propan-2-ol + Na →

   b) Propan-2-ol + HBr →

   c) methanol + CH_3CH_2-COOH →

   d) butan-1-ol + PCl_5 →

   e) butan-2-ol + $SOCl_2$ →

   f) 2-methylpentan-3-ol + PBr_3 →

11.6. Nomenclature, physical properties and isomers of ethers

ACTIVITY 11.6

1) Write structural formulae of all isomers with the formula $C_4H_{10}O$. Which of them are functional isomers?

2) Suggest the names of the above isomers and indicate the ones which are soluble in water.

Ethers are organic compounds in which two hydrocarbon groups are connected to single oxygen. The general formula of ether is **R-O-R'**. Based on the general structure of ether, they are classified as symmetrical, unsymmetrical and epoxide.

- **For symmetrical ethers, R and R' are identical.**

Examples:

$CH_3\text{-}O\text{-}CH_3$

$CH_3\text{-}CH_2\text{-}O\text{-}CH_2CH_3$

- **For unsymmetrical ethers, R and R′ are different (R≠R′);**

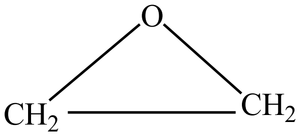
Examples:

$CH_3\text{-}O\text{-}CH_2\text{-}CH_3$

$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$

- **Cyclic ethers are called epoxides**

Examples:



a) Nomenclature

Ethers can be named by naming each of the two carbon groups as a separate word followed by a space and the word ether. The -OR group can also be named as a substituent using the group name, **alkoxy.**

Examples:

$CH_3\text{-}CH_2\text{-}O\text{-}CH_3$: ethyl methyl ether or methoxyethane.

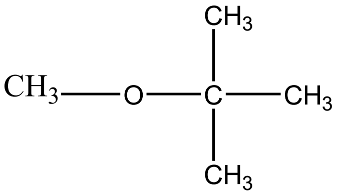
$CH_3\text{-}O\text{-}CH_3$: dimethyl ether or methoxy methane

The smaller, shorter alkyl group becomes the alkoxy substituent. The larger, longer alkyl group side becomes the alkane base name. Each alkyl group on each side of the oxygen is numbered separately. The numbering priority is given to the carbon closest to the oxygen. The alkoxy side (shorter side) has an "-oxy" ending with its corresponding alkyl group.

Examples:

$CH_3CH_2CH_2CH_2CH_2\text{-}O\text{-}CH_2CH_2CH_3$: 1-propoxypentane

$CH_3CH_2OCH_2CH_3$: ethoxyethane or diethyl ether



$$CH_3-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$

2-methoxy-2-methylpropane

b) Isomerism in ethers

Ethers are functional isomers of alcohols. Functional isomerism occurs when substances have the same molecular formula but different functional groups. For example: ethanol and methoxymethane are functional group isomers with molecular formula C_2H_6O.

CH_3CH_2OH Ethanol

CH_3OCH_3 Methoxymethane

c) Physical properties

1) Ethers are sparingly soluble in water but are soluble in organic solvents.

2) The polar nature of the C-O bond (due to the electronegativity difference of the atoms) results in intermolecular dipole-dipole interactions.

3) An ether cannot form hydrogen bonds with other ether molecules since there is no H to be donated (no -OH group).

4) Their melting and boiling points increase with the increase in molecular mass because of increasing the magnitude of Van der Waal's forces with size.

5) The boiling points of ethers are much lower than those of alcohols of similar molecular mass. This is because of the intermolecular hydrogen bonding which are present in alcohols but are not possible in ethers.

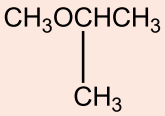
Table: 11.2: Boiling points of alcohols compared to those of their isomers

Molecule	Molecular mass	Boiling points °C
CH_3-O-CH_3	46	-24.9
CH_3-CH_2-OH	46	78
CH_3-CH_2-O-CH_2-CH_3	74	35
CH_3-CH_2-CH_2-CH_2OH	74	117.7

APPLICATION ACTIVITY 11.6

1. Give the IUPAC name for each of the following compounds:

   a) $CH_3CH_2OCH_2CH_2CH_2CH_3$

   b) 
   $CH_3O\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$

2. Given dipropyl ether and 2-ethoxybutane,

   a) Draw the condensed formulas for each,

   b) The two compounds are isomers or not? Explain your answer.

   c) State the one which has the higher boiling point and explain your answer.

11.7. Preparation reactions of ethers

ACTIVITY 11.7

Complete the following reactions and give the names of the main products.

a) $CH_3CH_2CH_2OH \xrightarrow{H_2SO_4\ /170^0C}$

b) $CH_3CH_2CH_2OH \xrightarrow{H_2SO_4\ /140^0C}$

1) Intermolecular dehydration of alcohols

This is done by heating excess primary alcohol with concentrated sulphuric acid or phosphoric acid at about 140°C.

$$2R\text{-}CH_2OH \xrightarrow{H_2SO_4\ \ /140^0C} R\text{-}CH_2\text{-}O\text{-}CH_2\text{-}R + H_2O$$

Example:

$$2CH_3CH_2OH \xrightarrow{H_2SO_4\ /140^0C} CH_3CH_2OCH_2CH_3 + H_2O$$

$$R-O-R + H_2SO_4 \xrightarrow{\text{Heat}} R-OH + RHSO_4$$

Examples :

$$CH_3-O-CH_3 + H_2SO_4 \xrightarrow{\text{Heat}} CH_3OH + CH_3HSO_4$$

$$CH_3-CH_2-O-CH_2-CH_3 + H_2SO_4 \xrightarrow{\text{heat}} CH_3-CH_2-OH + CH_3CH_2HSO_4$$

(b)Reaction with hydrohalic acids

Ethers react with cold hydrohalic acids to form alkyl halides and alcohols.

$$R\text{-}O\text{-}R' + HX \rightarrow ROH + R'X$$

Examples:

$$CH_3CH_2OCH_2CH_3 + HI \rightarrow CH_3CH_2OH + CH_3CH_2I$$

Note: For unsymmetrical ethers, the halogen is attached to the smaller alkyl group.

$$CH_3CH_2OCH_3 + HI \rightarrow CH_3CH_2OH + CH_3I$$

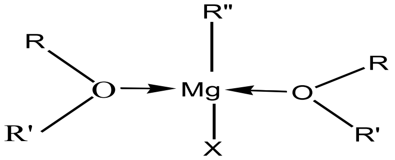
Ethers react with hot hydrohalic acids to form only alkyl halides.

$$ROR' + 2HX \xrightarrow{\text{Heat}} RX + R'X + H_2O$$

$$CH_3CH_2OCH_2CH_3 + 2HI \xrightarrow{\text{Heat}} 2CH_3CH_2I + H_2O$$

c) Reaction with the Grignard reagents

Ethers can act as the Lewis base due to the two non-bonded electron pair on oxygen to form coordinative bonds with Grignard reagent. This explains clearly why organomagnesium compounds are manipulated in ether solvent but not in water since in water, there is a reaction which generates alkanes.



d) Combustion

The combustion of ethers gives carbon dioxide and water:

$$C_nH_{2n+1}\text{-}O\text{-}C_m H_{2m+1} + \frac{3(n+m)}{2} O_2 \longrightarrow (n+m)\,CO_2 + (n+m+1)\ H_2O$$

Example: $C_2H_5OC_3H_7 + 15/2O_2 \rightarrow 5CO_2 + 6H_2O$

2) From halogenoalkanes

(a) In this method halogenoalkanes are heated together with sodium or potassium alkoxides.

$$R - OH + 2Na \rightarrow 2RO^{-}Na^{+} + H_2$$

$$R\,O^{-}Na^{+} + R' - X \rightarrow R\text{-}O\text{-}R' + NaX \text{ (Heat at about } 250^{0}C)$$

This is the **Williamson's synthesis**

(b) In the second method, the halogenoalkane is heated with dry silver oxide.

$$2R - X + Ag_2O \xrightarrow{heat} R - O - R + 2AgX$$

Example :

$$2CH_3 - Cl + Ag_2O \xrightarrow{heat} CH_3 - O - CH_3 + 2AgCl$$

$$2CH_3 - CH_2 - Br + Ag_2O \xrightarrow{heat} CH_3 - CH_2 - O - CH_2 - CH_3 + 2AgCl$$

APPLICATION ACTIVITY 11.7

Complete the following equations:

a) $CH_3CH_2O^{-}Na^{+} \quad + \quad CH_3CH_2Cl \longrightarrow$

b) $CH_3CH_2CH_2CH_2OH \xrightarrow{H_2SO_4\ /140^{0}C}$

11.8. Chemical properties of ethers

ACTIVITY 11.8

A compound with molecular formula C_3H_8O has three isomers. Write the displayed formulae of these three isomers and identify the one of them which does not react with sodium metal.

1) Reactions in which the carbon – oxygen bond is broken

a) Reaction with sulphuric acid

Ethers react with hot concentrated sulphuric acid to form alcohols according to the following reaction.

2) Oxidation reaction

Ethers react with oxygen of air to form **peroxides**

$$\text{ROR'} + O_2 \xrightarrow{\text{Many steps}} \text{ROOR'} \text{ (less volatile than the parent ether)}$$

In concentrated or solid form, these peroxides are dangerous because they are highly explosive. The presence of peroxides contaminates the ether. This type of contamination is purified by treatment with a reducing agent such as **alkaline ferrous sulphate.**

APPLICATION ACTIVITY 11.8

Complete the following equations:

a) $CH_3OCH_2CH_2CH_3 + O_2 \longrightarrow$

b) $CH_3CH_2CH_2OCH_2CH_3 + HI \xrightarrow{\text{Heat}}$

c) $CH_3CH_2CH_2OCH_2CH_2CH_3 + H_2SO_4 \xrightarrow{\text{Heat}}$

11.9. Uses of alcohols and ethers

a) Uses of alcohols

ACTIVITY 11.9(a)

In Rwanda, different types of alcoholic drinks are produced.

a) Give examples of these alcoholic drinks.

b) Give one example of an alcoholic drink which is prohibited in Rwanda and explain why it is prohibited?

Ethanol is the alcohol found in alcoholic drinks. Alcoholic fermentation converts starch, sugar into ethanol. For example grapes are used to produce wine (ripe banana produce *urwagwa*).

Drinking alcohol, i.e. the ethylic alcohol also called ethanol, is a normal social activity; but excess of it is dangerous for our health. Hence excess of alcoholic consumption must be avoided.

For non-adult youth, consumption of alcohol in any form is illegal in Rwanda and many other countries.

There are some alcoholic drinks produced in Rwanda and in the Region that are prohibited to be sold in Rwanda. However, alcohols have many other applications in daily life as indicated in the Table 11.3.

Table 11.3. Application of some alcohols

Kind	Manufacture	Uses
Methanol	• By destructive distillation of wood. • By synthesis from hydrogen and carbon monoxide under high pressure.	Solvent for fats, oils, resins, nitrocellulose. Manufacture of dyes, formaldehyde, antifreeze solutions, special fuels, plastics.
Ethanol	• By fermentation of sugar, starch, or waste sulphite liquor. • Synthesis from ethylene or acetylene. Direct hydration of ethylene.	Solvent for products such as lacquers, paints, varnishes, glues, pharmaceuticals, explosives; vinegar preparation, perfume synthesis. Source of energy as well as biofuels or gasohol. Alcoholic drink(as wine, beer). Also as 'building block' in making high-molecular-weight chemicals.
Propan-2-ol	• By hydration of propylene from cracked gases. • By-product of certain fermentation processes.	Solvent for oils, gums, alkaloids, resins. Making acetone, soap, antiseptic solutions.
Propan-1-ol	• As a coproduct of air oxidation of propane and butane mixtures.	Solvent for lacquers, resins, coatings, films, waxes. Also as brake fluid, in manufacture of propanoic acid, plasticizers.

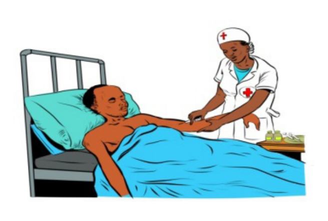
Butan-1-ol	• By fermentation of starch or sugar. • By synthesis, using ethyl alcohol or acetylene.	Solvent for nitrocellulose, ethyl cellulose, lacquer, urea-formaldehyde, urea-melamine plastics. Diluent of hydraulic fluids, extracting of drugs.
Methylpropan-1-ol	• By synthesis from carbon monoxide and hydrogen at high pressure, then distillation from products formed.	Solvent for castor-oil-base brake fluids. Substitute for n-butyl alcohol in making urea resins.
Butan-2-ol	• By hydration of but-1-ene, formed in petroleum cracking.	In making other chemicals such as butanone. Solvent in nitrocellulose lacquers. Production of brake fluids, special greases.
Methylpropan-2-ol	• By hydration of methylprop-1-ene, derived from petroleum cracking.	In perfume making. As wetting agent in detergents. Solvent for drugs and cleaning compounds.
Propane-1,2,3-triol	• From treatment of fats in soap making. Synthetically from propene.	In explosives, cellophane. Tobacco humectant.
Cyclohexanol	• By catalytic hydrogenation of phenol. By catalytic air oxidation of cyclohexane.	Intermediate in making chemicals used in nylon manufacture. Stabilizer and homogenizer of soaps, synthetic detergents. Solvent.

Ethanol produced by sugar cane fermentation has been used as alternative fuel to gasoline (petrol). It has been mixed with gasoline to produce gasohol.

b) Uses of ethers

ACTIVITY 11.9(b)

In the image below, a nurse is injecting anaesthesia to a patient.



Question: Suggest some examples of chemicals which can be used as anaesthesia.

Lower ethers are used as **anesthesia** since they produce inert local cooling when sprayed on a skin. Ethers are also used as local anesthesia for minor surgery operation.

Lower ethers are volatile liquid which on evaporation produce low temperature. They are therefore used as **refrigerants.**

Ether itself is one of the most important organic solvents for fats, oils, resins, and alkaloids.

APPLICATION ACTIVITY 11.9

Describe the uses of alcohols and ethers in daily life.

SKILLS LAB 11

Preparation of concentrated ethanol

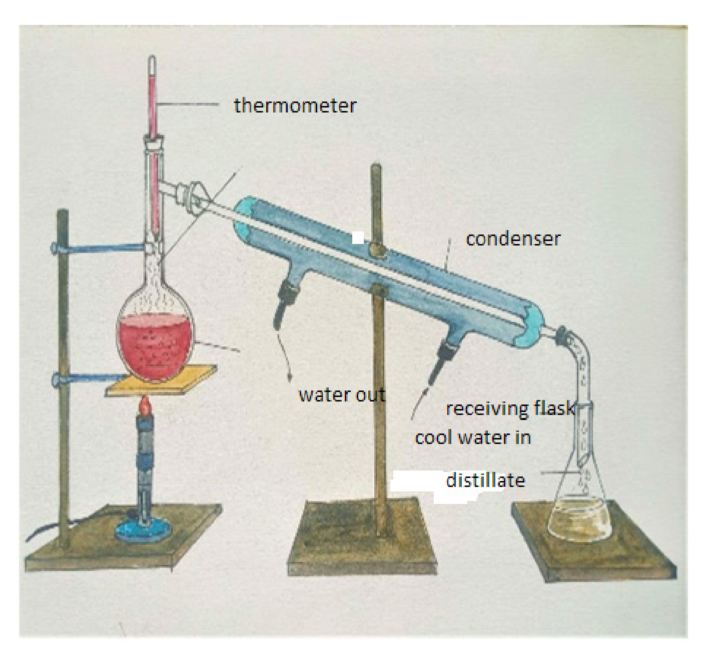
(a) Prepare banana wine or sorghum beer.

(b) Perform fractional distillation of banana wine or sorghum beer; Collect the fraction between 72^0C- 78^0C.

(c) Take $5cm^3$ of the distillate on watch glass, ignite and note the time it takes to burn completely; measure the amount of water left on watch glass and then calculate the percentage of ethanol.

(d) Outline the uses of this ethanol produced after fractional distillation.

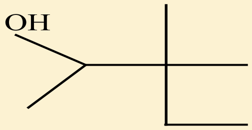
Set up for distillation



END UNIT ASSESSMENT 11

I. Multiple choice questions

1. What is the correct name of the molecule with the skeletal formula shown below?



A 1,2, 2-trimethylbutan-3-ol

B 2-ethyl-2-methylbutan-2-ol

C 3,3-dimethylpentan-2-ol

D 4-hydroxy-3,3-dimethylpentane

2. Compound X, $C_4H_8O_2$, has an unbranched carbon chain. An aqueous solution of X has an approximate pH of 3. Compound Y, C_3H_8O, is a secondary alcohol. X and Y are reacted together in the presence of a little concentrated sulphuric acid to form Z as the major organic product. What is the structural formula of Z?

   A. $(CH_3)_2CHCO_2CH_2CH_2CH_3$.

   B. $CH_3(CH_2)_2CO_2CH(CH_3)_2$

   C. $CH_3(CH_2)_2CO_2(CH_2)_2CH_3$

   D. $(CH_3)_2CHCO_2CH(CH_3)_2$

3. The ester $CH_3CH_2CH_2CO_2CH_2CH\ (CH_3)_2$ was hydrolysed under acidic conditions.

   What are the organic products of this hydrolysis?

   A butanoic acid and 2-methylpropan-1-ol

   B butanoic acid and 2-methylpropan-2-ol

   C butan-1-ol and 2-methylpropanoic acid

   D propanoic acid and 2-methylpropan-1-ol

II. Open questions

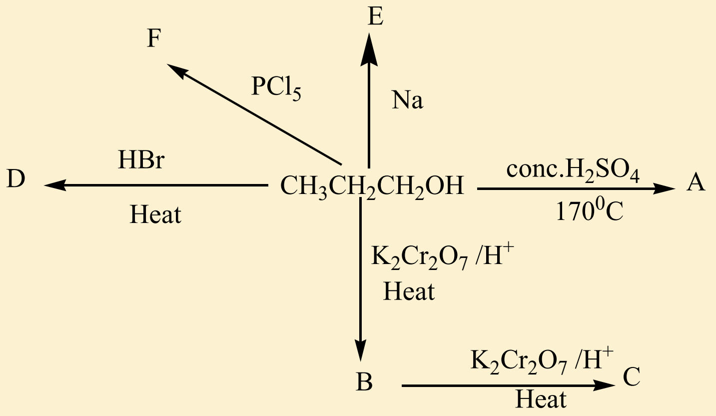
4) (a) Give the systematic names of three alcohols whose molecular formula is C_4H_9OH.

(b) One of the alcohols in (a) can be oxidized to form a ketone.

i) Give the structural formula of this alcohol.

ii) Give the structural formula of the ketone produced.

5) Some reactions of propan-1-ol are shown in the scheme below:



Give the structural formulae of the organic compounds A, B, C, D, E and F

6) This question concerns some reactions of a compound X which has the structure:

$CH_3CH_2CH_2$ CH_2CH_2-OH

a) Give the systematic name of compound X.b) Is X a primary, secondary or tertiary alcohol?

c) What name is given to the intermolecular forces in compound X?

d) Give the structural formulae for two organic compounds which could be obtained by reacting X with a hot mixture of potassium dichromate and sulphuric acid.

UNIT 12

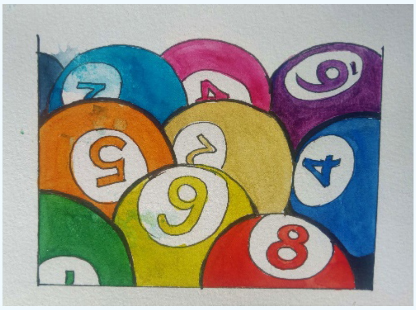
CARBONYL COMPOUNDS.

Key unit competence: Compare the chemical nature of carbonyl compounds to their reactivity and uses.

INTRODUCTORY ACTIVITY

Observe the following pictures and answer the questions asked below.

A



B

Honey

Mangoes

1. The objects shown in the pictures A and B are made of an alcohol and another organic compound containing carbon, hydrogen and oxygen. Suggest the name and formula of this organic compound.

2. Honey, mangoes and other fruits contain some sugars like glucose and fructose. Draw displayed structural formulae of glucose and fructose.

3. Describe the similarities and differences between glucose and fructose in terms of structural formulae.

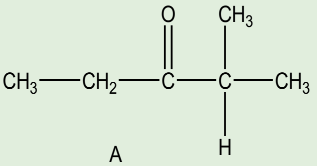
4. State the functional groups found in fructose and glucose.

5. What will happen if Brady’s reagent reacts with glucose or fructose?

12.1. Nomenclature and isomerism in carbonyl compounds.

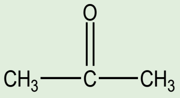
ACTIVITY 12.1

Observe the following molecules and answer to the questions.



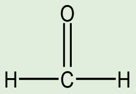
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{CH_3}{C}}-CH_3$

A



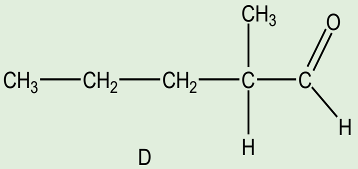
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

B

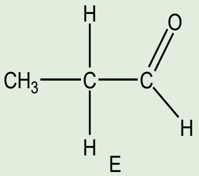


$H-\overset{O}{\overset{\|}{C}}-H$

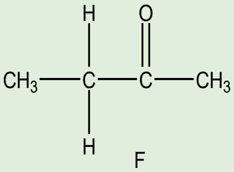
C



D



E



$CH_3-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$

F

1. From the list above, identify the ones which are isomers to each other.

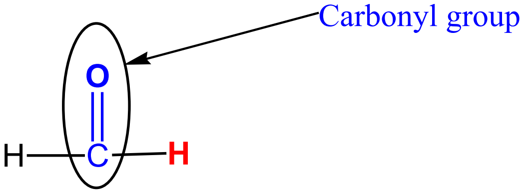
2. Suggest the names of the above molecules.

Carbonyl compounds are compounds that contain carbon-oxygen double bond (C=O). Carbonyl compounds are classified into two general categories based on the kinds of chemistry they undergo. In one category there are **aldehydes** and **ketones**; in the other category there are **carboxylic acids** and their **derivatives**. This unit deals with aldehydes and ketones.

- **Aldehyde molecules**

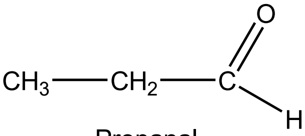
For aldehydes, the carbonyl group is attached to at least hydrogen atom and alkyl group as shown in the molecule of propanal below. Methanal is the smallest aldehyde, it has two hydrogen atoms attached to carbonyl group.

Examples:



$H-\overset{O}{\overset{\|}{C}}-H$

Methan**al**



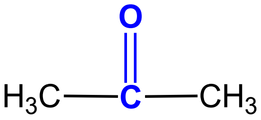
Propanal

If you are going to write this in a condensed form, you write aldehyde as –CHO, **don't write it** as -COH, because that looks like an alcohol functional group.

- **Ketone molecules**

A ketone has two alkyl groups attached to the carbonyl group.

Example:



$H_3C-\overset{O}{\overset{\|}{C}}-CH_3$

Propan**one**

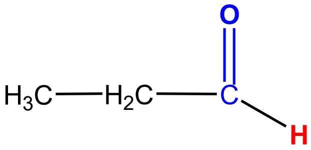
Note: ketones **don't** have a hydrogen atom attached to the carbonyl group.

Nomenclature of aldehydes

The systematic name of an aldehyde is obtained by replacing the terminal **"e"** from the name of the parent hydrocarbon with **"al".** In numbering the carbon chain of an aldehyde, the carbonyl carbon is numbered one.

1st Example: Write the formula of **propanal.**

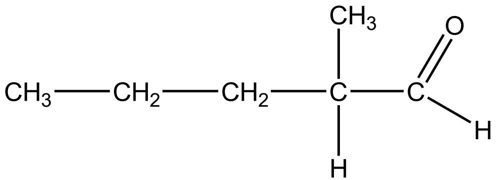
Propanal has a chain of 3 carbons without carbon-carbon double bonds. The **suffix 'al'** indicates the presence of the -CHO group. The carbon in carbonyl functional group is counted as first of the chain.



Propan**al**

2nd Example: Write the formula of **2-methylpentanal**.

This molecule has 5 carbons in the longest chain, including the one in the -CHO group. There aren't any carbon-carbon double bonds. A methyl group is attached to the number 2 carbon



2-methylpentanal

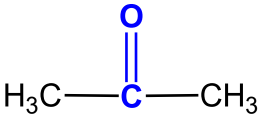
Note: In aldehydes, the carbon in the -CHO group is always counted as first carbon.

- **Nomenclature of ketones**

The systematic name of a ketone is obtained by removing the terminal **"e"** from the name of the parent hydrocarbon and adding **"one".** The chain is numbered in the direction that gives the **carbonyl carbon the smallest number**. Ketones contain a carbon-oxygen double bond just like aldehydes, but for ketones carbonyl group is bonded to two alkyl groups.

1st Example: Write formula of **propanone**.

Propanone has a chain of 3 carbons. The **suffix "one"** indicates the presence of the >C=O in the middle of the carbon chain. The carbon-oxygen double bond has to be in the middle of the carbon chain, for this molecule, the carbonyl group is on carbon 2.



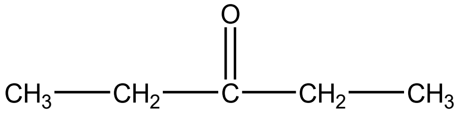
$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Propan**one**

2nd Example: Write the formula of **pentan-3-one**.

In pentanone, the carbonyl group could be in the middle of the chain or next to the end - giving either pentan-3-one or pentan-2-one.

The position of the carbon-oxygen double bond has to be indicated because there is more than one possibility. This molecule has its carbon-oxygen double bond at carbon 3. If it was on the second carbon, it would be pentan-2-one.



$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$$

- **Isomerism in aldehydes and ketones**

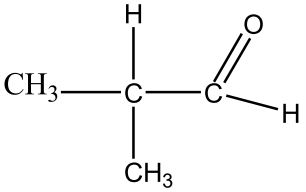
Aldehydes and Ketones exhibit chain and position isomerisms.

a) Chain isomerism

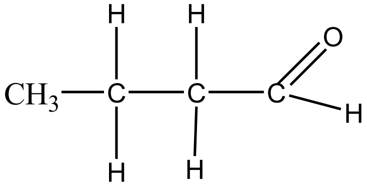
Aldehydes with 4 or more carbon atoms and ketones with five or more carbon atoms show chain isomerism.

Examples:

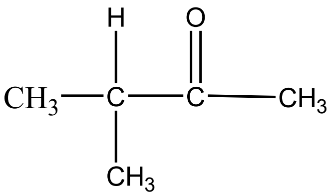
C_4H_8O has the following chain isomers:



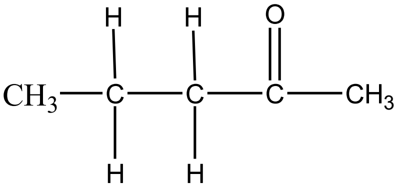
and



$C_5H_{10}O$ has the following chain isomers:



and

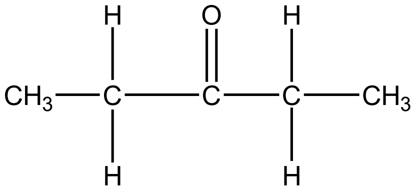


b) Position isomerism

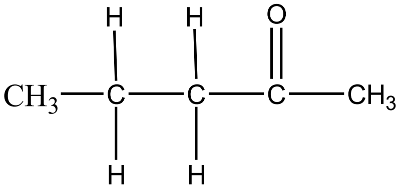
Aromatic aldehydes and higher ketones give position isomers.

Example:

$C_5H_{10}O$ has the following position isomers:

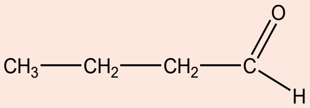


and

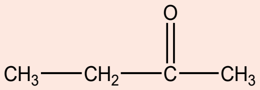


APPLICATION ACTIVITY 12.1

1. Write the names of the following compounds:

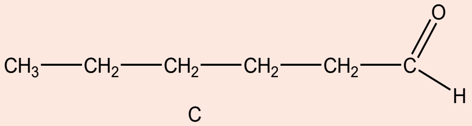


A

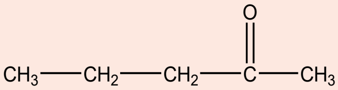


$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

B



C



$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

D

2. Draw the structural formula of hexan-3-one and write the name and formula of its isomer which is an aldehyde.

3. Draw the structural formula of 2-methylpropanal and write the name and formula of its isomer which is a ketone.

12.2. Physical properties of aldehydes and ketones

ACTIVITY 12.2

- Take 50ml for each substance: ethanal, butanal and propanone.
- Mix ethanol (or formaldehyde) with 50ml of water in beaker
- Mix butanal with 50ml of water in beaker
- Mix propanone (or acetone) with 50ml of water in beaker

(1) Compare the solubility of ethanal, butanal and propanone in water.

(2) State intermolecular forces present in each substance.

(3) Explain what happen in terms of intermolecular forces during mixing those above substances with water.

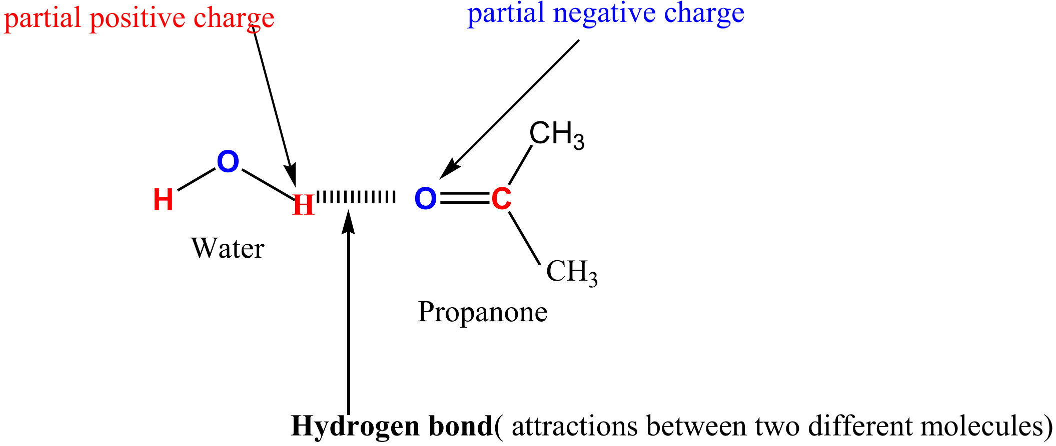
(4) Explain why some substances have high solubility in water than others.

(5) Explain how the intermolecular forces present in ethanal, butanal and propanone affect other physical properties like boiling and melting point of these substances.

- **Solubility of aldehydes and ketones in water**

The small molecules of aldehydes and ketones are soluble in water but solubility decreases with increase of carbon chain. Methanal, ethanal and propanone - the common small aldehydes and ketones are soluble in water at all proportions.

Even though aldehydes and ketones don't form hydrogen bond with themselves, they can form hydrogen bond with water molecules.



The slightly positive hydrogen atoms in a water molecule can be sufficiently attracted to the lone pair on the oxygen atom of an aldehyde or ketone to form a hydrogen bond.

Other intermolecular forces present between the molecules of aldehyde or ketone and the water are dispersion forces and dipole-dipole attractions

The occurring of attractions releases energy which helps to supply the energy needed to separate the water molecules and aldehyde or ketone molecules from each other before they can mix together.

Apart from the carbonyl group, hydrocarbon chains are non polar, they don't dissolve in water. By forcing hydrocarbon chain to mix with water molecules, they break the relatively strong hydrogen bonds between water molecules without replacing them by other attractions good like hydrogen bonds. This makes the process energetically less profitable, and so solubility decrease.

- **Boiling points of aldehydes and the ketones**

Methanal is a gas and has a boiling point of -21°C, and ethanal has a boiling point of +21°C. The other aldehydes and ketones are liquids or solids, with boiling points rising with increasing of molecular mass as the strength of Van der Waals force increases.

Physical properties of covalent compounds depend on intermolecular forces.

Compounds that have similar molecular mass but different intermolecular forces have different physical properties.

Table: 12.1. Example of comparison between molecules of similar mass but different functional groups and boiling points

Molecule	Molecular mass	Type	Boiling point (°C)
$CH_3CH_2CH_3$	44	alkane	-42
CH_3CHO	44	aldehyde	+21
CH_3CH_2OH	46	alcohol	+78
CH_3COCH_3	54	ketone	+56

Alcohols have higher boiling point than aldehydes and ketones of similar lengths. In the alcohol, there is hydrogen bonding, but the molecules of aldehydes and ketones don't form hydrogen bonds. Aldehydes and ketones are polar molecules but alkanes are non polar molecules.

APPLICATION ACTIVITY 12.2

The table below shows the boiling points of an alkane, an aldehyde and an alcohol.

Molecule	Molecular mass	Type	Boiling point (°C)
$CH_3CH_2CH_3$	44	Alkane (Propane)	-42
CH_3CHO	44	Aldehyde (Ethanal)	+21
CH_3CH_2OH	46	Alcohol (Ethanol)	+78

a) Explain why the boiling point of an aldehyde is greater than that of an alkane?

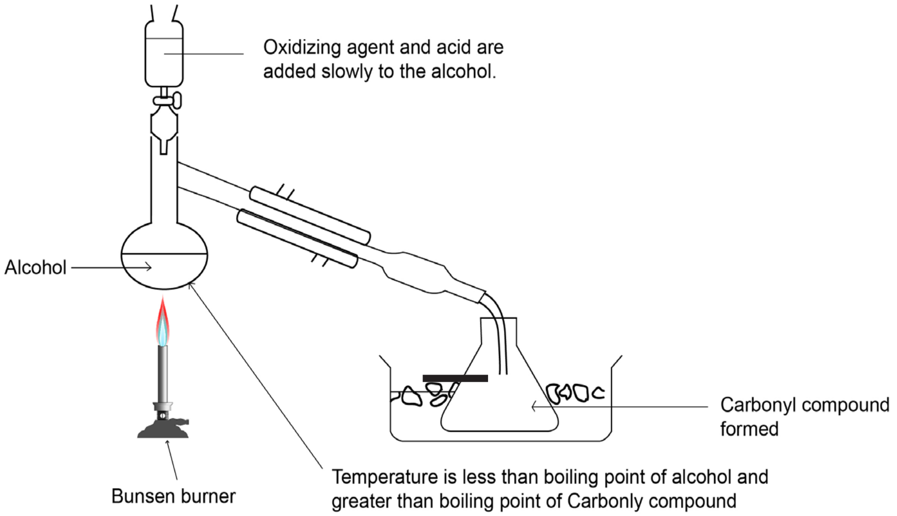
b) Why is the boiling point of the alcohol still higher?

c) Explain why, unlike the similar-sized alkanes, the small aldehydes and ketones are soluble in water.

12.3. Preparation methods of aldehydes and ketones.

ACTIVITY 12.3.(a)

(1) The set up below represents the method of preparation of ethanal from ethanol.



Procedure:

(a) Place 50 cm^3 of water in a 500 cm^3 round-bottomed flask, and add slowly, with shaking, 17 cm^3 of concentrated sulphuric acid: then add some anti-bumping granules.

Note: The granules are silica, and prevent the sudden formation of large gas bubbles that lead to 'bumping' or succussion.

(b) Assemble the flask containing the sulphuric acid into a distillation apparatus. The flask carries a tap funnel instead of a thermometer, and the receiving flask should be surrounded by an iced water bath.

Note: The boiling temperature of ethanal is 21°C, so the cooling reduces evaporation of the ethanal.

(c) Dissolve 50 g of sodium dichromate (VI) in 50 cm^3 of water contained in a small beaker, and add 40cm^3 of ethanol. Stir thoroughly, and place this mixture in the tap funnel.

(d) Heat the dilute acid in the flask until it begins to boil gently, and then remove the flame and run the alcohol/dichromate (VI) solution very slowly into the flask. Directly the solution enters the hot acid in the flask a vigorous reaction occurs, and a mixture of ethanal and water containing a little ethanoic acid distils over. The reaction mixture becomes green. The addition of the alcohol/dichromate (VI) mixture should take about 20 minutes; towards the end of this time it will be necessary to replace the flame under the distilling flask to maintain gentle boiling.

(e) When the addition of the alcohol/dichromate (VI) mixture is complete, collected and moderately concentrated aqueous solution of ethanal is obtained in the receiver flask.

Questions:

i. Write down chemical equations of the reactions that take place in this experiment

ii. Ethanol reacts with $K_2Cr_2O_7/H^+$, does ethanol undergoes oxidation or reduction in this reaction?

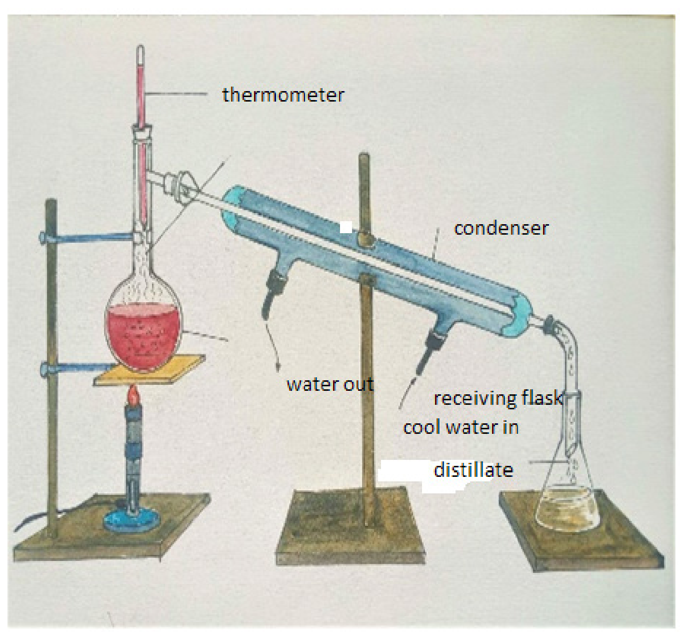
iii. Why does the mixture turn green?

ACTIVITY 12.3(b)

Preparation of ketones

Procedure:

Transfer 15g of calcium acetate in 50mL round bottom flask fixed on a stand, and place it on a Bunsen burner . Fit it with a condenser connected to a receiver flask. Adjust the temperature until the condensation starts. Heat the flask and collect the carbonyl compound in receiver flask. The obtained product is not pure and needs to be purified. Set up a distillation apparatus and distil the crude product to obtain pure carbonyl compound (56^{0}c). Do not forget to use stirrer bar which must be placed in the round bottom flask containing the ketone.



Set up for preparation of a carbonyl compound

Questions:

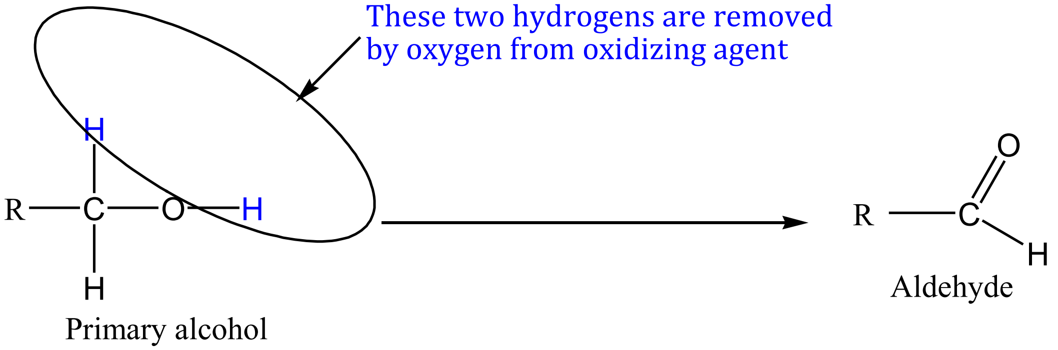
i. Write the balanced equation of the reaction which takes place in this experiment.

ii. Suggest the name and structural formula of the carbonyl compound produced.

a) Oxidation of alcohol by $K_2Cr_2O_7/H^+$

Potassium dichromate (VI) acidified with dilute sulphuric acid is used as oxidizing agent during the preparation of aldehydes or ketones. Primary alcohols is oxidized to aldehydes, oxygen atom from the oxidising agent removes two hydrogens; one from the -OH group of the alcohol and the other hydrogen comes from the carbon that is attached to hydroxyl group.

- **Primary alcohol undergoes oxidation to produce aldehyde**

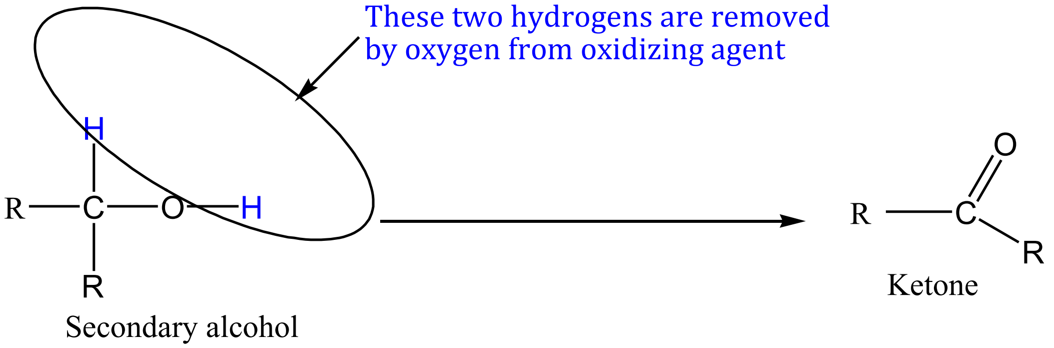


These two hydrogens are removed by oxygen from oxidizing agent

Primary alcohol

Aldehyde

- **Secondary alcohol undergoes oxidation to produce ketone**

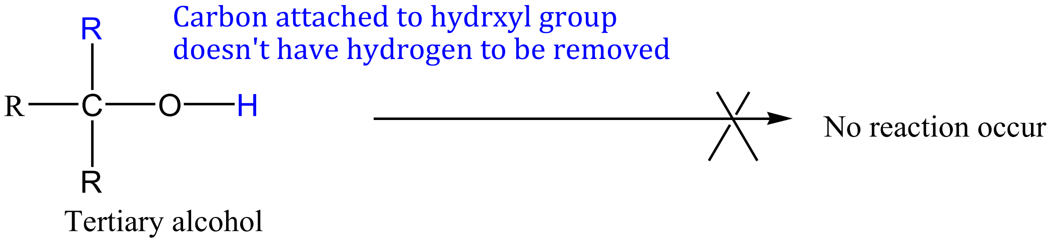


These two hydrogens are removed by oxygen from oxidizing agent

Secondary alcohol

Ketone

- **Tertiary alcohol doesn't undergo oxidation because the carbon bonded to hydroxide doesn't have hydrogen to be removed.**



Carbon attached to hydrxyl group doesn't have hydrogen to be removed

No reaction occur

Tertiary alcohol

The solution of dichromate (VI) ions, $Cr_2O_7^{2-}$, is orange. During chemical reaction dichromate (VI) ions re reduced to chromium (III) ions, Cr^{3+} which are green.

$$3CH_3CH_2OH + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O$$

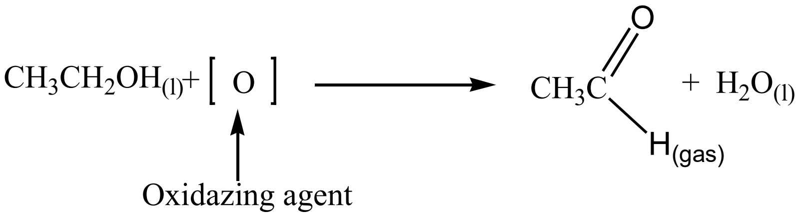
Technique of stopping oxidation of aldehyde

The aldehyde produced by oxidation of alcohol could undergo further oxidation to a carboxylic acid if the acidified potassium dichromate (VI) is still present in solution where the reaction takes place. In order to prevent this further oxidation of aldehyde to carboxylic acid the following techniques are used.

- Use an excess of the alcohol than potassium dichromate (VI). Potassium dichromate (VI) is limiting reactant hence there isn't enough oxidising agent present to carry out the second stage of oxidizing the aldehyde formed to a carboxylic acid.
- Distil off the aldehyde as soon as it forms. Removing the aldehyde as soon as it is formed this means that aldehyde is removed from solution where oxidizing agent is, to prevent further oxidation. Ethanol produces ethanal as shown by the following reaction.

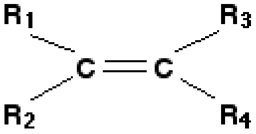
$$3CH_3CH_2OH + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O$$

To simplify the writing of the reaction, [O] represents oxygen from an oxidising agent. Then the reaction is written as follows:



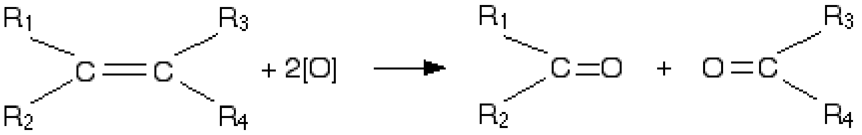
Oxidation of alkene by $KMnO_4/H^+$

Oxidation of alkenes with hot concentrated acidified potassium manganate (VII) solution produces carbonyl compounds. Consider the general formula of alkene below:

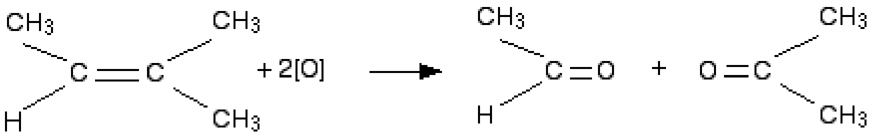


Where R_1, R_2, R_3 and R_4 represent alkyl groups or hydrogen atoms

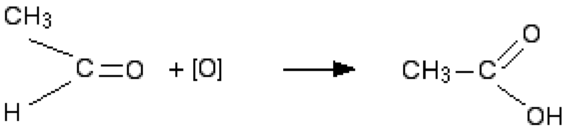
Carbon-carbon double bond of alkene is broken by acidified potassium manganate (VII) and is replaced by two carbon-oxygen double bonds to each carbon from double bond. General equation:



Example 1:

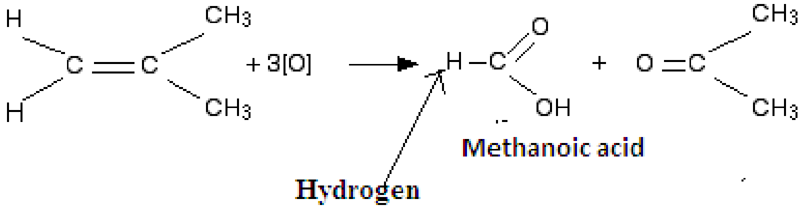


If acidified potassium manganate (VII) is still present in solution, aldehyde makes further oxidation to carboxylic acid

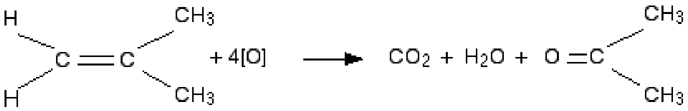


Example 2:

The molecule below has two hydrogens attached to a carbon with double bond

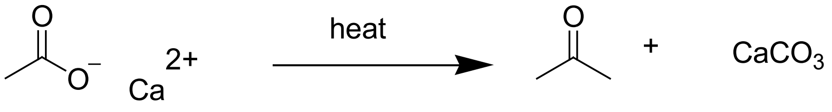


Methanoic acid has hydrogen attached on carbonyl group hence it makes further oxidation to carbon dioxide. Final equation is written as follow:



- **Preparation of ketone by distillation of calcium acetate**

Example: preparation of acetone



calcium acetate acetone calcium carbonate

APPLICATION ACTIVITY 12.3

1. Draw the structure of the aldehyde or ketone that would be formed if each of the following alcohols is oxidised. You can assume that conditions are fulfilled to avoid further oxidation of the aldehyde to a carboxylic acid.
   i. $CH_3CH_2CH_2OH$
   ii. $CH_3CH_2CH(CH_3)CH_2OH$
   iii. $CH_3CH_2CHOHCH_3$
2. Draw the structure of the alcohol you would oxidize in order to obtain each of the following compounds.
   i. pentan-2-one
   ii. butanal
3. Write a balanced equation of the reaction between propan-2-ol and $K_2Cr_2O_7/H^+$

12.4. Chemical reactions of carbonyl compounds

ACTIVITY 12.4.(a)

You are provided with the following: propanal, propanone, ethanol, glucose solution and 2,4-dinitrophenylhydrazine (Brady's reagent).

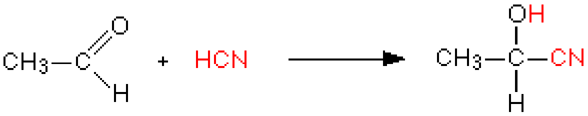
Take about 2 ml of each solution; propanal, propanone, ethanol and glucose solution in test tubes. Add 6 drops of the 2,4-dinitrophenylhydrazine to each of the test tubes containing: propanal, propanone, ethanol or glucose solution. If no precipitate forms immediately, warm for 5 minutes in the water bath. Record your observations in the table below.

Substance	Observations	Deductions
Aldehydes (propanal)		
Ketones (propanone)		
Alcohol(ethanol)		
Sugar(glucose)		

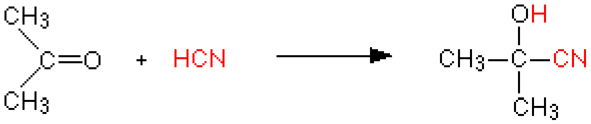
a) Nucleophilic addition reactions

- **Reaction of HCN with aldehydes and ketones**

Hydrogen cyanide adds to aldehydes or ketones to form ***cyanohydrins or hydroxynitriles.*** The product has one more carbon atom than the reactant. For example, ethanal reacts with HCN to form 2-hydroxypropanenitrile:



When HCN reacts with propanone, the product is 2-hydroxy-2-methylpropanenitrile:

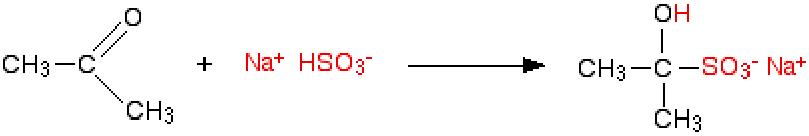


Because hydrogen cyanide is a toxic gas, the best way to carry out this reaction is to generate hydrogen cyanide during the reaction by adding HCl to a mixture of the aldehyde or ketone and excess sodium cyanide. Excess sodium cyanide is used in order to make sure that some cyanide ion is available to act as a nucleophile. The solution will contain hydrogen cyanide (from the reaction between the sodium or potassium cyanide and the HCl)

The pH of the solution is maintained in range 4 - 5, because this gives the fastest reaction. The reaction takes place at room temperature.

- **Reaction of $NaHSO_3$ with aldehydes or ketones**

The aldehyde or ketone is shaken with a saturated solution of sodium hydrogensulphite in water. Hydrogen sulphite with negative charge act as nucleophile, where the product formed is separated as white crystals. Propanone react hydrogensulphite, as below:



Impure aldehyde and ketone can be purified by using this reaction. Impure aldehyde or ketone is shaken with a saturated solution of sodium hydrogensulphite to produce the crystals. Impurities don’t form crystals; these crystals formed are filtered and washed to remove any impurities. Addition of dilute acid to filtered crystals regenerates the original aldehyde. Dilute alkali also can be added instead of dilute acid.

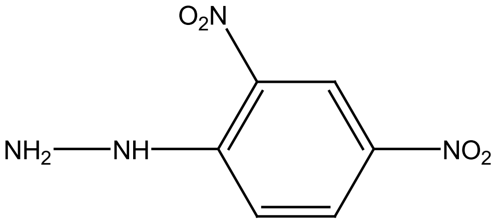
b)Condensation reactions

A condensation reaction is one in which two molecules join together with the loss of a small molecule in the process.

The reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine (Brady's reagent)

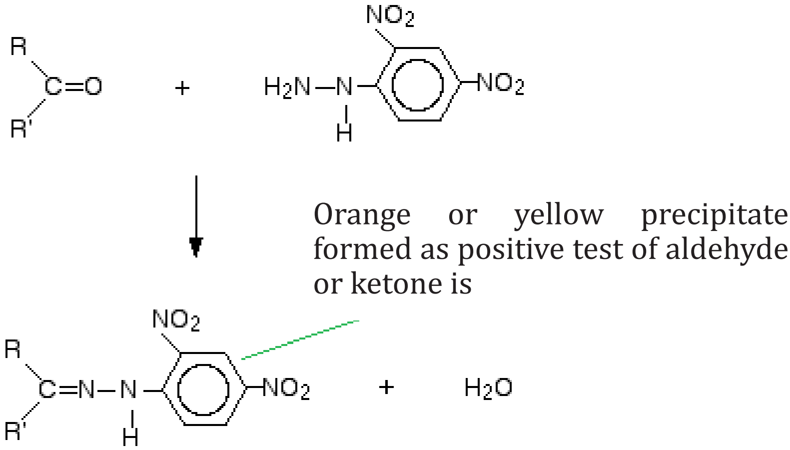
Brady's reagent is a solution of the 2,4-dinitrophenylhydrazine in methanol and sulphuric acid.

2,4-dinitrophenylhydrazine is often abbreviated as 2,4-DNP or 2,4-DNPH.



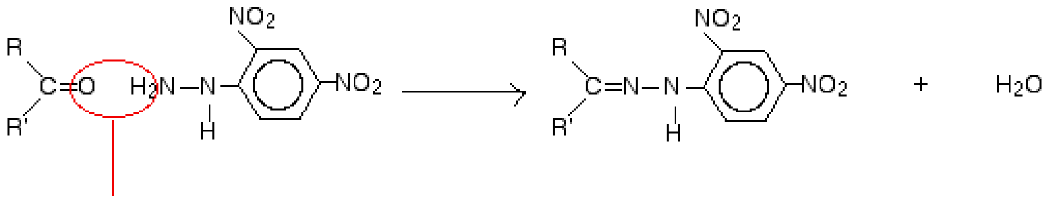
2,4 -dinitrophenylhydrazine

The overall reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine is:



Orange or yellow precipitate formed as positive test of aldehyde or ketone is

Where R and R' represent alkyl groups or hydrogen(s); if both or only one is hydrogen the starting carbonyl compound is an aldehyde. If both R and R' are alkyl groups the carbonyl compound is a ketone. The following molecule shows clearly how the product is formed.


H₂O is lost then carbon bonds to nitrogen

The product formed is named”2,4-dinitrophenylhydraz**one**”. The simple difference consists in replacing suffix “**-ine**” by “**-one**”.

The reaction of 2,4-dinitrophenylhydrazine with ethanal produces ethanal 2,4-dinitrophenylhydraz**one**; The reaction of 2,4-dinitrophenylhydrazine with butanal produces butanal 2,4-dinitrophenylhydraz**one**. This is an example of ***condensation reaction.***

c) Oxidation reactions of carbonyl compounds

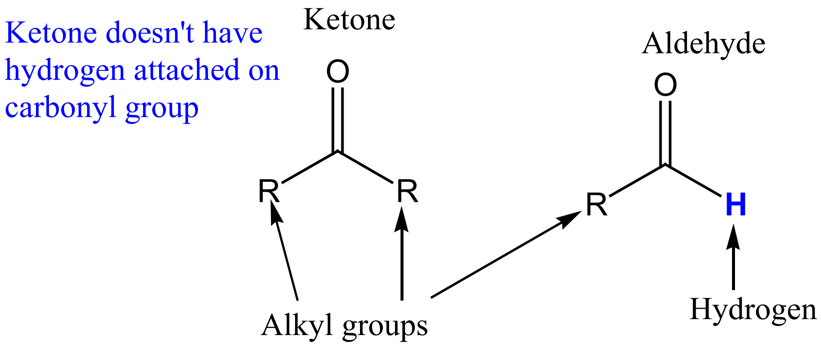
ACTIVITY 12.4.(b)

You are provided with the following: propanal, propanone and potassium dichromate (VI) solution acidified with dilute sulphuric acid.

Take about 2ml of each solution; propanal and propanone; add 6 drops of the potassium dichromate(VI) solution acidified with dilute sulphuric acid. Record your observations in the table below and give your deductions.

Substance	Observations	Deductions
Aldehydes (propanal)		
Ketones (propanone)		

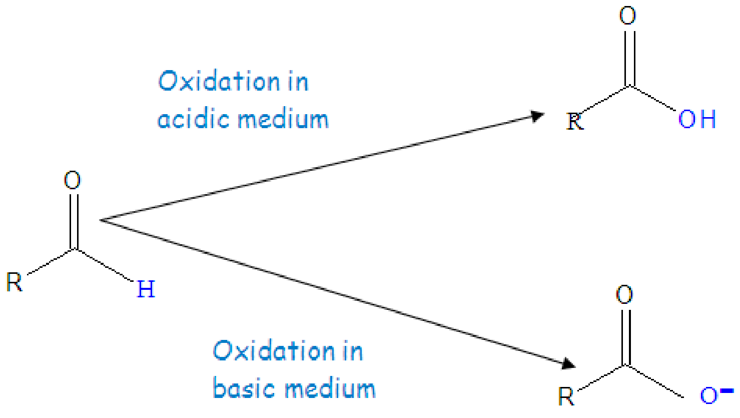
By considering the structural formulae of aldehydes and ketones, the difference is only the presence of a hydrogen atom attached to the carbonyl functional group in the aldehyde whereas ketones have an alkyl group instead.



During chemical reaction aldehydes react with oxidizing agent; hydrogen on carbonyl functional group is replaced by oxygen, as illustrated below. The presence of hydrogen atom makes aldehydes very easy to oxidize. In other words, aldehydes are strong reducing agents.

For ketone, absence of hydrogen on carbonyl functional group makes ketones to resist oxidation. But very strong oxidising agents like potassium permanganate solution oxidize ketones - and they do it in a destructive way, by breaking carbon-carbon bonds.

Aldehyde oxidation can take place in acidic or alkaline solutions. Under acidic solutions, the aldehyde is oxidized to a carboxylic acid. Under alkaline solutions, acid formed react with base to form a salt of carboxylic acid.



- **Oxidation of aldehyde by $K_2Cr_2O_7/H^+$ solution**

Add few drops of the aldehyde or ketone to a solution of potassium dichromate (VI) acidified with dilute sulphuric acid. If the color doesn’t change in the cold, the mixture is warmed gently in a beaker containing hot water.

Tested substances	Observations
Aldehydes	Orange color of $K_2Cr_2O_7$ solution turns green of Cr^{3+}solution.
Ketones	Orange color of $K_2Cr_2O_7$ solution doesn't change.

The dichromate (VI) ion, $Cr_2O_7^{2}$, is an oxidizing agent, it oxidizes aldehyde to carboxylic acid, and it is reduced to Cr^{3+}ion

$$3RCHO + Cr_2O_7^{2-} + 8H^+ \rightarrow 3RCOOH + 2Cr^{3+} + 4H_2O$$

- **Oxidation reactions using Tollens' reagent**

ACTIVITY 12.4.(c)

You are provided with the following: propanal, propanone and Tollens' reagent.

Take about 2ml of each solution; propanal and propanone. Add 6 drops of the Tollens' reagent to each of the following in the test tubes; propanal or propanone. Warm gently the mixture in a hot water bath for a few minutes. Record your observations and deductions in the table below.

Substance	Observations	Deductions
Aldehydes (propanal)		
Ketones (propanone)		
Sugar(glucose)		

Tollens' reagent is a solution of diamminesilver (I) ion, $[Ag(NH_3)_2]^+$ and OH^-.

In order to identify if a substance is aldehyde or ketone, add few drops of Tollens' reagent to test tubes containing aldehyde or ketone and warm gently in a hot water bath for a few minutes. The formation of sliver mirror or grey precipitate is an indication of the presence of aldehyde.

Tested substances	Observations
Aldehydes	The colourless solution produces a grey precipitate of silver, or a silver mirror on the test tube.
Ketones	Colourless solution doesn't change: no reaction

Equation of reaction:

$$2Ag(NH_3)_2{}^+{}_{(aq)} + RCHO_{(l)} + 3OH^-{}_{(aq)} \rightarrow 2Ag_{(s)} + ROO^-{}_{(aq)} + 4NH_{3(aq)} + 2H_2O_{(l)}$$

- **Oxidation reactions using Fehling or Benedict solution**

ACTIVITY 12.4.(d)

You are provided with the following: ethanal, propanone, Fehling's solution and Benedict's solution.

Put about 2ml of ethanol in the first test tube and about 2ml of propanone in the second test tube. Add 6 drops of the Fehling's or Benedict's solution to each of the tubes containing 2ml of ethanal or propanone to be tested. Warm gently the mixture in a hot water bath for a few minutes. Record your observations and give deductions in the table below.

Substance	**Observations**	**Deductions**
Ketones (propanone)		
Aldehydes (propanal)		

Fehling's solution and Benedict's solution react with aldehyde in the same way; both solutions contain Cu^{2+} and OH^-. In Fehling's solution Cu^{2+} is complexed with tartrate ligand but in Benedict's solution Cu^{2+} is complexed with citrate ligand.

Don't worry about ligands, important reagents are Cu^{2+} and OH^-, ligands tartrate and citrate are used to prevent formation of copper (II) hydroxide or copper (II) carbonate precipitate.

A few drops of Fehling's or Benedict's solution is added to the aldehyde or ketone and the mixture is warmed gently in a hot water bath for a few minutes.

Tested substances	**Observations**
Aldehydes	The blue solution produces a dark red precipitate of copper (I) oxide (Cu_2O).
Ketones	The blue color of Cu^{2+} solution doesn't change. Reaction doesn't occur.

Fehling's and Benedict's solutions are oxidizing agent, they oxidize aldehydes to carboxylic acid. Remember that the reaction takes place in basic solutions, acid formed is neutralized by base, and hence the products area salt of carboxylic acid instead of carboxylic acid.

Equation of reaction:

$$RCHO(l) + 2\,Cu^{2+}\text{ (in complex)} + 5OH^-(aq) \longrightarrow RCOO^-(aq) + Cu_2O(s) + 3H_2O(l)$$

- **Iodoform reaction with aldehydes and ketones**

ACTIVITY 12.4.(e)

You are provided with the following: propanone, propanal, 6M NaOH solution and KI_3 solution.

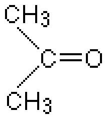
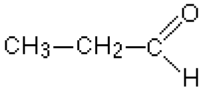
Put 4 drops of each tested substance, propanone, propanal, into different test tubes.

Add to this 0.5 mL distilled water to each test tube.

Add 0.25mL 6M NaOH and 0.25 mL of water to each test tube.

Add 6 drops of I_3^- solution to each test tube.

If no precipitate forms immediately, warm the mixture very gently. Record your observations and deductions in the table below.

Substance	**Observations**	**Deductions**
 Propanone		
 Propanal		

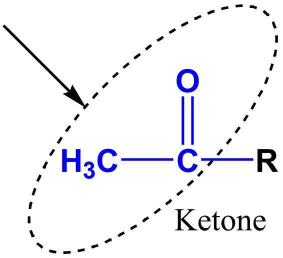
- **Reagents for iodoform reaction**

There are two different mixtures that can be used to do iodoform test, these mixture are:

- Iodine and sodium hydroxide solution
- Potassium iodide and sodium chlorate (I) solutions

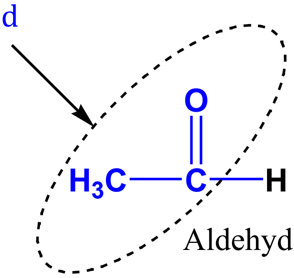
Don't worry about Potassium iodide and sodium chlorate (I) solutions, Potassium iodide and sodium chlorate(I) react to form final solution containing I_2 and OH^-. Both mixtures contain the same reagents.

Each of these mixtures contains important reagent $\mathbf{I_2}$ and $\mathbf{OH^-}$which react with aldehyde or ketone. When I_2 and OH^- is added to a carbonyl compound containing the group CH_3CO (blue in the cycle) as shown below, pale yellow precipitate (triiodomethane) is formed.


Carbonyl compound that has this group reacts with I_2 and OH^- to form a pale yellow precipitate

Ketone

Where **R** is an alkyl group for ketone


Carbonyl compound that has this group reacts with I_2 and OH^- to form a pale yellow precipitate

Aldehyde(Ethanal)

Note: iodine, I_2, is dissolved in iodide solution to form I_3^- which is soluble in water

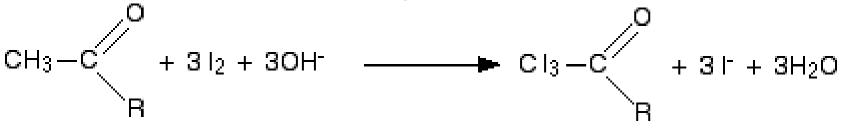
- **Description of iodoform test**

For iodine and sodium hydroxide solution: Iodine solution, I_3^-, is added to aldehyde or ketone, followed by just enough sodium hydroxide solution to remove the colour of the iodine. If pale yellow precipitate doesn't form in the cold, it may be necessary to warm the mixture very gently. The positive result is pale yellow precipitate of CHI_3.

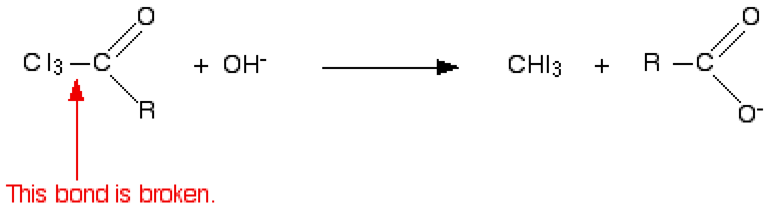
For potassium iodide and sodium chlorate (I) solutions: Potassium iodide solution is added to a small amount of aldehyde or ketone, followed by sodium chlorate (I) solution. If pale yellow precipitate doesn't form in the cold, warm the mixture very gently. The positive result is a pale yellow precipitate of CHI_3.

Reaction of iodoform test: The reagents of iodoform test are I_2 and OH^- solution. The reaction takes place into two main steps:

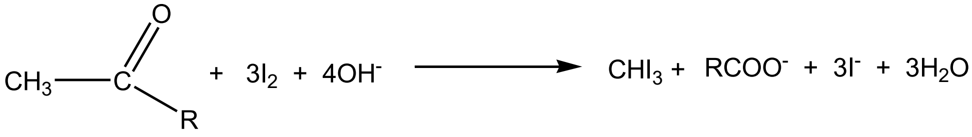
- Three hydroxides, OH^-, remove three hydrogens from methyl group and the place of hydrogen is taken by iodide.



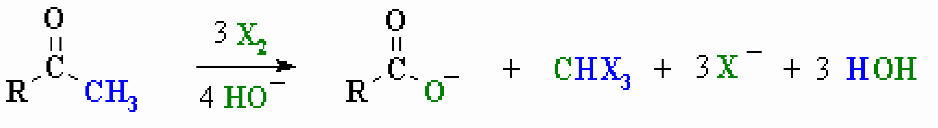
CI_3^- group is a good leaving group; CI_3^- is replaced by OH^- to form carboxylic acid, because CI_3^- is a base according to Bronsted-Lowry, it reacts with acid to form the following product:



The overall equation for reaction of iodoform test:



The same reaction takes place for other halogen elements in the same way. The general equation is given below



When methyl ketones or methyl aldehyde, ethanal, are treated with the halogen element in basic solution, hydrogens of the methyl group are replaced by halogen element followed by cleavage of the methyl group. The products are the salt of carboxylic acid and trihalomethane. The reaction is fast until the 3 hydrogens at the methyl group have been replaced by halogen atoms.

APPLICATION ACTIVITY 12.4

1. **A** has the formula $C_5H_{12}O$. Its oxidation gives **B** with the formula $C_5H_{10}O$. **B** reacts with 2,4-dinitrophenylhydrazine to give a positive test but B does not give a positive test with Tollens reagent. **A** is dehydrated by concentrated H_2SO_4 to **C** **(**pent-2-ene**)**. Identify the compound **A** and draw the formulae of B and C**.**

2. Brady's reagent is a solution of 2,4-dinitrophenylhydrazine in a mixture of methanol and sulphuric acid. What do you observe when a Brady's reagent is added to an aldehyde or ketone?

12.5. Uses of carbonyl compounds.

ACTIVITY 12.5

Observe the following materials made by bakelite polymers and answer the questions below:

Questions:

1) The above objects are made using carbonyl compounds. Suggest the name and formula of a compound which can be used to make the above objects.

2) Outline other uses of carbonyl compounds.

a) Formaldehyde:

Formaldehyde is a gas at room temperature but is sold as a 37 percent solution in water (this solution is called **formalin)**.

Formaldehyde is used as preservative and germicide, fungicide, and insecticide for plants and vegetables. Formaldehyde is mainly used in production of certain polymers like Bakelite. Formaldehyde is used as monomer in production of Bakelite.

b) Acetone as solvent:

Acetone is soluble in water at all proportions and also dissolves in many organic compounds. Boiling point of acetone is low, 56^0C, which makes it easier to be removed by evaporation. Acetone is an industrial solvent that is used in products such as paints, varnishes, resins, coatings, and nail polish removers.

c) Aldehydes and ketones in living organisms

Organic molecules that contain ketones or aldehydes functional group are found in different foods such as irish potatoes, yellow bananas, etc.

Aldehydes and ketones functional group are found in humans hormones like progesterone and testosterone.

APPLICATION ACTIVITY 12.5

Outline the common uses of acetone and methanol in our daily life.

SKILLS LAB 12

Formaldehyde can be used to produce formalin which is commonly used as preservative or antiseptic. Using the skills acquired from unit eleven (alcohols) of this textbook and unit twelve (carbonyl compounds) prepare this formalin from banana of sorghum.

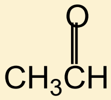
END UNIT ASSESSMENT 12

1. Answer the following questions by choosing the best alternative represented by letters from A, B, C and D:

   a) The compound ($CH_3CO\ CH_2CH_3$) belongs to which class of organic compound?

   A) alcohols B) alkenes C) ketones D) aldehydes

   b) The compound that follows belongs to which class of compounds?

   $CH_3\overset{O}{\overset{\|}{C}}H$

   A) alkenes B) aldehydes C) ketones D) alcohols

2. One of the compounds responsible for the flavor of butter is butane-2,3-dione. Give the structural formula of butane-2, 3-dione.

3. Three compounds **E, F,** and **G** all have the molecular formula C_3H_6O. **E** is an alcohol, **F** is ketone and **G** is aldehyde. Draw the structural formulae of **F** and **G.**

4. Carbonyl compound **X** undergoes the following reactions

   X gives an orange precipitate with 2, 4-dinitrophenylhydrazine.

   X gives pale yellow precipitate with mixture of potassium iodide and sodium iodate (I)

X Doesn’t react with warm acidified $K_2Cr_2O_7$ solution.

X doesn’t react with aqueous bromine.

X is reduced by hydrogen in the presence of catalyst to a mixture of isomers **Y** and **Z** of formula $C_4H_{10}O$. Identify **X**, and give the structural formulae of **X, Y** and **Z.**

5. Three alcohols A, B and C of molecular formula $C_4H_{10}O$ were separately heated with acidified $K_2Cr_2O_7$ (potassium dichromate). Alcohol C did not undergo any change while A and B did. Alcohol A produced compound D which reacted further to form compound E. Alcohol B reacted to form a compound F. Compound F did not react with Fehling’s solution but reacted with 2,4-dinitrophenylhydrazine.

a) Suggest structural formulae of C and E.

b) Give the structural formulae of compounds D and F.

c) Give the structural formulae of alcohols A and B.

UNIT 13

CARBOXYLIC ACIDS AND ACYL HALIDES

Key unit competency: Compare the chemical nature of carboxylic acids and acid halides to their reactivity.

INTRODUCTORY ACTIVITY

1. You have certainly drunk and tasted fresh milk and fresh banana juice or any other fruit juice. What happen if the milk or juice stays for long time: how does it taste? Can you explain the change?
2. After an ant's stings, you feel a prolonged pain and sometimes the part of the body that was stung swells.
   a) Explain the reasons of these observations and sensations.
   b) Is there any other substance that accompanies the ant's stings?
3. Lemon juice and vinegar, both have a sour test and they can be used in treatment of salad before they are eaten.

a) Why are they used for this purpose?

b) Which chemical substance do they have in common that is responsible for this sour taste?

c) Identify the part that is common in the structures of the main chemical responsible for their sour taste.

13.1. Nomenclature and isomers of carboxylic acids and acyl halides

13.1.1. Nomenclature of carboxylic acids

ACTIVITY 13.1.1

1. With help of the general rules of naming organic compounds, studied in unit 1, suggest the IUPAC names of the following compounds.

   a) CH_3-COOH

   b) CH_3-CH(CH_3)-COOH

   c) HCOOH

   d) HOOC-CH_2-COOH

   e) CH_3-CH_2-CH(CH_3)-COOH

2. Find the structures that correspond to the systematic names below

   a) 2,2-dimethylpropanoic acid

   b) 3-methylbutanoic acid

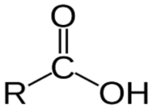
3. You are provided with molecular formulae of different organic compounds: $C_2H_4O_2$, $C_3H_6O_2$. Identify all possible isomers of these compounds.

4. A student was given two samples of enantiomers; L-lactic acid and D-lactic acid, which are both colorless liquids.

   a. How are these two isomers related?

   b. Briefly describe how the two samples can be distinguished so that they can be properly labeled.

Carboxylic acid is classified in the family of organic compounds due to the presence of carboxyl group (-COOH) in their chemical formula. The general formula for carboxylic acids is R-COOH where R- refers to the alkyl group of the molecule.



a. Nomenclature

Carboxylic acids are named by following the general rules of naming organic compounds, where the suffix **'oic acid'** is added to the stem name of the longest carbon chain that contains the acid functional group. The side branches are also positioned by starting from the carbon with carboxylic functional group.

The carboxylic group takes priority to other functional group when numbering carbons in the case of substituted chain.

Table 13.1: Nomenclature of carboxylic acids

Formula	Systematic name	Common name
HCOOH	Methanoic acid	formic acid
CH_3COOH	Ethanoic acid	acetic acid
CH_3-CH_2-COOH	Propanoic acid	propionic acid
CH_3-$(CH_2)_2$ –COOH	Butanoic acid	butyric acid
CH_3-$(CH_2)_{10}$ –COOH	Dodecanoicacid	lauric acid
CH_3-$(CH_2)_{12}$ –COOH	Tetradecanoic acid	myristic acid
CH_3-$(CH_2)_{14}$ –COOH	Hexadecanoic acid	palmitic acid
CH_3-$(CH_2)_{16}$ –COOH	Octadecanoic acid	stearic acid

For diacids, the suffix of the IUPAC name becomes **'dioic acid'.** They have a general formula of $HOOC$-C_nH_{2n}-COOH.

Table 13.2. Nomenclature of carboxylic acids with two carboxyl groups

Formula	Systematic name	Common name
HOOC-COOH	Ethanedioic acid	Oxalic acid
$HOOC-CH_2-COOH$	Propanedioic acid	Malonic acid
$HOOC – CH_2-CH_2-COOH$	Butanedioic acid	Succinic acid
$HOOC-(CH_2)_4-COOH$	Hexanedioic acid	Caproic acid or adipic acid
$HOOC-(CH_2)_8-COOH$	Decanedioic acid	Sebacic acid

Unsaturated acids (alkenoic acids) are systematically named by changing the stem suffix **'-an'** to**'-en'.**

Table 13.3. Nomenclature of unsaturated carboxylic acids

Formula	Systematic name	Common name
$CH_2=CH-COOH$	Prop-2-enoic acid	Acrylic acid
$CH_3-CH=CH-COOH$	But-2-enoic acid	Crotonic acid
$CH_2=C (CH_3)-COOH$	2-methylprop-2-enoic acid	Metacrylic acid
$CH_3 -(CH_2)_7- CH=CH-(CH_2)_7- COOH$	Octadec-9-enoic acid	Oleic acid

Hydroxy-acids are named by considering -hydroxyl group as a substituent on the longest carbon chain that contains carboxylic functional group.

Table 13.4. Nomenclature of hydroxy-acids

Formula	Systematic name	Common name
$HOCH_2-CH_2-COOH$	3-hydroxy-propanoic acid	β–lactic acid
$CH_3-CHOH-COOH$	2-hydroxypropanoic acid	α–Lactic acid
$HOCH_2-CHOH-COOH$	2,3-dihydroxypropanoic acid	Glyceric acid
HOOC-CHOH-COOH	Hydroxypropanedioic acid	Malic acid
HOOC-CHOH-CHOH-COOH	Dihydroxybutanedioic acid	Tartaric acid

b. Isomerism

Carboxylic acids show diverse types of isomers either among themselves or with other compounds that have different functional groups:

- **Chain isomers**

Chain isomers have the same molecular formula and they differ in the length of the carbon chain (carbon backbone) of the molecule.

Example: CH_3-CH_2-CH_2-COOH (butanoic acid) and CH_3-CH(CH_3)-COOH (2-methylprpanoic acid) are chain isomers of $C_4O_2H_8$

- **Functional isomers with esters**

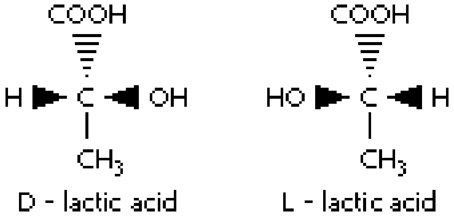
Functional isomers have the same molecular formula and they differ from the functional groups that are found in the structure of the molecule.

Example: CH_3-CH_2-COOH (propanoic acid) and CH_3-COO-CH_3 (methyl ethanoate) are functional isomers of $C_3O_2H_{6.}$

- **Optical isomers**

Optical isomers have the same molecular formula and the same structural formula, but they are different in the spatial arrangement of atoms and their optical properties. An organic compound shows optical isomerism, when there is **chiral carbon** (a carbon atom attached to four diverse groups) in its structure. A chiral carbon is also known as **asymmetric carbon**.

For example, lactic acid can exist in two isomers that are mirror images of one other and they cannot be superimposed on each other. This is caused by the molecule which has an asymmetric carbon.



Just as the right hand and left hand are mirror images of one another but not superimposable, optical isomers, also known as enantiomers, are different from each other and can have different properties. For example, muscles produce D-lactic acid when they contract, and a high amount of this compound in muscles causes muscular pain and cramps.

These molecules are optical isomers, because they have opposite optical activities.They can be distinguished by a plane-polarized light where one enantiomer rotates the light to the right while the other rotates it to the left.

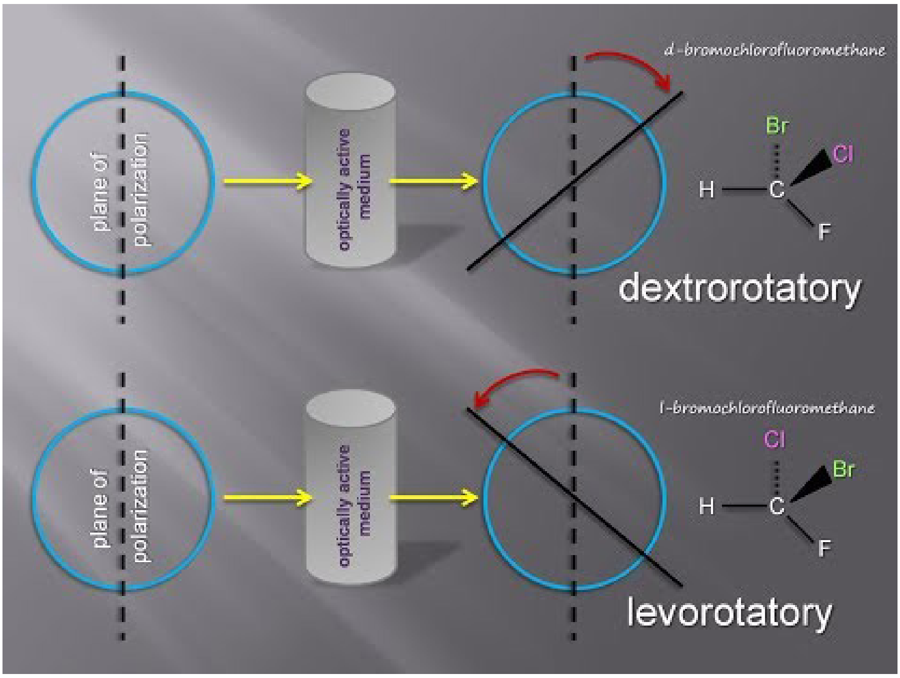


Figure13.1. Dextrorotatory compound D) and laevorotatory compound (L)

Enantiomers are often identified as D- or L- prefixes because of the direction in which they rotate the plane polarized light as shown in figures 13.1. Enantiomers that rotate plane polarized light in clockwise direction are known as dextrorotatory (right-handed) molecules and enantiomers that rotate plane polarized light in anticlockwise direction are known as levorotatory (left-handed) molecules.

A solution containing equal amounts of enantiomers, 50% levorotatory and 50% dextrorotatory is known as a **racemic mixture** that will not rotate polarized light, because the rotations of the two enantiomers cancel each other out.

APPLICATION ACTIVITY 13.1

1. Write the structures of the following compounds:

   a) 2,3-Dimethylpentanoic acid

   b) 2-Methylhexanedioic acid

2. Give the IUPAC names of the organic acids below:

   a) CH_3-$CH(CH_3)$-$CH=CH$-CH_2-CH_2-$COOH$

   b) CH_3-$CH(OH)$-CH_2-$COOH$

3.Identify the type of isomers that are in the following group of compounds:

   a) CH_3-CH_2-$CH(CH_3)$-CH_2-$COOH$ and CH_3-CH_2-COO-$CH(CH_3)_2$

   b) $CH_3CH_2CH_2CH_2COOH$ and $CH_3C(CH_3)_2COOH$

2. Explain which of the compounds below is/are optically active: 2-hydroxybutanoic acid, 3-hydroxybutanoic acid, 2-methylpropanoic acid and 2-methylbutanoic acid.

13.1.2. Acyl chlorides and their nomenclature

ACTIVITY 13.1.2

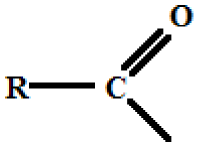
a) Write the reaction between ethanoic acid and phosphorus pentachloride.

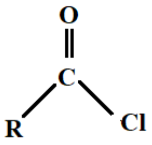
b) What is the functional group in product of the reaction a)?

c) How can this organic product be named?

d) How is the nomenclature of the compound related to that of carboxylic acids?

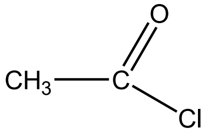
Acyl halides are compounds with the general formula where the–OH group of carboxylic acid has been substituted by a halogen atom. The acyl remaining structure is represented as:

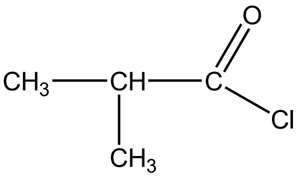

Acyl group

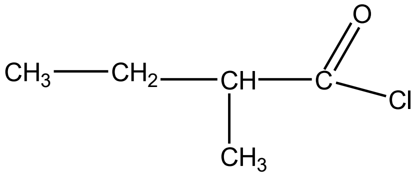

Acyl chloride

They are named in the same way as carboxylic acids where the suffix'-ic acid' of the acid is replaced by 'ylchloride'. Like in carboxylic acids, in acyl chlorides side branches are given positions by starting from the acyl functional group.

Examples:


Ethanoyl chloride
(acetyl chroride)


2 -methylpropanoyl chloride


2 -methylbutanoyl chloride

C_6H_5COCl: benzoylchloride

Their isomers can be chain isomerism, positional isomerism and functional isomerism with chloro aldehydes and ketones, alcohols with double bond C=C and chlorine as a substituent, cyclic ethers with chlorine.

Acyl chlorides have not many applications in our everyday life, but industrially they are used in synthesis of perfumes and nylons, which are polymers of high importance in textile industry. They can also be used in pharmaceutical industries to synthesize drugs with aromatic ester or amide functional groups like aspirin or paracetamol.

APPLICATION ACTIVITY 13.1.2

1. Draw structures for the following.
   a) Propanoyl chloride
   b) Butanoyl chloride
   c) 4-Methylpentanoyl chloride
2. Answer by True or False. Also give relevant explanations for your answer in each case.
   a) In naming acyl chlorides, side branches are given positions on the main chain from the opposite extremity to the acyl chloride functional group.
   b) Acyl chloride can show optical isomerism.
3. Name this compound: CH_3-$C(CH_3)_2CH_2COCl$

13.2. Physical properties and uses of carboxylic acids and physical properties of acyl chlorides

13.2.1 Physical properties of carboxylic acids

ACTIVITY 13.2.1

1. Imagine a scenario of two balls tied together by a metallic wire and other two balls attached to one another by a thin banana leaf rope. If you are asked to separate them by breaking what ties them together; explain in which case it will require much energy.
2. Use a diagram to explain the type of intermolecular forces that hold molecules of carboxylic acids together.
3. How do you compare the melting and boiling points of carboxylic acids and alcohols which have the same number carbon atoms? From your research give supporting examples with relevant experimental values.

a. Physical state

Many carboxylic acids are colorless liquids with disagreeable odors. Aliphatic carboxylic acids with 5 to 10 carbon atoms are all liquids with a "goaty" odors (odor of cheese). These acids are also produced by the action of skin bacteria on human sebum (skin oils), which accounts for the odor of poorly ventilated storerooms. The acids with more than 10 carbon atoms are wax-like solids, and their odor diminishes with increasing molar mass and resultant decreasing volatility. Anhydrous acetic acid freezes at (17°C) slightly below ordinary room temperature, reason why it is called glacial acetic acid (Figur14.2). But a mixture of acetic acid with water solidifies at much lower temperature.

Figure 13.2. Glacial ethanoic acid at 17^{0}C

b. Melting and boiling point

Carboxylic acids show a high degree of association through hydrogen bonding. Because of this, they have high melting and boiling points compared to other organic compounds of the same mass or number of carbon atoms.

Table 13.3. Comparison of melting and boiling points of carboxylic acids and alkanes

Formula	Molar mass (g/mol)	Melting point (^{0}C)	Boiling point (^{0}C)
HCOOH	46	8	100.5
$CH_3CH_2CH_3$	44	-190	-42
CH_3COOH	60	17	118
$CH_3CH_2CH_2CH_3$	58	-138	-0.5

Carboxylic acids have high melting and boiling points because their hydrogen bonds enhance the possibility of bringing two acid molecules together by forming a kind of **dimer**.

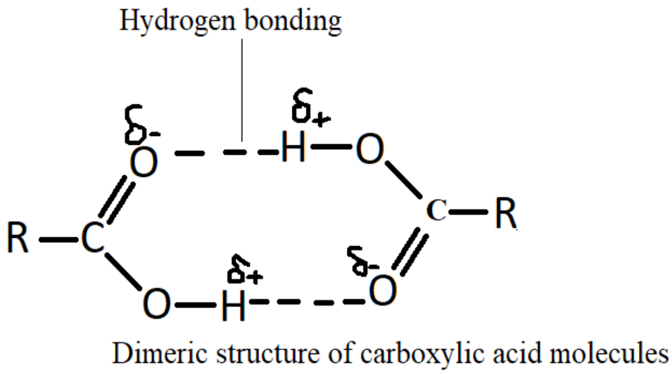


Figure 13.3. Carboxylic acids form hydrogen bonds in a dimeric structure

c. Solubility

The carboxyl group readily engages in hydrogen bonding with water molecules (Figure 13.4). The acids with one to four carbon atoms are completely miscible with water. Solubility decreases as the carbon chain length increases because of increasing of the non-polar hydrocarbon chain which is insoluble in water. Hexanoic acid $CH_3(CH_2)_4COOH$ is slightly soluble in water. Palmitic acid $CH_3(CH_2)_{14}COOH$, with its large non polar hydrocarbon part, is essentially insoluble in water. The carboxylic acids generally are soluble in organic solvents such as ethanol, toluene, and diethyl ether.

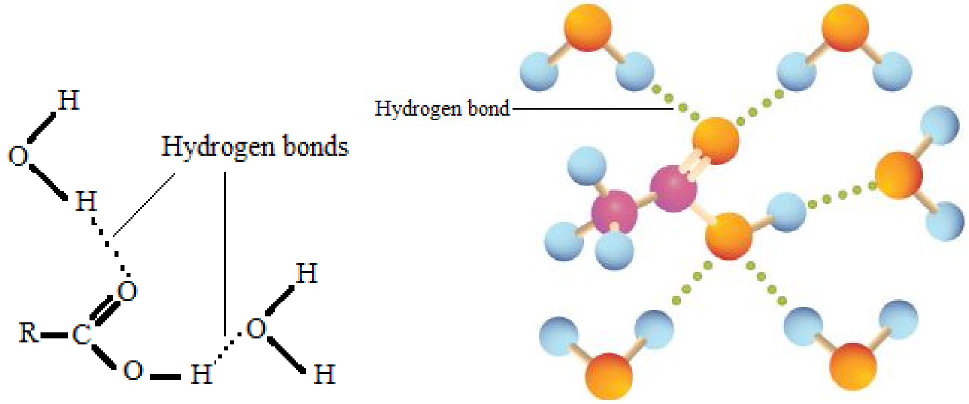


Figure 13.4. Carboxylic acids form hydrogen bonds with molecules of water

13.2.2.Physical properties of acyl chlorides

ACTIVITY 13.2.2

Use the information about the structure and intermolecular forces to compare the physical properties (solubility, melting and boiling points) of carboxylic acids and acyl chlorides.

a. Appearance

Acyl chlorides are colourless fuming liquids. Their characteristic strong smell is caused by hydrogen chloride gas that is produced when they get in contact with moisture . For example, the strong smell of ethanoyl chloride is a mixture of vinegar odour and the acrid smell of hydrogen chloride gas.

b. Solubility

Acyl chlorides are slightly soluble in water due to their small dipole that can interact with the polarity of water molecule. They cannot be said to be soluble in water because they readily react with water. It is impossible to have a simple aqueous solution of acyl chlorides, rather we have the products of their reaction with water.

c. Boiling and melting points

Acyl chloride molecules interact by Van der Waals forces whose strength increases with the increase in molecular masses of the compounds.

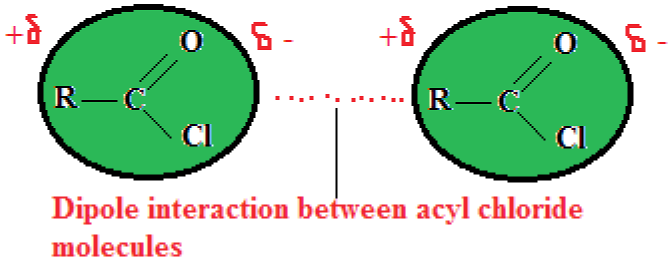


Figure 13.5. Intermolecular forces between molecules of acyl chlorides

The boiling and melting points of acyl chlorides increase as their molecular masses rise. They have lower boiling and melting points than alcohols and carboxylic acids of the same number of carbon atoms, because they lack hydrogen bonds.

APPLICATION ACTIVITY 13.2

.I.Carboxylic acids

1. How do you compare the melting points of hexadecanoic acid and octadecanoic acid?

2. Butanoic acid has molar mass of 88 and pentan-2-one has a molar mass of 86. Which of these compounds has the higher boiling point? Explain.

3. Would you expect butyric acid (butanoic acid) to be more soluble than butan-1-ol in water? Explain.

II.Acyl chlorides

4. When you mix ethanoyl chloride with water, a clear solution is obtained; yet it is meaningless to talk about the solubility of ethanoyl chloride in water? Explain why.

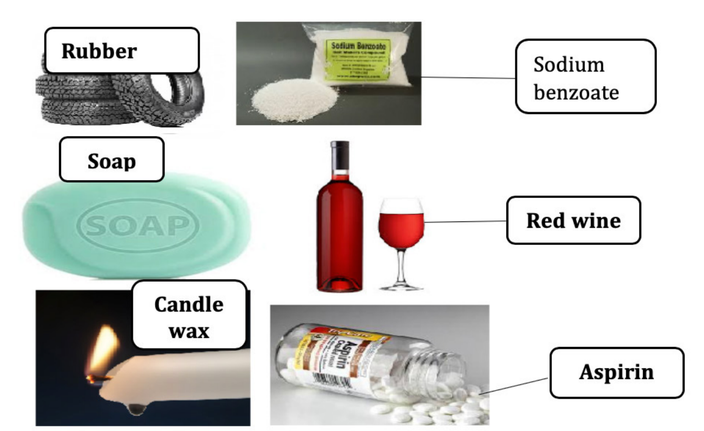
5. Ethanoyl chloride is a colourless fuming liquid. Why does it fume?

6. What types of intermolecular forces are there in liquid ethanoyl chloride? How do these forces account for the boiling points of acyl chlorides?

13.2.3. Uses of carboxylic acids

ACTIVITY 13.2.3

Observe the following images and answer the questions related.



a) Do you find any relationship between carboxylic acids and the manufacture process of each the substances represented in the above images?

b) Suggest other instances where carboxylic acids are used in our daily life.

Carboxylic acids occur naturally in fats, acidic dairy and citrus fruits, and among their most important uses are:

Food industry and nutrition

- Food additives: Sorbic acid, benzoic acid, etc.
- Main ingredient of common vinegar (acetic acid).
- Elaboration of cheese and other milk products (lactic acid).

Pharmaceutical industry

- Antipyretic and analgesic (acetylsalicylic acid or aspirin).
- Active in the process of synthesis of aromas, in some drugs (butyric or butanoic acid).
- Antimycotic and fungicide (caprylic acid and benzoic acid combined with salicylic acid).
- Active for the manufacture of medicines based on vitamin C (ascorbic acid).

- Manufacture of some laxatives (hydroxybutanedioic acid).

Other industries

- Manufacture of varnishes, resins and transparent adhesives (acrylic acid).
- Manufacture of paints and varnishes (linoleic acid).
- Manufacture of soaps, detergents, shampoos, cosmetics and metal cleaning products (oleic acid).
- Manufacture of toothpaste (salicylic acid).
- Production of dyes and tanned leather (methanoic acid).
- Manufacture of rubber (acetic acid).
- Preparation of paraffin candles (stearic acid)

APPLICATION ACTIVITY 13.2.3

Make a research and explain 5 uses of carboxylic acids either in our daily life or in industries.

13.3. Acidity of carboxylic acids.

ACTIVITY 13.3

1. What characterizes acidic substances?

2. Explain what is meant by;

   a) Arrhenius acid.

   b) Bronsted-Lowry acid

   c) Lewis acid

3. Explain which acid-base theory explains properly the acidity of carboxylic acids.

4. Experiment

To test for the acidic properties of carboxylic acids.

Materials

- Test tubes and test tube rack
- Droppers

Chemicals

- Ethanoic acid/ vinegar (0.1M)
- Distilled Water
- Dilute HCl (aq) solution (0.1M)
- Methyl orange indicator/ Blue litmus paper/Red litmus paper

Procedure

1. Take about 5cm^3 of distilled water in a test tube

2. Test it with the indicator provided and note your observations.

3. To 5cm^3 of distilled water add 2-3 drops of ethanoic acid and note your observations; repeat the same test in steps 1 to 3 for HCl (aq).

4. Analyze your findings and try to draw relevant conclusions.

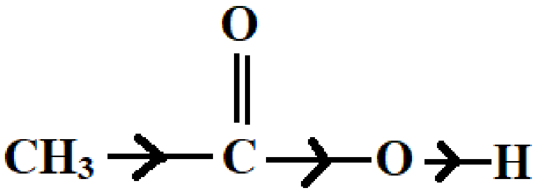
Solutions of carboxylic acid turn blue litmus paper red; they do not change the color of red litmus paper; therefore, they are acids as other mineral acids such as HCl (aq).

Organic or carboxylic acids are weak acids in opposition to some mineral acids such as hydrochloric acids which are strong acids. According to Arrhenius' theory of acids and bases, strong acids dissociate completely in water to give hydrogen ion, $H^+(aq)$ or H_3O^+, whereas weak acids dissociate partially. The hydrogen ion released combines with a water molecule to form H_3O^+ a hydrate positive ion called hydronium, ion.

$$\underset{\text{acid}}{\text{R-COOH(aq)}} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{base}}{\text{R-COO}^-(aq)} + \underset{\text{acid}}{H_3O^+(aq)}$$

The carboxylate ion formed by ionization of the acid is more stable than the acid because it has many resonance structures.

Ethanoic acid is a weaker acid than methanoic because its methyl group has a **positive inductive effect**; that is to mean that it pushes electrons towards the O-H bond hence make hydrogen ion stable and not easily leaving.



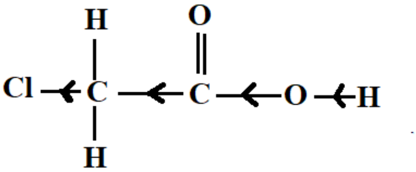
$$CH_3 \rightarrow \overset{\overset{\displaystyle O}{\|}}{C} \rightarrow O \rightarrow H$$

Positive inductive effect of alkyl group

The greater the number of such groups, the greater the effected and therefore the weaker will be the acid.For example, 2,2-dimethylpropanoic is weaker than 2-methylpropanoic acid which is in turn weaker than propanoic.

The same rule applies to the increase in the length of the alkyl group chain. Butanoic acid is a weaker acid than propanoic acid which shows that the acidity strength decreases as the alkyl chain increases.

On the other hand, when an electron withdrawing group (a group with a **negative inductive effect**) is present, the opposite effect is observed. For example, chloroethanoic acid is a stronger acid than ethanoic acid. This is because chlorine being electronegative, will withdraw electron towards itself thus reducing the electron density around the O-H bond thus weakening it. It causes O-H bond to easily break, and the concentration of hydrogen ions will be high in the solution.



Negative inductive effect of chlorine

The more the number of groups with negative inductive effect, the greater is the effect and hence the more acidic will be the solution. Trifluoroacetic acid is more acidic than trichloroacetic, dichloroacetic, chloroacetic and acetic acid because fluorine is more electronegative than chlorine and hydrogen. It will strongly withdraw electron towards itself, hence makes easier for the proton to leave.

It must also be noted that the further away the electronegative element, the less the effect. For example, 3-chlorobutanoic acid is therefore a weaker acid than 2-chlorobutanoic acid.

APPLICATION ACTIVITY 13.3

1. Explain the reasons of the following observations:
    a) Propanoic acid releases more hydrogen ions in solution than 2-methyl propanoic acid.
    b) Fluoroethanoic acid is stronger than ethanoic acid.
2. Consider the molecules in the following table, analyze them and rank the following acids according to increasing order of their acidity strength as 1, 2, 3 and 4. Give reasons for your answer.

Molecule	Ranking
2-chlorobutanoic acid	
3-chlorobutanoic acid	
4-chlorobutanoic acid	
Butanoic acid	

13.4. Preparation methods carboxylic acids and acyl halides.

13.4.1.Preparation methods of carboxylic acids

ACTIVITY 13.4.1

1. We normally prepare or manufacture substances because we need them in our daily life to solve some of the problems we have. Are carboxylic acids useful to us?

2. Now that we accept that carboxylic acids are in the category of organic compounds that are widely used in our daily life; either in industry or in our household activities. Since they are needed, they must be obtained from somewhere.

   a) Suggest diverse ways carboxylic acids can be obtained.

   b) Describe how acetic acid that is used to make vinegar can be prepared.

Carboxylic acids are common and vital functional group; found in amino acids, fatty acids etc. and provide the starting raw material for acid derivatives such as acyl chlorides, amides, esters and acid anhydrides. There are several methods of preparation of carboxylic acids where the most common are discussed in this section.

a. From primary alcohols and aldehydes

Different carboxylic acids can be prepared by oxidation of either primary alcohols or aldehydes. In the process, the mixture of alcohol is heated under reflux with an oxidizing agent such acidified potassium permanganate or potassium dichromate. Primary alcohols are first oxidized to aldehydes then further oxidation of aldehydes produces carboxylic acids.

$$R-CH_2OH \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+(aq)} R-CHO \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+(aq)} R-COOH$$

$$CH_3-CH_2OH \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+(aq)} CH_3-CHO \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+(aq)} CH_3-COOH$$

In fact, when excess oxidizing agents like acidified $K_2Cr_2O_7$ or $KMnO_4$ are used, primary alcohols are oxidized to carboxylic acids.

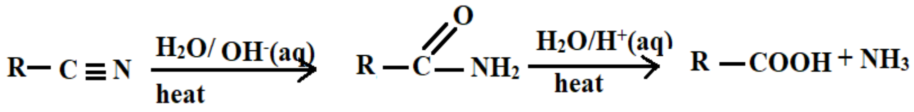
b. Hydrolysis of acid nitriles and amides with acid or alkali

When nitriles are hydrolyzed by water in acidic medium and the mixture is submitted to heat, the reaction yields carboxylic acids.

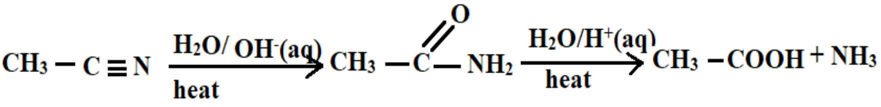
$$R-C\equiv N \xrightarrow[\text{heat}]{H_2O/H^+(aq)} R-COOH + NH_3$$

$$CH_3-C\equiv N \xrightarrow[\text{heat}]{H_2O/H^+(aq)} CH_3-COOH + NH_3$$

The preparation of carboxylic acids from nitriles passes through formation of amides as an intermediate products and further hydrolysis leads to the formation of carboxylic acids.



$$R-C\equiv N \xrightarrow[\text{heat}]{H_2O/\,OH^-(aq)} R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\text{heat}]{H_2O/H^+(aq)} R-COOH + NH_3$$



$$CH_3-C\equiv N \xrightarrow[\text{heat}]{H_2O/\,OH^-(aq)} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\text{heat}]{H_2O/H^+(aq)} CH_3-COOH + NH_3$$

c. From dicarboxylic acid

Monocarboxylic acids can be prepared by heating carboxylic acids which have two carboxylic functional groups attached to the same carbon atom.

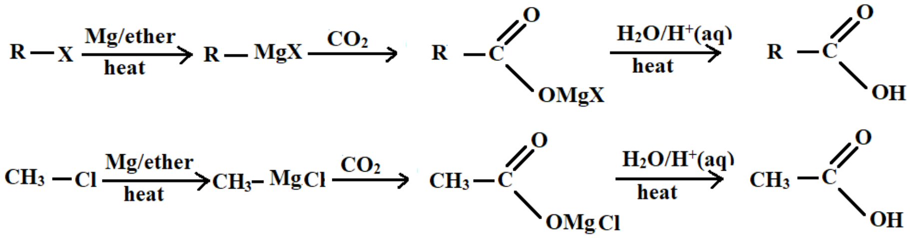
$$HOOC-COOH \xrightarrow{\text{heat}} HCOOH + CO_2$$

$$HOOC-CH_2-COOH \xrightarrow{\text{heat}} CH_3-COOH + CO_2$$

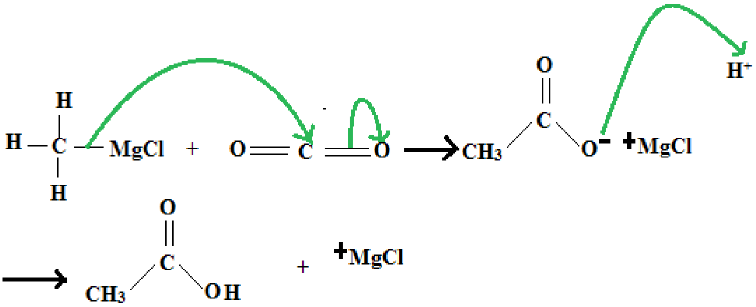
Note that the reaction is used to reduce length of the carbon chain. The mono carboxylic acid prepared has one carbon atom less than the starting dicarboxylic acid.

d. From organomagnesium compounds (Carboxylation reaction)

Grignard reagents react with carbon dioxide gas, and when the intermediate compound formed is hydrolyzed it finally forms carboxylic acid.



