CHEMISTRY

FOR TTCs

STUDENT'S BOOK

3

OPTION:

SME

FOREWORD

Dear Student teacher, Rwanda Basic Education Board is honored to present to you this Chemistry Book for Year three 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 student teacher 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

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

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Joan MURUNGI,

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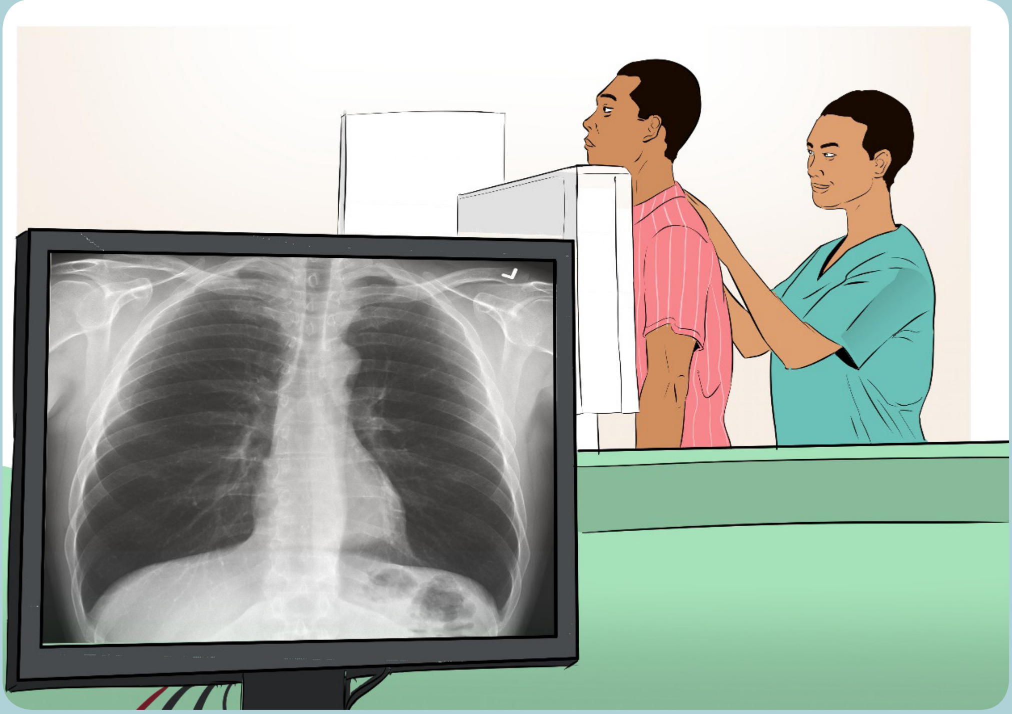
UNIT 1

RADIOACTIVITY

Key Unit Competence:

Explain the importance and dangers of radioisotopes in everyday life.

Introductory activity



The above photos show different ways through which radiations reach into our body (cells). The most familiar to you is radiation from sun rays! However, everything present in the pictures above, and many others that are not included, emits radiation. Now, discuss on the following points.

Point 1: Can you see or feel the presence of radiations?

Point 2: How are we exposed to natural ionizing radiation? (Radiation with the ability to rip out one or several electrons from an atom or molecule is referred to as ionizing radiation and radiation which does not have sufficient energy to damage atoms or molecules is called non-ionizing radiation).

Point 3: What do you understand by "radioactive materials"? Do you think all of them are natural? Do you think all of them (i.e, radioactive materials) are harmful?

All living beings have been exposed to a constant flux of natural radiations on the surface of our friendly planet, but these radiations have no negative effect.

Natural radiations are everywhere in the universe

Figure 1.1: Some natural sources of radiations

We are constantly being bombarded by particles of cosmic radiations: several hundred go through our bodies every second. Rocks like granite, which have become symbols of permanence and durability (hence used in building), contain light traces of radioactive uranium. Sitting on or walking near a block of granite exposes you to many sources of radioactivity. Even the food we eat or the air we breathe contains radioactive elements (such as radon) either formed by the intervention of cosmic rays, or as old as the solar system itself.

The radioactivity is an integral part of our environment.

1.1. Definition of radioactivity and radioisotopes

Activity 1.1

1. Define the word “isotope”
2. Given the following atoms calculate A, Z, and N

   ${}^{27}_{13}\text{Al}$, ${}^{12}_{6}\text{C}$, ${}^{87}_{38}\text{Sr}$

3. Given the following elements, identify the isotopes among them

   ${}^{1}_{1}\text{H}$, ${}^{2}_{1}\text{D}$, ${}^{3}_{1}\text{D}$

   ${}^{27}_{13}\text{Al}$, ${}^{12}_{6}\text{C}$, ${}^{87}_{38}\text{Sr}$ Explain the reason you have selected like that

The discovery of the electron towards the end of the nineteenth century was the starting point of new avenues of research in science, which were to give physicists an insight into the structure and nature of the atoms of matter. They discovered that there is a nuclear phenomenon in some elements that pushes them to emit radiations. This phenomenon was called **radioactivity** as proposed by **Marie Curie** to describe those emissions of nuclear radiation by some of the heavy elements.

The radioactivity is a nuclear phenomenon. It is the process by which an unstable atomic nucleus changes into another more stable atomic nucleus by emitting energy in form of radiation. Substances which have the property of emission of radiation are called **radioactive substances**. Radioactivity is also known as **radioactive disintegration** or **radioactive decay.** Particles and rays are emitted when a nucleus of a radioactive isotope of element breaks down. They break down to acquire stability as all atoms want to be stable.

A radioactive decay results when an atom with one type of nucleus, called “**the parent radioactive nuclide**” transforms into another atom with a different nucleus. The new product or element is named “**the daughter nuclide**”, and thus the decay process results in “**transmutation**”. **Transmutation**, in this case, means creation of an atom of a new element. In this way, the energy or radiation emitted may take the form of particles such as **alpha** (α) or **beta** (β) **particles**.

During the transmutation process, daughter nuclides are often in metastable or excited state; they lose energy in form of **gamma** (γ) **ray** to become de-excited. Gamma rays, here, can be compared to the heat of reaction that accompanies an exothermic reaction.

In nuclear chemistry, the term '**nuclide**' is used to designate a nucleus of an element.

'Nucleons' is the term used for nuclear particles such as protons and neutrons. In radiochemistry, the nucleon number stands for mass number (sum of protons and neutrons present in the nucleus of a given atom).

Different nuclides, which have the same proton number but different nucleon numbers are called **isotopes** or **isotopic nuclides**.

Radioisotopes or radioactive isotopes are the atoms of an element whose atomic nuclei undergo decay by emitting radiation(s).

Example of radioisotopes

$^{238}_{92}\text{U}$, $^{234}_{90}\text{Th}$

Application activity 1.1

1. Explain what is meant by each of the following terms:

   a) Radioactive decay

   b) Daughter nuclide

   c) Transmutation

2. Differentiate between isotopes and radioactive isotopes

1.2. Emission of alpha, beta and gamma rays and their properties

Activity 1.2

1. State the types of radiation as revealed in the previous discussions.
2. Use your search engine or any textbooks available to find out the properties of the three types of radiation and the effect of electric and magnetic fields on them.

Different forms of radiation are emitted from an unstable nucleus as it decays. The main types of emitted particles are alpha particles, beta particles and gamma rays. The detailed information on each particle is provided below.

1.2.1. Alpha particles

An alpha particle contains two protons and two neutrons (so, its mass number, A=4 and atomic number, Z=2). Because it has 2 protons, an alpha particle has a charge of 2+ (α^{2+}). That makes it identical to helium nucleus. In equations, it is written as the Greek letter "alpha (α)" or as the symbol for helium (He). The charge of an alpha particle was found experimentally by passing it in an electric field between two plates where it was attracted towards the negative plate.

The main properties of an alpha particle are the following:

- Alpha particle bears a positive charge of +2
- It has a mass of 4 amu
- It is deflected toward the negative pole of electric and magnetic fields. Look at Figure 1.2 below.
- It affects a photographic plate and causes fluorescence on striking a fluorescent material.
- It ionizes the gas through which it passes.
- Not very penetrating; a very thin sheet of aluminium foil or a sheet of paper stops it.
- It can be shielded by paper or clothing.
- It destroys living cells and causes biological damage.
- It is strongly ionizing

When a nuclide decays by alpha emission, it loses 2 atomic number units and 4 mass units; in other words the daughter nuclide is the element located at 2 places before the parent nuclide in the periodic table.

Examples: $^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He$

$$^{226}_{88}Ra \rightarrow {}^{222}_{88}Rn + {}^{4}_{2}He$$

1.2.2. Beta particles

A beta particle, which is a high energy electron, has a charge of -1 and because its mass is so much less than that of a proton, it is given a mass number of zero (0). It is represented by the Greek letter "beta (β)" or by the symbol for electron with the charge, -1, written on the lower left "${}^{0}_{-1}e$". Beta particle is deflected toward the positive plate of an electric and magnetic field.

The main properties of a beta particle are the following.

- It bears a negative charge of -1
- It is deflected toward positive plate of an electric and magnetic fields. The deflection is large since a beta particle is lighter than an α particle.
- It affects photographic plates.
- It is ionizing but less than alpha ray.
- It travels at speeds close to that of light (of the order of 10^8 m/s).
- Its penetrating power is 100 times greater than that of α particles.
- It causes fluorescence on striking a fluorescent material.
- It can be stopped by $\frac{1}{16}$ inch of lead.
- It causes greater radiation damage as it can easily pass through the skin of the body.

Beta particles are produced from unstable nuclei when a neutron is transformed into a proton and an electron. The high-energy electron is emitted from the nucleus as a "beta radiation"

$$ {}_{0}^{1}\mathbf{n} \rightarrow {}_{1}^{1}\mathbf{p}\left({}_{1}^{1}\mathrm{H}\right) + {}_{-1}^{0}\mathbf{e}\left({}_{-1}^{0}\beta\right) $$

This shows that the number of neutrons decreases by one and the number of protons increases by one: ${}_{Z}^{A}\mathrm{X} \rightarrow {}_{Z+1}^{A}\mathrm{X} + {}_{-1}^{0}e$

It is noteworthy that a β-emission results in the production of **isobars** (nuclides having the same mass numbers but different atomic numbers). The beta emission produces a new element with 1 more atomic number unit, or the element that directly follows in the periodic table.

Examples: ${}_{6}^{14}C \rightarrow {}_{7}^{14}N + {}_{-1}^{0}e$

${}_{94}^{241}Pu \rightarrow {}_{95}^{241}Am + {}_{-1}^{0}e$

A positron note β^{+} or ${}_{+1}^{0}e$ is similar to an electron except that a positron has a positive (+1) charge. A positron is produced by an unstable nucleus when a proton is transformed into a neutron and a positron: ${}_{1}^{1}\mathbf{p} \rightarrow {}_{0}^{1}\mathbf{n} + {}_{+1}^{0}\mathbf{e}\left(\beta^{+}\right)$. This shows that the number of neutrons increases by one and the number of protons decreases by one; the element just preceding the parent nuclide in the periodic table is formed.

$$ {}_{Z}^{A}\mathrm{X} \rightarrow {}_{Z\text{-}1}^{A}\mathrm{X} + {}_{+1}^{0}e $$

Example:

$$^{49}_{25}Mn \rightarrow ^{49}_{24}Cr + ^{0}_{+1}e$$

Note that a positron is an example of "**antimatter**", a term physicists use to describe a particle that is the exact opposite of a particle, in this case, an electron. When an electron and a positron collide, their minute masses are completely converted to energy in the form of "**gamma rays**"

$$^{0}_{-1}e + ^{0}_{+1}e \rightarrow 2^{0}_{0}\gamma$$

Electron capture: an electron is captured by the nucleus from the same isotope which combines with a proton to form a neutron.

$$^{1}_{1}\mathrm{p} + ^{0}_{-1}e \rightarrow ^{1}_{0}\mathrm{n}$$

Isotopes that undergo electron capture have got fewer neutrons than stable isotopes of the same element and as such a proton must be changed to a neutron. Electron capture results in decreasing of the atomic number by one unit as in positron emission.

$$^{\mathrm{A}}_{\mathrm{Z}}\mathrm{X} + ^{0}_{-1}e \rightarrow ^{\mathrm{A}}_{\mathrm{Z\text{-}1}}\mathrm{X}$$

Examples: $^{38}_{19}\mathrm{K} + ^{0}_{-1}e \rightarrow ^{38}_{18}\mathrm{Ar}$

$$^{37}_{18}\mathrm{Ar} + ^{0}_{-1}e \rightarrow ^{37}_{17}\mathrm{Cl}$$

Note that in few cases, both positron emission and electron capture may occur in the same element. For example, zinc-63 can undergo both electron capture and positron emission forming copper-63. Observe the following equations:

$$^{63}_{30}\mathrm{Zn} + ^{0}_{-1}e \rightarrow ^{63}_{29}\mathrm{Cu}$$

$$^{63}_{30}\mathrm{Zn} \rightarrow ^{63}_{29}\mathrm{Cu} + ^{0}_{+1}e$$

1.2.3 Gamma rays

Gamma rays, γ, are high-energy radiation released as an unstable nucleus undergoes a rearrangement of its particles to give a more stable, lower energy nucleus.

Because gamma ray is an electromagnetic radiation, it has no mass and no charge.

The main properties of gamma radiation (gamma ray) are the following:

- It is an electromagnetic radiation of short wavelength and higher frequency, hence high energy
- It is not deflected by electric and magnetic fields. Refer to figure 15.4 for more understanding.
- It affects photographic plates.
- Its ionizing power is very low compared to alpha-particles and beta-particles.
- It travels at the same speed as that of light.
- It has the greatest penetrating ability, 5000-10000 times that of alpha particles.
- It causes fluorescence when they strike a fluorescent material.
- It is diffracted by crystals.
- It can be stopped by several inches (5cm thick piece) of lead or a thick concrete.
- It can easily pass through the human body and cause immense biological damage.

Normally, there are very few pure gamma emitters. In radiology, one of most commonly used gamma emitter is technetium (Tc). The excited state called “metastable technetium” is written as technetium-99m, **Tc-99m**. By emitting energy in the form of gamma rays, the excited nucleus becomes more stable.

$$^{99m}_{43}\mathrm{Tc} \rightarrow ^{99}_{43}\mathrm{Tc} + ^{0}_{0}\gamma$$

Stable nuclides are usually in the state of least energy or ground state. But these nuclides can be excited by particles or photon bombardment. The excited nucleus returns into the ground state by emission of excess energy as Υ-rays.

$$^{A}_{Z}\mathrm{X}^{*} \rightarrow ^{A}_{Z}\mathrm{X} + \gamma$$

Examples:

$$^{27}_{13}\mathrm{Al}^{*} \rightarrow {}^{27}_{13}\mathrm{Al} + \gamma$$

$$^{87}_{38}Sr^{*} \rightarrow {}^{87}_{38}Sr + \gamma$$

$$^{99}_{43}\mathrm{Mo} \rightarrow {}^{99}_{42}\mathrm{Tc}^{*} + {}^{0}_{1}\mathrm{e} \rightarrow {}^{99}_{42}\mathrm{Tc} + {}^{0}_{0}\gamma$$

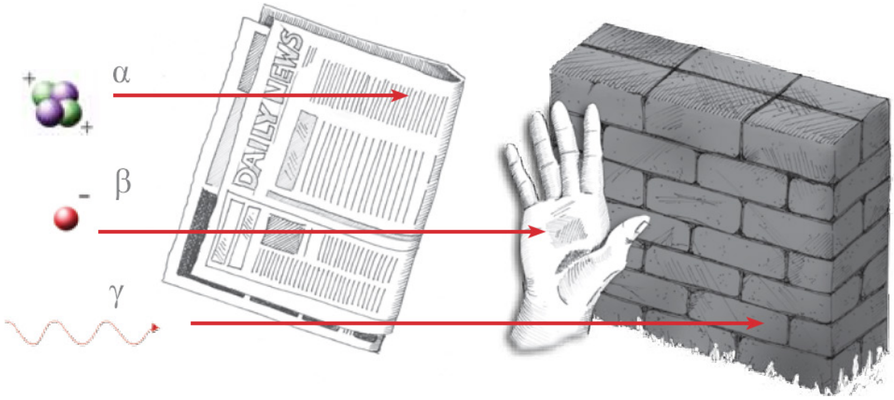


Figure 1.2.(a) Penetration power and shielding of the main radioactive particles

1.2.4. Effect of electric and magnetic fields on nuclear radiations

a) Effect of electric field on nuclear radiation

Experiments involving emissions of radiations cannot be performed in an ordinary school laboratory but can be carried out in research laboratories.

In 1899, the study of radioactivity was taken up by **Ernest Rutherford.** He placed a little radium at the bottom of a small lead box and subjected the rays that emerged from it to the action of a very strong magnetic field at right angles to their direction. He found that the rays separated into three distinct constituents as shown in the figure 1.2 below.

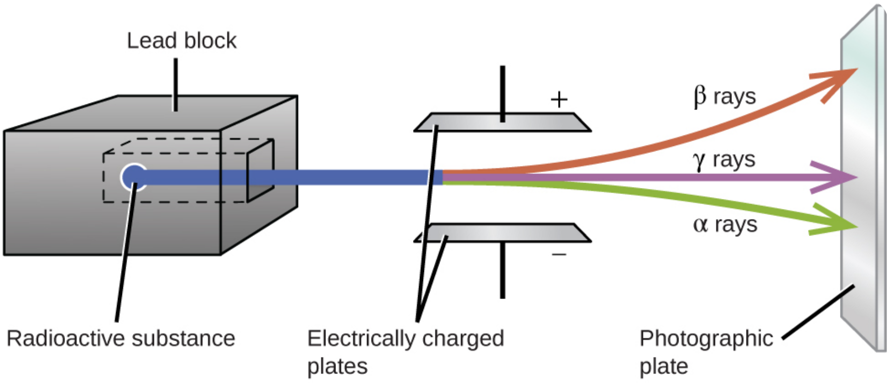


Figure 1.2 (b) Effect of electric field on radioactive emissions

It is clear that when these radiations pass through a magnetic field or an electric field, they are affected differently. The heavy alpha particles are slightly deflected towards the **negatively charged plates**; this shows that they bear a **positive charge**. The lighter beta particles are deflected more sharply towards the **positively charged plates**, showing that they are bear a **negative charge**. The gamma rays are not affected by the magnet, showing that they bear no charge.

b) Effect of magnetic field on nuclear radiation

A magnetic field (only one pole is shown) affects radioactive rays differently depending on the type of ray. Alpha rays (heavy, positively charged particles) are deflected slightly in one direction. Beta rays (light, negatively charged electrons) are deflected strongly in the opposite direction. Electromagnetic gamma rays are not deflected.

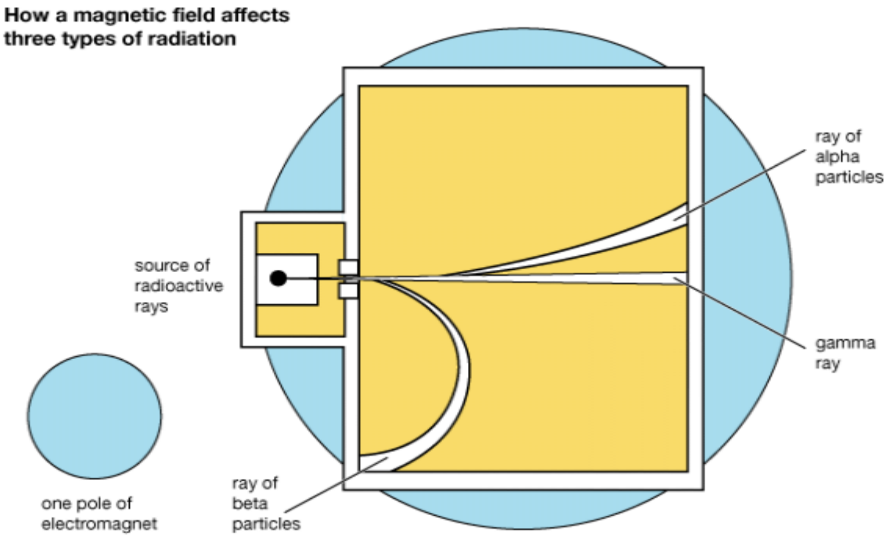


Fig.1.2 (c)effect of magnetic field on nuclear radiation

Summary of properties of radiations and their differences

***Table 1.1*. Distinction between the properties of α, β and γ radiations (summary)**

Property	α-particle	β-particle	γ-radiation
Nature	Stream of positively charged particles i.e, helium nuclei	Stream of negatively charged particles i.e, high-energy electrons	Electromagnetic waves i.e, high-energy rays
Speed	Nearly 10^{7} ms^{-1}	About 90% of the speed of light or 2.7 x 10^{8} ms^{-1}	3 x l0^{8} ms^{-1} (in vacuum)
Rest mass	4 times the mass of proton i.e., 6.64 x 10^{-27} kg	Mass of electron i.e. 9.1x10^{-31} kg	No mass
Charge	Positive charge +3.2 x 10^{-19} C (+2)	Negative charge -1.6 x 10^{-19}C (-1)	No charge (0)
Effect of electric and magnetic fields	Deflected toward negative plate	Deflected toward positive plate	Unaffected
Ionizing power	Maximum (10,000 times γ)	Less than alpha (100 times of γ)	Minimum
Penetrating power	Small (2-4 cm in air)	High (about 1 mm of lead or about 5 mm of Al) 200-300 cm in air	Very high (about 30 cm of iron) 500 m in air
Biological damage	Cause some damage	Cause more damage	Cause immense biological damage

Application activity 1.2

1. How are an alpha particle and a helium nucleus similar? Different?
2. Naturally occurring potassium consists of three isotopes: potassium-39, potassium-40 and Potassium-41.

   a) Write the atomic symbols for each isotope.

   b) In what ways are the isotopes similar and in what ways do they differ?
3. Give the missing information in the following table:

Medical use	**Atomic symbol**	**Mass number**	**Number of protons**	**Number of neutrons**
Heart imaging	$^{201}_{81}\text{Tl}$			
Radiation therapy		60	27	
Abnormal scan			31	36
Hyperthyroidism	$^{131}_{53}\text{I}$			
Leukemia treatment		32		17

4. Explain why alpha particles are not greatly deflected by an electric or magnetic field as beta particles
5. Briefly describe the effect of a magnetic field on different nuclear radiations.

1.3 Nuclear equations and radioactive decay series

Activity 1.3

1. Use your search engine or any available resources to learn about nuclear equations, how they are balanced and radioactive decay series and make a summary to be presented. While carrying out your research try to answer to question number 2 below.

2. Complete the following nuclear equations and balance them:

a) $^{226}_{88}\mathrm{Ra} \rightarrow ? + {}^{4}_{2}\mathrm{He}$

b) $^{241}_{95}\mathrm{Am} \rightarrow ? + {}^{4}_{2}\mathrm{He}$

c) $^{60}_{27}\mathrm{Co} \rightarrow ? + {}^{0}_{-1}\mathrm{e}$

d) $^{118}_{54}\mathrm{Xe} \rightarrow ? + {}^{0}_{+1}\mathrm{e}$

e) $^{4}_{2}\mathrm{He} + {}^{10}_{5}\mathrm{B} \rightarrow ? + {}^{1}_{0}\mathrm{n}$

When a nucleus spontaneously breaks down by emitting radiation, the process is called **natural radioactive decay**. It can be shown as **a nuclear equation** using the symbols for the original radioactive nucleus, the new nucleus and the radiation emitted.

Radioactive nucleus → new nucleus + radiation (α, β, β^+ or γ)

(Parent) **(Daughter)**

If the first daughter nuclide is stable, the activity of the radioactive source ends there. But in many cases, the daughter nuclide is also radioactive and we obtain a **"decay series (chain)"**.

A → B → C → ... Z (sterile)

More stable

A nuclear equation is balanced when the sum of the mass numbers and the sum of the atomic numbers of the particles and atoms on one side of the equation are equal to their counterparts on the other side.

The changes in mass and atomic numbers of an atom that emits a radioactive particle are shown in the table below.

Table 1.3: Mass number and atomic number changes due to radiation

Decay process	Radiation symbol	Mass number	Atomic number	Charge
Alpha emission	or α	4	2	+2
Beta emission	or β	0	-1	-1

Positron emission	or	0	+1	+1
Gamma emission	or γ	0	0	0
Proton		1	1	+1
Neutron		1	0	0

1.3.1. Nuclear equations

A nuclear reaction is represented by a nuclear equation as follows:

Example 1:

Radium-226 emits an alpha particle to form a new isotope whose mass number, atomic number and identity we must determine.

Step 1: Write the incomplete nuclear equation.

$$^{226}_{88}\mathrm{Ra} \rightarrow \ ^{A}_{Z}\mathrm{X} + \ ^{4}_{2}\mathrm{He}$$

Step 2: Determine the missing mass number, A.

$$226 = A + 4$$

$$226 - 4 = A$$

$$222 = A$$

Step 3: Determine the missing atomic number, Z.

$$88 = Z + 2$$

$$88 - 2 = Z$$

$$86 = Z$$

Step 4: Determine the symbol of the new nucleus.

Use the periodic table to find out the element with the atomic number corresponding to that obtained in step 3 above. In this case the element is Radon (Rn). The symbol of this isotope of Radon is written as $^{222}_{86}\mathrm{Rn}$.

Step 5: Write the complete nuclear equation.

$$^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

Step 6: Check if the equation is balanced, i.e:

i) If the sum of mass numbers at the left side of the equation is equal to the sum of mass number at the right side (226 = 222+4)

ii) If the sum of atomic numbers at the left side of the equation is equal to the sum of atomic numbers at the right side (88 = 86+2)

Example 2:

When a proton bombards Nickel-58, the products are a new nucleus and an alpha particle. Write the balanced nuclear equation for this bombardment reaction.

Step 1: Write the incomplete nuclear equation.

$$^{58}_{28}\text{Ni} + {}^{1}_{1}\text{H} \rightarrow ? + {}^{4}_{2}\text{He}$$

Step 2: Determine the missing mass number

58 + 1 =? + 4

59 – 4 = **55**

Thus, the mass number for the new nucleus is 55.

Step 3: Determine the missing atomic number

28 + 1 =? + 2

29 – 2 = **27**

Step 4: Determine the symbol for the new nucleus.

On the periodic table, the element that has the atomic number of 27 is Cobalt, Co. the symbol of this isotope of Cobalt is written as $^{55}_{27}\text{Co}$.

Step 5: Complete the nuclear equation.

$$^{58}_{28}\text{Ni} + {}^{1}_{1}\text{H} \rightarrow {}^{55}_{27}\text{Co} + {}^{4}_{2}\text{He}$$

Step 6: the equation is balanced.

Note: Nuclear reactions involving hitting a nuclide by a particle such as proton or neutron as in the example 2 are referred to as '**bombardment reactions**'. Bombardment reactions are not natural; they are **induced (or artificial) nuclear reactions**.

For the case of example 1, when a radioactive particle is emitted, the type of nuclear reaction is **emission reaction**; those are natural radioactive isotopes.

1.3.2. Radioactive decay series

Radioactive decay Series is the series of steps by which a radioactive nucleus decays into a non-radioactive nucleus. The element goes from radioactive to non-radioactive.

A radioactive element disintegrates by emission of an α- or β-particle from the nucleus to form a new "daughter element." This again disintegrates to give another "daughter element'. This is why the whole series of elements starting with the parent radioactive element to the stable end-product is called **radioactive disintegration series** or **radioactive decay series** as seen above.

Naturally radioactive nuclides disintegrate to acquire stability.

In nature, there are three radioactive decays which are Uranium, Thorium and Actinium series. Each series starts with a radioactive element and then ends with a reasonable stable element. Uranium series is the most important.

The three series are similar because they all involve loss of alpha and beta particles ending with isotopes of Lead. Uranium series gives Lead-206, the most stable isotope of Lead; Thorium gives Lead-208 and actinium series gives Lead-207.

a) The uranium series

It starts with the parent element Uranium-238 and ends with the stable element Lead-206. It derives its name from Uranium-238 which is the starting nuclide of the series and has the longest half-life. In the process, 8 alpha and 6 beta particles are emitted before Lead-206 is attained. The whole process is shown below:

$$^{238}_{92}U \xrightarrow{\alpha} {}^{234}_{90}Th \xrightarrow{\beta} {}^{234}_{91}Pa \xrightarrow{\beta} {}^{234}_{92}U \xrightarrow{\alpha} {}^{230}_{90}Th \xrightarrow{\alpha} {}^{226}_{88}Ra \xrightarrow{\alpha} {}^{222}_{86}Rn \xrightarrow{\alpha} {}^{218}_{84}Po$$

$$\xrightarrow{\alpha} {}^{214}_{82}Pb \xrightarrow{\beta} {}^{214}_{83}Bi \xrightarrow{\beta} {}^{214}_{84}Po \xrightarrow{\alpha} {}^{210}_{82}Pb \xrightarrow{\beta} {}^{210}_{83}Bi \xrightarrow{\beta} {}^{210}_{84}Po \xrightarrow{\alpha} {}^{206}_{82}Pb$$

b) The Thorium series

It begins with the parent element thorium-232 and ends with Lead-208 which is stable.

$$ {}^{232}_{90}Th \xrightarrow{\alpha} {}^{228}_{88}Ra \xrightarrow{\beta} {}^{228}_{89}Ac \xrightarrow{\beta} {}^{228}_{90}Th \xrightarrow{\alpha} {}^{224}_{88}Ra \xrightarrow{\alpha} {}^{220}_{86}Rn \xrightarrow{\alpha} {}^{216}_{84}Po \xrightarrow{\alpha} $$

$$ {}^{212}_{82}Pb \xrightarrow{\beta} {}^{212}_{83}Bi \xrightarrow{\beta} {}^{212}_{84}Po \xrightarrow{\alpha} {}^{208}_{82}Pb $$

c) The Actinium series

It starts with the radioactive element Actinium-235. The end-product is the stable element Lead-207.

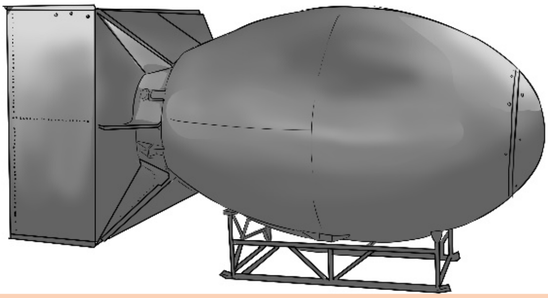
Application activity 1.3

1. Complete the following nuclear equations:
   a) ${}^{28}_{13}Al \longrightarrow ? + {}^{o}_{-1}e$
   b) $? \longrightarrow {}^{86}_{36}Kr + {}^{1}_{0}n$
   c) ${}^{210}_{83}Bi \longrightarrow ? + {}^{4}_{2}He$
   d) ${}^{40}_{18}Ar + ? \longrightarrow {}^{43}_{19}K + {}^{1}_{1}H$
   e) ${}^{238}_{92}U + {}^{1}_{0}n \longrightarrow ?$
2. Cobalt-60 decays by emitting a beta particle. Write the nuclear equation for its decay.
3. A new isotope is produced by the bombardment of Zinc-66 by a proton. Write the equation for this nuclear bombardment.
4. Complete the Thorium series starting with. 2 beta particles emitted, then 3 alpha particles; followed by a beta particle; then alpha particle; beta particle and then 2 alpha particles. Note that 2 beta particles are emitted consecutively.

1.4. Nuclear fission and fusion and their applications

Activity 1.4

1. What happens when the glass is fallen down?
2. The picture below illustrates the "Fat Man" which was the codename for the nuclear bomb that was detonated over Japanese city by the United States on 9 August 1945



Make a research and write the nuclear reaction which was used to fabricate the same bomb.

While many elements undergo radioactive decay naturally, some nuclear reactions are not spontaneous but are brought about when stable isotopes are bombarded with high-energy particles (like neutrons, α-particles, protons ...). Nuclear fission and fusion are good examples **artificial radioactivity** as they do not take place spontaneously.

1.4.1. Nuclear fission and fusion

a) Nuclear Fission

Nuclear fission is a process in which a large atomic nucleus is split into two smaller nuclei.

Large nuclei obviously have a large number of protons. The close proximity of so many protons makes these nuclei unstable due to the repulsion forces between protons. Thus, the nucleus of the unstable isotope splits to form smaller atoms by bombardment with a suitable sub-atomic particle. Those stable isotopes that are bombarded by a neutron to undergo fission reactions (to become fissionable) are known to be "**fertile radioisotopes**".

Among the three natural isotopes of uranium $^{238}_{92}U$, $^{235}_{92}U$ and $^{234}_{92}U$, the $^{235}_{92}U$ nucleus undergoes nuclear fission when bombarded with slow neutrons. Uranium-236 is formed which being unstable, further breaks up in several different ways.

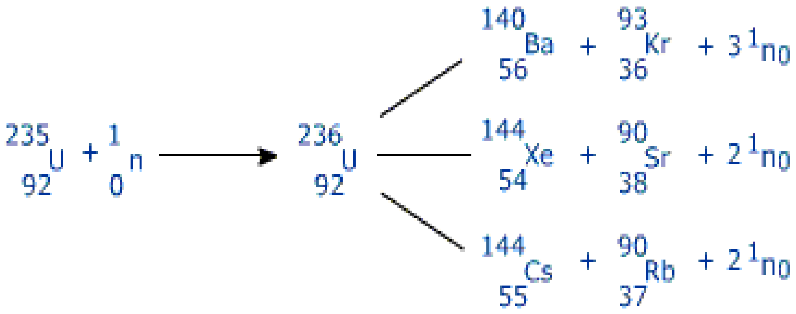


Figure 1.4 (a)nuclear fission of Uranium-235 nucleus

The neutrons emitted, in this fission reaction, bombard more uranium nuclei available to form a "**reaction chain**". This chain reaction is the basis of nuclear power. As uranium atoms continue to split, a significant amount of energy is released, in form of heat, from the reaction. This heat released is used to produce electricity (in a nuclear plant) or used in atomic/nuclear bombs.

Other examples: nitrogen-14 and oxygen-16 undergoing alpha and neutron bombardment respectively.

$${}^{14}_{7}N + {}^{4}_{2}He \rightarrow {}^{17}_{8}O + {}^{1}_{1}H$$

$${}^{16}_{8}O + {}^{1}_{0}n \rightarrow {}^{13}_{6}C + {}^{4}_{2}He$$

The tremendous amount of energy released during nuclear fission results from the principle of mass-energy equivalence; during the nuclear reaction, there is loss of mass but the mass lost is transformed into energy.

b) Nuclear Fusion

Nuclear fusion is a process that consists of joining two atomic nuclei of smaller masses to form a single nucleus of a larger mass.

A good example is the fusion of two "heavy" isotopes of hydrogen (deuterium, Hydrogen-2, and tritium, Hydrogen-3) into the element helium.

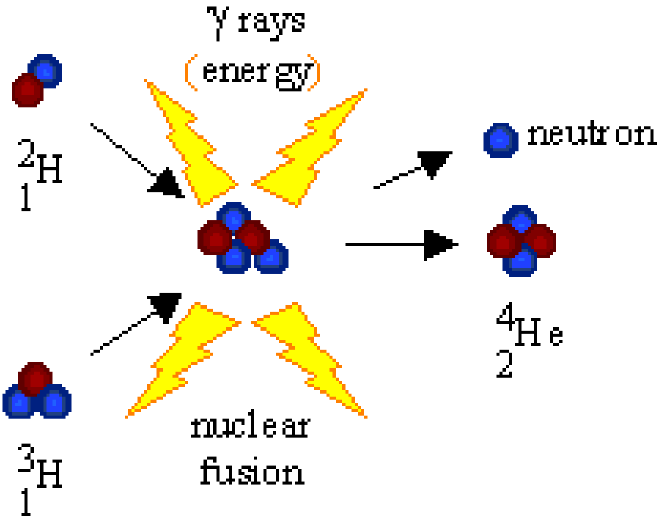


Figure 1.4. (b)Nuclear fusion of deuterium (^2H) and tritium (^3H)nuclei

Similarly, when two atoms of deuterium (hydrogen-2) collide at high speed, they might combine (fuse) to form a helium atom (He-3).

$$2{}^2_1H \rightarrow {}^3_2He + {}^1_0n$$

However, very high temperatures and pressures are required for the fusion to take place because of the repulsion between the positive nuclei. Thus, for the fusion to take place the nuclei must have enough kinetic energy to overcome these repulsion forces between like charges.

Like fission, in the fusion process large quantity of energy is liberated in the form of heat. This energy is also used in atomic/nuclear bombs (Hydrogen bomb).

Note that it is very difficult to carry out nuclear fusion between two large nuclei due to the highly strong repulsion forces that are between their positively charged nuclei. Table 15.6 provides the differences between nuclear fission and nuclear fusion.

Table 1.4: Differences between nuclear fission and nuclear fusion

Nuclear fission	Nuclear fusion
– A bigger (heavier nucleus) splits into smaller nuclei. – It does not require extreme high temperature and pressure as the nuclear fusion – A chain reaction sets – It can be controlled and energy released can be used for producing electricity in nuclear power reactors – The products of the reaction are radioactive; hence high risks of radioactive pollution.	– Lighter nuclei fuse together to form the heavier nucleus. – Extremely high temperature and pressure are required. – It is not a chain reaction. – Up to now it has not been controlled to produce electricity – The products of fusion reaction are non-radioactive in nature; hence non-pollutant

1.4.2 Application of nuclear fission and nuclear fusion

Both fission and fusion are nuclear reactions that produce energy as described above.

Fission is used in nuclear power reactors since it can be controlled, while fusion is not utilized to produce power since the reaction has not yet controlled up to now. The two processes have an important role in the past, present and future in energy creation.

Example: ${}^{235}_{92}\text{U}+{}^{1}_{0}\text{n} \rightarrow {}^{144}_{56}\text{Ba}+{}^{90}_{36}\text{K}+2{}^{1}_{0}\text{n}$

This reaction produces the energy of 1.73 x 10^{9}kJ mol^{-1} which is equivalent to the energy that can be produced by burning 300,000 tons of petrol!

Like other forms of energy, nuclear energy can be either renewable (nuclear fusion) or non-renewable (nuclear fission).

- Nuclear fission is non-renewable because uranium or other fissile nuclides needed for this process are not renewable.

  For example: In Atomic Bomb, there are fission reactions of uranium. The energy produced is uncontrolled and this principle is used to manufacture the bombs and missiles. When controlled, the nuclear fission is also useful in the production of electricity.

- Nuclear fusion energy (if mastered) could be renewable because hydrogen needed for this process is available in nature in large amount.

  For example: In Hydrogen Bomb, the nuclear reaction involves the fusion of deuterium and tritium nuclei to form helium.

  $${}_{1}^{2}H + {}_{1}^{3}H \rightarrow {}_{2}^{4}He + {}_{0}^{1}n$$

The deuterium comes from the ocean and has a near infinite supply and will not run out in the next few million years. With advancements in technology, we might be able to fuse protium itself. As it comes from water, the fuel supply is also near infinite and thus nuclear fusion is a renewable source of energy.

Application activity 1.4

1. Classify the following as pertaining to nuclear fission, nuclear fusion, or both:

   a) Small nuclei combine to form larger nuclei.

   b) Large amounts of energy are released.

   c) Very high temperatures are needed for the reaction.

2. In a fission reaction, U-235 bombarded with a neutron produces Sr-94, another small nucleus and 3 neutrons. Write the complete equation for this fission reaction.

1.5. Comparison between Nuclear and Chemical reactions.

Activity 1.5

1. Compare the following reactions and predict the possible differences

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$$Zn + H_2SO_4 \longrightarrow ZnSO_4$$

$$HCl + NH_3 \longrightarrow NH_4Cl$$

$${}_{28}^{58}Ni + {}_{1}^{1}H \rightarrow {}_{27}^{55}Co + {}_{2}^{4}He$$

2. Describe the following as pertaining to chemical reaction or nuclear reaction:
   a) Isotopes have the same chemical properties as they have the same number of electrons
   b) Hydrogen nuclei are the reactants
   c) Large amounts of energy are released.
   d) The mass is strictly conserved

Nuclear reaction and chemical reaction differ as shown in the following table:

Table 1.5: Differences between a chemical reaction and a nuclear reaction

Ordinary chemical reaction	Nuclear reaction
Valence electrons are used	Nuclei are involved
Atoms do not change their nature	New atoms are produced
Affected by external factors (temperature, pressure)	Not affected by external factors
Low energy involved	Gigantic energy involved

Application activity 1.5

Referring to your own examples of balanced equations establish the difference between chemical reaction and nuclear reaction

1.6. Uses of some radioisotopes

Activity 1.6

1. According to your own understanding, how do you think radioactivity is important in daily life?
2. Consult different sources (textbooks and search engines) to carry out a deep research on the uses of radioisotopes.

Radioactive isotopes have a variety of applications. Generally, they are useful because either we can detect their radioactivity or we can use the energy they release.

Radioactive isotopes are effective tracers because their radioactivity is easy to detect. A tracer is a substance that can be used to follow the pathway of that substance through some structures. For instance, leaks in underground water pipes can be discovered by running some tritium-containing water through the pipes and then using a Geiger counter to locate any radioactive tritium subsequently present in the ground around the pipes.

Tracers can also be used to follow the steps of a complex chemical reaction. After incorporating radioactive atoms into reactant molecules, scientists can track where the atoms go by following their radioactivity. One excellent example of this is the use of carbon-14 to determine the steps involved in photosynthesis in plants.

1. Radioactive Dating

Radioactive isotopes are useful for establishing the ages of various objects. The half-life of radioactive isotopes is unaffected by any environmental factors, as seen above, so the isotope acts like an internal clock.

For example, if a rock is analyzed and is found to contain a certain amount of uranium-235 and a certain amount of its daughter isotope, we can conclude that a certain fraction of the original uranium-235 has radioactively decayed. If half of the uranium has decayed, then the rock has an age of one half-life of uranium-235, or about 4.5×10^9 years. Many analyses like this, using a wide variety of isotopes, have indicated that age of the earth itself is over 4×10^9 years.

In another interesting example of radioactive dating, hydrogen-3 dating has been used to verify the stated vintages of some old fine wines.

One isotope of carbon, carbon-14, is particularly useful in determining the age of once-living artifacts. A tiny amount of carbon-14 is produced naturally in the upper reaches of the atmosphere, and living things incorporate some of it into their tissues, building up to a constant level. Once a living thing dies, it no longer acquires carbon-14. As time passes the carbon-14 that was in the tissues decays. The half-life of carbon-14 is 5,730 years. If an artifact is discovered and analyzed many years after its death and the remaining carbon-14 is compared to the known constant level, an approximate age of the artifact can be determined.

Radiocarbon dating is used in many fields to learn information about the past conditions of organisms and the environments present on Earth.

2. In Medicine

Radioactive isotopes have many medical applications in diagnosing and treating illness and diseases.

When a radiologist wants to determine the condition of an organ in the body, the patient is given a radioisotope that is known to concentrate in that organ. After a patient receives a radioisotope, a scanner produces an image of the organ. The scanner moves slowly across the region of the body where the organ containing the radioisotope is located. The gamma lays emitted from the radioisotope in the organ are used to expose a photographic plate with a scan of the organ.

One example of a diagnostic application is using radioactive iodine-131 to test for thyroid activity. The thyroid gland in the neck is one of the few places in the body with a high concentration of iodine.

To evaluate thyroid activity, a measured dose of ^{131}I is administered to a patient, and the next day a scanner is used to measure the amount of radioactivity in the thyroid gland. The amount of radioactive iodine that collects there is directly related to the activity of the thyroid, allowing radiologists to diagnose both hyperthyroidism and hypothyroidism.


image from a scanner of a patient suffering from the thyroidism disorder

Figure 1.6: **Examination of thyroid activity in radiography**

Iodine-131 has a half-life of only 8 days. So, it has low cell damage due to the minimum exposure. Technetium-99 can also be used to test thyroid function.

Bones, the heart, the brain, the liver, the lungs, and many other organs can be imaged in similar ways by using the appropriate radioactive isotope.

Other medical applications of radioisotopes include:

- Radiation from Co-60 (γ-rays) is used to irradiate the tumors (for instance, diagnosis and treat thyroid disorders).
- Iodine-125 (I-125) is used in treatment of brain cancer and in osteoporosis (a disease which causes bones to become weaker and easily broken) detection.
- Iodine-131 (I-131) is used to diagnose and treat thyroid disorders, in treatment of Graves' disease, goiter and prostate cancer.
- Phosphorus-32 (P-32) is used in the treatment of leukemia, excess red blood cells (tumors) and pancreatic cancer.
- Technetium-99m is used in imaging of skeleton and heart muscle, brain, liver, heart, lungs, bones, spleen, kidney and thyroid. This is the most widely used radioisotope in nuclear medicine.
- Cerium-141 (Ce-141) is used in gastrointestinal tract diagnosis and in measuring blood flow to the heart.
- Sodium-24 (Na-24) in the form NaCl is used as a tracer in blood.
- Strontium-85 (Sr-85) is used in detection of bone lesions and brain scans
- Radio Gold (Au-198) is used in Liver disease diagnosis.
- Radio iron (Fe-59) is used in Anemia diagnosis.
- In addition, radioisotopes are also used in sterilization of medical devices.

3. In Agriculture

Obviously, we obtain **food to eat and some drinks** as a result of agriculture. But contaminated food causes some diseases. Thus, there are some radioisotopes that kill dangerous microorganisms present on food by "**irradiation**".

The radiation emitted by some radioactive substances can be used to kill microorganisms on a variety of foodstuffs thereby increasing the shelf life of these produces. Produces such as tomatoes, mushrooms, sprouts, and berries are irradiated with the emissions from cobalt-60 or caesium-137. This exposure kills a lot of the bacteria that could cause spoilage and so the produce stays longer. Eggs and some meat, such as beef, pork, and poultry, can also be irradiated. Normally, irradiation of food does not make it radioactive.

By using known vintages (qualities of wines), oenologists (wine scientists) can construct a detailed analysis of the cesium-137 of various wines through the years.

The verification of a wine's vintage requires the measurement of the activity of cesium-137 in the wine. By measuring the current activity of cesium-137 in a sample of wine (the gamma rays from the radioactive decay pass through glass wine bottles easily, so there's no need to open the bottle), comparing it to the known amount of cesium-137 from the vintage, and taking into account the time passed, researchers can collect evidence for or against a claimed wine vintage.

In addition in plant research, radiation is used to develop new plant types to speed up the process of developing large amount of agricultural products. This involves insect control, drastic reduction of pest populations and, in some cases, elimination of insects by exposing the male ones to sterilizing doses of radiation. Radiation pellets are used in grain elevators to kill insects and rodents. Irradiation prolongs the shelf-life of foods by destroying bacteria, viruses, and molds as seen above.

Other agricultural uses of radioisotopes include the following:

- Radioactive phosphorus (P-32) is used in the study of metabolism of plants.
- Radioactive sulphur (S-35) helps to study advantages and disadvantages of fungicides.
- Pests and insects on crops can be killed by gamma - radiations.
- Gamma - rays are used for preservation of milk, potatoes etc.
- Yield of crops like carrot, root, apples or grapes can be increased by irradiation with radioisotopes.

4. In Industry

The applications of radioisotopes in industry are so many. Many types of thickness gauges exploit the fact that gamma rays are attenuated when they pass through the material. By measuring the number of gamma rays, the thickness can be determined. This process is used in common industrial applications such as:

a) **The automobile industry**: to test steel quality in the manufacture of cars and to obtain the proper thickness of tin and aluminum

b) **The aircraft industry**: to check for flaws in jet engines

c) **Road construction**: to gauge the density of road surfaces and sub surfaces

d) **Pipeline companies**: to test the strength of welds and leakage

e) **Oil, gas, and mining companies**: to map the contours of test wells and mine bores, and

f) **Cable manufacturers**: to check ski lift cables for cracks.

The isotope ^{241}Am is used in smoke detectors , in thickness gauges designed to measure and control metal foil thickness during manufacturing processes, to measure levels of toxic lead in dried paint samples, and to help determine where oil wells should be drilled.

The isotope ^{252}Cf (a neutron emitter) is used for neutron activation analysis, to inspect airline luggage for hidden explosives, to gauge the moisture content of soil and other materials, in bore hole logging in geology, and in human cervix-cancer therapy

Application activity 1.6

a) The radioisotopes are mostly used in different domains, such as in medicine, agriculture, dating …

Establish their usage in those domains and establish the importance of using them

b) Compare and contrast the relationship between the importance and the inconvenience of using the radioisotopes in the above domains

1.7. Health hazards of radioactive substances

Activity 1.7

1. By accident you have broken your leg, and reaching at hospital they are administrating you with x- rays (radiography) by using medical imaging, they are giving you different protection in different organs especially near the sex, suggest why they are protecting you before treatment? Find explanations about that.
2. Use your search engine or any available resources to find out how we are all exposed to radiation and the hazards that are brought to us by radiation.

Radioactive materials in the environment, whether natural or artificial, do expose people to risks.

This can happen in two ways:

- The radiation from the material can damage the cells of the person directly. This is damage by ***irradiation*.**
- Some of the radioactive materials can be swallowed or breathed in. While inside the body, the radiation it emits can produce damage. This is damage by **contamination.**

Some health Hazards are: **radiation burns, hair loss** (temporary or permanent), **cancer, reproductive sterility, mutations in offspring, etc.**

We are all exposed to low levels of radiation every day. Naturally occurring radioisotopes are part of atoms of wood, brick and concrete in our homes and the buildings of schools, hospitals, supermarkets, etc. This radioactivity is called "background radiation" and is present in the soil, in the food we eat, in the water we drink, and the air we breathe. For instance, one of the naturally occurring isotopes of potassium, potassium-40, is radioactive. This one is found in the body because it is present in any potassium-containing food. Other naturally occurring radioisotopes in air and food are carbon-14, radon-222, strontium-90 and iodine-131.

In addition to naturally occurring radiation from construction materials in our homes, we are constantly exposed to radiation (cosmic rays) produced in space by the sun.

The larger the dose of radiation received at one time, the greater the effect on the body. Exposure to low amount of radiation cannot be detected, but at medium levels the whole-body exposure produces a temporary decrease in number of white blood cells. If the exposure is very high, the person suffers the symptoms of radiation sickness such as nausea, vomiting, fatigue, and a reduction of white-cell count which can even be lowered to zero. So the victim suffers from diarrhea, hair loss, hair loss and infection. Too much exposure is expected to cause death.

You can ask yourself how radiation (which is in the air all around you) might lead to lung cancer. This is explained by the presence of Radon gas (mainly from granite rock) which is the main source of background radiation, and which is in turn responsible for almost all the radiation we get exposed to over our lifetime. When we breathe in; some of the radioactive atoms in the air undergo radioactive decay and emit alpha, beta or gamma radiation. These radiations can collide with and ionize atoms in our lung tissue, which could ultimately lead to lung cancer.

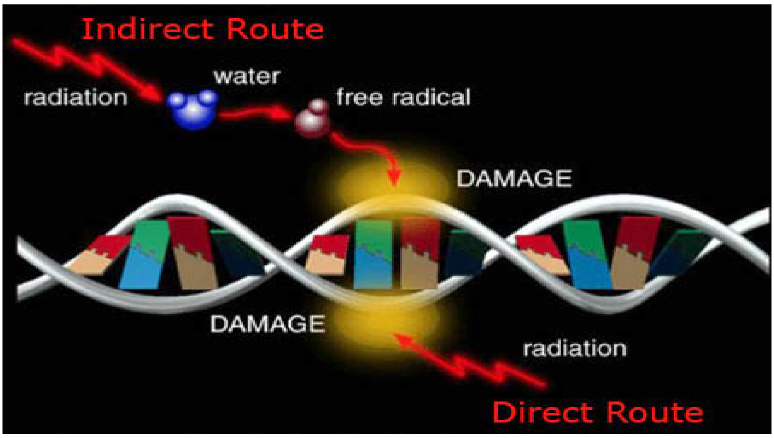


Figure 1.7: Ways through which radiations reach the body cells

Skills Lab 1

1. Today, the different organizations are fighting against the usage of nuclear weapons which are found in different countries, those countries are the strongest and giant even many countries fear them so much. Make a consultation on the internet (https://web.stanford.edu/class/e297c/war_peace/atomic/hfatman.html) and answer the following questions

   a) What is a nuclear weapon?

   b) Why nuclear weapons are not good especially for human and environment

   c) Little boy and fat man are the two hydrogen bombs which was used in the second world war those bombs annexed two cities Hiroshima and Nagasaki, till now those cities are facing different consequences associated to those bombs. Make a research and answer to the following questions

      ii) Try to describe the scenario

      iii) As human being and peace makers, why are we supposed to fight against the nuclear weapons?

      iv) Explain the side effect related to the use of nuclear power plant

      v) Write the nuclear reaction which has been used in fabrication of hydrogen bomb.

End of unit assessment 1

I. MULTIPLE CHOICE QUESTIONS. Choose the letter corresponding to the appropriate answer

1. Elements which emit natural radioactivity are known as

   A. Radio elements

   B. Active elements

   C. Radioactive elements

   D. Nuclear elements

2. Spontaneous emission of radiation by unstable nuclei is called

   A. Positive radioactivity

   B. Artificial radioactivity

   C. Natural radioactivity

   D. Negative radioactivity

3. What change occurs in the nucleus of an atom when it undergoes beta emission?

   A. The outer shell of electrons is filled.

   B. The number of neutrons decreases by one.

   C. A high speed electron is produced.

   D. A proton is produced.

   E. There is a release of energy.

4. Which one of the following does not occur in nuclear reaction?

   A. Nuclear radiation is released.

   B. There is a change in mass.

   C. It involves a rearrangement of electrons.

   D. New elements are made.

5. When beta decay occurs in a radioactive isotope, the atomic number (Z) always

   A. Increases by one

   B. Stays the same

   C. Increases by two

   D. Decreases by one

6. Which of the following statements is not correct concerning alpha-particles?

   A. They are composed of helium nuclei

   B. They are emitted from unstable nuclei

   C. They have a positive charge

   D. They can penetrate thick sheets of lead

7. Which one of the following is true when a nucleus undergoes radioactive decay?

   A. A new element is always formed

   B. Alpha-particles are always emitted

   C. Beta-particles are always emitted

   D. The unstable nucleus loses energy

8. Why would the occupants of a house fitted with smoke detectors containing americium–241 not be at risk from alpha radiation emitted by these devices?

   A. It has very low penetrating power through the air.

   B. Alpha radiation has very low ionizing power.

   C. The occupants wear protective clothing at all times

   D. Alpha radiation is not harmful

9. Which of these metals is used as a shield against radioactive emissions?

   A. Uranium

   B. Lead

C. Radium

D. Gold

10. Which one of the following reactions is not correct? Explain.

A. ${}^{238}_{92}\mathrm{U} - {}^{4}_{2}\mathrm{He} \rightarrow {}^{234}_{90}\mathrm{Th}$

B. ${}^{24}_{11}\mathrm{Na} \rightarrow {}^{20}_{9}\mathrm{F} + {}^{0}_{-1}\mathrm{e}$

C. ${}^{198}_{79}\mathrm{Au} \rightarrow {}^{198}_{80}\mathrm{Hg} + {}^{0}_{-1}e$

D. ${}^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}e$

11. Polonium-210 decays by emitting an alpha particle. What are the values of x, y and Z in the equation? Refer to ${}^{Y}_{X}Z$.

A. x = 206, y = 82, Z = Pb

B. x = 82, y = 206, Z = Pb

C. x = 83, y = 206, Z = Bi

D. x = 82, y = 204, Z = Pb

12. Radium-226 may decay by the emission of an alpha-particle. Which one of the following sets of products would result in such decay? (Radium has an atomic number of 88).

A. ${}^{226}_{89}\mathrm{Ac} + {}^{0}_{-1}\mathrm{e}$

B. ${}^{230}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$

C. ${}^{222}_{86}\mathrm{Rn} + {}^{4}_{2}\mathrm{He}$

D. ${}^{227}_{88}\mathrm{Ra} + {}^{0}_{-1}\mathrm{e}$

13. Which of the following would not be the use of radioisotopes?

A. Dating of silverware found in an archaeological site

B. Putting a date on the remains of a dinosaur

C. Irradiation of tropical fruits before consuming them

D. Tracing leaks from underground pipes

II. Matching: Choose the letter of the correct word for each of the questions below. Each letter will be used only once.

A. Decay series

B. Half-life

C. Helium

D. Longer

E. Nuclear fission

F. Nuclear fusion

G. Radioactive

H. Radioactive decay

I. Radioactivity

J. Transmutation

1. An element that gives off nuclear radiation is known to be ….
2. When an element changes to another, more stable element, there is …
3. The amount of time for half the atoms in a radioactive sample to decay is referred to as …
4. The more stable a nucleus is, the ______ its half-life.
5. The process in which the nucleus of an unstable atom releases radiation in order to become stable is known as …
6. The changing of an atom into another, more stable atom during decay is …
7. The splitting of an atom into 2 smaller nuclei (nuclear power plant) is known as …
8. An alpha particle is actually a nucleus of ___________.
9. The name given to the several steps required to get a radioactive element to a stable element is the …
10. The joining of 2 atoms to form a single, larger nucleus is known as ……………

III. Short and long answer open questions

1. Define radioactivity.
2. Describe an alpha particle. What nucleus is it equivalent to?
3. Plutonium has an atomic number of 94. Write the nuclear equation for the alpha particle emission of plutonium-244. What is the daughter isotope?
4. Francium has an atomic number of 87. Write the nuclear equation for the alpha particle emission of francium-212. What is the daughter isotope?
5. Write balanced equations for the following nuclear reactions:

   a) Nuclide carbon-14 undergoes beta decay

   b) Uranium-238 decays by alpha particle emission

   c) Carbon-11 decays by position emission
6. a) Give values for a, b, c and d in the following nuclear equations:

   i) ${}^{35}_{17}Cl + {}^{1}_{0}n \rightarrow {}^{a}_{b}X + {}^{1}_{1}H$ ii) ${}^{7}_{3}Li + {}^{2}_{1}H \rightarrow 2\,{}^{c}_{d}Y + {}^{1}_{0}n$

   b) ${}^{238}_{92}U$ undergoes radioactive decay as shown below:

   $${}^{238}_{92}U \xrightarrow{\alpha-emission} A \xrightarrow{\beta-emission} B \xrightarrow{\beta-emission} X \xrightarrow{\alpha-emission} Y$$

   Calculate the mass number and atomic number of element Y.

UNIT 2

BENZENE

Key Unit Competence:

Relate the chemistry and uses of benzene to its nature and structure

Introductory activity

From your prior studies in organic chemistry, it is believed that carbon is tetravalent while hydrogen is monovalent and compounds constituted by the two elements are known as 'hydrocarbons'. The structures and chemistry of the hydrocarbons reflects to their uses as fuels and starting materials for many substances important in life such as pharmaceutical drugs, solvents, packaging materials, clothes and so on. In this activity you need to follow instructions given to explain how the structure of a substance determines its chemical properties and uses.

1. Write down the molecular formulae for these five hydrocarbons
    a) A molecule with 6 carbon atoms and 14 hydrogen atoms
    b) A molecule with 6 carbon atoms and 12 hydrogen atoms
    c) A molecule with 6 carbon atoms and 10 hydrogen atoms
    d) A molecule of 6 carbon atoms with 8 hydrogen atoms
    e) A molecule of 6 carbon atoms with 6 hydrogen atoms
2. From the molecules in 1) above, choose molecule(s) that fit(s) in the description provided, and then draw its (their) structural formula (e).
    a) Unsaturated hydrocarbon (s) that decolorize (s) bromine water and alkaline potassium manganate (VII)
    b) Saturated hydrocarbon (s)

c) Hydrocarbon (s) with empirical formula of CH

d) Unsaturated hydrocarbon (s) which do (es) not decolorize bromine water and potassium manganate (VII).

e) Unsaturated hydrocarbon (s) that form(s) a white precipitate when treated with ammoniacal silver nitrate and forms a reddish-brown precipitate when treated with ammoniacal copper (I) chloride.

3. It is believed that unsaturated hydrocarbons decolorize both bromine water and alkaline potassium manganate (VII). Explain any assumption you can suggest about the compound in question 2.d)

Some or all people are unique in their living attitudes and values. But being unique does not mean to be isolated from others as people need each other in order to complement and build a strong nation.

This is true for benzene. From the above activity question 3 you may have been stuck while discussing on why this unsaturated compound has properties that are different from other unsaturated hydrocarbons provided within the same activity. But this does not mean that it is quite different from them. It will share some properties with others but exhibit its identity or its unique properties from others.

In this unit, you will discover what makes benzene resistant towards some reactants and its importance will be highlighted.

2.1. Structure of benzene

Activity 2.1

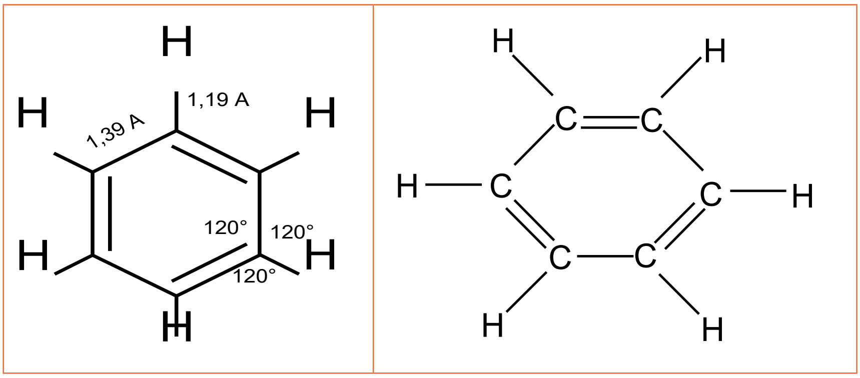
- Research in books or search engine about the structure of benzene.
- Read and make a summary on the historical development of benzene's structure.

Michael Faraday was the first to isolate benzene from coal. Benzene was found to have the molecular formula of C_6H_6. However, its structural formula posed a problem for many years.

For example, you can work out the structures of compounds whose molecular formula is C_6H_6 and see how many you can find.

The structure of benzene must be only one, in which all the six hydrogen atoms occupy equivalent positions. This was discovered by Friedrich August Kékulé Von Stradonitz while daydreaming of a snake seizing its own tail. From this, he proposed a ring structure of six carbon atoms with double bonds alternating with single bonds.

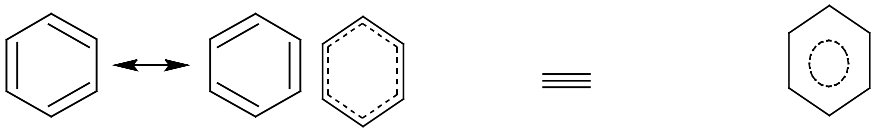
Furthermore, X-ray diffraction studies, first carried out by Kathleen Lonsdale, showed that benzene is planar and all its C-C bonds are of the same length (0.139 nm which is intermediate of C-C single bond and C=C double bond in alkenes) and bond angles of the same size (120°).



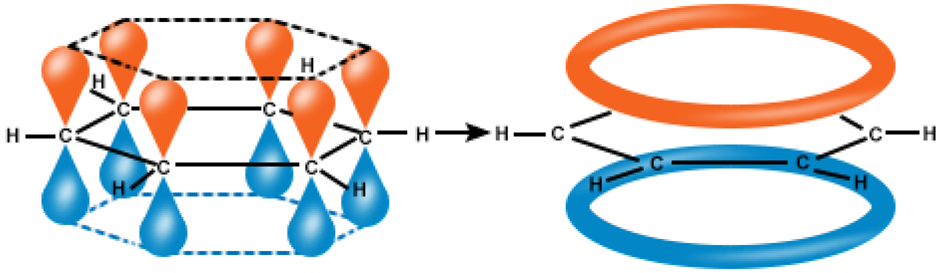
By comparing benzene with alkenes, the following points are noticed:

- Benzene fixes 3 moles of hydrogen, thus it has 3 double bonds,
- Benzene does not decolorize bromine water or acidified potassium manganate (VII) and does not turn green the acidified potassium dichromate,
- Benzene does not react with water and hydracids under normal conditions.

From the above points it can be easily noticed that benzene is not quite an alkene, due to its double bonds which do not occupy fixed positions. This change of positions of the double bonds is referred to as ‘resonance’.



The sp^2 hybridized orbitals of carbon is involved in sigma bond formation with other two carbon atoms and one hydrogen atom to make a hexagonal ring. The remaining unhybrid p-orbital is involved in side-ways overlapping with a neighbor carbon atom to form a pi-bond. Since there is an equal probability of making the pi-bond with either neighbor carbon atom, pi-electron remains delocalized over six carbon atoms of the ring.



Application activity 2.1

Discuss and provide appropriate answers for the following questions:

1. (a) Benzene has the molecular formula C_6H_6. Draw the Kékulé structure for this showing all the atoms.

   (b) Draw the skeletal structure showing the way the Kékulé structure is normally drawn.

2. How does the structure of benzene differ from the cyclohexane structure?

3. Describe the Structure and Bonding of Benzene

2.2. Physical properties, uses and toxicity of benzene

Activity 2.2

1. You are provided the following substances
   - Benzene
   - Water
   - Any other organic solvent (cyclohexane, ethanol or propanol, …
   - Match box

And you are asked to carry out the following experiment and take conclusion

i) Mix benzene and water and shake

ii) Mix benzene and each of the organic solvent

iii) Take 25milliliters of benzene then burn it

For each case write your observation and draw the properties of benzene and explain.

a) Take a time to make a possible research either at internet or any other resources like books from library, predict some dangers which can be associated with benzene

b) Establish at least four uses of benzene referring to the structure and different experiments you have carried out.

2.2.1. Physical properties of benzene

Benzene is known to have the following physical properties

- Benzene is a colorless volatile liquid with an aromatic (pleasant/sweet) smell.
- Benzene boils at 80.1 °C
- Benzene melts at 5.5°C.
- Benzene is insoluble in water.
- It is less dense than water (specific gravity or relative density is 0.88).

2.2.2. Uses of benzene

It has been used by chemists since 1800 it is a good solvent for other organic compounds. Benzene itself is an excellent solvent for certain elements, such as sulphur, phosphorus, and iodine. It is found in crude oil. It is used to make plastics, resins, synthetic fibers, rubber, lubricants, dyes, detergents, drugs and pesticides.

2.2.3. Toxicity of benzene

Benzene is highly toxic and is said to be carcinogenic.

A person exposed for long time to benzene (even at low levels), can develop anemia and leukaemia.

Figure 2.1: Benzene is a component of compact discs and explosives

Application activity 2.2

1. Benzene is flammable and carcinogenic. What do you understand by the term “carcinogenic”?
2. What advice can you give to your friend who smokes?

2.3. Preparation of benzene

Activity 2.3

Referring to the hydrocarbons especially alkanes

i) Define Reforming

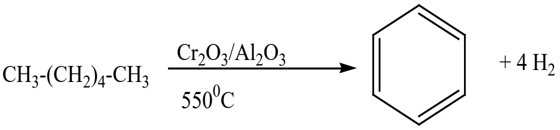
ii) Write the equation of reaction of reforming of hexane and describe the main product and predict its structure.

All the raw materials provided in the activity above are from the topics covered in senior five, so hopefully you performed them very well. The methods used for preparing benzene are based on reduction reaction and decomposition reaction and even addition reaction.

2.3.1. Industrial preparation (on large scale)

a) From petroleum oils: By catalytic reformation of petroleum products

By fractional distillation followed by reforming. Fraction of naphtha is heated over $Cr_2O_3 - Al_2O_3$ at 500-550°C and 15atm pressure (aromatisation).

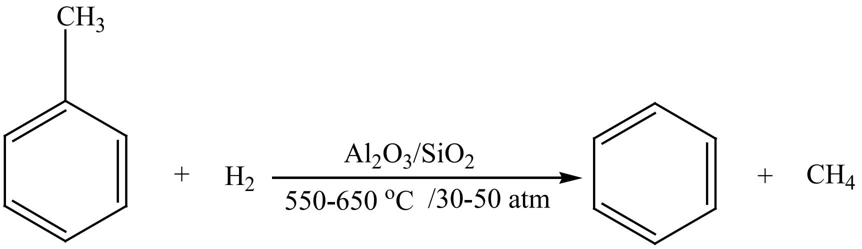


When platinum is used at 15atm and at 500°C, the process is called **‘platforming’**.

b) By converting methylbenzene into benzene

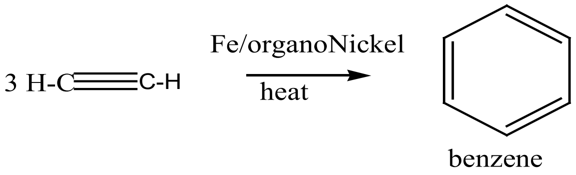
Methylbenzene is much less commercially valuable than benzene. The methyl group can be removed from the ring by a process known as **“demethylation”.**

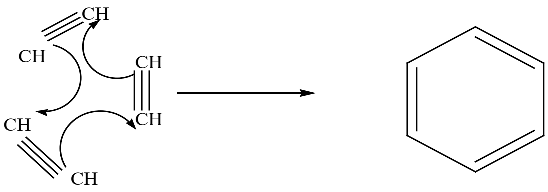
The methylbenzene is mixed with hydrogen at a temperature of between 550°C and 650°C, and a pressure between 30atm and 50atm, with a mixture of silicon dioxide and aluminium oxide as catalyst.



c) From ethyne

When ethyne is heated in the presence of iron as catalyst or organo-Nickel, it undergoes ***cyclization***.

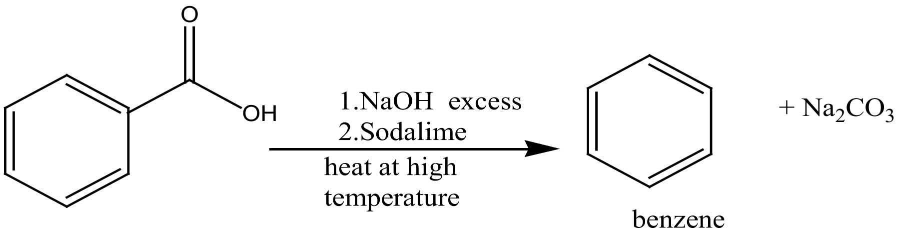




2.3.2. *Laboratory Preparation*

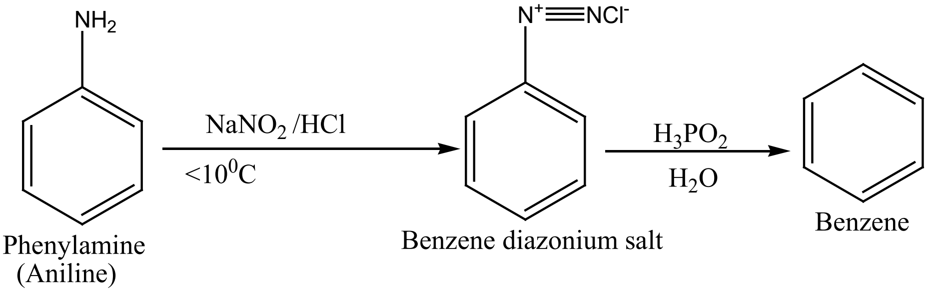
a. From benzoic acid

In this method benzoic acid is heated with soda lime.

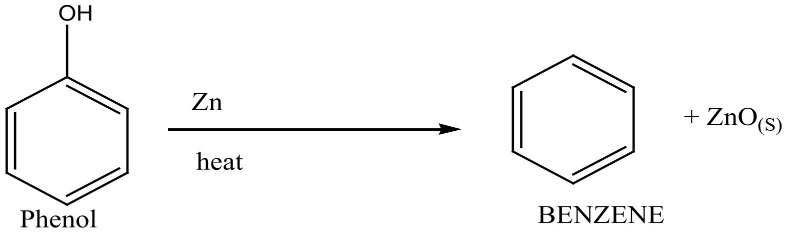


b. From benzenediazonium salt

In this method, the benzenediazonium salt formed by reacting phenylamine with sodium nitrite and a mineral acid is treated with phosphorous acid (H_3PO_2) and water.

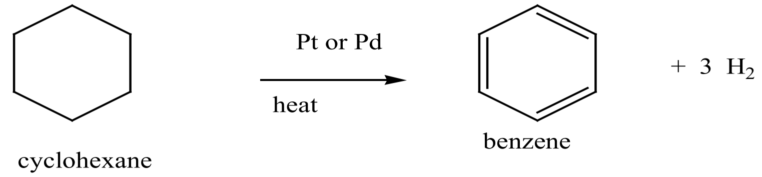


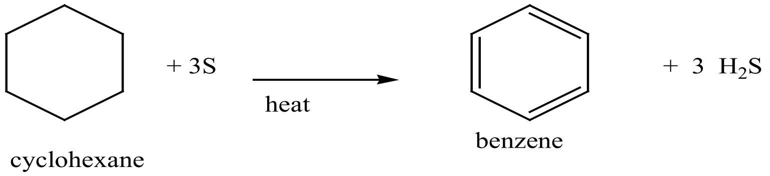
c. From phenol by heating phenol with zinc dust.



d. From cyclohexane

When cyclohexane is heated with Palladium or Platinum as catalyst, it undergoes dehydrogenation forming benzene. When cyclohexane is heated with sulphur, benzene is also produced.





Application activity 2.3

Discuss and describe how you can obtain benzene starting with inorganic reagents, showing necessary conditions at every step.

2.4. π-bond delocalization and Chemical stability of benzene

Activity 2.4

In chemical energetics (senior five), you learnt many forms of enthalpy changes that take place when various reactions take place. In this activity, you have to use some of the concepts of these enthalpy changes in order to understand the stability of benzene. By following instructions provided as questions and using the following data:

Enthalpy change of atomization of carbon, C(s):	+715 kJ (mol of C atoms)$^{-1}$
Enthalpy change of atomization of hydrogen, H_2(g):	+218 kJ mol^{-1}
Bond energy of C=C (average):	610 kJ mol^{-1}
Bond energy of C-C (average):	346 kJ mol^{-1}
Bond energy of C-H (average):	413 kJ mol^{-1}

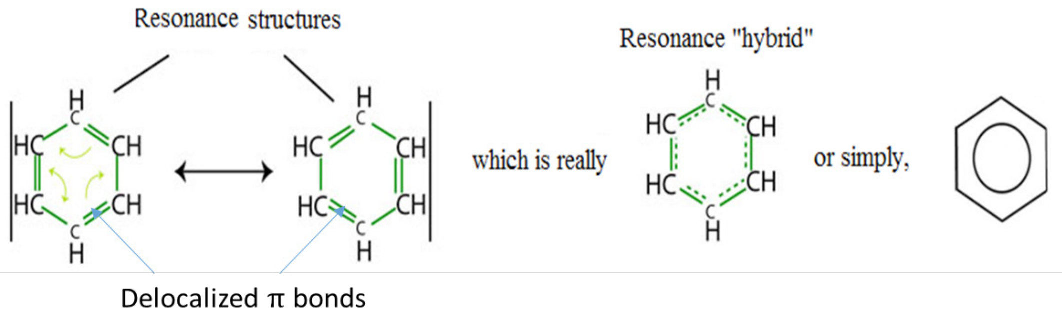
Discuss and work out the enthalpy change of formation of benzene by the following stages.

1. Calculate the energy needed to produce
   a) Six moles of gaseous carbon atoms from C(s)
   b) Six moles of gaseous hydrogen atoms from H_2(g)
2. Calculate the energy released when
   a) Three moles of C-C bonds are formed from gaseous atoms
   b) Three moles of C=C bonds are formed from gaseous atoms
   c) Six moles of C-H bonds are formed from gaseous atoms.

3. Use your answers to **[1]** and **[2]** to calculate the total energy change when a mole of gaseous benzene is formed from its elements.
4. Compare your answer with experimental value of +82 kJ mol^{-1}.
5. Now, use the available resources (books or internet) to find out what you can present about the stability of benzene.

2.4.1. π-bond delocalization

Benzene is an aromatic compound with molecular formula of C_6H_6. It is a planar hexagonal ring with three pi-bonds (π bonds) in an alternate manner. The π bonds are said to **be delocalized** since the ϖ electrons move freely throughout the entire system and can't belong to any particular carbon atom. These electrons are resonating around the carbon atoms in the benzene molecule resulting into two possible resonance structures (or forms) of benzene molecule that are in such a rapid equilibrium. The resonance hybrid of benzene molecule is represented with a circle at the center of hexagonal ring of carbon atoms as shown below:



The delocalization of 3 π-electrons in benzene molecule leads to its **'aromaticity'.**

Benzene is the smallest aromatic molecule and it is not the only aromatic molecule known, for eg. naphthalene, anthracite, etc are aromatic molecules. Thus, for a molecule to be aromatic, it has to fulfill the **Huckel's rule** of aromaticity with the following criteria:

- It must be cyclic and flat
- It must be conjugated (i.e, all atoms around the ring must be able to participate in pi-bonding through resonance)
- It must have a number of pi-delocalized electrons that is even and corresponding to **(4n + 2)** delocalized electrons, where n (number of benzene rings) = 0,1,2,3 and so on.

2.4.2. Chemical stability of benzene

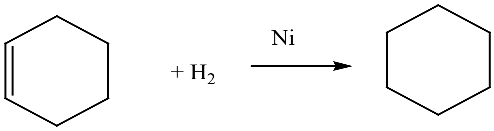
The stability of benzene can be explained on the basis of resonance in the molecule. There are two possible resonance structures (or forms) of benzene molecule that are in such a rapid equilibrium (see figure above). The regular-hexagonal planar ring of benzene is attributed to resonance stabilization of this conjugated cyclic alkene. Thus, an approaching reagent (such as bromine for instance) cannot be attracted to a double bond before the structures changes.

The delocalization of ϖ-electrons in benzene molecule provides its extra stability. Benzene is more stable than expected as compared to aliphatic alkenes or the cyclic alkenes with three double bonds. Thus, it does not undergo addition reaction like alkenes do. In other words, benzene is less reactive than alkenes for addition reactions as this type of reactions can be responsible for loss of aromaticity (or resonance).

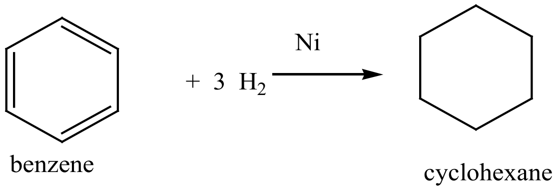
Benzene reacts preferably through substitution reactions in which one of its bonded H-atoms is replaced by an electrophile. Another measurement of stability of benzene is the tendency of benzene to undergo electrophilic substitution reactions rather than electrophilic addition reactions as alkenes. The presence of the π electron cloud makes a negative zone that could be attacked by electrophilic reagents, by giving electrophilic substitution reactions.

The thermochemical data show that benzene does not have true double bonds. The theoretical heat of formation of gaseous benzene, taking into consideration 3 double bonds, is +252 kJ/mol while experimental value is +82 kJ/mol, therefore the true structure is more stable by 170 kJ/mol than cyclohexa-1,3,5-triene (Kekulé structure).

The enthalpy of hydrogenation of cyclohexane is -120 kJ/mol.



Therefore, since Kekulé (cyclohexa-1,3,5-triene) structure has 3 double bonds, the expected heat of hydrogenation is 3 times i.e. 3 x (-120) kJ/mol = -360 kJ/mol.



However the experimental enthalpy of hydrogenation of benzene is only -208 kJ/mol! Therefore benzene is more stable by 152 kJ/mol than it would be if it was cyclohexa-1,3,5-triene. This stabilization energy is called ***delocalization energy or resonance energy*.**

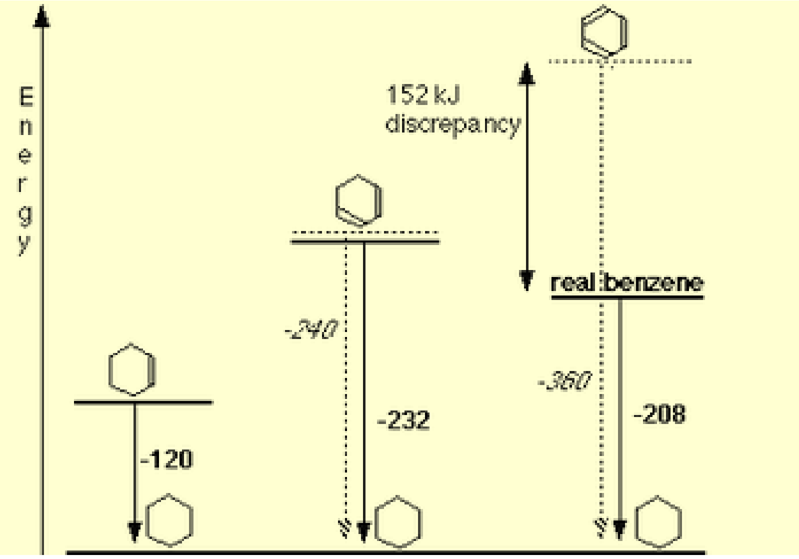


Figure 2.4: comparison between enthalpy change of hydrogenation of benzene and that of cyclohexene

Note: Because of this ***extra stability***, benzene:

- Does not undergo reactions with halogens and halogen acids which are characteristic of alkene,
- Does not react with water in the presence of H^+ and does not react with acidified $KMnO_4$,
- Cannot be represented by these structures because of its inertness,
- $CH_2=C=CH-CH=C=CH_2$ nor $CH_3-C\equiv C-C\equiv C-CH_3$
- Under drastic conditions, it however reacts with Cl_2 or Br_2 in the presence of ultraviolet light/light or halogen carrier,
- Reacts so fast with oxygen, by producing yellow luminous flame which is sooty.

Application activity 2.4

Refer to your results from the ***activity 4.4*** to discuss and conclude on this:

Real benzene is more or less stable than the Kékulé structure? Explain your answer.

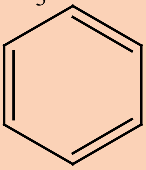
2.5. Reactions of Benzene

Activity 2.5

Complete the following chemical reaction

1. $CH_3CH{=}CHCH_3 + H_2 \xrightarrow{Pt}$

2.



$+ \; H_2 \longrightarrow$

3. $CH_3CH_2\,CCH_3{=}CH_2 + HCl \longrightarrow$

4. $C_6H_6 + Cl_2 \xrightarrow{UV}$

5. $CH_3CH_2CH(CH_3)CH_2 \xrightarrow{KMnO_4/H^+}$

Establish the differences you are observing in the reactions above

As seen in the previous discussions, since benzene contains carbon-carbon double bonds, it might be expected to undergo electrophilic addition reactions readily as it is the case for alkenes. This is not the case, however, and benzene does not decolorize bromine water. Neither does it readily undergo any other addition reactions.

