

S.6 CHEMISTRY NOTES TERM I 2020

CLASS S.6 SCIENCES--CAB/BCM/PCB/PCM/BCG.

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SCHOOL: ST LAWRENCE ACADEMY SCHOOLS AND COLLEGES:

INSTRUCTIONS

- ORGANISATION.
 1. Physical chemistry.
 2. Inorganic chemistry.
 3. Organic chemistry.
- *Forward these notes to your friend/classmates immediately*
- *Check where you stopped with your teacher and copy the rest of the notes in your class work books.*

PHYSICAL CHEMISTRY NOTES

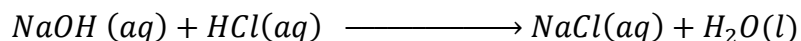
CHEMICAL EQUILIBRIA

Equilibrium reactions do not undergo complete reactions thus they are reversible.

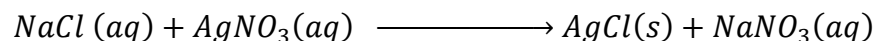
Chemical reactions can be classified as:

(a) Irreversible Reactions:

Reactions occur only in one direction. e.g. $C(g) + O_2(g) \longrightarrow CO_2(g)$



These reaction proceeds to completion in the forward direction. Similarly when a solution of silver nitrate is added to a solution of sodium chloride silver chloride is precipitated immediately.

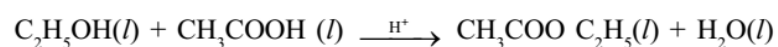


(b) Reversible reactions

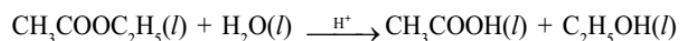
Heat transfer, vapourisation, melting and other phase changes are physical changes and are reversible.

A reversible reaction is one which can be made to go in either direction depending on the conditions. It doesn't undergo to completion thus the reaction proceeds in two direction i.e. back ward and forward reaction.

Consider the reaction between ethanol and acetic acid. When mixed in the presence of dilute sulphuric acid they react and form ethyl acetate and water.

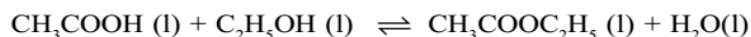


On the other hand, when ethyl acetate and water are mixed in the presence of dilute sulphuric acid the reverse reaction occurs.



The two reactions occur simultaneously.

Thus the above reaction is more appropriately written as



When ethyl acetate and water are formed in the forward reaction the reverse reaction also starts in which ethanol and acetic acid are formed. After some time the concentrations of all the reactants and products become constant. This happens when the rates of forward and reverse reactions become equal; and all the properties of the system become constant (system has attained state of equilibration).

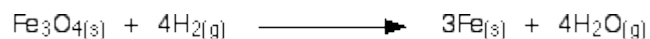
However it may be noted that the state of equilibrium is reached only if the reaction is carried out in a **closed system**. At the time of equilibrium, forward and reverse reactions are taking place and it is in a state of dynamic equilibrium because no change is taking place.

E.g. passing steam over hot iron the steam reacts with the iron to produce a black, magnetic oxide of iron called triiron tetroxide, Fe_3O_4 .



The hydrogen produced in the reaction is swept away by the stream of steam.

Under different conditions, the products of this reaction will also react together. Hydrogen passed over hot triiron tetroxide reduces it to iron. Steam is also produced.



This time the steam produced in the reaction is swept away by the stream of hydrogen.

The above two reactions are reversible

Reversible reactions happening in a closed system

A **closed system** is one in which no substances are either added to the system or lost from it. Energy can, however, be transferred in or out at will.

In the example of iron being heated in steam in a closed container. Heat is being added to the system, but none of the substances in the reaction can escape. The system is closed.

As the triiron tetroxide (Fe_3O_4) and hydrogen start to be formed, they will also react again to give the original iron and steam. So, if you analysed the mixture after a while, a **dynamic equilibrium** is achieved.

The state of equilibrium has following characteristics properties:

(Chemical Equilibrium is dynamic in nature)

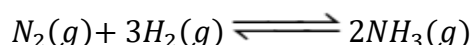
(i) The chemical equilibrium is the result of two equal but opposite processes occurring in the forward and reverse directions and there is no “net” change occurring in the system.

(ii) Equilibrium can be attained from either side e.g.

$N_2O_4 \rightleftharpoons 2NO_2$: is established whether we start the reaction with N_2O_4 or NO_2 .

(iii) Equilibrium can be attained only in a closed system

Any system consisting of gaseous phase or volatile liquids must be kept in a closed container, e.g.



A system consisting of only non-volatile liquid and solid phases can be kept even in an open container because such substances have no tendency to escape, e.g.



(iv) A catalyst cannot change the equilibrium state:

Addition of a catalyst speeds up the forward and reverse reactions by same extent and help in attaining the equilibrium faster. However, the equilibrium concentrations of reactants and products are not affected in any manner.

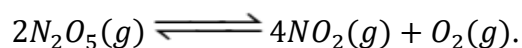
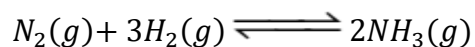
THE LAW OF MASS ACTION: EQUILIBRIUM CONSTANTS: K_c

The two different types of equilibrium (homogeneous and heterogeneous) are looked at separately, because the equilibrium constants are defined differently.

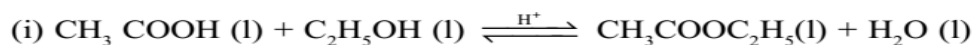
A homogeneous equilibrium has everything present in the same phase.

Examples:-

For gas phase:

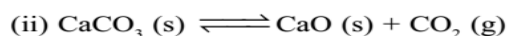


For liquid phase:



A heterogeneous equilibrium has things present in more than one phase.

examples include



The law of mass action is universal

Using a general chemical reaction in which reactants A and B react to give Products C and D



where a,b,c and d are coefficients for a balanced chemical reaction

The mass action law (concentration equilibrium constant) states that if the system is at equilibrium then the following ratio is constant provided no change in temperature.

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (\text{Relation is known as the law of equilibrium.})$$

The law can be stated as follows: If a reversible reaction is allowed to reach equilibrium, then the product of the concentrations of the products raised to their appropriate powers divided by the product of the concentrations of the reactants raised to the appropriate powers has a constant value at a particular temperature.

Derivation:

Now we consider a general reversible reaction: $aA + bB \rightleftharpoons cC + dD$

In the forward reaction A and B react to give C and D as products in the back ward reaction C and D react to give A and B as the products. Thus the back ward and forward reactions proceed until a point is reached and at this point a dynamic equilibrium is attained

If K_1 and K_2 are the rate constant for the forward and backward reactions of the above reaction respectively

The rate of forward reaction = $k_1[A]^a[B]^b$

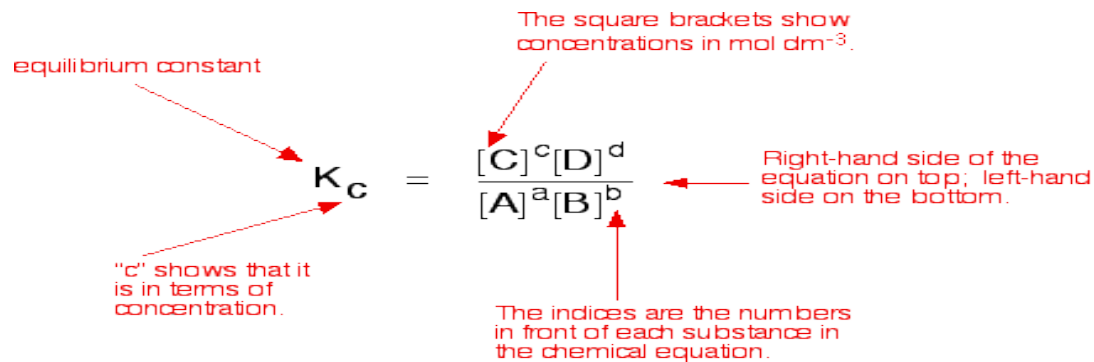
The rate of backward reaction = $k_2[C]^c[D]^d$ Where K_1 and K_2 are the respective rate constants.

At Equilibrium

$$K_1[A]^a[B]^b = K_2[C]^c[D]^d$$

$$\text{or } k = \frac{K_1}{K_2} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Where 'K' is equilibrium constant



As stated above the active mass is expressed in terms of mole/ litre (for solutions) or partial pressure (for gases). Similarly, equilibrium constant K is expressed as for solutions or gases, respectively.

For the above reaction, K_p and K_c are related as follows: $K_c \text{ or } K_p$

Relation ship between K_c and K_p

For a general gas phase reaction at equilibrium: $a A(g) + b B(g) \rightleftharpoons c C(g) + d D(g)$

The pressure and concentration equilibrium constants K_p and K_c are

$$K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} \quad \text{and} \quad K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

For a gaseous substance, the ideal gas equation is, $PV = nRT$ where p and n are its partial pressure and amount in a gaseous mixture and V and T are its volume and temperature and R is the gas constant. The relation may be written as $P = \frac{n}{V} RT$

But $\frac{n}{V} = C$ (Molar Concentration in moles/litre) thus $P = C \cdot RT$

This relation can be used for replacing the partial pressure terms in the expression for K_p

$$K_p = \frac{(c_C RT)^c (c_D RT)^d}{(c_A RT)^a (c_B RT)^b} \quad \text{or} \quad K_p = \frac{[C]^c [RT]^c \times [D]^d [RT]^d}{[A]^a [RT]^a \times [B]^b [RT]^b}$$

Using the square bracket notation for molar concentration the relation can be written as

$$K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(n_p - n_R)}$$

$$= K_c (RT)^{\Delta n_g}$$

where Δn_g is the change in the moles of gaseous substances in the reaction and is equal to the difference in the moles of gaseous products n_p and the moles of gaseous reactants, n_R

Δn_g may be zero, positive or negative.

R = gas constant, T = absolute temperature.

Value of Δn : > 0 or (+) Ve

Relation: $K_p > K_c$

Units of K_c : $(\text{mol L}^{-1})^{\Delta n}$ or Units of K_p : $(\text{atm})^{\Delta n}$

In the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Here n_p = moles of gaseous product is equal to 2

n_R = moles of gaseous reactant is equal to 2 as 1 from H_2 and 1 from I_2

$$\text{Hence } \Delta n_g = n_p - n_R = 2 - 2 = 0.$$

In the reaction. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$\text{Hence } \Delta n_g = n_p - n_R = 2 - 4 = -2.$$

In a reaction involving solids and gases. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$\text{Hence } \Delta n_g = n_p - n_R = 1 - 0 = 1.$$

Expressions of Equilibrium Constant for Some Reactions:

The law of equilibrium can be applied to write down expressions of K_c and K_p for some reactions

(a) Homogeneous Equilibria

Examples

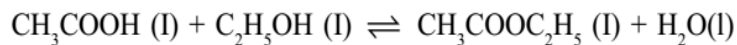
(i) Decomposition of N_2O_4 . $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} ; K_p = K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}}$$

(ii) Oxidation of sulphur dioxide in the contact process. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} ; K_p = \frac{p_{SO_3}^2}{p_{SO_2}^2 \cdot p_{O_2}}$$

(iii) Esterification of acetic acid with ethanol:



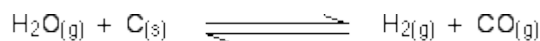
$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

In this case no gas is evolved thus K_p is meaningless.

(b) Writing an expression for K_c for a heterogeneous equilibrium:

The important difference this time is that you *don't include any term for a solid in the equilibrium expression*.

- (i) The equilibrium produced on heating carbon with steam.

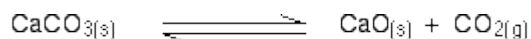


$$K_p = \frac{P_{\text{H}_2} \times P_{\text{CO}}}{P_{\text{H}_2\text{O}}}$$

Qn, Write for K_c :

- (ii) The equilibrium produced on heating calcium carbonate

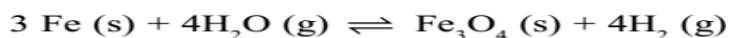
This equilibrium is only established if the calcium carbonate is heated in a closed system, preventing the carbon dioxide from escaping.



$$K_c = [\text{CO}_2] \text{ and } K_p = P_{\text{CO}_2}$$

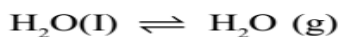
- (iii) Other examples:

(i) Reaction between iron and steam



$$K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4} ; K_p = \frac{P_{\text{H}_2}^4}{P_{\text{H}_2\text{O}}^4}$$

(ii) Liquid – Vapour Equilibrium



$$K_c = [\text{H}_2\text{O; g}] ; K_p = P_{\text{H}_2\text{O}}$$

Note

For reactions in which water is one of the reactants the concentration of water is taken as unchanged since it is assumed that the water is present in excess and not considered in the K_c .

Question

Describe: Experimental methods of verification of the law of mass action: determination of K_c .

Equilibrium Constant and Chemical Equation:

The expression of equilibrium constant depends upon the manner in which the chemical equation representing it is written.

For the reaction: $I_2(g) + H_2(g) \rightleftharpoons 2HI(g)$

The equilibrium constant K is given as $K_c = \frac{[HI]^2}{[H_2][I_2]}$

When the same reaction is written as $\frac{1}{2}I_2(g) + \frac{1}{2}H_2(g) \rightleftharpoons HI(g)$

The corresponding equilibrium constant K_1 is given as $K_{c1} = \frac{[HI]}{[H_2]^{\frac{1}{2}}[I_2]^{\frac{1}{2}}}$

It may be noted that equilibrium constant K and K_1 are related: $K_{c1} = \sqrt{K_c}$.

Where the reaction is written as reverse: $2HI(g) \rightleftharpoons I_2(g) + H_2(g)$.

$K_{c2} = \frac{[H_2][I_2]}{[HI]^2}$ here it can be seen that $K_{c2} = \frac{1}{K_c}$

Units of Equilibrium Constant

Units of equilibrium constant K_c or K_p depend upon the fact whether during the reactions there is any change in the moles of substance or not.

(a) The reactions in which there is no change in moles of substance i.e. $\Delta n = 0$.

The equilibrium constant for such reaction has no units. E.g. $I_2(g) + H_2(g) \rightleftharpoons 2HI(g)$

Hence K_p and K_c have no units in such cases.

(b) The reaction where there is change in the moles of substance i.e. $\Delta n \neq 0$.

The equilibrium constant for such reactions has units which depend upon the change in moles of substances. e.g. : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta n = n_p - n_R = 2 - 4 = -2$.

The units of K_c for this reaction would be $(\text{mol l}^{-1})^{-2}$ or $\text{l}^2\text{mol}^{-2}$ and those of

K_p would be bar⁻² or atm⁻² as shown below:

The equilibrium constant for such reactions are:

$$K_C = \frac{[NH]^2}{[H_2]^3[N_2]} \quad \text{or} \quad K_p = \frac{(P_{NH})^2}{(P_{H_2})^3(P_{N_2})}$$

$$K_C = \frac{(\text{mol/l})^2}{(\text{mol/l})^3 \times \text{mol/l}} \quad \text{or} \quad K_p = \frac{\text{pressure}^2}{\text{pressure}^3 \times \text{Pressure}}$$

$$K_C = \text{l}^2/\text{mol} \quad \text{or} \quad K_p = \text{pressure}^{-2} \text{ or bar}^{-2} \text{ or atm}^{-2}$$

For the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

$\Delta n = 2 - 1 = 1$. Therefore,

The units for K_c and K_p are

K_c = mol L⁻¹ and K_p = bar

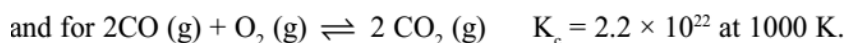
Significance of the Magnitude of K_c

The equilibrium constant of a reaction has a constant and characteristic value at a given temperature. The changes in starting concentration, pressure and the presence of a catalyst do not change the value of the equilibrium constant. However if the temperature is changed.

The value of the equilibrium constant also changes.

The magnitude of the equilibrium constant is a measure of the extent up to which a reaction proceeds before the equilibrium is reached. The magnitude of K is large when the products are present in larger amounts than the reactants in the equilibrium mixture.

For the reaction



A large value of K_c for the second reaction indicates that amount of products is much more than the reactants present at the time of equilibrium. Thus the magnitude of equilibrium constant tells us about the position of the equilibrium.

The magnitude of K_c indicates the extent to which the reaction has occurred. Large K_c value indicates high proportion of the products to the reactants.

Calculation of Equilibrium Constants:

Equilibrium constants K_c and K_p can be calculated if the equilibrium concentrations or partial pressures are known or can be obtained from the given data. The following examples illustrate the calculations.

Example 1.

Calculate the equilibrium constant for the reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$

If at equilibrium 1 mol of A, 0.5 mole of B, 3.0 mole of C and 10 mol of D are present in a one litre vessel.

From the law of equilibrium $K_c = \frac{[C][D]}{[A][B]}$

Since the volume of the vessel is one litre, the number of moles of A, B, C and D are equal to their concentrations. Thus $[A] = 1.0 \text{ mol/l}$, $[B] = 0.5 \text{ mol/l}$, $[C] = 3.0 \text{ mol/l}$ and $[D] = 10 \text{ mol/l}$

$$K_c = \frac{3.0 \text{ mol/l} \times 10 \text{ mol/l}}{1 \text{ mol/l} \times 0.5 \text{ mol/l}}$$

$$K_c = \frac{3 \times 10}{1 \times 0.5} = 60$$

Example 2:

When 1.00 mol hydrogen and 1.00 mole of Iodine are allowed to reach equilibrium in 1.00 dm^3 flask at 450°C and $1.01 \times 10^5 \text{ Nm}^{-2}$, the amount of hydrogen iodide at equilibrium is 1.56 mol. Calculate K_p at 450°C .

Let P = Total pressure of the system = 1.01×10^5

Equation at equilibrium:	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$			Total
Initial moles:	1.00	1.00	0	2.00
Equilibrium moles:	1-a	1.a	2a	2

Since $2a = 1.56$

thus $a = 0.78 \text{ moles}$

Thus

Equilibrium moles	0.22	0.22	1.56	2.00
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Equilibrium partial pressure **Remember partial pressure = mole fraction total pressure.**

$\frac{0.22}{2.00} \times P$	$\frac{0.22}{2.00} \times P$	$\frac{1.56}{2.00} \times P$	P
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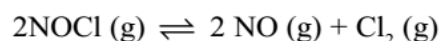
11,110 11,110 78,780

Using
$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = \frac{(78,780)^2}{(11110 \times 11110)}$$

= 50.3.

Example 3:

In an experiment carried out at 298 K, 4.0 mol of NOCl were placed in a 2 litre flask and after the equilibrium was reached 1.32 mol of NO were formed. Calculate K_c at 298 K for the reaction.



Solution Calculation of equilibrium concentrations

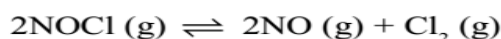
(i) $[\text{NO}] = \frac{\text{No. of moles of NO}}{\text{Volume}} = \frac{1.32 \text{ mol}}{2\text{L}} = 0.66 \text{ mol L}^{-1}$

(ii) $[\text{Cl}_2] = \frac{\text{No. of moles of Cl}_2}{\text{Volume}} = \frac{\frac{1}{2} (\text{No. of moles of NO})}{\text{Volume}} = \frac{1.32 \text{ mol}}{2 \times 2\text{L}} = 0.33 \text{ mol L}^{-1}$

(iii) $[\text{NOCl}] = \frac{\text{No. of moles of NOCl}}{\text{Volume}} = \frac{(\text{Initial moles} - \text{moles decomposed})}{\text{Volume}}$

$$= \frac{(4.0 - 1.32) \text{ mol}}{2 \text{ L}} = \frac{2.68 \text{ mol}}{2 \text{ L}} = 1.34 \text{ mol L}^{-1}$$

For the reaction



$$K_c = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(0.66 \text{ mol L}^{-1})^2 (0.33 \text{ mol L}^{-1})}{(1.34 \text{ mol L}^{-1})^2} = \frac{(0.66)^2 \times 0.33}{(1.34)^2}$$

$$= 0.080 \text{ mol L}^{-1}$$

$$K_c = 0.080 \text{ mol L}^{-1}$$

Example 4:

2 moles of HI were heated in a vessel of one litre capacity at 713 K till the equilibrium was reached. At equilibrium HI was found to be 25% dissociated. Calculate K_c and K_p for the reaction.

Solution Initial moles of HI = 2

$$\text{Moles of HI dissociated} = \frac{25 \times 2}{100} = 0.5 \text{ mol}$$

$$\text{Moles of HI at equilibrium} = 2.0 - 0.5 = 1.5 \text{ mol}$$

The dissociation of HI occurs as

	2HI (g)	$\rightleftharpoons$	H ₂ (g)	+	I ₂ (g)
Initial moles	2		0		0
Equilibrium moles	(2 – 0.5)		0.25		0.25
	1.5 mol		0.25 mol		0.25 mol
Volume of reaction vessel	1L		1L		1L
Equilibrium concentration	1.5 mol L ⁻¹		0.25 mol L ⁻¹		0.25 mol L ⁻¹

For the reaction

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.25 \text{ mol L}^{-1})(0.25 \text{ mol L}^{-1})}{(1.5 \text{ mol L}^{-1})^2}$$
$$= \frac{(0.25)^2}{(1.5)^2} = 0.028$$

$$\text{Also } K_p = K_c (RT)^{\Delta n_g}$$

$$\text{For this reaction } \Delta n_g = n_p - n_R = 2 - 2 = 0$$

$$\therefore K_p = K_c = 0.028$$

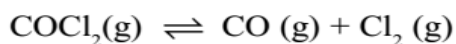
Example 5:

Calculate K_p for the reaction $COCl_2(g) \rightleftharpoons CO + Cl_2(g)$ in atm and Nm^{-2}

The equilibrium partial pressures of $COCl_2$, CO and Cl_2 are 0.20, 0.16 and 0.26 atm respectively.

