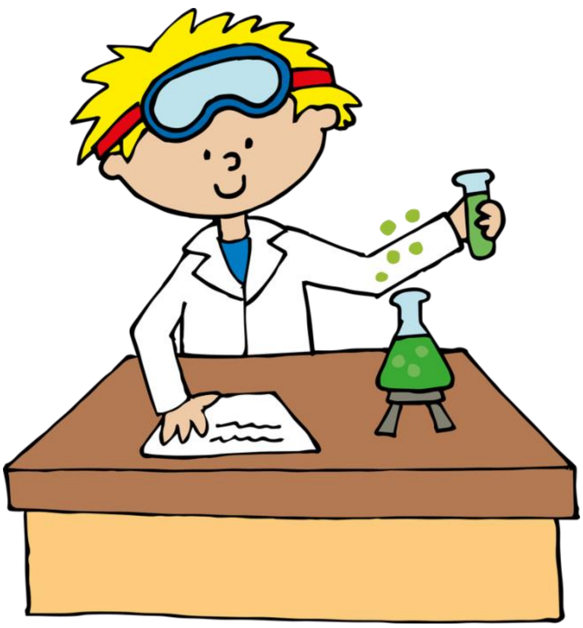
Ministry of Higher Education
Mustansiriyah University
College of Pharmacy
Pharmaceutical Chemistry department

وزارة التعليم العالي والبحث العلمي
الجامعة المستنصرية
كلية الصيدلة
فرع الكيمياء الصيدلانية

Organic Chemistry Laboratory

Part (I)

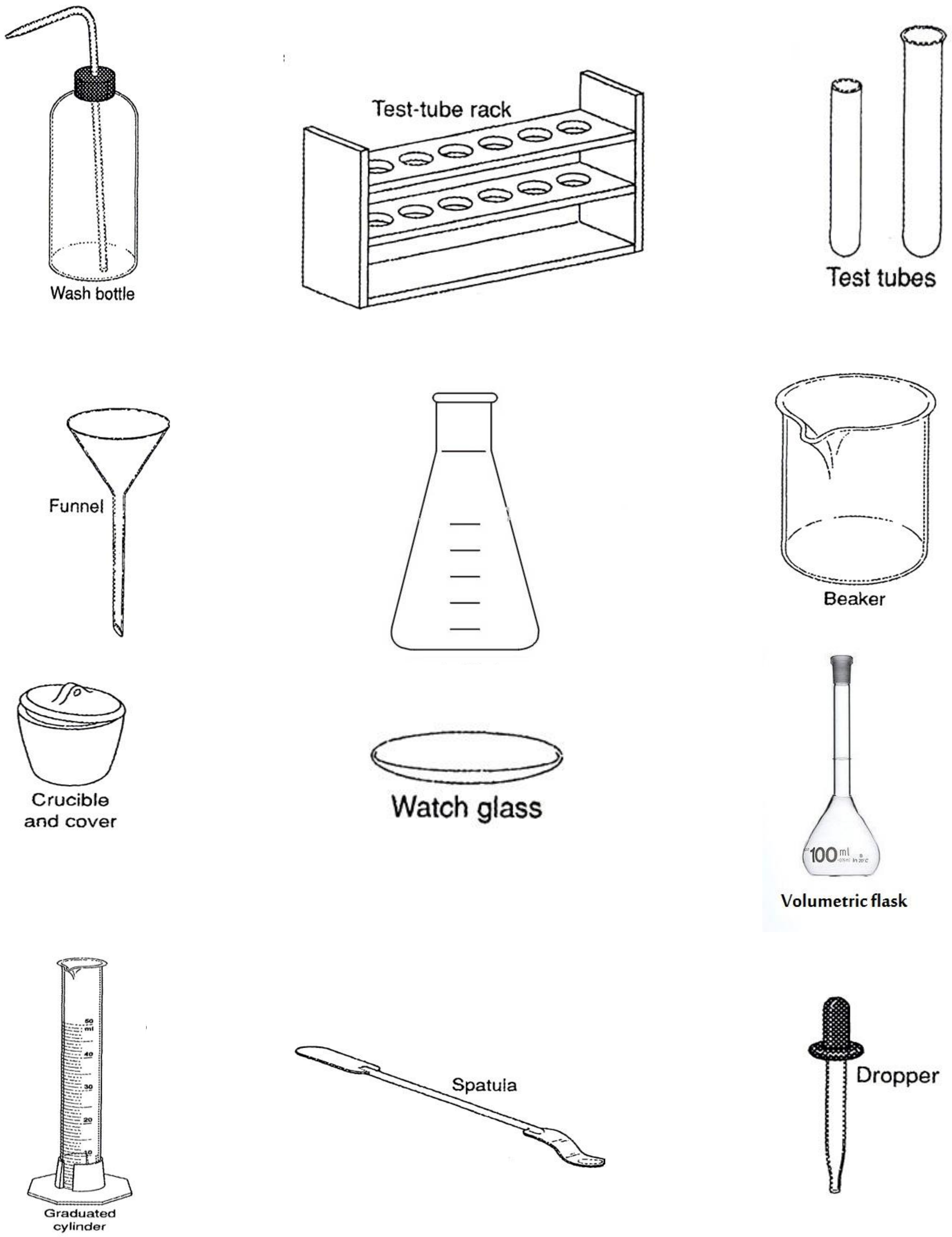


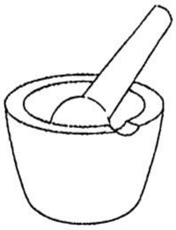
1. Always wash your hands before and after experiments. (bring small towel and a bar of soap with you)
2. Read all directions for the experiment carefully before beginning. Follow all the directions exactly as written or explained by the supervisor.
3. Never perform unauthorized activities.
4. Never mix chemicals or other materials for fun.
5. Maintain a clean work area.
6. When an experiment is completed always clean up the glass ware and working area and return all equipment's to its proper place.
7. Never eat in lab (DO NOT CHEW GUM)

8. Know the location of safety equipment's (e.g. Fire extinguisher) and how to use it.
9. Always wear safety goggles when working with chemicals, burners, or any substance or object that might injure eyes.
10. Wear your lab. coats as soon as you enter the lab. and keep it on the whole time. (student NOT ALLOWED to enter the lab unless he has his coat on)