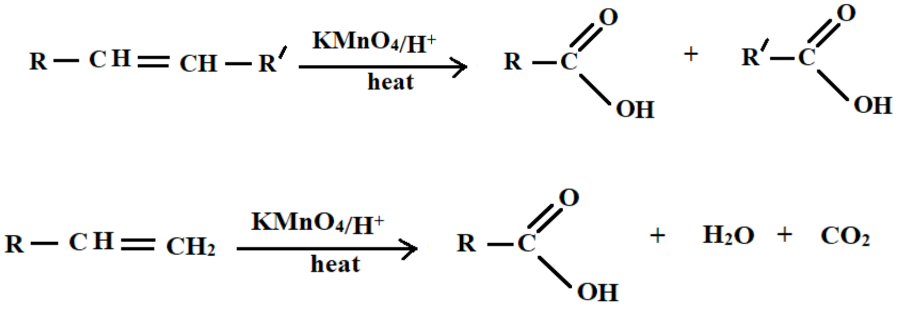
Mechanism:



It should be noted that this method of preparation yields a carboxylic acid with one carbon atom more than the starting alkyl halide.

e. From alkenes (Oxidation of alkenes)

Carboxylic acids are also obtained by heating alkenes with concentrated acidified potassium permanganate. The reaction unfortunately forms a mixture of compounds that must be later separated.



Note that the hydrolysis of carboxylic acid derivatives such as amides, esters, acyl chlorides and acid anhydrides also produce the corresponding acids.

f. Laboratory preparation of acetic acid

Acetic acid can be prepared in the laboratory.

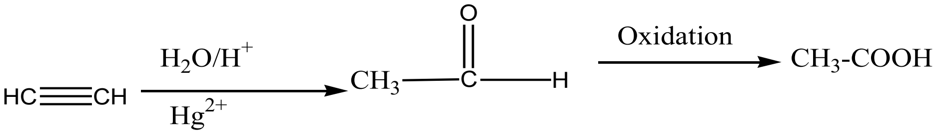
- From its salt:

$CH_3COONa + H2SO4 \xrightarrow{\triangle} CH_3 - COOH + NaHSO_4$

Or

$2CH_3COONa\,(aq) + H_2SO_4(aq) \rightarrow 2CH_3COOH(aq) + Na_2SO_4(aq)$

- From acetylene:



- From ethanol:

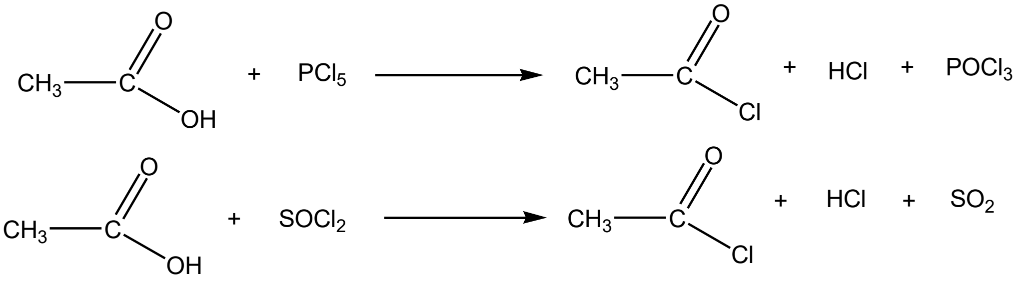
$CH_3\text{-}CH_2OH + O_2 \rightarrow CH_3\text{-}COOH + H_2O$

APPLICATION ACTIVITY 13.4.1

1. Describe how the following interconversions can be carried out in one or more than one steps:
   a) Propanoic acid from monobromoethane
   b) Propanoic acid from ethanol
2. When banana wine (the wine obtained locally from the fermented juice from ripe banana) stays for some time its taste becomes sour. Explain these observations by a chemical reaction.

13.4.2. Preparation methods of acyl halides.

Carboxylic acids react with halogenating agents such as PCl_5,$SOCl_2$,PCl_3 to produce acyl chloride.



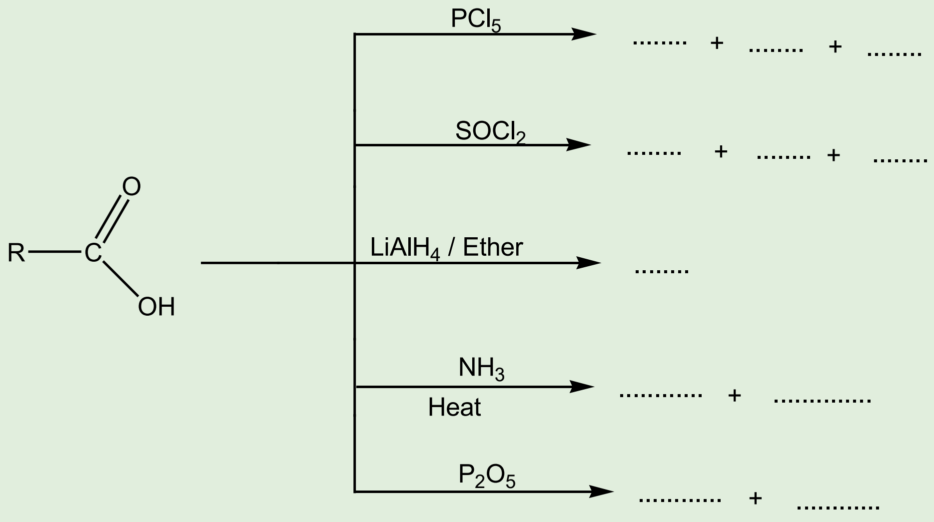
13.5. Reactions of carboxylic acids

ACTIVITY 13.5

1. Carboxylic acids are starting materials for the synthesis of many other important organic substances such as esters used to make sweets and wines, acetic anhydrides used to make aspirin, etc. Explain the reason why it is possible to transform carboxylic acids into other compounds. What property of carboxylic acids is exploited in this regard?

2. Fatty acids are some of the raw materials used in the manufacture of soaps. How is it possible, to convert fatty acid into these important cleansing agents?

3. Complete the following reaction:



3. Experiment

Materials

- 2 Test tubes
- Rubber stopper
- A delivery tube

Chemicals:

- Sodium carbonate
- Acetic acid
- Lime water

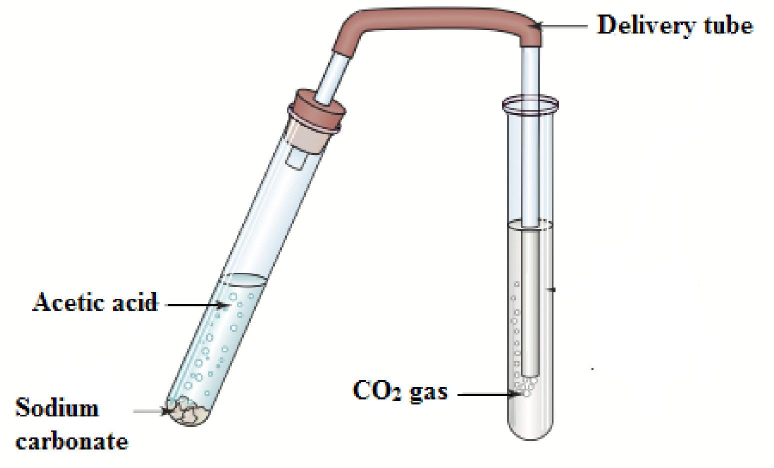
Procedure

1. Put an end full spatula of sodium carbonate in a test tube.

2. Add about 10cm^3 of acetic acid solution.

3. Immediately close it with a rubber stopper joined to a delivery tube, already immersed in lime water, as in the diagram below.

4. Note all your observations.



Write all equations of the reactions involved in this experiment.

13.5.1 Reaction involving hydrogen atom of the carboxyl group

Carboxylic acids react with reactive metals, metal oxide, sodium carbonate, sodium hydrogen carbonate, NH_4OH and alkalis. These are typical reactions of acids.

1. Reaction with metals

Carboxylic acids react with reactive metals to form salts of carboxylic acids and hydrogen gas. For example, acetic acid reacts with sodium metal to form sodium acetate and hydrogen gas.

$$2RCOOH\,(aq) + 2Na\,(s) \longrightarrow 2RCOO^-Na^+\,(aq) + H_2\,(g)$$

$$2CH_3COOH\,(aq) + 2Na\,(s) \longrightarrow 2CH_3COO^-Na^+\,(aq) + H_2\,(g)$$

2. Reaction with alkaline solutions

Strong alkalis such as sodium hydroxide react with carboxylic acids by the process of neutralization that forms salts of carboxylic acids and water.

$$RCOOH\,(aq) + NaOH(aq) \longrightarrow RCOO^-Na^+\,(aq) + H_2O\,(l)$$

$$CH_3COOH\,(aq) + NaOH\,(aq) \longrightarrow CH_3COO^-Na^+\,(aq) + H_2O\,(l)$$

3. Reaction with sodium carbonate and sodium hydrogencarbonate

Like mineral acids, carboxylic acids react with carbonates and bicarbonates of metals to form salts, water and carbon dioxide. The reaction is followed by observable effervescence (bubbles of carbon dioxide in the solution) as illustated in figure 13.6.

$$\mathbf{2R\text{-}COOH\,(aq) + Na_2CO_3\,(aq) \longrightarrow 2R\text{-}COONa\,(aq) + H_2O\,(l) + CO_2\,(g)}$$

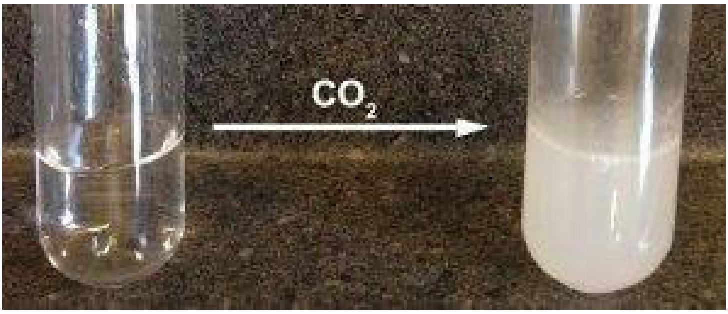
Example:

$$\mathbf{CH_3\text{-}COOH\,(aq) + Na_2CO_3\,(aq) \longrightarrow CH_3\text{-}COONa\,(aq) + H_2O\,(l) + CO_2\,(g)}$$

Figure 13.6. Effervescence when acetic acid is added to sodium carbonate

The reaction of acids with carbonates is the basis for the chemical test of carboxylic acid functional group and it can be used to distinguish carboxylic acids from other functional groups in qualitative analysis.

Carbon dioxide produced is also tested by lime water and it turns lime water milky (Figure 13.7)



Lime water before

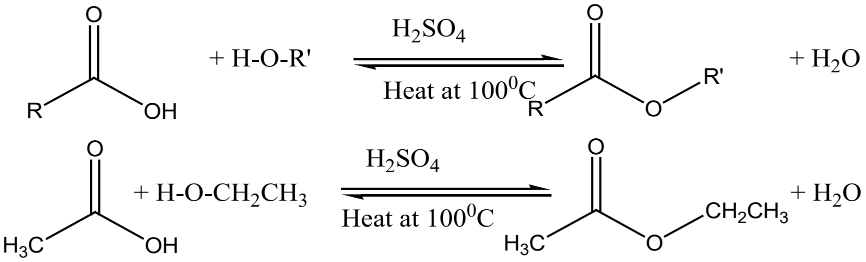
After CO_2 is buble through

Figure 13.7. Testing carbon dioxide by lime water

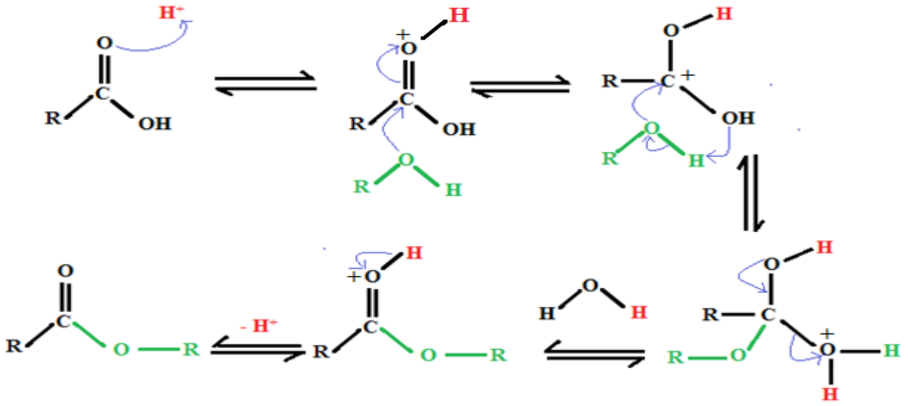
13.5.2. Reaction involving the whole group –O-H

1°. Reaction with alcohols (Esterification)

Carboxylic acids react with alcohols to form esters and the reaction is known as esterification reaction. The reaction requires heating under reflux and in the presence of concentrated H_2SO_4. It is a reversible reaction because all the reactants are not converted into products.



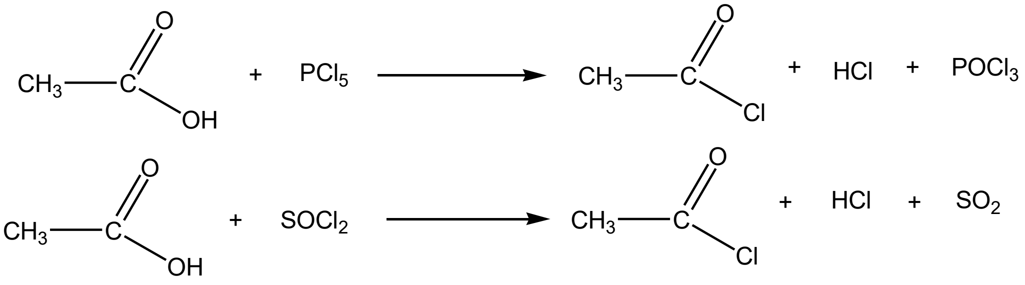
The mechanism of esterification reaction:



It is noted that the oxygen atom in the ester formed comes from the alcohol and the one in water is from the acid. In the mechanism of esterification, the acid loses -OH group while the alcohol loses H-atom.

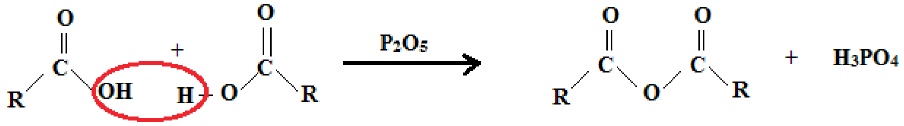
2⁰. With phosphorus halides, thionyl chloride

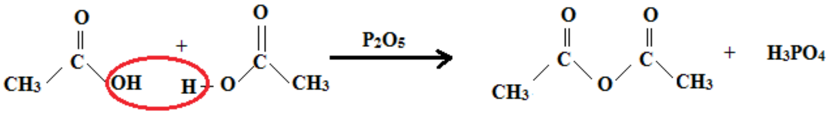
Due to the presence of -OH group in carboxylic acids, like alcohols, they react with PCl_5 and $SOCl_2$ and the organic product is acyl chloride. This is the basis reaction of the synthesis of acyl chlorides from carboxylic acids.



3. Reaction with phosphorous pentoxide

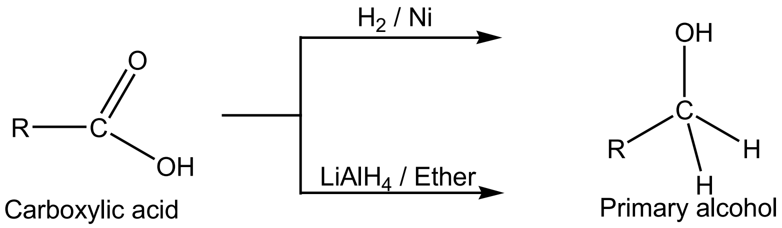
Carboxylic acids molecules can be dehydrated by phosphorous pentoxide to yield corresponding acid anhydrides.





13.5.3. Reduction of carboxylic acids

Carboxylic acids are reduced to primary alcohols on treatment with reducing agent such as $LiAlH_4$ in dry ether or by use of hydrogen in the presence of Ni catalyst. The reduction does not form aldehyde as an intermediate product, like in oxidation of primary alcohols.



APPLICATION ACTIVITY 13.5

1.Explain the following observations:

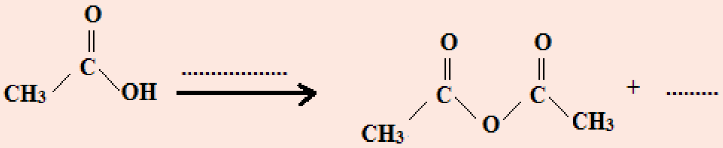
a) Sodium hydroxide dissolves in acetic acid, but it does not dissolve in ethanol

b) A student took a $10cm^3$ of $0.1moldm^{-3}$potassium hydroxide solution, she/he then added 2 drops of phenolphthalein and the solution turned purple. When she/he added $10cm^3$ of $0.1moldm^{-3}$ ethanoic acid the mixture of solutions turned colorless.

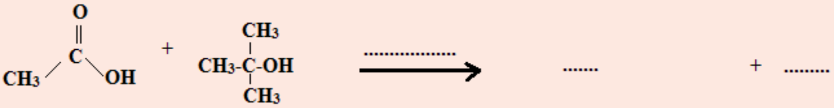
2. Complete the following reactions:

a) CH_3CH_2COOH + … → CH_3CH_2COCl +….

b)



c)



3. Describe the chemical test that can be used to distinguish the following pairs of compounds:

a)Ethanoic acid and 2-methylpropan-2-ol

b)Ethanoic acid and phenol

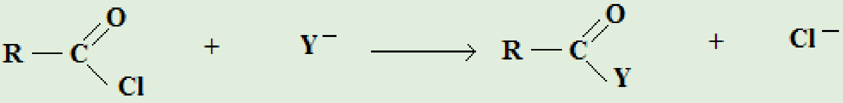
13.6. Reactions of acyl chlorides with water, strong base, Grignard reagents, alcohols, ammonia and amines, salts of carboxylic acid and reduction of acyl halide

ACTIVITY 13.6

1. Acyl chlorides mostly react when there is a substitution of chloride ion by another negatively charged ion or molecule with a free lone pair of electrons.

a) How is this type of reaction mechanism called?

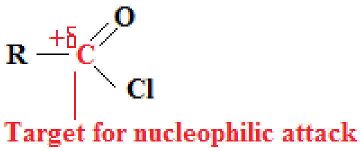
b) Given the following acyl chloride molecule and a reagent with a substituting group Y-. Propose the appropriate mechanism for this reaction.



Explain the chemical properties that Y^- should possess so that it can be a good substituent of Cl^- from the acyl chloride.

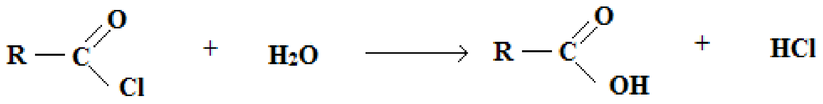
The chemistry of acyl chlorides is dominated by nucleophilic substitution, where a stronger nucleophile replaces chlorine atom of acyl chloride. They undergo nucleophilic substitution reactions more easily than alkyl halides and carboxylic acids because the nucleophile targets the carbon which is deficient in electrons and -Cl is better leaving group than -OH group.

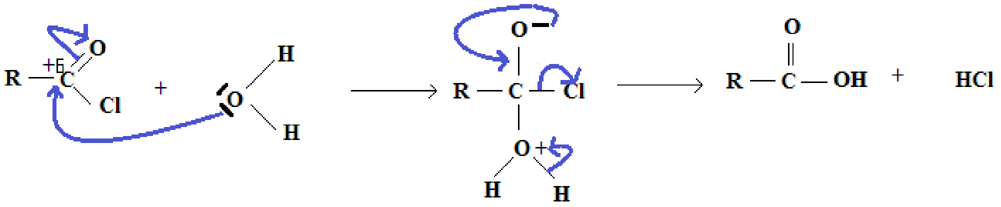
The common reactions of acyl chlorides include reactions with water, alcohols and ammonia and amines. These reactants have a very electronegative element that has a free lone pair of electrons to act as a nucleophile.



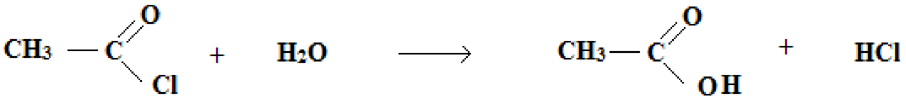
Reaction with water (hydrolysis)

Acyl chlorides violently react with water to form corresponding carboxylic acids and in each case white acidic fumes of hydrogen chlorides are also observed (Figure 13.8).





Example:



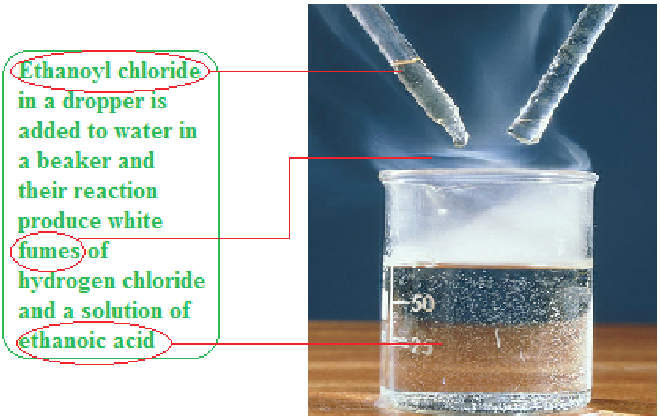
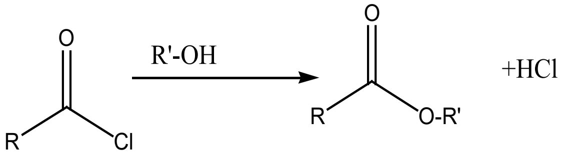


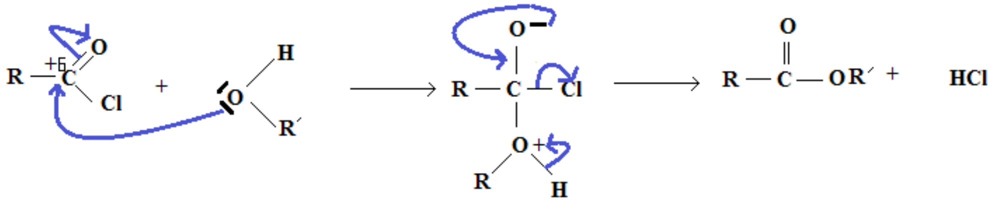
Figure 13.6.a. Reaction of ethanoyl chloride with water produces white fumes

Reaction with alcohols

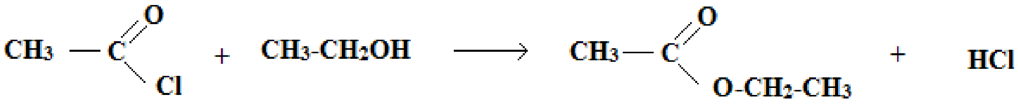
They react with alcohol to produce esters with high yields than esterification of an alcohol and carboxylic acid, since Cl-atom in acyl chloride is a better leaving group than O-H for the case of carboxylic acid. The difference in electronegativity is the main reason for this observation.



Mechanism



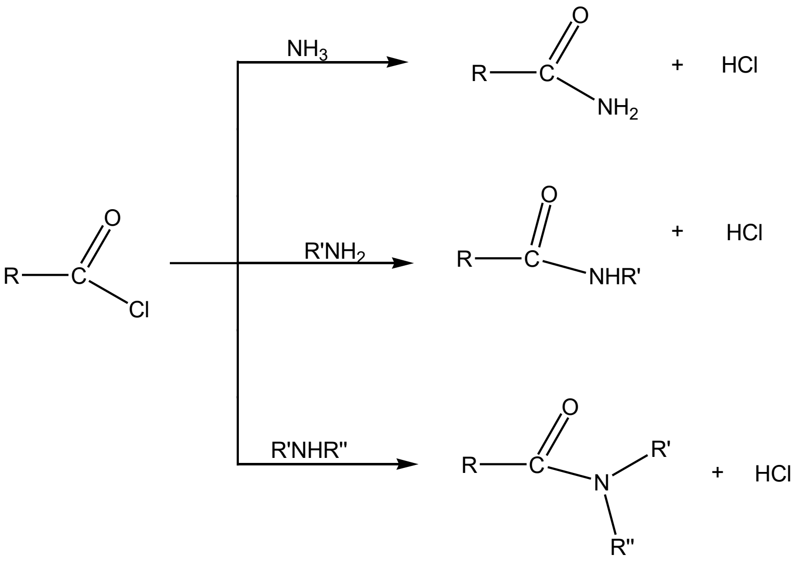
Example:



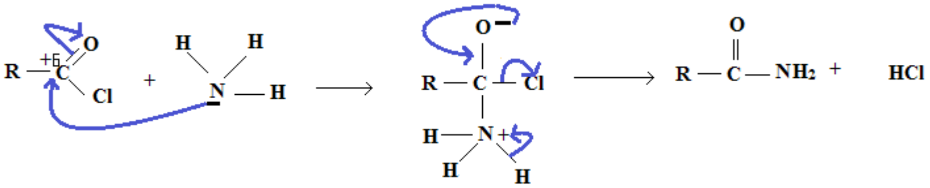
In addition, this reaction is very important in preparation of aromatic esters which would not be possible by the reaction of phenol with carboxylic acids.

Reaction with ammonia and amine

Acyl chlorides react with ammonia and amines to yield amides. Ammonia, primary amines and secondary amines form primary amides, secondary amides and tertiary amides respectively.



Mechanism:



APPLICATION ACTIVITY 13.6

1. Explain if tertiary amines can react with acid chloride. If it is possible what would be the expected product.
2. Acyl chlorides are acid derivatives and they contain an acyl group. Using ethanoyl chloride as an example, explain what is meant by the terms acid derivative.
3. Explain these observations:
   a) Ethanoyl chloride is more reactive towards water than is chloroethane.
   b) Acyl chlorides are more reactive by nucleophilic substitution than carboxylic acids.

SKILLS LAB 13

1. A student was given two samples of organic compounds A and B. Both are colourless liquids in transparent glass bottles. The student was asked to use the provided chemicals to distinguish the two compounds. When she added drops of sodium carbonate solution to both samples in separate test tubes, she observed effervescence for B and there was no effervescence for A. She then added few drops of water to both liquids; she observed white fumes with irritant gas with A, while on B there was no observable change. Identify the two compounds by précising the functional group to which A and B belong to.

2. Copy the following table and complete it by writing the structural formulae for ethanol and ethanoic acid.

Ethanol	**Ethanoic acid**

a. Describe a simple chemical test that could be used to distinguish ethanol and ethanoic acid.

b. Name the functional group produced when ethanol reacts with ethanoic acid and state how it could be tested?

c. What are the conditions needed to carry out the reaction in b?

3. Take a wine bottle such as local banana beer and leave it open to air during one week .

a. Taste it. What do you feel after tasting it?

b. Explain this statement and use the equation of reaction that takes place if any.

c. What would you expect to happen to the PH of the wine over a number of days?

END UNIT ASSESSMENT 13

Multiple choice questions

1. Choose the correct answer from the four options given. CCl_3COOH is the strongest
   a. Acid
   b. Base
   c. Alkali
   d. Compound
2. The reaction of acyl chlorides with alcohols and phenols will give
   a. Esters
   b. Ketones
   c. Aldehydes
   d. Haloalkanes
3. Acyl chlorides are made by reacting carboxylic acids with
   a. PCl_5,
   b. $PCl_{3,}$
   c. $SOCl_2$,
   d. All of them
4. Vinegar contains a carboxylic acid known as
   a. Citric acid
   b. Ethanoic acid
   c. Acetic acid
   d. Both b and c

5. For synthesis of carboxylic acid intermediate product needed is

a. Aldehyde

b. Aryls

c. Benzene

d. Carboxylic acid,

Open questions

6. Arrange the compounds below in increasing order of boiling point:

Propanoic acid, Propanal, Propan-1-ol . Explain your answer

7. Draw the isomer that is:

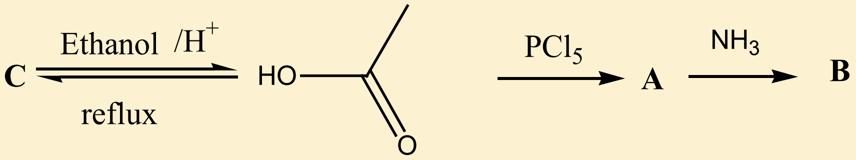
a) The most acidic of dichlorobutanoic acid

b) The least acidic of fluoropentanoic acid

8. Naturally occurring fats and oils are the esters of acids with an even number of carbon atoms. Acids with an odd number of carbon atoms are very rare. Suggest a method of increasing the length of an aliphatic acid chain by one carbon atom. More than one steps may be needed.

$$R\text{-}CH_2\text{-}CO_2H \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}CO_2H$$

9. Study the reaction chart flow given below and answer related questions



a) Give the names and structures of the compounds A, B, and C

b) Outline the appropriate mechanism for the reaction that converts A into B.

10. Given the following boiling points: 141^{0}C, 186^{0}C, 118^{0}C, 299^{0}C, match them with the compounds in the table below.

CH_3—CO_2H	
$CH_3(CH_2)_{10}$—CO_2H	
$CH_3(CH_2)_3$—CO_2H	
CH_3CH_2—CO_2H	

11 Starting from any aliphatic carboxylic acid, how could you make its derivatives.

a) An acyl chloride

b) An acid anhydride

In each case, give the necessary conditions and equations for the reaction.

12. Describe how the following interconversions can be carried out. In each case, indicate the appropriate reagents and conditions.

a) Propan-1-ol from Propanoic acid

b) Acetic anhydride from acetic acid

UNIT
14

ESTERS, ACID ANYDRIDES, AMIDES AND NITRILES

Key unit competency: Relate the functional groups of esters, acid anhydrides, amides and nitriles to their reactivity, preparation methods and uses.

INTRODUCTORY ACTIVITY

The development of organic chemistry has led scientists to the production of new substances and materials that are necessary in our everyday life which could not be provided by our natural environment. Others were produced to satisfy the high demand of consumers which cannot be assured by natural products only. Analyze the items presented below and answer the questions listed down.

1. What kind of textile is used to make umbrellas? How did scientists make this kind of textiles?

2. One of the substances used to improve soil fertility so as to ensure food security is urea? How is it synthesized?

3. Why is it possible to make artificial drinks with flavours of natural fruits?

4. How are pain killer drugs manufactured?

5. What kinds of substances provide perfumes with their fragrances?

14.1. Structure and nomenclature of esters

ACTIVITY 14.1

1. The compounds listed below contain acid derivatives and other organic molecules. Classify them in the following table.

   $CH_3CH_2CH_2COOH$, $CH_3CH_2CH_2COOC(CH_2)_2CH_3$, $CH_3CH_2CH_2CONH_2$, $CH_3CH_2CH_2CONHCH_3$, $CH_3CH_2CH_2CONHCH_3$, $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2CH_2COH$,$CH_3CH_2COCH_3$, $CH_3CH(CH_3)CN$, $CH_3CH(CH_3)COOH$, $CH_3CHOHCH_2CH_3$.

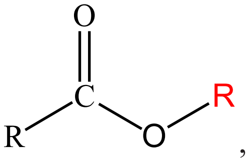
Acid derivatives	Carboxylic acids	Alcohols	Carbonyl compounds

2. Draw all possible isomers with molecular formula $C_4H_8O_2$ and label esters with letter A and acids with letter B.

14.1.1. Structure of esters

In unit 13, the reactions of carboxylic acids were discussed. The reactions of carboxylic acids produce the derivatives of acids such as esters, acid halides, acid anhydrides ,amides and nitriles.

The general molecular formula of esters is $C_nH_{2n}O_2$ and their general structural formula is: RCOOR’ or



Where R may be a hydrogen atom or an alkyl group and R may be an alkyl group or an aryl group but not a hydrogen atom. In case that R is the hydrogen atom, the compound is no longer an ester but it is a carboxylic acid.

The following Figures, 14.1 and 14.2 show models for two common esters where green spheres = Hydrogen atoms, red spheres = oxygen atoms; blue spheres = carbon atoms

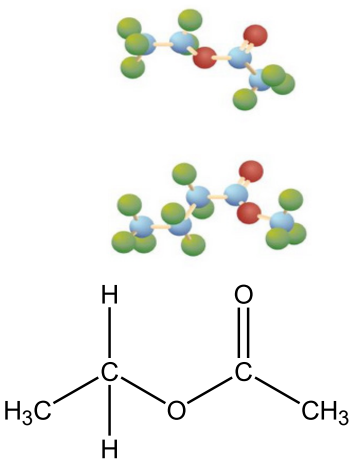


Figure 14.1. Structure of ethyl acetate

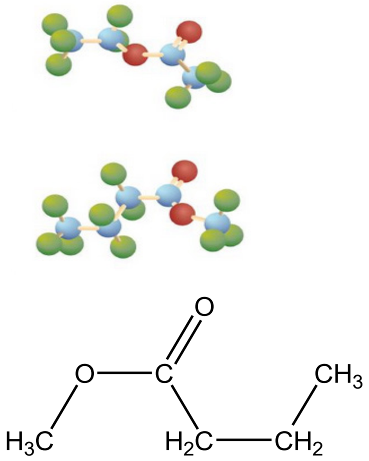
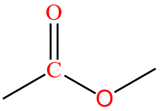


Figure14.2. Structure of methyl butanoate

The functional group of esters is 

Esters are compounds produced by the reaction involving an acid and an alcohol with the elimination of water molecule.

For example, the reaction between acetic acid and ethanol yields an ester with water.

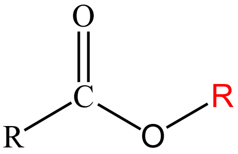
$CH_3COOH + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + H_2O$

Acetic acid ethanol ester water

Esters are known for their distinctive odor and they are commonly responsible for the characteristic of fruits aroma, flowers and fragrances. Esters are found in nature but they can be also synthesized. Both natural and synthetic esters are used in perfumes and as flavoring agents.

14.1.2. Nomenclature of esters

The nomenclature of esters follows some steps. When naming esters the alkyl group R' is named followed by the name of RCOO- group.



The group name of the alkyl or aryl portion is written first and is followed by the name of the acid portion. In both common and International Union of Pure and Applied Chemistry (IUPAC) nomenclature, the ***-ic*** ending of the corresponding acid is replaced by the suffix ***–ate***. Some examples of names of esters are given in Table 14.1.

Examples:

Table 14.1. Examples of structural formulae of some esters and their names

Structural formula	Common name	IUPAC name
CH_3COOCH_3	Methyl acetate	Methyl ethanoate
$HCOOCH_3$	Methyl formate	Methyl methanoate
$CH_3COOCH_2CH_3$	Ethyl acetate	Ethyl ethanoate
$CH_3CH_2COOCH_2CH_3$	Ethyl propionate	Ethyl propanoate
$CH_3CH_2CH_2COOCH(CH_3)_2$	Isopropyl butyrate	Isopropyl butanoate

APPLICATION ACTIVITY 14.1

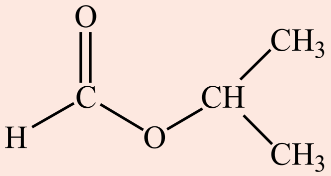
1. Name the following compounds by using the common and IUPAC names.

   a) $CH_3CH_2COOCH_3$,

   b) $CH_3CH_2COOCH_2CH_3$,

   c) $CH_3CH_2COOCH_2CH_2CH_3$

   (iv)



2. Draw the structural formulae corresponding to each of the following names.

   (a). Propyl methanoate (b) octyl ethanoate

14.2. Physical properties and uses of Esters

14.2.1 Physical properties

ACTIVITY 14.2

A. Analyzing the solubility of esters (fats and oils)

Materials and Chemicals

Cooking oil, margarine, water, ethanol, stirring rods and test tubes labeled A and B.

Procedure

1. Pour water in a test tube A and ethanol in test tube B and add some cooking oil in each test tube. Shake well to mix and record your observation.

2. Pour water in a test tube A and ethanol in test tube B and add a small piece of margarine in each test tube. Use a stirring rod to mix and record your observation.

B. Comparing boiling points of alcohols, carboxylic acids and esters

Materials and Chemicals

Propan-1-ol, propanoic acid and methyl ethanoate, test tubes, test tube holders (racks), heaters, and thermometers.

Procedure

1. Put 10 mL of each substance in a labeled test tube.
2. Boil carefully substances are volatile and flammable
3. Use a thermometer to measure the boiling point of each substance.
4. Record the results and compare them. Suggest a reason for the difference in boiling points of the three substances.

Esters are soluble in organic solvents such as ethanol and insoluble in water.

Small esters are fairly soluble in water but the solubility decreases as the length of the chain increases

Lower esters have sweet fruity smells.

Esters have lower boiling points than alcohols and carboxylic acids because they lack hydrogen bonds. A compound having hydrogen bonds has a high boiling point because, to break that bond requires higher energy.

Melting and boiling points of esters increase as the molecular mass increases.

14.2.2. Uses of Esters

Esters find various uses:

(i) They are used as organic solvents.

(ii) Due to their aroma, they are used as constituent of fragrance, essential oils, food flavoring and cosmetics.

(iii) They are used to manufacture soaps, detergents and glycerol.

(iv)They are used to provide energy in the body.

(v) Polyesters are used to produce plastics etc.

APPLICATION ACTIVITY 14.2

1. Discuss the solubility of esters
2. State one industrial and one biological use of esters.
3. Two compounds A and B of molecular formula C2H4O2 were analyzed to compare their relative boiling points. Compound A had lower boiling point than compound B
   a) Draw the structural formula of each compound.
   b) Identify the relationship that exists between compounds A and B. Explain your reasoning.

14.3. Preparation and chemical properties of esters

ACTIVITY 14.3

1. Perfumes are manufactured using flowers and fruit essential oils to give them pleasant fragrances. Each essential oil has a specific odour. Suppose that you are working in a perfume's factory as a chemist, how can you proceed to produce perfumes of new odours? Suggest one physical and one chemical method.
2. Ethyl propanoate is used to make juices with a pineapple flavor. State the organic compounds used to synthesize each ester. Write down the reaction equations showing their synthesis.

3. Using your research on internet and reading books, make a summary of each of the following terms:

   a. Reduction of esters

   b. Hydrolysis of esters

   c. Alkaline hydrolysis of esters

   d. Trans-Esterification

   e. Comparison of the reactivity of esters, acid chlorides and acid anhydrides

4. Give an example of an equation for each of the processes in 3.

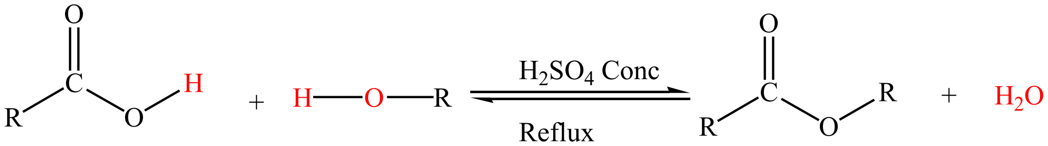
5. Express the technical name given to the process in 3.c.

14.3.1. Preparation of Esters

The preparation of esters involves different types of reaction such as esterification, reaction of an acid chloride with an alcohol and the reaction of acid anhydrides with alcohols.

1. Esterification reaction

Esters can be produced by a reaction between alcohols and carboxylic acids in strong acidic medium acting as a catalyst. The acid is commonly a concentrated sulphuric acid, under reflux (Figure 14.1). The reaction is generally called "Esterification" (a condensation reaction which involves the addition of the alcohol and acid molecules followed by an elimination of a water molecule).



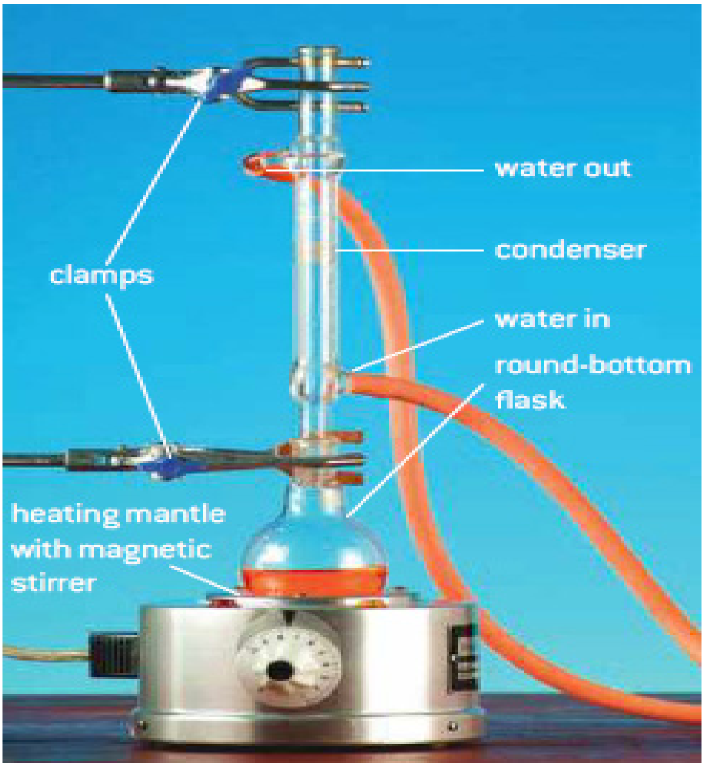
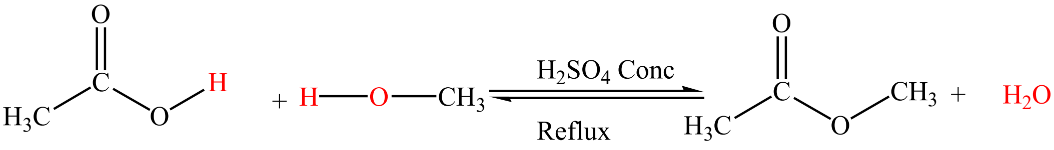


Figure 14.1 Ester preparation set up

Example: Esterification reaction between ethanoic acid and Methanol



2. Reaction of an acid chloride with an alcohol

$RCOCl + R'OH \rightarrow RCOOR' + HCl$

Example

$CH_3COCl + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCl$

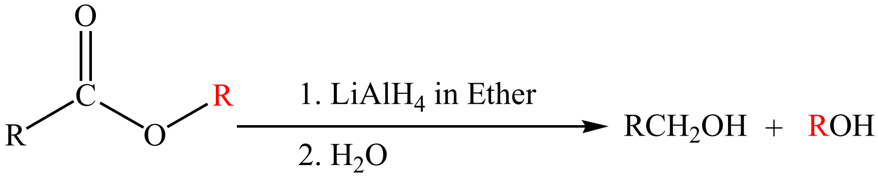
14.3.2. Chemical properties of esters

Chemical properties of esters involve their reactivity with other compounds.

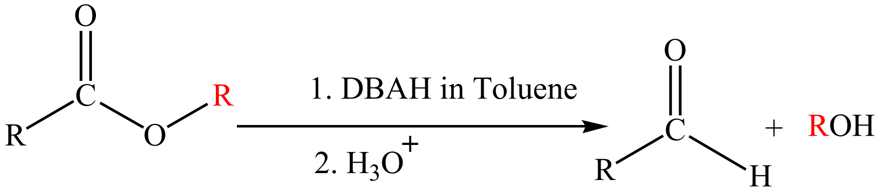
a. Reduction of esters

Compared to ketones and aldehydes, esters are relatively resistant to reduction.

Esters are reduced by Lithiumtetrahydridoaluminate ($LiAlH_4$) giving two alcohols, one from the acyl segment (RC=O) and one from the alkoxide segment (R-O) as shown by the reaction below.

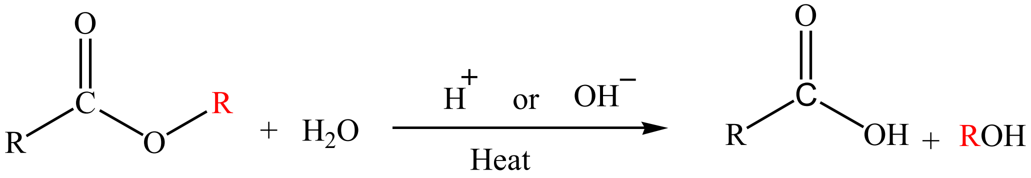


When a less reactive reducing agent such as diisobutylaluminium hydride (DIBAH) is used the acyl segment is converted into an aldehyde and the alkoxide group is still converted into an alcohol. Exactly one equivalent of the hydride must be used, and the reaction must be carried out at -78 ˚C



b. Hydrolysis of esters.

The reaction of an ester with water is called hydrolysis. This reaction is very slow unless catalyzed by a base or an acid.



The base catalyzed hydrolysis reaction is called ***saponification*** (derived from Latin word, "sapo", which means soap). Soaps are sodium or potassium salts made by hydrolyzing the vegetable oil which contain higher molecular weight esters in the presence of sodium or potassium hydroxides.

$$RCOOR + NaOH \xrightarrow{heat} RCOONa + ROH$$

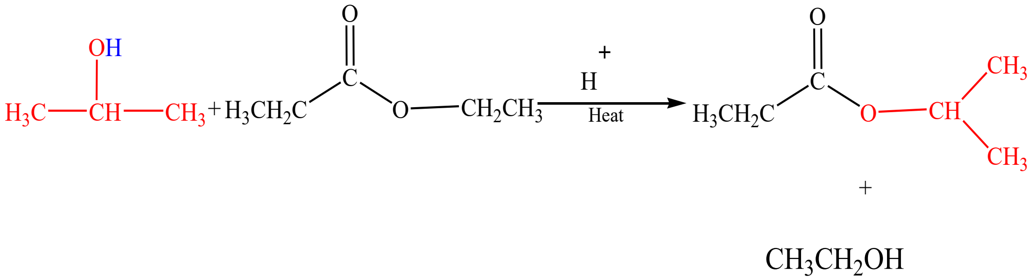
Ester Soap

C. Trans-esterification

Alcohols react with esters to undergo an exchange of the alkoxide segment. The reaction is acid catalyzed and the used alcohol must be in excess. This is a very common way of producing new esters from readily available esters.

$$RCOOR + ROH_{(excess)} \xrightarrow[Heat]{H^+} RCOOR + ROH$$

Example

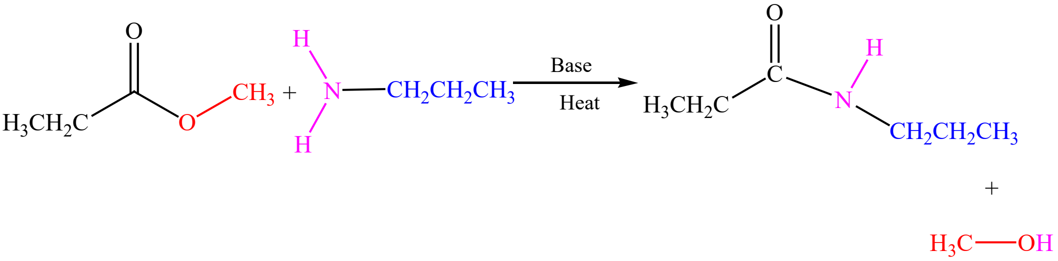


d. Reaction with ammonia and amines: *Aminolysis*

Esters react with ammonia, primary or secondary amines to produce amides. The reaction is carried out at high temperature in basic medium. However, this reaction is not often used because higher yields are normally obtained by using acyl chlorides.

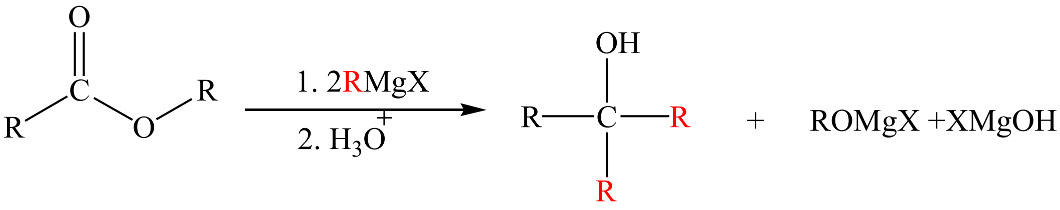
$$RCOOR + RNH_2 \xrightarrow[Heat]{Base} RCOHNR + ROH$$

Example



e. Reaction with Grignard reagents

Esters react with two equivalents of a Grignard reagent to form tertiary alcohols. This reaction produces ketone intermediates which undergo a fast conversion into the alcohol because of being more reactive than esters.



APPLICATION ACTIVITY 14.3

1. Write a balanced equation for the reaction between propanoyl chloride and butan-1-ol and name the product.

2. Investigate how to carry out the following conversions by using non-organic compounds other than the one cited. Use any inorganic substances you need.

   a) Propan-1-ol to propyl propanoate

   b) Ethanal to ethyl ethanoate

3. Ethanoic acid reacts with an alcohol of molecular formula $C_4H_{10}O$ to produce an ester which is optically active.

   a) Identify the structure of the alcohol.

   b) Sketch the structure of the ester formed.

4. Complete the equations below:

   a) $CH_3CH_2COOCH_3 + NaOH \rightarrow$

   b) $CH_3CH_2COOCH_3 + CH_3NH_2 \rightarrow$

   c) $CH_3COOCH_3 + CH_3MgCl \rightarrow$

5. For a reaction to take place, some conditions may be required depending on the type of reaction. Discuss the conditions to be used in order to carry out the reaction 4.a)

6. Reactions of amines with esters are not common. Explain briefly this statement.

7. You are provided with ethyl ethanoate and asked to prepare isobutyl ethanoate.

   Describe how you can proceed to prepare that compound. In your explanations, include reagents, conditions and equation(s) for the reaction(s) that take place.

   You are allowed to use any other organic compound you need.

14.4. Saponification and Detergents

ACTIVITY 14.4

Observe the above picture and answer the following questions.

1. Describe the use of the products above –mentioned in the picture.
2. Explain the properties that make these products have suitable for their use in 1.
3. Explain how these products are manufactured?
4. Propose the differences and similarities of these products?
5. Using NaOH and cooking oil, how can you prepare a solid soap in laboratory?

Surfactants like soaps and detergents are important cleaning products which play an essential role in our daily life. By safely and effectively removing soils, germs and other contaminants, they help us to stay healthy, care for our homes and possessions, and make our surroundings more pleasant.

SOAPS

Soaps are water-soluble sodium or potassium salts of fatty acids. Soaps are made from fats and oils, or their fatty acids, by reacting them with a strong alkali. The process is known as "***saponification***".

Fats and oils

The fats (solid lipids at room temperature and pressure) and oils (liquid lipids at room temperature and pressure) used to produce soaps find their sources from animal or plant. Each fat or oil is made up of a distinctive mixture of several different triglycerides.

In the formation of a triglyceride molecule, three fatty acid molecules reacted with one molecule of propane-1,2,3-triol or glycerol as shown in Figure 14.2. below.

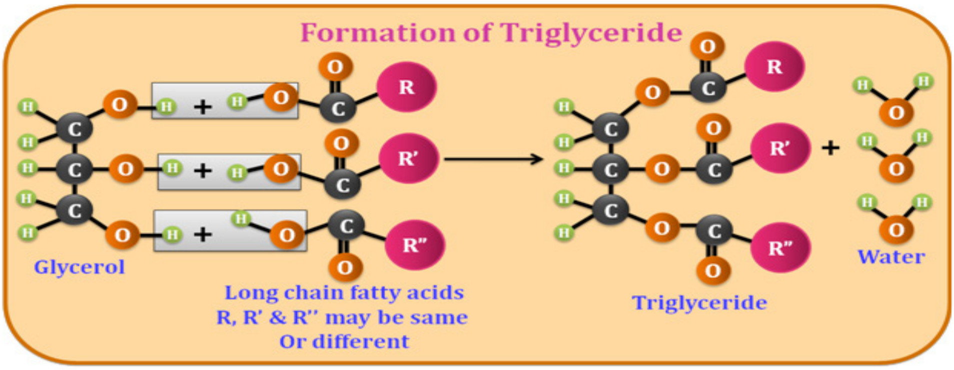


Figure 14.2. Formation of a triglyceride

Examples of other fatty acids include stearic acid ($CH_3(CH_2)_{16}CO_2H$), palmitic acid ($CH_3(CH_2)_{14}COOH$), ...

