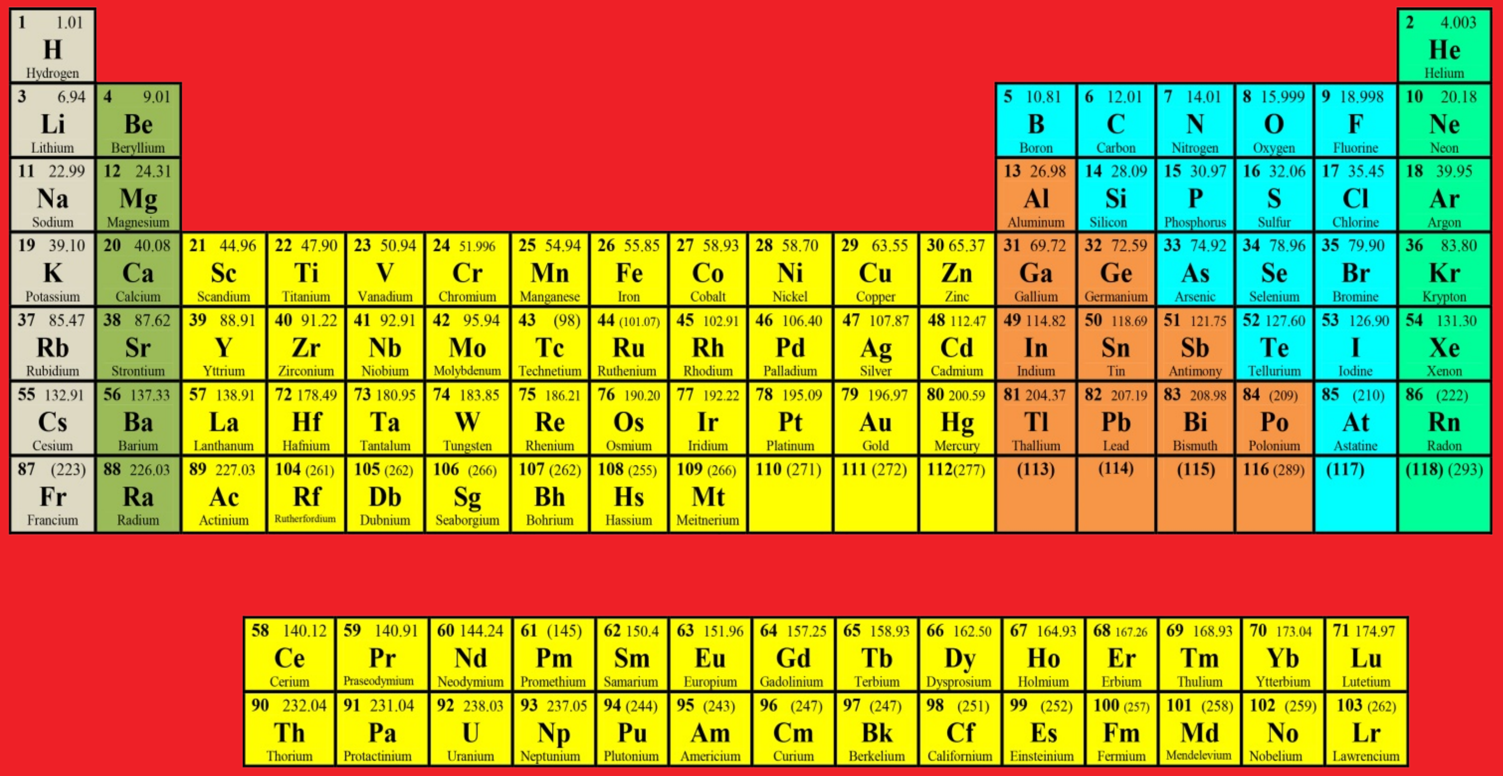
CHEMISTRY

Distance Module-II

GRADE 11



1 1.01 H Hydrogen																	2 4.003 He Helium
3 6.94 Li Lithium	4 9.01 Be Beryllium											5 10.81 B Boron	6 12.01 C Carbon	7 14.01 N Nitrogen	8 15.999 O Oxygen	9 18.998 F Fluorine	10 20.18 Ne Neon
11 22.99 Na Sodium	12 24.31 Mg Magnesium											13 26.98 Al Aluminum	14 28.09 Si Silicon	15 30.97 P Phosphorus	16 32.06 S Sulfur	17 35.45 Cl Chlorine	18 39.95 Ar Argon
19 39.10 K Potassium	20 40.08 Ca Calcium	21 44.96 Sc Scandium	22 47.90 Ti Titanium	23 50.94 V Vanadium	24 51.996 Cr Chromium	25 54.94 Mn Manganese	26 55.85 Fe Iron	27 58.93 Co Cobalt	28 58.70 Ni Nickel	29 63.55 Cu Copper	30 65.37 Zn Zinc	31 69.72 Ga Gallium	32 72.59 Ge Germanium	33 74.92 As Arsenic	34 78.96 Se Selenium	35 79.90 Br Bromine	36 83.80 Kr Krypton
37 85.47 Rb Rubidium	38 87.62 Sr Strontium	39 88.91 Y Yttrium	40 91.22 Zr Zirconium	41 92.91 Nb Niobium	42 95.94 Mo Molybdenum	43 (98) Tc Technetium	44 (101.07) Ru Ruthenium	45 102.91 Rh Rhodium	46 106.40 Pd Palladium	47 107.87 Ag Silver	48 112.47 Cd Cadmium	49 114.82 In Indium	50 118.69 Sn Tin	51 121.75 Sb Antimony	52 127.60 Te Tellurium	53 126.90 I Iodine	54 131.30 Xe Xenon
55 132.91 Cs Cesium	56 137.33 Ba Barium	57 138.91 La Lanthanum	72 178.49 Hf Hafnium	73 180.95 Ta Tantalum	74 183.85 W Tungsten	75 186.21 Re Rhenium	76 190.20 Os Osmium	77 192.22 Ir Iridium	78 195.09 Pt Platinum	79 196.97 Au Gold	80 200.59 Hg Mercury	81 204.37 Tl Thallium	82 207.19 Pb Lead	83 208.98 Bi Bismuth	84 (209) Po Polonium	85 (210) At Astatine	86 (222) Rn Radon
87 (223) Fr Francium	88 226.03 Ra Radium	89 227.03 Ac Actinium	104 (261) Rf Rutherfordium	105 (262) Db Dubnium	106 (266) Sg Seaborgium	107 (262) Bh Bohrium	108 (255) Hs Hassium	109 (266) Mt Meitnerium	110 (271)	111 (272)	112(277)	(113)	(114)	(115)	116 (289)	(117)	(118) (293)

58 140.12 Ce Cerium	59 140.91 Pr Praseodymium	60 144.24 Nd Neodymium	61 (145) Pm Promethium	62 150.4 Sm Samarium	63 151.96 Eu Europium	64 157.25 Gd Gadolinium	65 158.93 Tb Terbium	66 162.50 Dy Dysprosium	67 164.93 Ho Holmium	68 167.26 Er Erbium	69 168.93 Tm Thulium	70 173.04 Yb Ytterbium	71 174.97 Lu Lutetium
90 232.04 Th Thorium	91 231.04 Pa Protactinium	92 238.03 U Uranium	93 237.05 Np Neptunium	94 (244) Pu Plutonium	95 (243) Am Americium	96 (247) Cm Curium	97 (247) Bk Berkelium	98 (251) Cf Californium	99 (252) Es Einsteinium	100 (257) Fm Fermium	101 (258) Md Mendelevium	102 (259) No Nobelium	103 (262) Lr Lawrencium

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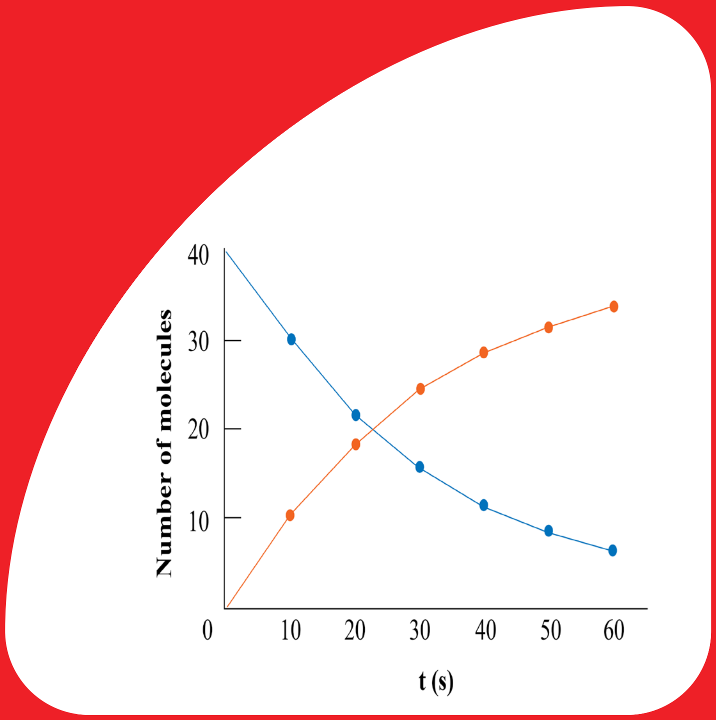
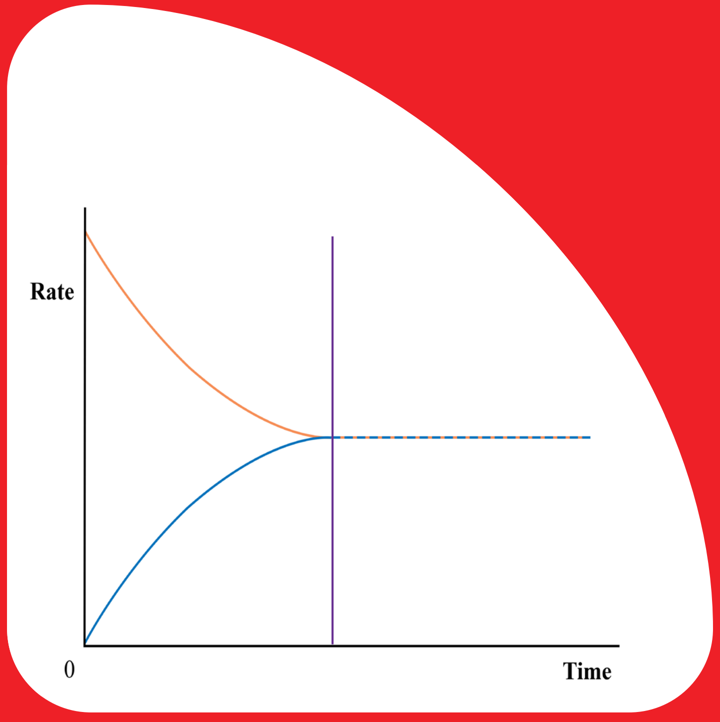
CHEMISTRY GRADE 11 DISTANCE MODULE - II

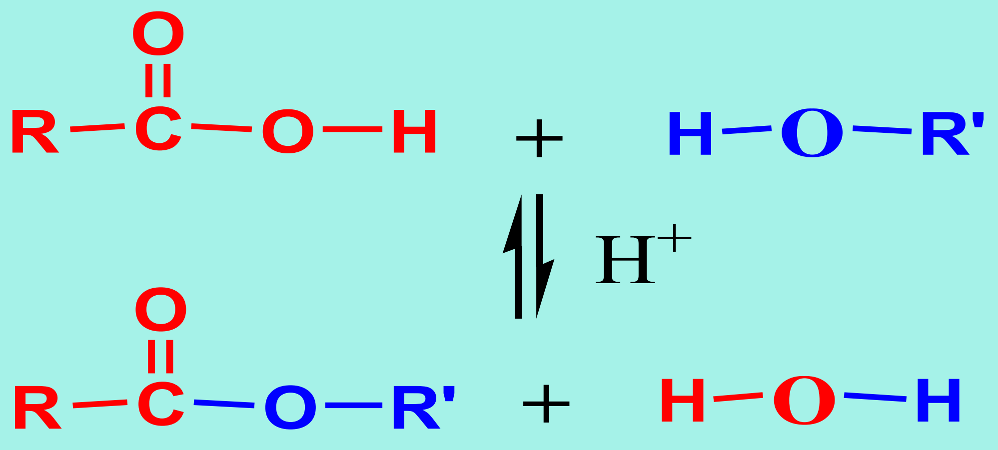
CHEMISTRY

Distance Module-II

GRADE 11







$$R-\overset{O}{\overset{\|}{C}}-O-H + H-O-R' \underset{}{\overset{H^+}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-O-R' + H-O-H$$

FEDERAL DEMOCRATIC REPUBLIC OF ETHIOPIA | MINSTRY OF EDUCATION

CHEMISTRY

Distance Module - II

GRADE 11

CHEMICAL KINETICS, EQUILIBRIUM, AND SOME IMPORTANT OXYGEN-CONTAINING ORGANIC COMPOUNDS

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Introduction to the Module

Dear learner! Grade 11 Chemistry course includes two modules. Module 1 is about the Atomic Structure, Chemical Bonding, and Physical States of matter. Module 2 deals with Chemical kinetics, equilibrium, and some important oxygen-containing organic compounds.

For each module, an assignment for submission is provided. After you go through the contents of each module try to answer the questions. Then, submit the assignment to your tutor. Ask your tutor for her/his response and comments so that you can improve your study. The assignments are part of the total evaluation of the course.

As a student enrolled in an independent study course, you have taken on a dual role that of a student and a teacher. As a student, you are responsible for mastering the lessons and completing the learning activities and assignments. As a teacher, you are responsible for checking your work carefully, noting areas in which you need to improve and motivating yourself to succeed.

This module deals with chemical kinetics, equilibrium, and some important oxygen-containing organic compounds.

Unit four is about **Chemical kinetics**, also known as **reaction kinetics**, is the branch of physical chemistry that is concerned with understanding the rates of chemical reactions. The rate of a reaction is a powerful diagnostic tool. By finding out how fast products are made and what causes reactions to slow down, we can develop methods to improve production. This information is essential for the large-scale manufacture of many chemicals, including fertilizers, drugs and household cleaning items. However, some questions have not been answered yet. These questions include: Do all reactions reach to completion? If not then how much of the reactants remain unreacted, that is, what is the extent of the reaction it took? etc. These questions can be answered after studying **chemical equilibrium** in **unit five**. In this unit, you will learn about chemical equilibrium, how it is attained, and factors that affect the position of chemical equilibrium.

Unit six is about some important oxygen-containing organic compounds. In Grade 10, you learned about some general organic reactions of hydrocarbons. In this unit, you will continue to learn more functional groups: oxygen-containing functional groups. The oxygenated hydrocarbons include alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, acid chlorides, amides and anhydrides. Alcohols occur widely in nature and have many industrial and pharmaceutical applications. Methanol, for example, is one of the most important of all industrial chemicals. Ethers are relatively resistant to chemical transformation and are often used as solvents in chemical reactions.

There are a number of symbols in the course materials so that it guides you as you study

☸ This tells you there is an overview of the unit and what the unit is about.

? This tells you there is an in-text question to answer or think about in the text.

☞ This tells you to take note of or to remember an important point.

⚒ This tells you there is a self-test for you to do

√ This tells you there is a checklist.

✍ This tells you there is a written assignment

🔑 This tells you that this is the key to the answers for the self-tests.

Module Content

UNIT 4: CHEMICAL KINETICS

UNIT 5: CHEMICAL EQUILIBRIUM

UNIT 6: SOME OXYGEN-CONTAINING ORGANIC COMPOUNDS

Module Assessment Methods

- You should complete regularly self-assessments by having them your progress will be evaluated.
- Contact your tutor regularly if possible face-to-face time to get oral feedback on your study progress for each section of a module.
- You should submit individual assignment on time and try to get feedback on your progress
- After completion of module 2, you will sit for final examination which composed of true/false items, multiple choice, fill in the black space, and short answer questions.

UNIT 4

CHEMICAL KINETICS

Unit Introduction

☸ Dear learner, this unit is about the rate of chemical kinetics. Chemical kinetics is the study of rates of chemical processes. This includes investigations of how different experimental conditions can influence the speed of a chemical reaction. The investigations yield information about the reaction's mechanism and transition states. The study of chemical kinetics also uses the construction of mathematical models that can describe the characteristics of a chemical reaction.

This unit is organized into three sections. The first section gives you the general introduction about the rate of a reaction. The second section is about how to determine rate of reaction. Rate of reaction tells us how fast a quantity of a reactant or a product is changing with time. The third section deals with factors that affecting the rate of a chemical reaction: the surface area of the reactants, the presence of a catalyst, the temperature and the concentration of the substances in the reaction mixture affect the rate of a reaction.

Unit Outcome

At the end of this unit, you will be able to:

- explain rate of reaction
- describe the pre-conditions for a chemical reaction to occur
- discuss factors that affect rate of chemical reaction.

The Required Study Time **2 weeks**

If you set an average of one hour per day, you will be able to complete unit one by the end of the assigned week. Try to do all the learning activities. And compare your answers with the one provided at the end of the Module.

If you do not get a particular exercise right in the first attempt, you should not get discouraged, but instead, go back and attempt it again. If you still do not get it right after several attempts, then you should seek help from your friend or even your tutor.

Unit Content

Unit Learning Strategies

- You should monitor your performance through planning, monitoring, and self-regulation
- You should manage the learning environment and available resources
- You should try all self-test exercises and written assignments
- You should surf on the internet for better understanding contents in the module.
- You should consult your tutor for further clarifications on some contents in the module.

Section 4.1: Introduction

Dear learner, this unit is about the rate of chemical reactions. Every chemical reaction proceeds at a different rates or speed. Some reactions proceed very slowly and may take a number of days to complete; while others are very rapid, requiring only a few seconds. For example, rusting of iron could start quickly, while ripening of fruits may be completed in a few days. On the other hand, weathering of stone may take more than a decade and the breakdown of plastics in the environment takes more than hundred years. However, other reactions, like the combustion of gasoline or the explosion of gunpowder occur in a few seconds.

Can you add more examples from your experience?

Activity 4.1

Dear learner, attempt to answer the following questions.

1. Does sugar dissolve faster in hot or in cold tea? Why?
2. How can we measure the rate of reaction?

To be useful reactions must occur at a reasonable rate. The area of chemistry that is concerned with reaction rates is called **chemical kinetics.** The word **"kinetic"** suggests movement or change.

Chemical kinetics is the study of reaction rates, the changes in the concentrations of reactants and products with time.

Section 4.2: The Rate of a Reaction

Dear learner, we know that some chemical reactions are very fast while other reactions occur moderately fast or slowly. In this section you will study how to accurately describe the rate of a given reaction. You will also investigate the conditions required for a chemical reaction to occur.

At the end of this section, you will be able to:

- define rate of reaction
- describe rate of reaction using graphs
- list the pre-conditions for a chemical reaction to occur, and
- explain how collision, activation energy and proper orientation of reactants cause a chemical reaction to occur.

Dear learner, can you work out the rate of reaction from its chemical equation? Equations only tell us how product we can get. They do not say how quickly it is made. We can only find the rate by actually doing experiments. The rate of a chemical reaction measures the change in concentration of a reactant or a product per unit time. The rate of a reaction determines how fast the concentration of a reactant or product changes with time.

The rate of reaction tells us how quickly a chemical reaction happens. For example, for a general reaction:

$$\text{Reactants} \rightarrow \text{Products}$$

The above equation tells us that, during the course of a reaction, reactant molecules are consumed while product molecules are formed. The progress of a reaction can be followed by monitoring either the decrease in concentration of the reactants or the increase in concentration of the products.

Consider the progress of a simple reaction in which A molecules are converted to B molecules:

$$A \rightarrow B$$

The decrease in the number of A molecules and the increase in the number of B molecules with time are shown in **Figure 4.1.** In general, it is more convenient to express the rate in terms of change in concentration with time.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of substance}}{\text{Change in time}} = \frac{\Delta c}{\Delta t}$$

Note that Δ denotes the difference between the final and initial state of concentration. Thus, for the preceding reaction we can express the rate as:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

in which, Δ[A] and Δ[B] are the changes in concentration (mol. L^{-1}) over a period Δt. Because the concentration of A decreases during the time interval, Δ[A] is a negative quantity. The rate of a reaction is a positive quantity, so a minus sign is needed in the rate expression to make the rate positive. On the other hand, the rate of product formation does not require a minus sign because Δ[B] is a positive quantity (the concentration of B increases with time).

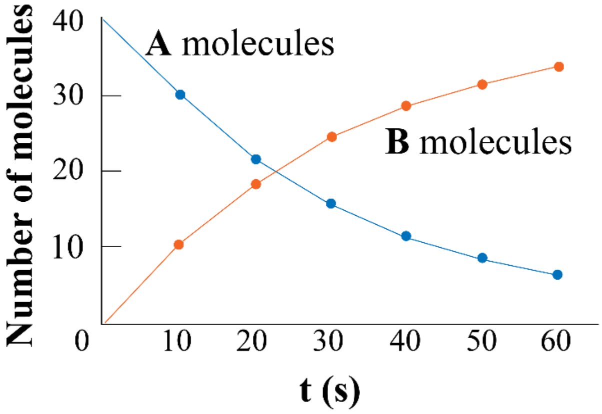


Figure 4.1: The rate of reaction A → B, represented as the decrease of A molecules with time and the increase of B molecules with time.

For more complex reactions, we must be careful in writing the rate expression. Consider, for example, the reaction:

$$2A \rightarrow B$$

Two moles of A disappear for each mole of B that forms, that is, the rate at which B forms half of the rate at which A disappears. We write the rate as either:

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

Similarly, for the reaction:

$$aA + bB \rightarrow cC + dD$$

$$\text{Rate} = -\frac{1}{\alpha}\frac{\Delta[A]}{\Delta t} = \frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Example 4.1

1. Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:

   a. $I^-(aq) + OCl^-(aq) \rightarrow Cl^-(aq) + OI^-(aq)$

   b. $3O_2(g) \rightarrow 2O_3(g)$

   c. $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Solution:

a. Because each of the stoichiometric coefficients equals 1,

$$\text{Rate} = -\frac{\Delta[I^-]}{\Delta t} = -\frac{\Delta[OCl^-]}{\Delta t} = \frac{\Delta[Cl^-]}{\Delta t} = \frac{\Delta[OI^-]}{\Delta t}$$

b. Here the coefficients are 3 and 2, so

$$\text{Rate} = -\frac{1}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[O_3]}{\Delta t}$$

c. In this reaction:

$$\text{Rate} = -\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = \frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

2. In the reaction of nitric oxide with hydrogen:

   $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

   If the rate of disappearance of NO is 5.0×10^{-5} mol $L^{-1}s^{-1}$, what is the rate of reaction for the formation of N_2?

   Solution:

   The rate of reaction for the formation of N_2

$$\text{Rate} = \frac{\Delta[N_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[NO]}{\Delta t} = -\frac{1}{2}\left(-5.0\times10^{-5}\ \text{mol L}^{-1}\ \text{s}^{-1}\right)$$

   rate = 2.5×10^{-5} mol $L^{-1}s^{-1}$

Self-test Exercise 4.1

1. The rate of a chemical reaction can be expressed in:

   a. grams per mole b. energy consumed per mole

   c. volume of gas per unit time d. moles formed per liter of solution

2. Consider the following reaction:

   $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

   a. the rate of formation of O_2 is four times the rate of NO_2 formation

   b. the rate of formation of NO_2 is twice the rate of N_2O_5 disappearance

   c. the rate of N_2O_5 disappearance half of the rate of O_2 formation

   d. the rate of O_2 formation is twice the rate of the rate of O_2 formation

3. Write the rate expression for the following reaction:

   $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

   a. the formation of CO_2 and H_2O

   b. the disappearance of CH_4 and O_2

4. The reaction for the formation of ammonia is given as:

   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

   Write the rate reaction for:

   a. the formation of NH_3

   b. the disappearance of N_2 and H_2

Determination of Rate of Reaction

Reaction rate is change in an observable property over time. The observable property should be selected based upon what can be measured in the laboratory. This could be a color change, a temperature change, a pressure change, a mass change, or the appearance of a new substance (for example, amount of precipitate formed).

Some reactions are exothermic, which means they release heat, while others are endothermic, they absorb heat.

By checking the temperature of the reaction mixture using a thermometer, it is possible to note if there is a reaction going on even if the formation of solid or a color change is absent.

How can we measure the rate of reaction?

The speed of reaction can be determined in three ways:

- measuring the time taken for a reaction to complete,
- measuring the amount of product formed against time, and
- measuring the amount of reactant used up or remaining against time

Consider, for example, the thermal decomposition of gaseous dinitrogen pentoxide, N_2O_5, to give the brown gas nitrogen dioxide:

$$\begin{array}{ccccc} 2N_2O_5(g) & \rightarrow & 4NO_2(g) & + & O_2(g) \\ \text{Colorless} & & \text{Brown} & & \text{Colorless} \end{array}$$

Changes in concentration as a function of time can be determined by measuring the increase in pressure as 2 gas molecules are converted to 5 gas molecules. Alternatively, concentration changes can be monitored by measuring the intensity of the brown color due to NO_2 formation. Reactant and product concentrations as a function of time at 55 °C are listed in **Table 4.1.** Using this data, we can calculate the rate:

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Table 4.1 Concentrations (mol $L^{-1}s^{-1}$) as a function of time at 55 °C for the thermal decomposition of gaseous dinitrogen pentoxide **(N_2O_5)**

Time (s)	N_2O_5	NO_2	O_2
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

Note: The concentration of NO_2 and O_2 increase as the concentration of N_2O_5 decreases.

In the decomposition of N2O5, the rate of formation of O2 is given by the equation:

$$\text{Rate of formation of } O_2 = \frac{\Delta[O_2]}{\Delta t}$$

$$= \frac{\text{Conc. of } O_2 \text{ at time } t_2 - \text{Conc. of } O_2 \text{ at time } t_1}{t_2 - t_1}$$

During the time period 300 to 400 s, for example, the average rate of formation of O_2 is 9×10^{-6} mol $L^{-1}s^{-1}$:

$$\text{Rate of formation of } O_2 = \frac{[O_2]}{t} = \frac{0.0049\ M - 0.0040\ M}{400\ s - 300\ s}$$

$$= 9 \times 10^{-6} \text{ mol } L^{1}\ s^{1}$$

The average rate of formation of NO_2 during the time period 300 – 4 00 s is 3.7 × 10^{-5} mol L^{-1} s^{-1}, which is four times the rate of formation of O_2, in accord with the 4:1 ratio of the coefficients of NO_2 and O_2 in the chemical equation for the decomposition of N_2O_5.

$$\text{Rate of formation of } NO_2 = \frac{\Delta[NO_2]}{t} = \frac{0.0197\ M - 0.0160\ M}{400\ s - 300\ s}$$

$$= 3.7 \times 10^{-5} \text{ mol } L^{1}\ s^{1}$$

Similarly, during the time period 300 – 400 s, the average rate of decomposition of N_2O_5 is 1.9 × 10^{-5} mol L^{-1} s^{-1};

$$\text{Rate of formation of } N_2O_5 = -\frac{\Delta[N_2O_5]}{t} = \frac{-(0.0101\ M - 0.0120\ M)}{400\ s - 300\ s}$$

$$= 1.9 \times 10^{-5} \text{ mol } L^{1}\ s^{1}$$

It's important to specify the time when quoting a rate because the rate changes as the reaction proceeds.

For example, the average rate of formation of NO_2 is 3.7 × 10^{-5} mol L^{-1} s^{-1} during the time period 300 – 400 s, but it is only 2.2 × 10^{-5} mol L^{-1} s^{-1} during the period 600 –700 s. In general, the rate of reaction at the beginning is fast and it decreases as the reaction proceeds.

What could be the possible reason for this decrease in the rate of reaction with time?

Plotting the data of **Table 4.1** gives the three curves in **Figure 4.2.** Looking at the time period 300 – 400 s on the O_2 curve, $\Delta[O_2]$ and Δt is represented, respectively, by the vertical and horizontal sides of a right triangle. The slope of the third side, the hypotenuse of the triangle, is $\Delta[O_2]/\Delta t$, the average rate of O_2 formation during that period.

> The steeper the slope of the hypotenuse, the faster the rate.

For example, compare the hypotenuse of the triangle defined by $\Delta[NO_2]$ and Δt during the time period 300–400 s and 600–700 s.

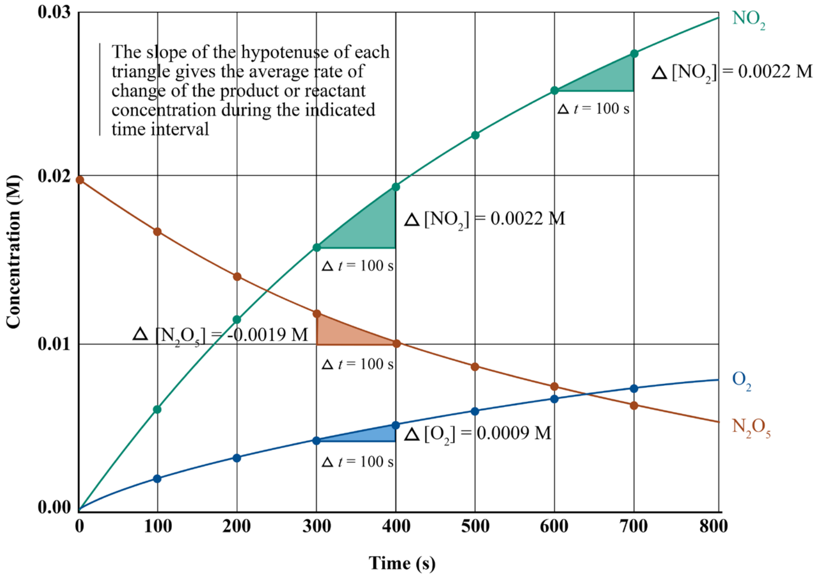


Figure 4.2: Concentrations as a function of time when gaseous N_2O_5 decomposes to gaseous NO_2 and O_2 at 55 °C.

It is important to realize that, given the initial concentrations in **Table 4.1** the concentrations of $NO_2(g)$ and $O_2(g)$ can be calculated from the concentration of $N_2O_5(g)$ at any time. The following example illustrates such a calculation.

Example 4.2

Using the data in **Table 4.1**, if $[N_2O_5] = 1.20 \times 10^{-2}$ mol L^{-1} at 300 s, calculate $[NO_2]$ and $[O_2]$ at t = 300 s.

Solution:

The chemical equation is: $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2} O_2(g)$. The number of moles per liter of $N_2O_5(g)$ that have reacted in 300 s is the difference between the initial concentration and the concentration at 300 s $[N_2O_5]$. From **Table 4.1**. $[N_2O_5]_0 = 2.00 \times 10^{-2}$ mol L^{-1}.

Molarity of $N_2O_5(g)$ reacted $= [N_2O_5]_0 - [N_2O_5] = 2.00 \times 10^{-2}$ mol $L^{-1} - 1.20 \times 10^{-2}$ mol $L^{-1} = 0.8 \times 10^{-2}$ mol L^{-1}.

According to the chemical equation, 2 moles of $NO_2(g)$ are provided for every mole of $N_2O_5(g)$ that reacts. So, per liter, we have:

$$\text{Molarity of } NO_2(g) \text{ produced} = 0.8 \times 10^{-2} \text{ mol } L^{-1}\ N_2O_5 \left(\frac{2 \text{ mol } L^{-1}\ NO_2}{1 \text{ mol} L^{-1}\ N_2O_5}\right)$$

$$= 1.6 \times 10^{-2} \text{mol } L^{1}$$

Similarly, for $O_2(g)$ we have:

$$\text{Molarity of } O_2(g) \text{ produced} = 0.8 \times 10^{-2} \text{ mol } L^{-1}\ N_2O_5 \left(\frac{\frac{1}{2} \text{ mol } L^{-1}\ NO_2}{1 \text{ mol} L^{-1}\ N_2O_5}\right)$$

$$= 0.4 \times 10^{-2} \text{ mol } L^{1}$$

Hello! Learner, often, chemists want to know the rate of a reaction at a specific time t rather than the rate averaged over a time interval Δt. For example, what is the rate of formation of NO_2 at time t = 350 s? Such instantaneous rate is calculated from the slope of a tangent drawn at any points on the graph of concentrations versus time (Figure 4.2). The slope of tangent taken at the initial point of the graph is assumed to be equal to its initial rate. In the initial rate the change in concentration of a reactant or product as a function of time is measured within minutes (or seconds) the reaction starts.

Example 4.3

Consider the gas-phase reaction that occurs when we mix 1.000 moles of hydrogen and 2.000 moles of iodine chloride at 230 °C in a closed 1.000 liter container.

$$H_2(g) + 2ICl(g) \longrightarrow I_2(g) + 2HCl(g)$$

From the experimental data given in the table below, determine the instantaneous rate of reaction at time, *t* = 2 s.

Time (s)	0	1	2	3	4	5	6	7	8
[ICl] (mol L^{-1})	2.000	1.348	1.052	0.872	0.748	0.656	0.586	0.530	0.484
[H_2] (mol L^{-1})	1.000	0.674	0.526	0.436	0.374	0.328	0.293	0.265	0.242

Solution:

First, plot of H_2 concentration versus time for the reaction of 1.000 M H_2 with 2.000 M ICl. Then, draw a tangent line to the curve. The instantaneous rate of reaction at any time, *t*, equals the negative of the slope of the tangent to this curve at time *t*. **Figure 4.3** shows how to find the instantaneous rate at *t* = 2 seconds.

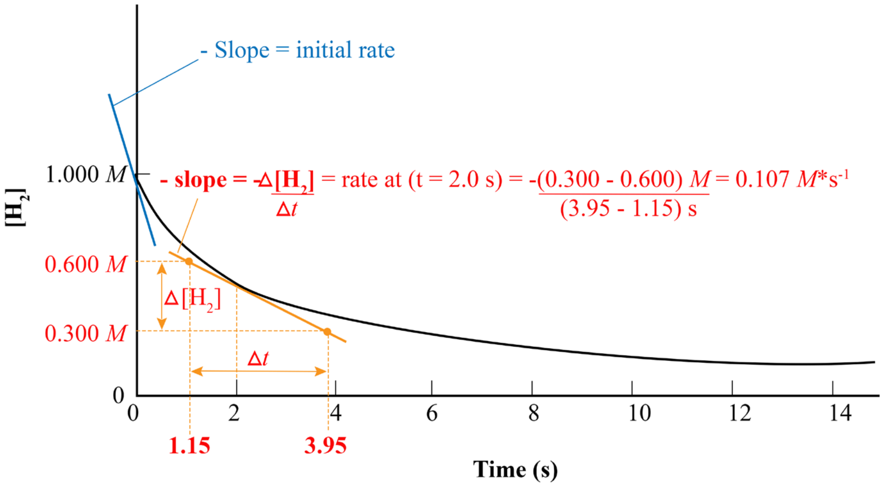


Figure 4.3: A plot of the hydrogen concentration versus time, using data of the above table.

Self-test Exercise 4.2

1. Consider the following reaction:

   $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

   under certain conditions, the rate of decomposition of N_2O_5 is 2.5×10^{-6} mol/s. The rate of formation of NO_2 is:

   a. 1.0×10^{-5} mol/s b. 1.3×10^{-6} mol/s

   c. 2.5×10^{-6} mol/s d. 5.0×10^{-6} mol/s

2. Consider the following reaction:

   $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

   At a certain temperature, 1.0 mol CH_4 is consumed in 4.0 minutes (refer question number 3). The rate of production of H_2O is:

   a. 0.25 mol/min b. 0.50 mol/min c. 2.0 mol/min d. 8.0 mol/min

3. The reaction for the formation of ammonia is given as:

   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

   Write the rate reaction for:

   If the rate of formation of NH_3 is 9.0×10^{-4} mol/s (refer question number 5), then the rate of consumption of N_2 is:

   a. 4.5×10^{-4} mol/s b. 6.0×10^{-4} mol/s

   c. 9.0×10^{-4} mol/s d. 1.4×10^{-3} mol/s

4. Using the initial concentrations and the fact that $[O_2] = 0.64 \times 10^{-2}$ mol. L^{-1} at $t = 600$ s in **Table 4.1**, calculate $[N_2O_5]$ and $[NO_2]$ at $t = 600$ s.

Experiment 4.1

Measuring the Rate Reaction

Objective: To measure the rate of reaction between marble chips ($CaCO_3$) and dilute HCl acid.

Apparatus: Direct reading balance, 100 mL conical flask, stopwatch, cotton wool.

Chemicals: 2M dilute HCl acid , and marble chips/$CaCO_3$.

Procedure:

1. Set up the apparatus as shown in Figure 4.4, but without the marble chips at first.
2. Add 20 g of pure marble chips, in a clean 100 mL conical flask.
3. Add 40 mL of 2M dilute HCl acid to the conical flask.
4. Plug the cotton wool in position immediately.
5. Read the mass of the flask and its contents and start the stopwatch.
6. Record the mass at one minute intervals for 10 minutes.

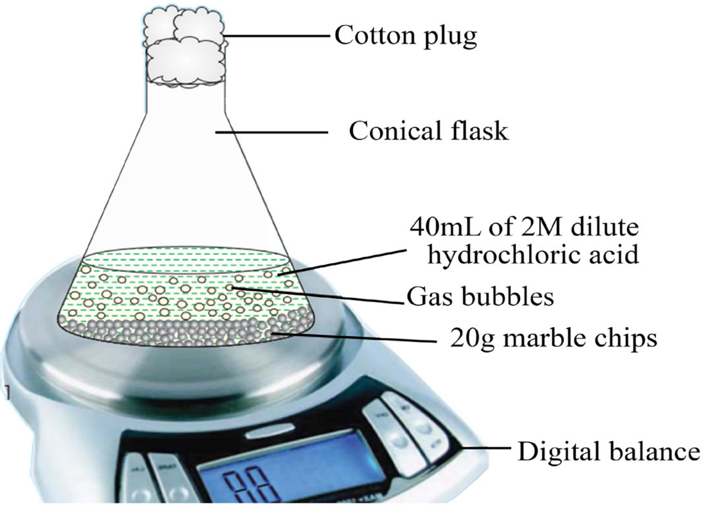


Figure 4.4: The laboratory set up for the measurement of rate of reaction

Observations and analysis:

1. Use the following table to record your observations.

Time (min)	0	1	2	3	4	5	6	7	8	9	10
Mass (g)											
Decrease in mass (g)											

Plot a graph with time (minutes) on the horizontal axis and rate on the vertical axis. Draw a smooth curve through as many points as possible. **Note** that in this experiment change in mass is proportional to change in concentration.

2. What happens to the mass during the reaction? Explain this with the help of a balanced equation.
3. What information can be obtained from the slope of this graph at any point?
4. Why is the graph
   a. steep at the start of the reaction?
   b. less steep in the middle of the reaction?
   c. horizontal at the end of the reaction?
5. Calculate:
   a. The average rate of the reaction. b. The rate of reaction at 2 minutes.
6. Describe how the rate of reaction changes with time.
7. Can we measure the rate of this reaction by measuring the amount / volume of CO_2 evolved?
8. Draw a graph of the expected result by plotting volume of CO_2 evolved vs time.

Conditions needed for a chemical reaction

Dear learner, different factors can affect the rate of reactions. In order to have a better understanding in each factor affecting the reaction rate, you need to know first the term **collision theory**. This theory used to predict the rates of chemical reactions. The assumption of the collision theory is that chemical reactions take place due to the collision between molecules.

☞ Collision theory is a model that describes how the rate of a chemical reaction is determined by the collisions between reacting particles.

Activity 4.2

Dear learner, ethanol can easily burn in air due to the following reaction.

$CH_3CH_2OH + O_2 \rightarrow CO_2 + H_2O$

In actual practice, you are required to use a lighter (igniter) to start the reaction. Why?

i. Collisions between reactants

The collision theory of rate of reaction is that, in order for a reaction to occur between reacting species (atoms, ions or molecules), they must first collide (come in contact).

> The rate of reaction is directly proportional to the number of collisions per second (the frequency of collision).

$$\text{Rate} \ \alpha \ \frac{\text{number of collisions}}{\text{second}}$$

ii. Proper Orientation

According to collision theory, the more collisions there are the faster the rate of reaction would be. Not all collisions between reacting species result in a reaction. This is because collisions between reactants can be either effective or ineffective. Thus, the collision between molecules should have the proper orientation (**Figure 4.5**).

> Effective collisions are collisions that result in a reaction to form the desired products.
>
> Ineffective collisions are collisions that do not result in a reaction to form the desired products.