(1 atm = 101300 Nm⁻²)

Solution : (i) K_p in atmospheres



$$K_p = \frac{p_{\text{CO}} \times p_{\text{Cl}_2}}{p_{\text{COCl}_2}} = \frac{(0.16 \text{ atm})(0.26 \text{ atm})}{(0.20 \text{ atm})} = \frac{0.16 \times 0.26}{0.20} \text{ atm} \\ = 0.21 \text{ atm.}$$

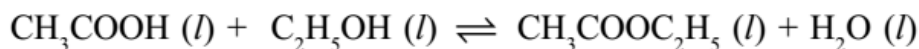
(ii) K_p in Nm⁻²

$$K_p = 0.21 \text{ atm and } 1 \text{ atm} = 101300 \text{ Nm}^{-2}$$

$$\therefore K_p = (0.21 \text{ atm}) (101300 \text{ Nm}^{-2} \text{ atm}^{-1}) = 21273 \text{ Nm}^{-2}$$

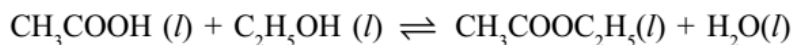
Example 6:

When equal number of moles of ethanol and acetic acid were mixed at 300 K, two-third of each had reacted when the equilibrium was reached. What is the equilibrium constant for the reaction?



Solution : Let n moles each of acetic acid and ethanol be mixed initially. Then the

Let V be the volume of the reaction mixture in litres.



Initial mole	n	n	0	0
Equilibrium concentration in moles	$(n - \frac{2}{3}n)$	$(n - \frac{2}{3}n)$	$\frac{2}{3}n$	$\frac{2}{3}n$
	$\frac{1}{3}n$	$\frac{1}{3}n$	$\frac{2}{3}n$	$\frac{2}{3}n$
Equilibrium concentration	$\frac{n}{3V}$	$\frac{n}{3V}$	$\frac{2n}{3V}$	$\frac{2n}{3V}$

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

$$= \frac{\left(\frac{2n}{3V}\right)\left(\frac{2n}{3V}\right)}{\left(\frac{n}{3V}\right)\left(\frac{n}{3V}\right)} = 2 \times 2 = 4$$

$$K_c = 4$$

Example 7:

Nitrogen (1mole) and hydrogen (3 moles) react at constant temperature at a pressure of 1 atm. At equilibrium half the nitrogen has reacted. Calculate K_p .

	$N_2(g)$	$+ 3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initial moles	1	3		0
At equilibrium	$1 - 0.5(0.5)$	$3 - 1.5(1.5)$		2×0.5
Mole fraction	$0.5/3$	$1.5/3$		$1/3$
Partial pressure:	$(0.5/3) \times 1\text{MPa}$	$(1.5/3) \times 1\text{MPa}$		$(1/3) \times 1\text{MPa}$

Applying the law of equilibrium constant: $K_p = \frac{(P_{NH})^2}{(P_{H_2})^3(P_{N_2})}$

$$K_p = \frac{\left(\frac{1}{3} \times 1 \text{ MPa}\right)^2}{\left(\frac{0.5}{3} \times 1 \text{ MPa}\right)^3 \times \left(\frac{1.5}{3} \times 1 \text{ MPa}\right)}, = 5.3 \text{ MPa}^{-2}$$

Example 8:

If 2.6 moles of HI were heated to about 100°C and found out to be 20% dissociated, calculate:

- The concentration of H_2 , I_2 and HI present at equilibrium
- The K_c

Solution:



$$\begin{array}{ccc} 2n(1-x) & nx & nx \\ n(1-x) & \frac{nx}{2} & \frac{nx}{2} \end{array}$$

$$x = 20\% \quad 20/100 = 0.2$$

$$n = 2.6 \text{ moles.}$$

Conc. of	HI	H_2	I_2
	$2.6(1-0.2)$	$2.6 \times 0.2 / 2$	$2.6 \times 0.2 / 2$
	2.08 moles	0.26 moles	0.26 moles.

$$\begin{aligned} K_c &= 0.26 \times 0.26 / (2.08)^2 \\ &= 1.563 \times 10^{-2} \end{aligned}$$

Example 9

1.54 g of HI were heated in 600cm^3 bulb at 530°C , when equilibrium was attained the bulb was rapidly cooled to room temperature and broken under KI solution. The iodine formed from the decomposition required 67.0cm^3 of 0.1M $\text{Na}_2\text{S}_2\text{O}_3$ solution for complete reaction.

Calculate:

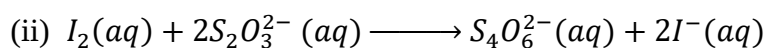
- (i) The number of moles of HI in 1.54g.
- (ii) The number of moles of KI formed.
- (iii) The value of K_c at 530°C .

Solution

(i) From moles = $\frac{\text{Mass dissolved}}{\text{Relative formula mass}}$

RFM of HI = $1 + 127 = 128$

Moles = $1.54/128 = 0.01203$ moles.



1000cm^3 $\text{S}_2\text{O}_3^{2-}(\text{aq})$ contain 0.1 moles of mole

1cm^3 of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ contains $(\frac{0.1}{1000})$ moles

67.0cm^3 of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ used contain $(\frac{0.1}{1000} \times 67.0)$ moles = 0.0067 moles

From the equation mole ratio is 1: 2

2 moles of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ reacted with 1 mole of I_2 .

0.0067 moles $\text{S}_2\text{O}_3^{2-}(\text{aq})$ reacts with $\frac{0.0067}{2} = 0.00335$ moles of I_2 .

(iii) Using the decomposition equilibrium equation. $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$

HI : n = $0.01203 \approx 0.012$ moles : Let the degree of dissociation be x .

$2n(1-x)$	nx	nx
$n(1-x)$	$\frac{nx}{2}$	$\frac{nx}{2}$

But $\frac{nx}{2} = 0.00335$ of I_2 . Also n = 0.012

Thus x = 0.558

HI = $n(1-x) = 0.012(1-0.558) = 0.0053$ moles HI

600cm^3 contain 0.0053 moles of HI

1000cm^3 of will contain $(\frac{0.0053}{600} \times 1000)$ moles = 0.0088M

Number of moles of H_2 = Number of moles of I_2

Number of moles of I_2 at equilibrium = 0.00335 moles in 600cm^3 .

600cm^3 contain 0.00335 moles of I_2

1000cm³ of will contain $(\frac{0.00335}{600} \times 1000) \text{ moles} = 0.0056\text{M}$

Also $[\text{H}_2] = 0.0056\text{M}$

Using the equilibrium constant $K_C = \frac{0.0056\text{mol/l} \times 0.0056\text{mol/l}}{(0.0088\text{ mole/l})^2} = 0.4.$

UNEB QUESTIONS:

1. 2006 P1 Qn 14

Part C

At a certain temperature, the equilibrium constant for the reaction between nitrogen and hydrogen K_p was $4.82 \times 10^{-5} \text{ atm}^{-2}$ and the partial pressure of nitrogen are 30 and 120 atmosphere respectively.

- Write an expression for equilibrium constant K_p .
- Calculate the partial pressure of ammonia at equilibrium.

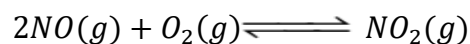
Solution: $K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3}$

Using the above expression.

$$4.82 \times 10^{-5} = \frac{P_{\text{NH}_3}^2}{10 \times 120} \quad P_{\text{NH}_3} = \sqrt{4.82 \times 10^{-5} \times 10 \times 120} = 50 \text{ atm.}$$

2. Qn 5 2006 p.2

Nitrogen (II) oxide combines with oxygen at 80°C and 200 atm to form nitrogen(IV)oxide according to the following equation.



Calculate K_p , if the mixture contained 67% nitrogen (VI) oxide at equilibrium.

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \times P_{\text{O}_2}}$$

Percentage of NO and O₂ at equilibrium = 100% - 67% = 33%

Total moles of NO and O₂ = 2+1 = 3

Percentage of NO = $\frac{2}{3} \times 33 = 22\%$ and for O₂ = 33-22 = 11%

Partial pressure for NO₂, $P_{\text{NO}_2} = \frac{67}{100} \times 200 = 134 \text{ atm.}$

NO, $P_{\text{NO}} = \frac{22}{100} \times 200 = 44 \text{ atm.}$

$$O_2, P_{O_2} = \frac{11}{100} \times 200 = 22 \text{ atm.}$$

$$\text{Thus } K_p = \frac{134^2}{44^2 \times 22} = 0.4216 \text{ atm}^{-1}$$

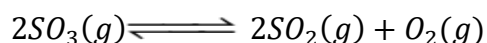
3. Qn 14 2003 p1

1 mole of sulphur trioxide was introduced into a 1 dm³ vessel. The vessel was heated to 100K until equilibrium was attained. At equilibrium, 0.35 moles of sulphur trioxide was present.

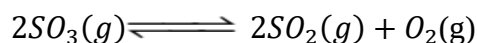
Write:

- (i) Equation for the decomposition of sulphur trioxide.
- (ii) An expression for equilibrium constant K_c

Calculate the K_c value



$$K_c = \frac{[SO_2]^2 [O_2]}{[SO_3]^2}$$



Initial moles	1	0	0.
Moles at equilibrium	0.35	0.65	0.325

$$K_c = \frac{[0.65]^2 [0.325]}{[0.35]^2} = 1.121 \text{ mol dm}^{-3}.$$

LE-CHATELIER'S PRINCIPLE AND THE FACTORS WHICH AFFECT EQUILIBRIUM CONSTANT:

The state of equilibrium is in a dynamic balance between forward and backward reaction.

This balance can be disturbed by changing concentration, temperature or pressure. If done so a certain net change occurs in the system. The direction of change can be predicted with the help of Le-Chatelier principle

Le Chatelier's Principle

It states that when a system in equilibrium is disturbed by a change in concentration, pressure or temperature, a 'net' change occurs in it in a direction that tends to decrease the disturbing factor.

If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change.

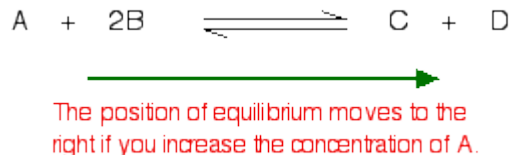
a. Using Le Chatelier's Principle with a change of concentration

Suppose you have an equilibrium established between four substances A, B, C and D.



Considering a change by increasing the concentration of A.

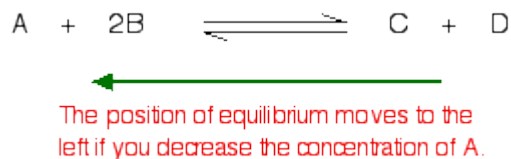
According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the concentration of A decreases again - by reacting it with B and turning it into C + D. The position of equilibrium moves to the right.



This will continue until a maximum possible amount of B has been converted into C and D by A.

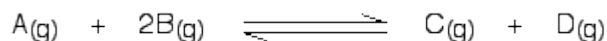
If you changed the conditions by decreasing the concentration of A.

According to Le Chatelier, the position of equilibrium will move so that the concentration of A increases again. That means that more C and D will react to replace the A that has been removed. The position of equilibrium moves to the left.



b. Using Le Chatelier's Principle with a change of pressure

This only applies to reactions involving gases:



What would happen if you changed the conditions by increasing the pressure?

According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the pressure is reduced again. In this case, there are 3 molecules on the left-hand side of the equation, but only 2 on the right. By forming more C and D, the system causes the pressure to reduce.

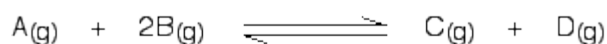
Increasing the pressure on a gas reaction shifts the position of equilibrium towards the side with fewer molecules. E.g in formation of NH_3 and SO_3 gas where there's decrease in volume.




 The position of equilibrium moves to the right
 if you increase the pressure on the reaction.

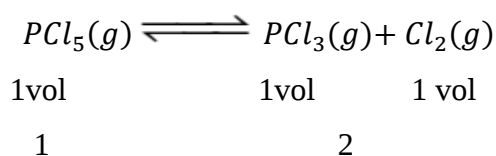
What would happen if you changed the conditions by decreasing the pressure?

The equilibrium will move in such a way that the pressure increases again. It can do that by producing more molecules. In this case, the position of equilibrium will move towards the left-hand side of the reaction.




 The position of equilibrium moves to the left
 if you decrease the pressure on the reaction.

For example: in the decomposition of phosphorous pentachloride where there's increase in volume.



Any reaction which occur with increase in volume will be favoured by use of low pressure.

What happens if there are the same number of molecules on both sides of the equilibrium reaction?

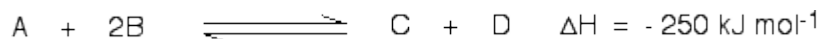
e.g in formation of HI(g)

In this case, increasing the pressure has no effect whatsoever on the position of the equilibrium.

Because you have the same numbers of molecules on both sides, the equilibrium can't move in any way that will reduce the pressure again.

c. Using Le Chatelier's Principle with a change of temperature

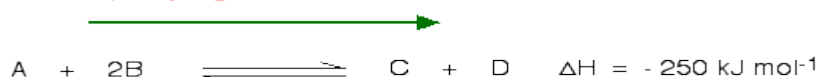
This depends whether heat is given out or absorbed during the reaction. Assume that our forward reaction is exothermic (heat is evolved):



This shows that 250 kJ is evolved (hence the negative sign) when 1 mole of A reacts completely with 2 moles of B. For reversible reactions, the value is always given as if the reaction was one-way in the forward direction.

The back reaction (the conversion of C and D into A and B) would be endothermic by exactly the same amount.

250 kJ is **evolved** when A and B react completely to give C and D.



250 kJ is **absorbed** when C and D react completely to give A and B.

(i) increasing the temperature

According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the temperature is reduced again.

Suppose the system is in equilibrium at 400°C, and you increase the temperature to 650°C.

To cool down, it needs to absorb the extra heat that you have just put in. In the case we are looking at, the *back reaction* absorbs heat. The position of equilibrium therefore moves to the left. The new equilibrium mixture contains more A and B, and less C and D.



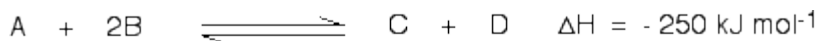
The position of equilibrium moves to the left if you increase the temperature.

If you were aiming to make as much C and D as possible, increasing the temperature on a reversible reaction where the forward reaction is exothermic.

(ii) decreasing the temperature

Suppose the system is in equilibrium at 650°C and you reduce the temperature to 400°C. The reaction will tend to heat itself up again to return to the original temperature. It can do that by favouring the exothermic reaction.

The position of equilibrium will move to the right. More A and B are converted into C and D at the lower temperature.



The position of equilibrium moves to the right if you decrease the temperature.

Summary.

- Increasing the temperature of a system in dynamic equilibrium favours the endothermic reaction. The system counteracts the change you have made by absorbing the extra heat.
- Decreasing the temperature of a system in dynamic equilibrium favours the exothermic reaction.

The system counteracts the change you have made by producing more heat.

d. Effect of catalyst:

A catalyst increases both the forward and backward reactions equally, this is because the addition of a catalyst does not affect the relative rate of the two reactions thus can't affect the position of the equilibrium.

e. Effect of inert gas on equilibrium:

1. Addition of an inert gas does not affect the concentration of any reacting species at equilibrium hence K_c does not change:

Thus $K_p = K_c (RT)^{\Delta n}$ where Δn = number of moles of (product- reactant)

2. Reaction where $\Delta n = 0$ then $K_p = K_c$.

In this case the addition of an inert gas will only increase the total pressure of the system without affecting the partial pressure of the reacting species.

3. Reaction where $\Delta n > 0$ e.g. decomposition of PCl_5 :

In this case the addition of inert gas at constant volume, equilibrium of the species is not affected since concentration of the species does not appear in the K_c expression thus it remains constant.

At constant pressure, the addition of an inert gas leads to an increase of the volume and this causes the dilution of the concentration of the species. This increase in volume leads to the increase in the degree of dissociation thus K_c constant will shift to the right.

4. Reaction where $\Delta n < 0$ e.g. in formation of $NH_3(g)$

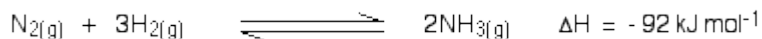
Addition of an inert gas at constant pressure will favour the formation of the reactants thus shifting the equilibrium to the left and the equilibrium will not be affected if the inert gas is added at constant volume.

APPLICATION OF FACTORS ON INDUSTRIAL PROCESSES:

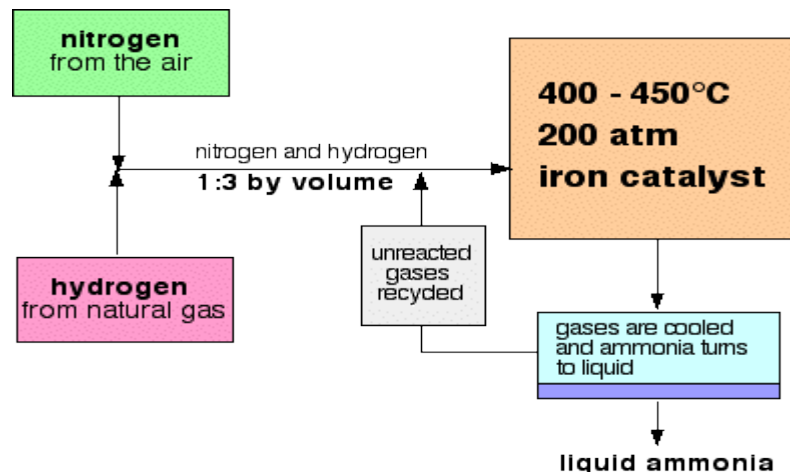
1. THE HABER PROCESS

The Haber Process describes the manufacture of ammonia from nitrogen and hydrogen, and it involves conditions such as temperature, pressure and catalyst on the composition of the equilibrium mixture.

The Haber Process combines nitrogen from the air with hydrogen derived mainly from natural gas (methane) into ammonia. The reaction is reversible and the production of ammonia is exothermic.



A flow scheme for the Haber Process looks like this:



The catalyst is iron, though potassium hydroxide added to it as a promoter - a substance that increases its efficiency.

At each pass of the gases through the reactor, only about 15% of the nitrogen and hydrogen converts to ammonia. (This figure also varies from plant to plant.) By continual recycling of the unreacted nitrogen and hydrogen, the overall conversion is about 98%.

Explaining the conditions

(i) The proportions of nitrogen and hydrogen

The mixture of nitrogen and hydrogen going into the reactor is in the ratio of 1 volume of nitrogen to 3 volumes of hydrogen.

Avogadro's Law says that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. That means that the gases are going into the reactor in the ratio of 1 molecule of nitrogen to 3 of hydrogen. That is the proportion demanded by the equation.

(ii) The temperature

Equilibrium considerations

You need to shift the position of the equilibrium as far as possible to the right in order to produce the maximum possible amount of ammonia in the equilibrium mixture.

The forward reaction (the production of ammonia) is exothermic.



According to Le Chatelier's Principle, this will be favoured if you lower the temperature. The system will respond by moving the position of equilibrium to counteract this - in other words by producing more heat.

In order to get as much ammonia as possible in the equilibrium mixture, you need as low a temperature as possible. However, 400 - 450°C isn't a low temperature!

400 - 450°C is a compromise temperature producing a reasonably high proportion of ammonia in the equilibrium mixture (even if it is only 15%), but in a very short time.

(iii) The pressure



Notice that there are 4 molecules on the left-hand side of the equation, but only 2 on the right.

According to Le Chatelier's Principle, if you increase the pressure, the system will respond by favouring the reaction which produces fewer molecules. That will cause the pressure to fall again.

In order to get as much ammonia as possible in the equilibrium mixture, you need as high a pressure as possible. 200 atmospheres is a high pressure.

(iv) The catalyst

The catalyst has no effect whatsoever on the position of the equilibrium. Its only function is to speed up the reaction for a dynamic equilibrium to be set up within the very short time that the gases are actually in the reactor.

In the absence of a catalyst the reaction is so slow that virtually no reaction happens in any sensible time.

Separating the ammonia

When the gases leave the reactor they are hot and at a very high pressure. Ammonia is easily liquefied under pressure as long as it isn't too hot, and so the temperature of the mixture is lowered enough for the ammonia to turn to a liquid. The nitrogen and hydrogen remain as gases even under these high pressures, and can be recycled.

Uses of ammonia:

- Manufacture of fertilizers e.g. ammonium nitrate.
- Manufacture of Nylon.
- Manufacture of nitric acid.
- In wood pulp production. etc.

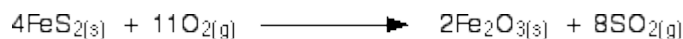
2. THE CONTACT PROCESS:

(a) Making the sulphur dioxide

This can either be made by burning sulphur in an excess of air:



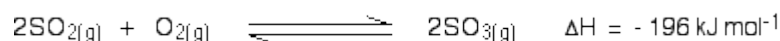
... or by heating sulphide ores like pyrite in an excess of air:



Or Burning H₂S in excess air (write the equation)

(b) Converting the sulphur dioxide into sulphur trioxide.