Saponification reaction

The reaction of saponification involves the collision between triglycerides in fat/oil and aqueous NaOH or KOH. The result is the formation of soap and glycerol (Figure 14.3).

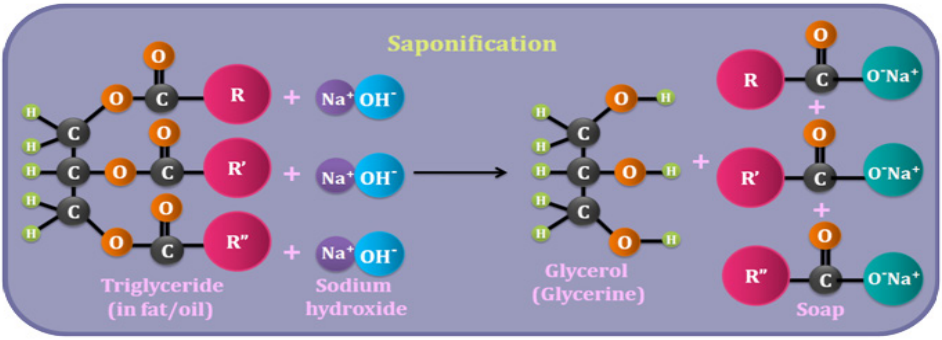
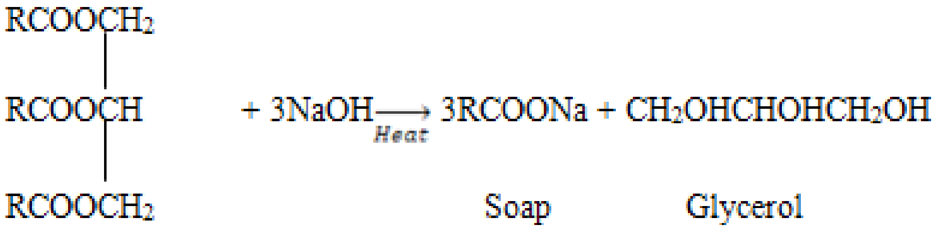


Figure 14.3. Saponification

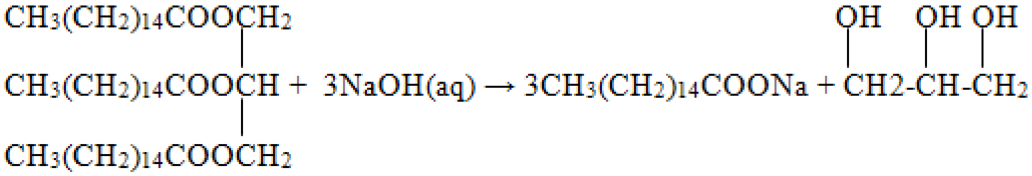
Or



$$\begin{array}{l} RCOOCH_2 \\ \quad | \\ RCOOCH \qquad + 3NaOH \xrightarrow[Heat]{} \underset{\text{Soap}}{3RCOONa} + \underset{\text{Glycerol}}{CH_2OHCHOHCH_2OH} \\ \quad | \\ RCOOCH_2 \end{array}$$

The reaction of saponification is exothermic because there is liberation of heat and the soap formed remains in suspension form in the mixture. Soap is precipitated as a solid from the suspension by adding common salt to the suspension.

Example:



$$\begin{array}{l} CH_3(CH_2)_{14}COOCH_2 \\ \qquad\qquad | \\ CH_3(CH_2)_{14}COOCH + 3NaOH(aq) \rightarrow 3CH_3(CH_2)_{14}COONa + \overset{OH}{\overset{|}{CH2}}-\overset{OH}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH_2}} \\ \qquad\qquad | \\ CH_3(CH_2)_{14}COOCH_2 \end{array}$$

The other major soap-making process is the neutralization of pure fatty acids with an alkali.

Note: Sodium soaps are “hard” soaps whereas potassium soaps are soft.

DETERGENTS

Detergents are organic liquid or water-soluble solid cleaning substances that, unlike soap, are not prepared from fats and oils.

The chemical composition of detergents is different from that of soaps but they have the same cleaning mechanism and are not adversely affected by hard minerals in the water and this makes them more effective than soaps. However, they are less environmental friendly because of a reduced biodegradability.

Detergents may be used for household cleaning, laundry or for body and hand washing. They exist in the powder or liquid form.

How do soaps and detergents work?

When a soap or detergent is added to water, a polar solvent, the molecules form clusters, known as *micelles*(Figure 14.4), in which the polar ends of the molecules are on the outside of the cluster and the non-polar ends are in the middle.

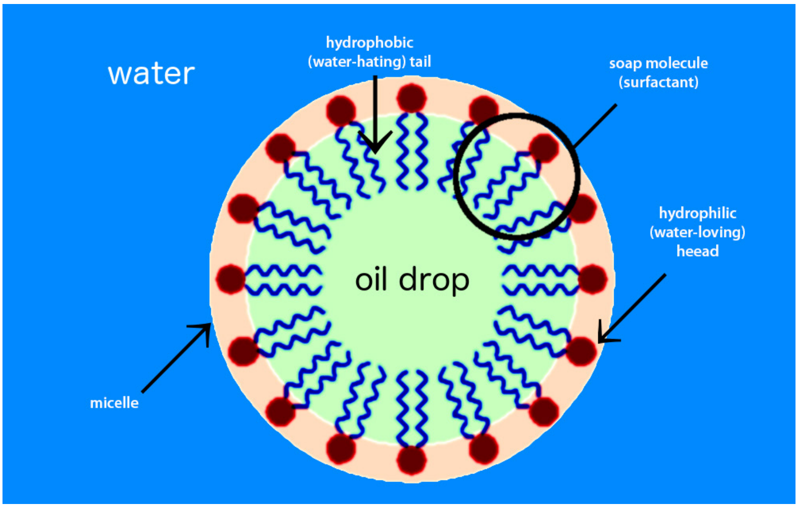


Figure 14.4. Soap or detergent micelle

The carboxylate end of the soap molecule is attracted to water. It is called the hydrophilic (water-loving) end. The hydrocarbon chain is attracted to oil and grease and repelled by water. It is known as the hydrophobic (water-hating) end. When washing, the hydrophobic part of the soap molecule (Figure 14.5) dissolves oil or grease the main source of dirt and it gets washed away by water as it is insoluble in it.

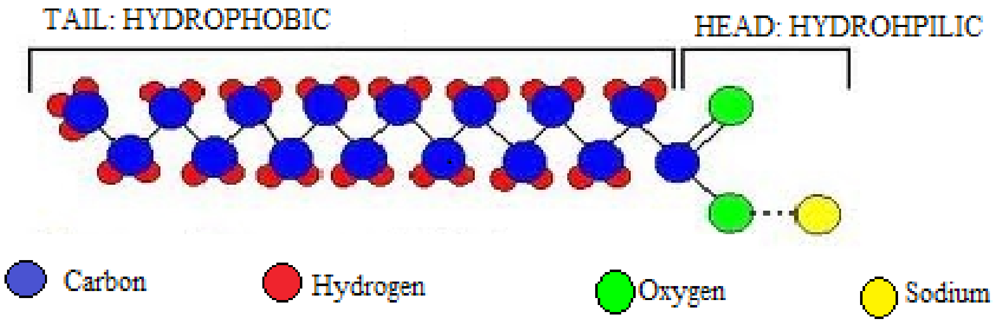


Figure 14.5. Representation of soap molecule

The cleaning property of both soaps and detergents results from their capacity to emulsify water-insoluble materials (dirt, oil, grease, etc.) and hold them in suspension in water. This ability originates from the molecular structure of soaps and detergents. When a soap or detergent adds on to water that contains oil or other water-insoluble materials, the soap or detergent molecules surround the oil droplets. The oil or grease is "dissolved" in the alkyl groups of the soap molecules while the ionic end allows the micelle to dissolve in water. As a result, the oil droplets are dispersed throughout the water (this is referred to as *emulsification)* and can be rinsed away.

APPLICATION ACTIVITY 14.4

1. Propyl tristearate reacts with sodium hydroxide to form soap.
   a) Write a balanced equation for the reaction which takes place.
   b) Calculate the mass of sodium hydroxide needed to react exactly with 4kg of this oil and the mass of the produced soap.
2. Describe the chemical difference of solid and liquid soaps.
3. Distinguish soaps from detergents.
4. Why are detergents more effective than soaps?
5. Describe briefly in your own words how soaps and detergents work.
6. Give the importance of soaps and detergents in our everyday life.

14.5. Structure and nomenclature of acid anhydrides

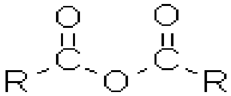
ACTIVITY 14.4

One of the most used pain killers is aspirin (image above). This is a medical drug which can be prepared using salicylic acid and ethanoic acid. However, ethanoic acid is not used. Instead, one of its derivatives is used. Search from internet or the school library and answer the questions below:

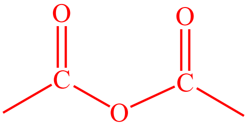
1. Propose a derivative of acetic acid used in this preparation.
2. Explain why is it used in preference to acetic acid.
3. Write down its molecular formula and structure.
4. Suggest how it is produced from acetic acid.

14.5.1. Structure of acid anhydrides

The acid anhydrides are derivatives of carboxylic acids. The general structure of acid anhydrides is RCOOOCR, or



The functional group of acid anhydrides consists of two acyl groups held together by an oxygen atom.



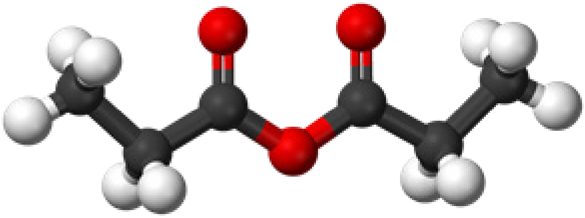
When the two R groups are identical, the acid anhydride is symmetric and when the two R groups are different, the acid anhydride is asymmetric. The general molecular formula of acid anhydride is $C_nH_{2n-2}O_3$

14.5.2. Nomenclature of acid anhydrides

The nomenclature of acid anhydride is based on whether they are symmetrical or unsymmetrical. Symmetrical acid anhydrides are named as parent acid followed by the term anhydride

Examples: $CH_3COOOCCH_3$: Ethanoic anhydride

$CH_3CH_2COOOCCH_2CH_3$: Propanoic anhydride (Illustration below)



Unsymmetrical acid anhydrides are named by writing alphabetically the names of parent acids followed by the term **"anhydride"**.

Examples: $CH_3CH_2COOOCCH_3$ Ethanoic propanoic anhydride

$CH_3COOCOCH_2Cl$: Acetic chloroacetic anhydride

APPLICATION ACTIVITY 14.5

1. Write the molecular formula of an acid anhydride which has 6 carbon atoms
2. Draw the structure of one straight and one branched isomers of the molecular formula in (1) above.
3. Name the isomers from (2).

14.6. Preparation, chemical properties and uses of acid anhydrides

ACTIVITY 14.6

1. Two carboxylic acids can react to form an acid anhydride and a water molecule. However, this method is not suitable when preparing mixed (unsymmetrical) acid anhydrides.

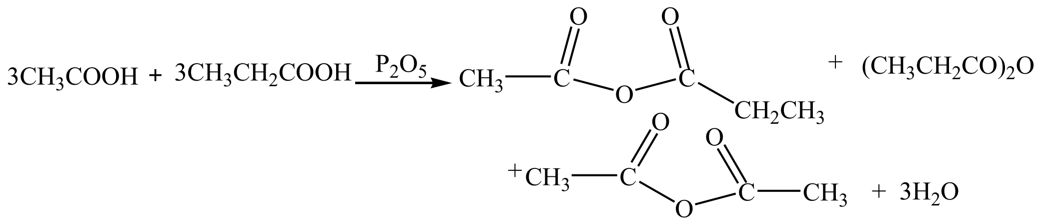
   Suggest a reason why this method is not suitable.
2. Using your knowledge in organic chemistry so far, suggest a method which may be suitable to prepare ethanoic propanoic anhydride. Write the equation for the reaction. (Hint: you may refer to the preparation of ethers).
3. Prepare ethanoic anhydride using ethanoic acid and phosphorous pentoxide.
4. Aspirin is synthesized using ethanoic anhydride and salicylic acid. Suggest an equation for the reaction that occurs.

14.6.1. Preparation

Anhydride means "without water". Two carboxylic acids can react, eliminating a water molecule to yield an acid anhydride.

The commonly used dehydrating agent is phosphorous pentoxide, P_2O_5. If two different acids are used, a mixed anhydride is produced. The method is less efficient however, as one obtains the two symmetrical anhydrides in addition to the desired mixed anhydride.

Example:



A better method of making mixed anhydrides is to react an acid halide with a salt of a carboxylic acid. This method can be used to make symmetrical anhydrides too.

Examples: * $CH_3CH_2COONa + CH_3COCl \rightarrow CH_3CH_2COOOCCH_3 + NaCl$

* $CH_3COONa + CH_3COOCl \rightarrow CH_3COOOCCH_3 + NaCl$

14.6.2. Chemical properties of acid anhydrides and their uses

The term″chemical propertieš indicates the reactivity between two or more compounds. In the case of acid anhydrides, their reactivity involves the electron-deficient carbonyl-carbon which is attacked by nucleophiles. This reaction occurs slowly.

There are mainly four types of reactivity of acid anhydrides such as hydrolysis, reaction with alcohols, reaction with ammonia and amines and the reduction reaction.

1. Hydrolysis

This reaction of acid anhydride in water leads to the formation of parent carboxylic acids which were used to prepare the anhydride. The reaction is carried out in acidic medium under reflux.

$$RCOOCOR + H_2O \xrightarrow[\text{Heat}]{H^+} RCOOH + RCOOH$$

Example:

$$CH_3COOOCCH_2CH_3 + H_2O \xrightarrow[\text{Heat}]{H^+} CH_3COOH + CH_3CH_2COOH$$

2.Reaction with alcohols

Anhydrides react readily with primary, secondary, tertiary alcohols to form esters and carboxylic acid.

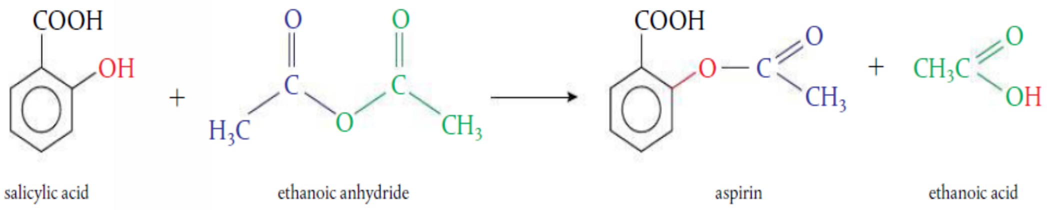
$RCOOOCR + ROH \xrightarrow{H^+} RCOOR + RCOOH$

Aspirin synthesis is an application of this reaction

Example:

$CH_3CH_2COOOCCH_3 + CH_3CHOHCH_3 \xrightarrow{H^+} CH_3CH_2COOCH(CH_3)_2 + CH_3CH_2COOH$

This reaction is very important in pharmaceutical industries and it indicates the main use of acid anhydrides as it is the basis of aspirin manufacture as shown below.



3. Reaction with ammonia and amines

Anhydrides react with ammonia, primary and secondary amines to produce amides.

The reaction with amine: $RCOOCR + R'NHR' \rightarrow RCON(R')_2 + RCOOH$

Amide Acid

Example: $CH_3COOOCCH_3 + CH_3NH_2 \rightarrow CH_3CONHCH_3 + CH_3COOH$

Reaction with ammonia: $(RCO)_2O + NH_3 \rightarrow RCONH_2 + RCOOH$

Example: $(C_2H_5CO)_2O + NH_3 \rightarrow C_2H_5CONH_2 + C_2H_5COOH$

Amide

4. Reduction of acid anhydrides

Anhydrides are reduced by Lithium tetrahydridoaluminate, $LiAlH_4$, to yield two moles of primary alcohols.

$RCOOOCR' \xrightarrow{LiAlH_4} RCH_2OH + R'CH_2OH$

Example: $*CH_3COOOCCH_3 \xrightarrow{LiAlH_4} 2\ CH_3CH_2OH$

$*CH_3CH_2COOOCCH_3 \xrightarrow{LiAlH_4} CH_3CH_2CH_2OH + CH_3CH_2OH$

14.6.3 Uses of acid anhydrides

1. Ethanoic anhydride is used in the synthesis of acetate esters.

   Examples: aspirin, cellulose acetate,...

2. Maleic anhydride is used in the synthesis of various resins when copolymerized with styrene.

3. They are used to synthesize polyesters and polyamides.

APPLICATION ACTIVITY 14.5

1. Write the equations that can be used to synthesize the following acid anhydrides from ethanol.

   a. Ethanoic anhydride

   b. Propanoic anhydride

   c. Ethanoic propanoic anhydride

2. Students of senior five MCB were asked to prepare butanoic propanoic anhydride and group A used a method similar to Williamson's method of synthesizing ethers whereas group B decided to use a dehydrating agent. Which group chose a better method? Explain your reasoning

3. Complete the equations below

   $(CH_3CH_2CO)_2O + NH_3 \rightarrow$

   $CH_3CH_2COOOCCH_2CH(CH_3)_2 \xrightarrow{LiAlH_4}$

4. Propose the products from the reaction below:

   $CH_3CH_2COOOCCH_3 + H_2O \xrightarrow{H^+}$

5. Draw the structures of products formed when propanoic anhydride reacts with 2-methylpropan-2-ol

6. State the necessary chemicals and conditions to prepare aspirin.

7. Chemists prefer using acid anhydrides than acyl chlorides when preparing esters. Discuss this statement.

14.7. Structure , nomenclature ,physical properties and uses of amides.

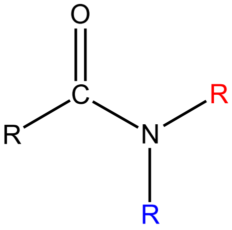
ACTIVITY 14.7

In the previous unit, it has been mentioned that carboxylic acids react with ammonia and amides to produce new organic compounds.

1. Draw and name their functional group.
2. Draw their general structure and determine their general molecular formula.
3. What natural and artificial polymers contain the same functional group?
4. Suggest how their boiling points would be relative to those of esters. Provide an explanation for your suggestion.
5. What kind of textile is used to make this wedding dress below?

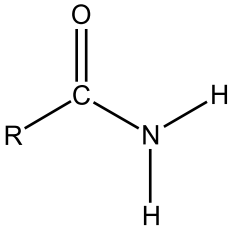
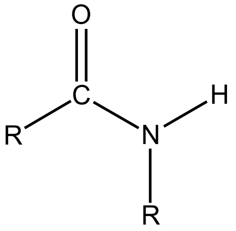
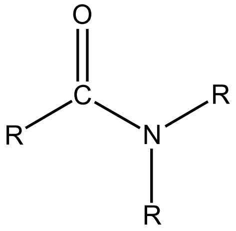
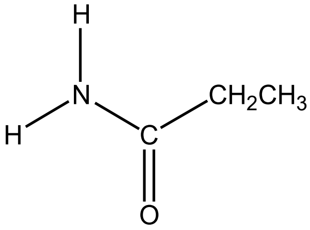
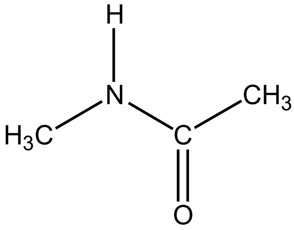
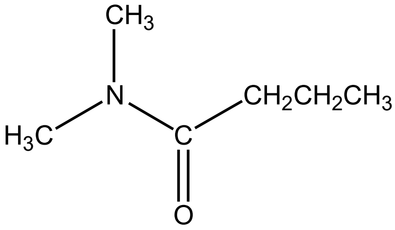
14.7.1. Structure of amides

Amides are acid derivatives in which the –OH group is replaced by -NH_2, -NHR or –$N(R)_2$. The functional group comprises nitrogen atom which is attached to the carbonyl carbon atom. The carbonyl group linked to nitrogen atom is called ***an amide linkage***. The general structure of amides is:



Where R and R can be hydrogen atoms (for primary amides), alkyl groups (for tertiary amides). For secondary amides only one R is a hydrogen atom. Their general molecular formula is $C_nH_{2n+1}ON$. Examples of some amides are given in the Table 14.1

Table 14.1. Examples of some amides

Primary amide	Secondary amide	Tertiary amide
		
		
$CH_3CH_2CONH_2$	$CH_3NHCOCH_3$	$(CH_3)_2NCOCH_2CH_2CH_3$

14.7.2. Nomenclature of amides

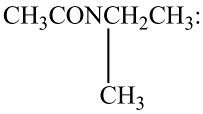
The nomenclature of amides is derived from the name of corresponding acid. The –oic acid suffix or –ic acid is replaced by –amide.

As for other organic compounds, the first step is to consider the number of carbon atoms forming the chain.

The alkyl group bonded to nitrogen atom is indicated by a capital N preceding the alkyl name.

Examples: $CH_3CH_2CONH_2$: propanamide, $CH_3CONHCH_3$: N-methylethanamide

$CH_3CON(CH_3)_2$: N,N-dimethylethanamide

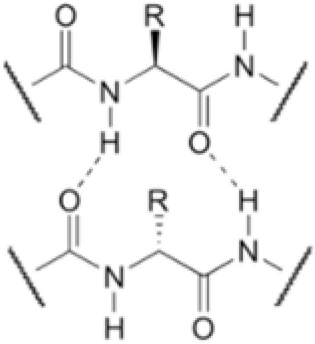


$\underset{\displaystyle CH_3}{CH_3CONCH_2CH_3}$: N-ethyl-N-methylethanamide

14.7.3. Physical properties and uses of amides

1) Physical properties of amides

Except formamide, all the amides are crystalline solids at room temperature. Amides have higher melting and boiling points than corresponding esters due to hydrogen bonding as shown below.



The melting and boiling points increase as molecular mass increases. Lower members are soluble in water but this solubility decreases as the molecular mass increases. All the amides are soluble in organic solvents. The Table 14.6.3 shows the comparison of melting and boiling points of some amides.

Table 14.2. Some physical properties of lower amides

Name	Melting point (°C)	Boiling point (°C)	Solubility in water
Methanamide	2	193	Soluble
Ethanamide	82	222	Soluble
Propanamide	81	213	Soluble
Butanamide	115	216	Soluble
Benzamide	132	290	Slightly soluble

Source: https://chem.libretexts.org

2) Uses of Amides

Amides are used in the production of many useful chemicals and materials such as fertilizers (urea), nylon textiles and skin care substances.

Urea manufacture

Urea can be prepared in three ways:

a. Reaction of phosgene and ammonia

$\underset{\text{Phosgene}}{O=CCl_2} + NH_3 \rightarrow \underset{\text{Urea}}{O=C(NH_2)_2} + 2HCl.$

The diagram below shows the representation of Urea.

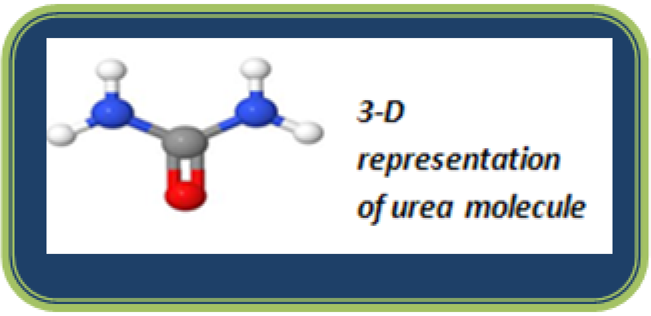


Figure 14.6 -D Urea molecule

b. From calcium cyanamide, $CaCN_2$

Calcium carbide reacts with nitrogen to produce calcium cyanamide and carbon. The produced $CaCN_2$ is then treated with a mixture of water and carbon dioxide to produce urea.

$CaC_2 + N_2 \rightarrow CaCN_2 + C$

$CaCN_2 + H_2O + CO_2 \rightarrow H_2N\text{-}C\equiv N \xrightarrow{H_2O} O=C(NH_2)_2$

c. Reaction of carbon dioxide and ammonia

$CO_2 + NH_3 \rightarrow H_2N\text{-}CO\text{-}NH_2 + H_2O$

Urea is also naturally present in animal urines.

It is widely used in agriculture as a source of nitrogen, chemical fertilizer. It also finds use in animal feeding and in resins manufacture.

Nylon manufacture

Nylon-6,6 is a synthetic textile produced when hexane-1,6-dioic acid(adipic acid) reacts with hexane-1,6-diamine. Nylon is a polyamide. Some materials and clothes are made from nylo-6,6.

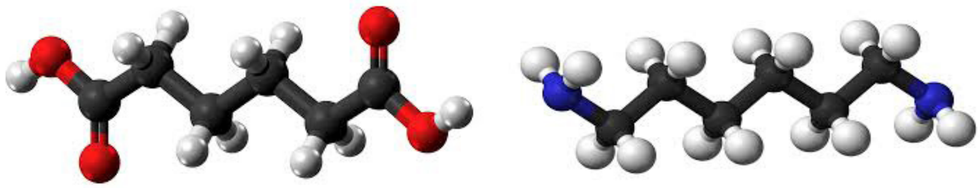


Figure 14.7. Adipic acid and Hexane-1,6-diamine

Medical use of urea

Urea containing creams are used in skin treatment to promote its rehydration. It softens the skin.

APPLICATION ACTIVITY 14.7

1. Write the molecular formula of amides with 4 carbon atoms.
2. Draw all possible structural formulae of primary, secondary and tertiary amides with molecular formula in (1) above and name them
3. Compare the solubilities of butanamide and N,N-dimethylethanamide in water.
4. The solubility of amides decreases with the increase in molecular mass. Suggest a reason for this observation.
5. Which one between ethanol and ethanamide do you expect to have a higher boiling point? Explain your answer.
6. Discuss the benefits and dangers of using animal urine as a source of nitrogen for plants.

14.8. Preparation and chemical properties of amides

ACTIVITY 14.8

1. Draw the structure of propanamide.

2. Suggest how this compound can be prepared from propanoic acid. Include an equation in your answer and state working conditions.

3. Draw the structure of ethanoyl chloride and write an equation for its reaction with CH_3NH_2

4. Suggest other possible reactions that can be used to prepare amides in general.

5. What reagents and conditions which can be used to reduce amides?

14.8.1. Preparation of amides

Amides can be prepared from all of the other acid derivatives when they react with ammonia and primary or secondary amines. Their production of amides involves the following reactions.

1. $RCOCl + H\text{-}NH_2 \rightarrow RCONH_2 + HCl$

Acyl chloride Ammonia

Example: $CH_3COCl + H\text{-}NH_2 \rightarrow CH_3CONH_2 + HCl$

2. $RCOCl + H_2NR' \rightarrow RCONHR' + HCl$

Acyl chloride Primary amine

Example: $CH_3COCl + CH_3CH_2\text{-}NH_2 \rightarrow CH_3CONH_2 + CH_3CH_2Cl$

3. $RCOOR' + RNHR \rightarrow RCON(R)_2 + R'OH$

Ester Secondary amine

Example: $CH_3CH_2COOCH_3 + CH_3NHCH_3 \rightarrow CH_3CH_2CON\ (CH_3)_2 + CH_3OH$

4. $RCOOOCR + RNH_2 \rightarrow RCONHR + RCOOH$

Acid anhydride primary amine

Example: $CH_3COOOCCH_3 + CH_3CH_2NH_2 \rightarrow CH_3CONHCH_2CH_3 + CH_3COOH$

5. Amide can also be prepared from a reaction of a carboxylic acid and ammonia or an amine. The produced salt must be heated to dehydrate it.

$$RCOOH + RNH_2 \rightarrow RCOON^{+}H_3R' \xrightarrow[\text{Heat > 100°c}]{} RCONHR' + H_2O$$

Example:

$$CH_3COOH + C_2H_5NH_2 \rightarrow CH_3COON^{+}H_3C_2H_5 \xrightarrow[\text{Heat > 100°c}]{} CH_3CONHC_2H_5 + H_2O$$

6.The hydrolysis of nitriles also produces amides

$$RC\equiv N + H_2O \xrightarrow{H^+} RCONH_2$$

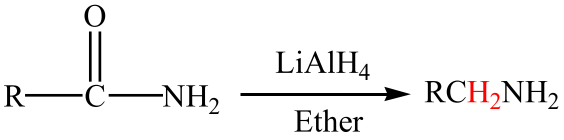
Example: $CH_3CH_2C\equiv N + H_2O \xrightarrow{H^+} CH_3CH_2CONH_2$

14.8.2. Chemical properties of amides

The reactivity of amides involves different types of reaction to form various organic compounds.

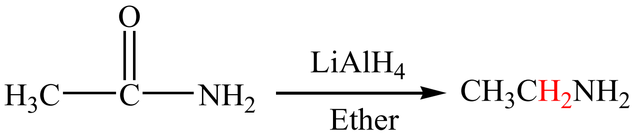
1. Reduction reaction

Amides are reduced with sodium and ethyl alcohol or with lithium aluminium hydride ($LiAlH_4$) to yield primary amines.



$$R-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{Ether}]{LiAlH_4} RCH_2NH_2$$

Example:



$$H_3C-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{Ether}]{LiAlH_4} CH_3CH_2NH_2$$

2. Hydrolysis

Amides react with water in acidic medium (dilute) at high temperatures to form acids.

$$RCONH_2 + H_2O \xrightarrow{\textit{high temperature}} RCOOH + NH_3$$

Example: $CH_3CH_2CONH_2 + H_2O \xrightarrow{\textit{high temperature}} CH_3CH_2COOH + NH_3$

3. Hoffman degradation

Primary amides react with a mixture of sodium hydroxide and bromine or sodium hypobromite to produce amines. The reaction is called degradation as the carbon chain is reduced by one carbon.

$RCONH_2 + 4NaOH + Br_2 \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

Example: $CH_3CONH_2 + 2NaOH + Br_2 \rightarrow CH_3NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

This equation can be simplified as follows:

$CH_3CONH_2 + NaOBr \rightarrow CH_3NH_2 + NaBr + CO_2$

Note: Hoffman degradation reaction is used to test the presence of the amide functional group. When an amide is treated with sodium hypobromite, a colorless gas which turns milky lime water is evolved, $CO_{2.}$

4. Reaction with nitrous acid

Primary amides react with nitrous acid to produce an acid, water and nitrogen gas.

$RCONH_2 + HNO_2 \xrightarrow[\text{at 5 °c}]{\text{HCL}} CH_3COOH + N_2 + H_2O$

Example: $CH_3CH_2CONH_2 + HNO_2 \xrightarrow[\text{at 5 °c}]{\text{HCL}} CH_3CH_2COOH + N_2 + H_2O$

5. Dehydration reaction

Dehydrating reagents, like thionyl chloride ($SOCl_2$), remove one molecule of water from amides to give nitriles. Phosphorous pentoxide can also be used. The reaction is done under reflux.

$RCONH_2 \xrightarrow[\text{Reflux}]{SOCl_2} RC{\equiv}N + H_2O$

Example: $CH_3CH_2CONH_2 \xrightarrow[\text{Reflux}]{SOCl_2} CH_3CH_2C{\equiv}N + H_2O$

APPLICATION ACTIVITY 14.8

1. Referring to the hydration of alkynes, draw the structure of the intermediate compound formed during the preparation of amides from nitriles.

2. Identify the compounds corresponding to each letter in the scheme of reactions below

$$\text{Ethene} + HBr \rightarrow \mathbf{A} \xrightarrow{\text{Mg/dry ether}} \rightarrow \mathbf{B} \xrightarrow{CO_2\ /H_2O} \mathbf{C}$$

$$\mathbf{C} + CH_3CH_2NH_2 \xrightarrow{\text{heat}} \mathbf{D}$$

$$\mathbf{E} + SOCl_2 \rightarrow \mathbf{F}$$

$$\mathbf{F} + CH_3NH_2 \rightarrow CH_3CH(CH_3)CONHCH_3 + HCl$$

3. Explain how you can distinguish between these pairs of compounds. State the reagents to be used and the expected observations.

   a. Butanamide and ethyl ethanoate

   b. Aqueous sodium carbonate and ethanamide.

4. How can you perform the following conversions?

   a. $CH_3CH_2CH_2OH$ to CH_3CH_2CN(your conversion must include an amide formation step)

   b. CH_3CHO to CH_3NH_2

14.9. Structure, nomenclature, physical properties and uses of nitriles

ACTIVITY 14.9

In the previous lesson of this unit you learnt different reactions of amides. From your knowledge and understanding, answer the questions that follow:

1. Draw the structure of compound A:

$$CH_3CONH_2 \xrightarrow{SOCL_2} A$$

2. To what homologous series does product A belong?

3. Write the molecular formula of A.

4. Suggest the general structure and the general molecular formula for all compounds belonging to the same homologous series as A.

5. At room temperature, these compounds are liquids or solids depending on the molecular mass and yet they lack hydrogen bonding. Suggest a brief explanation for this specialty.

14.9.1. Structure of nitriles

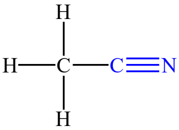
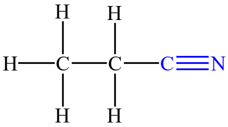
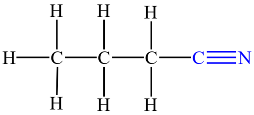
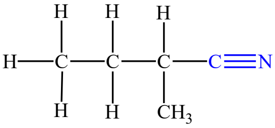
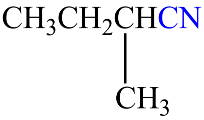
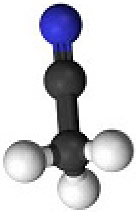
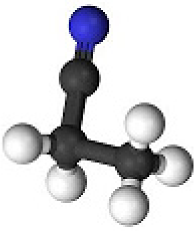
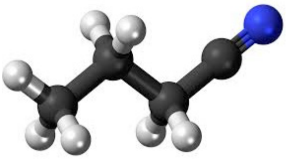
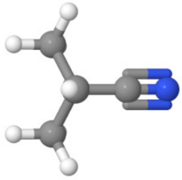
Nitriles are organic compounds with the general structure RC≡N where -C≡N is its functional group. The nitrile compounds include a nitrogen atom attached to a carbon atom by a triple covalent bond. Their general molecular formula is $CnH_{2n-1}N$. Unlike other acid derivatives they do not contain an acyl group.

14.9.2. Nomenclature of nitriles

The nitriles are named using the name of the alkane parent followed by the term –nitrile. The carbon attached to the nitrogen atom is given the location position number 1.

Structure and name of some nitriles are shown in the Table 14.2.

Table 14.2. Examples of some nitriles

Ethanenitrile	Propanenitrile	butanenitrile	2-methylbutananenitrile
			
CH_3CN	CH_3CH_2CN	$CH_3CH_2CH_2CN$	 $CH_3CH_2\underset{CH_3}{\underset{\vert}{CH}}CN$
			

14.9.3. Physical properties and uses of nitriles

Physical properties

The physical properties of nitriles are summarized below.

1. The nitrile compounds are present as colorless solids and liquids having a characteristic odour.

2. Nitriles have boiling points ranging between 82 and 118 °C. The high boiling points are due to strong dipole-dipole moments caused by the polarity of the C≡N bond.

3. Nitriles compounds exhibit high polar and electronegativity

4. Lower nitriles are highly soluble in water but this solubility decreases with the increase in molecular mass as the non-polar part becomes lager.

Uses of nitrile compounds

Nitriles find many uses:

- Nitriles are used in the manufacture of nitrile gloves, seals, and pipes or tubes as they exhibit resistance to chemicals.
- They are used as an antidiabetic drug which is used in the treatment of breast cancers.
- This compound is found in many plant and animal sources.

- They are utilized in the applications of oil resistant substances and also for low-temperature uses.
- They are also employed in automotive systems, hydraulic tubes and also in aircraft systems.

APPLICATION ACTIVITY 14.9

1. Draw the structure of each of the compound below:

   a. Butanenitrile

   b. 3-methylpentanenitrile

2. Name these compounds:

   a. $CH_3CH_2CH_2CH(CH_3)CN$

   b. $CH_3CH(CH_3)CH(CH_3)CN$

3. Draw all possible isomers of molecular formulaC_4H_7N and name them.

14.10. Preparation and chemical properties of nitriles

ACTIVITY 14.10

One method of preparing nitriles is to dehydrate an amides.

1. Use your knowledge about chemistry of alkyl halides and suggest another preparation method.

2. Name the reaction mechanism involved in that method.

3. Write an equation of the preparation of propanenitrile using the method you have suggested.

14.10.1. Preparation of nitriles

Nitriles are prepared by dehydration of amides under reflux in the presence of phosphorous (V) oxide, P_2O_5 or sulphur dichloride oxide, $SOCl_2$ and there is elimination of water molecule.

1. Dehydration of amides

$$CH_3CH_2CH_2CONH_2 \xrightarrow[Reflux]{SOCl_2} CH_3CH_2CH_2C{\equiv}N + H_2O$$

2. Nucleophilic substitution of halogenoalkanes

The halogenoalkane is heated under reflux with a solution of sodium or potassium cyanide in ethanol. The halogen is replaced by a -CN group and a nitrile is produced.

$RX + CN^- \rightarrow RCN + X^-$

Example: $CH_3CH_2Cl + KCN_{(aq)} \rightarrow CH_3CH_2CN + KCl_{(aq)}$

14.10.2. Chemical properties of Nitriles

Nitrile compounds undergo various reactions. Nitriles are hydrolyzed in the presence of an acid or a base to form carboxamides and carboxylic acids. This is the reason why they are considered to be acid derivatives while they have no acyl group.

1. Hydrolysis

$$RC{\equiv}N + H_2O \xrightarrow{H^+} RCONH_2 + \xrightarrow[Heat]{H_2O} RCOOH + NH_3$$

Example:

$$CH_3CH_2C{\equiv}N + H_2O \xrightarrow{H^+} CH_3CH_2CONH_2 + \xrightarrow[Heat]{H_2O} CH_3CH_2COOH + NH_3$$

2. Reduction reaction

Nitriles can be reduced by $LiAlH_4$ or hydrogen to produce primary amines in the presence of catalysts such as palladium.

$$RC{\equiv}N + 2H_2 \xrightarrow{Pd} RCH_2NH_2 \text{ or } RCN \xrightarrow[2)\ H_2O]{1)\ LiAlH_4} RCH_2NH_2$$

Example: $CH_3CH_2CH_2C{\equiv}N + 2H_2 \xrightarrow{Pd} CH_3CH_2CH_2CH_2NH_2$

$$CH_3CH_2CH_2CN \xrightarrow[2)\ H_2O]{1)\ LiAlH_4} CH_3CH_2CH_2CH_2NH_2$$

APPLICATION ACTIVITY 14.10

1. An aldehyde of molecular formula C_3H_6O reacts with hydrogen cyanide in strong basic medium to give compound A. compound A undergoes a reduction to give compound B.

   a. Suggest a reducing agent which can be used to reduce A.

   b. Draw the structure of the product formed when compound A is treated with hot acidified water.

2. What is meant by the term hydrolysis?

3. Nitriles are considered to be acid derivatives even though they do not have the acyl group. Search from the internet or library a reason for this consideration.

SKILLS LAB 14

1. Follow the procedure below and collect the required raw materials and try to prepare the soap in your laboratory.

PROCEDURE FOR SOAP MANUFACTURE

- **Caution : wear gloves and goggles as sodium hydroxide is caustic**. Dissolve 3.25 g of sodium hydroxide in 8 mL of water contained in 25 mL Erlenmeyer flask. Swirl to help dissolve the solution. Set aside and allow cooling to room temperature.
- In a beaker add 25 grams of your oil (or fat) and heat gently to about 40 ° C. If using a fat it should be melted.
- Combine the sodium hydroxide solution and oils. Stir the mixture until it starts to harden (about 15-20 minutes). Once the mixture starts to harden then stir for 5 minutes at 15 minute intervals. At the point when it starts to harden you can also add any ‘essential oil’ ingredients to scent your soap. • Once the soap is relatively firm (your stir marks will remain for several seconds) pour raw soap into your prepared molds or keep it in the beaker. After a few days the soap can be turned out of the mold. If the soap is very soft, allow it to cure for a few days to firm the outside.
- Eventually remove the soap and set the bar out to cure and dry. This will allow the bar to firm and finish saponification. (This can actually take days to cure properly—the longer you wait the less unreacted sodium hydroxide that will be present.

END UNIT ASSESSMENT 14

Part I: Objective questions

1. The esters are ……. acyl chlorides

   a. more reactive than

   b. equal in reactivity

   c. less reactive than

2. Secondary amines react with acid chloride to give

   a. amines

   b. carboxylic acids

   c. amides

   d. imines

3. A mixture of acetic acid and propanoic acid undergo dehydration to give

   a. acetic anhydride

   b. propanoic anhydride

   c. acetic and propanoic anhydrides

   d. acetic, propanoic and acetic propanoic anhydrides

4. Ethanoyl bromide reacts with sodium propanoate to give

   a. ethanoic anhydride

   b. propanoic anhydride

   c. ethanoic propanoic anhydride

   d. all of the above

5. Esters are made from the reaction between

   a. carboxylic acid molecules

   b. alcohol molecules

c. alcohol and carboxylic acid molecules

d. acid anhydride and water molecules

6. Ethyl acetate is hydrolyzed by water to give a/an

a. lactone

b. ester

c. acid anhydride

d. carboxylic acid and an alcohol

7. The reaction between ethyl ethanoate and dimethylamine gives an

a. amide

b. imide

c. acid anhydride

8. $LiAlH_4$ reduces Ethanamide to give a/an

a. carboxylic acid

b. amide

c. alcohol

d. amine

9. Nitriles can be hydrolyzed with water to give

a. alcohols

b. aldehydes

c. acids

d. acids and amides

10. Reduction of nitriles gives

a. amides

b. amines

c. imines

d. carboxylic acids

Part II: Structured questions

11.Use equations to show how you could prepare the following compounds, using the organic compounds cited as the only organic substances and any inorganic substance you need:

a. CH_3CH_2COOH to $CH_3CH_2NH_2$

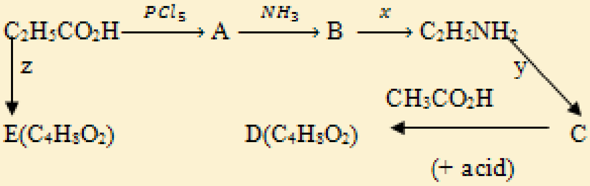
b. ethyl propanoate to ethanamide

c. propanoic acid to propanoic anhydride

d. butanenitrile to $CH_3CH_2CH_2NH_2$

e. propanoic acid to N-propylpropanamide

12. Identify compounds A, B, C, D and E, and reagents x, y and z in the following scheme of reactions. Write equations for the reactions involved:



13. Identify the compound corresponding to each letter in the scheme of reactions below:

(a) + HBr $\leftrightharpoons$ (b) + H_2O

(b) + Mg $\rightarrow$ (c)

(c) + CO_2 plus H_2O $\rightarrow$ (d) + BrMgOH

(d) + NaOH $\rightarrow$ (e) + H_2O

(d) + PCl_5 $\rightarrow$ (f) + $POCl_3$ + HCl

(e) + (f) $\rightarrow$ (g) + NaCl

(a)+ (g) $\rightarrow$ $CH_3CH_2CO_2CH_2CH_3$ + CH_3CH_2COOH

14. Name the following:

a. $CH_3CH_2COOCH_3$

b. $CH_3CH_2CONHCH_3$

c. $CH_3COOOCCH_2CH_3$

d. CH_3CH_2CN

e. $CH_3CON(CH_3)_2$

15. Draw the structural formula of:

a. 2-chloropropanamide

b. Methylpentanoate

c. Butanoic anhydride

d. Propanoyl chloride

e. N-ethyl-N-propylbutanamide

16. Give the organic products of the following reactions:

a. Propanoic acid and ammonia.

b. Ethanoyl chloride plus methanol.

c. Butanoic anhydride plus water.

d. Propanamide plus sodium hypobromite

e. Ethanol plus propanoyl chloride

17. Give reagents, essential conditions and equations for the conversion of ethanoic acid into:

a. Ethanoic anhydride

b. Ethanamide

c. Ethyl ethanoate

18. Ethanoic anhydride is a liquid at room temperature but ethanamide is a solid. Comment briefly on this.

19. Discuss the uses of esters.

20. a. Write an equation for the formation of ethyl ethanoate from ethanoyl chloride and ethanol. Name the mechanism for the reaction taking place.

b. Explain why dilute sodium hydroxide will cause holes in clothing made from polymers such as Terylene while polythene containers can store caustic soda.

21. Ethyl oleate is an ester with the structural structure below:

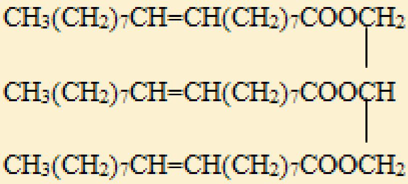
$CH_3(CH_2)_6CH_2\text{-}CH{=}CHCH_2(CH_2)_6COOCH_2CH_3$

It is possible the body could synthesize this compound from the ethanol present in alcoholic drinks and the natural fatty acid, oleic acid.

a. Write the structural formula of oleic acid

b. Construct a balanced equation for the production of ethyl oleate from ethanol and oleic acid.

c. Suggest how oleic acid can be obtained from the triglyceride below



$$\begin{array}{l} CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_2 \end{array}$$

22. This question is about the reactions of carboxylic acids and their derivatives.

a. A carboxylic acid derivative X was found to contain C, H, N and O. An analysis gave the following percentage composition by mass: 49.4%, 9.6% and 19.1% for carbon, hydrogen and nitrogen respectively. Compound X had a relative molecular of 73.

i. Calculate the empirical and molecular formulae of X.

ii. Suggest three possible structures of X.

b. Acyl chlorides such as ethanoyl chloride undergo several reactions due to their high reactivity. What could be produced when ethanoyl chloride reacts with:

i.Water

ii. Propan-2-ol

ii. Ammonia

iii. Sodium acetate

UNIT
15

AMINES AND AMINO ACIDS

Key unit competency: Relate the chemical nature of the amines and aminoacids to their properties, uses and reactivity.

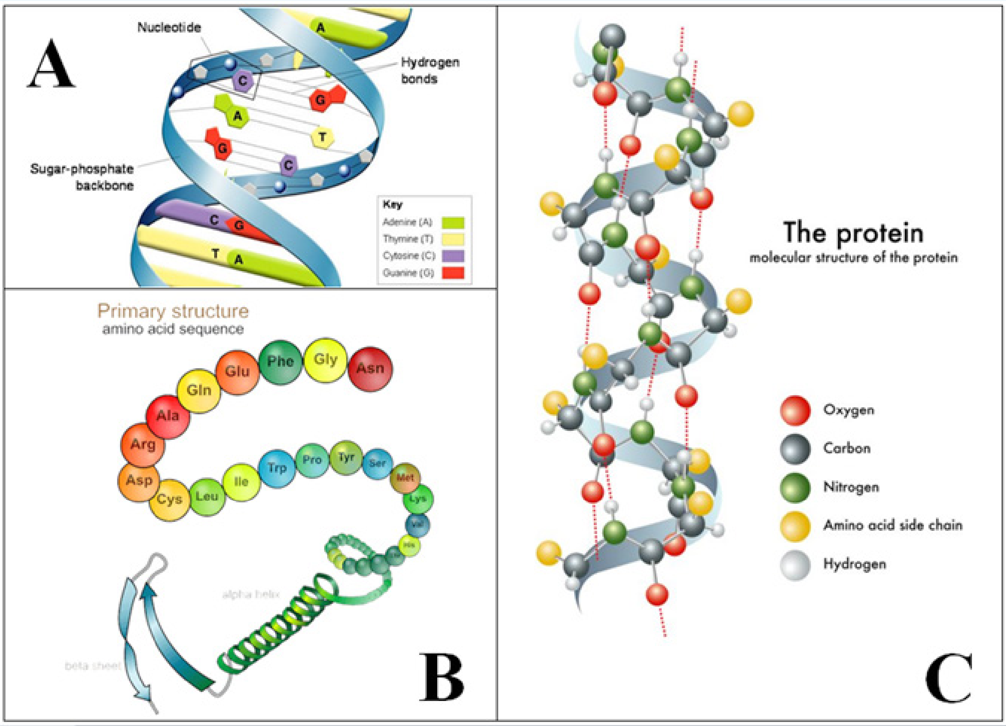
INTRODUCTORY ACTIVITY

Read the text below, observe the accompanying images and answer to the questions.

The cell is the basic structural, functional, and biological unit of all known living organisms. A cell is the smallest unit of life. All cells are made up of Inorganic compounds and organic compounds. ***Inorganic compounds*** are in general compounds that do not contain carbon atoms while ***organic compounds*** are compounds that mainly contain carbon (C) and hydrogen (H) atoms, and eventually other elements such as oxygen (O) and nitrogen (N) in biological macromolecules that include the ***carbohydrates***, ***lipids***, ***proteins*** and ***nucleic acids***.

Proteins are macromolecules consisting of one or more long chains of *amino acid residues*. Proteins differ from one another primarily in their sequence of ***amino acids*** which is dictated by the nucleotide sequence of their genes, and which usually results in protein folding into a specific three-dimensional structure that determines its activity. ***Nucleic acids*** [Deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)] alongside proteins, lipids and complex carbohydrates (polysaccharides), are one of the four major types of macromolecules that are essential for all known forms of life. They are a thread-like chain of nucleotides carrying the genetic instructions used in the growth, development, functioning and reproduction of all known living organisms and many viruses.

The image below shows the partial molecular structure of ***DNA*** (A) and of a ***protein*** (B, C).



1. Identify the common point between DNA and proteins. Explain your answer.

2. The terminology ***"amino acid"*** is found in the text and image above. According to you, what is it, and what is its role in living organisms?

3. If protein molecules are made essentially of Carbon, Hydrogen, Oxygen, Nitrogen and amino acid side chains (figure C),

   a. What kind of bonds do you expect to see in those structures?

   b. What kind of reactions do you expect in those molecules?

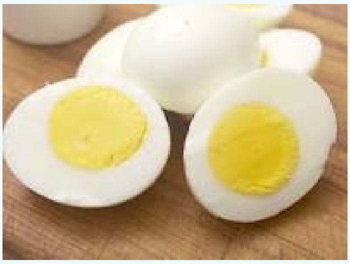
4. a) Have your ever checked the smell of the following substances?

   i.Ammonia in laboratory
   ii. Fish
   iii. Rotting fish
   iv. Decaying animal tissues
   v. Rotting egg

b) How are their smell and where do you think the smell is coming from?

c) What types of chemicals do you think the substances ii, iii,iv,v in a) are made up of ?

d) What are the common main constituents that we find in the following food? From you knowledge in biology what type of food are they representing?



15.1. Nomenclature and classification of amines

ACTIVITY 15.1

1. Pentan-2-ol, butan-1-ol and 2-methylpropan-2-ol are alcohols.

For each one:

a. give its molecular formula

b. give its structural formula

c. give its displayed formula

d. give its skeletal formula

e. State whether it is a primary, secondary or tertiary alcohol.

A. Give the general formula that is used to represent alcohols.

B. Two of the alcohols in this question are isomers of each other. Identify which two and identify the type of isomerism they show.