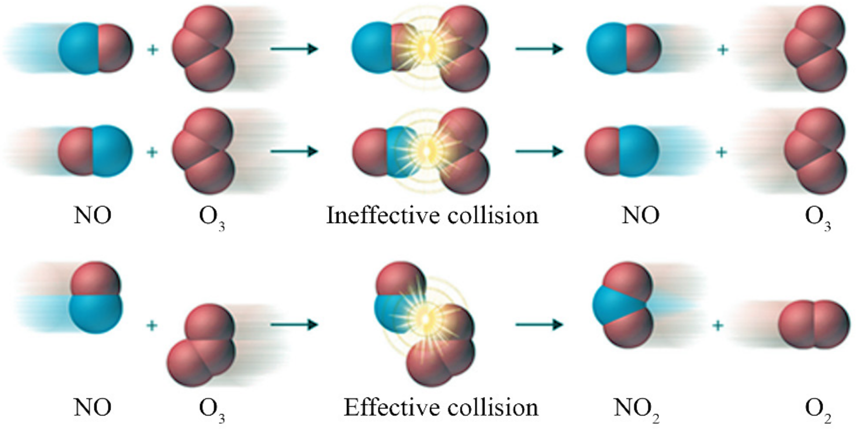


Figure 4.5: The effect of molecular orientation on the reaction of NO and O_3

iii. Activation energy

If the collisions between the reactant molecules do not have sufficient energy, then no reaction will occur. Therefore, for the reaction to take place collision must always occur with sufficient energy to break the bonds in the reactants and form new bonds in the product.

☞ The minimum amount of energy needed for the reaction is known as activation energy, E_a.

According to the kinetic molecular theory, the average kinetic energy of the particles of a substance is directly proportional to the absolute temperature. As the temperature of the reacting species is raised, the average kinetic energy of the reacting particles increases considerably. This causes the particles of the reactants to collide more frequently and with greater energy. This results in increase in reaction rate.

√ CHECKLIST 4.1

In the boxes provided for each of the following tasks put a tick mark (√) if you can perform or concepts you are familiar with them.

I can…

- define rate of reaction ☐
- describe rate of reaction using graphs ☐
- list the pre-conditions for a chemical reaction to occur, and ☐
- explain how collision, activation energy and proper orientation of reactants cause a chemical reac-tion to occur ☐

Section 4.3: Factors Affecting the Rate of a Chemical Reaction

Dear learner, the rates at which reactants are consumed and products are formed during chemical reactions vary greatly. Even a chemical reaction involving the same reactants may have different rates under different conditions. For example, sugar crystals dissolve more easily in hot water than in cold water. Powdered sugar dissolved easily as compared to equivalent amounts of sugar crystals. In this section you will study how the change in temperature, concentration, nature of reactant, surface area and presence of a catalyst affect the rate of reaction.

At the end of this section, you will be able to:

- list factors that affect the rate of a chemical reaction
- describe the effects of changes in temperature, concentration or pressure and surface area on the rates of a chemical reaction
- explain the effect of catalysts on the rates of chemical reaction.

I. Nature of the reactants

The rate of a reaction depends on the chemical nature of the substances in the reaction. The combination of two oppositely charged ions usually occurs very rapidly. For example, the reaction of an acid with a base is:

$$H_3O^+ + OH^- \longrightarrow 2H_2O$$

Activity 4.3

Dear learner, compare how fast the following substances burn.

a. paper b. wood charcoal c. alcohol

Dear learner, consider **Experiment 4.2** to study the effect of the nature of reactants on rate of reaction.

Experiment 4.2

The Effect of Nature of Reactants on Rate of Reaction

Objective: To study the effect of the nature of reactant for the reaction of copper and magnesium metals with hydrochloric acid.

Apparatus: Balance, test tubes, test tube stand.

Chemicals: Copper (Cu), magnesium (Mg), 2M hydrochloric acid (HCl).

Procedure:

1. Measure equal masses of copper and magnesium metals using a balance.
2. Record the weighed mass of these metals and add each to separate test tubes.
3. Assemble the test tubes as shown in Figure 4.6.
4. Add equal volume of 5 mL of 1M HCl to both the test tubes.
   Wear your safety goggles and gloves.
5. Observe relative rates of reaction in both test tubes and record your observations.

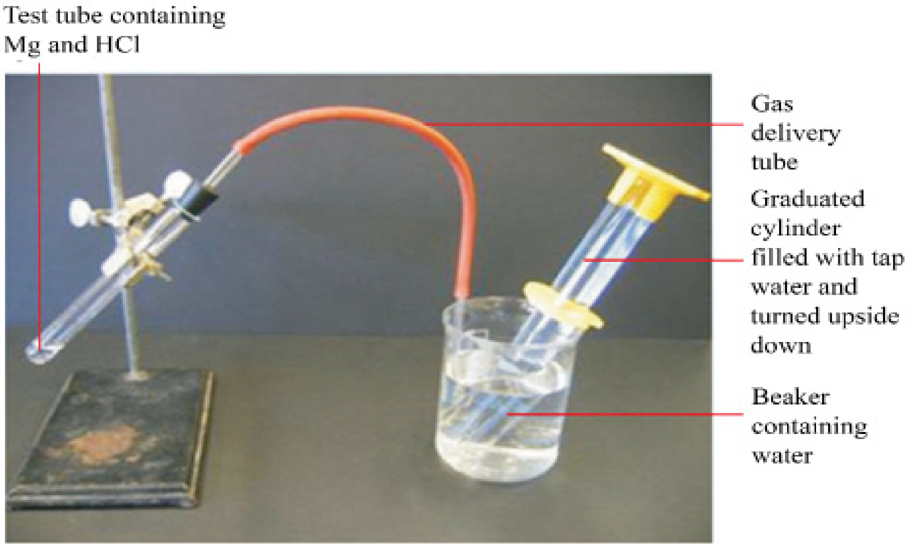


Figure 4.6: The reaction of magnesium with HCl acid

Observations and analysis

1. Which of these two metals, copper or magnesium, reacts faster? Why?
2. Write the balanced chemical equation for the reaction of
   a. copper with HCl acid   b. magnesium with HCl acid
3. What do you learn from this experiment?
4. Perform a similar activity using different metals such as aluminum, and zinc. In which case do you expect the reaction to be faster and why?

The acid-base reaction of HCl and NaOH is much faster than the decomposition of hydrogen peroxide, which involves the reorganization of molecules.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Even similar reactions may have different rates under the same conditions. For example, if small pieces of the metal iron and sodium are left in air, the sodium reacts completely overnight, whereas the iron is barely affected.

? Can you write the balanced equation for the reaction of sodium and calcium with water?

II. Surface Area of Reactants

Hello! Dear learner, you know that meat and vegetables can be cooked more quickly by cutting them into small pieces. This is because the smaller the size of the particles, the faster the reaction. By increasing the surface area of any solids involved in a chemical reaction, you can increase the speed of the reaction.

Activity 4.4

Dear learner, why powdered sugar dissolved easily in water as compared to equivalent amounts of sugar crystals?

Dear learner, consider the Experiment 4.3 to study the effect of surface area on rate of reaction.

Experiment 4.3

Effect of surface Area on Reaction Rate

Objective: To study the effect of surface area of reactants on the rate of reaction using cube chalk and powdered chalk with dilute hydrochloric acid.

Apparatus: Direct reading balance, 100 mL conical flask, stopwatch, cotton wool.

Chemicals: Cube chalk, powered chalk and 2M dilute HCl solution

Procedure: Repeat **Experiment 4.1** but use 20 g of small cubical chalk and then powdered chalk in place of marble chips.

Observations**:** In which case is the gas produced faster?

Observations and analysis:

1. Compare the rate curve, average rate and reaction rate at 2 minutes with that of Experiment 4.1. Explain your observations.
2. Sketch a graph for the consumption of each size of chalk (cube chalk and powdered chalk) against time on the same graph sheet.
3. Write a conclusion to the experiment.

Reactions can be classified as homogeneous (same phase) and heterogeneous (different phases). For example, the combustion of graphite is a heterogeneous reaction because it involves a solid with gas.

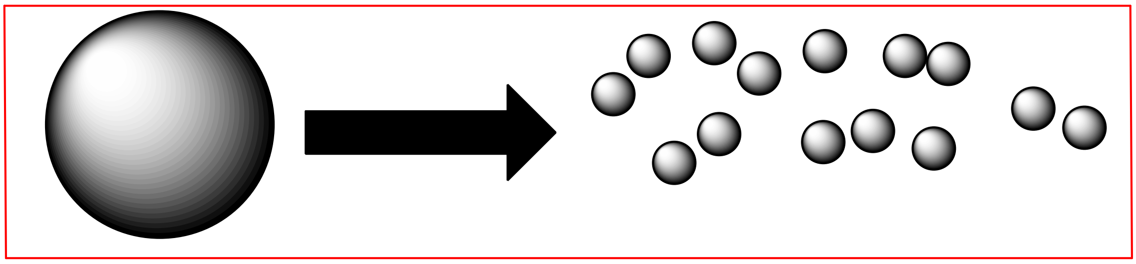
☞ In a heterogeneous, the reaction occurs only at the interface (boundary) between two phases.

? Why does a wood fire burn faster if the logs are chopped into smaller pieces?

☞ A homogeneous reaction occurs only in one phase.

For example: NO (g) $\longrightarrow$ ½N_2(g) + ½O_2(g)

Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. The rate of reaction between two phases depends to a great extent on the surface area of contact between them. Finely divided solids, react more rapidly than the same amount of the substance in a large body because of the greater surface area available.



A large particle has smaller surface

Smaller particles have a larger total surface area

III. Concentration of Reactants

Dear learner, recognize that at a fixed temperature, the rate of a given reaction depends on the concentration of the reactants.

Dear learner, consider Experiment 4.4 to study the effect of concentration of acid on the rate of reaction between $CaCO_3$ and hydrochloric acid.

Experiment 4.4

Effect of Concentration on Reaction Rate

Objective: To study the effect of concentrations of hydrochloric acid on rate of reaction with marble chips.

Apparatus: Direct reading balance, 100 mL conical flask, stopwatch, cotton wool

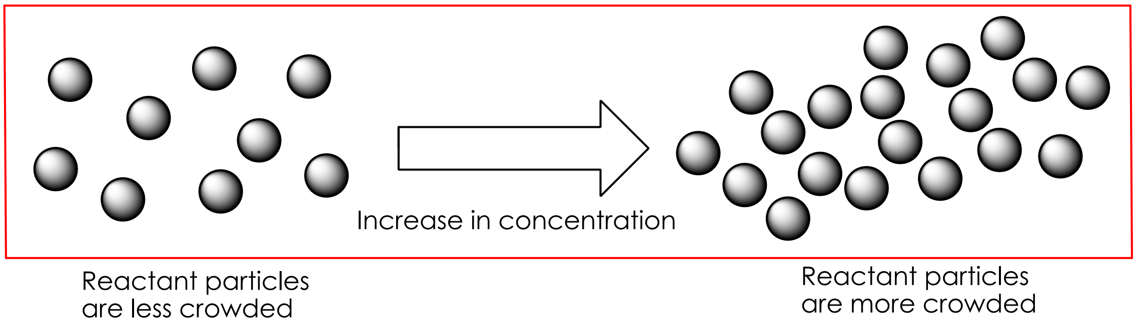
Chemicals: 1M HCl, 2M HCl dilute solutions and marble chips ($CaCO_3$).

Procedure: Repeat **Experiment 4.1** but you have to use 1M dilute HCl acid in place of 2M dilute HCl acid.

Observations and analysis:

1. Compare the rate of reaction with that in **Experiment 4.1.** Which reaction is more vigorous? Explain.
2. Which of the two reactions will produce more carbon dioxide? Explain your answer.
3. What would happen to the rate curve and average rate if:
   a. 1M HCl is replaced with 4M dilute HCl acid? Explain.
   b. 1M HCl is replaced with 0.5M dilute HCl acid? Explain.
4. Sketch a graph for each of 0.5 M, 1M, 2M and 4M dilute HCl acid against time on the same graph sheet.

? Why does limestone ($CaCO_3$) deteriorate more rapidly in highly polluted air than in less polluted air?



Reaction rates often increases when the concentration of one or more of the reactants increases.

This is because increasing the concentration produces more contacts between the reacting particles, which results in increasing the rate of reaction. In the case of reactions that involve gaseous reactants, an increase in pressure can increase the concentration of the gases which may lead to an increase in the rate of reaction.

Pressure change has no effect on the rate of reaction if the reactants are either solids or liquids.

IV. Temperature of Reactants

Dear learner, you know that temperature is very important in influencing the speed of reactions.

Activity 4.5

Dear learner, try to answer the following questions.

1. Why sugar crystals dissolve more easily in hot water than in cold water?
2. Why do we keep foods in refrigerator rather than at room temperature?

In Experiment 4.5, you will study the effect of temperature on the rate of reaction of $Na_2S_2O_3$ with HCl.

Experiment 4.5

The Effect of Temperature on Reaction Rate

Objective: To study the effect of temperature on the rate of reaction between sodium thiosulphate and hydrochloric acid.

Apparatus: 100 mL beakers, test tubes, thermometers, white paper, pencil.

Chemicals: 0.5M HCl acid, 0.1M $Na_2S_2O_3$ solution, pieces of ice.

Procedure:

1. Take 25 mL of 0.1M $Na_2S_2O_3$ solution in a test tube and 25 mL of 0.5M HCl acid in another test tube.
2. Prepare three such sets and maintain them at different temperatures.
   Set (i) at 0 °C [by keeping them in an ice bath as shown in Figure 4.7 (a)].
   Set (ii) at room temperature.
   Set (iii) at 40 °C (by heating the two solutions in a water bath).
3. Put a cross sign on a white cardboard and place a clean dry 100 mL beaker above it.
4. Now, pour the contents of set (i) in the beaker and start a stopwatch immediately.
5. Carefully stir the mixture with thermometer and record the time taken for the cross to disappear [Figure 4.7 (b)].
6. Repeat steps 3, 4, and 5 with set 2 and set 3, respectively.
7. Tabulate your results as temperature in °C versus time in minutes.

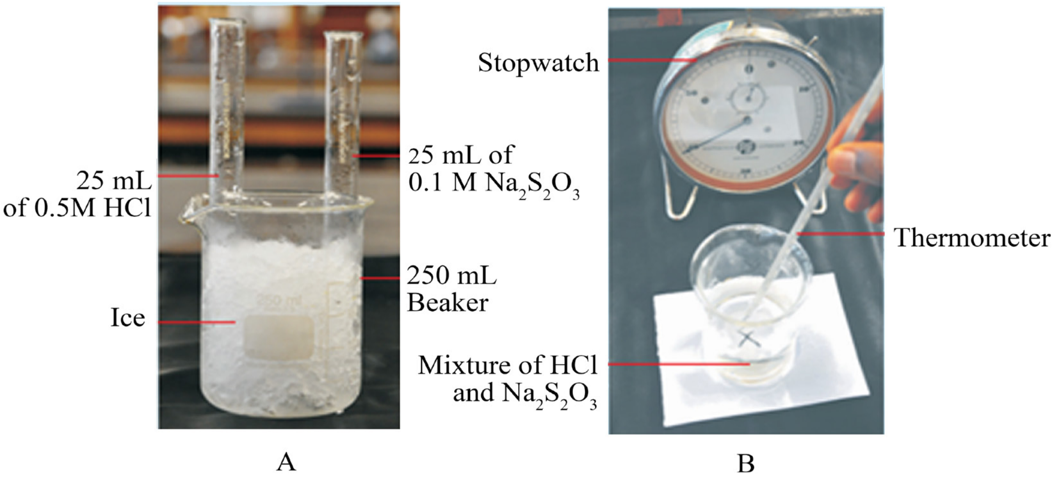


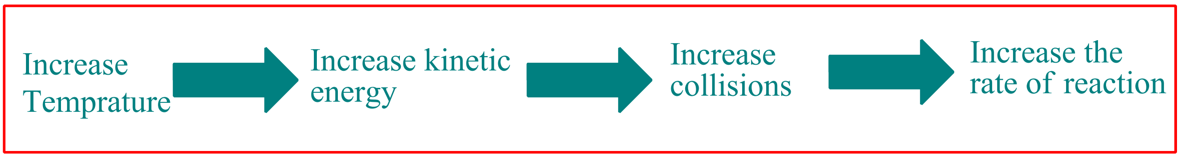
Figure 4.7: Laboratory set-up for the study of the effect of temperature on rate of reaction

Observations and analysis:

1. What was the appearance of the mixture at the start of the reaction, and at the end of the reaction? Explain the changes using the equation for the reaction.
2. Plot the graph of time (minutes) on the horizontal axis against rate on the vertical axis.
3. Under which condition of temperature does the cross take:
   a. the shortest time to disappear, and
   b. the longest time to disappear.
4. Draw a conclusion about the relationship between the average reaction rate and temperature.

Molecules at higher temperatures have more thermal energy.

Generally, an increase in the temperature of a reaction mixture increases the rate of chemical reactions. This is because, as the temperature of the reaction mixture raises, the average kinetic energy of the reacting particles increases. So, they collide more frequently and with greater energy.



The effect of temperature on rate of reaction can be experienced in our daily life. For example, foods cook faster at higher temperature than at lower ones. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures.

The rate of a reaction in a homogeneous system is approximately doubled by an increase in temperature of only 10 °C.

V. Presence of a Catalyst

Activity 4.6

Dear learner, answer the following questions from your experience.

1. What catalyst do you know in your body and the surroundings?
2. Why is yeast added to the dough in the making of bread? What happens if you don't add yeast to the dough?

Now, you will perform Experiment 4.6 to study the effect of a catalyst on the rate of decomposition of hydrogen peroxide, H_2O_2

Experiment 4.6

The Effect of a Catalyst on the Rate of Reaction

Objective: To investigate the effect of a catalyst on rate of decomposition of hydrogen peroxide.

Apparatus: Conical flask, gas syringe, delivery tube.

Chemicals: 0.5% by volume H_2O_2 solution, MnO_2.

Procedure:

1. Set-up the apparatus as shown in Figure 4.8. Set the volume of the gas syringe at 0 mL. Add 25.0 mL of 0.1M H_2O_2 solution, but without manganese (IV) oxide, MnO_2, and start stopwatch immediately.
2. Record the volume of gas collected in gas syringe at minute intervals until each reaction is almost complete.
3. Repeat steps 1 and 2 with 1 g of MnO_2.

Observations and analysis:

1. Identify the gas and write a balanced chemical equation for the reaction.
2. Under which condition does gas syringe contains more of the gas at any one time? Give an explanation for this observation.
3. Describe the appearance of MnO_2 before and after the reaction.
4. Plot graphs of rate on the vertical axis and time (minutes) on the horizontal axis for two different sets of readings. Which set of reading were used? Why?
5. Write a conclusion about the reaction rate:
   a. in the presence of a catalyst
   b. in the absence of a catalyst

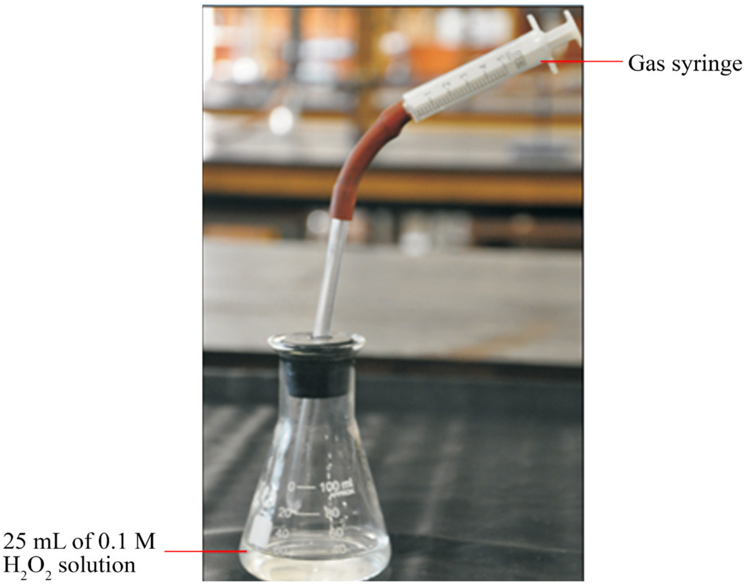


Figure 4.8: Investigation into the effect of manganese (IV) oxide on hydrogen peroxide

A catalyst is a substance that changes reaction rate by providing a different reaction mechanism one with a lower activation energy, E_a.

A catalyst lowers the activation energy.

An activation energy is the minimum energy required to start a chemical reaction.

Catalyst are not used up by the reactions, rather they are recovered at the end of the reaction. Although a catalyst speeds up the reaction, it does not alter the position of equilibrium.

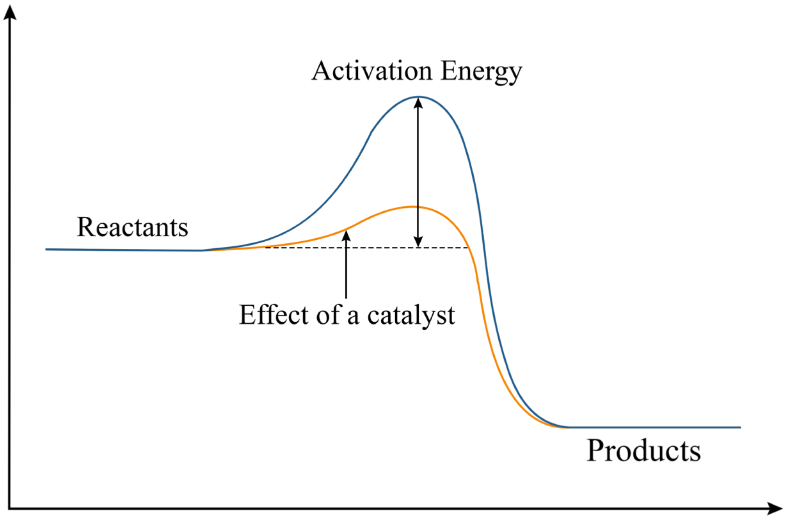


Figure 4.9: A catalyst provides an alternate pathway with a lower activation energy barrier for the reaction

Chemical catalysts can be either positive or negative.

☞ Positive catalysts increase the rate of reaction by lowering the *Ea*.

Example 4.4:

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$; $V_2O_5(s)$ as catalyst.

☞ Negative catalysts or Inhibitors decrease the rate of reaction by increasing the value of E_a.

Example 4.5:

$OCl^-(aq) + I^-(aq) \longrightarrow OI^-(aq) + Cl^-(aq)$; $OH^-(aq)$ as inhibitor.

Example 4.4 represents heterogeneous catalysts as state of reactants and catalyst is different, while Example 4.5 represents homogeneous catalyst as both reactants and catalyst are in same state.

? What catalyst do you know in your body and the surroundings?

A substance that catalyzes one reaction may have no effect on another reaction, even if that reaction is very similar. Many of the most highly specific catalysts are those designed by nature.

☞ The chemical reactions in living things are controlled by biochemical catalysts called enzymes.

Self-test Exercise 4.3

1. Which of the following properties could be used to measure the rate of the following reaction taking place in an open container?

   $$Zn\,(s) + 2HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

   a. mass of Zn b. solubility of HCl

   c. concentration of Cl^- d. color of the solution

2. Consider the following reaction:

   $$2S(s) + 3O_2(g) \longrightarrow SO_3(g) + \text{heat}$$

   The rate of this reaction could be increased by:

   a. decreasing temperature

   b. adding a catalyst

   c. increasing the concentration of S(s)

   d. increasing the concentration of $SO_3(g)$

3. Which combination of factors will affect the rate of the following reaction?

   $$Zn\,(s) + 2HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

   a. temperature and surface area only

   b. temperature and concentration only

   c. concentration and surface area only

   d. temperature, concentration and surface area

4. In general, reaction rates double when the temperature is increased by 10 °C. The temperature of a reaction is increased by 40 °C. The rate of the reaction will increase by a factor of:

   a. 2 b. 4 c. 8 d. 16

5. An untreated sugar cube does not burn when held over a lighted match. A sugar cube coated with cigarette ash readily ignites and burns. All of the cigarette ash remains after the reaction. The factor that caused this change in rate is the:

   a. nature of reactants b. presence of a catalyst

   c. increase in surface area d. increase in concentration

√ CHECKLIST 4.2

In the boxes provided for each of the following tasks put a tick mark (√) if you can perform or concepts you are familiar with them.

I can…

- list factors that affect the rate of a chemical reaction ☐
- describe the effects of changes in temperature, concentration or pressure and surface area on the rates of a chemical reaction ☐
- explain the effect of catalysts on the rates of chemical reaction ☐

UNIT SUMMARY

- Chemical kinetics is the study of the rates and mechanisms of chemical reactions.
- A chemical reaction occurs when atoms, molecules or ions undergo effective collisions.
- The higher the activation energy, the slower a chemical reaction and vice versa.
- In general, reaction rates increase with temperature, because higher temperature increases both the frequency of collisions and the number of molecules possessing enough energy to undergo effective collision.
- Reaction rate is expressed as the change in concentration of a reactant or product, per unit time.
- Reaction rates must be determined experimentally, often by gathering data on the variation of concentration over time.
- Reaction rates are influenced by the concentrations of reactants, temperature, catalysts and the degree of contact between reactants (surface area).

Self-Assessment

Part I: Choose the correct answer from the suggested options

1. When the concentration of reactant molecules is increased, the rate of reaction increases. The best explanation is: As the reactant concentration increases,
   a. the average kinetic energy of molecules increases.
   b. the frequency of molecular collisions increases.
   c. the rate constant increases.
   d. the activation energy increases.

2. A catalyst:
   a. actually, participates in the reaction.
   b. changes the equilibrium concentration of the products.
   c. does not affect a reaction energy path.
   d. always increases the activation energy for a reaction.

3. Which items correctly complete the following statement?

   A catalyst can act in a chemical reaction to:

   (I) increase the equilibrium constant.
   (II) lower the activation energy.
   (III) provide a new path for the reaction.
   a. only I & II
   b. only II
   c. c. only II & III
   d. only I & III

4. Milk is refrigerated in order to slow the rate of decomposition by bacterial action. The decrease in reaction rate is due to:
   a. a decrease in surface area.
   b. a decrease in ΔH for the reaction.
   c. a decrease in the fraction of particles possessing sufficient energy.
   d. the introduction of an alternate pathway with greater activation energy

5. The speed of a chemical reaction
   a. is constant no matter what the temperature is.
   b. is independent of the amount of contact surface of a solid involved.
   c. between ions in aqueous solution is extremely rapid because there are no bonds that need to be broken.
   d. varies inversely with the absolute temperature.

Part II: Give short answers to each of the following questions

6. What variable of a chemical reaction is measured over time to obtain the reaction rate?
7. How does an increase in pressure affect the rate of a gas phase reaction? Explain.
8. A reaction is carried out with water as the solvent. How does the addition of more water to the reaction vessel affects the rate of the reaction? Explain.
9. How does an increase in temperature affect the rate of a reaction? Explain the two factors involved.

Answer for the Activities - Unit Four

Activity 4.1

1. Sugar dissolves more easily in hot water than in cold water since increasing temperature generally increases the solubility of solids in liquid.
2. We can measure rate of a reaction by monitoring either the decrease in concentration of the reactants or the increase in concentration of the products.

Activity 4.2

This is because we need a minimum amount of energy to start combustion of ethanol.

Activity 4.3

Each reaction has its own characteristic rate, which is determined by the chemical nature of the reactants: alcohol burns very fast, paper burns at moderately, whereas wood charcoal slowly.

Activity 4.4

Sugar in the powdered state has more surface area of compared to the crystalline sugar. As a result, the powdered sugar is expected to dissolve in water at a faster rate than crystalline sugar.

Activity 4.5

1. Sugar dissolves in water due to the random motion of the molecules of water and colliding with the stationary molecules of sugar imparting them kinetic energy. This process is faster in hot water as the molecules of water move with higher velocity in hot water than in cold water. Thus, as the molecules of water are moving with higher velocity they collide more and impart more kinetic energy leading to a faster dissolution of sugar in hot water.
2. The lower the temperature, the less energy the molecules have, and the slower they therefore go. A fridge provides quite low temperatures, meaning fewer molecules have Ea or higher. As there are fewer molecules to create a reaction, the food is kept fresher.

Activity 4.6

1. An enzyme is a substance that acts as a catalyst in living organisms, regulating the rate at which chemical reactions proceed without itself being altered in the process.
2. Yeast is one of the leavening agents used in baking. Yeast reacts with sugar, causing it to ferment. The fermentation then results in the production of carbon dioxide. The carbon dioxide gets trapped in bread dough and becomes little air bubbles responsible for making bread rise. If you have not added yeast, the bread will rise very slowly and have a high risk of drying out.

Answer key for self-test Exercises

Answer key to self-test Exercise 4.1

1. c
2. b
3. a. $\text{Rate} = \frac{[CO_2]}{\Delta t} = \frac{1}{2}\frac{[H_2O]}{\Delta t}$

   b. $\text{Rate} = \frac{[CH_4]}{\Delta t} = \frac{1}{2}\frac{[O_2]}{\Delta t}$
4. a. $\text{Rate} = \frac{1}{2}\frac{[NH_3]}{\Delta t}$

   b. $Rate = \frac{[N_2]}{t} = \frac{1}{3}\frac{[H_2]}{t}$

Answer key to self-test Exercise 4.2

1. d
2. b
3. a
4. $[NO_2] = 0.0256 \text{ mol L}^{-1}$ and $[N_2O_5] = 0.0072 \text{ mol L}^{-1}$

Answer key to self-test Exercise 4.3

1. a
2. b
3. d
4. d
5. b

Answer to Self-Assessment

Part I: Choose the correct answer from the suggested options

1. b 2. a 3. d 4. c 5. c

Part II: Give short answers to each of the following questions

6. This could be a colour change, a temperature change, a pressure change, a mass change, or the appearance of a new substance (for example, amount of precipitate formed).
7. Reaction rate is proportional to concentration. An increase in pressure will increase the concentration, resulting in an increased reaction rate.
8. The addition of water will dilute the concentrations of all dissolved solutes, and the rate of the reaction will decrease.
9. An increase in temperature affects the rate of a reaction by increasing the number of collisions between particles, but more importantly, the energy of collisions increases. Both these factors increase the rate of reaction.

UNIT 5

CHEMICAL EQUILIBRIUM

Unit Introduction

Dear learner, in this unit you will learn the concept of chemical equilibrium. The unit is structured into two sections.The first section 5.1 introduces concepts to be covered in this unit and the second section 5.2 deals with reversible and irreversible reactions, the attainment of equilibrium, equilibrium constant expressions, application equilibrium constant, and Le-Chatelier's principle. In this unit, solved examples, self-assessment questions and practical activities are given to provide you the opportunities to practices. To successfully complete this unit, a minimum of 5 weeks are required.

Unit Outcome

At the end of this unit, you will be able to:

- discuss how equilibrium is established
- explain characteristics of dynamic equilibrium
- state the law of mass action and write an expression for equilibrium constants, K_C and K_P, from a given chemical reaction
- apply the law of mass action to calculate K_{C}, K_P, concentration and pressure of substances in equilibrium
- explain how the reaction quotient is used to indicate position of the equilibrium

- state Le-Chatelier’s principle and use it to predict and explain the effects of changes in temperature, pressure, concentration and presence of a catalyst on a reaction
- perform an activity to demonstrate the effects of changes in concentration on the position of equilibrium and to determine K_C or KP values
- explain how equilibrium principles may be applied to optimize the production of industrial chemicals (e.g., production of ammonia and sulphuric acid)
- describe scientific enquiry skills along this unit: observing, predicting, comparing & contrasting, communicating, asking questions and making generalization.

Unit Content

The Required Study Time **5 weeks**

If you set an average of one hour per day, you will be able to complete this unit in four weeks. Try your best to answer self-assessment questions, the experimental activities, and the unit review questions. Cross check your observations for the experimental activities and answers for the self-assessment and unit review questions with the suggested answers at the end of the Module.

If you do not get a right answer to a particular self-assessment question in your first attempt, you should not get discouraged, but instead, attempt to answer it over and over again. If you still do not get it right after several attempts, then you should rather seek help from your friends or even your tutor.

Unit Learning Strategies

- You should monitor your performance through planning, monitoring, and self-regulation
- You should manage the learning environment and available resources
- You should try all self-test, Self-assessments and written assignments
- You should use additional reference materials for better understanding of contents in the module.
- You should perform experimental activities to better understand of the lesson given in the module
- You should consult your tutor for further clarifications on some contents in the module.

Section 5.1: Introduction

Dear learner, in unit 4 you have learned about the rate of reaction. You have also studied the time taken for half of the reaction to be completed. However, some questions have not been answered yet. These questions include: Do all reactions reach to completion? If not then how much of the reactants remain unreacted, that is, what is the extent of the reaction it took? Why does the reaction reach to completion? Why does it attain equilibrium? These questions can be answered after studying chemical equilibrium.

In this unit, you will learn about chemical equilibrium, how it is attained, and factors that affect the position of chemical equilibrium.

Section 5.2. Chemical Equilibrium

Dear learner, in this section you will learn in detail about the chemical equilibrium. You will begin your study with a brief introduction of reversible and irreversible reactions and dynamic chemical equilibrium. You will proceed your study with the nature of the equilibrium state and important relationships involving equilibrium constants. Then, you will learn how you can predict the conditions of equilibrium. You will also perform various equilibrium calculations. Finally, you will learn how the equilibrium condition affects the methods used to produce industrial chemicals.

At the end of this section, you will be able to:

- explain reversible and irreversible reactions
- define dynamic chemical equilibrium
- state the necessary conditions for attainment of equilibrium
- describe the microscopic event that occur when a chemical system is in equilibrium
- explain the characteristics of chemical equilibrium
- state the law of mass action
- define equilibrium constant
- write the equilibrium constant expression for chemical reactions that involve concentration
- calculate values for equilibrium constant involving concentration
- state the relationship of K_{eq} to the relative amounts of products and reactants in a given reaction
- write the equilibrium constant expression for chemical reactions that involve partial pressure
- calculate values for equilibrium constant involving partial pressure
- show the relationship between K_C and K_P
- distinguish between homogeneous and heterogeneous equilibrium reactions
- define reaction quotient
- use the equilibrium quotient to predict the direction of the reaction and the position of equilibrium
- calculate equilibrium concentrations given initial concentrations
- determine whether the reactants or products are favored in a chemical reaction given the equilibrium constant
- list factors that affect chemical equilibrium
- state Le-Chatelier's principle
- use Le-Chatelier's principle to explain the effect of changes in temperature, pressure, concentration and presence of catalyst on a reaction
- state the effect of changes in concentration, pressure/volume and temperature on K_{eq}
- perform an activity to demonstrate the effect of changes in concentration on the position of equilibrium

- perform an activity to demonstrate the effect of changes in temperature on the position of equilibrium
- perform an activity to determine K_C for esterification of an organic acid;
- define optimum conditions
- explain how Le-Chatelier's principle is applied in the Haber process (production of NH_3) and in the Contact process (production of H_2SO_4)

5.2.1 Reversible and irreversible reactions

? What is the difference between reversible and irreversible reactions?

Dear learner, many chemical reactions proceed to completion. In such types of reactions, the reactants are completely converted to the products. Such reactions are called irreversible reactions or one-way reactions. When the equation for irreversible reaction is written, a single arrow (→) is used to indicate that the reaction proceed in only one direction.

For instance, the reaction between carbon and oxygen is irreversible reaction.

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

However, several reactions do not go to completion. Such reactions are called reversible reactions or two-ways reactions. These reactions usually precede both in the forward and reverse reactions. The reaction in which the original reactants form products is called the forward reaction and the reaction in which the products converted to the original reactant is called the reverse (backward) reaction. When the equation for a reversible reaction is written, a double arrow ($\rightleftharpoons$) indicates the reaction that go from reactants to products side and also from the products to the reactants side.

Activity 5.1

Dear learner, consider a reaction that involves both gaseous reactants and products. What will happen if the reaction takes place in:

a. an open vessel (container)?
b. a closed vessel?

Reversible reactions have the following general form

$$aA + bB \rightleftharpoons cC + dD$$

Where A and B are reactants, C and D are products and a, b, c, and d are balancing coefficients.

In this reaction:

$aA + bB \longrightarrow cC + dD$ Forward reaction
$cC + dD \longrightarrow aA + bB$ Reverse reaction

For example, formation of ammonia and hydrogen iodide are reversible reactions.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g$$
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Self-Test Exercise 5.1

Answer the following questions:

1. How do you distinguish between the reversible and irreversible reactions?
2. Give examples of reversible and irreversible reactions.

5.2.2 Attainment and characteristics of chemical

When can equilibrium be attained in a chemical reaction?

Dear learner, in a reversible reaction, the rate with which the reactants form products is known as the forward reaction rate (r_f) and the rate with which the products react to form the original reactants is called the reverse reaction rate (r_r). At the beginning of the reaction, the forward reaction has a high rate, but gradually decreases with time. The reverse reaction has almost negligible rate at the beginning, but gradually increases (as the products concentration increase) until equilibrium is established. The equilibrium is attained when the rate of two opposing reactions become equal. That is at equilibrium:

$$\text{Rate of forward reaction } (r_f) = \text{Rate of reverse reaction } (r_r)$$

5.2.3 Conditions for Attainment of Chemical Equilibrium

What happens to the rate of the forward and backward reactions as the reaction progresses?

Dear learner, chemical equilibria are dynamic equilibria, i.e., reactants and products are interconverted continually, even if the overall composition of the reaction mixture does not change. Once the equilibrium is established, changes in one direction is balanced by changes in other direction.

To understand the concept, consider **Figure 5.1** which shows the change in the reaction rate with time for the forward and reverse reactions. The rate of forward reaction depends upon the concentration of reactants whereas the rate of reverse reaction depends upon the concentration of products. Initially, only the reactants are present, therefore, the rate of forward reaction is fast. The reaction in the reverse direction does not take place as no product is present.

As the reaction progresses, the concentration of the reactants decreases and hence, the rate of forward reaction also decreases. However, due to the increase in the concentration of products, the rate of the reverse reaction increases. As the reaction further progresses a point will be reached when the rate of forward reaction becomes equal to the rate of reverse reaction. When this stage is attained, the concentrations of reactants and products do not change. The reaction has attained chemical equilibrium.

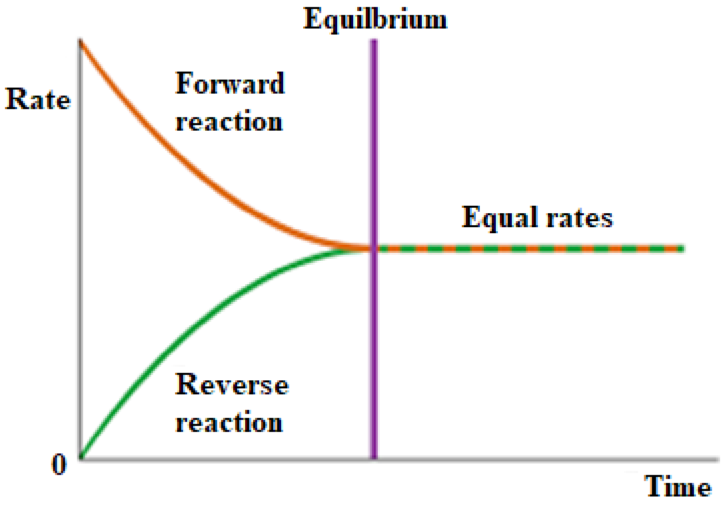


Figure 5.1. Change in the rate of reaction with time for forward and reverse reactions.

Does chemical reaction stop when equilibrium is attained?

For example, synthesis of ammonia from nitrogen and hydrogen is a reversible process.

$$N_2(g) \quad + \quad 3H_2(g) \rightleftharpoons 2NH_3(g$$

At the beginning of the reaction, only nitrogen and hydrogen are present. They combine to form ammonia at large rate. As the reaction progresses, the concentrations of nitrogen and hydrogen decreases, so the rate of formation of ammonia decreases. As more and more ammonia molecules are formed, some of the molecules start decomposing to give back nitrogen and hydrogen molecules. As the reaction progresses, the number of ammonia molecules increases, the rate of decomposition of ammonia also increases. As the reaction proceeds, the rate of formation of ammonia decreases while the rate of decomposition of ammonia increases. At a given point the two rates become equal and equilibrium is attained.

> It should be noted that the concentrations of products and reactants are not necessarily equal at equilibrium, only the rate of forward and reverse reactions are equal.