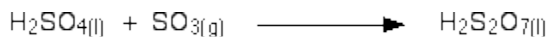
This is a reversible reaction, and the formation of the sulphur trioxide is exothermic.



This step requires a catalyst V₂O₅ at 1-2 atm and temperature of 400-500°C.

(c) Converting the sulphur trioxide into sulphuric acid.

This can't be done by simply adding water to the sulphur trioxide - the reaction is so uncontrollable that it creates a fog of sulphuric acid. Instead, the sulphur trioxide is first dissolved in concentrated sulphuric acid



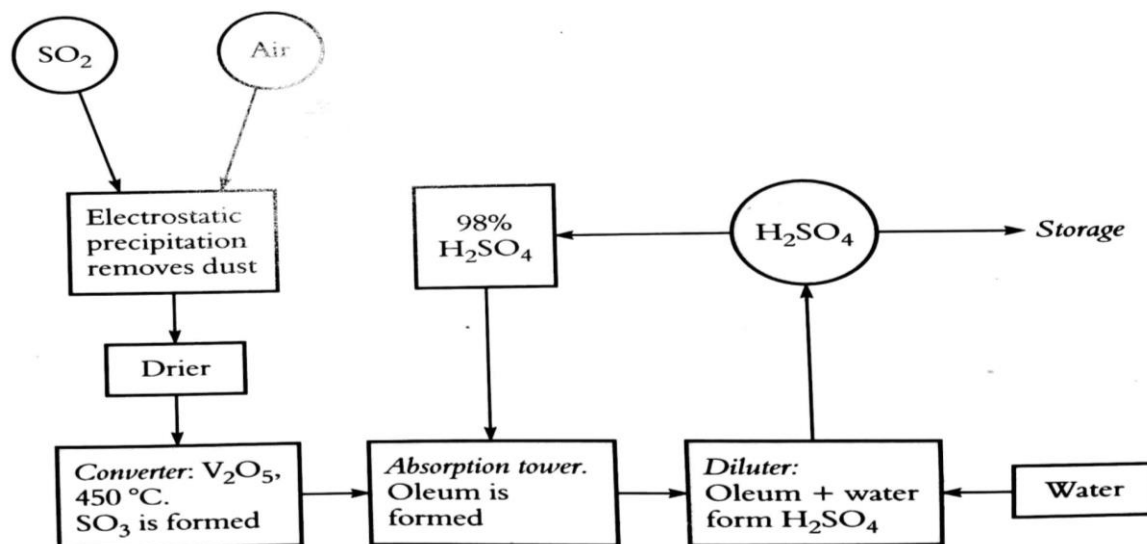
The product is known as fuming sulphuric acid or oleum.

This can then be reacted safely with water to produce concentrated sulphuric acid - twice as much as you originally used to make the fuming sulphuric acid.



The sulphuric acid obtained from this method is 98% conc.

The Flow chart.

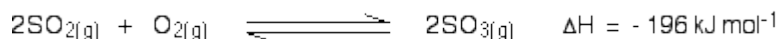


Explaining the conditions

The proportions of sulphur dioxide and oxygen

The mixture of sulphur dioxide and oxygen going into the reactor is in equal proportions by volume. Using Avogadro's Law. That means that the gases are going into the reactor in the ratio of 1 molecule of sulphur dioxide to 1 of oxygen.

That is an excess of oxygen relative to the proportions demanded by the equation.

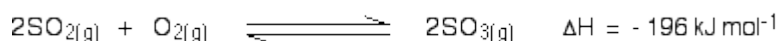


According to Le Chatelier's Principle, Increasing the concentration of oxygen in the mixture causes the position of equilibrium to shift towards the right. Since the oxygen comes from the air, this is a very cheap way of increasing the conversion of sulphur dioxide into sulphur trioxide.

The temperature

You need to shift the position of the equilibrium as far as possible to the right in order to produce the maximum possible amount of sulphur trioxide in the equilibrium mixture.

The forward reaction (the production of sulphur trioxide) is exothermic.

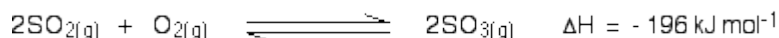


According to Le Chatelier's Principle, this will be favoured if you lower the temperature. The system will respond by moving the position of equilibrium to counteract this - in other words by producing more heat.

In order to get as much sulphur trioxide as possible in the equilibrium mixture, you need as low a temperature as possible. However, 400 - 450°C isn't a low temperature!

400 - 450°C is a compromise temperature producing a fairly high proportion of sulphur trioxide in the equilibrium mixture, but in a very short time.

The pressure



Notice that there are 3 molecules on the left-hand side of the equation, but only 2 on the right.

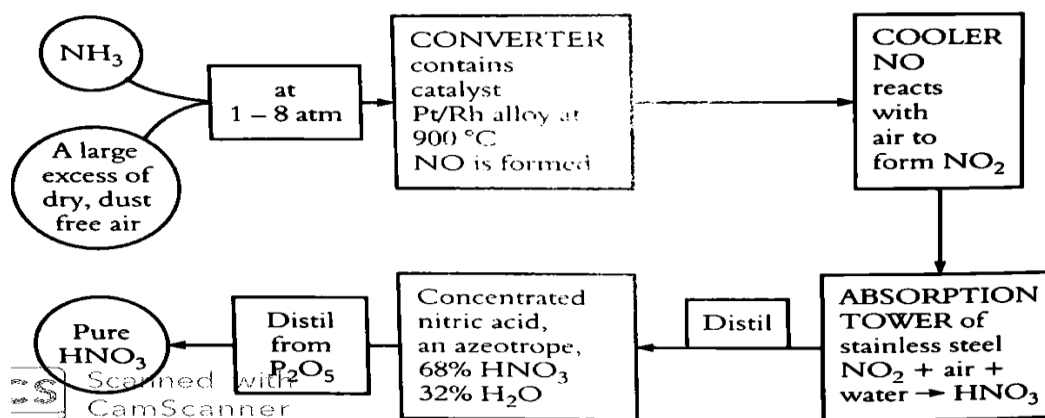
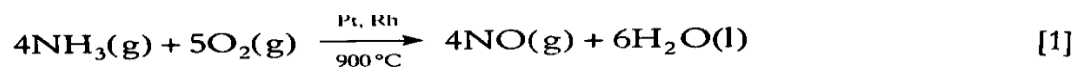
According to Le Chatelier's Principle, if you increase the pressure the system will respond by favouring the reaction which produces fewer molecules. That will cause the pressure to fall again.

In order to get as much sulphur trioxide as possible in the equilibrium mixture, you need as high pressure as possible. High pressures also increase the rate of the reaction. However, the reaction is done at pressures close to atmospheric pressure!

3. MANUFACTURE OF NITRIC ACID.

The industrial method of making nitric acid is the catalytic oxidation of ammonia.

A flow diagram for the process, which was invented by Ostwald, is shown below:



INORGANIC CHEMISTRY NOTES

Do research about the remaining transition elements

Especially: Manganese, Chromium, iron and copper.

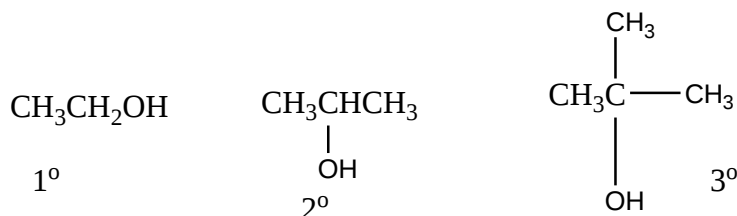
ORGANIC CHEMISTRY NOTES

ALCOHOLS OR ALKANOLS AND PHENOL

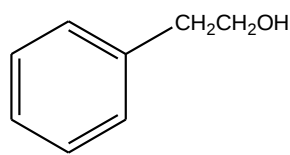
Introduction

Aliphatic Monohydric Alcohols are monohydroxyl derivatives of alkanes and have a general formula $C_nH_{2n+1}OH$ or $C_nH_{2n+2}O$

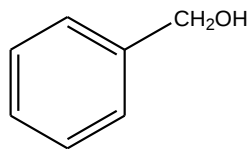
Aliphatic Monohydric Alcohols may be classified as 1° , 2° or 3° according to the nature of the carbon atom to which the hydroxyl group is attached i.e.



Aromatic Alcohols have aryl group attached to aliphatic portion of the alcohol separated by at least a methylene group. E.g

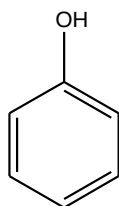


2-Phenylethanol

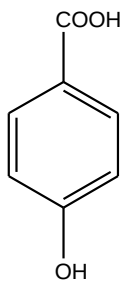


Phenylmethanol

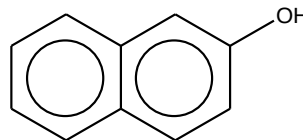
Compounds in which the hydroxyl group is attached directly to the benzene (Aromatic) ring are classified as **Phenol**. E.g.



Phenol

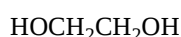


p-Hydroxybenzoic acid



2-Naphthol

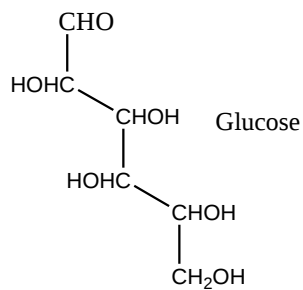
Alcohols containing two hydroxyl groups are described as **dihydric alcohols or diols** and those with three hydroxyl groups are **triols** while those containing many hydroxyl groups are **polyols**. E.g.



Ethane-1,2-diol



Propane-1,2,3-triol



Glucose

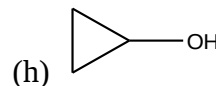
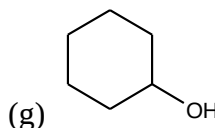
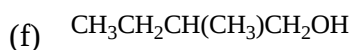
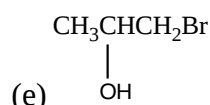
NOMENCLATURE OF ALCOHOLS

The IUPAC Names are obtained by dropping the ending “-e” of alkane and replacing it with suffix “-ol”. The position of the hydroxyl group is indicated by inserting an appropriate number between the stem name and ol.

Example:

Name the following compounds using the IUPAC System

- (a) CH_3OH (b) $\text{CH}_3\text{CH}_2\text{OH}$ (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (d) $(\text{CH}_3)_3\text{CCH}_2\text{OH}$



Solution

- (a) Methanol (b) Ethanol (c) Propan-1-ol (d) 2,2-dimethylpropan-1-ol
 (e) 1-bromopropan-2-ol (f) 2-methylbutan-1-ol (g) Cyclohexanol (h) Cyclopropanol

ISOMERISM

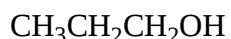
Aliphatic monools have structural isomers .i.e. Chain, functional and Positional Isomers.

Ethers are functional isomers of monools.

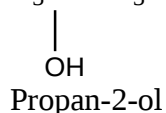
Example:

A compound X has molecular formula C_3H_8O . Write down the structural formulae and names of the possible isomers of X.

Solution:



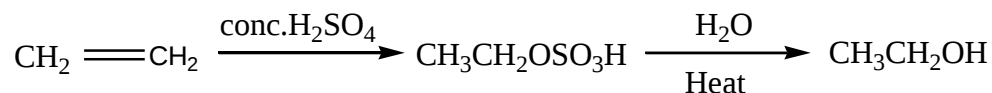
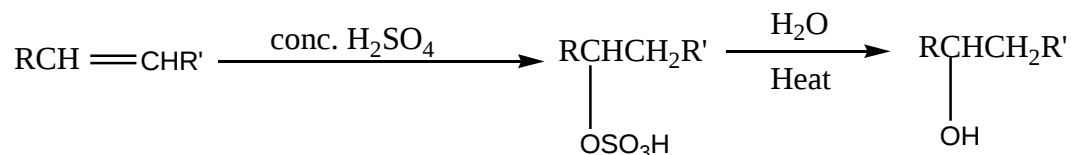
Propan-1-ol



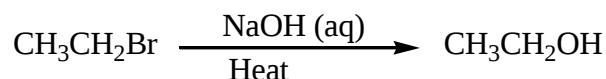
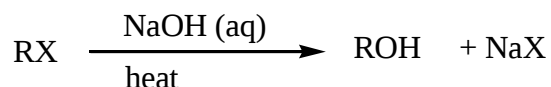
Methoxyethane

SYNTHETIC PREPARATION OF ALCOHOLS

1. From Alkenes



2. From Alkyl halides

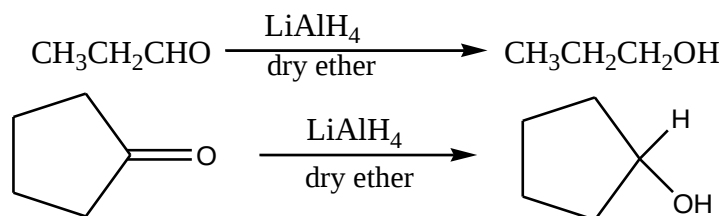


3. From Carbonyl compounds

Reduction of carbonyl compounds generates alcohol. Aldehydes are reduced to Primary Alcohol while Ketones to Secondary Alcohol.

The reducing agents commonly used are Na/ethanol, $LiAlH_4$ in dry ether, $NaBH_4$ and water, amalgamated Zinc and concentrated Hydrochloric acid, finely divided Ni or Pt with hydrogen gas.

Lithium Aluminium hydride does reduce a double bond if it is present in the carbonyl compound.

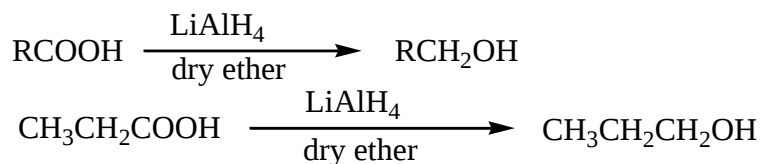


4. Grignard Reagent Synthesis

See Reactions of Haloalkanes.

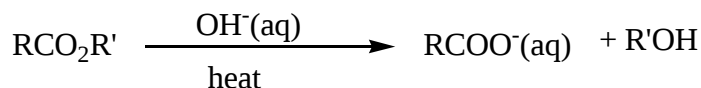
5. Reduction Of Carboxylic acids

Carboxylic acids are reduced to Primary Alcohols using LiAlH_4 in dry ether.



6. From Esters

Esters are hydrolysed by aqueous sodium hydroxide solution to generate an alcohol. However this is not usually done since esters are obtained from alcohols.



7. Cannizzaro Reaction

Aromatic Aldehydes without α -hydrogen atoms undergo self-reduction and oxidation in sodium hydroxide solution.

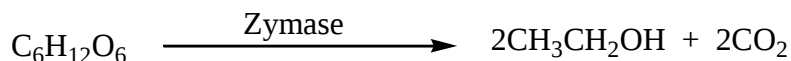
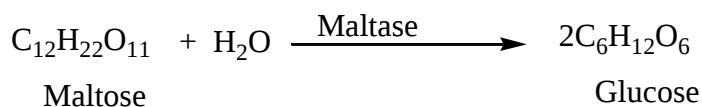
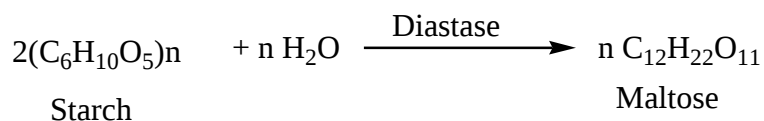


DOMESTIC PRODUCTION OF ETHANOL

Ethanol is mainly prepared by fermentation process. Fermentation is a process where starch or sugar is converted to ethanol by yeast enzymes.

The main sources of the starch materials include maize, millet, cassava, sorghum, potatoes, banana, rice, molasses, etc.

The enzymes that participate in the fermentation process and their stages include:



Qn:

- Describe the processes involved in the production of ethanol from a named material domestically
- State briefly how the purification of the ethanol produced can be done
- State four uses of ethanol
- State two effects of over consumption of ethanol on the human body.

Physical Properties of Alcohols

a) Solubility

Lower members of the series are soluble however, solubility decreases as the hydrocarbon portion increases. The miscibility of alcohols is due to ability of the formation of hydrogen bond with water molecule.

b) Boiling Points

Alcohols boil at higher temperatures expected because the molecules associate through hydrogen bonding which requires an extra energy to break.

Within the series, boiling points increase with molecular mass.

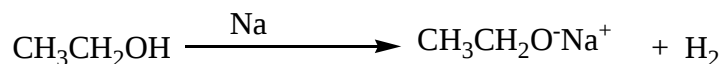
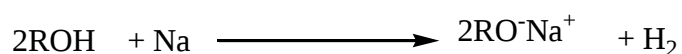
c) Density

Density increases with increasing molecular mass although branching reduces the factor. Aliphatic alcohols are less dense than water while Aromatic alcohols tend to be slightly denser than water.

REACTIONS OF ALCOHOLS

1. With Electropositive Metals

Although Alcohols are neutral to neutralization indicators, the hydroxyl group can be replaced by metals of Group I and II of the periodic table. The products are hydrogen gas and metal Alkoxide.

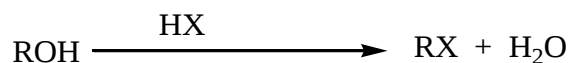


2. Halogenation

This can be done by:

a) Using Hydrogen Halide

They react with hydrogen halides to form alkyl halides. The order of reactivity for alcohols is $3^\circ > 2^\circ > 1^\circ$ while for hydrogen halides is $\text{HI} > \text{HBr} > \text{HCl}$.



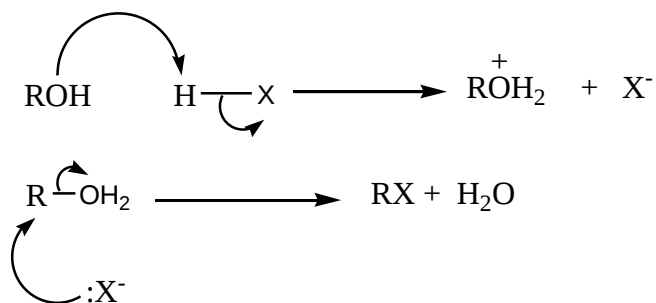
1° Alcohols undergo bromination with hydrogen bromide which is generated from sodium bromide and concentrated sulphuric acid.

In case of hydrogen chloride, the reaction is carried by using anhydrous Zinc chloride and concentrated hydrochloric acid. (Luca's Reagent)

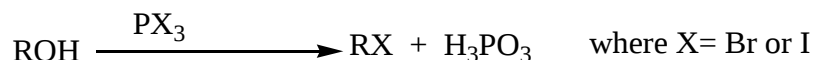
The reagent is used to distinguish the classes of monools i.e.

- 3° Alcohol forms a cloudy solution immediately
- 2° Alcohols forms cloudiness between 5-10 minutes
- 1° Alcohol no observable change.

Mechanism

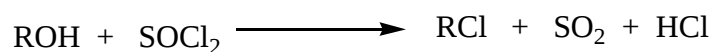
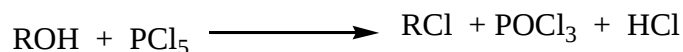


b) Using Phosphorous Halides



c) Using Thionyl chloride

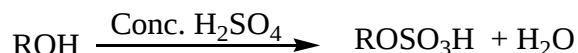
Thionyl Chloride and Phosphorous pentachloride generate alkyl chloride.

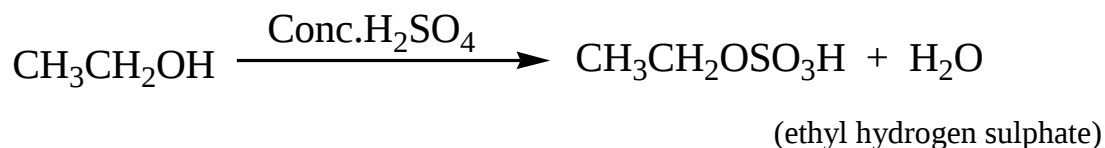


3. Concentrated Sulphuric acid

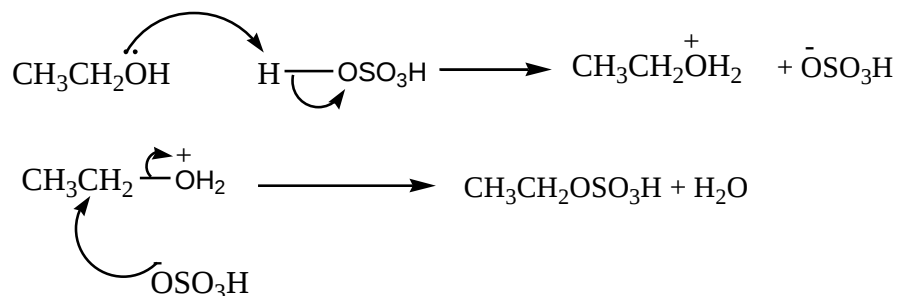
The products of the reaction depend on the conditions of the reaction under which it is carried out.

