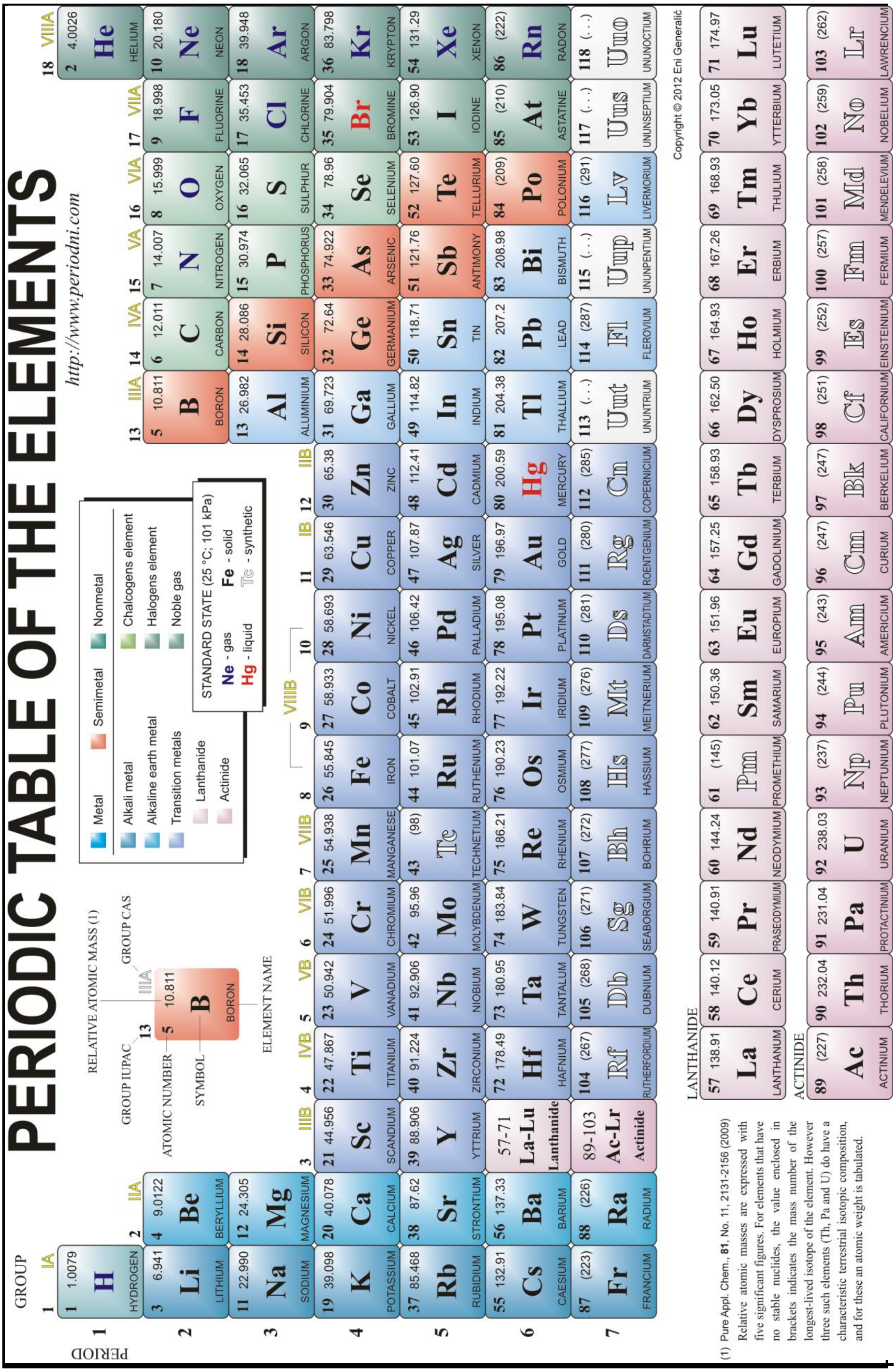
Periodic Table



PERIODIC TABLE OF THE ELEMENTS

http://www.periodni.com

PERIOD	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.38 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.798 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.96 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (267) Rf RUTHERFORDIUM	105 (268) Db DUBNIUM	106 (271) Sg SEABORGIUM	107 (272) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (276) Mt MEITNERIUM	110 (281) Ds DARMSTADTIUM	111 (280) Rg ROENTGENIUM	112 (285) Cn COPERNICIUM	113 (...) Uut UNUNTRIUM	114 (287) Fl FLEROVIUM	115 (...) Uup UNUNPENTIUM	116 (291) Lv LIVERMORIUM	117 (...) Uus UNUNSEPTIUM	118 (...) Uuo UNUNOCTIUM