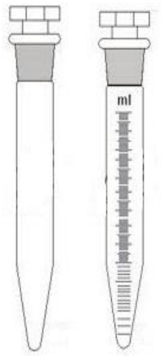
11. Keep all lids closed immediately when a chemical is not being used.
12. Many chemicals and hazardous materials might be corrosive or even poisonous. never touch, taste, or smell any chemical. If instructed to smell the fumes in an experiment, gently wave a hand over the opening of the container and direct the fumes tower the nose.
13. Dispose of all chemicals as instructed by the supervisor.
14. Take care not to spill any chemicals on you bench or in the lab. If spilling does occur, notify the supervisor for clean-up directions.
15. Be careful if you work with acids and bases. Always pour acid into water gradually when diluting the acid. NEVER pour water into acid.
16. Rinse any acids or bases off skin or clothing with water.
17. Never reach across a flame.
18. Pull back long hair and push up long sleeves if necessary.
19. Always point a test tube or bottle being heated away from you and others.
20. Never heat chemicals in a closed container.
21. Always use a clamp, tong, or heat-resistant gloves when handling with hot containers.
22. Use a wire screen to protect glassware when heating.
23. Never heat glassware that is not thoroughly dry.
24. Never use broken or chipped glassware. If glassware break notifies the supervisor.
25. Notify the supervisor immediately if you are cut or injured in lab. (For first aid)
26. All sharp glass ware and broken glass are to be disposed of in the proper container. (Notify the supervisor)