C. Name the alcohol whose structural formula is $CH_3CH_2COH(CH_3)_2$

2. a) What is meant by nucleophilic substitution?

b) Differentiate between SN_1 and SN_2 with the help of relevant examples

c) What type of reaction is the following? SN_1 or SN_2? Justify your answer

$$NH_3 + RCl \longrightarrow RNH_2 + HCl$$

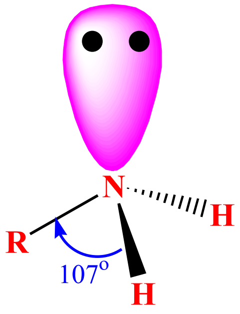
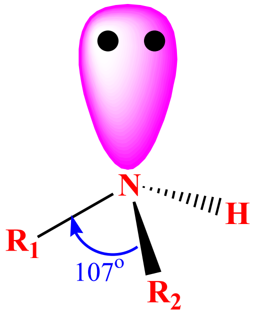
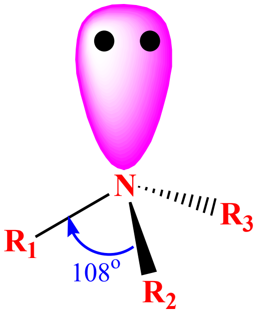
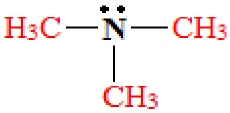
d) Write the formula of successive nucleophilic substitution between alkyl iodide CH_3-CH_2-I and ethyl amine and exhibit the differences between the products.

Amines are one of organic compounds containing nitrogen. They are one of the most important classes of organic compounds which are ***obtained by replacing one or more hydrogen atoms by an alkyl or aryl group in a molecule of ammonia (NH_3)***. They are present in vitamins, proteins, hormones, etc. They are extensively used in the manufacturing of many drugs and detergents.

15.1.1 Classification of amines

The general formula of amines contains NH_2 functional group. Amines have as general formula, RNH_2, where R may be a hydrocarbon group. Depending upon the number of hydrogen atoms that are replaced by an alkyl or aryl group in ammonia, amines are classified as primary, secondary and tertiary (Table 15.1).

Table 15.1. Classification of amines and examples

	Primary amine	*Secondary amine*	*Tertiary amine*
General structure	 One of the three hydrogens of ammonia is replaced by an alkyl group	 Two of the three hydrogens of ammonia are replaced by alkyl groups	 All the three hydrogens of ammonia are replaced by alkyl groups
Examples	$CH_3-CH_2-NH_2$	$CH_3-NH-CH_3$	 $H_3C-\ddot{N}(CH_3)-CH_3$

15.1.2 Nomenclature of amines

In organic chemistry, the names of the compounds are given according to the guidelines provided by IUPAC. In this regards, amines are named by ending with –*amine.*

The ***IUPAC*** system names amine functions as substituents on the largest alkyl group.

Examples:

$CH_3CH_2CH_2NH_2$:1-aminopropane or propanamine

If there is another priority functional group as well as the amine group then the prefix amino is used. Example:

$CH_3CH(CH_3)CH_2CH(NH_2)CH_2CH_3$: 3-amino-5-methylhexane

If the amine is secondary and has two alkyl groups attached to the nitrogen, then each chain is named and the smaller alkyl group is preceded by an –N which plays the same role as a number in positioning a side alkyl chain.

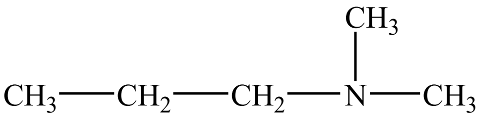
Example: $CH_3CH_2CH_2NHCH_3$: N-methylpropylamine is the common name and N-methyl-1-aminopropane is the IUPAC name.

If in the common naming the lengths of the chain are the same, an –N is not used as shown in the following example:

CH_3CH_2-NH-CH_2CH_3 (Diethylamine is the common name which does not contain N because the chains have the same length and N-ethylethanamine is the IUPAC where N does appear.

In case of a tertiary amine, the use of N is applied at each alkyl side group.

Example:



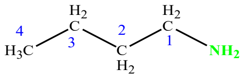
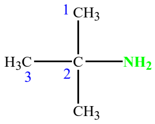
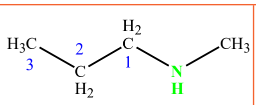
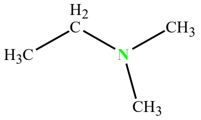
$$CH_3-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{N}}-CH_3$$

N,N -dimethylpropylamine (common name)

N,N -dimethyl -1 -aminopropane (IUPAC name)

The following are examples of primary, secondary and tertiary amines (Table 15.2) with their corresponding names using IUPAC of common name.

Table 15.2. Some examples of primary, secondary and tertiary amines

				
	A primary amine	*A primary amine*	*A secondary amine*	*A tertiary amine*
IUPAC name	1-aminobutane	2-amino-2-methylpropane	1-methylamino-propane	dimethylaminoethane
Common name	n-butylamine	tert-butyl-amine	methylpropyl-amine	ethyldimethyl-amine

Aliphatic and Aromatic and heterocyclic amines are named after the groups surrounding the ***nitrogen + amine***.

Examples:

1°Aliphatic amines

$C_2H_5NH_2$: ethyl*amine*

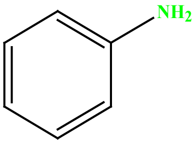
$(CH_3)_2NH$: dimethyl*amine*

$(CH_3)_3N$: trimethyl*amine*

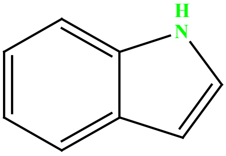
2° Aromatic amines

C_6H_5**NH_2**: phenyl***amine*** or aniline

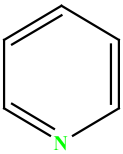
In case of heterocyclic amines, there is a common nomenclature of these compounds as indicated in the following examples.



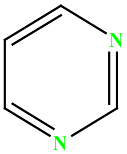
aniline



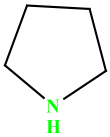
Indole



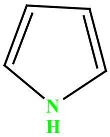
pyridine



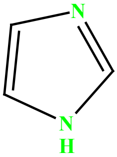
pyrimidine



pyrrolidine



Pyrrole

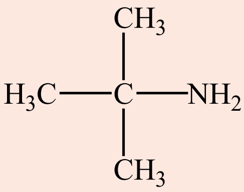


imidazole

APPLICATION ACTIVITY 15.1

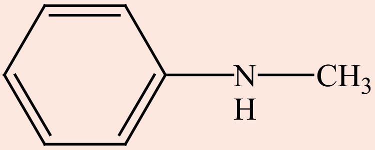
1. Classify the following as primary, secondary and tertiary amines.

a.

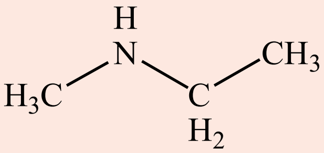


$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-NH_2$

c.

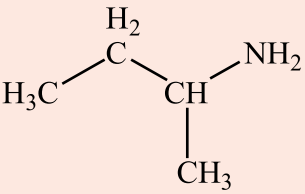


e.



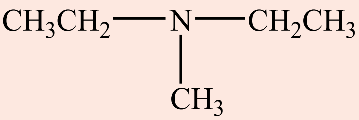
$H_3C-\overset{H}{N}-\underset{H_2}{C}-CH_3$

b.



$H_3C-\overset{H_2}{C}-\underset{CH_3}{CH}-NH_2$

d.



$CH_3CH_2-\underset{CH_3}{N}-CH_2CH_3$

2. For each compound below, provide the respective IUPAC name.

	IUPAC name
CH_3NH_2	
$CH_3CH_2CH_2NH_2$	
$CH_3CHNH_2CH_3$	
$CH_3NHCH_2CH_3$	
$CH_3CH_2N(CH_3)CH_2CH_2CH_3$	

3. Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

i. $(CH_3)_2CHNH_2$

ii. $CH_3(CH_2)_2NH_2$

iii. $CH_3NHCH(CH_3)_2$

iv. $(CH_3)_3CNH_2$

v. $C_6H_5NHCH_3$

15.2 Physical properties, natural occurrences and uses of amines

ACTIVITY 15.2

Calculate the molecular mass of the given products and justify the difference between boiling points of amines, alkanes and alcohols

Compound	Molecular mass	Boiling point
Methanol (CH_3OH)		65°C
Methylamine (CH_3NH_2)		−6°C
Ethane (CH_3CH_3)		−89°C
1-propanol ($CH_3CH_2CH_2OH$)		97°C
Propyl amine ($CH_3CH_2CH_2NH_2$)		48°C
Ethylmethylamine ($CH_3NHCH_2CH_3$)		36°C
Trimethylamine $N(CH_3)_3$		2.9°C
Butane ($CH_3CH_2CH_2CH_3$)		-0.5°C
Butylamine (n-$C_4H_9NH_2$)		77.65°C
Diethyl-amine [$(C_2H_5)_2NH$]		56.15°C
Ethyl-dimethyl-amine [$C_2H_5N(CH_3)_2$]		37.35°C
2-Methyl-butane [$C_2H_5CH(CH_3)_2$]		27.65°C
Butan-1-ol (n-C_4H_9OH)		117.15°C

15.2.1 Physical properties of amines

Primary and secondary amines can form a hydrogen bond to each other (as shown in the Figure 15.1 below where two molecules of $H_3C–NH_2$ are bonded together).

Because Nitrogen is less electronegative than oxygen, the N—H bond is not quite as polar as the O—H bond; reason why hydrogen bonds in amines are less strong than those of alcohol molecules. Primary and secondary amines have lower boiling points than alcohols of similar molecular weight due to their weaker hydrogen bonding.

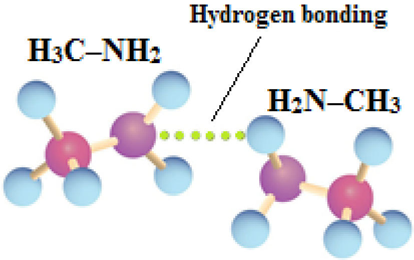
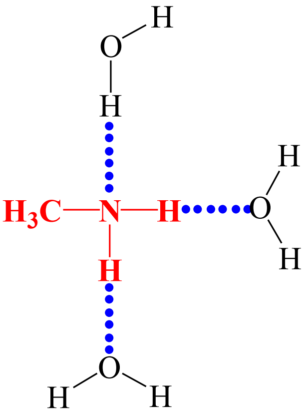


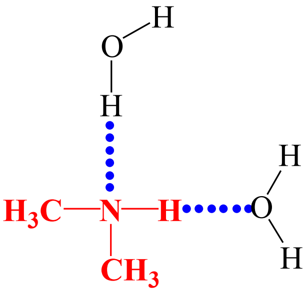
Figure 15.1. Hydrogen bonding between two amine molecules

Tertiary amines do not bond to each other by hydrogen bond and they have boiling points similar to hydrocarbons of the same molecular weight. However, primary, secondary and tertiary amines form hydrogen bond with water and amines with low-molecular weight are generally soluble in water.

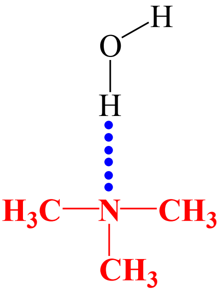
Example of hydrogen bond between amines and water:



Primary amine



Secondary amine



Tertiary amine

Generally the boiling point of amines increases as the molecular weight increase and they boil at higher temperatures than alkanes but at lower temperatures than alcohols of comparable molar mass.

The amines are soluble in organic solvent and the solubility decreases as the molecular weight increases. The table 15.3 summarizes some physical properties of some amines.

Table 15.3. Physical Properties of Some Amines Compared to some Oxygen-Containing Compounds

Name	Condensed Structural Formula	Class	Molar Mass	Boiling Point (°C)	Solubility at 25°C (g/ 100g Water)
Butylamine	$CH_3CH_2CH_2CH_2NH_2$	Primary amine	73	78	miscible
Diethylamine	$(CH_3CH_2)_2NH$	Secondary amine	73	55	miscible
Butylalcohol	$CH_3CH_2CH_2CH_2OH$	—	74	118	8
Dipropylamine	$(CH_3CH_2CH_2)_2NH$	Secondary amine	101	111	4
Triethylamine	$(CH_3CH_2)_3N$	Tertiary amine	101	90	14
Dipropylether	$(CH_3CH_2CH_2)_2O$	—	102	91	0.25

Amines tend to be gases at low molecular weight (e.g. up to $(CH_3)_3N$, trimethylamine) and the heavier ones are liquids at room temperature. In fact, Methyl, dimethyl, trimethyl, and ethyl -amines ***are gases*** under standard conditions. Most common alkyl amines are ***liquids***, and high molecular weight amines are, quite naturally, ***solids*** at standard temperatures. Additionally, gaseous amines possess a characteristic ***ammonia smell***, while liquid amines have a distinctive "fishy" smell: higher molecular-weight amines often **smell like rotting fish**, and are often **found in decaying animal tissues**. Cadaverine [$H_2N(CH_2)_5NH_2$] and putrescine [$H_2N(CH_2)_4NH_2$] are some of the examples. The lower molecular- weight amines with up to about five carbon atoms are ***soluble in water***. The higher-molecular-weight amines that are ***insoluble in water*** will dissolve in acid to form ionic amine salts.

15.2.2 Natural occurrence of amines and their usage

Naturally amines occur in proteins, vitamins, hormones, etc. and they are also prepared synthetically to make polymers, drugs and dyes.

Amines can be used as dyes (colorants) or as drugs. Primary aromatic amines are used as a starting material for the manufacture of azo dyes. They react with nitrous (II) acid to form diazonium salt which can undergo a coupling reaction in order to form an azo compound. As azo compounds are highly coloured, they are widely used in dyeing industries. Examples include Methyl orange and Direct brown 138.

In medicine, amines can be used as drugs.

- ***Chlorpheniramine*** is an antihistamine that helps to relief allergic disorders due to cold, hay fever, itchy skin, insect bites and stings.
- ***Diphenhydramine*** is the common antihistamine.
- ***Chlorpromazine*** is a tranquillizer that anaesthetizes without inducing sleep. It is used to relieve anxiety, excitement, restlessness or even mental disorder.
- ***Acetaminophen*** is also known as ***paracetamol*** or ***p-acetaminophenol***, it is an analgesic that relieves pains such as headaches. It is believed to be less corrosive to the stomach and is an alternative to aspirin.

Amines are widely encountered in biological and pharmacological studies. Some important examples are the 2-phenylethylamines, some vitamins, antihistamines, tranquilizers, and neurotransmitters (noradrenaline, dopamine and serotonin) which act at neuromuscular synapses.

APPLICATION ACTIVITY 15.2

1. Which compound of each pair has the higher boiling point? Explain.

   a. butylamine or pentane

   b. CH_3NH_2 or $CH_3CH_2CH_2CH_2CH_2NH_2$

2. Between the two compounds $CH_3CH_2CH_3$ and $CH_3CH_2NH_2$, explain which is more soluble in water.

15.3 Preparation of amines

ACTIVITY 15.3

Ammonia (NH_3) molecules react with water molecules. Write the detailed chemical equation of that reaction.

The amines can be prepared based on the following reactions:

15.3.1 Alkylation of ammonia

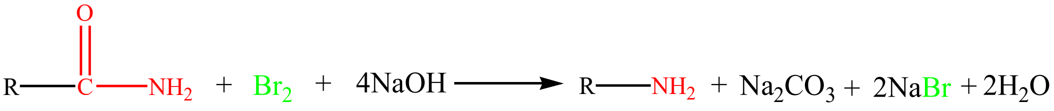
Primary amines can be synthesized by alkylation of ammonia. The reaction involves nucleophilic substitution of an alkyl halide when ammonia is used as nucleophilic agent. The reaction is carried out in a sealed tube at 100 °C or 373 K.

$$CH_3—CH_2—Cl + NH_3 \rightleftharpoons CH_3—CH_2—NH_2 + HCl$$

15.3.2. Hoffmann bromamide degradation reaction

Hoffmann developed a method for the preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. This is a degradation reaction with migration of an alkyl or aryl group taking place from carbonyl carbon of the amide to the nitrogen atom.

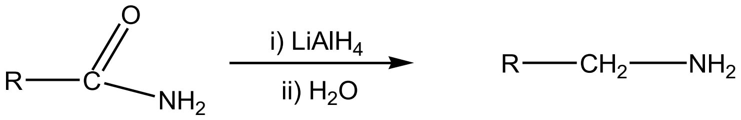
The reaction is valid for the preparation of primary amines only, and it yields uncontaminated compound with other amines.



$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

15.3.3 Reduction of amides

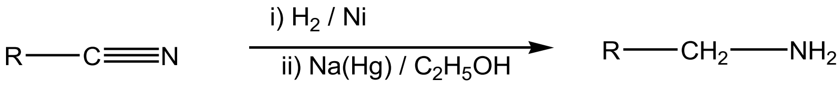
The reduction of amides, using lithium aluminium hydride ($LiAlH_4$) convert them to amines.



$$R-C(=O)NH_2 \xrightarrow[\text{ii) } H_2O]{\text{i) } LiAlH_4} R-CH_2-NH_2$$

15.3.4 Reduction of nitriles

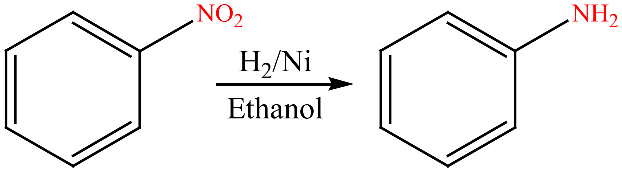
Nitriles are reduced to amines using hydrogen in the presence of a nickel catalyst, although acidic or alkaline conditions should not be used to avoid the possible hydrolysis of the -CN group. $LiAlH_4$ is more commonly employed for the reduction of nitriles on the laboratory scale.

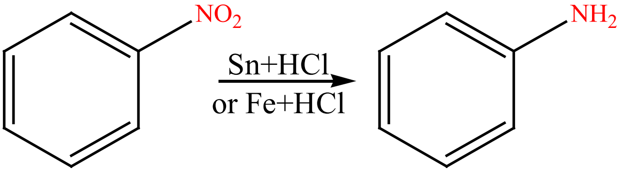


$$R-C\equiv N \xrightarrow[\text{ii) } Na(Hg) / C_2H_5OH]{\text{i) } H_2 / Ni} R-CH_2-NH_2$$

15.3.5 Reduction of nitro compounds

Aromatic nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium. Nitroalkanes can also be similarly reduced to the corresponding alkanamines.





Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

APPLICATION ACTIVITY 15.3

1. a)Give two reagents that could be used to synthesize $(CH_3)_2CHCH_2NH_2$ from the following substance $(CH_3)_2CHCN$.

   b)Discuss the required conditions to use in each case of the reagents chosen.

2. Write chemical equations for the following reactions:

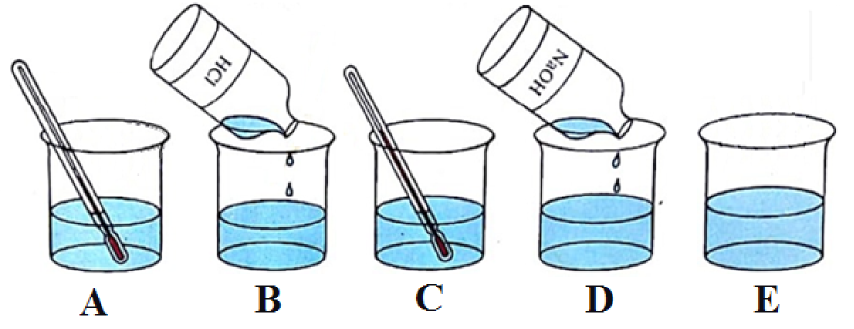
   a. Reaction of NH_3 with C_2H_5Cl.

   b. Ammonolysis of benzoyl chloride and reaction of amine so formed with two moles of CH_3Cl.

15.4. Chemical properties of amines

ACTIVITY 15.4

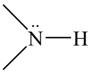
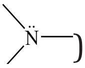
Experiment: In a solution of ethylamine at room temperature (A), add dilute hydrochloric acid (B). After a while (C), add excess of sodium hydroxide in the solution (D) to obtain the solution E.



Question:

1. A fishy smell is detected in solution A .Explain why?
2. What evidence is there for a chemical reaction between ethylamine and hydrochloric acid in solution?
3. Why does the smell of ethylamine disappear when hydrochloric acid is added in solution B?
4. Why does the smell reappear in E when excess sodium hydroxide is added in D?

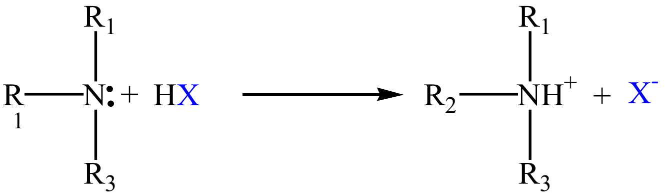
Difference in electronegativity between nitrogen and hydrogen atoms and the presence of unshared pair of electrons over the nitrogen atom makes amines reactive. The number of hydrogen atoms attached to nitrogen atom also is involved in the reaction of amines; that is why the reactivity of amines differs in many reactions. Amines behave as nucleophiles due to the presence of unshared electron pair as shown below in primary, secondary and tertiary functional group of amines).

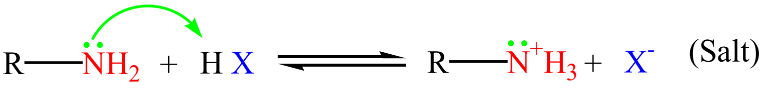
Primary ($-\ddot{N}H_2$), secondary () and tertiary amines ().

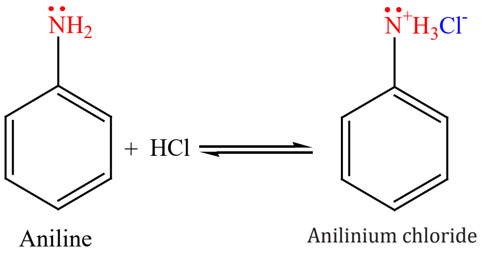
15.4.1 Reactions of amines with dilute acids

Amines, like ammonia, are bases. Being basic in nature, they react with acids to form salts.

Tertiary amines (R_3N) react with strong acids such as hydroiodic acid (HI), hydrobromic acid (HBr) and hydrochloric acid (HCl) to give ammonium salts R_3NH^+.







Amine salts on treatment with a base like NaOH, regenerate the parent amine.

$$R-N^+H_3X^- + O^-H \longrightarrow R-\ddot{N}H_2 + H_2O + X^-$$

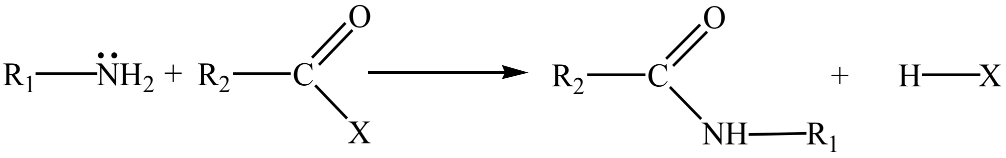
Example:

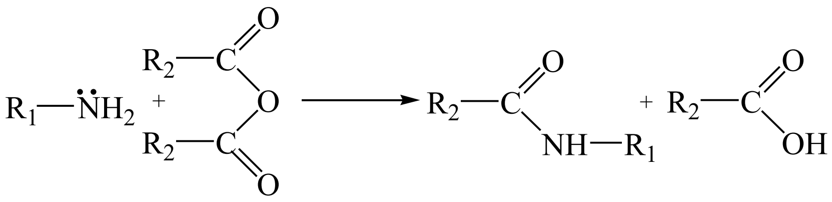
$CH_3NH_2 + HCl \rightarrow CH_3NH_3^+Cl^-$

$CH_3NH_3^+Cl^- + NaOH \rightarrow CH_3NH_2 + NaCl + H_2O$

15.4.2 Reactions of amines with carboxylic acid derivatives

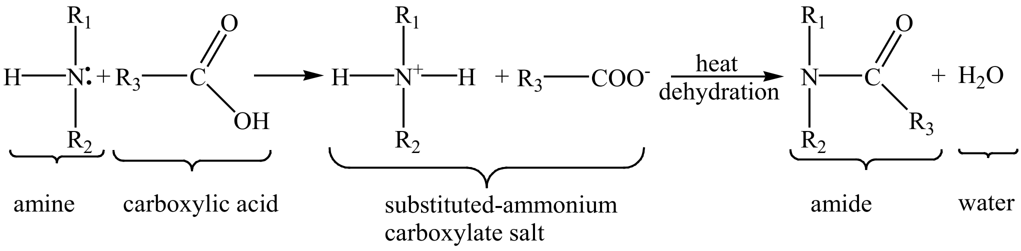
Acyl chlorides and acid anhydrides react with primary and secondary amines to form amides. Tertiary amines cannot be acylated due to the absence of a replaceable hydrogen atom.





15.4.3. Reaction with carboxylic acid

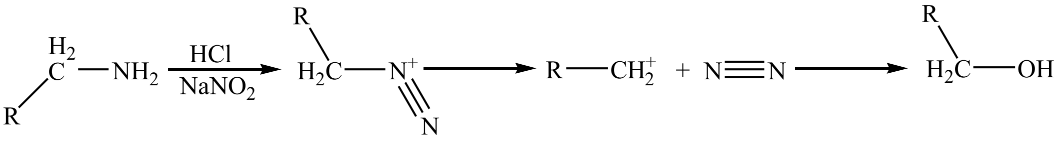
Because amines are basic, they neutralize carboxylic acids to form the corresponding ammonium carboxylate salts. Upon heating at 200°C, the primary and secondary amine salts dehydrate to form the corresponding amides.



15.4.4. Reaction with nitrous acid

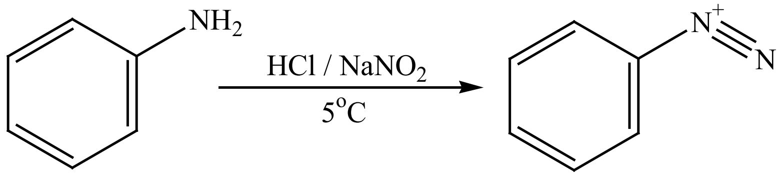
Nitrous acid, HNO_2 is unstable. It is produced indirectly using a mixture of $NaNO_2$ and a strong acid such as HCl or H_2SO_4 in diluted solution. Primary aliphatic amines react with nitrous acid to produce very unstable diazonium salts which spontaneously decompose by losing N_2 to form a carbanium ion. Further, the carbenium ion is used to produce a mixture of alkenes, alkanols or alkyl halides, with alkanols as major product.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$



diazonium ion

Primary aromatic amines, such as aniline (phenylamine) form a more stable diazonium ion at 0°C –5°C. Above 5°C, it will decompose to give phenol and N_2. Diazonium salts can be isolated in the crystalline form but are usually used in solution and immediately after preparation, due to its rapid decomposition.



APPLICATION ACTIVITY 15.4

1. Draw the structures of all amines of molecular formula $C_4H_{11}N$. Classify them as primary, secondary and tertiary amines

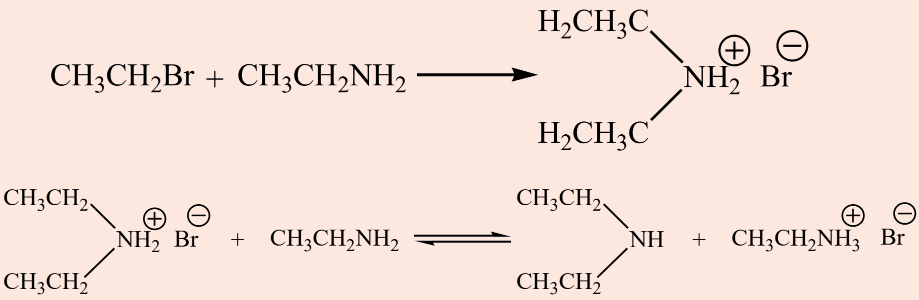
2. a. Write the equation for the reaction which happens when dimethylamine, $(CH_3)_2NH$, reacts with water.

   b. Write the formula of the product of the reaction between trimethylamine gas, $(CH_3)_3N$, and hydrogen chloride gas, showing the essential details of its structure.

3. Nitrous acid is unstable and has to be produced in the same test tube as the reaction is happening in. If you were to test an amine with nitrous acid, how would you do it?

4. This question is about the reactions between amines and halogenoalkanes (alkylhalides).

   a. The reaction between bromoethane and ethylamine produces a complicated mixture of products, but the first to be formed are given by the equations below:



Describe in words what is happening.

15.5. General structure of amino acids and some common examples

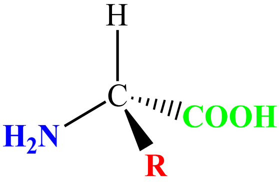
ACTIVITY 15.5

Amines are molecules that have as general formula, R–NH_2 while ***carboxylic acids*** have as general formula, R–COOH. Predict a general structure (skeletal formula) of a molecule that contains an ***amino group*** and ***a carboxyl group*** on an aliphatic chain.

15.5.1. General structure of amino acids

Amino acids are organic compounds containing amine (-NH_2) and carboxyl (-COOH) functional groups, along with a side chain (R group) specific to each amino acid. The key elements of an amino acid are carbon (C), hydrogen (H), oxygen (O), and nitrogen (N). About 500 naturally occurring amino acids are known.

The general structure of the most common amino acids is shown by the functional group (-NH_2) and a carboxylic acid group (-COOH) attached to the same carbon and they are called ***α-amino acids.***



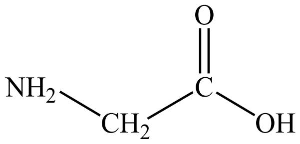
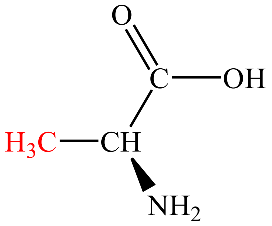
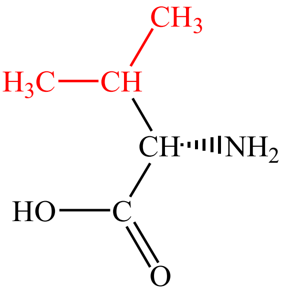
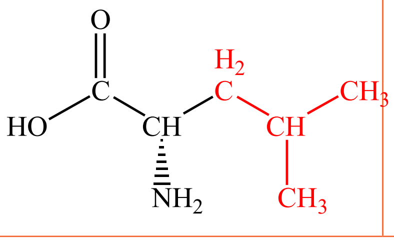
2-amino acid

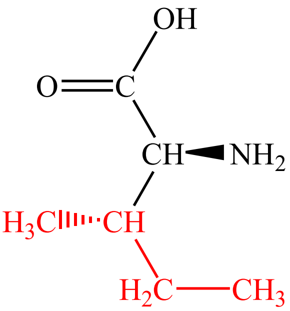
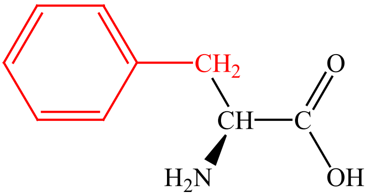
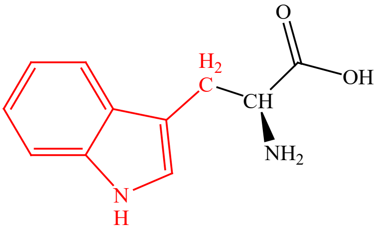
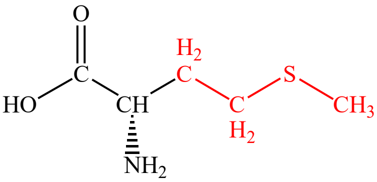
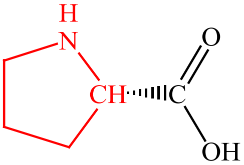
The **R** group is the part of the amino acid that can vary in different amino acids. It can be a hydrogen (in that case, the amino acid is called *Glycine*) or a –CH_3 group (Alanine) or other radicals.

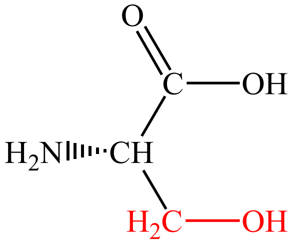
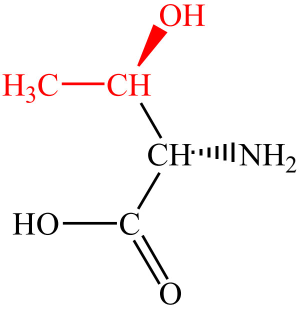
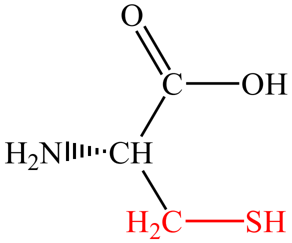
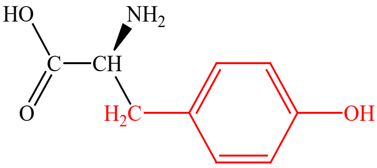
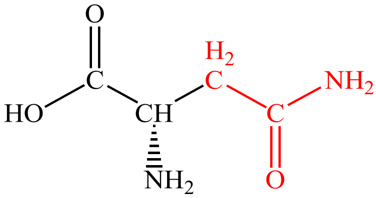
15.5.2. Common Amino Acids

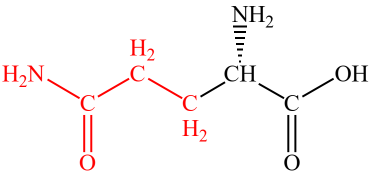
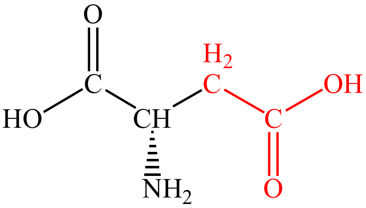
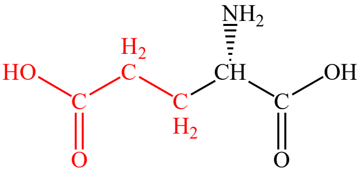
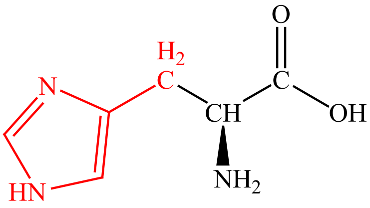
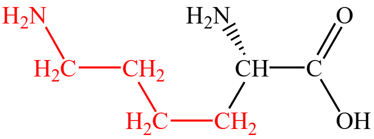
Among the 500 known amino acids, there are 20 important α-amino acids, as shown in the Table 15.4 below. Each amino acid has a ***common name***. You will notice that the names in common used for amino acids are not descriptive of their structural formulas; but at least they have the advantage of being shorter than the ***systematic names***. The ***abbreviations*** (Gly, Glu,) that are listed in table below, are particularly useful in designating the sequences of amino acids in proteins and peptides.

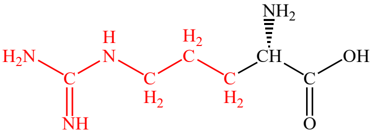
Table 15.4: Common amino acids and their formulas [adapted from (Chang, 2005) and (Schmitz, 2018)]

#	Common Name & Systematic name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
1	Glycine *2-Amino acetic acid*	Gly (G)		75	the only amino acid lacking a chiral carbon
2	Alanine *2-Amino-propionic acid*	Ala (A)		89	—
3	Valine *2-Amino-3-methyl-butyric acid*	Val (V)		117	a branched-chain amino acid
4	Leucine *2-Amino-4-methyl-pentanoic acid*	Leu (L)		131	a branched-chain amino acid

#	Common Name & Systematic name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
5	Isoleucine *2-Amino-3-methyl-pentanoic acid*	Ile (I)		131	an essential amino acid because most animals cannot synthesize branched-chain amino acids
6	Phenylalanine *2-Amino-3-phenyl-propionic acid*	Phe (F)		165	also classified as an aromatic amino acid
7	Tryptophan *2-Amino-3-(1H-indol-3-yl)-propionic acid*	Trp (W)		204	also classified as an aromatic amino acid
8	Methionine *2-Amino-4-methylsulfanyl-butyric acid*	Met (M)		149	side chain functions as a methyl group donor
9	Proline *Pyrrolidine-2-carboxylic acid*	Pro (P)		115	contains a secondary amine group; referred to as an *α-imino acid*

#	Common Name & Systematic name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
10	Serine *2-Amino-3-hydroxy-propionic acid*	Ser (S)		105	found at the active site of many enzymes
11	Threonine *2-Amino-3-hydroxy-butyric acid*	Thr (T)		119	named for its similarity to the sugar threose
12	Cysteine *2-Amino-3-mercapto-propionic acid*	Cys (C)		121	oxidation of two cysteine molecules yields *cystine*
13	Tyrosine *2-Amino-3-(4-hydroxy-phenyl)-propionic acid*	Tyr (Y)		181	also classified as an aromatic amino acid
14	Asparagine *2-Amino-succinamic acid*	Asn (N)		132	the amide of aspartic acid

#	Common Name & Systematic name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
15	Glutamine *2-Amino-4-carbamoyl-butyric acid*	Gln (Q)		146	the amide of glutamic acid
16	Aspartic acid *2-Amino-succinic acid*	Asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
17	Glutamic acid *2-Amino-pentanedioic acid*	Glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
18	Histidine *2-Amino-3-(1H-imidazol-4-yl)-propionic acid*	His (H)		155	the only amino acid whose R group has a pK_a (6.0) near physiological pH
19	Lysine *2,6-Diamino-hexanoic acid*	Lys (K)		147	—

#	Common Name & Systematic name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
20	Arginine *2-Amino-5-guanidino-pentanoic acid*	Arg (R)		175	almost as strong a base as sodium hydroxide

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek glykys, meaning "sweet"). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids.

APPLICATION ACTIVITY 15.5

1. Write the side chain of each amino acid.

   a. serine

   b. arginine

   c. phenylalanine

2. Draw the structure for each amino acid.

   a. alanine

   b. cysteine

   c. histidine

3. Identify an amino acid whose side chain contains:

   a. amide functional group.

   b. aromatic ring.

   c.carboxyl group.

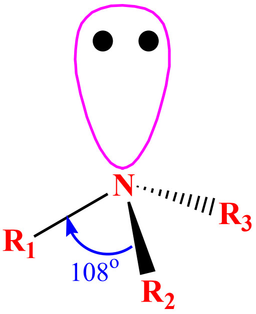
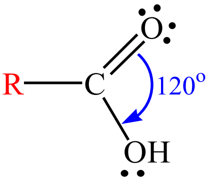
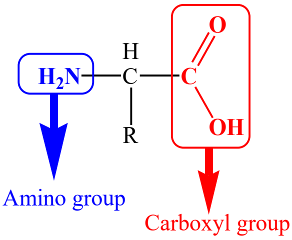
15.6. Comparison of physical properties amino acids to those of carboxylic acids and amines

ACTIVITY 15.6

By using examples, distinguish amines, carboxylic acids and amino acids (in different states: gas, liquid, solid) based on their characteristic feature.

The amino acids, carboxylic acids and amines have different functional groups; this is the base of their different physical properties as shown in the Table 15.5.

Table 15.5. Comparison of physical properties of amines, carboxylic acids and amino acids

	Amines	Carboxylic acids	Amino acids
General structure			

	Amines	Carboxylic acids	Amino acids
Hydrogen bond	• Primary and secondary amines can form hydrogen bond with one to other. • As a result of hydrogen bonding, primary and secondary amines have higher boiling points than alkanes of similar size. • Lone pairs on amines imply their hydrogen bond to water. (water solubility better than alkanes)	• Carboxylic acids are able to form a hydrogen bond. • Carboxylic acids have high boiling points due to their ability to form hydrogen bond with one another. • The ability to form hydrogen bonds, in addition to the presence of polar C=O, C-O, and O-H bonds, gives small carboxylic acids a significant water solubility. • An increasing number of carbon atoms leads to a reduction in water solubility. • Their hydrogen bonds enhance the possibility of bringing two acid molecules together by forming a dimer	• No hydrogen bond is found between two amino acids molecules. Rather, they undergo a peptide bond which generates loss of one molecule of water. • Hydrogen bonds exist between two polypeptide chains (chain of many amino acids)..

	Amines	Carboxylic acids	Amino acids
Physical state	• Low molecular weight Amines tend to be gases and many heavier ones are liquids or *solids* at normal standard temperatures. • Gaseous amines possess a characteristic *ammonia smell*, while liquid amines have a distinctive “fishy” smell. • Volatile amines have strong odors. -Amines smell like rotten fish. • Many amines are physiologically active. • -Smaller amines are irritating to the skin, eyes, and mucous membrane and are toxic by ingestion.	• Many carboxylic acids are colorless liquids with disagreeable odours. • Aliphatic carboxylic acids with 5 to 10 carbon atoms are all liquids which have “goaty” odors. • The acids with more than 10 carbon atoms are wax-like solids, and their odour diminishes with increasing of molar mass and these results in the decreasing degree of volatility.	The amino acids are crystalline solids with surprisingly high melting points.

	Amines	Carboxylic acids	Amino acids
Melting and boiling point	• *Primary* and *secondary amines* boil at higher temperatures than alkanes but at lower temperatures than alcohols of comparable molar mass. • The boiling points of *tertiary amines* is low because they do not form a hydrogen bond.	• Carboxylic acids have high melting and boiling points compared to other organic compounds of the same mass or number of carbon atoms.	• The α-amino acids *crystallize as the dipolar forms*, $H_3N^+–CHR–CO_2^-$, and the strong intermolecular electrical forces in the crystals lead to higher melting points than those of simple amines or monocarboxylic acids. • The melting points are so high that decomposition often occurs on melting and tend to be in the 200 – 300°C range.

	Amines	**Carboxylic acids**	**Amino acids**
Solubility	All three classes of amines can engage in hydrogen bonding with water. Amines of low molar mass are quite *soluble in water*; the borderline of solubility in water is at four or five carbon atoms. The higher-molecular-weight amines that are *insoluble in water* will dissolve in acid to form ionic amine salts.	• The carboxyl group readily engages in hydrogen bonding with water molecules. • The acids with one to four carbon atoms are *completely miscible with water*. • Solubility decreases as the carbon chain length increases because dipole forces become less important and dispersion forces become more predominant. • The carboxylic acids generally are *soluble in such organic solvents* as ethanol, toluene, and diethyl ether.	• Amino acids are generally soluble in water and insoluble in non-polar organic solvents such as hydrocarbons. The extent of the solubility in water varies depending on the size and nature of the “R” group. • The dipolar structures of amino acids greatly reduce their solubility in nonpolar organic solvents compared to simple amines and carboxylic acids.

APPLICATION ACTIVITY 15.6

Discuss the solubility of amino acids, referring on the solubility of amines and carboxylic acids

15.7. Chemical properties of amino acids

ACTIVITY 15.7

A and B are organic products formed from the reactions in a) and b) respectively and identify A and B.

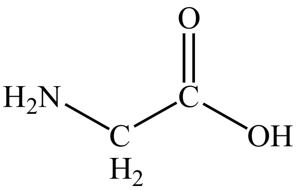
(a) $CH_3(CH_3)_2CH_3NH_2 + HCl \rightarrow A$

(b) $CH_3CH_2COOH + NaOH \rightarrow \ B$

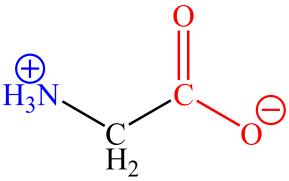
The reactivity of amino acids involves the reactions of both amines and carboxylic acids. Some of these reactions are given below.

15.7.1. Acid–base properties of amino acids

As the name suggests, amino acids are organic compounds that contain both a carboxylic acid group and an amine group. Amino acids are crystalline, high melting point (>200°C) solids. Such high melting points are unusual for a substance with molecules of this size — they are a result of internal ionisation. Even in the solid state, amino acids exist as ***zwitterions*** in which a proton has been lost from the carboxyl group and accepted by the nitrogen of the amine group:



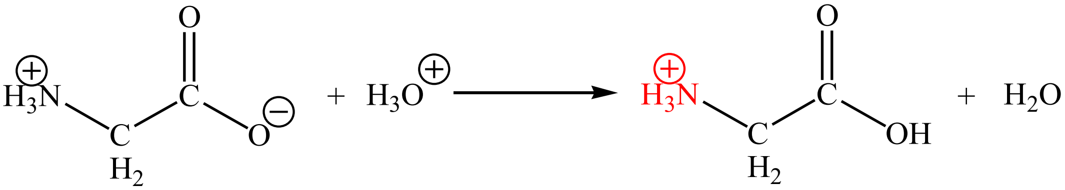
Glycine



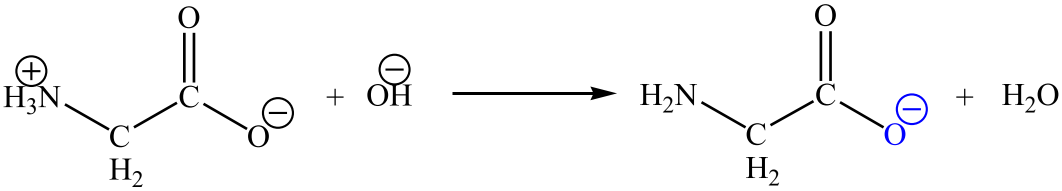
Zwitterion of glycine

So instead of hydrogen bonds between the amino acid molecules there are stronger ionic (electrovalent) bonds. This is reflected in the relative lack of solubility of amino acids in non- aqueous solvents compared with their solubility in water.

Zwitterions exhibit acid–base behaviour because they can accept and donate protons. In acids a proton is accepted by the carboxylic acid anion, forming a unit with an overall positive charge:



In alkalis the reverse occurs with the loss of a proton from the nitrogen atom:



The species present in a given solution depends on the pH of the solution.

Carboxylic acids have acidic properties and react with bases. Amines have basic properties and react with acids. It therefore follows that amino acids have both acidic and basic properties.

15.7.2. Isoelectric point in aminoacids (pI)

The isoelectric point (pI), is the pH at which a particular molecule carries no net electrical charge in the statistical mean. This means it is the pH at which the amino acid is neutral, i.e. the zwitterion form is dominant. The pI is given by the average of the pKas that involve the zwitterion, i.e. that give the boundaries to its existence.

The table below shows the pKa values and the isoelectronic point, pI, is given below for the 20 α-amino acids (Table 15.6).

pKa_1= α-carboxyl group, pKa_2 = α-ammonium ion, and pKa_3 = side chain group

Table 15.6 pKa and pI values for the 20 α-amino acids

Amino acid	pKa_1	pKa_2	pKa_3	pI
Glycine	2.34	9.60	---	5.97
Alanine	2.34	9.69	---	6.00
Valine	2.32	9.62	---	5.96
Leucine	2.36	9.60	---	5.98
Isoleucine	2.36	9.60	---	6.02
Methionine	2.28	9.21	---	5.74
Proline	1.99	10.60	---	6.30
Phenylalanine	1.83	9.13	---	5.48
Tryptophan	2.83	9.39	---	5.89
Asparagine	2.02	8.80	---	5.41
Glutamine	2.17	9.13	---	5.65
Serine	2.21	9.15	---	5.68

Threonine	2.09	9.10	---	5.60
Tyrosine	2.20	9.11	---	5.66
Cysteine	1.96	8.18	---	5.07
Aspartic acid	1.88	9.60	3.65	2.77
Glutamic acid	2.19	9.67	4.25	3.22
Lysine	2.18	8.95	10.53	9.74
Arginine	2.17	9.04	12.48	10.76
Histidine	1.82	9.17	6.00	7.59

There are 3 cases to consider:

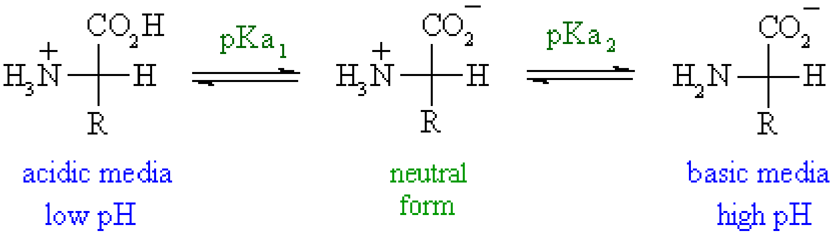
1. Neutral side chains

These amino acids are characterised by two pKas: pKa_1 and pKa_2 for the carboxylic acid and the amine respectively. The isoelectronic point will be halfway between, or the average of, these two pKa:

$$pI = \frac{1}{2}(pKa_1 + pKa_2)$$

This is most readily appreciated when you realise that at very acidic pH (below pKa1) the amino acid will have an overall positive charge and at very basic pH (above pKa2) the amino acid will have an overall negative charge.

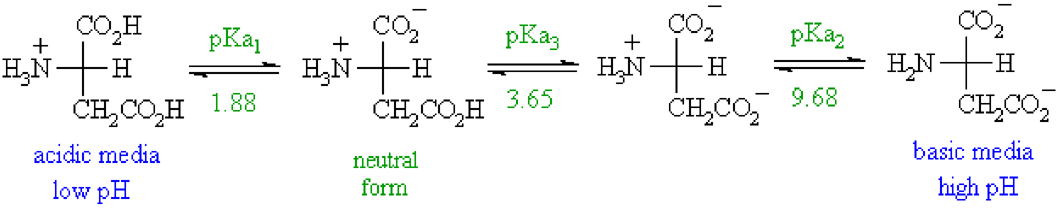
Example: For the simplest amino acid, ***glycine***, pKa_1= 2.34 and pKa_2 = 9.6, pI = 5.97.



The other two cases introduce other ionisable groups in the side chain "**R**" described by a third acid dissociation constant, $\mathbf{pKa_3}$

2. Acidic side chains

The pI will be at a lower pH because the acidic side chain introduces an "extra" negative charge. So the neutral form exists under more acidic conditions when the extra -ve has been neutralised. For example, for ***aspartic acid*** shown below, the neutral form is dominant between pH 1.88 and 3.65, pI is halfway between these two values, i.e. pI = 1/2 (pKa_1 + pKa_3), so pI = 2.77.



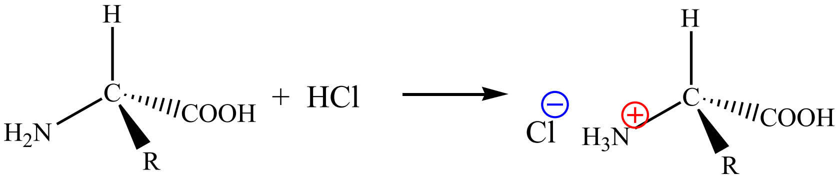
3. Basic side chains

The pI will be at a higher pH because the basic side chain introduces an “extra” positive charge. So the neutral form exists under more basic conditions when the extra positive has been neutralised. For example, for histidine, which has three acidic groups of pKa’s 1.82 (carboxylic acid), 6.04 (pyrrole NH) and 9.17 (ammonium NH), the neutral form is dominant between pH 6.04 and 9.17; pI is halfway between these two values,

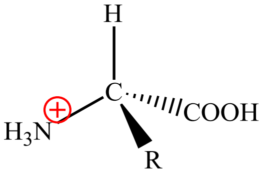
i.e. $pI = \frac{1}{2}(pKa_2 + pKa_3)$, so pI = 7.60.

15.7.3. Reaction with strong acids

In the following reaction, amino acids react with strong acids such as hydrochloric acid:

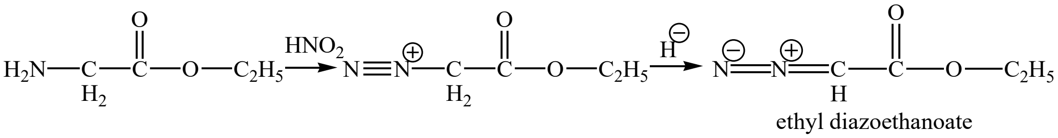


In **low pH**, therefore, amino acids exist in cationic form:



15.7.4. Reaction with nitrous acid (deamination)

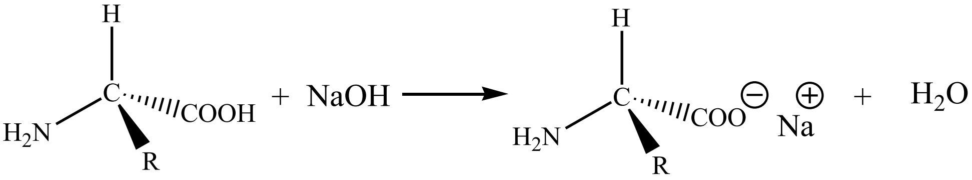
The amine function of ***α-amino acids*** and ***esters*** reacts with nitrous acid in a similar manner to that described for primary amines. The *diazonium ion* intermediate loses molecular nitrogen in the case of the acid, but the diazonium ester loses a proton and forms a relatively stable diazo compound known as ethyl diazoethanoate:



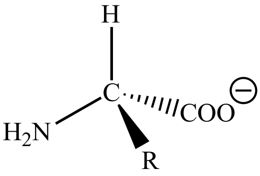
The diazo ester is formed because of the loss of N_2 from the diazonium ion which results in the formation of a quite unfavourable carbocation.