LANTHANIDE

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.05 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

(1) Pure Appl. Chem., **81**, No. 11, 2131-2156 (2009)
Relative atomic masses are expressed with five significant figures. For elements that have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element. However three such elements (Th, Pa and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

General instructions

ان منهج السلامة في المختبر يتضمن رغبة الشخص العامل لانجاز عمله بطريقة صحيحة, وهناك بعض الارشادات العامة للعاملين في المختبرات ومنها الالمام بطريقة العمل في الحالات الاضطرارية او الفجائية مثل اجهزة اخماد الحريق وصندوق الاسعافات الاولية , ويمنع العمل الفردي في الاعمال المحذورة , ويمنع التعامل مع مواد او اجهزة لم يتم الاطلاع على كيفية عملها, يجب ارتداء صدرية المختبر و النظارات الزجاجية بصورة دائمية مع توفير منشفة و اسفنجة و صابونة, ويمنع التدخين و الاكل و الشرب داخل المختبر . يجب ان يتجنب العامل في المختبر اضافة الماء الى الحامض او القاعدة لان ذلك يؤدي الى حدوث حرائق ولاكن يمكن اضافة الحامض او القاعدة الى الماء

ان تسجيلا كاملا ودقيقا لنتائج العمل المختبري مهم جدا لكل طالب في المختبر ويجب ان يحتفظ الطالب بسجل لعمله في المختبر يحتوي على وصف كامل و دقيق لكل تجربة قام بها. ان التفصيل في الكتابة يجب ان يكون كافيا حتى يتمكن باحث اخر من اعادة العمل و معرفة نتيجة التجربة بصورة مضبوطة. في ادناه مقترحات تنظيمية لسجل مختبري لتسجيل اية تجربة:

1. ابدأ بتسجيل كل تجربة على صفحة جديدة مدونا في السطر الاول تاريخ وعنوان ورقم التجربة المراد القيام بها.
2. اكتب المعادلة الكيميائية الموزونة للتفاعل و المصدر المتبع في التجربة
3. يمكنك كتابة كميات المواد الكيميائية المستعملة في جدول او ادراجها في وصف التجربة ويجب ذكر اوزان المواد الكيميائية و عدد المولات و حجوم المذيبات المستعملة.
4. يجب ان تحتوي الطريقة العملية على:

أ- وصف لكل جهاز غريب و جديد, واذا كانت هناك طريق تبريد معينة او خاصة فيجب وصفها او ذكرها.

ب- التسلسل في اضافة الكواشف واوقات الاضافة و مدد التفاعل.

ت- درجات الحرارة وخروج الغازات وتغيرات الالوان

ث- طريقة العمل وبضمنها المذيبات المستعملة.

ج-وزن منتوج المادة الخام و كذلك المادة النقية ودرجات انصهار المواد الصلبة.

<u>ينظم تقرير كل تجربة حسب الترتيب التالي</u>

اسماء الطلبة المشاركين: The names of participating students

اسم التجربة : Name of experimental

تاريخ اجراء التجربة: Data of experimental

الغرض من التجربة: Purpose of experimental

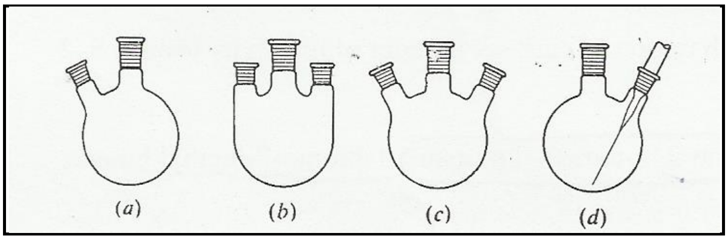
الادوات و المواد المستخدمة: Chemical and apparatus

