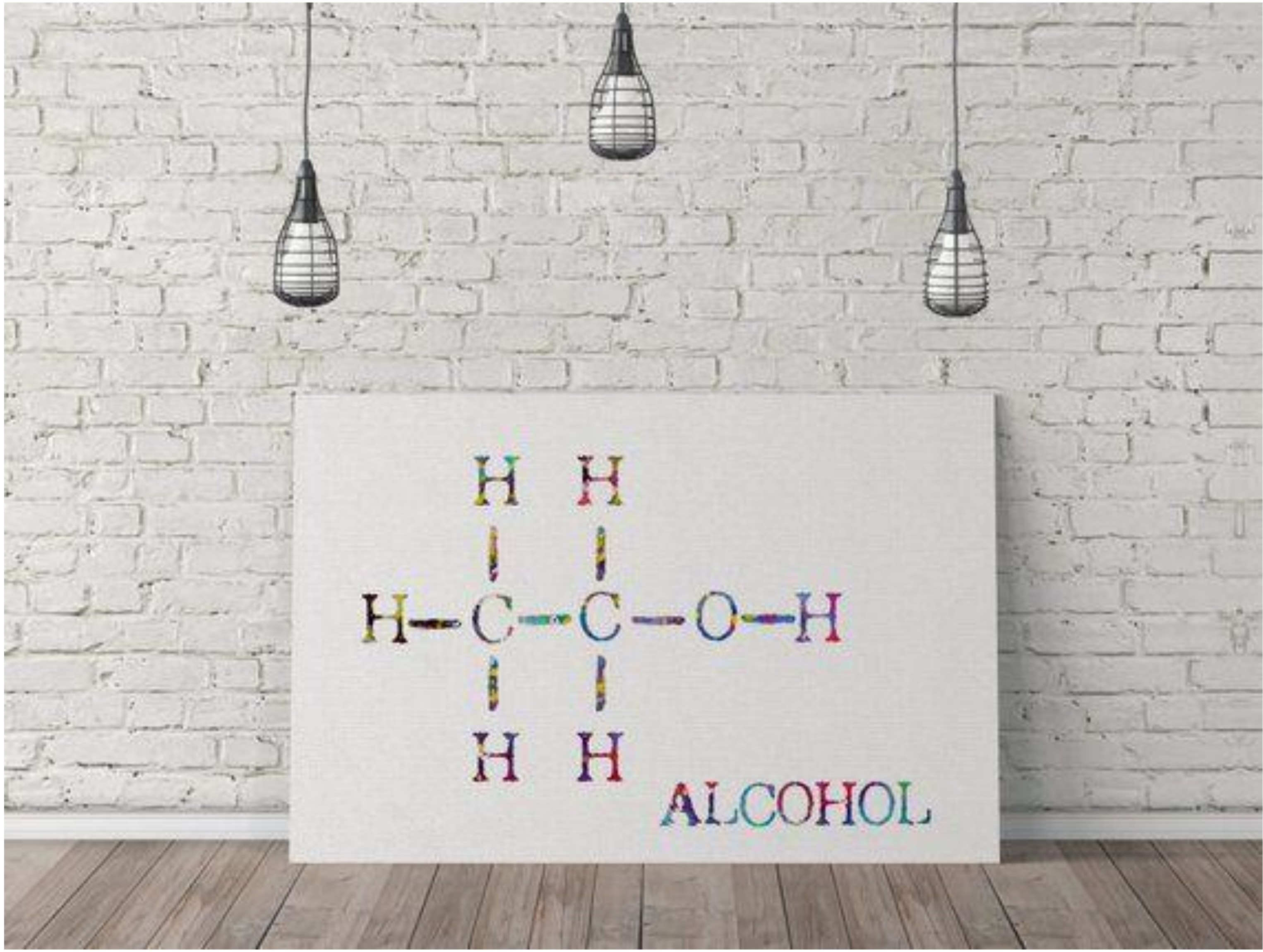
Chapter 9

Alcohols



Hussein Semaan

1- definition :

- **Alcohol** is an organic compound that carries at least one hydroxyl functional group (−OH) bound to a saturated carbon atom.