What are the characteristics of a reaction at equilibrium?

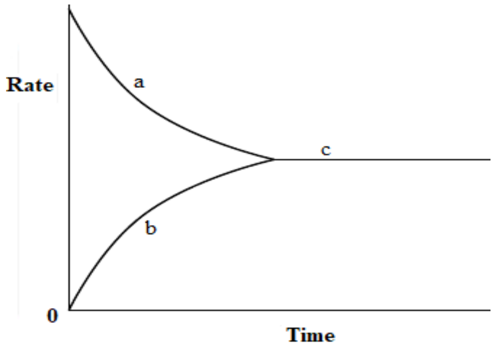
Generally, a reaction at equilibrium has the following characteristics:

- The reaction is reversible in nature.
- There is no net change in the concentrations of the reactants and products of the reaction.
- The rates of the forward and reverse reactions are equal
- The reaction should take place in a closed vessel to react at equilibrium.
- The equilibrium is a dynamic in nature.
- The concentrations of reactants and products are generally not equal.

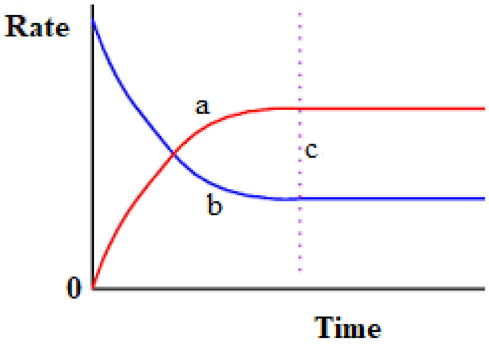
Activity 5.2

Answer the following questions

1. Label a, b and c are given for the following Figure. Explain trends of the rates of the forward and reverse reactions.



2. Labeled a, b and c are given for the Figure below. Explain what happens to the concentration of the reactants and the concentration of the products.



3. What are the conditions that remain constant at equilibrium?

5.2.4 Equilibrium expression and equilibrium constant

A. Law of Mass Action

? Can you describe the law of mass action?

Dear learner, mathematically the equilibrium constant is written based on the law of mass action or law of concentration action.

The law of mass action states that “the rate at which A and B combine is directly proportional to the product of their concentration terms each raised to the power of its respective coefficient in the balanced chemical reaction.”

The general equation that represents a reversible reaction is:

$$aA \quad + \quad bB \rightleftharpoons cC \;+\; dD$$

For the forward, reaction A and B are reactants and C and D are products.

Assume that the reaction is homogeneous, in which all the reactants and the products are in the same state.

The rate of forward reaction (r_f) depends upon the concentrations of A and B as well as the rate of reverse reaction (r_r) depends upon the concentrations of C and D. These relationships are expressed as follows:

$$r_f \propto [A]a\ [B]b \qquad \text{or} \qquad r_f = k_f\ [A]a\ [B]b$$

$$r_r \propto [C]c\ [D]d \qquad \text{or} \quad r_r = k_r\ C]c[D]d$$

Where [A], [B], [C] and [D] are the concentrations of A, B, C and D as well as k_f and k_r are rate constants for forward and reverse reactions, respectively.

> At equilibrium, the rate of forward reaction is equal to the rate of reverse reaction. Therefore,

$$r_f = r_r \qquad \text{or} \qquad k_f\ [A]a\ [B]b = k_r\ C]c\ [D]d$$

k_f and k_r are constant. Therefore, the ratio of k_f to k_r is also constant.

$$\frac{k_f}{k_r} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} = K_{eq}$$

The ratio of k_f and k_r is represented by K_{eq}, which is called equilibrium constant. [A], [B], [C] and [D] are concentrations of A, B, C, and D at equilibrium, respectively. When their concentrations are expressed in molarities, the K_{eq} is designated by K_C.

> When the reaction reactants and the products are gaseous, their concentrations can be expressed in terms of partial pressures. In such cases, the K_{eq} is denoted by K_p.

B. Equilibrium constant expression involving concentration, K_C.

What is homogeneous reaction? What rules do you follow to write such equations?

In homogeneous reactions all reactants and products are present in the same physical state. While writing equilibrium constant expressions for such reactions the following rules are followed.

- The concentrations of all the substances formed as products are written in the numerator
- The concentrations of all the reactants are written in the denominator.
- The equilibrium concentrations of each species are raised to a power equal to the coefficient of that species written in the balanced chemical equation.

For a general reaction at equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

The expression for Kc is:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

What is the unit of K_C?

The unit of K_C depends upon the number of moles of the reactants and products involved in the reaction. Therefore, for the above general reaction, the K_C unit will be:

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{[\text{mol L}^{-1}]^c [mol L^{-1}]^d}{[\text{Amol L}^{-1}]^a [\text{mol L}^{-1}]^b}$$

$$= (\text{mol L}^{-1})^{(c+d)-(a+b)}$$

Example 5.1

K_C expressions and units as well as K_C value determinations

1. NH_3 (g) + CH_3COOH (aq) $\rightleftharpoons$ NH_4^+ (aq) + CH_3COO- (aq)

$$K_C = \frac{[NH_4^+][CH_3COO^-]}{[NH_3][CH_3COOH]} = \frac{(\text{mol L}^{-1})(\text{mol L}^{-1})}{(\text{mol L}^{-1})(\text{mol L}^{-1})} = 1$$

2. HF (aq) $\rightleftharpoons$ H^+ (aq) + F^- (aq)

$$K_C = \frac{[H^+][F^-]}{[HF]} = \frac{(\text{mol L}^{-1})(\text{mol L}^{-1})}{(\text{mol L}^{-1})} = \text{mol L}^{-1}$$

3. $2NO\ (g) + Br_2\ (g) \rightleftharpoons 2NOBr\ (g)$

$$K_C = \frac{[NOBr]^2}{[NO]^2[Br_2]} = \frac{[mol\ L^{-1}]^2}{[mol\ L^{-1}]^2(mol\ L^{-1})} = mol\ L^{-1}]^{-2}$$

For the reaction

$H_2\ (g) + F_2\ (g) \rightleftharpoons 2HF\ (g)$

An equilibrium mixture at 425 °C contains 4.79×10^{-4} mol/L of H_2, 4.79×10^{-4} mol/L of F_2 and 3.53×10^{-3} mol/L of HF. Determine the equilibrium constant of the reaction.

Solution:

Given: $[H_2] = [F_2] = 4.79 \times 10^{-4}$ mol/L

$[HF] = 3.53 \times 10^{-3}$ mol/L

1. K_C expression for the reaction is
2. $K_C = \dfrac{[HF]^2}{[H_2][F_2]}$
3. Substitution of the give values in the expression gives:

$$K_C = \frac{[3.53 \times 10^{-3}\ mol/L]^2}{(4.79 \times 10^{-4}\ mol/L)(4.79 \times 10^{-4}\ mol/L)} = 5.43$$

Self-Test Exercise 5.2

1. Write the equilibrium constant expressions (K_C) for the following reactions:
   a. $NH_3\ (aq) + HF\ (aq) \rightleftharpoons NH_4^+\ (aq) + F^-\ (aq)$
   b. $2PBr_3\ (g) + Cl_2\ (g) \rightleftharpoons 2PCl_3\ (g) + 3Br_2\ (g)$
2. For the reaction $N_2\ (g) + 3Cl_2\ (g) \rightleftharpoons 2NCl_3\ (g)$ an analysis of an equilibrium mixture is performed at a certain temperature. It is found that $[NCl_3] = 1.9 \times 10^{-1}$ M, $[N_2] = 1.4 \times 10^{-3}$ M, and $[Cl_2] = 4.3 \times 10^{-4}$M. Calculate K_C for the reaction at this temperature

C. Equilibrium constant expression involving partial pressure, K_P

How can you express equilibrium constant in terms of partial pressure?

Hello learner, when all the reactants and the products are gases, their concentrations can be written in terms of partial pressures. In such cases the equilibrium constant is denoted by K_p, which is expressed as

$$\frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b} = K_P$$

For the formation of ammonia: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

The expression of equilibrium constant in terms of molarities is:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = K_C$$

The expression of K_p is:

$$\frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = K_P$$

What is the unit of K_p?

The unit of K_p is decided by the unit of pressure. If the partial pressure is expressed in atm, then the unit of K_p, will be:

$$K_P = \frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b} = \frac{[atm]^c[atm]^d}{[atm]^a[atm]^b} = (atm)^{(m+n)-(a+b)}$$

If the partial pressure is measured in kPa, then the unit of Kp will be:

$$(kPa)^{(m+n)-(a+b)}$$

Example 5.2

K_P expressions and units as well as K_P value determinations

1. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_P = \frac{[P_{NH3}]^2}{[P_{N2}][P_{H2}]^3} = \frac{(\text{atm})^2}{(\text{atm})(\text{atm})^3} = \frac{1}{\text{atm}^2} = \text{atm}^{-2}$$

2. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$K_P = \frac{[P_{HI}]^2}{[P_{H2}][P_{I2}]} = \frac{(\text{atm})^2}{(\text{atm})\,(\text{atm})} = 1$$

3. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$K_P = \frac{[P_{NO2}]^2}{[P_{N_2O4}]} = \frac{(\text{atm})^2}{(\text{atm})} = \text{atm}$$

4. The reaction for the formation of nitrosyl chloride was studied at 25 °C

$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$

At equilibrium, the partial pressures were found to be 1.2, 5.0×10^{-2} and 3.0×10^{-1} atm for NOCl, NO and Cl_2, respectively. Calculate the value of K_P for this reaction at 25 °C

Solution:

Given: = 1.2 atm, = 5.0×10^{-2} atm and = 3.0×10^{-1} atm

K_P expression for the reaction is:

1. $$K_P = \frac{(P_{NO})^2}{(P_{NO})^2\ P_{Cl_2}}$$

Substitution of the give values in the expression gives:

$$K_P = \frac{[1.2\ \text{atm}]^2}{(5.0 \times 10^{-2}\ \text{atm})^2(3.0 \times 10^{-1}\ \text{atm})} = 1.920\ \text{atm}^{-1}$$

Self-Test Exercise 5.3

1. Write the equilibrium constant expressions (K_P) for the following reactions:
   a. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
   b. $N_2(g) + O_2(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$
2. The following equilibrium pressures were observed at a certain temperature for the reaction

   $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ = 0.55 atm

   = 6.5×10^{-5} atm,

   = 4.5×10^{-5} atm
3. Calculate the value for the equilibrium constant at this temperature

a. Equilibrium constant for heterogeneous reactions

Activity 5.3

Dear learner, consider the following reaction to answer the related questions.

$Na(s) + HCl(aq) \rightleftharpoons NaCl + H_2(g)$

1. dentify the phases of the reactants and the products. Are the reactants and the product in the same or different phases?
2. What is the name of the equilibrium that involves such reactants and the product?

? What is a heterogeneous reaction? How can you equilibrium constant expression for heterogeneous reactions?

In heterogeneous reactions, the reactants and products are present in more than one physical state. For example, thermal decomposition of calcium carbonate is an example of a heterogeneous reaction.

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

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

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

When you write equilibrium constant expression for heterogeneous reactions, you do not include the concentration of pure solids or pure liquids in the expression. This is because, the position of equilibrium does not depend on the amounts of pure solids or pure liquids preset. The molar concentrations of pure solids liquids are constant (take to unity) at a given temperature.

Example 5.3

The equilibrium constant expression for some heterogeneous reactions is shown below:

1. $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

   $K_C = [CO_2]$ or $K_P = P_{CO_2}$

2. $NH_4Cl\,(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)$

   $K_C = [NH_3]\,[HCl]$ or $K_P = P_{NH_3}P_{HCl}$

3. $CO_2\,(g) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)$

   $$K_C = \frac{\left[H^+\right]\left[HCO_3^-\right]}{\left[CO_2\right]}$$

Self-Test Exercise 5.4

Write the equilibrium constant expression of the following reactions:

1. $Fe^{3+}\,(aq) + OH^-\,(aq) \rightleftharpoons Fe(OH)_3\,(s)$
2. $PCl_5\,(s) \rightleftharpoons PCl_3\,(l) + Cl_2\,(g)$
3. $2NBr_3\,(s) \rightleftharpoons N_2\,(g) + 3Br_2\,(g)$
4. $HCl\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$

b. Relation between K_C and K_P

? What is the relationship between K_C and K_P?

For the general reaction

$$aA + bB \rightleftharpoons cC + dD$$

K_C and K_P expressions are:

$$K_C = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} = \frac{C_C^c C_D^d}{C_A^a C_B^b}$$

$$K_P = \frac{[P_C]^c\,[P_D]^d}{[P_A]^a\,[P_B]^b}$$

Dear learner, assume that all gaseous species behave like an ideal gas. Thus, according to the ideal gas equation, the partial pressure, P, of a gas is given by:

$$P = nRT/V \quad \text{and} \quad n/V = C$$

Where n is the amount of gaseous species in moles, R is a gas constant, T is temperature in kelvin, V is volume of the reaction mixture and C is concentration in molarity.

Thus, partial pressure of each species for the above general reaction is:

$$P_A = n_A RT/V = C_A RT$$

$$P_B = n_B RT/V = C_B RT$$

$$P_C = n_C RT/V = C_C RT$$

$$P_D = n_D RT/V = C_D RT$$

$$K_P = \frac{[nCRT/V]^c\,[nDRT/V]^d}{[nART/V]^a\,[nBRT/V]^b} = \frac{C_C^c\,C_D^d}{C_A^a C_B^b}(RT)^{\Delta n}$$

Where, $\Delta n = (c + d) - (a + b)$ for gaseous species

$$KP = K_C(RT)\Delta n$$

When the number of gaseous reactants and products are equal then, $a + b = c + d$. Therefore, $\Delta n = 0$ and, hence $Kp = Kc$

Example 5.4

1. The equilibrium constant (K_P) for the reaction:

   $2SO_3$ sg) $\rightleftharpoons$ $2SO_2$ (g) + O_2 (g)

   is 1.8 × 10^{-3} kPa at 427 °C. Calculate K_C for the reaction at the same temperature.

Solution:

Given: $K_P = 1.8 \times 10^{-3}$ kPa = 1.8 Nm^{-2}, T = 427°C = 700 K and R = 8.314 N m K^{-1} mol^{-1}

We know that $K_P = K_C\,(RT)^{\Delta n}$

For the given reaction, $\Delta n = (2 + 1) - 2 = 1$

Therefore, $K_c = K_p/(RT)$

$$K_C = \frac{K_P}{RT} = K_C = \frac{1.8\,\cancel{N}m^{-2}}{8.314\,\cancel{N}\ m\,\cancel{K}^{-1}\ mol^{-1} \times\ 700\,\cancel{K}} = 3.1\ \times 10^{-4}\ m^{-3}\ mol$$

2. What are the values of Kp and Kc at 1000 °C for the reaction

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

   If the pressure of CO_2 in equilibrium with $CaCO_3$ and CaO is 3.87 atm?

Solution:

Enough information is given to find *Kp* first. Writing the *Kp* expression for the reaction:

$Kp = P_{CO2}$ = 3.87 atm,

R = 0.082 L atm K^{-1} mol^{-1} and

T = 1273 K

Then to get *Kc*, rearrange the equation,

$Kp = Kc(RT)^{\Delta n}$

Where n, the change in the number of moles of gas in the reaction is +1.

$$K_C = \frac{3.87\,\cancel{atm}}{0.082\ L.\cancel{atm}.\ \cancel{K}^{-1}\ mol^{-1} \times 1273\,\cancel{K}} = 0.037\ mol/L = 0.037\ M$$

3. At 400 °C, *Kc* = 64 for the reaction

   H_2 (g) + I_2 (g) $\rightleftharpoons$ 2HI (g)

   a. What is the value of Kp for this reaction?

   b. If at equilibrium, the partial pressures of H_2 and I_2 in a container are 0.20 atm and 0.50 atm, respectively, what is the partial pressure of HI in the mixture?

Solution:

a. The equation relating K_P to K_C is

$K_p = K_C(RT)^{\Delta n}$

The change in the number of moles of gas Δn is:

$\Delta n = 2\text{ mol HI} - 1\text{ mol } H_2 - 1\text{ mol } I_2 = 0$

Since, $\Delta n = 0$, $K_p = K_C$

$K_p = K_c(RT)^0 = Kc = 64$

b. Write the equilibrium constant expression

$$K_P = \frac{[P_{HI}]^2}{[P_{H2}][P_{I2}]}$$

By rearranging the above equation, we can find P_{HI}

$$P_{HI} = \sqrt{K_P[P_{H2}][P_{I2}]} = \sqrt{64 \times 0.2\text{ atm} \times 0.5\text{ atm}} = 2.53\text{ atm}$$

Self-Test Exercise 5.5

1. At 327 °C, the equilibrium concentrations are $[CH_3OH] = 0.15$ M, $[CO] = 0.24$ M and $[H_2] = 1.1$ M for the reaction

   $CH_3OH\,(g) \rightleftharpoons CO\,(g) + 2H_2\,(g)$

   Calculate K_P at this temperature

2. At 1100 K, $K_P = 0.25$ for the reaction

   $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$

   What is the value of K_C at this temperature?

3. When 0.500 mol of N_2O_4 is placed in a 4.00 L reaction vessel and heated at 400 K, 79.3% of the N_2O_4 decomposes to NO_2. The decomposition reaction is:

   $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g$

   Calculate K_C and K_P of the reaction at 400 K

What is the rule for writing the equilibrium constant for the overall reaction involving two or more reactions?

Dear learner, consider the reactions in which the product species in one equilibrium system are involved in the second equilibrium process.

$$A + B \rightleftharpoons C + D \qquad (i)$$

$$C + D \rightleftharpoons E + F \qquad (ii)$$

The equilibrium constant expressions for reaction (i) and (ii), respectively, are

$$K_1 = \frac{[C][D]}{[A][B]} \quad \text{and} \quad K_2 = \frac{[E][F]}{[C][D]}$$

The overall reaction is given by the sum of the two reactions

$$\begin{array}{l} A + B \rightleftharpoons C + D \\ C + D \rightleftharpoons E + F \\ \hline \end{array}$$

Overall reaction: $A + b \rightleftharpoons E + F$

The equilibrium constant expression for the overall reaction is

$$K_{overall} = \frac{[E][F]}{[A][B]} = K_1 \times K_2 = \frac{[C][D]}{[A][B]} \times \frac{[E][F]}{[C][D]}$$

Note that if a reaction is the sum of two or more reactions, the equilibrium constant of the overall reaction is equal to the product of the aquarium constants of the individual reaction.

That is: $K_{overall} = K_1 \times K_2 \times K_3 \ldots$

Example 5.5

1. Determine K_C for a reaction

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) + \tfrac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$$

from the following information at 298 K.

$2NO(g) \rightleftharpoons N_2(g) + O(g)$ (i) $K_1 = 2.4 \times 10^{30}$

$NO(g) + \tfrac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$ (ii) $K_2 = 1.4$

Solution:

To calculate K_C of the overall reaction, reactions (i) and (ii) must add up to give the overall reaction. To do this, first reverse reaction (i) and multiply ½, so that it will have the form

$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons NO(g)$ (iii)

Since the reaction equation is reversed and multiplied by ½, the equilibrium constant for reaction (iii), is calculated as

$$K_1' = \left(\frac{1}{K_1}\right)^{1/2} = \left(\frac{1}{2.4 \times 10^{30}}\right)^{1/2} = 6.5 \times 10^{-16}$$

Now, add reactions (ii) and (iii)

$NO\ (g) + ½Br_2\ (g) \rightleftharpoons NOBr\ (g)$ $\quad K_2 = 1.4$

$½N_2\ (g) + ½O_2\ (g) \rightleftharpoons NO\ (g)$ $\quad K_1' = 6.5\ \ 10^{-16}$

Overall reaction: $½N_2\ (g) + ½O_2\ (g) + ½Br_2\ (g) \rightleftharpoons NOBr\ (g)$ $\quad K_{overall} = K_2\ K_1'$

Thus, the equilibrium constant for the overall reaction is:

$$K_{overall} = K_2 \times K_1' = 1.4 \times 6.5 \times 10^{-16} = 9.1 \times 10^{-16}$$

Self-Test Exercise 5.6

1. The following equilibrium constants were determined at 1123 K:

   $C\ (s) + CO_2\ (g) \rightleftharpoons 2CO\ (g)$ $\quad = 1.4 \times 10^{12}$

   $CO\ (g) + Cl_2\ (g) \rightleftharpoons COCl_2\ (g)$ $\quad = 5.5 \times 10^{1}$

2. Write the equilibrium constant expression K_c and calculate the equilibriumconstant at 1123 K for the following reaction:

   $C\ (s) + 2CO_2\ (g) + 2Cl_2\ (g) \rightleftharpoons 2COCl_2\ (g)$

   For the reaction:

   $H_2\ (g) + Br_2\ (g) \rightleftharpoons 2HBr\ (g)$

3. $Kp = 7.1 \times 10^4$ at 700 K. What is the value of Kp for the following reactions at the same temperature?

   a. $2HBr\ (g) \rightleftharpoons H_2\ (g) + Br_2\ (g)$

   b. $½H_2\ (g) + ½\ Br_2\ (g) \rightleftharpoons HBr\ (g)$

4. Calculate a value for the equilibrium constant for the reaction:

   $O_2\ (g) + O\ (g) \rightleftharpoons O_3\ (g)$ from the following information:

   $NO_2\ (g) \rightleftharpoons NO\ (g) + O\ (g)$ $\quad K_C = 6.8\ \ 10^{-49}$

   $O_3\ (g) + NO\ (g) \rightleftharpoons NO_2\ (g) + O_2\ (g)$ $\quad K_C = 5.8\ \ 10^{-34}$

5.2.5 Applications of equilibrium constant

What information can be obtained from the value of the equilibrium constant of a reaction?

Dear learner, you can obtain useful information from the value of equilibrium constant of a given reaction at a particular temperature. The equilibrium constant of a reaction enable us to:

- predict the composition of an equilibrium mixture (or predict extent of reaction);
- predict the direction of the net reaction; and
- Calculate the equilibrium concentrations of reactants and products from initial concentrations.

A. Predict the composition of an equilibrium mixture

How does the values of equilibrium constant (K_C or K_P) predict the extent of reaction?

Hello learner, K_C or K_P value is used to predict the extent of the reactions at equilibrium. Very large values of K_C or K_P indicates that at equilibrium the reaction system consists of mainly products and the equilibrium lies far to the right, i.e., the reaction goes near to completion. An equilibrium mixture contains about as much product as can be formed from the given initial amounts of reactants.

However, if K_C or K_P value very small, the equilibrium mixture consists of mainly reactants and the reaction lies far to the left. An equilibrium mixture contains reactants, in essentially their initial amounts, and very small amounts of products.

Note that a reaction goes essentially to completion if K_C or $K_P > 10^{10}$ and not at all if K_C or $K_P < 10^{-10}$.

Self-Test Exercise 5.7

1. Predict whether the formation of product is favored for the following reactions:

   a. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_C = 3.6 \times 10^8$

   b. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_C = 5.0 \times 10^{-3}$

   c. $CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$ $K_C = 4.45 \times 10^{-24}$

2. Arrange the following reactions in order of their increasing tendency to proceed towards completion (least extent to greatest extent).

   a. $CO + Cl_2 \rightleftharpoons COCl_2$ $K_c = 13.8$

   b. $2CO_2 \rightleftharpoons 2CO + O_2$ $K_c = 2.0 \times 10^{-6}$

   c. $2NOCl \rightleftharpoons 2NO + Cl_2$ $K_c = 4.7 \times 10^{-4}$

B. Predict the direction of the reaction

What is reaction quotient (Q_C)?

Dear learner, to predict the direction of a reaction, you should first calculate reaction quotient (Q_C) and compare it with the value of the equilibrium constant. Reaction quotient is the ratio of concentrations of products to the concentrations of reactants each raised to the power equal to its stoichiometric coefficient.

> Q_C has the same form with K_C, but it involves concentrations that are not necessarily equilibrium concentrations.

For the general reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Where, [A], [B], [C] and [D] are concentrations at any stage during the reaction.

At the initial stages of the reaction, the amount of product formed is low, therefore, the value of Q is small. As the reaction progresses, the value of Q also increases due to the increase in concentration of the products. When the reaction attains equilibrium, Q becomes equal to the equilibrium constant.

? How do you predict the direction of a reaction using Q_C and K_C?

To predict the direction of the reaction, Q is compared with K_{eq}. Accordingly, if

(i) $Q = K_{eq}$, the reaction is at equilibrium

(ii) $Q < K_{eq}$, then the reaction will proceed to the right (the forward direction) to consume the reactants and to form more products untill the equilibrium is reached.

(iii) $Q > K_{eq}$, the reaction will proceed to the left (the reverse direction) to reduce the products until the equilibrium is reached.

Example 5.6

At a certain temperature, the reaction:

$$CO\ (g) + Cl_2\ (g) \rightleftharpoons COCl_2\ (g)$$

has an equilibrium constant $K_c = 13.8$. Is the following mixture an equilibrium mixture? If not, to which direction (forward or backward) will the reaction proceed to reach equilibrium? $[CO]_0 = 2.5$ mol L^{-1}, $[Cl_2]_0 = 1.2$ mol L^{-1}, and $[COCl_2]_0 = 5.0$ mol L^{-1}.

Solution:

Given: $[CO]_0 = 2.5$ mol L^{-1} $\quad [COCl_2]_0 = 5.0$ mol L^{-1}

$[Cl_2]_0 = 1.2$ mol L^{-1} $\quad K_C = 13.8$

The expression for Q_C is

$$Q_C = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{5.0 \text{ mol L}^{-1}}{2.5 \text{ mol L}^{-1} \times 1.2 \text{ mol L}^{-1}} = 1.67$$

$Qc < Kc$ thus the reaction mixture is not an equilibrium mixture. So, the reactants should combine to form more products to reach equilibrium, i.e., the reaction should proceed further to the right (the forward direction).

Self-Test Exercise 5.8

1. At a start of a reaction, there are 0.0218, 0.0145, ad 0.0783 moles of H_2, I_2 and HI, respectively, in a 3.5 liter reaction vessel at 430 °C. Decide whether the reaction is at equilibrium. If not predict in which direction the reaction will proceed. The equilibrium reaction is

   $H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_C = 54.3$ at 430 °C
2. At a very high temperature, the following reaction has $KC = 1.0 \times 10^{-13}$

   $2HF(g) \rightleftharpoons H_2(g) + F_2(g)$

   At a certain time, the detected concentrations of HF, F_2 and H_2 were 0.4 M, 0.004 M and 0.001 M, respectively. Is the system is at equilibrium? If not what must occur for the equilibrium to be established?
3. The decomposition of NOBr is represented by the equation:

   $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g) \qquad K_C = 0.0169$

   At equilibrium the concentrations of NO and Br_2 are 1.05×10^{-2} M and 5.24×10^{-3} M, respectively. What is the concentration of NOBr?

B. Calculating the equilibrium concentrations

How do you find the concentrations of reactants or products in an equilibrium mixture?

Hello learner, once equilibrium constant is determined for a reaction, it can be used to calculate the concentrations or partial pressures in an equilibrium mixture. To calculate equilibrium concentrations we usually follow the following procedure:

1. Write the balanced equation for the reaction and then K_C or K_P expression.
2. List the initial concentrations.
3. Calculate Q_C or Q_P to determine the direction of the reaction, if initial concentrations of the reactants and products are given.
4. Define the change in concentration needed to reach equilibrium and find the equilibrium concentrations by using the change of the initial concentrations.
5. Substitute the equilibrium concentrations into the K_C or K_P expression, solve for the unknown.
6. Check whether the calculated equilibrium concentrations give the correct value of K_C or K_P.

Example 5.7

The equilibrium constant, $K_C = 69$ for the following reaction

$H_2(g) \quad + \quad I_2(g) \rightleftharpoons \quad 2HI(g)$

Given that 1 mole of H_2 and 2 moles of I_2 were added in 500 mL reaction vessel. Determine the molar concentrations in the mixture at equilibrium.

Solution:

1. The equation for the reaction is

$$H_2(g) \quad + \quad I_2(g) \rightleftharpoons 2HI(g) \qquad K_C = \frac{[HF]^2}{[H_2][I_2]} = 69$$

$$[HI]_{initial} = [HI]_0 = 0$$

$$[H_2]_0 = \frac{1\text{ mol}}{0.5\text{ L}} = 2\frac{\text{mol}}{\text{L}} = 2\text{ M}$$

$$[I2]_0 = \frac{2\text{ mol}}{0.5\text{ L}} = 4\frac{\text{mol}}{\text{L}} = 4\text{ M}$$

2. No need to calculate Q_C since $[HI]_0 = 0$
3. Let the number of moles of H_2 (or I_2) consumed per liter to reach an equilibrium is x. Since the stoichiometric proportion of each reactant (H_2 and I_2) and the product HI is 1:2, for every x of both reactants consumed the concentration of HI formed is 2x. These changes are presented the table below.

Concentration	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial	2.0 M		4.0 M		0
Change	-x		-x		+2x
Equilibrium	2.0 M - x		4.0 M – x		2x

4. Substituting the equilibrium concentrations from the table into and the value of Kc I the equilibrium constant expression,

$$K_C = \frac{[HI]^2}{[H_2][I_2]}$$

$$64 = \frac{(2x)^2}{(2.0\text{ M} - x)(4.0\text{ M} - x)} = \frac{(2x)^2}{x^2 - 6x + 8}$$

By rearranging, we get

$4x^2 = 64x^2 - 384x + 512$

By rearranging again, we get

$60x^2 - 384x + 512 = 0$

This is a quadratic equation of the general formula $ax^2 + bx + c = 0$

The values of x can be obtained from the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this example a = 60, b = -384 and c = 512. Therefore:

$$x = \frac{-(-384) \pm \sqrt{(-384)^2 - 4(60 \times 512)}}{2 \times 60}$$

$$= \frac{384 \pm \sqrt{2.5 \times 10^4}}{120} = \frac{384 \pm 158}{120}$$

x = 1.9 M or 4.5 M

But the change in concentration cannot be greater than the initial concentrations of the H_2, i.e., 2 M. Thus, only 1.9 is reasonable value. Therefore, the equilibrium concentration of each species is

$[H_2] = 2.0 - x = 2.0\ M - 1.9\ M = 0.1\ M$

$[I_2] = 4.0 - x = 4.0\ M - 1.9\ M = 2.1\ M$

$[HI] = 2x = 2(1.9\ M) = 3.8\ M.$

5. Check

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(3.8\ M)^2}{0.1\,M \times 2.1\,M} = 68.76 \approx 69$$

Therefore, the calculated equilibrium concentrations are correct.

Self-Test Exercise 5.9

1. For the equilibrium:

   $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g) \qquad K_C = 0.36$ at 100 °C

   a sample of 0.25 mol N_2O_4 is allowed to dissociate and come to equilibriumin a 1.5 L flask at 100°C. What are the equilibrium concentrations of NO_2 and N2O4?

2. At 400 °C, the equilibrium constant for the reaction:

   $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$

   is 64. A mixture of 0.250 mol H_2 and 0.250 mol I_2 was introduced into an empty 0.75 L reaction vessel at 400 °C, find the equilibrium concentrations of all components

5.2.6 Changing Equilibrium Conditions: Le-Chatelier's principle

Can you state Le-Chatelier's principle? What happens when the equilibrium conditions change?

Dear learner, consider a chemical reaction that is initially at equilibrium. Often a change in conditions will displace the reaction from equilibrium. The reaction then shifts toward one direction (left to right or right to left as the equation is written) as it proceeds to a new equilibrium state. The direction in an equilibrium reaction will shift when a change in conditions occurs is predicted by Le Châtelier's principle.

Le Châtelier's principle stated that if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.

The factors that change may affect a reaction equilibrium include:

- concentration of a reactant or product,
- reaction volume or applied pressure, and
- temperature.

A. **Effect of Change in the Concentration**

How is an equilibrium system affected by a change in concentration?

Hello learner, when a system at equilibrium is disturbed by a change of concentration of one of the components, the system reacts in the direction that reduces the change. That is:

- If the concentration increases, the system reacts to reduce some of it.
- If the concentration decreases, the system reacts to produce some of it.

Consider the general reaction:

$$A \quad + \quad B \rightleftharpoons C \quad + \quad D$$

Dear learner, an increase in the concentration of A or B, or both, shifts the equilibrium position to the right, that is, toward the formation of more products. Similarly, a decrease in the concentration of C or D, or both, shifts the equilibrium position to the right. However, an increase in the concentration of C or D, or both (or a decree in A or B, or both) shift the equilibrium position to the left.

Consider the following reversible reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

If you wish to convert as much H_2 to HI as possible, you might increase the concentration of I_2. To understand the effect of this, first suppose that a mixture of H_2, I_2, and HI is at equilibrium. If I_2 is now added to this mixture, the equilibrium is disturbed. Thus, the reaction will now go in the direction that will use up some of the added I_2. Consequently, adding more I_2 has the effect of converting a greater quantity of hydrogen to HI.

☞ Note that adding or removing reactants or products changes the value of Q_C. It does not change the value of K_C.

Activity 5.4

Dear learner, suppose A and B react to produce C according to the following chemical equation:

$$A + B \rightleftharpoons C$$

If you add certain amounts of A and B to this equilibrium reaction mixture containing A, B, and C, the reaction again attains an equilibrium. Suppose at the new equilibrium, the amounts of A and B in the reaction mixture are doubled. How is the amount of C changed?

Dear learner, to understand the effect of change in concentration on equilibrium position you need to perform the following experiment. To conduct the experiment, visit a high school in your vicinity and request Grade 11 chemistry teacher to support you in performing or demonstrating the experiment. Note that the experiment should be performed only in the laboratory, or do not attempt to perform at your home. In case, if high school is not available in your vicinity, request your tutor to get support and advices.

Experiment 5.1

Effect of change in concentration on equilibrium position

Objective: To study the effect of concentration on the position of equilibrium.

Apparatus: Test tubes (5), test tube stands, 100 mL beakers (2),

Chemicals: 0.05 M $Fe(NO_3)_3$ solution, 0.01M KSCN solution, 0.1M H NO_3.

Procedure:

1. Take 5 test tubes and label them as 1, 2, 3, 4 and 5. Keep them on a testtube rack.
2. Take 50 mL of 0.05 M solution of $Fe(NO_3)_3$ in a beaker.
3. In separate beakers take 10 mL of 0.01 M KSCN solution and 20 mL of 0.1 M HNO_3 acid solution.
4. Mix the solutions according to the given table to prepare 5 different solutions

Test tube No.	**Volume in mL of**		
	0.05 M $Fe(NO_3)_3$	**0.1 M HNO_3**	**0.01 M KSCN**
1	1.0	4.0	1.0
2	2.0	3.0	1.0
3	3.0	2.0	1.0
4	4.0	1.0	1.0
5	5.0	0.0	1.0

Note the color of the solution in each test tube.

5. Arrange the test tubes in the increasing order of color intensity.

Observations and analysis:

1. Which direction is exothermic and which is endothermic? How do you explain your results?
2. Correlate the color intensity with the concentration of Fe^{3+} in the test tube.

   Hint: Fe3+ forms deep red color complex with SCN^- ions.

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons \underset{\text{Deep red}}{Fe(SCN)^{2+}(aq)}$$

3. By taking different volumes of $Fe(NO_3)_3$ in the test tubes the concentration of Fe3+ is varied in the solution. Calculate the concentration of Fe3+ ions ineach test tube and correlate with the color intensity.
4. In the test tube take 1.0 mL of $Fe(NO_3)_3$ solution and add 4.0 mL of HNO_3 solution followed by 1.0 mL of KSCN solution. Mix well and notethe color. Add 1.0 mL of $Fe(NO_3)_3$ solution and again note the color ofthe solution.

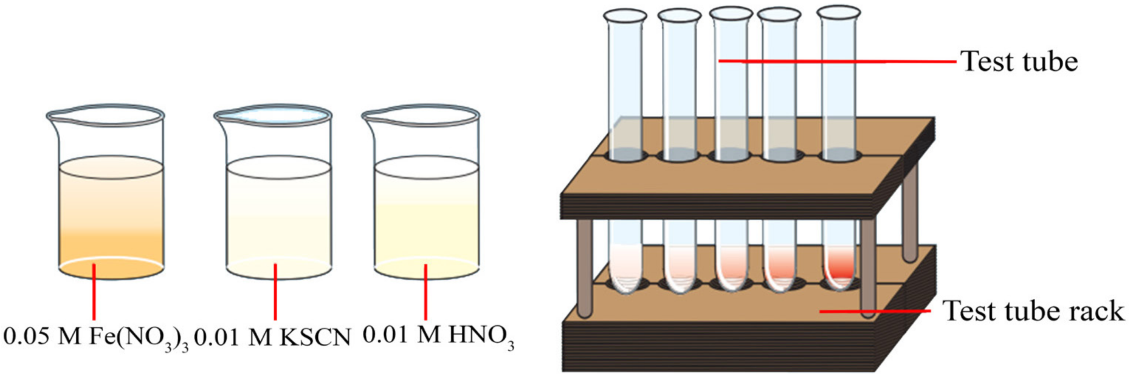


Figure 5.2: Laboratory set-up for the effect of changes in concentration onequilibrium of Fe^{3+} (aq) and SCN^- (aq).

B. Effect of Change in Pressure

How does changing of the pressure affect a chemical reaction in equilibrium? Can pressure change do affect equilibrium system of every chemical reaction?

Dear learner, a change in pressure affects only equilibrium systems that involve gases. Pressure changes can occur in three ways:

- changing the concentration of a gaseous component
- adding an inert gas, and
- changing the volume of the reaction vessel

Adding an inert gas has no effect on the equilibrium position because, inert gas molecules does not participate in the reaction and thus cannot affect the equilibrium in any way. However, the addition of an inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants or products.

Dear learner, a pressure change obtained by changing the volume can affect the yield of product in a gaseous reaction if the reaction involves a change in total moles of gas. According to Le Chatelier's principle, if a pressure at equilibrium is increased (volume decreased) then the reaction will proceed in that direction that relieve the pressure. Thus, an increase in pressure of the system at a constant temperature, shifts the equilibrium in the direction that produces smaller number of gaseous molecules whereas a decrease in pressure shifts in the direction of greater number (moles) of gaseous molecules.

For a general reaction:

$$aA + bB \rightleftharpoons cC + dD$$

The effect of pressure is decided by Δn.

$$\Delta n = (c + d) - (a + b)$$

- If $\Delta n > 0$, implies the total moles of products is greater than the total moles of reactants. Lowering of pressure will favor the reaction in forward direction.
- If $\Delta n < 0$, implies the total moles of products is less than the total moles of reactants. Increasing the pressure will favor the reaction in forward direction.
- If $\Delta n = 0$, the change in pressure has no effect on the position of equilibrium.

For example, in the formation of ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta n = 2 - (1 + 3) = -2$$

Therefore, an increase in pressure at equilibrium will favor the forward reaction.

For the dissociation of dinitrogen tetroxide:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta n = 2 - 1 = 1$$

The decrease in pressure at equilibrium, favors the forward reaction.

Self-Test Exercise 5.10

Look at each of the following equations and decide whether an increase of pressure obtained by decreasing the volume will increase, decrease, or have no effect on the amounts of products.

a. $CO (g) + Cl_2 (g) \rightleftharpoons COCl_2 (g)$

b. $2H_2S (g) \rightleftharpoons 2H_2 (g) + S_2 (g)$

c. $C (s) + S_2 (g) \rightleftharpoons CS_2 (g)$

A. Effect of Change in Temperature

What is the effect of a temperature change on a chemical equilibrium?

Hello learner temperature has a profound effect on most reactions. Reaction rates usually increase with an increase in temperature, meaning that equilibrium is reached sooner. Many reactions are sluggish or have very low rates at room temperature but speed up enough at higher temperature.

Change of temperatures also varies equilibrium constant values of a reaction.

Consider the K_C values of methanation reaction at different temperatures:

$$CO (g) + 3H_2 (g) \rightleftharpoons CH_4 (g) + H_2O (g) \qquad \Delta H° = -206.2 \text{ kJ}$$

K_C for methanation at different temperatures

Temperature (K)	K_C
298	4.7×10^{27}
800	1.38×10^{5}
1000	2.54×10^{2}
1200	3.92

How do you distinguish between endothermic and exothermic reactions? Does increasing the temperature favor the exothermic or endothermic reaction?

Reversible reactions are endothermic in one direction and exothermic in the other.