The reason for this is that the delocalized system in benzene is stable, and addition reactions would break up this delocalization and lead to the formation of the products which are less stable than benzene itself. Benzene thus tends to undergo electrophilic substitution reactions rather than addition reactions.

2.5.1. Electrophilic aromatic substitution reactions

Aromatic compounds undergo substitution reactions with ***electrophiles*** in which one or more hydrogen atoms of the benzene ring are substituted.

Since the reagents and conditions employed in these reactions are electrophilic, these reactions are commonly referred to as **"Electrophilic Aromatic Substitution"**. The catalysts and co-reagents serve to generate the strong electrophilic species needed to perform the initial step of the substitution.

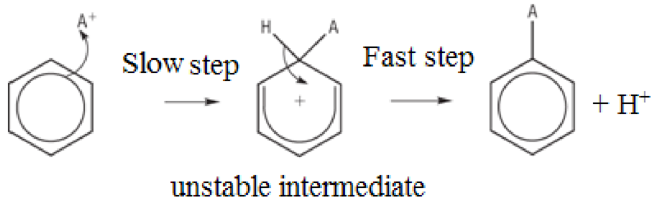
Many substitution reactions of benzene have been observed and the five most useful are listed below.

Reaction Type	Typical Equation
Halogenation:	$C_6H_6 + Cl_2 \xrightarrow[\text{FeCl}_3\text{ catalyst}]{\text{room temperature}} C_6H_5Cl + HCl$ Chlorobenzene
Nitration:	$C_6H_6 + HNO_3 \xrightarrow[\text{H}_2\text{SO}_4\text{ catalyst}]{\text{heat}} C_6H_5NO_2 + H_2O$ Nitrobenzene
Sulfonation:	$C_6H_6 + H_2SO_4 + SO_3 \xrightarrow{\text{heat}} C_6H_5SO_3H + H_2O$ Benzenesulfonic acid
Friedel-Crafts Alkylation:	$C_6H_6 + R\text{-}Cl \xrightarrow[\text{AlCl}_3\text{ catalyst}]{\text{heat}} C_6H_5\text{-}R + HCl$ Alkyl benzene
Friedel-Crafts Acylation:	$C_6H_6 + RCOCl \xrightarrow[\text{AlCl}_4\text{ catalyst}]{\text{heat}} C_6H_5COR + HCl$ Aryl Ketone

Mechanism for electrophilic substitution reactions of benzene

All electrophilic substitution reactions of benzene follow the same mechanism. After the formation of the electrophile, a two-step mechanism has been proposed for these electrophilic substitution reactions.

In the first, ***slow or rate-determining step, the electrophile forms a sigma-bond*** to the benzene ring, generating a positively charged benzenonium intermediate. In the second, ***fast step, a proton is removed*** from this intermediate, yielding a substituted benzene ring.



Briefly, electrophilic aromatic substitution reaction is realized in 3 steps:

1. Electrophile formation
2. Attack of the ring by electrophiles
3. Deprotonation = loss of H^+

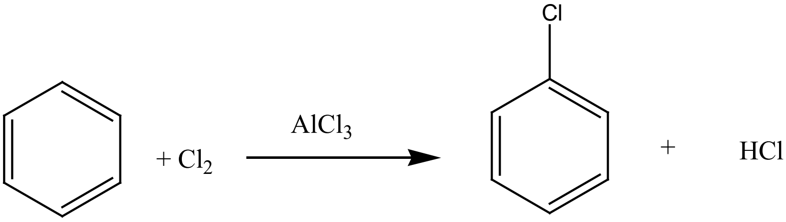
1) Halogenation

Benzene reacts with halogens (chlorine or bromine) in the presence of a catalyst, replacing one of the hydrogen atoms on the ring by a chlorine or bromine atom.

- The reactions happen at ***room temperature***.
- The catalyst has to be a Lewis acid known as “halogen carrier”. The most commonly used catalysts are: aluminium (or iron) chloride, $AlCl_3$/ $FeCl_3$ or aluminium (or iron) bromide, $AlBr_3$/ $FeBr_3$ if you are reacting benzene with bromine.

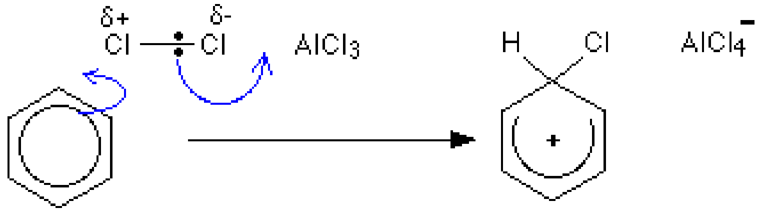
Example*:* The reaction with chlorine (Chlorination)

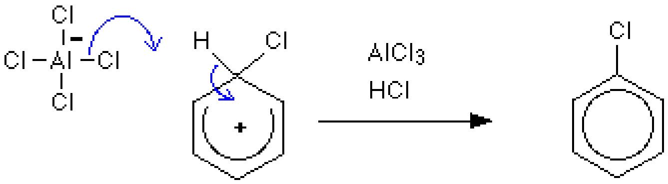
The reaction between benzene and chlorine in the presence of either aluminium chloride or iron chloride gives chlorobenzene.



Or $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$

Mechanism:

Step one:	

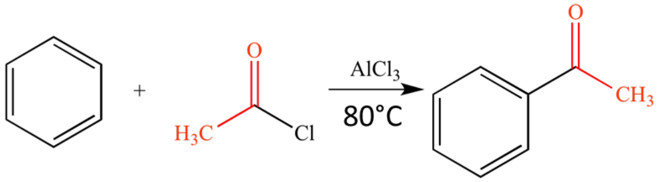
Step two:	

2) Friedel-craft-acylation

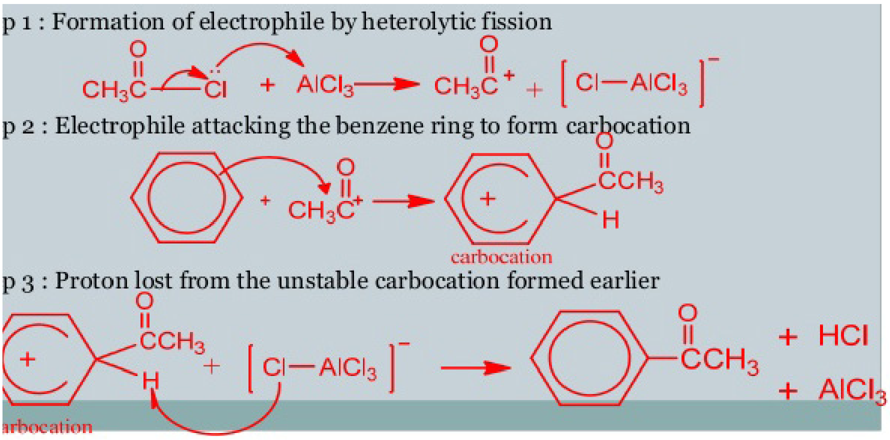
Acylation involves substituting an acyl group, RCO^-, into a benzene ring.

The most reactive substance containing an acyl group is an acyl chloride (also is known as an acid chloride). These have the general formula of RCOCl.

Example: Ethanoyl chloride reacts with benzene under the presence of $AlCl_3$ at 80°C to produce phenylethanone



The mechanism of acylation is:



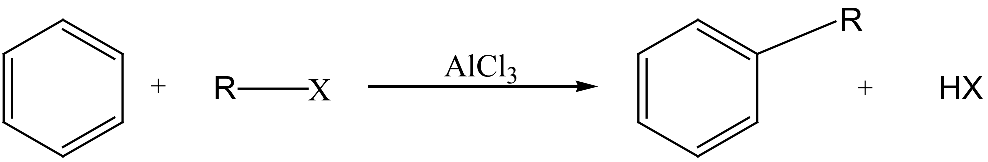
Note: An acid anhydride such as ethanoic anhydride, $CH_3CO\text{-}O\text{-}COCH_3$ can also be used for acylation purposes.

3) Friedel-Crafts Alkylation

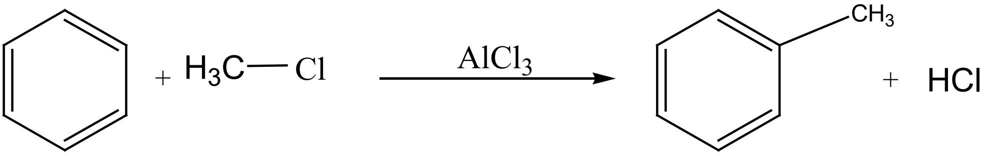
This reaction involves substituting an alkyl group into a benzene ring. Hydrogen on the ring is replaced by a group like methyl or ethyl and so on.

a) Using haloalkanes

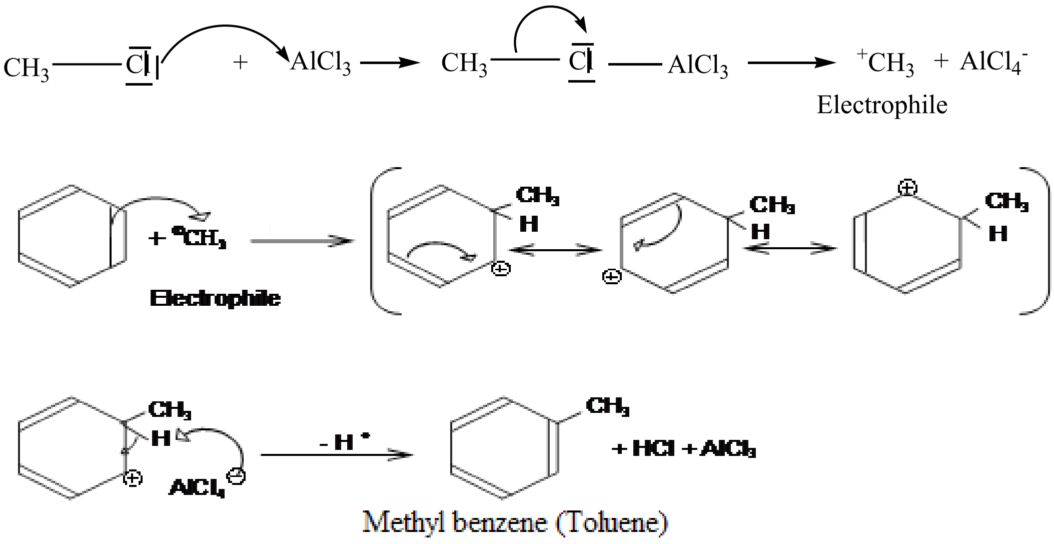
Benzene reacts with chloroalkanes in the presence of anhydrous $AlCl_3$ or $FeCl_3$ as a catalyst under reflux at 50°C to form alkyl benzenes



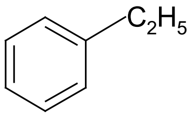
Example:



Mechanism:



If chloroethane (C_2H_5Cl) is used, then ethylbenzene ($C_6H_5C_2H_5$) is formed.



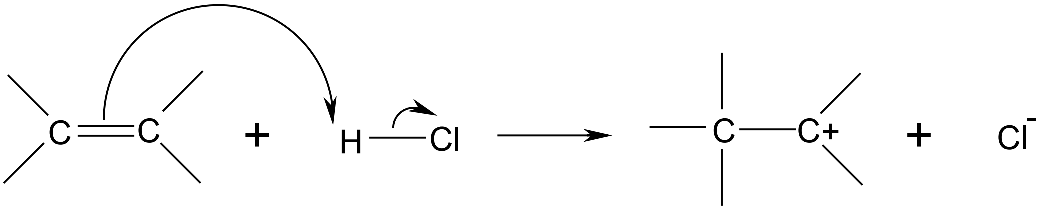
b) Using alkenes

Alkylbenzenes other than methylbenzene can be formed by reacting benzene with alkenes in the presence of HCl and $AlCl_3$, under reflux at temperatures below 50°C.

Mechanism:

***Step 1*:** The alkene reacts with the HCl in the same way as in electrophilic addition

reactions:

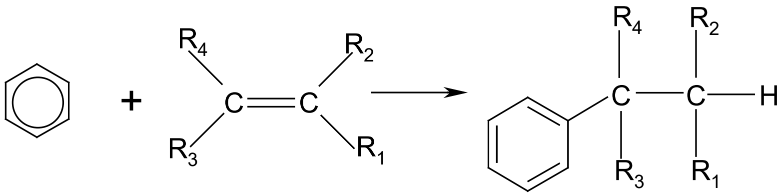


The carbocation behaves as the electrophile.

Step 2 and ***Step 3*** proceed in the same way as in the alkylation reaction described above.

The overall reaction can be written as follows: $\mathbf{C_6H_6 + R_1R_2C{=}CR_3R_4 \rightarrow C_6H_5CR_1R_2CR_3R_4}$

It can also be written as follows:

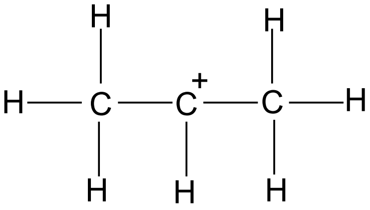


The $AlCl_3$ and the HCl act as catalysts.

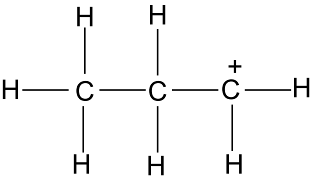
If ethene is used, the main product is ***ethylbenzene*.**

Unsymmetrical alkenes can give two possible carbocations when HCl is added. In such cases two different products are possible. In most cases one carbocation is produced in greater quantities than the other. Thus, a major product and a minor product are formed.

Example: Propene can react with HCl to give two possible carbocations:



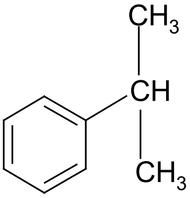
or



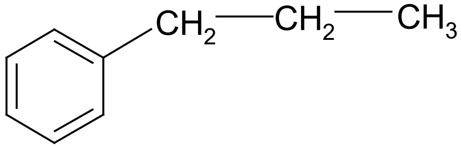
more stable

less stable

The more stable cation gives the major product, methylethylbenzene (or isopropylbenzene).



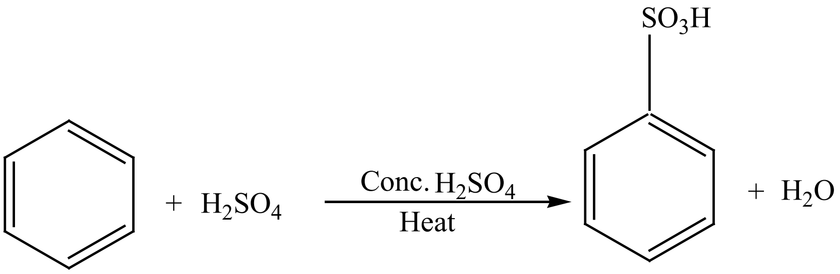
The less stable cation gives the minor product, propylbenzene.



4) Sulphonation

Sulphonation involves replacing one of the hydrogen on a benzene ring by the sulphonic acid group, -SO_3H^+. There are two equivalent ways of sulphonating benzene:

- Heat benzene under reflux with concentrated sulphuric acid for several hours.
- Warm benzene under reflux at 40°C with fuming sulphuric acid, **$H_2S_2O_7$,** for 20 to 30 minutes.

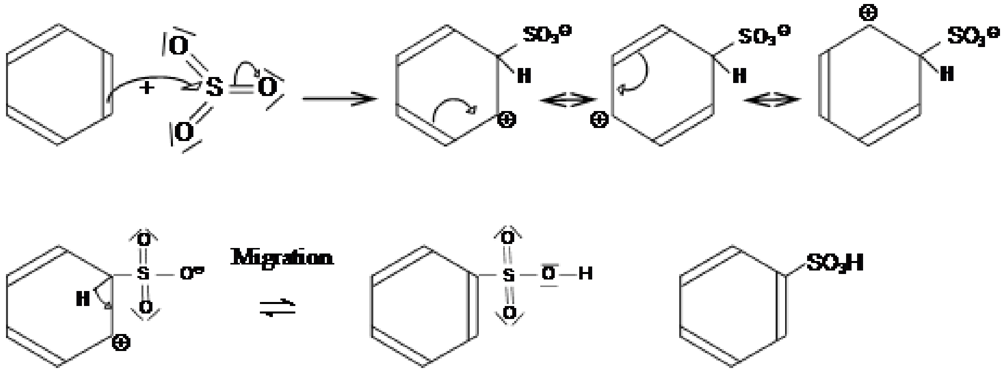


$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$

The product is ***benzenesulphonic acid***.

Mechanism:

$2\ H_2SO_4 \rightarrow SO_3 + H_3O^+ + HSO_4^-$



5) Nitration

Nitration happens when one (or more) of the hydrogen atoms on the benzene ring is replaced by a nitro group, $-NO_2$.

Benzene is treated with a 50:50 mixture of concentrated nitric acid and concentrated sulphuric acid at a temperature not exceeding 50°C. The mixture is held at this temperature for about half an hour. Yellow oily nitrobenzene is formed.

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

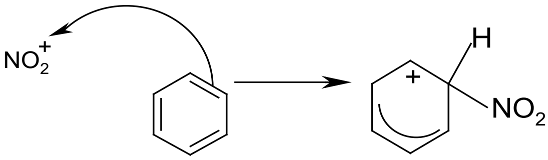
The concentrated sulphuric acid is acting as a catalyst and so is not written into the equations.

Mechanism:

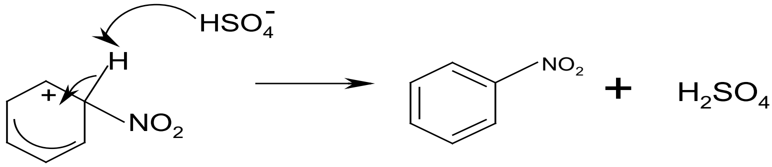
***Step 1*:** Nitric acid is a less strong acid than sulphuric acid, and acts as a base as the electrophile is formed.

$$H_2SO_4 + HNO_3 \rightarrow H_2O + NO_2^+ + HSO_4^-$$

Step 2: The NO_2^+ is the electrophile and attacks the delocalized ring, breaking it temporarily:



Step 3: The delocalized system then reforms itself by pulling in the electrons from the C-H bond. The H^+ recombines with the HSO_4^- to form H_2SO_4.



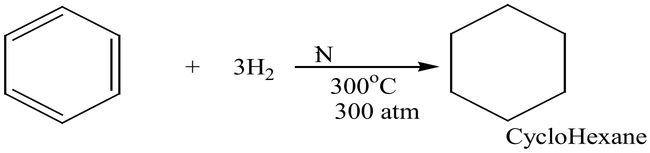
The overall reaction is $\mathbf{C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O}$

The sulphuric acid behaves as a catalyst. The product is known as ***nitrobenzene***.

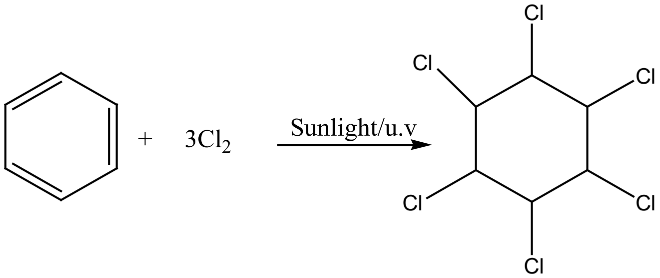
2.5.2. Some addition reactions and combustion reaction

The benzene ring can undergo addition reaction under drastic conditions, breaking down its resonance.

1. Hydrogenation



2. Addition of chlorine



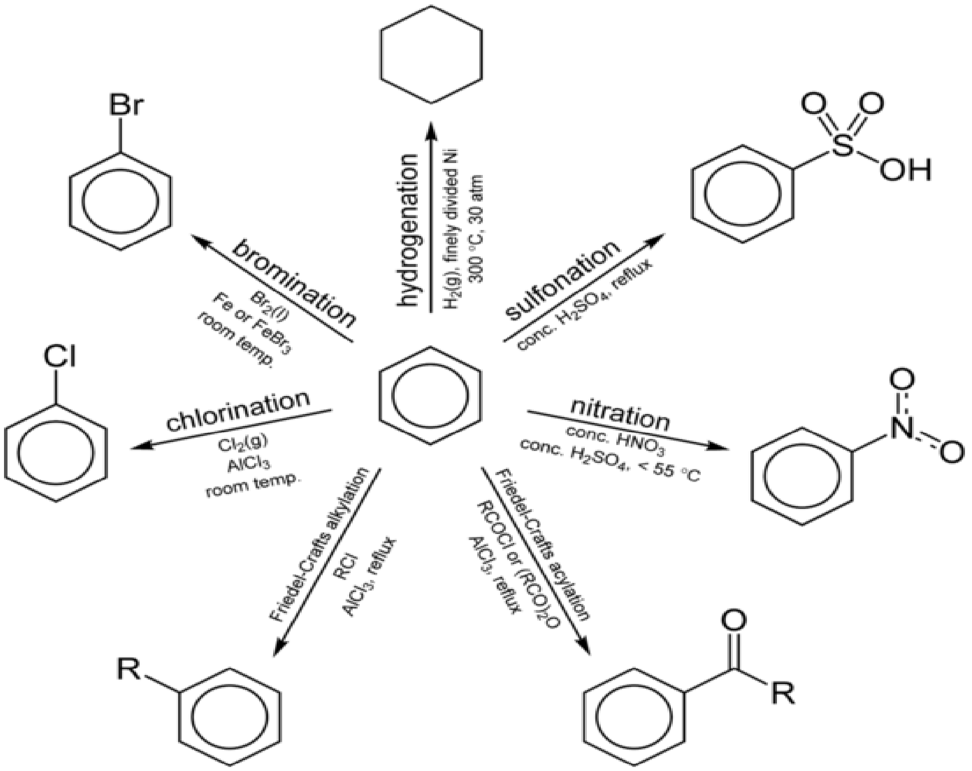
Hexachloro cycloHexane
(it is used as an insecticide and is very unstable)

3. Combustion reaction

As other hydrocarbons, benzene burns in air forming carbon dioxide (or carbon monoxide in a limited supply of air) and water.

$C_6H_6(l) + 15/2\ O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(l)$ or $C_6H_6(l) + 9/2O_2(g) \rightarrow 6\ CO(g) + 3\ H_2O(l)$

The following is a summary of benzene reactions



Application activity 2.5

Discuss and find out the answers to the following questions:

Benzene can be nitrated to form nitrobenzene, $C_6H_5NO_2$.

a) Draw the structural formula for benzene and give its empirical formula

b) State the reagents needed for the nitration of benzene

c) An electrophile is formed during the nitration of benzene

   i) What is the formula of this electrophile?

   ii) Write an equation for the production of the electrophile

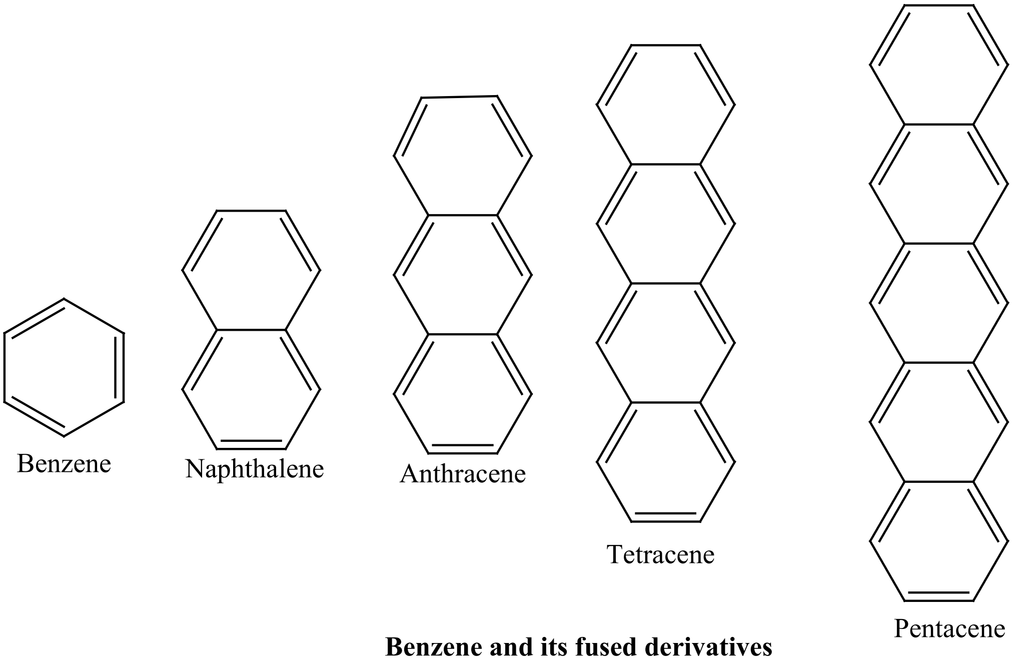
   iii) Use curly arrows to show the mechanism for the nitration of benzene

2.6. Nomenclature and positional isomerism in derivatives of benzene

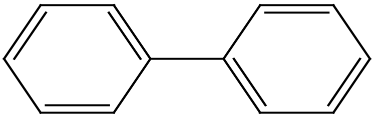
Activity 2.6

1. Name the following molecules:
   a) $CH_3CH_2CH(CH_3)CH_3$
   b) $ClCH_2CH_2CHOHCH_3$
   c) $CH_3CH(C_6H_5)CH_2CH_2CH_3$
   d) $C_6H_5NO_2$
   e) C_6H_4ClBr
2. Discuss about rules for naming aromatic compounds in this book or any other source (textbook or internet). Then, make a summary to be presented.

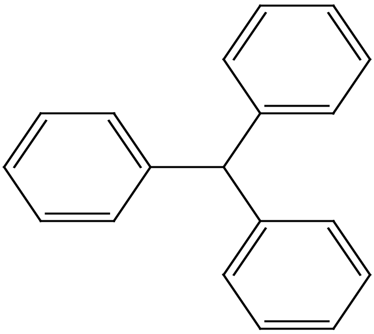
As you have seen from the previous lessons of this unit, benzene and its derivatives are referred to as aromatic compounds. The following diagram provides the structures of some aromatic compounds starting with benzene with one ring and then others with more than one ring and their respective names:



Benzene and its fused derivatives



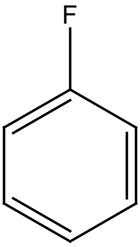
Biphenyl



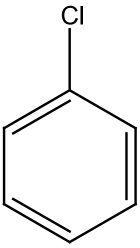
Triphenylmethane

Benzene derivatives, as seen, are obtained by replacing one or more hydrogen atoms on benzene ring with other substituent groups. According to the systematic nomenclature, the naming of benzene derivatives is purely based on the substitution part.

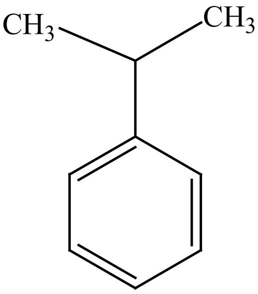
1. The IUPAC system of naming mono substituted benzene derivatives uses the name of the substituent as prefix to benzene. Examples: fluorobenzene, chlorobenzene, isopropyl benzene and ethyl benzene, and so on.



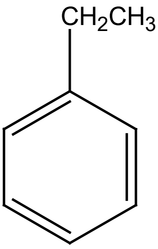
Fluorobenzene



Chlorobenzene

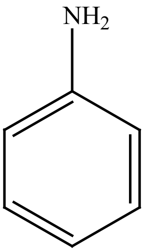


Isopropylbenzene

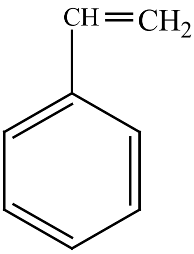


Ethylbenzene

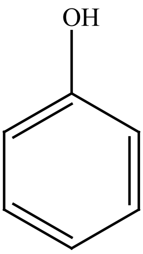
Some benzene derivatives have their traditional or popular names such as the following:



Aniline

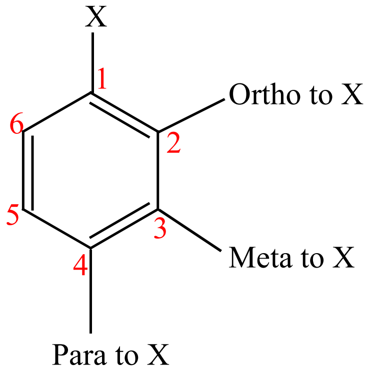


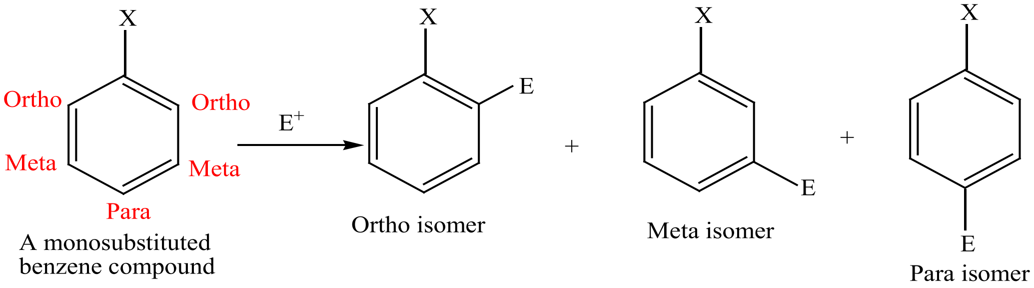
Styrene



Phenol

2. Di-substituted benzene derivatives with the prefixes “Ortho- or o-” for substituent groups on adjacent carbons (e.g, C1 and C2) in benzene ring. “Meta- or m-” for substituents separated by one carbon atom (e.g, C1 and C3). “Para- or p-” for substituent groups on carbons on opposite sides of ring (e.g, C1 and C4). The positions on the benzene ring are as follow

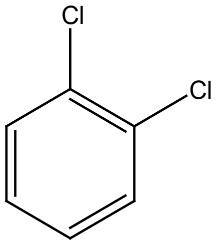




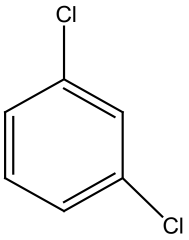
Benzene derivatives consisting of two substituents attached to the ring could be distinguished among three **positional isomers** (ortho- , meta- and para-isomers).

These are named either by numbers or by using non-numerical prefixes (Ortho, Meta and Para).

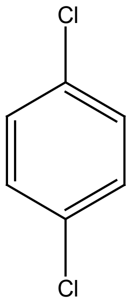
Notice that there are 2 identical ortho positions (2, 6), and 2 identical Meta positions (3,5).



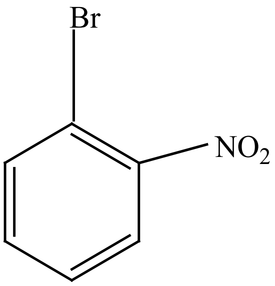
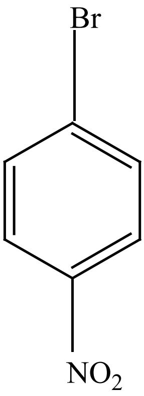
1,2-dichlorobenzene
or ortho-dichlorobenzene



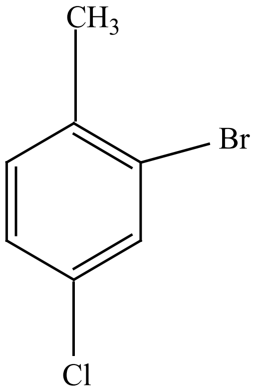
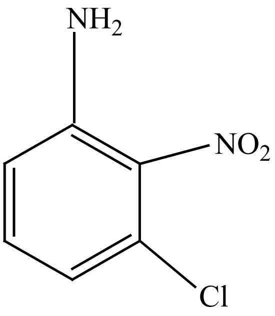
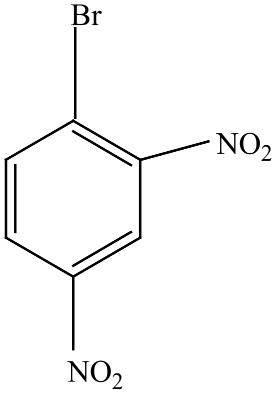
1,3-dichlorobenzene
or meta-dichlorobenzene



1,4-dichlorobenzene
or para-dichlorobenzene

 1-Bromo-2-nitrobenzene o-Bromonitrobenzene	 1-Bromo-4-nitrobenzene p-Bromonitrobenzene

3. When there is presence of more than two groups, ring substituent's positions are indicated with specific numbers. The ring thus gets numbered in a specific way in order to obtain the lowest number possible for these carbon atoms having substituents.

		
2-Bromo-4-chloromethylbenzene	3-Chloro-2-nitroaminobenzene	1-Bromo-2,4-dinitrobenzene

4. Some benzene derivatives are named by using their common names (or commercial names).

Table: Common and IUPAC names of some benzene derivatives

Substituent of benzene	Common name	IUPAC name
-CN	Benzonitrile	Benzenecarbonitrile
-OH	Phenol	Benzenol
–CH_3	Toluene	Methylbenzene
-COOH	Benzoic acid	Benzene carboxylic acid
–C_2H_2	Styrene	Vinyl benzene
–OCH_3	Anisole	Methoxybenzene
–NH_2	Aniline	Benzenamine
–SO_3H	Benzenesulphonic acid	Benzenesulphonic acid
-CHO	Benzaldehyde	Benzenecarbaldehyde

Application activity 2.6

Discuss and provide appropriate answers to the following questions:

1. You are provided with $C_6H_4Br_2$. Give three different structural formulae of isomers of $C_6H_4Br_2$ and name them.
2. Provide all the structures and names of compounds having the same molecular formula as Br-$C_6H_4NO_2$.

Skills Lab 2

1. Use internet or any other resources, and try to describe the different usage of benzene, where it can be found its difference from other organic compounds especially hydrocarbons and make conclusion on the research you made how special is benzene differently from others.

End of unit assessment 2

I. MULTIPLE CHOICE QUESTIONS: write the letter corresponding to the right answer.

1. Which of the following features is **not** characteristic of aromatic compounds?

   (a) They are planar.

   (b) They are cyclic

   (c) They contain an odd number of pairs of pi electrons.

   (d) The ring atoms must be carbon atoms.

   (e) They have an uninterrupted cloud of delocalized pi electrons.

2. What is the hybridization of the ring atoms in an aromatic compound?

   (a) s

   (b) sp^3

   (c) sp

   (d) p

   (e) sp^2

3. What kind of catalyst is essential for halogenation of aromatic compounds with Cl_2 or Br_2?

   (a) A Lewis acid

   (b) Light

   (c) A Lewis base

   (d) A Brönsted acid

   (e) A Brönsted base

   (f) Arrhenius acid

4. Why do aromatic compounds undergo electrophilic substitution rather than electrophilic addition?

   (a) Formation of the substituted benzene is highly exergonic.

   (b) Aromatic compounds are not very stable.

(c) The addition product is much less stable than the substitution product, since it is non-aromatic.

(d) Aromatic compounds are not nucleophiles.

5. Resonance forms are in equilibrium with each other. State true or false
   (a) True
   (b) False

6. Identify the incorrect statement regarding aromaticity
   (a) It is the extra stability possessed by a molecule
   (b) p-orbitals must be planar and overlap
   (c) Cyclic delocalization takes place
   (d) It does not follow Huckel's rule

7. Aromatic rings do not have resonance structures. State true or false
   (a) False
   (b) True

8. Select the incorrect statement:

   (a) A resonance may sometimes cause sp3 atoms to become sp2 hybridized

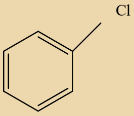
   (b) Delocalizing one lone pair causes aromaticity

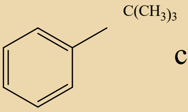
   (c) One lone pair will be counted as two pi electrons according to Huckel's equation

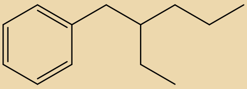
   (d) Two sigma bonds make up a double bond

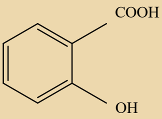
II. OPEN QUESTIONS

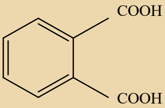
1. Give the proper ***IUPAC*** name for each of the compounds shown below.

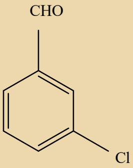
a)


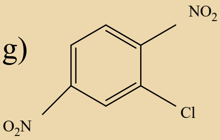
b)


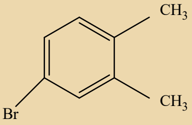
c)


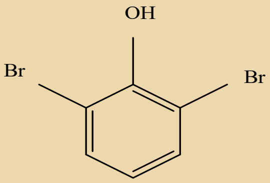
d)


e)


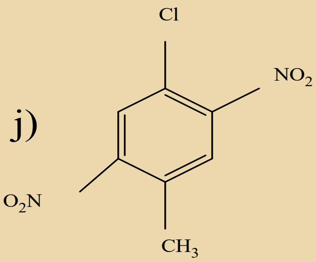
f)


g)


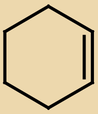
h)


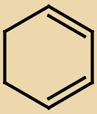


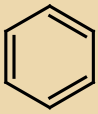
j)



2. Draw the structure corresponding to each of the following ***IUPAC*** names.
   (a) Ortho-bromopropylbenzene
   (b) 2, 3, 5-trinitrophenol
   (c) 1-fluoro-2, 4- dinitrobenzene
   (d) (1-bromoethyl) benzene
   (e) 2-methyl-6-phenylheptane
   (f) 1-Bromo-2,4-diethylbenzene
   (g) Sulfanilic acid
   (h) Benzaldehyde
   (i) Benzyl bromide
   (j) Vinyl benzene
3. Give four reasons for unusual stability of benzene.
4. Compare the stability of cyclohexene, 1, 3-cyclohexadiene, and benzene based on heat of hydrogenation.







5. What type of reactions benzene and benzene derivatives typically undergo? Provide at least two examples.

6. a)Bromine reacts with benzene in the presence of a suitable catalyst.

   (i) Give the name or formula of a suitable catalyst for this reaction.

   (ii) State the general name of this type of catalyst.

   (iii) Write a balanced equation for this reaction.

   (iv) State the name of the product obtained.

   (v) The reaction between bromine and benzene is an electrophilic substitution reaction. Outline the likely mechanism for this reaction. Show clearly all the curly arrows as well as the structures of the intermediate and the products.

   b) Bromine reacts much more readily with cyclohexene than it does with benzene.

   The reaction with cyclohexene does not need a catalyst.

   - Describe with the aid of diagrams, the bonding in cyclohexene and benzene.
   - Use your answer to explain why bromine reacts much more readily with cyclohexene than it does with benzene.

7. The nitration of benzene is an important industrial reaction.

   (a) State the conditions required for the nitration of benzene using nitric acid.

   (b) Write a balanced equation for the nitration of benzene.

   (c) (i) Outline the mechanism for the nitration of benzene.

   (ii) Explain what curly arrow means in this type of mechanism.

   - Give the name of the NO_2^+ ion and state its function in the mechanism of nitration of benzene.

UNIT
3

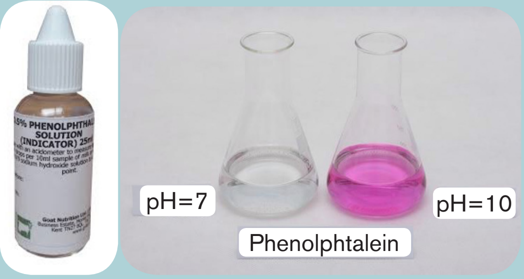
DERIVATIVES OF BENZENE

Key Unit Competence:

Compare and explain chemical reactivity of aromatic ketones, aldehydes, carboxylic acids and amines.

Introductory activity

Observe carefully the following pictures and answer the questions below:

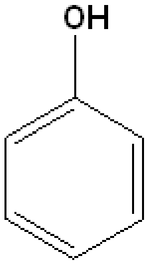
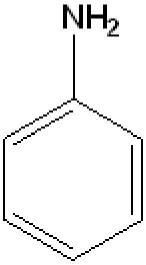
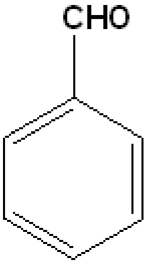
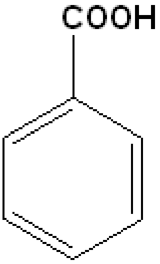
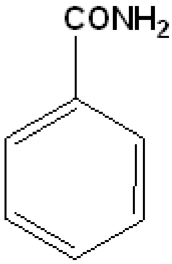
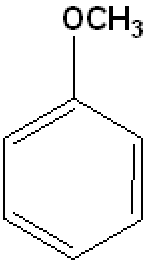
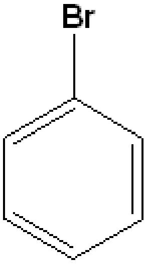
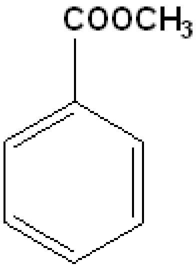
	
Aspirin	**Phenolphthalein**
	
Detergent	**Quinine**
	
DDT	**Dettol**

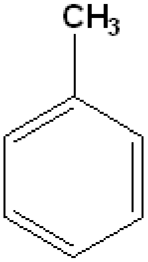
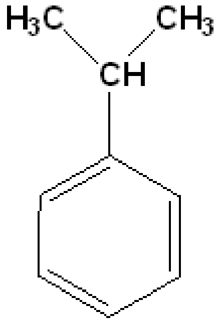
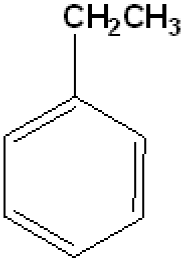
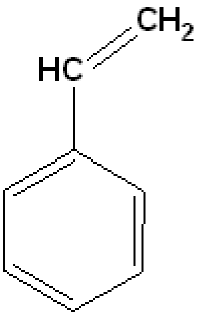
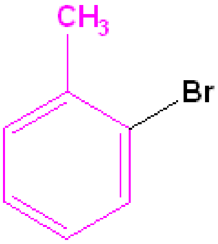
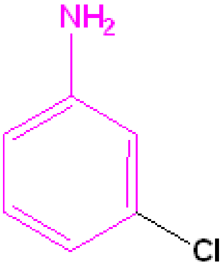
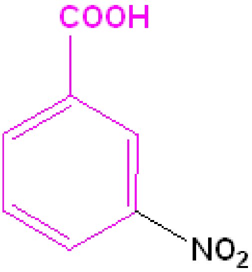
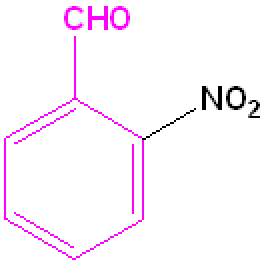
1. State the uses of the above substances
2. Make a research (in books or internet) and then suggest the chemical formulae of the above substances
3. Identify the similarities, if any, in their formulae.
4. Suggest other similar compounds.

The simplest and most important member of aromatic hydrocarbons is ***benzene* (*C_6H_6*).** The benzene ring is particular because of its stability and certain properties.

Many important chemical compounds are derived from benzene by replacing one or more of its hydrogen atoms with another functional group. It is a typical compound from which **many of compounds** of common properties derive.

Some examples of derivatives of benzene are given below:

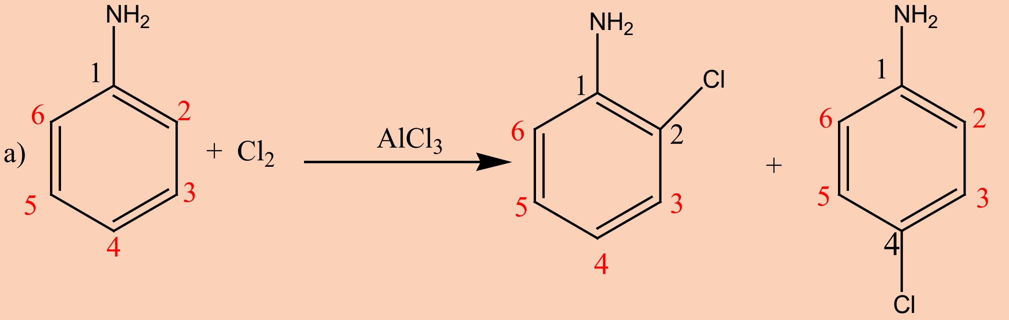
			
Phenol (Hydroxybenzene)	Aniline (Aminobenzene)	Benzaldehyde	Benzoic Acid
			
Benzamide	Anisole	Bromobenzene	Methylbenzoate

			
Toluene (Methylbenzene)	Cumene (Isopropyl benzene)	Ethylbenzene	Styrene (Vinylbenzene)
			
Toluene is the parent name	Aniline is the parent name	Benzoic acid is the parent name	Benzaldehyde is the parent name
2-Bromotoluene	3-Chloroaniline	3-Nitrobenzoic acid	2-Nitrobenzaldehyde
o-Bromotoluene	m-Chloroaniline	m-Nitrobenzoic acid	o-Nitrobenzaldehyde

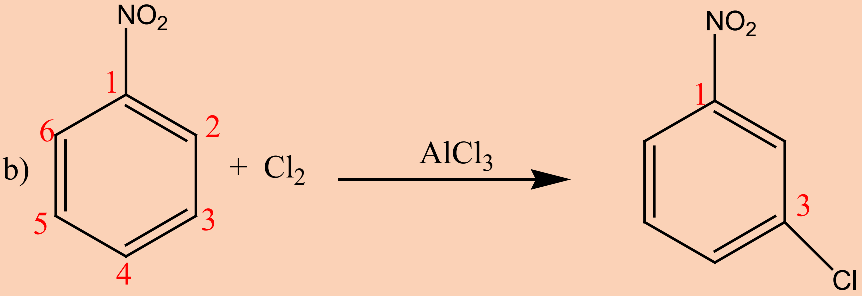
3.1. Effect of substituent groups on the benzene ring

Activity 3.1

1. When aminobenzene reacts with chlorine in the presence of Lewis acid such as $AlCl_3$ or $FeCl_3$, two major products shown below are produced:



when nitrobenzene, reacts with chlorine in the presence of Lewis acid such as $AlCl_3$ or $FeCl_3$, only one major product shown below is produced:



After comparing the two reactions, it was found that aniline is more reactive than nitrobenzene with chlorine respectively.

Using different books or internet make a research and find out why:

1. Aminobenzene is more reactive than nitrobenzene towards chlorine and all other electrophiles.
2. In reaction (a) the second substituent is oriented in ortho and para positions.
3. In reaction (b) the second substituent is oriented in only Meta position
4. In your research, find other substituents attached to benzene ring which orient second substituent in ortho and para positions; find other substituents attached to benzene ring which orient second substituent in Meta positions. .

The nature of a substituent already present in the benzene ring, not only determines the position of the next incoming group but also influences the rate of the second substitution reaction compared to the rate of substitution in benzene itself.

A substituent might increase the rate of the second substitution reaction, i.e. make the ring more reactive relative to benzene. Another group if present in benzene ring could decrease the rate of further substitution reaction, i.e. make the ring less reactive compared to benzene.

Groups already on the ring affect both the rate of the reaction and the site of attack. We say, therefore, that substituent groups affect both **reactivity** and **orientation** in electrophilic aromatic substitutions.

3.1.1. Deactivating and activating substituents

We can divide substituent groups into two classes according to their influence on the reactivity of the ring. The substituents which cause the compounds to undergo second substitution faster than benzene are called **Activating Substituents** (**electron-releasing groups**); they increase the electronic density on the benzene ring. On the other side, substituents which retard the rate of further substitution are referred to as **Deactivating Substituents** (**electron-withdrawing groups**); they decrease the electronic density on the benzene ring.

Examples

Activating Substituents (Activators)	**Deactivating Substituents (*Deactivators*)**
$-NH_2$, - NHR, - NR_2, - OH, -NHCOR, -OR, -R, -Ar, $-CH=CR_2$ (Alkenyl),	-CN, $-SO_3H$, $-CO_2H$, $-CO_2R$, -CHO, -COR, $-NO_2$, $-CF_3$, $-CCl_3$, Halogens (-F, -Cl, -Br, -I)

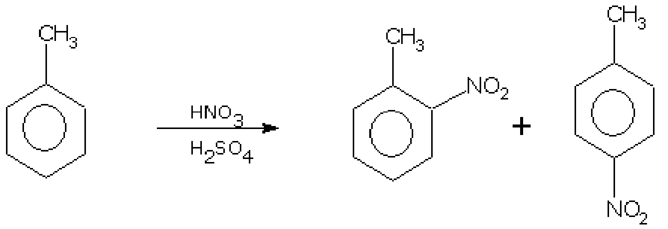
3.1.2. Regioselectivity

During the formation of monosubstituted products in benzene, the electrophile can be attached at any position on the benzene ring. But, when the monosubstituted product is to be converted into disubstituted one, the substituent already present in the ring directs the incoming group to a particular position. This is referred to as **directive influence of the group** or **regioselectivity**. Depending on their directive influence, various groups (substituents) can be divided into two categories:

- Ortho and Para Directors
- Meta Directors

a) Ortho and Para Directors

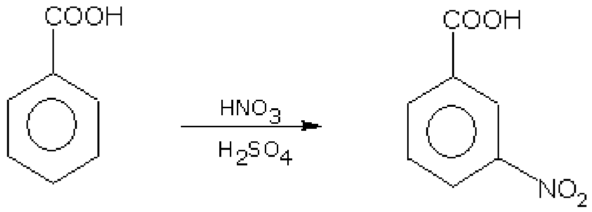
These direct the new substituents to enter the ring primarily in **Ortho** and **Para** positions to themselves. These groups increase the electron density at the ring. Thus the reactivity of benzene ring towards electrophilic substitution reactions increases. Therefore, all Activators are Ortho and Para directors. For example if we carry out nitration of toluene, the mixture of ortho and paranitrotoluenes is formed.



Toluene o-Nitrotoluene (30%) p-Nitrotoluene (70%)

b) Meta Directors

These direct the new substituents to enter the ring primarily in **Meta** position to themselves. For example, the nitration of benzoic acid produces **m**-nitrobenzene.



Benzoic acid m-Nitrobenzoic acid

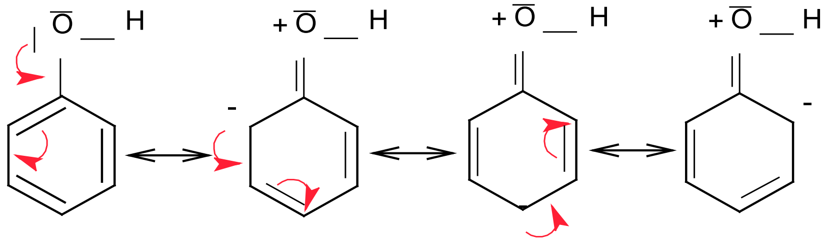
These groups withdraw the electrons from benzene ring reducing the electron density at the benzene ring. They decrease the reactivity of benzene ring towards electrophilic substitution reaction and make it less susceptible to the electrophilic attack. Therefore, all Deactivators are Meta directors.

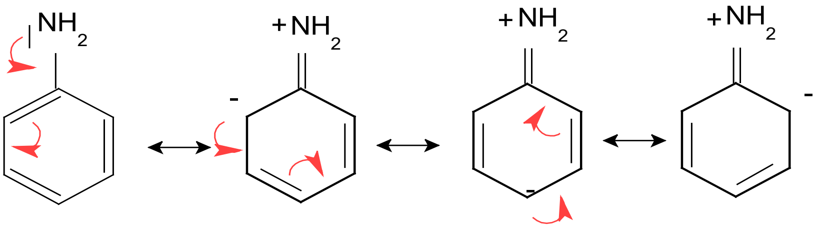
i) Explanation on the activators Regioselectivity

When the substituent present on the ring, has one or more lone pairs of electrons on the atom attached to the ring, it interacts with ϖ-electron system of the ring by providing its lone pair and it acts as electron donor (electron-donating substituent).

The presence of an electron-donating group such as –OH or -NH_2 activates the ring and causes further electrophilic substitution in ortho-para positions.

Let us take the example of phenol (C_6H_5-OH) and aniline (C_6H_5-NH_2) which have available electron pairs on the atom directly attached to benzene ring. Thus phenol and aniline exhibit resonance and can be represented as hybrid of the following forms:





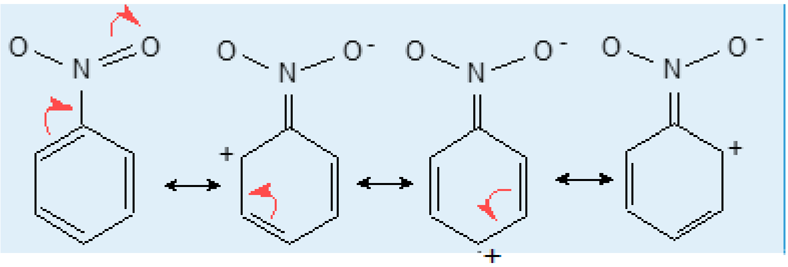
In the above two examples, positions 2 and 4 are relatively richer in electrons than position 3 and this makes them susceptible to electrophilic attack. The electrophile would attack the ring preferentially at ortho and para positions where the electron density relatively is greater as compared to the meta positions. The second electrophile will be directed where sites are negatively charged, i.e ortho and para positions.

From the above considerations, we conclude that all groups which are electron-donating are ortho-para directing and facilitate electrophilic substitution in the benzene ring.

ii) Explanation on the deactivators Regioselectivity

When the substituent has at least one strongly electronegative atom and/or a multiple bond in conjugation with benzene ring, the substituent acts as electron-withdrawing substituent.

Consider the nitrobenzene which contains $-NO_2$ is able to exist as the following resonance forms:



In the above example, it may be noted that resonance causes the decrease of electron density in the ring of nitrobenzene, and specifically at the ortho and para positions.

In general, the electron withdrawing substituents decrease the electron density of benzene ring and thereby act as deactivators and meta-directors.

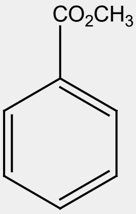
iii) Anomalous Behavior of Halogen Substituents

Halogens possess many electrons which would activate the ring, but contrary they have higher electronegativities which make them to be deactivators. These two properties are respected and they are the deactivators but ortho and para directors.

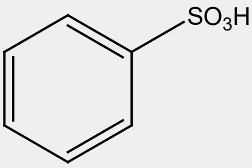
Application activity 3.1

1. Explain how the following substituents attached to benzene ring are going to direct further substitutions.

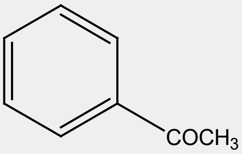
a)



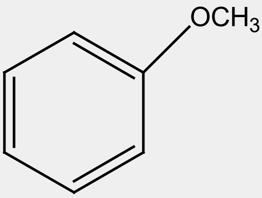
b)



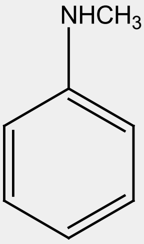
c)



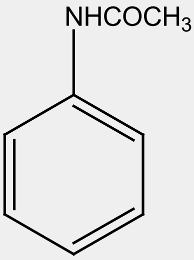
d)



e)



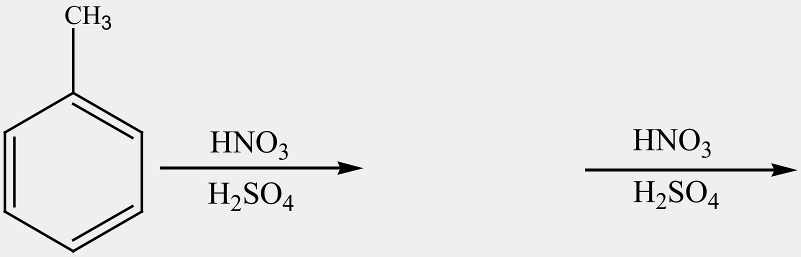
f)



2. Classify the following as ortho, para orienting and meta orienting substituents:

   Methyl, nitro, cyano, methoxyl.

3. Explain the following statement: Chlorine is deactivating, yet it is ortho and para-directing in electrophilic aromatic substitution reactions.
4. Predict the major product for the following reaction:



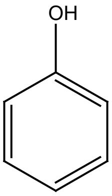
3.2. Phenol

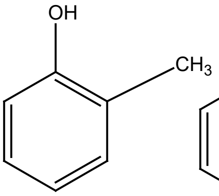
Activity 3.2

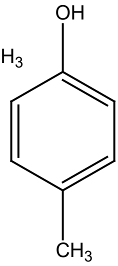
Aspirin, phenolphthalein indicator, Dettol, and other many compounds like dyes are produced from a substance containing only one hydroxyl (-OH) group attached to benzene ring. Make a research and find out:

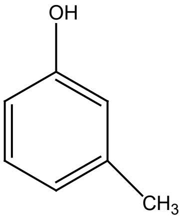
1. The name and the structural formula of this substance
2. Its physical and chemical properties
3. The uses of that very important substance.

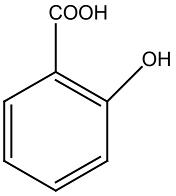
The phenols are organic compounds with one or more groups directly attached to a carbon atom in a benzene ring. The following are examples of phenols:

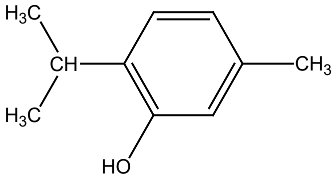

Phenol


2-Methyl phenol
O-methyl phenol
O-Cresol


P-cresol

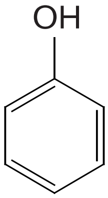

Meta-cresol


2-hydroxy benzoic acid
salicylic acid


2-Isopropyl 5-Methyl phenol
Thymol

Phenols occupy an important position in the modern synthetic organic chemistry for the preparation of dyes, antioxidants, phenolic resins and certain pharmaceutical products.

The most important member in this family is phenol (hydroxybenzene):



Phenol (hydroxybenzene) is a colorless crystalline solid which melts at 43°C and boils at 182°C. On exposure to air or light, it becomes colored due to oxidation.

Phenol is soluble in organic solvents and slightly soluble in water at room temperature, but infinitely soluble above 66 °C.

Phenol exhibits intermolecular hydrogen bonding and this makes its melting point higher than that of hydrocarbons of comparable molecular mass.

3.2.1. Sources and preparations of phenol

Activity 3.2.1

Complete equations of reactions that follow:

a) CH_3-CH_2-NH_2 + HNO_2 + HCl

b) Benzene + CH-CH_2-CH=CH_2/H^+

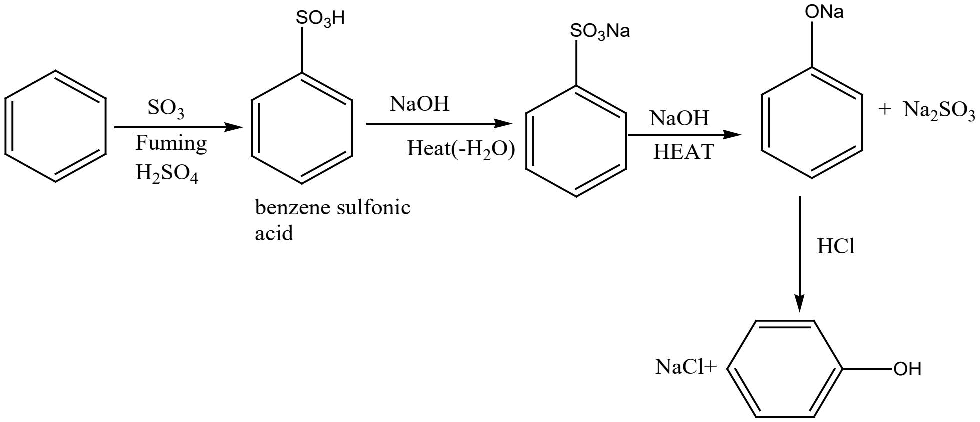
Phenols are common in nature; examples include tyrosine, one of the standard amino acids found in most proteins. Many of the more complex phenols used as flavorings and aromas are obtained from essential oils of plants. Other phenols obtained from plants include thymol, isolated from thyme, and eugenol, isolated from cloves.

Phenol, the cresols (methylphenols), and other simple alkylated phenols can be obtained from the distillation of coal tar or crude petroleum.

Phenol can be prepared:

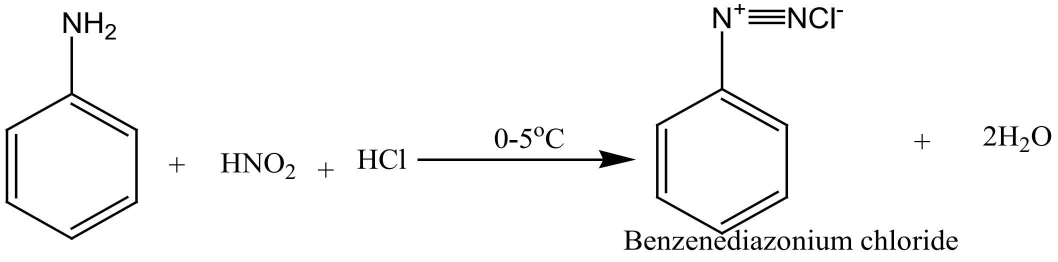
a) From benzene sulfonic acid

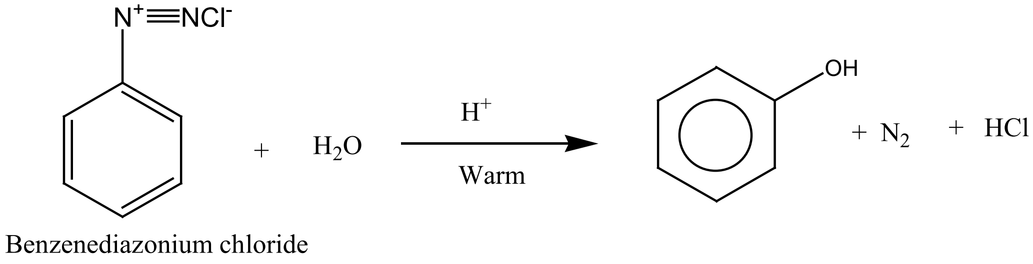
In this method, benzenesulphonic acid obtained from sulphonation of benzene reacts with sodium hydroxide to produce phenol.



b) From aniline via diazonium salts

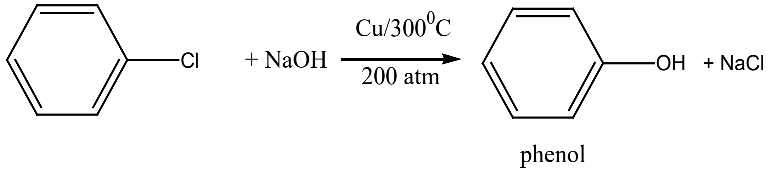
On warming a diazonium salt solution with diluted acid, phenol is obtained.





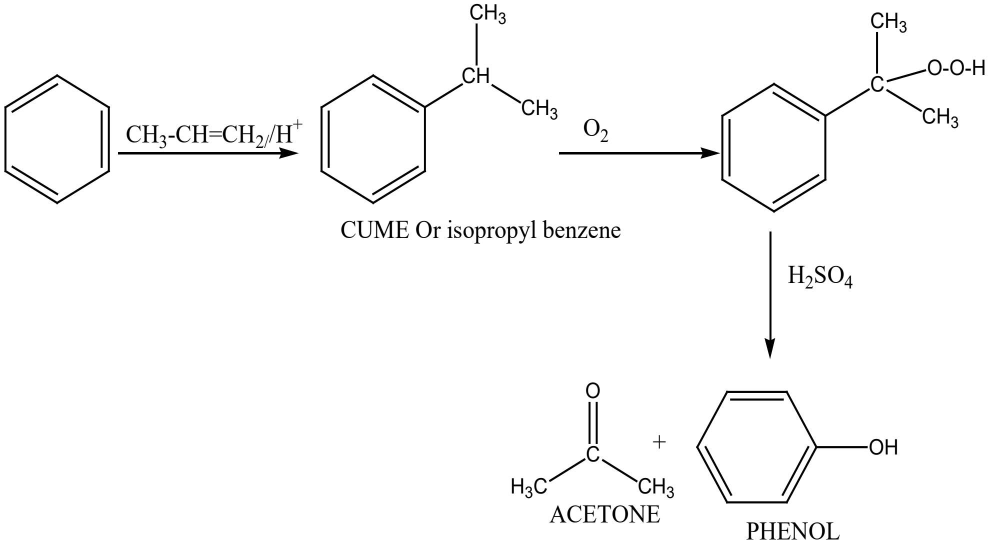
c) From aromatic halides

Phenol can be prepared by heating aromatic halides with caustic soda at temperature of 300°C and pressure of about 200 atmospheres in the presence of copper as catalyst.



d) By cumene process

Isopropyl benzene or cumene is treated with air and concentrated H_2SO_4.



Application activity 3.2.1

Write equations to show how to prepare phenol from benzene, aniline, aromatic halides and cumene.

3.2.2. Acidity of phenol

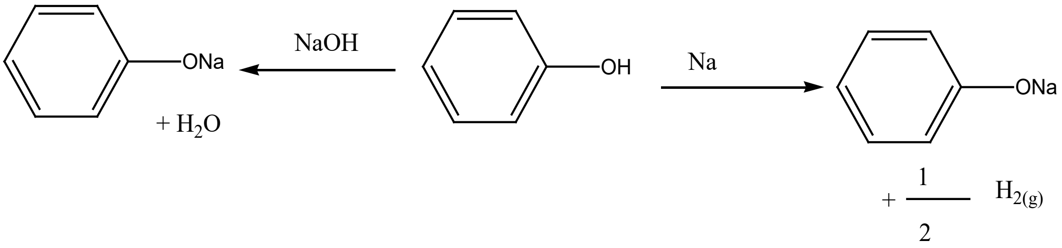
Activity 3.2.2

- Dissolve 5g of phenol in 20 mL of distilled water and put that aqueous solution in the beaker number 1,
- Put 20ml of ethanol in the beaker number 2,
- Put 20ml of ethanoic acid in the beaker number 3,

Put a blue a litmus paper in each beaker and note down your observations then explain.

The O-H bond is weaker in phenol than in alcohol. This is because the lone pair of electrons on the oxygen atom becomes associated with delocalized electrons of the ring. Because of this partial double bond develops between carbon and oxygen with the result that C-O bond is strengthened and the O-H weakened as the electronic density is displaced towards the ring. This gives to phenol a more acidic nature than alcohols.

Therefore, phenol is more acidic than phenylmethanol and ethanol or cyclohexanol and this explains why phenol and not cyclohexanol nor phenylmethanol is soluble in sodium hydroxide solution. Because of this acidic property, phenol unlike alcohols reacts with alkali metal and sodium hydroxide or potassium hydroxide solution. Alcohols are not acidic enough to react with sodium hydroxide or potassium hydroxide solution but react only with alkali metal.



Note: Phenol is a weaker acid it does not react with sodium carbonate or sodium hydrogen carbonate unlike carboxylic acids. The reaction with sodium carbonate or sodium hydrogen carbonate is also used to distinguish a carboxylic acid like benzoic acid from a phenol. Carboxylic acids give effervescence (liberate CO_2) with sodium carbonate or sodium hydrogen carbonate while phenols do not.

Application activity 3.2.2

Explain why phenol is more acidic than alcohols

3.2.3. Reactions of phenols

Activity 3.2.3

1. Is the hydroxyl group OH ortho, meta and or para orientor, activator or desactivator group?

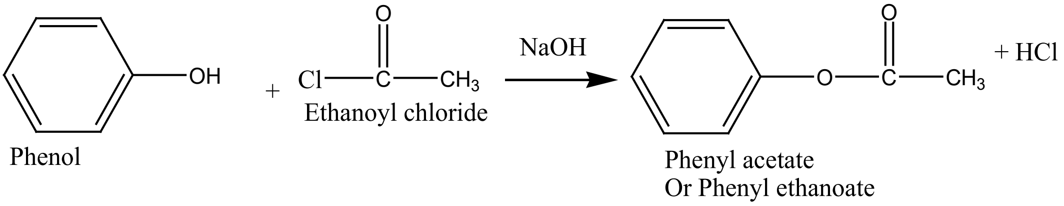
The reactions of phenol are of two types:

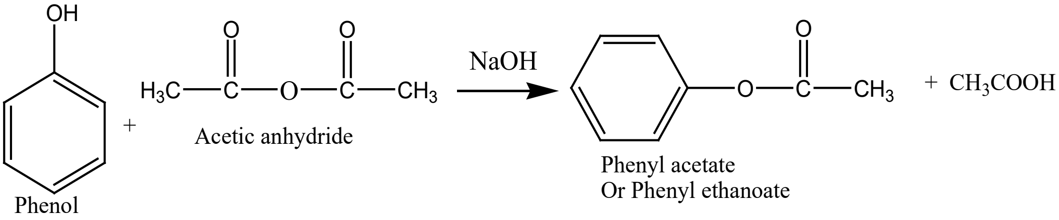
i) Reactions in which the O-H is broken;

ii) Those involving the aromatic ring (Electrophilic substitution reactions).

a) Esterification

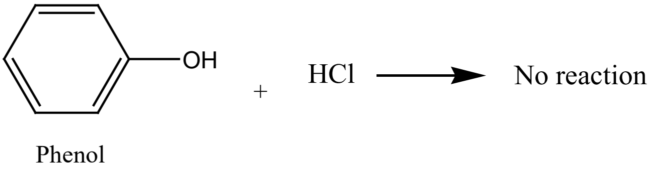
Phenols are weaker nucleophiles compared to alcohols because their lone pairs of electrons are partially delocalized over the benzene ring; that is why they do not form esters by direct reaction with carboxylic acids. However, the phenoxide ion ($C_6H_5O^-$) is a better nucleophile and it reacts with acid derivatives such as **acid chloride** or **acid anhydride,** which are themselves more reactive than the parent acid:



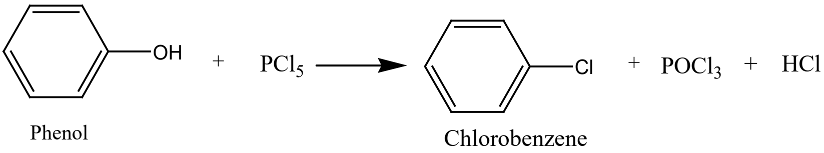


b) Replacement of OH by Halogens

Unlike alcohols, phenolic OH cannot be replaced by halogen by reaction with hydrogen halides.



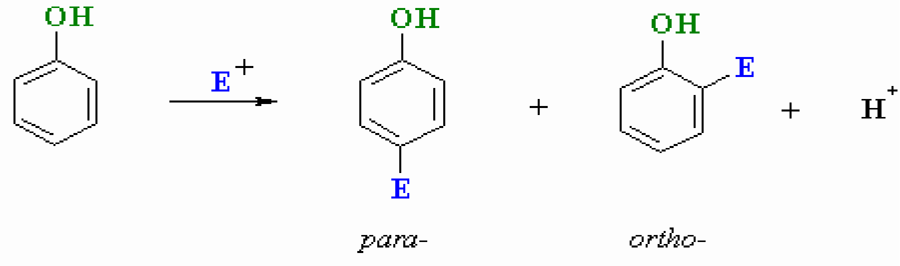
However, PCl_5 or PBr_5 reacts with phenol to form aryl halide:



c) Electrophilic substitution reactions of phenol

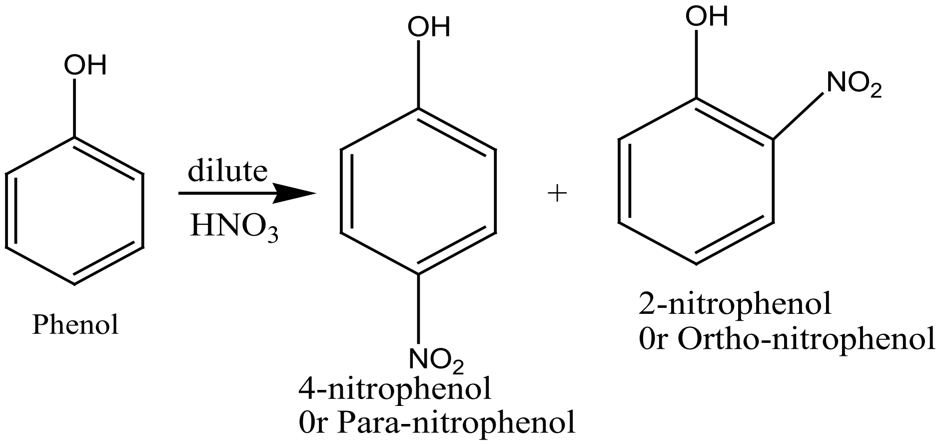
These reactions involve the replacement of hydrogen atoms at **Para** and **Ortho positions** of the ring, since the –OH is a an activator and ortho-para directing. The hydroxyl group increases the availability of electrons in the aromatic ring especially at para and ortho positions.

Because of this ring activation, phenols react more readily with electrophiles than benzene itself.

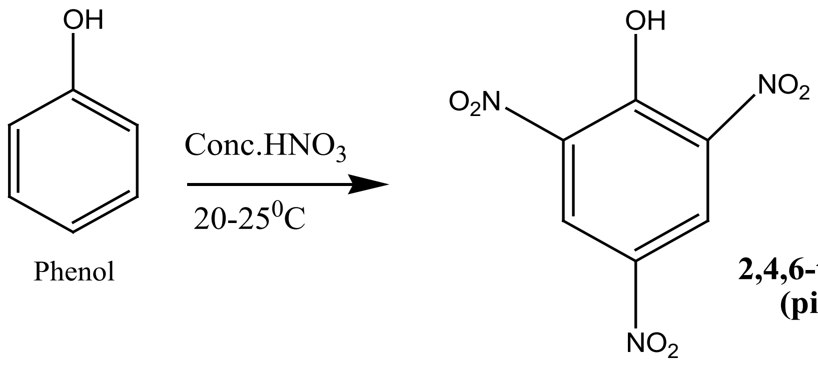


i) Nitration

At room temperature, phenol reacts with dilute nitric acid to yield a mixture of 2-nitrophenol and 4-nitrophenol:

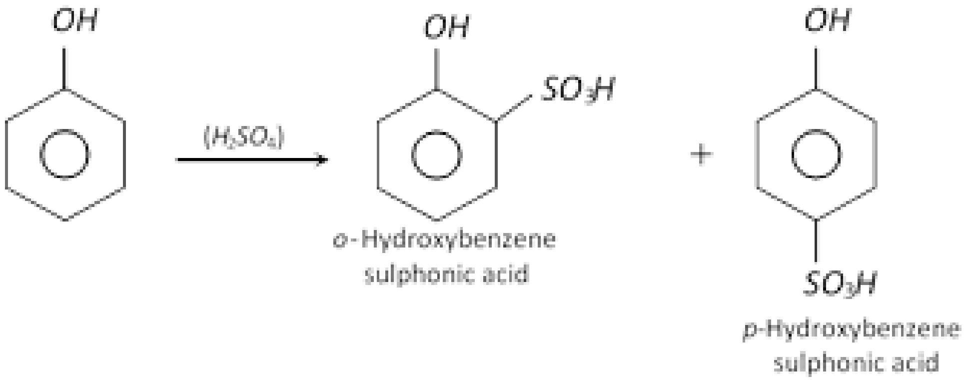


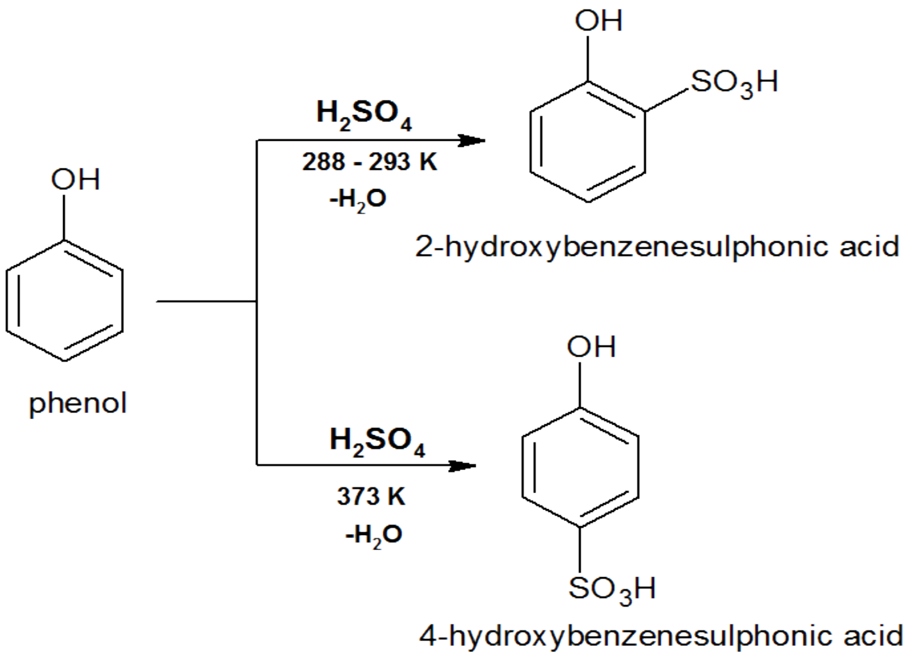
With concentrated nitric acid, phenol forms a yellow crystalline solid known as 2,4,6-trinitrophenol (**picric acid**) widely used in the manufacture of explosives and in solution as a yellow dye.



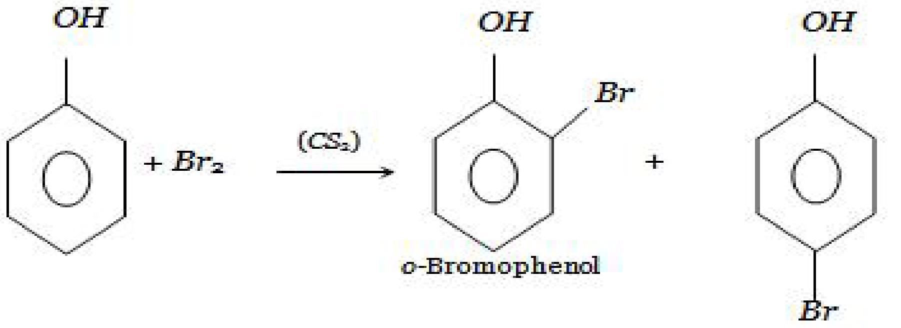
2,4,6-trinitrophenol (picric acid)

ii) Sulphonation

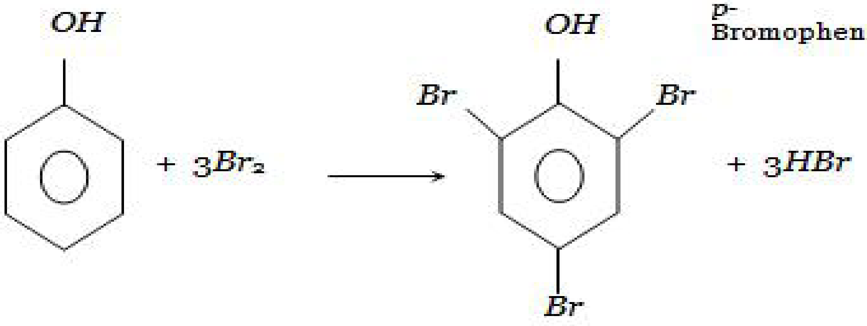




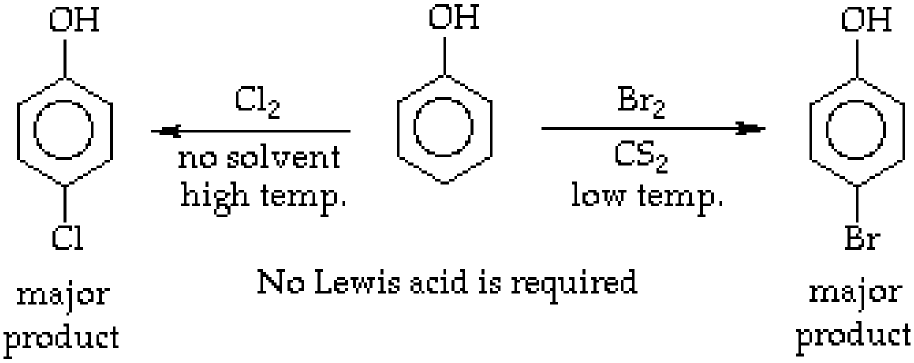
iii) Halogenation



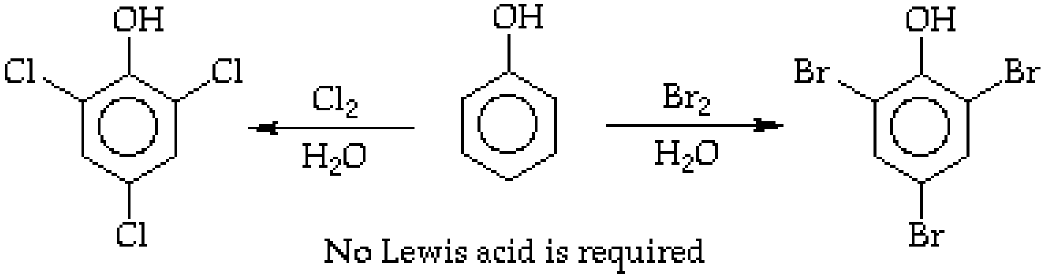
p-Bromophenol



2, 4, 6-Tribromophenol

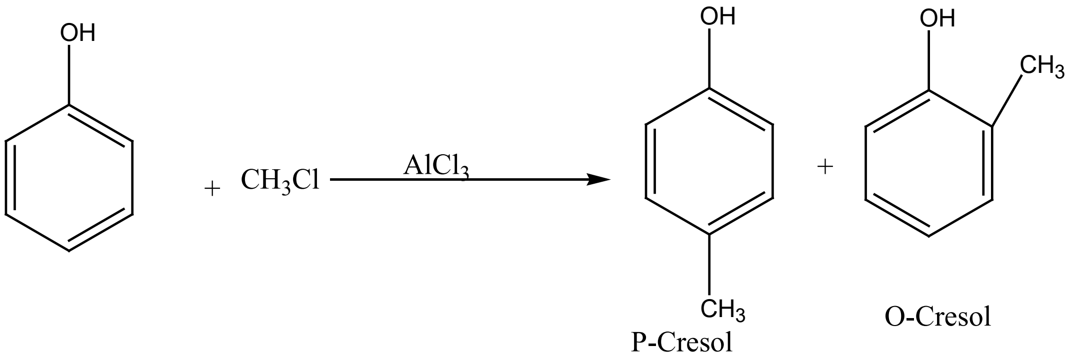


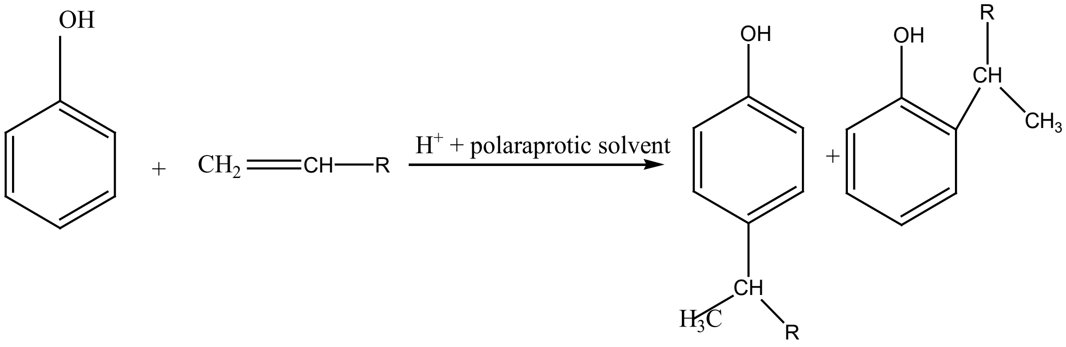
No Lewis acid is required



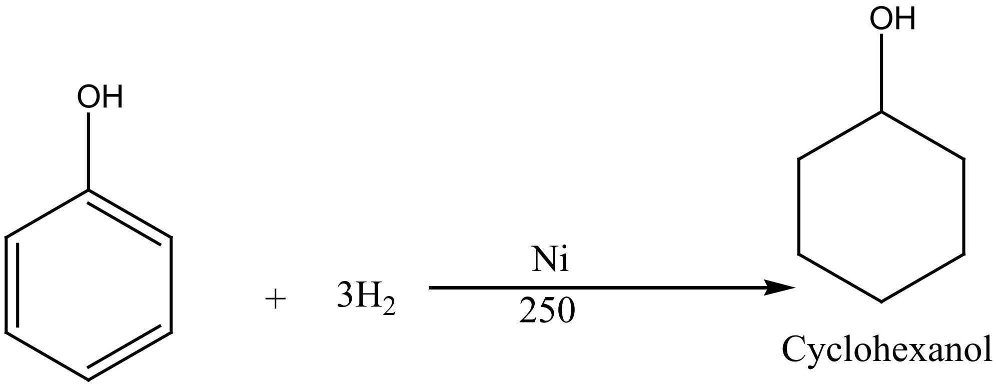
No Lewis acid is required

iv) Alkylation



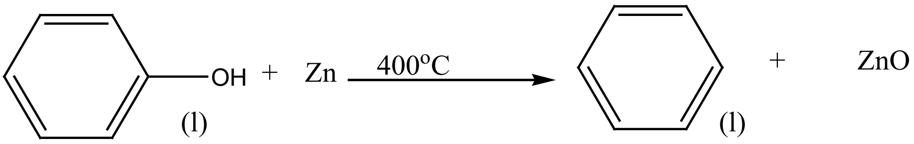


v) Hydrogenation



vi) Reduction

Phenol can be reduced by heating molten phenol with zinc dust (powdered zinc) to produce benzene.