2- molecular formula :

$C_nH_{2n+2}O$ or $C_nH_{2n+1}OH$

3- molar mass:

$14n + 18$

4- structural formula:

R-OH

5- functional group:

Hydroxyl group **-OH**

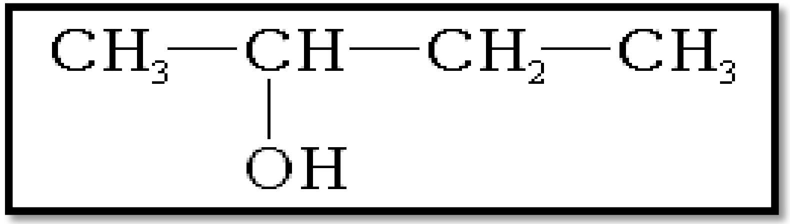
6- nomenclature :

Alkane → **Alkanol**

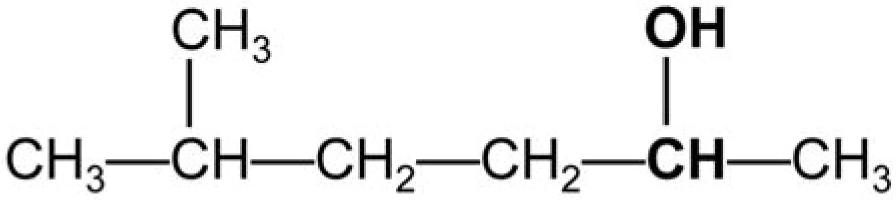
The position of hydroxyl group should be indicated in nomenclature if the main chain contain 3 or more carbon atoms