Consider a general reaction:

$$A + B \rightleftharpoons A + D + \text{heat} \qquad \text{(exothermic reaction)}$$

Dear learner, if you consider heat as a reaction component of the equilibrium system, a rise in temperature "adds" heat to the system and a drop in temperature "removes" heat from the system. As with a change in any other component, the system shifts to reduce the effect of the change. Therefore, an increase in temperature at a constant pressure and concentration favors the endothermic reaction whereas a decrease in temperature favors the exothermic reaction.

For example, formation of ammonia is an exothermic process:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92\ \text{kJ} \qquad \Delta H^\circ_{rxn} = -92\ \text{kJ}$$

Dear learner, from the equation you can see that 92 kJ of heat is released when NH_3 is produced from N_2 and H_2. Therefore, the forward reaction is exothermic while the reverse reaction is endothermic. Thus, an increase in temperature favors the decomposition of ammonia to N_2 and H_2, (i.e, shifts the equilibrium to the left or reactant side). Whereas, a decrease in temperature favors the formation of ammonia (shifts the equilibrium to the right or product side).

Self-Test Exercise 5.11

Consider the possibility of converting CO_2 to CO by an endothermic reaction:

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

Is a high or a low temperature more favorable to the production of carbon monoxide? Explain.

Dear learner, to understand the effect of change in temperature on equilibrium position you need to perform the following experiment. To conduct the experiment, visit a high school in your vicinity and request Grade 11 chemistry teacher to support you in performing or demonstrating the experiment. Note that the experiment should be performed only in the laboratory, or do not attempt to perform at your home. In case, if high school is not available in your vicinity, request your tutor to get support and advices.

Experiment 5.2

Effect of change in temperature on the equilibrium position

Objective: Determination of the effect of changes in temperature on the position of equilibrium of iodine and starch.

Apparatus: Test tubes, water bath, stands, Bunsen burner, thermometer.

Chemicals: Iodine, starch.

Procedure:

1. Add a few drops of tincture of iodine to some starch solution in a test tube. Record your observations.
2. Heat the solution to about 80 °C using a water bath. Record your observation. What can we deduce from this?
3. Cool the container by placing it in an ice box. Record your observation.

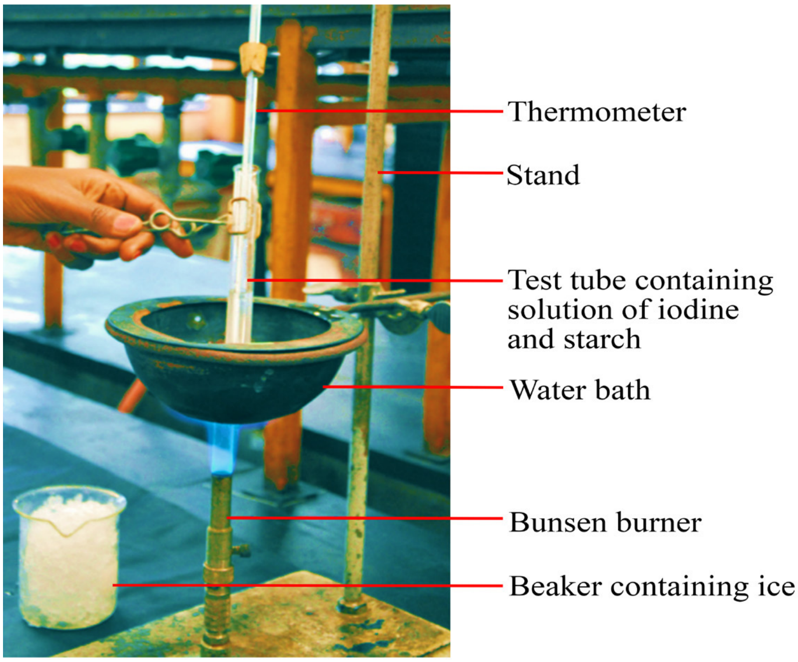


Figure 5.3 Laboratory set-up for the effect of changes in temperature on equilibrium of iodine and starch.

Observations and analysis:

1. Is this reaction an example of equilibrium reactions?
2. Which direction is exothermic and which is endothermic? How do you explain your results?
3. What can you conclude from your observations?

D. Effect of Catalyst

? What is a catalyst? How does a catalyst affect a reaction?

Dear learner, as you learned in Unit 1, a catalyst is a substance that increases the rate of a reaction but is not consumed in the reaction. Catalyst is shown over the arrow in equation for a chemical reaction and do not appear in equilibrium constant expressing or in the reaction quotients.

For instance, consider SO_3 is formed by the reaction of SO_2 with O_2:

$$2SO_2\,(g) \;+\; O_2\,(g) \;\xrightleftharpoons{\text{Catalyst}}\; 2SO_3\,(g) \qquad \square H°rxn = -197.6 \text{ kJ/mol}$$

Dear learner, , the reaction is very exothermic, but ordinarily very slow. It is catalyzed commercially in the contact process by spongy Pt, SiO_2, or V_2O_5, at high temperatures (400 to 700 °C).

? Does addition of a catalyst affect equilibrium position?

Addition of a catalyst does not shift the equilibrium position. Because a catalyst increases the rates of both forward and reverse reactions by the same factor. It has no effect on the equilibrium composition of a reaction mixture.

> Catalysts merely speed up the attainment of equilibrium but do not change either the value of the equilibrium constant or the equilibrium concentrations.

Self-Test Exercise 5.12

Predict the effect of the following changes on equilibrium:

$$2SO_2\,(g) \;+\; O_2\,(g) \;\rightleftharpoons\; 2SO_3\,(g) \qquad \Delta H°_{rxn} = 197.78 \text{ kJ}$$

a. increasing pressure at constant temperature
b. increasing temperature at constant pressure
c. adding a catalyst

5.2.7 Equilibrium and Industry

How is yield increased in industry?

Dear learner, industrial processes are designed to give maximum possible yield of the products. The conditions for carrying out the reactions are varied based on Le Chatelier's principle. The following processes demonstrate application of Le Chatelier's principle in the industry.

A. Haber Process for the Manufacture of Ammonia

How does ammonia produced from atmospheric nitrogen, N_2?

Dear learner, Fritz Haber (1909) established the conditions under which atmospheric nitrogen, N_2, would be converted to ammonia, NH_3, by reacting it with hydrogen, H_2. The Haber synthesis was developed into an industrial process by Carl Bosch.

Hello learner, the reaction between N_2 and H_2 to produce NH_3 is an exothermic equilibrium reaction. It releases 92.4 kJ/mol of energy at 298 K.

$$N_2\,(g) + 3H_2\,(g) \underset{\text{Catalyst}}{\overset{\text{heat, pressure}}{\rightleftharpoons}} 2NH_3\,(g) \quad \triangle H = -92\ \text{kJ mol}^{-1}$$

How does Haber process utilize Le Chatelier's principle to maximize the production of ammonia?

Dear learner, according to Le Chatelier's principle, the production of ammonia is favored by high pressure and low temperature. However, the rate of the reaction at lower temperature is extremely slow, so a higher temperature must be used to speed up the reaction which results in a lower yield of ammonia. The equilibrium expression for the reaction is:

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

As the temperature increases, the equilibrium constant decreases and the yield of ammonia decreases.

Temperature (°C)	Keq
25	6.4×10^{2}
200	4.4×10^{-1}
300	4.3×10^{-3}
400	1.6×10^{-4}
500	1.5×10^{-5}

In the industrial production of NH_3 by Haber process, the reaction rate is increased by

- adding catalyst such as an iron. It speeds up the reaction by lowering the activation energy so that the N_2 bonds and H_2 bond can be more readily broken.
- increasing reaction temperature. When temperature is increased reactant molecules will get sufficient energy to overcome the energy barrier (activation energy) so that the reaction is faster at higher temperatures, but the yield of ammonia is lower at higher temperature.

Hello learner, at 200 °C and pressure above 750 atm, the yield of ammonia is almost 100 %, i.e., the reactants are completely converted to ammonia. Increasing the pressure increases the final yield of ammonia, however high pressures are expensive to produce and difficult to manage. So, The Haber process is typically carried out at pressures between 200 and 400 atm and temperature of 500 °C. The effects of temperature and pressure, on the percentage yields of ammonia for the Haber process is shown in **Figure 5.4.**

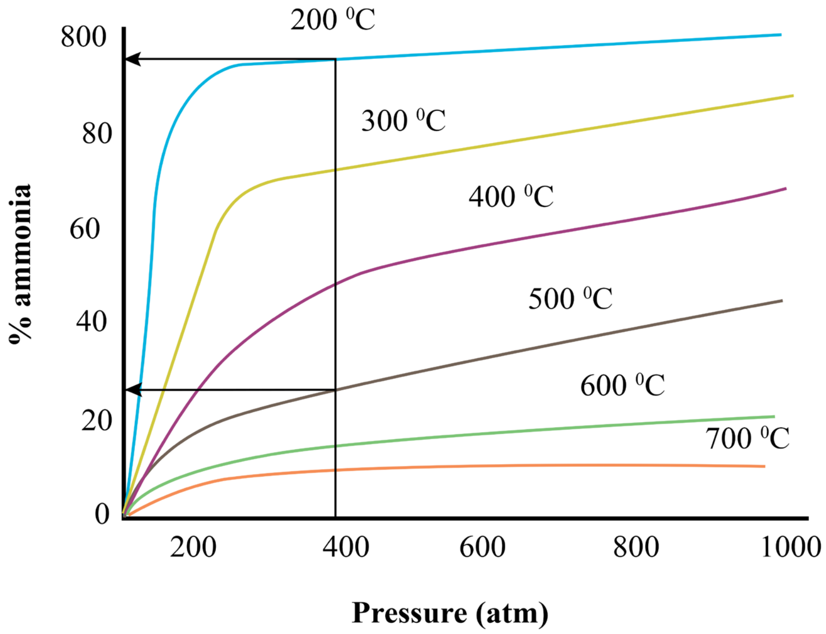


Figure 5.4: The effects of temperature and pressure on the percentage yields of ammonia for the Haber process.

Dear learner, in the commercial production of ammonia, NH_3 is continuously removed as it is produced. Removing the products causes more N_2 and H_2 to combine according to Le Chatelier's principle. The reaction never reaches equilibrium as the gas mixture leaving the reactor is cooled to liquefy and remove the ammonia. The remaining mixture of reactant gases is recycled through the reactor. The heat released by reaction is removed and used to heat the incoming gas mixture. **Figure 5.5** shows a simplified flow diagram for the Haber process:

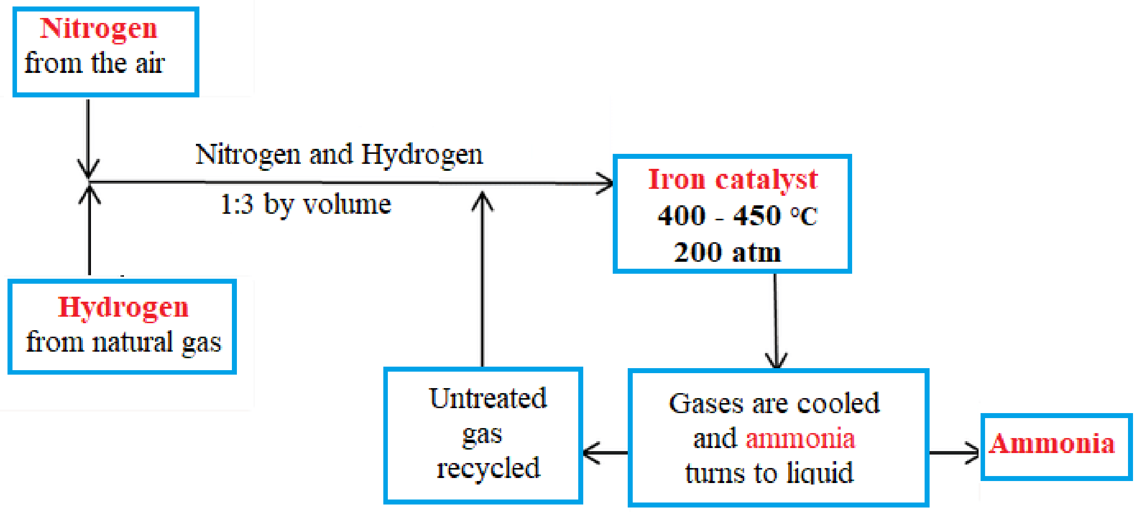


Figure 5.5 A simplified flow scheme of the Haber process.

Activity 5.5

Dear learner, answers the following questions:

1. Which compound is manufactured by Haber process?
2. What are the raw materials used in Haber process?
3. What is the role of iron in Haber process?

B. Contact Process for the Manufacture of Sulphuric acid

What is Contact process? How does Le-Chatelier's Principle used in Contact process?

Dear learner, contact process is the production of sulphuric acid, H_2SO_4, by the catalytic oxidation of sulphur dioxide, SO_2, to sulphur trioxide, SO_3. It is a reversible reaction:

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) \qquad \Delta H = -196\ kJ$$

Contact process involves the following steps:

i. Preparation of sulphur dioxide gas, SO_2, by burning pure sulphur in the presence of excess air:

$$S\,(s) + O_2\,(g) \longrightarrow SO_2\,(g)$$

To enhance the efficiency of a catalyst (in the next step), various impurities present in the mixture of SO_2 and air are first removed.

ii. Conversion of SO_2 to sulphur trioxide, SO_3

Oxidation of SO_2 to SO_3 takes place at 450 °C in the presence of a catalyst, a vanadium (V) oxide (V_2O_5):

$$2SO_2\,(g) + O_2\,(g) \xrightarrow[450\ ^\circ C]{V_2O_5} 2SO_3\,(g)$$

iii. Converting sulfur trioxide into sulfuric acid, H_2SO_4

In this case, SO_3 (g) is dissolved in concentrated H_2SO_4 (98 %) to produce disulphuric acid or pyrosulpuric acid, also known as fuming sulphuric acid or oleum, $H_2S_2O_7$:

$$SO_3\,(g) + H_2SO_4\,(l) \longrightarrow H_2S_2O_7\,(l)$$

Converting sulfur trioxide to sulfuric acid cannot be done just by adding water, as the reaction is so uncontrollable that it creates a fog of sulfuric acid.

iv. Dilution of $H_2S_2O_7$ to obtain H_2SO_4

A calculated amount of water is added to obtain sulphuric acid of desired strength:

$$H_2S_2O_7\,(l) + H_2O\,(l) \longrightarrow 2H_2SO_4\,(l)$$

Dear learner, the oxidation of SO_2 to SO_3 (step ii) is an exothermic reaction. So, according to Le Chatelier's principle, higher temperatures will force the equilibrium position to shift to the left, favoring the production of SO_2 whereas lower temperatures would favor the production of SO_3. However, the rate of reaching equilibrium at the lower temperatures is extremely low. At higher temperature, equilibrium is achieved rapidly but the yield of SO_3 is lower. The temperature about 450 °C is a compromising situation whereby a faster reaction rate results in a slightly lower yield.

Similarly, at higher pressures, the equilibrium position shifts to the least numbers of gaseous molecules, i.e., SO_3. In contact process, V_2O_5 is also used to speed up the rate of the reaction. **Figure 5.6** shows contact process for the manufacture of H_2SO_4.

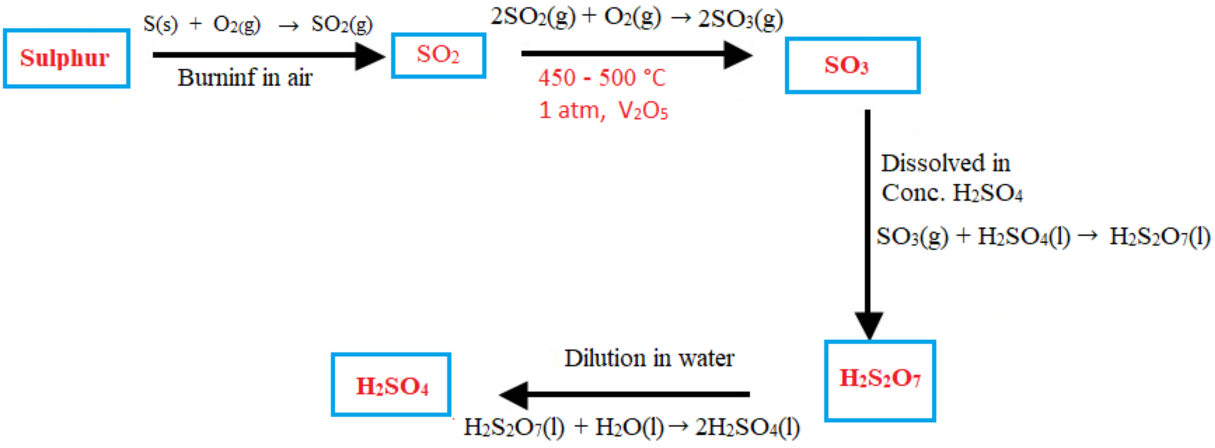


Figure 5.6: A flow scheme of Contact process for manufacture of H_2SO_4

Self-test Exercise 5.13

Answers the following questions:

1. What is a mixture of H_2SO_4 and free SO_3?
2. What are the raw materials for making SO_2 in the contact process?
3. Why SO_3 is not directly added to make H_2SO_4?

√ CHECKLIST-5.1

In the boxes provided for each of the following terms or concepts put a right mark (√) if you can respond to them or put a cross mark (x) if you cannot.

I can...

- explain reversible and irreversible reactions ☐
- define dynamic chemical equilibrium ☐
- state the necessary conditions for attainment of equilibrium ☐
- describe the microscopic event that occur when a chemical system is in equilibrium ☐
- explain the characteristics of chemical equilibrium ☐
- state the law of mass action ☐
- write the equilibrium constant expression for chemical reactions that involve concentration ☐
- calculate values for equilibrium constant involving concentration ☐
- state the relationship of Keq to the relative amounts of products and reactants in a given reaction ☐
- write the equilibrium constant expression for chemical reactions that involve partial pressure ☐
- calculate values for equilibrium constant involving partial pressure ☐
- show the relationship between KC and KP ☐
- distinguish between homogeneous and heterogeneous equilibrium reactions ☐
- define reaction quotient and use it to predict the direction of the reaction and the position of equilibrium ☐
- calculate equilibrium concentrations given initial concentrations ☐
- determine whether the reactants or products are favored in a chemical reaction given the equilibrium constant ☐
- list factors that affect chemical equilibrium ☐
- state Le-Chatelier's principle and use the principle to explain the effect

of changes in temperature, pressure, concentration and presence of catalyst on a reaction

- state the effect of changes in concentration, pressure/volume and temperature on Keq ☐
- perform an activity to demonstrate the effect of changes in concentration on the position of equilibrium ☐
- perform an activity to demonstrate the effect of changes in temperature on the position of equilibrium ☐
- perform an activity to determine KC for esterification of an organic acid; ☐
- explain how Le-Chatelier's principle is applied in the Haber process (production of NH3) and in the Contact process (production of H_2SO_4) ☐

UNIT SUMMARY

- Chemical equilibrium is the state of the reaction when the macroscopic properties like temperature, pressure, volume and concentration of the reaction do not change with time.
- According to the law of mass action the rate at which A and B combine is directly proportional to the product of their concentration terms each raised to the power of its respected coefficient in the balanced chemical reaction.
- For a general reaction at equilibrium $aA + bB \rightleftharpoons mM + nN$ the expression for K_C is:

$$K_C = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

- The expression for KP is $K_P = \frac{[P_M]^m [P_N]^n}{[P_A]^a [P_B]^b}$ provided that all A, B, M and N are in gaseous state.
- Reaction quotient is the ratio of concentrations of products to the concentrations of reactants raised to the power of their respective coefficients at any stage after the start of the reaction.

- For the reaction, aA + bB $\rightleftharpoons$ mM + *n*N the expression for the reactionquotient is

$$Q = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

- When Q < *K*, then the reaction will proceed in the forward direction and more products will be formed till the equilibrium is reached.
- When Q > *K*, then the reaction will proceed in the reverse direction and more reactants will be formed till the equilibrium is reached.
- When *Q* = *K*, then the reaction has attained equilibrium.
- Le Chatelier's principle gives the effect of any one or more of the reaction parameters namely, temperature, pressure or concentration on equilibrium.
- In Haber Process the atmospheric nitrogen, N_2, is converted to ammonia, NH_3, by reacting it with hydrogen, H_2,
- Haber process is an industrial process for producing ammonia from nitrogen and hydrogen, using an iron catalyst at high temperature and pressure.
- Contact process is the production of sulphuric acid, H_2SO_4, by the catalytic oxidation of sulphur dioxide, SO_2, to sulphur trioxide, SO3.
- For exothermic reactions the yield of products is increased by performing the reaction at lower temperatures.

SELF-ASSESSMENT QUESTIONS

Part I: Multiple choice questions

Choose the correct answer from the given alternatives

1. Which of the following is correct about a reaction at equilibrium?
   a. The concentrations of reactants and products are equal.
   b. The system is static in nature.
   c. The forward and backward rates are equal.
   d. None.

2. For a reaction to shift towards the product direction, which of the following condition holds true?
   a. $Q_C = K_C = 0$
   b. $Q_C < K$
   c. $Q_C > K_C$
   d. $Q_C = K_C$

3. Given the equation $2C\,(s) + O_2\,(g) \rightleftharpoons 2CO\,(g)$, the expression for K_C is:
   a. $\frac{2[CO]}{2[C][O_2]}$
   b. $\frac{[CO]^2}{[C]^2[O_2]}$
   c. $\frac{[CO]^2}{[O_2]}$
   d. $\frac{2[CO]}{[O_2]}$

4. In which of the following cases does the reaction go fastest towards completion:
   a. $K = 10^3$
   b. $K = 10^{-2}$
   c. $K = 10$
   d. $K = 1$

5. For the reaction $C\,(s) + CO_2\,(g) \rightleftharpoons 2CO\,(g)$, the partial pressures of CO_2 and CO are 2.0 atm and 4.0 atm, respectively, at equilibrium. What is the value of K_P for this reaction?
   a. 0.5 atm
   b. 4.0 atm
   c. 8.0 atm
   d. 32.0 atm

6. The equilibrium partial pressures of SO_2, O_2 and SO_3 are 0.1 atm, 0.25 atm and 0.5 atm respectively. The equilibrium constant for the reaction $SO_3\,(g) \rightleftharpoons SO_2\,(g) + \frac{1}{2}O_2\,(g)$ is:

   a. 0.1
   c. 0.05
   b. 10
   d. 20

7. Which of the following is likely to happen when pressure is applied to the following system at equilibrium:

   $H_2O\ (s) \rightleftharpoons H_2O\ (l)$

   a. More water will be formed
   c. Water will evaporate
   b. More ice will be formed
   d. d. No change occurs

8. The equilibrium constant for the reaction $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$ is K_1 and for the reaction $2NH_3\ (g) \rightleftharpoons N_2\ (g) + 3H_2\ (g)$ is K_2. The relation betweenK_1 and K_2 is:

   a. $K_1 = K_2$
   c. $K_1 = -K_2$
   b. $K_1 = 1/K_2$
   d. d. $K_1 = (K_2)0.5$

9. What will happen when CaO is added to the following reaction at equilibrium?

   $CaCO_3\,(s) \rightleftharpoons CaO\ (s) + CO_2\,(g)$

   a. No change occurs.
   b. c. More $CaCO_3$ is formed.
   c. Reaction shifts in the forward direction
   d. d. Total pressure increases.

10. Under what conditions are KP and KC equal?

   a. $\Delta n = 1$
   c. $\Delta n = -1$
   b. $\Delta n = 0$
   d. They can never be equal

Part II: Solve the following problems

11. For the reaction at equilibrium: $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$ $\Delta H = -196$ kJ/mol. Predict the direction of the change on:
    a. Removal of SO_2.
    b. Addition of noble gas (argon) at constant pressure.
    c. Decreasing volume of the system.
    d. Increasing temperature of the system.
    e. Addition of a catalyst.

12. Balance the following equations and write the equilibrium constant expressions, in terms of K_C and K_P.
    a. $NH_3\,(g) + O_2\,(g) \rightleftharpoons N_2\,(g) + H_2O\,(g)$
    b. $N_2\,(g) + H_2\,(g) \rightleftharpoons NH_3\,(g)$
    c. $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

13. For the reaction at 200°C: $2A\,(g) + B\,(g) \rightleftharpoons 3C\,(g)$ the equilibrium constant is 3.0. Given the following information,

Species	Concentration
[A]	2.0 M
[B]	3.0 M
[C]	2.0 M

Predict the direction in which the reaction should proceed to reach equilibrium.

14. Hydrogen and iodine react according to the equation;

$H_2(\,g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$

Suppose 1.00 mol H2 and 2.00 mol I2 are placed in a 1.00 L vessel. How many moles of substances are in the gaseous mixture when it comes to equilibrium at 458 °C? The equilibrium constant Kc at this temperature is 49.7.

15. Calculate K_P for the following reactions at the indicated temperature.

a. $2NOBr\,(g) \rightleftharpoons 2NO\,(g) + Br_2\,(g)$ $K_C = 6.50 \times 10^{-3}$ at 298 K

b. $NH_4I\,(s) \rightleftharpoons NH_3\,(g) + HI\,(g)$ $K_C = 7.00 \times 10^{-5}$ at 673 K

ANSWER KEYS TO ACTIVITIES

Activity 5.1

a. In an open vessel, the gaseous reactants completely convert to gaseous products, but there is no chance for the products to convert back to their reactants. Thus, the reaction is irreversible.

b. In a closed vessel, the reactions do not go to completion. Because, sometimes, the gaseous products begin to convert back to the reactants. In other words, the reaction proceeds spontaneously toward equilibrium. Thus, the reaction is irreversible.

Activity 5.2

1. In the given figure (a) rate of forward reaction (b) rate of reverse reaction, and (c) equilibrium point. The rate of the forward reaction decreases and the rate of the reverse reaction increases.
2. In the given figure (a) Concentration of product (b) concentration of reactants, and (c) equilibrium point. Concentration of reactants decreases, and concentration of product increases.
3. The conditions that remain constant at equilibrium include:
   a. concentration of the reactants and the products.
   b. the rate of forward and reverse reactions.

Activity 5.3

1. Na is in a solid phase, HCl is in aqueous phase, NaCl is in aqueous phase and hydrogen is in a gas phase. Therefore, the reactants and the products are in different phases.
2. The equilibrium that involves reactants and products in different phases is called heterogeneous equilibrium.

Activity 5.4

The amount of C is also doubled when the equilibrium is re-established.

KEYS TO EXPERIMENTAL OBSRVATIONS

Experiment 5.1

This is the main reaction that you consider in this experiment:

$$Fe^{3+}(aq) \quad + \quad SCN\text{-}(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$$

colorless colourless deep red

You observe that when the concentration of $Fe(NO_3)_2$ increases, by Le Chatelier's principle, the position of equilibrium shifts to the right so as to remove some of the extra $SCN^-(aq)$. Thus, more $FeSCN^{2+}(aq)$ is produced, and the solution becomes deep (darker) red.

Experiment 5.2

When a few drops of tincture of iodine is added to some starch solution, a blue-black color solution is formed. When the solution is heated to about 80 °C, the blue-black color disappears. The answers to the questions listed under observation and analysis are:

1. When iodine reacts with starch, starch-iodine complex is formed. The reaction is an example of an equilibrium reaction.
2. The forward reaction, which is in the direction of starch-iodine complex formation, is exothermic. The reverse is endothermic as shown below.

$$\text{Iodine} \quad + \quad \text{Starch} \underset{\text{Endothrmic}}{\overset{\text{Exothemic}}{\rightleftharpoons}} \text{Starch-Iodine complex}$$

3. As we apply to the system under equilibrium, the equilibrium position shifts in the direction that favors the reactant side. This is because the forward reaction is exothermic. As a result of this, the blue-black color gradually disappears and the solution becomes colorless.

Answer Keys to Self-assessment questions

Self-Test Exercise 5.1

1

Irreversible reaction	**Reversible reaction**
• Products do not convert back to reactants • The reaction stops completely and almost goes to completion • It can be carried out in an open or closed vessel • It takes place in one direction. It is represented by single arrow "→"	• Products are convert back to reactants • The reaction never goes to completion all the time, some reactants and products are present in the reaction mixture • It is generally carried out in a closed vessel • It takes place in both directions. It is represented by double arrow "⇌"

2. i. Irreversible reactions

$S(s) + O_2(g) \longrightarrow SO_2(g)$

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

$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(s)$

ii. Reversible reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

Self-Test Exercise 5.2

1. a. $K_C = \dfrac{[NH_4^+][F^-]}{[NH_3][HF]}$ b. $K_C = \dfrac{[PCl_3]^2[Br_2]^3}{[PBr_3]^2[Cl_2]^3}$

2. $K_C = \dfrac{[NCl_3]^2}{[N_2]][Cl_2]^3} = \dfrac{(1.9 \times 10^{-1})^2}{(1.4 \times 10^{-3}) \times (4.3 \times 10^{-4})^2} = 3.2 \times 10^{11} M^{-2}$

Self-Test Exercise 5.3

1. a. $K_P = \dfrac{\left(P_{SO_3}\right)^2}{\left(P_{SO_2}\right)^2 \times P_{O_2}}$ b. $K_P = \dfrac{\left(P_{NOBr}\right)^2}{P_{N_2} \times P_{O_2} \times P_{Br_2}}$

2. $\dfrac{(NO)^2 \times P_{O_2}}{\left(P_{NO_2}\right)^2} = \dfrac{\left(6.5 \times 10^{-5}\right)^2 \times 4.5 \times 10^{-5}}{(0.55)^2} = 6.28 \times 10^{-13}$ atm

Self-Test Exercise 5.4

1. $K_C = \dfrac{1}{\left[Fe^{3+}\right]\left[OH^-\right]}$

2. $K_C = [Cl_2]$ or $K_P = P_{Cl_2}$

3. $K_C = [N_2][Br_2]^3$ or $K_P = \left[P_{N_2}\right]\left[P_{Br_2}\right]^3$
4. $K_C = \left[H_3O^+\right]\left[OH^-\right]$

Self-Test Exercise 5.5

1. $K_P = 4{,}686.34$ atm
2. $K_C = 22.55$
3. $K_C = 1.51$, $K_P = 49.6$

Self-Test Exercise 5.6

1. $K_C = \dfrac{[COCl_2]^2}{[CO_2]^2[Cl_2]^2} = K_{C1} \times (K_{C2})^2 = 4.24 \times 10^{15}$
2. a. 1.41×10^{-5} b. 2.66×10^{2}
3. 2.53×10^{81}

Self-Test Exercise 5.7

1. a. Formation of the product is favored, since K_c is extremely large.
   b. Formation of the product is not favored, since K_c is small.
   c. Formation of the product is favored, since K_c is extremely small.
2. Increasing tendency to proceed towards completion (least extent to greatest extent).
   (b) $K_c = 2.1 \times 10^{-4}$ < (c) $K_c = 4.7 \times 10^{-4}$ < (a) $K_c = 13.8$

Self-Test Exercise 5.8

1. $Q_C = 19.4$ which is less than $K_{C.}$ Thus, the reaction mixture is not an equilibrium mixture. The reactants should combine to form more products to reach equilibrium, i.e., the reaction should proceed further to the right (the forward direction).
2. $Q_C = 2.5 \times 10^{-5}$ which is greater than $K_{C.}$ Implies that the reaction mixture is not an equilibrium mixture. The reaction should proceed to the left (the reverse direction) to reduce the products until the equilibrium is reached.
3. 5.7×10^{-2} M

Self-test Exercise 5.9

1. For the equilibrium: $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

   The equilibrium constant expression is written as:

   $$KC = \frac{[NO_2]^2}{[N_2O_4]} = 0.36$$

   Initial concentration of N_2O_2 is 0.25 mol/1.5 L, which is 0.167 M.

   $$\text{Therefore } \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x)^2}{(0.167 - x} = 0.36$$

   By solving the equation, be sure you get $[NO_2] = 0.17$ M, $[N_2O_4] = 0.085$ M

2. The concentration table may be constructed as follows:

Concentration	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial (M)	0.33		0.33		0
Change (M)	-x		-x		+2x
Equilibrium (M)	0.33 - x		0.33 - x		2x

   The equilibrium constant expression becomes:

   $$\frac{[HI]^2}{[H_2][I_2]} = \frac{[(2x)^2}{(0.33 - x)(0.33 - x)} = 64$$

   After solving for x, we get:

   $[HI] = 0.532$ M and $[H_2] = [I_2] = 6.7 \times 10^{-2}$ M

Self-test Exercise 5.10

a. The increase in pressure at equilibrium, favors the forward reaction.
b. The increase in pressure at equilibrium, favors the reverse reaction.
c. The change in pressure has no effect on the position of equilibrium

Self-test Exercise 5.11

Higher temperature favors converting of CO_2 to CO. i.e., higher temperature shifts the equilibrium to the right. Whereas, low temperature favors the reverse reaction or shifts the equilibrium to the left.

Self-test Exercise 5.12

a. Favors forward reaction

b. Favor forward reaction

c. Equally affect both forward and reverse reaction or it cannot shift the equilibrium position

Self-test Exercise 5.13

1. It is disulphuric acid or pyrosulpuric acid, also known as fuming sulphuric acid or oleum, $H_2S_2O_7$
2. Elemental sulphur
3. Because the reaction is explosive or uncontrollable.

Answer to Self-Assessment Questions

Part I

1. c
2. b
3. c
4. a
5. c
6. a
7. d
8. b
9. c
10. b

Part II

11. a. removal of SO_2 shifts the equilibrium to the left direction.
    b. addition of noble gas (argon) at constant pressure does not affect the equilibrium.
    c. decreasing the volume of the system shifts the equilibrium to the right direction.
    d. increasing the temperature of the system shifts the equilibrium to the left direction.
    e. addition of a catalyst has no effect on the equilibrium.

12. a. $2NH_3(g) + 3/2O_2(g) \rightleftharpoons N_2(g) + 3H_2O(g)$

$$K_C = \frac{[N_2][H_2O]^3}{[NH_3]^2[O_2]^{3/2}} \quad \text{or} \quad K_P = \frac{[P_{N_2}][P_{H_2O}]^3}{[P_{NH_3}]^2[P_{NH_3}]^{3/2}}$$

b. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_C = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} \quad \text{or} \quad K_P = \frac{[P_{NH_3}]^2}{[P_{N_2}]\,[P_{H_2}]^3}$$

c. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_C = [P_{CO_2}] \quad \text{or} \quad K_P = [P_{CO_2}]$$

13. $Q_C = 0.67$; $QC\ (0.67) < KC\ (3.0)$, hence, the reaction should proceed to the right to reach equilibrium

14. The equilibrium composition is 0.07 mol H_2, 1.07 mol I_2, and 1.86 mol HI

15. a. $K_P = 0.159$ b. $K_P = 0.213$

UNIT 6

SOME OXYGEN-CONTAINING ORGANIC COMPOUNDS

Unit Introduction

☸ Dear learner! this unit deals about oxygen-containing hydrocarbons. It includes the chemistry of alcohols, ethers, aldehydes, ketones, carboxylic acids and its derivatives: esters, fats and oils. The unit is structured into six sections: the first section revises the classifications of organic compounds that you learned in Grade 10. The next section is about alcohols and ethers, which contain the functional groups (−OH) and (R−O−R'), respectively. The third section is about aldehydes and ketones, which consists of the carbonyl group (C=O). Section four emphases on the carboxylic acids functional group (−COOH), which consists of the carbonyl group (C=O) and the hydroxyl group (−OH) bonded to the carbonyl carbon. The fifth section is concerned with chemistry of esters. Esters are formed when an acid react with an alcohol. The last section deals about the chemistry of fats and oils.

Unit Outcomes

At the end of this unit, you will be able to:

- classify organic compounds
- write the structural formula and IUPAC names of alcohols, ethers, aldehydes, ketones, carboxylic acids and esters
- give the general formulas of alcohols, ethers, aldehydes, ketones, carboxylic acids and esters
- describe some physical and chemical properties of alcohols, ethers, aldehydes, ketones, carboxylic acids and esters
- develop skills in naming and writing the molecular and structural formulas of alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, anhydrides, amides, and acid chlorides
- predict and correctly name the products of organic reactions, including substitution, addition, elimination, esterification, hydrolysis and oxidation reactions
- write the general formula of fats and oil and the structures for some common triglycerides
- give the structures, properties and uses of fats and oils.

Unit Content

The Required Study Time **4 weeks**

1. If you set an average of one hour per day, you will be able to complete unit six by the end of the assigned week. Try to do all the learning activities. And compare your answers with the one provided at the end of the Module.
2. If you do not get a particular exercise right in the first attempt, you should not get discouraged, but instead, go back and attempt it over and over again. If you still do not get it right after several attempts, then you should seek help from your friend or even your tutor.

Unit Learning Strategies

- You should monitor your performance through planning, monitoring, and self-regulation
- You should manage the learning environment and available resources
- You should try all self-test exercises and written assignments
- You should surf on the internet for better understanding of contents in the module.
- You should consult your tutor for further clarifications on some contents in the module.

Section 6.1: Introduction

Dear learner, in Grade 10, you learned about some general reactions of hydrocarbons. In this unit, you will continue to learn more about hydrocarbons that contain oxygen in their functional groups: alcohols, ethers, aldehydes, ketones, carboxylic acids and esters.

Can you mention some use of organic compounds in your daily life?

At the end of this section, you will be able to:

- classify organic compounds.

Classification of organic compounds

The organic compounds are mainly divided into two categories: acyclic (open chain) compounds and cyclic (closed chain) compounds. These compounds can be subdivided into different compounds. Open chain compounds (aliphatic compounds) can be classified broadly into two categories: saturated compounds and unsaturated compounds.

☞ Saturated compounds are those compounds that do not have a double or triple bond between carbon and hydrogen.

? Can you give examples of saturated compounds?

☞ Unsaturated compounds are those organic compounds that have a double or triple bond between the carbon-carbon atoms.

Activity 6.1

Dear learner, attempt to answer the following questions.

1. Why is classification of organic compounds needed?
2. Can you name the common functional groups?

√ CHECKLIST 6.1

In the boxes provided for each of the following tasks put a tick mark (√) if you can perform or concepts you are familiar with them.

I can…

- classify organic compounds ☐
- name the common functional groups ☐
- give an example for each functional group ☐

Section 6.2: Alcohols and Ethers

☸ Dear learner, in this section you will study the functional group of alcohols and ethers, their naming systems, general methods of preparation, and the chemical reactions of alcohols and ethers. Alcohols occur widely in nature and have many industrial and pharmaceutical applications. While, ethers are relatively resistant to chemical transformation and are often used as solvents.

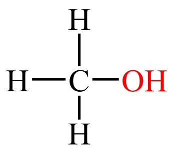
At the end of this section, you will be able to:

- define alcohols
- tell the functional group of alcohols
- classify alcohols based on the number of hydroxyl groups
- write the general formulas of monohydric alcohols
- write the molecular formulas and the names of the first six members of the monohydric alcohols
- give the IUPAC names for the given alcohols
- classify monohydric alcohols based on the number of alkyl groups attached to the carbon atom carrying the hydroxyl group
- give some examples for primary, secondary and tertiary alcohols
- describe the physical properties of alcohols
- explain general methods of preparation of alcohols
- explain the industrial preparation of ethanol
- explain the chemical reactions of alcohols such as oxidation, reaction with active metals, esterification and dehydration
- write the molecular formulas and names of the first six members of ethers
- give the IUPAC names for given ethers
- describe the physical properties of ethers
- explain the general methods of preparation of ethers
- explain the use of ethers, such as solvent inorganic reactions.

Hello! dear learner, alcohols are derivatives of hydrocarbons in which one or more of the hydrogen atoms in the hydrocarbon have been replaced by a hydroxyl group (–OH). In alcohols, the hydroxyl group is directly attached to carbon atom(s) of an aliphatic system. The hydroxyl group is responsible for imparting certain chemical and/or physical properties to the compound.

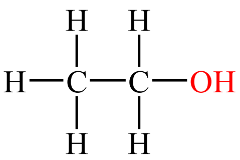
The functional group in an alcohol is an –OH (hydroxyl) group.

Example 6.1



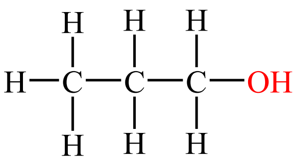
$H-\overset{H}{\underset{H}{C}}-OH$

Methanol



$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$

Ethanol



$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$

1-Propanol

Which alcohol (s) is present in hand sanitizers?