3.2.4. Test and uses of phenol

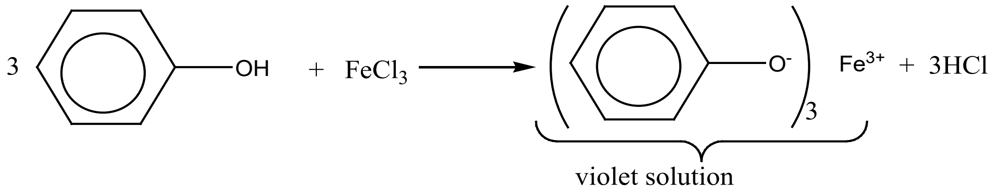
Activity 3.2.4

Put 5 mL of phenol in a test tube and add drop by drop bromine water. Write your observations and use books or internet for interpretation of your observations. Research other ways of testing the presence of phenol.

a) Chemical tests of phenol

i) Reaction with $FeCl_3$

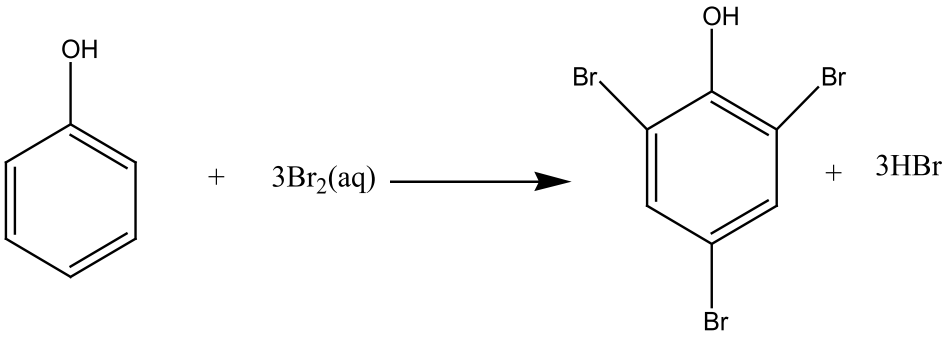
Phenol, unlike alcohols, reacts with aqueous neutral ferric chloride (iron (III) chloride) to form colored complexes. The product is mainly of violet color. This reaction is used to distinguish phenol from tertiary alcohol since formation of ***violet product*** with $FeCl_3$ confirms phenol.



$$C_6H_5OH(l) + FeCl_3(aq) \longrightarrow \underset{\textbf{Violet complex}}{C_6H_5O^-FeCl_2^+} + HCl$$

ii) Reaction with bromine water

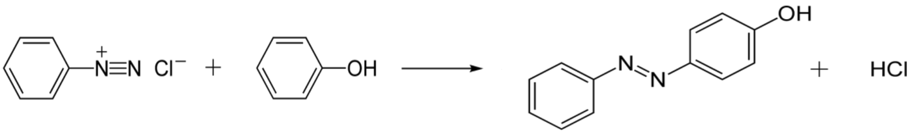
Add dropwise bromine water to aqueous solution of phenol, the ***white precipitate*** of 2, 4, 6-tribromophenol is formed



White precipitate

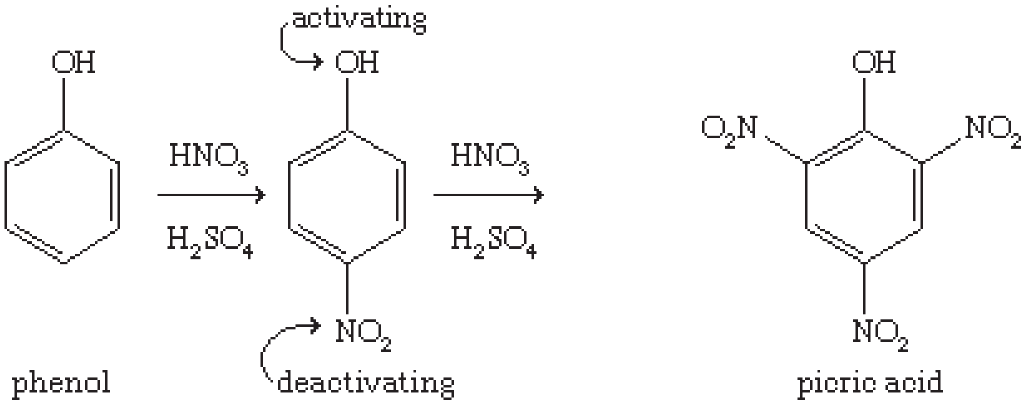
iii) Coupling with diazonium ions

Add dropwise solution of benzene diazonium chloride to aqueous solution of phenol, ***orange precipitate*** is formed.



b) Uses of phenol

- The major use of phenol is its conversion to plastics or related materials. Phenol condenses with aldehydes to form phenol-aldehyde derivatives which are useful plastics for example phenol-methanal plastic (**Bakelite**).
- Phenol is used in the manufacture of picric acid (used as a yellow dye) and other azo dyes when phenol reacts with diazonium compounds
- Phenol is a low material for the manufacture of explosives as shown in the following equation



Picric acid (2,4,6-trinitrophenol) is an explosive that was used in world war I.

- Phenol is a starting material for the manufacture of weed killers (example: 2,4-dichlorophenoxyethanoic acid known as 2,4-D).
- Phenol is used in the manufacture of phenolphthalein indicator ($C_{20}H_{14}O_4$).
- Phenol is also used in the manufacture of antiseptics (example: 2,4-dichloro-3,5-dimethylphenol which is present in "**Dettol**")
- Phenol is used as an oral anesthetic/analgesic in the treatment of throat infections.

Application activity 3.2.4

1. Explain the following observations:

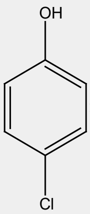
   (a) Phenol is a strong acid than phenylmethanol

   (b) Phenoxide ion is a weaker base than ethoxide ion

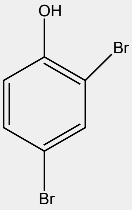
   (c) 4-nitrophenol is less volatile than 2-nitrophenol

2. Name the following compounds:

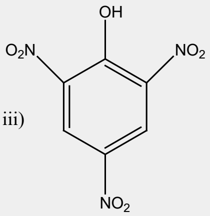
i)



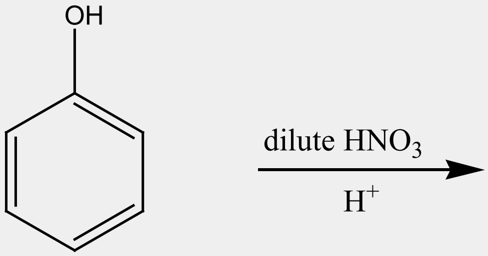
ii)



iii)



3. Predict the major product of the following reaction:



3.3. Aromatic hydrocarbons

Activity 3.3

a) What is a hydrocarbon compound?

b) Write general balanced equations of the reactions described and name the mechanism of the reaction.

   i) An alkane reacts with a halogen in the presence of light. Name the mechanism of the reaction.

   ii) An alkene reacts with hydrogen and halogenoacids. State the conditions of the reaction and name their mechanisms.

An **aromatic hydrocarbon** or **arene** (or sometimes **aryl hydrocarbon)** isa hydrocarbon with sigma bonds and delocalized π electrons between carbon atoms forming a circle. In contrast, aliphatic hydrocarbons lack this delocalization.

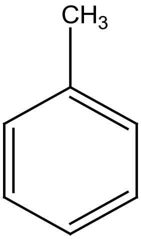
3.3.1. Structure and nomenclature of aromatic hydrocarbons

The trivial name of the parent monocyclic arene is benzene. The other members of this class are a large extent assigned the systematic IUPAC names. However IUPAC has adopted the trivial names of lower arenes particularly, which have become popular by long usage. This has been done for brevity and convenience. Thus methylbenzene is invariably named as **Toluene.**

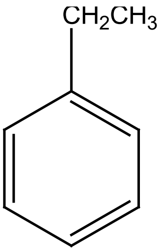
a) Structure and nomenclature of aromatic alkanes

In the IUPAC system, arenes of this class are named in straight forward manner as substituted-benzenes.

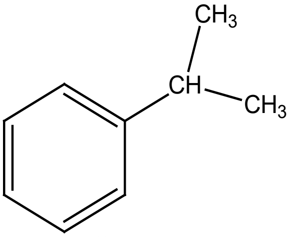
For example,



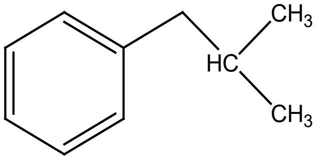
methylbenzene
(TOLUENE)



ethylbenzene

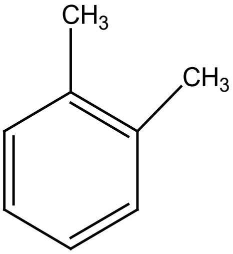


isopropylbenzene
(CUMENE)

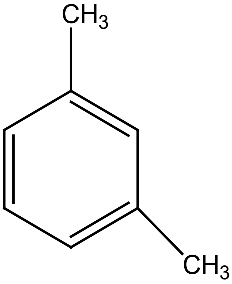


isobutylbenzene

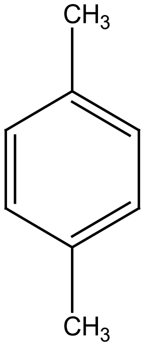
When there are two substituents on the benzene ring, then positions are indicated by numbers, or by the prefixes ***ortho* (o-), *meta* (m-)** and ***para* (p-).** Thus the isomeric dimethylbenzenes are named as:



1,2-dimethylbenzene
(o-XYLENE)

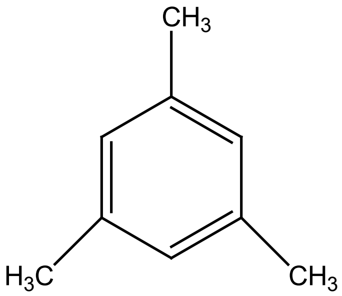


1,3-dimethylbenzene
(m-XYLENE)

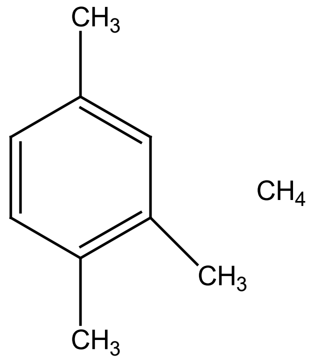


1,4-dimethylbenzene
(p-XYLENE)

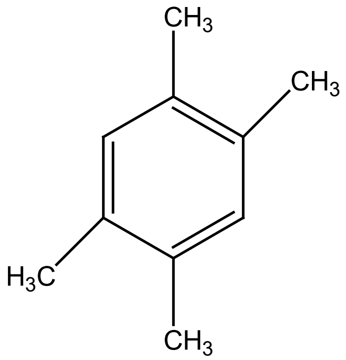
If there are three or more substituent groups present on the ring, the arenes are preferably designated by IUPAC names. One of the groups is written at the top position of the hexagon, which becomes number 1. The six carbon atoms of the benzene are then numbered from 1 to 6 around the ring so that the substituents groups get the lower numbers. The substituent groups are preferably named in the alphabetical order. Thus,



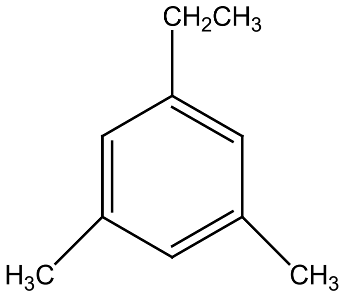
1,3,5-trimethylbenzene
(MESITYLENE)



1,2,4-trimethylbenzene
NOT 1,3,4-trimethylbenzene



1,2,4,5-tetramethylbenzene
NOT 1,3,4,6-tetramethylbenzene

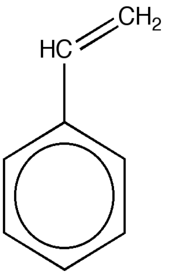
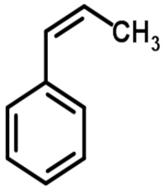
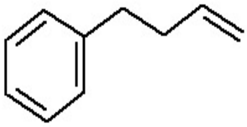
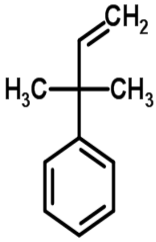


1-ethyl-3,5-dimethylbenzene

S

Note: The hydrocarbon group left after the removal of a hydrogen atom of the benzene itself is called **phenyl group (C_6H_5-).** The group left after the removal of a hydrogen atom of the CH_3- group of toluene is called **benzyl (C_6H_5-CH_2-).**

b) Structure and nomenclature of some aromatic alkenes

Structure				
Name	Phenylethene	Phenyl propene	4-Phenylbut-1-ene	3-Methyl-3-phenyl-1-butene

3.3.2. Reactions of alkylbenzenes

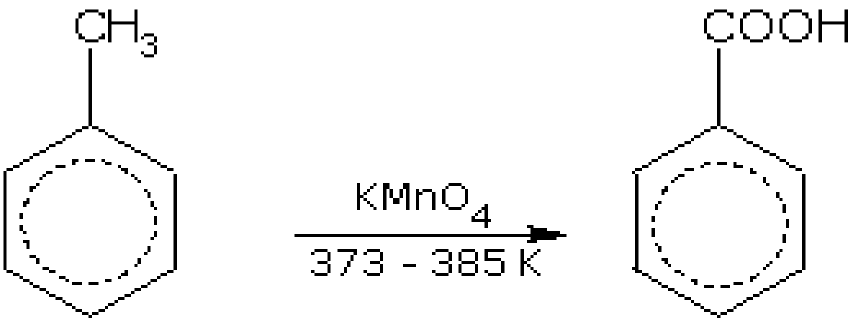
Alkylbenzenes involve two parts of their structures in chemical reactions:

- The **side chain** which can be oxidized by strong oxidizing agents like $KMnO_4$ and $Na_2Cr_2O_7$
- The **benzene ring** which can take place in electrophilic substitution. In electrophilic substitution alkylbenzenes react more strongly than benzene itself since the alkyl groups donate electrons. Alkyl groups are ortho and para directing.

a) Oxidation of the side chain

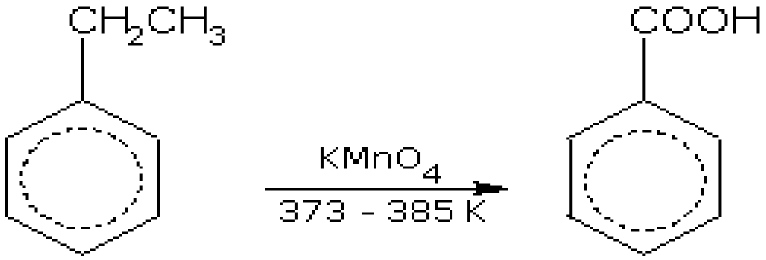
When alkylbenzenes are oxidized by powerful oxidizing agents (such as hot acidified or alkaline $KMnO_4$ and $Na_2Cr_2O_7$), the entire side chain, regardless of length, are oxidized to benzoic acid.

For example,



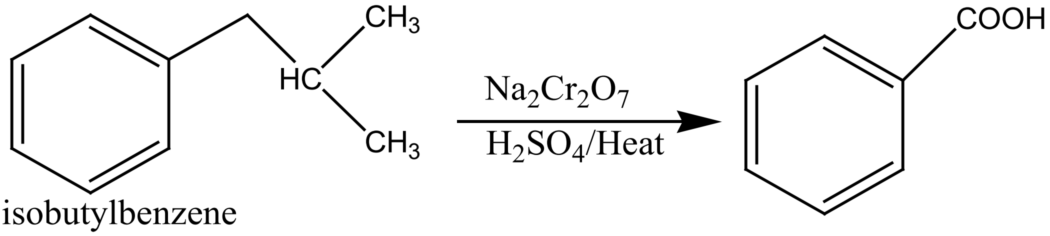
Toluene

Benzoic acid



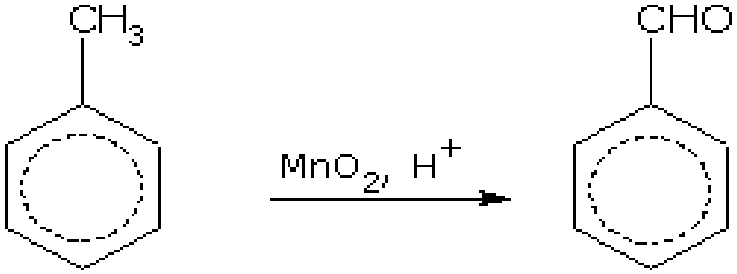
Phenylethane

Benzoic acid



isobutylbenzene

With weak oxidizing agents such as acidic manganese dioxide (MnO_2) or chromylchloride (CrO_2Cl_2), the side chain is oxidized to aldehyde (-CHO) group.

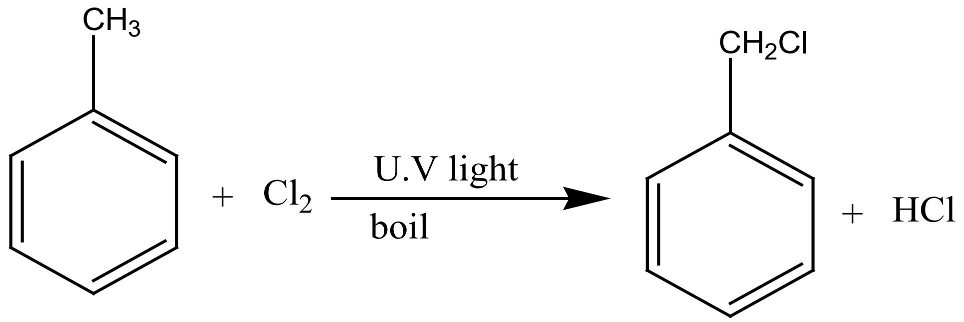


Toluene

benzaldehyde

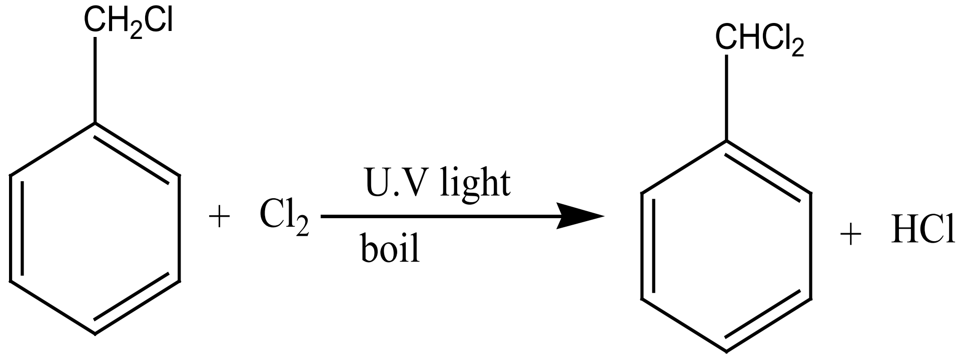
b) Radical substitution

Radical substitution takes place in three steps as for aliphatic alkanes: initiation, propagation and termination. The side chain substitution of hydrogen atom (s) occurs when chlorine or bromine is bubbled through boiling alkylbenzene in the presence of ultraviolet light or strong sunlight.

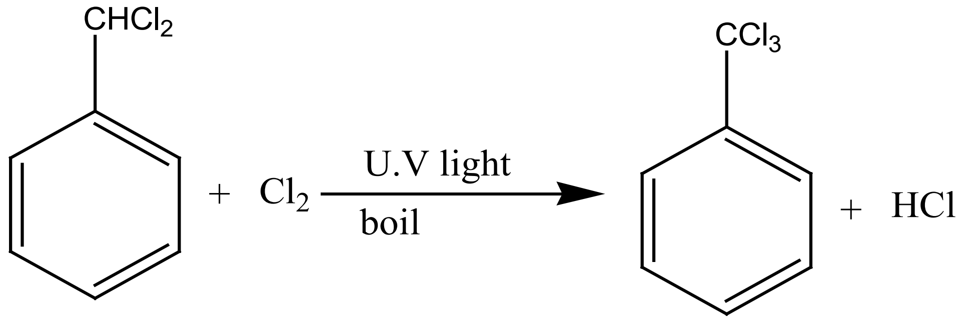


Benzyl chloride
or Chloromethylbenzene

Note that the above reaction may continue until all hydrogen atoms are replaced by halogen atoms.



dichloromethylbenzene



trichloromethylbenzene

Note: Bromine gives similar products under similar conditions.

Application activity 3.3

1. How can you prepare:

   Ortho-xylene (1, 2-dimethyl benzene) and para-xylene (1,4-dimethyl benzene) from benzene.

2. What will be the end product when propyl benzene reacts with Cl_2/ UV
   - Cl_2/ $AlCl_3$
   - HNO_3/H_2SO_4
   - MnO_2/H^+
   - $K_2Cr_2O_7/H^+$/373-385K

3.4. Aromatic carbonyl compounds

Activity 3.4

1. Write the functional group of carbonyl group
2. Give the structure formula of ethanal and propanone and ttheir common names
3. Write a balanced equation of the reaction when propanal and propanone react with

   a) MnO_4^-/H^+/heat

   b) NaOH/heat

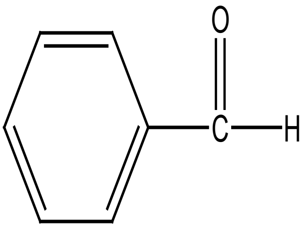
   c) PCl_5
4. Describe different ways of the preparation of propanal and propanone

The compounds with carbonyl group attached to the benzene ring are known as aromatic aldehydes and aromatic ketones.

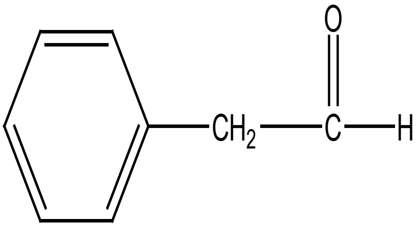
3.4.1. Structure and nomenclature of aromatic carbonyl compounds

a) Aromatic Aldehydes

These carbonyl compounds contain a phenyl group in their structures. Aromatic aldehydes are of two types: (a) those in which the aldehyde group (CHO) is directly attached to a carbon of the aromatic ring; and (b) those in which the aldehyde group (CHO) is directly attached to a carbon of the side chain. Aldehydes of type (a) are called aromatic aldehydes, while those of type (b) are best regarded as aryl-substituted aliphatic aldehydes.

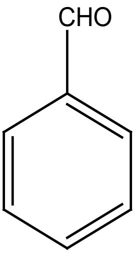


Aromatic aldehyde

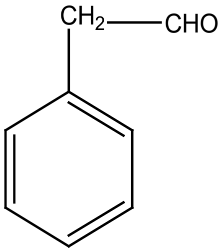


aryl-substituted aliphatic aldehyde

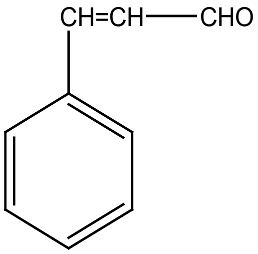
Benzaldehyde is a typical aromatic aldehyde, while phenylacetaldehyde and cinnamic aldehyde are to be designated as aryl-substituted aliphatic aldehydes.



Benzaldehyde

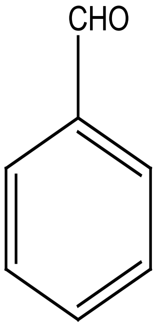


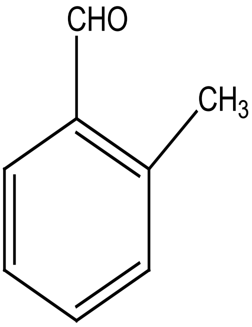
Phenylacetaldehyde

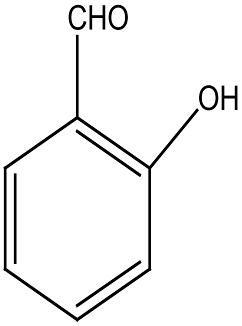


Cinnamic aldehyde

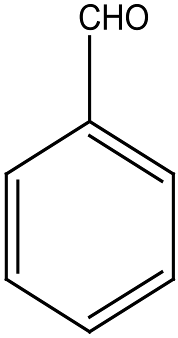
The IUPAC name of an aromatic aldehyde is derived by dropping the ending **–ene** of the name of the parent hydrocarbon and appending the suffix **–al.** Thus,

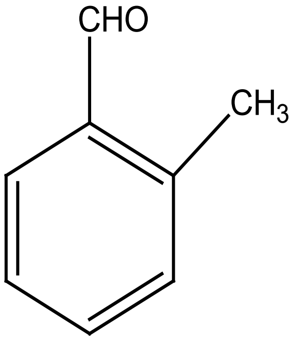

Benzal


2-methylbenzal


2-hydroxybenzal

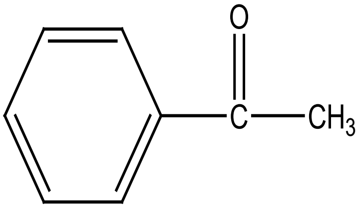
Aromatic aldehydes are generally called by their common names which are derived from the names of the corresponding carboxylic acid by replacing the **–ic** or **–oic acid** by **–aldehyde.** Thus the name benzaldehyde is derived from benzoic acid; ortho-tolualdehyde is derived from ortho-toluic acid, and salicylaldehyde from salicylic acid.


Benzaldehyde
(Benzal)

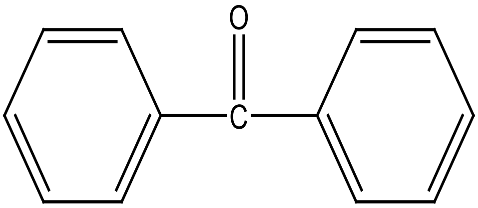

ortho-tolualdehyde
(2-methylbenzal)

b) Aromatic ketones

Ketones containing the carbonyl group attached to a benzene ring are named **phenones.** The individual name of such a ketone is derived by adding **phenone** to the stem formed by removing **–ic** from the name of the corresponding acid.



Acetophenone
(Methylphenylketone)



Benzophenone
(diphenylketone)

The common names of aromatic ketones are obtained as usual by naming the alkyl or aryl groups attached to the carbonyl group, followed by the word ketone. These are given in the brackets above.

3.4.2. Preparation of aromatic carbonyl compounds

a) Preparation of aromatic aldehydes

Benzaldehyde is the simplest member in this family and it may be prepared by the following methods which are applicable to aromatic aldehydes in general.

Benzaldehyde can be prepared using different methods. However, the main method is oxidation of methylbenzene. The methods of preparation include:

i) $$C_6H_5CH_3 \xrightarrow[\text{Heat}]{MnO_2/H_2SO_4} C_6H_5CHO$$

ii) $$C_6H_5CH_3 + 2Cl_2 \xrightarrow{\text{U.V light}} C_6H_5CHCl_2 + 2HCl$$

$$C_6H_5CHCl_2 \xrightarrow[\text{Reflux}]{H_2O/OH^-} C_6H_5CHO$$

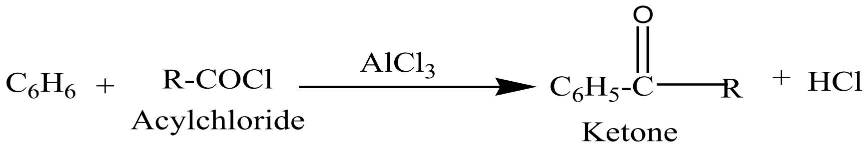
iii) $$C_6H_5CH_3 + O_2 \xrightarrow[\text{Heat}]{V_2O_5} C_6H_5CHO + H_2O$$

iv) $$C_6H_5COCl + H_2 \xrightarrow{Pd\text{-}BaSO_4} C_6H_5CHO + HCl$$

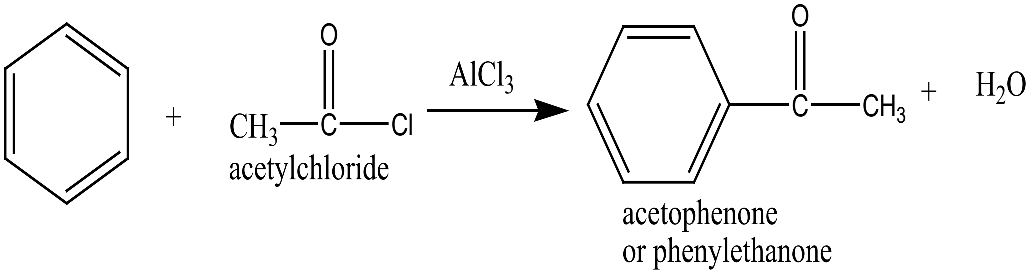
b) Preparation of aromatic ketones

Although aromatic ketones may be prepared by any of the methods used for aliphatic ketones, they are generally prepared by Friedel-Crafts reaction between an aromatic hydrocarbon and acylchloride or acid anhydride. The benzene is treated with acylchloride or acid anhydride in the presence of a halogen carrier.

1. **From acyl chloride**



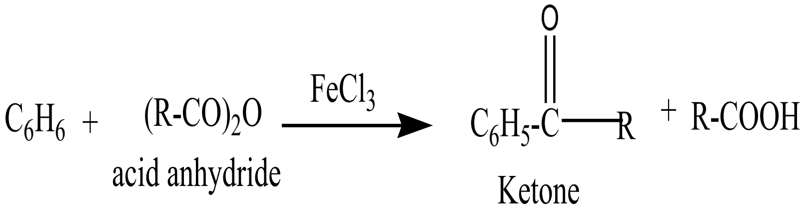
$$C_6H_6 + \underset{\text{Acylchloride}}{R\text{-}COCl} \xrightarrow{AlCl_3} \underset{\text{Ketone}}{C_6H_5\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}R} + HCl$$



acetylchloride

acetophenone
or phenylethanone

2. **From acid anhydride**



$$C_6H_6 + \underset{\text{acid anhydride}}{(R\text{-}CO)_2O} \xrightarrow{FeCl_3} \underset{\text{Ketone}}{C_6H_5\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}R} + R\text{-}COOH$$

3.4.3. Reactions of aromatic carbonyl compounds

The most typical reactions of the carbonyl groups are **nucleophilic addition**. In the carbon-oxygen double bond of the carbonyl group, oxygen is more electronegative than carbon, hence it has a strong tendency to pull electrons towards itself. This makes the carbon-oxygen double bond highly polar.

The partially positive carbon atom can be attacked by nucleophiles. During the reaction, the carbon-oxygen bond gets broken and the net effect is that the carbonyl group undergoes addition reaction.

The carbonyl group of aromatic aldehydes and ketones withdraws electrons from the benzene ring by inductive effect and resonance effect. Hence this group deactivates the benzene ring towards electrophilic substitution. The presence of the carbonyl group directs the substitution in **meta-position.** The electrophilic substitution of aromatic aldehydes and ketones is more difficult than electrophilic substitution of non-substituted benzene.

a) Reactions of aromatic aldehydes

Aromatic aldehydes present the same properties as aliphatic aldehydes. They give a positive test with ***Brady's reagent*** (2, 4- Dinitrophenyl Hydrazine; observation: yellow or orange precipitate), with ***Fehling solution*** (observation: red solution brown precipitate), with ***Tollen's reagent*** (observation: silver mirror) and with ***Schiff reagent*** (pink colour will be observed).

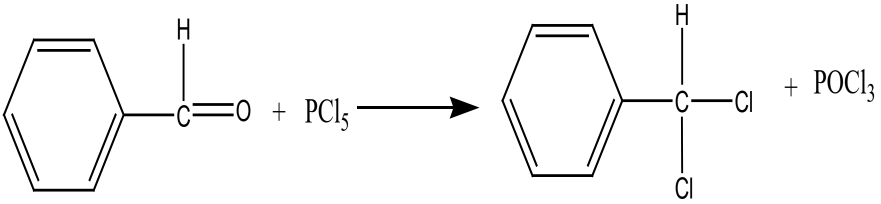
i) Benzaldehyde is not oxidized as readily as aliphatic aldehydes by oxidizing agents. While it reduces ammoniacal silver nitrate forming a silver mirror, it does not reduce Fehling's solution. Nevertheless, it undergoes oxidation by atmospheric oxygen at ordinary temperature in presence of light to form benzoic acid.

$$2C_6H_5CHO + O_2 \xrightarrow{hv} 2C_6H_5COOH$$

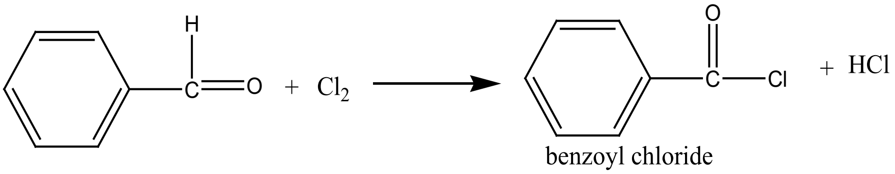
ii) When benzaldehyde is reduced with zinc and hydrochloric acid, benzyl alcohol is produced:

$$C_6H_5CHO \xrightarrow[Zn/HCl]{[H]} C_6H_5CH_2OH$$

iii) Benzaldehyde reacts with phosphorous pentachloride to form the **geminal dihalide:**

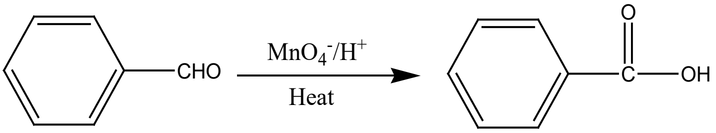


iv) The aldehyde group attached directly to the benzene ring is deactivating and hence chlorine does not substitute hydrogen in the ring in the absence of a catalyst. Instead, the chlorine substitutes hydrogen of the aldehyde group and benzoyl chloride is formed.

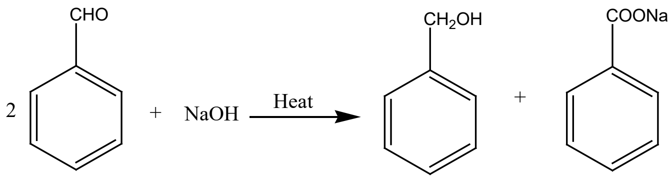


benzoyl chloride

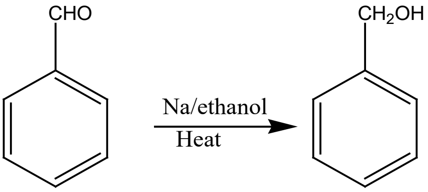
v)



vi) Benzaldehyde, on treatment with concentrated sodium hydroxide solution gives benzyl alcohol and sodium benzoate this reaction is called **Cannizzaro** reaction:



vii)



viii) Benzaldehyde undergoes nitration, sulphonation and halogenation. The substitution takes place in the meta-position to the group CHO.

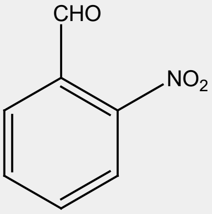
b) Reactions of aromatic ketones

The reactivity of the carbonyl group in aromatic ketones is not greatly affected by the aryl groups attached to it. In consequence, they undergo the same general reactions as aliphatic ketones. However, they do not form the bisulphite compound, and in addition give the usual substitution reactions in the aromatic ring.

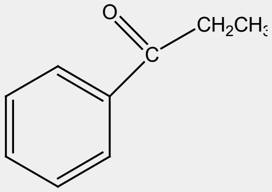
Application activity 3.4

1. Assign the systematic names of the following compounds:

a)



b)



2. Discuss the methods of preparation of benzaldehyde as a representative of the aromatic aldehydes.
3. Starting from benzene, chloroethylene and aluminium chloride even potassium permanganate, prepare banzaldehyde

3.5. Aromatic carboxylic acids

Activity 3.5

1. What is the general functional group of carboxylic acid?
2. How generally carboxylic acid are prepared?
3. Write equations of reactions their ethanoic acid react with:

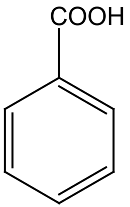
   a) Ethanol

   b) $LiAlH_4$, NaOH, Na_2CO_3, NH_3, Na, $NaHCO_3$, PCl_5
4. Discuss how alkyl carboxylic acids are prepared

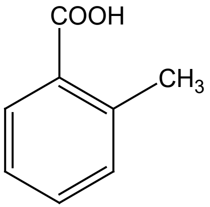
Aromatic acids contain one or more carboxyl groups **(–COOH)** attached directly to the benzene ring. The acids in which the **–COOH** group is attached to the side-chain group may be regarded as aryl-substituted aliphatic acids. However, there are no characteristics differences in the behavior of the ring and side-chain acids. The term "**aromatic acids**" includes both classes of compounds.

3.5.1. Structure and nomenclature of aromatic carboxylic acids

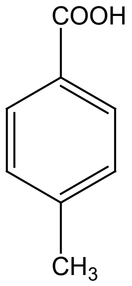
Aromatic carboxylic acids are called by their common names or after the name of the parent hydrocarbon. Thus:



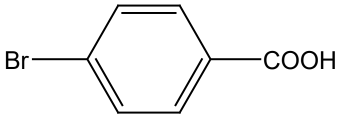
benzoic acid
(benzenecarboxylic acid)



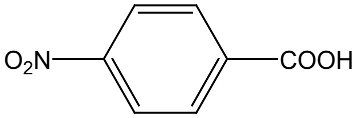
o-methylbenzoic acid
(2-methylbenzenecarboxylic acid)
(o-toluic aci)



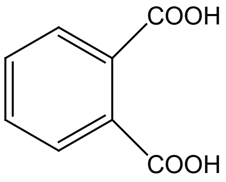
p-methylbenzoic acid
(4-methylbenzenecarboxylic acid)
(p-toluic aci)



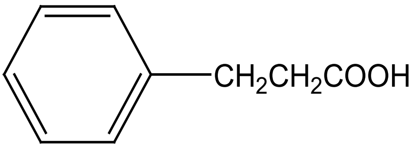
4-bromobenzoic acid



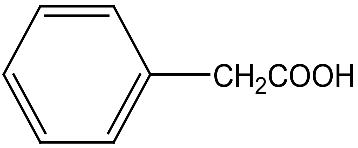
4-nitrobenzoic acid



benzene-1,2-dicarboxylic
acid (phthalic acid)



3-phenylpropanoic acid

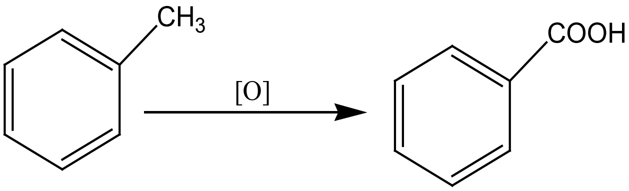


2-phenylethanoic acid

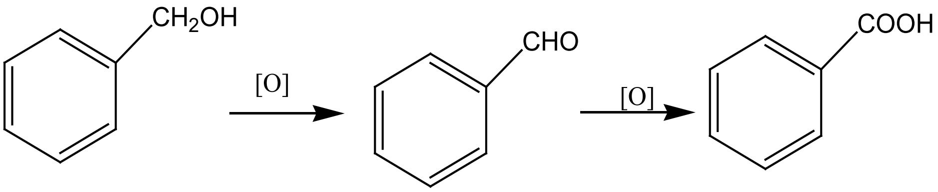
3.5.2. Preparation of aromatic carboxylic acids

Aromatic acids can be prepared by the same general methods which are available for aliphatic acids. In addition they may be obtained by oxidation of aromatic hydrocarbons having a side-chain.

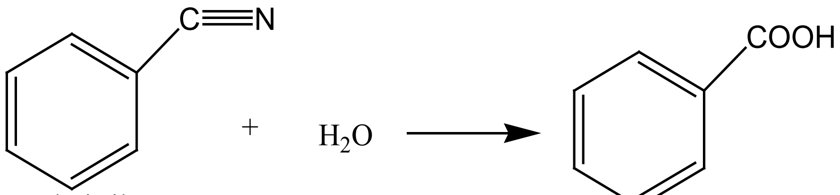
a) Oxidation of alkylbenzenes



b) Oxidation of primary alcohols and aldehydes

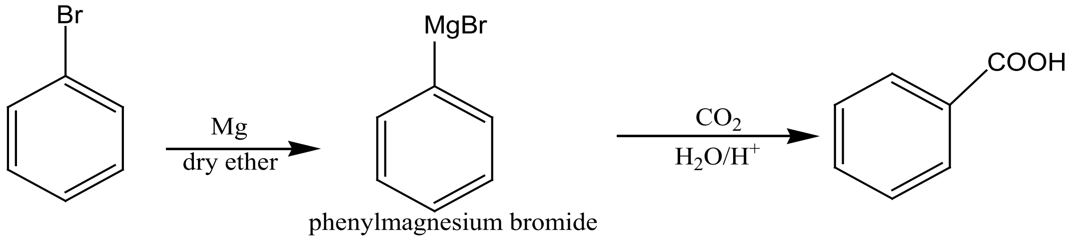


c) Hydrolysis of nitriles:

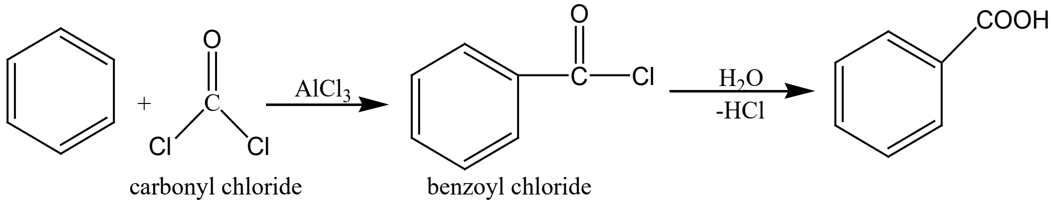


phenyl nitrile

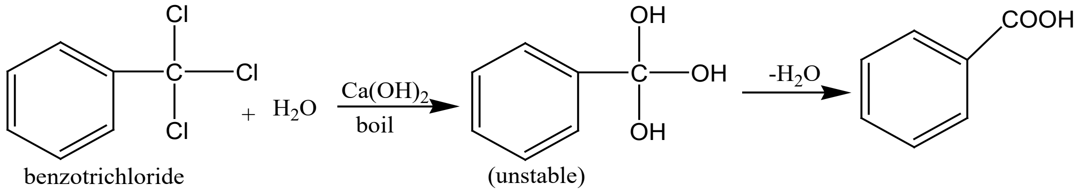
d) Carbonation of Grignard reagents:



e) Friedel-Crafts reaction:



f) Hydrolysis of trichlomethyl group on benzene ring:



3.5.3. Reactions of aromatic carboxylic acids

Aromatic acids are white crystalline solids, having higher melting points than aliphatic acids. They are slightly soluble in cold water but dissolve readily in hot water to form a colorless solution and on cooling, the acids recrystallize.

Aromatic carboxylic acids with unsubstituted benzene ring are slightly stronger acids than the aliphatic acids. Thus benzoic acid is stronger acid than acetic acid.

For the most part, the reactions of aromatic carboxylic acids are identical with those of aliphatic acids, the more important differences being in their rates.

Benzoic acid, the simplest aromatic carboxylic acid is more acidic than phenol since it can react with Na_2CO_3 or $NaHCO_3$ to liberate carbon dioxide gas. Its reactivity is attributed to its two parts: the carboxylic acid group and the benzene ring.

a) Side chain reactions

i) Benzoic acid dissolves in water to form acidic solution which turns blue litmus paper into red.

$C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$

ii) Like aliphatic acids, aromatic carboxylic acids also form salts:

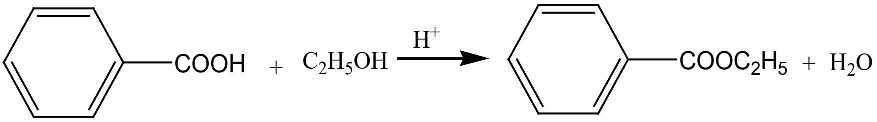
$C_6H_5COOH + NaOH \rightarrow C_6H_5COONa + H_2O$

$2C_6H_5COOH + Na_2CO_3 \rightarrow 2C_6H_5COONa + CO_2 + H_2O$

$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + H_2O + CO_2$

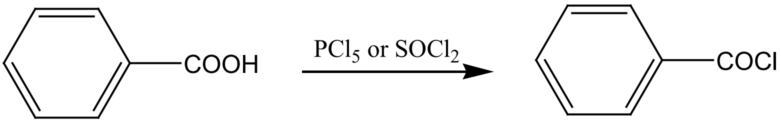
$2C_6H_5COOH + Na \rightarrow 2\ C_6H_5COONa + H_2$

iii) **Esterification**: Aromatic acids having no substituent in the ortho-position to COOH group, are readily converted into esters by direct reaction with alcohols in the presence of mineral acids (HCl or H_2SO_4) as catalyst. If, however, an ortho substituent is present, the rate of esterification is considerably reduced. When both ortho positions are occupied, esterification does not occur at all.



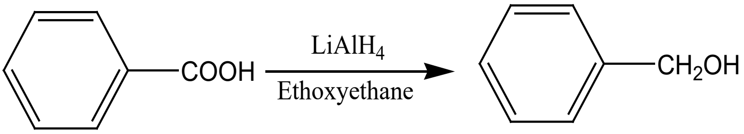
Ethylbenzoate

iv) **Acid halides:** Aromatic acids, like the aliphatic acids, are converted to corresponding acid halides by heating with phosphorous pentachloride or with thionyl chloride.



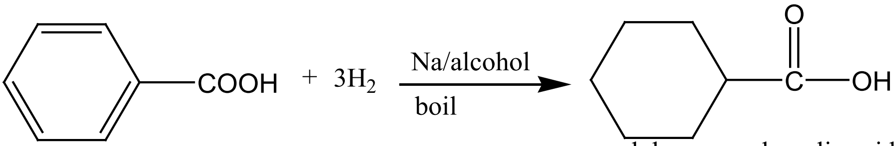
benzoylchloride

v) **Benzyl alcohols**: Aromatic acids on reduction in the presence of lithium aluminium hydride and ethoxyethane conditions give benzyl alcohols.



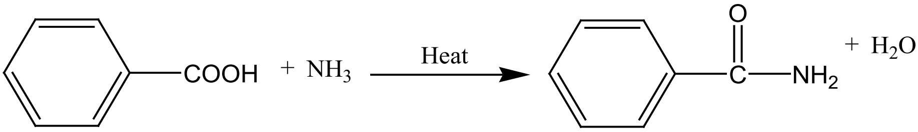
vi) **Reduction**: Ordinary reducing agents, like hydrogen and metal catalyst or sodium and alcohol, do not reduce the carboxyl group and rather reduce the aromatic ring. Thus benzoic acid when reduced with sodium and boiling alcohol is converted to cyclohexane carboxylic acid.

Remember here, in organic chemistry, that reduction of an organic compound means increase the hydrogen content in its molecule.



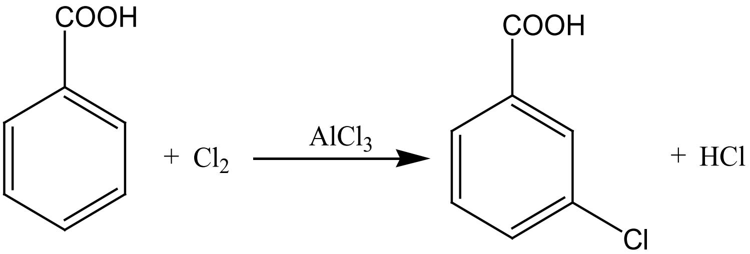
cyclohexanecarboxylic acid

vii) Aromatic acids form ammonium carboxylates which on heating give acid amides.



b) Benzene ring reactions

Aromatic acids undergo electrophilic substitution reactions in the benzene ring. The COOH group is meta-director and the substitution takes place less readily than in the parent hydrocarbon ring. For example,



m-chlorobenzoic acid

3.5.4 Uses benzoic acid and its derivatives

- Benzoic acid is used in medicine, in the dye industry for making aniline blue.
- Sodium benzoate being less toxic is used for preserving food products such as tomato ketchup and fruit juices.

Application activity 3.5

1. Write all equations showing how to prepare acid dichloro-3,5-benzoic acid from ethyl benzoic acid.
2. Complete equations of reactions that occur when from benzoic you want to prepare :

   a) benzylmethanol

   b) benzoylchloride

   c) cyclohexanemethanoic acid

3.6. Aromatic amines

Activity 3.6

1. What is the main functional group representing the amines
2. With demonstrative example, show how you can prepare ethyl amine (show the reagents that are used for its preparation).
3. Illustrate with formulas the different classes of amines.

The amino derivatives of the aromatic hydrocarbons are of two types:

(a) Aromatic amines or aryl amines in which the **$-NH_2$** group (or substituted **$-NH_2$ group**) is attached directly to a carbon of the benzene ring.

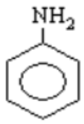
(b) Aryl-alkyl or aralkyl amines in which the **$-NH_2$** group is attached to a carbon of the side-chain.

Like the aliphatic amines, the aromatic amines may also be divided into primary, secondary and tertiary amines.

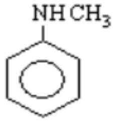
3.6.1. Structure and nomenclature of aromatic amines

In systematic naming, the numbering of carbon depends on the whole structure of the aromatic compound and the nature of the group attached to the benzene ring. In general, when more than one group are attached to the benzene ring, some groups are given priority as functional group.

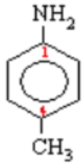
Here is a simple list for guidance on precedence (priority) of groups: **COOH > COO- > COOR >COCl> CONH$_2$ > CN > CHO > COR > OH >NH$_2$** which means that from the list given, the amino is the least important, whereas the carboxylic acid group is the most important.



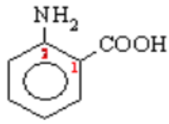
phenylamine



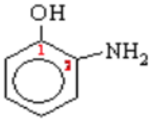
N-methylphenylamine



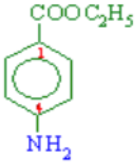
4-methyl phenylamine



2-aminobenzoic acid



2-aminophenol



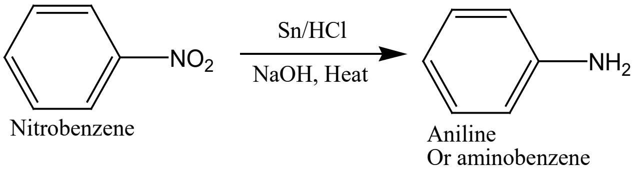
4-aminoethyl benzoate

3.6.2. Preparation of Phenylamine and uses of its derivatives

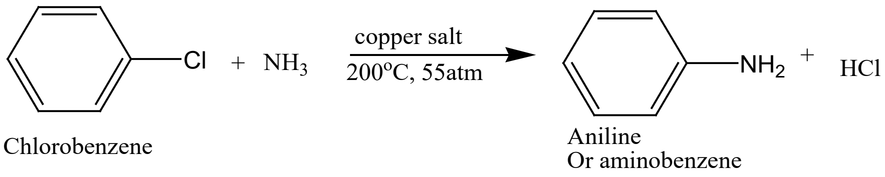
a) Preparation of phenylamine

i) Phenylamine, like other arylamines, can be prepared by the reduction of nitro compounds.

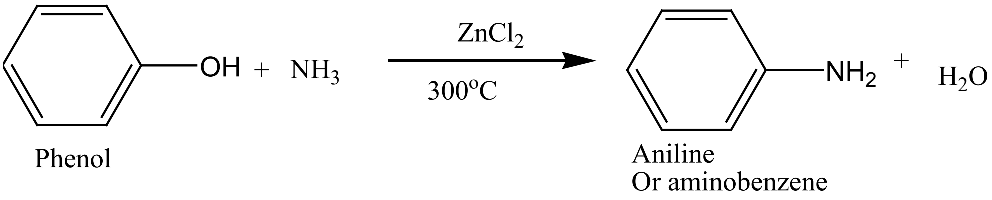
The nitro compounds are treated with granulated tin, zinc or iron and HCl.



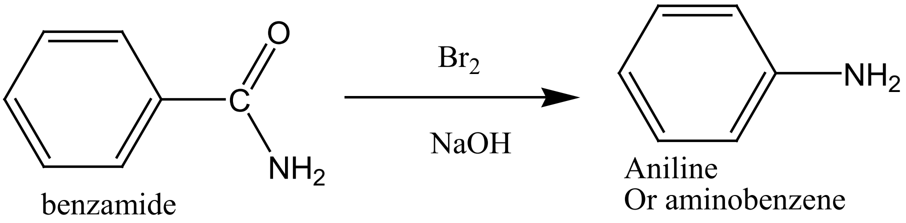
ii) Phenylamine can also be prepared by the addition of ammonia to chlorobenzene using copper (II) salts as catalyst at high temperature and high pressure.



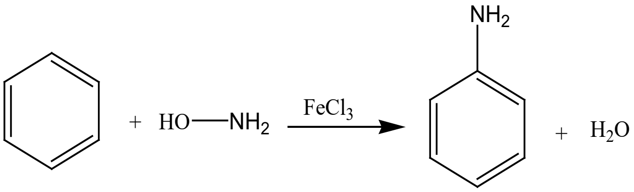
iii) Phenols react with ammonia in the presence of zinc chloride at about 300°C to form the corresponding amines.



iv) Like primary aliphatic amines, primary aromatic amines can be obtained by the degradation of aryl amides with bromine in alkaline solution (**Hofmann Degradation)**.



v) Aromatic hydrocarbons react directly with hydroxylamine in the presence of catalyst like $FeCl_3$ or $AlCl_3$ to give monoamines.



b) Uses of aniline and its derivatives

Derivatives of phenylamine or aniline are known as "**Anilines**". These are used in various fields of science and everyday life as given below:

i) Anilines are used in the rubber industry for the processing of rubber material such as car tyres, balloons, gloves, etc.

ii) It is used as a dyeing agent in the manufacture of clothes such as jeans, etc…

iii) It is employed in the production of drugs such as Paracetamol, Tylenol, and Acetaminophen.

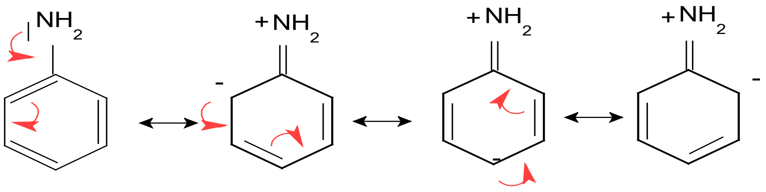
iv) It is used as a pesticide and fungicides in the agricultural industry.

v) It is utilized in the manufacture of polyurethane, which is in turn used in the making of plastics.

3.6.3. Alkalinity of phenylamine

Amines, both aliphatic and aromatic are basic. They are soluble in water. Phenylamine is weaker base than ammonia and aliphatic amines because the non-bonded electrons on the nitrogen atom are delocalized into the pi-system of the benzene ring. This makes the lone pair of electrons less available for reaction with a proton.

The delocalization of the lone pair of electrons on the nitrogen atom in phenylamine can be represented by the following resonance forms:



Thus aniline structure is greatly resonance stabilized.

3.6.4. Reactions of Phenylamine

Aniline, also called phenylamine or aminobenzene ($C_6H_5NH_2$), is a colorless oily liquid, slightly soluble in water and soluble in organic solvents. It turns brown on exposure to sunlight.

The aromatic amines in general give all the reactions of the amine group of aliphatic amines. However, the reactivity of the amine group is modified by delocalization of the non-bonded electrons on nitrogen atom into the pi-system of the aromatic ring.

a) Reaction of aniline with water (H_2O)

$$C_6H_5\text{-}NH_2 + H_2O \rightleftharpoons \underset{\text{anilinium ion}}{C_6H_5\text{-}NH_3^+} + OH^-$$

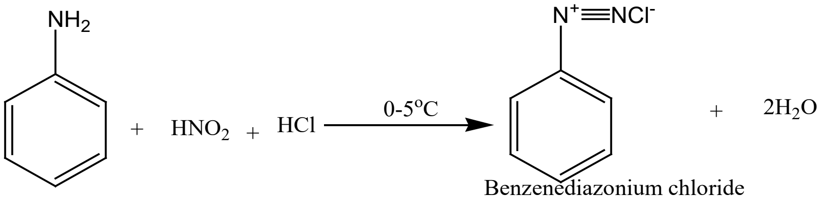
b) Reaction of aniline with hydrochloric acid (HCl)

Aniline is able to react with acids to produce salts. Phenylamine reacts with mineral acids to form phenylammonium chloride.

$$C_6H_5\text{-}NH_2 + HCl \longrightarrow C_6H_5\text{-}NH_3^+Cl^-$$

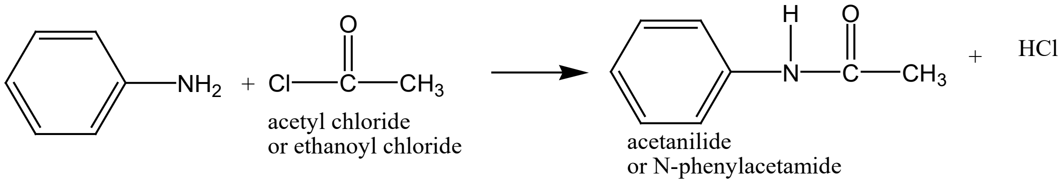
c) Reaction of aniline with nitrous acid (HNO_2)

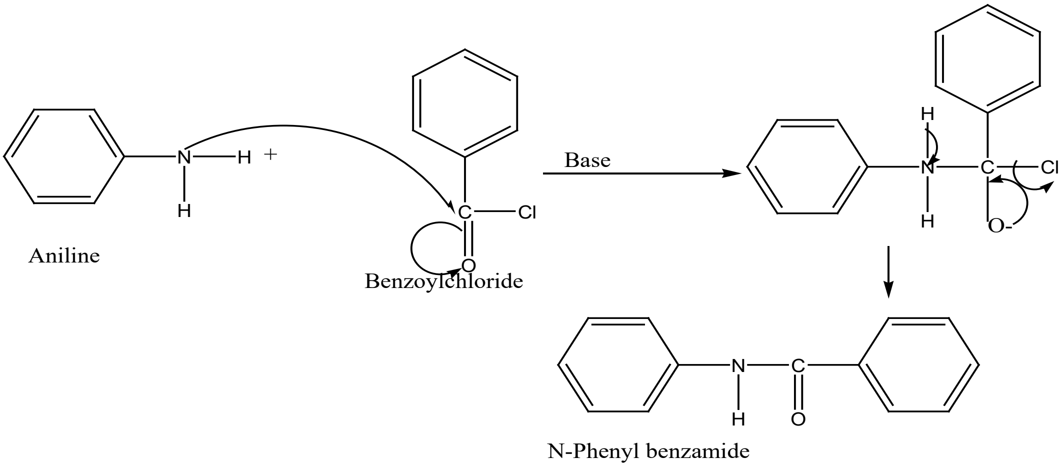
This is a very important reaction in the manufacture of dyes. The starting material is an aromatic amine such as phenylamine.



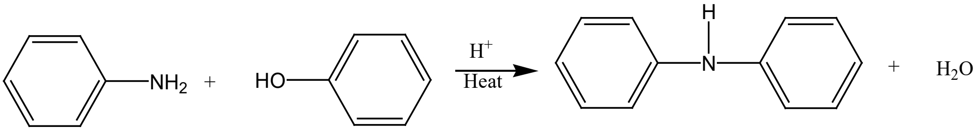
d) Reaction of aniline with ethanoyl chloride and benzoyl chloride

Phenylamine undergoes acylation to produce substituted amides.



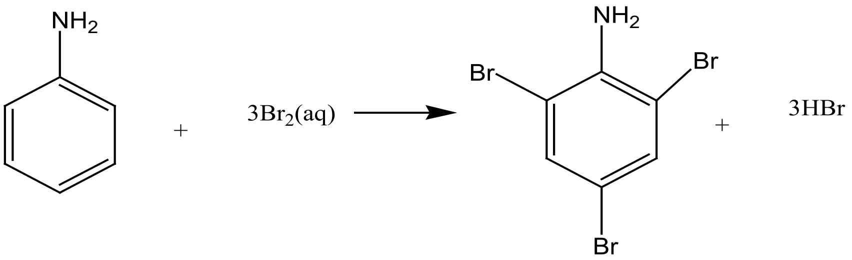


e) Reaction of aniline with phenol



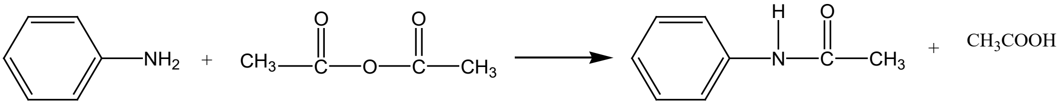
f) Reaction of aniline with halogens

The presence of amino group activates the ring and directs the incoming electrophiles to ortho and para positions. For example, addition of bromine water to phenyl amine, results in formation of immediate white precipitate of 2,4, 6-tribromophenylamine.



2,4,6-tribromophenylamine
(white precipitate)

g) Reaction of aniline with acid anhydride



Application activity 3.6

1. Starting from benzene, outline how a sample of phenylamine can be made. Give equations and all essential reagents and conditions.
2. Aniline is treated with nitrous acid in presence of tin under 5^0C, what will be the end product
3. Write equations of the reaction between aniline with:
   - a) Chlorine Cl_2
   - b) Methylphenol
   - c) Propanoyl chloride

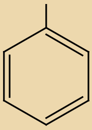
Skills Lab 3

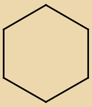
Rwanda is among the first cleanest countries in Africa and the world as well. To clean we use different substances including soaps and soapless detergents. Make a research and outline the different substances that constitute the detergent.

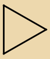
Make your procedure and buy them in the local shop to make your own detergent and try to share with others what you have done.

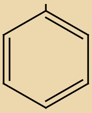
End of unit assessment 3

1. Which of the following compounds are not aromatic?

a) 

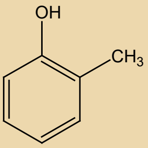
b) 

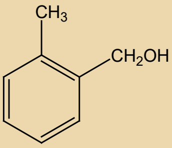
c) 

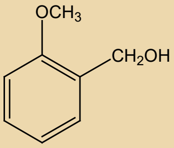
d) 

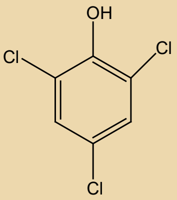
e) $CH_3CH_2CH_2CH_2CH_2CH_3$ f) C_6H_5Cl

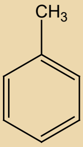
2. Which of the following structures are phenols and which are alcohols?

A: 

B: 

C: 

D: 

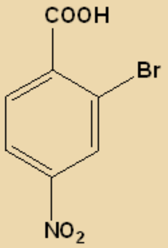
E: 

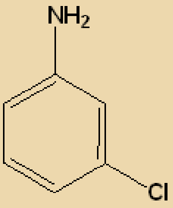
3. (a) What would you expect to see when bromine is added to aqueous phenol?

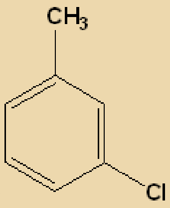
(b) Why does bromine react more readily with phenol than with benzene?

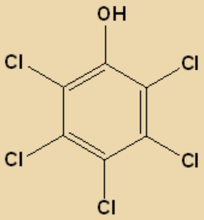
(c) Give three uses of phenol.

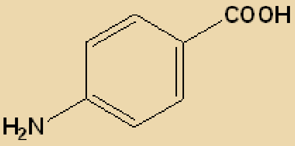
4. Write the IUPAC names of the following structures:

a) 

b) 

c) 

d) 

e) 

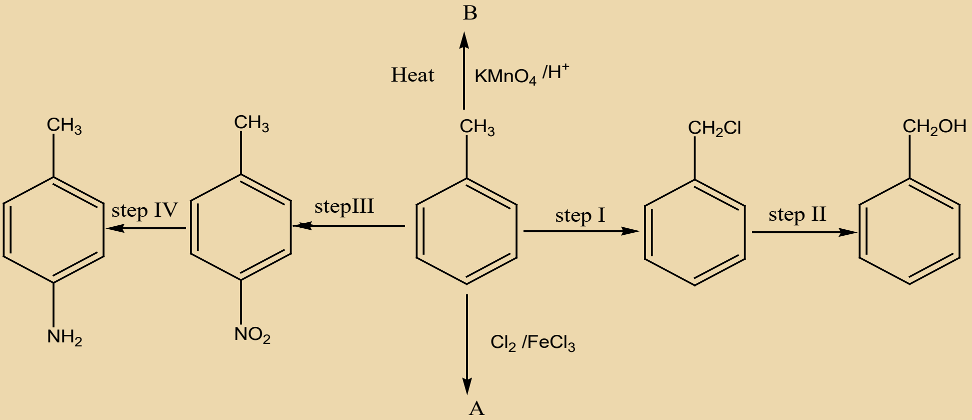
5. Write equations indicating the reagent and condition to show how the following conversions can be done:

a) Benzene to 2-hydroxybenzoic acid (salicylic acid)

b) Aniline to 3-bromophenol

c) Benzene to paranitrobenzoic acid

6. The scheme below shows some reactions starting with methylbenzene



a) Give the reagents and conditions used to carry out reactions in the steps below

i) Step I

ii) Step II

iii) Step III

b) What type of reaction is involved in step IV?

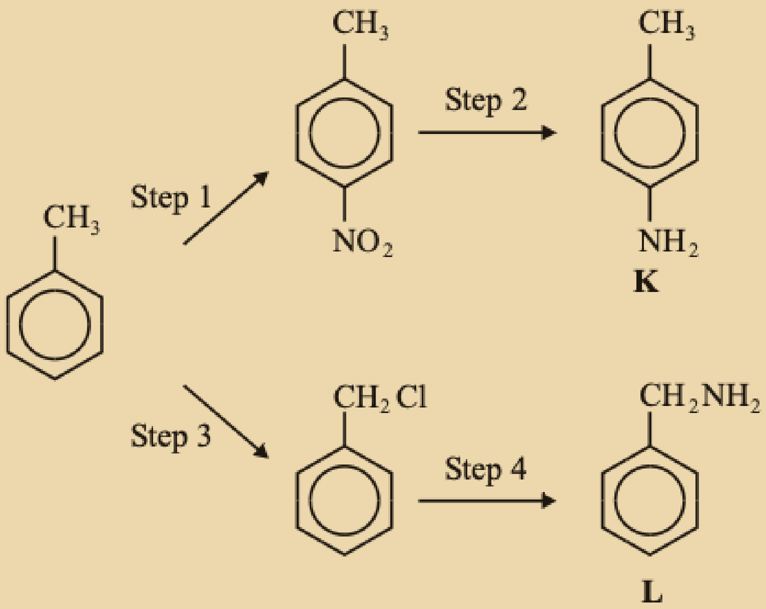
c) Give the structural formula and name of compounds A and B

d) What is the name of the mechanism involved in

i) Step I

ii) Step II

7. The following reaction scheme shows the formation of two amines, K and L, from methylbenzene.



a) (i) Give the reagents needed to carry out step 1.

(ii) Name and outline a mechanism for step 1.

b) Give the suitable reagent or combination of reagents for Step 2.

c) (i) Give the reagent for Step 4 and state the condition to ensure that the primary amine is the major product.

(ii) Name and outline a mechanism for Step 4.

d) Explain why amine **K** is a weaker base than ammonia.

e) Draw the structure of the organic compound formed when a large excess of bromomethane reacts with amine L.

f) Draw the structure of the organic compound formed when ethanoyl chloride reacts with amine L in an addition–elimination reaction.

UNIT 4

POLYMERS AND POLYMERIZATION

Key Unit Competence:

Relate the types of polymers to their structural properties and uses

Introductory activity

The images below show materials commonly used in our daily life.

Observe carefully the following images and answer the questions below:

1

2

3

4

5

6

7

a) Give the name for each material and one of its uses

b) Search in library (textbooks) and on internet, the chemical nature of each material mentioned above

c) Discuss the characteristics of the above materials and identify what do they have in common

Nowadays the materials made of plastics such as fibers, plastic and rubber materials, are all around us and are commonly called **polymers** by chemists.

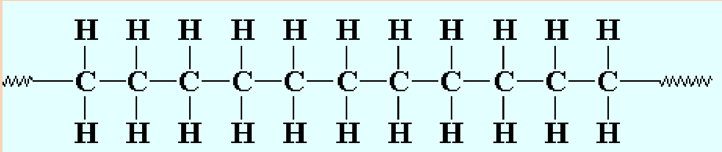
Polymers are commonly used in household utensils, automobiles, clothes, furniture, space-aircraft, biomedical and surgical components. Polymeric materials are light weight but can possess excellent mechanical properties and can be easily processed by different methods. In this unit you will learn more about polymers, their types and some important-synthetic and natural polymers.

4.1. Definition of monomer, polymer and polymerization

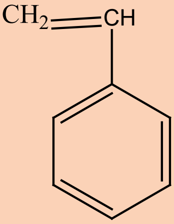
Activity 4.1

Compare the following substances and see their differences even the resemblance they have between them

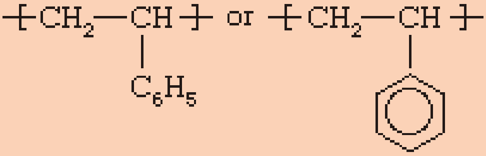
i) $CH_2{=}CH_2$ and ,



ii)



and



4.1.1. Monomer

The term monomer comes from mono "one" and meros "part", which expresses a single unit or a small molecular subunit that can be chemically bind to another identical or different molecule to form larger molecule (polymer).The monomer is repeated in the polymer chain and it is the basic unit which makes up the polymer. For instance in the large compound formed by $nA \rightarrow -A_n-$ where A is a monomer and the polymer is given by the repeated monomers in the chain; i.e. –A-A-A-A-A-A-. The larger molecules such as carbohydrates, lipids, nucleic acids and proteins are found in living systems, like our own bodies.

$nCH_2{=}CH_2 \rightarrow [-CH_2-CH_2-]_n$, ethylene ($CH_2 = CH_2$) is a monomer

4.1.2. Polymer

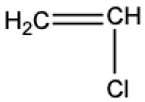
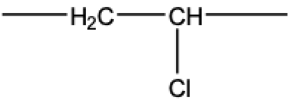
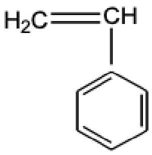
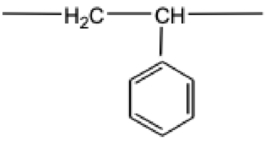
The term polymer comes from poly- meaning "many"; and meros meaning "part". A polymer is a large molecule (macromolecule or giant molecule) composed of smaller molecules (monomers) linked together by intermolecular covalent bonds. Polymers have a high molecular weight in the range of 10^3 to 10^7. A polymer can be represented as $(-A_n-)$ or $(- A - A - A - A - A\text{-}\ldots\ldots)$ which is a polymer of the monomer A.

Example: $nCH_2 = CH_2 \rightarrow [\text{-}\ CH_2 - CH_2 -]_n$,

Polyethylene, $[\text{-}\ CH_2 - CH_2 -]_n$ is a polymer while ethene,$CH_2 = CH_2$ is a monomer

More examples of polymers are given in the Table 4.1.

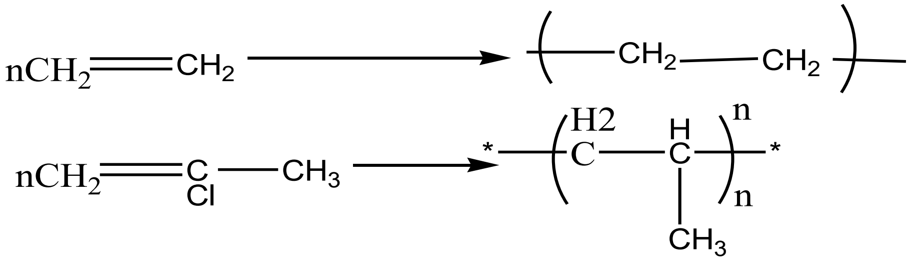
Table 4.1. Some examples of polymers and monomers

Monomer		Repeating unit/ monomeric unit	Polymer
$H_2C{=}CH_2$	Ethylene	$-H_2C-CH_2-$	Polyethylene
 $H_2C{=}CH{-}Cl$	vinyl chloride	 $-H_2C-CH(Cl)-$	poly(vinyl chloride)
	Styrene		Polystyrene

4.1.3. Polymerization

Polymerization is the process in which monomer units are linked by chemical reaction to form long chains (polymers). The individual units of molecules from which a polymer is created or evolved are better known as monomers and the process by which these monomers are linked with one another to form a big polymer molecule is called 'Polymerization'.

Examples



For example, a gaseous compound, Butadiene, with a molecular weight of 54 g/mole combines nearly 4000 times by polymerization and gives a polymer, known as polybutadiene.

Butadiene + butadiene + butadiene + … + butadiene → Polybutadiene

Note:

1. The **degree of polymerization (n)** is defined as the number of monomeric units in a macromolecule or polymer or oligomer (a polymer consisting of few number of monomers units) molecule.
2. A polymer formed by identical monomers is called **homopolymer** while a polymer formed by different monomers is a **copolymer**.

Preparation protocol of plastic from milk

Experimental activity for the preparation of plastic from Milk

Materials

- 500ml 2% milk
- 60ml vinegar
- One beaker of 100 mL
- 2 beakers of 1 L each
- 1 spoon
- 1 strainer
- Aluminum foil
- Thermometer
- Hot plate or Bunsen burner and stand
- Matches if using a Bunsen burner

Procedure

1. Assemble all materials and chemicals
2. Turn on the Bunsen burner or hotplate.
3. Place beaker of milk over heat. Stir constantly.
4. Place thermometer into the milk. Heat milk until it reaches 37°C.
5. Remove from heat and immediately add vinegar, stirring constantly. The solution will rapidly separate into curds suspended in a clear yellow liquid.
6. Strain the solution through the strainer into the empty 1L beaker. Hold up the beaker to see the clear liquid.
7. Scoop the curd onto a large piece of aluminum foil and press out into a thin layer. Pass the aluminum foil around the class. Then dry especially overnight. Describe the substance formed

Milk is a colloid, which is defined as a suspension of large molecules such as proteins in a solution such as water. Essentially, milk is a suspension of protein globules in water.

This protein can go through polymerization to create a natural plastic, as the casein molecules are associated together in long chains. Proteins are generally unstable and are prone to unfolding, which changes the natural state of the protein. This process is called denaturing. The addition of acid, in this case vinegar, causes the casein protein to unfold and rearrange into the long chains of a polymer. The process then causes the casein to precipitate out of the milk, leaving a clear watery substance behind. The casein can then be formed into various shapes before drying. In our experiment, thermal energy in the form of heat was applied to speed the process and cause a more complete separation.

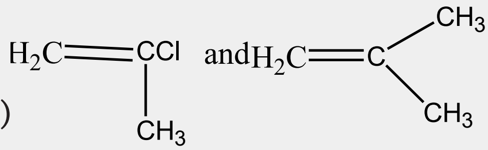
Application activity 4.1

1. Draw structure of the polymer formed from each of the following monomers or pair of monomers.

   a) $CH_2=CH\text{-}OCOCH_3$

   b)$CH_2=CCl\text{-}CH=CH_2$

   c)



2. Draw the monomers from which the following polymers are made:

   a) $\text{---}CH_2\text{-}CH(CN)\text{-}CH_2\text{-}CH(CN)\text{-}CH_2\text{—}$

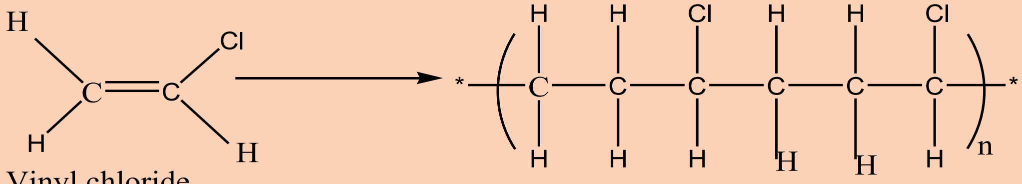
   b) $\text{---}CH_2\text{-}C(CN)=CH\text{-}CH(CN)\text{-}CH_2\text{-}C(CN)=CH\text{-}CH(CN)\text{-}CH_2\text{---}$

4.2. Types of polymerization

Activity 4.2

1. Observe carefully the following chemical reactions, and then answer the questions;

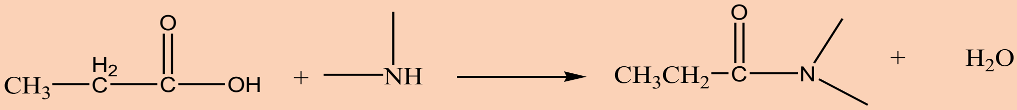
   A.



Vinyl chloride

polyvinyl chloride

B.



Compare and contrast the two chemical reactions

There are two types of polymerization reaction such as addition polymerization and condensation polymerization.

4.2.1. Addition polymerization

Addition polymerization is a process whereby monomers are linked together to form a polymer, without the loss of atoms from the molecules.

Some examples of addition polymers are polyethylene, polypropylene, polystyrene, polyvinyl acetate, polyvinyl chloride (PVC), rubber, polytetrafluoroethylene (Teflon), etc.

Example 1: Formation of polyethene or polyethylene

Polyethene is formed by addition of $CH_{2=}CH_2$ monomer molecules linked together as follows

$$n\,CH_2 = CH_2 \rightarrow [-\,CH_2 - CH_2 -]_n$$

Ethene Polyethene

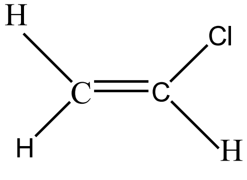
Example 2: Formation of PVC (polyvinylchloride)

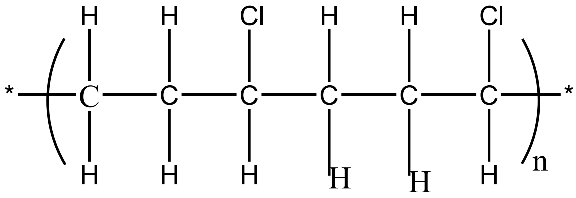
PVC (polyvinyl chloride) is found in plastic wrap, simulated leather, water pipes, and garden hoses, it is formed from vinyl chloride ($H_2C{=}CHCl$).

Vinyl is a common name for ethylene, PVC is formed from the following reaction:

$nCH_2{=}CHCl \rightarrow [-CH_2\text{-}CHCl\text{-}]_{n,}$ where **n** can be between 700-1500

Vinyl chloride Polyvinylchloride


Vinyl chloride


polyvinyl chloride

Example 3: Formation of rubber: Rubber can be natural or synthetic

Rubber is a natural polymer of isoprene (2-methyl-1, 3-butadiene). It is formed by a linear 1, 4- addition polymer of isoprene.

Natural rubber has elastic properties because it has the ability to return to its original shape after being stretched or deformed. Therefore it is known as Elastomer. Natural rubber is prepared from latex which is a colloidal solution of rubber in water.

4.2.2. Condensation polymerization

Condensation polymerization is a process where two or more monomers chemically combine to form a polymer with elimination of simple molecules like water, ammonia, hydrogen chloride, alcohol, etc.

In this type of reaction, each monomer generally contains two functional groups for the condensation reaction to take place.