المناقشة (متضمنة المعادلات ان وجدت او التركيب): Discussion

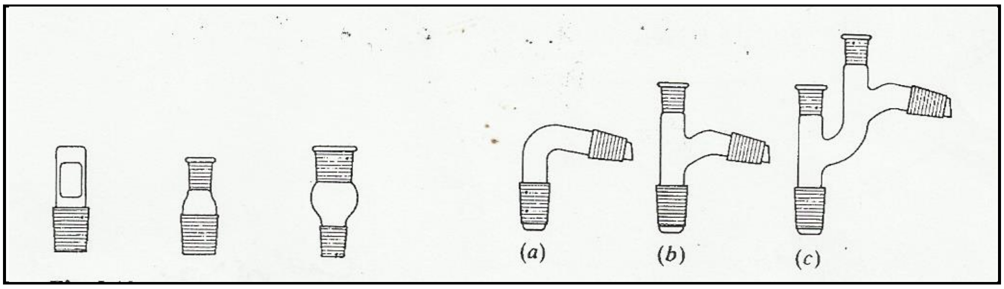
الحسابات و النتائج (متضمنا القوانين وجداول الكشوفات):

Results and calculations

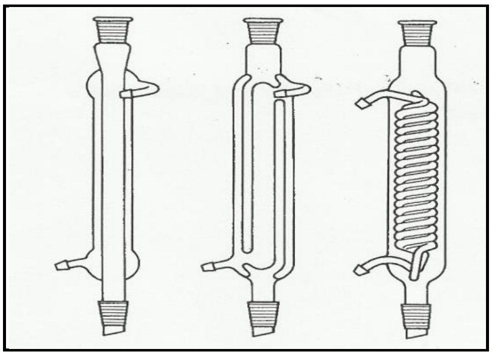
Classes and Apparatus

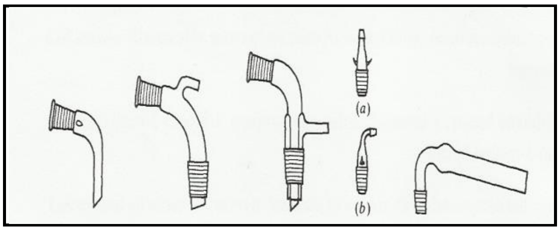


Round – bottomed flasks



Joint adapters distillation heads



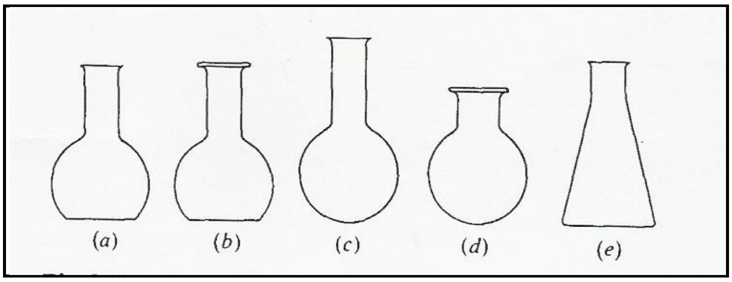


Condenser (1) (2) (3)

(1): receiver adapters or connectors ;

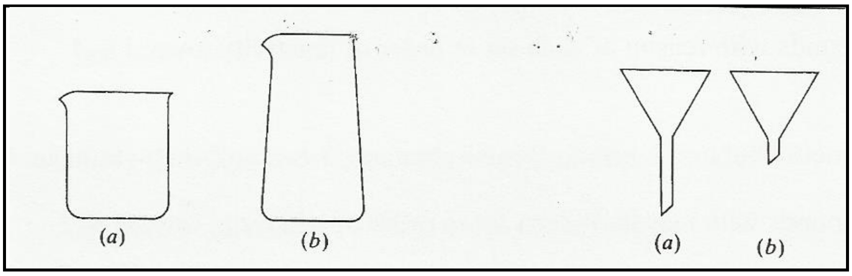
(2): a,b, rubber tubing adapters ;