15.7.5. Reaction with sodium hydroxide

Amino acids react with strong bases such as sodium hydroxide:



In **high pH**, therefore, amino acids exist in anionic form:



15.7.6. Reaction of amino acids with sodium carbonate

Amino acids are instantly dissolved by strong hydrochloric acid but are in part recovered unchanged on dilution and evaporation. They are not decomposed by ***sodium carbonate*** but are easily decomposed by sodium hydroxide. (Dakin & West, 1928)

APPLICATION ACTIVITY 15.7

1. Draw the structure for the anion formed when glycine (at neutral pH) reacts with a base.

2. Draw the structure for the cation formed when glycine (at neutral pH) reacts with an acid.

3. Calculate the Isoelectric point of Glycine? ($pKa_1 = 2.4$; $pKa_2 = 9.8$)

4. Calculate the Isoelectric point of Lysine? ($pKa_1 = 2.2$, $pKa_2 = 8.9$; $pKa_3 = 10.5$)

15.8. Optical isomers of amino acids

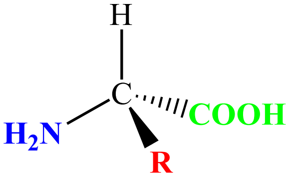
ACTIVITY 15.8

The molecule CHBrClF exhibits optical isomerism. Draw the 3D displayed formulae of both optical isomers.

In chemistry, the term "isomer" means *molecules that have the same molecular formula, but have a different arrangement of the atoms in space*.

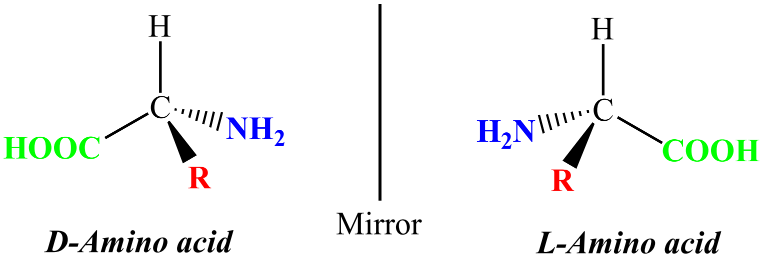
Simple substances which show optical isomerism exist as two isomers known as ***enantiomers***. Where the atoms making up the various isomers are joined up in a different order, this is known as ***structural isomerism***. Structural isomerism is not a form of stereoisomerism, which involve the atoms of the complex bonded in the same order, but in different spatial arrangements. ***Optical isomerism*** is one form of stereoisomerism; ***geometric isomers*** are a second type.

The general formula for an amino acid let us see that (apart from **glycine**, 2-aminoethanoic acid) the carbon at the centre of the structure has four different groups attached. In glycine, the "R" group is another hydrogen atom.



The lack of a plane of symmetry means that there will be two stereoisomers of an amino acid (apart from glycine) - one the non-superimposable mirror image of the other.

For a general 2-amino acid, the isomers are:



D-Amino acid ***L-Amino acid***

The R group, usually referred to as a side chain, determines the properties of each amino acid. Scientists classify amino acids into different categories based on the nature of the side chain. A tetrahedral carbon atom with four distinct groups is called **chiral**. The ability of a molecule to rotate plane polarized light to the left, L (**levorotary**) or right, D (**dextrorotary**) gives it its optical and stereo chemical fingerprint.

All the naturally occurring amino acids have the right-hand structure in the diagram above. This is known as the **"L-" configuration**. The other one is known as the **"D-" configuration**.

When asymmetric carbon atoms are present in a molecular compound, there are two ways in which the groups attached to that carbon can be arranged in the three dimensions, as we have just shown with the two models above. ***Chemically***, optical isomers behave the same. ***Biologically***, they do not. One will react properly, but the other will not.

APPLICATION ACTIVITY 15.8

1. Write the optical isomers of 2-aminopropanoic acid
2. Using diagrams, explain why glycine is not chiral.

15.9. Peptides and polypeptides

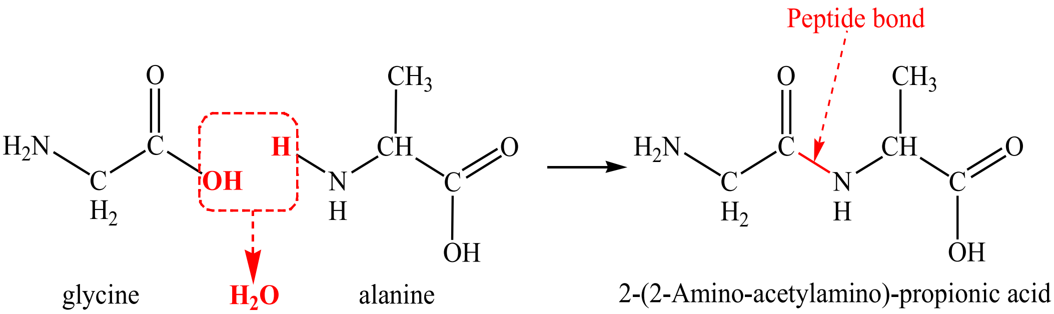
ACTIVITY 15.9

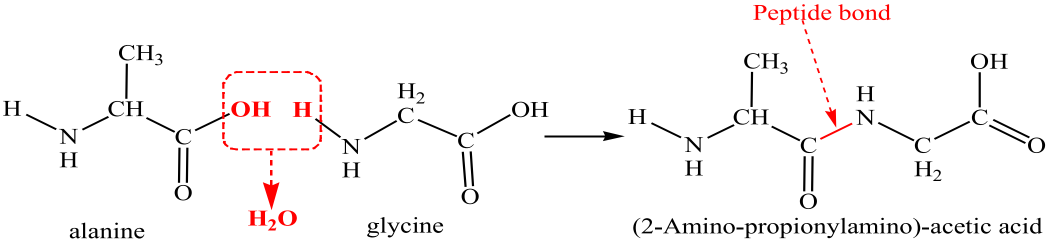
Ethyne (C_2H_2) is a compound which can undergo a polymerisation reaction. Deduce the reaction of polymerisation of ethyne, showing the mechanism of reaction.

15.9.1. Formation of peptide bonds

Amino acid molecules can also react with each other; the acidic –COOH group in one molecule reacts with the basic $–NH_2$ group in another molecule. When two amino acids react together, in the resulting molecule is called a **dipeptide**, forming *an amide linkage* (***peptide bond***), with the elimination of a water molecule.

Each amino acid possesses a carboxylic acid group and an amine group. The possibilities for constructing polypeptides and proteins are enormous. Let us consider two simple amino acids, **glycine** (2-aminoethanoic acid) and **alanine** (2-aminopropanoic acid). The figures below show that these can be joined in two ways:

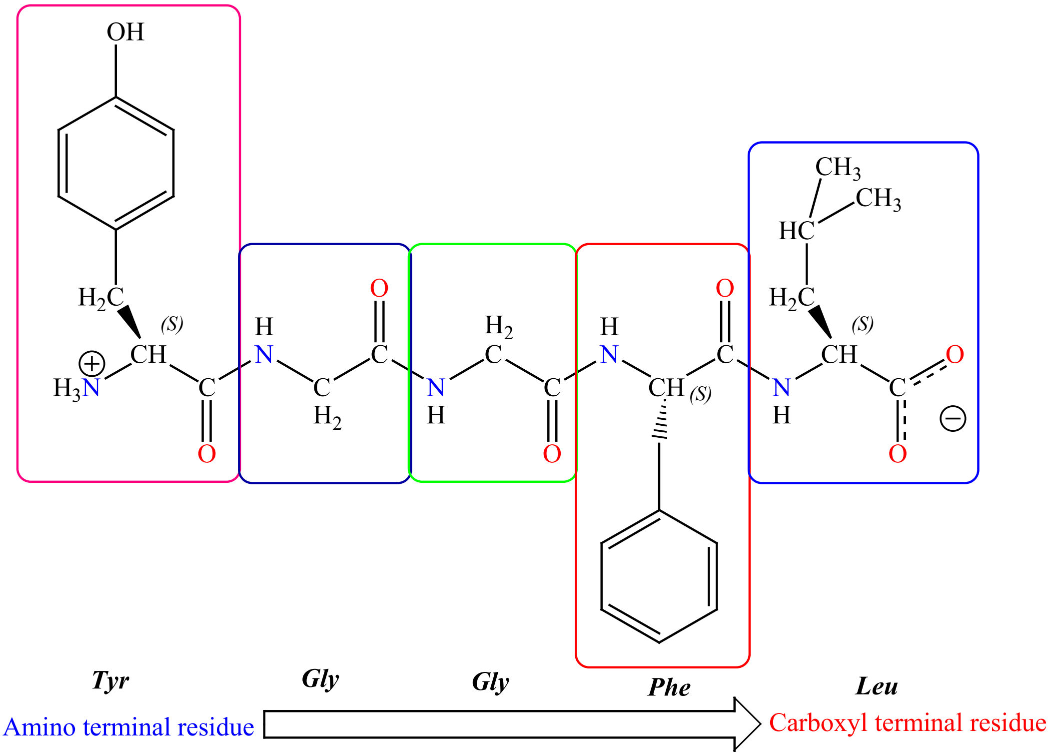




Note the amide link between the two amino acids. An amide link between two amino acid molecules is also called a **peptide link**. The reaction is a **condensation reaction** as the two amino acids join to one another with the loss of a small molecule. The **dipeptide** product still has an $-NH_2$ group at one end and a $-COOH$ group at the other end. Therefore the reaction can continue, to form a **tripeptide** initially, and then ever-longer chains of amino acids. The longer molecules become known as **polypeptides**, and then **proteins** as they get even longer sequences of amino acids. A typical protein is formed from between 50 and 200 amino acids joined in a variety of sequences.

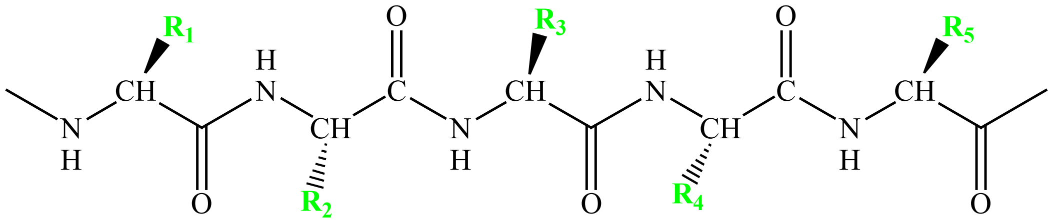
15.9.2. Structure of peptides and polypeptides

A series of amino acids joined by peptide bonds form a polypeptide chain, and each amino acid unit in a polypeptide is called a **residue**. A polypeptide chain has polarity because its ends are different, with α-amino group at one end and α-carboxyl group at the other. By convention, the amino end is taken to be the beginning of a polypeptide chain, and so the sequence of amino acids in a polypeptide chain is written starting with the aminoterminal residue. Thus, in the pentapeptide Tyr-Gly-Gly-Phe-Leu (YGGFL), phenylalanine is the amino-terminal (N-terminal) residue and leucine is the carboxyl-terminal (C-terminal) residue. Leu-Phe-Gly-Gly-Tyr (LFGGY) is a different pentapeptide, with different chemical properties.



This above illustration of the ***pentapeptide Tyr-Gly-Gly-Phe-Leu (YGGFL)*** shows the sequence from the amino terminus to the carboxyl terminus. This pentapeptide, Leu-enkephalin, is an opioid peptide that modulates the perception of pain. The reverse ***pentapeptide, Leu-Phe-Gly-Gly-Tyr (LFGGY)***, is a different molecule and shows no such effects.

A **polypeptide chain** consists of a regularly repeating part, called the ***main chain or backbone***, and a variable part, comprising the distinctive ***side chains***. The polypeptide backbone is rich in ***hydrogen-bonding potential***. Each residue contains a carbonyl group, which is a good hydrogen-bond acceptor and, with the exception of proline, an NH group, which is a good hydrogen-bond donor. These groups interact with each other and with functional groups from side chains to stabilize particular structures, as will be discussed later.



Components of a Polypeptide Chain

A polypeptide chain consists of a constant backbone (shown in blue) and variable side chains (shown in green).

15.9.3. Uses of amino acids as building blocks of proteins

Like carbohydrates and lipids, proteins contain the elements **carbon** (C), **hydrogen** (H) and **oxygen** (O), but in addition they also **always** contain **nitrogen** (N). **Sulphur**(S) is often present as well as **iron** (Fe) and **phosphorus (P)**. Before understanding how proteins are constructed, the structure of amino acids should be noted.

The process of construction of proteins begins by amino acids bonding together, as seen earlier, through **peptide bonds**. When many amino acids join together a ***long-chain polypeptide*** is produced. The linking of amino acids in this way takes place during ***protein synthesis***.

The simplest level of protein structure, ***primary structure***, is simply the sequence of amino acids in a polypeptide chain. ***The primary structure*** (Figure 15.2) of a protein refers to its linear sequence of amino acids. One of those sequences is: –Gly–Ile–Val–Cyst–Glu–Gln–Ala–Ser–Leu–Asp–Arg–Asp–Arg–Cys–Val–Pro–

The primary structure is held together by peptide bonds that are made during the process of protein biosynthesis. The two ends of the polypeptide chain are referred to as the carboxyl terminus (C-terminus) and the amino terminus (N-terminus) based on the nature of the free group on each extremity.

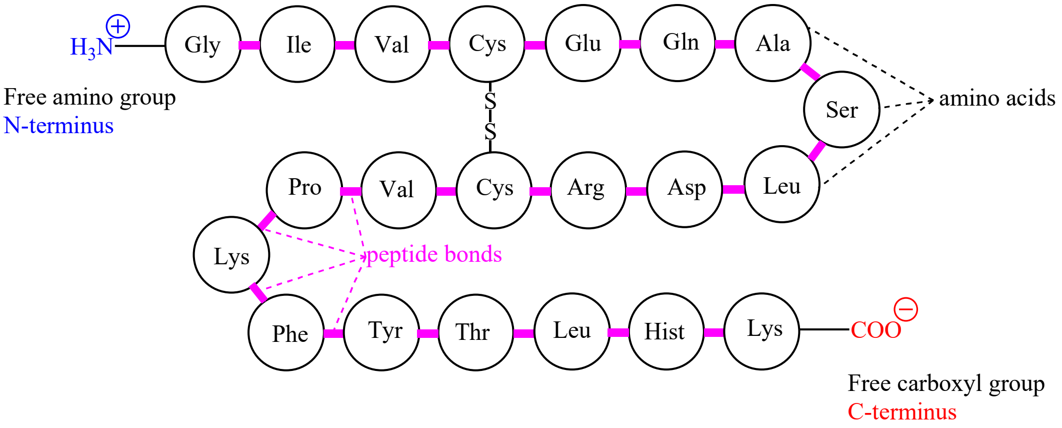


Figure 15.2. Structure of a primary protein

For example, the ***hormone insulin*** (Figure 15.3) has two polypeptide chains, A and B, shown in diagram below. Each chain has its own set of amino acids, assembled in a particular order. For instance, the sequence of the A chain starts with ***glycine at the N-terminus*** and ends with ***asparagine at the C-terminus***, and is different from the sequence of the B chain. You may notice that the insulin chains are linked together by ***sulfur-containing bonds between cysteines***.

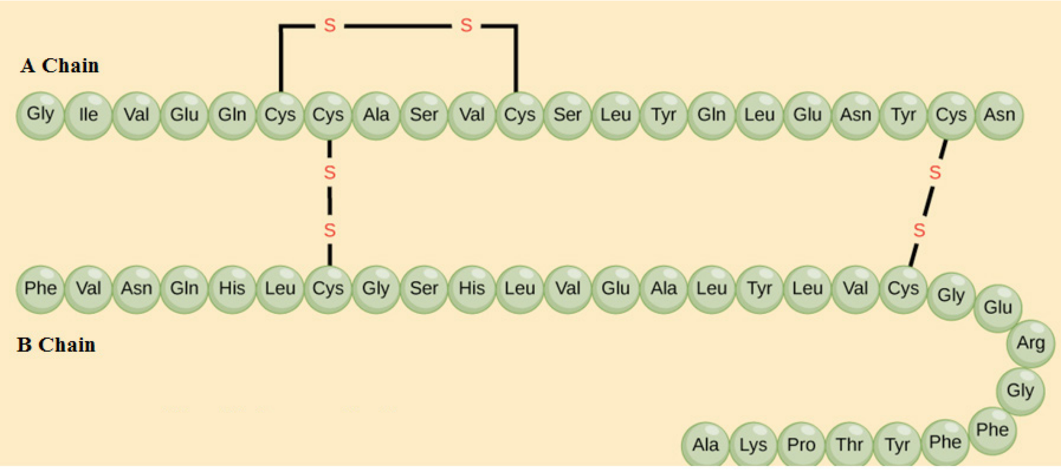


Figure 15.3 Structure of insulin

APPLICATION ACTIVITY 15.9

1. Distinguish between the N– terminal amino acid and the C– terminal amino acid of a peptide or protein.

2. Describe the difference between an amino acid and a peptide.

3. Amino acid units in a protein are connected by peptide bonds. What is another name for the functional group linking the amino acids?

4. Draw the structure for each peptide.

   a. gly-val

   b.val-gly

5. Identify the C– and N– terminal amino acids for the peptide lys-val-phe-gly-arg-cys

SKILLS LAB 15

1. Fats and proteins are found in organic compounds. You are provided with milk and in a well equipped laboratory. Make research , design and perform an experiment to identify the fats and protein compounds that are expected to be present in the milk.

END UNIT ASSESSMENT 15

1. Ethylamine and phenylamine are two organic compounds and both are basic.

   a. Draw the displayed formula of each compound, including lone pairs.

   b. Write a balanced symbol equation for the reaction between one of these compounds and an acid to form a salt.

   c. Which structural feature of each compound accounts for the basicity?

2. The formulae of two amino acids, glycine (Gly) and alanine (Ala), are given:

   Glycine: H_2NCH_2COOH and alanine: $H_2NCH(CH_3)COOH$.

   a. i. Give the systematic names of both amino acids.

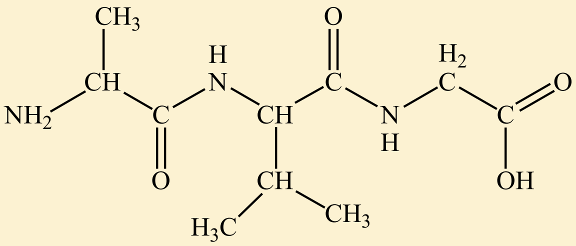
   ii. Draw their skeletal formulae.

   b. Alanine can exist as two stereoisomers.

   i. Draw these two stereoisomers, showing how they differ in their spatial arrangements.

   ii. Explain why glycine does not have stereoisomers.

3. The structure of a certain tripeptide is shown here:



   a. i. Draw the displayed formulae of the three amino acids that make up the tripeptide.

   ii. Which of these amino acids has two chiral carbon atoms?

   b. This tripeptide can be split up into the three amino acids by refluxing with aqueous hydrochloric acid.

   i.Which bond is broken in this reaction?

   ii. The reaction can be described as hydrolysis. Explain why, using a diagram.

UNIT 16

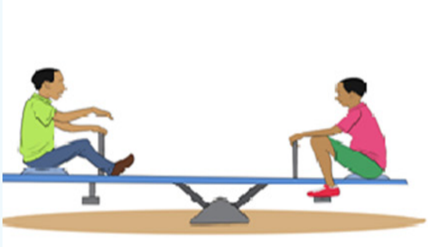
FACTORS THAT AFFECT CHEMICAL EQUILIBRIUM

Key unit competency: Deduce how concentration, pressure, catalyst and temperature affect the chemical processes in industry.

INTRODUCTORY ACTIVITY

Observe the figures bellow.

1. What is the difference between the figure a and b?
2. What conditions for the figure b to be like figure a?
3. What will happen if one person on the right side leaves his/her group in figure C?



a

b

C

4.a. What does it happen if :

i. there is a sudden earthquake?

ii. you throw a stone in a swimming pool?

b. What does it happen after a certain period of time after the occurring events stated in a) i and ii) ?

16.1. Difference between complete and incomplete reactions, concept and characteristics of a dynamic equilibrium

ACTIVITY 16.1

1. Write any two equations of your choice to show a reaction that undergo completion.

2. Write any two equations of your choice to show a reaction that does not go to completion.

3. Explain the terms used in equilibrium reactions.

   (a)Reversible reaction (b) equilibrium state (c) dynamic equilibrium (d) position of equilibrium.

4. Suggest and explain the characteristics of dynamic equilibrium and how it can be attained.e.

5. In a given Hotel, clients enter others leave. At a certain moment if the number of leavers and arrivals is equal, the number of the clients in the Hotel doesn’t change.

   (i) Has the movements of clients coming in and out stopped?

   (ii) How can you qualify that status?

   (iii) How can you compare this with chemical equilibrium?

a. Complete(irreversible) versus incomplete(reversible) reactions

In chemistry, a chemical reaction is a process where old bonds are broken and new bonds are formed. For a chemical reaction to take place, two or more substances called reactants are interacted. In general, when reactants collide with sufficient energy and in a proper orientation, the products are formed. Many chemical reactions proceed to a certain extent and stop. In some cases, reactants combine to form products and the products also start combining to give back the reactants. When such opposing processes take place at equal rates, no reaction appears and it is said that a state of equilibrium is reached.

A chemical reaction can proceed in either *non-reversible (irreversible or complete)* or *reversible* reaction.

During chemical processes, many chemical reactions do not undergo completion but instead they attain a state of chemical equilibrium.

A non-reversible reaction is a reaction which proceeds in only *one direction,* in other words, the reactants are completely transformed into products.

Examples:

$$CaCO_3(s) \rightleftarrows CaO\,(s)+CO_2(g)$$

$$NaOH(aq)+HCl(aq) \longrightarrow NaCl(aq)+H_2O(l)$$

In reversible reactions, both the forward and reverse reactions occur at different rates at the beginning but approach the same rate at equilibrium state.

Reversible reactions are indicated by placing two half arrows pointing in opposite directions between the reactants and products. The forward reaction is indicated by an arrow orientedd from left to right and the reverse reaction from right to left.

Note that all reactions at equilibrium can be forced to go in either direction depending on change of external factors.

Examples of reversible reactions

(i) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2\,SO_{3(g)}$

(ii) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

b. Concept of chemical equilibrium reactions

When a chemical reaction takes place in a container which prevents the entry or escape of any of the substances involved in the reaction, the quantities of these components change as some are being consumed and others are being formed at the same time.

Chemical equilibrium is ***the state at which the rate of forward reaction becomes equal to the rate of backward reaction.***

At the initial state, the rate of forward reaction is greater than the rate of backward reaction. However as the products are formed, the concentration of reactants decreases and the concentration of products increases.

For example in a reaction

$$A+B \longrightarrow C$$

and $C \longrightarrow A+B$

The state of chemical equilibrium can be shown graphically as follows in Figures 16.1 and 16.2

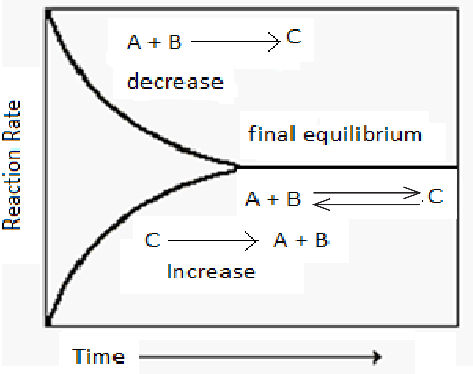


Figure 16.1 Plot of reaction rate versus time at equilibrium

At the equilibrium, the rate of formation of products is equal to that of formation of reactants.

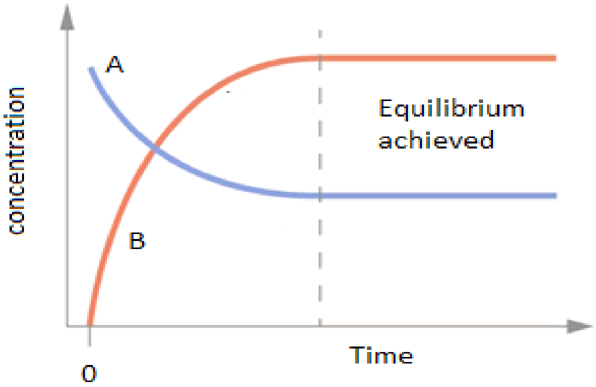


Figure 16.2 Variation of concentration of A and B with time for a reversible reaction

Consider the reaction $A \longrightarrow C$; the figure16.2 indicates how the concentration of A decreases while that of B increases for the reaction. The dotted vertical line indicates the time when the concentrations of A and B are no longer changing.

If the reversible reaction is carried out in a closed system, the reaction is said to be in the equilibrium state when the forward and backward reaction occur simultaneously at the same rate and the concentrations of reactants and products do not change with time (Figure 16.2).

At this point, the rates of forward and reverse reactions are the same and the system is said to have reached a state of ***dynamic equilibrium***.

A dynamic equilibrium is a process where the forward and reverse reactions proceed at the same rate; at that moment the concentrations of reactants and products remain constant (do not change).

However, in dynamic equilibrium, even if the concentrations of reactants and products do not change, it does not mean that the reaction has stopped. Rather, the reaction is proceeding in a way that it keeps the concentrations unchanged (the net change is zero).

There are two types of chemical equilibrium: **homogeneous** and **heterogeneous** equilibria.

In a homogeneous equilibrium, all the reactants and the products are in the same phase.

$$N_{2(g)}+O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

In heterogeneous equilibrium, the reactants and the products are present in different phases. This is the case of an aqueous solution in which the ions combine to produce a slightly soluble solid that forms a precipitate or an equilibrium reaction where solid and gaseous phases are present.

$$CaCO_{3(g)} \rightleftharpoons CaO\,(s) + CO_2(g)$$

$$Ag^{+}(aq) + Br^{-}(aq) \rightleftharpoons AgBr(s)$$

c. Characteristics of a system in a dynamic equilibrium

A chemical equilibrium is a process where reactants are converted into products and products can react to give back the reactants at equal rate. The characteristics of a system in dynamic equilibrium are the following;

1. The rate of the forward reaction is equal to the rate of the reverse reaction,
2. Microscopic processes (the forward and reverse reactions) continue in a balance which yields no macroscopic changes (nothing appears to be happening),
3. The system is closed and the temperature is constant and uniform throughout the process,
4. The equilibrium can be approached from the left (starting with reactants) or from the right (starting with products).

APPLICATION ACTIVITY 16.1

1. Identify the reactions which are non-reversible and reversible by writing the words irreversible and reversible.

(a) $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$

(b) $BaCl_2 + 2AgNO_3 \longrightarrow 2AgCl + Ba(NO_3)_2$

(c) $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$

(d) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

(e) $SO_{2(g)} + 1/2\ O_{2(g)} \rightleftharpoons SO_{3(g)}$

(f) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

(g) $2H_2O_{(g)} + 2SO_{2(g)} \rightleftharpoons 2H_2S_{(g)} + 3O_{2(g)}$

(h) Burning pieces of paper

(i) Rusting of iron

(j) fruit ripening

(k) heating chocolate and then cooling the product after heating

2. Briefly explain the characteristics of reactions at equilibrium.

3. Compare the homogeneous and heterogeneous reactions using specific examples.

4. By giving an example, describe the term dynamic equilibrium.

5. When does a reaction attain equilibrium state?

6. Using a graph and specific examples, explain what happens during a reaction before, at and after the equilibrium has been attained.

16.2. Factors that affect the reactions in equilibrium and Le Châtelier's principle

ACTIVITY 16.2

1. When one is cooking beans what are the different conditions he/she should take into consideration to obtain cooked beans in moderate time? Are those conditions applicable to any other chemical system? Explain.

2. Around 1908-1909 a young German research chemist, Fritz Haber, had discovered that nitrogen and hydrogen would form an equilibrium mixture containing ammonia.

   (a) Write a balanced equation for the formation of ammonia.

   (b) Haber's experiment yielded an equilibrium mixture containing only 8% by volume of ammonia. What conditions of temperature and pressure does Le Châtelier's principle predict for maximum yield of ammonia at equilibrium?

   (c) Why do you think Haber employed the catalyst accompanied with promoters and heat exchanger in his equipment?

Many industrial processes involve reversible reactions. It is important to understand how the variation of conditions can affect the composition of a chemical equilibrium. Some reactions to take place involve some conditions. For example, the rate of a chemical reaction depends on factors that affect the reaction.

Different factors which can affect the chemical equilibrium include:

1. Temperature

2. Pressure

3. Concentration of reactants and products

The effect of the above-mentioned factors on chemical equilibrium can be explained by the Le Châtelier's Principle.

Le Châtelier's Principle

According to Le Châtelier's Principle, when the temperature, pressure or concentration of a reaction in equilibrium is changed, the reaction shifts in the direction where the effect of these changes is reduced.

16.2.1. Effect of Temperature on equilibrium

ACTIVITY 16.2.1

1. If you have ever had the opportunity of adding sulphuric acid to water what did you detect when touching the wall of the container in which the reaction was taking place? Explain why it is not allowed to add water in concentrated sulphuric acid. How this reaction is termed considering heat exchange?

2. Explain the following terms:

   (a)Endothermic (b)Exothermic

3. Suggest how the temperature affects the position of equilibrium.

When dealing with temperature, we distinguish exothermic and endothermic reactions. A change in the temperature of a system already in equilibrium could either *shift the equilibrium to the right* (favoring the forward reaction) or *to the left* (favoring the backward reaction). This depends on whether the forward reaction is exothermic or endothermic. Heat can be considered as a reactant in an endothermic reaction and as a product in an exothermic reaction. For a reversible reaction, when the forward reaction is exothermic, the enthalpy change is negative ($\Delta H < 0$), then the backward reaction is endothermic and the enthalpy change is positive ($\Delta H > 0$).

For *exothermic forward reactions*, an increase in temperature will cause the system to counter balance it by favoring the reaction that consumes heat, hence the backward reaction will be favored or promoted. On the contrary, if the temperature is decreased, the system reacts to produce more heat by favoring the forward reaction.

Example: $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\Delta H = -92$ kJ/mol

In this equilibrium the forward reaction is exothermic, and the backward reaction is endothermic. If the temperature is increased, the reverse reaction will be favored and we say the equilibrium is displaced toward the left side. If the temperature is decreased, then the forward reaction is favored and the equilibrium is displaced toward the right side.

For *endothermic forward reaction*, an increase in temperature favors the forward reaction, while a decrease in temperature favors the reverse reaction.

In summary:

Increase in temperature $\xrightarrow{\text{shifts the equilibrium in the direction of}}$ Endothermic reaction

Decrease in temperature $\xrightarrow{\text{shifts the equilibrium in the direction of}}$ Exothermic reaction

APPLICATION ACTIVITY 16.2.1

Determine whether the following reactions are favored by high or low temperature? Justify your answer.

1) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\Delta H^o = -180$ kJ

2) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$); $\Delta H^o = -46$ kJ

3) $CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$; $\Delta H^o = -108$ kJ

4) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta H^o = +57$ kJ

5) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta H^o = -270$ kJ

16.2.2. The effect of change in concentration on equilibrium

ACTIVITY 16.2.2

Consider the reaction below

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

1.What do you think would happen if more and more nitrogen and hydrogen are added in the vessel where the reaction is taking place?

2. What would happen if:

(a) The concentration of ammonia is increased?

(b) Ammonia is removed from the vessel as it is produced?

According to Le Châtelier's principle, if the concentration of reactants is increased, the reaction will shift in the forward direction. Adding a reactant or product, the equilibria shifts away from the increase in order to consume the part of the added substance. By removing a reactant or product, the equilibria shifts toward the decrease to replace part of the removed species.

APPLICATION ACTIVITY 16.2.2

1. Explain Le Châtelier's principle.

2. What factors did Fritz Haber employ to determine the changing positions of equilibrium reactions in manufacture of ammonia using nitrogen gas and hydrogen gas?

3. Determine what would happen to the following reactions if the concentration of any one of the reactants is increased or decreased?

   a. $2SO_{2(g)}+O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

   b. $CO_{(g)}+H_2O_{(g)} \rightleftharpoons CO_{2(g)}+H_{2(g)}$

   c. $CO_{(g)}+Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$

   d. $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

   e. $CO_{(g)}+2H_{2(g)} \rightleftharpoons CH_3OH(g)$

4. Given this reaction at equilibrium: $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$

   In which direction—toward reactants or toward products—does the reaction shift if the equilibrium is stressed by each change?

   (a) H_2 is added.

   (b) NH_3 is added.

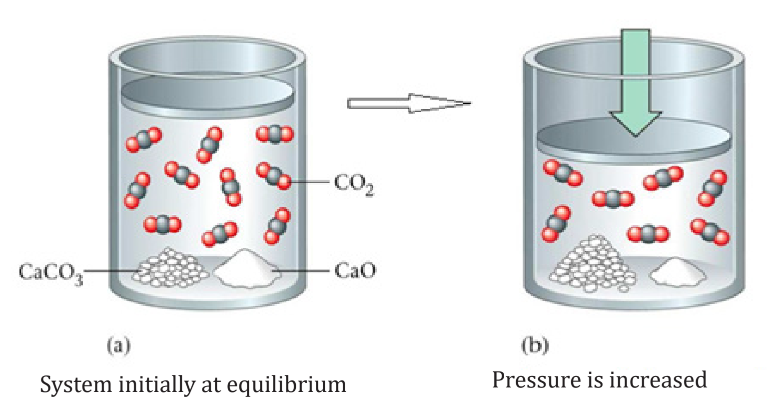
   (c) NH_3 is removed.

16.2.3. *Effect of Changing Pressure*

ACTIVITY 16.2.3

Consider the reaction: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
which takes place in a closed container,

1. Compare the molecules of carbon dioxide in both(a) and (b) in the diagram below.
2. Why is there change in the number of molecules in both diagrams?
3. What can you do to make sure the molecules in (b) go back to their original number as in a.



System initially at equilibrium

Pressure is increased

4. Assume the reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$,

   What would happen if the pressure was increased in the above equilibrium? Explain your prediction.

According to Le Châtelier's principle, an increase in pressure favours the reaction in the direction where the volume of reactants is reduced, or less molecules of gas are formed, and a decrease in pressure favours the reaction in the direction where the volume of reactants is increased, or more molecules of gas are formed.

Example

Consider the reaction:

$$N_{2\,(g)} + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

1 unit of volume	3 units of volume	2 units of volume

Because the pressure of gases is related directly to the concentration by P = n/V, changing the pressure by increasing/decreasing the volume of a container will disturb an equilibrium system. In the above example, the volume of reactants is 4 units while the volume of products is 2 units. Therefore, according to Le Châtelier's principle an increase in pressure of this reaction will favor the forward reaction to form more ammonia while a decrease in pressure of the reaction will favor the backward reaction to form more nitrogen and hydrogen.

$$\text{Increase in pressure} \xrightarrow{\text{shifts the equilibrium in the direction of}} \text{decreased volume}$$

$$\text{Decrease in pressure} \xrightarrow{\text{shifts the equilibrium in the direction of}} \text{increased volume}$$

To obtain much ammonia in the equilibrium mixture, a high pressure of 200 atmospheres is needed.

APPLICATION ACTIVITY 16.2.3

Predict whether each of the following reactions are favored by high or low pressures? Justify your answer

1. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
2. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
3. $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH(g)$
4. $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
5. $H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$
6. (a) What is the effect on this equilibrium if pressure is increased?

   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

   (b) What is the effect on this equilibrium if pressure is decreased?

   $3O_{2(g)} \rightleftharpoons 2O_{3(g)}$

16.2.4. The effect of a catalyst on equilibrium

ACTIVITY 16.2.4

1. What is an enzyme?
2. What is a catalyst? Name the catalyst used in the Haber process and contact process.
3. What would happen if the enzymes involved in the digestion of food were not present?
4. Most of the metabolic processes in the body are controlled by enzymes. What would happen to these metabolic processes if the enzymes were missing?

The function of a catalyst is to speed up the reaction by lowering the activation energy. The catalyst lowers the activation energy of the forward reaction and reverse reaction to the same extent. Adding a catalyst doesn't affect the relative rates of the two reactions and therefore the catalyst has no effect on the equilibrium system. But the catalyst helps the system to reach the equilibrium more quickly. The catalyst does not appear in the overall equation of the reaction.

APPLICATION ACTIVITY 16.2.4

1. Sulphuric acid is produced by the contact process.

Stage 1: Sulphur is burnt in air

$$S_{(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} \quad \Delta H = -297 \text{ kJ mol-1}$$

Stage 2: Sulphur dioxide is reacted with oxygen

$$SO_{2(g)} + 1/2\ O_{2(g)} \rightleftharpoons SO_{3(g)} \quad \Delta H = -98 \text{ kJ mol-1}$$

Stage 3: Sulphur trioxide is dissolved in concentrated sulphuric acid

$$SO_{3(g)} + H_2SO_{4(l)} \rightleftharpoons H_2S_2O_{7(l)} \quad \Delta H = -230 \text{ kJ mol-1}$$

Stage 3 constantly removes the SO_3 formed in stage 2.

(a) What effect does this have to the position of equilibrium in stage 2?

(b) What effect would increasing temperature and pressure have on the yield of SO_3 and the rate of reaction?

(c) A V_2O_5 catalyst is used. What effect does it have on the yield of SO_3 and the rate of reaction?

(d) Why is the concentration of SO_2 kept high?

(e) The conditions used are 450°C (moderately high) and 10 atmospheres.

(i)Why is this temperature used?

(ii) Why is a much higher pressure not used?

2. The following reaction is exothermic.

$$2NO_{(g)}+2H_{2(g)} \rightleftharpoons N_{2(g)}+2H_2O_{(g)}$$

In which direction does the equilibrium shift as a result of each change?

(a) Removing the hydrogen gas;

(b) Increasing the pressure of gases in the reaction vessel by decreasing the volume;

(c) Increasing the pressure of gases in the reaction vessel by pumping in argon gas while keeping the volume of the vessel constant.

(d) Increasing the temperature

(e) Using a catalyst

3. Use Le Châtelier's principle to explain what will happen to the position of equilibrium in the reaction $CO_{(g)}+H_2O_{(g)} \rightleftharpoons CO_{2(g)}+H_{2(g)}$ when the amount of water is increased.

16.3 Application of factors that affect the equilibrium on industrial processes

ACTIVITY 16.3

1. What do you think about the use of promoter on the efficiency of a catalyst on the yield of a chemical reaction?

2. State the factors that can increase the yield of ammonia in Haber process.

1. Haber process.

This is the indusrial manufacture of ammonia from nitrogen and hydrogen

a. The effect of pressure can be summarized by the graph indicated below

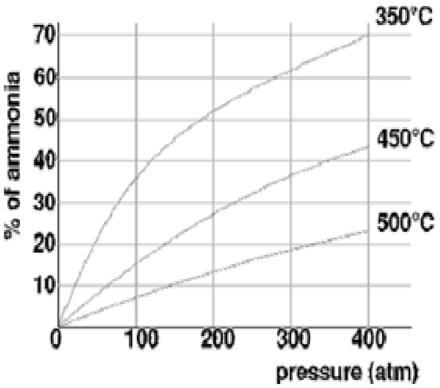


Figure 16.3: Graph of percentage yield changing with increase in pressure

If pressure is increased then the equilibrium will move to reduce the pressure. it will move to the side with fewer molecules of gas. In this case towards the products.

High Pressure gives a good yield of ammonia as indicated from the graph above, at 400 atmosphers the yield of ammonia is 70%.

Higher pressure increases the rate of reaction.

However, the higher the pressure used, the higher the cost of the equipment needed to withstand the pressure.

The higher the pressure the higher the electrical energy costs for pumps to produce the pressure.

A moderately high pressure of between 150 – 300 atmospheres is used.

b. Effect of temperature on Haber process

The industrial production of ammonia is based on the reaction, shown above, between nitrogen and hydrogen gases following the Haber process.

The Haber process combines nitrogen from the air with hydrogen derived mainly from natural gas (methane) into ammonia. The reaction is reversible and the production of ammonia is exothermic.

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92\ kJ/mol$$

The reaction of the production of ammonia is ***exothermic***. According to the Le Châtelier's Principle, since this reaction is exothermic and if only the factor temperature is considered, lowering the temperature would thermodynamically favors the forward reaction, i.e. the formation of ammonia. Nevertheless, working at low temperature will result in a low rate of the reaction (reaction kinetics), hence low yield or low production.

On the other hand, if you look at the state of reactants and products, you notice that at the reactants side, there are 4 gaseous molecules, whereas at the products side there are 2 gaseous molecules. If the pressure is increased, the system reacts by producing more products or less number of molecules; hence increasing pressure moves the equilibrium toward the formation of more products, i.e. less number of gaseous molecules.

Taking account of all those theoretical considerations, combined with financial and economical aspects of the operations, the Haber process adopts intermediate of compromise conditions: 400-450^{o}C, 150-300 atm and catalyst. The Haber process yields 15% of ammonia.

c. Effect of catalyst on Haber process

In addition to temperature and pressure, the catalyst is a vitally important variable in any industrial process. A more efficient catalyst permits lower operating temperatures. Experience has shown that the best catalyst is iron mixed with small amounts of promoters such as potassium oxide and aluminium oxide .These improve its catalytic activity.

Table 16.1 The effect of promoters on the efficiency of iron as catalyst for the Haber process (200 atm and 400^{0}C)

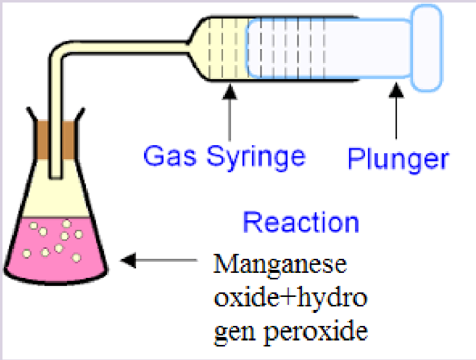
Catalyst	Promoter	% of ammonia in exit gases
Fe	nil	3-5
Fe	K_2O	8.-9
Fe	$K_2O+Al_2O_3$	13-14

APPLICATION ACTIVITY 16.3

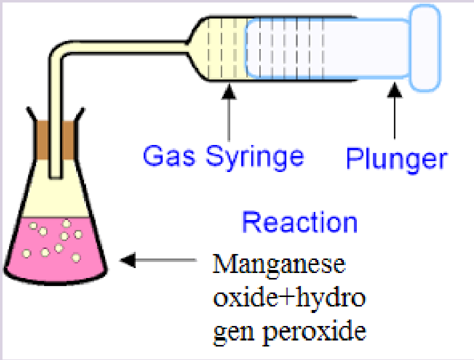
Make research and discuss the chemical principles of the optimum operating conditions for industial manufacture of sulphuric acid in contact process

SKILLS LAB 16

Perform a laboratory experiment to establish how effective manganese (IV) oxide acts as a catalyst for the decomposition of hydrogen peroxide.



EXPERIMENT 1



EXPERIMENT 2

1. Use the following procedure and record your results in the table shown

   In the experiment 1 use 0.3g of manganese (IV) oxide,and use 0.5g of manganese (IV) oxide in the experiment 2.

2. Record the results in the following table as the gas is produced

Time(S)	0	30	60	90	120
Volume of oxygen for 0.3g(cm^3)					
Volume of oxygen for 0.5g(cm^3)					

3. Plot a graph of the results.

4. Is the manganese acting as catalyst? Explain your answer

5. i)At which stage does the reaction proceed most quickly?

   ii) How can you tell this on the graph you have drawn?

6. Why does the slope of the graph become less steep as the reaction proceeds?

7. What volume of gas has been produced when using 0.3 g of manganese (IV) oxide after 50s?

8. How long did it take for 60 $cm^3$of gas to be produced in each case? Explain why.

2. Experiment to investigate the effect of changing concentration on equilibrium

Equipment/materials

100 ml beaker , Glass stir rods , hot plate , 250 ml beaker for waste collection , distilation water squirt bottle , enough test tubes, 3 ml of 0.010 M $Fe(NO_3)_3$, 1 ml of 0.10 M $Fe(NO_3)_3$, 1 ml 0.05 M NaSCN , 0.1 ml of 0.10 M $AgNO_3$, ~0.1 ml of 1.0 M $NaNO_3$, 15 ml of 0.10 M $Co(NO_3)_2$ (plus some in a dropper bottle) , 10 ml of 12 M HCl

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)}$$

Yellow reddish brown

Procedure

In five test tubes , place 2 drops of 0.05 M NaSCN (sodium thiocyanate), 2 drops of 0.01 M $Fe(NO_3)_3$ solution, and 3 drops of deionized water. Make sure you have taken the correct concentrations of each solution. Mix each with a stirring rod; all of the solutions should appear **red/ brown**

Add 2 drops of deionized water to test tube 1. This will serve as your color comparison for the following experiments.

Add 2 drops of 0.10 M $Fe(NO_3)_3$ to test tube 2. Record your observations in table.

Add 2 drops of 0.05 M NaSCN to test tube 3. Record your observations in table.

Add 1 drop of 0.10 M $AgNO_3$ to test tube 4. Record your observations in table.

Add 1 drops of 1.0 M $NaNO_3$ to test tube 5. Record your observations in table.

Test tube #	Stress applied	observations made
1	None , control for comparison	
2	Add 0.10M $Fe(NO_3)_3$	
3	Add 0.05 M NaSCN	
4	Add 0.10 M $AgNO_3$	
5	Add 1.0 M $NaNO_3$	

Study questions:

1. When $Fe(NO_3)_3$ was added to the system,

   (a) Which ion in the equilibrium system caused the “stress”?

   b) Which way did the equilibrium shift?

   (c) What happened to the concentration of SCN^-?

   (d) What happened to the concentration of $FeSCN^{2+}$?

2. When NaSCN was added to the system,

   (a) Which ion in the equilibrium system caused the “stress”?

   (b) Which way did the equilibrium shift?

   (c) What happened to the concentration of Fe^{3+}?

   (d) What happened to the concentration of $FeSCN^{2+}$?

3. When $AgNO_3$ was added to the system, it caused the precipitation of solid AgSCN.

   (a) Which ion in the equilibrium had its concentration changed by addition of $AgNO_3$?

   (b)Did the concentration of that ion increase or decrease?

   (c)When $AgNO_3$ was added, which way did the equilibrium shift?

4. When you added $NaNO_3$, did anything happen? Can you explain this result?

END UNIT ASSESSMENT 16

1. Consider the following equilibrium reaction:

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) What happens if we increase the concentration of N_2 by adding more N_2?

(b) What happens if we increase the concentration of H_2 by adding more H_2?

(c) What happens if we increase the concentration of NH_3 by adding more NH_3?

(d) What happens if we decrease the concentration of N_2 by removing some N_2?

(e) What happens if we decrease the concentration of H_2 by removing some H_2?

(f) What happens if we decrease the concentration of NH_3 by removing some NH_3?

2. Read the passage and answer the questions that follow:

Carbon dioxide and formation of Stalactites and Stalagmates in limestone caves

In addition to being a component of the atmosphere, carbon dioxide also dissolves in the water of the oceans. The dissolving process can be described by the following equations.

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)}+HCO_3^-{}_{(aq)} \qquad (1)$$

In nature, surface water often becomes acidic because atmospheric carbon dioxide dissolves in it; this acidic solution can dissolve limestone.

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)}+HCO_3^-{}_{(aq)} \qquad (2)$$

Openings formed in the limestone as the calcium carbonate dissolves

Slight cooling of the water saturated with carbon dioxide can reduce the solubility of the carbon dioxide. The position of the equilibrium shifts, resulting in the precipitation of calcium carbonate. This precipitate , the statalctite is formed immediately when the seeping water comes in contact with air currents in a cave . Stalagmites form on the floors of the caves in the same way.

a) Suggest why the balance between $CO_2(g)$ in the atmosphere and $CO_2(aq)$ in the oceans cannot be regarded as a true dynamic equilibrium.

b) Based on equations (1) and (2), explain the likely effect of the increasing concentration of atmospheric carbon dioxide on the pH of water at the ocean surface.

c) Use Le Châtelier's principle to explain why slight cooling of the water saturated with carbon dioxide will result in the precipitation of calcium carbonate.

3. The hydrogen used in the Haber process is made by the following reaction:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \quad \Delta H = +206\ kJ$$

Discuss how the yield of hydrogen in the process is affected by changing the pressure, changing the temperature and using a catalyst. (For this question, you are required to give answers in paragraph form.)

4. Read the following passage and answer the questions that follow.

Chlorine for disinfection

Chlorine is used in water treatment for disinfection.

When chlorine is added to pure water, hypochlorous acid (HOCl) and hydrochloric acid (HCl) are formed.

$$Cl_{2(g)} + H_2O_{(l)} \rightleftharpoons HCl_{(aq)} + H^+_{(aq)} + ClO^-_{(aq)}$$

The principal disinfecting action of aqueous chlorine is due to hypochlorous acid formed.

Hypochlorous acid is dissociated into hydrogen ions and hypochlorite ions

$$HOCl_{(aq)} \rightleftharpoons H^+_{(aq)} + OCl^-_{(aq)}$$

The concentration of hypochlorous acid and hypochlorite ions in chlorine water depend on the pH of water. Instead of using chlorine gas, some plants apply sodium hypochlorite or calcium hypochlorite in water. Sodium hypochlorite completely dissociate in water to form sodium ions and hypochlorite ions. In solution, the hypochlorite ions hydrolyze to form the disinfectant hypochlorous acid according to the following equation.

$$OCl^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HOCl_{(aq)} + OH^-_{(aq)}$$

a) State Le Châtelier's principle.

b) Use Le Châtelier's principle to explain how the pH of the chlorinated water will affect the concentrations of hypochlorous acid and hypochlorite ions in the water.

c) The hypochlorous acid produced in a solution of sodium hypochlorite can react further to produce small amount of chlorine according to the following equation:

$$HOCl_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons Cl_{2(g)} + H_2O_{(l)}$$

What will happen to the concentration of chlorine if a little sodium hydroxide solution is added to a sodium hypochlorite solution? Explain your answer.

Conditions

5. In the Contact process, sulphur dioxide is catalytically oxidized to sulphur trioxide according to the equation:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H < 0$$

The following table summarizes several possible conditions for the preparation of sulphur trioxide:

case	Conditions		
	reactants	Pressure / atm	Temperature/ ^0C
A	$SO_2(g)$ + excess $O_2(g)$	500	400
B	excess $SO_2(g)$+ $O_2(g)$	500	1000
C	excess $SO_2(g)$+ air	1	1000
d	$SO_2(g)$ + excess air	1	400

Which of the cases would represent?

(a) the theoretical conditions for obtaining the maximum yield of sulphur trioxide? Explain your answer.

b) the most economical conditions for the industrial preparation of sulphur trioxide? Explain your answer.

6. Ethanol is manufactured by catalytic hydration of ethene:

$$CH_2{=}CH_{2(g)} + H_2O_{(g)} \rightleftharpoons CH_3CH_2OH_{(l)}$$

a) The reaction represented by the above equation can reach a position of dynamic equilibrium. State two features of a system that is in dynamic equilibrium.

(b)The following table lists the percentage conversion of ethene using excess steam at various reaction conditions used in industry.