6.2.1 Classification of Alcohols

Dear learner, alcohols can be classified as *mono–*, *di–*, *tri-* or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl (–OH) groups respectively in their structures.

Monohydric alcohols are alcohols containing only one hydroxyl group.

Example 6.2

CH_3-CH_2-OH

Ethanol

CH_3-CH_2-CH_2-OH

1-Propanol

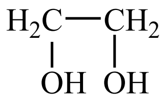
CH_3-CH_2-CH_2-CH_2-OH

1-Butanol

Which one of the above monohydric alcohols is present in drinking alcohol?

Dihydric alcohols contain two hydroxyl groups per molecule. They are also named glycols or diols.

Example 6.3



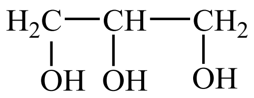
$\underset{OH}{\underset{|}{H_2C}}-\underset{OH}{\underset{|}{CH_2}}$

Ethane-1,2-diol (Ethylene glycol)

Can you give more examples of dihydric alcohols?

Trihydric alcohols contain three hydroxyl groups in their molecular structure.

Example 6.4



$\underset{OH}{\underset{|}{H_2C}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

Propane-1,2,3-triol (Glycerine or glycerol)

Polyhydric alcohols are those alcohols containing three or more hydroxyl groups in their molecular structure.

Can you give examples of polyhydric alcohols?

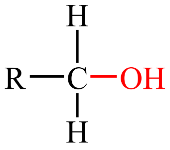
Classification of Monohydric Alcohols

Dear learner, monohydric alcohols may be further classified according to the carbon atom to which the hydroxyl group is attached.

Primary alcohols

In a primary alcohol, the carbon with the hydroxyl group is only attached to one alkyl group.

General structure:



$R-\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}-OH$

Primary (1°) alcohol

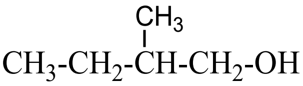
Example 6.5

$CH_3\text{-}CH_2\text{-}OH$

Ethanol

$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH$

1-Propanol



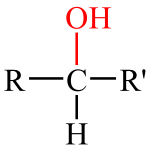
$CH_3\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{C}}H\text{-}CH_2\text{-}OH$

2-Methyl-1-butanol

Secondary alcohols

In a secondary alcohol, the carbon with the hydroxyl group is attached to two alkyl groups.

General structure:

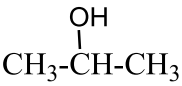


$R-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R'$

Where, R and R' may be same or different

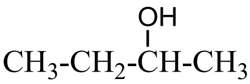
Secondary (2°) alcohol

Example 6.6



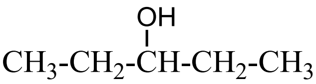
$CH_3\text{-}\overset{OH}{\overset{|}{C}}H\text{-}CH_3$

2-Propanol



$CH_3\text{-}CH_2\text{-}\overset{OH}{\overset{|}{C}}H\text{-}CH_3$

2-Butanol



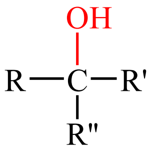
$CH_3\text{-}CH_2\text{-}\overset{OH}{\overset{|}{C}}H\text{-}CH_2\text{-}CH_3$

3-Pentanol

Tertiary alcohols

In a tertiary alcohol, the carbon with the hydroxyl group is attached to three other alkyl groups.

General structure:

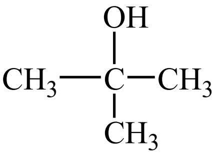


$R-\underset{R''}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R'$

Where, R,R' and R" may be the same or different

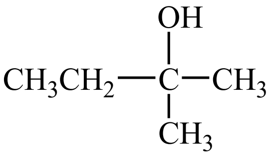
Tertiary (3°) alcohol

Example 6.7



$CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$

2-Methyl-2-propanol



$CH_3CH_2-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$

2-Methyl-2-butanol

6.2.2 Nomenclature of Alcohols

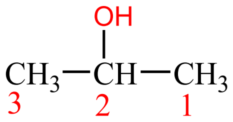
Dear learner, do you recognize that the common name of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it. In the IUPAC system, an alcohol is named by replacing the *e* of the corresponding alkane name with *ol*.

Example 6.8

CH_3-H	CH_3-OH	CH_3-CH_2-H	CH_3-CH_2-OH
Methane	Methanol (methyl alcohol)	Ethane	Ethanol (ethyl alcohol)

When an alcohol consists of a chain with three or more carbon atoms, the chain is numbered to give the position for the –OH group and any substituents on the chain. For this, the longest carbon chain (parent chain) is numbered starting at the end nearest to the hydroxyl group. The positions of the –OH group and other substituents are indicated by using the numbers of carbon atoms to which these are attached.

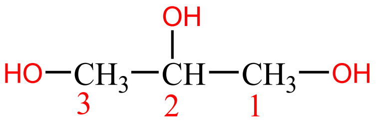
Example 6.9

	$\underset{3}{CH_3}-\underset{2}{CH_2}-\underset{1}{CH_2}-OH$	 $\underset{3}{CH_3}-\underset{2}{\overset{\overset{OH}{|}}{CH}}-\underset{1}{CH_3}$
IUPAC name:	1-Propanol	2-Propanol
Common name:	(propyl alcohol)	(isopropyl alcohol)

Is neopentyl alcohol a 1°, 2°, or 3° alcohol?

In IUPAC naming of polyhydric alcohols, the ‘*e*’ of alkane is retained and the ending ‘*ol*’ is added. The number of –OH groups is indicated by adding the multiplicative prefix, *di*, *tri*, etc., before ‘*ol*’.

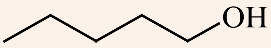
Example 6.10

	$HO-\underset{2}{CH_2}-\underset{1}{CH_2}-OH$	 $HO-\underset{3}{CH_3}-\underset{2}{\overset{\overset{OH}{|}}{CH}}-\underset{1}{CH_3}-OH$
IUPAC name:	1,2-Ethanediol	1,2,3-Propanetriol
Common name:	(ethylene glycol)	(glycerol)

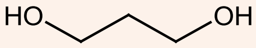
Self-test Exercise 6.1

1. Give the general formula for the homologous series of monohydric alcohols.
2. Classify the following alcohols as monohydric, dihydric and trihydric alcohols.
   a. 2-propanol b. 1,3-propanediol c. 1,2,3-butanetriol
3. Classify the following monohydric alcohols as primary, secondary or tertiary alcohols.
   a. 1-pentanol b. 2-pentanol c. 2-methyl-2-butanol
4. Give the IUPAC name for the following alcohols:

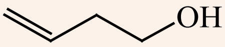
a.



b.



c.



6.2.3 Physical Properties of Alcohols

Dear learner, note that the hydroxyl group in an alcohol is polar due to the high electronegativity of oxygen. As a result, there is significant hydrogen bonding in alcohols (**Figure 6.1**).

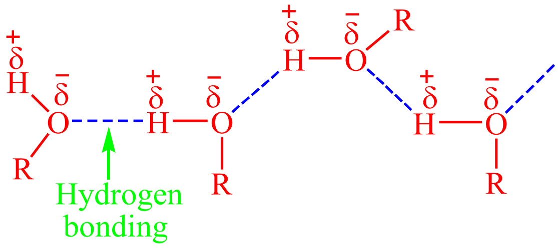


Figure 6.1: Hydrogen bonding between molecules of an alcohol.

Alcohols have higher melting and boiling points than hydrocarbons of comparable molecular size (mass).

Activity 6.2

Dear learner, try to answer the following questions.

1. Compare the physical state of the first four members of monohydric alcohols and alkanes.
2. Lower alcohols, like methanol and ethanol, are miscible with water in all proportions, while lower hydrocarbons are not so. Explain.

Table 6.1 gives some physical constants of the first six monohydric alcohols. Hydrogen bonding is also the cause for even lower members to be liquids at room temperature.

Table 6.1 IUPAC Names, Condensed Structure and Physical Constants of the First Six Monohydric Alcohols

Structure of monohydric alcohol	IUPAC name	Melting point (°C)	Boiling point (°C)	Density (g/mL)
CH_3OH	Methanol	–97	64.7	0.792
CH_3CH_2OH	Ethanol	–117	78.3	0.789
$CH_3CH_2CH_2OH$	1-Propanol	–126	97.2	0.804
$CH_3(CH_2)_2CH_2OH$	1-Butanol	–90	117.7	0.810
$CH_3(CH_2)_3CH_2OH$	1-Pentanol	–78.5	138	0.817
$CH_3(CH_2)_4CH_2OH$	1-Hexanol	–52	156.5	0.819

The general trends in physical properties of alcohols are:

Dihydric and the trihydric alcohols have higher boiling points than monohydric alcohols of similar molecular size (mass).

The solubility of alcohols in water decreases with increasing carbon number.

The water solubilities of dihydric and trihydric alcohols are higher than those of monohydric alcohols of similar molecular mass.

The boiling point of a branched isomer is lower than that of its isomeric straight-chain alcohol.

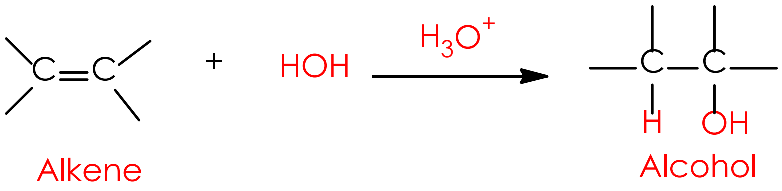
6.2.4 Preparation of Alcohols

Dear learner, recognize that the following are the general laboratory methods of preparation of alcohols:

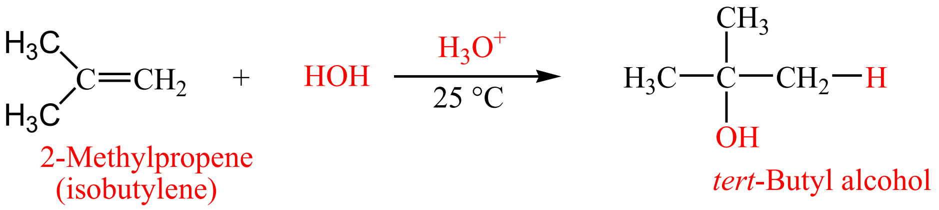
a. Acid-catalyzed hydration of alkenes:

Water is added to the double bond of an alkene in the presence of dilute acid such as H_2SO_4 or H_3PO_4.

General reaction:



Example 6.11



Note that hydrogen of the water goes to the carbon of the alkene that contains more hydrogens following the Markonikov's rule.

> Markonikov's rule: When an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of the reagent is attached to the unsaturated carbon atom having less number of hydrogen atoms.

b. Hydrolysis of alkyl halides:

Warming alkyl halides with sodium hydroxide forms alcohols.

What does hydrolysis mean?

General reaction:

$$\underset{\substack{(X = Cl, Br, I)\\ \text{Alkyl halide}}}{R{-}CH_2X} + NaOH \xrightarrow{\text{heat}} \underset{\text{Alcohol}}{R{-}CH_2OH} + NaX$$

Example 6.12

$$\underset{\text{Ethyl chloride}}{CH_3{-}CH_2Cl} + NaOH \xrightarrow{\text{heat}} \underset{\text{Ethanol}}{CH_3{-}CH_2OH} + NaCl$$

c. Hydrolysis of Esters:

Heating esters with potassium hydroxide produces alcohols.

General reaction:

$$\underset{\text{Ester}}{RCOOR'} + KOH \xrightarrow{\text{heat}} RCOOK + \underset{\text{Alcohol}}{R'OH}$$

Example 6.13

$$\underset{\text{Ethyl acetate}}{CH_3COOCH_2CH_3} + KOH \xrightarrow{\text{heat}} CH_3COOK + \underset{\text{Ethanol}}{CH_3CH_2OH}$$

Methods **b** and **c** involve the replacement of other groups by the –OH group. Hence, they are examples of substitution reactions.

Ethanol (Ethyl Alcohol), CH_3CH_2OH

Activity 6.3

Dear learner, attempt to answer the following questions.

1. Why is the shelf-life of some alcoholic beverages low, while for others it is high?
2. How can you improve the shelf-life of those alcoholic beverages with a low shelf-life?

Ethanol is the second member of the homologous series of monohydric alcohols. It is one of the constituents of all alcoholic beverages. 'Tella', 'Tej', beer, wine, 'Katikalla', ouzo, gin and whisky contain ethanol. There are a number of methods for preparing ethanol using different materials.

? Can you categorize the alcoholic beverages as distilled and non-distilled?

Industrial preparation of ethanol

Ethanol is manufactured industrially by:

1. **Fermentation of carbohydrates** such as sugar. Fermentation is the slow decomposition of carbohydrates such as sucrose, starch and cellulose in the presence of a suitable enzyme. It results in the formation of ethanol and carbon dioxide:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Ethanol}}{2CH_3CH_2OH} + 2CO_2$$

Fermentation can produce an alcoholic beverage whose ethanol content is 12-15% only.

Why is it difficult to produce a higher percentage of alcohols by fermentation?

How can a higher ethanol-containing beverages be produced?

Dear learner, most liquor factories in Ethiopia use molasses, a by-product of sugar industries, as a raw material to produce ethanol. In the brewing industry, germinated barley called malt is used as the starting material. The whole process taking place in breweries is summarized as follows:

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}} \xrightarrow[\text{Maltase}]{nH_2O} \underset{\text{Glucose}}{2nC_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{2CH_3CH_2OH} + 2CO_2$$

2. **Catalytic Hydration of Ethene**. Most ethanol is manufactured at present by this method. In this process, ethene is treated with steam at 573 °K and 60 atm pressures in the presence of phosphoric acid, H_3PO_4, catalyst.

$$\underset{\text{Ethene}}{CH_2{=}CH_2\,(g)} + H_2O\,(g) \xrightarrow[\text{573 K/60 atm}]{H_3PO_4} \underset{\text{Ethanol}}{CH_3CH_2OH\,(g)}$$

Experiment 6.1

Preparation of Ethanol by Fermentation

Objective: To prepare ethanol from sugar.

Materials and chemicals: Conical flask, glass rod, distillation flask, condenser, spatula, thermometer, watch glass, Bunsen burner, tripod, boiling chips, beaker, stopper and delivery tube. Sugar, ammonium phosphate or ammonium sulphate, yeast, $Ca(OH)_2$.

Procedure:

1. Take 50 mL of distilled water in a conical flask, add 15 g of sugar to it and stir. Add about 1 gram of yeast and a small amount of ammonium phosphate or ammonium sulphate to the solution. Arrange the setup, as shown in Figure 6.2, and let the flask stand for three days at a warm place.

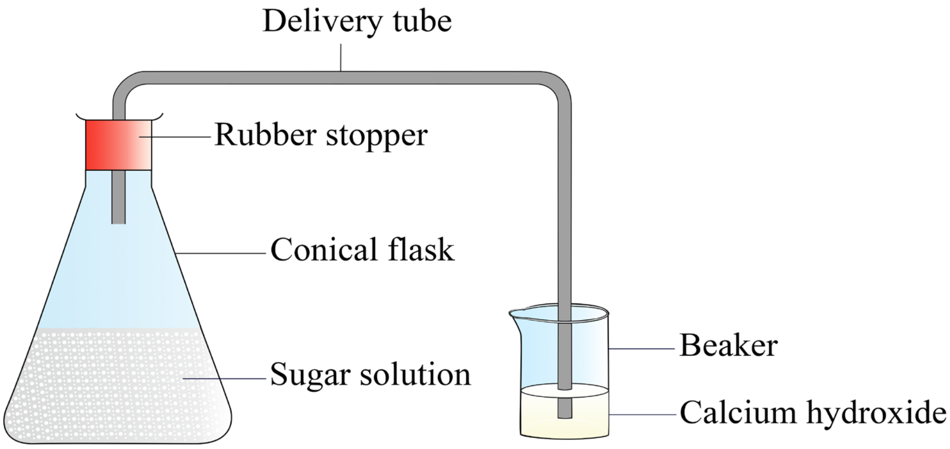


Figure 6.2: The fermentation of sugar

Observations and analysis:

A. What is the purpose of adding yeast to the solution?
B. Why do we add ammonium phosphate or ammonium sulphate to the sugar solution?
C. What happened to the calcium hydroxide solution at the end of the first or second day? Which gas is produced?
D. What is the smell of the solution in the flask after three days?
E. What has happened in the flask containing the sugar solution as it stood for three days?
F. After three days, filter the solution, and arrange the set up as in **Figure 6.3.** Pour 20 mL of the filtrate in a distilling flask, with a few boiling chips, heat the solution, and collect the liquid in a receiver.

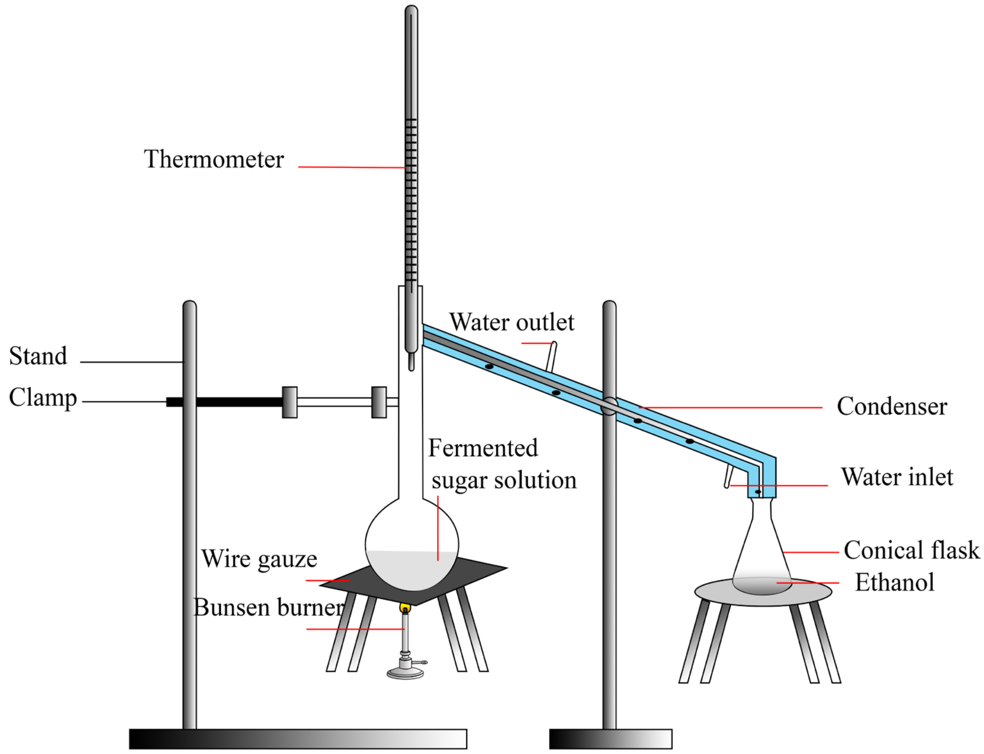


Figure 6.3: Separation of ethanol by distillation

Points to observe:

A. Observe the colour and identify the smell of the distillate.

B. Pour a small amount of the distillate on a watch glass, strike a match and bring the flame close to the distillate. Does it catch fire?

C. Write a complete laboratory report on this experiment and submit it to your teacher.

6.2.5 Chemical Properties of Alcohols

Activity 6.4

Dear learner, why do alcoholic beverages such as “Tela”, “Tej”, beer and wine turn sour if they are not properly stored? Which reaction of alcohols is responsible for this phenomenon?

Reactions of alcohols may involve the cleavage of the oxygen-hydrogen bond (— O — H) or the carbon-oxygen bond (— C — O).

1. Reactions of alcohols involving cleavage of –O–H bond

a. Reaction with Active Metals

Alcohols react with Li, Na, K, Mg, and other active metals to liberate hydrogen and to form metal alkoxides.

General reaction:

$$\underset{\text{Alcohol}}{2\,R-CH_2-O-H} + 2\,Na \longrightarrow \underset{\text{Sodium alkoxide}}{2\,R-CH_2-\overset{-}{O}\overset{+}{Na}} + H_2$$

Example 6.14

$$\underset{\text{Ethanol}}{2\,CH_3-CH_2-O-H} + 2\,Na \longrightarrow \underset{\text{Sodium ethoxide}}{2\,CH_3-CH_2-\overset{-}{O}\overset{+}{Na}} + H_2$$

Experiment 6.2

Reactions of Alcohols with Active Metals

Objective: To observe the reaction of alcohols with sodium and magnesium.

Materials required: Ethanol, sodium and magnesium metal. Test tubes, test tube holder, test tube rack, measuring cylinder, Bunsen burner, scissors or knife.

Procedure:

Take two test tubes and add 2-5 mL of ethanol to each of the test tubes. Cut a very small piece of sodium with a knife and drop it into the first test tube. Take magnesium ribbon and drop it in the second test tube.

Observations and analysis:

A. What do you observe
   a. in the first test tube? b. in the second test tube?

B. Is there an evolution of gas? How do you check this gas is hydrogen?

C. If no reaction occurs in any of the test tubes, heat the mixture gently using a Bunsen burner and write your observation.

D. Which bond of the alcohol is broken in the reaction?

E. Write a general reaction for such reactions.

F. What type of metals reacts in this manner?

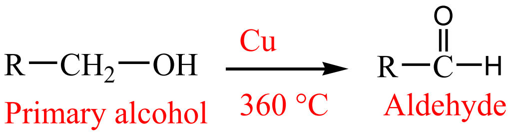
b. Oxidation of alcohols

Dear learner, note that the oxidation products of alcohols depend on the type of alcohol and the nature of oxidizing agents. Oxidation of alcohols is a very important method for the production of other oxygen-containing organic compounds, such as aldehydes, ketones and carboxylic acids.

i. Oxidation of primary alcohols

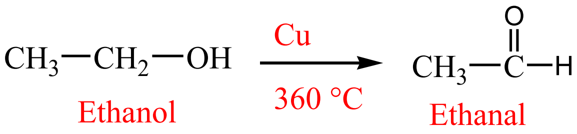
Depending on the oxidizing agent used, a primary alcohol is oxidized to an aldehyde which in turn is oxidized to a carboxylic acid. In the presence of mild oxidizing agents such as copper metal, primary alcohols yield aldehydes.

General reaction:



$$\underset{\text{Primary alcohol}}{R-CH_2-OH} \xrightarrow[360\ °C]{Cu} \underset{\text{Aldehyde}}{R-\overset{\overset{\Large O}{\|}}{C}-H}$$

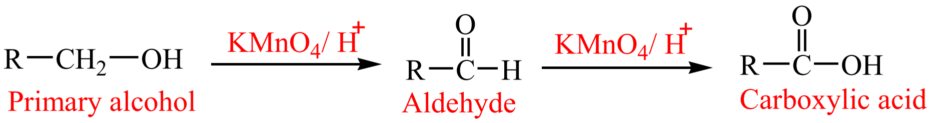
Example 6.15



$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[360\ °C]{Cu} \underset{\text{Ethanal}}{CH_3-\overset{\overset{\Large O}{\|}}{C}-H}$$

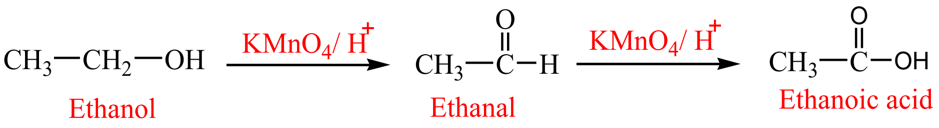
Strong oxidizing agents, such as acidified $KMnO_4$ or $K_2Cr_2O_7$ or CrO_3 in H_2SO_4, oxidize primary alcohol first to aldehydes and then to carboxylic acids. It is difficult to stop the reaction at the aldehyde stage.

General reaction:



$$\underset{\text{Primary alcohol}}{R-CH_2-OH} \xrightarrow{KMnO_4/\ H^+} \underset{\text{Aldehyde}}{R-\overset{\overset{\Large O}{\|}}{C}-H} \xrightarrow{KMnO_4/\ H^+} \underset{\text{Carboxylic acid}}{R-\overset{\overset{\Large O}{\|}}{C}-OH}$$

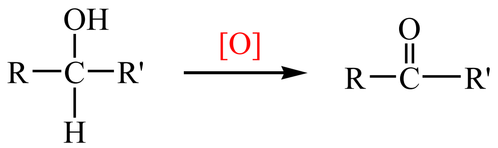
Example 6.16



$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow{KMnO_4/\ H^+} \underset{\text{Ethanal}}{CH_3-\overset{\overset{\Large O}{\|}}{C}-H} \xrightarrow{KMnO_4/\ H^+} \underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{\Large O}{\|}}{C}-OH}$$

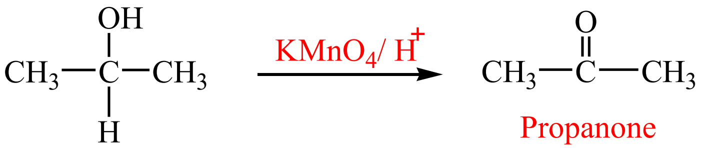
ii. Oxidation of secondary alcohols yields ketones

General reaction:



Secondary alcohol Ketone 3

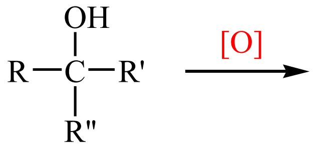
Example 6.17



2- Propanol

Propanone
(acetone)

iii. Tertiary alcohols and ketones are generally resistant to oxidation



No reaction
Under normal conditions

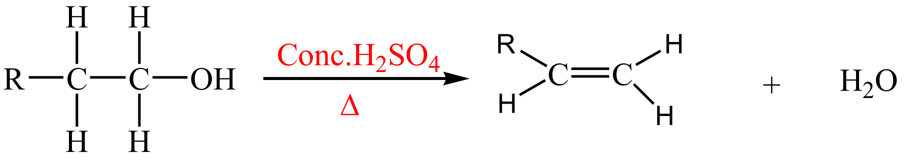
Tertiary alcohol

What happens if 3° alcohols subject to oxidation under drastic conditions?

2. Reactions involving cleavage of carbon–oxygen (C – O) bond in alcohols

a. Dehydration of alcohols: Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with an acid such as concentrated H_2SO_4 or H_3PO_4 and heating.

General reaction:

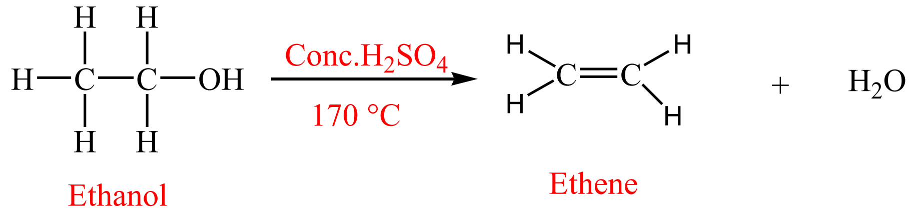


Alcohol Alkene

Dehydration of primary alcohols is difficult and requires concentrated acid and high temperature.

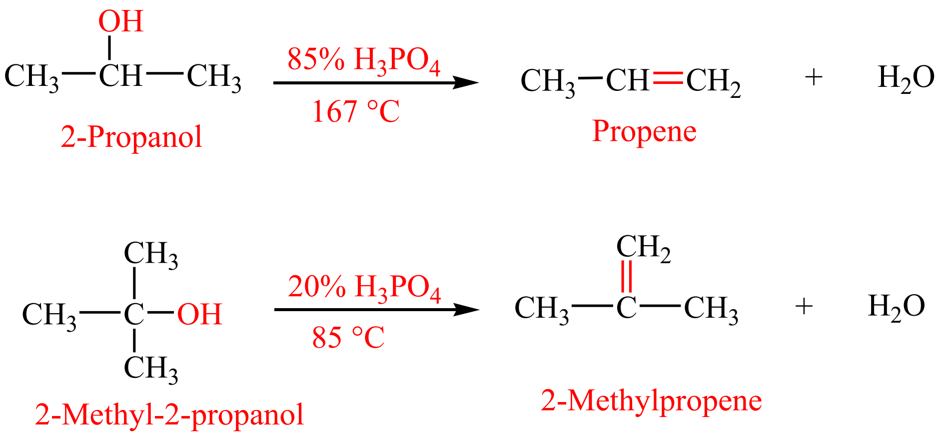
Example 6.18

Ethanol dehydrates in the presence of concentrated H_2SO_4 and heating at 170 °C.



Secondary and tertiary alcohols dehydrate under milder conditions.

Example 6.19



b. Reactions of alcohols with hydrogen halides: Alcohols react with hydrogen halides to form alkyl halides.

General reaction:

$$R{-}CH_2{-}OH \quad + \quad HX \longrightarrow R{-}CH_2{-}X \quad + \quad H_2O$$

Alcohol

(X = Cl, Br, I)
Alkyl halide

Example 6.20

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + HBr \longrightarrow \underset{\text{Ethyl bromide (1-bromoethane)}}{CH_3-CH_2-Br} + H_2O$$

Is it possible to produce alcohols from alkyl halides?

Self-test Exercise 6.2

1. What is the general formula of alcohols?

   Classify the following alcohols as primary, secondary and tertiary alcohols:

   a. 3-hexanol
   b. 2-methyl-2-pentanol
   c. 3-methyl-2-butanol
   d. 1-heptanol
   e. 2-methyl-1-propanol
   f. 2,3-dimethyl-2-butanol

2. Compare boiling points of alcohols and hydrocarbons of similar molecular mass. Explain if there is any difference.

3. Complete the following chemical reactions in your exercise book:

   a. $CH_3CH_2CH_2CH_2OH \xrightarrow{CrO_3/H_2SO_4}$

   b. 

   $$H_3C-CH_2-\overset{\overset{OH}{|}}{C}H-CH_2CH_3 \xrightarrow{K_2Cr_2O_7/\ H^+}$$

6.2.6 Structure and Nomenclature of Ethers

Dear learner, note that ethers are compounds in which an oxygen is bonded to two alkyl substituents (R–O–R'), where R and R' may be the same or different. If the alkyl substituents are identical, the ether is a symmetrical ether. If the substituents are different, the ether is an unsymmetrical ether.

$R-O-R$

a symmetrical ether

$R-O-R'$

an unsymmetrical ether

Activity 6.5

Dear learner, diethyl ether (CH_3CH_2-O-CH_2CH_3) is prepared from ethyl alcohol (CH_3CH_2-OH). Based on this information and your prior knowledge of molecular structures, try to answer the following questions.

1. From CH_3CH_2-OH and CH_3CH_2-O-CH_2CH_3, which one do you expect to have higher boiling point? Why?
2. Which one of these compounds is more soluble in water? Why?

The common name of an ether consists of the names of the two alkyl substituents (in alphabetical order), followed by the word "ether". The smallest ethers are almost always named by their common names.

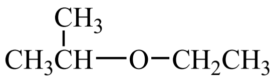
Example 6.21

a. $CH_3-O-CH_2CH_3$

ethylmethyl ether

b. $CH_3CH_2-O-CH_2CH_3$

diethyl ether

c. 

$CH_3\overset{\overset{CH_3}{|}}{C}H-O-CH_2CH_3$

ethylisopropyl ether

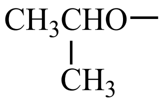
The IUPAC system names an ether as an alkane with an RO– substituent. The substituents are named by replacing the "yl" ending in the name of the alkyl substituent with "oxy".

CH_3O-

methoxy

CH_3CH_2O-

ethoxy



$CH_3\underset{\underset{CH_3}{|}}{C}HO-$

isopropoxy

Example 6.22

a. 

$CH_3\overset{\overset{OCH_3}{|}}{C}HCH_2CH_3$

2-methoxybutane

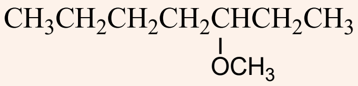
b. $CH_3CH_2CH_2CH_2CH_2-OCH_2CH_3$

1-ethoxypentane

Self-test Exercise 6.3

1. Give the systematic (IUPAC) name for each of the following ethers:

a. $CH_3CH_2CH_2OCH_2CH_2CH_2CH_3$

b. 

$CH_3CH_2CH_2CH_2\underset{\underset{OCH_3}{|}}{C}HCH_2CH_3$

2. What are the common names of the compounds given in question 1?

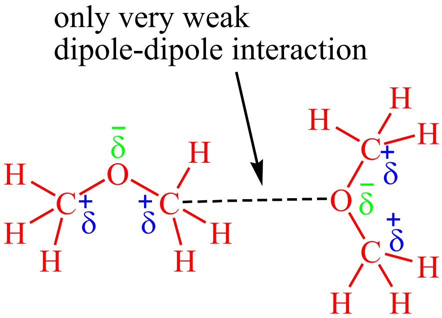
6.2.7 Physical Properties of Ethers

Dear learner, ethers are polar compounds in which oxygen bears a partial negative charge and each carbon bonded to it bears a partial positive charge **(Figure 6.4).**

How do ethers differ from alcohols?

The boiling points of ethers are much lower than those of alcohols of comparable molecular weight. For example, the boiling points of ethanol (78 °C) is much higher than its constitutional isomer dimethyl ether (-24 °C). The difference in boiling points between these two compounds is due to the polar O–H group in the alcohol, which is capable of forming intermolecular hydrogen bonds.

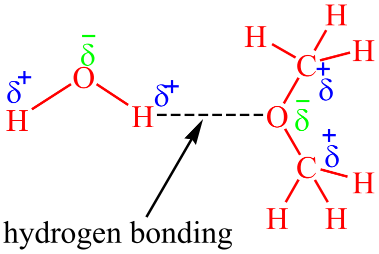
How do you rate the boiling points of ethers and hydrocarbons of comparable molecular weight?



only very weak
dipole-dipole interaction

Figure 6.4: Weak attractive interactions exist between diethyl ether molecules in the pure liquid

Because the oxygen atom of an ether carries a partial negative charge, ethers form hydrogen bonds with water **(Figure 6.5)** and are more soluble in water than are hydrocarbons of comparable molecular weight and shape.



hydrogen bonding

Figure 6.5: Hydrogen bonding between diethyl ether and water

Self-test Exercise 6.4

1. Arrange these compounds in order of increasing solubility in water:
   a. $CH_3OCH_2CH_2OCH_3$ b. $CH_3CH_2OCH_2CH_3$ c. $CH_3CH_2CH_2CH_2CH_2CH_3$
2. Arrange these compounds in order of increasing boiling point:
   a. $CH_3OCH_2CH_2OCH_3$ b. $HOCH_2CH_2OH$ c. $CH_3OCH_2CH_2OH$
3. Write the condensed structures of both isomers with the formula C_2H_6O Label the functional group of each isomer.

6.2.8 Preparation of Ethers

1. Dehydration of alcohols

Dear learner, note that alcohol undergoes dehydration in the presence of protic acids (sulphuric acid, phosphoric acid) to produce alkenes and ethers under different conditions. For example, ethanol is dehydrated to ethene at 170 °C in the presence of sulphuric acid. On the other hand, ethanol yields diethyle ether in the presence of sulphuric acid at 140 °C. The method is limited to use with primary alcohols.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[170\ ^{o}C]{H_2SO_4} \underset{\text{Ethene}}{CH_2{=}CH_2} + \underset{\text{Water}}{H_2O}$$

$$\underset{\text{Ethanol}}{2\ CH_3CH_2OH} \xrightarrow[140\ ^{o}C]{H_2SO_4} \underset{\text{Diethyl ether}}{CH_3CH_2OCH_2CH_3} + \underset{\text{Water}}{H_2O}$$

? What is the problem if we use secondary and tertiary alcohols?

? Does this method work for the synthesis of both symmetrical and unsymmetrical ethers?

2. Williamson ether synthesis

In this method, an alkyl halide is made to react with an alkoxide which leads to the formation of ether.

$$\underset{\text{Alkyl halide}}{R{-}X} + \underset{\text{Alkoxide ion}}{R{-}O^-} \longrightarrow \underset{\text{Ether}}{R{-}O{-}R} + X^-$$

Can this method be used for the preparation of both symmetrical and unsymmetrical ethers?

Example 6.23

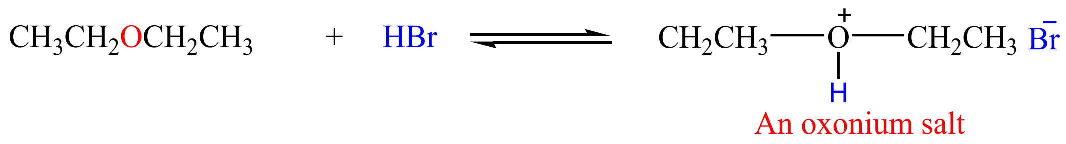
$$\underset{\text{ethyl bromide}}{CH_3CH_2Br} + \underset{\text{methoxide ion}}{CH_3O^-} \longrightarrow \underset{\text{ethyl methyl ether}}{CH_3CH_2OCH_3} + Br^-$$

$$\underset{\text{butyl iodide}}{CH_3CH_2CH_2CH_2I} + \underset{\text{ethoxide ion}}{CH_3CH_2O^-} \longrightarrow \underset{\text{butyl ethyl ether}}{CH_3CH_2CH_2CH_2OCH_2CH_3} + I^-$$

6.2.9 Reactions of Ethers

Dear learner, ethers, R–O–R, resemble hydrocarbons in their resistance to chemical reaction. They do not react with oxidizing agents, such as $K_2Cr_2O_7$ or $KMnO_4$. Ethers are not affected by bases, however, they can react with proton donors to form oxonium salts. Why?

Example 6.24



$$CH_3CH_2OCH_2CH_3 + HBr \rightleftharpoons \underset{\text{An oxonium salt}}{CH_2CH_3-\underset{\displaystyle H}{\overset{+}{O}}-CH_2CH_3\ Br^-}$$

Heating dialkyl ethers with very strong acids (HI, HBr, and H_2SO_4) cleaves the ether linkage:

$$CH_3CH_2OCH_2CH_3 + 2\,HBr \xrightarrow{\Delta} 2\,CH_3CH_2Br + H_2O$$

Ethers are not affected by most reagents at moderate temperatures. Because of their good solvent properties and general inertness to chemical reaction, ethers are excellent solvents in which to carry out many organic reactions.

Self-test Exercise 6.5

1. What are the common use of ethers?
2. Outline how the alkoxide ion is prepared for the Williamson ether synthesis using a chemical equation.

CHECKLIST 6.2

In the boxes provided for each of the following tasks put a tick mark (√) if you can perform or concepts you are familiar with them.

I can…

- define alcohols ☐
- classify alcohols based on the number of hydroxyl groups ☐
- write the general formulas of monohydric alcohols ☐
- write the molecular formulas and the names of monohydric alcohols ☐
- give the IUPAC names for the given alcohols ☐
- describe the physical properties of alcohols ☐
- explain general methods of preparation of alcohols ☐
- explain the chemical reactions of alcohols ☐
- write the molecular formulas and names of ethers ☐
- give the IUPAC names for given ethers ☐
- describe the physical properties of ethers ☐
- explain the general methods of preparation of ethers ☐
- explain the use of ethers ☐

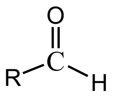
Section 6.3: Aldehydes and Ketones

Dear learner, in this section you will study the functional group of aldehydes and ketones, their naming systems, general methods of preparation, and chemical reactions. Aldehydes and ketones are widespread in nature, often combined with other functional groups. Aldehydes and ketones are known for their **sweet** and sometimes **pungent odors**. For example, the odor from vanilla extract comes from the molecule vanillin.

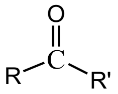
At the end of this section, you will be able to:

- write the general structural formulas of aldehydes and ketones
- give the structures and names of common members of each group
- describe the physical properties of aldehydes and ketones
- explain some methods of preparation of aldehydes and ketones
- explain the chemical reactions of aldehydes and ketones such as addition, oxidation and reduction
- give some chemical tests that differentiate aldehydes from ketones.

The functional group of an aldehyde is a carbonyl group (C=O) bonded to a hydrogen atom, whereas in a ketone the carbonyl group is bonded to two carbon atoms.


or RCHO

Aldehyde


or RCOR' where R and R' may be same or different.

Ketone

Activity 6.6

Dear learner, try to answer the following questions.

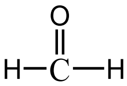
1. What functional group form if one of the carbons in the C=C is replaced by an oxygen atom?
2. What are the simplest ketone and simplest aldehyde?

6.3.1 Nomenclature

Dear learner, in the IUPAC system aldehydes and ketones are named by selecting the longest chain of carbon atoms that contains the functional group as the parent alkane.