(3) calcium chloride guard – tube

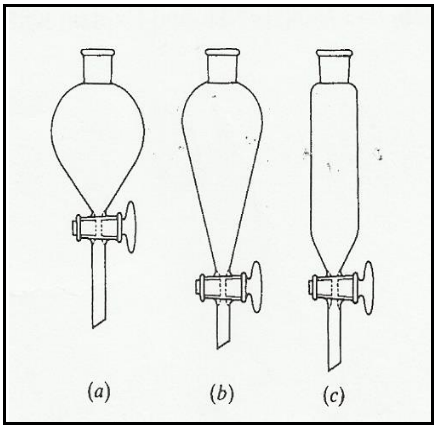


a,b : flat bottomed flasks ; c, d: round bottomed flasks

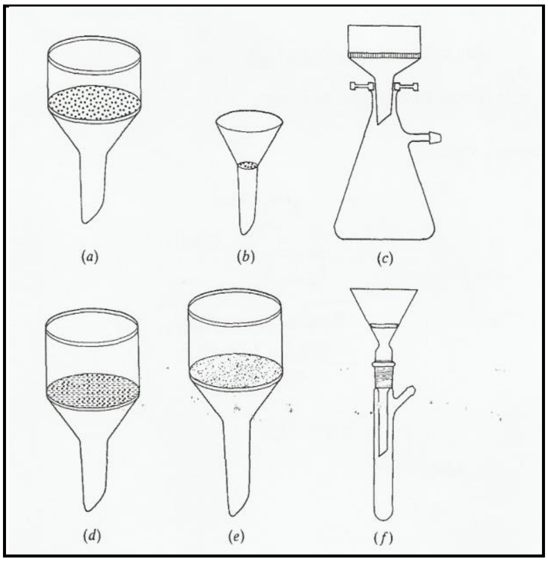
e: short – necked boiling flask



a : beaker ; b : conical beaker   /   a: long funnel ; b: short funnel



Separatory funnels



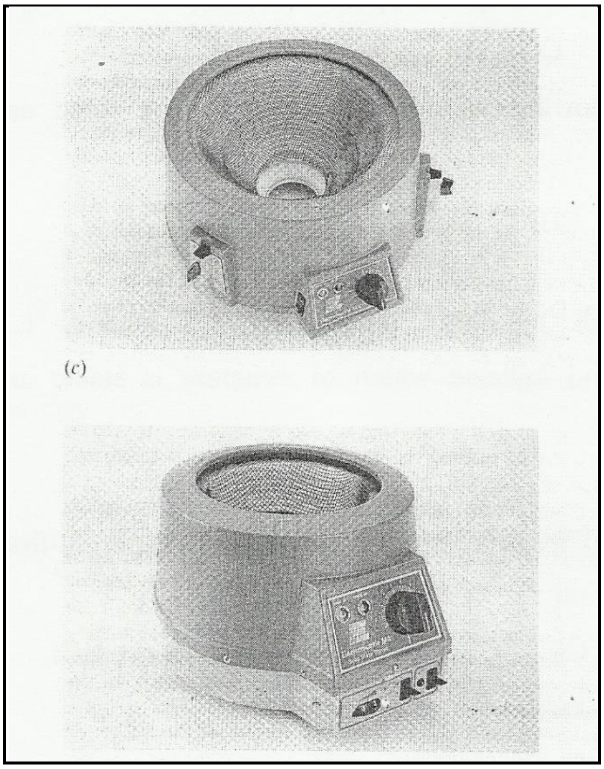
a: Buchner funnel; b : Hirsch funnel;

c: Buchner funnel and flask

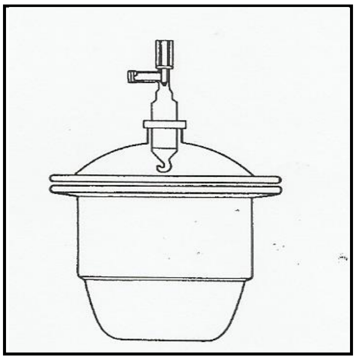
d: slit sieve funnel;

e : sintered glass funnel ;