Pressure /atm	Temperature/ °C	Percentage conversion / %
50	200	45
50	320	30
80	200	60
80	320	45

i) State and explain the effect of increasing the pressure on the percentage conversion.

ii) Deduce the sign of the enthalpy change for the forward reaction. Explain your answer.

iii) The equation for the formation of ethanol shows that equal numbers of moles of ethene and steam are required. In industry however excess steam is used.

Suggest why excess steam is used.

7. The following reaction is exothermic.

$$2NO_{(g)}+2H_{2(g)} \rightleftharpoons N_{2(g)}+2H_2O_{(g)} \quad \Delta H= -ve$$

In which direction does the equilibrium shift as a result of each change?

(a) Removing the hydrogen gas;

(b) Increasing the pressure of gases in the reaction vessel by decreasing the volume;

(c) Increasing the pressure of gases in the reaction vessel by pumping in argon gas while keeping the volume of the vessel constant;

(d) Increasing the temperature;

(e) Using a catalyst.

8. The reaction: $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ reaches dynamic equilibrium in a closed vessel. The forward reaction is exothermic. The reaction is catalyzed by V_2O_5.

(a) Explain the term dynamic equilibrium.

(b) What will happen to the position of equilibrium when:

  (i) Some sulfur trioxide, SO_3, is removed from the vessel?

  (ii) The pressure in the vessel is lowered?

  (iii) More V_2O_5 is added?

  (iv) The temperature of the vessel is increased?

(c) State LeChâtelier's principle.

(d) Use Le Châtelier's principle to explain what will happen to the position of equilibrium in the reaction: $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

when the concentration of hydrogen is decreased.

UNIT 17

QUANTITATIVE CHEMICAL EQUILIBRIUM

Key unit competence: Write expressions and calculate the values of equilibrium constant, interpret the values of Kc in relation to the yield of the products in reversible reactions.

INTRODUCTORY ACTIVITY

1. Observe carefully the following chemical equations and answer the questions.

   A: $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

   B: $2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$

   Differentiate the two chemical equations.

2. Consider the reversible reaction: $2SO_2\,(g) + O_2(g) \rightleftarrows 2SO_3(g)$ which is used in the Contact process for the manufacture of sulphuric acid in the presence of V_2O_5 catalyst. The reaction produces the energy $\Delta H = -196$ KJ/mol.

   a) State and explain the effect of raising the temperature on the position of equilibrium of this reaction.

   b) What is the effect of the catalyst on the position of equilibrium in this reaction?

   c) What is the effect of increasing the concentration of oxygen (at the same temperature)?

   d) What is the effect of increasing the concentration of SO_3?

3. Ethane can be cracked at high temperatures according to the equation :

   $C_2H_6\,(g) \rightleftarrows C_2H_4(g) + H_2(g)$. If the standard enthalpy of formation of ethene is positive, Explain the effect on the position of equilibrium of increasing temperature.

4. Ammonia is manufactured by the Haber - Bosch process according to the equation

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92Kjmol^{-1}$$

State and explain the effect of high temperatures on:

a) The rate of the above reaction

b) The yield of ammonia.

5. State, giving reasons, how an increase in pressure affects the position of equilibrium in the reaction above.

17.1. Definition, characteristics of equilibrium constant, and Deriving equilibrium constant K_c

ACTIVITY 17.1

1. Discuss the effect of a decrease in pressure on each of the following equilibrium?

a) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

b) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

c) $CO_{(g)}+2H_{2(g)} \rightleftharpoons CH_3OH(g)$

2. Explain the effect of an increase in temperature on each of the following reaction at the equilibrium.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)}+Cl_{2(g)} \ ; \Delta H = +87.9kJ/mol$$

In most of the chemical reactions, the reactants are not completely converted into products. The reaction proceeds to a certain extent and reaches a state at which the concentrations of both reactants and products remain constant with time.

Chemical equilibrium is the state in which both reactants and products of a chemical reaction are present in concentrations that do not change with time. Chemical equilibrium deals with the reversible reactions, which reach equilibrium state; where the forward reaction proceeds at the same rate as the reverse reaction. The scope of chemical equilibrium includes the study of characteristics and factors affecting the chemical equilibrium.

17.1.1. Definition

The equilibrium constant expresses ratio of the concentrations between the products and the reactants under the given conditions. The equilibrium constant is symbolized by K_c, and the ratio Q expresses the value of the reaction quotient when the forward and reverse reactions occur at the same rate. When the reaction reaches the equilibrium, no change is observed between the chemical composition of the mixture with time and the enthalpy of the products is equal to that of the reagents while the Gibbs free energy change for the reaction is equal to zero.

By definition: **The equilibrium constant, Kc, is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients at given temperature.**

17.1.2. Characteristics of equilibrium constant

Consider the following reversible reaction involving homogeneous system;

$aA + bB \rightleftarrows cC + dD$

The equilibrium constant Kc is equal to:

$$\mathbf{K_c =} \frac{[C]^d[D]^d}{[A]^a B^b}$$

Note: All the concentrations used to calculate Kc are measured at homogeneous equilibrium.

Where, **A, B, C,** and **D** are ***chemical species,*** and ***a, b, c,*** and ***d*** are ***their respective stoichiometric coefficients.***

If Kc value >> 1), the direct reaction is favored and the reaction mixture contains mostly products.

If Kc value <<1, the reverse reaction is favored and the reaction mixture contains mostly reactants.

If the Kc value is close to 1 (0.10 < Kc < 10), the mixture contains appreciable amounts of both reactants and products

Examples: Write the equilibrium constant expression, Kc, for the following reactions:

(1) $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$; $K_c = \frac{[HI]^2}{[H_2][I_2]}$

(2) $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$; $K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$

Note:

i) The equilibrium can be approached from either direction (forward or backward direction).

ii) The equilibrium constant Kc does not depend on the initial concentrations of reactants and products but it depends on temperature.

The equilibrium is described as homogeneous if all species are in the same phase and heterogeneous if they are in different phases.

Characteristics of the equilibrium constant Kc

The equilibrium constant, K_c is governed by temperature, which is the only factor that can change the internal potential energy of the reactants or products.

i) If the forward reaction is exothermic, K_c decreases with the increase in temperature.

ii) If the forward reaction is endothermic, K_c increases with the increase in temperature.

iii) The application of a catalyst to a reaction has no effect on a Kc value.

17.1.3. Deriving equilibrium constant Kc

ACTIVITY 17.1.3

1. Write an expression for the chemical equilibrium, K_c, for each of the following reactions;

$$Sn^{2+}(aq) + 2Fe^{2+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2Fe^{2+}(aq)$$

$$Ag^{+}(aq) + Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

$$2Cr^{3+}(aq) + Fe(s) \rightleftharpoons 2Cr^{2+}(aq) + Fe^{2+}(aq)$$

2. Equilibrium is established in the reaction

$$A(aq) + B(aq) \rightleftharpoons 2C(aq)$$

If equilibrium concentrations are [A] = 0.25, [B] = 0.40, [C] = 0.50 mol dm^{-3}, what is the value of K_c ?

3. The following reaction was allowed to reach equilibrium:

$$2D(aq) + E(aq) \rightleftharpoons F(aq)$$

The initial amounts of the reactants present in 1.00 dm^3 of solution were 1.00mol D and 0.75 mol E. At equilibrium, the amounts were 0.70 mol D and 0.60 mol E. Calculate the equilibrium constant K_c.

a. Deriving equilibrium constant Kc from thermodynamic approach

The equilibrium constant gives the rate of transformation and expresses the ratio of the concentrations between the products and the reagents under the given conditions.

A relation can be derived between the change of standard free enthalpy and the equilibrium constant. Enthalpies and entropies are important thermodynamic functions used for a wide variety of applications. Enthalpy and entropy expresses the energy of a reaction. In chemistry, the temperature is an important factor than can influence the rate of the reaction.

The application of thermodynamic data is expanded due to the introduction of the Gibb's energy, because of its link to the equilibrium constant, Kc.

A relationship is made between the equilibrium constant, Kc, and Gibb's energy, *G*, entropy *S* at temperature *T* have been introduced.

Since the mass action law is valid for many reactions, for a general reaction of ***a* moles** of **A** and ***b* moles** of **B** that produce ***c* moles** of **C** and ***d* moles** of **D** is represented by:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

The concentrations or activities of A, B, C, and D are represented by [A], [B], [C] and [D] respectively. For any system, a reaction quotient, ***Q*** can be expressed as:

$$Q = \frac{[C]^d[D]^d}{[A]^a[B]^b} \quad (1)$$

The data derived from experiments, show that, over time, the **quotient *Q*** tends to approach a constant ***K*** for a given reaction in a closed system. Such a state is called ***equilibrium.***

The constant *K* depends on temperature and the nature of the reactants and products. Thus, *K* is called the equilibrium constant.

$$K = \frac{[C]^d[D]^d}{[A]^a[B]^b} \quad (2)$$

The use of thermodynamic functions covers a wide range of concentrations rather than using concentrations to define the **reaction quotient** or **equilibrium constant *K*.** Furthermore, the energy is the driving force for reactions. The tendency for a reaction to reach equilibrium is driven by the Gibbs free energy, symbolized by G^o and the relationship between K and G^o has been determined by:

$$G^o = -R\,T \ln K \quad (3)$$

At the *standard conditions*, activities of all the reactants and products are unity (equal to 1). In this system, $Q = 1$.

Based on the equation (2), if $Kc > 1$, the ***forward reaction is spontaneous***.

To generalize the free Gibb's energy change, ***G* in a system, at non-standards,** we obtain:

$$\Delta G = \Delta G^o + R\,T \ln Q \quad (4)$$

At the equilibrium*, "$Q \rightarrow K$" and* $\Delta G = 0$*, the* equation (4) can be written as:

$$\Delta G = \Delta G^o + RT \ln Q = 0 \quad (5)$$

From the equation (5), we get:

$$\Delta G^o = -RT \ln Q \quad (6)$$

If ***$\Delta G = 0$),*** the system has reached an equilibrium state.

From the relations (3) and (4), we can summarize that: **$\Delta G = \Delta G^o + R\,T \ln Q$ and $\Delta G^o = - R\,T \ln K$**

The relation above can be written as $\Delta G = - R\,T \ln K + R\,T \ln Q$

$$\text{Or } \Delta G = R\,T \ln Q - R\,T \ln K \qquad (7)$$

Applying the law of logarithm, we have log a/b = log a –log b, then the relation (7) becomes:

$\Delta G = R\,T \ln Q/K$ (8)

The value of ΔG **can inform us on the spontaneity of a reaction:**

If *ΔG is positive ($\Delta G > 0$),* the reverse reaction is spontaneous

If ***ΔG is positive ($\Delta G < 0$),*** the forward reaction is spontaneous

The relation (8) allows to determine in which direction a reaction will proceed under non-standard conditions and the ratio Q/K determines the sign of ΔG:

1. If $Q/K < 1$, ΔG is negative and the reaction is spontaneous.
2. If $Q/K = 1$, $\Delta G = 0$ and the system is at equilibrium.
3. If $Q/K > 1$, ΔG is positive and the reaction is spontaneous in the opposite direction.

b. Deriving equilibrium constant Kc from kinetic approach

In kinetics, there is a relationship between the equilibrium constant and the rate constant which is used to express the rate law as constant of proportionality.

Consider the reaction: $N_2O_4\,(g) \rightleftharpoons 2NO_2(g)$

In chemical kinetics, the rate of forward reaction is written as: $R = k_f[N_2O_4]$ where R = rate of the forward reaction and kf is the rate constant for the said reaction.

Similarly, the rate of backward reaction at equilibrium is: $R = k_b[NO_2]^2$, k_b is the rate constant for backward reaction.

At the equilibrium, both the two rates are equal, therefore: $k_f[N_2O_4] = k_b[NO_2]^2$

The relation can be rearranged and we get: $= \frac{[NO_2]^2}{[N_2O_4]} = \frac{K_f}{K_b} = Kc$

Thus, the equilibrium constant is the ratio of the forward and reverse rate constants which are both constant values at a given temperature.

APPLICATION ACTIVITY 17.1

1. An important step in the manufacture of sulphuric acid is the catalytic oxidation of sulphur dioxide, SO_2 to sulphur trioxide, SO_3.

   $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ ΔH = -196kJmol-1

   For each of the following changes, state how the equilibrium will react to the change and give your reasoning.

   a) Decrease in pressure;

   b)Reduction of catalyst efficiency by 50%.

2. Ammonia is manufactured by the Haber - Bosch process by mixing hydrogen and nitrogen at 700K and 200 atmospheres pressure and using an iron catalyst with a potassium hydroxide promoter.

   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ΔH = -92kJ

   Explain why the use of high pressure favors ammonia formation.

3. Express the equlilibrium constant, K_c , and state its units in each of the following reactions.

   a) $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$

   b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

4. Consider the reaction between sulphur dioxide and oxygen to produce sulphur trioxide at 700°C:

   $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ ΔH = -ve

   a) Write the expression for the equilibrium constant, K_c, for the above reaction and give its units.

   b)The equilibrium mixture of the above reaction at 700° C contains 0.4 moles of sulphur dioxide, 0.03 moles of oxygen and 1.00 mole of sulphur trioxide in a 2.0 dm^3 container. Calculate the value of K_c

17.2. Mass action law and equilibrium constant expression

ACTIVITY 17.2

a) Explain briefly the mass action law by extending it to the reaction.

$$aA + bB \rightleftharpoons cC + dD$$

17.2.1. Mass action law

In chemistry, all the species involved in the chemical reaction must be equal in both sides of reaction (reactants and products). This is the basic explanation of the mass action law which can be defined as follows: **Law of Mass Action or Equilibrium states that "*The ratio of equilibrium concentrations of products and reactants each raised to the power of their coefficients in the balanced stoichemetric equations is a constant, Kc, at a constant temperature.***

The molar concentration i.e. number of moles per litre is also called ***Active Mass***. It is expressed by enclosing the symbols of formulae of the substance in brackets.

For example, **molar concentration of A** is expressed as **[A]**.

Consider a simple reversible reaction: $aA + bB \rightleftharpoons cC + dD$ (At a certain temperature)

According to law of mass action: the total mass of A and B involved in the collision must be equal to the total mass of new formed compounds.

Rate of **forward reaction** $\propto \mathbf{[A]^a[B]^b} = K_f\,[A]^a[B]^b$

Rate of **backward reaction** $\propto \mathbf{[C]^c[D]^d} = K_b\,[C]^c[D]^d$

17.2.2. Equilibrium constant expression

Consider a general reaction: $aA + bB \rightleftharpoons cC + dD$,

the equilibrium constant is expressed as:

$$\mathbf{K_c} = \frac{[C]^d[D]^d}{[A]^a[B]^b},$$

Where C and D are products formed and A and B are reactants; a, b, c and d are powers or stoichiometric coefficients.

Based on the types of reaction, some of reactants or products formed can be in different state such as gas, liquid or solid.

As a general rule, the concentration of pure solids and pure liquids *are not included in equilibrium constant expressions and calculations.*

Examples of equilibrium constant expressions

1. $CaCO_3(s) \rightleftharpoons CaO\ (s) + CO_2(g)$

$$K_c = [CO_2]$$

2. $C(s) + H_2O(g) \rightleftharpoons CO\ (g) + H_2$

$$K_c = \frac{[CO][H_2]}{[H_2O]}$$

3. $(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + H_2O(g) + CO_2(g)$

$$K_c = [NH_3]^2[H_2O][CO_2]$$

4. $HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+\ (aq) + NO_2\text{-}(aq)$:

$$K_c = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

5. $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_c = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

6. $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

$$Kc = [Pb^{2+}][Cl^-]^2$$

K_c expression and deriving units of K_c:

Kc values are listed without units; don't include units when calculating Kc. If the equilibrium concentrations are known, simply substitute the concentrations into the equilibrium constant expression.

Example:

For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, calculate Kc from the following equilibrium concentrations: $[N_2O_4] = 0.0613$ M; $[NO_2] = 0.1839$ M and deduce its units.

Answer: $Kc = [NO_2]^2/[N_2O_4]$

$= 0.1839\ M)^2/\ 0.0613\ M$

$=0.5517M$

Units of Kc = $M^2/M=M$

APPLICATION ACTIVITY 17.2

Express the equilibrium constant (K_c) for each reaction and state its units

$2P(g)+Q(g) \rightleftharpoons 2R(g)$

$Ag^+_{(aq)} + Fe^{2+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + Ag(s)$

$CO_{(g)}+H_2O_{(g)} \rightleftharpoons CO_{2(g)}+H_{2(g)}$

$2SO_{2(g)}+ O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)}+Cl_{2(g)}$

$2Cr^{3+}_{(aq)}+Fe_{(s)} \rightleftharpoons 2Cr^{2+}_{(aq)}+ Fe^{2+}_{(Aq)}$

17.3. Definition of equilibrium constant in terms of partial pressures “Kp”

ACTIVITY 17.3

Write down the ideal gas equation and explain all terms involved in.

Explain the term “partial pressure”.

For gaseous equilibria, the concentration of reactants and products can be expressed in terms of pressures of the different components. If the reaction mixture behaves as an ideal gas, the ideal gas equation is PV = nRT. The molecular concentration [X], which is n/V, is then equal to P/RT. This shows that, at a given temperature when T is constant, the pressure of a component is proportional to its molecular concentration.

The equilibrium constant with the concentrations of reactants and products expressed in terms of molarity is expressed by Kc.

Consider the generalized reaction **aA + bB ⇌ cC + dD, the equilibrium constant is:**

$$K_C = \frac{[C]^d[D]^d}{[A]^a[B]^b}$$

However, since the pressure is proportional to the concentration for gases in a closed system, the equilibrium constant can be written in terms of the pressures of the different components rather than their molecular concentrations and Kp expression is used.

For the above generalized reaction: $K_p = \frac{[pC]^c[pD]^d}{[pA]^a[pB]^b}$

Where P is the partial pressure

Example: Consider the reaction, $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$, where gaseous compounds are involved in the reaction, the equilibrium constant can be written as;

$$K_p = \frac{(p_{HI})^2}{p_{H_2} x p_{I_2}}$$

Where $p_{HI,}$ p_{H_2} and p_{I_2} are the partial pressures of the different compounds. If no other gases are present. The sum of the partial pressures is equal the total pressure P.

If $p_{HI} = 0.50$, $pH_2 = pI_2 = 0.30$, we have

$$K_p = \frac{(p_{HI})^2}{p_{H_2} x p_{I_2}} = \frac{(0.50)^2}{0.30x0.30} = 2.78$$

Determination of the partial pressure

The total pressure P of a mixture of gases is equal to the sum of partial pressures of the component present in the mixture of that gas. This commonly referred to as Dalton's law of partial pressure.

It is expressed as: $P_{total} = p_w + p_x + p_y + ...$ (1)

Where P is the partial pressure of the component w, x, y, etc.

For example, the partial pressures of the above components are given by ideal gas equation:

$$P_w = \frac{n_w RT}{V}, \quad P_x = \frac{n_x RT}{V}, \quad P_y = \frac{n_y RT}{V} \qquad (2)$$

$$\text{Thus } P_{total} = \frac{n_w RT}{V} + \frac{n_x RT}{V} + \frac{n_y RT}{V} \qquad (3)$$

In accordance with Dalton's law of gaseous mixture, the molar fraction of each gas is expressed as:

$$X_w = \frac{n_w}{n_T}, X_x = \frac{n_x}{n_T}, X_y = \frac{n_y}{n_T} \qquad (4)$$

Where X_w, X_x and X_y are molar fractions of gases w, x and y respectively.

From the relation (4), the number of total number of moles for each component forming the gas mixture can be calculated as follows:

$$n_w = X_w n_T, \ n_x = X_x n_T, \ n_y = X_y n_T \qquad (5)$$

By replacing the relation (5) in the equation (2), we get:

$$P_w = \frac{x_w n_T RT}{V}$$

$$P_x = \frac{x_x n_T RT}{V}$$

$$P_y = \frac{x_y n_T RT}{v}$$

Because $P_{total} = \frac{n_T RT}{V}$, then

$P_w = X_w P_{total}$

$P_x = X_x P_{total}$

$P_y = X_y P_{total}$

Where P_w, P_x and P_y are partial pressures for the gases w, x and y in the mixture. For any mixture of gases, the sum of all the molar fractions of all the components is given by $X_w + X_x + X_y + \ldots = 1$

APPLICATION ACTIVITY 17.3

1. The gases SO_2, O_2 and SO_3 are allowed to reach the equilibrium. The partial pressures of the gases are $P_{SO_2} = 0.050$ atm, $P_{O_2} = 0.025$ atm, $P_{SO_3} = 1.00$ atm .

Find the values of K_p for the equilibria.

a) $SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g)$

b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

2. Study the following equilibrium:

$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$

a) Write an expression for K_p

b) Would you expect an increase in total pressure to affect the yield of hydrogen? Explain your answer.

3. At certain temperature, the partial pressures of sulphur dioxide and oxygen are 0.25 and 0.64 atmospheres respectively. The total pressure of the system being 1.04 atmospheres.

Calculate the K_p of the reaction

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

17.4. Derivation of the relationship between Kc and Kp, Calculations on K_c and K_p

ACTIVITY 17.4

1. a) Derive the relationship between K_p and K_c for the reaction;

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

b) Calculate the K_p for the reaction at 4500^{0}C if K_c is 0.2 atm^{-1} (R = 0.082 atm mol^{-1}K^{-1})

c) 2000 cm^3 of sulphur dioxide was mixed with 1000 cm^3 of oxygen at 300^{o}C and 10 atmospheres pressure in the presence of a catalyst. When equilibrium had been attained, it was found that 1333 cm^3 of sulphur dioxide remained.

i) Write a balanced equation for the reaction between sulphur dioxide and oxygen.

ii) State the name of catalyst.

iii) Write an expression for the pressure equilibrium constant K_p.

iv) calculate the partial pressure of each of the gases at equilibrium.

v) Calculate the equilibrium constant,Kp, for the reaction.

17.4.1 Derivation of the relationship between Kc and Kp

The pressure and molarity are related by the Ideal Gas Law, PV = nRT where P = nRT/V

Consider the general reaction:

aA(g) + bB(g) → cC(g) + dD(g)

$$K_p = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b} \quad (6)$$

It is known that:

$$P_A = \frac{n_A RT}{V}, \text{ where } [A] = \frac{n_A}{V} \text{ and } P_A = [A]\,RT \quad (7)$$

$P_B = \frac{n_B RT}{V}$, where [A] = $\frac{n_B}{V}$ and P_A = [B] RT (8)

$P_C = \frac{n_C RT}{V}$, where [C] = $\frac{n_C}{V}$ and P_C = [C] RT (9)

$P_{D} = n_D RT/V$ Where [D] = n_D/V and P_D =[D]RT (10)

Replacing (7), (8), (9) and (10) in the relation (6), we get;

$$K_p = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b}$$

$$Kp = \frac{[C]^c [D]^d (RT)^{c+d}}{[A]^a [B]^b (RT)^{a+b}}$$

$$K_p = K_c (RT)^{(c+d)-(a+b)} \Rightarrow K_p \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b} = \frac{[C]^c [D]^d (RT)^{c+d}}{[A]^a [B]^b (RT)^{a+b}} \Rightarrow$$

$$K_p = \frac{[C]^c [D]^d (RT)^{c+d}}{[A]^a [B]^b (RT)^{a+b}} = K_c (RT)^{(c+d)-(a+b)}$$

$K_p = K_c(RT)^{\Delta n}$

Where R (ideal gas constant) = 0.0821 L.atm/K. mol^{-1}; T = temperature in Kelvin;

Δn = moles of gaseous products - moles of gaseous reactants;

K_p= equilibrium constant in gaseous phase expressed in partial pressures;

K_c = equilibrium constant in molar concentrations

Note: Kc = Kp when the number of gas molecules are the same in both sides (Δn = 0).

Characteristics of equilibrium constant

(i) The value of the equilibrium constant is independent of the original concentration of reactants.

(ii) The equilibrium constant has a definite value for every reaction at a particular temperature. However, it varies with change in temperature.

(iii) For a reversible reaction, the equilibrium constant for the forward reaction is inverse of the equilibrium constant for the backward reaction.

(iv) In general, **$K_{forward}$ reaction = 1/$K'_{backward}$ reaction**

(v) The value of equilibrium constant tells the extent to which a reaction proceeds in the forward or reverse direction.

(vi) The equilibrium constant is independent of the presence of catalyst.

17.4.2 Calculations on K_c and K_p

In general, calculations involving K_c and K_p requires the number of moles at the equilibrium state. K_c is derived from molar concentration of reactants and products at equilibrium state While K_p requires the partial pressure of all the reactants and products at equilibrium state.

Worked examples

The following table shows the equilibkium concectration for the reaction as below at 700k

$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$

[H2] / mol dn^{-3}	[I_2] / mol dn^{-3}	[HI] / mol dn^{-3}
1.71x10^{-3}	2.91x10^{-3}	1.65x10^{-2}

a. Calculations Involving K_c

The value of K_c is calculated using the concentrations of the reactants and products at equilibrium. **If these values are quoted they can be calculated from the initial concentrations of the reactants.**

Worked examples

a) Write an expression of the equilibrium constant K_c.

b) Calculate the values of K_c at 700K.

Answer:

$$\text{a) } K_c = \frac{[H]^2}{[H_2][I_2]}$$

b) Substitute the values quoted into this expression:

$$K_c = \frac{(1.65x10^{-2})^2}{(1.71x10^{-3})(2.91x10^{-3})} = 54.7$$

If the moles or molarity of the components of the reaction are not quoted at equilibrium then these need to be calculated:

Worked examples:

Consider the formation of hydrogen iodide: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Suppose a mole of hydrogen is mixed with b mole of iodide and allowed to reach the equilibrium so that x mol of HI are formed then;

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Mol at start	a	b	0
Mole at equilibrium	a-x/2	b-x/2	x

From the balanced equation, 1 mole of hydrogen reacts with 1 mole of iodine to form 2 moles of hydrogen

$$K_c = \frac{x^2}{(a-\frac{x}{2})(b-\frac{x}{2})}$$

2. Consider the esterification reaction:

$$CH_3COOH(l) + CH_3CH_2OH\ (l) \rightleftharpoons CH_3COOCH_2(l) + H_2O(l)$$

Mol at start	a	b	0	0
Mol at equilibrium	a-x	b-x	x	x

From the balanced equation, 1 mol of acid reacts with 1 mol of alcohol to form 1 mol of ester and 1 mol of water.

This means that:

- The amount of the two products formed is the same (x)
- The amount by which the two reactants are reduced equals the amount of each product formed (x)

$$Kc = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]} = \frac{(\frac{x}{v})x(\frac{x}{v})}{\frac{(a-x)}{v}x\frac{(b-x)}{v}}$$ where V= volume in dm^3

Cancelling V gives:

$$K_c = \frac{x^2}{(a-x)(b-x)}$$

3. For the equilibrium below:

$$CH_3COOH(l) + CH_3CH_2OH\ (l) \rightleftharpoons CH_3COOCH_2(l) + H_2O(l)$$

Mole at start	1	0.33	0	0
Mole at equilibrium	(1 - 0293)	(0.33-0.293)	0.293	0.293

Fnd the value of K_c

Answer: $K_c = \frac{(0.293x0.93)}{(0.707x0.037)} = 3.31$

4. 0.206 mol of hydrogen and 0.144 mol of iodine were heated at 683 K at equilibrium 0.258 mol of HI were present.

a) Calculate the value of K_c at this temperature.

b) If the value for K_c is 54 at 700K deduce whether this reaction is exothermic or endorthermic.

Answer:

a) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Mole at start	0.206	0.144	0
Mol at equilibrium	$0.206-\frac{0.258}{2}$	$0.114 - \frac{0.258}{2}$	0.258
	0.077	0.015	0.258

$$K_c = \frac{(0.258)^2}{(0.707x0.015)} = 57.63$$

b) As the temperature increases the value of Kc decreases so the forward reaction is exothermic.

5. Consider the gaseous equilibrium: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ At 300 K 1.0 mol of $N_2O_4(g)$ is 20% dissociated in a 2.0 dm^3 flask. Calculate the value of Kc for this reaction.

Answer:

If N_2O_4 is 20% dissociated then 80% remains at equilibrium i.e 1.0x80/100 = 0.8mol. 20% has been converted into nitrogen dioxide.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

	N_2O_4	NO_2
Mol at start	1.0	0
Mol at equilibrium	0.8	2x0.2 = 0.4

$$K_c = \frac{[NO_2]^2}{(N_2O_4)} \text{mol dm}^{-3}$$

It is possible to use moles in the K_c expression since the units for K_c are mol dm^{-3}.

$$K_c = \frac{\left(\frac{0.4}{v}\right)^2}{\frac{(0.8)}{v}} = \frac{0.16}{0.8xv} \text{ where V} = 2dm^3$$

$$K_c = \frac{0.16}{0.8x2} = 0.1 \text{mol dm}^{-3}$$

6. 3.00 mol of PCl_5 kept in 1L closed reaction vessel was allowed to attain equilibrium at 380K. Calculate composition of themixture at equilibrium. *Kc*= 1.80

Answer

Let x mol per liter of PCl_5 be dissociated,

Concentration(M)	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$		
Initial	**3**	**0**	**0**
Change	**-x**	**+x**	**+x**
Equilibrium	**3-x**	**x**	**X**

$Kc = [PCl_3][Cl_2]/[PCl_5]$

$1.8 = x^2/ (3 - x)$

$x^2 + 1.8x - 5.4 = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

a = 1, b = 1.8, c = −5.4

$x = [-1.8 \pm \sqrt{(1.8)^2 - 4(-5.4)}]/2$

$x = [-1.8 \pm \sqrt{3.24 + 21.6}]/2$

$x = [-1.8 \pm 4.98]/2$

$x = [-1.8 + 4.98]/2 = 1.59$

as value of x cannot be negative hence we neglect that value(x= -3.39)

$[PCl_5] = 3.0 - x = 3 - 1.59 = 1.41$ M

$[PCl_3] = [Cl_2] = x = 1.59$ M

b. Calculations involving K_p

(i) knowing the values of the partial pressures

Worked example

1. The partial pressures of the gases at equilibrium in the Haber process at 640 K are hydrogen 40kPa; nitrogen 10 kPa; ammonia 15kPa. Use these data to calculate a value for K_p at 640 K.

Answer:

First write the equation and then an expression for K_p, with units

$Kp = \dfrac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^2}$ and unit is $(1/(kPa)^2)$or $(kPa)^{-2}$

Now substitute the values quoted into the expressions:

$K_p = \dfrac{(15)^2}{(40)(40)^2} = 3.5\text{x}10^{-4}\ (1/(kPa)^2)$ or $(kPa)^{-2}$

It is important to note that K_p is a constant at constant temperature. Altering the partial pressures of the reactants will shift the equilibrium position but the value of K_p remains constant.

(ii) Using total pressure:

The sum of the partial pressures of the individual gases in a mixture is equal to the total pressure exerted by the mixture of gases.

Example: In the Haber process: total pressure = $P_{NH_3} + P_{N_2} + P_{H_2}$, this is useful expression that is needed in the calculations.

Worked examples:

1. In the contact process, at equilibrium and with a total pressure of 120 kPa, the partial pressures of sulphur dioxide and sulphur trioxide are 33 kPa and 39 kPa respectively. Calculate a value of K_p stating the units.

Answer:

First write the equation for the process and then an expression for K_p, with units:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$K_p = \frac{(P_{SO_3})^2}{(P_{O_2})^2(P_{SO2})^2} \quad \text{unit is } 1/\text{kPa or } (\text{kPa})^{-1}$$

Before the partial pressures can be substituted into the expression we need to find the partial pressure of oxygen, which is not quoted in the question

Using: Total pressure = the sum of the partial pressures ⇒ 120 = 33+39 + P_{SO_2}

$$P_{SO_2} = 120- (33 + 39) = 48$$

$$K_p = \frac{(39)^2}{(48)(33)^2} = 0.029\ (1/\text{kPa}) \text{ or } (\text{kPa})^{-1}$$

The partial pressure of each gas = mole fraction x total pressure.

2. A gaseous mixture contains 7 moles of X, 2 moles of Y and 1 mole of Z at equilibrium at a total pressure of 100 kPa. Calculate the value of K_p for the reaction:

$$X(g) + Y(g) \rightleftarrows 2Z(g)$$

Answer:

First calculate the mole fractions of each gas:

The total number of moles = 10

The mole fractions of the gases are: X = 7/10 = 0.7; Y = 2/10 = 0.2; Z = 1/10 = 0.1.

Using: the partial pressure of each gas = mole fraction x total pressure

The total pressure is: P_x =0.7x100 = 70kPa; P_y = 0.2x100 = 20kPa; P_z = 0.1x100 = $10kP_a$

Knowing the values of the partial pressures of the gases at equilibrium, we can now calculate the value of the equilibrium constant, K_p.

$$K_p = \frac{[P_z]^2}{(P_z)(P_y)}$$

$$K_p = \frac{(10)^2}{20x70} = 0.071$$

c. Relating K_c to K_p

Worked examples:

1. For contact process: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_p = \frac{P_{SO_3}{}^2}{(P_{O_2})(P_{SO_2})^2}$$

$$K_p = K_c\,(RT)^{2-(2+1)} = \frac{K_c}{RT}$$

For haber process:

$$K_p = \frac{P_{NH_3}{}^2}{(P_{H_2})(P_{N_2})^2} = K_c(RT)^{2-(1+3)} = \frac{K_c}{(RT)^2}$$

2. Iodine and hydrogen were allowed to react at 450^{0}C to give HI(g) according to the following equilibrium.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

a) Write down the mathematical expression of K_p.

b) 0.50 moles of hydrogen H_2(g) and 0.50 moles of I_2 (g) were allowed to react in a closed vacuum at 450^{o}C under the pressure of 2.0 atm and the equilibrium is established if the number of moles of I_2 is 0.11 moles.

i) Calculate partial pressure for each gas

ii) Calculate then the value of K_p

iii) Hence, deduce from the above the value of K_c.

Answer

a) The mathematical expression is $K_p = \dfrac{P_{HI}^{\ 2}}{(P_{H_2})(P_{I_2})^2}$

b) Let us consider the following table:

Number of moles (mol)	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
Initial	0.50 0.50 0
Changes	-0.39 -0.39 +0.78
Equilibrium	0.11 0.11 0.78

i) Let us define

$$X_{I_2} = X_{H_2} = \frac{n_{HI}}{n_{H_2} + n_{I_2} + n_{HI}} = \frac{0.78}{0.11 + 0.11 + 0.78} = 0.78$$

The partial pressure of each gas is given by:

$$P_i = X_i P_{total} \Rightarrow P_{H_2} = P_{I_2} = 0.11\ x2 = 0.22\ atm$$

$$P_{HI} = X_{HI}P_{total} = 0.78x2 = 1.56\ atm$$

ii) The partial pressure equilibrium constant is

$$K_p = \frac{(1.56\ atm)^2}{(0.22\ atm)x(0.22\ atm)} = 50.28$$

iii) K_c is equal to $K_p = 50.28$, since $\Delta n = 2-(1+1) = 0$

$K_c = 50.28$

3. Antimony pentachloride dissociates in antimony dichloride and chlorine. At 180^0C it was found that it is dissociated to 29.2%. Calculate K_p and K_c for the dissociation at this temperature, if we started with 2 moles of $SbCl_5$ in a container of 1 liter.

Answer:

Expression of K_c and K_p:

$$SbCl_5 \rightleftharpoons SbCl_3 + Cl_2$$

$$K_c = \frac{[SbCl_3][Cl_2]}{[SbCl_5]} = K_p(RT)^{-1}$$

V = 1L

	$SbCl_5 \rightleftharpoons$	$SbCl_3$ +	Cl_2
Initial state	2	0	0
Equilibrium	2(1-0.292)	0.292x2	0.292x2

$$K_c = \frac{0.292x0.292x2}{2(1 - 0.292)} = \frac{0.341056}{1.416} = 0.24$$

$$K_p = \frac{0.24}{(0.082x455)} = 0.24 \text{ x } 0.082 \text{ x } 455 = 8.95$$

APPLICATION ACTIVITY 17.4

a) Derive the relationship between K_p and K_c for the reaction;

$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)$

b) Calculate the K_p for the reaction at 4500^0C if K_c is 0.2 atm^{-1} (R = 0.082 atm $mol^{-1}K^{-1}$)

c) 2000 cm^3 of sulphur dioxide was mixed with 1000 cm^3 of oxygen at 300^oC and 10 atmospheres pressure in the presence of a catalyst. When equilibrium had been attained, it was found that 1333 cm^3 of sulphur dioxide remained.

i) State the name of catalyst.

ii) Write an expression for the pressure equilibrium constant K_p.

iii) Calculate the partial pressure of each of the gases at equilibrium.

iv) Calculate the equilibrium constant,Kp, for the reaction.

SKILLS LAB 17

OBJECTIVE: To investigate the effects of temperature and concentration upon the position of equilibrium in a solution of cobalt(II) containing excess chloride ions.

MATERIALS AND CHEMICALS REQUIRED

Chemicals

25 mL of solution in which [Co^{2+} (aq)] = 0.5M and [Cl^{-}(aq)] = 5M:

$CoCl_2.6H_2O$ = 3.0 g, concentrated HCl = 12.0 mL, deionised water

Small stock supplies of concentrated hydrochloric acid and of solid cobalt (II) chloride, deionised water.

Materials

25 mL volumetric flask, 25 mL graduated cylinder, balance, small funnel, dropper.

To test effects of changes of concentration of solutes:

white glazed tile, white glazed well-plate(or test tube and test tube rack as in image a), 1 mL graduated pipette with filler bulb (or automatic

delivery pipette), pasteur pipettes, small spatula, four small glass stirring rods,

Image (a)https://opentextbc.ca/chemistry/chapter/20-2-alcohols-and-ethers/

INSTRUCTIONS

1. Weigh 3.00 g of solid cobalt(II) chloride and put it in a small funnel placed in the mouth of a 25 mL volumetric flask.

2. Measure 12 mL of concentrated hydrochloric acid in a graduated cylinder, then pour it slowly over the solid cobalt chloride in the funnel, so that the crystals dissolve and fall into the flask. Rinse the cylinder with a little deionised water and pour the rinse water slowly over any remaining crystals in the funnel. Continue to drop water slowly until all the crystals have fallen or dissolved into the flask, then finish filling the flask to the 25 mL graduation, and shake. The solution should be dark blue-purple in colour.

3. To show the reversibility of the reaction with changing temperature, place the flask, or a sample of solution taken from the flask into a small closed tube or bottle, into the coldest part of a refrigerator. Observe how the colour changes. Then remove the flask or sample from the refrigerator and watch the change of colour as the temperature of the solution rises.

   Steps 4 to 10, require the use of a 4 x 3 glazed well-plate, or a suitable alternative (test tube and test tube rack) as in image(a) above.

4. Label the wells of a white glazed well-plate 1 to 12. Transfer 0.40 mL of the blue solution, at room temperature, into ten wells, leaving wells 5 and 9 empty.

   At each of steps 5 to 9, all observed changes of colour should be recorded.

5. Using a pasteur pipette, add one drop of water to each of wells 2, 3 and 4, two drops of water to each of wells 6, 7 and 8, and three drops of water to each of wells 10, 11 and 12. (Well 1 should contain a sample of the initial solution, as a control.) Stir each sample gently with a small glass rod.

6. To each of wells 3, 7 and 11, add one drop of concentrated hydrochloric acid.

7. To each of wells 4, 8, and 12, add equal small amounts of crystals of cobalt (II) chloride.

8. With a small stirring rod, stir wells 3, 7, and 11; rinse and dry the rod after each use.

9. With a small stirring rod, stir wells 4, 8, and 12. Rinse and dry the rod after each use.

10. Record the final pattern of colours seen in the wells 1 to 12.

OBSERVATIONS

Design and construct tables to record the colours observed.

(Colours might be recorded as “blue”, “pinkish-blue”, “bluish pink”, or “pink”. Variations,

Table one: Effect of addition of water to solutions

Sample number	1	2,3,4	6,7,8	10,11,12
Water added	none	1 drop	2 drops	3 drops
Final color				

Table two: Effects of addition of a drop of concentrated HCl to solutions 3, 7 and 11.

Sample number	1	3	7	11
Water added	none	1 drop	2 drops	3 drops
Initial color				
Color before stirring	no acid added			
Color after stirring				

Table three: Effects of addition of solid cobalt(II) chloride to solutions 4, 8, and 12.

Sample number	1	4	8	12
Water added	none	1 drop	2drops	3 drops
Initial color				
Color before stirring	no $CoCl_2$ added			
Color after stirring				

EVALUATION

1. How well do the observed changes in the colours of the solutions agree with the expected changes:

a. with respect to the effect of dilution with water upon the position of the equilibrium?

b. with respect to the effect of an increase in the concentration of chloride ions upon the position of the equilibrium?

c. with respect to the effect of an increase in the concentration of cobalt(II) ions upon the position of the equilibrium?

2. How can any changes of colour observed in the solutions as a result of stirring be explained?

END UNIT ASSESSMENT 17

1. Nitrogen monoxide gas (NO) was allowed to react with hydrogen gas (H_2) in a litre container according to the equation

$$2NO_{(g)}+2H_{2(g)} \rightleftharpoons N_{2(g)}+2H_2O_{(g)}$$

Initially before the reaction started; the concentration of each gas was: NO(g) = 0.10 mol/litre, H_2(g) = 0.050 mol/litre, H_2O(g) = 0.10 mol/litre, N_2(g) = 0.00 mole/litre. When the reaction reached equilibrium, the concentration of each gas was equal to 0.062 mol/litre. When the reaction reached equilibrium, the concentration of each gas was equal to 0.062 mole/litre.

a) Write the mathematical expression of equilibrium constant, K_c.

b) Calculate the equilibrium constant, K_c .

c) Determine the mathematical expression of equilibrium constant, K_p in relation to the equilibrium constant K_c .

d) Calculate K_p, by using the value of K_c (in 1.b) above. (R =0.082 L.Atm. K^{-1} mol^{-1}, temperature K = 298 Kelvin)

2. This question refers to the Haber process for the synthesis of ammonia. The equation which presents the reaction is given below.

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H^o = -92kJ\ mol^{-1}$

a) Explain what is meant by the term '' dynamic equilibrium''.

b) i) Write the expression for the equilibrium constant K_p, for the above process.

ii) If the pressure is measured in atmospheres, what will be the units of K_p?

c) State and explain the effect on the above equilibrium:

i) Increasing the pressure

ii) Increasing the temperature

d) Name the catalyst used in the Haber process.

e) i) Describe the function of a catalyst in terms of activation energy and use a diagram to illustrate its effect.

ii) Describe the effect of catalysts on the position of equilibrium and its effects on the concentrations of reacting substances at equilibrium.

3. Nitrogen tetroxide, $N_2O_4(g)$, decomposes according to the equation

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

a) Write an expression for the equilibrium constant, K_c, for the above reaction

b) Explain the effect on the composition of the equilibrium mixture when the pressure is doubled.

4. Consider the following equilibrium reactions:

Reaction I:

$$3Fe(s)+4H_2O(g) \rightleftharpoons Fe_3O_{4(s)} +4H_{2(g)}$$

Reaction II:

$$CO_{(g)}+Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$$

a) Write expressions for the equilibrium constant, K_p.

i) for reaction I

ii) for reaction II

b) State, giving reasons, how an increase in pressure affects the position of equilibrium in each reaction above.

5. The production of ammonia in the Haber process involves the reaction:

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$

a) Write an expression for the equilibrium constant, K_c, for the above reaction.

b) 0.20 mol of $N_2(g)$ and 0.20 mol of $H_2(g)$ were reacted in a 1 dm^3 closed container. (Until equilibrium) was reacted. At equilibrium, the concentration of $NH_3(g)$ was 0.060 $moldm^{-3}$.

i) Calculate concentrations of $N_2(g)$ and $H_2(g)$ at equilibrium.

ii) Calculate the value of K_c and state its units.

c) How does an increase in pressure affect the yield of ammonia? Explain your answer.

d) The actual conditions used in the Haber process are a temperature of 500°C and a pressure of 200 atmospheres. Why are these conditions used instead of the conditions that would give the highest yield?

e) Give one large scale use of ammonia.

6. Methane gas reacts with steam according to the equation given below:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \quad \Delta H^o: +210\ kJmol^{-1}$$

a) How does an increase in pressure affect the equilibrium position? Explain your answer.

b) Write an expression for the equilibrium constant, K_c, and state its units.

UNIT 18

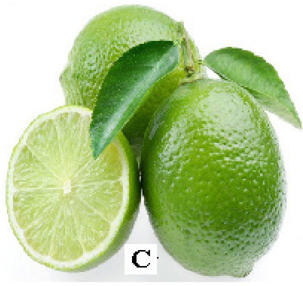
ACIDS AND BASES

Key unit Competence: Explain the acid-base theories (Arrhenius, Bronsted–Lowry, Lewis).

INTRODUCTORY ACTIVITY

1. Have you heard the words acid and base? Yes or No. If yes what do they mean? Give an example of an acid and an example of a base?

2. Observe the pictures shown below. Identify the name and main use(s) of the substance in each picture.



3. Answer the following questions using information given in question 2

(i) Match the names of substance in question 2 with the ones in the following table.

(ii) In how many main groups would you classify the substance above?

(iii) Name the groups you referred to in 2 (ii)?

Substance	**pH range**
Butter	6.1-6.4
Soap	9-10
Citric acid	2.2-2.4
Magnesium hydroxide	≈ 10.5
Pepper	4.6-5.5

Acids were first recognized as a class of substances that taste sour. Vinegar tastes sour because it contains acetic acid; citric acid is responsible for the sour taste of a lemon. Bases, sometimes called alkalis, are characterized by their bitter taste and slippery feel. The bitter tastes of quinine or extract from some plants such as Vernonia amygdalina (Umubirizi) are characteristics of bases.

18.1 Acid-Base Theories

ACTIVITY 18.1

Determining the acidity/alkalinity nature of substance using acid-base indicators.

Procedure

Using a dropper, collect 3-4 drops of each of the 7 chemical substances in 7 test tubes.

1. Hydrochloric acid (HCl)
2. Sodium hydroxide ($NaOH$)
3. Sodium chloride ($NaCl$)
4. Glucose ($C_6H_{12}O_6$)
5. Sulphuric acid (H_2SO_4)

6. Distilled water (H_2O)

7. Ammonia (NH_3).

8. Ethanoic acid (CH_3COOH)

   a. To each chemical test whether it is an acid, a base or neutral by using blue litmus paper, red litmus paper and universal indicator (better). Record your observations and colour intensities in Table that follows

   b. Comparing the colour intensities of the indicators, explain the source of their difference.

Reagent	**Red Litmus**	**Blue Litmus**	**Acid, base or neutral?**
Hydrochloric acid (HCl)			
Sodium hydroxide (NaOH)			
Sodium chloride (NaCl)			
Distilled water (H_2O)			
Glucose ($C_6H_{12}O_6$)			
Sulphuric acid (H_2SO_4)			
Ammonia (NH_3)			
Ethanoic acid (CH_3COOH)			

Study Questions

1. Which of the chemicals are acids?

2. Which of the chemicals are bases?

3. Which of the chemicals are neutral?

18.1.1. Arrhenius' Theory of Acid-Base

The first person to recognize the essential nature of acids and bases was the Swedish scientist **Svante Arrhenius** (1859–1927). On the basis of his experiments with electrolytes, Arrhenius postulated that acids produce hydrogen ions in aqueous solution, while bases produce hydroxide ions.

(i) **An acid** is a substance which dissociates in aqueous solution to produce hydrogen ions (H^+) as the only positive ions.

(ii) **A base** is any substance that dissociates in aqueous solution to produce hydroxyl ions (OH^-) as the only negative ions.

Notice that the Arrhenius concept of acid and base requires the presence of water.

In this theory, the products of an acid-base reaction are: salt and water:

$$NaOH(aq)+HCl(aq) \longrightarrow NaCl(aq)+H_2O(l)$$

Base Acid Salt Water (Neutral solution)

This reaction acid-base shows that when an acid reacts with a base, the result is a neutral solution of a salt in water; this explains why the reaction is called an **acid-base neutralization reaction**: acidic properties and basic properties neutralize each other.

Examples of acids
1. $HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$ 2. $H_2SO_{4(aq)} \longrightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$
Examples of bases
1. $NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$ 2. $Mg(OH)_{2(aq)} \longrightarrow Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$

Notice

The observations in activity 18.1 show that all acids and bases do not show the same intensity of colours; this means that although all are acids or bases they give different concentrations of H^+ or OH^- ions.

This means that not all acids and bases dissociate into their ions at the same extent. Some dissociate completely in water, other dissociate partially.

Acids and bases that dissociate completely into their ions when dissolved in water are qualified as "**strong**".

Examples of strong acid and strong base:

$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$ **strong acid, complete dissociation into ions**

$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$ **strong base, complete dissociation into ions**

Acids and bases that dissociate partially in water are qualified as "**weak**":

Examples of weak acid and weak base:

$H_3PO_{4(l)} + H_2O(l) \rightleftharpoons H^+_{(aq)} + H_2PO_4^-{}_{(aq)}$ **partially dissociated, weak acid.**

$NH_4OH_{(aq)} + H_2O(l) \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$ **partially dissociated, weak base.**

Since strong acids and strong bases dissociate completely in water whereas weak acids and weak bases dissociate partially, the concentration $[H^+]$ in a solution of a strong acid will be higher than the concentration $[H^+]$ in the solution of a weak acid of the same concentration. In other words, pH of the strong acid solution will be lower that pH of the weak acid solution of the same concentration.

For the same concentration: pH of HCl (aq) < pH of H_3PO_4(aq)

In the same way, the concentration OH^- in a strong base solution will be higher than the concentration OH^- of a weak base solution of the same concentration; in this case the concentration H^+ in a strong base solution will be lower than the concentration H^+ in a weak base solution of the same concentration, or pH of strong base solution will be higher than pH of the weak base solution of the same concentration.

For the same concentration: pH of NaOH(aq) > pH of NH_4OH(aq).

APPLICATION ACTIVITY 18.1(a)

1. Fill in the following table

Substance	Acid/Base	Positive ions in water	Negative ions in water
HCl			
HBr			
HNO_3			
KOH			
$Ca(OH)_2$			
NH_4OH			
HCOOH			

2. Use the information in the table below to answer the following questions.

The pH Values of Some Common Solutions(*)

Solution	pH / pH range
Battery acid	0.3
Stomach acid	1–2
Lemon or lime juice	2.1
Vinegar	2.8–3.0
Coca-Cola	3
Wine	2.8–3.8
Beer	4–5
Coffee	5
Milk	6
Urine	6
Pure H_2O	7
(Human) blood	7.3–7.5
Sea water	8
Antacid (Milk of magnesia)	10.5
NH_3 (1 M)	11.6
Bleach	12.6
NaOH (1 M)	14.0

(*)Adapted from: https://chem.libretexts.org

3. (i) Take two different solutions with equal concentrations of acids such as HCl and CH_3COOH, and measure their pHs.

   (ii) Take two different solutions with equal concentrations of bases such as NaOH and NH_4OH, and measure their pHs.

Questions:

a. Record your observations about the results?

b. How do you interpret those results?

18.1.2. Brønsted-Lowry's Acid-Base Theory: Acid-base conjugate pairs

The weakness of the Arrhenius acid-base theory is that it requires the presence of water and the acid and base properties are due only to the presence of H^+ and OH^- ions respectively in an aqueous solution. Hence, for example, hydrogen chloride, HCl (g), is not an acid and NH_3 is not a base according to this theory.

In 1923, the Danish Chemist Johannes Nicolaus Brønsted (1879–1947) and English Chemist Thomas Martin Lowry (1874 – 1936) independently developed the definitions of acids and bases based on the compounds' abilities to either donate or accept protons (H^+ ions). In this theory, acids are defined as proton donors whereas bases are defined as proton acceptors. A compound that acts as both a Brønsted-Lowry acid and base is called ***amphoteric.***

Briefly in this theory, **an acid is a proton (H^+) donor**, and **a base is a proton acceptor**.