Common Laboratory Apparatus

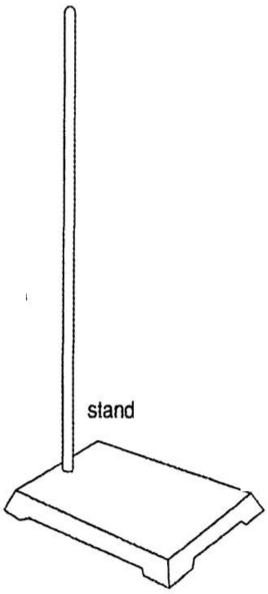



Mortar and pestle

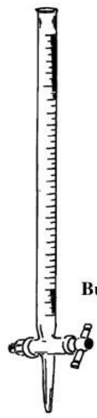

Glass rode



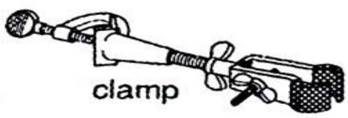
Centrifuge tube


stand

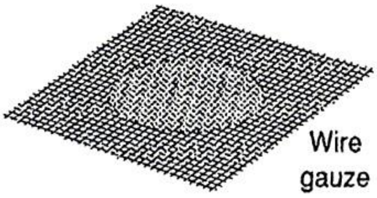

pipettes

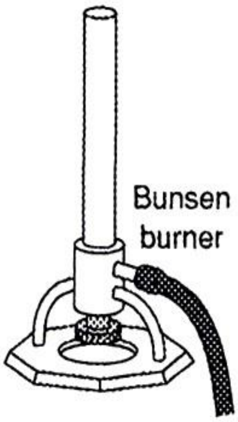

Burette

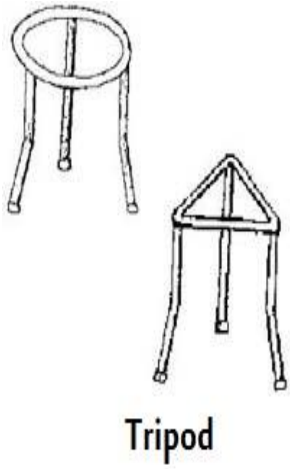

Bruch

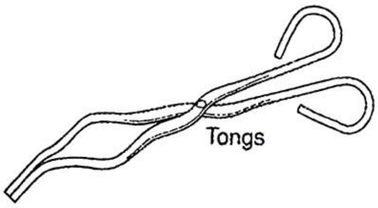

clamp

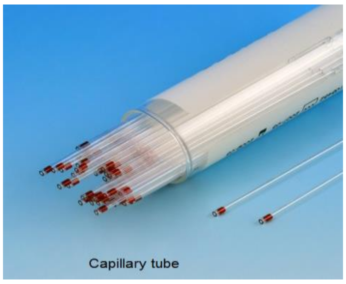

Reagent Bottle

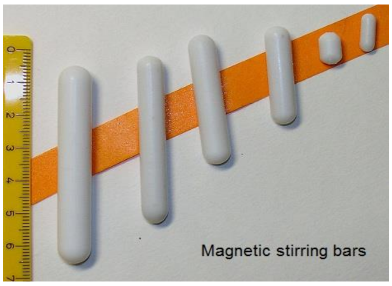


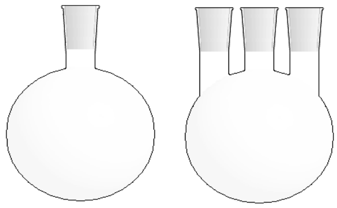




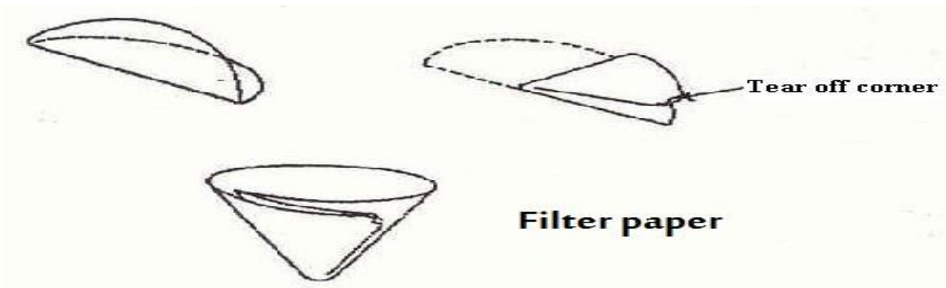




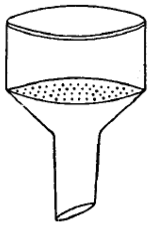




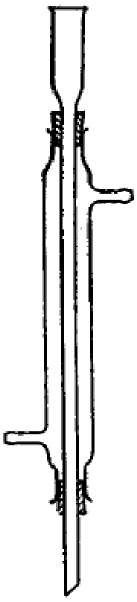
Round bottom flask



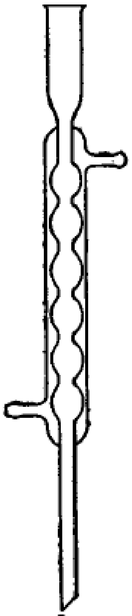
Buchner Flask



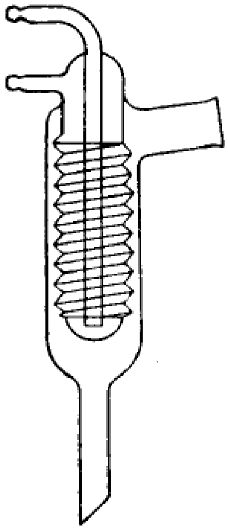
Buchner Funnel



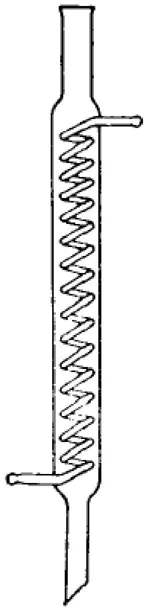
Liebing Condenser



Allihn Condenser



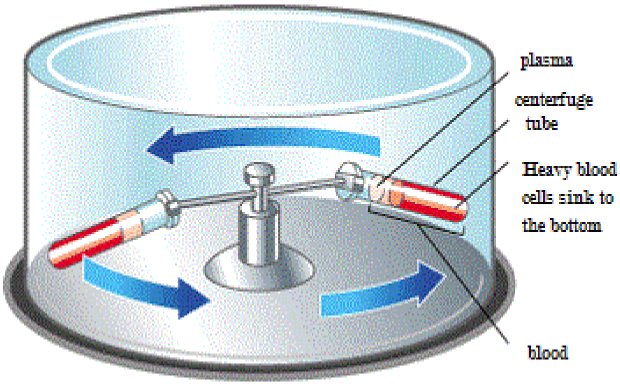
Friedrichs Condeser



Coiled Condenser

Folden filter paper

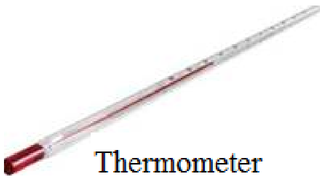
Litmos paper



Centerfuge

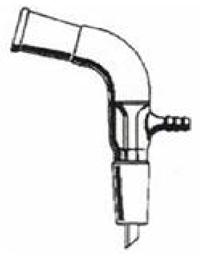
Electronic Balance

Test tube holder



Thermometer

Distil head



Receiving adapter

Identification of Organic Compounds

It is identified of the molecular structure of the chemical organic compounds. Many of organic compounds may contain impurities which are by product results during storage under unsuitable condition or decomposed of compound. When identify of organic compounds. The compounds must be pure as they will affect the chemical and physical properties. The following steps were using to identify your unknown compounds: -

I. Physical Properties:

a. Physical state of the compound: - liquid or solid.
b. Color of the compound.
c. Odor: - bad smell or nice smell.
d. Determine the melting point, boiling point depending on the physical state of the compound.
e. Determination of solubility class using H_2O, ether, NaOH solution, $NaHCO_3$ solution HCl dil, conc. H_2SO_4 it's very important step and gives an idea about the unknown and its functional group.

II. Chemical Properties:

a. The effect of the compound on the litmus paper: -
   i. Litmus blue turns red - acidic compound.
   ii. Litmus red turns blue - basic compound.
   iii. Litmus no change color – neutral compound.

b. Sodium fusion: - elemental analysis for N, S, halogen (Cl, Br, I) in compound.

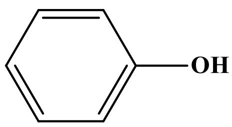
c. Determination of functional group by general tests and specific tests. Functional groups of organic compounds divided into: -

1. Compounds have (O) atom: alcohol, phenol, aldehyde, ketone, carboxylic acid and ester.
2. Compounds have (N) atom: - amine, amide, nitro compounds
3. Hydrocarbon compounds.
4. Unsaturated compounds.

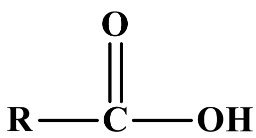
Alcohol

R—OH

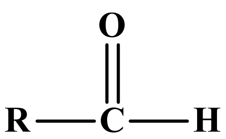
Phenol



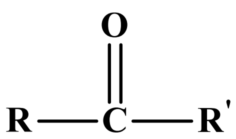
Carboxylic acid



Aldehyde



Ketone



Amine

R—NH_2

III. *Instrumentation:*

a. IR (infrared radiation).
b. UV (ultraviolet radiation).
c. NMR (nuclear magnetic resonance).

EXPERIMENT 1

MELTING-POINT DETERMINATION

The melting point (m.p) of a substance is one of the physical properties that used to identify a substance. ***The melting point*** of solid crystalline compound is the temperature at which the solid begins to change into liquid under a pressure of one atmosphere, ***or*** it is the temperature at which there is equilibrium between liquid and solid states.

The melting point and the freezing point for a pure substance are identical. The melting point is considered as a criterion of purity of a compound and is useful for identification of organic compound.

A pure crystalline organic compound usually has a sharp and characteristic melting point rang of (0.5-1) °C. ***The melting point range*** is determined by recording the difference between the temperature where the sample state to melt T_1 and the temperature where melting is complete T_2. Actual melting begins when the first drop of liquid becomes visible. You may recall that impurities depress the melting (freeing) point of substance. They also increase the range of melting. When a sample melts at a lower-than-expected temperature over an extended range, this is a sign that the sample was not pure. The same idea will apply for pure organic compound, if they undergo slight decomposition that decrease the melting point and increase the melting rang.

A technique known as ***a mixed melting point*** may be used as additional evidence in identifying a given compound. Suppose that you have two samples (A and B) with the same melting point. If you do not know whether these two samples are the same or different, you can mix them and measure the melting point for the resultant mixture. If A and B are different, one of them will act as an impurity for the other and the measured melting point will be lower than the original one with a higher melting point range. On the other hand, if the measured melting point is the same as the original one, A and B represent the same compound.

There are two methods used for determination of melting point:

i. Capillary tube method.
ii. Apparatuses method.

****

Melting point Procedure:

A. Capillary tube method

1. A (0.1 gram) of the dry organic substance is placed on a glass slide (watch glass) and finely powdered with glass spatula. The open end of the capillary tube is pushed into the powder, the solid is then shaken down the tube by tapping the closed end on the bench top until most of the solid vibrates down to the closed end, and your sample should be about 3-5 mm high.
2. The capillary tube is attached to a thermometer (by a rubber ring) as shown in (fig. 1) in such a way that its closed end is attached to the bottom of the thermometer's bulb.