There are two main types: **polyamides** which are formed between a diol with a dicarboxylic acid and **polyesters** which are formed when a dicarboxylic acid and a diamine react to form nylons.

The condensation polymers include synthesis of Nylons, Terylene, Kevlar polymer, proteins, cellulose, Bakelite, Dacron, etc.

Example 1: FORMATION OF POLYAMIDES

This type of polymers is formed by the result of generation of amide bonds in the polymerization reaction.

i) Formation of Nylon

Nylon -6, 6 is produced by the condensation reaction between two monomer units adipic acid and 1,6-hexanediamine in the presence of heat. This is formed from a six-carbon diacid and a six-carbon diamine as shown below.

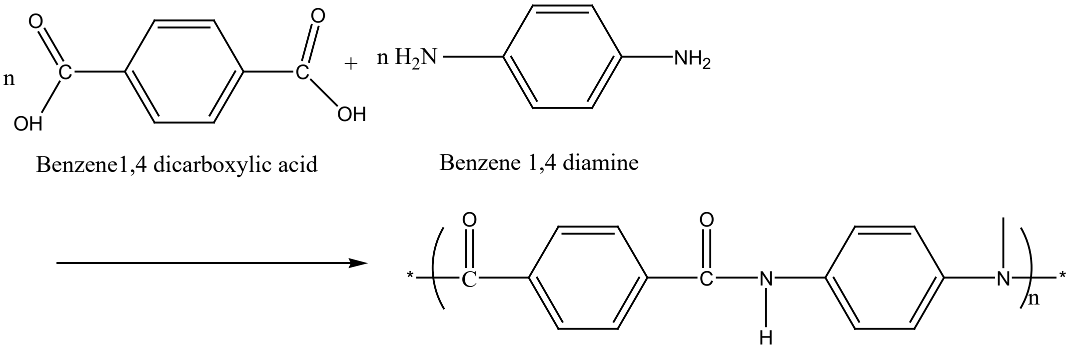
$$nH_2N{-}(CH_2)_6{-}NH_2 + nHOOC{-}(CH_2)_4{-}COOH \xrightarrow{-2nH_{2}0} {-}(NH{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_4{-}CO)_n{-}$$

1, 6-Hexanediamine Adipic acid Nylon -6, 6

ii) Formation of Kevlar

Kevlar is formed from the polymerization of benzene -1,4-diamine and benzene-1,4-dioic acid as follows:

Benzene-1,4-dioic acid + Benzene-1,4-diamine → Kevlar + water



Benzene1,4 dicarboxylic acid

Benzene 1,4 diamine

Kevlar

In that polymerization –NH_2 group of hexamethylenediamine reacts with –COOH group of adipic acid to form –NH-CO- amide linkage with elimination of H_2O.

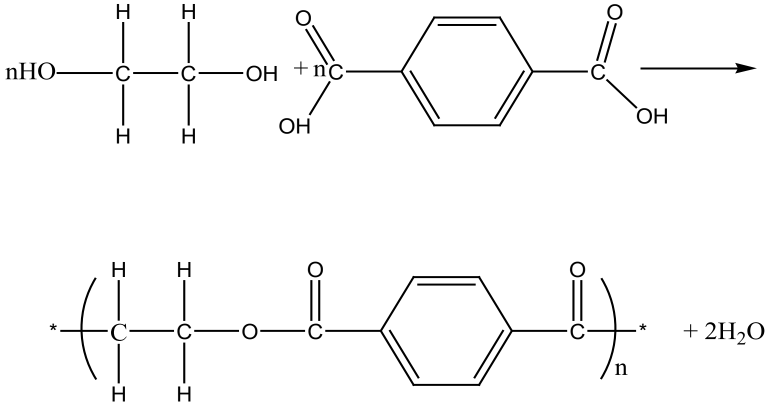
Polyamides such as nylon-6,6 and Kevlar are widely used in clothing. Kevlar has some remarkable properties, including fire resistance and higher strength than steel. It is used to make protective clothing-for example for fighters, bullet proof vests and helmets

Example 2: FORMATION OF POLYESTERS

i) Formation of Terylene

Terylene is formed by reacting 1, 2- ethanediol and benzene -1, 4-dicarboxylic acid with loss of water molecules. Terylene comes from terephtalic acid and ethylene glycol.

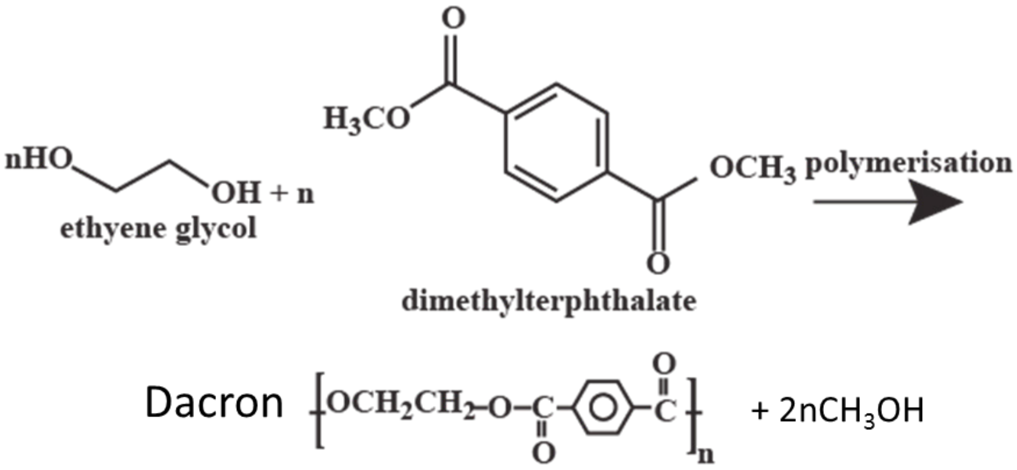
Benzene -1,4-dicaboxylic acid + ethane-1,2-diol (ethylene glycol) → Terylene + water



ii) Formation of Dacron

It is made from dimethyl -1,4-benzene dicarboxylate and 1,2-ethane diol:

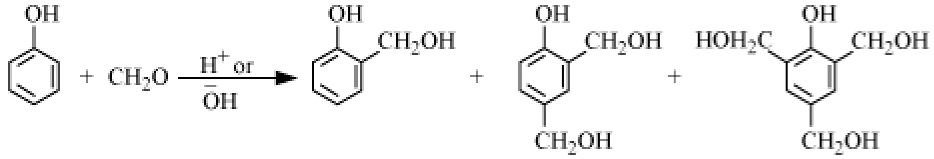
Dimethyl -1,4-benzene dicarboxylate + 1,2-ethane diol → Dacron + methanol

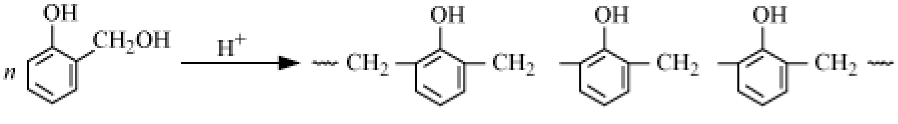


$$\text{Dacron}\ \left[OCH_2CH_2-O-\underset{\underset{O}{\|}}{C}-C_6H_4-\overset{\overset{O}{\|}}{C} \right]_n + 2nCH_3OH$$

Example 3: FORMATION OF BAKELITE:

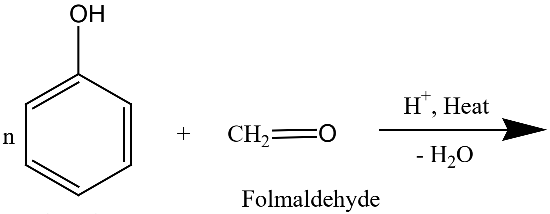
Bakelite (polyoxybenzylmethyleneglycolanhydride) is the oldest synthetic polymer. It is formed from phenol and formaldehyde in the presence of either an acid or a base catalyst. The initial product could be Novalac, then novalac on heating with formaldehyde undergoes cross linking to form Bakelite.



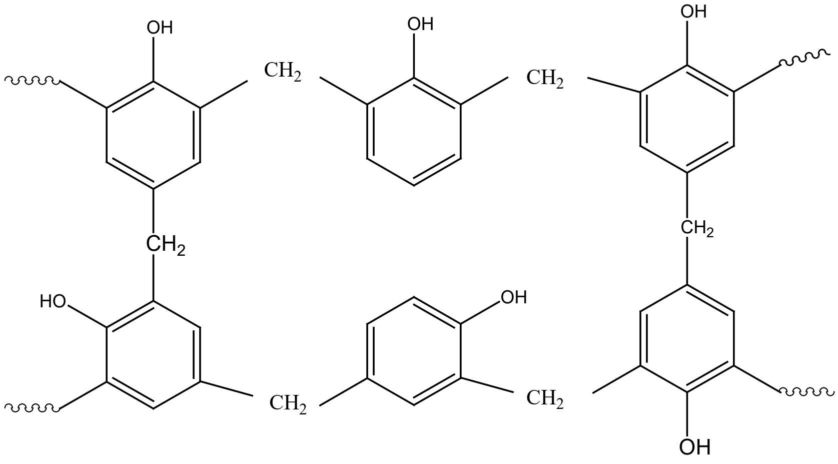


Novolac

The general equation is:



Phenol



Bakelite

Experiment on the preparation of phenol formaldehyde resin (bakelite)

Chemicals

- Glacial acetic acid,
- 40% formaldehyde solution,
- Phenol, conc. H_2SO_4

Apparatus Required:

- Glass rod,
- beakers,
- funnel,
- measuring cylinder,
- dropper
- Filter paper

Procedure:

1. Place 5ml of glacial acetic acid and 2.5ml of 40% formaldehyde solution in a 500ml beaker and add 2 grams of phenol.
2. Add few ml of conc. Sulphuric acid into the mixture carefully. Within 5 min, a large mass of plastic is formed
3. The residue obtained is washed several times with distilled water, and filtered product is dried and yield is calculated.

Conclusion:

A mixture of phenol and formaldehyde are allowed to react in the presence of a catalyst. The process involves formation of methylene bridges in ortho, para or both ortho and para positions. This results first in the formation of linear polymer (Called NOVALAC) and then in to cross-linked polymer called phenol-formaldehyde resin or Bakelite.

Some differences between addition polymerization and condensation polymerization are summarized in Table 6.2.

Table 4.2. Comparison between addition and condensation polymerization

Addition polymerization	Condensation polymerization
1. Involves unsaturated monomer like ethylene, vinyl chloride, styrene etc. 2. Fast addition of monomers. 3. Initiator is necessary to catalyze the polymerization 4. No elimination products 5. Polymers made are, for example, polyethene, polypropylene, polybutadiene, polyvinylchloride.	1. Involves substanceswith at least 2 different reacting functional groups like ethylene glycol (2-COOH groups). 2. Step-wise slow addition 3. Catalyst is not necessary 4. Small molecule like H_2O, HCl, or CH_3OH is often eliminated. 5. Polymer made are, for example, Terylene, nylon, formaldehyde-resins, silicones

Application activity 4.2

1. Write down a balanced chemical equation for reaction between hexane -1,6-diamine and hexane -1,6-diolchloride.
2. Differentiate addition polymers and condensation polymers by using examples.
3. Nylon is a condensation polymer formed from two monomers represented by NH_2-X-NH_2 and HOOC-Y-COOH.

   a) Draw a structure to represent the repeat unit of the nylon polymer from two monomers and indicate the linkage group by a ring.

   b) What is the name given to the linkage group in nylon polymer?
4. Nylon 6,6 has a structure containing the following repeat unit:

   $-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH-$

   a) What type of polymer is this?

   b) Give the structural formulae of the monomers of this polymer.

   c) What natural polymer has the same linkage as Nylon 6,6.

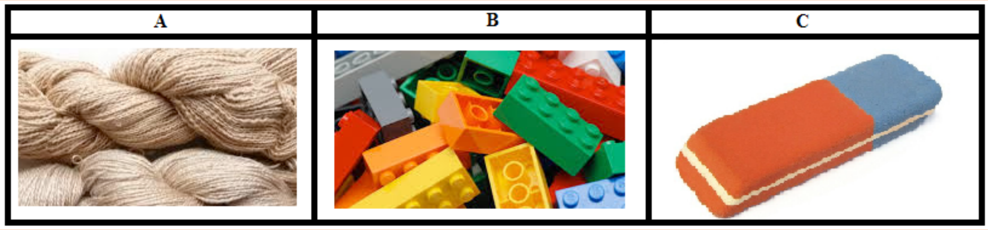
4.3. Classes and types of polymers

Activity 4.3

1. Among the following names, according to your knowledge class them among natural and synthetics

   Cellulose, starch, Bakelite, amylopectin, plastic bags, nylon, Kevlar, explain the cause of your classification

2. Discuss the use of plastics versus metals
3. Observe carefully the following image and then answer to the questions;



a) Explain the materials used to make each image

b) Compare the materials represented by the above images

4.3.1 Classes of polymers

Classes of polymers

In general, polymers are classified into two classes such as natural polymers and synthetic polymers.

A. Natural polymers

Natural polymers are those that are obtained from natural sources. They are made naturally and are found in plants and animals or other living beings.

For examples: cotton, silk, wool, natural rubber, cellulose and proteins.

1. **Silk**

A silk is a fine continuous protein fiber produced by various insects' larvae usually for cocoons. It is mainly a lustrous elastic fiber produced by silkworms and used for textiles.

For example, orb-weaving spiders produce a variety of different silks with diverse properties, each tailored to achieve a certain task. Most arthropod species produce silks used for building structures to capture prey and protect their offspring against environmental hazards.

2. Cotton

Cotton is soft, fluffy staple fiber that grows in a boll, or protective case, around the seeds of the cotton plants. Cotton is natural cellulosic fiber.

3. Proteins

Proteins are highly complex substance made up of hundreds of thousands of smaller units called amino acids which are attached to one another to make along chain. There are around 20 different amino acids that occur naturally in proteins. Many proteins act as enzymes that catalyze biochemical reactions and are essential to metabolic functions.

4. Natural rubber

Natural rubber is an elastic material obtained from the latex sap of trees that can be vulcanized and finished into a variety of products. It is a hydrocarbon polymer of isoprene (2-methylbuta-1,3-diene) obtained from latex. Latex is an emulsion of rubber particles in water that coagulate by addition of ethanoic acid.

The molecular formula of natural rubber is: $-CH_2-C(CH_3)=CH-CH_2-C(CH_3)=CH-CH_2-$ which is polyisoprene, having the monomer of isoprene $(CH_2=C(CH_3)CH=CH_2$.

5. Cellulose

Cellulose is an insoluble substance which is the main constituent of plant cell walls and the vegetable fibers such as cotton. It is a polysaccharide consisting of chains of glucose monomers.

B. Synthetic polymers

Except the natural polymers, there are also synthetic polymers which are synthesized in the laboratory. They are manufactured from lower mass molecular compounds. Synthetic polymers (polymer made by two different monomers) are copolymers formed when many molecules of buta-1,3-diene or its derivatives chemical are joined with unsaturated compounds. They can also be either thermosetting or thermoplastic polymers.

Examples: Polyethene is a polymer formed by linking together a large number of ethene molecules. PVC, Nylons, Terylene and Polystyrene. etc, ..

Examples of natural and synthetic polymers and their uses

Table 4. Natural and synthetic polymers

	Polymer	Monomer	Source (Where you can find it)
Natural	Protein	Amino acids	Wool, silk, muscles…
	Starch	Glucose	Potato, wheat, etc…
	Cellulose	Glucose	Paper, wood, dietary fibers
	DNA	Nucleotides	Chromosomes
Synthetic	Poy(ethene)	Ethene	Bags, washing up bowls, etc…
	Polyvinyl chloride PVC (polychloroethene)	Chlororethene (vinyl chloride)	Fabric coating, electrical insulation, etc...
	Poly(phenylethene)	Phenylethene	Toys, expanded polystyrene
	Polyesters	Ethane-1,2-diol and benzene-1,2-dicarboxylic acid	Skirt, shirts, trousers

4.3.2 Types of polymers

The polymers can be classified into three main different types such as (i) plastics, (ii) rubber, and (iii) fibers.

a) Plastics

The plastics are types of polymers that are the most commonly used. Plastics are polymerized organic substances, solid of high molar mass, which at some time in its manufacture can be shaped by flow. They are electrical and thermal insulators. Their advantage is recycling and this allow them to be used many times. Plastics are materials that can be softened (melted) by heat and re-formed (molded) into another shape. Plastics are typically composed of artificial synthetic polymers

The disadvantage of plastics is in their temperature resistance as they get quite fast soft and loose mechanical properties.

Examples: Polyethylene, Teflon, Plexiglas, PVC, etc.

b) Rubbers

Rubber is a tough elastic polymeric substance made from the latex of a tropical plant or synthetically made. There are two types of rubbers; natural rubber and synthetic rubber. Rubbers are soft and springy and return to their original shape after being deformed.

– Natural rubber

Natural rubber is an elastic material obtained from the latex sap of trees that can be vulcanized and finished into a variety of products. Natural rubber is extracted from rubber producing plants, most notably the tree “Hevea brasiliensis”, which originates from South America.

Natural rubber is a polymer of the monomer 2-methylbuta-1,3-diene (isoprene). Poly(2-methylbuta-1,3-diene) can exist in cis- and trans- isomeric forms. Natural rubber is the cis-form.

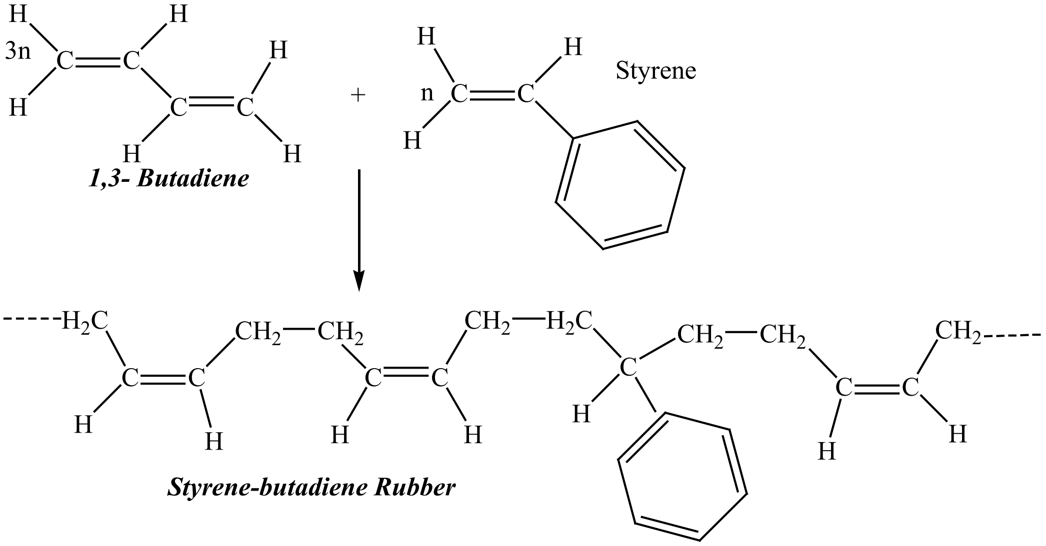
– Synthetic rubber

A synthetic rubber is any artificial elastomer (man-made polymer having elastic properties)

There are several synthetic rubbers in production. These are produced in a similar way to plastics, by a chemical process known as polymerization. They include neoprene, Buna rubbers, and butyl rubber. Synthetic rubbers have usually been developed with specific properties for specialist applications. Synthetic rubber can be made from polymerizing buta -1,3-diene, $CH_2=CH-CH=CH_{2.}$

The synthetic Rubber can be also obtained by polymerizing a mixture of two or more different monomers. An example is styrene-butadiene rubber (SBR), a synthetic rubber formed by a mixture of 1,3-butadiene and styrene in a 3 to 1 ratio, respectively.

The structure of SBR is the following:



The combination of monomer units gives a new polymer product having the same empirical formula to the monomer but having a higher molecular weight. The monomer units are usually unsaturated compounds (i.e. alkenes and their derivatives).

Alkenes can be made to join together in the presence of high pressure and by adding a suitable catalyst. The ϖ-bond breaks and the molecules are held together.

c) Fibers

Fiber (from latin Fibra) is a natural or synthetic substance that is significantly longer. Fibers are often used in the manufacture of other materials. In manufacture of strongest engineering materials often fibers are incorporated, for example carbon fiber and ultra-high molecular-weight polyethylene.

Fibers are strong polymers that do not change shape easily. They are made into thin, strong threads which can be woven together, Nylon is an example.

– Natural fiber

Natural fibers are substances produced by plants and animals that can be turned into filament, thread or rope and further be woven, woolen, matted or bound.

– Synthetic fiber

A man made textile fibers including usually those made from natural materials such as rayon and acetate as well as fully synthetic fibers (such as nylon or acrylic fibers).

Application activity 4.2

1. Polymers found in natural materials can be formed by the reaction between amino acids
   a) Deduce the formula of the product formed when two molecules of alanine, $CH_3CH(NH_2)COOH$ react together and deduce the name of linkage present in the product.
   b) Give the name of the type of naturally occurring polymer containing this linkage.
1. Write the structural formula of;
   a) Polypropylene (PP)
   b) Polyvinyl chloride (PVC)
   c) Polystyrene (PS)
   d) Nylon 6, nylon-6,6
   e) Teflon (polytetrafluoroethylene)

4.3. Properties of polymers

Activity 4.3

1. Differentiate the biodegradable from non-biodegradable substances
2. What happens to something to be degraded?
3. Give at least 4 dangers for non-biodegradable substances
4. Propose a solution of what you can do in order decrease the danger associated to non-biodegradable substances.

Polymers or in general plastics have different properties depending on their nature. Among the properties, they can be thermosetting or thermosoftening whereas on the other side they can be biodegradable or non-biodegradable.

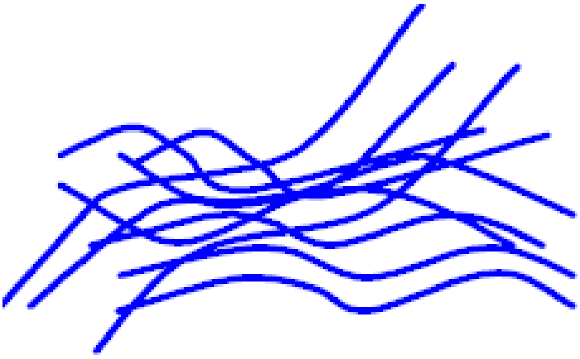
4.3.1. Thermosoftening and thermosetting properties

Thermosoftening (thermoplastics) and thermosetting (thermosets) are properties of polymers on how they soften on heating and harden on cooling.

a) Properties of Thermosoftening polymers

Thermosoftening polymers have weak intermolecular forces and they can be remolded into new shapes. They can be softened between 65°C and 200°C and can be returned to their original state by heating. At higher temperature **thermoplastic** becomes liquid and suitable for **injection molding**. After cooling, melt harden and keep a given shape. Disadvantage of thermoplastic is in their temperature resistance, meaning that they get quite fast soft and loose mechanical properties. Thermoplastics have linear and complex molecules.

Thermosoftening is a property by which some polymers can be softened on heating. This allows them to cool and harden, and then can be resoftened many times. The following is the structure of thermosoftening polymers.



For the thermosoftening polymers, the Van der Waal's forces between the chains are often very strong and the polymers have relatively high melting and boiling points. Due to their variable chain length, most polymers have different Van der Waal's forces and these polymers tend to melt gradually over a range of temperatures rather than sharply at a fixed temperature. As the chains are not rigidly held in place by each other, polymers tend to be reasonably soft.

The density and strength of addition polymers varies widely and they depend to a certain extent on the length of the hydrocarbon chain, but depend much more strongly on the nature and extent of the branching on the chain.

Polymers which have very few branches are very compact and the chains can thus pack together very efficiently.

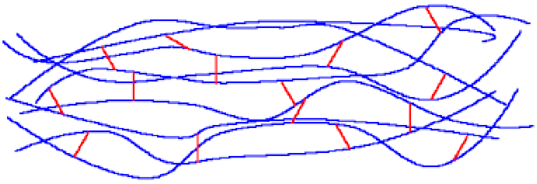
Examples: P.V.C, Dacron, Polypropene. Etc.

b) Properties of Thermosetting polymers

Thermosetting Polymers are some polymers which cannot be reshaped once heated as they are completely decomposed. Thermosetting polymers include phenol-formaldehyde, urea-aldehyde, silicones and allyls. Thermosetting Polymers have cross-links (covalent bonds between chains) that do not break on heating and they comprise three dimensional network structure. The greater the degree of cross-linking makes the polymer more rigid. These polymers are generally insoluble in solvents and have good heat resistance quality.

Thermosetting polymers are generally stronger than thermoplastic polymers due to strong covalent linkage between polymer chains.

When thermosetting plastics or thermosets are molded, covalent bonds are formed between the chains. They are more brittle in nature and their shape is permanent. Once they are softened, they cannot be returned to their original state by heating. Thermosetting polymers include phenol-formaldehyde, urea-aldehyde, silicones and allyls. The following is the structure of thermosetting polymers;



Examples :Bakelite ,epoxy-resins,silicones,formica .etc

Advantages and disadvantages of the above mentioned properties:

- ***Advantages***
  - Thermoplastics are convenient for manufacturers to use and they are not expensive. They are even recyclable.
  - Thermosets retain their strength and shape even when heated, they have high heat resistance and structural integrity.
- ***Disadvantages***
  - Thermoplasts melt and some degrade in direct sunlight or und high U.V light levels. Many suffer from creep, a relaxation of the material under long term loading. They tend to fracture rather than deform under high stress.
  - Thermosets absorb moisture and toxicity easily.
  - Thermosets are not recyclable.

4.3.2. Biodegradable and non-biodegradable properties

These are the properties of polymers depending on how they react overtime as a result of biological activity especially to be broken by microorganisms.

If they do not respond on the degradation or decomposition, they are said to be non-biodegradable polymers.

a) Biodegradable polymers

Biodegradable polymers are the polymers that are fully decomposed into carbon dioxide, methane, water, biomass and inorganic compounds under aerobic or anaerobic conditions and the action of living organisms. Therefore the biodegradable properties are all characteristics of some polymers to be decomposed under aerobic or anaerobic conditions and action of living organisms.

Biodegradation or biotic degradation is a specific property of certain plastic materials. Microorganisms (bacteria, fungi, algae) recognize polymers as a source of organic compounds (e.g. simple monosaccharides, amino acids, etc.) and energy that sustain them.

For biodegradation to happen there are two reactions that can allow it to proceed: biodegradation based on oxidation and the other based on hydrolysis. Those reactions can occur either simultaneously or successively. The decomposition of condensation polymers (example: polyesters and polyamides) take place through hydrolysis, while polymers with carbon atoms only in main chain (example: polyvinyl alcohol, lignin) decompose by oxidation which may be followed by hydrolysis of products of oxidation.

The advantage of biodegradable plastics is that they decompose into natural substances and do not require separate collection, sorting, recycling or any other final waste solution (disposal at landfills or burning) as is the case with non-biodegradable plastics.

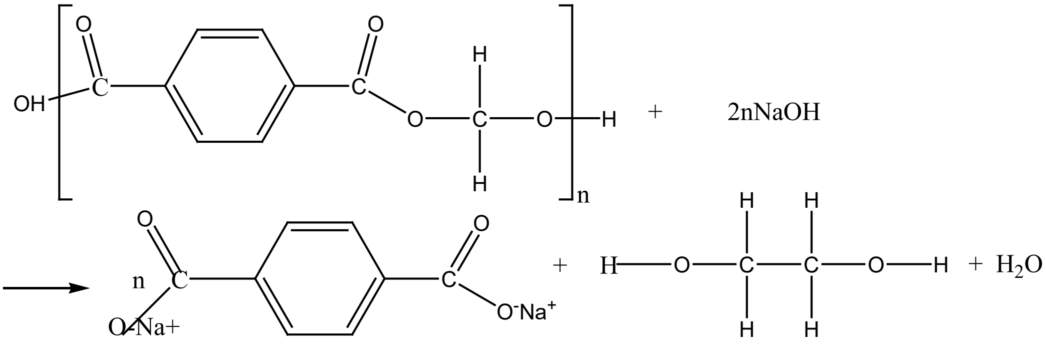
Characteristics of biodegradable polymers:

- They are slightly soluble in water;

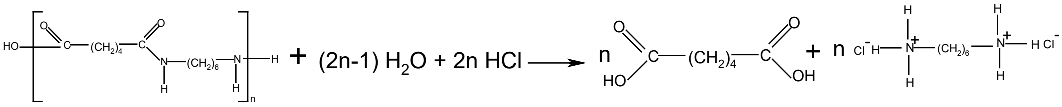
  Example: poly (ethanol)'' $–(CH_2\text{-}CHOH)_n\text{-}$'' also called poly(vinyl alcohol or PVA)
- They decompose slowly at the sunlight (they are photodegradable). They are incorporated while making polystyrene materials like cups. When they are exposed to sunlight for 60 days, their cups break down into dust particles.

The break-up of these polymers is carried out in aqueous solution and can be classed as hydrolysis reactions.

Polyesters are best hydrolyzed in strongly alkaline conditions, in which they undergo saponification:



Polyamides are best hydrolyzed in strongly acidic conditions:



The biodegradability of condensation polymers may compromise their effectiveness, since physical and chemical durability is one of the reasons for their widespread use. A balance must be struck between practical durability and long-term biodegradability. The degradable polymers are applied in many areas (Table 4.3).

Table 4.3: Application of biodegradable polymers

Category	Applications
Packaging	Food packaging, garbage bags, wrappers
Housewares	Disposable dinnerware, cups, bottles, containers
Biomaterials	Devices, surgical implants, absorbable sutures, tissue engineering, regenerative medicine.
Pharmaceuticals	Controlled Medical release of drugs, homeostatic agents, drugs delivery, tablet coatings, hydrogels
Agriculture	Mulch, Mulch films, plant covering, pots, bags, trays and containers, controlled release of fertilizers, chemicals, etc.
Personal care	Combs, diaper backing, shampoos

b) Properties of Non-biodegradable polymers

Most of the major synthesized polymers are non-biodegradable. All kind of plastics and synthetic fibers are non-biodegradable. They are polymers which are resistant to environmental degradation thus accumulate in form of waste. These polymers cannot be changed to a harmless natural state by the action of bacteria, and may therefore damage the environment.

Since the chains of non-biodegradable polymers are non-polar, addition polymers are insoluble in water. Their intermolecular forces are strong and the chains are often tangled, they are generally insoluble in non-polar solvents as well.

In fact the long saturated hydrocarbon chains result in polyalkenes being very unreactive generally, as they cannot react with electrophiles, nucleophiles or undergo addition reactions.

This results in their widespread use as inert materials; they are commonly used as insulators, packaging and in making containers.

However their low reactivity means that they are not easily decomposed in nature and as a result have a very long lifetime. Such substances are said to be non-biodegradable, and constitute an environmental hazard as they are very persistent in nature and thus difficult to dispose of.

Application activity 4.3

1. Poly(ethene) is a non-biodegradable plastic.

    a) Explain the term bio-degradable

    b) Give one environmental benefit of using biodegradable plastics.

    c) Developing biodegradable plastics involves compromise. Suggest one factor that requires careful consideration and explain your choice.

2. Multiple choice questions (choose the letter corresponding to the right answer);

    A) The word 'polymer' is said for material made from ______________.

    a) Single entity
    b) Two entities
    c) Multiple entities
    d) Any entity

B) One of characteristic properties of polymer material __________

e) High temperature stability
f) High mechanical strength
g) High elongation
h) Low hardness

C) Polymers are ___________ in nature.

a) Organic
b) Inorganic
c) Both (a) and (b)
d) None

D) These polymers cannot be recycled:

a) Thermoplasts
b) Thermosets
c) Elastomers
d) All polymers

E) In general, strongest polymer group is __________ .

a) Thermoplasts
b) Thermosets
c) Elastomers
d) All polymers

F) These polymers consist of coil-like polymer chains:

a) Thermoplasts
b) Thermosets
c) Elastomers
d) All polymers.

G) Strong covalent bonds exists between polymer chains in __________ .

a) Thermoplasts
b) Thermosets
c) Elastomers
d) All polymers

H) Following is the unique to polymeric materials:

a) Elasticity
b) Viscoelasticity
c) Plasticity
d) None.

I) Elastic deformation in polymers is due to _____________ .

a) Slight adjust of molecular chains
b) Slippage of molecular chains
c) Straightening of molecular chains
d) Severe of Covalent bonds

J) Kevlar is commercial name for ___________ .

a) Glass fibers
b) Carbon fibers
c) Aramid fibers
d) Cermets

4.4. Uses of polymers and their effect on the environment

Activity 4.4

1. List at least 3 commonly used polymers in daily life.
2. Explain why burning plastics such as PVC is particularly dangerous.
3. Look at the image below and answer the questions:

Analyze the above image and discuss the impacts of the materials contained in the said image on the environment.

Polymers are widely used materials in our daily life. To date, the importance of polymers is highlighted in their applications in different areas of sciences, technologies and industry from basic uses to biopolymers and therapeutic polymers.

4.4.1. Uses of polymers

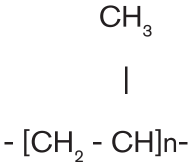
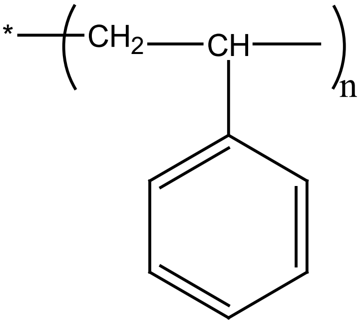
Polymers found many uses in our daily life:

Plastics are inexpensive, lightweight, strong, durable, corrosion-resistant materials, with high thermal and electrical insulation properties.

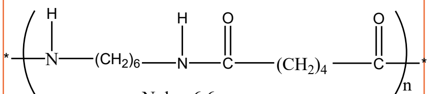
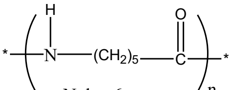
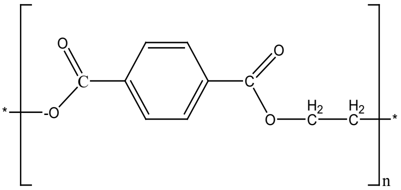
In general due to the properties of polymers, they are used to make a vast range of products that bring medical and technological advances, energy savings and numerous other societal benefits.

The following Table 4.4 shows the uses of the following commonly known polymers:

Table 4.4: Uses of common used polymers

Name	Chemical Formula	Properties	Uses
Polyethylene (PE)	$-[CH_2 - CH_2]n-$	Thermoplastic; translucent; Permeable by hydrocarbons, alcohol, and gas; resistant to X rays and chemical agents	Film, bags, pipe, insulating sleeves, bottle stoppers, lids, plastic wrap, toys
Polypropylene (PP)	 $\overset{\overset{CH_3}{\vert}}{-[CH_2 - CH]n-}$ Monomer is propene	Thermoplastic; low density; durable; resistant to X rays; permeable by water; impact resistant and temperature resistant 135°C	Household items, plastic wrap, automobile parts, batteries, bumpers, garden furniture, syringes, bottles, appliances
Polystyrene (PS)		Thermoplastic; transparent; nontoxic; optical and electrical properties; easy to color; resistant to X rays, oils, and grease.	Plastic wrap, kitchen utensils, furniture covers, thermal insulation, toys, office supplies, disposable razors

Polyvinyl Chloride (PVC) - [ClCH-CH_2]n–	- [Cl-CH - CH_2]n– Monomer is ClCH=CH_2 Vinyl Chloride	Thermoplastic; soft or rigid; opaque or transparent; fire resistant; resistant to X rays, acids, bases, oils, grease, and alcohol.	Household items, electric wire insulation, water pipes, floor coverings, window and door coverings, baggage, vinyl, sport and camping gear, items for chemical and automobile
Polytetrafluoroethylene (PTFE) or Teflon	-[CF_2 - CF_2]n- The monomer is $F_2C=CF_2$ Tetrafluoroethylene	Chemically inert, antiadhesive, impermeable to water and grease, heat and corrosion resistant	Orthopedic and prosthetic appliances, hearing aids, joints, upholstery, corrosion resistant mechanical parts, electrical insulation, frying pan coatings

Polyamides (PA) (examples: Nylon6,6; Nylon6)	 Nylon 6,6  Nylon 6	Thermoplastic, mechanical properties, durable to temperatures of 100°C, resistant to X rays and fuel, impermeable to odors and gas,	Food wrap, counters, electricity, fuel pipes, shoes, ski bindings, bicycle seats
Polyesters		Thermosetting, transparent, mechanical properties at high temperatures, electrical properties, resistant to impact, easy to work with	Textiles, plastic wrap, bottles, switches, electric Sockets and fuses, appliances.
Phenol formaldehyde polymers		Thermosetting, long lasting	Used in layers, Bakelite, Durable varnish

4.4.2. Effects of polymers on environment

Polymers or polymeric materials have eased the life of a man but there are some disadvantages related to polymers directly, especially their hazardous on the environment. On the other hand workers in the plastics industry are exposed to toxic substances is by inhalation and absorption through the lungs, which according to Lokensgard and Richardson (2004) accounts for nearly 90 percent of the toxic symptoms observed in the plastics industry.

However, concerns about usage and disposal are diverse and include accumulation of waste in landfills and in natural habitats, physical problems for wildlife resulting from ingestion or entanglement in plastic, the leaching of chemicals from plastic products and the potential for plastics to transfer chemicals to wildlife and humans. In the polymerization of compounds, some additive chemicals can be potentially toxic (for example lead and tributyl tin in polyvinyl chloride, PVC). Further substantial quantities of plastic have accumulated in the natural environment and in landfills.

The rural areas are more prone to this type of contamination and the related effects, as a majority of the people from these areas as there is over use of plastics on a large scale. Discarded plastics contaminate a wide range of natural terrestrial, freshwater and marine habitats.

When dumped in landfills, plastic materials interact with water and form hazardous chemicals which may be toxic to humans and other aquatic organisms. If these compounds seep down towards groundwater aquifers, they degrade the water quality, leading to groundwater pollution.

Many of plastic wastes lead to the formation of persistent organic pollutants (POPs), compounds which are very dangerous to the whole environment. These compounds persist in the environment and due to their property of bio-accumulation; they have high levels of toxicity in the food chain. Blockage due to plastic accumulation may form breeding grounds for mosquitoes and other harmful vector insects, which might cause numerous diseases in humans.

Burning plastic leads to the contamination of the atmosphere, due to the release of other poisonous chemicals, leading to air pollution. Recycling them requires much attention as they lead to the development of skin and respiratory problems due to inhalation of toxic chemicals. When plastic is burnt they release toxic chemicals that are deposited in soil and surface water and on plants.

Non-biodegradable polymers or long term biodegradable materials in the soil, especially plastic bags, they do not allow rain water for penetration which causes soil erosion.

NB: ***Rwanda has taken a tremendous decision of stopping the use of plastic bags in the country, which has got promising result for the environment and the users in general.***

Application activity 4.4

1. Give one large scale use for polyester polymers and state the property of polyesters on which the use depends.
2. Enumerate three environmental problems caused by the widespread use of plastics as polymers.

Skills Lab 4

In Rwanda there is a punishment of the people who are found using the plastic bags and other non-biodegradable packaging because they are not degraded and make the soil to be unproductive. Take a time and have a visit in the area where there is storage of the plastic bags and bottles and have observation even see the effect on plant in that area

By removing those plastic bags observe on the ground of their storage and make a conclusion about the rule sat and propose a solution of how to dispose those plastic things. In class come and present your findings and connect it with the environmental club. Give your support in protecting environment especially using plastic bags and plastic bottles even packages. Share your ideas with the local leaders by advising them how to dispose those dangerous materials.

End of unit assessment 4

1. Explain the terms cross-linking and thermosetting with reference to condensation polymers. For what purposes are thermosetting polymers suitable?

2. a) How the chemical inertness of poly(ethene) arise?

   b) How does it increase the usefulness of the material?

   c) How does it affect the disposal of waste polyethene?

3. a) What type of functional group joins the repeating units in nylon?

   b) In what way does the structure of nylon resemble that of a polypeptide?

   c) What type of interaction takes place between polymer molecules which contain the functional group present in polypeptide?

4. Identify 3 examples of synthetic polymers

5. What is the benefit of cross-linking polymer chains?

6. a) Give one example for each of the following type of polymer. Write the structural formula of the polymer and monomer unit. Give at least one use of the polymer named

   i) Natural addition polymer

   ii) Synthetic addition polymer

   iii) Natural condensation polymer

   v) Synthetic condensation polymer

b) State the role of each of the following in the manufacture of plastics

i) Fillers

ii) Plasticizers

c) i) what is meant by vulcanization?

ii) Discuss the effect of vulcanization on rubber molecules and state how it affects the physical properties of rubber.

iii) Name the monomer units in natural rubber

iv) Name one commercial synthetic rubber. Write equation to show how it is formed and give one use of it

UNIT 5

FACTORS THAT AFFECT THE RATE OF REACTIONS

Key Unit Competence:

Explain the factors that affect the rate of chemical reactions.

Introductory activity

Picture A

Picture B

Analyze these pictures and answer the questions below.

1. Name the reaction illustrated by each picture
2. Identify the fast reaction and the slow reaction
3. Suggest how the fast reaction can be slowed down and how the slow one can be speeded up.

The speeds at which chemical reactions occurs differ greatly. Some reactions, such as the combination of sodium and bromine, occur instantly. Other reactions, such as the rusting of iron, need a long time to take place. The area of chemistry concerned with the study of whether a reaction is fast or slow (reaction rates) is called **chemical kinetics**.

The profitability of many chemical processes depends on the reaction rates. For example, the economical synthesis of ammonia, used as a fertilizer, depends on the rate at which gaseous N_2 and H_2 can be converted into NH_3.

5.1. Concept of chemical kinetics

Activity 5.1

a) Burn a small amount (about 2 cm^3) of ethanol and record the time taken for this amount of ethanol to be completely burned.
b) Put 4ml of aqueous lead (II) nitrate solution in a test tube and add three drops of aqueous potassium iodide solution, then record the time taken for the yellow precipitate to be formed.
c) Put a piece of magnesium ribbon 1cm in a beaker containing ethanoic acid and record the time it takes for the whole ribbon to disappear.

Questions:

1. Suggest the name of the reaction that takes place in each of the above activities.
2. Write a balanced equation for each reaction.
3. Classify the above reactions using the table below:

Fast reactions	Slow reactions

The goal of chemical kinetics is to investigate how fast the reactants are consumed or the products are formed. It is important to predict the rate of processes and to find the influencing factors that promote a desired reaction or inhibit an undesired one.

Figure 5.1. Precipitation of silver chloride

During a chemical reaction, reactants are converted to products by breaking old bonds and forming new ones. Some chemical reactions are slow while others are fast. For example, precipitation of silver chloride is fast. It occurs instantaneously by mixing aqueous solutions of silver nitrate and sodium chloride.

$AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow AgCl_{(aq)} + NaNO_{3(aq)}$

However, the rusting of iron is a slow process that takes place over many days, even over the years. Similarly, the formation of diamond and other minerals in the earth's crust takes millions of years.

Apart from reaction rates, chemical kinetics is also a study of the mechanisms of chemical reactions. Any chemical process may be broken down into a sequence of one or more single-step processes known either as elementary processes, elementary reactions, or elementary steps.

The *rate of a reaction* is defined as the change in concentration of a reactant or a product in a given period of time. The reaction rate tells us how fast the reaction is taking place by indicating how much of a reactant is consumed or how much of a product is yielded in a given time.

Thus, $reaction\ rate = \frac{change\ in\ amount\ (or\ concentration)\ \text{of a substance}}{time\ taken}$

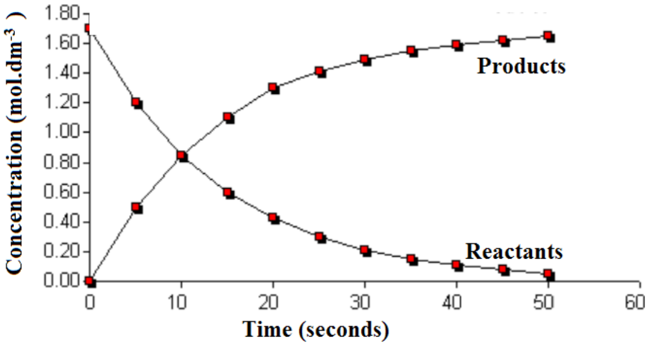


Figure 5.2 Change of concentration with time

In chemical kinetics, the rate of a reaction can be expressed as the initial rate, average rate or instantaneous rate.

The ***initial rate*** is the rate of a reaction measured at the beginning of the reaction. It is the change in concentration of a reactant, or product, per unit time at the start of reaction. The initial rate is simply the instantaneous rate at time equal to zero, or at the beginning of the reaction.

The ***average rate*** is defined as the change in concentration of a reactant or product of a chemical reaction in a given interval of time.

$$\text{Average rate of reaction} = \frac{\text{change in concentration of reactants or products}}{\text{Time interval}}$$

Average rate of reaction

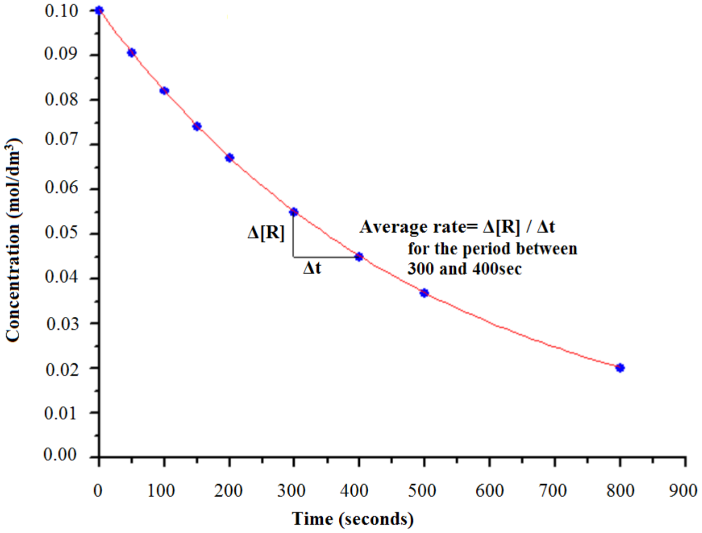


Figure 5.3 Average rate of a reaction

For example, consider the following reaction:

$$R \longrightarrow P$$

In this reaction, one mole of the reactant R produces one mole of the product P. If $[R]_1$ and $[P]_1$ are concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are concentrations of R and P respectively at time t_2 then,

$\Delta t = t_2 - t_1$

$\Delta[R] = [R]_2 - [R]_1$

$\Delta[P] = [P]_2 - [P]_1$

$$\text{The average rate of disappearance of R} = \frac{\text{Decrease in concentration of R}}{\text{Change in time}} = -\frac{\Delta[\text{R}]}{\Delta \text{t}}$$

By convention, the rate is always expressed as positive quantity. Because the concentration of reactants is decreasing with time, Δ[R] is a negative number. We use the negative sign to make the rate of reaction a positive quantity.

$$\text{The average rate of appearance of P} = \frac{\text{Increase in concentration of P}}{\text{Change in time}} = +\frac{\Delta[\text{P}]}{\Delta \text{t}}$$

For a better understanding, consider the following examples:

1. Consider the following reaction at 300°C: **$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$**

If in the first 150 seconds, the concentration of nitrogen dioxide has decreased from 0.0100 mol/L to 0.0055 mol/L, the average rate for the disappearance of nitrogen dioxide for the first 150 seconds is:

$$Rate = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{(0.005 mol/L - 0.0100 mol/L)}{150s} = \frac{0.0045 mol/L}{150s} = 3.0\,x10^{-5}\,mol/L.s$$

2. Consider the reaction of the acidified hydrogen peroxide (H_2O_2) added to a solution of potassium iodide (KI) and iodine is liberated.

$H_2O_{2\,(aq)} + 2KI_{(aq)} + H_2SO_{4(aq)} \rightarrow H_2O_{(aq)} + I_{2(aq)} + O_{2(g)} + K_2SO_{4(aq)}$

In this reaction, initially the concentration of iodine is zero. But as time goes on it increases, and the reacting mixture becomes brownish. The concentration of iodine can be measured at different intervals of time by titration against sodium thiosulphate. If the concentration of iodine rises from 0 to 10^{-5} mol L^{-1} in 10 seconds, the average rate becomes:

$$Rate = \frac{\Delta[I_2]}{\Delta t} = \frac{10^{-5}\,mol/L}{10s} = 10^{-6}\,mol\,L^{-1}s^{-1}$$

The ***instantaneous rate*** is the change in concentration of a reactant or product of a chemical reaction at a given instant. This rate is measured when the reaction is in progress at any point of time.

It is obtained when we consider the average rate at the smallest time interval ***dt*** (i.e. when Δt approaches zero***).***

Mathematically, for an infinitesimally small dt, the instantaneous rate is given by:

$$Rate, R = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Where d[R] = small change in concentration of R and dt = small change in time

For the general reaction:

$$aA + \ bB \longrightarrow cC \ + \ dD$$

The rate is given by:

$$Rate = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Where a, b, c and d are stoichiometric coefficients of reactants and products.

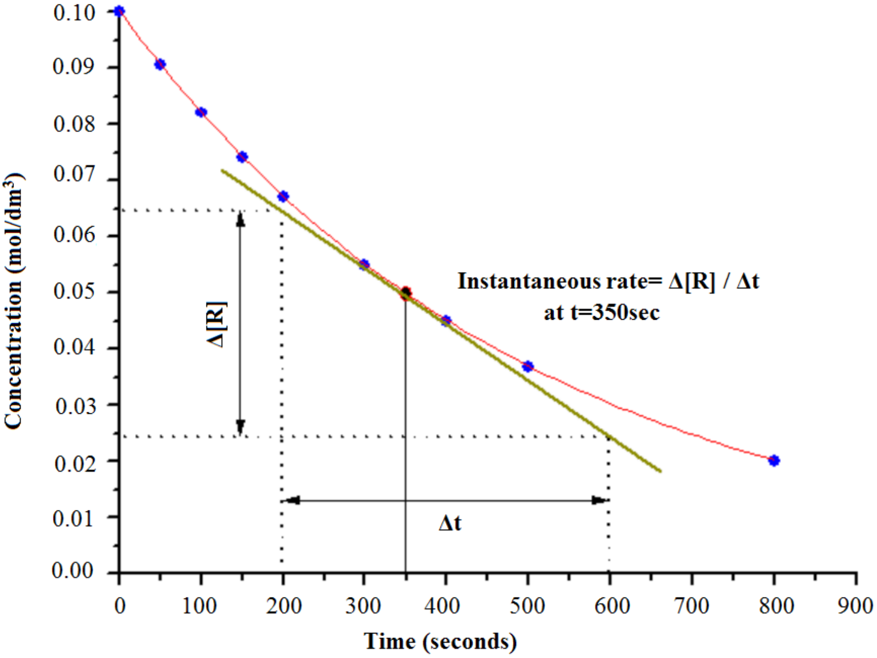


Figure 5.4 Instantaneous rate of reaction

Example:

The decomposition of dinitrogen pentoxide: 2 $N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$ was performed in the laboratory and the rate of formation of NO_2 was found to be 0.53 M/s.

a) What was the rate of formation of $O_2(g)$?

b) What was the rate of consumption $N_2O_5(g)$?

Answer:

a) First determine the relationship between $NO_2(g)$ and $O_2(g)$ in terms of rate using the coefficients of the balanced equation:

$$Rate = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Next substitute in the given values and solve the rate of formation of $O_2(g)$:

Rate of formation of $O_2(g)$ = (1/4) (0.53 M/s) = 0.13 M/s

b) First determine the relationship between $NO_2(g)$ and $N_2O_5(g)$ in terms of rate using the coefficients of the balanced equation:

Reaction $Rate = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$

Next, substitute the given values and solve for the rate of consumption of $N_2O_5(g)$:

$-(\frac{1}{2})$ rate of consumption of $N_2O_5(g)$ = +1/4 rate of formation $NO_2(g)$

Rate of consumption of $N_2O_5(g)$ = $\frac{2}{4}$ (0.53 M/s) = 0.27 M/s.

The rate of a chemical reaction is important in our daily life as well as in industry. At home, it is interesting to know the rate at which a kind of food is cooked (i.e. boiling an egg or baking a cake). It is interesting to know the rate at which the seeds of maize or beans are growing till the time of harvesting. In the body, chemical reactions must take place at the correct rate to supply exactly the needs of the cells.

The rate of reaction dictates the rate of production of our daily products. In order to meet the demand and safety standards, optimization of rate of reaction is nonetheless the most important subject to control and study. Kinetic studies are important in understanding reactions, and they also have practical implications. In industry, reactions are conducted in reactors in which compounds are mixed, possibly heated and stirred for a time, and then moved to the next phase of the process. It will be important to know how long to hold the reaction at one stage before moving on, to make sure that reaction has finished before starting the next one. By understanding how a reaction takes place, many processes can be improved.

Another importance of kinetics is to understand the biological processes, especially enzyme-catalyzed reactions.

Application activity 5.1

1. What is meant by the expression rate of a reaction?
2. In the following reaction:

   $$\text{A} \longrightarrow \text{Products,}$$

   The concentration of A decreases from 0.5 mol/L to 0.4 mol/L in 10 minutes. Calculate the average rate of this reaction in mol/dm^{-3}/s.

5.2. Factors that change the rates of reactions

Activity 5.2.a

1. Chemicals and apparatus: 0.1M $Na_2C_2O_4$ (FA1), 0.1M $KMnO_4$ (FA_2), H_2SO_4conc, test tubes, heater.

Procedure: -Put 10ml of FA_1 into 2 separate beakers labelled A and B.

Note: Beaker A will be heated to raise up the temperature of the solution.

- Add 3drops of H_2SO_4conc into each beaker and mix well.
- Add 2ml of FA_2 into each beaker and shake it to mix both solutions well.
- Record the time it takes for the solution in each beaker to become colorless.

Suggest a reason for the observations made.

In chemical kinetics, the determination of how quickly or slowly reactants turn into products is a measure of the ***reaction rate***. All factors that can change the number of collisions of reacting particles can also change the rate of reaction, based on collision theory.

These factors are:

a) Temperature
b) Concentration
c) Pressure
d) Surface area
e) Light
f) Catalyst

According to collision theory, for a chemical reaction to occur it is necessary for the reacting species (atoms or molecules) to collide with energy equal to or greater than the activation energy and with proper orientation.

Thus, a factor that increases the number of collisions between particles will increase the reaction rate and a factor that decreases the number of collisions between particles will decrease the chemical reaction rate.

5.2.1. Temperature

Temperature is a factor that plays a big role in chemical reactions. In general, the rates of most chemical reactions increase as the temperature rises. When the temperature of a reaction is increased, the heat is supplied to the particles involved in the reaction. Since heat is a form of energy, these particles acquire more energy which enables them to move more quickly and they collide with each other more frequently and with more energy. Therefore, more particles will overcome the activation energy barrier to form products. If temperature is decreased, particles will move more slowly, therefore decreasing the rate of reaction.

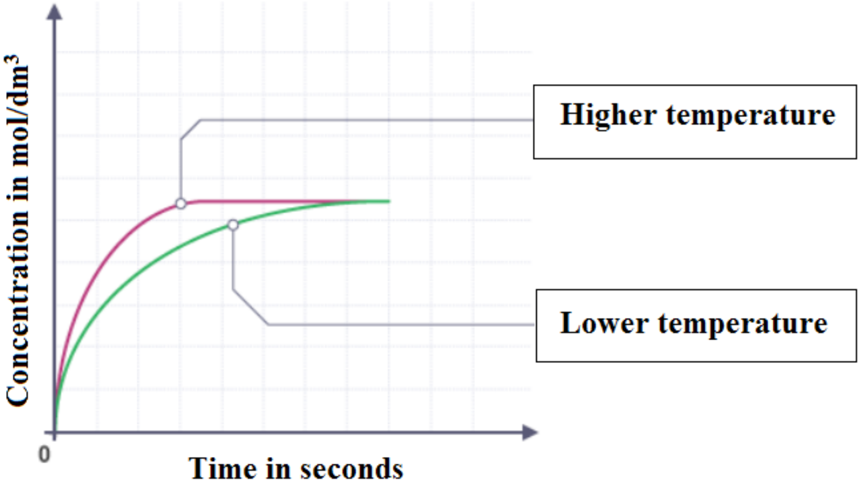


Figure 5.5 Effect of temperature change on rate of reaction

Increasing the temperature of the reactants sometimes provides the activation energy needed to initiate a chemical reaction.

Examples:

i) Some types of food such as meat get spoilt quickly when kept out of a refrigerator. However, when they are kept in a refrigerator, the lower temperature inside the refrigerator slows down the proliferation of microorganisms that destroy the meat.

ii) Consider the chemical reaction: $CaCO_3(s) + 2\ HCl(aq) \rightleftharpoons CaCl_2(aq) + CO_2(g) + H_2O(l)$

At **273 K (0 °C),** the reaction is extremely slow, and the amount of CO_2 produced is very small. When the temperature is raised to **323 K (50 °C),** the reaction becomes fast and more quantity of CO_2 is obtained.

The temperature dependence of the rate of a chemical reaction can be explained by the following Arrhenius equation.

$$K = Ae^{-\frac{Ea}{RT}}$$

Arrhenius Svante

Where:

K is Rate constant

A is Arrhenius constant

Ea is Activation energy

R is Gas constant

T is Temperature

The logarithmic form of the Arrhenius equation is:

$$\ln K = \ln A - \frac{Ea}{RT} \text{ or } logK = logA - \frac{EA}{2.303RT}(\frac{1}{T})$$

When temperature changes from T_1 to T_2 the Arrhenius equation becomes:

$$\ln\frac{K_1}{K_2} = \frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{or} \quad \log\frac{K_2}{K_1} = -\frac{Ea}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Using the above equations, we can calculate the ratio of rate constants or activation energy if we know the rate constants of a reaction at two different temperatures.

Example:

The rate constant for the reaction: $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$ is 2.7×10^{-4} at 600 K and 3.5×10^{-3} at 650 K. Calculate the activation energy of the reaction. ($R = 8.31 Jmol^{-1}K^{-1}$).

Answer:

$$\log\frac{K_2}{K_1} = -\frac{Ea}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\log\frac{3.5x10^{-3}}{2.7x10^{-4}} = -\frac{Ea}{2.303x8.31}\left(\frac{1}{650} - \frac{1}{600}\right)$$

Ea $= 1.03 \text{ x}10^{5} \text{ J mol}^{-1}$

Application activity 5.2.a

1. Using the collision theory, describe the effect of carrying out a reaction at a low temperature.
2. The rate constant for the reaction: $A_{(g)} + B_{(g)} \rightarrow C_{(g)}$ is 1.7×10^{-3} at 500 K and 4.5×10^{-2} at 600 K. Calculate the activation energy of the reaction. ($R = 8.31 Jmol^{-1}K^{-1}$).
3. The rate constants of reaction at 700 K and 760 K are $0.011 M^{-1}s^{-1}$ and $0.105 M^{-1}s^{-1}$ respectively. What are the values of ‘A’ and ‘Ea’?

5.2.2 Concentration, Pressure, surface area and light

Activity 5.2.b

A. Chemicals and Apparatus: 0.2M sodium thiosulphate, 2.0M hydrochloric acid, distilled water, measuring cylinder, stop clock (or stopwatch), conical flask and white paper.

Procedure:

1. Prepare sodium thiosulphate solution (about 0.2M) by adding 2g of sodium thiosulphate solid to 60cm^3 of water in a conical flask.
2. Divide the solution into three equal portions, put them in three different conical flasks and place each conical flask on white paper marked with a cross (X).
3. To one conical flask add 1cm^3 of 2M HCl solution and swirl the mixture gently for uniform mixing, you must start the stop clock immediately after adding the acid into the sodium thiosulphate solution. Record the time it takes for sulphur to be precipitated enough to obscure the cross when viewed from the top.
4. To the remaining two conical flasks, add 2cm^3 and 3cm^3 of the 2M HCl respectively. Record the time taken in each case for the cross to be obscured.

Questions:

1. State, in which conical flask, the reaction was fast. Suggest a reason for your answer.
2. Write balanced equation for the reaction that takes place.

B.

Procedure:

1. To approximately 10 cm^3 sodium chloride solution in a large test tube add a few cm^3 of silver nitrate solution. An immediate precipitate of silver chloride will be formed.
2. Quickly divide the precipitate formed into three parts and, put them into three separate test tubes.
3. Put one of the test tubes immediately into a dark cupboard, the second may be left out on the bench and the third may be placed near a source of strong light (example: in direct sunshine or near to a lamp).

Question:

Examine the color of the precipitates at regular intervals and interpret your observations.

i) Concentration

Concentration refers to the number of particles dissolved in a given volume of a solution. The more the reacting particles are present in a given volume, the more opportunities of the collisions involving those particles will occur.

The rates of many reactions depend on the concentrations of the reactants. It has been observed that the rate of chemical reaction is directly proportional to the concentration of the reactants. Thus, increasing the concentration of the reactants usually results in a higher reaction rate. At lower concentrations, there is less chance for collisions between particles. Thus, decreasing the concentrations of reactants results in a lower reaction rate.

At the beginning of a reaction, when the concentration of reactants is maximum, the rate of reaction is also maximum. However, as the reaction proceeds the concentration of the reactants decreases as some amount of reactants is converted into products. The rate of the reaction decreases as the reactants are consumed and it increases when the products are formed **(Figure 5.6).** The reaction rate is directly proportional to the concentration.

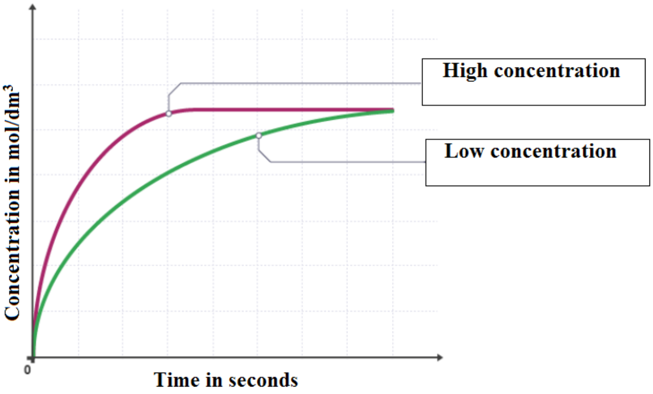


Figure 5.6.Effect of concentration on the rate of reaction

For example, consider the reaction: **$2NO + O_2 \rightarrow 2NO_2$**

The rate of this reaction doubles ***when the concentration of oxygen is doubled.*** On the other hand, when the concentration of nitric oxide is ***doubled,*** the rate of reaction ***increases four times.***

ii) Pressure

The pressure affects the rate of chemical reactions when the reactants or products are in gaseous state only. This is because solids and liquids cannot be compressed.

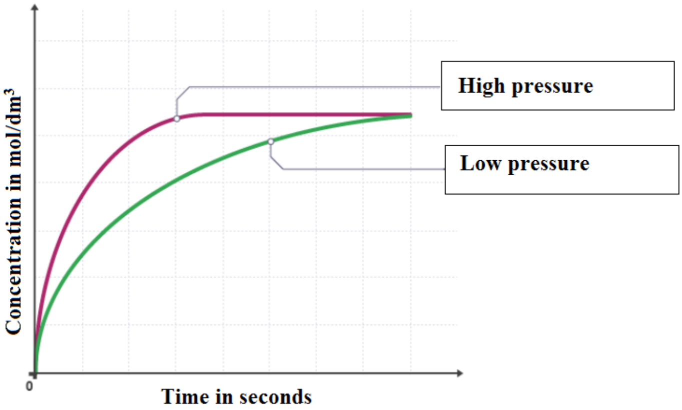


Figure 5.7Effect of pressure on the rate of reaction.

Pressure has a similar effect as concentration on the reaction rate. When the pressure increases in the gaseous system, the number of collisions between reactants also increases. Consequently, the rate of reaction is increased. At high pressure, the gas particles are closer together which increases the collisions.

iii) Light

Light is a form of energy that can affect the rate of a reaction. The rate of some photochemical reactions increases with increase in the intensity of suitable light used. The energy provided by light increases with the increase in its intensity. Hence, a greater number of reactant molecules gets enough energy to undergo a chemical change.

Examples:

1. When methane reacts with chlorine in dark, the reaction rate is very low. It can be speeded up when the mixture is put under diffused light. In bright sunlight, the reaction is explosive.

2. The rate of photosynthesis reaction is more on brighter days. At low light intensities, as light intensity increases, the rate of the light-dependent reaction (photosynthesis) generally, increases. The more photons of light that fall on a leaf, the greater the number of chlorophyll molecules that are ionized and the more ATP and NADPH are generated.

However, some photochemical reactions involving free radicals, generated in a chain process, are not greatly affected by the intensity of the light. Only one photon is sufficient to trigger the formation a free radical. This, in turn, initiates a chain process in which more free radicals are formed repeatedly in each cycle without the need of extra photons.

When photons strike the reactant molecules, they provide necessary activation energy to the reactant molecules.

There are many reactions influenced by light. For example: photosynthesis and photography. Such reactions are known as **photochemical reactions.** Other examples are:

$$H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$$

$$2AgCl \xrightarrow{\text{sunlight}} 2Ag + Cl_2$$

$$SO_2 + Cl_2 \xrightarrow{\text{sunlight}} \underbrace{SO_2Cl_2}_{\text{sulphuryl chloride}}$$

$$CO + Cl_2 \xrightarrow{\text{sunlight}} \underbrace{COCl_2}_{\text{phosgene}}$$

iv)Surface area

Surface area is the measure of how much area of an object is exposed. For the same mass, many small particles have a greater surface area than one large particle. The more surface contact between reactants, the higher the rate of reaction. The less surface contact, the lower the reaction rate.

The rate of a reaction between two phases greatly depends on the surface contact between them. For instance, a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid, because the finely divided solid has a larger surface area.

Examples:

1. Large pieces of wood burn slowly, smaller pieces burn rapidly, and sawdust burns explosively.
2. Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total surface area:

   $$2Fe(s) + 6HCl(aq) \longrightarrow 2FeCl_3(aq) + 3H_2(g)$$

   An iron nail reacts more slowly.
3. Powdered calcium carbonate reacts much faster with dilute hydrochloric acid than if the same mass was present as lumps of marble chips or limestone.

   $$CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$$

In general, the more finely divided a solid reactant is, the greater the surface area per unit volume and the more the number of collisions between reactants. Increasing the collisions increases the rate of reaction.

Application activity 5.2.b

1. Two students Anna and Derrick want to measure the volume of carbon dioxide produced when 50g of calcium carbonate react with excess HCl. Anna decides to use large particles whereas Derrick uses the powder form. Who will get the results first? Explain your answer.
2. Consider the following reaction: $3H_{2\ (g)} + N_{2\ (g)} \leftrightarrow 2NH_{3\ (g)}$ at equilibrium. What will be the effect of increasing the total pressure of the system on the rate of formation of ammonia? Explain your answer.

5.2.3. Effect of Catalyst on rate of reaction

Activity 5.2.c

Apparatus and chemicals: Hydrogen peroxide, test tubes, wooden splint, manganese (IV) oxide, test tube racks and propane-1,2,3-triol.

Procedure

1. Put 15cm^3 of dilute hydrogen peroxide in a clean beaker (B_1) and place it in the test tube rack. Observe the test tube from time to time and record your observations.
2. Put another 15 cm^3 of fresh dilute hydrogen peroxide in a beaker (B_2) and add a half-spatula of manganese (IV) oxide. Test the gas produced with a glowing splint.
3. Put 15 cm^3 of dilute hydrogen peroxide in a clean beaker (B_3) and put a very small amount of manganese (IV) oxide. When the reaction starts add about 1cm^3 of propane-1,2,3-triol and shake the contents of the beaker.

Question:

Compare the rate of oxygen gas production in beakers B_1 and B_2 to that in B_3.

For a reaction to take place, the molecules must possess a certain energy called **activation energy**, which is the minimum amount of energy required for a chemical reaction to take place. If the activation energy is high, the reaction will be slow, and a catalyst is required for lowering this activation energy.

A catalyst is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Catalysts reduce the amount of energy required to break and form bonds during a chemical reaction.

The effect of adding a catalyst on a reaction can be demonstrated on a Potential Energy Diagram **(Figure 5.8)**

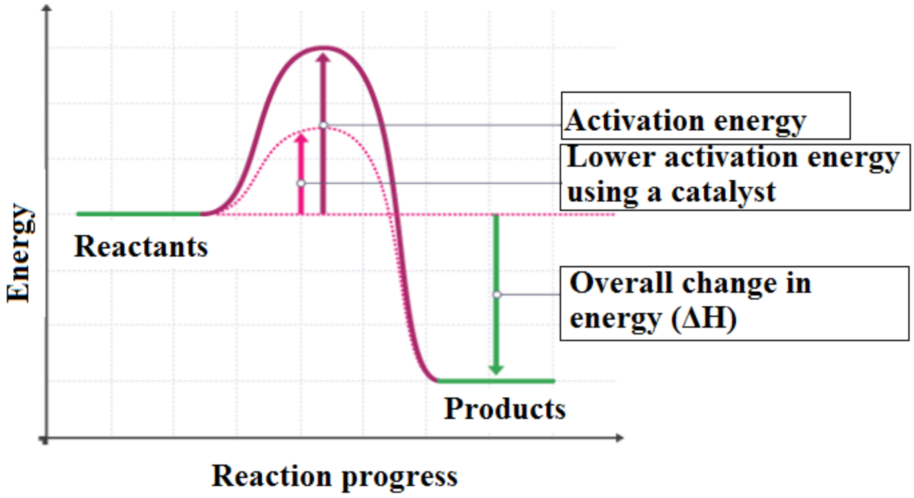


Figure 5.8 Effect of catalyst on the rate of reaction

Most catalysts are highly selective; they often determine the product of a reaction by accelerating only one of several possible reactions that could occur.

Note: Except a catalyst that can lower the activation energy (Ea), increasing the temperature, concentration or surface area has no effect on the activation energy (Ea).

Examples of catalysts:

- The decomposition of hydrogen peroxide (H_2O_2) is relatively slow; however, exposure to light accelerates this process and in the presence of MnO_2 as a catalyst, the reaction goes very fast.
- In the manufacture of ammonia, iron is used as a catalyst to increase the rate of reaction.

  $N_2\,(g) + 3H_2\,(g) \rightarrow 2\,NH_3\,(g)$

- Similarly, reaction of Sulphur dioxide and oxygen to produce sulphur trioxide takes place in the presence of catalyst vanadium (V) pentoxide (V_2O_5).

  $2SO_2\,(g) + O_2\,(g) \rightarrow 2\,SO_3\,(g)$

Types of Catalysts

The main types of catalysts are homogeneous and heterogeneous. Others are positive, negative, auto and induced catalysts.

a) Homogeneous Catalyst

A **homogeneous catalyst** is the one which is in the same phase as the substances it catalyzes.

Example

- In the oxidation of iodide ions by peroxodisulphate ions, ion is a homogeneous catalyst.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \xrightarrow{Fe^{2+}(aq)} 2SO_4^{2-}(aq) + I_2(aq)$$

b) Heterogeneous Catalyst

A heterogeneous catalyst is the one which is in a physical state other than that of reacting substances. A process involving this catalyst is also known as surface catalysis or contact catalysis.

Examples:

- Haber's Process:

$$N_2(g) + 3H_2(g) \overset{Fe(s)}{\rightleftharpoons} 2NH_3(g)$$

- Hydrogenation of alkenes (catalyzed by nickel or platinum):

$$RCH{=}CHR(g) + H_2(g) \xrightarrow{\text{Ni or Pt}} RCH_2 - CH_2R$$

c) Positive catalyst

The substance which increases the rate of reaction is known as a **positive catalyst**. It acts by decreasing the activation energy of the reaction

Figure 7.2 Decomposition of H_2O_2 in MnO_2

An example of a positive catalyst is vanadium pentoxide, V_2O_5, used in Contact Process:

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_{5(s)}} 2SO_{3(g)}$$

d) Negative catalyst (Inhibitor or retarder)

The substance which decreases the rate of reaction is known as a **negative catalyst**. It acts by increasing the activation energy of a reaction.

Example:

Acetanilide prevents the oxidation of Na_2SO_3 by air; it is a negative catalyst. Similarly,

H_3PO_4 prevents the decomposition of H_2O_2.

e) Auto catalyst

This is a substance that catalyzes the reaction which is producing it.

Example:

In the oxidation of ethanedioic acid (oxalic acid) by potassium permanganate ($KMnO_4$), Mn^{2+} ion formed acts as catalyst and increases the rate of reaction.

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2C_2O_4(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(aq)$$

The initial stages of the reaction are slow but as the reaction proceeds, the reaction rate increases. The increase in the rate is caused by the accumulation of the catalyst Mn^{2+} which is formed in the initial stages of the reaction.

f) Enzymes

Enzymes are **biological catalysts** which catalyze the chemical reactions occurring in living organisms. Enzymes are higher molecular mass proteins.

Examples:

Oxidoreductases: Responsible for catalysis of reduction or oxidation of molecules.

Transferases: Catalyze transfer of functional group from one chemical compound to the other.

Hydrolases: Catalyze the hydrolysis reactions and the reverse reactions.

Application activity 5.2.c

1. Give the name and the type of catalyst used in each of the following reactions:

   a. Production of ammonia in the Haber process.

   b. Hydrogenation of alkenes.

2. Explain in details why it is necessary to use a catalyst when a reaction is carried out at a low temperature.

Skills Lab 5

1. Suppose that you are hired to be a chemist of a milk processing factory. Discuss how the knowledge of factors that affect the rates of chemical reactions will help you to fulfill your responsibilities.
2. Explain the factor behind the use of cold packs to immediately treat physical injuries of footballers.
3. Referring to the factors that affect rates of reactions, explain why drinking water right after eating can cause indigestion.

End of unit assessment 5

1. For the following multiple-choice questions on the rate of reactions, choose the correct answer.

   The study of the rate of chemical reactions is called ....

   A) reaction rate

   B) reaction kinetics

   C) reaction speed

   D) reaction power

2. As the temperature of a reaction is increased, the rate of the reaction increases because the..............................

   A) reactant molecules collide less frequently

   B) reactant molecules collide more frequently and with greater energy per collision

   C) activation energy is lowered

   D) reactant molecules collide less frequently and with greater energy per collision

3. Rate of reaction is change in the concentration of reactants or products in a specific…

   A) volume

   B) density

   C) time

   D) area

4. Effect of pressure (in case of gases) is like the effect of

   A) concentration

   B) molarities

   C) temperature

   D) humidity

5. __________ will lower the activation energy for a reaction.

   A) increasing the concentrations of reactants

   B) raising the temperature of the reaction

   C) adding a catalyst for the reaction

   D) removing products as the reaction proceeds

6. Aluminium reacts with warm dilute hydrochloric acid to give aluminium chloride solution and hydrogen. Explain why the reaction of dilute hydrochloric acid with aluminium foil is fairly slow whereas the reaction with the same mass of aluminium powder can be extremely vigorous.

7. For the reaction A → B, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

8. The decomposition of dinitrogen pentoxide (N_2O_5) in tetrachloromethane(CCl_4) at 318K has been studied by monitoring the concentration of dinitrogen pentoxide in the solution.

   Initially, the concentration of dinitrogen pentoxide is 2.33mol/L and after 184 minutes, it is reduced to 2.08mol/L. The reaction takes place according to the equation:

$$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$$

   Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of nitrogen dioxide during this period?

9. Calculate the activation energy for a reaction whose rate constants are $2.15x10^{-1}dm^3mol^{-1}s^{-1}$ and $7.25x10^{-3}dm^3mol^{-1}s^{-1}$ at 991K and 500K respectively. ($R = 8.3145\ JK^{-1}mol^{-1}$).

10. How much faster will the reaction be at 781K than 550K if the activation energy of the reaction is 190 kJ/mol? ($R = 8.3145\ JK^{-1}mol^{-1}$).

UNIT
6

pH OF ACIDIC AND ALKALINE SOLUTIONS

Key Unit Competence:

Prepare solutions, measure and calculate their pH, explain the concept of buffer solution, and its applications in manufacturing and biological processes.

Introductory activity

The fruits we use in our everyday life are either acidic or alkaline.

1. Classify the fruits above as acidic or alkaline using universal indicator paper.
2. Which fruit is more likely to give the most acidic juice?
3. You are provided with lemon and orange juices. Describe a simple technique you can use to compare the acidity degree of both juices.

Many fruit juices and other soft drinks contain acids, and this can be identified by their sour or sharp taste. They contain many dissolved compounds of which acids are among. Some acids are chemicals that can be harmful or dangerous to human and should never be tested by drinking them (i.e. sulphuric acid used in car batteries).

Bases are products commonly used in our daily life such as soap, toothpaste, milk, magnesium syrup, baking soda. Solutions of bases are slippery on touch because they attack oils on the skin and convert them into soaps. This makes them to be good cleaning agents. Bases dissolve in water to form solutions called **alkaline solutions**.

Acids can react with bases to form compounds known as **salts** which are of great importance in nature. For example, ammonium chloride is used as an electrolyte in dry cells, calcium carbonate is used in the manufacture of cement, potassium nitrate is used as a fertilizer, magnesium sulphate and iron (II) sulphate are used to manufacture drugs.

6.1. Degree of ionization in relation to the strength of acids and bases

Activity 6.1

a) Define the following terms and give an example of each:

  (i) a Brønsted-Lowry acid

  (ii) a Lewis base

b) Describe the difference between strong and weak acids.

c) Write an equation of the dissociation of ethanoic acid in water and identify the acid/base conjugate pairs.

6.1.1. Acids and bases

Previously, an acid has been defined as a substance that donates hydrogen ions while a base was defined as a substance that accepts hydrogen ions. Acidity and alkalinity are measured with a logarithmic scale called pH.

– **Strong and weak acids**

When an acid is dissolved in water, there are more hydrogen ions than hydroxide ions in the solution meaning that the solution is acidic. We distinguish strong and weak acids.

A strong acid ***is completely ionized (dissociated)*** when dissolved in water. For example, hydrochloric acid ionizes completely in water to form hydrogen or hydroxonium ions, $H^+_{(aq)}$, and chloride ions, $Cl^-_{(aq)}$, as illustrated below. **The single arrow indicates that the compound is completely ionized.**

$HCl_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

Other strong acids include sulphuric acid (H_2SO_4), nitric acid (HNO_3), perchloric acid ($HClO_4$) and many more.

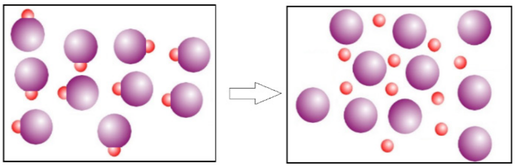


Figure 6.1. Complete dissociation of a strong acid.

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

A weak acid ***is partially ionized*** when dissolved in water. Only a small portion of its molecules ionizes. For example, ethanoic acid ionizes partially in water to form ethanoate ions and hydroxonium ions as shown below. **The double arrow symbolizes the partial dissociation.**

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

Other weak acids include sulphurous acid (H_2SO_3), carbonic acid (H_2CO_3), phosphoric acid (H_3PO_4), methanoic acid (HCOOH), etc. Generally, organic acids are known as weak acids.

- **Strong and weak bases**

When a base is dissolved in water, there are more hydroxide ions in the solution than hydrogen ions and the solution is **alkaline**. We distinguished strong and weak bases.

A strong base **dissociates (ionizes) completely** when dissolved in water. For example, sodium hydroxide (NaOH) ionizes in water to form sodium ions and hydroxide ions as illustrated below:

$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$

Potassium hydroxide is another example of a strong base.

A weak base **dissociates partially** when dissolved in water.

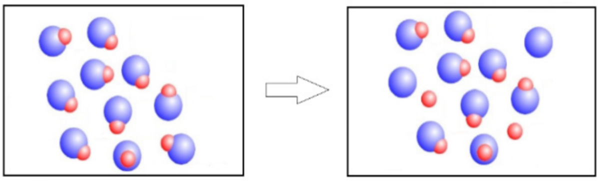


Figure 6.2 Partial dissociation of a weak base.

For example, ammonium hydroxide ionizes partially in water to form ammonium ions and hydroxide ions as shown below:

$$NH_{4(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

Phenylamine ($C_6H_5NH_2$) and Hydroxylamine (NH_2OH) are other examples of weak bases.

6.1.2 Degree of ionization (α)

The degree of ionization is the extent to which a molecule is dissociated into its constitutive ions when dissolved in water. In other words, it is ***the ratio of the number of ionized molecules to the total number of molecules dissolved in water.*** It is symbolized by α_a for acids and α_b for bases.

$$\alpha = \frac{\text{number of ionized molecules}}{\text{total number of molecules dissolved in water}}$$

When a weak acid or weak base is dissolved in water, partial ionization occurs such that equilibrium is set up between the undissolved molecules and the ions formed in water. This equilibrium is known as ***ionic equilibrium*** of an acid or base.

The degree of ionization can have values ranging from 0 to 1.

α is equal to zero for non-electrolytes (i.e. substances which do not ionize in water).

α is equal to 1 for strong electrolytes such as strong acids or bases because they ionize completely in water.

α is less than 1 and greater than 0 in the case of weak electrolytes such as weak acids or bases because they ionize partially in water.

The degree of ionization can also be expressed as a percentage as shown by the relation below.

$$\alpha = \frac{\text{concentration of ions formed}}{\text{Original concentration of electrolyte}} \times 100\%$$

The greater the degree of ionization, the stronger the acid or base. For example, the concentration of an acid, HA, that undergoes ionization is equal to the concentration of hydrogen ions formed as shown below:

$$HA_{(aq)} \longrightarrow A^{-}_{(aq)} + H^{+}_{(aq)}$$

$$\text{Percentage ionization} = \frac{[H^{+}]}{[HA]} \times 100\ \%$$

Example

What is the degree of dissociation of a weak acid in a 0.25M solution, given the concentration of H^+ as 0.001 mol dm^{-3}?