- a) At lower temperatures (below 140°C), alkyl hydrogen sulphate is obtained

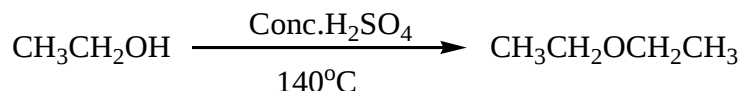
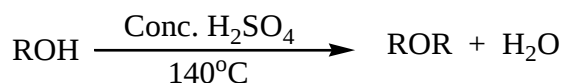




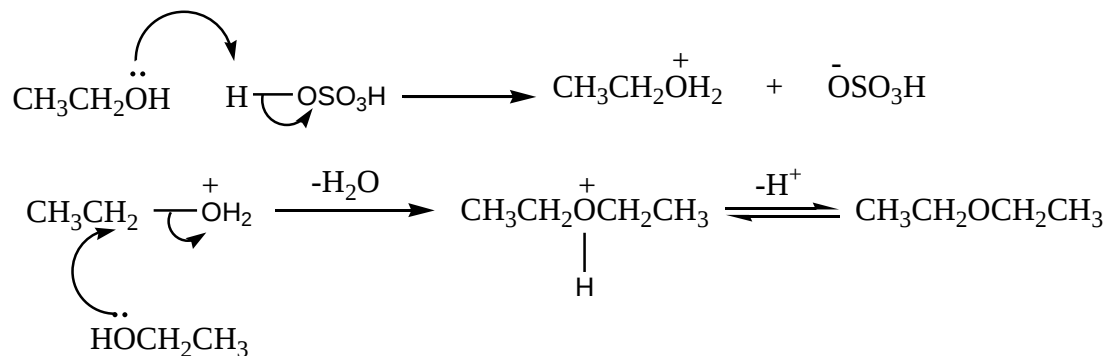
Mechanism



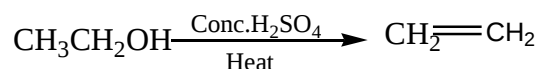
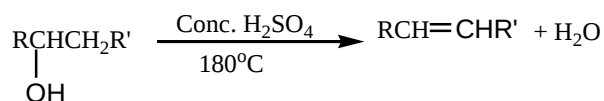
b) At about 140°C when excess alcohol, ether is obtained.



Mechanism



c) When the reaction is carried out at about 180°C, an alkene is obtained. Aluminium Oxide at 350°C or concentrated orthophosphoric acid can be used.



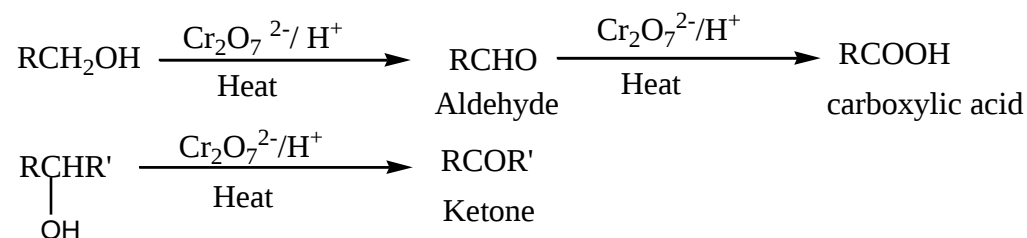
4. Oxidation reaction

The product oxidation depends on the type of alcohol and partly the power of oxidizing agent.

Primary Alcohols are oxidized to Aldehydes and the reaction proceeds to carboxylic acid while Secondary Alcohols are oxidized to Ketones.

Tertiary Alcohols are resistant to oxidation.

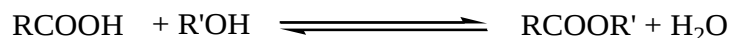
The oxidizing agents commonly used are acidified potassium dichromate or acidified chromium (VI) oxide



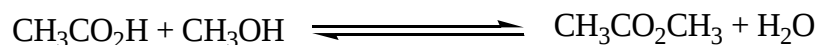
5. Esterification reaction

The process whereby a primary alcohol reacts with a monocarboxylic acid is known as esterification.

The reaction usually takes place in presence of concentrated sulphuric acid and it is reversible reaction.

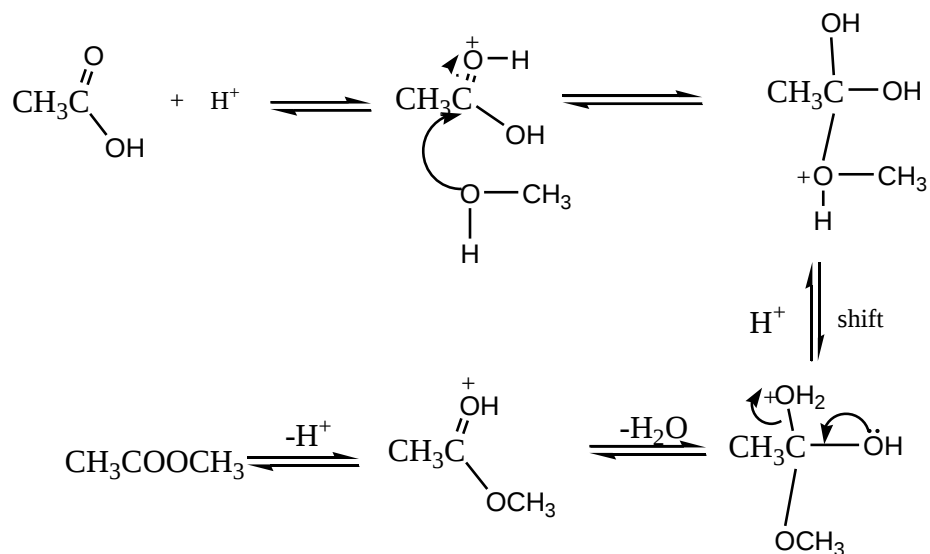


Example:



Mechanism:

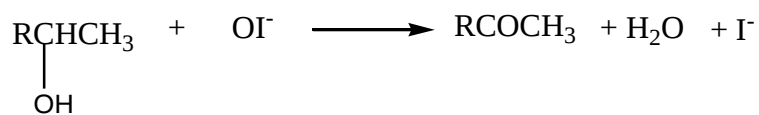
This was determined using radioactive Oxygen (18). The primary alcohol containing oxygen-18 is reacted with monocarboxylic acid. The mass spectrometer is used to analyse the ester and water formed. The oxygen-18 is found in the ester only and not water indicating that carbon-oxygen single bond in the acid and oxygen-hydrogen bond in the alcohol are bonded.



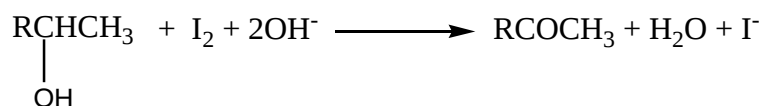
6. Iodoform reaction

Alcohols of the form $\begin{array}{c} \text{H} \\ | \\ \text{CH}_3\text{C}-\text{R} \\ | \\ \text{OH} \end{array}$ react with iodine in presence of sodium hydroxide solution to form a yellow solid.

Iodine is an oxidizing agent and can oxidize alcohols to Aldehydes or Ketones.



OR



Ethanol is the only primary alcohol which gives a positive.

N.B. Chlorine forms chloroform which is colourless liquid, Bromine forms bromoform which is reddish-brown.

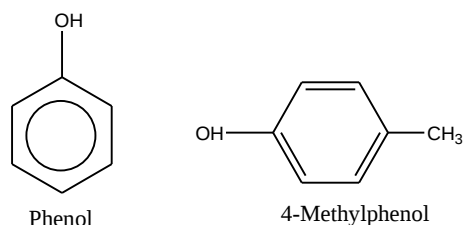
PHENOL

Introduction

These are compounds containing a hydroxyl group attached directly to aromatic nucleus (Benzene) and have a general formula $ArOH$.

Like alcohols they may be monools or polyols depending on the number of the hydroxyl groups they contain.

Examples include:



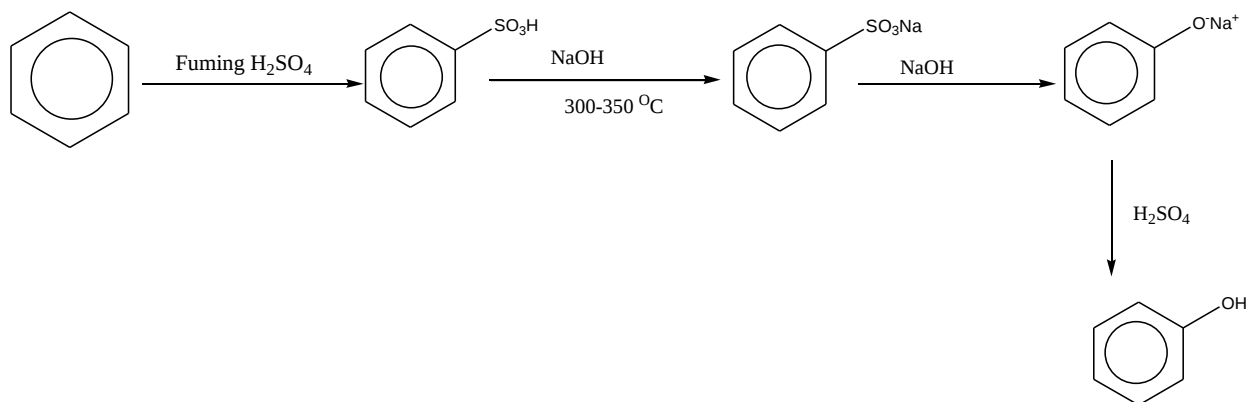
Physical Properties

Phenol is colourless crystalline solid although often found red tint due to presence of oxidation products. It is slightly soluble but very soluble in organic solvents.

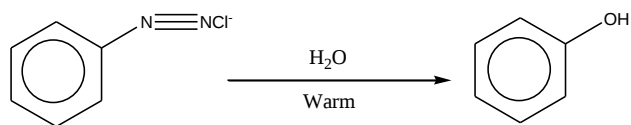
N.B. The introduction of the hydroxyl group into an already substituted aromatic ring especially in position-4 produces a marked increase in the boiling point. E.g. the greater volatility of 2-nitrophenol is attributed to intramolecular hydrogen bonding while the higher boiling points of 3- and 4- isomers are direct result of intermolecular hydrogen bonding.

Preparation of Phenol

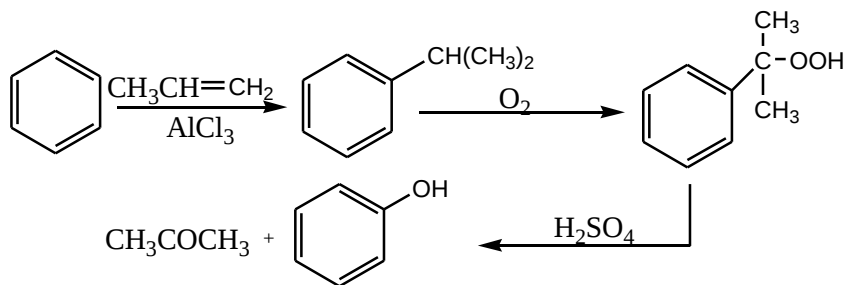
a) From Benzene sulphonic acid



b) From Benzene Diazonium salt.



c) Cumene process



Reactions of Phenol

Phenol undergoes two distinct reactions i.e.

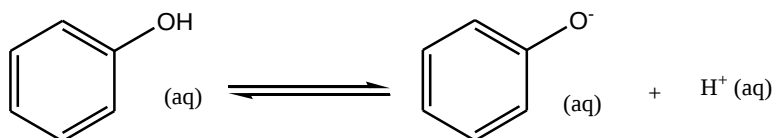
- Side-chain substitution reactions which generally involves replacement of the acidic proton
- Electrophilic substitution in the ring.

Phenol as an acid

Phenol is a stronger acid than alcohols but weaker acid compared to carboxylic acid.

Qn: Explain briefly why phenol is more acidic compared to Ethanol

Soln: In phenol, the lone pair of electrons on the oxygen atom interacts with delocalized electrons of the benzene ring. This strengthens the carbon-hydrogen bond while weakening the oxygen-hydrogen bond consequently; phenol loses a proton easily making it acidic.



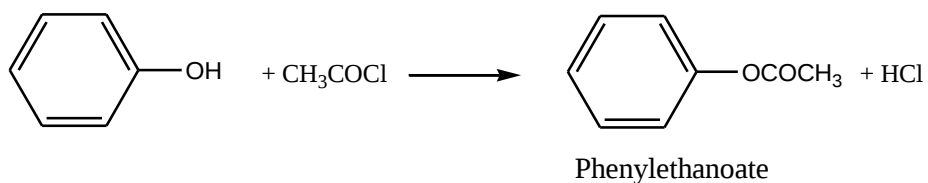
In ethanol, the oxygen-hydrogen bond is not weakened and the proton is not easily lost. This is because there are no delocalized electrons to interact with lone pairs of electrons on the oxygen atom.

Note: Due to the above reason, phenol differs from alcohols in that it does not react with halogen acids or Phosphorus halides and does not undergo elimination reaction

a) Side-chain reactions include:

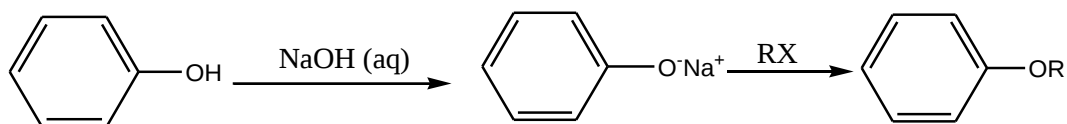
1) Esterification reaction

Phenol reacts with acid chlorides and acid anhydrides to form esters



2) Ether Formation

Sodium phenate (Sodium phenoxide) reacts with alkyl halides to form ethers



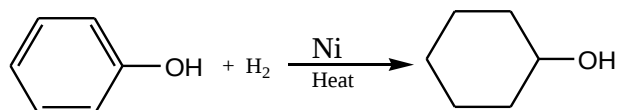
3) With Neutral Iron (III)chloride solution

Phenol reacts with neutral Iron (III) chloride solution to form a violet colouration due to a complex formed.

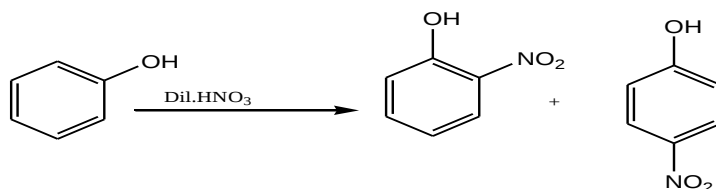
b) Electrophilic Substitution of the ring

Phenol is more reactive towards Electrophilic reagent than Benzene since it activates position 2- and 4- therefore the products formed at those positions.

1) Reduction reaction



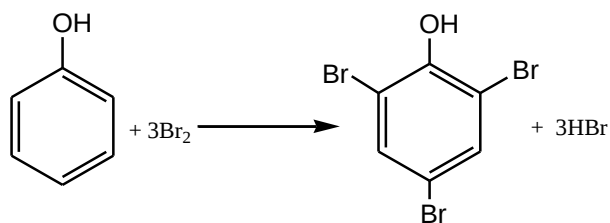
2) Nitration reaction



3) Bromination

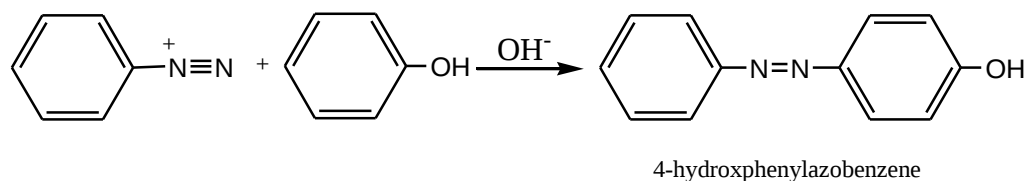
In aqueous solution, phenol reacts with bromine to form a white precipitate of 2, 4, 6-tribromophenol.

This reaction is used also to test for presence of phenol and estimate phenol quantitatively.



4) Coupling with Benzene Diazonium salts

Benzene Diazonium salt solution is added to alkaline solution of phenol to generate bright yellow precipitate of 4-hydroxyphenylazobenzene.



Question

1. Explain the following observation:
 - a) Ethanol is more acidic than 2-methylpropan-2-ol but less acidic than phenol
 - b) Phenol is easily nitrated using nitric acid whereas Benzene is nitrated using a mixture of concentrated nitric acid and sulphuric acid
 - c) Butan-1-ol is more soluble in 5M hydrochloric acid than in water
 - d) The boiling point of ethanol (78°C) is greater than Ethoxyethane (35°C)
2. Write the half and overall equation of reaction for:
 - a) Ethanol and acidified potassium dichromate solution
 - b) Ethene and acidified potassium manganate (VII) solution.

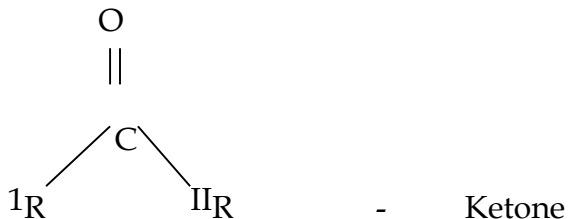
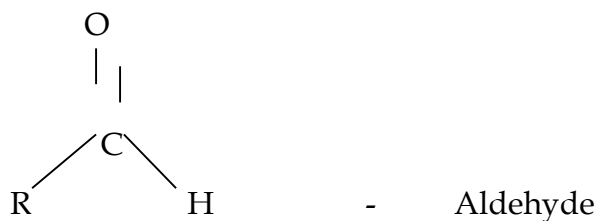
CARBONYL COMPOUNDS

Introduction

These are compounds containing a carbonyl functional group. They are alkanals (Aldehydes) and alkanones (Ketones).

The saturated aliphatic series are homologous and correspond to a general molecular formula $C_nH_{2n}O$.

Aldehydes possess single hydrogen attached to the carbonyl carbon whereas Ketones always contain two hydrocarbon groups



Aldehydes are more reactive therefore easily oxidized and also more susceptible to Nucleophilic addition.

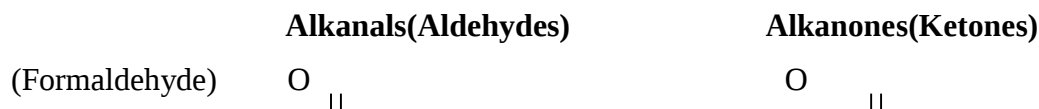
Nomenclature of Aldehydes and Ketones

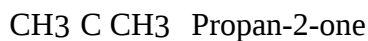
For Aldehydes, the IUPAC names are obtained by dropping the ending “-e” of the corresponding alkane and replacing it with suffix “-al” for Aldehydes name.

The IUPAC names for Ketones is also obtained by dropping the ending “-e” of alkanes and replacing it with suffix “-one”

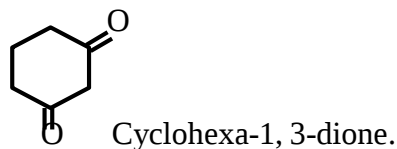
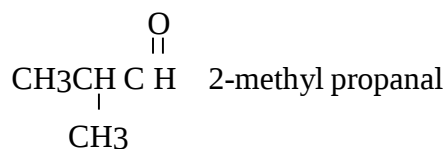
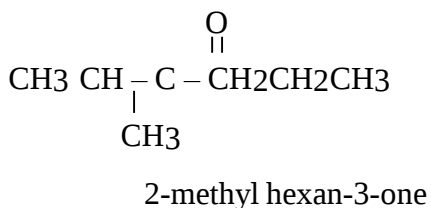
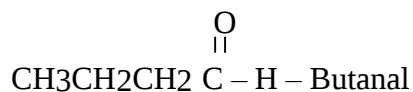
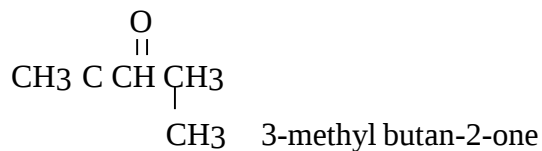
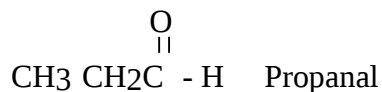
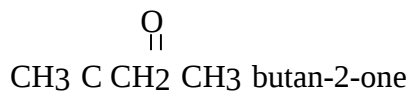
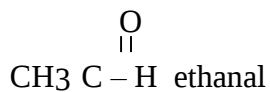
The position for carbonyl group is indicated by inserting an appropriate number between stem name and -one.

Example



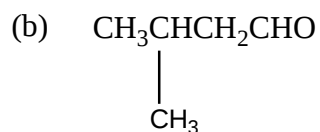
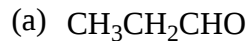


(Acetaldehyde)



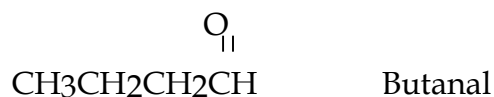
Question

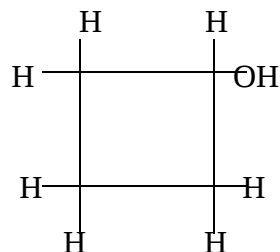
Name the following organic compounds:



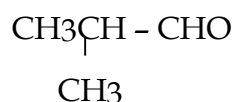
ISOMERISM IN CARBONYL COMPOUNDS

Carbonyl compounds exhibit chain and position isomerism.

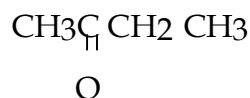




Cyclic butanol (cyclic alcohol)



2-methyl propanal (Aldehyde)



Butan-2-one (Ketone)

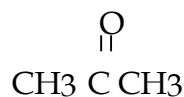


But-en-4-ol (Unsaturated alcohol)

Example: Write all the isomers of the compounds with the molecular formula $\text{C}_3\text{H}_6\text{O}$.