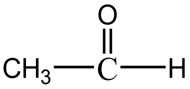
Aldehydes are named by changing the suffix *-e* of the parent alkane to *–al*. The suffix "*-al*" indicates the functional group –CHO.

Example 6.25



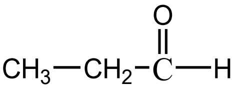
$H-\overset{\overset{O}{\parallel}}{C}-H$

Methanal



$CH_3-\overset{\overset{O}{\parallel}}{C}-H$

Ethanal

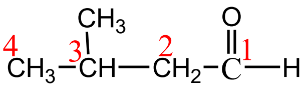


$CH_3-CH_2-\overset{\overset{O}{\parallel}}{C}-H$

Propanal

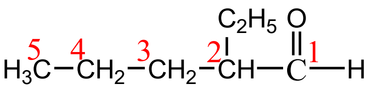
The carbonyl carbon atom in aldehydes is always considered to be C-1; there is no need to use a number to locate it.

Example 6.26



${}^{4}CH_3-\overset{\overset{CH_3}{|}}{{}^{3}CH}-{}^{2}CH_2-\overset{\overset{O}{\parallel}}{{}^{1}C}-H$

3-Methylbutanal



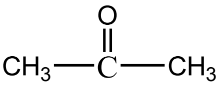
$H_3{}^{5}C-{}^{4}CH_2-{}^{3}CH_2-\overset{\overset{C_2H_5}{|}}{{}^{2}CH}-\overset{\overset{O}{\parallel}}{{}^{1}C}-H$

2-Ethylpentanal

The functional group of a ketone is a carbonyl group bonded to two carbon atoms.

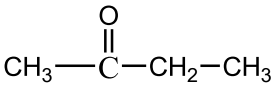
The IUPAC names of ketones are obtained by using the suffix *-one* to replace the terminal *-e* in the corresponding alkane name. The suffix '*-one*' indicates the functional group –ROR'.

Example 6.27



$CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3$

Propanone

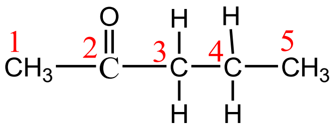


$CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_3$

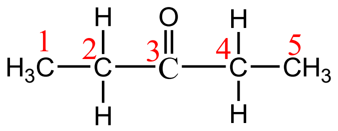
Butanone

Dear learner, in the name of higher ketones, the longest chain containing the functional group is chosen as a parent structure and then the carbon atoms of the chain are numbered starting from the end closer to the carbonyl group.

Example 6.28



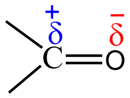
2-Pentanone or pentan-2-one



3-Pentanone or pentan-3-one

6.3.2 Physical properties of Aldehydes and Ketones

Dear learner, recognize that a carbon–oxygen double bond is polar, with oxygen bearing a partial negative charge and carbon bearing a partial positive charge:



Polarity of a carbonyl group

Aldehydes and ketones are polar compounds.

There is dipole–dipole interactions in aldehydes and ketones, as a result, they have higher boiling points than those of non-polar compounds with comparable molecular weight. For example, butanal and butanone both have a molecular mass (MM) of 72. The boiling point of butanal is 72, 76 °C and of butanone is 80 °C, which is much higher than the boiling points of diethyl ether (MM) 74, 34 °C and pentane (MM) 72, 36 °C.

The carbonyl groups of aldehydes and ketones can form hydrogen bonding with water molecules. Thus, low-molecular-weight aldehydes and ketones are more soluble in water than are non-polar compounds of comparable molecular weight. **Table 6.2** lists the boiling points and solubilities in water of several low-molecular-weight aldehydes and ketones.

Table 6.2 Physical properties of selected aldehydes and ketones

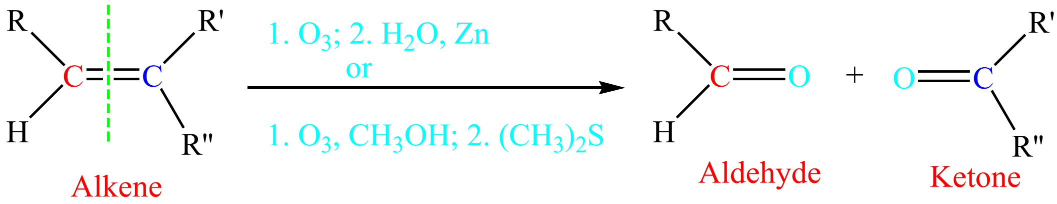
Name	Common Name	Structural Formula	Boiling Point (°C)	Solubility (g/100 g water)
Methanal	Formaldehyde	HCHO	-21	infinity
Ethanal	Acetaldehyde	CH_3CHO	20	infinity
Propanal	Propionaldehyde	CH_3CH_2CHO	49	16
Butanal	Butyraldehyde	$CH_3CH_2CH_2CHO$	76	7
Hexanal	Caproaldehyde	$CH_3(CH_2)_4CHO$	129	slight
Propanone	Acetone	CH_3COCH_3	56	infinity
2-Butanone	Methyl ethyl ketone	$CH_3COCH_2CH_3$	80	26
3-pentanone	Diethyl ketone	$CH_3CH_2COCH_2CH_3$	101	5

6.3.3 Method of preparation of Aldehydes and Ketones

Dear learner, you should recognize the common preparation methods of aldehydes and ketones: ozonolysis of alkenes and oxidation of alcohols.

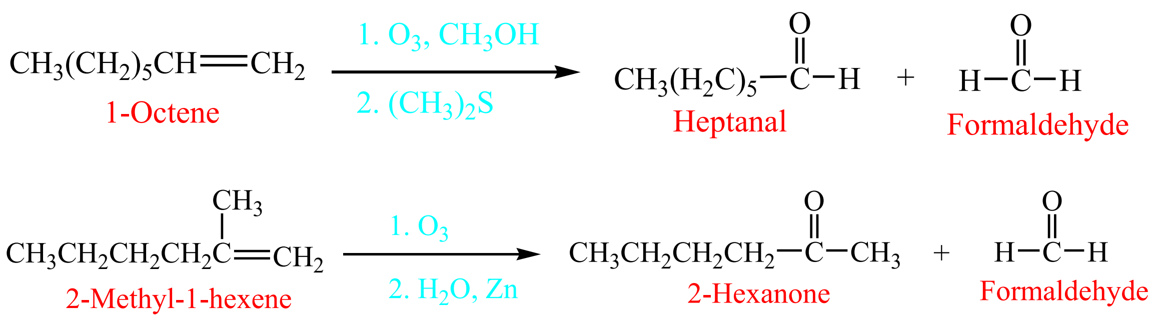
a. Ozonolysis of alkenes

When an alkene is treated with ozone (O_3) followed by hydrolysis of the resulting ozonids, two aldehydes, two ketones, or one aldehyde and one ketone may be formed. The two-stage reaction sequence is called ozonolysis and is represented by the general equation:



Each carbon of the double bond becomes the carbon of a carbonyl group.

Example 6.29



$$CH_3(CH_2)_5CH{=}CH_2 \xrightarrow[2.\ (CH_3)_2S]{1.\ O_3,\ CH_3OH} CH_3(H_2C)_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$

1-Octene, Heptanal, Formaldehyde

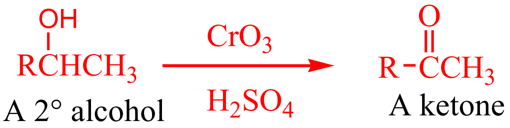
$$CH_3CH_2CH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2 \xrightarrow[2.\ H_2O,\ Zn]{1.\ O_3} CH_3CH_2CH_2CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$

2-Methyl-1-hexene, 2-Hexanone, Formaldehyde

b. Oxidation of Alcohols

Oxidation of a secondary alcohol leads to a ketone.

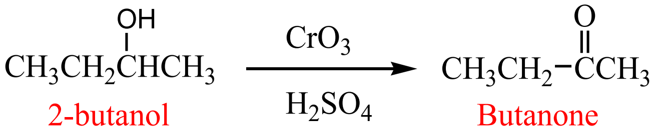
The common oxidizing agent is chromic acid (H_2CrO_4), which is formed when chromium trioxide (CrO_3) or sodium dichromate ($Na_2Cr_2O_7$) is dissolved in aqueous acid.



$$R\overset{\overset{\displaystyle OH}{|}}{C}HCH_3 \xrightarrow[H_2SO_4]{CrO_3} R{-}\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

A 2° alcohol, A ketone

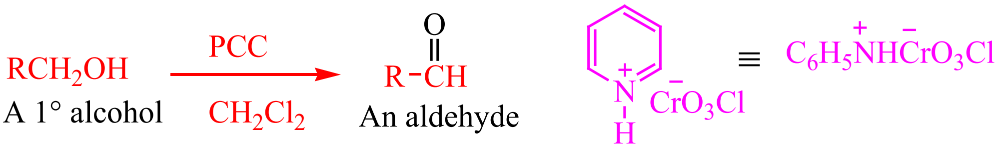
Example 6.30



$$CH_3CH_2\overset{\overset{\displaystyle OH}{|}}{C}HCH_3 \xrightarrow[H_2SO_4]{CrO_3} CH_3CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

2-butanol, Butanone

An aldehyde can be prepared by oxidation of a primary alcohol under mild oxidizing agent such pyridinium chlorochromate (PCC) in an anhydrous solvent such as dichloromethane (CH_2Cl_2).

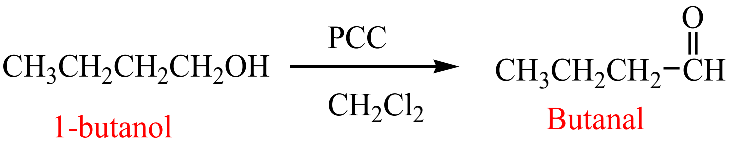


$$RCH_2OH \xrightarrow[CH_2Cl_2]{PCC} R{-}\overset{\overset{\displaystyle O}{\|}}{C}H \qquad \equiv C_6H_5\overset{+}{N}H\overset{-}{Cr}O_3Cl$$

A 1° alcohol, An aldehyde

PCC = Pyridinium chlorochromate

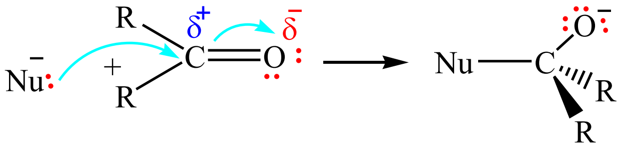
Example 6.31



$$\underset{\text{1-butanol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[CH_2Cl_2]{PCC} \underset{\text{Butanal}}{CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}H}$$

6.3.4 Reactions of aldehydes and ketones

Dear learner, the partially positive charge on the carbonyl carbon is the cause of the most common reaction theme of the carbonyl group, the addition of a nucleophile (Nu:⁻) to form a tetrahedral carbonyl addition intermediate.



Tetrahedral carbonyl addition intermediate

a. Addition

i. Addition of Grignard Reagents to Aldehydes and Ketones

The addition of carbon nucleophiles is the most important type of nucleophilic addition to a carbonyl group because these reactions form new carbon–carbon bonds.

The Grignard reagent is an alkylmagnesium halide.

$$\underset{\substack{\text{Alkyl halide}\\(X = Cl, Br, I)}}{R-X} \xrightarrow[\text{ether}]{Mg} \underset{\text{Grignard reagent}}{\overset{-}{R}:\overset{+}{Mg}X} \qquad R = \text{alkyl or aryl}$$

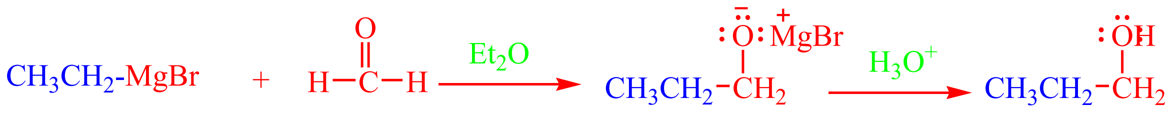
Example 6.32

$$CH_3CH_2Br \xrightarrow[Et_2O]{Mg} CH_3\overset{-}{CH_2}:\overset{+}{Mg}Br$$

1. Addition to Formaldehyde Gives a 1°Alcohol

Dear learner, note that treatment of a Grignard reagent with formaldehyde, followed by hydrolysis in aqueous acid, gives a primary alcohol:

Example 6.33

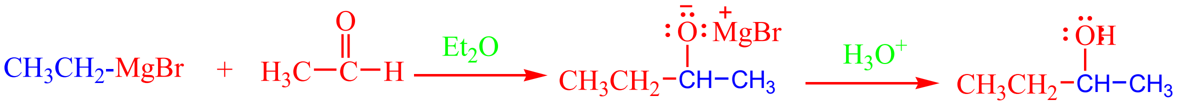


1- propanol
(1° alcohol)

2. Addition to an Aldehyde (Except Formaldehyde) Gives a 2°Alcohol

Treatment of a Grignard reagent with any aldehyde other than formaldehyde, followed by hydrolysis in aqueous acid, gives a secondary alcohol:

Example 6.34

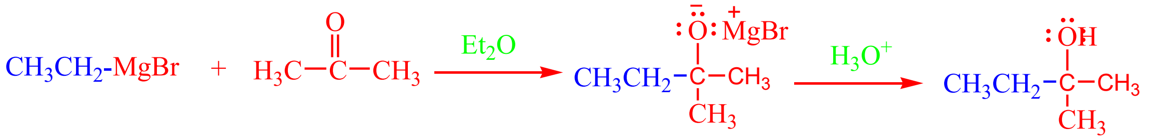


2- butanol
(2° alcohol)

3. Addition to a Ketone Gives a 3°Alcohol

Treatment of a Grignard reagent with a ketone, followed by hydrolysis in aqueous acid, gives a tertiary alcohol.

Example 6.35

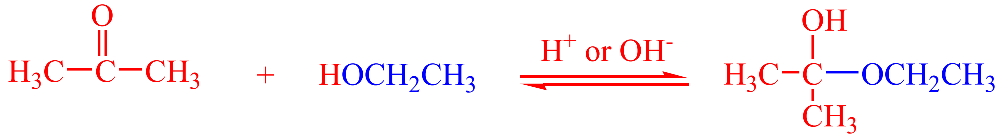


2- methyl-2- butanol
(3° alcohol)

ii. Addition of Alcohol: formation of Acetals

The addition of a molecule of alcohol to the carbonyl group of an aldehyde or a ketone forms a hemiacetal (a half-acetal). This reaction is catalyzed by both acid and base: Oxygen adds to the carbonyl carbon and hydrogen adds to the carbonyl oxygen.

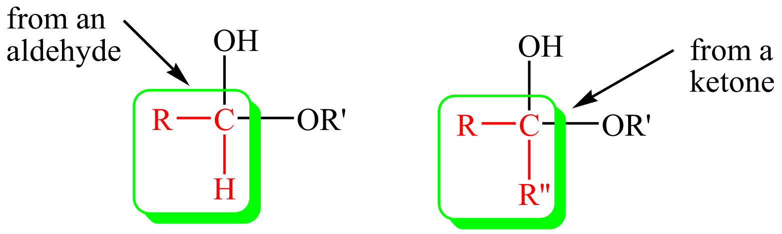
Example 6.36



$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 + HOCH_2CH_3 \xrightleftharpoons{H^+ \text{ or } OH^-} H_3C-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-OCH_2CH_3$$

A hemiacetal

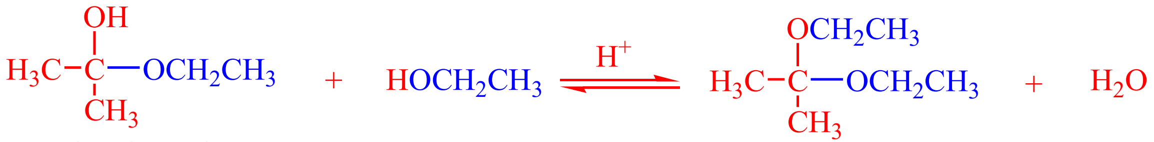
The functional group of a hemiacetal is a carbon bonded to an –OH group and an –OR or –OAr group.



Hemiacetals

Hemiacetals can react further with alcohols to form acetals plus a molecule of water. This reaction is acid catalyzed.

Example 6.37

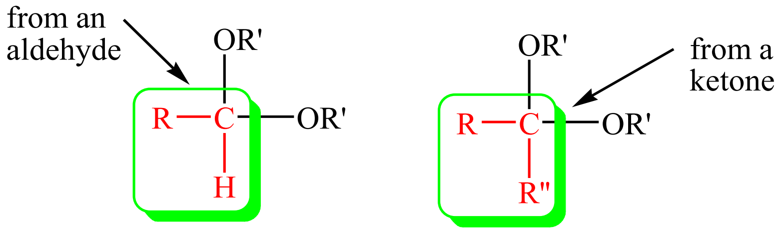


$$H_3C-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-OCH_2CH_3 + HOCH_2CH_3 \xrightleftharpoons{H^+} H_3C-\overset{\overset{OCH_2CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OCH_2CH_3 + H_2O$$

A hemiacetal

A diethyl acetal

The functional group of an acetal is a carbon bonded to two –OR or –OAr groups.



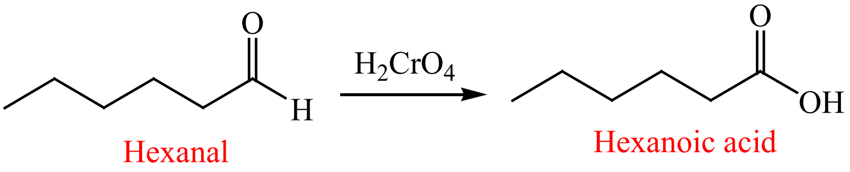
Acetals

b. Oxidation

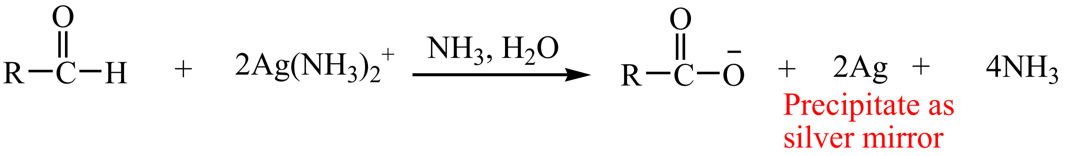
i. Oxidation of Aldehydes to Carboxylic Acids

Aldehydes are oxidized to carboxylic acids by a variety of common oxidizing agents, including chromic acid and molecular oxygen. Aldehydes are one of the most easily oxidized of all functional groups.

Example 6.38



When **Tollens' reagent** ($Ag(NH_3)_2^+$) is added to an aldehyde, the aldehyde is oxidized to a carboxylic anion, and Ag^+ is reduced to metallic silver. If this reaction is carried out properly, silver precipitates as a smooth, mirror like deposit—hence the name silver-mirror test:



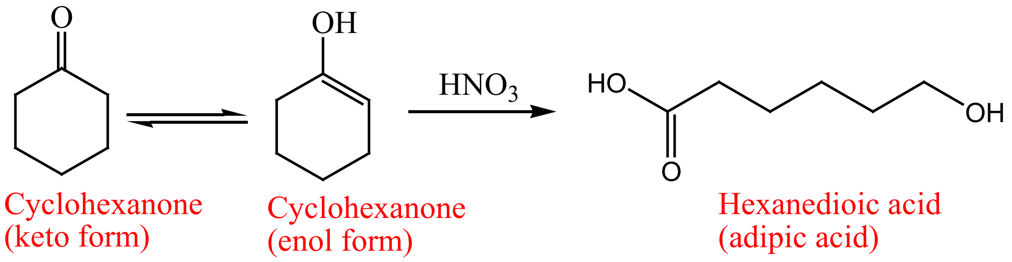
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \quad + \quad 2Ag(NH_3)_2^+ \xrightarrow{NH_3,\ H_2O} R-\overset{\overset{\displaystyle O}{\|}}{C}-\bar{O} \quad + \quad \underset{\text{Precipitate as silver mirror}}{2Ag} \quad + \quad 4NH_3$$

Tollens' reagent does not react with most ketones, which can be used to distinguish aldehydes from ketones.

ii. Oxidation of Ketones to Carboxylic Acids

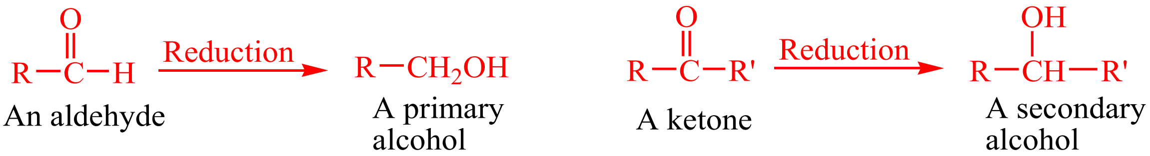
Ketones are much more resistant to oxidation than are aldehydes. For example, ketones are not normally oxidized by chromic acid or potassium permanganate. Ketones undergo oxidative cleavage, via their enol form, by potassium dichromate and potassium permanganate at higher temperatures and by higher concentrations of nitric acid, HNO_3.

Example 6.39



c. Reduction

Aldehydes are reduced to primary alcohols and ketones to secondary alcohols:

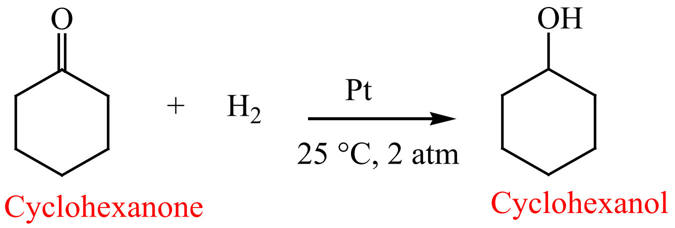


$$\underset{\text{An aldehyde}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H} \xrightarrow{\text{Reduction}} \underset{\text{A primary alcohol}}{R-CH_2OH} \qquad \underset{\text{A ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-R'} \xrightarrow{\text{Reduction}} \underset{\text{A secondary alcohol}}{R-\overset{\overset{\displaystyle OH}{|}}{CH}-R'}$$

i. Catalytic Reduction

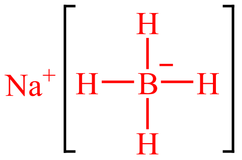
The carbonyl group of an aldehyde or a ketone is reduced to a hydroxyl group by hydrogen in the presence of a transition metal catalyst, most commonly finely divided palladium, platinum, nickel, or rhodium.

Example 6.40

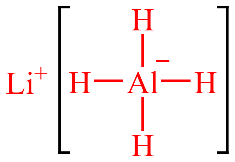


ii. Metal Hydride Reductions

By far the most common laboratory reagents used to reduce the carbonyl group of an aldehyde or a ketone to a hydroxyl group are sodium borohydride and lithium aluminum hydride. Each of these compounds behaves as a source of hydride ion, a very strong nucleophile.



Sodium borohydride

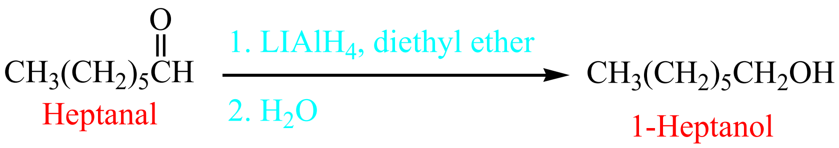


Lithium aluminum hydride

Hydride ion

Lithium aluminum hydride is a very powerful reducing agent; it rapidly reduces not only the carbonyl groups of aldehydes and ketones, but also those of carboxylic acids and their functional derivatives. Sodium borohydride is a much more selective reagent, reducing only aldehydes and ketones rapidly.

Example 6.41



$$CH_3(CH_2)_5\overset{\overset{O}{\|}}{C}H \xrightarrow[\text{2. } H_2O]{\text{1. LIAlH}_4\text{, diethyl ether}} CH_3(CH_2)_5CH_2OH$$

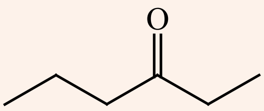
Heptanal

1-Heptanol

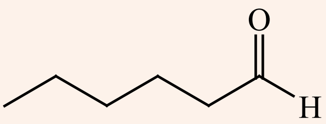
Self-test Exercise 6.6

1. Which of the following statements is false? Give your reason.
   a. The carbonyl carbon in all aldehydes is bonded to a hydrogen and to an alkyl group.
   b. Ketones are more soluble in water than alcohols of comparable molecular weight.
   c. Any reaction that oxidizes an aldehyde to a carboxylic acid will also oxidize a ketone to a carboxylic acid.
2. Draw a structural formula for the one ketone with molecular formula C_4H_8O and for the two aldehydes with molecular formula C_4H_8O.
3. Draw structural formulas for these compounds:
   a. 1-Chloro-2-propanone
   b. 3-Hydroxybutanal
   c. 4-Hydroxy-4-methyl-2-pentanone
4. Give the IUPAC name of the following compounds:

a.



b.



5. Formalin helps in the preservation of biological specimens. What is the main constituent of formalin?

√ CHECKLIST 6.3

In the boxes provided for each of the following tasks put a tick mark (√) if you can perform or concepts you are familiar with them.

I can…

- write the general structural formulas of aldehydes and ketones ☐
- give the structures and names of common members of each group ☐
- describe the physical properties of aldehydes and ketones ☐
- explain some methods of preparation of aldehydes and ketones ☐
- explain the chemical reactions of aldehydes and ketones such as addition, oxidation and reduction ☐
- give some chemical tests that differentiate aldehydes from ketones. ☐

Section 6.4: Carboxylic Acids

☸ Dear learner, in this section you will study the functional group of carboxylic acids, their naming systems, physical and chemical properties, and general methods of preparations. Carboxylic acids are widespread in nature, often combined with other functional groups. Simple alkyl carboxylic acids, composed of four to ten carbon atoms, are liquids or low melting solids having very unpleasant odors. Carboxylic acids and their derivatives are used in the production of polymers, biopolymers, coatings, adhesives, and pharmaceutical drugs. They also can be used as solvents, food additives, antimicrobials, and flavorings.

At the end of this section, you will be able to:

- list common organic acids and name their sources
- write the general formula of saturated monocarboxylic acids
- write the molecular formulas and names of the first six members of the saturated monocarboxylic acids
- give the structural formula for the first four members of the saturated monocarboxylic acids
- give the examples of mono, di and tricarboxylic acids
- name some branched carboxylic acids]
- describe the physical and chemical properties of saturated monocarboxylic acids
- explain the general methods of preparation of saturated monocarboxylic acids
- name and write structural formulas of some fatty acids
- describe some uses of common carboxylic acids.

6.4.1 Structure and Nomenclature of Carboxylic Acids

6.4.1.1 Structure of Carboxylic Acids

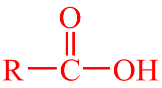
Carboxylic acid is one of the class of organic compounds containing the carbonyl functional group (C=O). A carboxyl group (COOH) is a functional group consisting of a carbonyl group (C=O) with a hydroxyl group (O–H) attached to the same carbon atom. The carboxyl group is represented as **—COOH** or **—CO_2H.**

Activity 6.7

Dear learner, can you give the names of some common house hold carboxylic acids? Which acid is commonly present in most fruits?

a. Saturated monocarboxylic acids

Hello! dear learner, the general formula for saturated monocarboxylic acids can be written as:



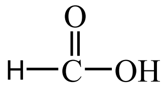
$$R-\overset{O}{\overset{\parallel}{C}}-OH$$

where R is either hydrogen or an alkyl group for aliphatic carboxylic acids. When R is phenyl (aryl) group, the structure represents aromatic carboxylic acids.

Example 6.42

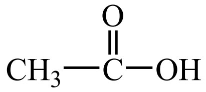
1. The structure of the first three saturated monocarboxylic acids are written as follows:

a.



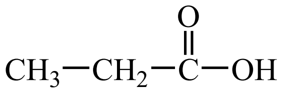
$H-\overset{O}{\overset{\parallel}{C}}-OH$ Methanoic acid

b.



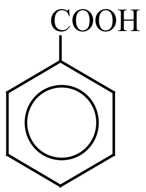
$CH_3-\overset{O}{\overset{\parallel}{C}}-OH$ Ethanoic acid

c.



$CH_3-CH_2-\overset{O}{\overset{\parallel}{C}}-OH$ Propanoic acid

2. The simplest aromatic acid is benzoic acid.



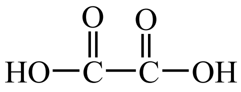
Benzene carboxylic acid (Benzoic acid)

b. Di- and tricarboxylic acids

Carboxylic acids containing two carboxyl groups in their structure are called dicarboxylic acids.

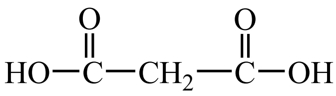
Example 6.43

1. The structure of the first three saturated dicarboxylic acids are shown below:

a.


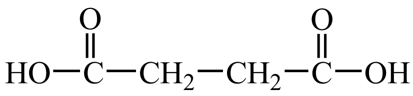
$\mathrm{HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH}$

Ethanedioic acid

b.


$\mathrm{HO-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OH}$

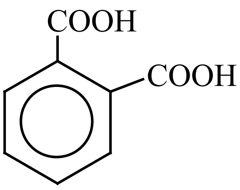
Propanedioic acid

c.


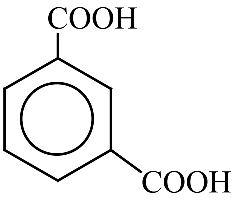
$\mathrm{HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH}$

Butanedioic acid

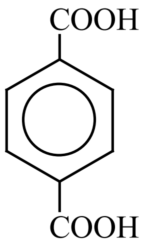
2. The simplest aromatic dicarboxylic acid occurs in three isomeric forms: phthalic acid, isophthalic acid, and terephthalic acid. Their structures and IUPAC names are given below.



Phthalic acid



Isophthalic acid



Terephthalic acid

Carboxylic acids that contain three carboxyl groups in their structure (e.g. citric acid) are called tricarboxylic acids.

Can you give the structure of citric acid?

Self-test Exercise 6.7

1. Write the structure of the following monocarboxylic acids:
   a. Butanoic acid b. Pentanoic acid
2. Write the structure of the following dicarboxylic acids:
   a. Pentanedioic acid b. Hexanedioic acid
   c. 1,3-Benzenedicarboxylic acid
3. A great many carboxylic acids are encountered in nature. List some of them and their respective sources.

6.4.1.2 Nomenclature of Carboxylic Acids

i. Common names carboxylic acids

a. Straight chain monocarboxylic acids

Dear learner, do you know that a large number of carboxylic acids are named by their common names. The common names of some basic carboxylic acids are derived from Latin names that indicate the first original natural source of the carboxylic acid. **Table 6.3** lists common names of some of the most important monocarboxylic acids.

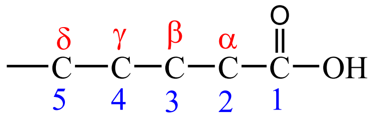
Table 6.3 Common names of some monocarboxylic acids.

Structure of Acid	Natural Source	Common Name
HCOOH	Ants (Formica)	Formic acid
CH_3COOH	Vinegar (Acetum)	Acetic acid
CH_3CH_2COOH	Basic Fat (Propio)	Propionic acid
$CH_3CH_2CH_2COOH$	Rancid butter (Butyrum)	Butyric acid
$CH_3CH_2CH_2CH_2COOH$	Present in a Valerian herb	Valeric acid
$CH_3CH_2CH_2CH_2CH_2COOH$	Goat (Caper)	Caproic acid

Note that the common name of carboxylic acids end with the suffix –ic acid.

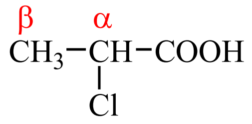
b. Branched chain and substituted carboxylic acids

Dear learner, in common naming system, the branched chain and substituted acids are named as derivatives of straight chain carboxylic acids. The position of the side chain or substituents is indicated by Greek letters, α, β, γ, δ... for designating the 1st, 2nd, 3rd,... position of carbon atoms as shown below:



Example 6.44

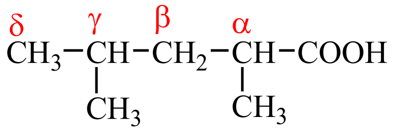
a.



$\overset{\beta}{CH_3}-\underset{\underset{Cl}{|}}{\overset{\alpha}{CH}}-COOH$

α-chloropropionic acid

b.



$\overset{\delta}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{\gamma}{CH}}-\overset{\beta}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{\alpha}{CH}}-COOH$

α,γ-dimethyvaleric acid

c. Dicarboxylic acids

Dicarboxylic acids also possess common names which are based on their sources. **Table 6.4** lists common and IUPAC names of some of the most important dicarboxylic acids.

Table 6.4 Common and IUPAC names of some dicarboxylic acids

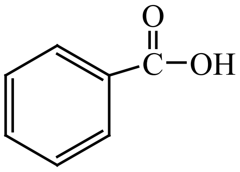
Structure	Common Name	IUPAC Name
HOOC–COOH	Oxalic acid	Ethanedioic acid
$HOOC–CH_2–COOH$	Malonic acid	Propanedioic acid
$HOOC–(CH_2)_2–COOH$	Succinic acid	Butanedioic acid
$HOOC–(CH_2)_3–COOH$	Glutaric acid	Pentanedioic acid
$HOOC–(CH_2)_4–COOH$	Adipic acid	Hexanedioic acid
$HOOC–(CH_2)_5–COOH$	Pimelic acid	Heptanedioic acid

d. Aromatic carboxylic acids

Do you know what aromatic carboxylic mean? What is the simplest aromatic compound?

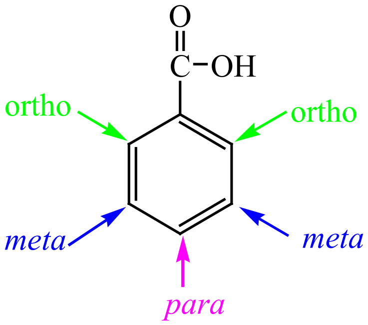
Aromatic carboxylic acids are compounds which have a carboxyl group directly attached to an aromatic ring.

The common name of the simplest aromatic carboxylic acid is benzoic acid.



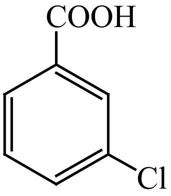
Benzoic acid

In common naming system, the position of the substituent is indicated by the prefixes *ortho* (o-), *meta* (m-), *para* (p-) as it is shown in the structure below.



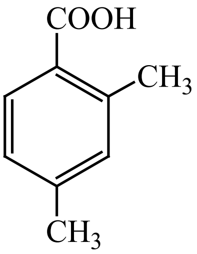
Example 6.45

a.



m-chlorobenzoic acid

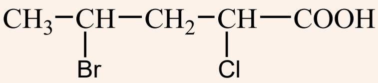
b.



o,p-dimethylbenzoic acid.

Self-test Exercise 6.8

1. Write the common names for the following carboxylic acids:

   a. 

   $CH_3-\underset{Br}{\underset{|}{CH}}-CH_2-\underset{Cl}{\underset{|}{CH}}-COOH$

   b. $HOOC-(CH_2)_2-CH_2-COOH$

2. Write the structures of carboxylic acids for the given common names:

   a. β-Bromobutyric acid b. p-bromobenzoic acid c. glutaric acid

ii. IUPAC names of carboxylic acids

a. Straight chain monocarboxylic acid

Dear learner, in IPUAC system, monocarboxylic acids are named by replacing the terminal "–e" of the corresponding alkane name with "–oic acid." They are named as **alkanoic acids**.

Example 6.46

1. Write the IPUAC names for:

   a. $H\text{-}COOH$ Methanoic acid

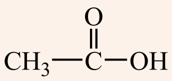
   b. $CH_3\text{-}CH_2\text{-}COOH$ Propanoic acid

   c. $CH_3\text{-}CH_2\text{-}CH_2\ CH_2\text{-}COOH$ Pentanoic acid

2. Write the structure of the following carboxylic acids:

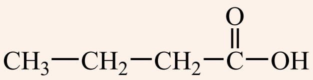
   a. Ethanoic acid b. Butanoic acid c. Hexanoic acid

3\. a.



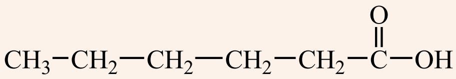
$CH_3-\overset{\overset{\Large O}{\|}}{C}-OH$

b.



$CH_3-CH_2-CH_2-\overset{\overset{\Large O}{\|}}{C}-OH$

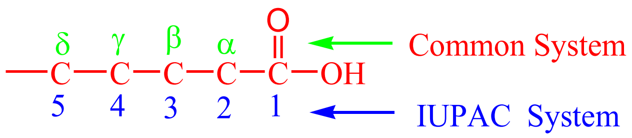
c.



$CH_3-CH_2-CH_2-CH_2-CH_2-\overset{\overset{\Large O}{\|}}{C}-OH$

b. Branched chain and substituted monocarboxylic acids

Dear learner, the IUPAC name of a branched carboxylic acid is derived from that of the longest carbon chain that contains the carboxyl group. The positions of the substitutes are indicated by Arabic numerals as 1, 2, 3. The numbering of the chain starts from the carboxyl carbon and it is always assigned C-1 position. Note that C-2 position in the IUPAC system corresponds to the α-position in the common naming system.



Example 6.47

a. $CH_3\text{–}CH(CH_3)\ CH_2\text{–}COOH$

3-methylbutanoic acid

b. $CH_3\text{–}CH_2CH(Cl)\text{–}CH(CH_3)\text{–}COOH$

3-Chloro-2-methylpentanoic acid

c. Dicarboxylic acids

In the IUPAC system, dicarboxylic acids are named as **alkanedioic acids**. These names are obtained by replacing the suffix ''–e'' in the name of corresponding alkane by ''–dioic acid''. **Table 6.4** above gives the common and IUPAC names of the first six dicarboxylic acids.

Example 6.48

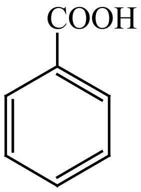
$HOOC\text{–}CH_2\text{–}CH_2\text{–}COOH$

Butanedioic acid

Can you write the structure of hexaneanedioic acid?

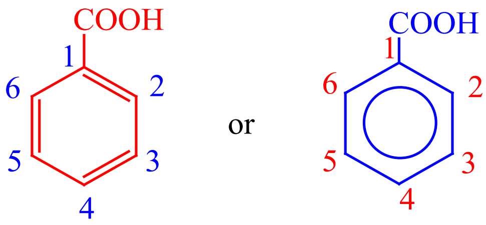
d. Aromatic carboxylic acids

IUPAC name of the simplest aromatic carboxylic acid is benzenecarboxylic acids.

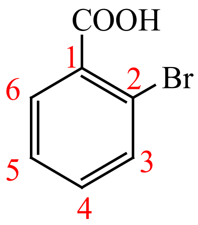


Benzenecarboxylic acid

Substituted aromatic acids with one carboxyl group are named as derivatives of benzenecarboxylic acids. The position of substituents is indicated using the Arabic numerals 2, 3, etc according to their position on the benzene ring relative to the carboxyl group. The carbon on which the carboxyl group is attached is by convention C-1.



Example 6.49

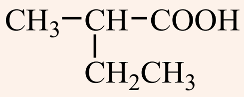


2-bromobenzenecarboxylic acid

Self-test Exercise 6.9

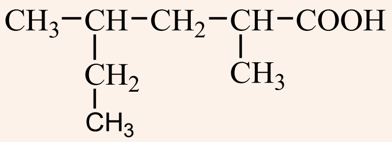
1. Write the IUPAC names for the following carboxylic acids:

a.



$CH_3-\underset{\underset{\displaystyle CH_2CH_3}{|}}{CH}-COOH$

b.

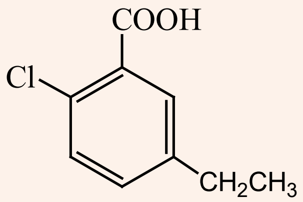


$CH_3-\underset{\underset{\underset{\underset{\displaystyle CH_3}{|}}{\displaystyle CH_2}}{|}}{CH}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-COOH$

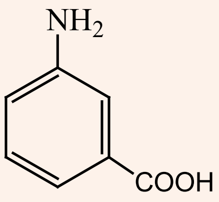
c. $Cl-CH_2-CH_2-CH_2-COOH$

d. $HO\text{-}CH_2-CH_2-CH_2-COOH$

e.



f.