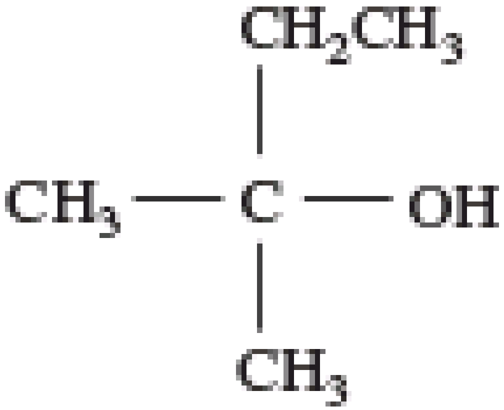
The name become : x-alkanol

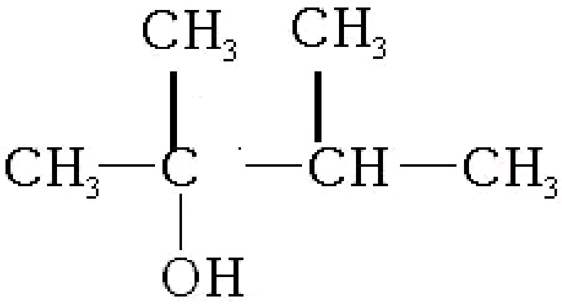
$\boxed{CH_3-CH_2-OH}$



$CH_3-CH_2-CH_2-CH_2-OH$



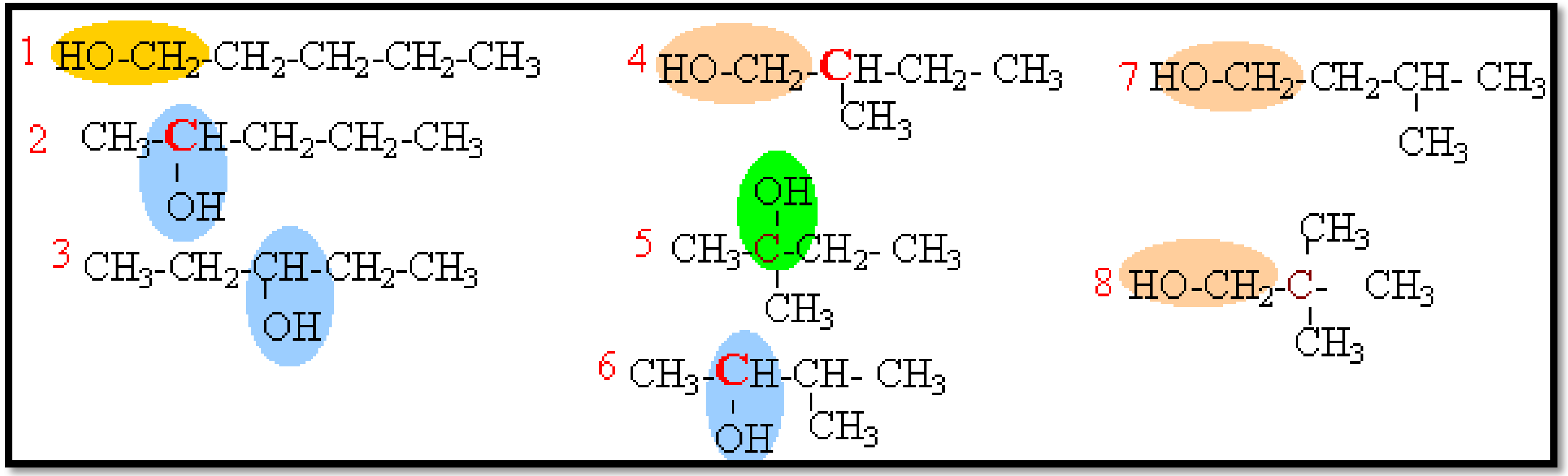




$(CH_3)_2CH-CH_2-CH_2OH$

6- isomers of alcohol:

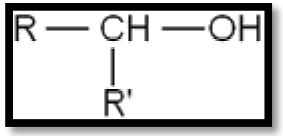
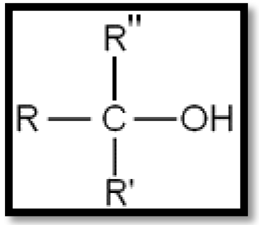
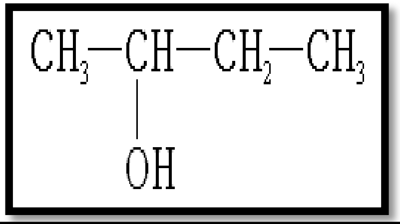
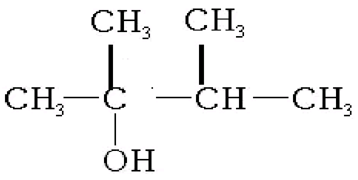
Write all possible condensed structural formulas of $C_5H_{12}O$



- 1 and 2 are examples of positional isomers
- 1 and 4 are examples of a skeletal isomers

Alcohol have a functional isomers which is ether

7- classes of alcohol:

Class	Primary	Secondary	Tertiary
Condensed structural formula	$R-CH_2-OH$		
Definition	The carbon connected to hydroxyl group is connected to 1 carbon atom (2 hydrogen atoms)	The carbon connected to hydroxyl group is connected to 2 carbon atoms (1 hydrogen atoms)	The carbon connected to hydroxyl group is connected to 3 carbon atoms (0 hydrogen atoms)
Example	CH_3-CH_2-OH		

8- reactions of alcohol:

8.1- mild oxidation:

Mild oxidation is a reaction which takes place without breaking of carbon chain.

It can be carried out by three ways:

1- Catalytic oxidation in the presence of oxygen gas (air).

2- Catalytic dehydrogenation in the absence of oxygen gas.

3- Oxidation by oxidant such as $Cr_2O_7^{2-}$, MnO_4^-…

In general :

- Primary alcohol $\xrightarrow{\text{Oxidation}}$ aldehyde $\xrightarrow{\text{Oxidation}}$ carboxylic acid
- Secondary alcohol $\xrightarrow{\text{Oxidation}}$ ketone $\xrightarrow{\text{Oxidation}}$ X
- Tertiary alcohol $\xrightarrow{\text{Oxidation}}$ X

8.1.1- Catalytic oxidation in the presence of oxygen gas (air).