3. Then both of them are placed in an oil bath (paraffin, glycerin), the rubber ring should be above the surface of the oil bath.
4. Heating is started gradually with continuous stirring.
5. The range between the temperature at which the powdered solid inside the capillary tube beings to liquefy T_1 and the temperature at which a clear liquid is observed inside the capillary tube T_2 is recorded as observed melting point range.
6. After completing the experiment, the oil liquid must be allowed to cool before using it again.

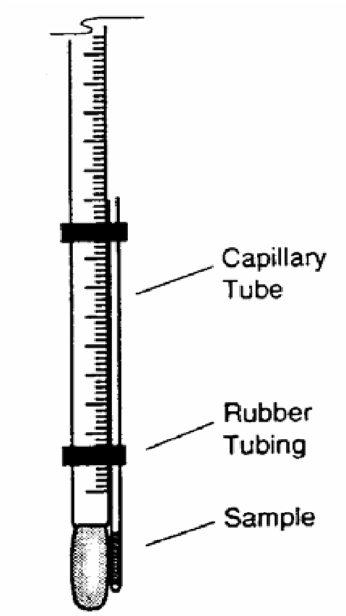


Fig.1- Thermometer for the melting point

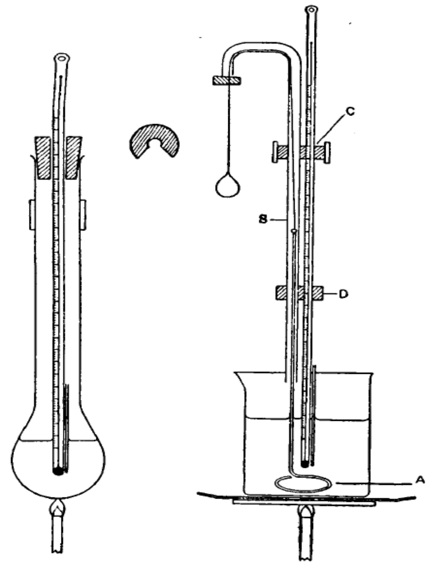


Fig.2- Apparatus for melting point determination

B. Melting point apparatus: -

The electrically-heated melting point apparatus (fig.3) is a precision instrument designed for the determination of single or mixed melting point of solid up to a maximum temperature of 350 °C.

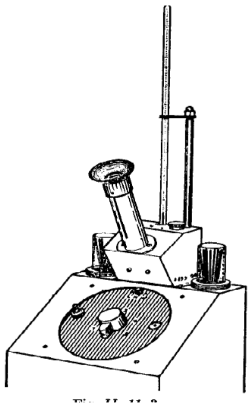


Fig.3- electrically-heated melting point apparatus

1- Make sure the melting temperature apparatus has cooled to near room temperature if it has been used recently.
2- Insert your capillary tube into a slot that will hold the tube next to the heating block.
3- Make sure the thermometer is set to zero and switch “ON”, (the on-off switch for the heating block).
4- Look through the eyepiece to see the solid sample as the temperature is increasing.
5- Observed both the temperature at which melting begins T_1 and at which the last crystal disappears T_2 report a range such as 88-90°C, turn off the apparatus.
6- Once a melting point range is determined, prepare another capillary tube (tubes should only be used once and then discarded).

EXPERIMENT 2

BOILING-POINT DETERMINATION

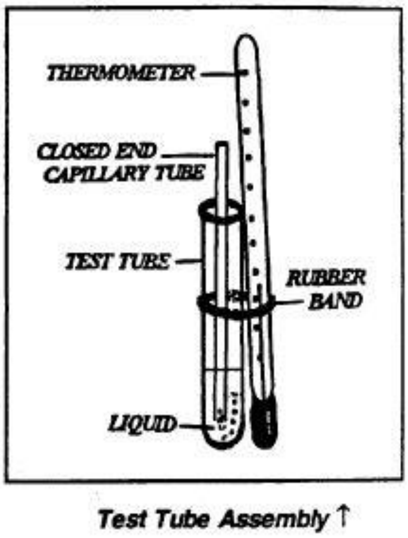
The poling point (B.p) of an organic liquid is the temperature at which its vapor pressure equals the atmospheric pressure over the liquid, ***or*** it's the temperature at which the vapor and liquid phases are in equilibrium of a given pressure. The boiling is considered as a criterion of purity of a compound and is useful for identification of organic compound.

Similar to the melting point the boiling point may be sharp or may vary over a temperature rang. Pure liquid has sharp boiling point while mixtures show a boiling point range.

The atmospheric pressure plays an important role in determination of the boiling point correctly. Reduction of the pressure leads to a decrease or a depression in the boiling point and vice versa.

Boiling point Procedure:

1- A (5cm) capillary tube closed from one end is inverted upside down and is attached to a thermometer by a rubber ring.
2- Place them in a clean and dry test tube containing a small quantity of a liquid whose boiling point is to be measures (the rubber ring should be above the surface of the liquid).
3- The whole assembly is to be placed in an oil bath.
4- Start heating with continuous stirring until a rapid stream of bubbles comes out of the capillary tube (inside the liquid).
5- Remove the flame and allow the oil bath to cool so that the bubble stream will become slower and slower as the temperature drops until a point is reached at which bubbling ceases and the liquid starts to rise inside the capillary tube.
6- Record this temperature as the boiling point.



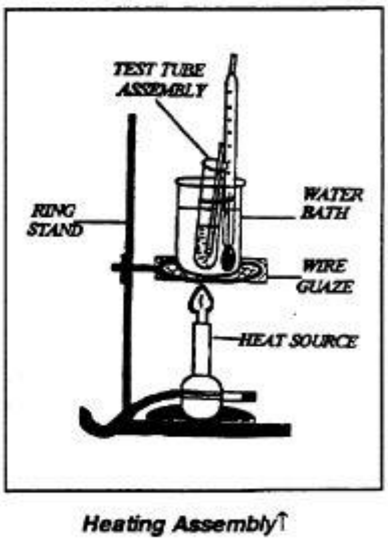


Fig.4-(a) Thermometer for the Boiling (b) Apparatus for Boiling point determination

EXPERIMENT 3

SOLUBILITY CLASSIFICATION

Solubility is the property of a solid or liquid chemical substance called (solute) to dissolve in liquid called (solvent). Solubility is controlled by intermolecular forces. **Solvent used:** H_2O, NaOH 5%, $NaHCO_3$ 5%, HCl dil., and H_2SO_4 con.