Examples

1) $CH_3COOH_{(aq)} + H_2O(l) \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$

Acid **Base**

2) $NH_4^+{}_{(aq)} + H_2O(l) \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)}$

Acid **Base**

3) $NH_{3(aq)} + H_2O(l) \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$

Base **Acid**

4) $CO_3^{2-}{}_{(aq)} + H_2O \rightleftharpoons HCO_3^{-}{}_{(aq)} + OH^{-}{}_{(aq)}$

Base **Acid**

5) $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$

Base **Acid**

In this theory you notice that OH^- ion is not the only base; any chemical species that can accept a proton is a base, be it in aqeous solution or not. H^+ continues to be the only source of acid properties except that the presence of water is no more a prerequisite.

Example: $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$

Acid (proton donor) base (proton acceptor)

Conjugate acids and bases

Let us consider an acid HA which ionizes partially in aqueous solution according to a reversible reaction below:

$$HA + H_2O \rightleftharpoons H_3O^{+}{}_{(aq)} + A^{-}{}_{(aq)}$$

- *Forward reaction:*

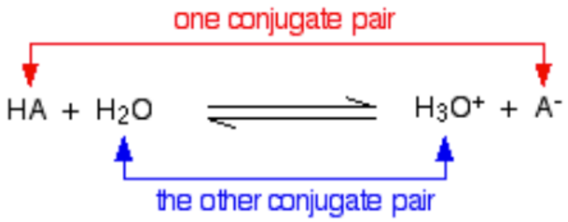
HA is an acid because it is donating a proton to H_2O.

The water (H_2O) is a base because it is accepting a proton from the acid (HA).

- Reverse *reaction*

The H_3O^+ is an acid because it is donating a proton to the A^- ion.

The A^- ion is a base because it is accepting a proton from the H_3O^+. The reversible reaction contains *two* acids and *two* bases. We take them as pairs, called ***conjugate pairs***.



According to the forward reaction, HA is the acid and its conjugate base is A^-. According to the reverse reaction, H_3O^+ is an acid whose conjugate base is H_2O.

The above reaction can be represented as:

$$HA + H_2O \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Acid1 Base2 Acid 2 Base 1

The acid-base conjugate pairs are written as Acid1/ Base 1 and Acid 2/ Base2.

Examples

1) When an acid loses a proton a **conjugate base** is produced.

$$CH_3COOH_{(aq)} + H_2O(l) \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

Acid1 Base2 Base1 Acid2

The conjugate acid-base pairs for this reaction are the following: CH_3COOH/CH_3COO^- and H_3O^+/H_2O

2) $NH_3(aq) + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$

Base1 Acid2 Acid1 Base2

The conjugate acid-base pairs for this reaction are: NH_4^+/NH_3 and H_2O/OH^-.

In general, when an acid is strong, its conjugate base is weak and vice-versa.

Examples:

In the reaction above, HCl is a strong acid, the conjugate base Cl^- is weak; similarly, H_2O is a weak base and its conjugate acid H_3O^+ is strong.

In the conjugate acid base couples of the previous example:

NH_4^+/NH_3: NH_4^+ is a strong acid whereas NH_3 is a weak base.

H_2O/OH^-: H_2O is a weak acid whereas OH^- is a strong base.

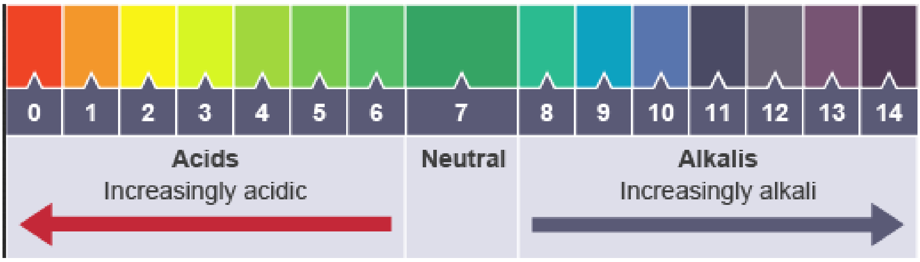


Figure18.1: pH scale

Remark

The observation of the above examples shows that water can act as both Brønsted-Lowry base or a Brønsted-Lowry acid. Thus, water is known as an **amphoteric solvent.**

APPLICATION ACTIVITY 18.1(b)

1. Label the acid (A), base (B), conjugate acid (CA), and conjugate base (CB) in each of the following reactions.

a. $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$

b. $H_2PO_4^-{}_{(aq)} + NH_{3(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + HPO_4^{2-}{}_{(aq)}$

c. $NH_4^+{}_{(aq)} + CN^-_{(aq)} \rightleftharpoons HCN_{(aq)} + NH_{3(aq)}$

d. $H_2SO_{4(aq)} + H_2O(l) \rightleftharpoons H_3O^+_{(aq)} + HSO_4^-{}_{(aq)}$

2. Give the conjugate base for each of the following Brønsted-Lowry acid.

a. HI

b. NH_4^+

c. H_2CO_3

d. HNO_3

3. Give the conjugate acid for each of the following Brønsted-Lowry bases.

a. CN–

b. O^{2-}

c. CH_3COO^-

d. NH_3

18.1.3. Lewis's Acid-Base Theory

In 1938, an American chemist **Gilbert Newton Lewis** (1875–1946) introduced another theory which extends the concept of acids and bases further than those of Arrhenius and Brønsted-Lowry.

An acid is a chemical species that has a vacant orbital and can accept a pair of electrons from another chemical species. **An acid is an electron pair acceptor or electron deficient.**

In this theory, hydrogen ion, H^+, is electron deficient and can accept a pair of electrons as any electron deficient species; it is no more the only responsible of acidic properties.

Other various species can act as Lewis acids. They include the following chemical species.

a. All cations, but particularly cations of transition metals; e.g. Cu^{2+}, Fe^{2+}, Fe^{3+}.

b. Chemical molecules whose central atom does not fulfill the octet rule; e.g BF_3, $AlCl_3$, BH_3, …

A base is a substance that possesses one or more lone pairs of electrons which may be used for the formation of a coordinate bond. **A base is an electron pair donor.**

A Lewis base can be an anion, such as OH^{-}, Cl^{-} , CN^{-} or a neutral molecule with lone pair of electrons such as $H_2\ddot{O}$:, :NH_3, etc…

Examples

1) The reaction between ammonia, NH_3, H_2O with H^+, to form ammonium ion, NH_4^+ and H_3O^+ respectively:

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

Electron donor   electon deficient
(lewis base)   (lewis acid)

$$H_2O + H^+ \rightleftharpoons H_3O^+$$

Lewis base   Lewis acid

2) The reaction between ammonia, NH_3, and boron trifluoride, BF_3, involves a Lewis acid,

$$BF_3 + NH_3 \rightleftharpoons F_3B{:}NH_3$$

3) The formation of complex ions by transition metals is an example of reactions involving Lewis acids and Lewis bases. For instance, consider the following reactions:

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons Cu\,(NH3)_4{}^{2+}{}_{(aq)}$$

$$Fe^{2+}(aq) + 6CN^{-}(aq) \rightleftharpoons Fe(CN)_6{}^{4-}{}_{(aq)}$$

In this wider concept of Lewis acid and base, all cations and neutral molecules, deficient in electrons are Lewis acids, whereas all anions and neutral molecules with lone pair(s) of electrons are Lewis bases.

Therefore, H^+ ion becomes a Lewis acid among many other Lewis acids and OH^- ion becomes a Lewis base among many other Lewis bases.

APPLICATION ACTIVITY 18.1(c)

1) Write equations of reactions between the following species and state which species are acids and which one are bases.

   a. Fe^{3+} and H_2O to form hexaaquairon (III).

   b. Cu^{2+} and NH_3 to form tetraamminecopper (II).

   c. Cr^{3+} and H_2O to form hexaaquachromium (III).

2) What is the name of the bond formed between a Lewis acid and a Lewis base?

   a. Covalent bond b. Double bond c. Coordinate covalent bond
   d. Ionic bond

3) Why is BH_3 (boron trihydride) a Lewis Acid? Identify the correct answer.

   a. It is a cation.

   b. It is electron deficient.

   c. It can accept more than 8 valence electrons.

   d. It contains double bonds.

SKILLS LAB 18

Make the internet research on how to prepare natural indicators from the extract of plants such as red cabbage, hibiscus flowers and make a simple test for acidity in the following vegetables tomatoes, spinach, lemon, soap.

Compare your results to the test of common acids such as hydrochloric acid and base such as sodium hydroxide

Draw a conclusion by filling the following table

Indicator subsatnce	Extract of red cabbage	Extract of hibiscus flower	conclusion
Hydrochloric acid			
Sodium hydroxide			
Soap			
Tomatoes extract			
Spinach extract			
Lemon juice			

END UNIT ASSESSMENT 18

1. Write an equation for the dissociation of the following acids in water:

   a) $HClO_4$ b) H_2SO_4 c) CH_3COOH d) H_2S e) HNO_3

2. Write the balanced equation of that reaction that happens when nitric acid is put in water.

3. Write the balanced equation of reaction that happens when acetic acid is put in water.

4. Write an equation for the dissociation of $Ba(OH)_2$ in water.

5. What is the conjugate base of HSO_4^-?

6. Write the formula and name for the conjugate acid for the following bases:

a) NH_3 b) PO_4^{3-} c) CN^- d) HCO_3^-

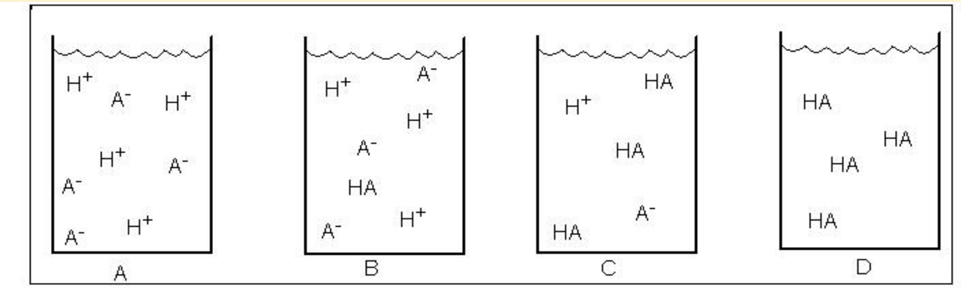
Write a balanced equation for the Bronsted-Lowry acid HPO_4^{2-} in water.

8. Write and balance the equation of the dissociation of ammonia in water.

9. The acidity strength of group VII oxoacids increases with the number of oxygen atoms. With reference to Bronsted-Lowry theory of acids and bases, rank their conjugate bases hereafter in increasing order of alkalinity strength.

a) ClO^- b) ClO_2^- c) ClO_3^- d) ClO_4^-

10. Rank the following chemical species in decreasing order of acidity strength.



UNIT
19

ENERGY CHANGES AND ENERGY PROFILE DIAGRAMS

Key unit Competency: Explain the concept of energy changes and energy profile diagrams for the exothermic and endothermic processes.

INTRODUCTORY ACTIVITY

You are provided with the following chemicals and apparatus

- Zinc granules
- Dilute hydrochloric acid (2HCl)
- Quicklime or Calcium oxide (CaO).
- Ammonium chloride (NH_4Cl)
- Sodium thiosulphate ($Na_2S_2O_3.5H_2O$)
- Distilled Water
- A thermometer
- 4 Beakers labeled A, B, C and D.
- 4 Spatulas
- 4 test tubes

Procedure:

1. In beaker labeled A put dilute hydrochloric acid.

In beaker labeled B put water.

Read and record the initial temperatures of both substances.

2. In beaker A put zinc granules using a spatula.

In beaker B put calcium oxide using a spatula.

Read and record the final temperatures of both solids.

3. In beaker labeled C put 100 cm^3 distilled water.

In beaker labeled D put 100 cm^3 distilled water

Read and record the initial temperatures of both solutions.

4. In beaker C put one end full spatula of ammonium chloride.

In beaker D put one and full spatula of sodium thiosulphate.

Read and record the final temperatures of both solids.

Study questions

1. Fill the following table.

Substance

Initial Temperature (°C)

Final Temperature (°C)

1. Fill the following table

Substance	Initial Temperature (°C)	Final Temperature (°C)
A		
B		
C		
D		

2. Which reactions produce heat?

3. Which reactions absorbed heat?

4. List 2 uses of heat in everyday life.

19.1. Concept of a system

ACTIVITY 19.1

1.You are provided with two different beakers labeled 1 and 2 containing 100ml of water:

a)in beaker 1: add slowly 5 ml of concentrated sulphuric acid and stir using a stir rod

b)in beaker 2 :add 5 g of ammonium nitrate and stir.

2. a)touch the wall of each beaker and write what you feel.

b)Classify the system as open or closed and justify your answer

Thermochemistry is the study of heat and energy associated with a chemical reaction or a physical transformation. Thermodynamics is the study of the relationship between heat, work, and other forms of energy. A reaction may release or absorb energy, and a phase change may do the same, such as in melting and boiling. Energy is exchanged between a closed system and its surroundings during the heating and cooling processes.

A system is a part of the universe which is studied using laws of thermodynamics. Everything outside the system is the **surroundings**. An infinitely small region separating the system from the surroundings is called **boundary**. In Chemistry **the chemical system** consists of reactants and products. The systems are classified according to the number of factors including the composition and the interaction with the surroundings. A system can be homogeneous or heterogeneous. It can be in gaseous, liquid or solid state. A system is said to be in equilibrium when its properties do not change with time. The state of a system is described using its composition, temperature and pressure.

Three types of systems can be distinguished according to the exchange between the system and the surroundings in terms of matter and/ or energy.

1) **An open system** is a system that can exchange both matter and energy with the surroundings (Figure 19).

Examples:

- All reactions carried out in open containers.
- Evaporation of water in a beaker.
- Hot coffee in a cup.

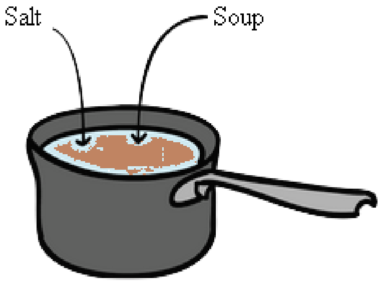


Figure 19.1 Example of an open system

2) A closed system is a system that can exchange energy but not matter with the surroundings (Figure 19).

Examples:

- All the reactions carried out in a closed container.
- Boiling water in a closed steel vessel.
- Boiling soup in a closed saucepan.

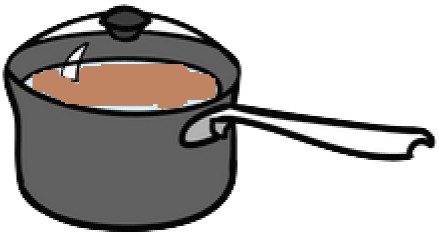


Figure 19.2: Example of a closed system

According to **Figures 19.1** and **19.2,** both the saucepans without a lid and with a lid, respectively, can absorb heat from the stove and get heated. There is exchange of energy taking place in both cases from the stove (surroundings) to the water (system). However, the saucepan with the lid prevents any change of matter. That is, no matter is added to or removed from the saucepan. On the other hand, in the case of the saucepan without the lid various substances can be added or removed from the saucepan and thus changing the mass of the content. As a conclusion, the lid prevents the exchange of matter between the system and the surroundings.

3) An isolated system is a system which is both sealed and insulated. It can't exchange neither matter nor energy with its surroundings.

Examples

Hot coffee in a thermos flask *(Figure 19.3)*.The latter is a closed system. The outer surface is insulated and thus neither heat nor matter transfer take place between the system and the surrounding.

Figure 19.3: Example of an isolated system

APPLICATION ACTIVITY 19.1

1. Which type of thermodynamic system is an ocean? An aquarium? A greenhouse?
2. A closed system contains 2 g of ice. Another 2 g of ice are added to the system. What is the final mass of the system?
3. An isolated system has an initial temperature of 30 ^{o}C. It is then placed on top of a Bunsen burner for an hour. What is the final temperature? What type of system is the final one?

19.2. The internal Energy of a system and first Law of Thermodynamics

ACTIVITY 19.2

1. a) Calculate the kinetic energy of a running object that has a mass of 80 kg and is running at a speed of 8 m/s.

   b) An apple of 154 g is placed in 1.5 m above the ground. Determine its gravitational potential energy? ($g = 9.81\ m\ s^{-2}$)

   c) What is the kinetic energy of a cyclist who, at a certain point in his run down the hill, has a potential energy of 34 300 J and a mechanical energy of 50 725 J?

2. Indicate the direction of heat (from one compartment to another) and explain your answer for each of the following phenomena.

   a) When you touch water in a saucepan on top of a stove with your hand and you feel it is warm.

   b) when you touch water from the tap with your hand and you feel it is cold.

   c) when you mix cold water and warm water.

3. What type of energy does a pencil on the table have? And what type of energy does a falling pencil have?

19.2.1. Internal energy

The first Law of Thermodynamics deals with energy that is transferred between a given system and its surroundings in form of heat. The exchange of energy is related to the energy that is stored in the system called **internal energy E.** The internal energy is the sum of the kinetic and potential energies of the particles that form a system.

- ***Kinetic energy (K.E)*** is the energy possessed by an object in motion such as translation, rotation or vibration.

$$K.E = \frac{1}{2} mv^2$$

Where m is the mass of a moving object and v is its speed.

- ***Potential energy (P.E)***

In physics potential energy of an object is defined as energy that an object has because of its position.

$$P.E = mgh$$

Where m = mass in kilograms (kg),

g = acceleration of gravity (9.81 m s^{-2})

h = position of the object in meters (m).

In chemistry, the potential energy of an object is the energy contained or stored in its chemical bonds.

The total internal energy of a system is the sum of its kinetic energy and its potential energy.

Mathematically, the internal energy (U) of a system is given by the expression:

$$U = K.E + P.E$$

19.2.2. Heat energy and temperature

The heat or thermal energy of an object is the total energy of all the molecular motion inside that object. When two bodies are in contact, heat always flows from the object with the higher temperature to that of lower temperature. Heat transfer ceases when a thermal equilibrium is attained. The heat content of a body will depend on its temperature, its mass, and the material it is made of. Because heat is a form of energy, it is measured in Joules (J) or kilojoules (kJ) or calorie (cal). A calorie is defined as the amount of energy needed to raise the temperature of one gram of water by one degree Celsius.

1 calorie (cal) = 4186 joules (J); 1000 cal = 1 kcal = 4.186 kJ.

The temperature is a measure of the average heat energy (thermal energy) of the molecules in a substance. When an object has a temperature of 100 °C, for example, it does not mean that every single molecule has that exact thermal energy. In any substance, molecules are moving with a range of energies, and interacting with each other. The temperature is a physical measure expressing how an object is hot or cold. The temperature is measured using a variety of temperature scales. The most commonly used are degree Celsius (°C) and Kelvin (K):

$$K = °C + 273$$

N.B: In thermodynamic calculation, degree Kelvin, not degree celcius, is used.

First Law of Thermodynamics

Thermodynamics is part of physical chemistry that deals with the relationships between heat and other forms of energy. In particular, it describes how thermal energy is converted to and from other forms of energy and how it affects matter. The first Law of Thermodynamics is a statement about conservation of energy and it categorizes the method of energy transfer into two basic forms: work (W) and heat (Q). The First Law of Thermodynamics states that **energy can be converted from one form to another with the interaction of heat, work and internal energy, but it cannot be created or destroyed, under any circumstances**. Internal energy refers to all the energies within a given system, including the kinetic energy of molecules and the energy stored in all of the chemical bonds between molecules.

For a closed system (without mass input and output), the internal energy is the sum of the heat energy and the work done by the system or the surroundings

$$\Delta U = Q + W$$

Where W is the energy transferred to the system by doing work and Q is the energy transferred to it by heating.

Let us consider a gas occupying a volume V_1 in cylinder with a movable piston on which an external pressure P is applied. If the temperature of the gas increases, it expands and occupies a new volume V_2. The change in volume is represented as ΔV, as shown in **Figure 19.4.** The sign of the work depends on whether it is done by the surroundings on the system or vice versa (**Table 19.1**).

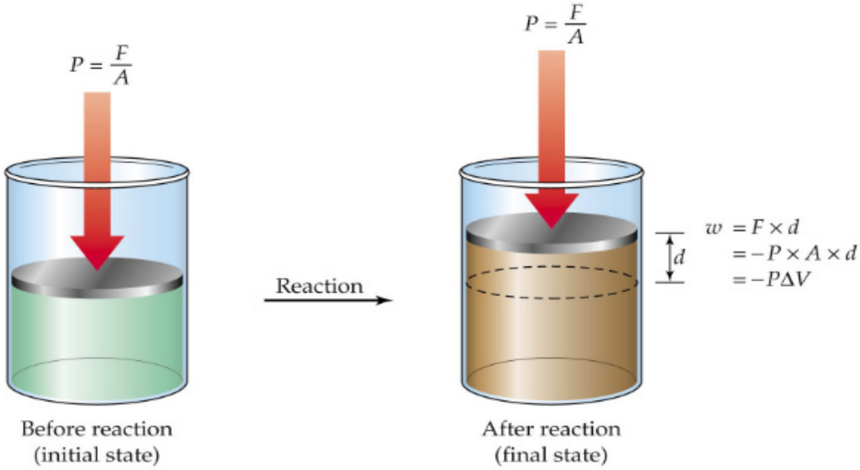


Figure 19.4. Interaction between a closed system and its surroundings.

The work done by the system on the surroundings is negative. Therefore, the first law of Thermodynamics is written as:

$$\Delta U = Q - W$$

Work (W) is also equal to the negative external pressure on the system multiplied by the change in volume. It can be expressed as:

$$W = -P\Delta V$$

Where P is the external pressure on the system, and ΔV is the change in volume. This is specifically called ***pressure-volume work.*** Therefore, the first Law of Thermodynamics is expressed using ***equation:***

$$\Delta U = Q - P\Delta V$$

Table 19.1. Sign convention for Q, W and ΔU

Variable	Sign	Meaning
Q	+	The system gains heat
	-	The system loses / releases heat
W	+	The work is done by the surroundings on system.
	-	The work is done by system on the surroundings.
ΔU	+	Net gain of energy by the system
	-	Net loss of energy by the system

Example:

What is the work of the gas that expands by 10.0 L against an external pressure of exactly 5.5 atmospheres?

Solution

Given that 1atm = 101,325 Pa,

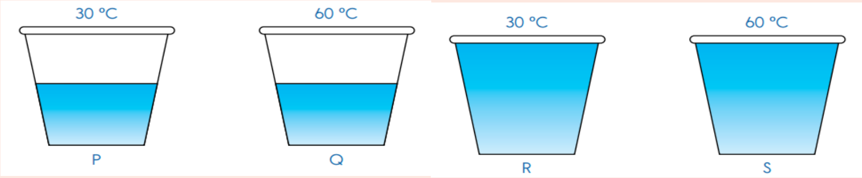
$\Delta H = -P\Delta V$

$= -5.5 \times 101{,}325\ \text{Pa} = 557{,}287.5\ \text{Pa} \times 10.0\ \text{L} = 5{,}572{,}875\ \text{J}.$

N.B: Pascal, SI unit, is used in calculations.

APPLICATION ACTIVITY 19.2

1. Four glasses of water are represented below.



Glasses P and Q have the same amount of water. Glasses R and S have the same amount of water.

The water in Glasses P and R are at the same temperature. The water in Glasses Q and S are at the same temperature.

1. Fill in the blanks below with the correct answers.

   a. The water in Glass……..has the most heat.

   b. The water in Glass……..has the least heat.

2. Ari touched a metal spoon. The metal spoon felt cold. Choose the best answer.

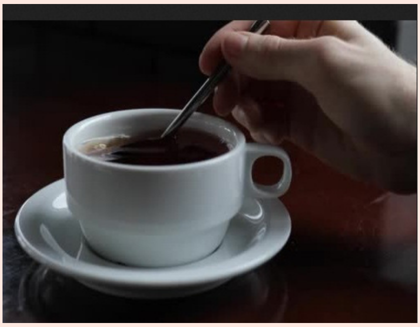
   A. Heat flows from hand to spoon

   B. Heat flows from spoon to hand

   C. Heat does not flow

   D. Heat flows in both directions

3. Tom placed a metal spoon in a mug of hot coffee as shown below. The metal spoon got hot. Choose the best answer.



A. Heat flows from hand to spoon

B. Heat flows from spoon to hand

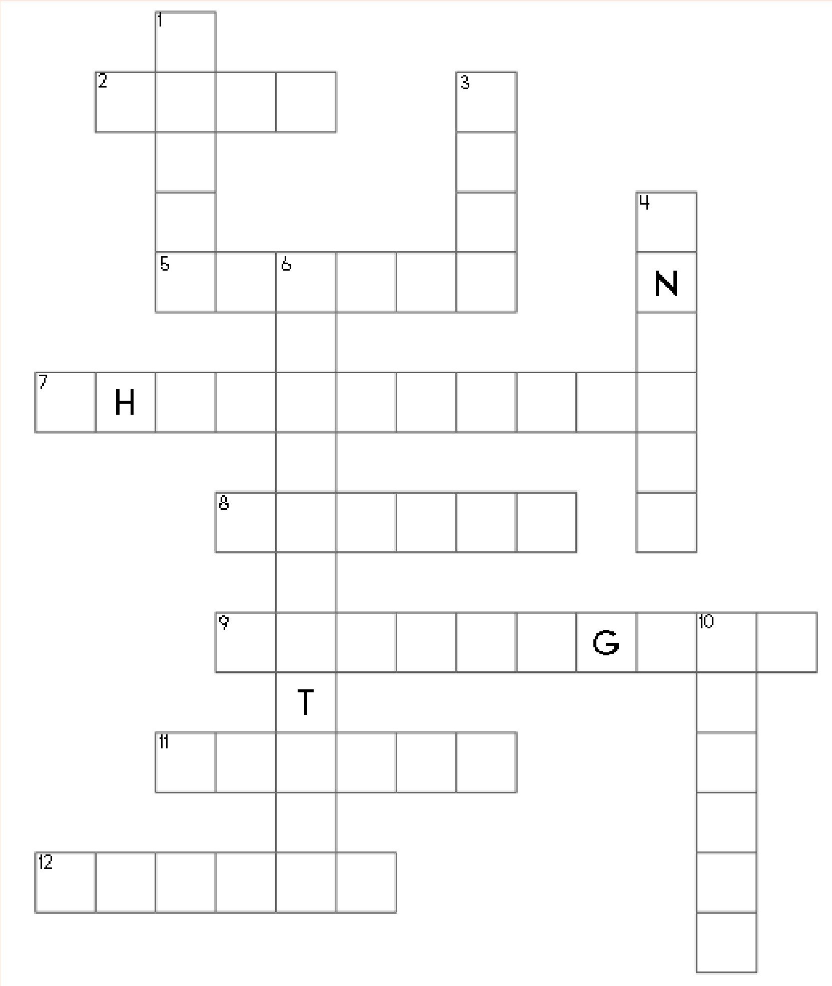
C. Heat does not flow

D. Heat flows in both directions

4. Complete the statement below.

If two objects are near each other and one object is hotter than the other, then heat will flow from the ……………………object to the…………………..object.

5. Complete the crossword puzzle using the clues given below.



Down

1. Our sense of …………………..cannot measure temperature accurately.

3. Wood is a ……………………conductor of heat.

4. Heat is a form of ……………………...

6. …………………………is a measure of how hot or cold an object is.

10. Metals can ………………………………when heated.

Across

2. Heat is used to …………………………… food.

5. When two objects of different temperatures are in contact, heat will travel from the ………… object to the other object.

7. The instrument used to measure temperature accurately is a ……………………………...

8. Temperature is measured in the unit ………………………Celsius (°C).

9. A……………, when used with a temperature sensor, can be used to measure and record temperatures.

10. The Sun is an important …………………………of heat.

11. A hotter object will has a ………………………temperature.

12. A gas is compressed and during this process the surroundings does 462 J of work on the gas. At the same time, the gas loses 128 J of energy to the surroundings as heat. What is the change in the internal energy of the gas?

13. What does the first law of thermodynamics have to do with systems?

19.3. Standard Enthalpy changes

ACTIVITY 19.3

1. What is meant by standard conditions of temperature and Pressure?
2. Which term describes the sum of kinetic energy and Potential energy?

The standard conditions referring to thermo chemical measurements are:

Temperature = 0^0C or 273 K.

Pressure = 1 atmosphere (atm) or 101, 325 Pa.

The concentration of solutions is 1.0 mol. dm^{-3} or 1.0 mol L^{-1}.

1. *Standard enthalpy change of formation (ΔH^o_f)*

The Standard enthalpy change of formation of a substance is the amount of heat released or absorbed when one mole of that substance is formed from its elements under the standard conditions. It is represented by ΔH^o_f

Examples:

$$Mg(s) + 1/2O_2(g) \longrightarrow MgO(s) \quad \Delta H^0_f\,(MgO\,(s)) = -\,602\ kJ\ mol^{-1}.$$

It shows that the enthalpy change of formation of one mole of magnesium oxide from 1 mole of Mg and ½ mole of O_2 molecules is – 602 kJ mol^{-1} (Figure 19.3.a)

The states of reactants and products are the states of those substances at standard conditions (statndard states): solid for Mg, gaseous for O_2 and solid for MgO.

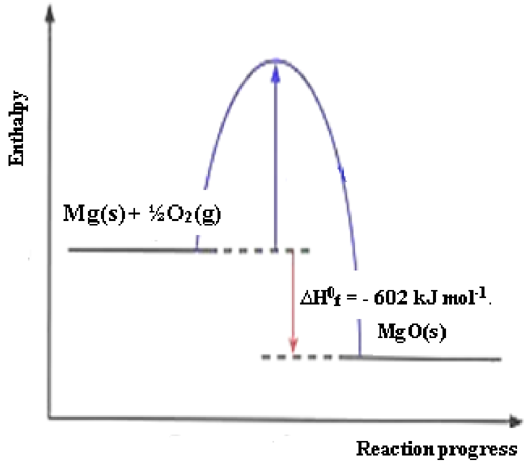


Figure 19.5. Energy profile diagram for the combustion of magnesium

ii) $2C(s) + H_{2(g)} \longrightarrow C_2H_{2(g)}$ $\Delta H^0f\ (C_2H_2\ (g)) = +226\ kJ\ mol^{-1}$ (Figure 19.3.b)

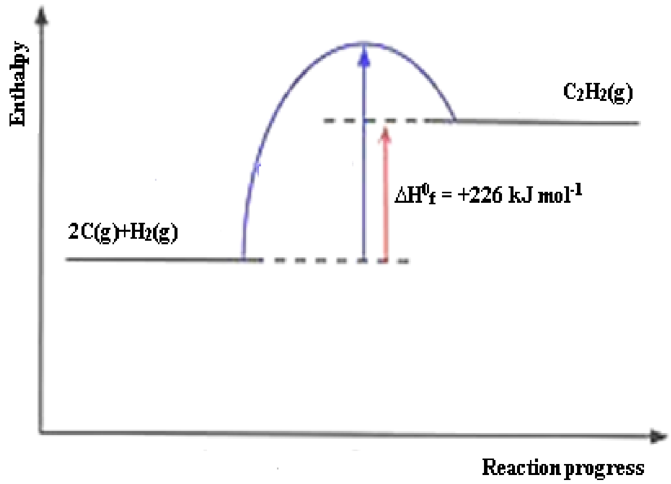


Figure 19.6. Energy profile diagram for the formation of acetylene (C_2H_2)

iii) $H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O(l)$ $\Delta H^0_f\ (H_2O\ (g)) = -286\ kJ\ mol^{-1}$.

Note: The standard enthalpy of formation of substances can be either negative or positive.

The compounds with more negative ***ΔH^o_f values are more stable than compounds with more positive ΔH^o_f values.*** The standard enthalpy of formation of elements is zero. However, for elements that exist in more than one allotropic form, only the most stable form under standard conditions is given zero standard enthalpy of formation.

2. Standard enthalpy change of Combustion ($\Delta H^o c$)

The standard enthalpy change of combustion ***(ΔH^o_c)*** of a substance ***is*** the heat evolved when 1 mole of the substance burns completely in excess oxygen under standard conditions.

Examples

1) $H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O(l)$ $\Delta H^o_c = -286\ kJ\ mol^{-1}$

2) $C_2H_{6(g)} + 7/2\ O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O(l)$ $\Delta H^o_c = -890\ kJ\ mol^{-1}$

$Mg(s) + 1/2O_2(g) \longrightarrow MgO(s)$ $\Delta H^o_c = -602\ kJ\ mol^{-1}$

Note: *For compounds resulting from a direct combination of an element (metal* *or non-metal) and oxygen, the standard enthalpy of combustion is equal to the standard enthalpy of formation.*

Examples:

$\Delta H^{\theta}_{c}(H_2) = \Delta H^{\theta}_{f}(H_2O) = -286\ kJ\ mol^{-1}$.

$\Delta H^{\theta}_{c}(Mg) = \Delta H^{\theta}_{f}(MgO) = -602\ kJ\ mol^{-1}$

$\Delta H^{\theta}_{c}(C) = \Delta H^{\theta}_{f}(CO_2) = -394\ kJ\ mol^{-1}$

3. Standard enthalpy change of neutralization (ΔH^{o}_{n})

The standard enthalpy of neutralization, ΔH^{o}_{n} is the enthalpy change which occurs when one gram equivalent of an acid is neutralized by one gram equivalent of a base to produce a salt and water under the standard conditions. The equation of the neutralization reaction is:

$$H^{+}_{(aq)} + OH^{-}_{(aq)} \longrightarrow H_2O(l)$$

Examples:

1) $CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)\quad \Delta H^{o}_{n} = -56.1\ kJ\ mol^{-1}$

2) $1/2H_2SO_{4(aq)} + NaOH_{(aq)} \longrightarrow 1/2Na_2SO_{4(aq)} + H_2O(l)\quad \Delta H^{o}_{n} = -66.5\ kJ\ mol^{-1}$

4. Lattice enthalpy (ΔH^{θ}_{LE})

The lattice enthalpy is the amount of heat released when one mole of an ionic solid is formed from its gaseous ions under standard conditions. It is also the amount of heat absorbed when an ionic solid dissociates into its gaseous ions under standard conditions.

The lattice enthalpy is negative for the formation of the lattice and positive for the breaking of the lattice. There is a relationship between the size and charge of ions with the lattice enthalpy.

i. The higher the ***charge of the ions, the higher*** the strong electrostatic attractions and the higher is the lattice enthalpy.

ii. ***The smaller is the size of ions, the higher is the strong*** electrostatic attractions and the higher the lattice enthalpy.

Examples:

1) $NaCl(s) \longrightarrow Na^{+}_{(g)} + Cl^{-}_{(g)}\quad \Delta H_{LE} = +771\ kJ\ mol^{-1}$

2) $Na^{+}_{(g)} + Cl^{-}_{(g)} \longrightarrow NaCl(s)\quad \Delta H^{\theta}_{LE} = -771\ kJ\ mol^{-1}$

5. Standard enthalpy of Hydration (ΔH^{θ}_{Hyd})

The standard enthalpy of Hydration also called **Standard enthalpy of solvation** is the amount of heat released when one mole of isolated gaseous ions dissolves in water forming one mole of aqueous ions under standard conditions. The positive terminal of the water molecule is attracted to the anion while its negative terminal is attracted to the cation. This is an ion-dipolar attraction which is typically an electrostatic interaction. This latter is accompanied by the release of heat energy.

Examples:

1) $Cl^-_{(g)} + H_2O(l) \longrightarrow Cl^-_{(aq)}$ $\Delta H_{Hyd} = -364$ kJ mol^{-1}

2) $K^+_{(g)} + H_2O(l) \longrightarrow K^+_{(aq)}$ $\Delta H_{Hyd} = -322$ kJ mol^{-1}

6. The standard enthalpy change of solution (ΔH^{0}_{s})

The standard enthalpy change of solution is the change in enthalpy that occurs when one mole of a substance is dissolved in water to form an infinitely dilute solution under standard conditions. The dissolution involves the breaking of the lattice into the ions and then there is hydration of these ions. Therefore, the standard *enthalpy change of solution is the sum of standard lattice enthalpy* and *standard enthalpy change* of hydration. It may be either positive or negative.

Examples:

1) $NaCl(s) + H_2O(l) \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$ $\Delta H^{o}_{s} = +6$ kJ mol^{-1}

2) $MgCl_{2(s)} + H_2O(l) \longrightarrow Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}$ $\Delta H^{o}_{s} = -186$ kJ mol^{-1}

7. Standard enthalpy change of atomization (ΔH^{o}_{atm})

The **Standard enthalpy change of atomization** is the amount of heat required to form one mole of free gaseous atoms from its chemical substance under standard conditions. The enthalpy change of atomization is always positive.

Examples:

1) $CH_{4(g)} \longrightarrow C(g) + 4H(g)$ $\Delta H^{0}_{atm} = +1662$ kJ mol^{-1}

2) $1/2Cl_{2(g)} \longrightarrow 2Cl(g)$ $\Delta H^{0}_{atm} = +121$ kJ mol^{-1}

Note:

For diatomic molecules, this type of enthalpy is equal to the bond dissociation energy(B.D.E).

Bond energy also called ***bond enthalpy*** is a form of potential energy defined as the amount of energy required to break a given chemical bond. It has always positive values which depict the endothermic nature of the bond breaking. The energy required to form a chemical bond is equal in magnitude but opposite in sign to the energy required to break that bond. For example, the energy for breaking a hydrogen-hydrogen bond is 436 $kJ.mol^{-1}$, and when a hydrogen-hydrogen bond is formed the process releases 436 $kJ.mol^{-1}$. In a chemical reaction several bonds are broken and new ones are formed.

- ***Energy change of reaction = Energy used to break bonds - Energy used to form bonds***

APPLICATION ACTIVITY 19.3

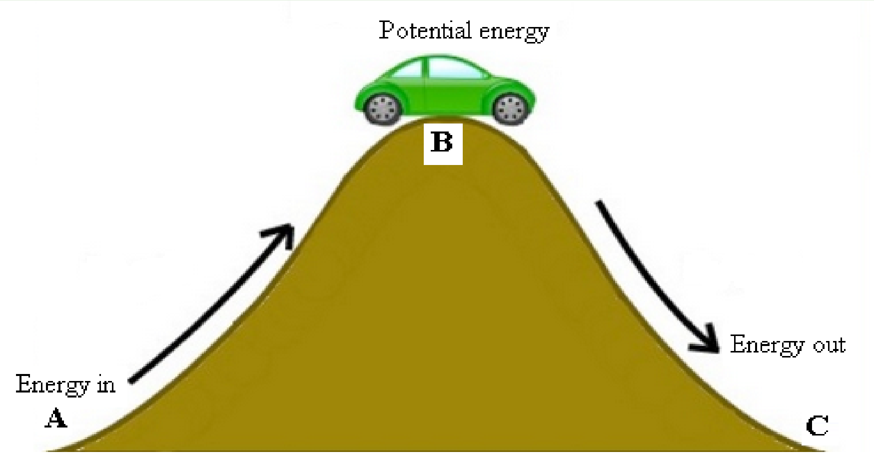
1. A gas is compressed and during this process the surroundings does 462 J of work on the gas. At the same time, the gas loses 128 J of energy to the surroundings as heat. What is the change in the internal energy of the gas?

2. Why enthalpy of atomization is always positive?

19.4 Energy profile diagrams for Exothermic and Endothermic reactions.

ACTIVITY 19.4

Observe the following image and answer the related questions.



1. Discuss the type of energy form present in points A, B and C of the pathway followed by the vehicle.
2. Discuss how each form of energy changes from point A to point C.
3. Which points corresponds to maximum stability and minimum stability, respectively? Relate your answer to energy concept.

When a chemical reaction happens, the energy is transferred to or from the surroundings and often there is a temperature change. For example, when a bonfire burns, it transfers the heat energy to the surroundings. The objects near the bonfire become warmer and the temperature rise can be measured with a thermometer.

There are some chemical reactions that must absorb energy in order to proceed. These are **endothermic reactions**. Some other chemical reactions release energy to the surroundings. The energy released can take the form of heat, light, or sound. These are **exothermic reactions.**

1) Exothermic reactions

They are characterized by an increase in the temperature of the surroundings, i.e. energy is given up. Heat is lost to the surroundings and by convention it is negative and represented as: **$\Delta H < 0$.**

For exothermal reaction (Figure 19.7), total energy of the reactants is higher than in the product, because the heat energy absorbed during bond breaking is lower than the heat energy released during bond formation.

Examples of exothermic reactions are:
1) Burning different substances

2) Neutralization reactions between acids and alkalis

3) The reaction between water and calcium oxide

4) Termite reaction: This is the reduction of metal oxides in which a large amount of heat is liberated. It is very useful for the connecting of broken metal parts. When Aluminum powder reacts with iron oxide or chromium oxide, a large amount of heat is released (about 3500 °C is attained to weld broken metallic part.

5) The reaction of sodium and chlorine to yield table salt is an exothermic reaction. This reaction produces 411 kJ of energy for each mole of salt that is produced:

$$NaCl(s) + 1/2Cl_2(g) \longrightarrow NaCl(s)$$

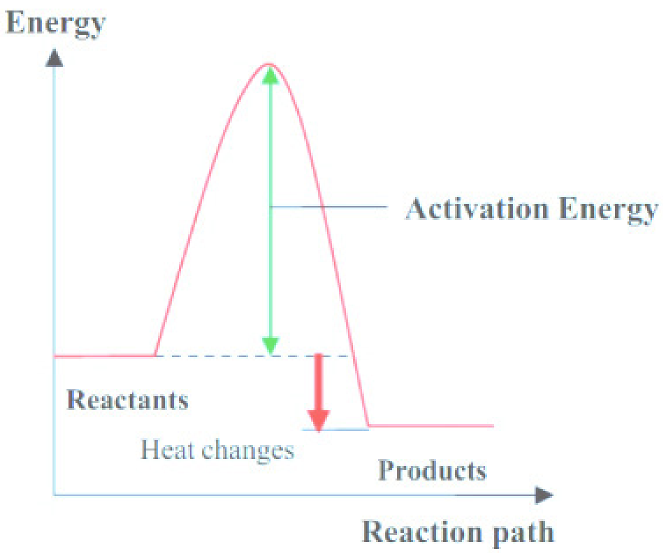


Figure 19.7. Energy profile diagram for exothermic reaction

2. Endothermic reactions

These are reactions that take place by absorbing the energy from the surroundings. The energy is usually transferred as heat energy; in this case the surroundings loses energy to the reactants causing the surroundings to get colder. Endothermic reactions cannot occur spontaneously. Work must be done in order to get these reactions to occur. When endothermic reactions absorb energy, a temperature drop in the surroundings is observed during the reaction. Endothermic reactions are characterized by positive heat flow (into the reaction) and an increase in enthalpy, by convention it is represented by: $\Delta H > 0$.

For endothermic reaction (Figure 19.8), the total energy of the reactants is lower than the product, because the heat energy absorbed during bond breaking is higher than the heat energy released during bond formation.

You have certainly experienced this effect when you put a drop of methanol or any other volatile substance on your skin; you feel cold because that part of your skin is supplying energy to evaporate the volatile liquid.

Examples

1) Water evaporation

2) The thermal decomposition of calcium carbonate to produce quicklime, CaO.

3) Cooking

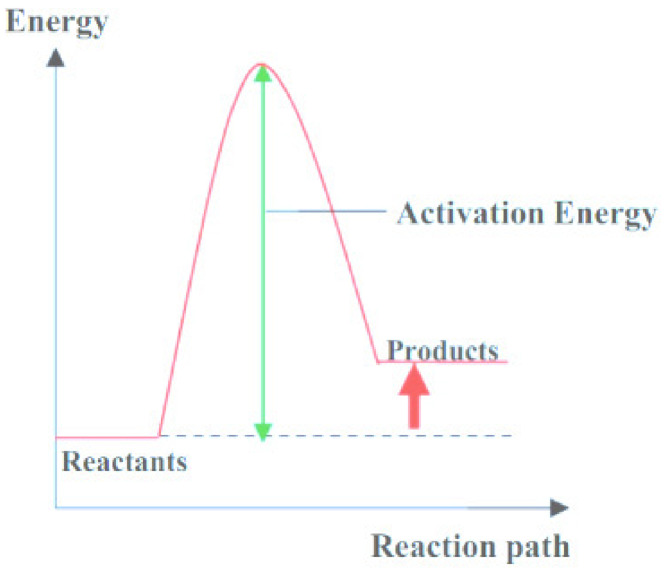


Figure 19.8. Energy profile diagram for endothermic reaction

Activation energy, Ea

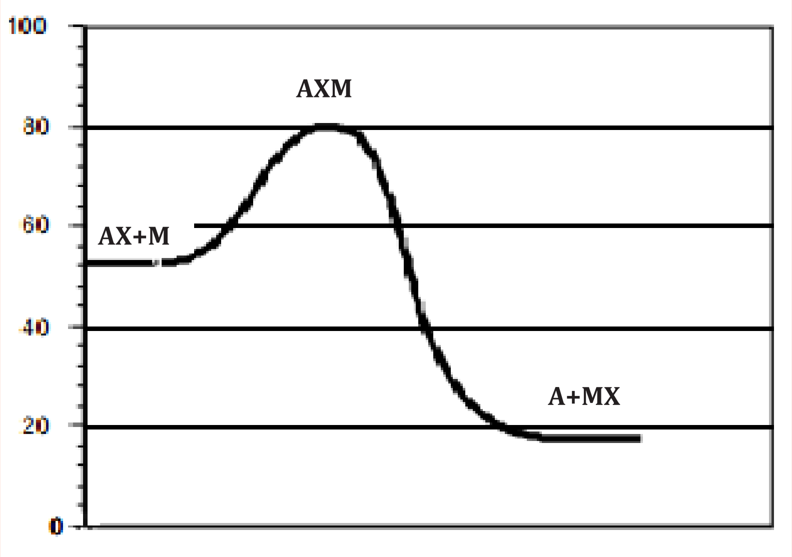
The activation energy is the minimum energy required for a chemical reaction to take place. It is the energy barrier that has to be overcome for a reaction to proceed. Without that minimum energy, the reaction will not take place. That is why, for example, the only fact that a dry wood is in contact with oxygen of air will not start burning; there is a need of supplying the minimum energy to overcome the activation energy barrier, this is done by using a burning match.

Activated complex

The activated complex is the intermediate species, where former chemical bonds are being broken, whereas new chemical bonds are being formed. In term of energy, it corresponds to the activation energy.

APPLICATION ACTIVITY 19.4

1.Use the following potential energy diagram to answer the questions below:



i) What is meant by ***activation energy?***

ii) Determine the energy of the reactants.

iii) Determine the energy of the products.

iv) Determine the activation energy for the forward reaction.

v) Determine the activation energy for the reverse reaction.

iv) Determine the activation energy for the forward reaction.

v) Determine the activation energy for the reverse reaction.

vi) Determine the enthalpy change of reaction for the forward reaction.

vii) Determine the enthalpy change of reaction for the reverse reaction.

viii) Fill in using exothermic or endothermic.

a. The forward reaction is ....

b. The reverse reaction is ....

ix) Which chemical species or set of chemical species represent the activated complex?

x) Which one of the chemical bonds A-X and M-X is stronger? Explain.

xi) State the chemical species whose particles move the fastest. Explain your answer.

xii) State the chemical species whose particles move the slowest. Explain your answer.

xiii) The compound AX and the element M are in gaseous and solid states, respectively.

What effect would grinding M into a fine powder have on the above graph?

2. Draw an energy level diagram for the reaction

$$NaOH + HCl \longrightarrow NaCl + H_2O \quad \Delta H = -57 Kjmol^{-1}$$

i) Is this reaction endothermic or exothermic?

ii) Calculate the energy change associated with this reaction if 2moles of sodium hydroxide were neutralized by excess hydrochloric acid.

SKILLS LAB 19

To determine the enthalpy change of combustion of ethanol ,the heat produced by the burning fuel warm a known mass of water .By measuring the mass of fuel burnt and the temperature rise of water it is possible to obtain the approximate value of the enthalpy change of the combustion of the fuel(ex:ethanol)

Constuct an improvised calorimeter as shown on the diagram (figure 19.9) and calculate the enthalpy change when a mass X of ethanol is used to heat 400ml of water

i) Measure the initial temperature of water (before heating) and the final temperature (after heating).

ii) Measure the mass X of ethanol used before and after heating.

iii) Calculate the heat required to raise the temperature from the initial point to the final point(this is the amount of heat produced by the burnt mass of ethanol)

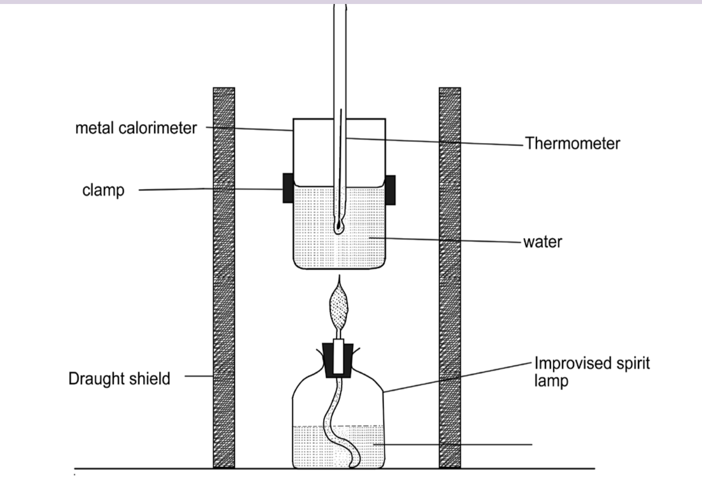
iv) Deduce the heat produced by one mole of burnt ethanol(this is the heat of the combustion of ethanol).

v) Compare the value obtained to the accurate value of -1368 Kj mol^{-1}

vi) Mention different sources of errors in the simple experiment which could be responsible for the poor results.

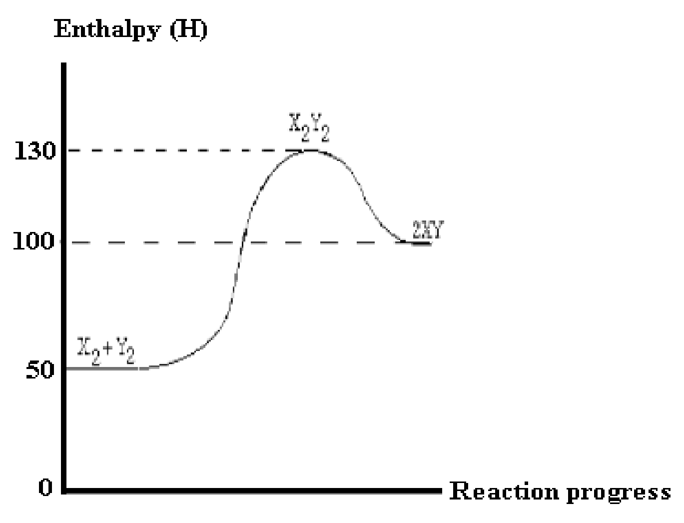
vii) Why is the answer in (iv) not described as the standard enthalpy change of combustion of ethanol?

Figure 19.9 Diagram of a simple colorimeter



END UNIT ASSESSMENT 19

Observe the diagram hereafter and answer the related questions



a. Regarding the absorption or release of energy, what is the nature of the overall reaction?

b. What is the activation energy for the forward reaction?

c. What is the activation energy for the reverse reaction?

d. Determine the enthalpy change of reaction for the forward reaction?

e. Is the reverse reaction endothermic or exothermic?

f. Which chemical species constitute the activated complex?

g. Which chemical species or set of chemical species have the maximum potential energy?

h. Which chemical species or set of chemical species have the maximum kinetic energy?

i. Which chemical species or set of chemical species have the strongest bonds?

j. Which chemical species or set of chemical species have the weakest bonds?

k. What is the enthalpy change of reaction for the reaction ?

$X_2Y_2 \longrightarrow X_2 + Y_2$

l. Which one of the forward reaction and reverse reaction is more likely to be faster?

m. As particles of the newly formed product move away from one another their potential energy goes ....while their kinetic energy goes ....

n. State the meaning of the term activated complex.

o. Which chemical species or set of chemical species correspond to the state of maximum stability? Why?

p. What is the effect of caltalyst if it is added to the above reaction

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