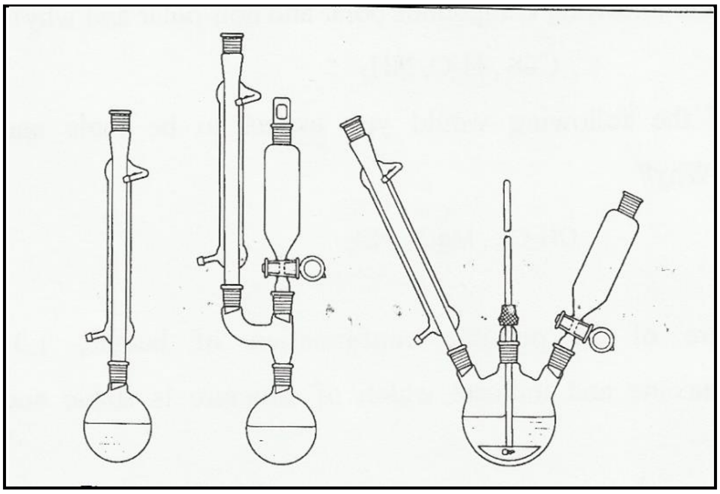
f: Buchner funnel or Hirsch funnel   with glass joints



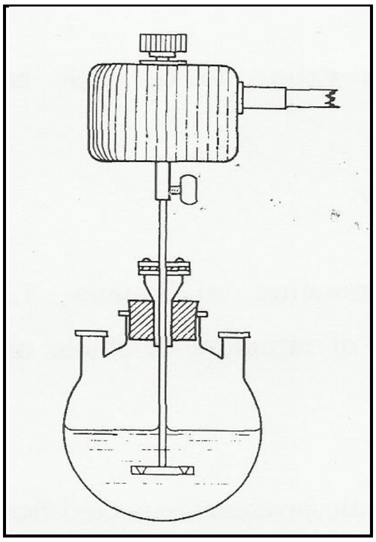
Heating mental



Desiccators



(a) (b) (c)

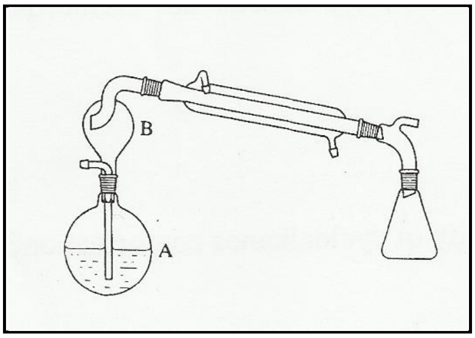


Mechanical shaking

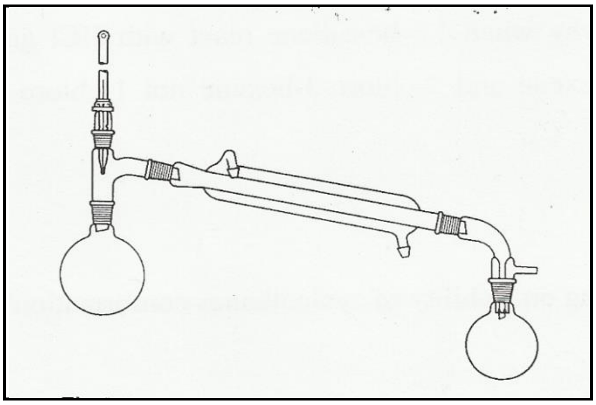
a : Heating a reaction mixture under reflux with addition of liquid

b: Heating a reaction mixture under reflux with addition of liquid

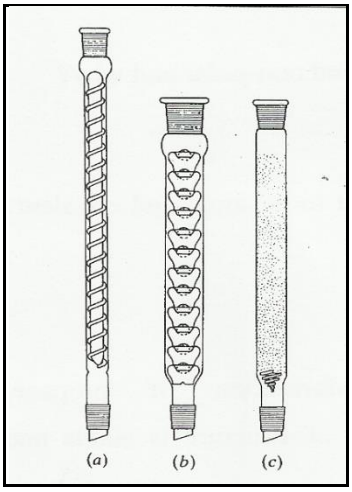
c: Heating a reaction mixture under reflux with addition of liquid and with stirring