Propanal (Aldehyde)



Propanone (Ketone)



Prop-1-en-3-ol.

Qn. Write the IUPAC names and structural formulae of all isomers to $\text{C}_5\text{H}_{10}\text{O}$.

PHYSICAL PROPERTIES OF CARBONYL COMPOUNDS

Simple aliphatic Aldehydes and Ketones with exception of methanal are all colourless liquids. The lower Aldehydes possess rather unpleasant smell whereas Ketones and Benzenecarbaldehyde have pleasant, sweet odours.

Methanal is a gas at room temperature and rest are liquids. Carbonyl group is polar therefore Aldehydes and Ketones have a higher boiling points but lower than those of alcohols since they do not form strong hydrogen bonds with each other.

Lower Aldehydes and Ketones are appreciably soluble in water due to their ability to form hydrogen bonds with water molecules and the resultant solution is neutral to litmus.

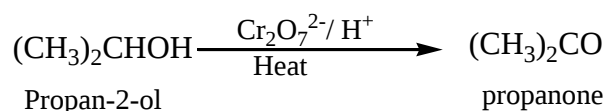
The density of the aliphatic compounds of both series is less than that of water but it increases with increase in molecular mass.

SYNTHETIC PREPARATIONS

1. Oxidation of Alcohols

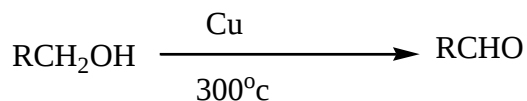
1° Alcohols are oxidized to Aldehydes while 2° Alcohols are oxidized to Ketones using acidified potassium dichromate or acidified chromium (VI) oxide.

During oxidation process, a colourless solution turns to green solution.



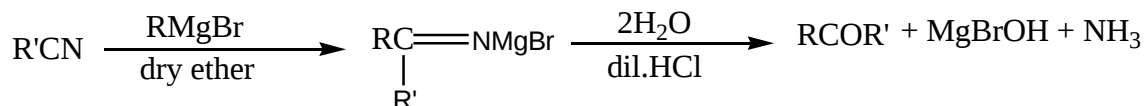
During the oxidation process, especially for primary alcohols, there will be further oxidation to carboxylic acid which renders this method ineffective but this further oxidation can be avoided by carrying out a reaction under low heat (temperatures) or limiting the amount of the oxidant used.

Oxidization can also be accomplished by dehydrogenation of the alcohol using copper catalyst heated at about 300°C



2. From Grignard reagent.

When Grignard reagent reacts with cyanide compounds and on hydrolysis Ketones are obtained.

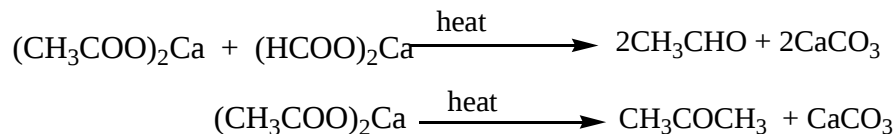


3. Decarboxylation method of Calcium salts

When a carboxylic acid salt of calcium is heated, an aldehyde is formed. More especially methanol is formed.



With other higher aldehydes, Ca salt of a carboxylic acid is heated with calcium methanoate.

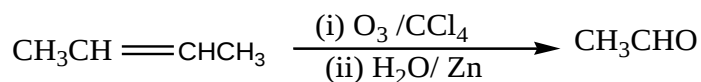
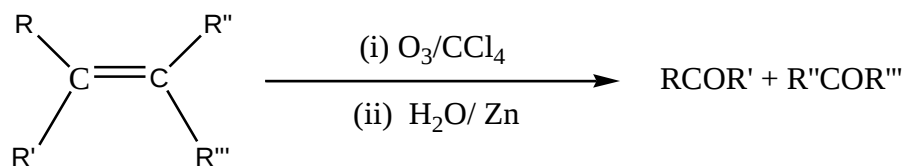


Question: Synthesise $\text{CH}_3\text{CH}_2\text{OH}$ $\xrightarrow{\quad\quad\quad}$ CH_3COCH_3

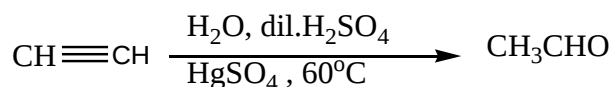
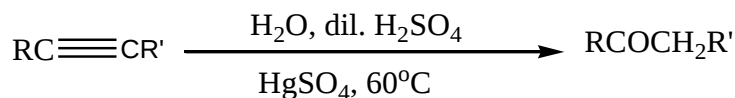
4. Ozonolysis of Alkenes

When an alkene is reacted with ozone, an ozonide is formed. When the ozonide is diluted in H_2O in presence of some zinc, a carbonyl compound is formed. Zinc dust is used to decompose H_2O_2 .

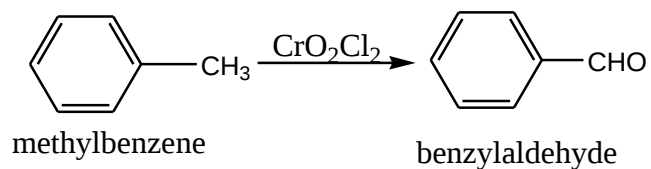
Note: Aldehydes formed depends on the types of alkene used. Symmetrical alkene gives one type of aldehyde while unsymmetrical will give you both carbonyls.



5. Hydration of Alkynes



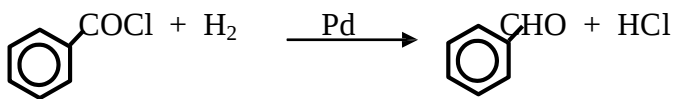
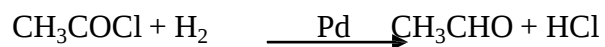
6. From methyl benzene



QN: Show how methyl benzene can be converted to Benzoic acid using equation (s) of reactions.

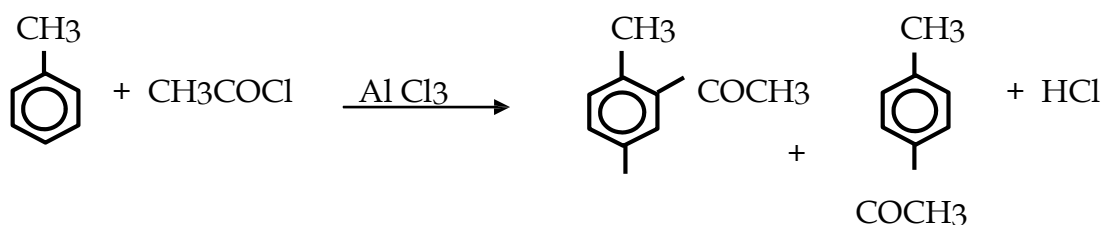
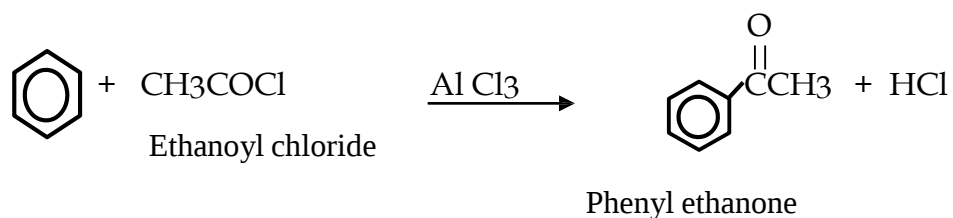
7. Hydrogenation of acid chlorides

Acid chlorides are reduced by hydrogen in presence of catalysts like Pd to form aldehydes.

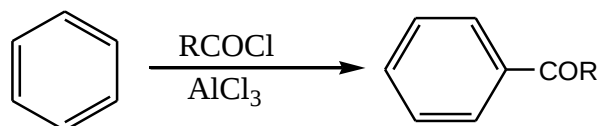


8. Acylation method

Alkyl acylation is a reaction between acid halides with a benzene ring compound. This reaction produces aromatic ketones when it is carried out in presence of a halogen carrier (AlCl_3 , FeCl_3)



Generally



Question:

- Write the mechanism of the reaction above
- Using equations show how 1-phenyl ethanol can be prepared from benzene.
- Write equations showing how Benzene can be obtained from 1-phenylethanol.

CHEMICAL PROPERTIES OF CARBONYL COMPOUNDS

Carbonyl compounds chemically react because of the property of the carbonyl carbon which is a common functional group present in both aldehydes and ketones.

A carbonyl carbon contains more electronegative oxygen bonded to carbon which pulls electrons towards itself and attains a negative charge while the carbon remains positive. Therefore, the carbon oxygen bond is polarised creating a good condition for Nucleophilic reagents to be added across the carbonyl carbon. The intermediate formed with a negative on oxygen reacts with an electrophile to form the final end product.

Carbonyl group in aldehyde is more reactive than in ketones.

Explanation:

In ketones, the presence of two alkyl groups having a positive inductive effect highly neutralizes the positive charge in the carbon resulting into a less attraction of a nucleophile.

Methanol is more reactive than other aldehydes. Explain.

In methanol only hydrogen is bonded to the carbonyl carbon that the partial positive charge formed is not neutralized making methanol more reactive.

Therefore, the more number of alkyl groups added to a carbonyl carbon, the less the reaction due to the following reasons:

- (i) The alkyl groups have got electron pushing (positive inductive) effect which neutralizes the partial positive charge on the carbon.
- (ii) Several alkyl groups will have a crowding effect preventing a nucleophile from being attached to the carbon.

When other atoms of a more electronegative effect are added next to the carbonyl group, the reactivity of the carbonyl carbon compound increases. E.g. if a hydrogen on the carbon atom next to the carbonyl group is replaced with a halogen, the reactivity increases.

Note: Aldehydes are more reactive than ketones. Why?

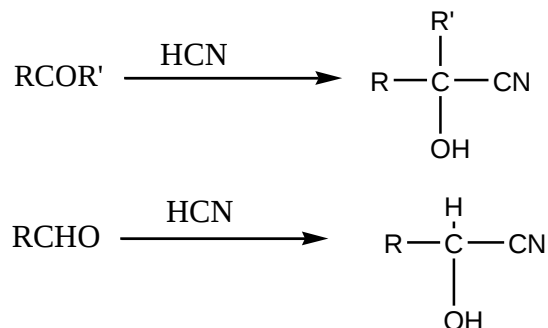
Both aldehydes and ketones have the same carbonyl group that is polarized since oxygen is more electronegative than carbon. I.e oxygen atom has a partial negative charge and the carbon atom has a partial positive charge. In a Nucleophilic addition reaction, nucleophiles attack the electron deficient carbon atom.

In aldehydes is one alkyl group bonded to the carbonyl carbon while in ketones are two alkyl groups bonded to the carbonyl carbon. These alkyl groups have a positive inductive effect thus reduce the positive charge on the carbonyl carbon. Thus any attacking nucleophile is less attracted in ketones than in aldehydes.

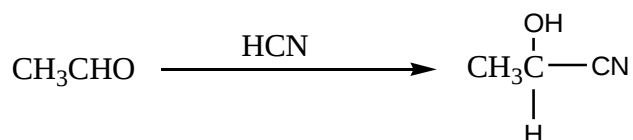
REACTIONS OF CARBONYL COMPOUNDS

Some of the Nucleophilic addition reactions include;

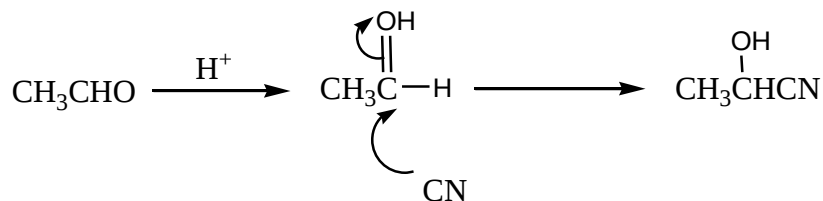
1) Addition of Hydrogen cyanide:



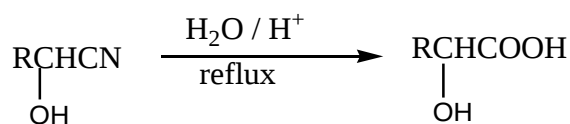
Hydrogen cyanide is usually prepared during a reaction of dilute sulphuric acid on alkali metal cyanide.



Mechanism



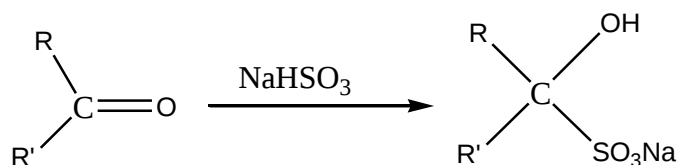
Cyanohydrins are used to synthesize 2-or α -hydroxy acids on hydrolysis.



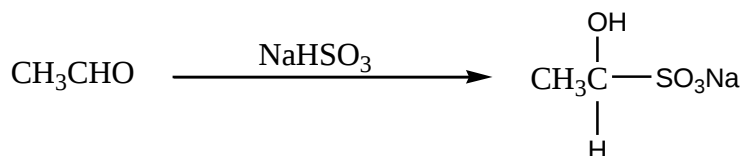
Qn: Using equations indicating the necessary conditions show Ethene can be converted to 2-hydroxypropanoic acid.

2) Addition of saturated sodium hydrogen sulphite solution

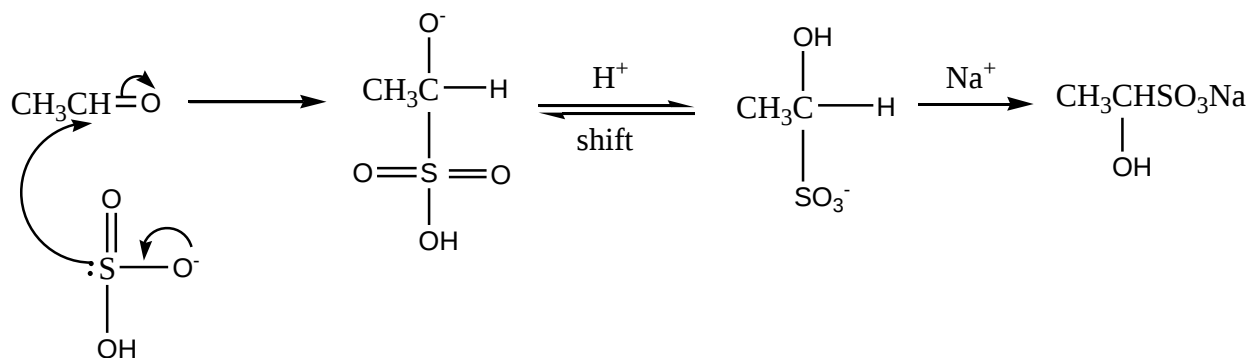
The reaction occurs readily with most Aldehydes and some Ketones especially methyl Ketones to form white solids of Aldehydes or Ketones hydrogen sulphite.



Aldehyde or Ketone hydrogen sulphite



Mechanism



Qn: Write equation showing show Propanone can be converted to Propanone hydrogen sulphite and indicate the mechanism of the reaction.

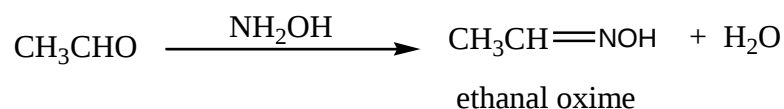
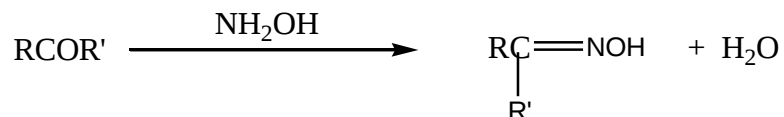
3. Condensation reaction or Elimination of water molecules.

In this reaction, carbonyl compounds react with derivatives of ammonia of general form X-NH₂ to release water molecules.

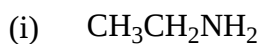
The final products are usually solids which are easily isolated and purified by recrystallisation.
Some of the addition reagents include:

a) With Hydroxylamine, NH_2OH

The product formed is white solid is Aldehydes or Ketone oxime.

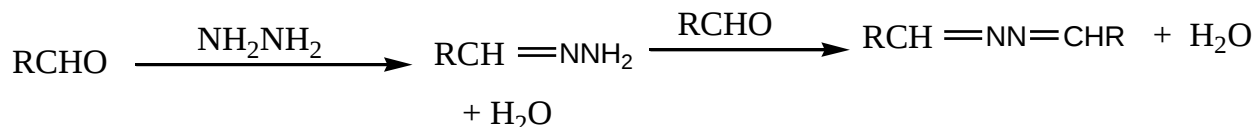


Qn: Write the mechanism of the reaction above and show how the product formed can be converted to:

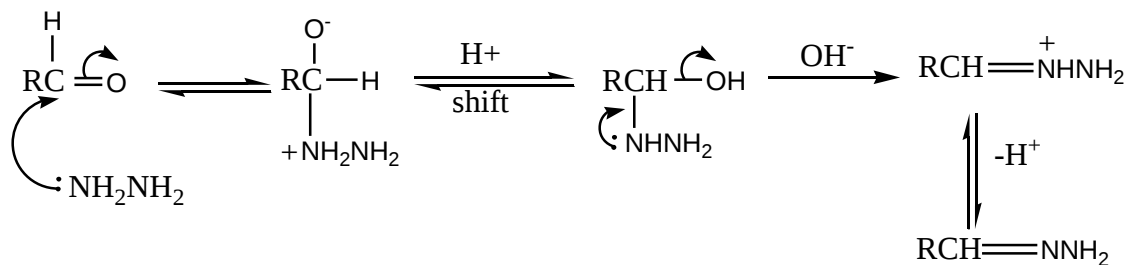


b) With hydrazine, NH_2NH_2

The product is Aldehydes or Ketones hydrazone which in excess yield azine.



Mechanism

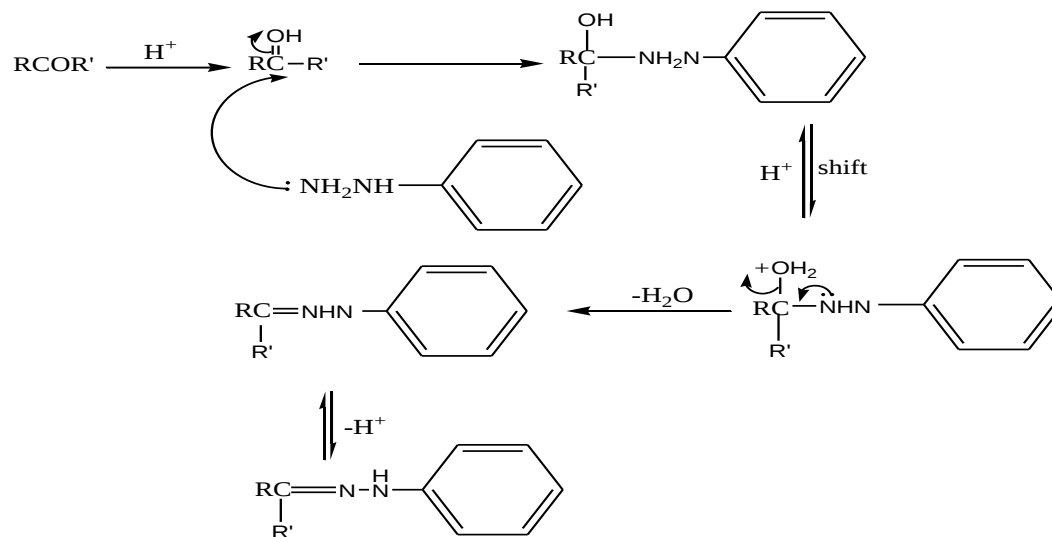


N.B. In presence of an acid, protonation is the first stage



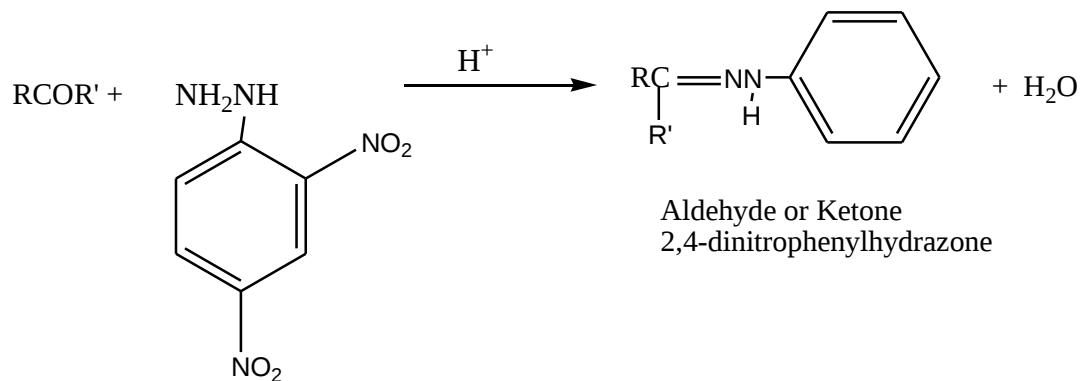
c) With Phenyl hydrazine $\text{C}_6\text{H}_5\text{NHNH}_2$

Carbonyl compounds generate phenyl hydrazone derivatives which are low melting point solids. The reaction occurs with or without an acid.



d) With 2,4-dinitrophenylhydrazine

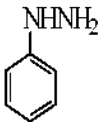
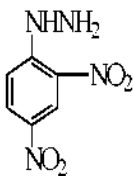
2,4-dinitrophenylhydrazine is utilized in Brady's reagent for detection of a carbonyl functional group. Yellow or orange solid crystallizes out in the form of 2,4-dinitrophenylhydrazone.



e) With semicarbazide, NH₂NHCONH₂

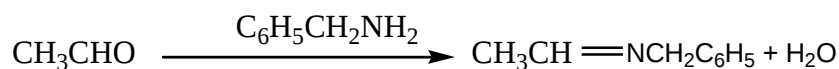
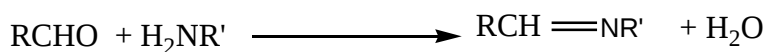


Summary

Reagent		Product
Hydroxylamine NH_2OH	$\text{R}-\text{C}(=\text{O})-\text{R}', \text{H}^-$	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{NHOH} \\ \diagup \\ \text{R}' \end{array}$ Oxime
Hydrazine NH_2NH_2		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{NHNH}_2 \\ \diagup \\ \text{R}' \end{array}$ Hydrazone
Semi carbazine $\text{NH}_2\text{NHCONH}_2$		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{NHNHCONH}_2 \\ \diagup \\ \text{R}' \end{array}$ Semi carbazone
Phenylhydrazine 		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{NN}-\text{C}_6\text{H}_5 \\ \diagup \\ \text{R}' \\ \\ \text{H} \end{array}$ Phenylhydrazone
2,4-dinitrophenylhydrazine 		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{NN}-\text{C}_6\text{H}_3(\text{NO}_2)_2 \\ \diagup \\ \text{R}' \\ \\ \text{H} \end{array}$ 2,4-dinitrophenylhydrazone

4. Reaction with Primary amines.

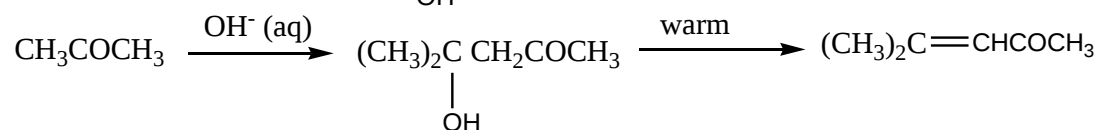
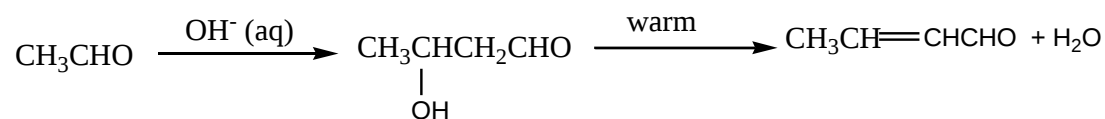
Aldehydes react with primary amines to form imines.