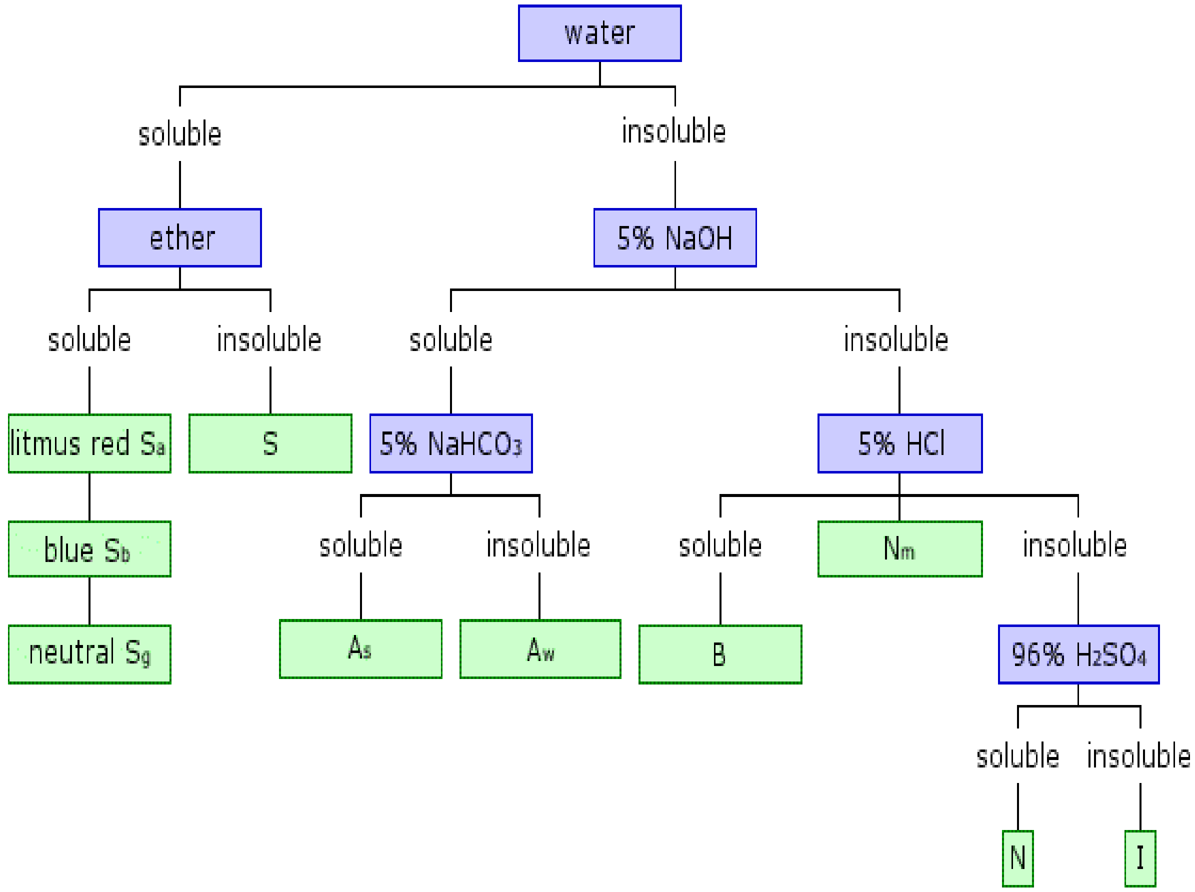
"**Like dissolves like**" is simple rule for solubility of organic compounds and it is based on the **polarity** of the systems. This statement indicates that a solute will dissolve best in a solvent that has a similar chemical structure to itself for example: - polar molecules dissolve in polar solvents (*e.g.* water, alcohols) and non-polar molecules dissolved in non-polar solvents (*e.g.* the hydrocarbon, hexane). This is showing why ionic compounds like table salt (sodium chloride) dissolve in water (polar) but not in most organic solvents. The polarity of organic due to the presence of electronegative atoms (*e.g.* N, O) which is found in polar functional groups such as amines ($-NH_2$) and alcohols (-OH).

In solubility classification will be obtained:

i. **Identification of functional group: -** unknown is partially soluble in water indicates that a polar functional group is present if not soluble indicate is non-polar functional group and leads to more specific information about the functional group present as show in scheme of solubility.

ii. **Information about molecular size of compounds: -** with fewer than five carbon atoms is water soluble, where as the higher is not.

Flow Chart for Classes of Organic Compounds

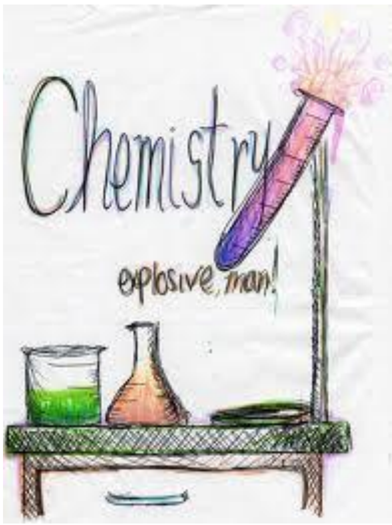


Class	Functional Group Possibilities
S_a	monofunctional carboxylic acids (≤5C), aryl sulfonic acids
S_b	monofunctional amines (≤6C)
S_g	monofunctional alcohols, aldehydes, ketones, esters, nitriles, and amides (all ≤5C)
S	salts of organic acids, amine hydrochlorides, amino acids, polyfunctional compounds with hydrophilic functional groups
A_s	strong organic acids: carboxylic acids (>6C), phenols with electron-withdrawing groups in the ortho and/or para position(s), diketones
A_w	weak organic acids: phenols, enols, oximes, imides, sulfonamides, thiophenols (all >5C), diketones, nitro compounds with hydrogens
B	aliphatic amines (≥8C), anilines (only one phenyl group attached to N), some ethers

N_m	miscellaneous neutral compounds containing N or S (>5C)
N	alcohols, aldehydes, ketones, monofunctional esters (>5C but <9C), ethers, epoxides, alkenes, alkynes, some aromatic compounds (with activating groups)
I	saturated hydrocarbons, haloalkanes, aryl halides, other deactivated aromatic compounds, diaryl ethers

Note: -

- Soluble: - solid compound dissolved in solvent.
- Insoluble: - solid compound not dissolved in solvent.
- Miscible: - liquid compound dissolved in solvent.
- Immiscible: - liquid compound not dissolved in solvent.



Solubility Test Procedure:

1. **Water Solubility.** Place 0.05 mL or 25 mg of compound in test tube, and add 0.75 mL of water. Shake test tube vigorously after the addition if not water soluble heated the solution, then let cool in room temperature if still soluble, the acid-base properties of the compound should be determined with litmus. If the compound is not soluble go to STEP (2).