A-Primary alcohol:

- Limited oxidation :

$$R\text{-}CH_2OH + 1/2O_2 \xrightarrow{Cu} R-\underset{\underset{O}{\|}}{C}-H\,(R\text{-}CHO) + H_2O$$

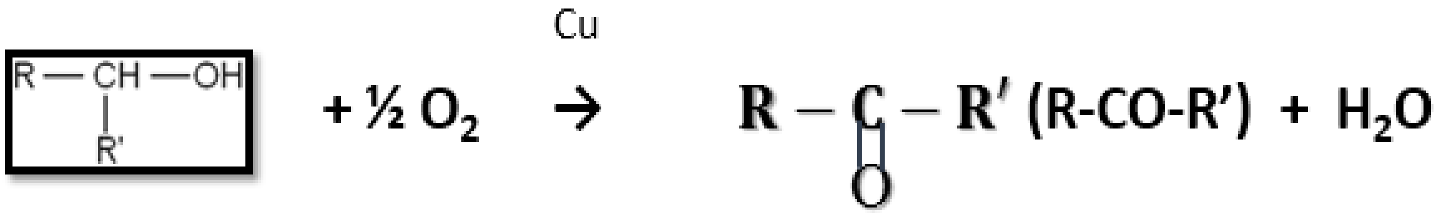
Primary alcohol aldehyde

- Continous oxidation:

$$R\text{-}CH_2OH + O_2 \xrightarrow{Cu} R-\underset{\underset{O}{\|}}{C}-OH\,(R\text{-}COOH) + H_2O$$

Primary alcohol carboxylic acid

B- secondary alcohol:



Secondary alcohol

ketone

8.1.2- Catalytic dehydrogenation in the absence of oxygen gas(air):

A- primary alcohol:

$$R\text{-}CH2OH \xrightarrow[T]{Cu} R_1\text{-}CHO + H_2$$

Primary alcohol **aldehyde**

B- secondary alcohol:

$$\underset{\displaystyle R'}{R\text{-}\overset{}{C}H\text{-}OH} \xrightarrow[T]{Cu} R\text{-}CO\text{-}R' + H_2$$

Secondary alcohol **ketone**

8.1.3- Oxidation by oxidant such as $Cr_2O_7^{2-}$, MnO_4^-…

- Dichromate ion (orange) : $Cr_2O_7^{2-}$
- Permanganate ion(purple) : MnO_4^-

A- primary alcohol :

- Limited oxidation:

Oxidation half-equation : $\times 3(R\text{-}CH_2OH \rightarrow R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H + 2H^+ + 2e^-)$

reduction half-equation : $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Overall equation : $3R\text{-}CH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3R\text{-}CHO + 2Cr^{3+} + 7H_2O$

Primary alcohol **aldehyde**

- Continous oxidation : in presence of an excess of oxidant

Oxidation half-equation : $x3(R\text{-}CH2OH + H2O \longrightarrow R\text{-}\overset{\overset{O}{||}}{C}\text{-}OH + 4H^{+} + 4e^{-})$

$$x2(Cr_2O_7^{-2} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H2O)$$

overall equation : $2\ Cr_2O_7^{2-} + 3R\text{-}CH_2\text{-}OH + 16H^{+} \rightarrow 2\ Cr_2O_7^{2-} + 3R\text{-}COOH + 11H_2O$

Primary alcohol **carboxylic acid**

B- secondary alcohol:

Oxidation half-equation : $x3(R\text{-}\overset{\overset{R'}{|}}{C}HOH + H2O \longrightarrow R\text{-}\overset{\overset{O}{||}}{C}\text{-}R' + 2H^{+} + 2e^{-})$