Answer:

Degree of dissociation: $\alpha_a = \frac{[H^{+}]}{[Acid]}$

$$\alpha = \frac{0.001}{0.25} = 0.004 = 0.4\%$$

Application activity 6.1

1. A 0.1moldm^{-3} methanoic acid solution contains 0.0042moldm^{-3} of hydrogen ions. Calculate the percentage of the acid that is ionized.
2. A solution of 0.035M nitrous acid contains 0.0037M of hydrogen ions. Calculate the percentage ionization of the acid.
3. Two acids A and B have α_{aA}= 0.5 and α_{aB}= 0.05. Which acid is stronger? Explain your reasoning.
4. If 0.750 M solution of the weak base ethylamine ($C_2H_5NH_2$) contains 2.04×10^{-2} M of OH^-, what is its degree of ionization?

6.2. Explanation of acid and base dissociation constants (K_a and K_b)

Activity 6.2

1. Write the expression of the equilibrium constant, Kc, for the reaction below:

   $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

2. (a) Write an equation to show the ionization of ethanoic acid in water.

   (b) Write an equation to show the hydrolysis of ammonia in water.

3. A 10.0cm^{3}mixture contains the equilibrium amounts/mol ethanol 0.0515; ethanoic acid 0.0525; water 0.0167; ester 0.0314 and $H^+_{(aq)}$ 1.00x10^{-3}. Calculate the value of Kc for this reaction.

Weak acids and bases dissociate partially when dissolved in water, in a reversible process which reaches equilibrium at a given time. Therefore, equilibrium constants can be used to explain the strength of acids and bases based on their ionization reactions.

In acid-base equilibrium, both forward reaction (to the right) and reverse reaction (to the left) involve proton transfer. The acid-base dissociation reaction leads to the formation of **conjugate acib-base** as follow:

Acid + Base $\rightleftharpoons$ Conjugate Base + Conjugate Acid

Examples:

6.2.1. Acid dissociation constant, K_a

The **acid dissociation constant** also known as **acidity constant** or **acid ionization constant** is the equilibrium constant for the ionization reaction of an acid. It is denoted by $\mathbf{K_a}$ and expressed in **mol/dm³**.

This constant is a quantitative measure of the strength of the acid in solution.

Acid dissociation constants are mostly associated with weak acids because strong acids are completely ionized in the aqueous solution and their K_a values are extremely large.

Consider a weak acid HA. Its ionization is represented as follows:

$$HA_{(aq)} \rightleftharpoons A^-_{(aq)} + H^+_{(aq)}$$

The equilibrium constant for the dissociation of HA is as follows:

$$K_a = \frac{[A^-][H^+]}{[HA]}$$

6.2.2. Base dissociation constant, K_b

The **base dissociation constant** also known as **base ionization constant** or **basicity constant** is the equilibrium constant for the ionization reaction of a weak base. It is denoted by $\mathbf{K_b}$ and expressed in **mol/dm³**. The equilibrium constant, K_b, measures the strength of the base in solution.

Base dissociation constants are mostly associated with weak bases because strong bases are completely ionized in the aqueous solution and their K_b values are extremely large.

Consider a weak base, BOH undergoing ionization as shown below:

$$BOH_{(aq)} \rightleftharpoons OH^-_{(aq)} + B^+_{(aq)}$$

The base dissociation constant, K_b, can be expressed by applying the equilibrium law:

$$K_b = \frac{[OH^-][B^+]}{[BOH]}$$

When K_b is large, the base is highly dissociated, and therefore it is strong. When it is small, a few molecules of the base dissociate, and the base is weak.

6.2.3 Relationship between equilibrium (dissociation) constant and the degree of ionization α; Ostwald's dilution law

The relationship between the equilibrium constant and the degree of dissociation of weak electrolytes has been introduced by Ostwald in 1888.

The Ostwald's dilution law states that "the degree of ionization of a weak electrolyte is inversely proportional to the square root of the molar concentration of the electrolyte".

$$\alpha = \sqrt{\frac{Ka}{c}}$$

Where C is the molar concentration and K_a is the equilibrium constant.

Consider the dissociation equilibrium of formic acid HCOOH which is a weak electrolyte in water.

$$HCOOH\,(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$$

$$Ka = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

To find the value of the equilibrium constant we need the equilibrium concentration of all species in the equilibrium mixture.

If the initial concentration of the acid is C and the value of dissociated acid molecules at equilibrium is α, then equilibrium concentrations can be determined as shown in the table:

Table 6.1 Equilibrium concentration of a weak acid

Equation	HCOOH	$\rightleftharpoons$	**H^+**	**$HCOO^-$**
Initial concentration	C		0	0
Concentration on ionization	$C\alpha$		$C\alpha$	$C\alpha$
Concentration at equilibrium	$C - C\alpha$ or $C(1-\alpha)$		$C\alpha$	$C\alpha$

Where the total concentration of the acid is **C** at the initial step and its degree of ionization is **αC.** At equilibrium, $C\alpha$, $C\alpha$ and $C\,(1-\alpha)$ represent the concentration of H^+, $HCOO^-$ and HCOOH respectively.Ka is then equal to

$$Ka = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

If α is too small, $K_a = \alpha^2 C$ because $1-\alpha \approx 1$

Therefore, $\alpha^2 = \dfrac{Ka}{C}$

$$\alpha = \sqrt{\frac{Ka}{C}}$$

The higher the Ka value, the greater the degree of ionization and the stronger the acid.

Similarly, for weak bases $Kb = \frac{C\alpha^2}{1-\alpha}$

And $\alpha = \sqrt{\frac{Kb}{C}}$ when α is too small.

The higher the Kb value, the greater the degree of ionization and the stronger the base.

Worked examples

1. (a) A solution of a weak acid, HA contains 0.25M and the concentration of $H^+$is 0.001 mol dm^{-3}.Calculate the dissociation constant of HA.

   (b) Determine the degree of ionization of this acid in 1M solution?

Answer:

(a) Dissociation Constant: $K_a = \frac{[A^-][H^+]}{[HA]}$

$$K_a = \frac{0.001 \text{ x } 0.001}{0.25}$$

$$K_a = 4.0 \text{ x } 10^{-6} \text{ mol dm}^{-3}$$

(b) Degree of dissociation in a 1 M solution:

$$\alpha = \sqrt{\frac{K_a}{[HA]}}$$

$$\alpha = \sqrt{\frac{4.0 \text{ x } 10^{-6}}{1}}$$

$$\alpha = 0.002$$

$$\alpha = 0.2\%$$

2. Calculate the degree of ionization of 0.1M acetic acid, CH_3COOH (K_a = 1.8 x10^{-5} mol dm^{-3}).

Answer

$$\alpha = \sqrt{\frac{Ka}{Ca}}$$

$$\alpha = \sqrt{\frac{1.8 \text{ x} 10{-}5}{0.1}}$$

α = 0.013 =1.3%

Application activity 6.2

1. Calculate the degree of ionization of a 0.04M ethanoic acid solution at 25 ^{0}C given that its K_a is 1.3 x 10^{-5} mol dm^{-3}.
2. The acid dissociation constant of a monobasic acid is 4.39 x 10^{-5} mol dm^{-3} at 25 ^{0}C.

   Calculate the degree of ionization of a 0.01M solution of the acid.
3. (a) Write an equation for the ionization of methylamine in water.

   (b) Express the dissociation constant Kb for methylamine.

   (c) The hydroxide ion concentration of a 1M methylamine solution is 0.04 $moldm^{-3}$.

   Calculate the K_b for methylamine.

6.3. Relationship between K_a and K_b

Activity 6.3

1. The hydrogen carbonate ion is a Bønsted-Lowry acid.
   a) Write an equation to represent the hydrolysis of hydrogen carbonate ions in water.
   b) Write down an expression for the acid dissociation constant, K_a of hydrogen carbonate ions in water.
2. The carbonate ion is a Brønsted-Lowry base.
   a) Write an equation to represent the hydrolysis of carbonate ions in water.
   b) Write down an expression for the acid dissociation constant, Kb of hydrogen carbonate ions in water

The relationship between Ka and Kb is derived from the dissociation of conjugate acid and conjugate base. For example, considering NH_4^+ and NH_3; NH_4^+ is a conjugate acid and NH_3 is a conjugate base.

The ionization of a conjugate acid in water is shown below:

$$NH_4^+(aq) + H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

The ionization of a conjugate base in water is indicated below:

$$NH_3(aq) + H_2O_{(l)} \rightleftharpoons NH_4^+(aq)\ ^{+}\ OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Multiplying Ka by $K_b = K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \,.\, K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

Ka × Kb= $[H_3O^+][OH^-]$

Ka x Kb = Kw

Ka x Kb = Kw=$1x10^{-14}mol^2dm^{-6}$ at 25^0C

$$K_a = \frac{K_w}{K_b} = \frac{1x10^{-14}}{K_b} \text{ and } K_b = \frac{K_w}{K_a} = \frac{1x10^{-14}}{Ka}$$ and at 25^0C

Ka x Kb (conjugate base)=Kw

If both sides of the above equation are multiplied by -log, it becomes

-log (Ka x Kb) = -logKw=14

-logKa + -logKb= pKw=14

pKa + pKb= pKw= 14

Application activity 6.3

1. Ethyl ammonium ion, $CH_3CH_2\text{-}NH_3^+$ is a conjugate acid.

   a) Write an equation for the ionization of this ion in water.

   b) Write the expression of acid dissociation constant, K_a, of ethyl ammonium ions in water.

2. At 0^0C, $Kw=1.14 \times 10^{-15} mol^2 dm^{-6}$.

   a) Find pKw at this temperature.

   b) Calculate Kb for a conjugate base of an acid which has $Ka=1.5 \times 10^{-6}$ mol dm^{-3} at 0^0C.

3. Calculate the acid dissociation constant of an acid whose conjugate base has $Kb=1.6 \times 10^{-5} mol\ dm^{-3}$.

6.4. Use of K_a or pK_a and K_b or pK_b to explain the strength of acids and bases

Activity 6.4

1. a) Ethanoic acid has pK_a of 4.77 at 25 ^0C. What is meant by pK_a of the acid?

   b) Given the following acids and their corresponding K_a values in the table below,

Acid	Formula	K_a / mol dm^{-3}
Phenol	C_6H_5OH	1.0×10^{-10}
Ethanoic acid	CH_3COOH	1.8×10^{-5}
Methanoic acid	HCOOH	1.8×10^{-4}

   State the strongest and the weakest acid and justify your answer.

2. The ionization of ethanoic acid in water is shown by the following equation :

$$CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-\ (aq) + H^+\ (aq)$$

Use the above equation to write an expression which relates the acid dissociation constant, K_a and the degree of ionization, α

The acid and base dissociation constants are respectively represented by K_a and K_b. On the other hand, pKa and pKb represent -log of Ka and Kb respectively. All these quantities, K_a, pK_a, K_b and pK_b are very helpful in predicting whether a species donates or accepts a proton, and the relative extent to which it is done.

K_a or K_b is a measure of the extent to which an acid or a base dissociates into ions in water.

Another way to express acid or basic strength of a substance is the use of pK_a or pK_b.

$pK_a = -\log K_a$ and $pK_b = -\log K_b$.

A smaller K_a value means that a little quantity of the acid dissociates into its ions in water thus weak acid. The pK_a gives the same information but in a different way. The smaller the pK_a value, the larger the K_a value and the stronger is the acid as shown in the table 6.1 and the same principle applies to bases as shown 6.2.

Table 6.2 K_a and pK_a of some acids at 25 ˚C

	Acid	**Conjugated base**	**K_a**	**pK_a**
STRONG ACID	HI	I^-	1.0x10^{10}	-10.0
	$HClO_4$	ClO_4^-	4.0x10^{8}	-8.6
	HBr	Br^-	1.0x10^{8}	-8.0
	HCl	Cl^-	1.0x10^{6}	-6.0
	H_2SO_4	SO_4^{2-}	1.0x10^{4}	-4.0
	HNO_3	NO_3^-	1.0x10^{2}	-2.0
	H_3O^+	OH^-	55.5	-1.75
WEAK ACIDS	HIO_3	IO_3^-	1.69x 10^{-1}	0.77
	H_3PO_4	$H_2PO_4^-$	7.5x10^{-3}	2.15
	HF	F^-	3.53x 10^{-4}	3.45
	C_6H_5COOH	$C_6H_5COO^-$	6.46x 10^{-5}	3.75
	CH_3COOH	CH_3COO^-	1.75x10^{-5}	4.76
	H_2CO_3	HCO_3^-	4.30x10^{-7}	6.37
	H_2S	HS^-	1.0x10^{-7}	7.00

VERY WEAK ACIDS	HSO_3^-	SO_3^{2-}	$6.43x10^{-8}$	7.19
	$H_2PO_4^-$	HPO_4^{2-}	$6.34\ x10^{-8}$	7.20
	HCN	CN^-	$4.93\ x10^{-10}$	9.31
	HCO_3^-	CO_3^{2-}	$5.618x10^{-11}$	10.25
	HPO_4^{2-}	PO_4^{3-}	$4.20x10^{-13}$	12.28
	HS^-	S^{2-}	$1.20x10^{-13}$	12.92
	H_2O	OH^-	$1.0x10^{-14}$	15.75

Generally, pK_a is greater than three ***($pK_a > 3$)*** when the acid is weak.

When K_a increases, pK_a decreases and the acid is strong due to large number of H^+ions in water.

For strong acids, pK_a is less than zero ***($pK_a < 0$).***

Table 6.3: K_b and pK_b of some bases in water at 25 ˚C

Base	**K_b (mol / dm³)**	**pK_b**
$C_6H_5NH_2$	4.2×10^{-10}	9.38
C_5H_5N	1.7×10^{-9}	8.77
NH_3	1.8×10^{-5}	4.75
$HO\text{-}CH_2CH_2\text{-}NH_2$	3.2×10^{-5}	4.49
$(CH_3CH_2)_3N$	5.2×10^{-5}	4.28
CH_3NH_2	4.4×10^{-4}	3.36
$CH_3CH_2NH_2$	5.4×10^{-4}	3.27
$(CH_3)_2NH$	5.9×10^{-4}	3.23
$(CH_3CH_2)_2NH$	8.6×10^{-4}	3.07

The larger the value of K_b the higher the level of dissociation and the stronger the base and the lower the pK_b value the stronger the base (Table 6.4.b).

Application activity 6.4

1. You are provided with the following acidic solutions and their respective K_a values

   1M HF, $K_a = 6.3 \times 10^{-4}$ mol dm^{-3}

   1M HCN, $K_a = 6.2 \times 10^{-10}$ mol dm^{-3}

   1M $H_2C_2O_4$, $K_a = 5.0 \times 10^{-2}$ mol dm^{-3}

   1M CH_3COOH, $K_a = 1.25 \times 10^{-3}$ mol dm^{-3}

   a) Calculate the pKa values of each of the acids listed above.

   b) State and explain which one is the strongest acid and which one is the weakest?

2. What is the pK_b of a base whose conjugate acid has a pK_a of 7.29 at 25^{0}C?

6.5. Explanation of ionic product of water

Activity 6.5

1. a) According to Brønsted-Lowry theory, water is both a proton donor and acceptor. This means that two water molecules can react. Write an equation showing how two water molecules react.

   b) Write an expression for the dissociation constant of water.Explain how the amount of H_3O^+ compares to that of OH^- in (1)

Water is a weak electrolyte and neutral in nature. However, it ionizes as shown by the equation below:

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

$$\text{Or } H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant for the above equation is given by:

$$K_c = \frac{[H^+]\,OH^-]}{[H_2O]} \text{ or } \frac{[H_3O^+]\,[OH^-]}{[H_2O]},$$

When Kc is multiplied by $[H_2O]$, a new constant is formed which is Kw.

$Kc\,[H_2O]=Kw$

Then, $K_w = [H^+]\,[OH^-]$ or $Kw = [H_3O^+]\,[OH^-]$

This new constant, **K_w**, is called the ***ionic product of water***.

At room temperature (25 °C or 298 K), K_w is equal to 1.0×10^{-14} mol^2dm^{-6} and this shows that the equilibrium concentrations of H_3O^+ and OH^- are equal and with a value of 1.0×10^{-7} $moldm^{-3}$.

$K_w = [H^+]\,[OH^-]$

$K_w = [H^+]^2$; since $[H^+] = [OH^-]$

$1.0\times10^{-14} = [H^+]^2$

$[H^+]= 1.0\times10^{-7}$ and $[OH^-] = 1.0\times10^{-7} moldm^{-3}$

Values of K_w vary with temperature just like other equilibrium constants.

The data in (**Table 6.4**) show how the value of the ionic product of water, Kw, increases with temperature. However, at all temperatures, the concentration of H^+ ions remains equal to the concentration of OH^- ions in pure water.

Table 6.4 Variation of the ionic product of water with temperature

Temperature (K)	K_w ($mol^2\ dm^{-6}$)
293	0.687×10^{-14}
298	1.008×10^{-14}
313	2.917×10^{-14}
323	5.474×10^{-14}
373	5.6×10^{-14}

The relationship between K_w and pK_w is the same as that between K_a and pK_a.

$pK_w = -\log_{10}K_w$. Because the value of K_w is $10^{-14} mol^2\,dm^{-6}$, this implies that the value of pK_w is equal to 14.

Application activity 6.5

1. a) Write an expression for the ionic product, K_w of water.

   b) State the units of K_w.

2. a) At 30 °C, K_w value is 1.471×10^{-14} mol^2dm^{-6}. Calculate the concentration of H^+ ions in pure water at this temperature.

3. a) How does Kw vary with temperature?

   b) Is the dissociation process of water exothermic or endothermic? Explain your reasoning using the answer you gave in (3.a)

6.6. Definition and calculations of pH and pOH of acidic and alkaline solutions

Activity 6.6

1. A fruit juice has pH of 3.5.

   a) After analyzing that juice and get pH = 3.5, what is your conclusion?

   b) Apply the expression of pH and Calculate the concentration of hydrogen ions in the juice

2. Calculate the concentration of H^+ ions and hence the pH of 0.025M nitric acid solution.

3. Calculate the pH of a 0.02 $moldm^{-3}$ sulphuric acid solution.

4. Calculate the pH of a 0.01M ammonia solution with a degree of dissociation of 0.04.

5. A solution with pH of 9.50 has a pOH of ____?

   A. 9.50 B. 0.50 C. 4.50 D. 19.0

6. The pH of a popular soft drink is 3.4. What is its hydroxonium ion concentration?

   A. 5.0×10^{-4} M B. 4.0×10^{-4} M

   C. 2.5×10^{3} M D. 5.0×10^{-5} M

7. A solution with a $[OH^-]$ of 1.20×10^{-7} M has a pOH and a pH of ____.

   A. 6.92 and 7.08 B. 7.08 and 6.92

   C. 5.94 and 8.06 D. 5.35 and 8.75

The pH is a scale commonly used to measure the degree of acidity or alkalinity of a solution. On a scale, commonly values range from 0 up to 14. The term pH is derived from "p," which is a mathematical symbol expressing the negative logarithm (antilog), and "H," the chemical symbol for Hydrogen.

Hence, mathematically $pH=-\log[H^+]$. Similarly, $pOH=-\log[OH^-]$.

For pure water, $[H^+] = 1.0\times10^{-7}M$

$pH= -\log_{10}(1.0\times10^{-7}) = -(-7)$

pH = 7

The value 7 is the pH of pure water at 25°C. It also defines the standard pH for all neutral solutions.

For pure water, $[OH^-] = 1.0\times10^{-7}$

$pOH= -\log_{10}(1.0\times10^{-7}) = -(-7)$

pOH = 7

Figure 6. 3 pH meters

Figure 6.4 shows the location of acidic, neutral and alkaline compounds on pH scale while **Figure 6.5** shows the pH or pOH scale (from 0 to 14). **Figure 6.6** shows some examples of compounds with different pH values on the scale.

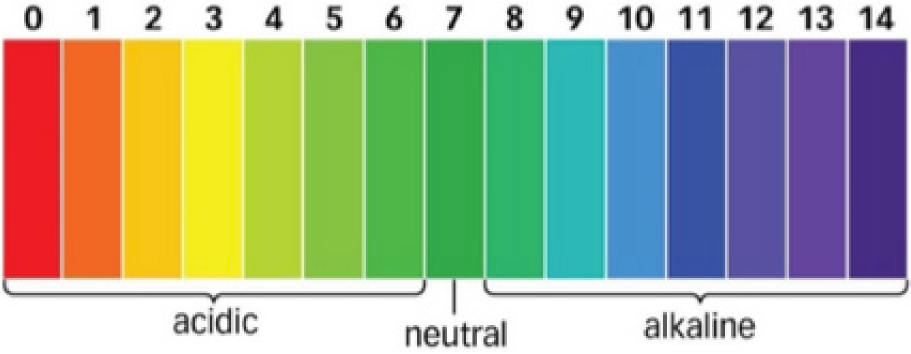


Figure 6.4 Values of pH for acidic, neutral and alkaline solutions.

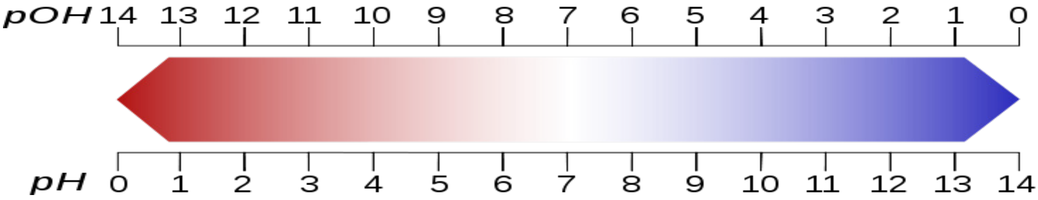


Figure 6.5 The pH scale

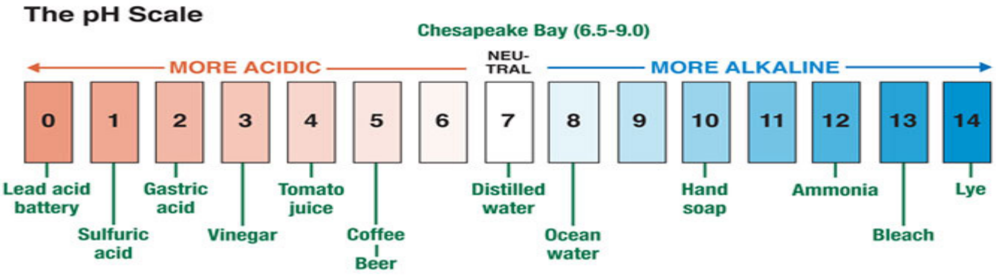


Figure 6.6 The pH of some solutions

The pH of strong acids ranges from 1up to 3 and weak acids from 4 up to 6. Strong bases have values of pH ranging from 11 up to 14 and weak bases have values of pH ranging from 8 up to 10.

Relationship between pH, pOH and pK_w

In any solution at 298 K, $K_w = [H^+][OH^-] = 1.0x10^{-14}$ mol^2dm^{-6}

If $pH= -log_{10}[H^+]$ and $pOH = -log_{10}[OH^-]$,

Then, $pK_w = -log_{10}[K_w]$

$pK_w = -log_{10}(1.0x10^{-14})$

$pK_w = 14$

From $[H^+][OH^-] = K_w$

$-\log_{10}[H^+] - \log_{10}[OH^-] = -\log_{10}[K_w]$

$pH + pOH = pKw$

It means that pH of alkaline solutions can be calculated from the following expression;

$pH = pK_w$ – pOH thus pH = 14 – pOH.

6.6.1. Calculation of the pH of strong acids

To calculate the pH of a strong acid, the concentration of H^+ ions present in the solution must be determined first. Next is to apply the formula $pH=-\log[H^+]$.

Examples:

1. Determine the pH of a 0.025 M solution of hydrobromic acid solution.

Hydrobromic acid, HBr, is a strong acid which ionizes completely in water to give H^+ and Br^- ions.

$HBr_{(aq)} \longrightarrow H^+_{(aq)} + Br^-_{(aq)}$.

For every mole of HBr, there will be 1 mole of H^+ and the concentration of H^+ will be the same as the concentration of HBr. Therefore, $[H^+] = 0.025$ M.

$pH = - \log [H^+]$

$pH = - \log (0.025)$

$pH = - (-1.602)$

pH = 1.602

2. Calculate the pH of a solution containing 0.32 $moldm^{-3}$ of sulphuric acid.

Answer

$H_2SO_4 (aq) \longrightarrow 2H^+ (aq) + SO_4^{2-} (aq)$

1 mole of H_2SO_4 ionizes to produce 2 moles of H^+ ions.

Thus, $[H^+] = 2[H_2SO_4]$

$= 2 \times 0.32 = 0.64M$

$pH= -\log_{10}[H^+]$

$pH= -\log_{10} (0.64)$

$pH= -\log_{10} (6.4 \times 10^{-1})$

pH = 0.194

3. Calculate the concentration in mol dm^{-3} of sulphuric acid solution of pH 3.5

   Answer

   $pH = -\log_{10}[H^+]$ and $[H^+]=10^{-pH}$

   $3.5 = -\log_{10}[H^+]$

   $[H^+] = 10^{-3.5}$

   $[H^+] = 3.16 \times 10^{-4}$ mol dm^{-3}

From the equation of ionization: $H_2SO_4\ (aq) \longrightarrow 2H^+\ (aq) + SO_4^{2-}\ (aq)$

2 moles of H^+ were produced by 1 mole of H_2SO_4

3.16×10^{-4} moles of H^+ are produced by moles of H_2SO_4

Concentration of H_2SO_4 = **1.58×10^{-4} mol dm^{-3}**

6.6.2. pOH and pH of strong bases

After calculating the concentration of OH^- ions in the solution, pOH is determined by using the formula

$pOH=-\log[OH^-]$.

$pH + pOH=pKw=14$

$pH=pKw-pOH$

$pH=14-pOH$

Examples

1. Calculate the pOH of a solution 0.024M sodium hydroxide.

   Answer

   $NaOH\ (aq) \longrightarrow Na^+\ (aq) + OH^-\ (aq)$

   1 mole of NaOH produces 1 mole of OH^-

   Therefore $[OH^-] = [NaOH] = 0.024M$

   $pOH = -\log_{10}[OH^-]$

   $pOH = -\log_{10}(0.024)$

   $pOH = -\log_{10}(2.4 \times 10^{-2})$

   pOH = 1.62

2. Calculate the pH of 0.02M sodium hydroxide solution.

Answer

$NaOH\ (aq) \longrightarrow Na^+\ (aq) + OH^-\ (aq)$

$[OH^-] = [NaOH] = 0.02M$

$pOH = -\log_{10}[OH^-]$

$pOH = -\log_{10}(0.02)$

$pOH = -\log_{10}(2.0 \times 10^{-2})$

<u>pOH = 1.699</u>

$pH = pKw - pOH$

$pH = 14 - 1.699$

<u>pH = 12.30</u>

3. What is the molarity of a solution of potassium hydroxide of pH=13.32 at 25°C?

Answer

$pOH = pKw - pH$

$pOH = 14 - 13.32$

$pOH = 0.68$

From $pOH = -\log_{10}[OH^-]$

$0.68 = -\log_{10}[OH^-]$

$[OH^-] = 10^{-0.68}$

$[OH^-] = 0.2$

$KOH\ (aq) \longrightarrow K^+\ (aq) + OH^-\ (aq)$

From the equation of ionization, 1 mole of OH^- was produced by 1 mole of KOH

Hence, the **molarity of KOH = $[OH^-]$ = 0.2M**

6.6.3. pH of weak acids

Because a weak acid is partially ionized in aqueous solution, the concentration of H^+ ions is not equal to the concentration of the acid. Therefore, the first thing to do is to determine the concentration of H^+ in the solution.

Consider a weak acid HA, whose concentration is C_a, which ionizes as shown below:

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \quad (1)$$

By applying the equilibrium law, we get acid dissociation constant K_a which is equal to

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (2)$$

Since the mole ratio is 1:1 from the equation (1), it means that $[H^+] = [A^-]$ and $[HA] = Ca$ since only a very small fraction of the acid is dissociated

$Ca\text{-}\alpha \approx Ca$ or $[HA]\text{-}\alpha \approx [HA]$). Hence,

$$K_a = \frac{[H^+]^2}{Ca} \qquad (3)$$

$$[H^+]^2 = Ka.Ca$$

$$[H^+] = \sqrt{Ka.Ca}$$

$$[H^+] = (K_a.C_a)^{\frac{1}{2}} \qquad (4)$$

With the concentration of H^+ ions in the solution, now the formula of the pH of a weak acid can be derived.

$$pH = -\log[H^+] \text{ and } [H^+] = (K_a.C_a)^{\frac{1}{2}}$$

$$pH = -\log 10(K_a.C_a)^{\frac{1}{2}} \qquad (5)$$

$$pH = -\log Ka^{\frac{1}{2}} + -\log Ca^{\frac{1}{2}} \qquad (6)$$

$$pH = \tfrac{1}{2}pKa - \tfrac{1}{2}\log Ca \qquad (7)$$

Examples

1. Calculate the pH of a 0.1mol dm^{-3} ethanoic acid solution if K_a of ethanoic acid is 1.0x10^{-5} mol dm^{-3}.

Answer

Method 1

C_a = 0.1mol dm^{-3}, K_a = 1.0x10^{-5} mol dm^{-3}

$[H^+] = \sqrt{Ka.Ca}$

$[H^+] = \sqrt{(1.0 \text{ x } 10^{-5}) x\ 0.1}$

$[H^+]$ = 1.0x10^{-3} mol dm^{-3}

From pH = $-\log_{10}[H^+]$

pH = -log(1.0x10^{-3})

pH = 3

Method 2.

pH = ½ pKa – ½ log Ca

= ½ x 5 + 0.5

pH = 3

2. The pH of a 0.01M methanoic acid is 3.63. Determine the value of:

a) the acid dissociation constant, K_a

b) pK_a of methanoic acid.

Answer

a) The equation of ionization is: $HCOOH (aq) \rightleftharpoons HCOO^- (aq) + H^+ (aq)$

$Ka = \frac{[H^+]2}{Ca}$; $[H^+]=[HCOO^-]$

pH = $-\log_{10}[H^+]$

3.63 = $-\log_{10}[H^+]$

$[H^+] = 10^{-3.63}$

$[H^+] = 2.399 x 10^{-4}$ mol dm^{-3}

$$Ka = \frac{[H^+]2}{Ca}$$

$$Ka = \frac{(2.399 \times 10^{-4})^2}{0.01}$$

Ka = 5.49 x 10^{-6}mol dm^{-3}

b) $pK_a = -\log_{10}K_a$

$pK_a = -\log_{10}(5.49 \times 10^{-6})$

pK*a* = 5.2

3. A solution of 0.01 mol dm^{-3} of chloroethanoic acid is 18% ionized, calculate:

a) The acid dissociation constant, K_a.

b) pH of the solution

Answer

a) From the equation of ionization: $ClCH_2COOH (aq) \rightleftharpoons ClCH_2COO^- (aq) + H^+ (aq)$

$K_a = \alpha^2.C_a$

$$K_a = \left(\frac{18}{100}\right)^2 x\ 0.01$$

K_a = 3.24 x 10^{-4} mol dm^{-3}

b) From $K_a = \frac{[ClCH_2COO^-]\,[H^+]}{[ClCH_2COOH]}$

$$K_a = \frac{[H^+]^2}{Ca}$$

$$[H^+] = \sqrt{Ka.Ca}$$

$$= \sqrt{(3.24\ x\ 10^{-4})x\ 0.01}$$

$[H^+] = 1.8 \times 10^{-3}$ mold m^{-3}

$pH = -\log_{10}[H^+]$

$= -\log_{10}(1.8 \times 10^{-3})$

pH = 2.745

6.6.4. pOH and pH of weak bases

Weak bases undergo a partial ionization in water and the consequence of this is that the concentration of OH^- ions is not equal to the concentration of the acid. Therefore, to calculate the pOH and pH of weak bases, we must first determine the concentration of OH^- ions.

$$BOH\ (aq) \rightleftharpoons B^+\ (aq) + OH^-\ (aq) \quad (8)$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} (9)$$

If C_b is the concentration of the solution, equation (9) becomes:

$$K_b = \frac{[B^+][OH^-]}{[BOH]} (9)$$

Since mole ratio is 1:1, then $[B^+] = [OH^-]$ and equation (9) becomes:

$$K_b = \frac{[OH^-]^2}{Cb} \ (10)$$

$$= K_b.C_b$$

$$[OH^-]^2 = K_b.C_b$$

$$[OH^-] = \sqrt{Kb.Cb}$$

$$[OH^-] = (K_b\,.\,C_b)^{\frac{1}{2}} \qquad (11)$$

Substituting the value of into equation $pOH = -\log_{10}[OH^-]$ gives us:

$$pOH = -\log_{10}() \ (12)$$

$$\boxed{pOH= pOH=- ½ \log K_b + - ½ \log C_b = ½ pK_b - ½ \log C_b \ (13)}$$

pH is then given by:

$$\boxed{pH=pKw-pOH= 14- ½ pK_b + ½ \log C_b (14)}$$

Examples

1. Calculate the pH of a 0.01M ammonia solution whose K_b is$1.584x10^{-5}$ mold m^{-3}

Answer

$$NH_4OH\ (aq) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

$$Kb = \frac{[OH^-]^2}{Cb}$$

$$[OH^-] = \sqrt{Kb.Cb}$$

$$[OH^-] = \sqrt{(1.584 \ x \ 10^{-5}) \ x \ 0.01}$$

$= 3.98\text{x}10^{-4}$ mol dm^{-3}

From pOH = -log[OH$^-$]

= -log(3.98x10^{-4})

pOH = 3.4

pH = 14 – pOH

pH = 14 – 3.4

pH = 10.6

2. What is the base dissociation constant, K_b for a 0.01M phenylamine solution of pH 10.9?

Answer

$C_6H_5\text{-}NH_2\ (aq) + H_2O\ (l) \rightleftharpoons C_6H_5\text{-}NH_3^+\ (aq) + OH^-\ (aq)$

pOH = 14 – pH

pOH = 14 – 10.9

pOH = 3.1

pOH = -log[OH$^-$]

3.1 = -log[OH$^-$]

$[OH^-] = 10^{-3.1}$

$[OH^-] = 7.9\text{x}10^{-4}$ mol dm^{-3}

From $Kb = \frac{[OH-]^2}{Cb}$

$$Kb = \frac{(7.9\text{x}\ 10^{-4})^2}{0.01}$$

Kb = 6.3 x 10^{-5} mol dm^{-3}

3. Calculate the base dissociation constant, K_b of a 0.01M phenylamine which is 8% ionized.

Answer

A= 8% = = 0.08

ph-NH_3OH (aq) $\rightleftharpoons$ ph-NH_3^+ (aq) + OH^- (aq)

Table 6.5 Equilibrium concentration of a weak base; phenylamine

Equation	ph-NH_3OH	$\rightleftharpoons$	ph-NH_3^+	OH^-
Original concentration	C		0	0
Concentrationon ionization	Cα		Cα	Cα
Concentration at equilibrium	C −Cα		Cα	Cα

From the dissociation equation,

$[OH^-] = C\alpha$

$[OH^-] = 0.01 \times 0.08$

$[OH^-] = 0.0008$ $moldm^{-3}$

Substituting the values from above values in the formula $Kb = \frac{[OH-]^2}{Cb}$ gives:

$$Kb = \frac{(0.0008)^2}{0.01}$$

$Kb = 6.4 \times 10^{-5}$ $moldm^{-3}$

Application activity 6.6

1. A solution of propanoic acid contains 0.05moles in $1dm^3$. It has a pH of 4. What is the acid dissociation constant, K_a of propanoic acid?
2. Methanoic acid solution contains 0.001mol dm^{-3} and is 1% ionized.

   Calculate its pH given that its K_a is 1.0×10^{-7} mol dm^{-3}
3. Determine the molarity of sodium hydroxide solution whose pH is 6.9
4. Calculate the pOH of a solution containing 2.2×10^{-5} mol dm^{-3} of potassium hydroxide
5. What is the pH of 0.4M sodium hydroxide solution?

6. Calculate the pOH and pH of a 0.005 mol dm^{-3} ammonia solution of $K_b = 1.85 \times 10^{-5} moldm^{-3}$
7. A solution of phenylamine contains 0.01mol dm^{-3} and is 8% ionized. Calculate the base dissociation constant, K_b and hence pH of the solution.
8. A solution of 0.01M ammonia has a pH of 10.6.Calculate its base dissociation constant, K_b and its degree of ionization.
9. Calculate the molarity of a solution of sulphuric acid whose pH is 4.36
10. Calculate the pH of a solution containing 0.05M hydrochloric acid.

6.7. Buffer solution

Activity 6.7

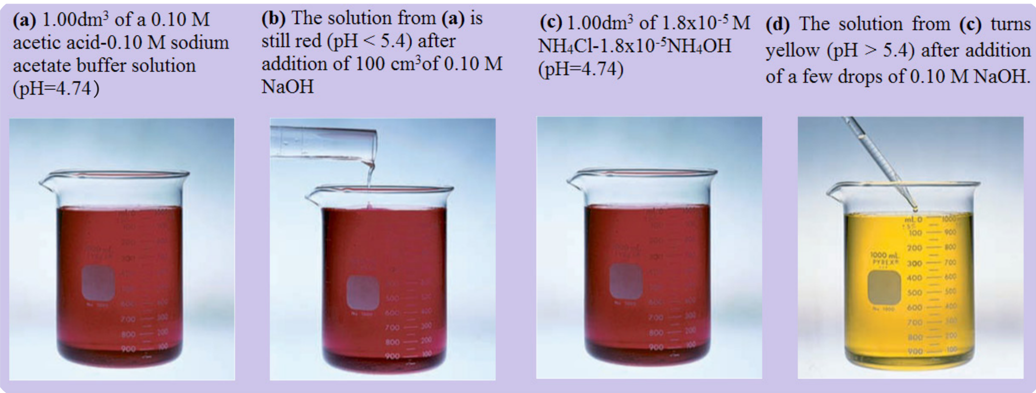
1. Write equations to show the behavior of the following substances in water

   a) CH_3COONa and CH_3COOH

   b) NH_4Cl and NH_4OH
2. Write expression of the dissociation constants of CH_3COOH and NH_4OH.
3. What is the relationship between $CH_3CO_2H_2^+$ and CH_3CO_2H?
4. Ka for ethanoic acid at 298K is $1.74 \times 10^{-5} moldm^{-3}$. Calculate the pH of a $0.1 moldm^{-3}$ solution of CH_3CO_2H at 298K.

6.7.1. Definition of buffer solution

A Buffer solution is a solution that resists a pH change when a small amount of a base or acid is added to it.



(a) $1.00 dm^3$ of a 0.10 M acetic acid-0.10 M sodium acetate buffer solution (pH=4.74)

(b) The solution from **(a)** is still red ($pH < 5.4$) after addition of 100 cm^3 of 0.10 M NaOH

(c) $1.00 dm^3$ of 1.8×10^{-5} M NH_4Cl-$1.8\times10^{-5} NH_4OH$ (pH=4.74)

(d) The solution from **(c)** turns yellow ($pH > 5.4$) after addition of a few drops of 0.10 M NaOH.

Figure 6.7 Comparison of acidic and buffer solutions

Two types of buffer solutions are known: an **acidic buffer** and a **basic buffer**.

An ***acidic buffer*** consists of a solution of a weak acid and its salt of its conjugate base.

Examples of acidic buffers: - Ethanoic acid and sodium ethanoate solution,
– Carbonic acid and sodium hydrogen carbonate.

A ***basic or alkaline buffer*** consists of a solution of a weak base and a salt of its conjugate acid.

Examples of basic buffers: -Ammonia and ammonium chloride solution,
– Ammonia and ammonium sulphate or ammonium nitrate.

6.7.2. pH of buffer solutions

The pH of a buffer solution or the concentration of the acid and base can be calculated using the **Henderson-Hasselbalch equation.** Henderson-Hasselbalch equation was given by Lawrence Joseph Henderson (1878-1942) and Karl Albert Hasselbalch (1874-1962).

Figure 6.8 Lawrence Joseph Henderson (left) and Karl Albert Hasselbalch (right)

a) pH of an acidic buffer

Suppose that you are given a solution of CH_3COOH and CH_3COONa.

The dissociation equations for both substances are:

Weak acid: $CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq)$ ***Equation (1)***

The salt of its conjugate base: $CH_3COONa\,(aq) \longrightarrow CH_3COO^-\,(aq) + Na^+\,(aq)$ ***Equation (2)***

The weak acid ionizes partially whereas its salt ionizes completely in solution.

From equation (1);

$$K_a = \frac{\left[CH_3COO^-\right] \times \left[H^+\right]}{\left[CH_3COOH\right]}$$ and

$$[H^+] = \frac{K_a\left[CH_3COOH\right]}{\left[CH_3COO^-\right]}$$

Since sodium ethanoate is completely ionized, the concentration of the salt is taken as [CH_3COO-]. The concentration of ethanoate ions from the weak acid is taken as negligible since only a very small fraction of it is ionized.

The acid is dissociated to a very small extent because of two factors:

1. The acid is weak
2. The presence of ethanoate ions in the solution from the salt makes the equilibrium position in the equation (1) shift to the left.

The concentration of H^+ ions is given by:

$$\left[H^+\right] = \frac{\mathrm{Ka}\left[\mathrm{Acid}\right]}{\left[\mathrm{Salt}\right]}$$

Taking negative logarithms to base 10 on both sides gives:

$$-log\left[H^+\right] = -logK_a - log\frac{\left[\mathrm{Acid}\right]}{\left[\mathrm{Salt}\right]}$$

$$-log\left[H^+\right] = -logK_a + log\frac{\left[\mathrm{Salt}\right]}{\left[\mathrm{Acid}\right]}$$

$$\boxed{pH = pK_a + log\frac{\left[\mathrm{Salt}\right]}{\left[\mathrm{Acid}\right]}}$$

This formula is known as the **Henderson-Hasselbalch** equation.

Therefore, the pH of an acidic buffer depends on the relative concentration of the salt and the acid in the mixture.

Examples

1. 0.61g of benzoic acid, C_6H_5COOH were dissolved in $1dm^{-3}$ of 0.02M sodium benzoate to form a buffer solution. Calculate the pH of the buffer solution formed. (C=12, H=1, O=16, $K_a=6.3x10^{-5}$ mol dm^{-3})

   Answer

   Molar mass of C_6H_5COOH = (12x7)+(1x6)+(16x2) = 122g/mole

   Remember that: Concentration C = $\frac{number\ of\ mole\ n}{volume\ V}$

$$\left[Acid\right] = \frac{\frac{0.61g}{122gmol-1}}{1dm-3} = 0.05\ mol\ dm^{-3}$$

$$pH = pK_a + log\frac{\left[Salt\right]}{\left[Acid\right]}$$

$$pH = -log\left(6.3x10^{-5}\right) + log\frac{\left[0.02\right]}{\left[0.05\right]}$$

<u>pH = 3.803</u>

2. a) Calculate the pH of a buffer solution containing 4.1g of sodium ethanoate, CH_3COONa per litre and 0.01M ethanoic acid of $K_a = 1.7x10^{-5}$ mol dm^{-3} (C=12, H=1, O=16, Na=23)

b) Calculate the pH change of the buffer solution when $1cm^3$ of 1M sodium hydroxide is added.

Answer

Molar mass of CH_3COONa = (12x2)+(1x3)+(16x2)+(23x1) = 82g/mole

$$[Salt] = \frac{4.1}{82} = 0.05\ moll^{-1}$$

$$pH = pK_a + log\frac{[Salt]}{[Acid]}$$

$$pH = -log\left(1.7x10^{-5}\right) + log\frac{[0.05]}{[0.01]}$$

pH = 5.469

b) Added OH- ions react with ethanoic acid. This decreases the concentration of ethanoic acid but increases the concentration of sodium ethanoate.

Moles of 1M NaOH added $= \frac{1x1}{1000}$ = 0.001moles

The new concetrations of acid and salt are calculated in the new volume (volume of the buffer + volume of added base/acid. Since the amount of added acid/base is too small (negligeable), the volume of the buffer is almost constant.

New volume = $1dm^{-3}$ + $1cm^{-3}$= $1.001dm^{-3}$

$$New\ [Acid] = \frac{(0.01 - 0.001)\text{mol}}{1.001\text{dm} - 3} = 0.009\ mol\ dm^{-3}$$

$$New\ [Salt] = \frac{(0.05 + 0.001)\text{mol}}{1.001\text{dm} - 3} = 0.051\ moldm^{-3}$$

$$New\ pH = pK_a + log\frac{[Salt]}{[Acid]}$$

$$pH = -log\left(1.7x10^{-5}\right) + log\frac{[0.051]}{[0.009]}$$

pH = 5.523

Therefore, pH change = 5.523 – 5.469 = **<u>0.054 units</u>**

pH and pOH of a basic buffer

Suppose that you are given a basic buffer containing NH_4OH and NH_4Cl.

The dissociation equations of the base and the salt of its conjugate acid are:

Weak base: $NH_4OH\ (aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$***Equation (3)***

Its salt of strong acid: $NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$ ***Equation (4)***

From equatin (3), the base dissociation constant, Kb is:

$$K_b = \frac{[NH_4^+] \text{ x } [OH^-]}{[NH_4OH]}, \text{ and}$$

$$[OH^-] = \frac{K_b[NH_4OH]}{[NH_4^+]}$$

Since the base is partially ionized, we assume that all the ammonium ions are from the fully ionized ammonium chloride. The concentration of ammonium ions from the weak base is negligible.

$$\text{Thus, } [OH^-] = \frac{K_b[\text{Base}]}{[\text{Salt}]}$$

$$-log[OH^-] = -log K_b - \left(log\frac{[\text{Base}]}{[\text{Salt}]}\right)$$

$$-log[OH^-] = -log K_b + \left(log\frac{[\text{Salt}]}{[\text{Base}]}\right)$$

$$pOH = pK_b + log\frac{[Salt]}{[Base]}$$

And the pH of this buffer solution is given by:

pH=pKw-pOH=14-pOH

$$pH = pKw - pKb + \log\frac{[Base]}{[Salt]} = 14 - pKb + \log\frac{[Base]}{[Salt]}$$

Examples

1. A one litre solution consists of 0.01M ammonia solution and 2.13g of ammonium chloride. K_b for ammonia solution is 1.8×10^{-5} mol dm^{-3}. (N=14, H=1, Cl=35.5)

   a) Calculate the pH of the buffer solution

   b) Calculate the pH change on addition of 1cm^3 of 1M hydrochloric acid.

   Answer:

   (a) Molar mass of NH_4Cl = (14x1)+(1x4)+(35.5x1) = 53.5g/mole

   $[Salt] = \frac{2.13}{53.5}/1 = 0.051$ mol dm^{-3}

   $pH = pK_w - pOH$, where $pK_w = 14$

   $$pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

   $$= -\log 1.8\times10^{-5} + \log\left(\frac{0.04}{0.01}\right)$$

   pOH = 5.347

   pH = 14 – 5.347

   pH = 8.653

   b) Addition of hydrochloric acid decreases the concentration of ammonia solution since it reacts with it to form ammonium chloride and the concentration of ammonium chloride increases.

   Moles of HCl added = $\frac{1x1}{1000}$ = 0.001moles

   The new concetrations of base and salt are calculated in the new volume (volume of the buffer + volume of added base/acid). Since the amount of added acid/base is too small (negligeable), the volume of the buffer is almost constant.

New volume = 1dm^{-3} + 1cm^{-3}= 1.001dm^{-3}

$$\text{New }[NH_4OH] = \frac{(0.01 - 0.001)\text{mol}}{1.001\text{dm}-3} = 0.009 \text{ mol dm}^{-3}$$

$$\text{New }[NH_4Cl] = \frac{(0.04 + 0.001)\text{mol}}{1.001\text{dm}-3} = 0.041 \text{ mol dm}^{-3}$$

$$pOH = -\log 1.8x10^{-5} + \log\left(\frac{0.041}{0.009}\right)$$

= 5.503

New pH = 14-5.503

pH = 8.497

Therefore, pH change = 8.653-8.497 = **0.156 units.**

2. Calculate the pH of a solution made by adding 30cm^3 of 0.1M hydrochloric acid to 80cm^3 of 0.1M ammonia solution. (K_b of ammonia solution = 1.8x10^{-5} mol dm^{-3})

Answer

Moles of HCl reacted = $\left(\frac{0.1x30}{1000}\right)$ = 0.003 moles

Moles of NH_4OH reacted = $\left(\frac{0.003}{0.005}\right)$ = 0.008 moles

From the equation of the reaction;

$NH_4OH\ (aq) + HCl\ (aq) \longrightarrow NH_4Cl\ (aq) + H_2O\ (l)$

Mole reaction is 1:1. This means that 0.003 moles of HCl reacted with 0.003 moles of NH_4OH to form 0.003 moles of NH_4Cl.

Therefore; moles of unreacted (excess) ammonia solution = 0.008 – 0.003 = 0.005 moles.

The resultant solution is a buffer solution consisting of 0.003 mol dm^{-3} of NH_4Cl and 0.005 mol dm^{-3} of NH_4OH

$$pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

$$pOH = -\log 1.8x10^{-5} + \log\left(\frac{\frac{0.003}{0.11}}{\frac{0.005}{0.11}}\right) = \left(\frac{0.003}{0.005}\right)$$

Note: Here we immediately use number of moles in the place of concentrations because both substances are in the same volume of solution;

$$\log\left(\frac{\frac{0.003}{0.11}}{\frac{0.005}{0.11}}\right) = \left(\frac{0.003}{0.005}\right)$$

pOH = 4.523

pH = pK_w – pOH

pH = 14 – 4.523

<u>pH = 9.477</u>

Application activity 6.7

1. A buffer solution of pH 4.0 is made using benzene carboxylic acid and sodium benzene carboxylate. Calculate the mass of sodium benzene carboxylate (molecular mass=144) that should be dissolved in 1.0 dm^3 of a 0.012 mol dm^{-3} solution of benzene carboxylic acid (Ka for C_6H_5COOH = 6.31 x 10^{-5} mol dm^{-3})

2. a) Calculate the pH of a buffer solution containing 7.2g of sodium benzoate in 1 dm^{-3} of 0.02M benzoic acid. (C=12, H=1, O=16, Na=23, Ka=6.25x10^{-5} mol dm^{-3})

   b) Evaluate how will the pH change if 1cm^3 of 0.01M of sodium hydroxide is added to the solution.

3. Calculate the pH of a buffer solution formed when 10cm^3 of 0.1M hydrochloric acid is added to 100cm^3 of 0.05M ammonia solution. K_b of ammonia solution is 1.8x10^{-5} mol dm^{-3}

4. a) Calculate the pH of a buffer solution formed when 80cm^3 of 0.4M ammonia solution is mixed with 100cm^3 of 0.1M hydrochloric acid.

   b) Calculate the pH change when 0.7cm^3 of 1M hydrochloric acid solution was added.

6.8. Preparation of buffer solutions of different pH

Activity 6.8

1. Explain the term buffer solution.
2. Describe the difference between the two types of buffer solutions.
3. Calculate the pH of acetic acid – sodium acetate buffer containing 0.1M acetic acid and 0.1M sodium acetate. ($Ka = 1.85 \times 10^{-5}$ mol dm^{-3}).
4. Calculate the pH of ammonium hydroxide – ammonium chloride buffer solution that is 0.1 M in ammonium hydroxide and 0.01 M in ammonium chloride. (pKb of $NH_4OH = 9.25$).

Figure 6.9. Commercially prepared buffer solutions

A buffer solution can resist a change in pH because it contains species in solution able to react with any added acid or base.

Generally, preparing a buffer solution requires either **a weak acid and a salt of the acid's conjugate base** or **a weak base and a salt of the base's conjugate acid**.

6.8.1. By mixing a weak acid and its corresponding salt or weak base and its corresponding salt

It is very important to prepare buffer solutions of known pH in the laboratory. From the **Henderson-Hasselbalch equation,** we identify two terms which determine the final pH of a buffer solution. These are pK_a and the ratio [conjugate-base]/ [acid].

So, to prepare an acidic buffer solution of known pH, select an acid whose pK_a is within the range of one unit of the desired pH and adjust the ratio of salt to acid concentrations to achieve the desired pH.

Example

Suppose you want to prepare an acidic buffer with a pH of 4.0. A suitable weak acid would be ethanoic acid CH_3COOH because its pK_a is 4.8. The conjugate base is ethanoate ion CH_3COO^-, which is provided by the sodium ethanoate salt, CH_3COONa. Ethanoic acid is available as a laboratory reagent with a concentration of 1.0 mol dm^{-3}.

The question is, what mass of sodium ethanoate should be added to ethanoic acid solution to make this buffer?

Using the Henderson-Hasselbalch equation;

$$pH = pK_a + log\left(\frac{[conjugate\ base]}{[acid]}\right)$$

Substitute the known quantities: $4.0 = 4.8 + log\left(\frac{[conjugate\ base]}{1.0}\right)$

$$4.0 = 4.8 + log[conjugate\ base]$$

Log[conjugate base] = -0.8

[Conjugate base] =$10^{-0.8}$

[Conjugate base] = 0.16 mol dm^{-3}

The concentration of the conjugate base is 0.16 mol dm^{-3}.

The molar mass of sodium ethanoate is 82.0 g mol^{-1}.

So, 0.16 moles of sodium ethanoate have a mass given by:

Mass =Moles × molar mass

= (0.16 moles) × (82.0 g mol^{-1})

= 13g

Therefore, an acidic buffer solution of pH 4.0 can be prepared by dissolving 13 g of sodium ethanoate in 1.0 dm^3 of 1.0 mol dm^{-3} ethanoic acid in a volumetric flask. Insert a calibrated pH meter to monitor the pH of the prepared acidic buffer solution.

Note that it is the ratio of acid to conjugate base that is important in determining the pH of the buffer solution not the concentrations.

6.8.2. By partial neutralization

Buffers can also be prepared by the partial neutralization of a weak acid by a strong base through titration process.

This is done by running excess weak acidic solution from the burette into a strong basic solution in the conical flask until half neutralization takes place. A weak acid is partially neutralized by the strong base to form a salt of the weak acid. This salt is formed together with excess of the weak acidic solution which makes the resultant solution a buffer solution. Do this while measuring the pH of the resultant buffer solution with a pH meter.

For example, reacting 40 ml of 1.0M propanoic acid (C_2H_5COOH) solution (pK_a is 4.87) with 60.0 ml of 0.10 M sodium hydroxide solution (NaOH). This will produce a buffer solution consisting of propanoic acid and sodium propanoate of pH 4.13.

Application activity 6.8

The following materials and chemicals are provided by the technician laboratory.

- 100ml Beaker,
- 10ml measuring cylinder,
- 50ml measuring cylinder,
- Electronic weighing scale,
- Calibrated pH meter,
- Glass rod,
- 100ml volumetric flask
- Ethanoic acid,
- Sodium ethanoate and distilled water

Procedure

1. Measure exactly 50 ml of distilled water to a 100 ml beaker.
2. Using a measuring cylinder, add 5 ml of 0.3M ethanoic acid to the beaker.
3. Then weigh exactly 0.3g sodium ethanoate (CH_3COONa)
4. Add a little of the sodium ethanoate at a time, stirring the mixture with a glass rod to dissolve.
5. Insert the calibrated pH meter into the resultant solution in the beaker and measure its pH.
6. Quantitatively transfer the buffer solution to a 100 ml volumetric flask. Add distilled water up to the mark. Cap and invert the flask twice to mix.

Questions

a) What is the pH of the prepared buffer solution from the pH meter?

b) Given K_a of ethanoic acid as 1.8×10^{-5} mol dm^{-3} and using the Henderson-Hasselbalch equation, Calculate the pH of the buffer solution.

6.9. Working of buffer solutions and their applications.

Activity 6.9

1. a) What is a buffer solution?

   b) Distinguish the components of an acidic buffer and those of a basic buffer.
2. Calculate the mass of sodium propanoate needed to prepare one litter of a buffer solution of propanoic acid and sodium propanoate which has a pH of 4.13. The concentration of propanoic acid is 1.0M propanoic acid and its K_a is 1.58×10^{-5}.
3. Buffer solutions contain various components and they can resist a change in pH when a small amount of an acid or a base is added. Suggest which of those components will work when an acid is added, and which one will work when a base is added in any acidic buffer of your choice.

Generally, in a buffer solution, the weak acid and its conjugate base or the weak base and its conjugate acid are responsible for controlling pH.

6.9.1 Working process of buffer solutions

a. An acidic buffer

Consider a buffer solution made of ethanoic acid and sodium ethanoate solutions. Ethanoic acid is partially ionized because it is a weak acid whereas sodium ethanoate is fully ionized because it's a strong electrolyte.

$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$

$CH_3COONa_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$

Such a solution contains few hydrogen ions from the acid and a large portion of ethanoate ions from the salt.

When a small amount of an acid is added, the added hydrogen ions react with ethanoate ions to form ethanoic acid. This prevents an increase in the concentration of hydrogen ions in the solution hence pH remains constant.

$CH_3COO^-_{(aq)} + H^+_{(aq)} \rightleftharpoons CH_3COOH_{(aq)}$

When a small amount of a base is added, the added hydroxide ions react with ethanoic acid to form water. This prevents an increase in the concentration of hydroxide ions hence pH is kept constant.

$CH_3COOH_{(aq)} + OH^-_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$

b. A basic buffer

Consider a buffer solution of aqueous ammonia and ammonium chloride. Aqueous ammonia is partially ionized while ammonium chloride is completely ionized because it is a strong electrolyte.

$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$

$NH_4Cl_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-_{(aq)}$

Such a solution contains a few hydroxide ions and a large portion of ammonium ions from the salt.

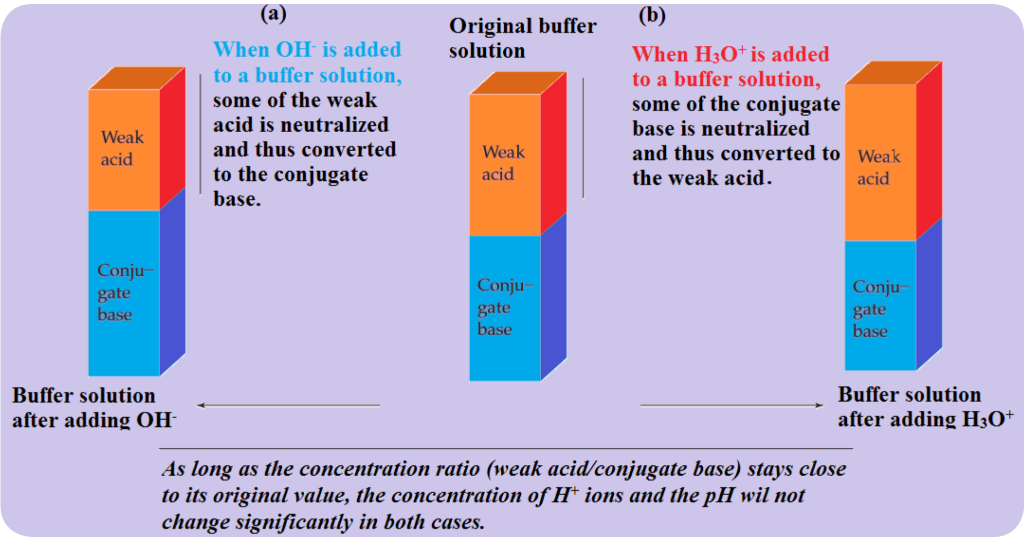
When a small amount of a base is added, the added hydroxide ions react with ammonium ions to form undissociated aqueous ammonium hydroxide. This prevents a change of both the concentration of hydroxide ions and pH.

$$NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \rightleftharpoons NH_4OH_{(aq)}$$

Similarly when a small amount of an acid is added, hydrogen ions react with undissociated aqueous ammonium hydroxide to form water. This prevents a significant increase in the concentration of hydrogen ions thus keeping pH almost constant.

$$NH_4OH_{(aq)} + H^+{}_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + H_2O_{(l)}$$

The diagram below summarizes how buffers work.



(a) When OH^- is added to a buffer solution, some of the weak acid is neutralized and thus converted to the conjugate base.

Original buffer solution

(b) When H_3O^+ is added to a buffer solution, some of the conjugate base is neutralized and thus converted to the weak acid.

Buffer solution after adding OH^-

Buffer solution after adding H_3O^+

As long as the concentration ratio (weak acid/conjugate base) stays close to its original value, the concentration of H^+ ions and the pH wil not change significantly in both cases.

Figure 6.10 Summary of how buffer solutions work

6.9.2. Definition of buffer capacity and buffer range

a. Buffer capacity

This is a measure of the ability of a buffer solution to resist changes in pH when a base or acid is added. On addition of a base or acid to a buffer system, the effect on pH change can be large or small depending on the initial pH of the solution and it's ability to resist that pH change.

Buffer capacity is therefore defined as the number of moles of acid or base which, when added to one litre of a buffer solution, changes its pH by 1.

Buffer capacity (β) ***has no units since it is a ratio of number of moles of acid or base added, to change in pH of a buffer solution.***

Mathematically;

$$\beta = \frac{\Delta n}{\Delta pH}$$

where; β = Buffer capacity

Δn = number of moles of acid or base added

ΔpH = Difference between final and initial pH

Example:

To a buffer solution, 0.02 moles of acid was added. If the initial and final pH of the buffer was 4.75 and 5.20 respectively, calculate the buffer capacity of the solution.

Answer:

$$\beta = \frac{\Delta n}{\Delta pH}$$

$$= \frac{0.02}{(5.20 - 4.75)}$$

$$= 0.044$$

Buffer capacity indicates the efficiency of the buffer solution to control pH.

The buffer capacity is maximum at pH=pKa where [acid]=[conjugate base].

b. Buffer range

Buffer range is the pH range within which the buffer solution is effective.

Buffer range corresponds to the change in pH of about ±1. For example, acetic acid/sodium acetate buffer works at optimum pH of 4.8. This means that it would work from pH 3.8 on addition of an acid to pH 5.8 when a base is added. Beyond this pH range, the buffer has no capacity to buffer the solution.

Effective buffer ranges of buffer solutions are different and they depend on the acid or base dissociation constant.

Table 6.6 pKa and pH ranges of different buffer solutions.

Buffer	pKa	pH range
Carbonate	10.3	9.3 – 11.3
Citrate	6.4	5.4 – 7.4
Phosphate	2.1	1.1 – 3.1
Borate	9.2	8.2 – 10.2
Ammonia	9.3	8.3 – 10.3
Acetate	4.8	3.8 – 5.8

6.9.3. Applications of buffer solutions

pH of various solutions must be controlled either in industries or in cells of living organisms because any slight change may greatly affect the functioning of the whole system.

In biological processes

- Buffer solutions are used to maintain the pH of human blood constant at 7.4. Intravenous injections must be correctly buffered so that they do not change the pH of blood in humans.
- Proteins in living organisms act as buffers by controlling pH in body cells. They are composed of amino acids linked together in long chains. Each amino acid has two functional groups; the amino group and acidic carboxyl group. The carboxyl group donates hydrogen ion when pH in body cells is high (alkaline). Amino group accepts hydrogen ion from body cells when pH is low (Acidic).
- Buffers keep the correct pH for enzymes to work in many organisms. Enzymes work best in a specific range of pH. If this pH is not controlled, the rate of enzyme activity slows down or enzymes stop working due to denaturation.
- In bacteriological research, culture media are generally buffered to maintain the pH as bacteria required a constant pH all the time to grow.

In agricultural processes

- Plants grow well in soils with a narrow pH range. Some soils become acidic due to acidic rains which is a serious problem to plant or crop growth. Organic matter and mineral salts in a fertile soil act as buffers. It is important to maintain pH of the soils for proper growth of vegetation and soil microorganisms.

In natural systems

- Water bodies such as lakes, rivers and streams are important habitats for aquatic organisms e.g. fish and young amphibians. They should have a stable pH to ensure survival of these organisms. Otherwise extreme pH may cause physical damage to the gills and fins of fish.

In industries

- Buffer solutions are used in fermentation to control pH changes such that anaerobic fermentation bacteria are not killed. This prevents the solutions from becoming too acidic and spoiling the product.
- Buffer solutions are used in manufacture of cosmetics whose pH must be controlled to prevent adverse effects on body cells.
- They are used in the production of pharmaceutical drugs to prevent deterioration when the drug is administered or stored. Buffers ensure stability and clinical effectiveness of the drugs.
- Dyes used in textile industries are buffered in order to maintain color strength in different fabrics after production.
- Buffers are used in leather industries to control pH during tanning and dyeing. This gives a product of fine texture and color.

Application activity 6.9

1. (a)(i) What is meant by a Bronsted-Lowry acid?

   (ii) Write an equation to show that ethanoic acid is a Bronsted-Lowry acid.

   (b) A buffer solution contains ethanoic acid and sodium ethanoate. With the aid of equations, explain how this buffer solution resists change in pH when a small amount of acid or base is added.

   (c) Calculate the pH of a buffer solution which consists of 0.20 mol dm^{-3} of ethanoic acid and 0.25 mol dm^{-3} of sodium ethanoate. (K_a of ethanoic acid is 1.75×10^{-3} mol dm^{-3})
2. Explain why most often buffer solutions are prepared such that the concentration of the conjugate acid or base are similar?
3. Explain why the pH does not change very much on addition of small amount of strong acid or base to a buffer solution?
4. What is meant by “buffer capacity”? What determines buffer capacity of a solution?

Skills Lab 6

1. Plants grow well in soils with a narrow pH range. Identify a plant which best grows in your school's farm and determine the pH of the soil under which that plant is well grown.
2. Discuss the effects of pH change on enzyme activity

End of unit assessment 6

SECTION A: Multiple choice questions

1. In the following reaction in aqueous solution, the acid reactant is _____ and its conjugate base product is ______.

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

A. CH_3COOH, CH_3COO^- B. NH_3, NH_4^+

C. CH_3COOH, NH_4^+ D. NH_3, CH_3COO^-

2. Which one of the following is the strongest acid?

A. HNO_2, Ka= $5.6x10^{-4}$ B. H_2SO_3, Ka=$1.0x10^{-2}$

C. H_2CO_3, Ka=$4.30x10^{-7}$ D. $HClO_4$, Ka=$4.0x10^{-8}$

3. What is the hydroxonium ion concentration of a 0.20M solution of ammonia? The K_b value of ammonia is 1.8×10^{-5} mol dm^{-3}.

A. 2.8×10^{-10} B. 5.2×10^{-12}

C. 1.25×10^{-9} D. 1.9×10^{-3}

4. A cup of coffee has a hydroxide ion concentration of 1.0×10^{-10} M. what is the pH of this coffee?

A. 10 B. 4

C. 7 D. 1

5. How would you calculate K_b for the formate ion, given that the K_a for formic acid is1.8×10^{-4}? ($K_w = 1.0 \times 10^{-14}$)

A. $K_b = Ka \times K_w$ B. $K_b = K_w + K_a$

C. $K_b = K_w/K_a$ D. $K_b = K_a/K_w$

SECTION B:

6. Benzoic acid is a weak acid.

   (a) What is meant by a weak acid?

   (b) The acid dissociation constant of benzoic acid (K_a) is 6.4×10^{-5} moldm^{-3}. Calculate the pH of 0.1moldm^{-3} benzoic acid (C_6H_5COOH) solution.

7. Calculate the pH of 0.1moldm^{-3} ethanoic acid (CH_3COOH) solution at 25^{0}C. Ka of CH_3COOH is 1.8×10^{-5}

8. (a) Write an equation of the reaction for the dissociation of propanoic acid in aqueous solution

   (b) Write an expression for the acid dissociation constant, K_a of propanoic acid

9. Some foodstuffs contain “acidity regulators” which have a buffering action on the pH. Mixtures of citric acid and its sodium salt are often used for this purpose.

$$C_5H_7O_4COOH\,(aq) \rightleftharpoons C_5H_7O_4COO^-\,(aq) + H^+\,(aq)$$

Citric acid $K_a = 7.4 \times 10^{-4}$ mol dm^{-3}

   (a) The concentration of citric acid in lemon juice is 0.23 mol dm^{-3}. Calculate the pH of lemon juice if no other acid is present.

   (b) Write equations to show how citric acid and sodium citrate buffer system regulates the acidity on addition of:

      (i) H^+ ions

      (ii) OH^- ions

   (c) Calculate the pH of the solution containing 0.20 mol dm^{-3} citric acid and 0.3 mol dm^{-3} sodium citrate.

10. A 0.01M solution of ammonia is 4.0% ionized.

   (a) Calculate the pH of the solution

   (b) Determine the base dissociation constant, K_b for the ammonia solution

11. (a) A 0.1M ethanoic acid solution was titrated with 0.1M sodium hydroxide solution until the acid was exactly half-way neutralized. Calculate the pH of the resultant solution. (K_a =1.8 x 10^{-5} mol dm^{-3})

    (b) Two drops of aqueous sodium hydroxide were added to the resultant solution in (a). State what happened to the pH of the solution and explain your answer.

12. A buffer solution of pH 4.5 was prepared from ethanoic acid (K_a = 1.8 x 10^{-5}) and sodium ethanoate. The concentration of sodium ethanoate was 0.2 mol $litre^{-1}$.

    (a) Write equation for the reaction that took place on addition of small amount of:

    (i) dilute hydrochloric acid

    (ii) dilute sodium hydroxide

    (b) Calculate the concentration of ethanoic acid in the buffer solution

13. At 27 ^{0}C, ammonia has a base dissociation constant, K_b of 1.8 x 10^{-5} mol dm^{-3}

    (a) Write an expression for K_b of ammonia

    (b) Calculate the concentration of OH^- ions in 0.1M ammonia solution at 25^{0}C. State any assumptions made.

    (c) Calculate the change in OH^- concentration which occurs when 0.01 moles of ammonium chloride are added to 1.0 dm^3 of the solution in (b) above.

14. A solution containing 2.3x10^{-3} $moldm^{-3}$ of potassium hydroxide ionizes in water (Kw = 1.0 x $10^{-14}mol^2dm^{-6}$)

    (a) Write the equation for the ionization of potassium hydroxide in water.

    (b) Calculate the pH of the resultant solution.

    (c) Explain what is meant by the term buffer solution?

    (d) Discuss some of the applications of buffer solutions in our everyday life.

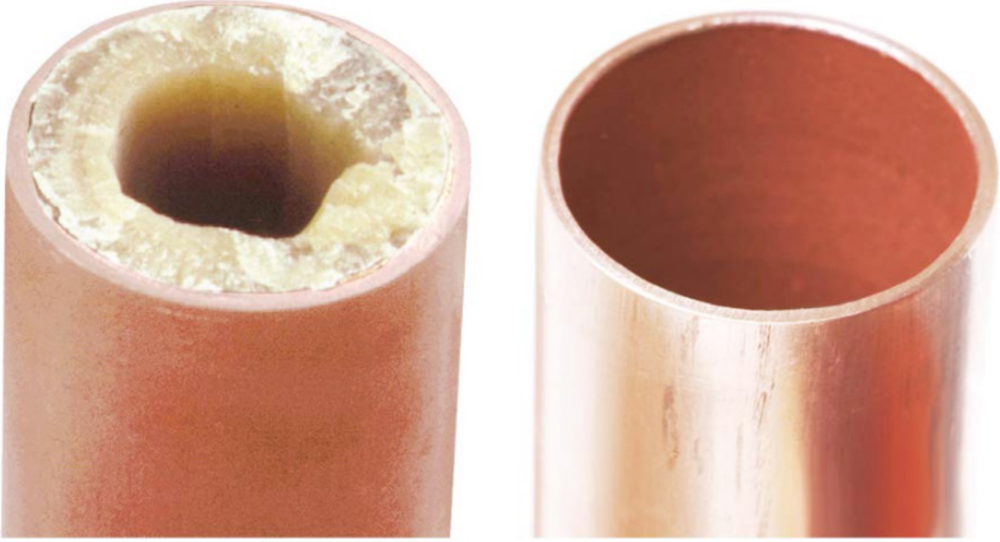
UNIT 7

SOLUBILITY AND SOLUBILITY PRODUCT OF SPARINGLY SOLUBLE SALTS

Key Unit Competence:

Calculate the solubility product constant of sparingly soluble salts and deduce the applications of common ion effect in the industry.

Introductory activity



Pipe with limescale

Pipe without limescale

Limescale is a hard, chalky deposit that often builds up inside kettles, hot water boilers, and pipework, especially that for hot water. It is also often found as a similar deposit on the inner surfaces of old pipes and other surfaces where «hard water» has evaporated.

1. Suggest possible cations found in limescale? Explain your reasoning.
2. Which property of limescale allows it to form in these materials?
3. Suggest possible means of removing limescale from these materials.

Though many ionic compounds are highly soluble in water, some others are only slightly soluble. When these slightly soluble salts are put in water, an extremely very small portion of them dissolves in water and a dynamic equilibrium is established between the dissolved ions and the undissolved salt. Such equilibrium is the focal point to be treated in this unit.

7.1. Definition of solubility and molar solubility

Activity 7.1

1. What is meant by the terms: molar concentration and mass concentration?
2. Calculate the molarity of a solution made by dissolving 4g of sodium hydroxide in distilled water to make 250ml of solution. Determine its mass concentration.
3. A solution of sodium hydrogen carbonate has a molarity of 0.5mol. dm^{-3}. what mass of sodium hydrogen carbonate must be dissolved to make 2dm^{3} of this solution?

Solubility

Solubility is a chemical property referring to the ability of a given substance, the solute, to dissolve in a solvent.

The solubility of a substance is the mass of that substance (expressed in grams) that completely dissolve in 100g of water at a given temperature.

Note:

1. Solubility of ionic salts increases with an increase in temperature. Therefore, the solubility is always expressed under a well-defined temperature
2. Some substances are soluble in all proportions in a given solvent, such as ethanol in water.

Molar solubility

Molar solubility is the maximum number of moles of a solute that can be dissolved in one liter of solution to make a saturated solution.

Most ionic salts are soluble in water while some are insoluble.

Specific examples of soluble salts include:

- All Nitrates,
- All Carbonates except calcium carbonate and silver carbonate
- All Chlorides except silver and lead Chlorides.
- Sodium, Potassium, and Ammonium Sulphate are also soluble, the rest of the sulphate are insoluble.

Soluble substances dissolve by forming free ions in solution; this forms a homogenous mixture

Application activity 7.1

1. Explain why solubility is always expressed under a well-defined temperature.
2. Classify the following compounds as water soluble and water insoluble: $CaCl_2$, $CuSO_4$, NH_3, $PbCr_2O_7$, CaC_2O_4 and LiI.
3. Suggest how the solubility of gases varies with an increase in temperature.
4. Is the dissolution of ionic salts in water an exothermic process or endothermic process? Explain your reasoning.

7.2. Unsaturated, saturated and super saturated solution

Activity 7.2

1. Dissolve a full spatula of sodium chloride in 50cm^3 of water and record your observation.
2. To the solution in (1) add more sodium chloride (25g) and stir well. State and explain your observation.
3. Suggest what you would observe if the experiment in (2) is done at a higher temperature and what would happen if the resulting solution is cooled down.

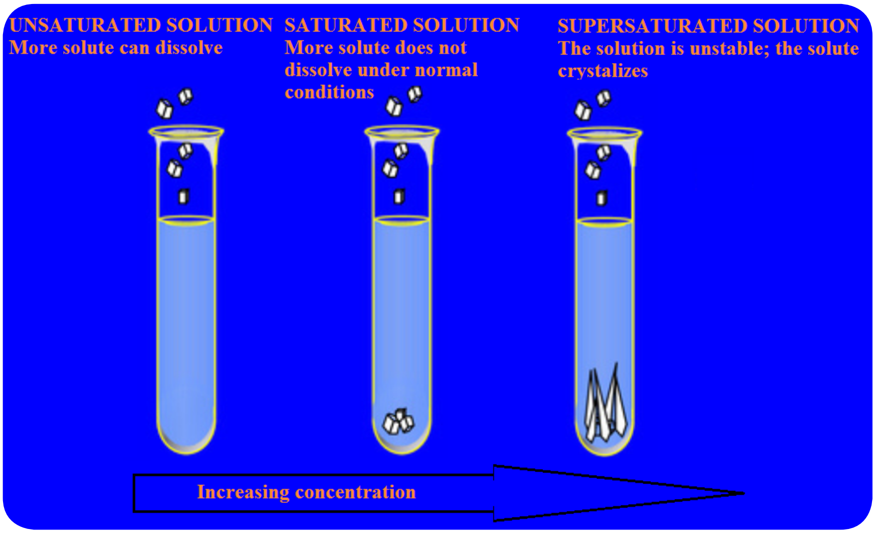


Figure 7.1. Unsaturated, saturated and super saturated solutions

An unsaturated solution is the one which does not contain the maximum amount of solute it can dissolve completely at a given temperature.

A saturated solution is the one which contains the maximum amount of solute it can dissolve at a given temperature. When more solute is added to such solution it does not dissolve. Instead, the excess solute remains in the solid state and it is in equilibrium with the solution.

A super saturated solution contains more solute than the normal maximum solute it can completely dissolve at a given temperature. It is prepared by raising the temperature of the solution to dissolve more solute and then carefully cool it down. This solution is very unstable and adding one crystal of solute to it precipitates the excess solute.

Application activity 7.2

1. Define the following word or expression

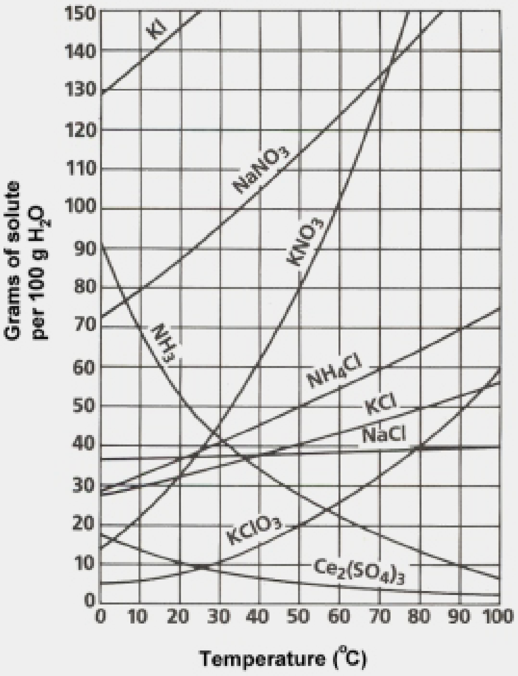
   a. Solubility.

   b. Saturated solution

   c. Supersaturated solution

2. At 90°C, you dissolved 10 g of KCl in 100g of water. Is this solution saturated or unsaturated? Explain your answer.

3. A mass of 100 g of $NaNO_3$ is dissolved in 100 g of water at 80°C. As the solution is cooled, at what temperature should a solid first appear in the solution? Explain.



4. Use the graph to identify the most soluble compound at 20°C.

5. A mass of 80 g of KNO_3 is dissolved in 100 g of water at 50°C. The solution is heated to 70°C. How many more grams of potassium nitrate must be added to make the solution saturated? Explain your reasoning.

7.3 Equations of the dissociation of sparingly soluble salts in water

Activity 7.3

Write equations to show the dissociation of the following substances in water.

1. Barium sulphate.
2. Silver iodide.
3. Silver carbonate.
4. Calcium phosphate.

A sparingly soluble solute is one which slightly dissolves in a solvent. It partially dissociates into its constituent ions.

Some examples of sparingly soluble salts are; Barium sulphate, $BaSO_4$; and Silver Chloride AgCl.

When a sparingly soluble salt is dissolved in a solvent a dynamic equilibrium between dissociated ions and the undissociated solid as shown in the equations below:

1. $AgCl_{(s)} \rightleftarrows Ag^{+}(aq) + Cl^{-}(aq)$
2. $BaSO_4 \rightleftarrows Ba^{2+}(aq) + SO_4^{2-}(aq)$

Biological processes in our bodies also give examples of internal equilibrium systems controlled by hormones, such as Calcium phosphate $Ca_3(PO_4)_2$, an insoluble constituent of bone, which is in equilibrium with its constituent ions in blood. The equilibrium is represented by the equation below: is given by the equation below.

$$Ca_3(PO_4)_2 \leftrightarrows 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

This explains why we need calcium providing food for stronger bones. When the concentration of $Ca^{2+}_{(aq)}$ ions in blood increases, equilibrium position shifts to the left hence preventing the dissolution of bones.

Application activity 7.3

1. Write equations to represent the dissociation of the following sparingly soluble compounds in water:

   a. Calcium carbonate

   b. Iron (III) hydroxide

   c. Silver chromate

2. The following pairs of ions are founds in aqueous solutions:

   a. Pb^{2+} and $Cr_2O_7^{2-}$

   b. Al^{3+} and OH^-

   Write the chemical formulae of the parent compound for each pair of ions

7.4. Solubility product, Ksp, and its relationship with solubility

Activity 7.4

1. Write equations to represent the solubility equilibria established when the compounds below are dissolved in water.

   a. AgCl

   b. $Ca_3(PO_4)_2$

2. Write the equilibrium constant expression Ka, for the partial dissociation of ethanoic acid in water.
3. Suggest the equilibrium constant expressions for each of the equation in (1)

a) Solubility product, Ksp.

In the previous sections, we have seen that solubility of a solid is expressed as the concentration of the “dissolved solid” in a saturated solution.

The solubility product is the equilibrium constant expressed in terms of concentrations of the ions produced from a sparingly soluble solid in contact with a saturated solution.

This equilibrium constant is denoted by the symbol **Ksp**, where the sp added to K tells us that this equilibrium constant is a solubility product. Table 7.1 shows the solubility constant values of some salts at 25⁰C.