2. **5% NaOH Solubility.** Place 0.05 mL or 25 mg of compound in test tube, and add 0.75 mL of NaOH solution. Shake test tube vigorously after the addition of If NaOH soluble, go on to STEP (3); If not proceed to STEP (4).

3. **$NaHCO_3$ Solubility.** Place 0.05 mL or 25 mg of compound in test tube, and add 0.75 mL of $NaHCO_3$ in small portions. Shake test tube vigorously after the addition of each portion of solvent. If produced bubbles then it is a strong organic acid. If not that mean is a weak organic acid.

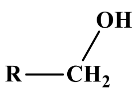
4. **5% HCl Solubility.** Place 0.05 mL or 25 mg of compound in test tube, and add 0.75 mL of HCl solution. Shake test tube vigorously after the addition If HCl soluble, then it is an organic base. If not HCl soluble, then go on to STEP (5).

5. **H_2SO_4 Solubility.** Place 0.6 mL of H_2SO_4 in test tube, and add 0.05 mL or 25 mg of compound. Shake test tube vigorously. If H_2SO_4 soluble, then it is a very weak based compound. If not H_2SO_4 soluble, then it is neutral compound.

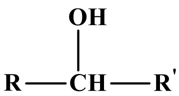
EXPERIMENT 4

IDENTIFICATION OF ALCOHOL COMPOUNDS

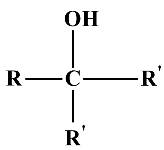
- Alcohols are compounds contain hydroxyl groups (OH) attached to carbon atoms (alkyl group = R). Suffix (-ol) used in the molecule of a hydroxyl group.
- Alcohols divided into three types:
  1. **Primary alcohol: -** (-OH) are attached to carbon atom that attached to one carbon atom.
  2. **Secondary alcohol: -** (-OH) are attached to carbon atom that attached to two carbon atoms.
  3. **Tertiary alcohol: -** (-OH) are attached to carbon atom that attached to three carbon atoms.



1^o alcohol



2^o alcohol



3^o alcohol

- Some of alcohol compounds: - ethanol, methanol, isopropanol, tert-butanol, cyclohexanol.

Physical properties:

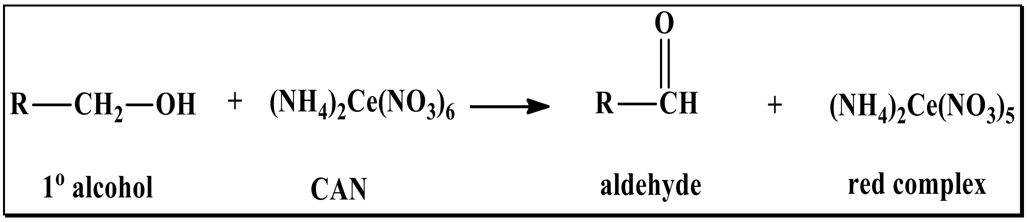
Colorless liquid, have characteristic odor, miscible in water, toxic, burned by blue flame.

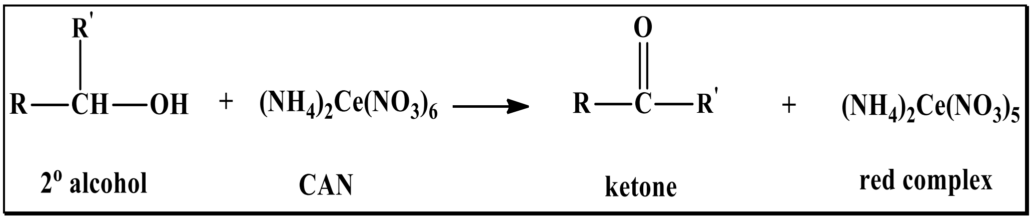
Chemical properties:

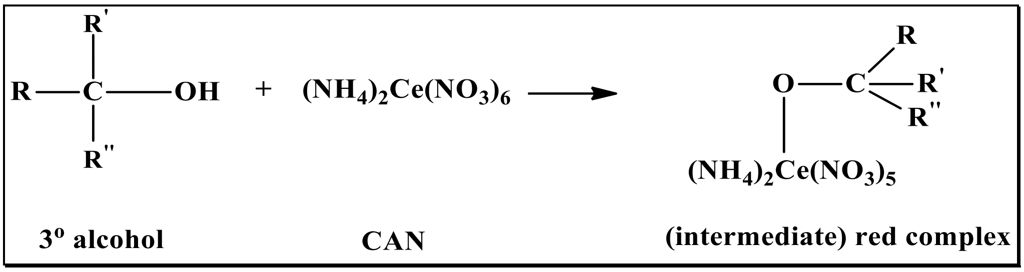
1. **The effect of the compound on the litmus paper: -** They are neutral compounds because they don't change the color of litmus paper.

2. **General test by (ceric ammonium nitrate test):**

(CAN) oxidizing agent that oxidized alcohol compounds to give positive result (red complex) by oxidation –reduction reaction. Phenol compounds give negative result brown to greenish brown precipitate while other functional group give yellow color.