5. Aldol condensation

Aldehydes react with alkali to generate Aldol product which dimerises on warming to enal.

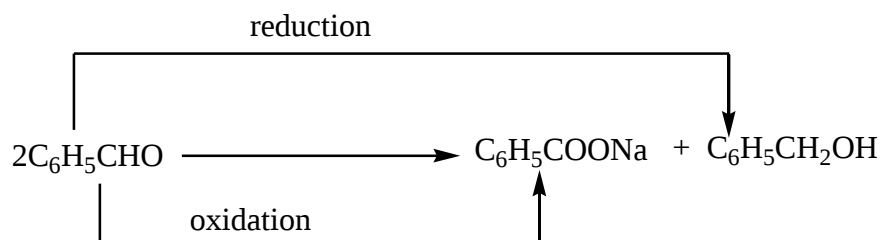
The reaction is undergone by carbonyl compounds with at least one- α -hydrogen atom.



6. Cannizzaro reaction

Aldehydes without at least one- α -hydrogen atom react with sodium hydroxide solution to undergo self oxidation and reduction reaction.

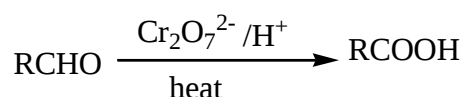
This reaction is limited to aromatic and aliphatic compounds in which the carbonyl carbon is attached to tertiary alkyl carbon atom.



7. Oxidation reaction

Aldehydes are oxidized to carboxylic acids by oxidising agents such as acidified potassium dichromate solution, acidified chromium (VI) oxide solution or dilute nitric acid.

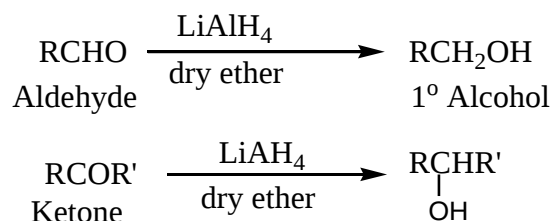
Ketones are resistant to oxidation by common oxidising agents.



8. Reduction reaction

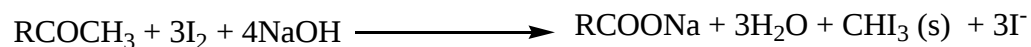
Aldehydes are reduced to Primary alcohol while Ketones are reduced to Secondary Alcohol.

Reducing agents commonly used are LiAlH_4 / dry ether, Hydrogen /Nickel at 150°C , Amalgamated Zinc and concentrated hydrochloric acid, NaBH_4 / Water.



9. Halo form reaction

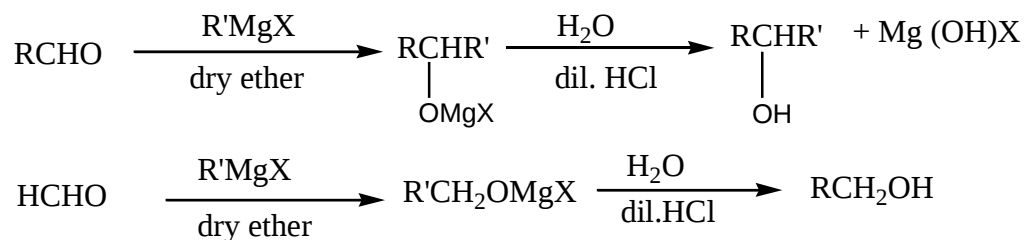
Ethanal and Methyl Ketones react with iodine in presence of sodium hydroxide solution to form a yellow solid.



This reagent is used to differentiate between the structure of Aldehydes and methyl Ketones.

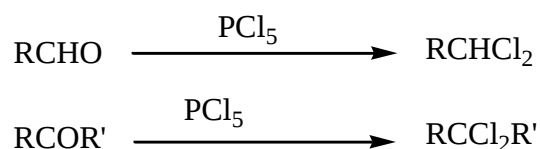
10. Addition of Grignard reagent

Aldehydes generate Secondary Alcohol except ethanal while Ketones generate tertiary alcohol.



11. With Phosphorous penta chloride

Carbonyl compounds generate dichloride.



Confirmatory test for carbonyl compounds.

Reagent. 2,4-dinitrophenylhydrazine solution.

Observations. Yellow precipitate with aliphatic carbonyl compounds

Brown precipitate with aromatic carbonyl compounds

Distinguishing between Aldehydes and Ketones

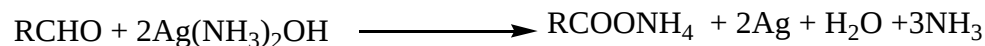
Aldehydes can be differentiated from Ketones by various reagents that are oxidizing agent's i.e.

- a) **Ammoniacal Silver nitrate solution.** (*Tollen's reagent*). (*Silver mirror test for aldehydes only*)

The reagent consists of silver nitrate in presence of excess ammonia solution.

Aldehydes react with ammoniacal silver nitrate form a silver mirror alongside a clean test tube on warming whereas no observable change for Ketones.

Ethanal reacts almost immediately.



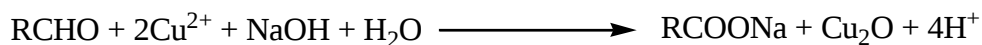
Observations.

A silver mirror with aldehydes.

No observable change with ketones.

- b) **Fehling's or Benedict's solution.** (*For aliphatic aldehydes only*)

Aliphatic Aldehydes reduce copper (II) ions to reddish-brown copper (I) oxide on heating.



Ketones and aromatic Aldehydes give no observable change.

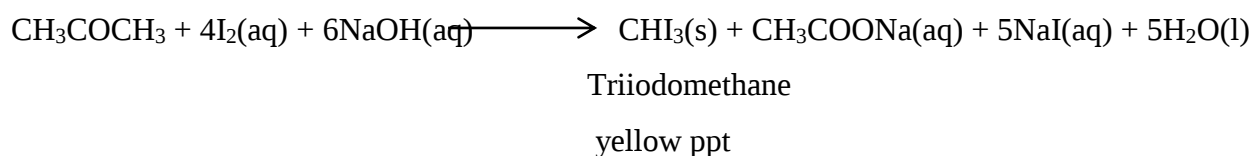
Observations.

Red precipitate with aliphatic aldehydes.

No observable change with ketones and aromatic aldehydes.

c) Iodine solution followed by sodium hydroxide solution. (Iodoform reagent)

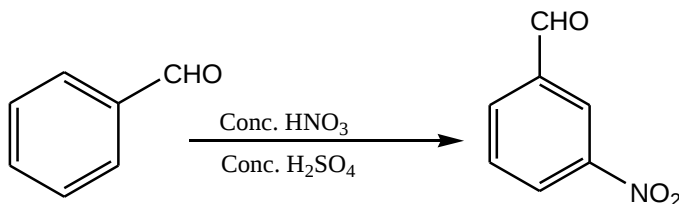
It tests for aldehydes, ketones and alcohols of the form $\text{CH}_3\text{-CO-}$, and $\text{CH}_3\text{-CH(OH)-}$ called methyl alcohols, methyl aldehydes or methyl ketones. All produce a yellow precipitate of triiodomethane.



Non-methyl alcohols, aldehydes or ketones give no observable change.

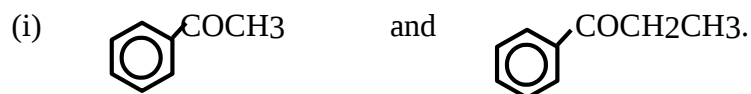
Reactions of Aromatic Aldehydes and Ketones involving substitution in Ring

Carbonyl group is deactivating group therefore the reaction involving the benzene ring generate meta-derivative product.



Question

Name the reagent that can be used to distinguish between the following pairs of compounds and in each case, state what would be observed when the reagent is separately treated with each compound.



Reagent: Hot iodine solution in aqueous sodium hydroxide.

With COCH₃ : A yellow precipitate.

With COCH₂CH₃ : No observable change.

(ii) CH₃COCH₃ and HCHO

(iii) CHO and COCH₂CH₃

(iv) CH₃CH₂COCH₃ and HCHO

CARBOXYLIC ACIDS

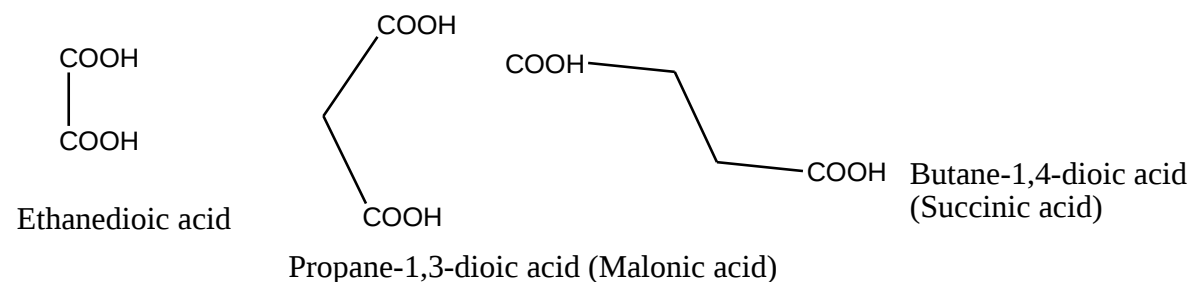
Introduction

Aliphatic monocarboxylic acids form a homologous series corresponding to the general molecular formula, $C_nH_{2n+1}COOH$.

Carboxylic acids are organic compounds contain the carboxyl group that is made of carbonyl group and hydroxyl group.

The number of the carboxyl group present in acid classifies acids as: Monocarboxylic acids which are monobasic have one carboxyl while dicarboxylic acid are dibasic.

The simplest dicarboxylic acid are:



Nomenclature

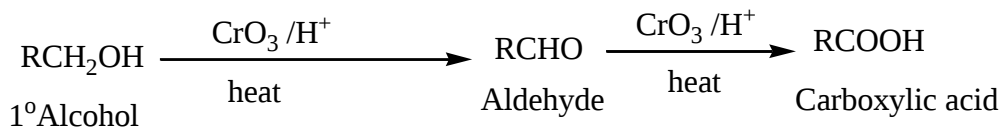
The IUPAC names are afforded by taking the name of the appropriate alkane and replacing the ending “-e” with the suffix “oic acid”. Positions of the substitution are denoted in the usual way by numbering the longest unbranched chain containing the carboxyl group.

Structure	Name
HCOOH	methanoic acid
CH ₃ CH ₂ COOH	Propanoic acid
CH ₃ (CH ₂) ₂ COOH	Butanoic acid
(CH ₃) ₂ CHCOOH	2-methylpropanoic acid
CH ₃ (CH ₂) ₁₄ COOH	Hexadecanoic acid
C ₆ H ₅ CH ₂ COOH	2-phenylethanoic acid
HOOC-COOH	ethanedioic acid
HOOCCH ₂ COOH	Propane-1,3-dioic acid

Synthetic Preparations

1) Oxidation of Primary Alcohol or Aldehydes

Primary Alcohols or Aldehydes are oxidized by acidified potassium dichromate solution or acidified chromium (VI) oxide to carboxylic acid.



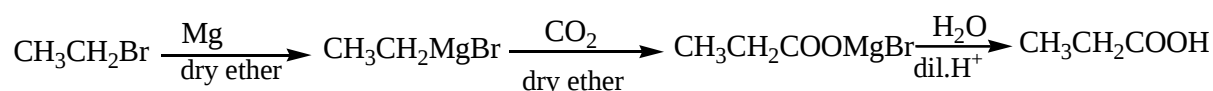
Orange solution turns green due to reduction of chromium (VI) ions to chromium (III) ions.

2) Grignard synthesis



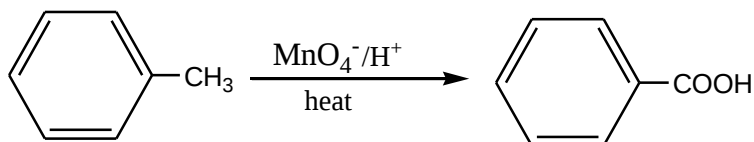
R may be 1°, 2°, 3° or Aromatic

Example

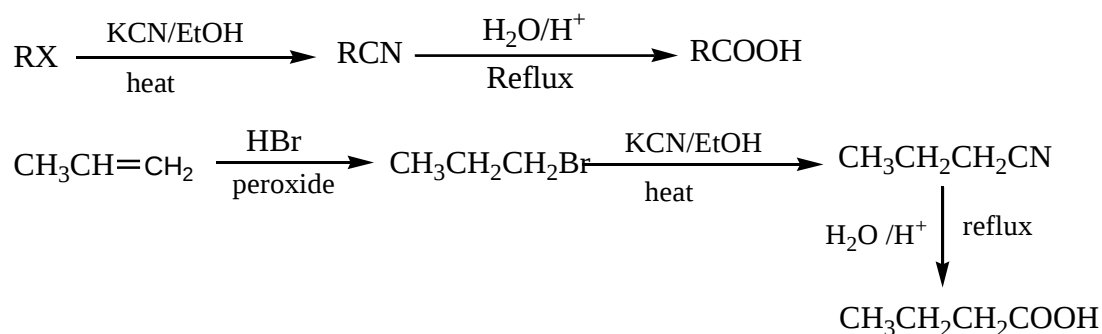


In Preparation of Benzoic acid, solid carbondioxide or dry ice is used.

3) From Methyl Benzene



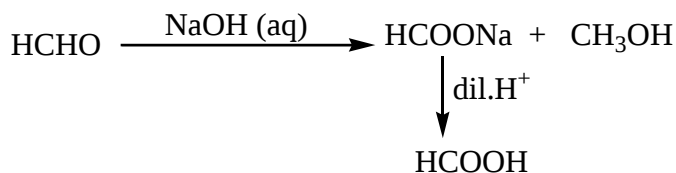
4) From Cyanide compounds.



The reaction is unsuitable for preparation of aromatic carboxylic acid.

5) Cannizzaro reaction

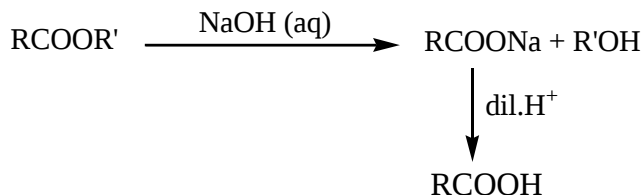
Aromatic Aldehydes and aliphatic ones containing no α -hydrogen atom undergo self oxidation and reduction.



6) Alkali Hydrolysis of Esters

The hydrolysis of Esters generates the corresponding alcohol and Acid.

The method is not commonly used since esters are obtained from carboxylic acid.



Physical Properties of Carboxylic acids

All simple aliphatic acids as far as C₁₀ are liquids at room temperature while aromatic acids are crystalline solids. Ethanoic acid has a sharp, pungent odour.

Boiling points of the acids increase with increase molecular mass. The boiling points are higher than expected because of the ability of the molecule to associate through hydrogen bonding which requires extra energy to break.

The first four aliphatic acids are completely miscible with water due to the ability of the functional group to form hydrogen bonds with water molecules.

Because of their greater hydrocarbon hence covalent character, the higher homologues become progressively less soluble in water.

Benzoic acid is only slightly soluble in cold water but dissolves readily in hot.

N.B. The molecular mass determination of carboxylic acids using Colligative properties such as freezing point in non-polar solvents gives the results that are twice than expected due to dimerisation of the molecule through hydrogen bonding in such solvents.

Acidic nature of carboxylic acids

Carboxylic acids are weak acids which partially dissociate in aqueous solutions. However, they are stronger acids than alcohols and phenols.

The acidic strength of carboxylic acids depend on degree of ionisation and the acid dissociation constant denoted K_a defined as

$$K_a = \frac{[H^+][X^-]}{[HX]} \text{ for a weak monobasic HX acid.}$$

The Nature of the groups close to the carboxyl group has a great effect on the acid strength therefore a phenomenon known as inductive effect.

Electron withdrawing groups' e.g halogens makes carboxylic acid stronger thus oxygen-hydrogen bond becomes weaken hence release of hydrogen ions in aqueous solution. i.e.

Acid	CH ₃ COOH	CH ₂ ClCOOH	CHCl ₂ COOH	CCl ₃ COOH
K _a	1.7x 10 ⁻⁵	1.3x10 ⁻³	5.0x10 ⁻²	2.3x10 ⁻¹
pK _a	4.76	2.86	1.29	0.65

Electron releasing groups' e.g alkyl groups makes carboxylic acid weaker thus oxygen-hydrogen bond strengthen hence less amount of hydrogen ions in aqueous solution.

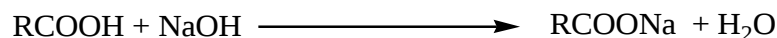
Reactions of carboxylic acids

The reactions of carboxylic acids involve the hydroxyl group which either undergoes the loss of proton or replaced by another atom or group.

Some of the reactions include:

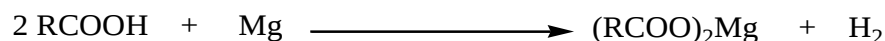
1) With Bases

The react to form salts and water



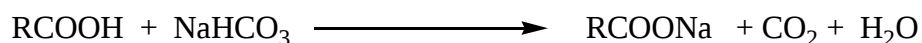
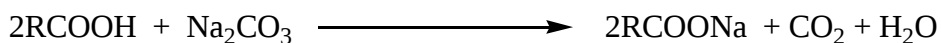
2) With electropositive metals.

The react to form salts and hydrogen



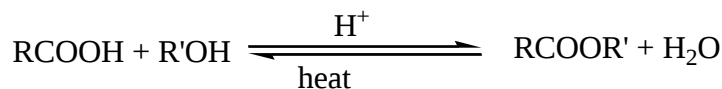
3) With sodium carbonate or Sodium hydrogen carbonate

They react to liberate carbondioxide gas. They are stronger acids than carbonic acid.



4) With Primary Alcohols

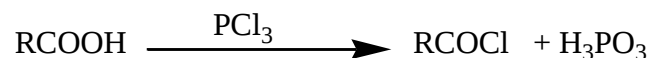
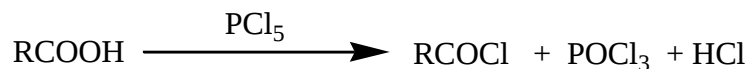
Carboxylic acids react with primary alcohols in presence of concentrated sulphuric acid as catalyst to form esters.



(See Alcohols for mechanism of the reaction)

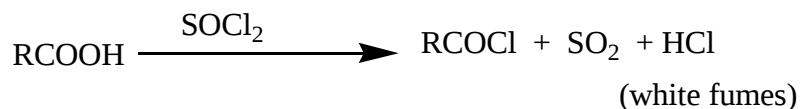
5) With Phosphorous Halides

They react to acid chlorides.