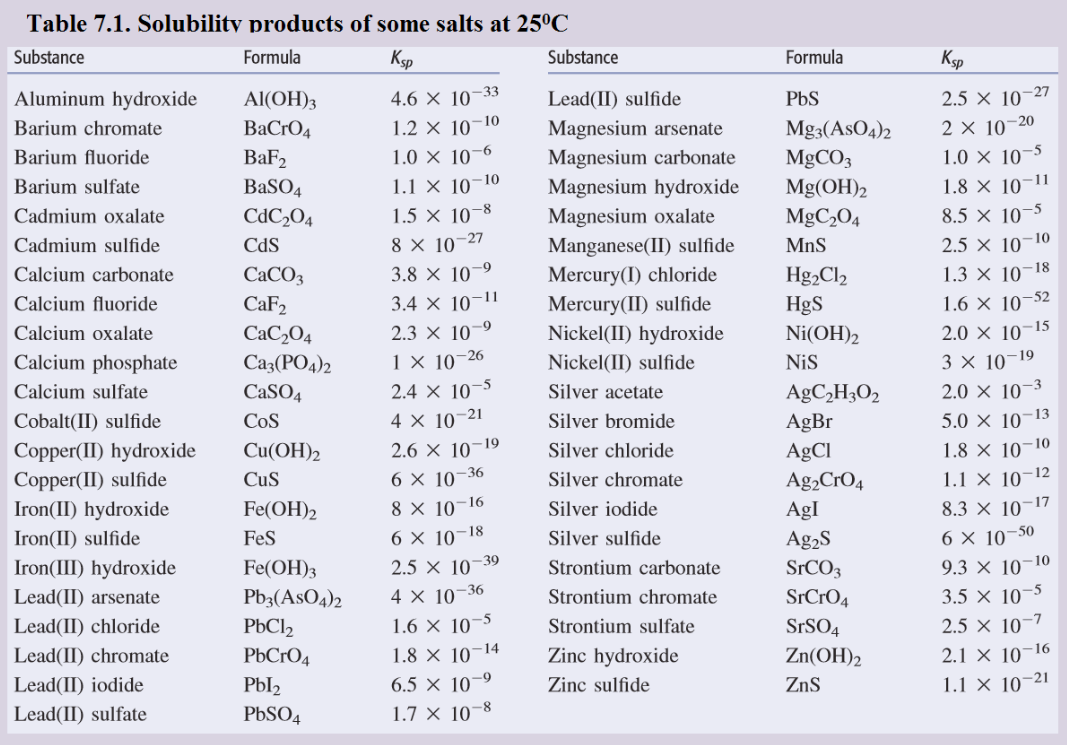


Table 7.1. Solubility products of some salts at 25⁰C

Substance	Formula	K_{sp}	Substance	Formula	K_{sp}
Aluminum hydroxide	$Al(OH)_3$	4.6×10^{-33}	Lead(II) sulfide	PbS	2.5×10^{-27}
Barium chromate	$BaCrO_4$	1.2×10^{-10}	Magnesium arsenate	$Mg_3(AsO_4)_2$	2×10^{-20}
Barium fluoride	BaF_2	1.0×10^{-6}	Magnesium carbonate	$MgCO_3$	1.0×10^{-5}
Barium sulfate	$BaSO_4$	1.1×10^{-10}	Magnesium hydroxide	$Mg(OH)_2$	1.8×10^{-11}
Cadmium oxalate	CdC_2O_4	1.5×10^{-8}	Magnesium oxalate	MgC_2O_4	8.5×10^{-5}
Cadmium sulfide	CdS	8×10^{-27}	Manganese(II) sulfide	MnS	2.5×10^{-10}
Calcium carbonate	$CaCO_3$	3.8×10^{-9}	Mercury(I) chloride	Hg_2Cl_2	1.3×10^{-18}
Calcium fluoride	CaF_2	3.4×10^{-11}	Mercury(II) sulfide	HgS	1.6×10^{-52}
Calcium oxalate	CaC_2O_4	2.3×10^{-9}	Nickel(II) hydroxide	$Ni(OH)_2$	2.0×10^{-15}
Calcium phosphate	$Ca_3(PO_4)_2$	1×10^{-26}	Nickel(II) sulfide	NiS	3×10^{-19}
Calcium sulfate	$CaSO_4$	2.4×10^{-5}	Silver acetate	$AgC_2H_3O_2$	2.0×10^{-3}
Cobalt(II) sulfide	CoS	4×10^{-21}	Silver bromide	$AgBr$	5.0×10^{-13}
Copper(II) hydroxide	$Cu(OH)_2$	2.6×10^{-19}	Silver chloride	$AgCl$	1.8×10^{-10}
Copper(II) sulfide	CuS	6×10^{-36}	Silver chromate	Ag_2CrO_4	1.1×10^{-12}
Iron(II) hydroxide	$Fe(OH)_2$	8×10^{-16}	Silver iodide	AgI	8.3×10^{-17}
Iron(II) sulfide	FeS	6×10^{-18}	Silver sulfide	Ag_2S	6×10^{-50}
Iron(III) hydroxide	$Fe(OH)_3$	2.5×10^{-39}	Strontium carbonate	$SrCO_3$	9.3×10^{-10}
Lead(II) arsenate	$Pb_3(AsO_4)_2$	4×10^{-36}	Strontium chromate	$SrCrO_4$	3.5×10^{-5}
Lead(II) chloride	$PbCl_2$	1.6×10^{-5}	Strontium sulfate	$SrSO_4$	2.5×10^{-7}
Lead(II) chromate	$PbCrO_4$	1.8×10^{-14}	Zinc hydroxide	$Zn(OH)_2$	2.1×10^{-16}
Lead(II) iodide	PbI_2	6.5×10^{-9}	Zinc sulfide	ZnS	1.1×10^{-21}
Lead(II) sulfate	$PbSO_4$	1.7×10^{-8}			

Examples of expression of Ksp for some compounds:

i) $AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$

Ksp of AgCl = $[Ag^+]\,[Cl^-]$

There is no denominator in the expression of the solubility product because the denominator is a pure solid and pure solids and liquids are never included in equilibrium constant expression as their concentrations do not change.

A solubility product is generally a special example of a heterogeneous equilibrium constant. It involves more than one phase and that is solids in contact with liquids.

ii) $PbSO_{4(s)} \leftrightarrow Pb^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$

$Ksp = [\,Pb^{2+}][\,SO_4{}^{2-}]$

iii) $PbI_{2(s)} \leftrightarrow Pb^{2+}{}_{(aq)} + 2I^-{}_{(aq)}$

$Ksp = [Pb^{2+}]\,[I^-]^2$

Note: 1. The concentrations of various ions are raised to the power of the respective stoichiometric numbers in the equation.

2. Like any other equilibrium constant, Ksp is temperature dependent.

b) Relationship between solubility product and solubility.

Consider the following hypothetical reaction:

$A_mB_n\ (s) \rightleftharpoons mA^{n+}\ (aq) + nB^{m-}(aq)$

Given that solubility is denoted '**s**' and solubility product is expressed by Ksp, the solubility product will be equal to:

$$Ksp = [A^{n+}]^m[B^{m-}]^n=(mS)^m x(nS)^n$$

$$= m^m x n^n x S^{m+n}$$

Solubility can then be calculated by using the formula below:

$$S = \sqrt[m+n]{\frac{Ksp}{m^m.n^n}}$$

Application activity

1. Write equations for the solubility equilibria of the following sparingly soluble salts and the corresponding solubility product expressions.

   a. $AgI(s)$

   b. $CaSO_4(s)$

   c. $Ag_2CO_3\ (s)$

   d. $Li_3PO_4(s)$.

2. A saturated solution of a sparingly soluble salt has the following equilibrium:

   $A_xB_y \rightleftharpoons xA^{y+}+yB^{x-}$

a) Write the solubility product expression Ksp for this system.

b) Using 's' as solubility of the salt in moles per liter calculate Ksp for this system.

7.5. Calculations involving solubility product

Activity 7.5

1. Write solubility product expressions, Ksp for each of the following solubility equilibria:

   a) $PbSO_{4(s)} \longleftrightarrow Pb^{2+}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$

   b) $PbI_{2(s)} \longleftrightarrow Pb^{2+}_{(aq)} + 2I^{-}_{(aq)}$

2. An inorganic compound XB_2 dissociates in aqueous solution according to the equation:

   $XB_{2(s)} \longleftrightarrow X^{2+}_{(aq)} + 2B^{-}_{(aq)}$. If 0.05mol of XB_2 is dissolved in water and the equilibrium concentration of of $X^{2+}_{(aq)}$ is found to be 0.0002, what is the equilibrium concentration of $B^{-}_{(aq)}$?

In solubility equilibria calculations, we use molar solubility, solubility and solubility product values. Molar solubility and solubility are always determined when the system is at equilibrium or when the solution is saturated. Hence, we use equilibrium concentrations of present ions to compute the Ksp value. Given Ksp value solubility can also be determined.

Calculating Ksp

Worked examples:

a) The solubility of calcium carbonate $CaCO_3$, at 298K is 6.9×10^{-3} $moldm^{-3}$. Calculate the solubility product at this temperature.

Solution

$CaCO_{3(s)} \leftrightarrow Ca^{2+}_{(aq)} + CO_3{}^{2-}{}_{(aq)}$

Every mole of calcium carbonate which dissolves gives 1 mole of calcium ions and 1 mole of carbonate ions in solution.

So, 6.9×10^{-3} moles of calcium carbonate in $1dm^3$ of solution will dissolve to give:

6.9×10^{-3} moles of Ca^{2+} ions and

6.9×10^{-3} moles of CO_3^{2-} ions both in $1dm^3$ of the solution.

$[Ca^{2+}]=6.9\times10^{-3}\,mol\,dm^{-3}$

$[CO_3^{2-}]=6.9\times10^{-3}\,mol\,dm^{-3}$

After determining equilibrium concentrations/molar solubilities of the ions, we write the equilibrium constant expression and substitute each concentration with its value.

$Ksp=[Ca^{2+}][CO_3^{2-}]$

$=(6.9\times10^{-3}\text{ mol dm}^{-3})^2$

$=4.761\times10^{-5}\text{mol}^2\text{dm}^{-6}$

b) The solubility of calcium sulphate $CaSO_4$ at 298K is $0.67g/dm^3$. Calculate the solubility product at this temperature. (O=16, S=32, Ca=40)

solution

$CaSO_{4(s)} \leftrightarrow Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

The solubility is given in g/dm^3; Convert it into mol/dm^3

Molar solubility = Molarity at equilibrium $=\dfrac{mass\ concentration\left(\frac{g}{dm^3}\right)}{molar\ mass\left(\frac{g}{mol}\right)}$

1 mole of $CaSO_4$ weighs: 40+32+(16×4)=136g

0.67 corresponds to $0.67/136=4.93\times10^{-3}\text{ mol/dm}^3$

The solubility of calcium sulphate is $4.93\times10^{-3}\text{ mol/dm}^3$

Each mole of calcium sulphate that dissolves produces1 mole of Ca^{2+} ions and 1 mole of SO_4^{2-} ions in solution.

$[Ca^{2+}]=4.93\times10^{-3}\text{ mol/dm}^3$

$[SO_4^{2-}]=4.93\times10^{-3}\text{ mol/dm}^3$

$Ksp=[Ca^{2+}][SO4^{2-}]$

$Ksp=(4.93\times10\text{-}3)^2$

$=2.4\text{ x }10^{-5}\text{ mol}^2\text{dm}^{-6}$

c) The solubility of lead II chloride, $PbCl_2$ is $0.016moldm^3$ at 298k. Calculate the solubility product at this temperature.

Solution

$PbCl_{2(s)} \leftrightarrow Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$

The mole ratio is $1PbCl_2:1Pb^{2+} : 2Cl^-_{(aq)}$or (1:1:2). So,

$[Pb^{2+}]=0.016\text{ mol dm}^{-3}$

$[Cl^-]=0.016\times2=0.032$ mol/dm^3

Ksp$=[Pb^{2+}][Cl^-]^2=0.016\times(0.032)^2$

$=1.6\times10^{-5}$mol^{3}dm^{-9}

d) The solubility of calcium phosphate, $Ca_3(PO_4)_2$is 7.7× 10^{-4}g/dm^3 at 25^{0}C. Calculate the solubility product at this temperature. (O =16, P =31,Ca=40)

Solution

$Ca_3(PO_4)_{2(s)}\leftrightarrow3\ Ca^{2+}_{(aq)}+2PO_4^{3-}{}_{(aq)}$

Convert the concentration in g/dm^3 to mol/dm^3

Molar solubility = Molarity at equilibrium $=\dfrac{mass\ concentration\left(\frac{g}{dm^3}\right)}{molar\ mass\left(\frac{g}{mol}\right)}$

1 mole of $Ca_3(PO_4)_2$ weighs 310g.

Concentration in mol dm^{-3}$=7.7\times10^{-4}/310=2.48\times10^{-6}$mol/dm^3

Mole ratio is 1:3:2

$[Ca^{2+}]=3\times2.48\times10^{-6}=7.45\times10^{-6}$mol/dm^3

$[PO_4^{3-}]=2\times2.48\times10^{-6}=4.96\times10^{-6}$ mol/dm^3

Ksp$=[Ca^{2+}]^3\ [PO_4^{3-}]^2$

$=(7.44\times10^{-6}$mol/dm$^3)^3\times(4.96\times10^{-6}mol/dm^3)^2=1.017\times10^{-26}$mol^5.dm^{-15}.

Calculating solubility from solubility product, Ksp.

Examples

a) Calculate the solubility in mol/dm^3 of silver chloride, AgCl, at 298Kif its solubility product is 1.8×10^{-10} mol^{2}dm^{-6}

Solution

$AgCl_{(s)}\leftrightarrow Ag^+_{(aq)}+Cl^-_{(aq)}$

The mole ratio is 1AgCl : 1Ag$^+$:1Cl$^-$.

So, if "s" moles of AgCl are dissolved, the solution will contain "s" moles of each ion.

$[Ag^+]=$ **s** mo ldm^{-3}

$[Cl^-]$= **s** moldm^3

Ksp= $[Ag^+][Cl^-]$

1.8×10^{-10}=s x s

$S=\sqrt{1.8\ x\ 10^{-10}}$

S =1.3×10^{-3}mol/dm^3

b) Calculate the molar solubility of $PbSO_4$ (lead II sulphate). Its solubility product is $1.6\times10^{-8}mol^2dm^{-6}$.

Solution.

$PbSO_{4(s)} \leftrightarrow Pb^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$

The mole ratio is 1$PbSO_4$: 1 Pb^{2+} :1 $SO_4{}^{2-}$

$[Pb^{2+}]$=smol.dm^{-3}

$[SO_4{}^{2-}]$=smol.dm^{-3}

Ksp=$[Pb^{2+}][SO_4{}^{2-}]=1.6\times10^{-8}$

1.6×10^{-8} = s x s

$s = \sqrt{1.6\ x\ 10^{-8}} = 1.26\ x\ 10^{-4}$mol.dm^{-3}

Molar solubility= 1.26×10^{-4}mol.dm^{-3}

c) Calculate the solubility in mol/dm^3 of silver (I) sulphide, Ag_2S. (At 298K, Ksp= 6.3×10^{-51} mol^{3}dm^{-9}).

Solution

$Ag_2S_{(s)} \leftrightarrow 2Ag^+{}_{(aq)} + S^{2-}{}_{(aq)}$

The mole ratio is 1Ag_2S : 2Ag^+: 1 S^{2-}

If the solubility of Ag_2S is S then those of Ag^{2+} and S^{2-} will be:

$[Ag^+]$=2s mol dm^{-3}

$[S^{2-}]$= s mol dm^{-3}

Ksp= $[Ag^+]^2[S^{2-}]$

6.3×10^{-51} mol^{3}dm^{-9}=$(2s)^2\times s$

$4s^3 = 6.3\times10^{-51}$ mol^{3}dm^{-9}

$$S = \sqrt[3]{\frac{6.3\ x\ 10^{-51}}{4}}$$

$S = 1.2\times10^{-17}$mol dm^{-3}

d) Calculate the solubility in g.dm^{-3} of chromium III hydroxide, $Cr(OH)_3$ at 25^{0}C if its solubility product is 1.0×10^{-33}mol^{4}dm^{-12}(H=1, O=16,Cr=52)

Solution

$Cr(OH)_{3(s)} \leftrightarrow Cr^{3+}_{(aq)} + 3OH^-_{(aq)}$

The mole ratio is 1$Cr(OH)_3$: Cr^{3+}: $3OH^-$

If the solubility of $Cr(OH)_3$ is S then those of Cr^{3+} and OH^- will be:

$[Cr^{3+}]$= S mol dm^{-3}

$[OH^-]$= 3S mol dm^{-3}

Ksp= $[Cr^{3+}][OH^-]^3$

$1.0\times10^{-33} = S\times(3S)^3$

$27S^4 = 1.0\times10^{-33}$

$$S = \sqrt[4]{\frac{1.0\ x\ 10^{-3}}{27}}$$

$S = 2.47\times10^{-9}$mol.dm^{-3}

Solubility expressed in g.dm^{-3}=molar solubility X molar mass= $2.47\ \times10^{-9}\ \times103$

$=2.5\times10^{-7}$g/dm^3

Application activity 7.5

1. Calculate the molar solubility of $Sr_3(AsO_4)_2$ if its solubility product equal 4.29×10^{-19}.Determine the units of this constant, Ksp.
2. Given that the molar solubility of Ag_2CO_3 is equal to 1.27×10^{-4}M. Calculate its solubility product.
3. The Ksp of $Mg(OH)_2$ is $1.8 \times 10^{-11} mol^3.dm^{-9}$. Calculate the solubility of $Mg(OH)_2$ in pure water.
4. Calculate the solubility constant of $B(OH)_2$ which forms a solution of pH 11.22.

7.6. Definition, calculation and use of ionic product (Q)

Activity 7.6

Barium sulphate is sparingly soluble in water.

a) Write an equation for the solubility of barium sulphate in water.
b) Write an equation for the solubility product of barium sulphate.
c) A solution of barium sulphate contains 0.002563g per liter of solution. Calculate the solubility product of barium sulphate.

The ionic product (Q) of a salt is the product of the concentrations of the ions in solution raised to the same power as in solubility product expression. Whereas the solubility product Ksp describes the equilibrium concentrations, the ionic product describes concentrations that are not necessarily equilibrium concentrations. Ksp is for saturated solutions only, whereas the ionic product can be for all types of solutions of any concentration.

The ionic product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

i) $Q > Ksp$: the solution is supersaturated and the ionic solid will precipitate
ii) $Q < Ksp$: the solution is unsaturated and more of the ionic solid, if available will dissolve. No precipitate forms.
iii) $Q = Ksp$: the solution is saturated, and no precipitate will form. Any addition of excess ions will precipitate the solid salt.

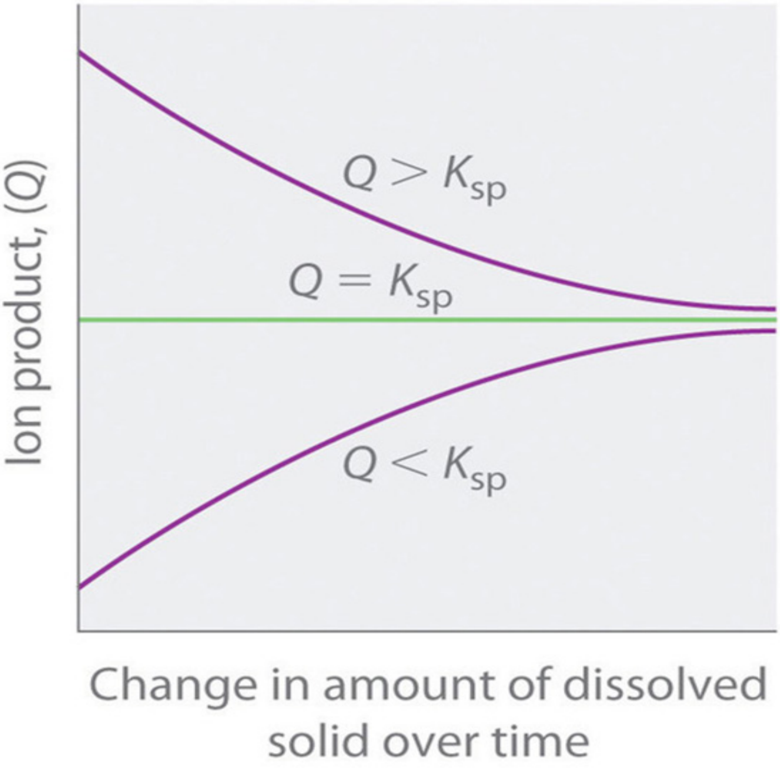


Figure 7.2 Change of the ionic product, Q, with time.

Calculation of the ionic product, Q.

i) Write the balanced equilibrium equation for precipitation reaction and the expression for Ksp.

ii) Substitute the concentrations of ions by their values.

iii) Find the value of Q

Worked examples

Calculate the ionic product of a 0.012 mol dm^{-3} lead II chloride solution at 298K. Ksp ($PbCl_2$) $=1.6\times10^{-5}$ mol^3dm^{-9} at 298K. Is this solution unsaturated or saturated ? Explain your answer.

$PbCl_{2(aq)} \leftrightarrow Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$

$Ksp=[Pb^{2+}]\,[Cl^-]^2$ and $[Pb^{2+}]=0.012M$, $[Cl^-]= 0.012M \times 2=0.024M$

$Q=[Pb^{2+}]\,[Cl^-]^2= (0.012)\,(0.024)^2$

$= 6.9 \times10^{-6} mol^3dm^{-9}$

The solution is unsaturated because Q is smaller than Ksp.

Predicting precipitate formation when two solutions are mixed.

The value of the ionic product is used to determine whether a precipitate will form or not when two solutions are mixed. The ionic product is compared to the solubility product.

- When Q is bigger than Ksp a precipitate is formed.
- When Q is smaller than Ksp the solution is unsaturated and no precipitate is formed..
- When Q is equal to Ksp the solution is saturated solution. No precipitate is formed.

Strategy

i) Write the balanced equilibrium equation for precipitation reaction and the expression for Ksp.

ii) Determine new concentrations of ions in the total volume after mixing the solutions and use them to calculate the ion product(Q)

iii) Compare the values of Q and Ksp to decide whether a precipitate will form.

Worked examples

1. Will a precipitate of lead II chloride be formed if 10 cm^3 of 0.10 $mol.dm^{-3}$ lead II nitrate solution $Pb(NO_3)_2$, is mixed with 10 cm^3 of 0.20 $mol.dm^{-3}$ hydrochloric acid, HCl? Ksp of $PbCl_2$ is 1.6×10^{-5} mol^3dm^{-9} at 298K.

Solution

$Ksp = [Pb^{2+}] [Cl^-]^2 = 1.6\times10^{-5}\ mol^3/dm^9$

When the solutions are mixed, all the ion concentrations will decrease. In this case each solution is being diluted from10cm^3 to a total volume of 20cm^3; so, each is diluted by a factor of 2.

The number of moles of Pb^{2+} and Cl^- ions in both solutions are:

$nPb^{2+} = M \times V = 0.01dm^3 \times 0.10mol\ dm^{-3} = 0.001mol$

$nCl^- = M \times V = 0.01dm^3 \times 0.20mol\ dm^{-3} = 0.002\ mol$

Total volume=$20 \times 10^{-3}dm^3$

New concentrations of Pb^{2+} and Cl^- ions in the total volume are:

$[Pb^{2+}] = n : V = 0.001mol / 0.02dm^3 = 0.05mol/dm^3$

$[Cl^-] = n : V = 0.002mol / 0.02dm^3 = 0.1mol/dm^3$

$Q = [Pb^{2+}] [Cl^{-}]^2 = 0.050 mol/dm^3 \times (0.10 mol/dm^3)^2 = 5.0\times10^{-4} mol^3/dm^9$

Q is bigger than Ksp and therefore a precipitate will form.

As precipitation continues, the value of Q decreases, and it eventually ends up by becoming equal to Ksp. At this point precipitation stop and we get a saturated solution in equilibrium with the precipitate.

2. Will a precipitate of calcium hydroxide form if 5.0 cm^3 of ammonia solution containing OH^- ions with concentration of 2.0×10^{-3} mol/dm^3 is added to 5.0 cm^3 0f 0.05 mol dm^{-3} is added to 5.0 cm^3 of 0.05 mol dm^{-3} calcium chloride solution. $CaCl_2$? Ksp $(Ca(OH)_2) = 5.5\times10^{-6}$ mol^3dm^{-9} at 298K.

Solution

$Ksp = [Ca^{2+}] [OH^-]^2 = 5.5\times10^{-6}$

Ion concentrations before reaction are

$[Ca^{2+}] = 0.025 mol\ dm^{-3}$

$[OH^-] = 1.0\times10^{-3} mol\ dm^{-3}$

Multiplying ion concentrations together gives $0.025 \times (1.0\times10^{-3})^2$

$Q = 2.5\times10^{-8}$ mol^3dm^{-9}

$Q < Ksp$ and no precipitate will be formed.

Application activity 7.6

1. At 298K, the solubility of silver chloride in water is 0.00188 $g.dm^{-3}$. What is its Ksp?
2. A solution is prepared by mixing equal volumes of 0.01M $MgCl_2$, and 0.02M MgC_2O_4 at 18°C. Would MgC_2O_4 precipitate out? Ksp of MgC_2O_4 at 18°C = 8.57×10^{-5}.
3. Will a precipitate form if 25.0 mL of 1.4×10^{-9} M NaI and 35.0 mL of 7.9×10^{-7} M $AgNO_3$ are mixed? (Ksp for AgI at 25°C is 8.5×10^{-17})

7.7. Separation of ions by fractional precipitation

Activity 7.7

A 1.0 $mol.dm^{-3}$ solution of ammonium hydroxide has $[OH^-] = 4.2\times10^{-3}$ $mol.dm^{-3}$. Equal portions of this solution were separately added to 10 cm^3 0.10 $mol.dm^{-3}$ solution of magnesium nitrate, calcium nitrate, strontium nitrate and barium nitrate. All the nitrates have the formula $X(NO_3)_2$. The experiments were then repeated with 10 cm^3 samples of a 1.0 M solution of sodium hydroxide. In which cases will a precipitate be formed?

Solubility products (in mol^3dm^{-9});

$Mg(OH)_2 = 1.1\times10^{-11}$

$Ca(OH)_2 = 5.5\times10^{-6}$

$Sr(OH)_2 = 3.2\times10^{-4}$

$Ba(OH)_2 = 5.0\times10^{-3}$

Ions of sparingly soluble salts can be separated from each other basing on the solubility of their salts in water. This is done by using a reagent that forms a precipitate with one or some of the ions in solution (fractional precipitation). Furthermore, if all ions can form a precipitate with the used reagent, **the solid which has a smaller Ksp will precipitate first** leaving other ions in the solution.

A smaller Ksp shows that lesser ions are needed to precipitate the solid out.

Examples

1. A solution contains both Ag^+ and Cu^{2+} ions. If hydrochloric acid solution is added to this solution, AgCl ($Ksp=1.8\times10^{-10}$) precipitates out while Cu^{2+} ions remain in solution because $CuCl_2$ is soluble. $Ag^+_{(aq)} + Cl^-_{(aq)} \leftrightarrow AgCl_{(s)}$
2. A solution contains 1.0×10^{-2} M Ag^+ and 2.0×10^{-2} M Pb^{2+}. When Cl^- ions are added to that solution, both AgCl ($Ksp = 1.8\times10^{-10}$) and $PbCl_2$ ($Ksp = 1.7\times10^{-3}$) precipitate out from the solution.

a) What concentration of Cl^- ions is necessary to begin the precipitation of each salt?

b) Which salt precipitates first?

Solution:

a) The salt requiring a lower concentration of Cl^- ions will precipitate out first.

For AgCl we have: Ksp $[Ag^+][Cl^-] = 1.8 \times 10^{-10}$.

Because [Ag+] =1.0×10^{-10} M, the greatest concentration of Cl- ions that can be present without causing precipitation of AgCl can be calculated from the Ksp expression

Ksp $=[1.0\times10^{-2}][Cl^-] = 1.8\times10^{-10}$.

$[Cl^-] = \frac{1.8x10-10}{1.0x10-2}$ $=1.8\times10^{-8}$ M. Any Cl^- ions in excess to this will cause AgCl to precipitate from solution.

For $PbCl_2$ we have Ksp $= [Pb^{2+}][Cl^-]^2 =1.7\times10^{-5}$

$[Cl^-]^2 =\frac{1.7X10-5}{2.0X10-2}$ $=8.5 \times 10^{-4}$ $[Cl^-] =\sqrt{8.5x10^{-4}}=2.9\times10^{-2}$ M.

Thus, the concentration of Cl^- ions in excess of 2.9×10^{-2} will cause $PbCl_2$ to precipitate.

b) Silver chloride will precipitate first as the Ag^+ ion requires a low concentration of Cl^- ions to precipitate out of solution.

Application activity 7.7

1. The concentration of Ca^{++} in blood is 0.0025M. If an oxalate solution with oxalate ion concentration 1×10^{-7}M is added to it, state whether precipitation occurs or not. Solubility product of calcium oxalate = 2.3×10^{-9}.
2. A solution is prepared by mixing equal volumes of 0.01M $MgCl_2$, and 0.02M MgC_2O_4 at 18°C. Would MgC_2O_4 precipitate out? (K_{sp} of MgC_2O_4 at 18°C = 8.57×10^{-5})
3. What is the minimum concentration of sodium sulfate that would cause a precipitate with 0.10 M strontium nitrate? (Ksp $SrSO_4$= 2.5×10^{-7})

7.8. Impact of Common ion effect, pH change, complex ion formation on solubility.

Activity 7.8

1. When aqueous sodium hydroxide is added to a solution of an aluminium salt it becomes white. When more NaOH$_{(aq)}$ is added the solution becomes colorless. Explain these observations.
2. Explain how a decrease in pH affects the following equilibrium

$$Cl_2 + H_2O \rightleftharpoons HClO + HCl$$

a) Common ion effect

It has known that the solubility of a sparingly soluble ionic substance is obviously decreased in a solution of another ionic compound when the two substances have an ion in common. This can be observed based on **Le Châtelier's Principle**. Generally, Common ion Effect is a decrease in the dissociation of a weak electrolyte when a common ion is added to the solution. This happens because the equilibrium position shifts to oppose the addition of that common ion.

Particularly for sparingly salts, Common ion Effect is the precipitation of a sparingly soluble compound (or salt) from its saturation by adding a soluble compound containing one of the ions contained by the sparingly soluble salt.

Consider the following example: $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

If sulphuric acid (H_2SO_4) is added to the solution of $BaSO_4$, the concentration of SO_4^{2-} ions increases and the equilibrium position shifts to the left side of the reaction. As a result, Barium gets precipitated as BaSO4$_{(s)}$. H_2SO_4 is a strong acid and it dissociates completely as indicated in the equation:

$$H_2SO_{4(aq)} \rightarrow 2H^+_{(aq)} + SO^{2-}_{4(aq)}$$

The sulphate ion (SO_4^{2-}) is the common ion among these two reactions thus when its concentration increases due to the dissociation of sulphuric acid, it shifts equilibrium to the left side of the reaction resulting in the precipitation of Barium as $BaSO_{4(s)}$.

$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

The solubility product expression tells us that the equilibrium concentration of the cation and the anion are inversely related. When the concentration of the anion increases; the maximum concentration of cation needed for the precipitation to occur decreases; and vice versa, reason why Ksp is constant. Consequently, the solubility of an ionic compound depends on the concentration of other salt that contain the same ions.

b) The pH

Some sparingly soluble salts produce basic ions such as, PO_4^{3-}, $C_2O_4^{2-}$, OH^-, CO_3^{2-} which can combine with hydrogen ions to form weak acid molecules. Thus, H^+ ions decrease the concentration of those ions in the solution and this allows the dissolution of more salt. Their solubility increases with a decrease in pH.

Example

Adding H^+ ions to a solution of $Ca_3(PO_4)_2$ increases the solubility of this compound.

$$Ca_3\left(PO_4\right)_{2(s)} \rightarrow 3Ca^{2+}_{(aq)} + PO^{3-}_{4(aq)} \quad \text{(equation1)}$$

$$3H^+_{(aq)} + PO^{3-}_{4(aq)} \rightarrow H_3PO_{4(aq)} \text{(equation 2)}$$

Equation 2 shows how H^+ ions combine with PO_4^{3-} ions and reduce them in the equilibrium shown by equation (1). As PO_4^{3-} ions reduces in the equilibrium, more $Ca_3(PO_4)_{2(s)}$ dissociates to reestablish the equilibrium.

c) Complex ion formation

Complex ions are formed when negatively charged ions such CN^- form a dative covalent bond with a central metal ion. The dative covalent bond can also be formed by neutral atoms which have lone pairs of electrons such as NH_3, and H_2O. Ligands are Lewis bases because they donate electrons. The number of ligands surrounding a central metal ion is called the coordination number.

Most transition metal ions possess empty d orbitals that are sufficiently low in energy to be able to accept electron pairs from electron donors from cations, resulting in the formation of a covalently bound complex ion.

Water is an active electron donor of this kind, so aqueous solutions of ions such as $Fe^{3+}_{(aq)}$ and $Cu^{2+}_{(aq)}$ exist as the octahedral complexes $\left[Fe(H_2O)_6\right]^{3+}$ and $\left[Cu(H_2O)_6\right]^{2+}$, respectively.

Ligands which are stronger Lewis bases can displace weaker Lewis bases from the central metal ion stepwise forming a variety of intermediate species. This is called Ligand exchange or Ligand displacement.

Hydrated cations contain the Ligand H_2O.This ligand is a weaker Lewis base compared to NH_3 being a stronger Lewis base; NH_3 will displace H_2O stepwise giving a series of intermediates.

If a sparingly soluble solid is placed in contact with a solution containing a ligand that can bind to the metal ion much more strongly than H_2O, then formation of a complex ion will be favored and the solubility of the solid will be greater.

Example:

1. When ammonia is added to a solution of copper (II) nitrate, in which the $Cu^{2+}(aq)$ ion is itself the complex ion shown at the left:

$$\left[M(H_2O)_4\right]^{2+}_{(aq)} + 4NH_{3(aq)} \longrightarrow \left[M(NH_3)_4\right]^{2+}_{(aq)} + 4H_2O$$

, where M is a central metal ion.

Because ammonia is a weak base, the first thing we observe is the formation of a cloudy precipitate of $Cu(OH)_2$ in the blue solution. As more acid is added, the precipitate dissolves, and the solution turns an intense deep blue, which is the color of tetrammine copper (II) and the various other related species such as $Cu(H_2O)_5(NH_3)^{2+}$, $Cu(H_2O)_4(NH_3)_2{}^{2+}$, etc.

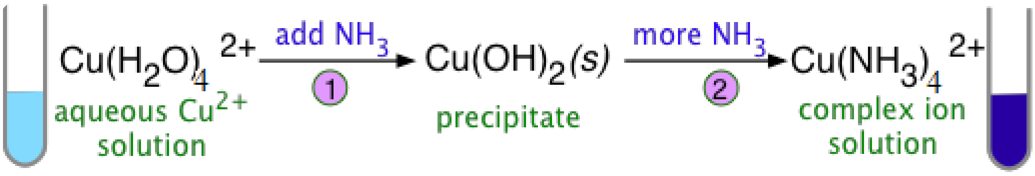


Figure 7.3 Precipitation of Cu^{2+} ions using ammonia solution

In many cases, the complexing agent and the anion of the sparingly soluble salt are identical. This is particularly apt to happen with insoluble chlorides, and it means that addition of chloride to precipitate a metallic ion such as Ag^+ will produce a precipitate at first, but after excess Cl^- has been added the precipitate will redisolve as complex ions are formed.

Application activity 7.9

1. The solubility product of silver oxalate $Ag_2C_2O_4$ is given by the expression, $Ksp = [Ag^+]^2 [C_2O_4^{2-}]$. Explain how the solubility of silver oxalate would be affected if a few drops of the following solutions are added.

   a) Concentrated ammonia solution

   b) Sodium oxalate

2. Strontium hydroxide is sparingly soluble in water.

   a) Write the equation for the solubility of strontium hydroxide in water.

   b) Write an expression for the solubility product (Ksp) of strontium hydroxide.

   c) Sodium hydroxide was added to a saturated solution of strontium hydroxide.

      (i) State what happened to the solubility of strontium hydroxide in water.

      (ii) Explain your answer in (i) above.

7.9. Applications of solubility product

Activity 7.9

1. Suggest a chemical test; reagents and procedure you can use to distinguish the ions in the following pairs:

   a) Mg^{2+} and Ca^{2+}

   b) Cu^{2+} and Fe^{3+}

   c) Cl^- and I^-

2. Define an acid-base indicator and explain why titrations involving $KMnO_4$ do not need an indicator.

a) **Volumetric analysis:** The concentration of Chloride ions in a solution of soluble Chloride salt can be determined by titration with a standard solution of silver nitrate. Potassium chromate is used as an indicator.

A white precipitate of silver Chloride forms first due to lower solubility of silver Chloride and the end point is indicated by the formation of a red precipitate of silver chromate. This can be seen from the solubility product (Ksp) values of silver chloride (Ksp AgCl = 1.2×10^{-10} mol^2dm^{-6}) and silver chromate (Ksp Ag_2CrO_4) = 2.4×10^{-12} mol^3dm^{-9}). A lower concentration of Ag^+ ions is needed to form a precipitate with chloride ions than that of chromate ions.

b) **Production of soap: saponification.**

To precipitate out the soap made by reacting a mixture of fats and oils with NaOH solution, a concentrated solution of sodium chloride (brine) is added to the soap- glycerol mixture. Soap and sodium chloride are present in the form of ions

Soap equilibrium: $C_{17}H_{35}COO^-Na^+(s) \longrightarrow C_{17}H_{35}COO^-(aq) + Na^+(aq)$

When brine is introduced to the soap mixture, it introduces a common ion Na^+ in a high concentration which shifts the equilibrium position to the left. As a result, the stearate ion ($C_{17}H_{35}COO^-$) combines with the excess sodium ions to form soap which floats on top.

c) **Qualitative analysis**

In the identification of ions, solubility of salts plays an important role. Some ions form characteristic insoluble precipitates with certain reagents. These precipitates are easy to identify.

Some precipitates are soluble in excess reagent while others are not. This also helps to identify the ions which may give precipitates of the same color.

The use of ammonia and sodium hydroxide also depends on solubility constant and the relative concentration of OH^- ions provided by both $NH_{3(aq)}$ and $NaOH_{(aq)}$.

Examples

1. Fe^{2+} forms a dirty green precipitate insoluble on excess NaOH.
2. Al^{3+} forms a white precipitate with NaOH as well as NH_3. This precipitate is soluble in excess NaOH but insoluble in excess NH_3.

Application activity 7.9

1. The solubility product of Bi_2S_3 is listed as an unimaginably small number, 1×10^{-97}. Calculate the solubility of Bi_2S_3 in pure water.
2. Use the data from table 7.1 to suggest an ion you can use as an indicator in the quantitative analysis of Fe^{3+} ions and $Cr_2O_4^{2-}$ ions using $NaOH_{(aq)}$ and $Ba(NO_3)_{2(aq)}$ respectively.

Skills Lab 7

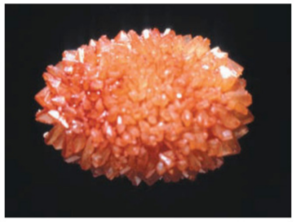


Figure 7.3

1. Most of kidney stones such as that shown in figure 7.3 are formed by calcium substances like calcium oxalate. Suggest a reason why people who suffer from this problem are advised to drink a lot of water.
2. Explain, in terms of solubility product concept, why hard water forms scum with soap while soft water does not.

End of unit assessment 7

1) The solubility product expression for tin (II) hydroxide, $Sn(OH)_2$, is

(a) $[Sn^{2+}][OH^-]$

(b) $[Sn^{2+}]^2[OH^-]$

(c) $[Sn^{2+}][OH^-]^2$

(d) $[Sn^{2+}]^3[OH^-]$

(e) $[Sn^{2+}][OH^-]^3$

2) The solubility product expression for silver (I) sulfide, using x to represent the molar concentration of silver (I) and y to represent the molar concentration of sulfide, is formulated as:

(a) xy

(b) x^2y

(c) xy^2

(d) x^2y^2

(e) xy^3

3. Consider the following solubility data for various chromates at 25°C

	K_{sp}
a. Ag_2CrO_4	9.0×10^{-12}
b. $BaCrO_4$	2.0×10^{-10}
c. $PbCrO_4$	1.8×10^{-14}

Which one is the least soluble chromate?.

4. The molar solubility of $PbBr_2$ is 2.17×10^{-3} M at a certain temperature. Calculate K_{sp} for $PbBr_2$.

(a) 6.2×10^{-6}

(b) 6.4×10^{-7}

(c) 4.1×10^{-8}

(d) 3.4×10^{-6}

(e) 1.4×10^{-5}

5) When we mix together, from separate sources, the ions of a slightly soluble ionic salt, the salt will precipitate if Q_{sp} _____ K_{sp}, and will continue to precipitate until Q_{sp} _____ K_{sp}.

(a) is greater than; equals

(b) is less than; is greater than

(c) is less than; equals

(d) equals; is less than

(e) equals; is greater than

6) A solution is 0.0010 M in both Ag^+ and Au^+. Some solid NaCl is added slowly until the solid AgCl just begins to precipitate. What is the concentration of Au^+ ions at this point? K_{sp} for AgCl = 1.8×10^{-10} and for AuCl = 2.0×10^{-13}.

(a) 2.0×10^{-10} M

(b) 4.5×10^{-7} M

(c) 1.8×10^{-7} M

(d) 3.0×10^{-4} M

(e) 1.1×10^{-6} M

7. Consider two compounds A and B where A has a solubility product of 3.3×10^{-3} while B has a solubility product of 4.4×10^{-7}. Can we conclude that compound A has a higher Molar solubility than B? Explain your answer.

8. Write the solubility product expressions for the following solubility equilibrium

i) $Hg_2Cl_{2(s)} \rightleftharpoons Hg_2^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$

ii) $Sr_3(AsO_4)_{2(s)} \rightleftharpoons 3Sr^{2+}{}_{(aq)} + 2AsO_4^{3-}{}_{(aq)}$

3. Consider a compound with the formula L_3X_4 that dissolve to produce $L^{4+}$and X^{3-}ions in solution. If the solubility product of this compound is 8.2×10^{-24}, calculate the molar solubility of the compound.

4. Explain what is meant by the term common ion effect and how it is accounted for by applying Le chatelier's principle.
5. Calculate the molar solubility of $Ba(IO_3)_2$ given that its Ksp is equal to $1.5x10^{-9}$.
6. Find the concentration of $PbCl_2$ in a saturated solution of $PbCl_2$. Ksp $=1.7\ x10^{-5}$.

UNIT 8

REDUCTION AND OXIDATION REACTIONS

Key Unit Competence:

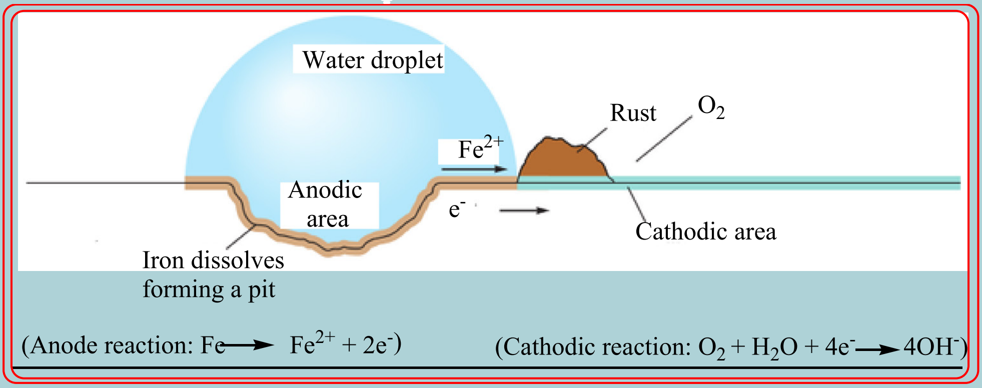
Explain the concept of reduction and oxidation and balance equations for redox reactions

Introductory activity

Introductory activity 8

The following figures illustrate the natural electrochemical process that is occurring on the surface of the metals. The figure A shows what we observe before and after the said process and the figure B shows what really happened chemically. Observe each of them carefully and answer the questions that follow.

Figure A



(Anode reaction: $Fe \longrightarrow Fe^{2+} + 2e^-$)

(Cathodic reaction: $O_2 + H_2O + 4e^- \longrightarrow 4OH^-$)

Figure B

1. Based on some features shown on the figures above, suggest the name of the phenomenon that is happening.
2. Write the overall chemical equation of the reaction that took place during the process.
3. What are the conditions for the process shown to occur?
4. Is this process reversible? Explain.
5. Discuss the economic impact of this process and suggest how it should be prevented.

8.1. Definition of electrochemistry and its relationship with redox reactions

Activity 8.1

1. Explain the terms “electricity” and “chemistry” and use available sources to explain the meaning of electrochemistry.
2. Using your knowledge acquired so far in chemistry, specifically from the unit 9 of senior 3, recall the concept of reduction and oxidation.

8.1.1. Definition of oxidation-reduction reactions and electrochemistry

Electrochemistry is defined as the study of the interchange of chemical and electrical energy. It is primarily concerned with two processes that involve oxidation–reduction reactions: the generation of an electric current from a spontaneous chemical reaction and, the opposite process, the use of a current to produce chemical change.

Electrochemistry is important in other less obvious ways. For example, the corrosion of iron, which has tremendous economic implications, is an electrochemical process. In addition, many important industrial materials such as aluminium, chlorine, and sodium hydroxide are prepared by electrolytic processes.

The name **"oxidation"** was initially applied to reactions where substances combined with the element oxygen. Thus any substance burning in air was said to be oxidized, the product being some type of oxide. For example, burning carbon to produce carbon dioxide is an oxidation, as shown by the equation

$$C + O_2 \rightarrow CO_2$$

Subsequently it was realized that reactions of substances with elements other than oxygen were of essentially the same type. For example, hydrogen can react with oxygen to form the compound water, but equally it can react with chlorine to form the compound hydrogen chloride. In both reactions the free element hydrogen is converted into a compound of hydrogen and another non-metal, and in both reactions, hydrogen atom tends to lose an electron whereas the other atoms tend to gain electron; so both were classified as **oxidations** even though no oxygen was involved in the second case.

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$H_2 + Cl_2 \rightarrow 2HCl$$

The reverse reaction, conversion of compounds such as oxides of metals to the elemental metal were called "**reduction**" reactions, for example, the reduction of copper (II) oxide to copper by heating with charcoal (carbon). The reduction reaction was then defined as the loss of oxygen by a compound.

$$2CuO + C \rightarrow 2Cu + CO_2$$

The gain or loss of oxygen is still a useful way of recognizing some oxidation or reduction reactions, but with knowledge of the structure of atoms, a rather wider definition of oxidation and reduction reaction has been adopted.

Oxidation reactions as a loss of electrons and reduction as a gain of electrons

Let's take the reaction between magnesium, Mg, and chlorine (Cl_2):

$$Mg(s) \quad + \quad Cl_2(g) \rightarrow \quad MgCl_2(s)$$

This reaction can be conceived into two parts, called half-reactions:

(1) $Mg\ (s) \rightarrow Mg^{2+}_{(aq)} + \cancel{2e^-}$ **oxidation reaction half-equation: loss of electrons**

(2) $Cl_2(g) + \cancel{2e^-} \rightarrow 2Cl^-$ **reduction reaction half-equation: gain of electrons**

(3) = (1) + (2): $Mg(s) + Cl_2(g) \rightarrow Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}$ overall redox reaction

or $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$

Hence a redox reaction is a combination of two half-reactions: an oxidation half-reaction and a reduction half-reaction. Nevertheless, one half-reaction cannot exist without the other, because electrons lost in the oxidation process must be captured in the reduction process, this explains why we talk of **oxidation-reduction** or **redox reaction**.

The characteristic of a redox reaction is that there is exchange or transfer of electrons between chemical species participating in the reaction.

We can compare this to the emigration-immigration movement: when a person leaves a country, emigration for that country, he/she must enter another country, immigration for that country and this constitutes an emigration-immigration movement.

We notice that any chemical species whose oxidation state increases is **oxidized**:

$Mg \rightarrow Mg^{2+} + 2e^-$, magnesium is oxidized.

And any chemical species whose oxidation state decreases is **reduced**:

$Cl_2 + 2e^- \rightarrow 2Cl^-$, chlorine is reduced

8.1.2 Relationship between electrochemistry and redox reactions

In oxidation–reduction (redox) reactions, electrons are transferred from one chemical species to another. This transfer of electrons provides a means for converting chemical energy to electrical energy or vice versa. The study of the relationship between electricity and chemical reactions is called **electrochemistry**.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two half-reactions, one representing the oxidation process and another the reduction process.

The electrons in a balanced half-reaction show the direct relationship between electricity and the specific redox reaction. **Electrochemical reactions are either spontaneous as in galvanic cells, or non-spontaneous as in electrolytic cells.** A spontaneous redox reaction generates a voltage itself. A non-spontaneous redox reaction occurs when an external voltage is applied.

The reactions that occur in an electric battery are electrochemical reactions**.** Thus, a galvanic cell ***uses*** the energy released during a spontaneous redox reaction to **generate** electricity. In contrast, an electrolytic cell ***consumes*** electrical energy from an external source, using it to cause a non-spontaneous redox reaction to occur. Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system. The oxidation half-reaction occurs at one electrode (**the anode**), and the reduction half-reaction occurs at the other (**the cathode**). When the circuit is closed, electrons flow from the anode to the cathode.

For instance, when a molten sodium chloride undergoes electrolysis the following reactions occur at electrodes.

Cathode: $Na^+ (l) + e^- \rightarrow Na(s)$ **reduction**

Anode: $Cl^- (l) \rightarrow 1/2Cl_2(g)$: **oxidation**

These reactions that require electricity are very useful in the preparation of sodium and chlorine from sodium chloride. Many other substances are prepared in the same way.

Likewise in a galvanic cell, oxidation and reduction occur at anode and cathode respectively. We will detail this in the following unit.

$Fe(s) + S(s) \rightarrow FeS(s)$

The Corrosion that is defined as “the degradation of materials by chemical reaction with the environment in which the material resides” also involves redox reaction since the metal get oxidized during the process.

Application activity 8.1

Which of the following transformations is a redox reaction? Justify your answer.

i) $H_2O(l) \rightarrow H_2(g) + O_2(g)$

ii) $N_2(g) + H_2(g) \rightarrow NH_3(g)$

iii) $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

iv) $H_2C{=}CH_2(g) + H_2(g) \rightarrow CH_3CH_3(g)$

v) $Ba(NO_{3)\,2}(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2HNO_3(aq)$

vi) $K(s) + \frac{1}{2} Br_2 \rightarrow KBr(s)$

vii) $Fe(s) + S(s) \rightarrow FeS(s)$

viii) $AgNO_3(aq) + KBr(aq) \rightarrow AgBr(s) + KNO_3(aq)$

ix) $KBr(\,l) \rightarrow K(s) + \frac{1}{2} Br_2(g)$

8.2. Oxidation numbers of elements in the compounds

Activity 8.2

1) How can you tell that a redox reaction takes place?

2) Recall the concept of:

   a) valence

   b) electronegativity

3) Explain how the concept of valence is related to that of oxidation number.

1) Definition

The **oxidation number** or **oxidation state** of an atom is the apparent or real charge that the atom has when all bonds between atoms of different elements are assumed to be ionic. By comparing the oxidation number of an element or chemical species before and after reaction, we can tell whether the atom has gained or lost electrons. Note that oxidation numbers don't necessarily imply ionic charges; they are just a convenient device to help keep track of electrons during redox reactions. Oxidation states are typically represented by integers, which can be positive, negative, or zero. In some cases, the average oxidation state of an element is a fraction.

2. Determination of oxidation numbers

Oxidation numbers are assigned following the rules below:

1) The oxidation number of an atom in its elemental form is always zero. Thus:
   - The oxidation number of H in H_2 is zero.
   - The oxidation number of Cl in Cl_2 is zero.
   - The oxidation number of P in P_4 is zero.
   - The oxidation number of S in S_8 is zero.
   - The oxidation number of Na metal is zero.

2. The oxidation number of:
   - an alkali metal in any its compounds is +1
   - an alkali earth metal in any of its compounds is +2
   - aluminium in any of its compounds is +3

3. Non-metals usually have negative oxidation numbers although they can sometimes have positive ones.

   (a) The oxidation number of oxygen is usually -2, except in peroxide where is equal to -1 in superoxides (e.g. KO_2), where it is equal to - ½ , and in OF_2 where it is +1.

   (b) The oxidation number of hydrogen is usually +1 when bonded to non-metals and -1 when boded to metals (in hydrides).

   (c) The oxidation number of a halogen in most binary compounds is -1 except chlorine, bromine and iodine when bonded to oxygen or another halogen which is above in the periodic table, in which case they have positive oxidation states.

4. For a monoatomic ion, the oxidation state is equal to the charge on the ion. Thus,
   - K^+ has an oxidation number of +1.
   - S^{2-} has an oxidation number of -2.
   - Cr^{3+} has an oxidation number of +3.

5. For a polyatomic ion, the sum of the oxidation numbers is equal to the charge on the ion.

6. For neutral compounds, the sum of the oxidation numbers is equal to zero.

Note: In writing oxidation numbers, the sign is written before the number to distinguish them from the actual electric charges for which the number is written before the sign.

Examples:

1. Find the oxidation number of the sulphur atom in sulphuric acid ($H_2\underline{S}O_4$).

Solution:

Since each H atom is +1 and each O atom bears -2, the S atom must have an oxidation number of +6 for the compound to have no net charge: $2(+1) + x + 4(-2) = 0$ net charge

$\mathbf{x} = 0 - 2(+1) - 4(-2) = \mathbf{+6}$

2. Find the oxidation number of the chlorine atom in the perchlorate anion (ClO_4^-),

Solution:

Each oxygen has an oxidation number of -2, so Cl atom must have an oxidation number of +7 for there to be a net charge of −1 on the ion:

$\mathbf{x} + 4(-2) = -1$ net charge

$\mathbf{x} = -1 - 4(-2) = \mathbf{+7}$

3. Calculate the oxidation number of:
   - a) nitrogen in N_2?
   - b) phosphorus in PF_5?
   - c) nitrogen in NH_4^+?
   - d) chromium in $Cr_2O_7^{2-}$
   - e) nitrogen in N_2H_4(hydrazine)?
   - f) nitrogen in NO_3^-?
   - g) manganese in MnO_4^-?
   - h) manganese in Mn_3O_4?
   - i) nitrogen in HN_3?
   - j) chlorine in $KClO_4$?

Solution:

a) 0
b) +5
c) -3
d) +6

e) -2

f) +5

g) +7

h) +(2)

i) −1/3

j) +7

Fractional oxidation numbers do not mean that electrons have been split. The oxidation number simply gives the average of the numbers of electrons still controlled by for instance the:

3 nitrogen atoms in hydrogen azide HN_3 See answer i) above

3 manganese atoms in Mn_3O_4, See answer h) above

Application activity

1. Calculate the oxidation number of:

   a) hydrogen in H_2SO_4, CaH_2, H_2O_2, $LiAlH_4$

   b) sulphur in SO_3, SO_4^{2-}, H_2SO_3, H_2S, $S_2O_3^{2-}$, $S_2O_7^{2-}$, $S_4O_6^{2-}$

   c) nitrogen in NO, N_2O_4, NH_2OH, NaN_3, N_2O, HNO_2

   d) lead in PbO_2, PbO, Pb_3O_4

   e) iron in $FeCl_2$, $Fe_2(SO_4)_3$, Fe_2O_3

   f) chlorine in KCl, Cl_2O, ClO_3^-, HClO

   g) silicon in $SiCl_4$, SiO_2, $[Si_6O_{18}]^{12-}$, $K_4Si_4O_9$

2. Identify in which of the following species nitrogen is in:

   a) its lowest oxidation state

   b) its highest oxidation state:

   NO_2, NO, HNO_3, N_2, HNO_2, N_2O, Na_3N

3. Determine the oxidation number of the underlined elements in the following compounds.

   $K_2\underline{Cr}_2O_7$, $Na_2\underline{C}_2O_4$, $K\underline{Mn}O_4$, $\underline{Mn}SO_4$, $\underline{C}O_2$, $\underline{Cr}Cl_3$, $H\underline{N}O_3(+5)$, $\underline{S}O_3(+6)$

8.3 Oxidation – reduction half-equations and concept of disproportionation reaction

Activity 8.3

Consider an example of the formation of potassium fluoride and answer the following questions.

1. What type of chemical bonding is this and what are the steps involved in the process?

   b) What step correspond to the: (i) oxidation process (ii) reduction process?

   c) Write an appropriate chemical equation for each of the processes in b) above.

2. Write equations of the reactions that occur when zinc metal react with copper sulphate solution.

Even if oxidation and reduction must take place simultaneously, it is often convenient to consider them as separate processes.

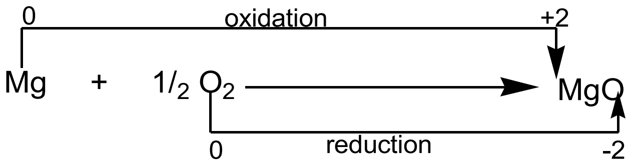
Oxidation:

Reaction in which a chemical species loses electrons and thus its oxidation number is increased.

Reduction:

Reaction in which a chemical species gains electrons and thus its oxidation number is decreased.

Examples



$$Mg + 1/_2\,O_2 \longrightarrow MgO$$

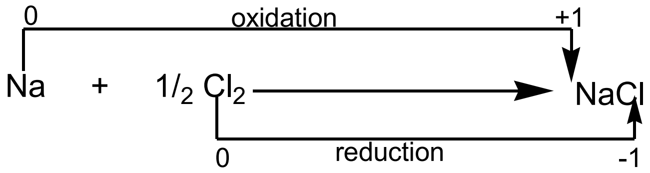
Using half-equations

$$Mg \longrightarrow Mg^{2+} + 2e^- \quad \text{and} \quad 1/_2O_2 + 2e^- \longrightarrow O^{2-}$$

Magnesium is oxidised because its oxidation number increases.
Oxygen is reduced because its oxidation number decreases.

$$Hg_2Cl_{2(s)} \longrightarrow Hg_2{}^{2+}{}_{(aq)} + 2Cl^-$$

$$Sr_3(AsO_4)_{2(s)} \longrightarrow 3Sr^{2+}{}_{(aq)} + 2AsO_{4aq}{}^{3-}$$



$$Na + 1/_2\,Cl_2 \longrightarrow NaCl$$

Using half-equations

$Na \longrightarrow Na^+ + e^-$ and $1/_2Cl_2 + e^- \longrightarrow Cl^-$

Sodium is oxidised because its oxidation number increases. Chlorine is reduced because its oxidation number decreases.

Most combinations and decompositions reactions are oxidation-reduction reactions.

e.g. $K + ½\,Br_2 \longrightarrow KBr$

$Al_2O_3 \xrightarrow{electrolysis} 2Al + O_2$

Single substitution and combustion reactions are oxidation-reduction reactions.

e.g.

$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$

$2KBr(aq) + Cl_2g) \rightarrow 2KCl(aq) + Br_2(l)$

$C(s) + O_2(g) \rightarrow CO_{2(}g)$

$S(s) + O_2(g) \rightarrow SO_2(g)$

Concept of disproportionation reactions

Disproportionation is a chemical reaction, typically a redox reaction, where an element in a molecule or chemical species is simultaneously oxidized and reduced. One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states. The element in the form of reacting substance is in the intermediate oxidation state; and both higher and lower oxidation states of that element are formed in the reaction.

An example is the disproportionation of copper in the following reaction:

$$\mathbf{Cu_2O_{(aq)} + H_2SO_{4\,(aq)} \rightarrow Cu_{(s)} + CuSO_{4\,(aq)} + H_2O_{(l)}}$$

Here the copper goes from oxidation state +1 in Cu_2O to oxidation state 0 in Cu (copper is reduced), and from oxidation state +1 to oxidation state +2 in $CuSO_4$(copper is oxidised).

Other examples:

a) Chlorine disproportionates in alkali:

$Cl_2 + 2OH^- \rightarrow Cl^- + OCl^- + H_2O$: Here chlorine goes from oxidation state 0 in Cl_2 to oxidation state -1 in Cl^- and oxidation state +1 in OCl^-

b) Disproportionation of copper (I) chloride

$2CuCl \rightarrow CuCl_2 + Cu$: Here copper goes from oxidation state +1 in CuCl to oxidation state +2 in $CuCl_2$ and oxidation state 0 in Cu

c) Disproportionation of hydrogen peroxide

$2H_2O_2 \rightarrow 2H_2O + O_2$: Here oxygen goes from oxidation state -1 in H_2O_2 to oxidation state -2 in H_2O and oxidation state 0 in O_2

Application activity 8.3

For each of the following reactions, represent by a suitable half-equation:

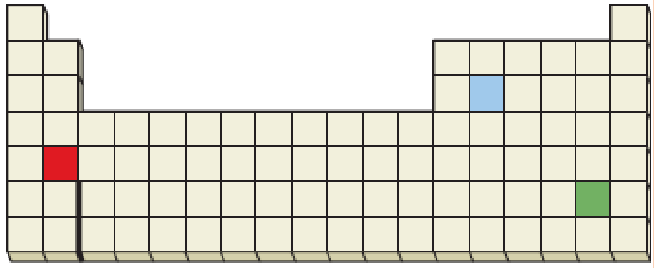
a) the oxidation process; b) the reduction process.

1. $Fe_{(s)} + Ni(NO_3)_{2(aq)} \rightarrow Fe(NO_3)_{2(aq)} + Ni_{(s)}$
2. $Cu_{(s)} + 4HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{2(g)}$
3. $Cu_{(s)} + 2Ag(NO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2Ag_{(s)}$
4. $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

8.4. Oxidizing and reducing agents

Activity 8.4

1. Based on the positions in the periodic table, which of the following reactions would you expect to occur? Explain.



   a) Red+ Green →Red^{+}+ Green^{-}

   b) Blue + Green → Green^{-} + Blue^{+}

   c) Red + Blue → Blue^{+} + Red^{-}

2. Aqueous copper (II) ion reacts with aqueous iodide ion to yield solid copper (I) iodide and aqueous iodine.
   a) Write the net ionic equation,
   b) Assign oxidation numbers to all species present, and
   c) Identify the chemical species that are oxidized and those that are reduced.

In any redox reaction, both oxidation and reduction must occur. In other words, if one substance is oxidized, then another must be reduced: The electrons formally have to go from one place to another. The substance that makes it possible for another substance to be oxidized is called **oxidizing agent** or **oxidant**. The oxidizing agent removes electrons from another substance by acquiring them itself; thus, the oxidizing agent is itself **reduced**.

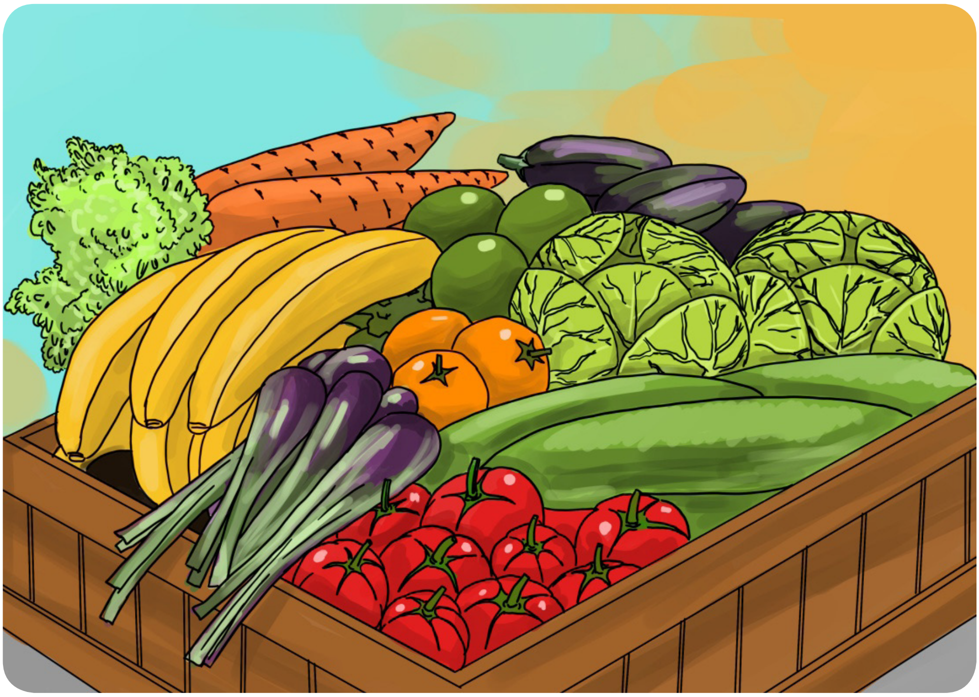


Figure 8.1: Portions of fruits and vegetables have per day enough of the antioxidants vitamin C and vitamin E to reduce the problems spoilage.

Similarly, **a reducing agent**, or **reductant**, is a substance that gives up electrons, thereby causing another substance to be reduced. The reducing agent is therefore **oxidized** in the process.

Let us consider the reaction between hydrogen chloride solution and zinc metal:

$HCl_{(aq)} + Zn_{(s)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$

In the above reaction, hydrogen in hydrogen chloride takes an electron from the zinc metal. The oxidation state of zinc metal increases from 0 to +2; **it is oxidized**. By taking the electrons from zinc metal, the oxidation state of hydrogen decreases from +1 to 0; it **is reduced**.

Hydrochloric acid is the oxidizing agent that causes oxidation of zinc to occur. Similarly, the zinc metal donates electrons to the hydrogen ion in hydrochloric acid, causing the oxidation state of hydrogen to decrease from +1 to 0. By providing the electrons necessary to reduce hydrogen ion, the oxidation number of zinc increases from 0 to +2. Therefore, zinc is acting as a reducing agent.

Table 8.1: Comparison between a reducing agent and an oxidizing agent

Reducing agent:	Oxidizing agent:
– Causes reduction by donating electron(s) – Loses one or more electrons – Undergoes oxidation; i.e. oxidation number of atom increases	– Causes oxidation by removing electron(s) from others – Gains one or more electrons – Undergoes reduction, i.e. oxidation number of atom decreases

In general, metals give up electrons and act as reducing agents, while reactive non-metals such as O_2 and the halogens accept electrons and act as oxidizing agents.

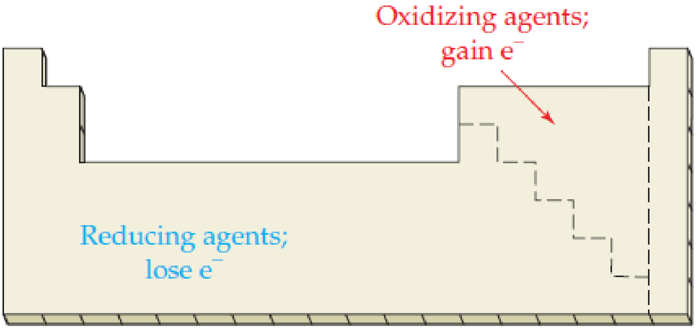


Figure 8.2: Oxidising and reducing agents and the periodic table

Application activity 8.4

1. For each of the following reactions, identify the oxidising agent and the reducing agent.

   a) $2I^- + Br_2 \rightarrow I_2 + 2Br^-$

   b) $2HI + H_2SO_4 \rightarrow H_2S + 4H_2O + I_2$

   c) $SO_2 + 2H_2O + 2Cu^{2+} + 2Cl^- \rightarrow H_2SO_4 + 2H^+ + 2CuCl$

   d) $Cr_2O_7^{2-} + 8H^+ + 3SO_3^{2-} \rightarrow 2Cr^{3+} + 4H_2O + 3SO_4^{2-}$

   e) $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

2. In the following reactions, indicate whether the underlined species is acting as an oxidising agent or a reducing agent.

   a) $\underline{\mathbf{Fe_2O_3}} + 3CO \rightarrow 2Fe + 3CO_2$

   b) $2\underline{\mathbf{Ca}} + O_2 \rightarrow 2CaO$

   c) $Zn + \underline{\mathbf{Fe^{2+}}} \rightarrow Zn^{2+} + Fe$

8.5. Balancing of redox equations

Activity 8.5.a

To study the redox reactions between iron (II) sulphate and hydrogen peroxide

Apparatus/materials

Iron powder, 2M sulphuric acid, Bunsen burner, hydrogen peroxide (20 cm^3), filter paper, test-tube and test-tube racks, 2M sodium hydroxide, filter funnel, 2M ammonia solution.

Procedure

1. Put about 0.5g of iron powder in a clean test tube and add 2cm^3 of dilute sulphuric acid(2M).Warm the mixture gently and test the gas produced with a burning splint. Name the gas formed in the reaction.
2. Allow the solution to cool then filter and divide the filtrate into three portions

3. To the first portion add a few drops of 2M sodium hydroxide and shake the contents of the test-tube then allow it to settle. Identify the product formed then add dilute sulphuric acid to the product. Record your observation. Empty the contents immediately and then rinse the test-tube with plenty of water brushing it thoroughly as you do so.
4. To the second portion add a few drops of hydrogen peroxide followed by one or two drops of dilute sulphuric acid and warm gently. Allow the solution to cool (or cool it under running tap water). To the cold solution add drop wise 2M NaOH until there is no further change. Record your observations. Add dilute sulphuric acid to the resultant product and note down your observations. Rinse the test tube thoroughly.
5. To the third portion, add about 1 cm^3 of dilute hydrogen peroxide solution followed by one or two drops of dilute sulphuric acid. Warm gently and test the gas produced with a glowing splint. Allow the solution to cool (or cool it using running tap water).To the cold solution add ammonia solution drop wise until no further change. Compare the product formed when ammonia solution to that obtained when sodium hydroxide was used.

Study Questions

1. Name the products formed when dilute sulphuric acid reacts with iron powder. Write a balanced formula equation for the reaction
2. When dilute sulphuric acid reacts with iron powder, iron atoms are oxidized and hydrogen ions are reduced. Write a balanced

   a) oxidation half-equation

   b) reduction half-equation and

   c) overall redox equations for the reaction between iron and sulphuric acid
3. What is the effect of adding sodium hydroxide in step 4?
4. What will be the effect of adding concentrated nitric acid to any iron salt? Explain why concentrated nitric acid does not react with pure iron metal

Rules for balancing equations of redox reactions

1. The Half-Reaction Method for balancing equations of Oxidation–Reduction Reactions in Aqueous Solutions

For oxidation–reduction reactions that occur in aqueous solution, it is useful to separate the reaction into two **half-reactions**: one involving oxidation reaction and the other involving reduction reaction. Then after balancing those half reactions, find the overall oxidation-reduction (redox) reaction by summing up the two half-reactions.

For example, consider the unbalanced equation for the oxidation– reduction reaction between cerium (IV) ion and tin(II) ion:

$$Ce^{4+}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow Ce^{3+}_{(aq)} + Sn^{4+}_{(aq)}$$

This reaction can be separated into two half-reactions:

- the reduction half-reaction: $Ce^{4+}_{(aq)} + e- \rightarrow Ce^{3+}_{(aq)}$
- the oxidation half-reaction: $Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2e$

Balance the equation and assure that the number of electrons given up by the reducing agent equals the number of electrons gained by the oxidizing agent

After balancing the equations, eliminating the terms that appear on both sides of the equations, if necessary, to get the overall redox reaction:

$2Ce^{4+}_{(aq)} + \cancel{2e}- \rightarrow 2Ce^{3+}_{(aq)}$ oxidation half-reaction

$Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + \cancel{2e}-$ reduction half-reaction

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$2Ce^{4+}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow 2Ce^{3+}_{(aq)} + Sn^{4+}_{(aq)}$ overall redox reaction

The half-reaction method for balancing oxidation–reduction equations differs slightly depending on whether the reaction takes place in aqueous, acidic or basic solution.

2. The half-reaction method for balancing equations for oxidation–reduction reactions occurring in acidic solution
   a) Write separate equations for the oxidation and reduction half-reactions.
   b) For each half-reaction balance,

      (i) Elements other than hydrogen and oxygen.

      (ii) Oxygen using H_2O.

      (iii) Hydrogen using H^+.

      (iv) The charge using electrons.

c) If necessary, multiply one or both balanced half-reactions by an integer to equalize the number of electrons transferred in the two half-reactions.

d) Add the half-reactions, and cancel identical species.

e) Checking that the elements and charges are balanced.

Example

$MnO_4^- + NO_2^- \rightarrow Mn^{2+} + NO_3^-$

Solution:

1) Dividing the equation into half-equations:

   a) $MnO_4^- \rightarrow Mn^{2+}$ reduction

   b) $NO_2^- \rightarrow NO_3^-$ oxidation

2) Balancing each half-equation

   a) Balancing atoms other than H and O:

   $MnO_4^- \rightarrow Mn^{2+}$

   $NO_2^- \rightarrow NO_3^-$

   b) Balancing of oxygen atoms by adding H_2O where oxygen atoms are missing:

   $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

   $NO_2^- + H_2O \rightarrow NO_3^-$

   c) Balancing of H atoms by adding H^+ ions where H is needed:

   $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

   $NO_2^- + H_2O \rightarrow NO_3^- + 2H^+$

   d) Balancing of charges by adding the number of electrons required to the side with higher positive charge:

   $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

   $NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$

3) If necessary, multiplying each half-equation by appropriate integers to balance the number of electrons in the two half-reactions:

   $2 \times [MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O]$

   $5 \times [NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-]$

4) Addition of the half-equations:

$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$

$5NO_2^- + 5H_2O \rightarrow 5NO_3^- + 10H^+ + 10e^-$

$2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$

5) Checking

On both sides, there are: 2Mn, 6H, 5N, 18O, net charge of 1-

Application activity 8.5.a

Use the half-reaction method and balance the following equations under acidic conditions.

1. $Cr_2O_7^{2-}{}_{(aq)} + I^-_{(aq)} \rightarrow Cr^{3+}_{(aq)} + IO_3^-{}_{(aq)}$
2. $MnO_4^-{}_{(aq)} + CH_3OH_{(l)} \rightarrow Mn^{2+}_{(aq)} + HCO_2H_{(l)}$
3. $As_{(s)} + ClO_3^-{}_{(aq)} \rightarrow H_3AsO_{3(l)} + HClO_{(l)}$

3. The half-reaction method for balancing equations for oxidation–reduction reactions occurring in basic solution

Activity 8.5.b

1) Explain the concept of “base” according to the Arrhenius theory.
2) Briefly recall the steps followed to balance of equations of reaction in acidic medium.
3) Referring to half-method technique used for the balancing of equations of reaction in acidic medium and to the available resources, explain the procedure applied to balance equations of redox reactions that happen in basic medium.

When balancing equations of oxidation-reduction reactions that take place in basic medium, we go through the first steps of the procedure as if the reaction were occurring in acidic solution.

We then add the appropriate number of OH^- ion to each side of the equation, combining H^+ and OH^- to form H_2O.

Examples

$I^- + MnO_4^- \rightarrow I_2 + MnO_2$

Solution:

(1) Dividing the equation into half-equations

$MnO_4^- \rightarrow MnO_2$

$I^- \rightarrow I_2$

(2) Balancing each half-equation

a) Balancing atoms other than H and O

$MnO_4^- \rightarrow MnO_2$

$2I^- \rightarrow I_2$

b) Balancing of oxygen atoms

$MnO_4^- \rightarrow MnO_2 + 2H_2O$

$2I^- \rightarrow I_2$

c) Balancing of H atoms

$MnO_4^- + 4H^+ \rightarrow MnO_2 + 2H_2O$

$2I^- \rightarrow I_2$

d) Addition of a number of OH^- ions equal to the number of H^+ ions to each side of each half-equation

$MnO_4^- + 4H^+ + 4OH^- \rightarrow MnO_2 + 2H_2O + 4OH^-$

$2I^- \rightarrow I_2$ or

$MnO_4^- + 4H_2O \rightarrow MnO_2 + 2H_2O + 4OH^-$

$2I^- \rightarrow I_2$

$MnO_4^- + 2H_2O \rightarrow MnO_2 + 4OH^-$

$2I^- \rightarrow I_2$

e) Balancing of charges

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

$2I^- \rightarrow I_2 + 2e$

(3) Multiplying each half-equation by appropriate integers

$2 \times [MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-]$

$3 \times [2I^- \rightarrow I_2 + 2e]$

(4) Addition of the half-equations

$2MnO_4^- + 4H_2O + 6e^- \rightarrow 2MnO_2 + 8OH^-$

$6I^- \rightarrow 3I_2 + 6e^-$

$2MnO_4- + 6I^- + 4H_2O \rightarrow 2MnO_2 + 3I_2 + 8OH^-$

(5) Checking

On both sides, there are: 2Mn, 6I, 8H, 12O, net charge of 8-

Application activity 8.5.b

Use the half-reaction method and balance the following equations under the alkaline conditions.

1. $CN^-_{(aq)} + MnO^-_{4\,(aq)} \rightarrow CNO^-_{(aq)} + MnO_{2(s)}$ (basic solution)
2. $H_2O_{2(l)} + ClO_{2(l)} \rightarrow ClO_2-_{(aq)} + O_{2(g)}$ (basic solution)

8.6. Reactivity series of metals

Activity 8.6

Carry out the following experiment regarding the displacement reaction and the reaction of sodium, magnesium, zinc, and copper with cold/hot water and dilute hydrochloric acid.

Equipments/materials

Metal samples (of consistent mass and surface area): Na, Mg, Zn, Cu

1.0 M solution of copper (II) sulphate, $Cu(SO_4)_2$,
Distilled water
Test tubes/ test tube rack
3 M HCl
400 mL beaker

Procedure

1. Place a small sample of each metal in test tubes containing 5mL of cold water. For metals like magnesium, it may be necessary to clean the outside of the metal with steel wool. Watch for evidence of reaction and note any changes you observe.
2. Place the test tubes, in which there was no reaction in the above experiment, in a 400 mL beaker that is about 1/3 full of boiling water. After a few minutes, look for evidence of reaction. Note any changes. Did some metals that didn't react with cold water, react with hot water?
3. Place a small sample of each metal in test tubes containing 5 mL of 1.0 mol/L hydrochloric acid, HCl. Watch for evidence of reaction. Note any changes
4. Place a small sample of magnesium ribbon in test tube containing 5 mL of 1M copper (II) sulphate. Watch for evidence of reaction and note any changes

Study questions

1. Considering sodium, magnesium, zinc, and copper: Arrange the metals in order of increasing reactivity (from least reactive to most reactive)
2. Which of the four metals are reacting with cold water? For those metals that did react, write a balanced symbolic equation.
3. Which of the four metals are reacting with hot water? For those metals that did react, write a balanced symbolic equation.
4. Which of the four metals are reacting with the hydrochloric acid? For those metals that did react, write a balanced symbolic equation.
5. Which metal did not react with either water or hydrochloric acid?
6. Which of the four metals would be suitable for making saucepans? Explain why the others are not.
7. Describe what you would see if you dropped a piece of magnesium ribbon into some copper (II) sulphate solution in a test tube. Write a chemical equation for the reaction.

The reactivity series is a series of metals, in order of reactivity, as reducing agents, from highest to lowest reducing agent. It is used to determine the products of single displacement reactions, whereby metal A will displace another metal B in a solution if A is higher in the series. Although hydrogen is not a metal, it is included in the reactivity series for comparison (Table 8.2).

When a metal is placed in a solution of another metal salt, and if the metal is more active than the metal in the salt, the more active metal displaces the other metal from its salt:

$$Zn(s) + CuCl_2(aq) \rightarrow ZnCl_2(aq) + Cu(s)$$

Blue solution Colourless solution Reddish deposit

In this example, since Zn is above Cu in the reactivity series, it displaces copper from its salts.

Examples of displacement reactions

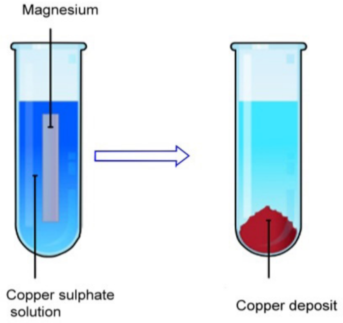
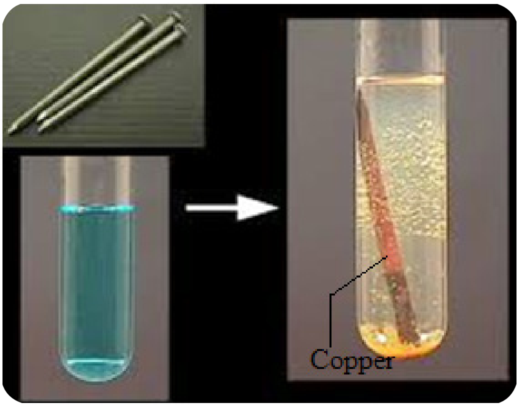
Chemical equation	**Chemical reaction**
$CuSO_{4(aq)}+Mg_{(s)}\rightarrow Cu_{(s)}+MgSO_{4(aq)}$ or $Cu^{2+}_{(aq)} + Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$	 Figure 8.3.a:Displacement of copper by magnesium
$Fe_{(s)}+CuSO_{4(aq)}\rightarrow Cu_{(s} + Fe_2(SO_4)_{3(aq)}$ Or $Fe_{(s)}+Cu^{2+}_{(aq)}\rightarrow Cu_{(s)} + Fe^{3+}_{(aq)}$	 Figure 8.3. b: Displacement of copper by iron

Table 8.2: Reactivity series of metals

	Metals	Metal Ion	Reactivity
Strongly reducing	K	K^+	These elements react with aqueous H^+ ions (acids) or with liquid water to release H_2 gas
	Na	Na^+	
	Li	Li^+	
	Ba	Ba^{2+}	
	Sr	Sr^{2+}	
	Ca	Ca^{2+}	
	Mg	Mg^{2+}	These elements react with aqueous H^+ ions (acids) or with steam to release H_2 gas
	Al	Al^{3+}	
	Mn	Mn^{2+}	
	Zn	Zn^{2+}	
	Cr	Cr^{2+}	
	Fe	Fe^{2+}	
	Cd	Cd^{2+}	
	Co	Co^{2+}	
	Ni	Ni^{2+}	
	Sn	Sn^{2+}	
	Pb	Pb^{2+}	
	H_2	H^+	included only for comparison
	Sb	Sb^{2+}	These elements do not react with aqueous H^+ ions (acids to release H_2 gas (they are **highly unreactive**)
	Bi	Bi^{2+}	
	Cu	Cu^{2+}	
	Hg	Hg^{2+}	
Weakly reducing	Ag	Ag^+	
	Au	Au^{3+}	
	Pt	Pt^+	

Only a metal higher in the reactivity series will displace another. A metal can displace metal ions listed **below** it in the activity series, but not above. For example, zinc is more active than copper and is able to displace copper ions from solution.

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

However, silver **cannot** displace copper ions from solution. It is important to distinguish between the displacement of hydrogen from an acid and hydrogen from water. Sodium is highly active and is able to displace hydrogen from water:

$$2\ Na_{(s)} + 2\ H_2O_{(l)} \rightarrow 2\ NaOH_{(aq)} + H_{2(g)}$$

The less active metals like iron or zinc cannot displace hydrogen from water but do readily react with acids:

$$Zn_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_{2(g)}$$

Those metals that can displace H^+ ions from acids are easily recognized by their position above hydrogen (H) in the activity series.