2. Draw the structures of the following carboxylic acids:
   a. 3-chloro-2,3-dimethylpentanoic acid
   b. 4-bromo-2-hydroxybenzoic acid
   c. *p*-Methylbenzoic acid
   d. 2-ethyl-3-methylpentanedioic acid

6.4.2 Physical Properties of Carboxylic Acids

1. State

Hello! Dear learner, note that the lower aliphatic acids containing up to 9 carbon atoms are liquids, whereas the higher members are colourless waxy solids. Benzoic acid and most of its derivatives are colourless solids.

2. Odor

The odors of the lower aliphatic acids progress from sharp, irritating odor of methanoic acid and ethanoic acids to the distinctly unpleasant odor of the butanoic, pentanoic and hexanoic acids.

Activity 6.8

Dear learner, try to explain the following observations.

1. The solubility of monocarboxylic acids in water decreases with increase in molecular mass.
2. Higher members of monocarboxylic acids are almost odourless.

3. Boiling Point

The melting points and boiling points of carboxylic acids are higher than those of hydrocarbons and oxygen-containing organic compounds of comparable size and shape and indicate strong intermolecular attractive forces. **Figure 6.6** gives boiling point comparison of carboxylic acid with alkene, ketone, and alcohol.

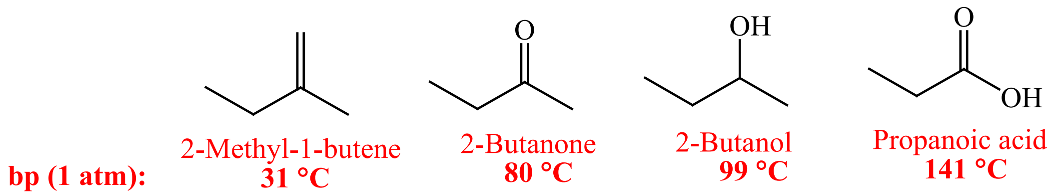


Figure 6.6: Boiling point comparison of carboxylic acid with alkene, ketone, and alcohol

A unique hydrogen-bonding arrangement, shown in **Figure 6.7**, contributes to these attractive forces. The hydroxyl group of one carboxylic acid molecule acts as a proton donor toward the carbonyl oxygen of a second. In a reciprocal fashion, the hydroxyl proton of the second carboxyl function interacts with the carbonyl oxygen of the first. The result is that the two carboxylic acid molecules are held together by two hydrogen bonds.

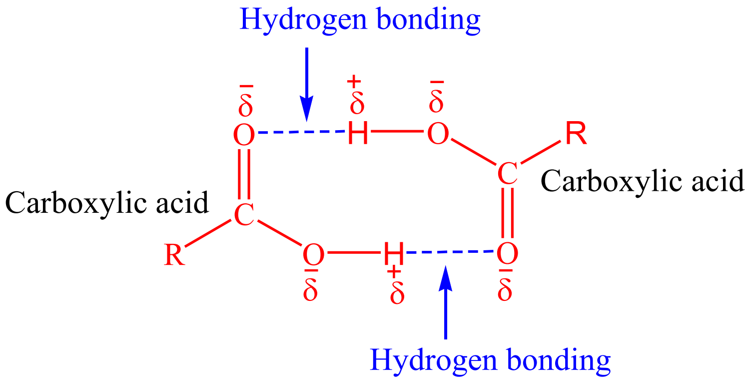


Figure 6.7: Carboxylic acid dimer

4. Solubility

In aqueous solution intermolecular association between carboxylic acid molecules is replaced by hydrogen bonding to water. The solubility properties of carboxylic acids are similar to those of alcohols. Carboxylic acids of four carbon atoms or fewer are miscible with water in all proportions. **Figure 6.8** shows hydrogen bonding between carboxylic acids and water molecules.

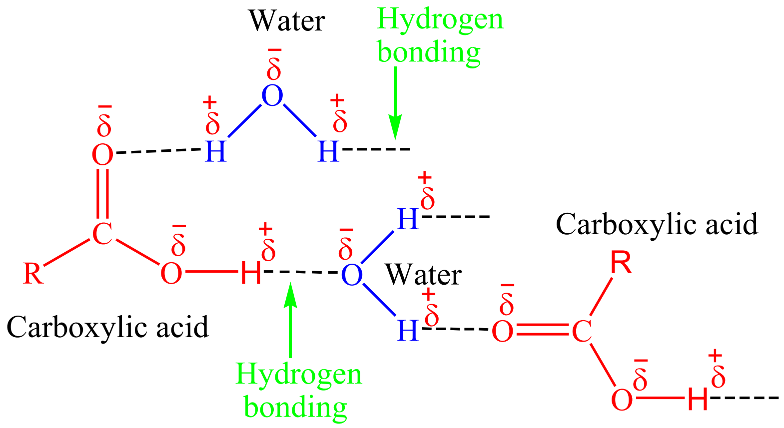


Figure 6.8: Formation of hydrogen bonding between carboxylic acids and water molecules.

The boiling points, melting points and solubilities of some carboxylic acids are given in **Table 6.5**.

Table 6.5 Physical constants of some carboxylic acids

Structure	IUPAC Name	Boiling point (°C)	Solubility (g/100 mL) H_2O at 25 °C
HCOOH	Methanoic acid	100.5	∞*
CH_3COOH	Ethanoic acid	118	∞*
CH_3CH_2COOH	Propanoic acid	141	∞*
$CH_3(CH_2)_2COOH$	Butanoic acid	164	∞*
$CH_3(CH_2)_3COOH$	Pentanoic acid	187	4.97
$CH_3(CH_2)_4COOH$	Hexanoic acid	205	1.08
$CH_3(CH_2)_5COOH$	Heptanoic acid	223	
$CH_3(CH_2)_6COOH$	Octanoic acid	239	0.07
$CH_3(CH_2)_7COOH$	Nonanoic acid	253	—
$CH_3(CH_2)_8COOH$	Decanoic acid	269	0.015

∞* means miscible in all proportions.

Self-test Exercise 6.10

1. Arrange the following aliphatic carboxylic acids in the decreasing order of boiling point:
    a. butanoic acid
    b. decanoic acid
    c. octanoic acid
    d. propanoic acid
2. Which of these aliphatic carboxylic acids has the lowest boiling point?
    a. pentanoic acid
    b. methanoic acid
    c. hexanoic acid
    d. propanoic acid
3. Arrange the following compounds in increasing order of their boiling points:
    a. C_5H_{12}
    b. C_2H_5COOH
    c. $C_4H_{11}OH$
    d. $CH_3(CH_2)_4COOH$

6.4.3 Chemical Properties of Carboxylic Acids

Dear learner, the carboxylic acids show reactions due to the alkyl or aryl group and the carboxyl group. The carboxyl group is further considered to be made up of a carbonyl and a hydroxyl group. All these groups modify the properties of each other due to their interaction.

Activity 6.9

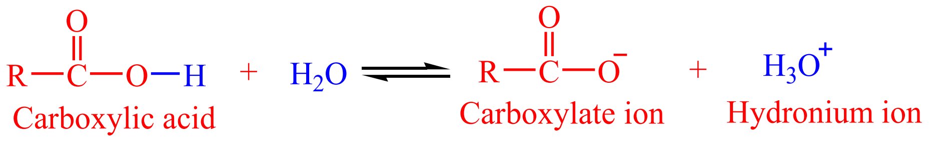
Dear learner, attempt to answer the following questions.

1. Why ‘tella’ or ‘tej’ turn sour when kept for longer time but not Katikalla?
2. Why beer has longer shell life than ‘Tella’?

Some of the common reactions of carboxylic acids are:

i. Reaction as an acid

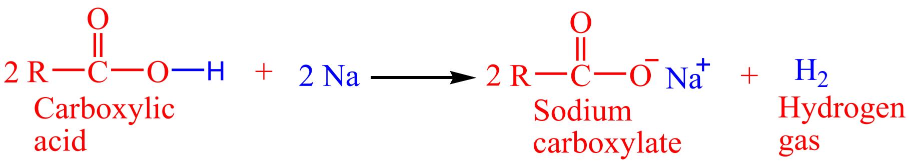
In aqueous solution, the cleavage of O–H bond occurs leading to the formation of carboxylate ion and hydronium ion. Carboxylic acids ionize partially and an equilibrium exists between the ionized and un-ionized forms.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + H_2O \rightleftharpoons R-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + H_3O^+$$

Carboxylic acids are weak acids and dissociates slightly. The following are examples of reactions of carboxylic acids as an acid.

a. Reaction with metals: Carboxylic acids react with active metals such as Na, K, Mg, Ca, etc. to give metal carboxylate salts, $RCO_2^-M^+$, and hydrogen gas.



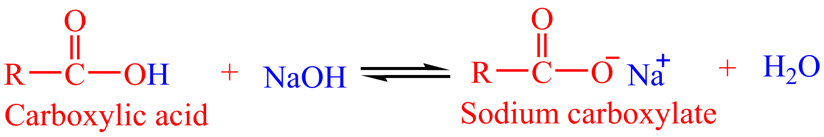
$$2\,R-\overset{\overset{O}{\|}}{C}-O-H + 2\,Na \longrightarrow 2\,R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\,\overset{+}{Na} + H_2$$

> The salts of carboxylic acids are named by writing the name of the metal first, followed by the name of the acid replacing the ending -*ic* acid by -*ate*.

For example, sodium reacts with ethanoic acid to form sodium ethanoate and hydrogen.

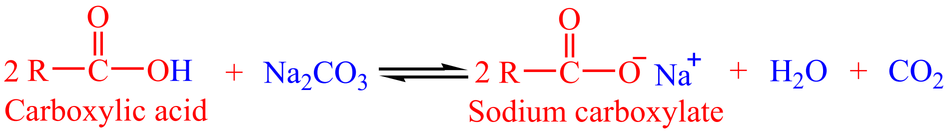
$$2\,CH_3-COOH + 2\,Na \longrightarrow 2\,CH_3-CO\overset{-}{O}\,\overset{+}{Na} + H_2$$

b. Reaction with Bases: Carboxylic acids react with strong bases to form the corresponding metal carboxylate salts and water.

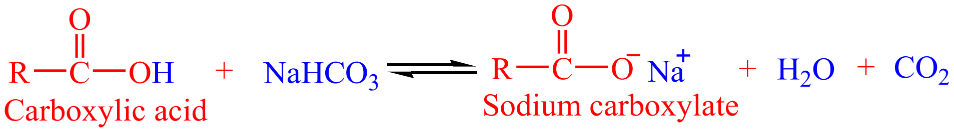


$$R-\overset{\overset{O}{\|}}{C}-OH + NaOH \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\,\overset{+}{Na} + H_2O$$

Carboxylic acids react with weak bases to form salt, water and carbon dioxide.

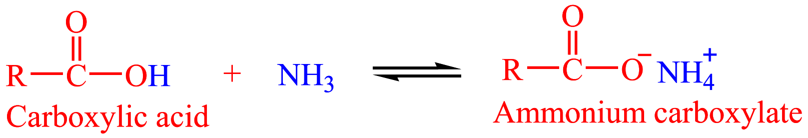


$$2\,R-\overset{\overset{O}{\|}}{C}-OH + Na_2CO_3 \rightleftharpoons 2\,R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\,\overset{+}{Na} + H_2O + CO_2$$



$$R-\overset{\overset{O}{\|}}{C}-OH + NaHCO_3 \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\,\overset{+}{Na} + H_2O + CO_2$$

Carboxylic acids react with ammonia to form ammonium salts of carboxylic acids.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NH_3 \rightleftharpoons R-\overset{\overset{\displaystyle O}{\|}}{C}-O^{-}\,NH_4^{+}$$

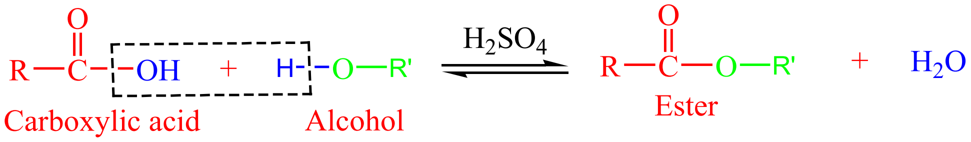
Carboxylic acid

Ammonium carboxylate

ii. Formation of Esters:

One of the important reactions of carboxylic acids involves the replacement of –OH group by an alkoxy group to form esters as products. In this reaction, carboxylic acids are heated with alcohols in the presence of concentrated sulphuric acid. The reaction is called esterification.

> **Esterification** is the process of combining an organic acid (RCOOH) with an alcohol (ROH) to form an ester (RCOOR) and water.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{OH + H}-O-R' \xrightleftharpoons{H_2SO_4} R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' + H_2O$$

Carboxylic acid

Alcohol

Ester

Self-test Exercise 6.11

1. Write the chemical equations for the reaction between ethanoic acid and each of the following reagents and write the names of the products formed:

   a. KOH b. Na_2CO_3 c. NH_3

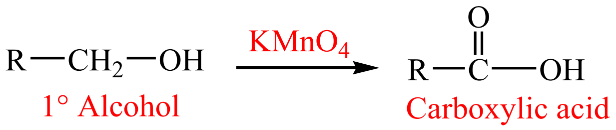
2. Write the chemical equations for the reaction between methanoic acid and ethanol and write the name of the product.

6.4.4 Preparation of Carboxylic Acids

One of the important methods for preparation of carboxylic acids is oxidation. Many saturated monocarboxylic acids are obtained by the oxidation of the corresponding primary alcohols whereas aromatic acids are obtained from the corresponding alkylbenzenes.

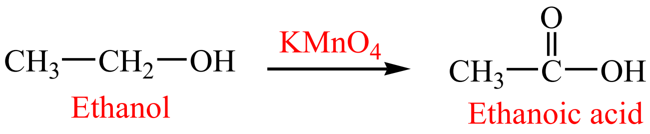
i. Oxidation of Primary Alcohols:

The primary alcohols are readily oxidized to the corresponding carboxylic acids by their reaction with common oxidizing agents like $K_2Cr_2O_7$ or $KMnO_4$.



$$R-CH_2-OH \xrightarrow{KMnO_4} R-\overset{\overset{O}{\|}}{C}-OH$$

Example 6.50

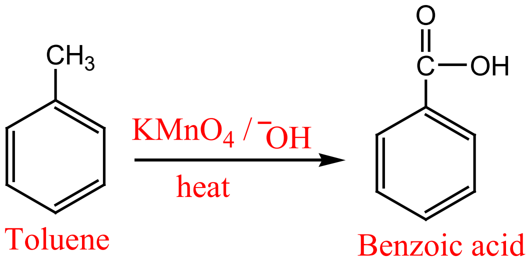


$$CH_3-CH_2-OH \xrightarrow{KMnO_4} CH_3-\overset{\overset{O}{\|}}{C}-OH$$

ii. Oxidation of Alkylbenzenes:

Aromatic compounds containing alkyl group as substituent undergo oxidation to form aromatic acids. The reaction involves oxidation with $KMnO_4$ or K_2CrO_7 under vigorous conditions. The alkyl group is oxidized to carboxyl group irrespective of its size. For example, toluene and ethylbenzene, both give benzoic acid on refluxing with $KMnO_4$ in alkaline medium.

Example 6.51



Can you write the chemical equations for the oxidation of ethylbenzene with $KMnO_4$ in alkaline medium?

iii. Preparation of acetic acid (Ethanoic acid):

Acetic acid is one of the important carboxylic acids which is used as food preservative. It can be prepared in laboratory by the oxidation of ethanol with potassium permanganate. It can also be obtained by passing the vapors of ethanol through copper oxide.

How do we prepare large quantities of acetic acid in industry?

Experiment 6.3

Laboratory Preparation of Acetic Acid

Objective: To prepare acetic acid in the laboratory by oxidation of ethanol.

Apparatus: Goggles, test tubes, test tube rack, quickfit distillation apparatus, 250 mL beaker, pipettes, Bunsen burner, stand, clamp, tripod, wire gauze, digital balance, blue litmus paper, boiling chips such as fine gravels, broken porcelain pieces, etc.

Chemicals: Ethanol, sodium dichromate, 1M sulphuric acid, 0.5M sodium carbonate solution.

Procedure:

Oxidation of ethanol to ethanoic acid

1. Set up the Quickfit distillation apparatus for refluxing as shown in **Figure 6.9a.**
2. Place about 10 mL of 1M sulphuric acid into the 250 mL round-bottom flask.
3. Add 2-3 g of sodium dichromate ($Na_2Cr_2O_7$) and a few pieces of boiling chips. Swirl the contents of the flask until the solution is complete (warm if necessary).
4. Cool the mixture under a running tap since the process is exothermic.
5. Add 1 mL of ethanol dropwise into the flask.
6. Boil under reflux **(Figure 6.9 a)** for 20 minutes
7. Arrange the distillation set up as shown in **(Figure 6.9 b)** and distil up to 2-3 mL
8. Notice the smell of the product (distilled liquid) and compare it with that of ethanol.
9. Add a few drops of the distilled liquid to a small amount of solid sodium carbonate.
10. Add a drop of the distilled liquid to moistened blue litmus paper.

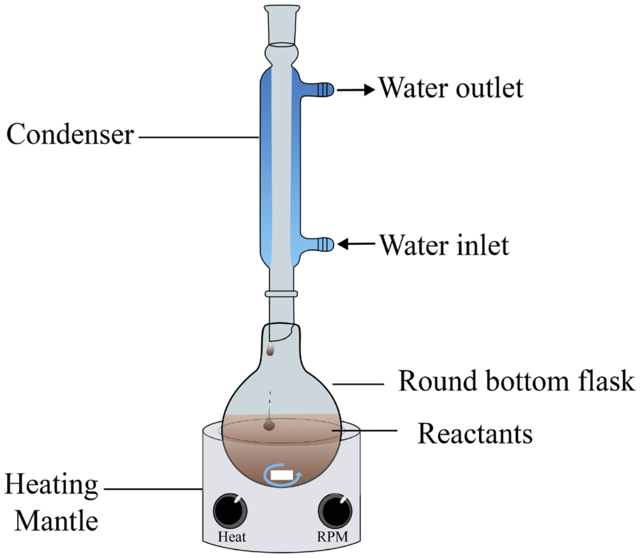


Figure 6.9a: Reflux set-up

Observation and analysis

1. What happened to the colour of the solution in the flask?
2. What is the role of sodium dichromate in the above reaction? Is it oxidized or reduced?
3. Write the chemical equation for this reaction.
4. What do you conclude from this experiment?

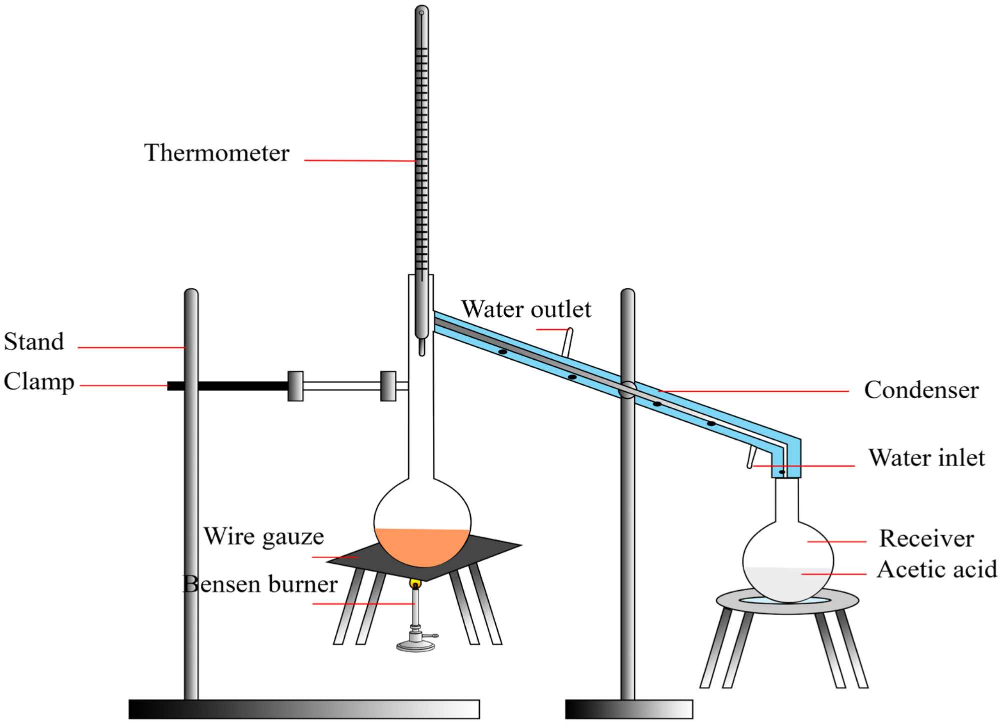


Figure 6.9b: Laboratory set-up for distillation of acetic acid

6.4.5 Fatty Acids

Activity 6.10

Dear learner, you have learned about the six foodstuffs in your lower grade biology lesson. Which one of these foodstuffs produces fatty acid during digestion?

Fatty acids are carboxylic acids with long hydrocarbon chains. The fatty acids most frequently found in nature are shown in **Table 6.6**. Most naturally occurring fatty acids contain an even number of carbon atoms and are unbranched. Double bonds in naturally occurring unsaturated fatty acids are never conjugated. Fatty acids can be classified as saturated or unsaturated.

? What is the main difference between saturated and unsaturated compounds?

Table 6.6 Some common naturally occurring fatty acids

Number of carbons	Common Name	Structure/Formula	Melting point (°C)
Saturated			
12	Lauric acid	$CH_3(CH_2)_{10}COOH$	44
14	Myristic acid	$CH_3(CH_2)_{12}COOH$	58
16	Palmitic acid	$CH_3(CH_2)_{14}COOH$	63
18	Stearic acid	$CH_3(CH_2)_{16}COOH$	69
20	Arachidic acid	$CH_3(CH_2)_{18}COOH$	77
Unsaturated			
16	Palmitoleic acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	0
18	Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	13
18	Linoleic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	-5
18	Linolenic acid	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	-11

Hello! dear learner, the physical properties of a fatty acid depend on the length of the hydrocarbon chain and the degree of unsaturation. The melting points of saturated fatty acids increase with increasing molecular weight because of increased van der Waals interactions between the molecules.

? Why do unsaturated fatty acids have lower melting points than saturated fatty acids with comparable molecular weights?

The melting points of the unsaturated fatty acids decrease as the number of double bonds increases. For example, an 18-carbon fatty acid melts at 69 °C if it is saturated, at 13 °C if it has one double bond, at -5 °C if it has two double bonds, and at -11 °C if it has three double bonds **(Table 6.6).**

6.4.6 Uses of Carboxylic Acids

Acetic acid is used as a solvent and as a starting material in the preparation of acetates, acetic anhydride, etc. It is also used to prepare the vinyl acetate polymer which is used in paints and adhesives. Vinegar contains about 8-10% acetic acid which is used in many food items. Perhaps one of the most important industrial applications of long chain carboxylic acid is for making soaps, detergents, and shampoos.

? Can you suggest some more examples of the use of carboxylic acids in daily life?

Self-test Exercise 6.12

1. Explain the difference in the melting points of the following fatty acids:
   a. palmitic acid and stearic acid
   b. palmitic acid and palmitoleic acid
   c. oleic acid and linoleic acid
2. What are omega fatty acids? Give some examples of omega fatty acids.
3. What is the difference between omega-3-fatty acids and omega-6-fatty acids?

√ CHECKLIST 6.4

In the boxes provided for each of the following tasks put a tick mark (√) if you can perform or concepts you are familiar with them.

I can…

- list common organic acids and name their sources ☐
- write the general formula of saturated monocarboxylic acids ☐
- write the molecular formulas and names of the first six members of the saturated monocarboxylic acids ☐
- give the structural formula for the first four members of the saturated monocarboxylic acids ☐
- give the examples of mono, di and tricarboxylic acids ☐
- name some branched carboxylic acids] ☐
- describe the physical and chemical properties of saturated monocarboxylic acids ☐
- explain the general methods of preparation of saturated monocarboxylic acids ☐
- name and write structural formulas of some fatty acids ☐
- describe some uses of common carboxylic acids ☐

Section 6.5: Esters

Dear learner, in this section you will learn about the common sources of esters, the general fula and naming of esters, the physical and chemical properties of esters, the general methods of preparation and uses of esters.

By the end of this section, you will be able to:

- list common sources of esters
- write the general structural formula of esters
- write the molecular formulas and names of some simple esters
- describe physical properties of esters
- explain the chemical properties of esters
- explain the general methods of preparation of esters
- describe some uses of common esters.

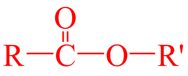
6.5.1 Sources of esters

Dear learner, esters are among the most widely occurring compounds in nature. Many esters are pleasant smelling substances and are responsible for the flavor and fragrance of many fruits, for example, bananas, apples, pineapples, pears, strawberries, etc. Oils, fats and waxes of plants or animal origin are all esters. Many esters are found in flowers and form the part of essential oils obtained from flowers.

6.5.2 Nomenclature

Dear learner, esters are derivatives of carboxylic acids in which the hydroxyl group (-OH) of a carboxylic acid is replaced by an alkoxy group (-OR). Esters can be formed by the reaction between acids and alcohols or phenols. In such cases, the hydroxyl group is replaced by an alkoxy group.

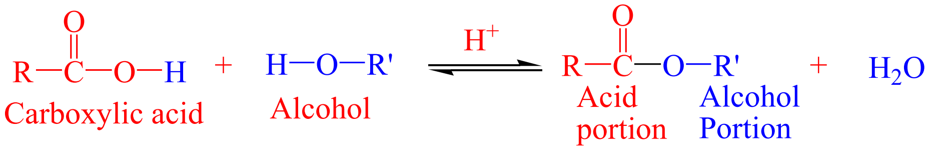
Esters have the general formula RCO_2R' (or $RCOOR'$), which can be represented by the general formula:



$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R'$ or RCO_2R' or $RCOOR'$

Where R = hydrogen, alkyl or an aryl group and R' = alkyl or an aryl group.

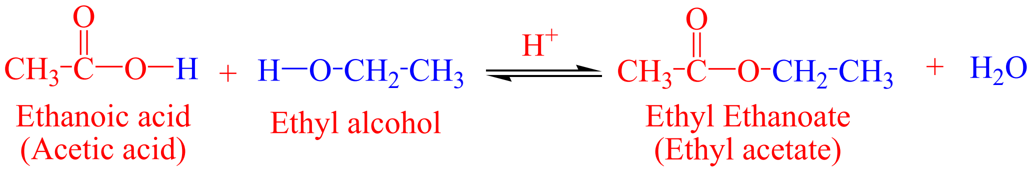
Esters are named by the common system and IUPAC system. In both the cases, the name consists of two parts. The first part is named using the part from alcohol. The second part of the name is based on the acid. Therefore, we have to identify the parts coming from alcohol and carboxylic acid. The reaction below shows the part coming from the alcohol is attached to the oxygen as an alkyl group, and the acid part is attached to the oxygen through the carbonyl group.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + H-O-R' \xrightleftharpoons{H^+} R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' + H_2O$$

The names of esters are derived from the names of the alcohol (with the ending -*yl*) and the acid (with the ending -ate or -oate). While writing their names the part of the name derived from the alcohol comes first.

When we use the common name of carboxylic acid, the name of the ester is a common name, and when the IUPAC name of the acid is used, we get the IUPAC name for the ester. For illustration, see the ester formed from ethyl alcohol and ethanoic acid.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + H-O-CH_2-CH_3 \xrightleftharpoons{H^+} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_3 + H_2O$$

The common name for this ester is ethyl acetate, and the IUPAC name is ethyl ethanoate.The formulas and names of some esters are listed in **Table 6.7.**

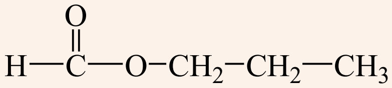
Table 6.7 Names and formulas of some common esters

Molecular Formula	Structure/Formula	Common Name	IUPAC Name
$C_2O_2H_4$	$HCOOCH_3$	Methyl formate	Methyl methanoate
$C_3O_2H_6$	CH_3COOCH_3	Methyl acetate	Methyl ethanoate
$C_3O_2H_6$	$HCOOCH_2CH_3$	Ethyl formate	Ethyl methanoate
$C_4O_2H_8$	$CH_3COOCH_2CH_3$	Ethyl acetate	Ethyl ethanoate
$C_4O_2H_8$	$HCOOCH_2CH_2CH_3$	Propyl formate	Propyl methanoate
$C_5O_2H_{10}$	$CH_3COOCH_2CH_2CH_3$	Propyl acetate	Propyl ethanoate

Self-test Exercise 6.13

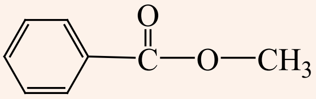
1. Name the following esters.

a.

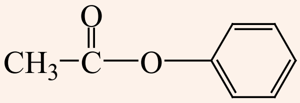


$H-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3$

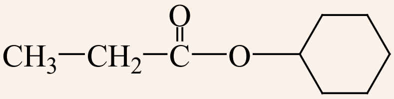
c.



b.



d.



2. Identify the acid and alcohol (or phenol) portions of carboxylic esters give in question 1.
3. Write the structure of the following esters:

d. Isopropyl methanoate b. Ethyl propanoate

6.5.3 Physical properties

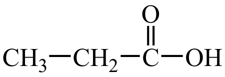
i. Boiling Points

Dear learner, the boiling points of esters increase with increasing molecular mass. Branched-chain esters have lower boiling points than their straight-chain isomers. Esters have lower boiling points than compounds of comparable molecular mass that are capable of forming hydrogen bonds such as carboxylic acids and alcohols. Because ester molecules cannot form hydrogen bonds with each other.

Activity 6.11

Dear learner, which one of the following compounds do you expect to have the highest boiling point? Why?

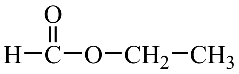
a.



$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$

b. $CH_3CH_2-O-CH_2CH_3$

c.



$H-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$

ii. Solubility

Esters of low molecular mass are fairly soluble in water. Esters have about the same solubility in water with that of the same molecular mass carboxylic acids. Because carboxylic esters can form hydrogen bonding with water

(Figure 6.10), the solubility of esters in water decreases as their molecular mass increase. All esters are soluble in organic solvents.

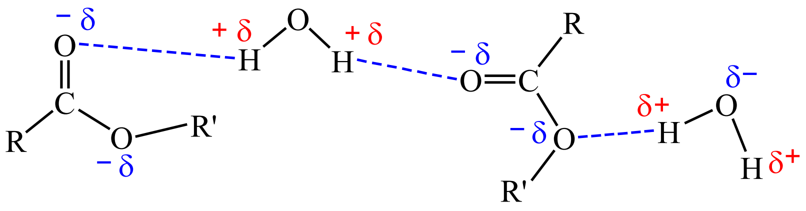


Figure 6.10: Hydrogen bonding between water and ester molecules

iii. Odor

Do you know what type of odor Esters have?

Esters have pleasant odors. Many of the odors of fruits and flowers result from mixtures of carboxylic esters, and many of them are used in perfumes and food flavorings.

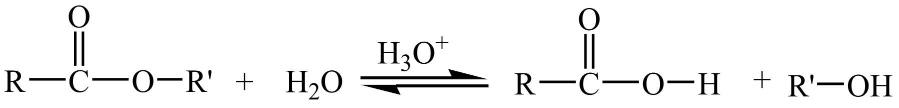
6.5.4 Chemical properties

What would happen when esters are treated with water?

i. Hydrolysis

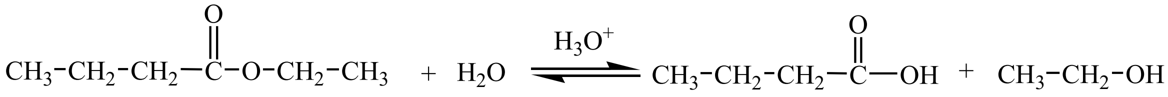
Hello! Dear learner, the most important reaction of carboxylic esters is their hydrolysis, which may be catalyzed by either mineral acids or bases. The reaction yields the corresponding carboxylic acid and alcohol of the ester.

The general reaction for acid-catalyzed hydrolysis of esters can be written as:



$$R-\overset{\overset{O}{\|}}{C}-O-R' + H_2O \xrightleftharpoons{H_3O^+} R-\overset{\overset{O}{\|}}{C}-O-H + R'-OH$$

Example 6.52

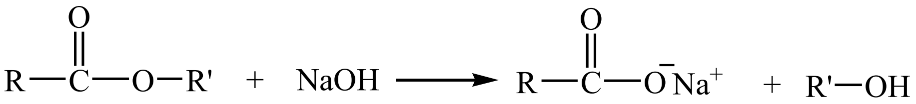


$$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3 + H_2O \xrightleftharpoons{H_3O^+} CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH + CH_3-CH_2-OH$$

For synthetic purposes, base catalysis is often preferred because the reaction is not reversible.

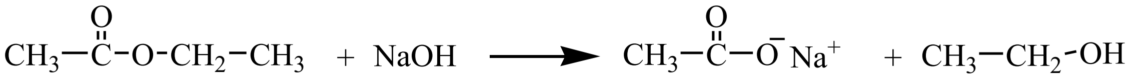
Base catalyzed ester hydrolysis is called saponification.

The general reaction for base-catalyzed hydrolysis of esters can be written as:



$$R-\overset{\overset{O}{\parallel}}{C}-O-R' + NaOH \longrightarrow R-\overset{\overset{O}{\parallel}}{C}-\bar{O}Na^+ + R'-OH$$

Example 6.53

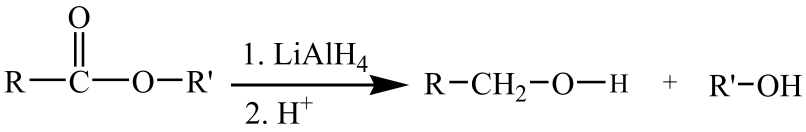


$$CH_3-\overset{\overset{O}{\parallel}}{C}-O-CH_2-CH_3 + NaOH \longrightarrow CH_3-\overset{\overset{O}{\parallel}}{C}-\bar{O}Na^+ + CH_3-CH_2-OH$$

In biological systems, many ester hydrolysis reactions take place, for example, in the digestion of fats. These reactions occur under very mild conditions, and in the presence of biological catalysts known as enzymes. Enzymes are proteins that speed up the chemical reactions in our bodies.

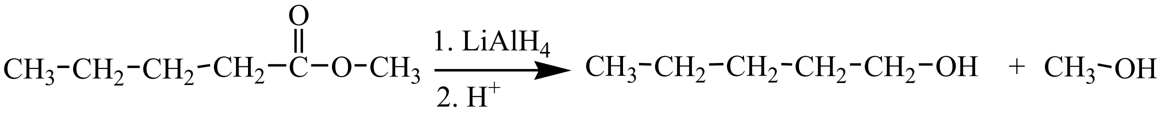
ii. Reduction

Esters are reduced to primary alcohols by special reducing agents like lithium aluminumhydride, $LiAlH_4$. The general reaction for reduction of esters is given by:



$$R-\overset{\overset{O}{\parallel}}{C}-O-R' \xrightarrow[2.\ H^+]{1.\ LiAlH_4} R-CH_2-O-H + R'-OH$$

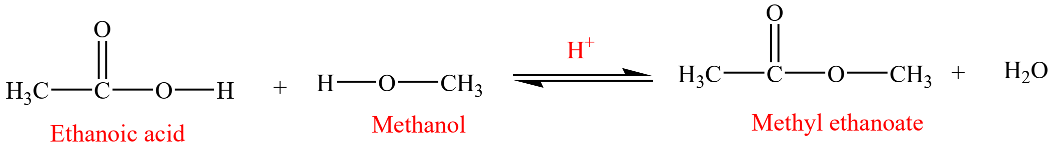
Example 6.54



$$CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\parallel}}{C}-O-CH_3 \xrightarrow[2.\ H^+]{1.\ LiAlH_4} CH_3-CH_2-CH_2-CH_2-CH_2-OH + CH_3-OH$$

6.5.5 Preparation of Esters

Hello! dear learner, esters can be synthesized by heating a mixture of a carboxylic acid and an alcohol in the presence of an acid (usually H_2SO_4) as catalyst. This reaction is called **esterification** and is a common method for the preparation of esters. In esterification, the -OH group from the carboxylic acid and the -H from the alcohol are removed and combine to form water molecule.



Self-test Exercise 6.14

1. Write the reactions for the preparation of each of the following esters using appropriate acids and alcohols:
   a. ethyl acetate
   b. ethyl butanoate
   c. methyl benzoate
   d. phenyl ethanoate
2. The esters formed from butyric acid are pleasant-smelling compounds found in fruits and used in perfumes. Draw the structural formula for the ester formed from the reaction of butyric acid with 2-propanol.

6.5.6 Uses of Esters

Dear learner, most simple esters are pleasant-smelling substances. They are responsible for the flavors and fragrances of most fruits. They are used in the manufacture of perfumes and as flavoring agents in the confectionery (cakes, candies, and ice cream) and soft-drink industries. Esters of low molecular mass are non-toxic liquids.

Esters are used as solvents for oils and fats, nail polishes, varnishes, paints, gums and resins; medicine (e.g. Aspirin); clothing, e.g. polyesters (Dacron); fragrance in perfumes; ad plasticizers (e.g. octyl phthalate). Some common esters which are responsible for many pleasant fragrances in nature are presented in **Table 6.8.**

Table 6.8 Esters naturally available in fruits and responsible for their pleasant fragrances

Fruit	Formula	Ester present
Apple	$C_4H_9COOC_5H_{11}$	Isoamyl isovalerate
Pineapple	$C_3H_7COOC_2H_5$	Ethyl butyrate
Banana	$CH_3COOC_5H_{11}$	Isopentyl acetate
Orange	$CH_3COOC_8H_{17}$	Octyl acetate
Grape	$C_6H_4(NH_2)(COOCH_3)$	Methyl anthranilate
Pear	$CH_3CO_2(CH_2)_2CH(CH_3)_2$	Isopentyl acetate

√ CHECKLIST 6.5

In the boxes provided for each of the following tasks put a tick mark (√) if you can perform or concepts you are familiar with them.

I can…

- list common sources of esters ☐
- write the general structural formula of esters ☐
- write the molecular formulas and names of some simple esters ☐
- describe physical properties of esters ☐
- explain the chemical properties of esters ☐
- discuss the general methods of preparation of esters ☐
- describe some uses of common esters ☐

Section 6.6: Fats and Oils

Dear learner, in this section you will learn about the differences between fats and oils, the general formula of fats and oils, their physical and chemical properties.

By the end of this section, you will be able to:

- define fats and oils
- write the general structural formula for fats and oils
- write the structures of some common triglycerides
- describe physical properties of fats and oils
- explain hardening of oils (process of converting oils to hard fats)
- explain rancidity.

6.6.1 Source of Fats and Oils

Dear learner, recognize that fats and oils are esters. They are triesters of glycerol which are collectivity known as triglycerides or triacylglycerols. Glycerol contains three alcohol groups and therefore can form three ester groups. Fats and oils are widely found in nature.

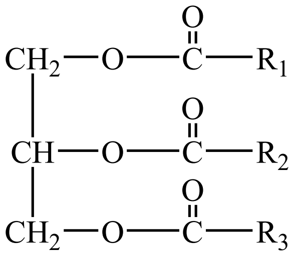
They have long hydrocarbon tails which are derived from carboxylic acids, which make them hydrophobic. Fats are solid or semi-solid at room temperature while oils are liquid. Triglycerides obtained from animals are usually solids, while those of plant origin are generally liquids. Therefore, we commonly say animal fats and vegetable oils.

Activity 6.12

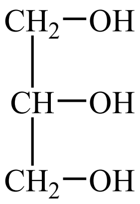
Dear learner, can you classify the following fats/oils (butter, lard, tallow, peanut oil, soybean oil and olive oil) as vegetable or animal origin based on their physical state? Is there any relation between the origin and the physical state of the fats/oils?

6.6.2 Structure of Fats and Oils

Hello, fats and oils are triesters. Variation in the structure of fats and oils occur in the fatty portion of the triglyceride (or triacylglycerol). Fats and oils are represented by the following general structural formula:



A triglyceride (triacylglycerol)

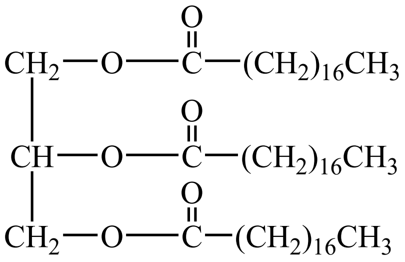


Glycerol

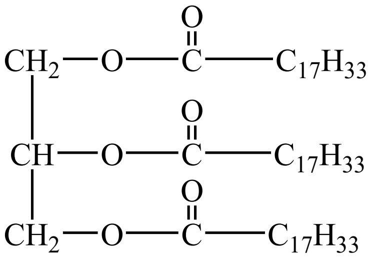
Where R_1, R_2 and R_3 may be the same or different hydrocarbon groups.