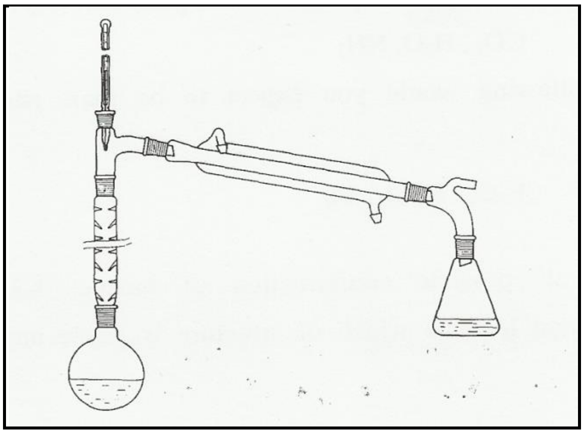
Steam distillation



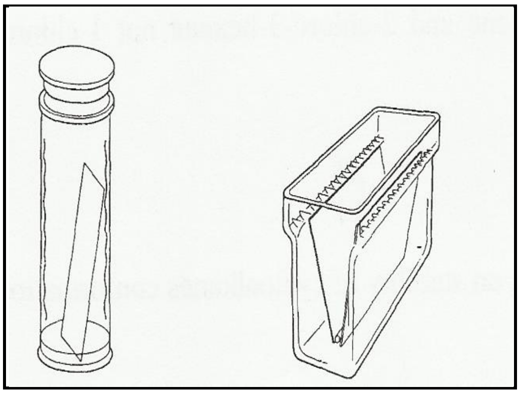
simple distillation at atmosphere pressure



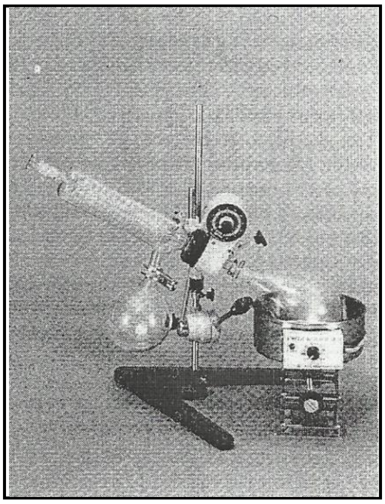
Fractional columns



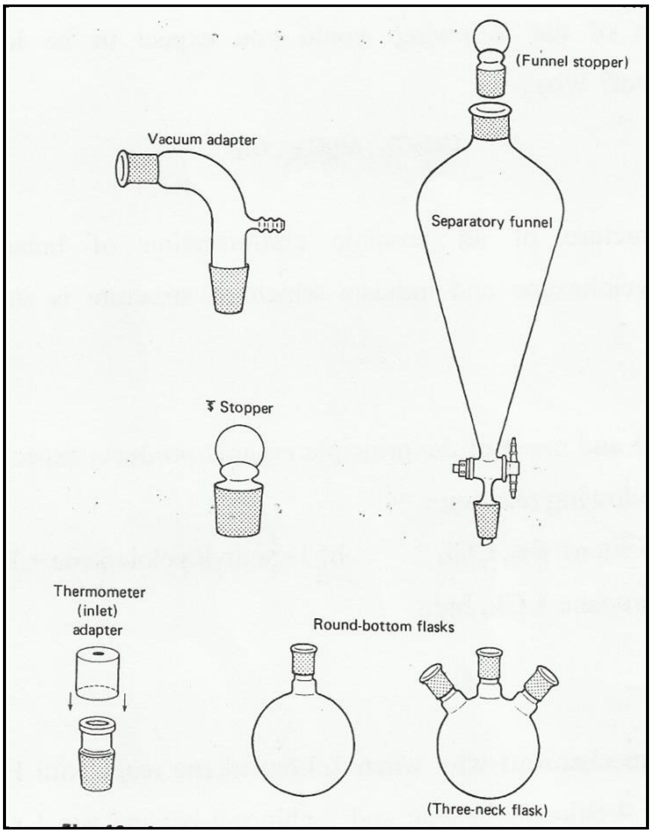
fractional distillation at atmospheric pressure