Conclusion: a more reactive metal will displace a less reactive metal from its salt solution (irrespective of which salt)

Application activity 8.6

1. Complete the following word equations.
   a) zinc + lead nitrate solution
   b) iron + zinc sulphate solution
   c) lead + copper nitrate solution
   d) magnesium + zinc chloride solution
   e) copper + sodium chloride solution
   f) zinc + iron sulphate solution
   g) gold + silver nitrate solution
   h) calcium + magnesium nitrate solution

2. Three metals **X**, **Y** and **Z** have the following reactions:

   Y will displace **X** from a solution of its salt.

   Z will displace both **X** and **Y** from solutions of their salts.

   Place the three metals in order of reactivity, starting with the ***least*** reactive.

3. Here is a list of metals in order of decreasing reactivity. **Q** and **R** are mystery metals.

   K >**Q**> Ca > Mg > Al > Zn >**R**> Fe > Cu
   a) Will Q react with cold water?
   b) Will R react with cold water?
   c) Will R react with dilute hydrochloric acid?
   d) Will R displace copper from copper sulphate solution?

4. a) Predict what will happen when

   i) magnesium is put into silver nitrate solution.

   ii) silver is put into copper sulphate solution.

   b) Write down the ionic equation for the reaction between calcium and lead nitrate solution.

5. Based on the activity series, what is the outcome (if any) of each of the following reactions?
   - a) Mn(s) + $NiCl_2$(aq) →
   - b) Cu(s) + $Cr(CH_3COO)_3$(aq) →
   - c) Cr(s) + $NiSO_4$(aq) →
   - d) Pt(s) + HBr(aq) →
   - e) H_2(g) + $CuCl_2$(aq) →

Skills Lab 8

Investigation of redox reactions in day-to-day life

Oxidation-reduction reactions are encountered in several domains of the daily life such us Metallurgy, food industry, production of substances like nitric acid, sulphuric acid, treatment of water, manufacture of bleaches, aging, energy production and so on.

Carry out a research and:

- Show how redox reactions are involved in the processes listed above, using suitable equations, where possible,
- Discuss the financial, environmental impact of these reactions.

End of unit assessment 8

1. Which of the following metals has an oxide which does not occur naturally? Explain.

   A. Copper B. Gold C. Lead D. Aluminium

2. In an acidified solution of potassium dichromate ($K_2Cr_2O_7$), dichromate ion ($Cr_2O_7^{2-}$) becomes reduced to:

   A. Chromate (V) ions

   B. Chromium (III) ions

   C. Chromium (II) ions

   D. Chromium (VI) ions

3. In a reaction between $CuSO_{4(s)}$ and $Zn_{(s)}$,

   A. Zinc experiences an increase in oxidation state

   B. Zinc losses electrons

   C. Zinc undergoes oxidation

   D. All of these

4. Oxidizing agents

   A. are mostly transition metals B. are mostly metals

   C. increase in oxidation state D. are mostly non-metals

5. In Copper Oxide (CuO) and carbon monoxide (CO) reaction to produce Cu and $CO_{2.}$ a reducing agent is: A. CuO B. CO C. Cu D. CO_2

6. In theory, most metals should easily corrode in air. Why? A group of metals called the noble metals namely gold, platinum, and silver are relatively difficult to corrode in air. Refer to the table 8.2 to come up with a possible reason why the noble metals are relatively difficult to corrode.

7. Gold metal will not dissolve in either concentrated nitric acid or concentrated hydrochloric acid. It will dissolve, however, in aqua regia, a mixture of the two concentrated acids. The products of the reaction are the $AuCl_4^-$ ion and gaseous NO. Write a balanced equation for the dissolution of gold in aqua regia.

8. Consider only the species Na^+, Cl^-, Ag^+, Ag, Zn^{2+}, Zn, Pb in answering the following questions. Give reasons for your answers. (Use data from table 8.2.)

   a. Which is the strongest oxidizing agent?

   b. Which is the strongest reducing agent?

   c. Which species can be oxidized by $SO_4^{2-}(aq)$ in acid?

   d. Which species can be reduced by Al(s)?

9. The blood alcohol (C_2H_5OH) level can be determined by titrating a sample of blood plasma with an acidic potassium dichromate solution, resulting in the production of $Cr^{3+}(aq)$ and carbon dioxide. The reaction can be monitored because the dichromate ion ($Cr_2O_7^{2-}$) is orange in solution, and the Cr^{3+}ion is green. The unbalanced redox equation is

   $$Cr_2O_7^{2-}(aq) + C_2H_5OH(aq) \rightarrow Cr^{3+}(aq) + CO_2(g)$$

   a) Establish a balanced oxidation and reduction half-reactions

   b) Hence write a balanced redox equation

10. When aluminium foil is placed in hydrochloric acid, nothing happens for the first 30 seconds or so. This is followed by vigorous bubbling and the eventual disappearance of the foil. Explain these observations.

11. Which of the following statements concerning corrosion is (are) true? For the false statements, correct them.

    a) Corrosion is an example of an electrolytic process.

    b) Corrosion of steel involves the reduction of iron coupled with the oxidation of oxygen.

    c) The key to cathodic protection is to connect via a wire a metal more easily oxidized than iron to the steel surface to be protected.

12. Suggest a list of the substances where nitrogen can exhibit oxidation states from -3 to +5.

13. When chlorine gas reacts with hot and concentrated sodium hydroxide solution, the oxidation number of chlorine changes from

    A. zero to + 1 and zero to -5

    B. zero to -1 and zero to +5

C. zero to +1 and zero to +5

D. zero to +1 and zero to -3

14. Explain the following terms: oxidation half equation; reduction half equation; oxidizing agent; oxidant; reducing agent; reductant.

15. Using the ion electron half equation method, balance the following redox equations.

a) $Fe^{3+}_{(aq)} + I^{-}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + I_{2(s)}$

b) $Sn^{2+}_{(aq)} + Fe^{3+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + Fe^{2+}_{(aq)}$

c) $Cu_{(s)} + Ag^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Ag_{(s)}$

d) $H^{+}_{(aq)} + Al_{(s)} \rightarrow H_{2(g)} + Al^{3+}_{(aq)}$

f) $H_2S_{(g)} + Fe^{3+}_{(aq)} \rightarrow H^{+}_{(aq)} + S_{(s)} + Fe^{2+}_{(aq)}$

16. Indicate which of the following equations represent redox reactions by writing "redox" after the equation. Where the reaction is redox, give the oxidized species, the reduced species and their oxidation numbers.

a) $Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$

b) $CaCO_{3(s)} + 2H^{+}_{(aq)} \rightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$

c) $Mg_{(s)} + 2H^{+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$

d) $MgO_{(s)} + 2H^{+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_2O_{(l)}$

e) $Cu_{(s)} + S_{(s)} \rightarrow CuS_{(s)}$

17. Record what you are expected to observe for the reactions between the metals and the solutions of their compounds. Write "no reaction" if no reaction took place.

	$Mg(NO_3)_2$	$FeSO_4$	$Cu(NO_3)_2$	$Pb(NO_3)_2$	$Zn(NO_3)_2$
Mg					
Fe					
Cu					
Pb					
Zn					

18. Sulphur dioxide reacts with water to form sulphite ion. Is this a redox reaction? Justify your answer.

19. In each of the following balanced redox equations, identify:

i) the species oxidized and their new oxidation numbers

ii) the species reduced and their new oxidation numbers.

iii) the reducing agent

iv) the oxidizing agent

a) $MnO_{2(s)} + 4H^+_{(aq)} + 2Cl^-_{(aq)} \rightarrow Mn^{2+}_{(aq)} + Cl_{2(g)} + 2H_2O_{(l)}$

b) $3SO_{2(g)} + 2NO_3^-{}_{(aq)} + 2H_2O \rightarrow 3SO_4^{2-}{}_{(aq)} + 2NO_{(g)} + 4H^+_{(aq)}$

c) $2Ag_{(s)} + H_2S \rightarrow Ag_2S_{(s)} + H_{2(g)}$

d) $H_2S_{(g)} + 2NO_3^-{}_{(aq)} + 2H^+_{(aq)} \rightarrow S_{(s)} + 2NO_{2(g)} + 2H_2O_{(l)}$

e) $5Fe^{2+}_{(aq)} + MnO_4^-{}_{(aq)} + 8H^+_{(aq)} \rightarrow 5Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)} + 4H_2O_{(l)}$

f) $6Fe^{2+}_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} \rightarrow 6Fe^{3+}_{(aq)} + 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

g) $Cl_{2(g)} + 2BrS_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2(g)}$

h) $CuO_{(s)} + H_{2(g)} \rightarrow Cu_{(s)} + H_2O_{(l)}$

i) $H_3AsO_{4(aq)} + Sn^{2+}_{(aq)} + 2H^+_{(aq)} \rightarrow H_3AsO_{3(aq)} + Sn^{4+}_{(aq)} + H_2O_{(l)}$

j) $Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} \rightarrow 2Pb^{2+}_{(aq)} + 2H_2O_{(l)}$

20. a) Put the metals used (magnesium, copper, iron, zinc) in order from the least reactive to the most reactive. The more reactive metal will displace the other metal from the solution of its metal salt.

b) Give the ionic equations for the reactions and explain why they are redox reactions.

c) Chromium is more reactive than copper but less reactive than magnesium. Use this information to complete the following word equations:

i) copper + chromium sulphate →

ii) magnesium + chromium sulphate →

iii) chromium + copper sulphate →

d) Suggest a simple experiment to compare the reactivity of chromium with those of iron and zinc.

UNIT 9

ELECTROCHEMICAL CELLS AND APPLICATIONS

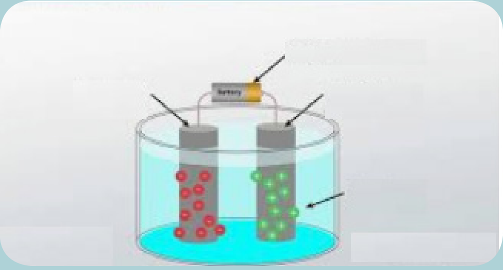
Key Unit Competence:

Explain the working of electrochemical cells and their industrial applications.

Introductory activity

Observe the pictures below and then answer the questions that follow:

(a)



(b)

1. What is represented by the figures above?
2. How do they work and what are the types of chemical reactions are involved in their functioning?
3. Point out some applications of the devices illustrated above.
4. Label the picture (b) above.

9.1. Electrochemical cells

Definition and description of electrochemical cells

Activity9.1

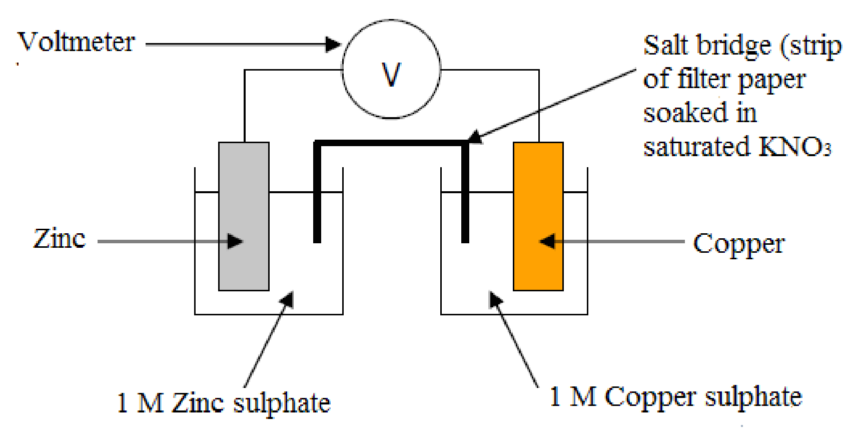
You are provided with the following materials and equipment. Use it to make the set up that is suggested below and answer the question that related.

Equipment and materials

- A piece of zinc rod or plate
- Two (2) beakers
- A piece of copper rod or plate
- One (1) voltmeter
- 1 mol dm^{-3} copper sulphate solution
- Connecting wires and crocodile clips (or similar)
- 1 mol dm^{-3} zinc sulphate solution
- A plastic tube (or a U-tube), full of 2 M potassium nitrate (or 2 M sodium chloride) solution stoppered on both sides by a cotton wool soaked in that potassium nitrate (or sodium chloride) solution, acting as a salt bridge.

Procedure

Set up the apparatus as shown below.



1. Connect the voltmeter leads to the two electrodes. Read the voltmeter.
2. With the voltmeter connected correctly (with the voltage positive), remove the salt bridge. Note what happens.

Discussion questions

The set up above may be described as being made up of two **compartments**. In each, a metal is dipped in a solution of its ions.

1. Recall the concept of oxidising agent and reducing agent.
2. What chemical species is acting as oxidising agent and reducing agent in the reaction between zinc and copper sulphate?
3. Write the ionic half-equations and the overall ionic equation of the reactions that are involved.
4. What does the set up above represent?
5. What reaction is happening in each compartment?

Redox reactions form an important class of reactions in which **oxidation** and **reduction** occur simultaneously.

The redox reactions find wide applications in the study of electrode processes and cells.

An **electrochemical cell** is a device which is capable of either producing electrical energy from chemical reactions or causes chemical reactions to take place through the introduction of electrical energy.

There are two types of electrochemical cells: **galvanic (voltaic) cells** and **electrolytic cells.**

A galvanic (voltaic) cell is a device used to convert chemical energy of a **spontaneous** redox reaction into electrical energy.

An electrolytic cell is a type of chemical cell in which the flow of electric energy from an external source causes a **non-spontaneous redox reaction** to occur.

Both types of cells contain electrodes where the ***oxidation and reduction reactions*** occur. Oxidation occurs at the electrode called the **anode** and reduction occurs at the electrode called the **cathode**.

Both types of electrochemical cells contain electrodes where the oxidation and reduction reactions occur. **Oxidation *occurs at the* anode** and **reduction *occurs at the* cathode**.

The **anode of an electrolytic cell is positive**, ***since it attracts anions from the solution, whereas the cathode is negative and attracts positive ions.***

In **a galvanic cell**, the **anode is negatively charged**, ***since the spontaneous oxidation at the anode is the source*** of the cell›s electrons or negative charge. The cathode of a galvanic cell is its positive terminal.

In both galvanic and electrolytic cells, **oxidation takes place at the anode** and **electrons flow from the anode to the cathode.**

Galvanic cells are commonly used as **batteries** or **sources of energy.** Galvanic cell reactions supply energy which is used to perform work. Galvanic cells are electrochemical cells which use the transfer of electrons in redox reactions to supply an electric current.

The energy is harnessed by putting the oxidation and reduction reactions in **separate containers**, connected by a **salt bridge**, or **separated by a porous membrane** (an apparatus that allows electrons to flow).

A galvanic cell generally consists of **two different metal rods** called **electrodes.** Each electrode is immersed **in a solution containing its own ions** (in the separate containers) and these form a **half cell**. The solutions in which the electrodes are immersed are called **electrolytes** i.e. **made of ions.**

One electrode acts as **anode** in which **oxidation takes place** and the other acts as the **cathode** in which **reduction takes place**.

1) HALF CELLS AND REDOX REACTIONS IN HALF CELLS

Each chamber of an electrochemical cell constitutes a **half-cell** containing an electrode and an electrolyte. **Half-cells** are sometimes known as ***redox electrodes* or *redox couples*.**

a) Types of half cells

The half cells may be categorized into three types: Metal, non-metal and ion half-cells.

(i) *Metal half cells*

This half cell is made of metal and its aqueous ions. It consists of a metal (electrode) dipped into an aqueous solution containing its own ions. For example: Zn/Zn^{2+} half cell.

(ii) ***Non-metal half cells***

This half cell is made from a non-metal and its aqueous ions. For example, hydrogen half cell comprises hydrogen gas in contact with hydrogen ions: $H_2/2H^+$

(iii) ***Ion half cell***

This type of half cell consists of an inert electrode such as platinum electrode dipping into a solution containing ions of the same metal in two different oxidation states. For example, a half cell containing $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ ions: $Fe^{3+}(aq)$, $Fe^{2+}(aq)/Pt$

b) Working of a half cell

The simplest half-cell consists of a metal placed in solution of its ions.

If a piece of metal is put into a solution of its own ions, atoms from the metallic structure pass into a solution and form hydrated metal ions. At the same time hydrated, metal ions gain electrons from the metal structure to form metal atoms. Eventually, an **equilibrium is established.**

For example, when a strip of zinc metal is dipped in aqueous solution of zinc sulphate, some zinc atoms are oxidized. Each zinc atom that is oxidized leaves behind 2 electrons and enters the solution as Zn^{2+} ion.

Oxidation: $$Zn_{(S)} \rightarrow Zn^{2+}_{(aq)} + 2e$$

At the same time, some Cu^{2+} ions in the solution gain 2 electrons from the zinc strip and deposit as copper atoms. They are reduced.

Reduction: $$Cu^{2+}_{(aq)} + 2e \rightarrow Cu_{(s)}$$

The opposing oxidation and reduction processes quickly come to an equilibrium:

$$Zn^{2+} + 2e^- \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} Zn$$

A strip of metal used in an electrochemical experiment is called an **Electrode.** By convention, the equilibrium is written with the electrons on the left-hand side. ***The electrode potential of the half-cell indicates its tendency to lose or gain electrons in the equilibrium.***

2) CONSTRUCTING CELLS FROM HALF CELLS

A simple electrochemical cell can be made by connecting together **two half cells** with different electrode potentials.

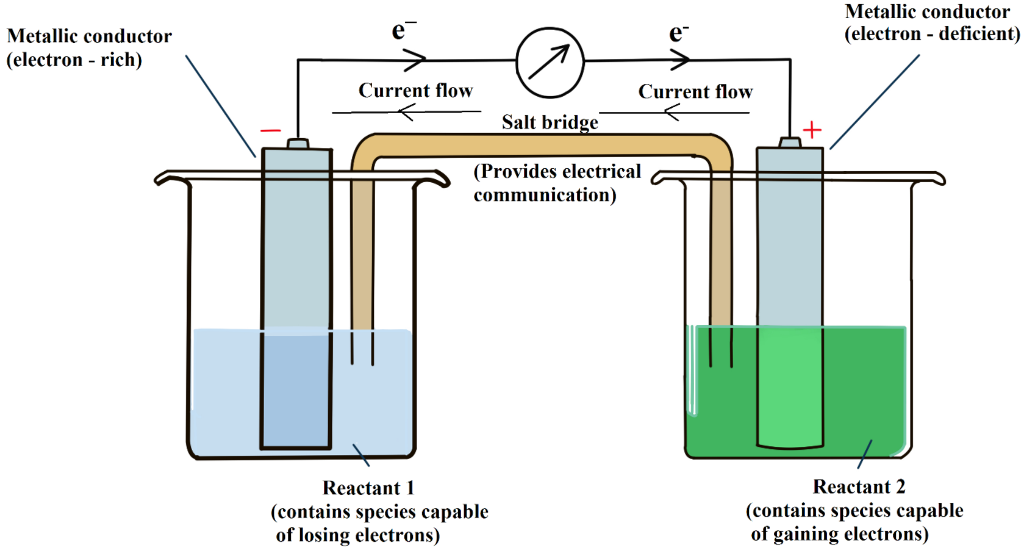


Figure 9.1: A general cell constructed from its half-cells

- One half cell **releases electrons (oxidation at the anode).**
- The other half cell **gains electrons (reduction at the cathode).**

Note that, in the electrochemical cell, ***the electrons flow*** from the negative terminal (anode) to the positive terminal (cathode) and the ***current flows in the opposite direction*** i.e. from cathode to anode.

The salt bridge is usually **an inverted U-tube** filled with a **concentrated solution of an inert electrolyte.** The inert electrolyte is neither involved in any chemical change, nor does it react with the solutions in the two half cells. Generally salts like KCl, KNO_3, Na_2SO_4 and NH_4NO_3 are used as the electrolytes.

a) The Significance of Salt Bridge

Its main function is to prevent the potential difference that arises between the two solutions when they are in contact with each other. This potential difference is called ***the liquid junction potential.***

- It completes the electrical circuit by connecting the electrolytes in the two half cells.
- It prevents the diffusion of solutions from one half-cell to the other.
- It maintains the electrical neutrality of the solutions in the two half cells.

b) How is the electrical neutrality of the solutions in the two half cells maintained using a salt bridge?

- In the **anodic half-cell**, there will be accumulation of positive charge when the positive ions that are formed pass into the solution. ***To maintain the electrical neutrality, salt bridge provides negative ions.***

For example, in Daniell cell, zinc oxidizes at the anode and passes into the solutions as Zn^{2+} ions, so there will be accumulation of positive charge in the solution. To maintain the electrical neutrality of the solution, ***the salt bridge provides negative ions*** (for example NO_3^- or Cl^-).

- In the **cathodic half-cell**, there will be accumulation of negative ions formed due to the reduction of positive ions. ***To maintain the electrical neutrality, salt bridge provides positive ions***.

For example, in Daniell cell, Cu^{2+} ions from the $CuSO_4$ solution is reduced by the electrons formed by the oxidation of zinc, and deposited on the copper cathode. As a result, the concentration of Cu^{2+} ions decreases in the solution and that of SO_4^{2-} ions (sulphate ions) increases. So there will be an accumulation of negatively charged sulphate ions around the cathode. To maintain the electrical neutrality, ***salt bridge provides positive ions*** (for example K^+ or NH_4^+).

Application activity 9.1

1. Explain the terms electrochemical cell and half-cell.
2. Briefly describe a simple galvanic cell.
3. What is the importance of salt bridge in an electrochemical cell?

9.2 Standard hydrogen electrode used to determine standard electrode potentials

Activity 9.2

1. Explain the concept of potential difference as applied to electric current.
2. How measurements of potential difference are carried out.
3. What are the units of potential difference?
4. Use reference books and attempt to explain the concept of Hydrogen Standard Electrode.

When a metal electrode is dipped in a solution containing its metal ions, a potential difference is developed at the metal /solution interface. This potential difference is called the ***electrode potential.***

For example, when a copper rod is dipped in a solution containing Cu^{2+} ions, the Cu^{2+} ions gain electrons from the copper rod leaving positive charge on the copper rod. As a result, a potential difference is set up between the copper rod and the solution and is called the electrode potential of copper.

In a **galvanic cell,** the ***anode has a negative potential and cathode has a positive potential.*** The potential of each individual half-cell cannot be measured. We can measure only the difference between the potential of the two half cells. While it is impossible to determine the electrical potential of a single electrode, ***we can assign an electrode the*** **value of zero** ***and then use it as*** **a reference.**

The electrode chosen as having the value of "zero" is called the **Standard Hydrogen**

Electrode (SHE). The SHE consists of ***1 atm of hydrogen gas*** bubbled through a ***1 M strong acid solution*****,** usually ***at room temperature. Platinum or graphite***, which is chemically inert, is used as the electrode.

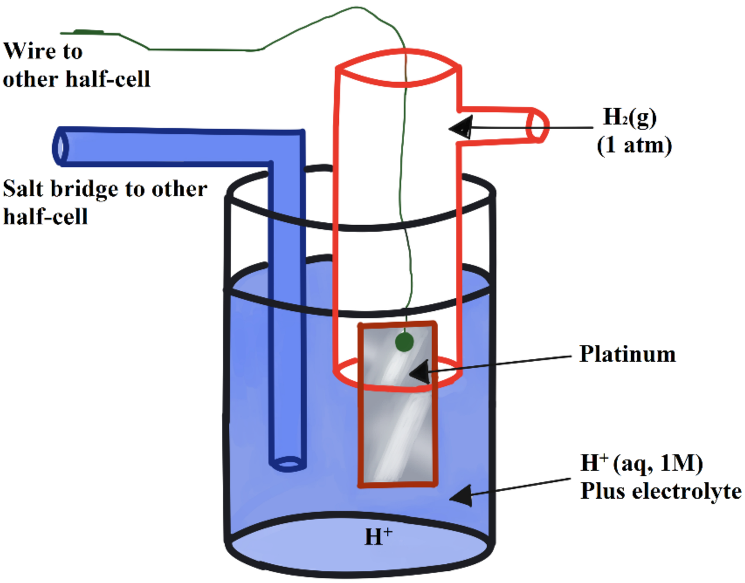


Figure 9.2: Standard Hydrogen Electrode

Thus, electrode potential at standard conditions (temperature of 25°C, pressure of 1 atm and concentration of 1 M concentration for the electrolyte) is called the "**standard electrode potential**". It is denoted by the symbol E^0 where the **superscript "0" on the *E*** denotes ***standard conditions*.**

Standard conditions are the following.

- Concentration of solutions : 1mol dm^{-3};
- Any gases involved have a pressure of 1 atmosphere;
- Temperature: 25°C
- Platinum is used as the electrode when the half-cell system does not include a metal.

Other standard electrode potentials can be determined using the SHE. The **standard electrode potential for SHE is zero ($E^0 = 0$)**. The **standard reduction (electrode) potential** can be determined by ***subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode.*** Here, the minus sign is necessary because oxidation is the reverse of reduction.

$$E^0_{cell} = E^0_{Cathode} - E^0_{Anode}$$

The diagram below shows how the standard potential ***E⁰*** of copper can be determined.

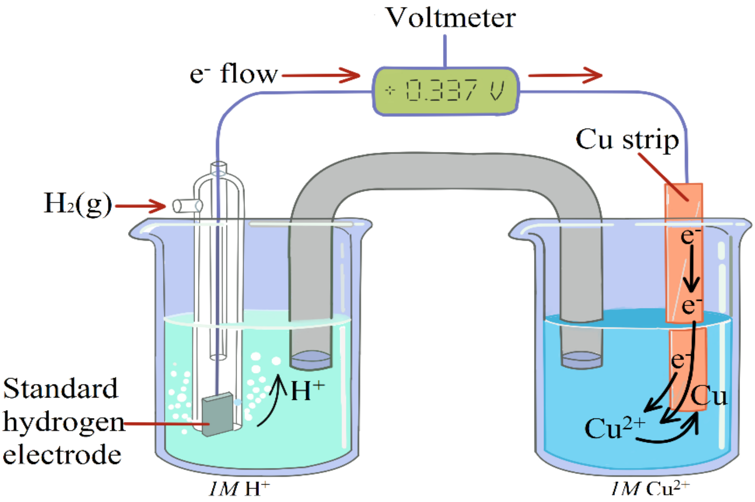


Figure 9.3 Measuring the electrode potential of copper

The copper electrode contains Cu^{2+} ions in equilibrium with copper metal. The hydrogen electrode is linked via a salt bridge to the solution in which the copper electrode is immersed. This permit ***charge transfer*** and ***potential measurement*** but ***not mass transfer*** of the acid solution in the electrode.

The oxidation and reduction at the electrodes leads to a standard electrode potential between the electrode and ions in solution. The standard electrode potential is expressed in ***Volts (V).***

Volt is **the *measure of electromotive force* (e.m.f.)** produced by a cell. Standard electrode potentials refer to ***redox potentials*** as well. A **voltmeter** measures ***a difference in electric potential between two points in an electrical circuit*.**

If the two points are the electrodes in voltaic cells, **the potential difference** is **the driving force that propels electrons *from the anode to the cathode*.** It is also called the **cell potential (E_{cell}).** Since the measurements are in volts, the cell potential is also called the **"Cell voltage".**

When ***E⁰*** are measured relative to the SHE (or some other reference electrode), a ***voltmeter*** is used. In order to resist any current flowing between the electrode and the SHE, the voltmeter must have high impedance and if a current were allowed to flow, the electrodes would become polarized and would no longer be at equilibrium.

Table 9.1: Standard Reduction Potentials in aqueous solution (at 25 °C)

				$E^0(V)$	
↑	$F_2(g)+2e^-$	$\longrightarrow$	$2F^-(aq)$	+ 2.870	INCREASING STRENGTH OF RED
	$H_2O_2(aq)+2H^+(aq)+2e^-$	$\longrightarrow$	$2H_2O(l)$	+ 1.770	
	$PbO_2(s)+SO_4^{2-}(aq)+4H^+(aq)+2e^-$	$\longrightarrow$	$PbSO_4(s)+2H_2O(l)$	+ 1.685	
	$MnO_4^-(aq)+8H^+(aq)+5e^-$	$\longrightarrow$	$Mn^{2+}(aq)+4H_2O(l)$	+ 1.520	
	$Au^{3+}(aq)+3e^-$	$\longrightarrow$	$Au(s)$	+ 1.500	
	$Cl_2(g)+2e^-$	$\longrightarrow$	$2Cl^-(aq)$	+ 1.360	
	$Cr_2O_7^{2-}(aq)+14H^+(aq)+6e^-$	$\longrightarrow$	$2Cr^{3+}(aq)+7H_2O(l)$	+ 1.330	
INCREASING STRENGTH	$O_2(g)+4H^+(aq)+4e^-$	$\longrightarrow$	$2H_2O(l)$	+ 1.229	
	$Br_2(l)+2e^-$	$\longrightarrow$	$2Br^-(aq)$	+ 1.066	
	$NO_3^-(aq)+4H^+(aq)+3e^-$	$\longrightarrow$	$NO(g)+2H_2O(l)$	+ 0.960	
	$OCl^-(aq)+H_2O(l)+2e^-$	$\longrightarrow$	$Cl^-(aq)+2OH^-(aq)$	+ 0.890	
	$Hg^{2+}(aq)+2e^-$	$\longrightarrow$	$Hg(l)$	+ 0.855	
	$Ag^+(aq)+e^-$	$\longrightarrow$	$Ag(s)$	+ 0.799	
	$Fe^{3+}(aq)+e^-$	$\longrightarrow$	$Fe^{2+}(aq)$	+ 0.771	
	$I_2(s)+2e^-$	$\longrightarrow$	$2I^-(aq)$	+ 0.535	
	$Cu^+(aq)+e^-$	$\longrightarrow$	$Cu(s)$	+ 0.521	
	$O_2(g)+2H_2O(l)+4e^-$	$\longrightarrow$	$4OH^-(aq)$	+ 0.400	
	$Cu^{2+}(aq)+2e^-$	$\longrightarrow$	$Cu(s)$	+ 0.337	
	$Sn^{4+}(aq)+2e^-$	$\longrightarrow$	$Sn^{2+}(aq)$	+ 0.150	
	$2H^+(aq)+2e^-$	$\longrightarrow$	$H_2(g)$	0.000	
	$Pb^{2+}(aq)+2e^-$	$\longrightarrow$	$Pb(s)$	- 0.126	
	$Sn^{2+}(aq)+2e^-$	$\longrightarrow$	$Sn(s)$	- 0.140	
	$Ni^{2+}(aq)+2e^-$	$\longrightarrow$	$Ni(s)$	- 0.250	
	$V^{3+}(aq)+2e^-$	$\longrightarrow$	$V^{2+}(aq)$	- 0.255	

H	$Co^{2+}(aq)+2e^-$	$\longrightarrow$	$Co(s)$	- 0.280	U
T	$Tl^+(aq)+e^-$	$\longrightarrow$	$Tl(s)$	- 0.340	C
	$PbSO_4(s)+2e^-$	$\longrightarrow$	$Pb(s)+SO_4^{2-}(aq)$	- 0.356	I
O	$Cd^{2+}(aq)+2e^-$	$\longrightarrow$	$Cd(s)$	- 0.403	N
F	$Fe^{2+}(aq)+2e^-$	$\longrightarrow$	$Fe(s)$	- 0.440	G
	$Zn^{2+}(aq)+2e^-$	$\longrightarrow$	$Zn(s)$	- 0.763	A
O	$2H_2O(l)+2e^-$	$\longrightarrow$	$H_2(g)+2OH^-(aq)$	- 0.828	G
X	$Al^{3+}(aq)+3e^-$	$\longrightarrow$	$Al(s)$	- 1.660	E
I	$Mg^{2+}(aq)+2e^-$	$\longrightarrow$	$Mg(s)$	- 2.370	N
D	$Na^+(aq)+e^-$	$\longrightarrow$	$Na(s)$	- 2.714	T
I S	$K^+(aq)+e^-$	$\longrightarrow$	$K(s)$	- 2.925	S
I N G A G E N T S	$Li^+(aq)+e^-$	$\longrightarrow$	$Li(s)$	- 3.045	↓

(Source:www.chemeddl.org/services/moodle/media/QBank/GenChem/Tables/EStandardTable.htm)

In the above table,

- The ***best oxidizing agents*** (**the poorest reducing agents**) i.e. those most easily reduced **appear up (top)**; for example F_2, O_2, Au^{3+}, etc.
- The ***poorest oxidizing agents*** (**the best reducing agents**) i.e. those most difficult to reduce **are on the bottom;** for example Na^+, K^+, Li^+, etc.

Thus,

The more positive the E°, the better oxidizing agent is the oxidized form (e.g., MnO_4^-).

The more negative the E°, the better reducing agent is the reduced form (e.g., Zn).

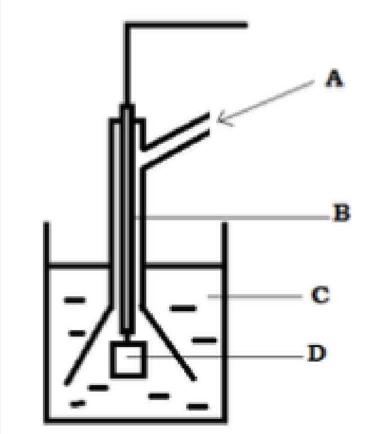
Indeed, Fluorine, F_2, is the most oxidizing agent and Lithium, Li, is the best reducing agent among the elements presented.

Application activity 9.2

1. Define standard electrode potential.
2. Is it possible to use another standard electrode than SHE? Justify your answer.
3. Answer by True or False.

   a) Hydrogen electrode which is the reference electrode can be used as Anode or Cathode.

   b) If hydrogen electrode acts as cathode, hydrogen is oxidised.
4. With the aid of a diagram, explain how the standard electrode potential of zinc is measured.
5. Given below is a diagram of hydrogen electrode. Identify **A, B, C** and **D** by choosing the words in the text below: ***Platinum, Inner glass tube, 1M HCl, Hydrogen at 1 atm***



9.3. Cell reactions and e.m.f. of the galvanic cells

Activity 9.3

1. Use your knowledge acquired so far about electrochemical cells to explain the concept of electrode potential;
2. How electrode potentials of half-cells are determined;

9.3.1. Electromotive force (emf) of a cell and cell notation

Electromotive force (**emf**) is a measurement of the energy that causes current to flow through a circuit. It can also be defined as the potential difference in charge between two points in a circuit. **Electromotive force** is also known as ***cell voltage*** or ***cell potential***, and it is measured in volts.

a) Calculations of electromotive force (emf)

To calculate the standard cell potential for a reaction:

- Write the oxidation and reduction half-reactions for the cell.
- Look up the standard reduction potential, $E^0_{reduction}$, for the reduction half-reaction in a table of reduction potentials.
- Look up the reduction potential for the reverse of the oxidation half-reaction and reverse the sign to obtain the oxidation potential. For the oxidation half-reaction, $E^0_{oxidation} = - E^0_{reduction}$.
- Add the potentials of the half-cells to get the overall standard cell potential.

$$E^0_{cell} = E^0_{cathode} + E^0_{anode} \qquad E_{cell} = E_{cathode} - E_{anode}$$

Example: Find the standard cell potential for an electrochemical cell with the following cell reaction. $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

1. Write the half-reactions for each process.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$$

$$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$$

2. Look up the standard potentials for the reduction half-reaction.

$E^o_{reduction}$ of Cu^{2+} = + 0.339 V

$E^o_{reduction}$ of Zn^{2+} = - 0.762 V

3. Add the cell potentials together to get the overall standard cell potential.

$$E_{cell} = + 0.339\ V - (- 0.762\ V) = + 1.101\ V\ 0.762\ V$$

WORKED EXAMPLE

Consider the following table of standard reduction potentials:

In aqueous solutions at 25 °C	
$Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$	**E° = +0.86 V**
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	**E° = +0.54 V**
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	**E° = 0.00 V**
$Zr^{4+}(aq) + 4e^- \longrightarrow Zr(s)$	**E° = – 1.53 V**
$Rb^+(aq) + e^- \longrightarrow Rb(s)$	**E° = – 2.93 V**

The potential generated by a cell constructed from standard **Zr** and **I_2** electrodes may be calculated. From the table, we write a balanced reduction half-reaction for each electrode and copy down the reduction potentials:

$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	**$E^0 = 0.54$ V**
$Zr^{4+}(aq) + 4e^- \longrightarrow Zr(s)$	**$E^0 = -1.53$ V**

Reversing which reaction will yield most positive standard reduction potential? Let us try both.

Case 1: *Reversing the iodine reduction:* E° = - 0.54 V

Case 2: *Reversing the zirconium reduction:* E° = + 1.53 V

Thus the highest positive potential is found by using the **Zr oxidation** half-reaction because:

+ 1.53 V > - 0.54 V

Thus the standard cell potential will be $E^o_{red}(I_2) - E^o_{red}(Zr)$

$$E^o_{cell} = (+0.54) - (-1.53)$$

$$E^o_{cell} = +2.07 \text{ V}$$

Making predictions

The spontaneous (Voltaic) cell reaction is the one that gives a positive cell voltage when subtracting one half-reaction from the other.

$$E^o_{cell} = E^o_{right} - E^o_{left} = E^o_{cathode} - E^o_{anode} = E^o_{+} - E^o_{-}$$

Which is the Anode? The Cathode?

Convention:

The anode is the electrode where oxidation occurs ➔ the more negative half-reaction potential

The cathode is the electrode where reduction occurs ➔ the more positive half-reaction potential

anode |solution | cathode

Even though we had to multiply the iodine reduction by a factor of 2 so that the electrons consumed would balance with those produced by the zirconium oxidation, we do **NOT** multiply the iodine reduction potential by this factor. In manipulating potentials, ***we should only change the signs of the values, not the magnitude.***

- ***A* negative reduction potential** tells us that the zirconium ion is harder to reduce (is a worse oxidizing agent) than hydrogen ion***;*** this also tells us that zirconium metal is a better reducing agent than hydrogen gas.
- ***A* positive reduction potential** tells us that the iodide ion is easier to reduce ***(is a better oxidizing agent)*** than hydrogen ion; this also tells us that iodine is a worse reducing agent than hydrogen gas.

In general, the ***electrode with the more positive value of electrode potential*** is the **cathode** (the one which undergoes reduction) and the ***electrode with more negative value of electrode potential*** is the **anode** (easily oxidised).

Under non standard conditions where the concentrations of the chemical species are not equal to 1mol dm^{-3}, the Nernst equation is used to calculate the e.m.f of a cell.

Nernst Equation

This equation was named after a German physicist Walther Nernst.

The Nernst Equation helps to calculate the cell potential under **non-standard conditions** and relates the measured cell potential to the reaction quotient and allows the exact measurement of equilibrium constants.

Let us consider an electrochemical reaction of the following type:

$aA + bB \rightarrow cC + dD$

Nernst equation for this can be written as follows:

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln Q$$

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Expressing the above equation in terms of common logarithms, we get

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Putting the values of R, F at T= 298 K, the equation above becomes

$$E_{cell} = E^0_{cell} - \frac{0.0592}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

In case of Daniel cell Nernst equation is as follows:

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln Q$$

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

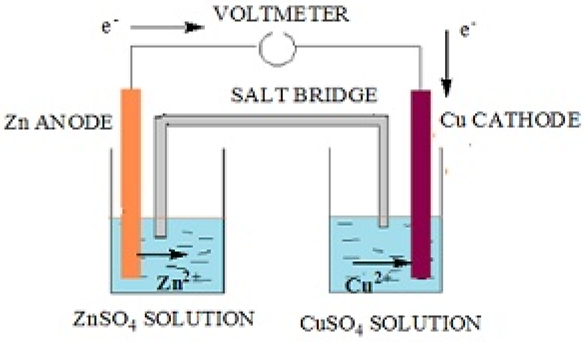
The above equation implies that the value of increases with the increase in the concentration of Cu^{2+} ion increases and decrease in the concentration Zn^{2+}

Putting the values of R, F at T= 298 K. the equation above becomes

$$E_{cell} = E^0_{cell} - \frac{0.06}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

If the circuit in Daniel cell is closed:

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$



With time, the concentration of Zn^{2+} increases and the concentration of Cu^{2+} decreases

Voltage reading of the cell on the voltmeter decreases.

After some time there is no alteration in the concentration of Cu^{2+} and Zn^{2+} ions and the voltmeter gives zero reading. At this point of time equilibrium has been reach and cell potential E_{cell} is zero.

The Nernst equation for the reaction is:

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E^0_{cell} = \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium,

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_c$$

At T = 298 K.

The equation can be rewritten as:

$$E^0_{cell} = \frac{0.06}{2} \log K_c$$

Example:

Calculate the emf of the cell in which the following reaction takes place:

$Ni_{(s)}$ **+ $2Ag^+$ (0.002 M) → Ni^{2+} (0.160 M) + $2Ag_{(s)}$**. Given that $E^ø_{cell}$ **= 1.05 V.**

Solution:

By using Nernst equation,

$$E_{cell} = E^0_{cell} - \frac{0.0592}{2} \log \frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$E_{cell} = 1.05 - \frac{0.0592}{2} \log \frac{[0.160]}{[0.002]^2}$$

$$E_{cell} = 1.05 - 0.0296 \log \frac{0.160}{0.000004}$$

$$= 1.05 - 0.0296(\log 4 \times 10^4)$$

$$= 1.05 - 0.0296(\log 10000 + \log 4)$$

$$= 1.05 - 0.0296(4 + 0.6021)$$

$$= 0.914 \text{ V}$$

Cell notation

An electrochemical cell consists of two electrodes: **Anode** and **Cathode**. The electrolyte solution containing each of these electrodes is called ***half-cells***. When the two half cells are combined, a **"cell"** is formed.

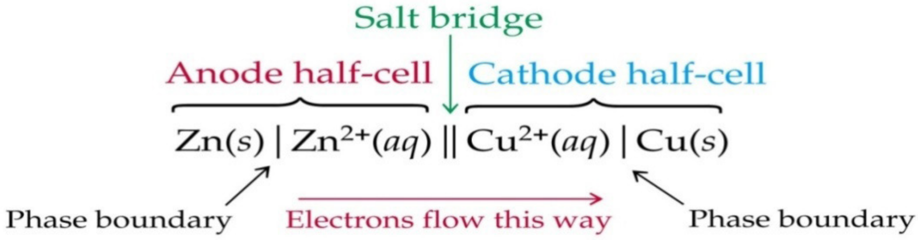
It is more convenient to represent an electrochemical cell **by writing a cell notation than by making a drawing.** Cell notation (usually called cell diagram) is short hand that expresses a certain reaction in an electrochemical cell.

By international agreement, the following conventions are used for electrochemical cell notations:

- Use a **single vertical line** (|) to represent the ***boundary between different phases*** such as between an electrode and a solution.
- Use a **double vertical line** (‖) to represent the ***salt bridge separating two half–cells.***
- **Double discontinuous vertical line (⁞⁞)** would be used to indicate ***porous barrier separating two half–cells instead of salt bridge.***
- **Place the anode where oxidation occurs** (A-O) ***on the left side of the diagram.***
- **Place the cathode where reduction occurs** (C-R) ***on the right side of the diagram.***

- **Aqueous solution concentrations** are written ***in parentheses after the symbol for the ion or molecule.***
- **A comma** is used to show ***the components that are in the same phase.***
- **The inert electrode used** is ***specified.***

Example 1: The following cell reaction is given: $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$



Under standard conditions, the cell notation is as follow:

$\mathbf{Zn_{(s)} \mid Zn^{2+}{}_{(aq)}(1.0\ M) \parallel Cu^{2+}{}_{(aq)}(1.0\ M) \mid Cu_{(s)}}$

Example 2

Ni- $AgNO_3$ cell

Oxidation half reaction $Ni(s) \rightarrow Ni^{2+}(aq) + 2e$

Reduction half reaction $2\ Ag^{+}(aq) + 2e^{-} \rightarrow 2\ Ag(s)$

Overall cell reaction $Ni(s) + 2\ Ag^{+}(aq) \rightarrow 2\ Ag(s) + Ni^{2+}(aq)$

***Cell Notation*: $\mathbf{Ni(s) \mid Ni^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)}$**

Note: In many cases, we use an electrode that does not participate in an oxidation –reduction equilibrium, rather the inert electrode (Pt or graphite) simply furnishes the surface on which an electric potential is established. Consider the following example.

Example 3

Zn – HCl reaction

Oxidation half reaction $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$

Reduction half reaction $2\ H^{+} + 2\ e^{-} \rightarrow H_2(g)$

Overall cell reaction $Zn(s) + 2\ H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

Cell Notation: $Zn(s) \mid Zn^{2+}(aq) \parallel H^{+}(aq) \mid H_2(g) \mid Pt(s)$

Application activity 9.3

1. An experiment was carried out to measure the e.m.f. of this cell.

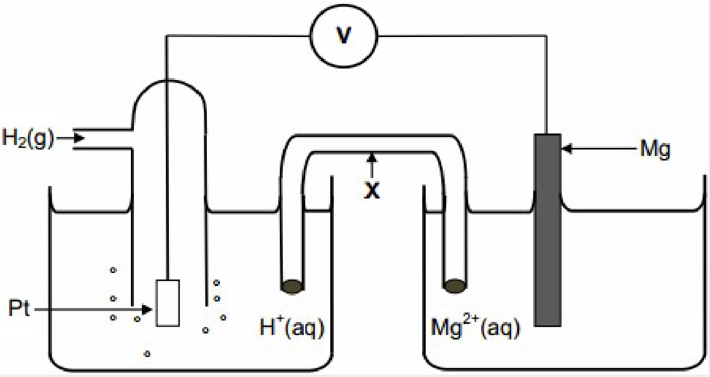
   $Al(s)|Al^{3+}(aq) \| H^{+}(aq) | H_2(g) | Pt(s)$

   a) The aluminium used as the electrode is rubbed with sand paper prior to use. Suggest the reason for this.

   b) Draw a labelled diagram of a suitable apparatus for the right-hand electrode in this cell. [You do not need to include the salt bridge or the external electrical circuit].

   c) A simple salt bridge can be prepared by dipping a piece of filter paper into K_2CO_3 solution. Explain why such a salt bridge would not be suitable for use in this cell.

2. The electrochemical cell represented below consists of a hydrogen half-cell and a magnesium half-cell at standard conditions.



The reading on the voltmeter is 2.36 V.

   a) Apart from concentration, write down two other conditions needed for the hydrogen half-cell to function at standard conditions.

   b) Write down the name of the item of apparatus labelled X.

   c) Is magnesium the anode or cathode in the cell above? Refer to the relative strengths of reducing agents to explain the answer.

   d) Write down the cell notation for this cell.

   e) Calculate the standard reduction potential of the magnesium half-cell. Show all your working.

   f) Write down the balanced net (overall) cell reaction that takes place in this cell. No spectator ions are required.

3. Student teachers conduct an investigation to determine which combination of two half-cells will provide the largest emf at standard conditions. Three half-cells, represented as **A**, **B** and **C** in the table below, are available.

Half-cell **A**	Half-cell **B**	Half-cell **C**
Mg/Mg^{2+}	Pb/Pb^{2+}	Al/Al^{3+}

The student teachers set up galvanic cells using different combinations of the above half-cells.

a) Write down the standard conditions under which these cells operate.

b) Write down the dependent variable in this investigation.

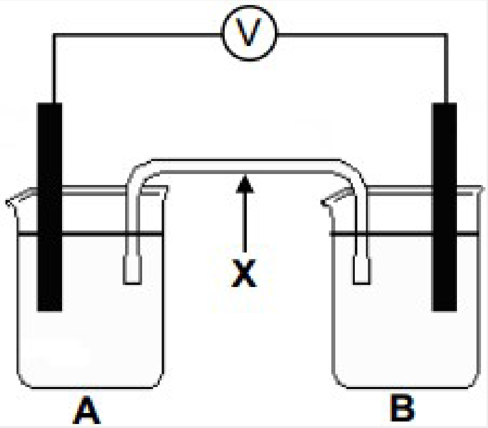
c) Use the Table of Standard Reduction Potentials to determine which one of the three half-cells (**A**, **B** or **C**) contains the:

(i) Strongest reducing agent

(ii) Strongest oxidising agent

e) Without any calculation, write down the combination of two half-cells which will produce the highest emf. Write down only **AB**, **BC** or **AC**.

f) One group of student teachers set up a galvanic cell using half-cells **A** and **B**, as shown below. **X** represents one of the components of the galvanic cell.



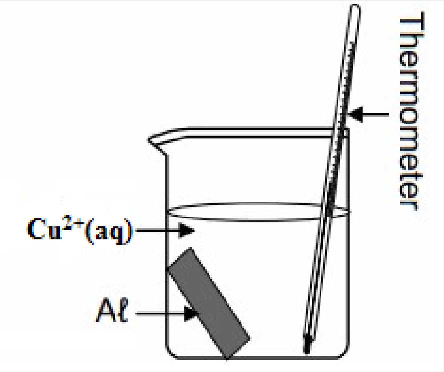
(i) Write down the name or symbol of the substance that will act as the anode in this cell. Give a reason for the answer.

(ii) Calculate the initial emf of this cell.

(iii) How will an increase in the concentration of the electrolyte in half-cell **B** affect the initial emf of the cell? Write down only increases, decreases or remains the same.

(iv) Briefly explain how component **X** ensures electrical neutrality while the cell is functioning.

4. A strip of aluminium is placed in a beaker containing a blue solution of a copper (II) salt. After a while the solution becomes colourless.

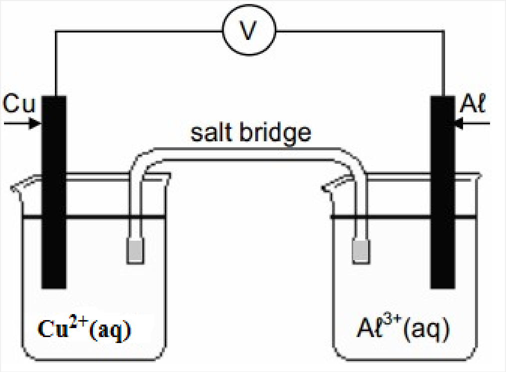


a) How would the reading on the thermometer change as the reaction proceeds? Write down increases, decreases or remains the same. Give a reason for the answer.

b) Refer to the reducing ability of aluminium to explain why the solution becomes colourless.

c) Write down the balanced net ionic equation for the reaction that takes place.

5. The electrochemical cell shown below functions at standard conditions.



a) Which electrode (Cu or Al) is the anode?

b) Write down the cell notation for this cell.

c) Calculate the emf of this cell.

d) What will the reading on the voltmeter be? Give a reason for your answer.

6. Rusting is an unwanted redox reaction. Iron rusts when exposed to oxygen and moisture.

   The unbalanced ionic equation for one reaction that occurs during rusting is represented below.

$$Fe(s)+O_2(g)+H_2O(l)\rightarrow Fe^{2+}(aq)+OH^-(aq)$$

   Use the Table of Standard Reduction Potentials to answer the following questions for this reaction.

   a) Write down the oxidation half-reaction.

   b) Write down the name of the substance that is reduced.

   Perform a calculation to verify that this reaction is spontaneous.

9.4. Corrosion and its effects on metallic objects

Activity 9.4

We have seen old metal materials with brown colour coating on their surfaces. Some metal materials are shown here below.

1. We usually call this rust, what is the other name given to this phenomenon?
2. How do metal objects cover themselves with this coat?
3. Suggest some effects of this phenomenon on the metallic objects.

Corrosion is defined as **"the degradation of materials by chemical reaction with the environment in which the material resides".** This is because of metal oxidation. As metals have a tendency to return to their natural state, it is a natural process which produces either salt or oxides. It requires four elements - anode, cathode, an electrolyte, and a metallic path.

9.4.1. Explanation of metal corrosion

In general, metals have tendency to lose electrons and convert into metal cations through metal oxidation reaction. Metal corrosion is the main cause of metal destruction, like steel rusts due to immersion in seawater. Similarly iron reacts with oxygen to form rust by exposure to moist air, thus the main conditions for rusting are ***oxygen*** and ***water*** (moisture or humidity). The most common corrosion process is the **rusting of iron** which is an ***electrochemical process***. Iron rust is iron oxide $\mathbf{Fe_2O_3 \cdot XH_2O}$ where **X** is the amount of water of crystallisation which can vary. It shows the colour of rust (yellow-brown).

It is a very complex process which is completed in the following steps.

1. First the ***iron*** gets oxidized into ***ferrous ions*** ($\mathbf{Fe^{2+}}$) ***with the loss of two electrons***.

   $Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$

2. The ***electrons*** are conducted through the iron to the cathode where ***water and oxygen are reduced to OH⁻***

   $O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$

3. The ***ferrous ions*** ($\mathbf{Fe^{2+}}$) and the ***OH^-(aq)*** ions diffuse from their respective poles and get deposited as ***iron (II) hydroxide***.

   $Fe^{2+}(aq) + 2\ OH^-(aq) \rightarrow Fe(OH)_2(s)$

4. The ***iron (II) hydroxide*** is then oxidised by air to ***iron (III) hydroxide*** which is then converted into ***rust.***

   $4\ Fe(OH)_2(s) + O_2(aq) + 2\ H_2O(l) \rightarrow 4\ Fe(OH)_3(s)$

   $2\ Fe(OH)_3(s) \rightarrow Fe_2O_3 \bullet XH_2O(s) + (3\text{-}x)\ H_2O(l)$

The figure below shows the mechanism for the rusting process.

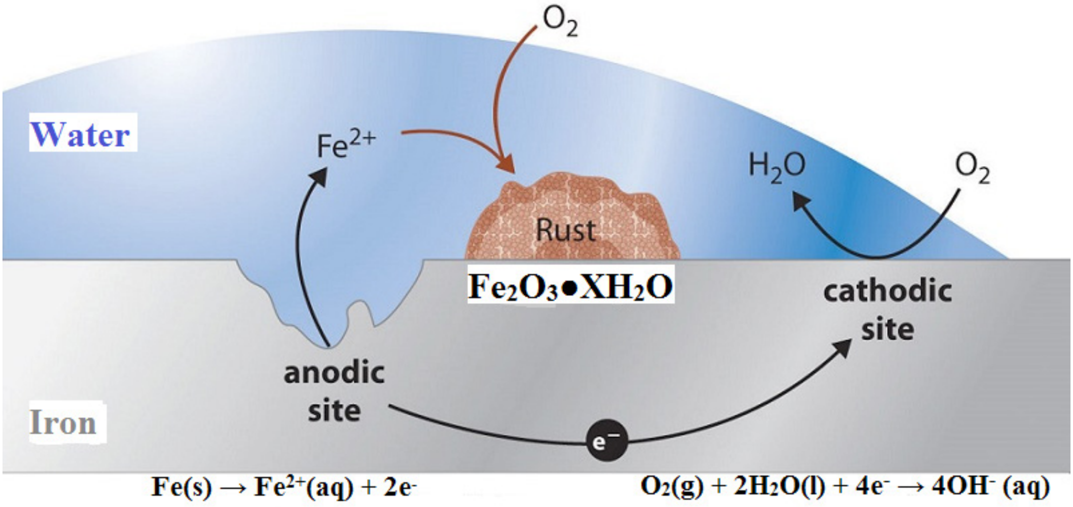


Figure 9.4: Mechanism for the rusting process

The **mechanism for the *rusting process* is similar to the *electrochemical cell.*** The electrons formed during the oxidation of iron are conducted through the metal. Thus, the iron ions diffuse from the water layer to the metal surface where oxygen is present.

This is an electrochemical cell where ***iron acts as the anode*** and ***oxygen gas as the cathode.*** The ***aqueous solution of ions behaves like a "salt bridge"*** as shown in the figure above.

Some of the noble and non-reactive metals like gold, platinum do not react with atmospheric oxygen and do not corrode.

Iron rusts faster under the following conditions:

- At elevated temperature
- Presence of dissolved electrolytes (especially salts)
- Iron in contact with a less electropositive element (where there are defaults); this is why corrosion accelerates at the contact point of two different metals because it undergoes oxidation.

The presence of salt enhances the conductivity of the aqueous solution formed at the surface of the metal. So the rusting of iron and steel is completed rapidly near the ocean (salty) or with salt.

For instance, in cold countries where the operations of road de-icing are done by spreading salt on the roads, corrosion of car bodies is accelerated.

9.4.2. Harmful effects of corrosion

There are many harmful effects of corrosion. Some of them are listed below.

- The loss of metallic object efficiency;
- The product is contaminated by these new impurities
- Metallic equipments are damaged;
- Accidents due to damage of metallic bridges, cars, aircrafts, etc.
- Pollution due to products from corrosion;
- Depletion of natural resources (metals);
- Loss of valuable materials such as blockage of pipes, mechanical damage of underground water pipes, etc.

9.4.3. Protection against corrosion

Since corrosion deteriorate the physical and chemical properties of metals, therefore we always try to protect metal surfaces against corrosion to make the material corrosion resistant.

The common example well known is to use ***anti-rust paints*** which is a physical isolation of the protected surface from contact with oxygen (air) and water.

There are other various ways to protect against corrosion such as:

- **Active corrosion protection:** Developing corrosion-resistant alloys, addition of inhibitors, etc.
- **Passive corrosion protection:** Coating by protective layer or film.
- **Permanent corrosion protection:** Electroplating (like tin plating or copper plating), Galvanization, etc.
- **Temporary corrosion protection:** Anodisation or protective coating.

Galvanisation is the process where the surface of iron is coated with a layer of zinc. Here the zinc acts as the ***sacrificial anode*** and undergoes oxidation instead of iron. This method is also called **"cathodic protection"**.

Anodisation is a method of increasing the corrosion resistance of a metal part by forming a layer of oxide on its surface. The part that is being treated forms the anode electrode of an electrical circuit.

Application activity 9.4

The rusting of iron is an electrochemical process. Different regions of the iron act as cathodes and anodes.

1. Write the equation for the reaction of iron at an anodic region.
2. Write the equation for the reaction of oxygen at a cathodic region.
3. Why does the presence of sodium chloride accelerate rusting?
4. Which of the following metals could be used for sacrificial protection of iron: zinc, nickel, tin, magnesium, lead? Explain your answer.

9.5. Applications of electrochemical cells

Activity 9.5

Electrochemical cells have very important daily applications. Some applications can be illustrated by the following images.

1. Use the images above to describe the main applications of electrochemical cells.
2. Use any documents or search engine and your knowledge on electrochemical cells acquired so far to answer the following questions.

   a) How do electrochemical cells like simple batteries work?

   b) How do the following work?

      (i) Leclanché dry cell

      (ii) Alkaline battery

      (iii) Mercury cell

      (iv) Lead-storage battery

      (v) Nickel-cadmium battery

      (vi) Lithium ion battery
3. Based on your research, suggest some explanations for the classification of electrochemical cells as primary cells, secondary cells, fuel cells, rechargeable cells and non-rechargeable cells.

Electrochemistry has a number of different uses, particularly in industry. The principles of cells are used to make **electrical batteries**. In science and technology, a battery is a device that stores chemical energy and makes it available in an electrical form. Batteries are made of electrochemical devices such as one or more galvanic cells or fuel cells.

The importance of electrochemical cells or galvanic cells lies in their ability to ***provide us with a portable source of electrical energy.*** We have already studied that a redox reaction is, primarily, the basis of all the electrochemical cells. Quite often, we use the term **"battery"** to represent the arrangement of two or more galvanic cells connected in series.

Batteries have many uses including in:

- Torches
- Electrical appliances such as cell phones (long-life alkaline batteries)
- Digital cameras (lithium batteries)
- Hearing aids (silver-oxide batteries)
- Digital watches (mercury/silver-oxide batteries)

- Military applications (thermal batteries)

The galvanic cells can be broadly classified into two categories, namely; ***primary cells*** and ***secondary cells.*** Here we add also ***fuel cells.***

9.5.1. Primary cells

This type of cells becomes dead over a period of time and the chemical reaction stops. They cannot be recharged or used again. Some common examples are dry cell, mercury cell, etc.

1. **Dry cell**

It is a compact form of Leclanché cell known after its inventor, a ***French chemist, G. Leclanché.*** In this cell, **anode consists of zinc container** while **cathode is a graphite rod** surrounded by powdered MnO_2 and carbon. The space between the electrodes is filled with the **paste of NH_4Cl and $ZnCl_2$** (which is **the electrolyte**).

The arrangement is shown in the figure below.

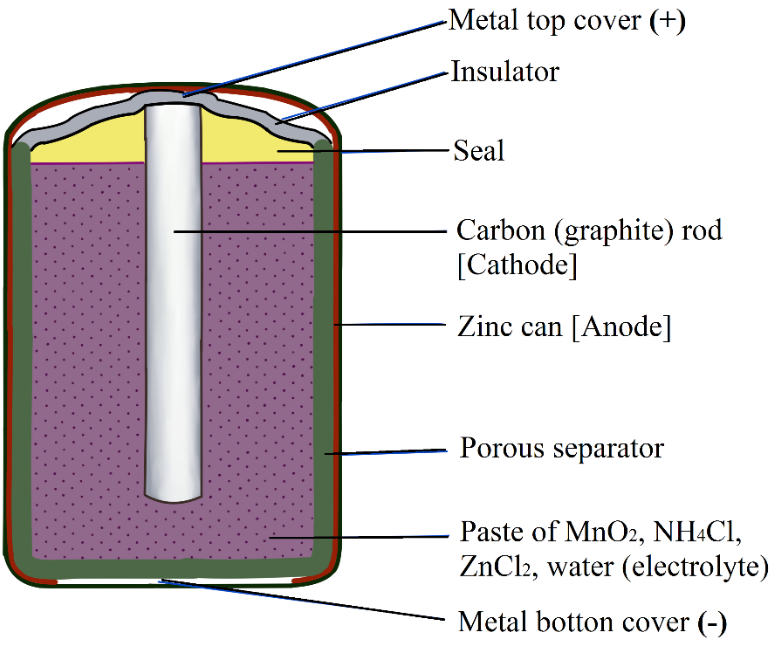


Figure 9.5 : Leclanché Dry Cell

The reactions taking place at the electrodes are given in their simplified form as follows:

- ***Cathode***: $2\ MnO_2 + 2NH_4^+ + 2e^- \rightarrow 2\ MnO(OH) + 2\ NH_3$
- ***Anode:*** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

The zinc ions (Zn^{2+}) so produced combine with ammonia liberated in cathodic reaction to form diammine zinc (II) cation.

$Zn^{2+}(aq) + 2NH_3(g) \rightarrow [Zn(NH_3)_2]^{2+}(aq)$

- **The overall reaction:**

$Zn(s) + 2\ MnO_2(s) + 2\ NH_4Cl(aq) \rightarrow ZnCl_2(aq) + 2\ MnO(OH)(s) + 2\ NH_3(aq)$

Or $Zn(s) + 2\ MnO_2(s) + 2\ NH_4Cl(aq) \rightarrow ZnCl_2(aq) + Mn_2O_3(s) + 2\ NH_3(aq) + H_2O(l)$

Alternately, the reduction reaction of Mn(IV) can proceed further, forming Mn(II) hydroxide.

$Zn(s) + 2MnO_2(s) + 2\ NH_4Cl(aq) \rightarrow ZnCl_2(aq) + Mn(OH)_2(s) + 2\ NH_3(aq)$

Dry cells do not have long life as NH_4Cl which is acidic, corrodes the zinc container even if the cell is not in use. The cell potential of dry cells lies in the range **1.25 V** to **1. 5 V.**

2. Alkaline batteries

Alkaline batteries were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries use ***alkaline electrolytes***.

They consist of ***Zn powder*** in the center of the pile as ***anode*** and ***MnO_2 + graphite*** as ***cathode***. Everything is contained in a steel housing. NH_4Cl is replaced by a solution of about 7 M of KOH, hence the term "alkaline".

The reactions are:

- **Anode:** $Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2\ e^-$
- **Cathode:** $MnO_2\ (s) + 2H_2O(l) + 2\ e^- \rightarrow Mn(OH)_2(s) + 2OH^-(aq)$
- **Overal reaction:** $Zn_{(s)} + MnO_{2(s)} + 2H_2O(l) \rightleftharpoons Zn(OH)_{2(s)} + Mn(OH)_{2(s)}$

  Or $Zn_{(s)} + 2MnO_{2(s)} \rightleftharpoons ZnO_{(s)} + Mn_2O_{3(s)}$

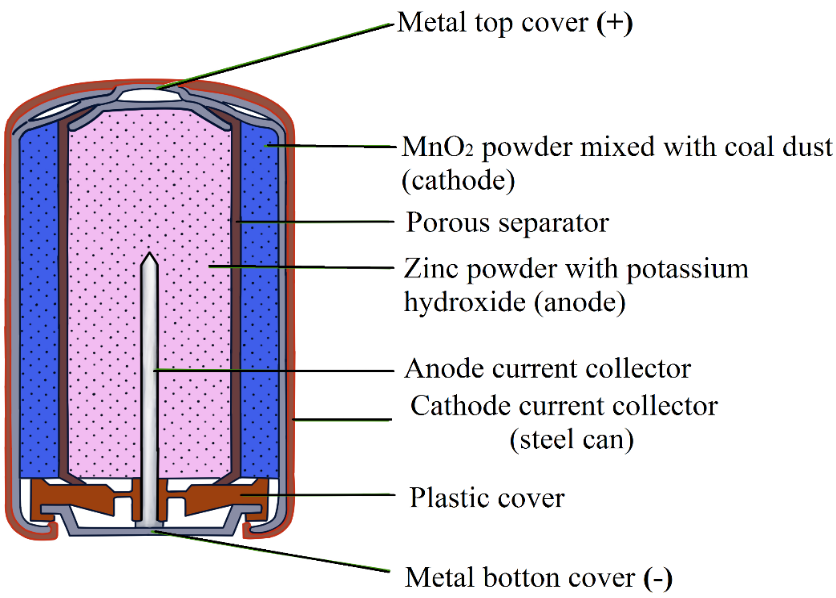


Figure 9.6: Alikaline battery

Alkaline cells last longer than ordinary dry cell. They have a longer shelf life and can be kept in service longer. An alkaline cell has NaOH or KOH in place of NH_4Cl as the electrolyte. It uses essentially the same reduction half-cell reaction as the ordinary dry cell, but in alkaline medium.

Alkaline cells develop a voltage of **1.5 V** as Leclanché cells but have advantage over dry cell.

Attempts to recharge an alkaline battery often lead to rupture of the battery and leakage of the potassium hydroxide electrolyte (this is because it is not rechargeable).

Advantages over the dry cell battery:

- It is more waterproof.
- A longer life because it contains more reagents.
- The voltage does not drop rapidly when current is drawn. This is because the concentration of zinc ion does not build up at the anode and the pH remains more nearly constant at cathode.

9.5.2. Secondary cells

This type of cells can be recharged by passing direct current through them and can be used again and again. These are the types of batteries found in devices such as smart phones, electronic tablets, and automobiles. Some examples are lead-storage battery, nickel-cadmium storage cell, etc.

a) Lead-storage battery

It is the most frequently used battery in automobiles. It consists of **six voltaic cells** connected in series. In ***each cell anode is made of spongy lead*** and ***cathode 'is a grid of lead packed with lead dioxide (PbO_2).*** The lead storage batteries are made of alternating lead electrodes on the one hand, and lead coated PbO_2 on the other. The ***electrolyte is the aqueous solution of 3M sulphuric acid*** (38% by mass).

These batteries provide a constant emf of about 12 V. Invented in 1859 by Gaston Planté, the lead-acid storage battery is still widely used in cars, trucks, and airplanes. The storage battery consists of a group of cells connected together in series. Each cell consists of a ***lead plate, a lead oxide plate, and an electrolytic solution of sulphuric acid.***

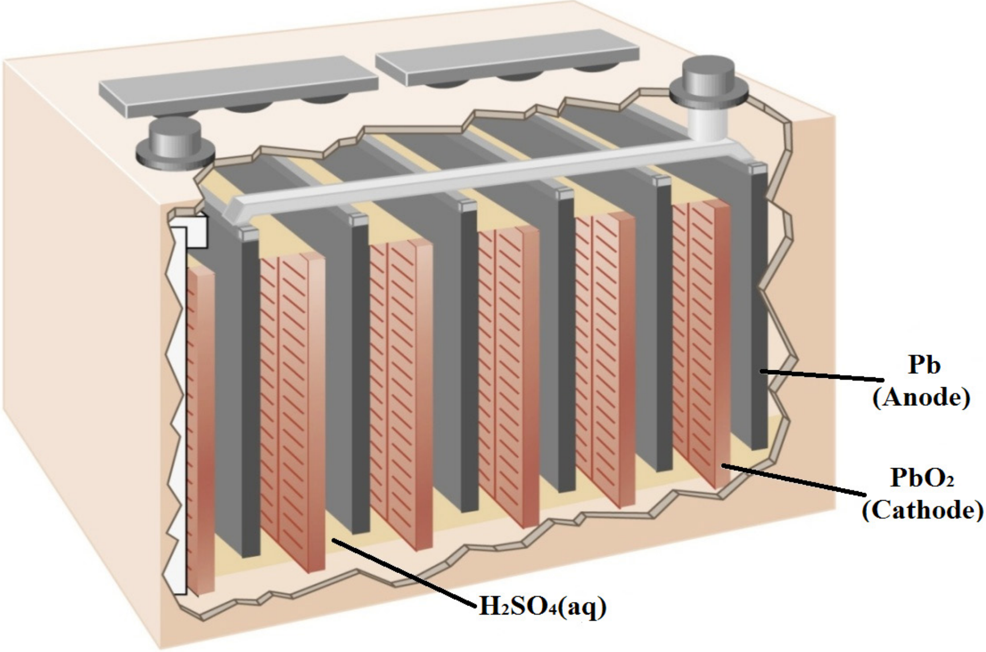


Figure 9.8: Lead storage battery

When these types of batteries run down, they can be recharged by forcing current through the battery in the direction opposite the direction the current flows when the battery is fully charged.

The following reactions occur:

i) Operation during discharge (cell phenomenon):

- Anode (Pb) : $Pb + SO_4^{2-} \rightarrow PbSO_4$
- Cathode (PbO_2) : $PbO_2 + SO_4^{2-} + 4\,H^+ + 2\,e^- \rightarrow PbSO_4 + 2\,H_2O$

- Overall reaction: $Pb + PbO_2 + 2\,H_2SO_4 \rightarrow 2\,PbSO_4 + 2\,H_2O$

Sulphuric acid is consumed.

ii) Operation when charging (electrolysis phenomenon):

- Anode (Pb) : $PbSO_4 + 2\,H_2O - 2e^- \rightarrow PbO_2 + SO_4^{2-} + 4\,H^+$
- Cathode (PbO_2) : $PbSO_4 + 2\,e^- \rightarrow Pb + SO_4^{2-}$

- Overall reaction: $2\,PbSO_4 + 2\,H_2O \rightarrow Pb + PbO_2 + 2\,H_2SO_4$

Sulphuric acid is generated

Note: When all of the ***Pb or PbO_2*** is converted to ***$PbSO_4$***, the battery is depleted. But by the electric current, the reaction ***changes direction*** and the battery is charging.

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

Their low cost and high current output makes these excellent candidates for providing power for automobile starter motors.

b) Nickel-Cadmium Storage Cell

The nickel-cadmium (known as **"Nicad"**) battery is another common secondary battery that is suited for low-temperature conditions with a long shelf life. However, their capacity in terms of watt-hours per kilogram is less than that of the nickel-zinc rechargeable batteries.

The anode is made of ***nickel oxyhydroxide coated by $Ni(OH)_2$*** and the cathode of ***iron or cadmium-covered by $Fe(OH)_2$ or $Cd(OH)_2$*** respectively. The electrolyte is a ***concentrated solution of KOH***.

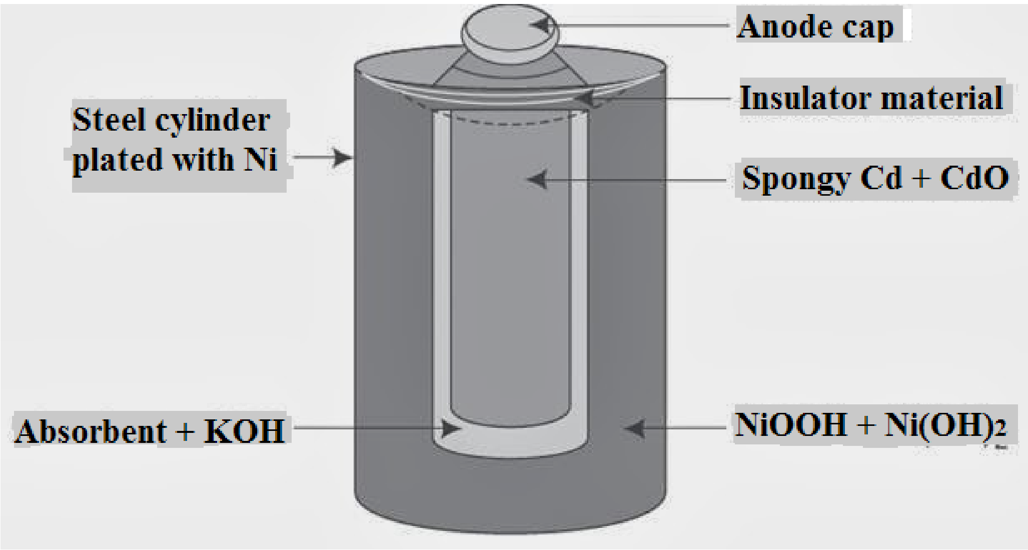


Figure 9.9: A Nickel-Cadmium cell

The reactions are:

- ***Operation during discharge:***
  - **Anode :** $Cd(s) + 2\ OH^-(aq) \rightarrow Cd(OH)_2(s) + 2\ e^-$
  - or $Fe(s) + 2\ OH^-(aq) \rightarrow Fe(OH)_2(s) + 2\ e^-$
  - **Cathode:** $2\ NiO(OH)(s) + 2\ H_2O(l) + 2\ e^- \rightarrow 2\ Ni(OH)_2(s) + 2\ OH–(aq)$
  - **Overall:** $Cd(s) + 2\ NiO(OH)(s) + 2\ H_2O(l) \rightarrow Cd(OH)_2(s) + 2\ Ni(OH)_2(s)$
- ***While charging,* the opposite phenomena take place.**
  - **Anode :**$Cd(OH)_2(s) + 2\ e^- \rightarrow Cd(s) + 2\ OH^-(aq)$
  - **Cathode:** $2\ Ni(OH)_2(s) + 2\ OH–(aq) \rightarrow 2\ NiO(OH)(s) + 2\ H_2O(l) + 2\ e^-$
  - **Overall:** $Cd(OH)_2(s) + 2\ Ni(OH)_2(s) \rightarrow Cd(s) + 2\ NiO(OH)(s) + 2\ H_2O(l)$

These batteries provide an electromotive force of 1.42 **V** (Fe-Ni) or **1.31 V** (Ni-Cd). The cell is also called **NiCad cell**.

As is evident, there are no gaseous products, the products formed adhere to the electrodes and can be reconverted by recharging process. This cell is becoming more popular these days and finds use in electronic watches and calculators.

Advantages of the nickel-zinc battery are its long life span, high voltage, and the sufficient energy to mass to volume ratio.

c) Lithium Ion Batteries

Lithium ion batteries are among the most popular rechargeable batteries and are used in many portable electronic devices. The most common lithium-ion cells have an **anode of graphite carbon (C)** and a **cathode of lithium cobalt oxide ($LiCoO_2$). The electrolyte is lithium perchlorate ($LiClO_4$).**

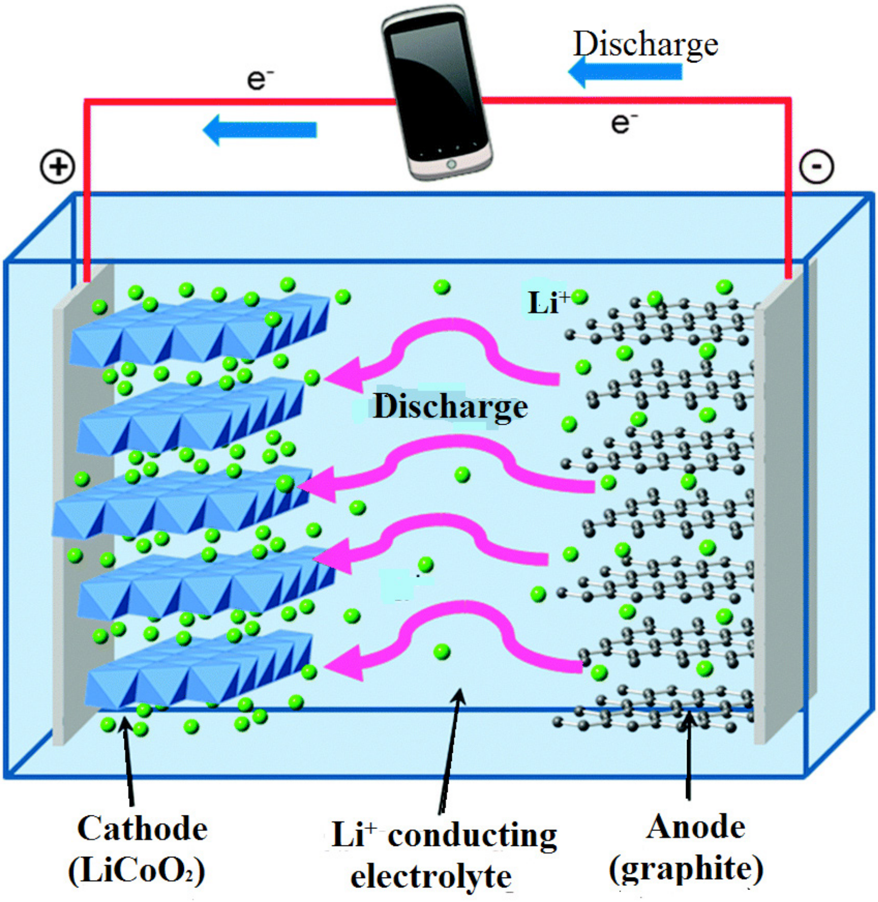


Figure 9.10: Lithium ion battery

♦ DURING DISCHARGE

At the anode, lithium is oxidised. Lithium ions are released from the carbon, along with electrons: $LiC_6 \rightarrow Li^+ + e^- + 6\,C$

At the cathode, lithium-ions are absorbed by the lithium dioxide, and the electrode is reduced as it also receives the electrons from the circuit: $CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$

The overall reaction is: $LiC_6 + CoO_2 \rightleftharpoons 6\,C + LiCoO_2$

The structure of **LiC_6** involves lithium inserted (intercalated) between the layers of graphite.

♦ *DURING RECHARGE*

The opposite reaction occurs.

In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode. The battery voltage is about **3.7 V**.

Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

9.5.3. Fuel cells

Fuel cells work like batteries but they do not run down or need recharging. They produce electricity and heat as long as fuel is supplied. A fuel cell consists of **two electrodes:** a negative electrode (or anode) and a positive electrode (or cathode) sandwiched around an **electrolyte.** A fuel, such as hydrogen, is fed to the anode, and air (oxygen) is fed to the cathode.

The ***anode is porous graphite coated with nickel***, the ***cathode is porous graphite coated nickel and nickel (II) oxide*** and potassium ***hydroxide solution is used as electrolyte***.

The reactions involved in a fuel cell are as follows:

- Anode side (an oxidation reaction): $H_2\ (g) + 2\ OH^-(aq) \rightarrow 2\ H_2O(l) + 2\ e^-$
- Cathode side (a reduction reaction): $O_2\ (g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$
- Net reaction (the "redox" reaction): $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

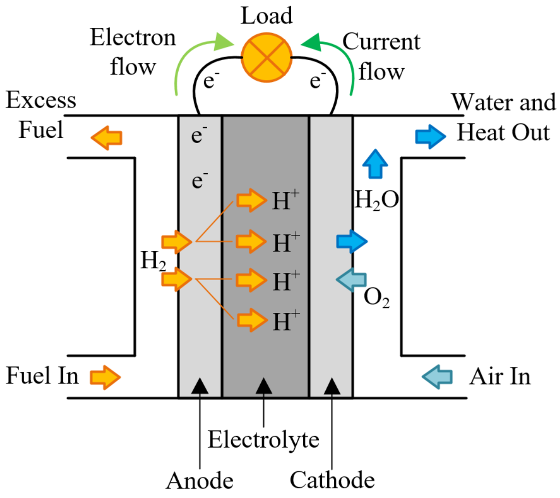


Figure 9.11: Hydrogen fuel cell

In a hydrogen fuel cell, a **catalyst** at the anode separates hydrogen molecules into protons and electrons, which take different paths to the cathode. The electrons go through an external circuit, creating a flow of electricity. The protons migrate through the electrolyte to the cathode, where they unite with oxygen and the electrons to produce **(drinking) water** and **heat**.

Platinum and platinum alloys (like Platinum-Ruthenium) are the most efficient catalysts for speeding up chemical reactions in hydrogen fuel cells.

The reaction in a single fuel cell typically produces only about **0.7 volts**. Therefore, fuel cells are usually stacked or connected in some way to form a fuel cell system that can be used in cars, generators, or other products that require power.

Application activity 9.5

1. A lead-acid battery (car battery) consists of six cells that can provide about 12 V. The half-reactions that take place in each cell and their respective standard reduction potentials are represented below:

$PbSO_4(s) + H^+(aq) + 2e^- \rightarrow Pb(s) + HSO_4^-(aq) \quad E^0 = -0.36\ V$

$PbO_2(s) + HSO_4^-(aq) + 3\ H^+(aq) + 2\ e^- \rightarrow PbSO_4(s) + 2\ H_2O(l) \quad E^0 = +1.7\ V$

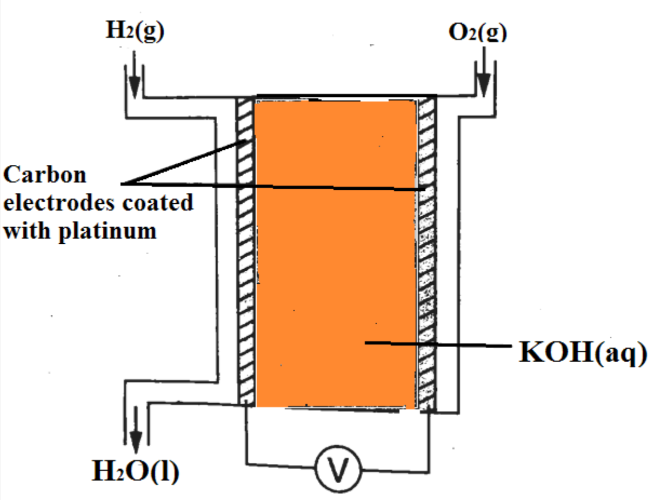
a) Are car batteries primary or secondary batteries? Explain.

b) Write down the equation for the net (overall) cell reaction that takes place in each cell of this battery.

c) Calculate the emf of the battery, consisting of six cells, under standard conditions.

d) State two environmental risks associated with the irresponsible disposal of lead-acid batteries.