> Fats are esters of glycerol and mostly saturated fatty acids, whereas oils are liquid esters primarily derived from unsaturated fatty acids and glycerol. The acid part of fats and oils almost always contain an even number of carbon atoms.

The structures of some common triglycerides are shown below:



Glyceryl tristearate (stearin) fat



Glyceryl trioleate (olein) oil

Can you give some more examples of saturated and unsaturated triglycerides?

Self-test Exercise 6.15

Write the structure of the following compounds

a. Glyceryl trimyristate

b. Glyceryl palmitooleostreate

6.6.3 Physical Properties of Fats and Oils

Dear learner, fats and oils have common physical properties including they are greasy to the touch, and have lubricating properties; they are not readily volatile; and may be burned without leaving any residue, that is, ash. Fats are solids at room temperature while oils are liquids. All oils and fats are colorless, odorless and neutral substances in their pure form. They are lighter than water and immiscible with it. They are soluble in organic solvents.

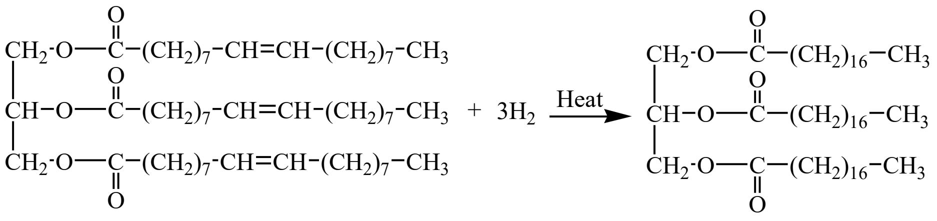
6.6.4 Hardening of oils

Oils can be converted to fats by addition of hydrogen (hydrogenation) at high pressure in the presence of nickel or palladium as a catalyst. The process of converting oils to hard fats is known as **hardening of oils**. This reaction is used in the preparation of margarine.

Hydrogenation of vegetable oils results in the formation of solid fat (e.g. Sheno Lega) which is not different in composition from animal fat.

Example 6.55

A glyceryl tristearate (found in animal fat) can be prepared by hydrogenation of glyoryl trioleate (oil found in olive oil and whole oil) is shown in the equation below:



Glyceryl trioleate

Glyceryl tristearate

Self-test Exercise 6.16

Write the equation for the hydrogenation of:

a. Glyceryl palmitooleostreate, and

b. Glyceryl trimyristate

6.6.5 Rancidity

Hello! Dear learner, fats and oils are quite reactive substances. When stored for any considerable length of time, they deteriorate and spoil. Among the various fats, spoilage takes the form of rancidity. Fats and oils develop an unpleasant odor due to rancidity. Rancidity is caused mainly due to the hydrolysis of ester linkage and oxidation across the double bonds. In this respect, different fats differ markedly. Some spoil very much more rapidly than others. The fat acquires a peculiarly disagreeable odor and flavor.

The rancidity of a given fat is not necessarily the result of long storage under unfavorable conditions. The fat may have been spoiled and rancid from the moment of its production. This will inevitably be true when the materials from which it was produced have undergone decomposition. In other words, to obtain a sound and sweet fat, the raw material must be sound and sweet; it must be processed speedily before it gets time to decompose; and this must be done under clean and sanitary conditions. The fat obtained must be stored under favorable conditions and its consumption should not be delayed.

√ CHECKLIST 6.6

In the boxes provided for each of the following tasks put a tick mark (√) if you can perform or concepts you are familiar with them.

I can…

- define fats and oils ☐
- write the general structural formula for fats and oils ☐
- write the structures of some common triglycerides ☐
- describe physical properties of fats and oils ☐
- explain hardening of oils (process of converting oils to hard fats) ☐
- explain rancidity ☐

UNIT SUMMARY

- Alcohols are compounds containing the hydroxyl (–OH) group as their functional group and represented by the general formula $CnH_{2n+1}OH$.
- Alcohols are classified depending on the number of hydroxyl groups they contain as monohydric, dihydric and trihydric alcohols.
- The names of alcohols contain the suffix '-*ol*' which indicates the presence of –OH group in the molecule.
- Primary alcohols oxidize to give aldehydes and then carboxylic acids, and secondary alcohols yield ketones on oxidation.
- The functional group of an ether is an atom of oxygen bonded to two carbon atoms. Ethers are used as solvents and in medicine as inhalation anesthetics.
- Ethers are weakly polar compounds. Their boiling points are close to those of hydrocarbons with comparable molecular weight.
- An aldehyde contains a carbonyl group bonded to a hydrogen atom and a carbon atom, whereas a ketone contains a carbonyl group bonded to two carbons.
- Aldehydes and ketones have higher boiling points and are more soluble in water than non-polar compounds of comparable molecular weight.
- Carboxylic acids are compounds with a –COOH functional group.
- Because of the –COOH functional group, carboxylic acids are polar compounds and can form hydrogen bonding with water and among themselves.
- Esters are mildly polar compounds that are widely distributed in nature.
- Fats are saturated fatty acids, whereas oils are unsaturated fatty acids.
- The process of converting oils into hard fats is known as hardening of oils.

Self-Assessment

Part I: Multiple choice Type Questions

1. The most common reaction that benzene undergo is:
   a. elimination
   b. substitution
   c. addition
   d. Polymerization

2. Which of the following compounds is an ether?
   a. $CH_3CH_2COOCH_3$
   b. $CH_3CH_2CH_2COOH$
   c. $CH_3CH_2CH_2CHO$
   d. $CH_3CH_2OCH_3$

3. The compounds CH_3OH and CH_3COOH react in the presence of an acid catalyst to form:
   a. a carboxylic acid
   b. an aldehyde
   c. a ketone
   d. an ester

4. Alcohols that yield ketones on oxidation are classified as:
   a. primary alcohols
   b. secondary alcohols
   c. dihydric alcohols
   d. trihydric alcohols

5. What is the product of the reduction of 3-methyl-2-pentanone?
   a. 3-methyl-2-pentanol
   b. 2-methyl-3-pentanol
   c. 3-methyl-2-pentanal
   d. 3-methyl-2-pentene

6. Acetic acid is manufactured by the fermentation of:
   a. ethanol
   b. methanol
   c. ethanal
   d. methanal

7. Fats and oils are:
   a. acids
   b. alcohols
   c. esters
   d. hydrocarbons

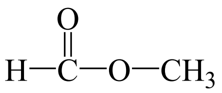
8. Which pair of compounds can react to form a hemiacetal?
   a. CH_3CH_2CHO and CH_3CH_2OH
   b. CH_3COCH_3 and CH_3CH_2CHO
   c. CH_3CH_2CHO and CH_3COOH
   d. CH_3COCH_3 and CH_3COOH

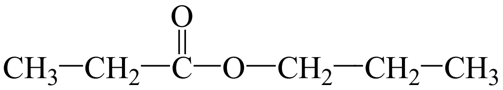
Part II: Answer the following questions:

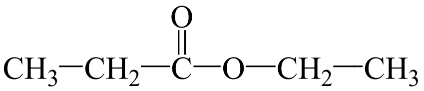
9. Why is there a large difference in the boiling points of butanal and 1-butanol?
10. Write a test to differentiate between 2-pentanone and pentanal.
11. Why are carboxylic acids more acidic than alcohols or phenols although all of them have hydrogen atom attached to an oxygen atom (—O—H)?
12. Draw the structural formula for the ester formed when each of the following reacts with methyl alcohol:

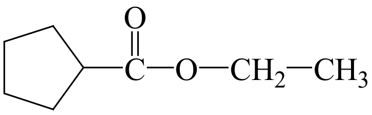
    a. Acetic acid
    c. Benzoic acid
    b. Formic acid
    d. Propionic acid

13. Give the IUPAC and common names, if any, for each of the following:

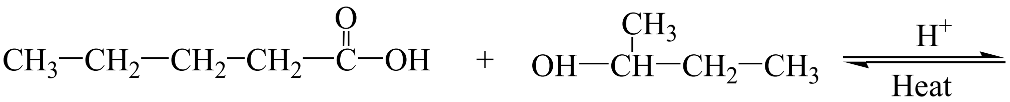
a.

$H-\overset{\overset{O}{\|}}{C}-O-CH_3$

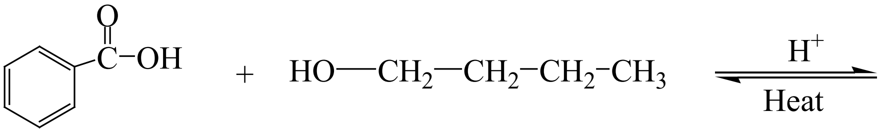
b.

$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-CH_3$

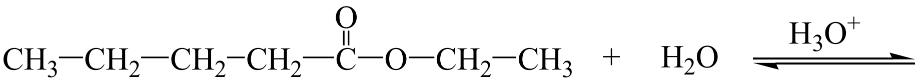
c.

$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

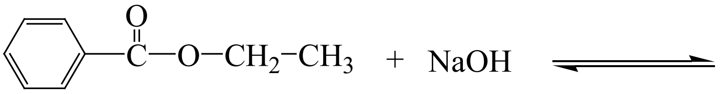
d.


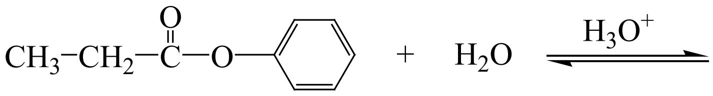
14. Draw the structural formula for each of the following reactions:

a.

$CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH + OH-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_3 \underset{Heat}{\overset{H^+}{\rightleftharpoons}}$

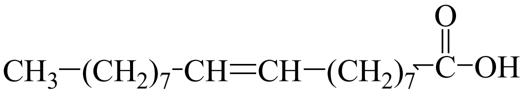
b.


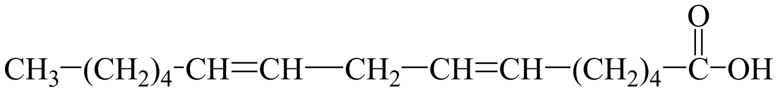
c.

$CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3 + H_2O \overset{H_3O^+}{\rightleftharpoons}$

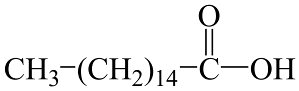
d.


e.


15. Identify each of the following as a saturated, monounsaturated, polyunsaturated:

a. 
$CH_3{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$

b. 
$CH_3{-}(CH_2)_4{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_4{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$

c. 
$CH_3{-}(CH_2)_{14}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$

Module-II Written Assignment Questions

Dear learner, you are supposed to work on the following assignment questions after completing Module II. The questions were designed from module 2 contents. Please, attempt to answer all the questions on separate answer sheet and submit it to your tutor for correction as a part of your assessment.

1. Express the rate of the following reaction equation in terms of the rate of concentration change for each of the three species involved:

   $2SO_2(g) \quad + \; O_2(g) \qquad\qquad 2SO_3(g)$

2. At a certain temperature, initial rate data for the decomposition of gaseous N_2O_5 are as follows:

Element	Initial $[N_2O_5]$	Initial Rate of Decomposition of N_2O_5 (m/s)
1	0.014	2.4×10^{-5}
2	0.040	6.8×10^{-5}
3	0.065	1.1×10^{-4}

What is the rate law?

   a. What is the value of the rate constant, including the proper units?
   b. What is the initial rate of decomposition of N_2O_5 when its initial concentration is 0.030 M?

3. Ammonia is manufactured in large amounts by the reaction:

   $N_2(g) + 3\,H_2(g) \qquad\qquad 2\,NH_3(g)$

   a. How is the rate of consumption of H_2 related to the rate of consumption of N_2?
   b. How is the rate of formation of NH_3 related to the rate of consumption of N_2?

4. Write expressions for K_c and for the following reactions:

   a. $2NH_2(g) + CO_2(g) \rightleftharpoons N_2CH_4O(s) + H_2O(g)$

   b. $2NBr_3(s) \rightleftharpoons N_2(g) + 3Br_2(g)$

   c. $Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

   d. $SO2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

   For which of reactions in (a – d) is K_p equal to K_C?

5. Carbon monoxide and hydrogen react according to the following equation:

   $$CO(g) + 3H_2(g) \rightleftharpoons 2CH_4(g) + H_2O(g)$$

   When 0.5 mol CO and 1.5 mol H_2 are placed in a 10.00-L vessel at 927 °C (1200 K) and allowed to come to equilibrium, the mixture is found to contain 0.22 mol H_2O. What is the molar composition of the equilibrium mixture? That is, how many moles of each substance are present?

6. The equilibrium constant, , is at a certain temperature for the reaction

   $$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

   For which of the following sets of conditions is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift?

   a. = 0.01 atm, ,

   b. = 0.0078 atm, ,

   c. = 0.0062 atm,

7. State LeChatelier's Principle. Which factors have an effect on a system at equilibrium? How does the presence of a catalyst affect a system at chemical equilibrium? Explain your answer.

8. Hydrogen for use in ammonia production is produced by the reaction

   $$CH_4\ (g) + H_2O(g) \underset{750\ °C}{\overset{\text{Ni catalyst}}{\rightleftharpoons}} CO(g) + 3H_2(g)$$

What will happen to a reaction mixture at equilibrium if:

   a. CH_4 is removed?

   b. $H_2O(g)$ is added

   c. the temperature is increased (the reaction is endothermic)?

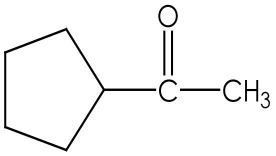
   d. an inert gas is added?

e. H_2 is removed?

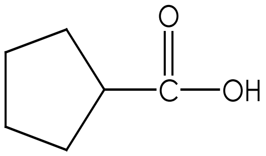
f. the volume of the container is doubled?

9. Give the IUPAC and common names, if any, for each of the following:

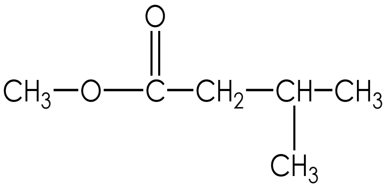
a.



b.

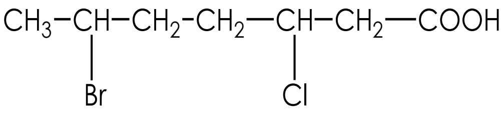


c.



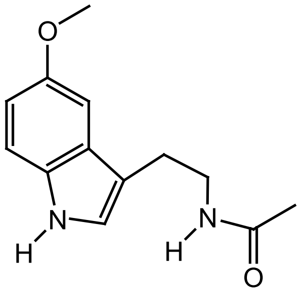
$CH_3-O-\overset{O}{\overset{\|}{C}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

d.



$CH_3-\underset{Br}{\underset{|}{CH}}-CH_2-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_2-COOH$

10. Melatonin is a naturally occurring compound in plants and animals, where it regulates the biological time clock. Melatonin is sometimes used to counteract jet lag. Identify the functional groups in melatonin.



Melatonin

11. Which compound in each pair would be more soluble in water? Explain.
    - a. pentane or 1-propanol
    - b. ethanol or ethyl methyl ether
    - c. methanol or 1-heptanol

12. When 2-butanol is heated with a strong acid, it dehydrates to form compounds A and B (C_4H_8). When 2-butanol is oxidized, compound C (C_4H_8O) forms. Draw the skeletal formulas and give the IUPAC names for compounds A, B, and C.

13. Ethyl octanoate is a flavor component of mangoes.
    - a. Draw the condensed structural formula for ethyl octanoate.
    - b. Write the balanced chemical equation for the formation of ethyl octanoate.
    - c. Write the balanced chemical equation for the acid hydrolysis of ethyl octanoate.
    - d. Write the balanced chemical equation for the base hydrolysis of ethyl octanoate with NaOH

14. Write the structure of the following fatty acids which are usually available in butter.
    a. palmitic acid .
    b. stearic acid
    c. myristic acid
    d. oleic acid

15. Sunflower seed oil can be used to make margarine. A triacylglycerol in sunflower seed oil contains two linoleic acids and one oleic acid.
    a. Draw the condensed structural formulas for two isomers of the triacylglycerol in sunflower seed oil.
    b. Using one of the isomers, write the reaction that takes place when sunflower seed oil is used to make solid margarine

Answer for the Activities - Unit Six

Activity 6.1

1. Chemists classify organic compounds based on bonding patterns in their structures (functional groups). That is, the functional groups in organic compounds determine what properties a compound will have and the types of chemical reactions in which it can participate.
2. Alkane, alkene, alkyne, alcohol, ether, carboxylic acid, etc

Activity 6.2

1. Lower members of alkanes are gas whereas alcohols are liquid because of the presence of strong intermolecular forces (H-bonding) in alcohols.
2. Alcohols can form H-bonding with water molecules, thereby, lower alcohols are soluble in water. However, the nonpolar hydrocarbons could not interact with water molecules by H-bonding or dipole system.

Activity 6.3

1. Most distilled spirits, such as whiskey, rum, brandy, gin, vodka and tequila, have a nearly indefinite shelf life if they are unopened. This is because the sugar content is low, limiting the growth of micro-organisms and the high alcohol content is deadly to bacteria.
2. Beverages can be preserved with chemical additives including Potassium Sorbate and Sodium Benzoate. These ingredients inhibit the growth of microorganisms (micros) that spoil beverages.

Activity 6.4

Alcoholic beverages like “Tella”, “Tej”, beer and wine turn sour if they are not properly

Kept (exposed to air). This is due to oxidation of ethanol to acetic acid. The reaction for the process is:

CH3CH2OH + O2 → CH3COOH + H2O

Activity 6.5

1. CH_3CH_2-OH has higher boiling point than CH_3CH_2-O-CH_2CH_3. This is because of alcohols can form H-bonding each other while ethers do not form H-bonding.
2. Similarly, CH_3CH_2-OH is more soluble than CH_3CH_2-O-CH_2CH_3 due to that fact that alcohols can readily form H-bond with water molecules.

Activity 6.6

1. Carbonyl (-C=O) functional group is formed.
2. The simplest aldehyde and ketone are formaldehyde (Methanal) and acetone (propanone), respectively.

Activity 6.7

1. Carboxylic acids occur in many common household items. (a) vinegar contains acetic acid, (b) aspirin is acetylsalicylic acid, (c) vitamin C is ascorbic acid, (d) lemons contain citric acid, and (e) spinach contains oxalic acid.
2. Citric acid

Activity 6.8

1. Because with increase of molecular mass size of hydrophobic carbon chain length increases.
2. The higher acids are wax like solids and are practically odorless due to their low volatility.

Activity 6.9

1. 'Tella' or 'tej' turn sour some days after they are made. This happens due to the oxidation of beverage alcohol, ethanol, to ethanoic acid by microorganisms. However, this reaction may not occur in "katikala" due to the high concentration of ethanol is not suitable for microbial growth.
2. Because Beer is pasteurized to avoid potential microorganisms and seal out oxygen to avoid oxidation of ethanol to ethanoic acid.

Activity 6.10

Lipids. During lipid digestion, triglycerides are broken into fatty acids and monoglycerides.

Activity 6.11

Therefore, CH_3CH_2COOH has the highest boiling point. This is because of carboxylic acids can form H-bonding each other but not in the cases of esters and ether molecules.

Activity 6.12

Peanut oil, soya bean oil and olive oil are vegetable in origin and butter, lard, and tallow are animal in origin. There is a relationship between the source and their physical state. Plant-origin fats are liquids, and animal-origin fats are solids.

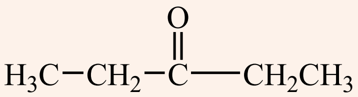
Answer key for self-test Exercises

Self-test Exercise 6.1

1. $C_nH_{2n+1}OH$, where $n \geq 1$.
2. a. monohydric b. dihydric c. trihydric
3. a. primary b. secondary c. teritiary
4. 1-pentanol b. 1, 3-propanediol c. 3-buten-1-ol

Self-test Exercise 6.2

1. The hydroxyl (–OH) group
2. a. secondary b. tertiary c. secondary
   d. primary e. primary f. tertiary
3. The boiling points of alcohols are higher than hydrocarbons of similar molecular weight because of the presence of strong intermolecular force, H-bonding in alcohols.
4. a. CH_3CH_2COOH

   b. 

   $$H_3C-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3$$

Self-test Exercise 6.3

1.	a. 1-propoxybutane	b. 3-methoxyheptane
2.	a. butylpropyl ether	b. methyl (1-ethylpentyl) ether

Self-test Exercise 6.4

1. a > b > c
2. b> c >a
3. CH_3-O-CH_3 (Ether) and CH_3CH_2OH (Alcohol)

Self-test Exercise 6.5

1. Ethers are not affected by most reagents at moderate temperatures. Because of their good solvent properties and general inertness to chemical reaction, ethers are excellent solvents in which to carry out many organic reactions. Diethyl ether is used as an anaesthetic in hospitals.
2. The alkoxide ion for the Williamson ether synthesis is prepared by using sodium metal or sodium hydride (NaH) to remove a proton from an alcohol.

$$2ROH + 2Na \longrightarrow 2RO^- + 2Na^+ + H_2$$

$$ROH + NaH \longrightarrow RO^- + Na^+ + H_2$$

Example:

$$\underset{\text{ethyl bromide}}{CH_3CH_2Br} + \underset{\text{methoxide ion}}{CH_3O^-} \longrightarrow \underset{\text{ethyl methyl ether}}{CH_3CH_2OCH_3} + Br^-$$

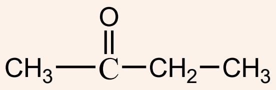
$$\underset{\text{butyl iodided}}{CH_3CH_2CH_2CH_2I} + \underset{\text{ethoxide ion}}{CH_3CH_2O^-} \longrightarrow \underset{\text{butyl ethyl ether}}{CH_3CH_2CH_2CH_2OCH_2CH_3} + I^-$$

1

Self-test Exercise 6.6

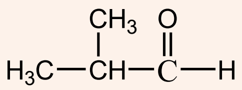
1. a. False b. False c. False

2.



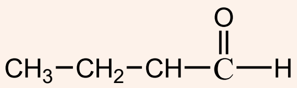
$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

Butanone



$H_3C-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-H$

2-Methylpropanal

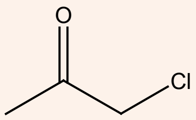


$CH_3-CH_2-CH-\overset{\overset{O}{\|}}{C}-H$

Butanal

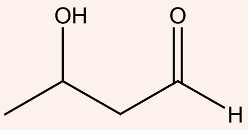
3.

a.



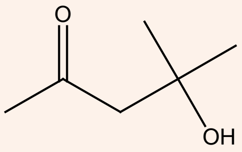
1-Chloro-2-propanone

b.



3-Hydroxybutanal

c.



4-Hydroxy-4-methyl-2-pentanone

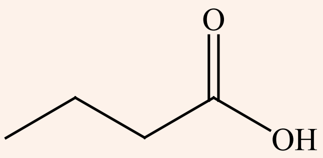
4. a. hexan-3-one b. hexanal

5. Formaldehyde (Ethanal)

Self-test Exercise 6.7

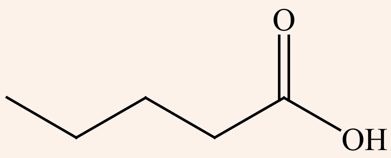
1.

a.



butanoic acid

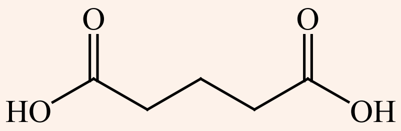
b.



pentanoic acid

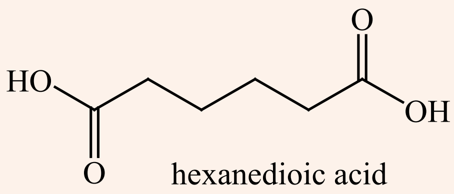
2.

a.



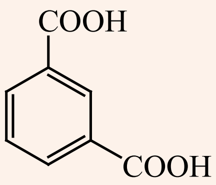
pentanedioic acid

b.



hexanedioic acid

c.



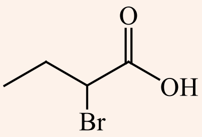
1,3-benzenedicarboxylic acid

3. A great many carboxylic acids are encountered in nature. List some of them and their respective sources.
   a. citric acid from lemons, orange,
   b. malic acid from bananas, apples,
   c. c. tartaric acid acids from avocados,
   d. d. citric and malic acids from salads, etc.

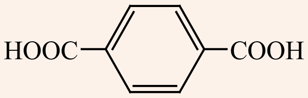
Self-test Exercise 6.8

1. a. γ−Bromo−α−Chlorovaleric acid b) Glutaric acid

2. a.



b.

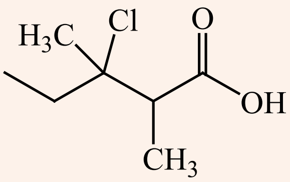


c. HOOC—$(CH_2)_3$—COOH

Self-test Exercise 6.9

1. a. 2-methylbutanoic acid b. 2,4-dimethylhexanoic acid
   c. 4-chlorobutanoic acid d. 4-hydroxybutanoic acid
   e. 2-chloro-5-ethylbenzoic acid f. 3-aminobenzoic acid

2. a.



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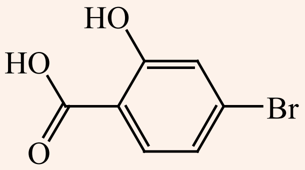
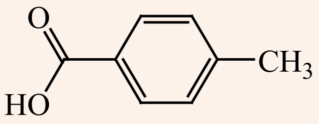
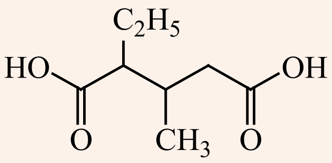


c.



d.

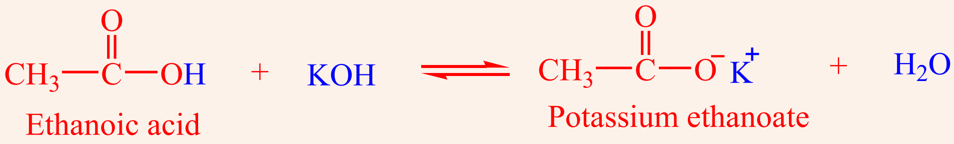


Self-test Exercise 6.10

1. Decanoic acid > octanoic acid > butanoic acid > propanoic acid
2. The aliphatic carboxylic acid, which has the lowest boiling point, is methanoic acid
3. $C_5H_{12} < C_4H_{11}OH < C_2H_5COOH < CH_3(CH_2)_4COOH$

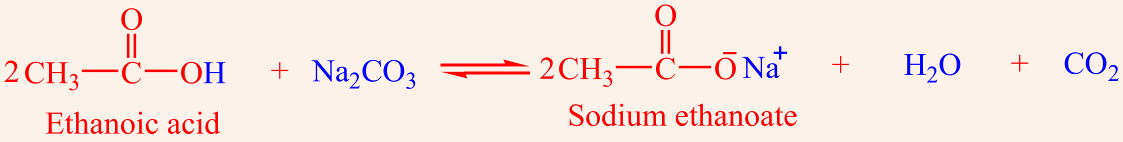
Self-test Exercise 6.11

1. a.



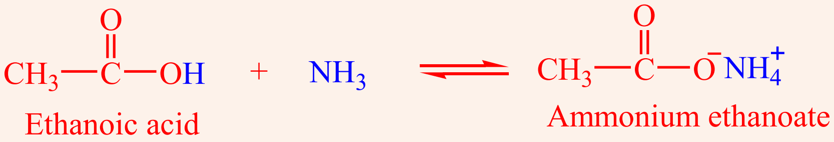
$$CH_3-\overset{O}{\overset{\|}{C}}-OH + KOH \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-O^-K^+ + H_2O$$

b.



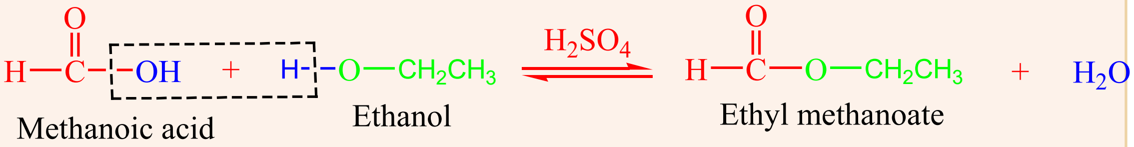
$$2CH_3-\overset{O}{\overset{\|}{C}}-OH + Na_2CO_3 \rightleftharpoons 2CH_3-\overset{O}{\overset{\|}{C}}-O^-Na^+ + H_2O + CO_2$$

c.



$$CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_3 \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-O^-NH_4^+$$

2.



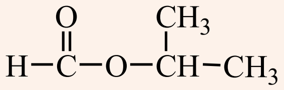
$$H-\overset{O}{\overset{\|}{C}}-\boxed{OH + H}-O-CH_2CH_3 \overset{H_2SO_4}{\rightleftharpoons} H-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3 + H_2O$$

Self-test Exercise 6.12

1. a. Stearic acid is a C_{18} fatty acid and palmitic acid is C_{16} fatty acid. Both are saturated fatty acids but stearic acid (C_{18}) has more molecular weight than palmitic acid (C_{16}) hence more melting point.
   b. The presence of a *cis*-double bond significantly lowers the melting point of a compound. Thus, palmitoleic acid melts at lower temperature than palmitic acid.
   c. The melting points of unsaturated fatty acids decreases with the increase in number of double bonds of comparable molecular weight. Linoleic acid has two double bonds whereas oleic acid has only one, so linoleic acid has a lower melting point.
2. "Omega-3" refers to the position of the final double bond in the chemical structure fatty acids, which is three carbon atoms from the "omega," or tail end of the molecular chain. Omega-3 fatty acids are found in foods, such as fish and flaxseed, and in dietary supplements, such as fish oil.
3. ω-3 fatty acids (FAs) have in common a terminal carbon-carbon double bond in the omega three-position, the third bond from the methyl end of the acid, whereas, ω-6 acids have it in the omega six-position, the sixth bond from the methyl end of the fatty acid, respectively.

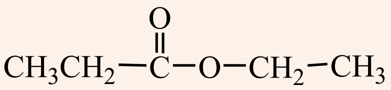
Self-test Exercise 6.13

1. a. propyl methanoate　　b. phenyl ethanoate
   c. methyl benzoate　　d. cyclohexyl propanoate
2. a. methanoic acid and n-propanol　　b. ethanoic acid and phenol
   c. benzoic acid and methano　　d. propanoic acid and cyclohexanol
3. a.



$H-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{CH_3}{|}}{CH}-CH_3$

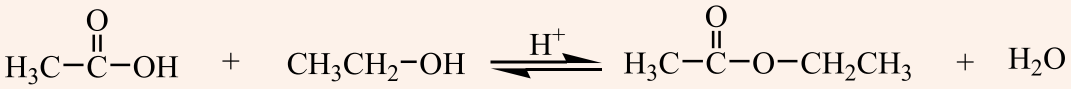
b.



$CH_3CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

Self-test Exercise 6.14

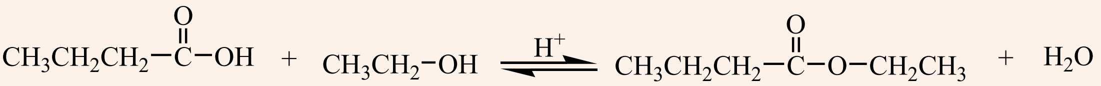
1. a.



$H_3C-\overset{\overset{O}{\|}}{C}-OH + CH_3CH_2-OH \overset{H^+}{\rightleftharpoons} H_3C-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3 + H_2O$

Acetic acid　Ethanol　Ethyl acetate

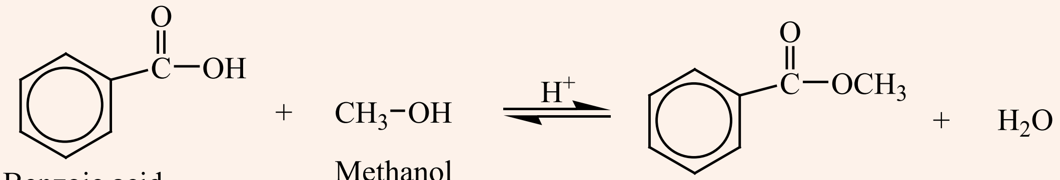
b.



$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH + CH_3CH_2-OH \overset{H^+}{\rightleftharpoons} CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3 + H_2O$

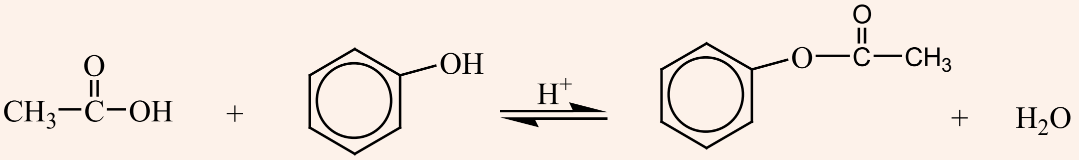
Butanoic acid　Ethanol　Ethyl butanoate

c.



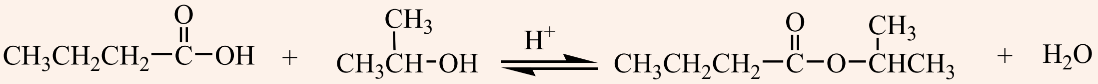
Benzoic acid　Methanol　Benzoic acid

d.



Ethanoic acid　Phenol　Phenol ethanoate

2.

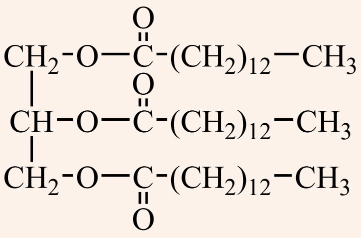


$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH + CH_3\overset{\overset{CH_3}{|}}{CH}\text{-}OH \overset{H^+}{\rightleftharpoons} CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{CH_3}{|}}{C}HCH_3 + H_2O$

Butric acid　2-propanol　2-propyl butyrate

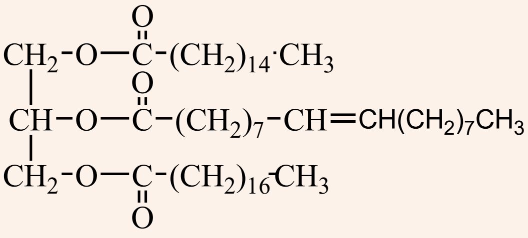
Self-test Exercise 6.15

1. a.



Glyceryl trimyristate

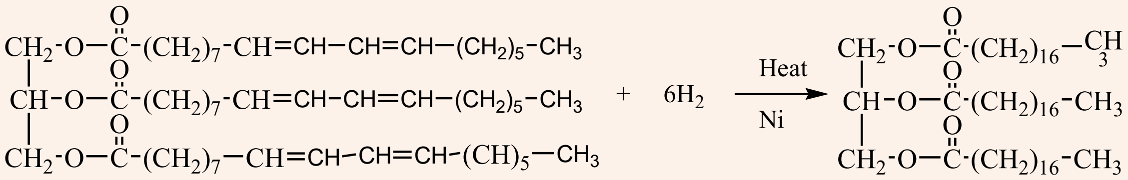
b.



Glyceryl palmitooleostreate

Self-test Exercise 6.16

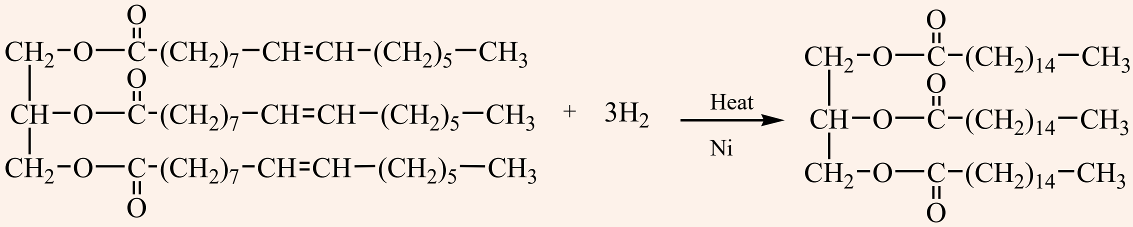
a.



Glyceryl trilinoleate

Glyceryl tristrerate

b.



Glyceryl tripalmitoleate

Glyceryl tripalmitate

Answer Key for Self-Assessment

Part I: Multiple choice Type Questions

1. c
2. d
3. d
4. b
5. a
6. a
7. c
8. a

Part II: Answer the following questions

9. Butan-1-ol contains an O-H group and hence undergoes intermolecular H-bonding. Therefore, its b.p. is much higher than that of butanal which does not contain an O-H group and hence does not undergo H-bonding.

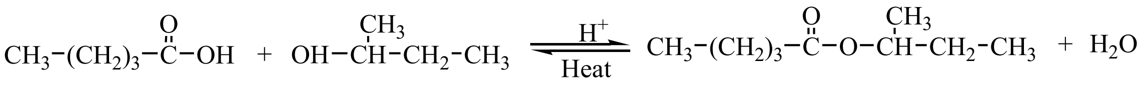
10. Pentanal and 2-pentanone can be distinguished by using Tollens' reagent. Pentanal is an aldehyde whereas 2-pentanone is ketone. Pentanal reacts with Tollens' reagent to give a silver mirror on glass surface.

11. Carboxylic acids are more acidic than alcohols or phenols, although all of them have a hydrogen atom attached to an oxygen atom (—O—H) because the conjugate base of carboxylic acids or the carboxylate ion is stabilized by resonance. Thus, carboxylic acids can release proton easier than alcohols or phenols.

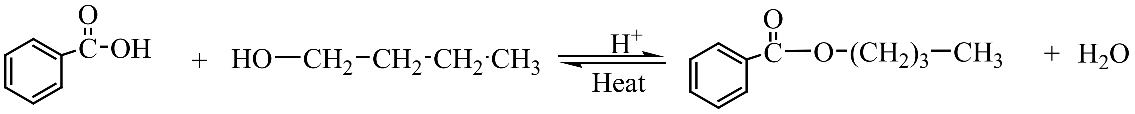
12. a. CH_3COOCH_3 b. $C_6H_5COOCH_3$ c. $HCOOCH_3$ d. $CH_3CH_2COOCH_3$

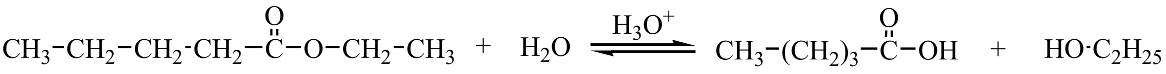
13. a. methyl methanoate b. propyl propanoate
c. ethyl propanoate d. ethyl cyclopentyl carboxylate

14.

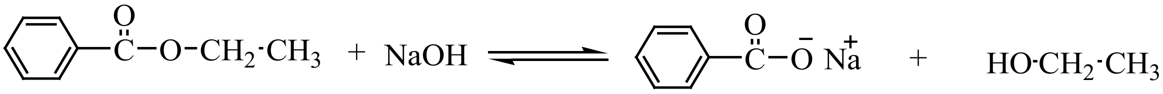
a. 

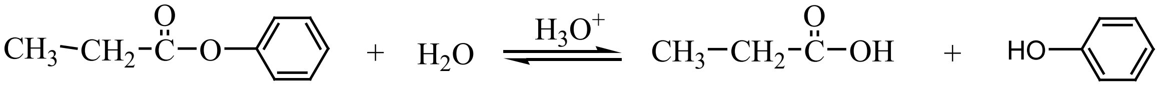
$$CH_3-(CH_2)_3-\overset{O}{\overset{\|}{C}}-OH + OH-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_3 \underset{Heat}{\overset{H^+}{\rightleftharpoons}} CH_3-(CH_2)_3-\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_3 + H_2O$$

b. 

c. 

$$CH_3-CH_2-CH_2\cdot CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + H_2O \overset{H_3O^+}{\rightleftharpoons} CH_3-(CH_2)_3-\overset{O}{\overset{\|}{C}}-OH + HO\cdot C_2H_{25}$$

d. 

e. 

15. a. monounsaturated b. polyunsaturated c. Saturated

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