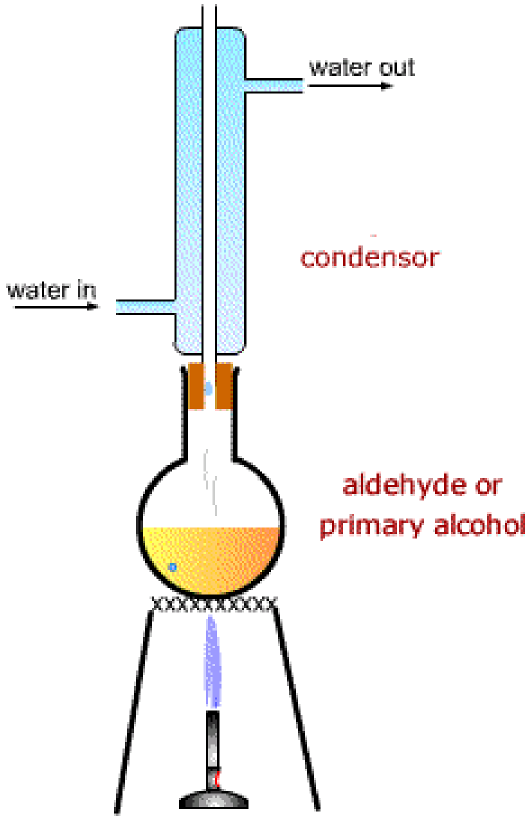
Reduction half-equation : $Cr_2O_7^{2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H2O$

overall equation : $3R\text{-}\overset{\overset{R'}{|}}{C}HOH + Cr_2O_7^{2-} + 8H^{+} \rightarrow 3R\text{-}\overset{\overset{O}{||}}{C}\text{-}R' + 2Cr^{3+} + 7H2O$