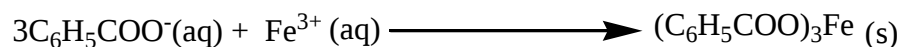
6) With Thionyl chloride

They react also to form acid chlorides. This is the convenient method for preparation of acid chlorides since the other two products are gaseous.



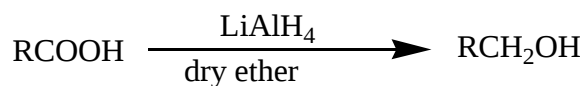
7) With Iron (III) chloride solution

They react forming a reddish-brown precipitate or solution. Lower molecular mass acids form a solution.



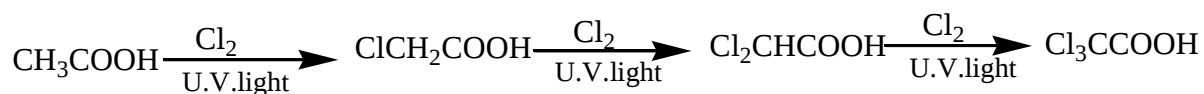
8) Reduction reaction

Carboxylic acids are reduced to primary alcohols using lithium aluminium hydride.



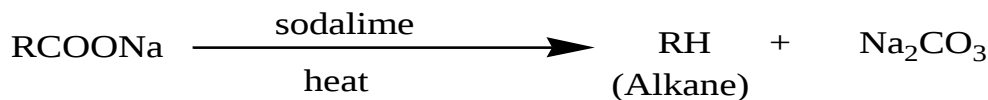
9) Reaction of the Alkyl group

When chlorine gas is bubbled through hot carboxylic acid in presence of ultraviolet light, one or all the hydrogen atoms adjacent are substituted.

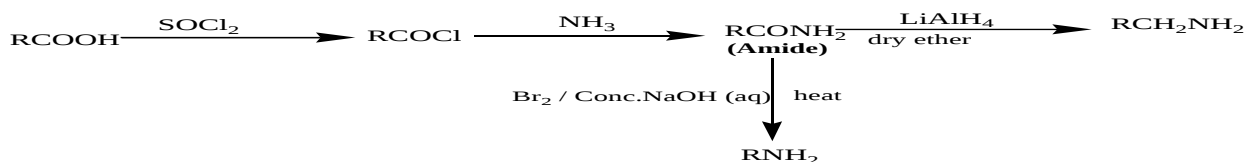


10) Decarboxylation reaction.

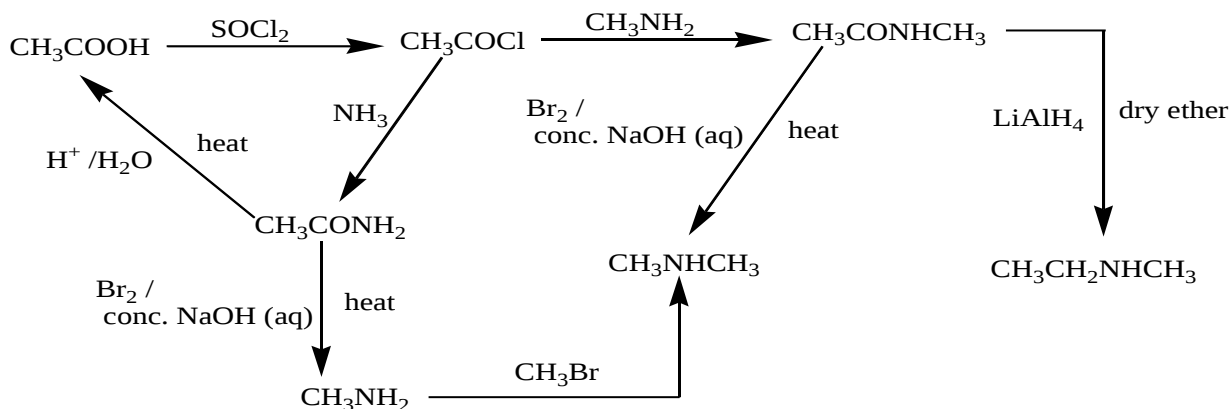
This reaction decreases the carbon length of the sodium salt of carboxylic acid to form an alkane.



11) Amide formation.

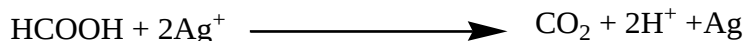


Sample reaction scheme is shown below



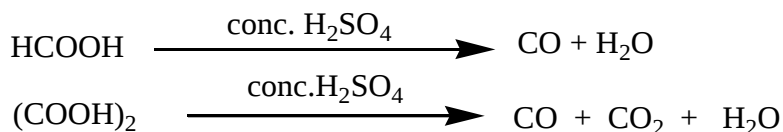
12) With Ammoniacal Silver nitrate solution

Methanoic acid is the only carboxylic acid that reacts with ammoniacal silver nitrate solution on warming due to presence of Aldehydes group to form silver mirror along side a clean test tube.



13) Dehydration reaction

Methanoic acid and Ethanedioic acid are the only carboxylic acid that can be dehydrated using concentrated sulphuric acid.



Question

- How would one carry out the following conversions in the laboratory? Indicate the necessary conditions of the reaction.
 - CH_3CHO to $\text{CH}_3\text{COOCH}_3$
 - $\text{CH}_2=\text{CH}_2$ to $\text{CH}_3\text{CH}_2\text{COOH}$
 - CH_3COOH to $\text{CH}_3\text{CH}_2\text{NHCH}_3$
 - $\text{C}_6\text{H}_5\text{CH}_3$ to $\text{C}_6\text{H}_5\text{COOCH}_3$
- Three isomeric acids **A**, **B** and **C** have molecular formula $\text{C}_8\text{H}_6\text{O}_4$ and all contain a benzene ring. In each case, one mole of the acid will react with 2moles of sodium hydroxide. Suggest structures for the acids. When the three acids are separately heated, **A** and **B** melt without decomposing, but **C** loses a molecule of water at about 250°C to form **D**, $\text{C}_8\text{H}_4\text{O}_3$. Suggest structures of **C** and **D**
- Explain the following observations:
 - When dilute hydrochloric acid is added to aqueous solution of soap, a white insoluble substance is formed.
 - Butane, Propan-1-ol, Propanal and Ethanoic acid have approximately the same molecular mass yet their boiling points are 273, 370 and 391K respectively.
 - Methanoic acid reacts with ammoniacal silver nitrate solution while Ethanoic acid does not.
 - Ethanedioic acid decolorizes potassium manganate (VII) solution on warming while Ethanoic acid does not.

READ ON THE FOLLOWING ASPECTS

DERIVATIVES OF CARBOXYLIC ACIDS

- *AMIDES*
- *ACID CHLORIDES*
- *ACID ANHYDRIDES AND ESTERS*

AMINES

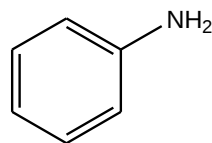
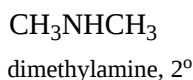
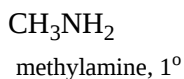
Introduction

Amines are alkyl or aryl derivatives of ammonia, and may be classified as Primary, secondary and tertiary according to the number of alkyl or aryl groups attached to the nitrogen atom.

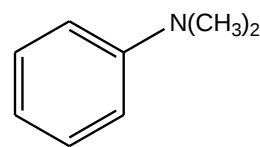
Aromatic amines are amines in which the nitrogen atom is attached directly to the aromatic ring.

Compounds containing two amine groups are known as diamines.

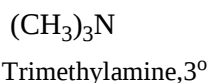
Examples of amines are their classes include



Phenylamine, 1°



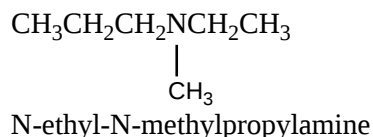
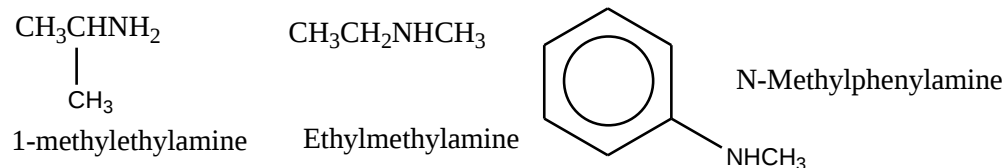
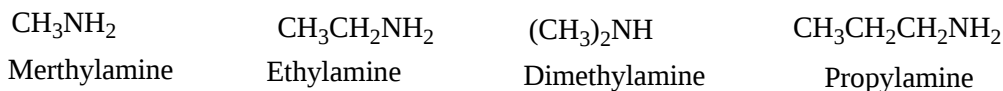
N,N-dimethylphenylamine, 3°



Nomenclature

Both aliphatic and aromatic amines can be named by inserting the ending “amine” to the name of alkane or other appropriate hydrocarbon.

Examples include:



More complex tertiary amines with different alkyl groups are named as derivatives of the longest chain and “N” is inserted before the named of each group.

For aromatic amines, the names are derived from the simplest aromatic amine i.e. Phenylamine.

Methylphenylamines are collectively termed as Toluidines.

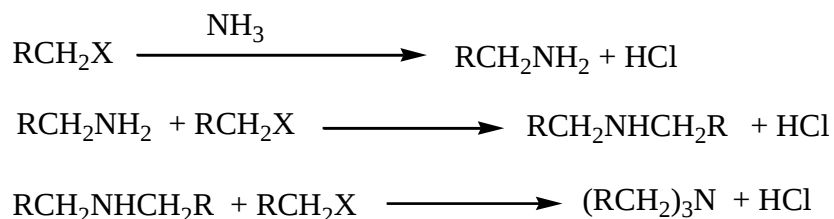
Synthetic Preparation

1) From Alkyl halides

This method generates a mixture of amines. Therefore their separation fractional distillation is used.

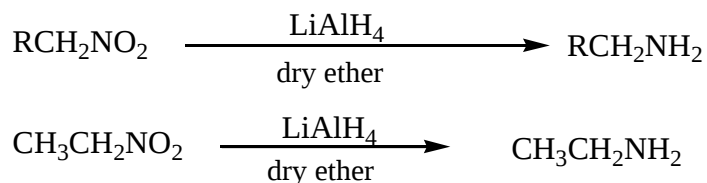
However better yield are obtained when Primary amine reacts with haloalkane compounds to generate secondary or tertiary amine.

The method also is suitable for preparation of Aromatic amine since aromatic halides do not react with ammonia under normal condition.

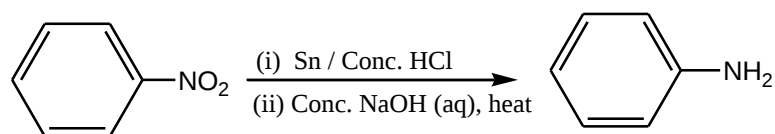


2) Reduction of Nitro compounds

Nitro compounds are reduced to Primary amines using Lithium Aluminium hydride or hydrogen gas in presence of a catalyst.

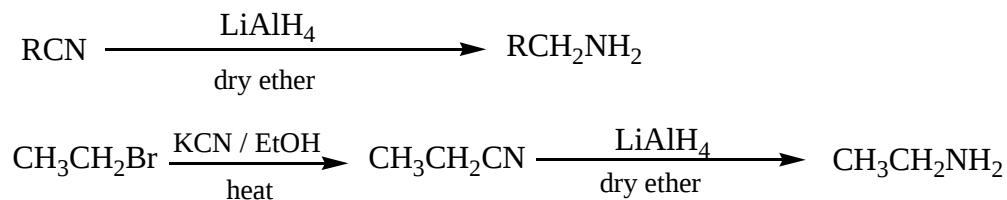


For aromatic amines, tin and concentrated hydrochloric acid is used for reduction of aromatic nitro compounds.

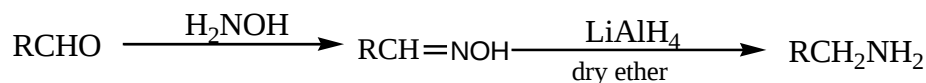


3) Reduction of Nitriles

Nitriles are reduced to primary amines by lithium aluminium hydride or hydrogen in presence of a catalyst.

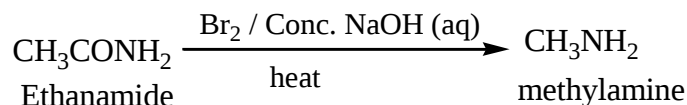
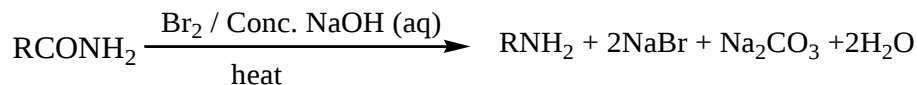


A further application is reduction of Oximes.



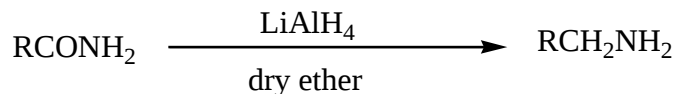
4) Hofmann degradation of Amides.

This reaction gives a good yield of primary amine of a lower carbon chain.



5) Reduction of amides

Primary or Secondary or tertiary amides are reduced to their respective amines using lithium aluminium hydride in dry ether.



Properties of Amines

Simple aliphatic amines are gases and possess a characteristic smell of ammonia. However most of the higher homologues are liquids with rotten fish smell.

They are polar compounds and the molecules form intermolecular hydrogen bonds with each other except tertiary amines.

For isomeric amines, the boiling points decrease in the order of 1^o > 2^o > 3^o due to progressive decrease in intermolecular hydrogen bond.

The hydrogen bonds in alcohols are stronger than those in amines because oxygen is more electronegative than nitrogen atom therefore the boiling points of alcohols are higher those of amines of relatively the same molecular mass.

Lower molecular mass amines are soluble in water because the molecules form hydrogen bond with water molecules and the resultant solution is basic .i.e. turns red litmus blue.

Basic Strength of Amines

The basic strength of amines depends on availability of lone pair of electrons on the nitrogen atom for protonation. Primary amines are more basic than ammonia due to presence of alkyl group which is electron releasing group therefore great salvation.

Secondary amines are more basic than Primary amines since they have two electron releasing groups hence more solvation.

Tertiary amines are less basic than both Primary and Secondary amines but more basic ammonia since they have three alkyl groups which are electron releasing groups' hence greater positive inductive effect or more electron releasing hence less solvation due to steric hinderance.

Aromatic amines are weaker or less basic than aliphatic amines because of the presence of benzene ring where the lone pair of electrons on the nitrogen atom gets delocalized. Thus lone pair of electrons on the nitrogen atom becomes less available for protonation.

The Table gives the base dissociation and their boiling points of amines.

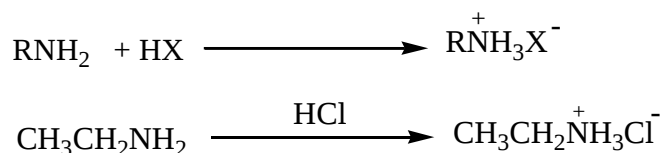
Amines	M.p.t (°C)	B.p.t(°C)	K _b
CH ₃ CH ₂ NH ₂	-84	17	5.6X10 ⁻⁴
CH ₃ CH ₂ NHCH ₂ CH ₃	-48	56	9.6X10 ⁻⁴
(CH ₃ CH ₂) ₃ N	-115	90	5.7X10 ⁻⁴
C ₆ H ₅ N(CH ₃) ₂	3	194	11.5X10 ⁻⁵

Reaction of Amines

Majority of the reactions of amines indicate amines as electron rich species (Nucleophiles). Therefore some of the reactions of amines include:

1) Salt formation

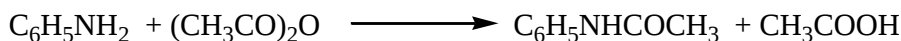
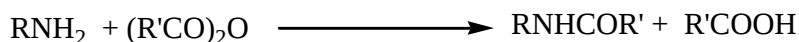
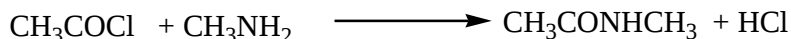
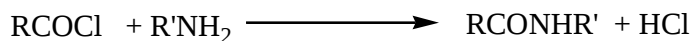
As bases, amines react with acids to form salts.



Generally the salts are soluble in water but insoluble in organic solvents. Therefore amines are soluble in dilute mineral acids.

2) Amide formation

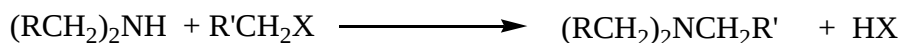
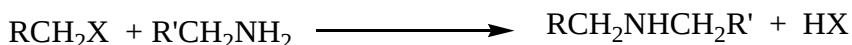
Both aliphatic and aromatic primary or secondary amines readily acylated using acyl halides or acid anhydrides



Qn: Write the mechanism of the above reaction

3) Alkylation of amines

Primary and secondary halides react with amines to form alkylated amine.



Qn: Write the mechanism of the above general reactions.

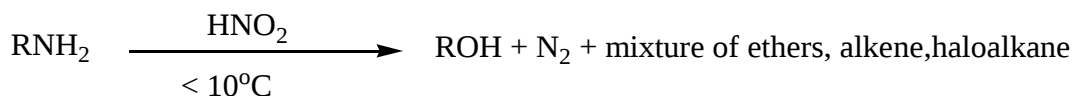
4) With Nitrous acid

Nitrous acid is unstable at room temperature therefore usually prepared in the reaction mixture using sodium nitrite and concentrated hydrochloric acid at low temperatures usually below 10°C.

The reaction mixture is used to differentiate between the classes of amines.

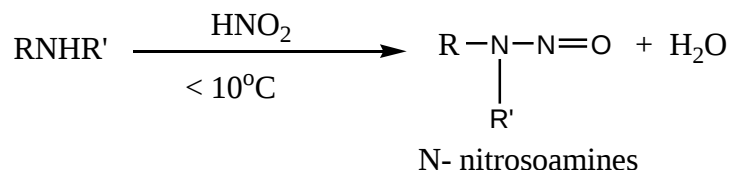
a) With Primary Aliphatic amines

They react to unstable alkyl Diazonium salt that decomposes to a colourless solution and bubbles of colourless gas.



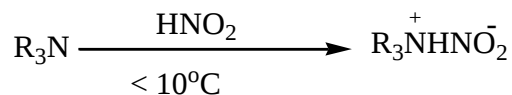
b) With Secondary amines

Both aliphatic and aromatic secondary amines react forming yellow oily liquids.



c) With Tertiary amines

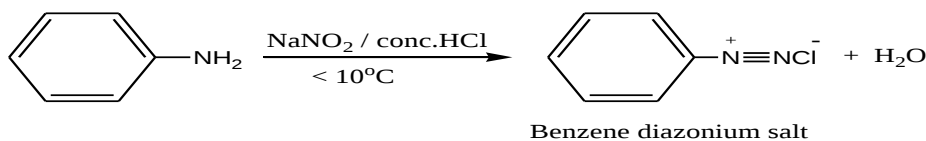
They with nitrous acid forming a colourless solution without evolution of bubbles of a colourless gas



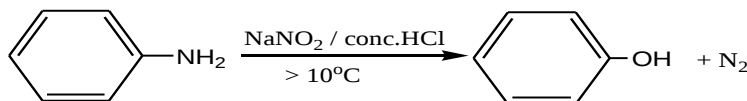
d) With Primary Aromatic amines

They react forming benzene Diazonium salt which is a stable colourless solution below 10°C .

The reaction between primary aromatic amine with nitrous below 10°C is known as diazotization.



Above 10°C , there is effervescence of a colourless gas and colourless liquid of phenol.



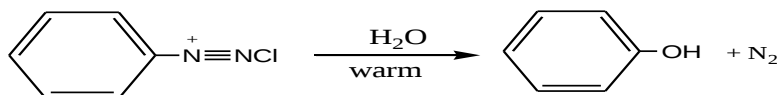
Reactions of Benzene Diazonium salt

Benzene Diazonium salt are prepared by action of nitrous acid on Phenylamine below 10°C .

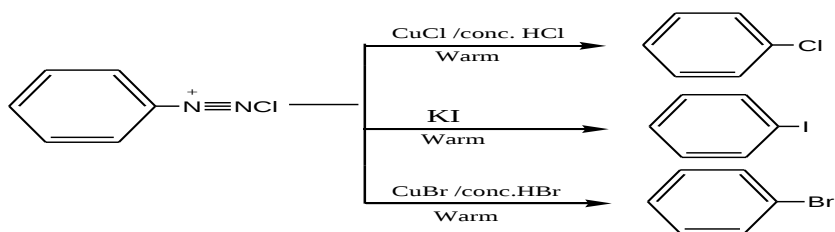
They undergo two types of reactions i.e.