2. The following is a simplified diagram for the hydrogen fuel cell used onboard space shutters.



a) The reaction at the hydrogen compartment is: 2 $H_2(g)$ + 4 $OH^-(aq)$ → 4 $H_2O(l)$ + 4 e-

(i) Write equation to represent the reaction taking place in the oxygen half-cell.

(ii) Write the balanced overall cell reaction.

(iii) Show the direction of flow of electrons.

b) Suggest the function of platinum in the above cell.

c) Give two advantages of fuel cells over those of ordinary batteries.

3. Hydrogen–oxygen fuel cells are used to provide electrical energy for electric motors in vehicles. In a hydrogen–oxygen fuel cell, a current is generated that can be used to drive an electric motor.

a) Deduce half-equations for the electrode reactions in a hydrogen–oxygen fuel cell.

b) Use these half-equations to explain how an electric current can be generated.

c) Explain why a fuel cell does not need to be recharged.

d) Explain why hydrogen-oxygen fuel cell can produce drinking water of potable quality.

e) To provide energy for a vehicle, hydrogen can be used either in a fuel cell or in an internal combustion engine.

(i) Suggest the main advantage of using hydrogen in a fuel cell rather than in an internal combustion engine.

(ii) Identify one major hazard associated with the use of that fuel cell in a vehicle.

4. The following half-reactions take place when a non-rechargeable alkaline cell is in use:

$Zn(s) + 2\ OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$ …………………… (1)

$MnO_2(s) + 2H_2O(l) + 2e^- \rightarrow Mn(OH)_2(s) + 2\ OH^-(aq)$ ………..... (2)

a) Write down the general name used for non-rechargeable cells.

b) Which one of the above equations (1) or (2) represents the half-reaction that takes place at the cathode? Give a reason for your answer.

c) Give a reason why the cell 'dies' after delivering current for a while.

5. Some cells, such as the nickel-cadmium cell used in calculators and electric shavers, can be recharged. Others, such as those used in watches and torches, cannot be recharged.

a) Are rechargeable cells primary or secondary cells?

b) The half-reactions occurring in a nickel-cadmium cell are shown below:

$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e-$

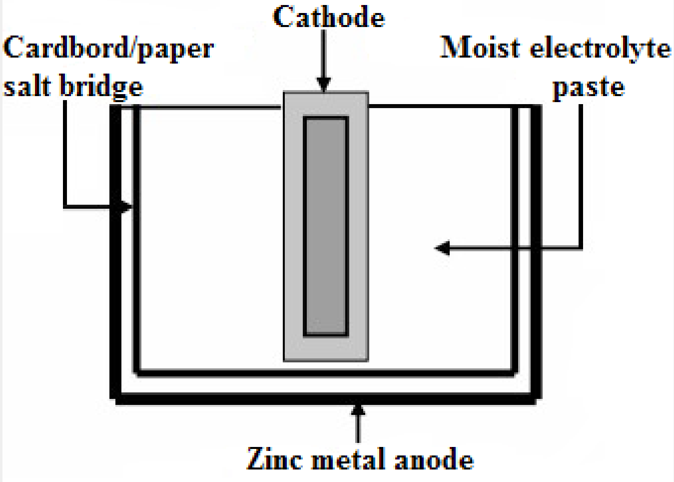
$NiO_2(s) + 2H_2O(l) + 2e- \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$

The emf of the nickel-cadmium cell is 1.4 V.

c) Which one of these half-reactions occurs at the cathode? Give a reason for your answer.

d) Write down the balanced equation for the overall cell reaction.

6. A sketch of a dry cell, such as the one used in a torch or radio, is shown below.



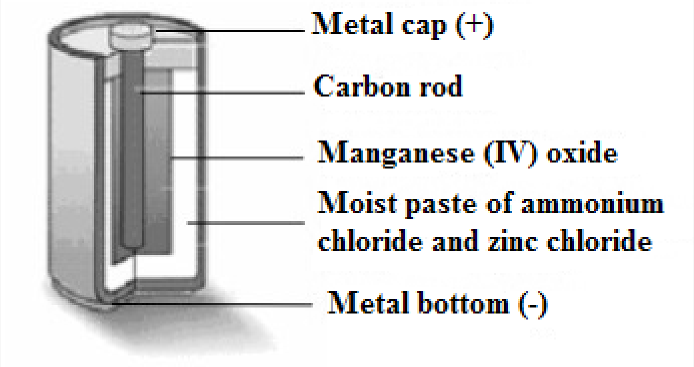
In some types of dry cells, the electrolyte paste is made of ammonium chloride which is acidic. In other types of cells the paste is alkaline, due to an alkali such as potassium hydroxide. The alkaline cells are known to last longer than those containing ammonium chloride.

a) Why is the above cell referred to as a dry cell?

b) Give a reason why alkaline cells last longer than cells that contain acid.

c) Give one reason why rechargeable batteries have less impact on global warming than non-rechargeable batteries.

7. A dry cell, as shown in the diagram below, does not contain a liquid electrolyte. The electrolyte in a typical zinc-carbon cell is a moist paste of ammonium chloride and zinc chloride.



The paste of ammonium chloride reacts according to the following half-reaction:

$2NH_4^+(aq) + 2e^- \rightarrow 2\ NH_3(g) + H_2(g)$

Manganese (IV) oxide is included in the cell to remove the hydrogen produced during half-reaction **(i)**, according to the following reaction:

$2\ MnO_2(s) + H_2(g) \leftrightarrow Mn_2O_3(s) + H_2O(l)$

The combined result of these two half-reactions can be represented by the following half reaction: $2\ NH_4^+(aq) + 2MnO_2(s) + 2e^- \leftrightarrow Mn_2O_3(s) + 2NH_3(g) + H_2O(l)$

a) Explain why it is important that the hydrogen produced in half-reaction (i) is removed by the manganese (IV) oxide

b) Write down the half-reaction occurring at the anode.

c) Write down the net ionic equation occurring in the zinc-carbon cell.

d) When in use the zinc casing of the dry cell becomes thinner, because it is oxidised. When not in use, it still corrodes. Give a reason for the latter observation.

e) Dry cells are generally discarded when ‘flat’. Why is the carbon rod the most useful part of the cell, even when the cell is flat?

9.6 Comparison between galvanic cell and electrolytic cell.

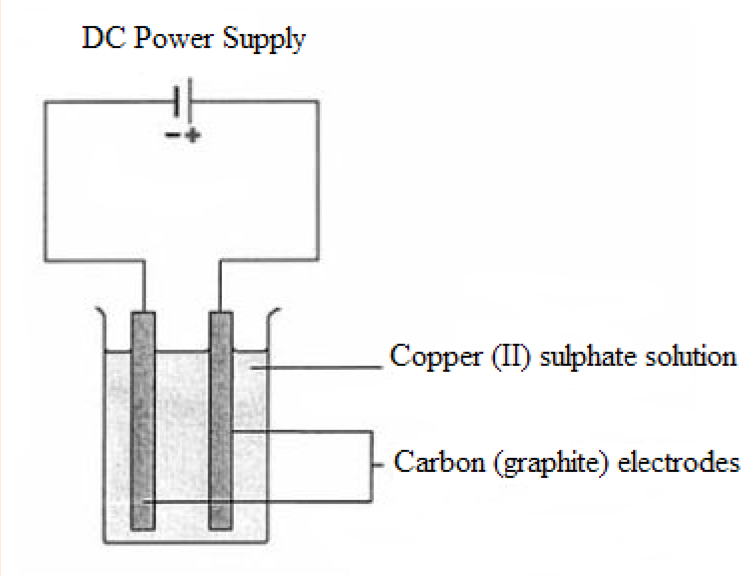
Activity 9.6

1. Electrolysis of copper (II) sulphate solution

Apparatus	Chemicals
– Beaker (250 cm^3) – Graphite electrodes (about 5 mm diameter), – Retort stands and clamps to hold electrodes – DC power supply – Leads and crocodile clips	Aqueous copper (II) sulphate, about 0.5 M, 200 cm^3

Procedure

- Set up the cell as shown in the diagram below.



- Watch for any activity on each of the electrodes,

Discussion questions

(a) Write down any observation.

(b) Write the reaction equations for the reactions at each electrode.

(c) Suggest any role of carrying out this experiment.

2. Give the definition of:

(a) Galvanic cell

(b) Electrolytic cell.

3. Compare and contrast these two types of electro chemical cells.

We have learnt that there are two types of cells namely galvanic cells and electrolytic cells. **Galvanic cell** is a device which converts chemical energy into electrical energy. On the other hand, **electrolytic cell** is a device which converts electrical energy into chemical energy.

9.6.1. Similarities

Electrolytic cells are very similar to voltaic (galvanic) cells in the sense that both

- Have a cathode and anode side,
- Have a consistent flow of electrons from the anode to the cathode.

9.6.2. Differences

Even though electrolytic and voltaic cells are very similar as we saw, there are also striking differences between the two cells. The main differences are outlined below.

Table 9.6.2: Differences between galvanic (voltaic) and electrolytic cell

Galvanic Cell	Electrolytic Cell
It converts chemical energy into electrical energy.	It converts electrical energy into chemical energy.
Electrical energy is produced.	Electrical energy is consumed.
It is based upon the redox reactions which are spontaneous.	The redox reactions are non-spontaneous and take place only when energy is supplied.
The chemical changes occurring in the two beakers are different.	Only one chemical compound undergoes decomposition.
Anode (-ve) - Oxidation takes place.	Anode (+ve) - Oxidation takes place.
Cathode (+ve) - Reduction takes place.	Cathode (-ve) - Reduction takes place
Anode is negative and cathode is positive.	Anode is positive and cathode is negative.
The electrons move from anode to cathode in external circuit.	The electrons are supplied by the external source. They enter through cathode and come out through anode.
The two half cells are set up in different containers and are connected through salt bridge or porous partition.	Both the electrodes are placed in the solution or molten electrolyte in the same container.

Application activity 9.6

1. State two differences and two similarities between an electrochemical cell and an electrolytic cell.
2. Which of these is a TRUE statement about voltaic cells?

   a) Voltaic cells convert chemical energy to electrical energy using an oxidation-reduction reaction.

   b) Voltaic cells convert electrical energy to chemical energy using an oxidation-reduction reaction.

   c) Voltaic cells convert chemical energy to electrical energy using a decomposition reaction.

   d) Voltaic cells convert electrical energy to chemical energy using electrolysis.
3. What is the anode in an electrolytic or voltaic cell?

   a) The site of oxidation

   b) The site of reduction

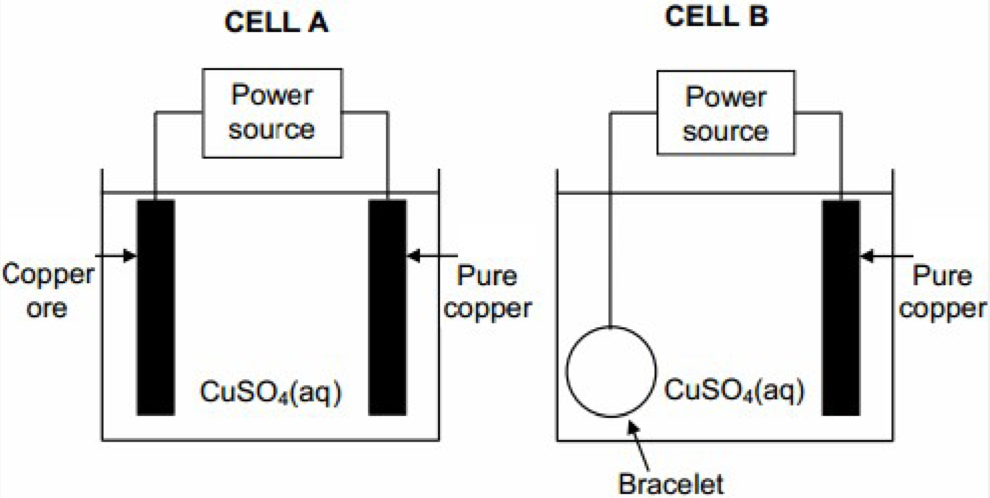
   c) The positive electrode

   d) The neutral electrode
4. What is the main difference between voltaic and electrolytic cells? Voltaic cells only contain a cathode and electrolytic cells only contain an anode.

   a) Voltaic cells convert chemical energy to electrical energy and electrolytic cells convert electrical energy back to chemical energy.

   b) Voltaic cells contain an electrolyte, while electrolytic cells do not.

   c) Electrolytic cells contain an electrolyte, while voltaic cells do not.
5. The simplified diagrams below represent two electrochemical cells, A and B, used in industry. Cell A is used in the purification of copper ore containing silver and platinum impurities. Cell B is used to electroplate a bracelet with a layer of copper.



a) Write down the name of the type of electrochemical cell of which the above two cells are examples.

b) Pure copper is used as one of the electrodes in each of the cells above.In which cell (A or B) is the pure copper the:

Cathode

Anode

c) Consider cell B. Initially the $CuSO_4$(aq) has a blue colour.

d) How will the intensity of the blue colour change whilst the cell is functioning?

Write down increases, decreases or remains the same. Give a reason for the answer.

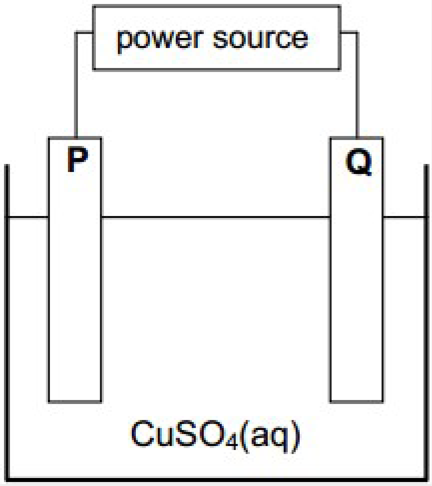
e) Write down the half-reaction that takes place at the pure copper electrode.

f) Consider cell A.

   i) Give a reason why the sludge formed in this cell is of economic importance.

   ii) Name one negative impact that the energy usage in this process has on the environment.

6. The simplified diagram below represents an electrochemical cell used in the refining of copper. One of the electrodes consists of impure copper and the other one of pure copper



a) What type of power source is used to drive the reaction in this cell? Write down only AC or DC.

b) Give a reason why the copper (II) sulphate is dissolved in water before it is used in this cell.

c) When an electric current passes through the solution, electrode P becomes coated with copper.

d) Is electrode P the cathode or the anode? Support your answer by writing the half-reaction that takes place at electrode P.

e) Write down the half-reaction that takes place at electrode Q.

f) It is found that the impure copper plate contains platinum. The platinum forms a residue at the bottom of the container during electrolysis.

g) Refer to the relative strengths of reducing agents to explain why platinum forms a residue at the bottom of the container.

h) How will the concentration of the copper (II) sulphate solution change during electrolysis? Write down only increases, decreases or remains the same. Give a reason for the answer.

Skills Lab 9

Electrochemical cells have several applications in a modern society. Some of them are used as alternatives to the uses of fossil fuels in order to limit the greenhouse effect and the global warming associated with their use. The environment friendly electrochemical cells include hydrogen cells, methanol fuel cells, microbial fuel cells, and so on.

However, these cells present some health/safety, financial, social problems. Discuss problems and suggest possible solutions.

End of unit assessment 9

MULTIPLE CHOICE QUESTIONS

1. What is the function of a voltaic electrochemical cell?

   (a) To convert electrical energy to light energy

   (b) To convert electrical energy to chemical energy

   (c) To convert electrical energy to heat energy

   (d) To convert chemical energy to electrical energy

2. What is a cathode?

   (a) The electrode where reduction takes place and electrons are lost.

   (b) The electrode where oxidation takes place and electrons are gained.

   (c) The electrode where oxidation takes place and electrons are lost.

   (d) The electrode where reduction takes place and electrons are gained.

3. Which of the following statements is FALSE?

   (a) Oxidation and reduction half-reactions occur at electrodes in electrochemical cells.

   (b) All electrochemical reactions involve the transfer of electrons.

   (c) Reduction occurs at the cathode.

(d) Oxidation occurs at the anode.

(e) All voltaic (galvanic) cells involve the use of electricity to initiate non-spontaneous chemical reactions.

4. For a galvanic (or voltaic) cell using Ag,Ag^+ (1.0 M) and Zn,Zn^{2+} (1.0 M) half-cells, which of the following statements is incorrect?

(a) The zinc electrode is the anode.

(b) Electrons will flow through the external circuit from the zinc electrode to the silver electrode.

(c) Reduction occurs at the zinc electrode as the cell operates.

(d) The mass of the zinc electrode will decrease as the cell operates.

(e) The concentration of Ag^+ will decrease as the cell operates.

5. Consider the standard galvanic (or voltaic) cell: Fe,Fe^{2+} versus Au,Au^{3+}. Which answer identifies the cathode and gives the E° for the cell?

(a) Fe, -0.44 V

(b) Au, 1.94 V

(c) Fe, 1.06 V

(d) Au, 1.06 V

(e) Fe, 1.94 V

6. What is the value of E for the half-cell:

MnO_4^- (0.010 M) + $8H^+$ (0.20 M) + $5e^-$ → Mn^{2+} (0.020 M) + 4 H_2O?

(a) 1.50 V

(b) 1.86 V

(c)1.44 V

(d) 1.58 V

(e)1.52 V

7. A concentration cell is constructed by placing identical Cu electrodes in two Cu^{2+} solutions. If the concentrations of the two Cu^{2+} solutions are 1.0 M and 0.0020 M, calculate the potential of the cell.

(a) 0.020 V

(b) 1.2 V

(c) 0.030 V

(d) 1.0 V

(e) 0.080 V

8. What is ΔG^o per mole of dichromate ions for the reduction of dichromate ions, $Cr_2O_7^{2-}$, to Cr^{3+} by bromide ions, Br^-, in acidic solution? (Hint: Use the standard cell potential.)

(a) +26.3 kJ

(b) -145 kJ

(c) +145 kJ

(d) -26.3 kJ

(e) -53.6 kJ

9. Estimate the equilibrium constant for the system indicated at 25°C.

$3\ Mg^{2+} + 2Al \leftrightarrow 3Mg + 2Al^{3+}$

(a) ~1069

(b) ~1023

(c) ~10-24

(d) ~10-36

(e) ~10-72

10. Which of the following statements is (are) true for all galvanic (or voltaic) cells?

(I) Reduction occurs at the cathode.

(II) The anode gains mass during discharge (note: this means operation of the cell.)

(III) The voltage is less than or equal to zero.

only III

only II

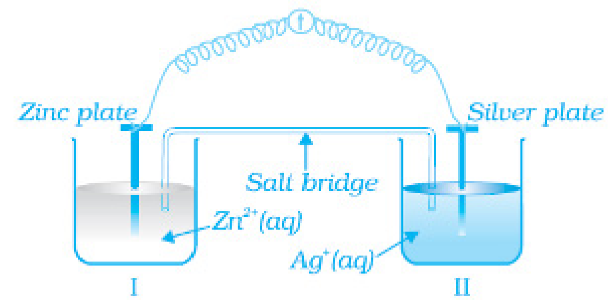
only I

II and III

I, II, and III

OPEN QUESTIONS

1. Consider figure below and answer the questions which follow.



(a) Redraw the diagram to show the direction of electron flow.

(b) Is silver plate the anode or cathode?

(c) What will happen if salt bridge is removed?

(d) When will the cell stop functioning?

(e) How will concentration of Zn^{2+} ions and Ag^{+} ions be affected when the cell functions?

(f) How will the concentration of Zn^{2+} ions and Ag^{+} ions be affected after the cell becomes ‘dead’?

2. Large blocks of magnesium are bolted onto the hulls of iron ships in an attempt to prevent the iron being converted into iron (II), one of the steps in the rusting process.

Use the data below, where appropriate, to answer the questions which follow.

	E^0 /V
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.37
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.44
$O_2(g) + 2H_2O(l) + 2e^- \rightarrow 4OH^-(aq)$	+0.40

(a) Calculate the e.m.f. of the cell represented by $Mg(s)|Mg^{2+}(aq)||Fe2^{+}(aq)|Fe(s)$ under standard conditions.

(b) Write a half-equation for the reaction occurring at the negative electrode of this cell when a current is drawn.

Deduce how the e.m.f. of the cell $Mg(s)|Mg^{2+}(aq)||Fe^{2+}(aq)|Fe(s)$ changes when the concentration of Mg^{2+} is decreased. Explain your answer.

(c) Calculate a value for the e.m.f. of the cell represented by

$Pt(s)|OH^{-}(aq)|O_2(g)||Fe^{2+}(aq)|Fe(s)$ and use it to explain why iron corrodes when in contact with water which contains dissolved oxygen.

3. The table below shows some values for standard electrode potentials.

Electrode	Electrode reaction	$E^{\ominus}$/ V
A	$Mn^{2+}(aq) + 2e^{-} \rightleftharpoons Mn(s)$	– 1.18
B	$Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s)$	– 0.44
C	$Ni^{2+}(aq) + 2e^{-} \rightleftharpoons Ni(s)$	– 0.25
D	$Sn^{2+}(aq) + 2e^{-} \rightleftharpoons Sn(s)$	– 0.14
E	$2H^{+}(g) + 2e^{-} \rightleftharpoons H_2(g)$	?

(i) Give the name of electrode E and indicate its role in the determination of standard electrode potentials.

(ii) What is the value of the standard electrode potential for electrode E°?

(iii) The electrochemical cell set up between electrodes C and D can be represented by the cell diagram:

$$Ni(s)\,|\,Ni^{2+}(aq)\,||\,Sn^{2+}(aq)\,|\,Sn(s)$$

(a) Calculate the e.m.f. of this cell.

(b) State which would be the positive electrode.

Write an equation to show the overall reaction in the cell.

(iv) Use the standard electrode potential data given in the table above:

(a) To explain whether or not you would expect a reaction to occur if a piece of tin were to be added to a test tube containing aqueous iron(II) sulphate;

(b) To predict and explain two observations you would expect to make if a small piece of manganese were to be added to a test tube containing hydrochloric acid of concentration 1 mol dm-3.

4. Calculate the voltage produced by the cell $Sn_{(s)}|Sn^{2+}||Ag^{+}|Ag_{(s)}$ at 25°C given:

$[Sn^{2+}] = 0.15$ M

$[Ag^{+}] = 1.7$ M

5. Hydrogen–oxygen fuel cells are used to provide electrical energy for electric motors in vehicles. In a hydrogen–oxygen fuel cell, a current is generated that can be used to drive an electric motor.

(a) Deduce half-equations for the electrode reactions in a hydrogen–oxygen fuel cell.

(b) Use these half-equations to explain how an electric current can be generated.

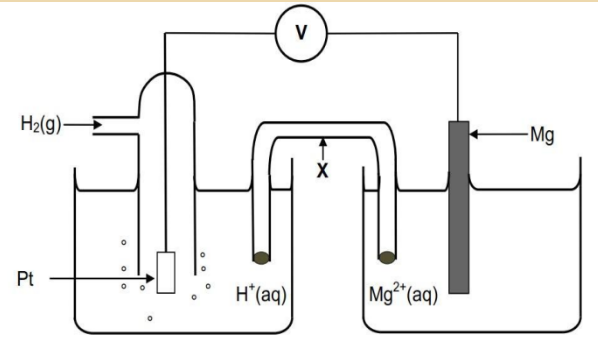
(c) Explain why a fuel cell does not need to be recharged.

(d) To provide energy for a vehicle, hydrogen can be used either in a fuel cell or in an internal combustion engine.

(i) Suggest the main advantage of using hydrogen in a fuel cell rather than in an internal combustion engine.

(ii) Identify one major hazard associated with the use of a hydrogen–oxygen fuel cell in a vehicle.

6. The galvanic cell represented below consists of a hydrogen half-cell and a magnesium half-cell at standard conditions. The reading on the voltmeter is 2.36 V.



a) Apart from concentration, write down two other conditions needed for the hydrogen half-cell to function at standard conditions.

b) Write down the name of the item of apparatus labelled X.

c) Is magnesium the anode or cathode in the cell above? Refer to the relative strengths of reducing agents to explain the answer.

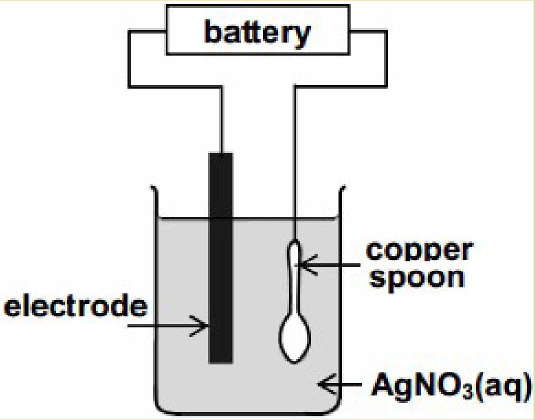
d) Write down the cell notation for this cell.

e) Calculate the standard reduction potential of the magnesium half-cell. Show all your working.

f) Write down the balanced net (overall) cell reaction that takes place in this cell.

No spectator ions are required.

7. Electroplating is one of the uses of electrolysis. The diagram below shows an electrolytic cell that can be used to plate a copper spoon with silver.



a) Define the term oxidation in terms of electron transfer.

b) What type of half-reaction takes place at the copper spoon? Write down only oxidation or reduction.

c) Write down a half-reaction that explains the change that occurs on the surface of the copper spoon during electrolysis.

d) Name the metal that is labelled 'electrode'.

e) Give a reason why the concentration of the $AgNO_3(aq)$ remains constant during electrolysis.

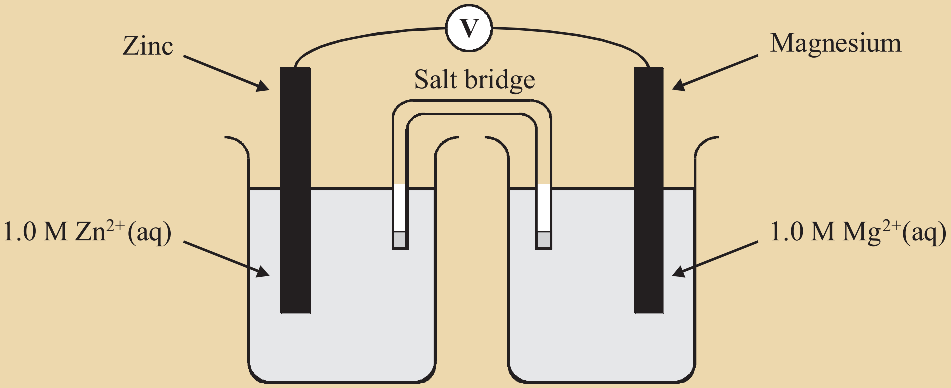
8. Use the data given below, where appropriate, to answer the questions which follow.

Standard electrode potentials in acid solution

	E^0 /V
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.37
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow V^{2+}(aq) + H_2O(l)$	+0.34
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$	+1.02
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.70

a) Give the components of the standard reference electrode used in determining the standard electrode potentials above. State the conditions under which this standard reference electrode has a potential of 0.00 V.

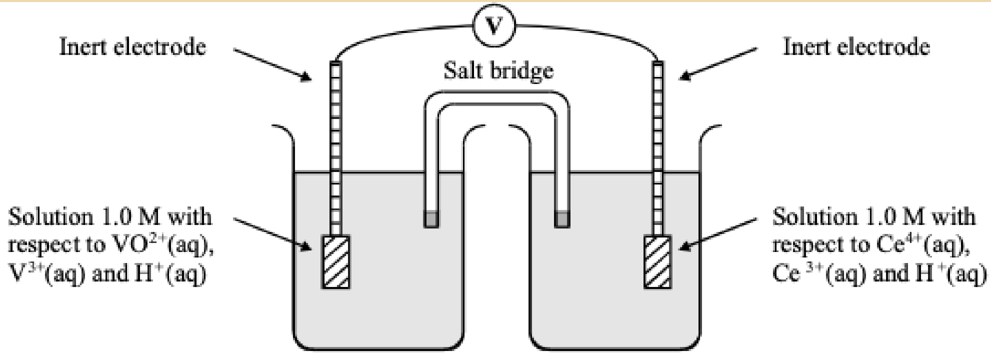
b) A diagram of a cell is shown below.



i) Calculate the overall standard potential of this cell.

ii) State the polarity of the zinc electrode.

c) Another diagram of a cell is shown below.



i) Calculate the overall standard potential of the cell.

ii) Deduce the direction of electron flow in the external circuit when the inert electrodes are connected together.

d) Using data from the table 12.1, derive an equation for the overall redox process which occurs when a solution containing Ce^{4+}(aq) is added to a solution containing V^{3+}(aq).

e) Which, if any, of the four vanadium-containing species, V^{2+}(aq), V^{3+}(aq), VO_2^+(aq) and

VO^{2+}(aq), will convert Sn^{2+}(aq) into Sn^{4+}(aq) in acid solution?

UNIT 10

ENTHALPY CHANGE OF REACTIONS

Key Unit Competence:

Design an experimental procedure to verify the enthalpy changes in a chemical reaction

Introductory activity

Observe the pictures below, analyze them and answer the questions that follow.


Airplane in flight


Cooking stove


Burning wood


Running of a vehicle's engine


Spacecraft launching


Bunsen burner

1. What is the origin of the energy used for the flight of airplanes, the functioning of vehicle's engines or some machines used in factories, launching of spacecrafts, energy used by our bodies, the energy released by a burning wood, Bunsen burner or a burning match or an exploding dynamite, etc?
2. What are the chemical reactions that are involved in the processes above?
3. How the energy used may be determined?

Our modern society greatly depends on energy for its existence.

Energy is needed for the functioning of different types of machines and appliances where electrochemical cells are required, to power our transportation vehicles, and to warm or cool our homes. Energy is also necessary for living beings where solar energy is used for the photosynthesis in plants. Food is transformed in energy to keep us warm or to mechanical energy in our muscles or to electrical energy in the signals within our nerve fibres.

The great amount of the energy on which we depend is derived from chemical reactions, whether those reactions are associated with the combustion of fuels, the discharge of a battery, or the metabolism of our foods. All of these processes involve energy changes.

That is the transfer of energy to or from chemicals plays a crucial part in industrial chemical process and living systems.

A good understanding of chemistry requires a good understanding of the energy changes that accompany chemical reactions.

The study of energy and its transformations is known as **thermodynamics**.

In this unit we will examine an aspect of thermodynamics that involves the relationships between chemical reactions and energy changes involving heat. This portion of thermodynamics is called **thermochemistry**.

10.1. Types of a system

Activity 10.1

To investigate the energy transfer between a system and surroundings

Requirements

Crucible, tongues, balance, Bunsen burner, conical flask with a stopper, Bunsen burner, distilled water, sodium hydroxide pellets,

Experiment A

Weigh a dry and clean crucible.

Weigh 5g of magnesium carbonate and transfer it into the crucible.

Record the mass of the crucible and magnesium carbonate.

Heat strongly the crucible and its content until there is no more change.

Let the crucible cool down.

Weigh again the crucible and its content. Record the new mass.

Experiment B

Weigh a conical flask with a stopper and containing 100ml of distilled water.

Remove the stopper and record the temperature of the distilled water.

Add 2g of sodium hydroxide to the content of the distilled water and weigh again the conical flak and its contents.

Shake strongly to dissolve the sodium hydroxide.

Record your observations and weigh again conical flak and its contents.

Study questions

Experiment A

1. Did the process releases or absorbs heat energy?
2. Did the mass of crucible and its contents increase or decrease during the process? Explain why.

Experiment B

1. Did the temperature of water in the conical flask goes down or rise?
2. Did the mass of the conical flask and its contents change appreciably or not? Explain.
3. What would be the observations if the experiment B was carried out in a thermos flask? Give a reason.

All chemical reactions involve the breaking of bonds in the reactants and the formation of new bonds in the products. The breaking of bond requires energy, whereas the formation of bond releases energy.

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 10.1).

Examples:

- All reactions carried out in open containers.
- Evaporation of water in a beaker.
- Hot coffee in a cup.

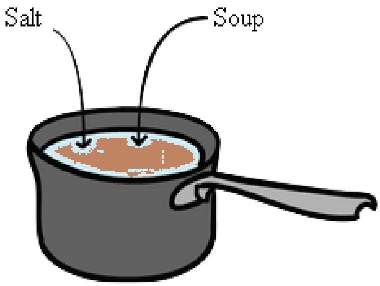


Figure 10.1 Example of an open system

2. **A closed system** is a system that can exchange energy but not matter with the surroundings (Figure 10.2).

Examples:

- All the reactions carried out in a closed container.
- Boiling water in a closed steel vessel.
- Boiling soup in a closed saucepan.

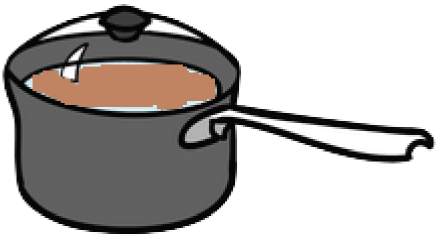


Figure 10.2 Example of a closed system

According to **Figures 10.1** and **10.2,** 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 exchange 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 asystem which is both sealed and insulated. It can exchange neither matter nor energy with its surroundings.

Examples

Hot coffee in a thermos flask (***Figure 10.3***).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 10.3 Example of an isolated system

Application activity 10.1

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 °C. It is then placed over the flame of a Bunsen burner for an hour. What is the final temperature?
4. What type of energy does a pencil on the table have? And what type of energy does a falling pencil have?
5. On which type of system is the first law of thermodynamics is based? What does it stipulate?

10.2. Heat energy and temperature

Activity 10.2

To investigate the relationship between heat and temperature

Requirements

- Weighing balance
- Thermometer
- Insulated plastic beaker(calorimeter)
- Measuring cylinder
- Sodium hydroxide pellets
- Distilled water

Procedure

1. Measure 100mL of water and transfer into the plastic beaker (calorimeter). Record the initial temperature T1.
2. Weigh 2g of sodium hydroxide pellets and transfer in the beaker containing water. Stir gently with a thermometer and record the highest temperature reached, T2.
3. Is the reaction exothermic or endothermic?
4. Repeat steps 1 through 2 using, 3, 4, 5, 6, 7, 8, 9, 10g of sodium hydroxide pellets and record the results in the table below.

Volume of water/ mL	Initial temperature/ °C	Mass of NaOH/g	Final temperature/ °C	Temperature change
100		2		
		3		
		4		
		5		
		6		
		7		
		8		
		9		
		10		

Interpretation

- Mass of the solution = m
- Change in temperature = ΔT
- Specific heat capacity of the solution C= 4.18J/g°C (Assumption)
- Relate the rise in temperature to the mass of sodium hydroxide.

Heat and temperature are related and often confused. More heat usually means a higher temperature.

When you heat a substance, either of two things can happen: the temperature of the substance can rise or/and the state of substance can change.

Heat versus Temperature comparison chart

	Heat	**Temperature**
Definition	Heat is energy that is transferred from one body to another as the result of a difference in temperature.	Temperature is a measure of hotness or coldness expressed in terms of any of several arbitrary scales like Celsius and Fahrenheit.
Unit	Joules	Kelvin, Celsius or Fahrenheit
Symbol	Q	T
SI unit	Joule	Kelvin
Particles	Heat is a measure of how many atoms there are in a substance multiplied by how much energy each atom possesses.	Temperature is related to how fast the atoms within a substance are moving. The 'temperature' of an object is like the water level – it determines the direction in which 'heat' will flow.
Ability to do work	Heat has the ability to do work.	Temperature can only be used to measure the degree of heat.

As thermodynamics is the study of the relationship between heat, work, and other forms of energy and its transformations, let us go through with all these types of energy.

- **Energy** is commonly defined as the capacity to do work or to transfer heat.
- **Work** is energy used to cause an object with mass to move.
- **Heat** is energy used to cause the temperature of an object to increase.

Heat is the exchange of thermal energy between the system and the surroundings that results in the temperature difference. Heat flows from matter with high temperature to matter with low temperature until both objects reach the same temperature. The quantity of heat is symbolized by "q".

When a system absorbs heat its temperature increases. The increase in temperature is directly proportional to the amount of heat absorbed.

The **heat capacity**, C of a substance is the amount of heat required to raise the temperature of a substance by 1°C. The **heat capacity** is expressed in J/°C or J/K.

The **molar heat capacity** is the amount of heat energy required to raise the temperature of one mole of a substance by 1°C. It is expressed in joules per mole per degrees Celsius (or Kelvin), (J/mol°C or J/mol. K).

For example, the molar heat capacity of lead is 26.65J/mol.°C, which means that it takes 26.65 Joules of heat to raise 1 mole of lead by °C.

The **specific heat capacity** is the amount of heat needed to increase the temperature of one gram of a substance by one degree. It is expressed in joules per gram per degree Celsius (J/g.°C). Water has a very high specific heat, 4.18J/g.°C.

The high specific heat of water allows it to absorb a lot of heat energy without large increase in temperature keeping ocean coasts and beaches cool during hot seasons. It allows it to be used as an effective coolant to absorb heat.

The relationship between heat and temperature is given by:

$q = m \times C \times \Delta T$

Where: q = quantity of heat
m = mass of substance
C = specific heat and
ΔT = change in temperature

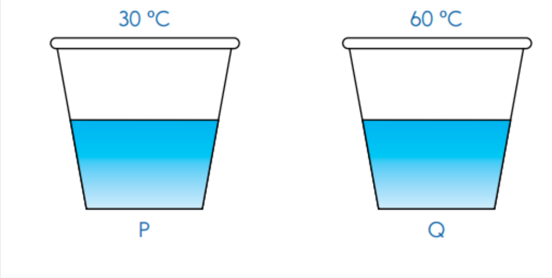
Note: Heat capacity, C, can never be negative for a mass or a substance, and similarly the specific heat of a substance can never be negative. Therefore, if the change in temperature is negative, the initial temperature is higher than the final temperature.

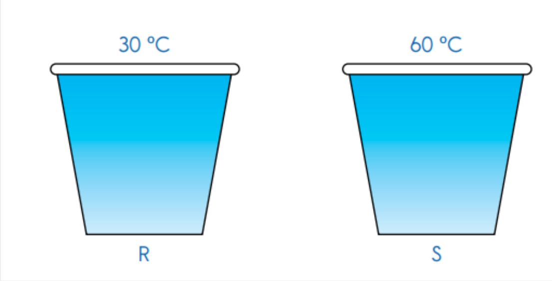
The heat capacity of an object depends on its mass: 200 g of water requires twice as much heat to raise its temperature by 1°C than 100 g of water. It also depends on the type of material: 1000 J of heat energy will raise the temperature of 100 g of sand by 12°C, but only raise the temperature of 100 g of water by 2.4°C.

Application activity 10.2

Multiple choice and short questions

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.

2. 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.

3. Ali 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

4. 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

5. 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.

Open Questions

1. Calculate the amount of heat needed to increase the temperature of 250g of water from 20°C to 56°C.
2. Calculate the specific heat capacity of copper given that 204.75 J of energy raises the temperature of 15g of copper from 25°C to 60°C.

10.3. Standard Enthalpy changes

Activity 10.3

1. Recall the concept of thermodynamic system and the different types of system.
2. The system can exchange heat with the surroundings. That heat which is exchanged has different names depending on the type of chemical process that is happening. Recall the different types of reactions and use available resources to find the proper name and the meaning of the heat that is exchanged for each specific process.

10.3. 1 Concept of enthalpy change

Using ***q*** to represent the heat added to or removed from the system, and w to represent work, the First Law of Thermodynamics can be represented by the equation: $\Delta E = q + w$

Table 10. 1: Energy changes of a system

F or q	F or w	F or ΔE
+ means system gains heat	+ means work is done on the system	**+** means net gain of energy by the system
- means system loses heat	**-** means work is done by the system	**-** means net loss of energy by the system

The work involved in the expansion or compression of gases is called **pressure-volume work**, or **P-V work**. When the pressure is constant, the sign and magnitude of the P-V work is given by $w = -P\Delta V$ where ***P*** is pressure and ΔV is the change in volume of the system ($\Delta V = V_{final} - V_{initial}$).

Enthalpy, H is the thermodynamic function that accounts for heat flow in processes occurring at constant pressure when no forms of work are performed other than P-V work.

$H = E + PV$

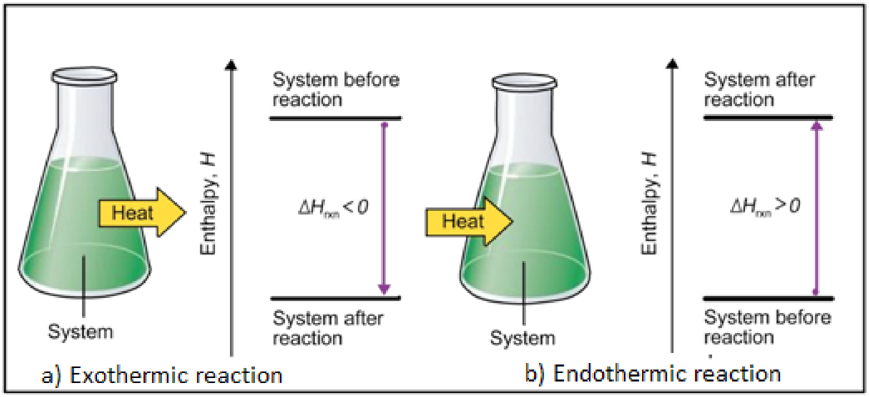
At constant pressure, a **change in enthalpy** equals the change in internal energy plus the product of the constant pressure times the change in volume.

$\Delta H = \Delta E + P\Delta V$

- When ΔH is positive, the system has gained heat from the surroundings - **endothermic.**
- When ΔH is negative, the system has lost heat to the surroundings - **exothermic.**

If heat flows from a system to its surroundings, the enthalpy of the system decreases, The enthalpy change is negative ($\Delta H < 0$) and the reaction is **exothermic**; it is energetically downhill.(Figure10.4a). Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, the enthalpy change is positive ($\Delta H < 0$), and the reaction is **endothermic**; it is energetically uphill (Figure10.4b).

The units of the enthalpy change of reaction (ΔH) are kilojoules per mole.
The heat change may be measured by a calorimeter.



a) Exothermic reaction b) Endothermic reaction

Figure 10.4: Enthalpy of reaction

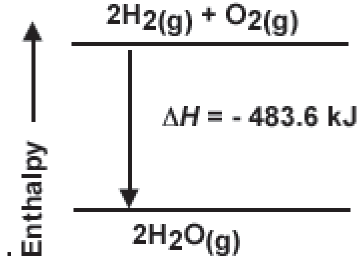
Source: https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_General_Chemistry_(Petrucci_et_al.)/07%3A_Thermochemistry/7.6%3A_Heats_of_Reactions_-_%CE%94U_and_%CE%94H

The enthalpy change for a chemical reaction is expressed by the equation:

ΔH = Hproducts – Hreactants

Here is an example of a thermochemical equation: $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$ ΔH = – 483.6 kJ

This equation indicates two moles of hydrogen gas burn to form two moles of water at a constant pressure, releasing 483.6 kJ of heat. Enthalpy change during a chemical reaction can also be represented in an enthalpy diagram, showing the reactants at the top and the products at the bottom



Rules of enthalpy change of reaction

Enthalpy changes of reaction follow some simple rules:

1. The enthalpy change of a reaction is proportional to the amount of reactants which are involved.

   Example:

   $2NO(g) \rightarrow N_2(g) + O_2(g)$ $\Delta H = -180$ kJ

   $6NO(g) \rightarrow 3N_2(g) + 3O_2(g)$ $\Delta H = -540$ kJ (180kJ x3)

2. The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to ΔH for the reverse reaction.

   Example:

   $N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H = 180$ kJ

   $2NO(g) \rightarrow N_2(g) + O2(g)$ $\Delta H = -180$ kJ

3. The enthalpy change of a reaction depends on the physical states of the reactants and the products.

   Example:

   $CH_4(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g) + \frac{1}{2} H_2O(l)$ $\Delta H = -890.4$ kJ/mol

   $CH_4(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g) + \frac{1}{2} H_2O(g)$ $\Delta H = -802.4$ kJ/mol

Enthalpy changes associated with the formation of a compound from its constituent elements is known as ***enthalpy of formation***, (or heat of formation), ΔH_f.

To compare enthalpies of different reactions, a set of conditions must be defined at which the enthalpies will be tabulated.

These conditions are called the **standard state**: a ***pure substance at 1 atmosphere of pressure at 298 K (25 °C)***

- **The standard enthalpy change, ΔH°, of a reaction** is defined as the enthalpy change when all reactants and products are in their standard states.
- **The standard enthalpy of formation of a compound, ΔH°_f,** is the change in enthalpy for the reaction that forms one mole of the compound from its elements, with all substances in their standard states.

By definition, ***the standard enthalpy of formation of the most stable form of any element is zero***, because there is no formation reaction needed when the element is already in its standard state.

Note:

Any reaction can be broken down into formation reactions: The standard enthalpy change of a reaction is ***the sum of the standard enthalpies of formation of the products minus the sum of the standard enthalpies of formation of the reactants***.

$$\boxed{\Delta Hrxn = \sum n\ \Delta Hf\ (products) - \sum m\ \Delta Hf\ (reactants)}$$

Where ***n*** and ***m*** are the coefficients from the balanced chemical equation

10.3.2. Some important enthalpy changes

1. Enthalpy change (ΔH)

In thermodynamics, the heat of reaction also known as enthalpy of reaction is the change in the **enthalpy (H) of a chemical reaction that occurs at a constant pressure. Enthalpy**, H is a state function used to describe the heat changes that occur in a reaction under constant pressure. It is a state function as it is derived from pressure, volume, and internal energy, all of which are state functions. The enthalpy is a measurement of the amount of energy per mole either released or produced in a reaction.

When a reaction is taking place in an open container, a quantity of heat which is proportional to the quantity of the matter present, will be released or absorbed.

The flow of heat is the **enthalpy change** noted ΔH. The units of ΔH are kJ or Kcal/mol.

2. Thermochemical equations

A **thermochemical equation** is a balanced equation that includes the amount of heat exchanged (produced or absorbed).

Examples

$NH_4NO_{3(s)}$ + 25 kJ → $NH_4NO_{3(aq)}$, 25 kJ is the energy absorbed for the reaction to take place.

$NaOH_{(s)} \rightarrow NaOH_{(aq)}$ + 44.2 kJ, 44.2 kJ is the energy released by the reaction.

Another way to express the heat change is the use of ΔH notation; the heat change for the system is shown outside the equation.

Examples

$NH_4NO_{3(s)} \rightarrow NH_4NO_{3(aq)}$ $\Delta H = +25 kJ/mol$

$NaOH_{(s)} \rightarrow NaOH_{(aq)}$ $\Delta H = -44.2 kJ/mol$

3. Types of enthalpy changes

There are various types of enthalpy change. Some examples of the types of enthalpy changes are given below.

a) The enthalpy of formation (ΔH_f)

The enthalpy of formation (ΔH_f) of a substance is the heat change (heat released or absorbed) for the chemical reaction in which one mole of the substance is formed from its constituent elements under given conditions of temperature T and pressure P.

The **standard enthalpy of formation (ΔH^o_f)** of a substance is the change in enthalpy for the reaction that forms one mole of the substance from its elements in their most stable form with all reactants and products at the pressure of 1 atm and usually at the temperature of 298 K.

Note: For any element in its stable state at 1 atm and 298 K, $\Delta H^o_f = 0$

The Standard conditions are:

Pressure = 1 atmosphere (1 atm)

Temperature = 25 °C = 298 K(remember that 0 °C = 273 K).

The concentration of solutions = 1mol/dm^3.

The **standard enthalpy change of a reaction,** is the enthalpy change when all reactants and products are taken at 1atm and 298K.

Consider a general reaction:

$$aA + bB \longrightarrow cC + dD$$

The standard enthalpy change for any reaction can be calculated from the standard enthalpies of formation of the reactants and the products in the reaction:

$$\Delta H^o_r = \sum n \, \Delta H^o_f \, \text{(products)} - \sum m \, \Delta H^o_f \, \text{(reactants)}$$

Example:

Determine the enthalpy of the reaction: $3Fe_2O_3(s) + CO(g) \rightarrow 2Fe_3O_4(s) + CO_2(g)$ using the following data.

Species	ΔH^o_f(kJ/mol)
$Fe_2O_3(s)$	-824
$CO(g)$	-111
$Fe_3O_4(s)$	-1118
$CO_2(g)$	-394

Answer:

ΔH^o_r = [2 x 1118 + 1 x (-394)] – [3 x (-824) =1 x (-111)] = - 47 kJ

b) Enthalpy of combustion

The ***enthalpy of the combustion*** of a substance (element or compound) ΔH^o_c, is the enthalpy change which occurs when one mole of a substance undergo complete combustion with oxygen in excess at 298 K and 1 atm.

Examples:

Reaction	Standard enthalpy of combustion/ kJmol^{-1}
$C(gr) + O_2(g) \rightarrow CO_2(g)$	-394
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$	-890
$H_2(g) + ½ O_2(g) \rightarrow H_2O(l)$	-286
$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + H_2O(l)$	-2220

c) Enthalpy of neutralization

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 of temperature and pressure.

The equation of the neutralization reaction is: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Example

Enthalpy change for the neutralisation of sodium hydroxide by hydrochloric acid is 57 $kJ.mol^{-1}$.

The enthalpy of neutralisation is the heat evolved for the reaction between the H^+ ions given by the acid with the OH^- ions given by the base to from one mole of H_2O.

d) Enthalpy of displacement

The **displacement enthalpy** is the enthalpy change of a reaction in which an element displaces another in a chemical reaction.

For example, zinc is more reactive than copper, so when zinc is added to copper (II) sulphate solution, copper is displaced.

$$CuSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Cu(s)$$

The reaction is associated with an enthalpy change converted into the heat energy equals to 217 $kJ\ mol^{-1}$.

e) Enthalpy of solution

The **enthalpy of solution** of a compound is the heat energy change at constant pressure when one mole of a compound is completely dissolved in a specific amount of water as solvent.

However, if a large volume of the solvent is used till further addition of the solvent does not produce any more heat change it is called **enthalpy of solution at infinite dilution.** The symbol **(aq)** is used to represent the solvent at large dilution.

Examples

The enthalpy of solution of sodium chloride solid:

$NaCl(s) + H_2O(l) \rightarrow NaCl(aq)\ \Delta H_{sol}(NaCl(s)) = +1\ kJmol^{-1}$

The enthalpy of solution of calcium fluoride solid

$CaF_2(s) + H_2O(l) \rightarrow CaF_2(aq)\ \Delta H_{sol}(CaF_2(s)) = +13.4\ kJ.mol^{-1}$

f) Enthalpy of atomisation

The **atomisation enthalpy** is the enthalpy change that accompanies the total separation of all atoms in a chemical substance (either an element or a compound). The enthalpy change of atomisation is always positive.

For a diatomic molecule, the atomisation enthalpy is equal to a half of the bond dissociation energy.

Examples:

Atomisation energy of sodium, $\Delta H_{at}(Na) = +107$ kJ mol^{-1}

Atomisation enthalpy of chlorine, $\Delta H_{at}(Cl_2) = +122$ kJ mol^{-1}

g) Lattice enthalpy

Lattice enthalpy is the energy released when one mole of an ionic compound is formed from its ions in the gaseous state.

Examples:

Lattice enthalpy of sodium chloride, $\Delta H_{LE}(NaCl) = -786$ kJ mol^{-1}

Lattice enthalpy of magnesium oxide, $\Delta H_{LE}(MgO) = -3890$ kJ mol^{-1}

h) Hydration enthalpy

Hydration enthalpy is the enthalpy change when one mole of gaseous ions dissolves in sufficient water to give an infinitely dilute solution.

Examples:

Hydration enthalpy of sodium ions, $\Delta H_{(hyd)}(Na^+) = -406$ kJ mol^{-1}

Hydration enthalpy of chloride ions, $\Delta H_{(hyd)}(Cl^-) = -364$ kJ mol^{-1}

i) Bond enthalpy

The bond enthalpy is the energy required to break a chemical bond. It is usually expressed in units of **kJ mol^{-1}**, measured at 298 K. The exact bond enthalpy of a particular chemical bond depends upon the molecular environment in which the bond exists. Therefore, bond enthalpy values given in chemical data books are averaged values.

The bond enthalpy values are used to:

- compare the strengths of bonds
- estimate the enthalpy change of a reaction
- explain the mechanisms of reaction
- explain the structure and bonding

In the calculation of reaction enthalpy using bond energy values, the following equation may be applied.

$$\Delta H = \sum \Delta \mathbf{H}_{\text{(bonds broken)}} - \sum \Delta H_{\text{(bonds formed)}}$$

This basically means that you add up all the energies of the broken bonds (in the reactants side), add up all the energies of the bonds that are reformed (in the products side) and subtract one from the other.

Example:

Calculate a value for the standard enthalpy of combustion of butan-1-ol $C_4H_9OH(g)$ using the following mean bond enthalpies.

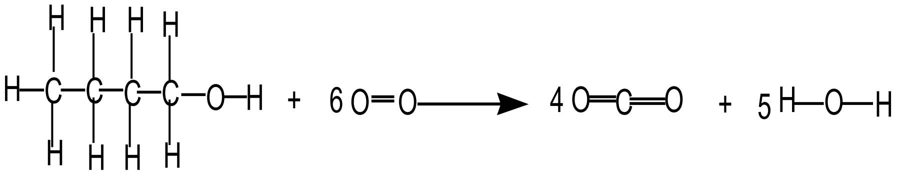
Bond	Mean bond enthalpy/kJ mol^{-1}
C- C	348
C -H	412
O -H	463
C-O	360
O=O	496
C=O	803

Solution

Equation for combustion of butan-1-ol

$C_4H_9OH(g) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$

Structural equation showing all the moles of covalent bonds:



Calculate the energy required for moles of bonds broken in the reactants:

3 moles of C- C = 3(348)

9 moles of C- H = 9(412) = 3708

1 mole of C-O = 360

1 mole of O-H = 463

6 moles of O= O = 6(496) = 2976

Total energy required for bonds broken = 8551 kJmol^{-1}

Calculate the energy released for moles of bonds formed in the products:

8 C =O = 8 x (803) = 6424

10 O-H = 10 x (463) = 4630

Total energy released for bonds made = 11 054 kJ mol^{-1}

ΔH_r =$\sum$(mean bond enthalpies of bonds broken) - $\sum$(mean bond enthalpies

of bonds formed)

ΔH_r = 8551 – 11054 = –2504 kJ mol^{-1}

j) Electron-gain enthalpy

The electron-gain enthalpy (previously called electron affinity) is the standard enthalpy change accompanying the addition of one electron to an atom in the gas phase. For example:

$$Cl(g)+e^- \longrightarrow Cl^-(g)+e^-(g); \quad \Delta H_{e.g}(298K)=-351kJ.mol^{-1}$$

Note that the process of electron gain for chlorine is exothermic, so the enthalpy change has a negative sign.

Application activity 10.3

1. Write an equation representing the formation of each of the following compounds from its constituent elements.

   a) hexane

   b) nitric acid

   c) methanol

   d) potassium bromide

   e) butanoic acid

2. Which of the following reactions do not represent the standard enthalpy of formation? Explain.

   a) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ ΔH^o= - 286 kJ

   b) $N_2(g) + O_2(g) \rightarrow 2NO(g)$ ΔH^o= - 180 kJ

c) $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2$ $\Delta H^o = -653.1\ kJ\ mol^{-1}$

d) $N_2(g) + 2H_2(g) \rightarrow N_2H_4(l)\Delta H^o = +50.63\ kJ\ mol^{-1}$

3. Write the equations that represent the standard enthalpy of combustion of:

   a) Hydrogen

   b) Methane

   c) Sulphur

   d) propanol

4. Write equations for which the enthalpy of atomisation is measured.

   a) Potassium

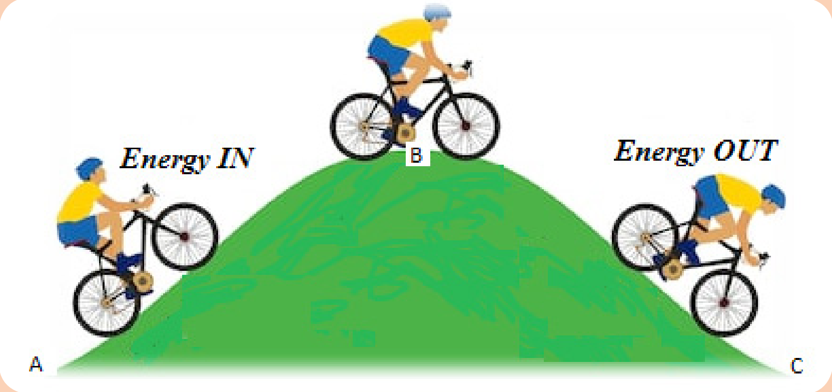
   b) Nitrogen

   c) Iodine

10.4 Energy profile diagrams for Exothermic and Endothermic reactions.

Activity 10.4

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 cyclist.
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 10.5), 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 parts.
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:

$$Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$$

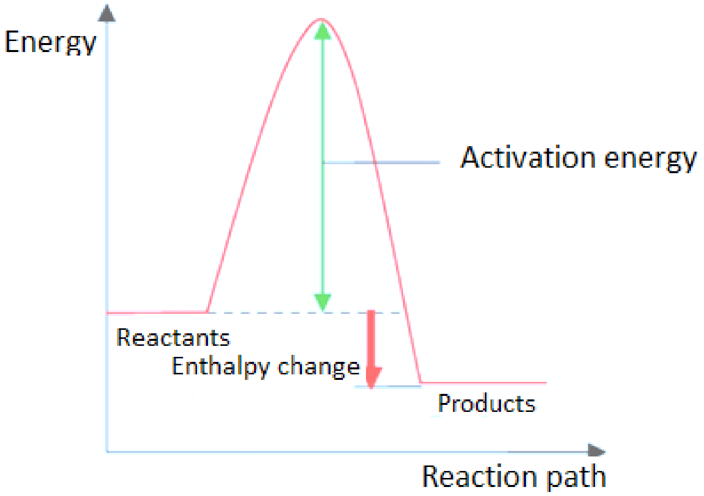


Figure 10.5: Energy profile diagram for exothermic reaction

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 18.9), 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

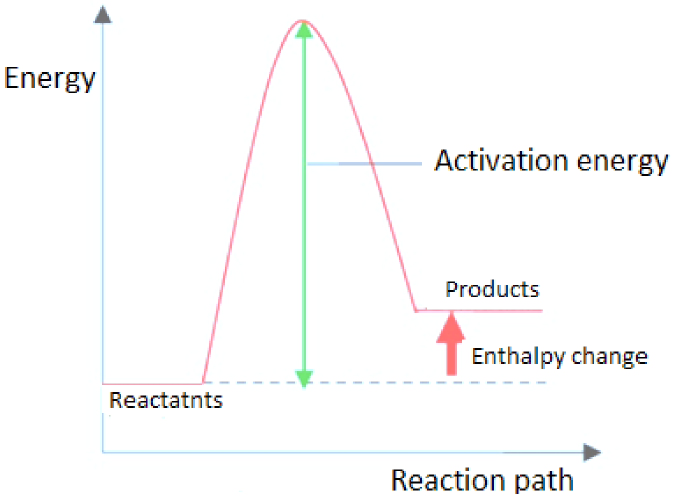


Figure 10.6: Energy profile diagram for endothermic reaction

3) Activation energy, E_a

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.

4) 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.

Examples

1. Let us consider the reaction between hydrogen and fluorine to form hydrogen fluoride.

$$H_2(g) + F_2(g) \rightarrow 2HF(g)$$

Determine the enthalpy change of the reaction and decide whether the reaction is endothermic or exothermic.

Data: The bond energies of H-H, F-F, and H-F are 436 $kJmol^{-1}$, 155$kJmol^{-1}$ and 567 $kJmol^{-1}$, respectively.

Solution:

The stoichiometric coefficients show that a hydrogen-hydrogen bond and a fluorine-fluorine bond are broken. Moreover, two hydrogen-fluorine bonds are formed. The overall energy change for this process is tabulated below.

Chemical species	**Bond type**	**Number of bonds**	**Bond enthalpy (kJ mol^{-1})**	**Total bond enthalpy (kJ mol^{-1})**
Reactants	H-H	1	436	436 × 1 = 436
	F-F	1	155	155×1 = 155
Products	H-F	2	567	567 × 2 = 1,134

Using the relation $\Delta\mathbf{H}_{rxn} = \Delta\mathbf{H}_{prod} - \Delta\mathbf{H}_{react,}$ gives

$\Delta H_{rxn} = [(436\times1)+(155\times1)-(567\times2)]$ kJ mol^{-1}

= (436+155-1134) kJ mol^{-1}

= - 543 kJ mol^{-1}

2. Consider the complete combustion of butane and answer to the related questions. Given the bond energies of reactants and products in the following table.

Bond type	**Bond enthalpy (kJ mol^{-1})**
C-C	348
C-H	413
O=O	495
C=O	799
O-H	463

(a) Use bond energies to estimate the enthalpy change for the said reaction.

(b) What is the nature of the reaction? Explain.

Solution:

a) The balanced equation for the reaction is:

$$\mathbf{2C_4H_{10}(g) + 10O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)}$$

Referring to the values of bond energy in the **Table 18.1** and taking into consideration the stoichiometric coefficients, the total bond enthalpy calculated is given as follows:

Chemical species	**Bond type**	**Number of bonds**	**Bond enthalpy ($kJ\ mol^{-1}$)**	**Total bond enthalpy ($kJ\ mol^{-1}$)**
Reactants	C-C	3×2 = 6	348	3481×6 = 2,088
	C-H	10×2 = 20	413	413×20 = 8,260
	O=O	1×13 = 13	495	495×13 = 6,435
Products	C=O	2×8 = 16	799	799×16 = 12,784
	O-H	2×10 = 20	463	463×20 = 9,260

Using the relation $\mathbf{\Delta H_{rxn}=\Delta H_{prod}-\Delta H_{react,}}$ gives

ΔH_{rxn} = [(2,088+8,260+6345)-(12,784+9,260)] $kJ\ mol^{-1}$

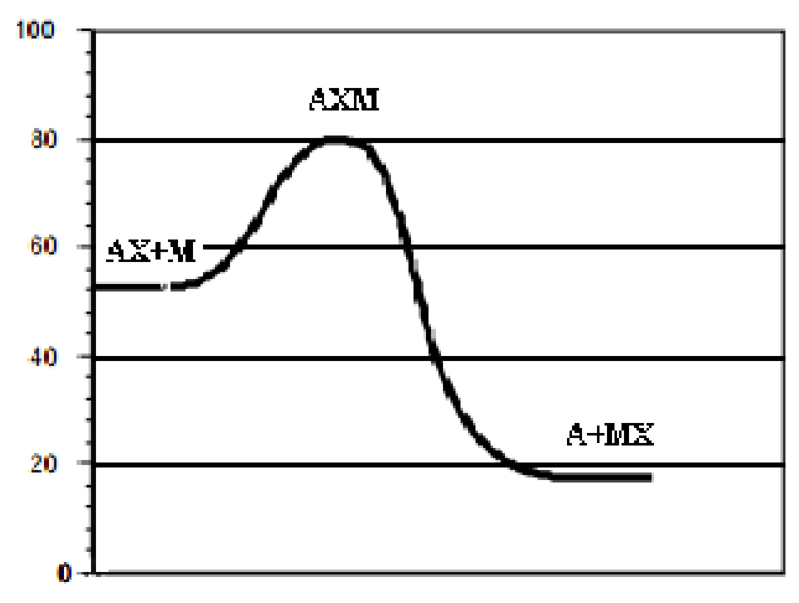
= (16,693-22,044) $kJ\ mol^{-1}$

= -5,351 $kJ\ mol^{-1}$

b) The reaction is exothermic, i.e it releases heat.

Application activity 10.4

Use the following potential energy diagram to answer the questions below:



1. What is meant by activation energy?
2. Determine the energy of the reactants.
3. Determine the energy of the products.
4. Determine the activation energy for the forward reaction.
5. Determine the activation energy for the reverse reaction.
6. Determine the enthalpy change of reaction for the forward reaction.
7. Determine the enthalpy change of reaction for the reverse reaction.
8. Fill in using exothermic or endothermic.

   a. The forward reaction is ……………………..

   b. The reverse reaction is ………………………

9. Which chemical species or set of chemical species represent the activated complex?
10. Which one of the chemical bonds A-X and M-X is stronger? Explain.
11. State the chemical species whose particles move the fastest. Explain your answer.

12. State the chemical species whose particles move the slowest. Explain your answer.
13. The compound AX and the element M are in gaseous and solid states, respectively.

What effect would grinding M into a fine powder have o the above graph?

10.5 Experimental determination of the standard enthalpy change of combustion

Activity 10.5

To investigate the enthalpy of combustion of ethanol

Requirements

- spirit burner (containing ethanol)
- thermometer
- copper can
- measuring cylinder
- retort stand and accessories
- balance
- breeze shield

Safety precautions

- Ethanol is highly flammable and the main risk is from burns.
- Since a small amount is burned the build-up of any products of incomplete combustion is negligible.
- Wear eye protection.
- Ensure the spirit burner is always sitting in a stable position.
- If you have to re-fill the spirit burner, allow it to cool and then fill it away from sources of ignition.

Procedure

1. Weigh the spirit burner (already containing ethanol) with its cap on and record its mass. (The cap should be kept on to cut down the loss of ethanol through evaporation)
2. Using the measuring cylinder, measure out 100 cm^3 of water into the copper can.

3. Set up the apparatus as directed by your teacher/lecturer.
4. Measure and record the temperature of the water.
5. Remove the cap from the spirit burner and immediately light the burner.
6. Slowly and continuously stir the water with the thermometer.
7. When the temperature has risen by about 10 °C, recap the spirit burner and measure and record the maximum temperature of the water.
8. Reweigh the spirit burner and record its mass.

Calculations

a) The heat energy gained by the water (q) can be calculated using the formula:

$$q = c\,m\,\Delta T$$

b) The difference in the initial and final masses of the spirit burner gives us the

mass of ethanol burned (say x g) and so the heat energy we calculate is equal to that released by burning x g of ethanol. It is assumed that all the heat energy released by the burning ethanol is absorbed only by the water.

c) We can work out the mass of one mole of ethanol and knowing how much heat energy is released when x g of ethanol is burned we can calculate the heat energy released when one mole of ethanol is burned. This will be equal to the enthalpy of combustion of ethanol.

A calorimeter is a device used to measure the amount of heat energy exchanged (released or absorbed) in a reaction. If a calorimetry experiment is carried out under a constant pressure, the heat transferred provides a direct measure of the enthalpy change of the reaction.

Simple determination of enthalpy of combustion can use a simple calorimeter.

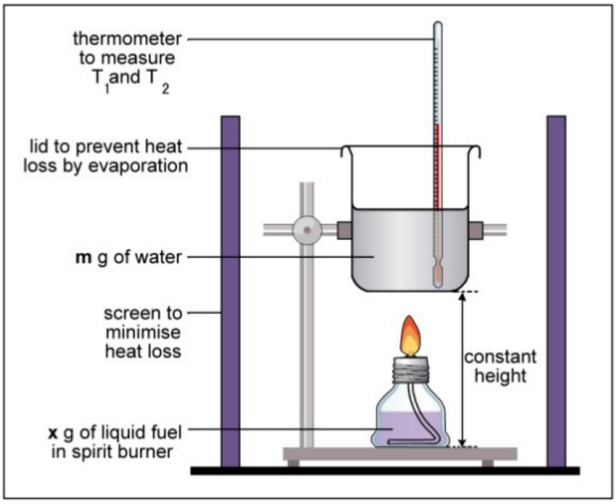


Figure 10.7: Determination of enthalpy of combustion using a simple calorimeter

The energy produced by the combustion of the fuel is used to heat a known mass (m) of water. Therefore, the heat provided by the fuel is equal to the heat received by water.

Its amount may be calculated using the relation: $q = m \times C_s \times \Delta T$

Where: m is the mass of water

Cs is the specific heat capacity of water

ΔT is the temperature change

Knowing the mass of the fuel used, its enthalpy of combustion may be calculated.

Example:

200 cm^3 of water were heated by burning ethanol in a spirit burner. The following mass measurements were recorded:

Mass of spirit burner and ethanol (before burning) = 58.25 g

Mass of spirit burner and ethanol (after burning) = 57.62 g

The initial temperature of the water was 20.7 °C and the highest temperature recorded was 41.0°C. The specific heat capacity of water is 4.18 $J\ g^{-1}\ K^{-1}$.

Calculate the value of the standard enthalpy change of combustion of ethanol in $kJ\ mol^{-1}$.

Answer:

$\Delta T = T_2 - T_1 = 41.0 - 20.7 = 20.3\ ^\circ C$

m = 200 g of water

x = mass of ethanol burned = 58.25 – 57.62 = 0.63 g

$n = \frac{\text{mass}}{M_m} = \frac{0.64}{46} = 0.01370\text{mol}$

$q = m \times C_s \times \Delta T = 200 \times 4.18 \times 20.3 = 16970.8\text{J}$

Heat energy change per mol of ethanol burned = $\frac{16970.8}{0.01370}$ = 1,238,744.526 J mol^{-1}

Standard enthalpy of combustion of ethanol is 1,238.744526 kJ mol^{-1}

Application activity 10.5

1. When 0.18 g of hexane underwent complete combustion, it raised the temperature of 100 g (0.1 kg) of water from 22 °C to 47 °C. Calculate its enthalpy of combustion.
2. The enthalpy of combustion of benzene is -3270 kJ mol^{-1}
   a) How much heat energy will be released if 30 g of C_6H_6 is burned in air?
   b) How many grams of carbon dioxide will be produced if 8800 kJ heat energy was released?

10.6 Experimental determination of the standard enthalpy change of neutralisation

Activity 10.6

To investigate the enthalpy of neutralization of hydrochloric acid by sodium hydroxide.

Requirements:

2 plastic beakers

50 mL of 1 M HCl

50 mL of 1 M NaOH

Thermometer

Scale

Weigh boats

Procedure:

1. Weigh an empty plastic beaker. Record the mass.
2. With a graduated cylinder, measure 50 mL of 1 M HCl and pour it into the plastic beaker.
3. With a thermometer, measure the temperature (T_1) of the HCl.
4. Rinse the graduated cylinder and measure 50 mL of 1 M NaOH.
5. Measure the temperature (T_2) of the NaOH.
6. Pour the NaOH into the plastic beaker and stir gently with the thermometer.
7. Record the highest temperature (T_3) that the thermometer reaches.
8. Weigh the plastic beaker and the liquid.

Discussion questions

1. Was the reaction exothermic or endothermic? How do you know?
2. Describe the flow of energy in the system.
3. Calculate the amount of heat the reaction gave off using

   $q = m \times C_s \times \Delta T$ ($C_s = 4.18$)
4. Calculate the moles of HCl and NaOH that reacted.
5. Calculate the molar enthalpy change, ΔH of this reaction using the relation above.
6. If the solutions used were more concentrated, would the value of q calculated be higher or lower?
7. If the solutions used were more concentrated, is the value of ΔH calculated higher or lower?

Calorimetry is also used to determine the enthalpy change of a reaction taking place in solution. For an exothermic reaction, the heat energy released increases the temperature of the water in solution while for an endothermic reaction, the heat energy absorbed is derived from water in the solution and the temperature of the solution falls.

When hydrochloric acid reacts with sodium hydroxide, the temperature of the mixture rises and the heat is transferred to the plastic beaker, the process is exothermic.

Example:

Consider the results from an experiment similar to the one described above:

The initial temperature: 26.7 ^{o}C

Final temperature: 33.5 ^{o}C

Temperature rise, ΔT = 33.5 ^{o}C - 26.7 ^{o}C = 6.8 ^{o}C

The mass of the solution = 100 g

Heat generated is used to heat the solution,

Enthalpy change = mass of the solution x specific heat capacity x temperature rise

$\Delta H = m \times Cs \times \Delta T$

$\Delta H = 100 \times Cs \times \Delta T$ joules

But 50ml of 1M HCl has 0.05mol and 50ml of 1M NaOH also has 0.05mol

Molar heat of the reaction = $\dfrac{-100 \text{ x } Cs \text{ x} \Delta T \text{ joules}}{0.05}$

$\Delta H = 2000 \times Cs \times \Delta T$ (J mol^{-1})

If the solutions used are more concentrated, the temperature increases and the amount of heat exchanged also increases. However, the molar enthalpy of neutralisation remains the same because when the concentration increases, the density increases as well as the number of moles.

Heat energy released = $q = m \times c \times \Delta t = 100 \times 4.18 \times 6.8 = 2842.4$J

Moles of acid used = 1mol dm^{-3}x 50 x10^{-3} dm^{-3} = 0.05 mol

Molar heat energy released in the neutralisation of 1 mole of the acid:

ΔH_{neut}= 2842.4 J/0.05 mol = 56,848 J mol^{-1} = 56.848 kJ mol^{-1}

The standard enthalpy of neutralisation between a strong acid and a strong base is approximately the same because a strong acid/base is completely dissociated in water.

The overall reaction of neutralization between a strong acid and a strong base is: $H^+ (aq) + OH^-(aq) \rightarrow H_2O (l)$

However, the reaction between a strong base and sulphuric acid releases more than 57 kJ.mol^{-1}. The addition of the base to sulphuric acid results in the dilution of the acid and this process (dilution of H_2SO_4) is exothermic.

The standard enthalpy of neutralisation involving weak acid or weak bases is less than 57 kJ because they are partially dissociated.

For example:

$$HCN(aq) \rightleftharpoons H+(aq) + CN-(aq)$$

When NaOH is added, the OH^- reacts with H^+ to yield H_2O following the reaction:

$$H^+ (aq) + OH^-(aq) \rightarrow H_2O (l) \qquad \Delta H = 57 \text{ kJ mol}^{-1}$$

The equilibrium will shift to the right side and more HCN will be dissociated. As the dissociation of HCN is endothermic, the total heat evolved will be less than 57 kJ mol^{-1}.

The standard enthalpy of neutralisation of HF (aq) (a weak acid) by a strong base is smaller than -57 kJ. $HF(aq) + NaOH(aq) \rightarrow NaF(aq) + H_2O(l)$ $\Delta H= - 68.6$ kJ mol^{-1} ***(heat released greater than 57kJmol^{-1})*** because the dissociation enthalpy of HF is negative due to the high hydration enthalpy of the fluoride ion which has a small radius. Therefore the overall heat evolved is more than 57 kJ mol^{-1}.

Application activity 10.6

1. An experiment was conducted to find out the enthalpy of neutralization of a weak acid, HX. 30 cm^3 of 1M HX solution were mixed with 40 cm^3 of 1M KOH (in excess) in a polystyrene cup. The temperature in the reaction was 5.0 °C. Calculate the enthalpy change of for the neutralization of the weak acid.
2. A student carried out an experiment to determine the enthalpy of the reaction when $NaHCO_3$ reacts with dilute hydrochloric acid. The student added 3.71g of $NaHCO_3$ to 30 cm^3 of 1M hydrochloric acid (excess) in a polystyrene cup. The temperature of the acid fell by 8.5 °C. Calculate the enthalpy change of the reaction.

10.7 Experimental determination of the standard enthalpy change of dissolution

Activity 10.7

To investigate the enthalpy of dissolution of ammonium nitrate.

Requirements

- spirit burner (containing ethanol)
- thermometer
- beaker
- measuring cylinder
- balance

Safety precautions

- Wear eye protection.

Procedure

Weigh 5g of ammonium nitrate (NH_4NO_3)

1. Using the measuring cylinder, measure out 50cm^3 into the beaker.
2. Set up the apparatus as directed by your tutor.
3. Transfer the ammonium nitrate in the can containing water.
4. Stir to 9dissolve
5. Record the temperature every 30 seconds until there is no more change in temperature

Study questions

1. What was the highest/lowest temperature recorded?
2. Was the reaction endothermic or exothermic?
3. Calculate the enthalpy change of potassium nitrate.

Some ionic compounds such as potassium iodide, sodium hydroxide and sodium chloride are very soluble while others like magnesium carbonate, are sparingly soluble or insoluble(calcium carbonate, magnesium hydroxide, barium sulphate). The dissolution of some compounds such as sodium hydroxide release the heat energy and the process is exothermic.

If a pair of oppositely charged gaseous ions is placed together, they are attracted to each other. The energy change (Lattice enthalpy) is highly exothermic. If the ions were placed in water, they would be attracted to the polar water molecules leading to the energy change (hydration enthalpy) which is highly exothermic. In both cases, the greater the charge density of the ions, the more exothermic will be the process.

The enthalpy change when one mole of a gaseous ion dissolves in water (excess) to give an infinitely dilute solution is called **Enthalpy change of hydration (ΔH_{hyd}).**

The solvent-solute interactions are referred as **"solvation".**

When an ionic compound dissolves in water, the process can either be exothermic or endothermic.

The enthalpy of solution of a compound is the heat energy change at constant pressure when one mole of a compound dissolves completely in water.

For example when sodium chloride dissolves in water, the overall process is represented as:

$$NaCl(s) + water \rightarrow Na^+(aq) + Cl^-(aq)$$

The first step is to separate the ions in the crystal. This requires energy to overcome the attractive forces between oppositely charged ions. The corresponding lattice dissociation energy according to the dissociation of the compound is:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq) \qquad \Delta H^o = +771 kJmol^{-1}$$

The second step involves the hydration of the ions:

$$Na^+(g) \rightarrow Na^+(aq) \quad \Delta H^o = -406 kJmol^{-1}$$

$$Cl^-(g) \rightarrow Cl^-(aq) \qquad \Delta H^o = -364 kJmol^{-1}$$

The hydration is an exothermic process as the ions form bonds with the water molecules.

The enthalpy of solution of an ionic compound can be calculated from the lattice enthalpy and the enthalpies of hydration.

Application activity 10.7

12.78g of solid potassium iodide were dissolved in 25.0 cm^3 of distilled water in an open polystyrene cup. The temperature of the water was observed to decrease by 13.7 °C. Assuming that the temperature drop was due to the dissolution of potassium iodide, calculate a value for the enthalpy change to 2 decimal places in $kJ\ mol^{-1}$.

The specific heat capacity of water is $4.18\ J\ g^{-1}\ K^{-1}$.

Skills Lab 10

Fossil fuels are called **non-renewable energy sources**, since it takes hundreds of millions of years for the Earth to produce new deposits of coal, oil and natural gas. In contrast, biofuels are considered **renewable energy sources** since corn, soy and other biomass can be grown indefinitely.

a) Evaluate the relevance of these statements in the context of our country.

b) Discuss the advantages of biofuels over fossil fuels.

End of unit assessment 10

1. a) Define the term enthalpy change.

   b) Define the term standard enthalpy change of reaction, using the following equation as an illustration: $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)\ \Delta H= -3120kJmol^{-1}$

   c) This reaction shows the combustion of ethane, but the standard enthalpy change of combustion of ethane is *not* $-3120\ kJ\ mol^{-1}$. Define the term *standard enthalpy change of combustion,* and explain why the standard enthalpy change of combustion of ethane isn't $-3120\ kJ\ mol^{-1}$.

2. 50.0cm^3 of 0.500M NaOH and 50.0cm^3 of 0.500M HNO_3 both at 20.0°C were mixed and stirred in a calorimeter with negligible heat capacity. The temperature of the mixture rose to 23.2°C.

   a) Calculate the change in enthalpy for the neutralization.

   b) Calculate the change in enthalpy per mole of water formed.

3. The standard enthalpy of combustion of propane is –2202 kJ mol^{-1}. Given that 0.015 mol of propane are burned completely and the fuel is used to heat 200 g of water (specific heat capacity 4.18 J g^{-1} K^{-1}), calculate the theoretical temperature change which would be measured.

4. 25.0cm^3 of 1M HCl at 21.5°C were placed in a polystyrene cup. 25.0cm^3 of 1M NaOH at 21.5°C were added. The mixture was stirred, and the temperature rose to 28.2°C. The density of each solution = 1.00g cm^{-3}, and the specific heat capacity of each solution = 4.18J$K^{-1}$$g^{-1}$. Calculate the standard molar enthalpy of neutralization.

5. The equation for the combustion of pentane is

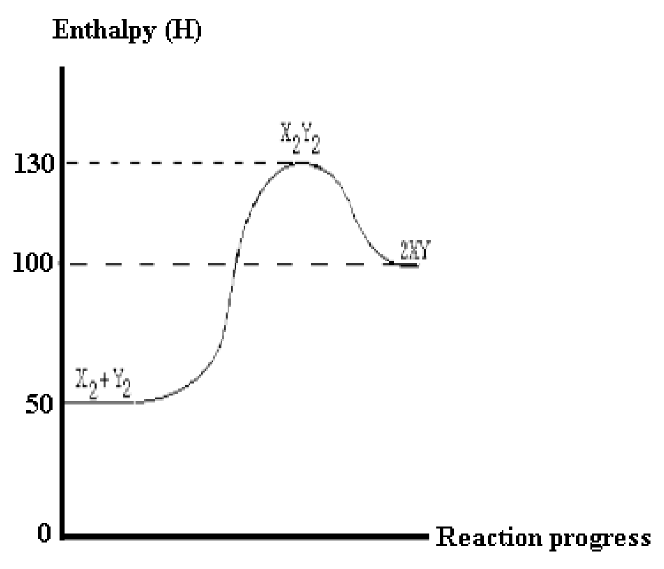
$$C_5H_{12}(l) + 8\,O_2(g) \rightarrow 5CO_2(g) + 6H_2O(g)$$

a) Use the mean bond enthalpy values given below to calculate the ΔH value for the combustion reaction. $\Delta H°$/ $kJmol^{-1}$ C-C = 348; C-H = 412; O-H = 463; O=O = 496; C=O = 743

b) Use the following enthalpy of formation data to calculate the ΔH value for the combustion reaction. $\Delta H°_f$/ $kJmol^{-1}$ $C_5H_{12}(l)$= -146; $CO_2(g)$= -394; $H_2O(g)$ = -242

c) Explain why the answers in a) and b) have different values.

Observe the diagram here after 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 2XY→X2 + Y2

l) Which one of the forward reaction and reverse reaction is more likely to be faster?

m) State the meaning of the term Activated complex.

n) Which chemical species or set of chemical species correspond to the state of maximum stability? Why?

o) What is the effect of catalyst if it is added to the above reaction

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