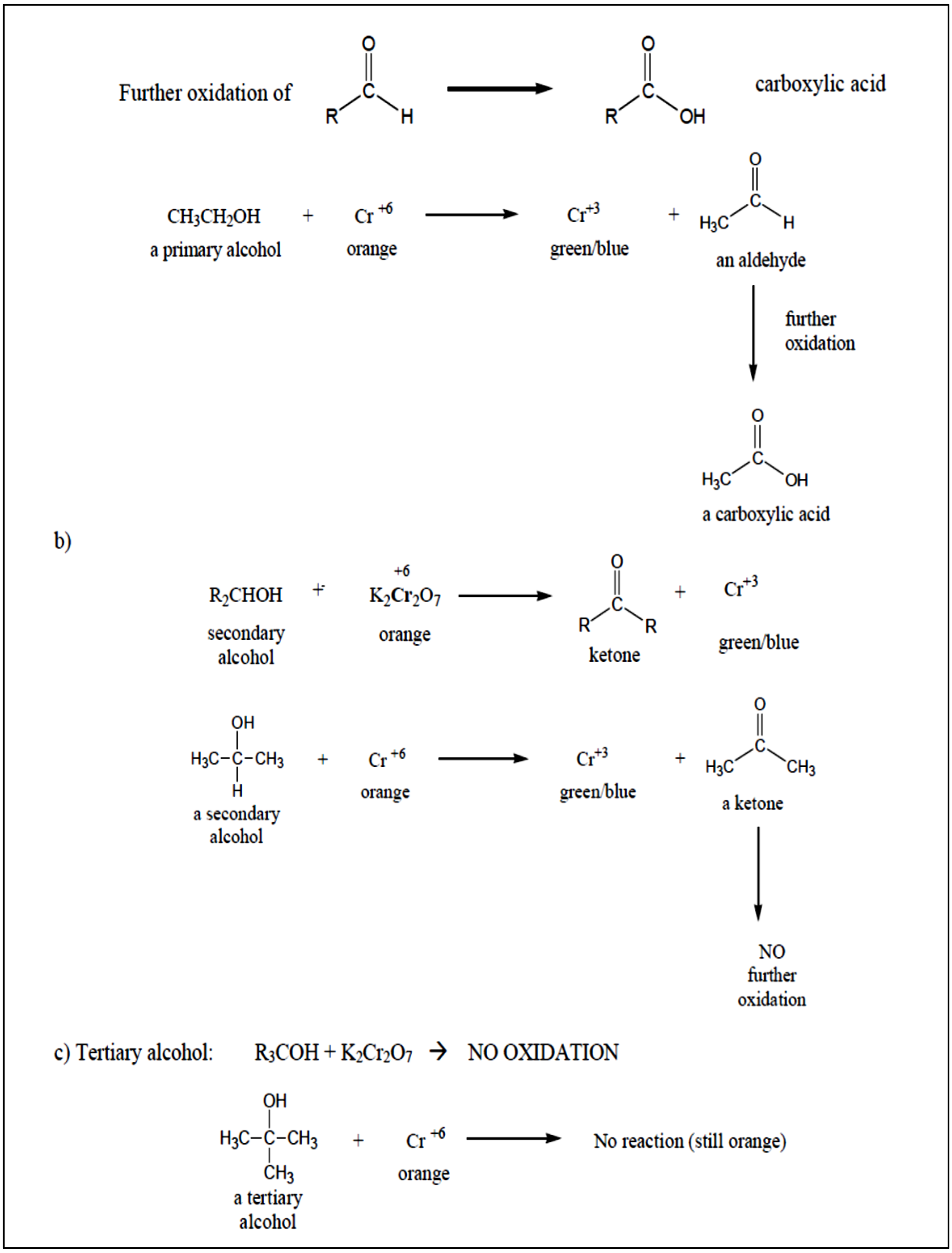






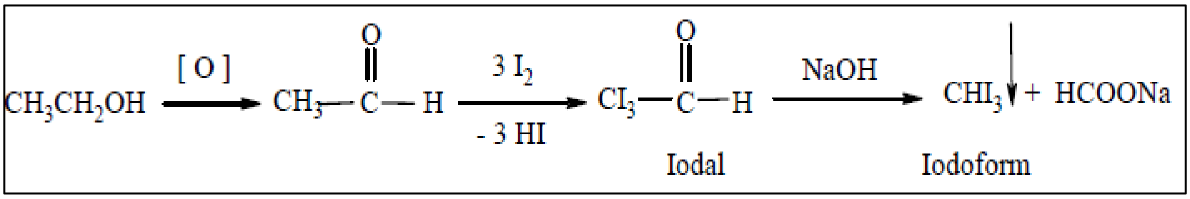
3. **Oxidation test:**

It was found that Primary alcohols oxidize to aldehyde while the Secondary alcohols oxidizing to ketone, but tertiary alcohols not oxidized when used strong oxidants such as $K_2Cr_2O_7$ in H_2SO_4 is according to the following equations.



4. Iodoforms Test:

This test is specific for terminal CH_3 group of alcohols. alcohol oxidized to aldehyde or ketone then addition (I_2) to ($-CH_3$) to form triiodo derivatives (Iodal) then formation (CHI_3) and carboxylic salt as pale-yellow ppt.



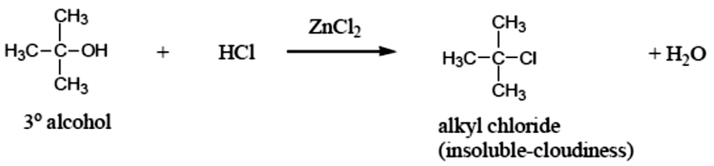
5. The Lucas test:

This test distinguishes among the three types of alcohols (1°, 2°, and 3°), by the speed with which they react. The reaction is a replacement reaction, where a Cl from (con. HCl+ $ZnCl_2$) replaces the hydroxyl group on the alcohol.

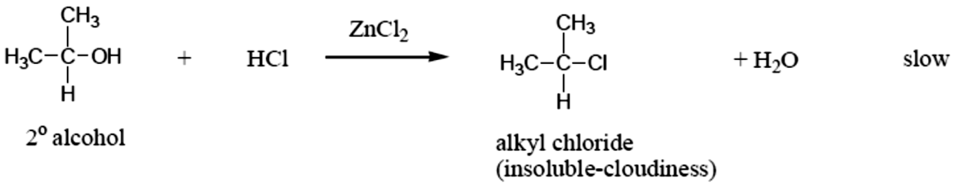
$$R{-}OH + H{-}Cl \xrightarrow{ZnCl_2} R{-}Cl + H_2O$$

alky chloride insoluble

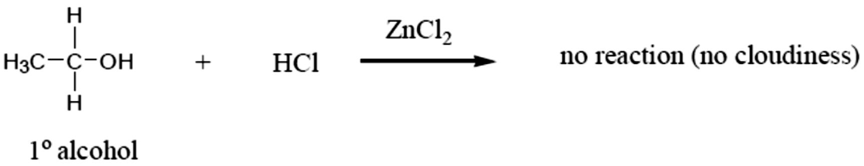
3° alcohol: R_3COH + HCl ($ZnCl_2$) → R_3Cl (alkyl chloride) + H_2O Very Fast
(insoluble/cloudiness)



2° alcohol: R_2CHOH + HCl ($ZnCl_2$) → R_2CHCl (alkyl; chloride) + H_2O Slow
(insoluble/cloudiness)



1° alcohol: RCH_2OH + HCl ($ZnCl_2$) → No reaction/very very slow



- ✓ 3° alcohols react very fast with the Lucas reagent (HCl mixed with$ZnCl_2$), and will turn cloudy almost immediately.
- ✓ 2° Secondary alcohols do react, but more slowly and must be heated in a water bath in order to react and turn cloudy.
- ✓ 1° Primary alcohols react so slowly (even in a warm water bath) that NO REACTION is observable. The color will stay the same without any precipitate is a **negative** result.