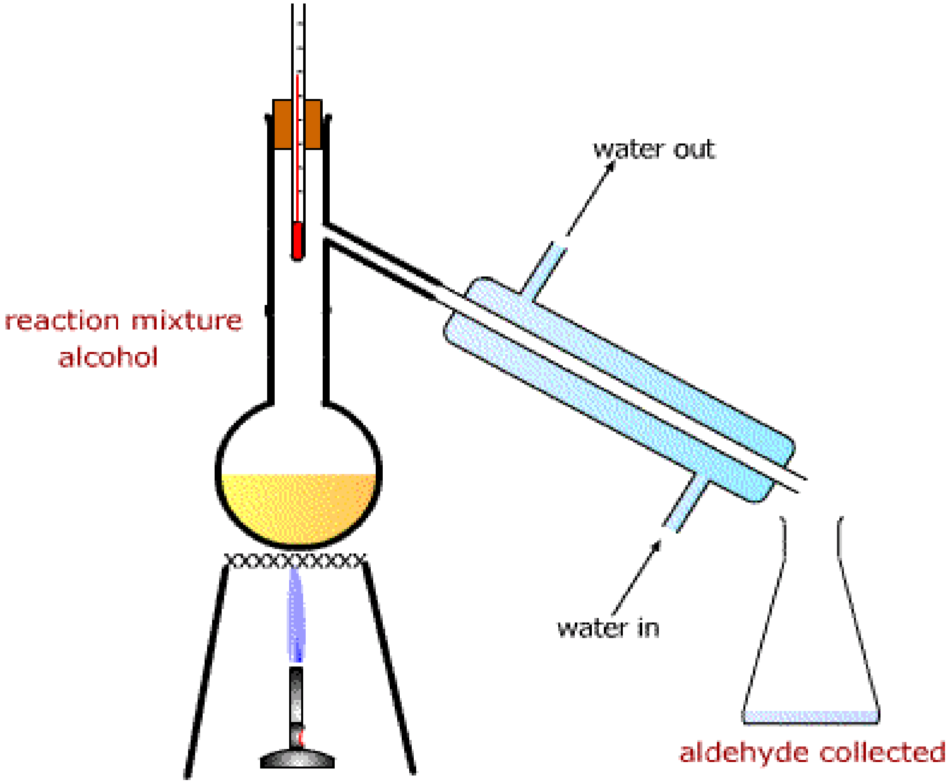
Secondary alcohol **ketone**

Mild oxidation in presence of permenganate

- Half equation : $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$



Reflux heating



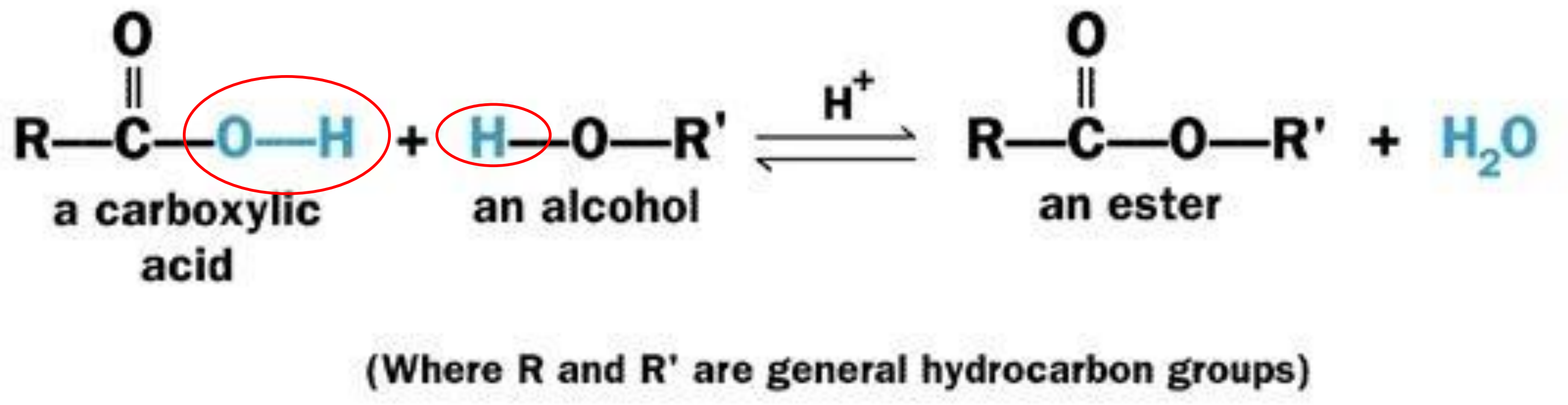
Simple distillation

In this preparation primary alcohol are oxidized into aldehyde which oxidized in a continuous reaction into carboxylic acid.

In this preparation primary alcohol are oxidized into aldehyde which are separated before continuous oxidation into carboxylic acid.

8.2- esterification reaction:

Esterification occurs when a carboxylic acid reacts with an alcohol. This reaction can only occur in the presence of an acid catalyst. This reaction lost an -OH from the carboxylic acid and a hydrogen from the alcohol. These two also combine to form water.

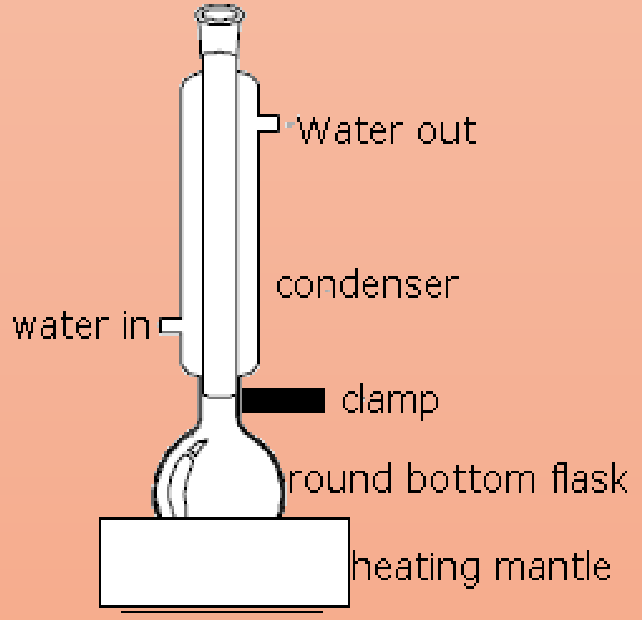


- Characteristics: slow, reversible, athermic.
- Sulfuric acid has a kinetic role as a catalyst, increases the rate of reaction
- Increasing the heat will increase the rate of reaction. At equilibrium, increasing heat will not effect the yield since this reaction is athermic.

If the mixture is an equimolar mixture of carboxylic acid and alcohol :

	% yield of esterification	% yield of hydrolysis
Primary alcohol	**66-67 %**	**33-34 %**
Secondary alcohol	**60%**	**40 %**
Tertiary alcohol	**< 5%**	**>95%**

Reflux heating:



- **Role of reflux:**
- Prevent the loss of reactants and products by condensation their vapors and returning them to the system of reaction.