1) Nucleophilic substitution reaction

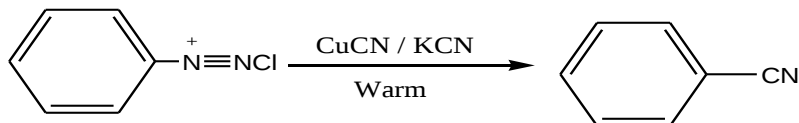
a) With water.



b) Halogen substitution



c) Cyanide substitution

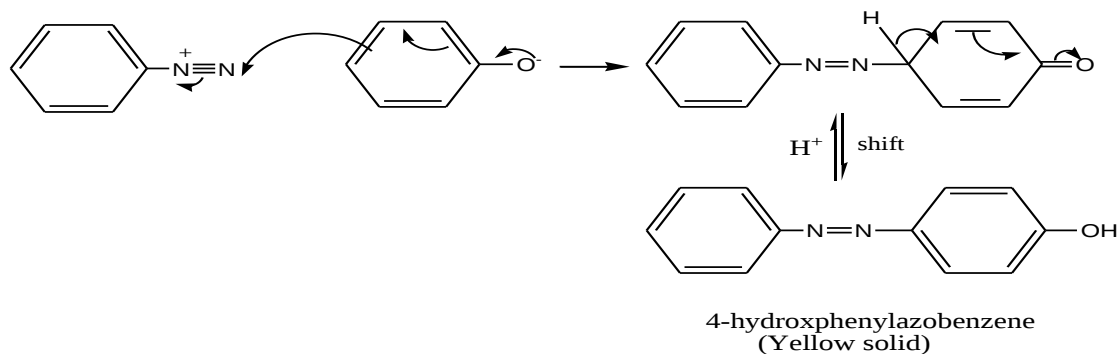


2) Coupling reactions

These reactions are usually used to generate azo dyes.

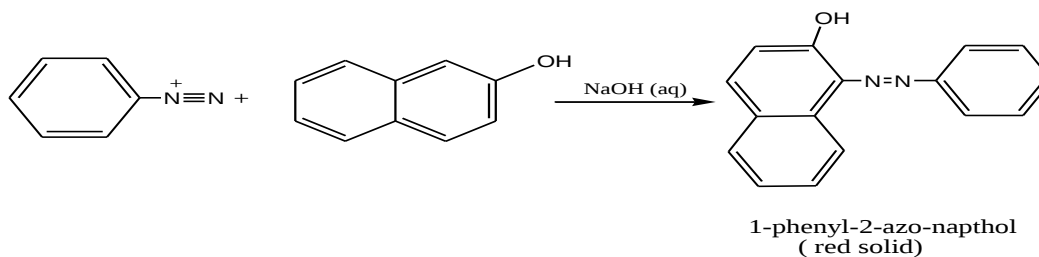
a) With Phenol

In alkaline medium benzene Diazonium salt react with phenol form a yellow azo dye.

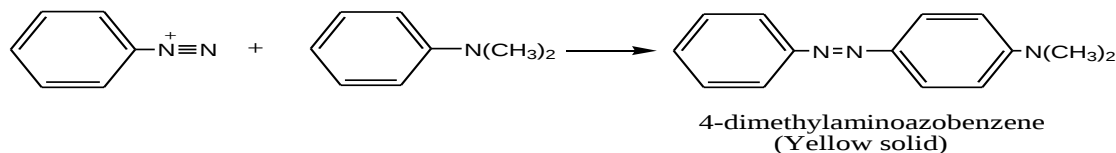


b) With Naph-2-ol

Benzene Diazonium salt forms a red azo dye in presence of alkaline medium also.



c) With amines

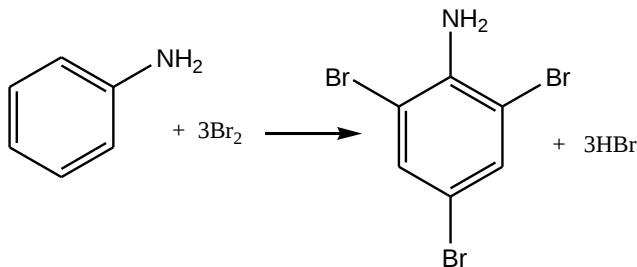


Qn: Write the mechanism of this reaction

Reaction of Aromatic amines (Substitution in the Benzene ring)

The amino group directs the incoming group to position 2 and 4 and activates the benzene ring towards Electrophilic substitution reactions.

Phenylamine reacts with Bromine forming a white precipitate of 2,4,6-tribromophenylamine.



SOAP AND DETERGENTS

SOAP

Sodium salt of long carboxylic acid is known as soap. Soap is usually obtained from Fats or Oils. Fats and Oils are complex mixtures of glycerol with a long chain carboxylic acid. Fats are solids at room temperature while Oils are liquids.

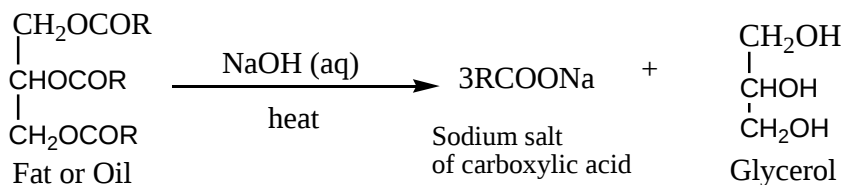
Fats tend to contain greater proportion of unsaturated acids while Oils tend to contain greater proportion of saturated acids.

The sources of oils are cotton seed, simsim, groundnut, sunflower seed, soya beans and coconut etc while fats are obtained from animals such as Pigs, Sheep or Cows.

Preparation of Soap

Soap is prepared by a reaction known as *saponification*.

Roast the dry seeds; crush/grind to make paste. Boil with water until oil floats on top and decant off the oil. Mix the oil with excess sodium hydroxide solution and boil while constant stirring for a long time.

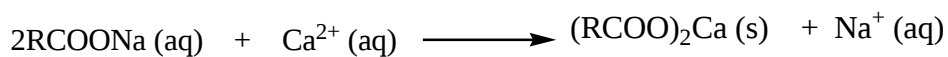


Add concentrated sodium chloride solution (Brine) to precipitate out the soap.

Cleansing Action of Soap

Soap lowers the surface tension between water and oil or insoluble material. They do so because they contain a polar group ($-\text{COO}^-$) and a non-polar alkyl chain (R-). The molecule of water congregates near the polar end while the molecules of oil congregate around the alkyl group. The non-polar oil particles are emulsified into suspension and removed.

N.B. Hard water affects the cleansing action of soap. Hard water contains calcium or magnesium ions. These ions react with soap to form a precipitate known as Scum.



Lather cannot be formed when the entire calcium or magnesium ions are completely removed as scum. This wastes soap in hard water.

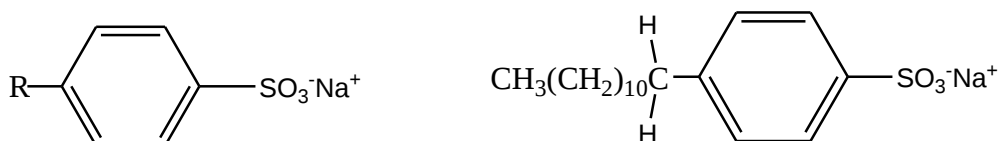
DETERGENTS

These are substances which improve the cleansing properties of water since they are sodium salts of long chain alkyl sulphonate or alkyl sulphate

Features of Detergents

Detergents have long chain hydrocarbon end which is oil or Fat soluble and hydrophilic part which is the sulphonate group. Thus detergents are sodium salts of sulphonic acids.

Since Detergents are alkyl benzene sulphonate examples include:



Common detergents include Nomi, Omo, surf, teepol etc.

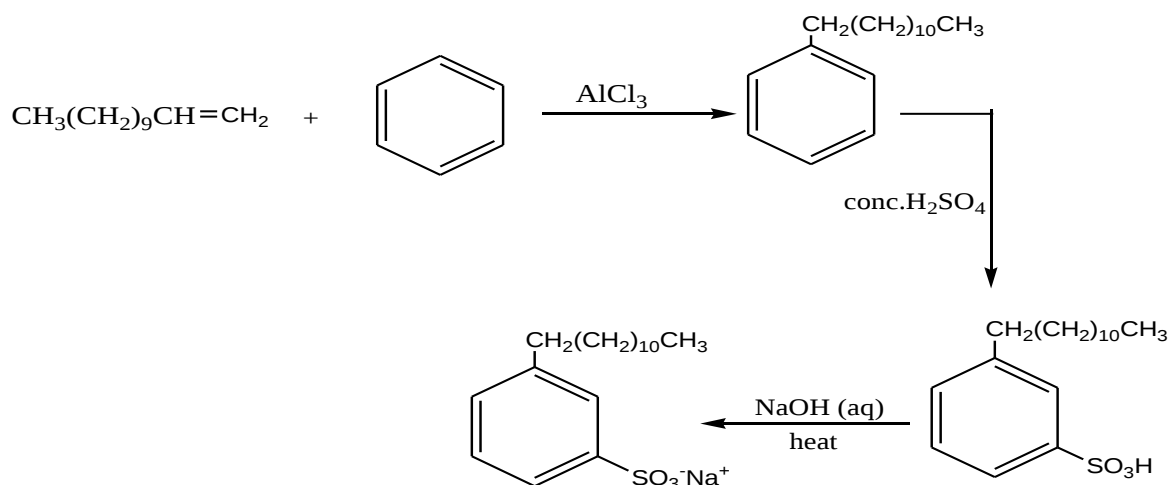
Properties of detergents

1. They are highly soluble in water
2. Detergents are emulsifying agents.

Preparation of Alkyl Benzene sulphonate

Soap less detergent is prepared as follows:

Benzene is alkylated in presence of a halogen carrier. The alkylated benzene is then sulphonated with concentrated sulphuric acid and the sulphonic acid formed is reacted with sodium hydroxide solution to form the detergent. i.e.



The table below shows the types of detergents and their uses.

Types	Nature	use
Anionic detergent	These have negative heads e.g $\text{CH}_3(\text{CH}_2)_{11}\text{CH}_2\text{OSO}_3^-\text{Na}^+$	Used for manufacture of toothpaste and shampoo
Cationic detergent	These have positive heads e.g $\text{C}_{15}\text{H}_{31}\text{N}(\text{CH}_3)_3\text{Br}$	Used for hair conditioners
Non-ionic detergents	These are neutral in water i.e. these carry no charge	Used for making liquid detergents

Action of Detergents on Fabrics

The action of detergents on fabrics is the same as that of soap.

Detergent Additives

- 1) **Sodium Sulphate:** This is used to increase the bulk of the detergent.
- 2) **Detergent builders (Inorganic phosphate):** These are used as water softeners because they form soluble complexes with calcium or magnesium ions in hard water.
- 3) **Peroxyborates:** These are used as bleaching agents.

Advantages of Soap over detergents

- a) Soap is biologically degradable
- b) Soap can be used for both bathing and washing

Disadvantage of Soap over detergents

They form undesirable scum with hard water which leads to wastage of soap

Advantages of detergents over soap

- a) They are used in any of water.
- b) Detergents have a brighter cleansing effect

Disadvantages of detergents over soap

- a) Detergents are non biodegradable
- b) Detergents contain fertilizer materials such as phosphates which nourish the growth of algae hence reducing oxygen supply in water.

Question:

- a) Some oils are used in the manufacture of soap.

- i. Name the reaction leading to the formation of soap
 - ii. Outline how soap is manufactured from oil.
 - iii. Write an equation of reaction between hard water and soap
 - iv. Explain briefly why soap is not commonly used in washing aluminium utensils
 - v. A sample of soap was prepared from 9.5g of oil containing an ester of hexadecanoic acid ($C_{15}H_{31}COOH$). Calculate the mass of soap formed.
- b) Synthetic detergents are gradually replacing soap as cleansing agents.
- i. Write equations to show how a soap less detergent can be prepared from $CH_3(CH_2)_5CH=CH_2$
 - ii. What problem does detergent cause to the environment
 - iii. State one structural difference between soap and detergent
 - iv. Describe the cleansing action of Omo as a detergent
 - v. $0.6cm^3$ of Jik was dissolved in water and solution made in $250cm^3$ volumetric flask. $25cm^3$ of this solution was acidified and $10cm^3$ of 0.2M potassium iodide solution added. The iodine liberated required $5.0cm^3$ of 0.2M Sodium thiosulphate solution for complete reaction. Calculate the mass of Chlorine in $1dm^3$ of Jik.

POLYMERISATION

This is the building of large molecules (polymer) by linking together very many small molecules (monomers) with or without loss of small molecules such as water, ammonia etc.

Polymers are long chain molecules with recurring structural units formed by polymerization process.

When the recurring units are different, a co-polymer is formed.

Factors that determine the properties of Polymers

- Chain length: Strength and melting points of polymers increase with increase chain length
- Branching: Increased branching reduces the molecular strength and lowers the melting point
- Cross linkage: Polymers with a cross link between the chains form a rigid network which increases the strength.
- Intermolecular forces: Stronger intermolecular forces between the chains result into higher melting points.

Types of Polymers

1. Natural Polymers

These are polymers whose formation is not controlled by man. These include Cellulose material (Cotton, paper), Protein material (wool, silk), Natural rubber and Rayon.

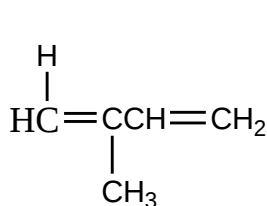
2. Synthetic Polymers

These are polymers that are man made. These include Plastics and fibers, addition polymers (polyethene, polypropene, and polyvinylchloride), Condensation polymers (Polyesters, nylon 6, 6)

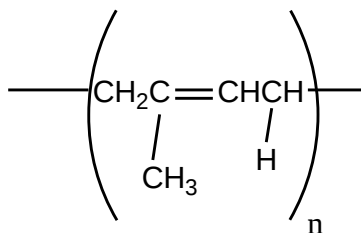
Natural Rubber

Rubber is obtained naturally from rubber trees as milky liquid called latex.

Natural rubber is a polymer derived from 2-methylbut-1, 3-diene I,e



2-methylbut-1,3-diene
(monomer)



Natural rubber (polymer)

Natural rubber is very soft and of little use. It is made hard and tough by heating it with sulphur by a process known as Vulcanisation.

Vulcanisation

This is the process of improving on the qualities of rubber by heating it with sulphur.

The sulphur atoms add to some double bonds of two neighbouring rubber molecules to form vulcanized rubber.

The hardness of vulcanized rubber is directly proportional to the amount of sulphur added.

The following are the effects of heating natural rubber with sulphur:

- It improves on temperature working range
- It improves on toughness
- It improves on elasticity
- It improves on Bulkiness

Vulcanized rubber therefore is used for making car tyres, shoe sole, gloves and insulating electric cables.

Synthetic Polymer

Addition Polymers

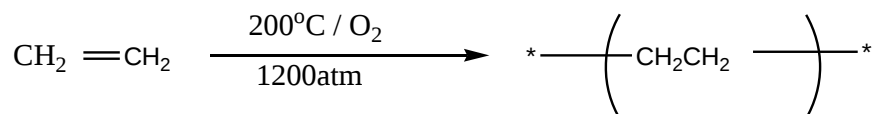
Addition Polymerization

This is the building up of a large molecule from a number of unsaturated monomers to form a single product.

Addition polymers include:

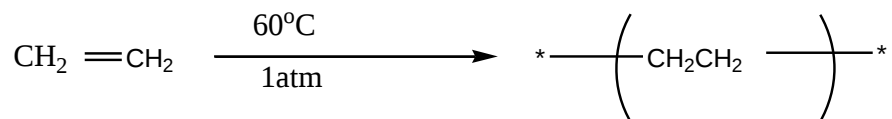
Polyethene: These exist in two forms i.e. High density and lower density polymer.

Low density polymer: This is formed in presence of a catalyst i.e.



Low density polyethene is used for making plastic bags, packing materials, electric cables, insulators.

High density polyethene: This is formed when ethene undergoes polymerization at 60°C and 1 atmosphere. i.e.

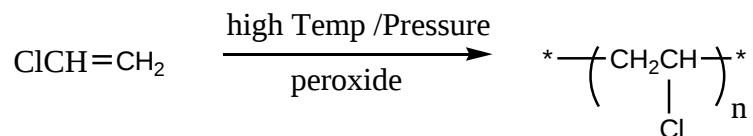


High density polyethene is used for manufacture of water tanks, plastic pipes, plastic bottles, crates, buckets and kitchen ware.

Polyethene doesn't rot, insoluble in most common solvents and less dense than water.

Polyvinylchloride (PVC)

The monomer is chloroethene. Chloroethene undergoes polymerization at high pressure and temperature in presence of peroxide i.e.

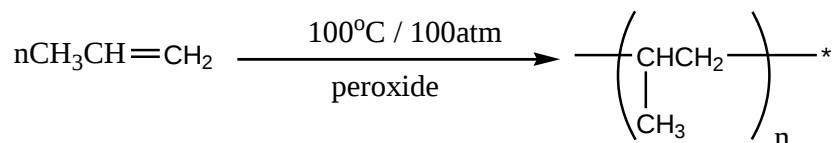


The properties of PVC are water proof, non-degradable, not attacked and easily destroyed on heating.

PVC is used for making plastic coats, umbrellas, electronic equipments, suitcases and insulating electric cables.

Polypropene

This is formed from propene at 100°C and 100atmosphere in presence of peroxide.



Polypropene is used for making beer bottle crates, drinking straws, ropes and surfaces of all weather football and hockey pitches.

Polystyrene / Polyphenylethene

The monomer is phenylethene. Polystyrene is used for making combs, packing materials, ceilings and toys.

Perspex

This is an addition polymer whose monomer is $\text{H}_2\text{C}=\overset{\text{CH}_3}{\underset{|}{\text{C}}}\text{COOCH}_3$.

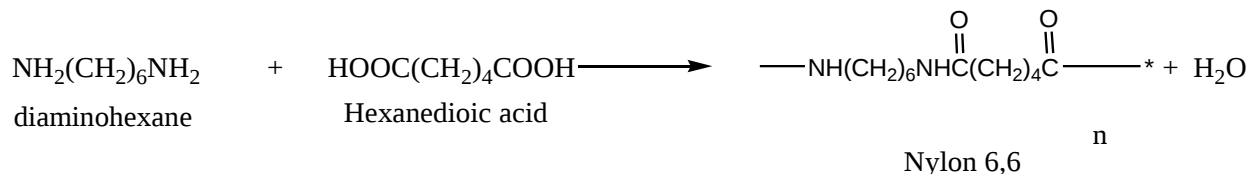
Perspex is used for making lenses, laboratory glass ware, windows of cars and airplanes, corrugated roof lights and in packaging.

Condensation Polymers

Condensation polymerization occurs when molecules that are bifunctional or polyfunctional react together to form a polymer and another product with small molecules.

Nylon 6,6

The monomers are diaminohexane and hexanedioic acid. It is called Nylon 6, 6 because each of the monomers has got six carbon atoms.



Nylon 6,6 has the following properties:

- It is water repellent hence dries easily
- It has got a hard warring tendency
- Insoluble in most solvents
- Fuses at temperatures above 200°C

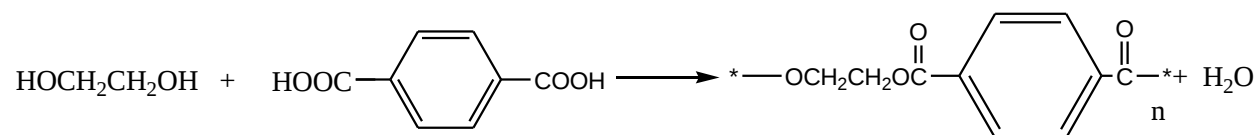
Nylon 6,6 is used for making of stockings, gloves, clothes, carpets and fishing nets.

N.B. Nylon 6,10 has monomers 1,6-diaminohexane and decanedicyldichloride and it is used for making surgical gloves, curtains , fishing nets and carpets.

Nylon polymers are also known as polyamides since they contain the peptide bond with in the molecule.

Polyester / Terylene

Made by condensing Ethane-1,2-diol and Benzene-1,4-dicarboxylic acid with loss of water molecules. i.e.



It is used for making clothes (textiles), ropes, safety belts and tents.

Differences between Addition polymerization and Condensation polymerization

	Addition polymerization	Condensation polymerization
1	Addition polymers are linear	Condensation polymers are non-linear
2	The monomers used are similar	Monomers used are different
3	Addition polymerization can be reversed	Condensation polymerization is irreversible

Advantages of Synthetic polymers over natural polymers

- Easier to manufacture
- Relatively stronger than the corresponding natural polymer

Disadvantages of Synthetic polymers over Natural polymers

- Non-biodegradable
- Its manufacture involves release of toxic fumes which cause a health hazards to Human.

PLASTICS

A plastic is a substance which when heated becomes soft and can be moulded into different shapes.

Properties of Plastics

- Become soft on heating
- Non-biodegradable
- Not attacked by acids or alkali

The properties of plastics can be modified by addition of:

- Plasticizers: these are substances which soften and make plastics easily moulded.
- Dyes and pigments: used to colour plastics
- Fillers: are used to increase the bulk of Plastics.

Types of plastics

1) Thermosoftening plastics (Thermoplastics)

These are plastics which when heated soften and can be remoulded into different shapes. This is because the binding forces between the polymer chains are weak and also have fewer cross-linkages between the polymer chains (or linear pattern arrangement).

Thermoplastics include Polypropene, polyethene, polystyrene, polyvinylchloride etc.

2) Thermosetting plastics (Thermosets)

These are plastics which when heated donot soften but harden and can not be remoulded in to different shapes. This is because they are held together by much cross-linkage between the polymer chains.

Thermosets include Bakelite used for making electric plugs, sockets and switches.

Advantages of Plastics over metals

- Plastics are resistant to attacks by acids, alkalis and atmospheric oxygen (corrosion).
- Easier to be recycled.
- Lighter than metals

Disadvantages of Plastics over metals

- Plastics items easily burn
 - Pollutants since they are non-biodegradable
 - You are provided with organic substance **Z** whose nature is required to be determined.
- Record your observation(s) and deduction(s) in the table below

END.