Alcohols tests Procedure:

1. **Ceric ammonium nitrate: -** In test tube add (4-5) drops of alcohol compounds, dissolved in water if not dissolved added few drops of dioxan. Add (2-4) drops of (CAN) shake the mixture well and observe the result. Positive result is red color.

2. **Oxidation test: -** In a test tube put 1ml of alcohol (ethanol) then 1ml of potassium dichromate $K_2Cr_2O_7$ and drops of conc. H_2SO_4.The green/blue color is chromium sulphate $Cr_2(SO_4)_3$ which formed due to the oxidation of primary or secondary alcohols.

3. **Iodoform test: -** in a test tube add 4 drops or (0.1g from solid) alcohol to 1ml of H_2O (if immiscible with water add 5ml of dioxin) then 3ml of iodine solution & heat in water bath for 3 min. then cool & add 10% NaOH drop wise till the color is pale yellowish ppt of iodoform is produced.

4. **Lucas's test: -** Add to one of alcohol few drops of Lucas reagent (6 drops) shakes well and observed the results: -

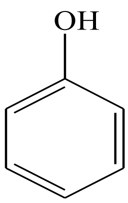
- ✓ 3° alcohols react very fast with the Lucas reagent (HCl mixed with$ZnCl_2$), and will turn cloudy almost immediately.
- ✓ 2° Secondary alcohols do react, but more slowly and must be heated in a water bath in order to react and turn cloudy.
- ✓ 1° Primary alcohols react so slowly (even in a warm water bath) that NO REACTION is observable. The color will stay the same without any precipitate is a **negative** result.

EXPERIMENT 5

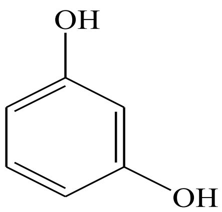
IDENTIFICATION OF PHENOLS COMPOUNDS

Phenol is aromatic compound contains one or more hydroxyl group (OH)connected directly to aromatic nucleus. Phenol classified according to the number of hydroxyls contained group into:

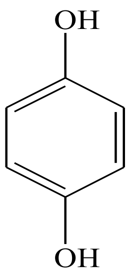
- Monohydric phenol
- Dihydric phenol
- Trihydric phenol



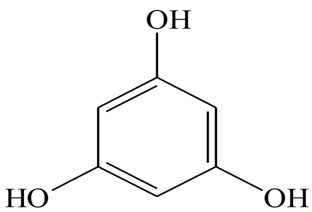
Phenol



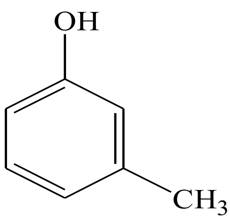
Resorcinol



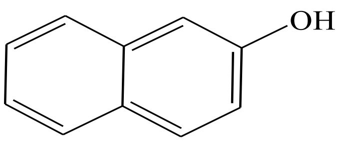
Hydroquinune



Benzen-1,3,5-triol



m-cresol



Naphthalen-2-ol

Physical Properties:

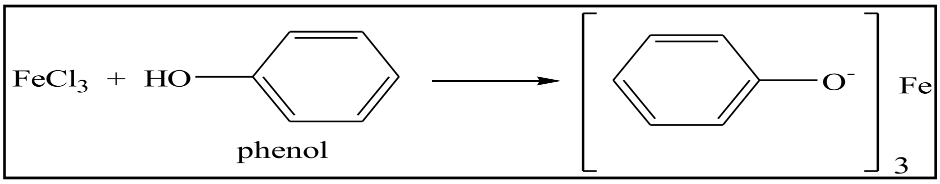
Most phenol is solids in pure state (except m-cresol), which turned to light red when exposed to air it has characteristic odor. Soluble in water, alcohols, ethers, and sodium hydroxide, ignite by yellow smoky flame.

Chemical Properties:

1. Ferric chloride test:

Phenols react with ferric chloride to give colored compounds due to the presence of [-C=C-OH] (enol) group. Indeed, this reaction is considered as a test for any compound with enol group the results:

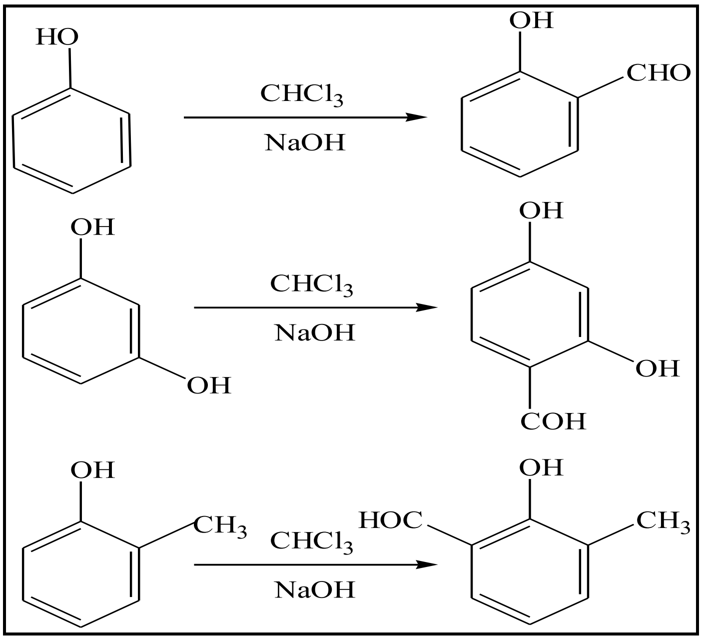
- Violet color→phenol or *m*-cresol
- a deep violet color→ resorcinol
- greenish blue → *o*- and *p*-cresol
- deep green → Hydroquinone
- no characteristic color→β- Naphthol



2. Riemer - Tiemann reaction:

Treatment of phenol with chloroform and aqueous sodium hydroxide solution introduces an aldehyde group (-CHO) into the aromatic ring at the ortho- or para-positions.

- If no color or yellow → Phenol
- If a red fluorescent→ Resorcinol
- If a brown color → hydroquinone
- if blue color change to green→β- Naphthol
- If a deep orange color → *o*-cresol
- If a pale orange color → *m*-cresol
- If a yellow color → *p*-cresol



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Phenols Test Procedure:

1. **Ferric chloride test: -** few crystals of the solid phenol or few drops dissolved in ethanol then add 2 drops of (5%) ferric chloride solution and observe the resulting color.

2. **Riemer - Tiemann reaction**: - few amounts of phenol add 1 ml of 30% NaOH solution and 1 ml of chloroform, heat on water bath, and observe the color.