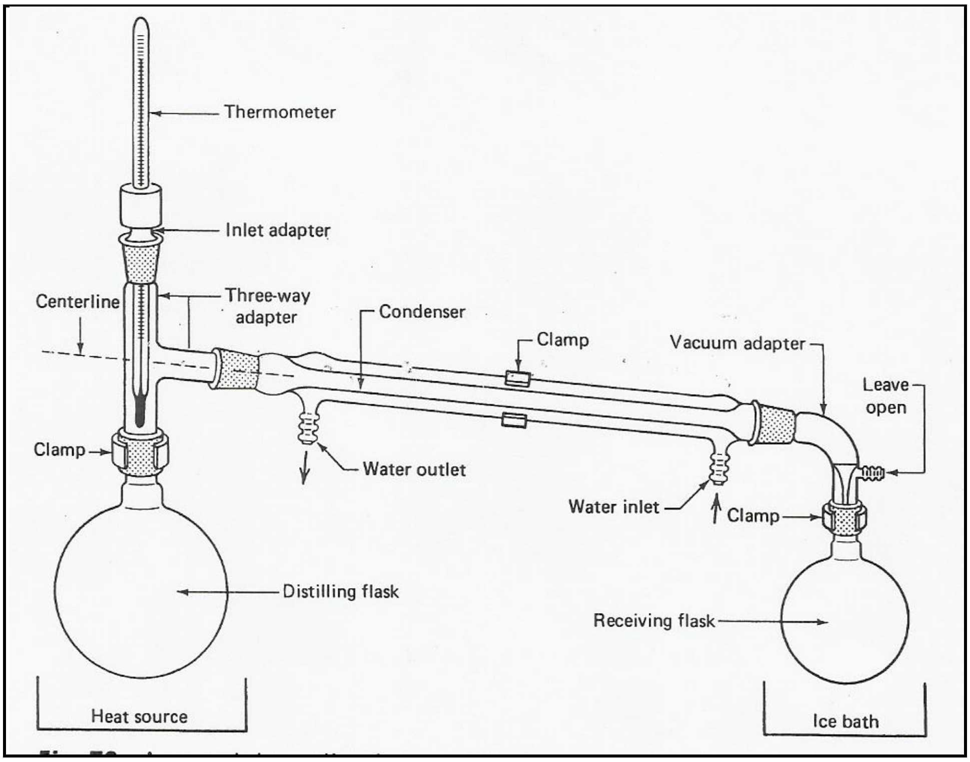


Cylindrical glass jar

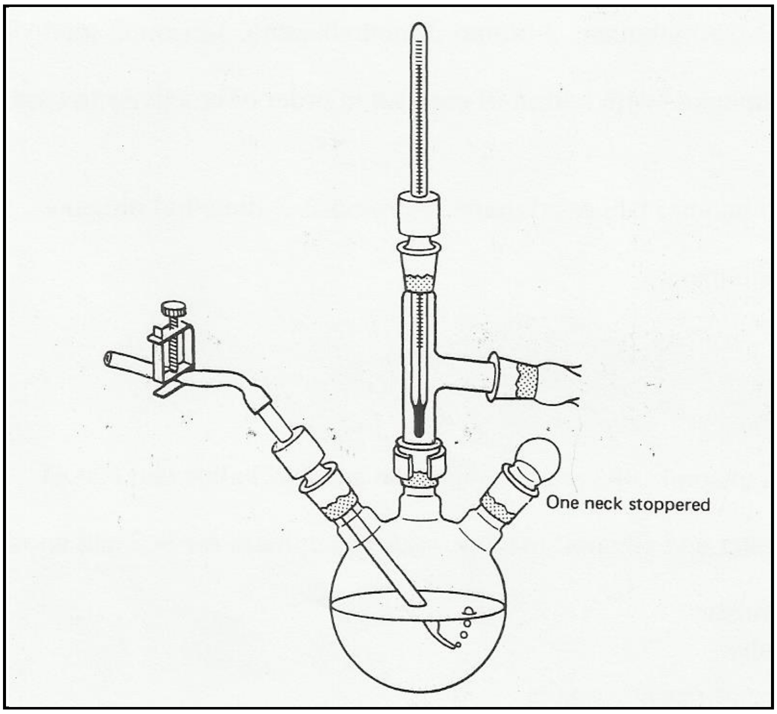


Vaccum distillation

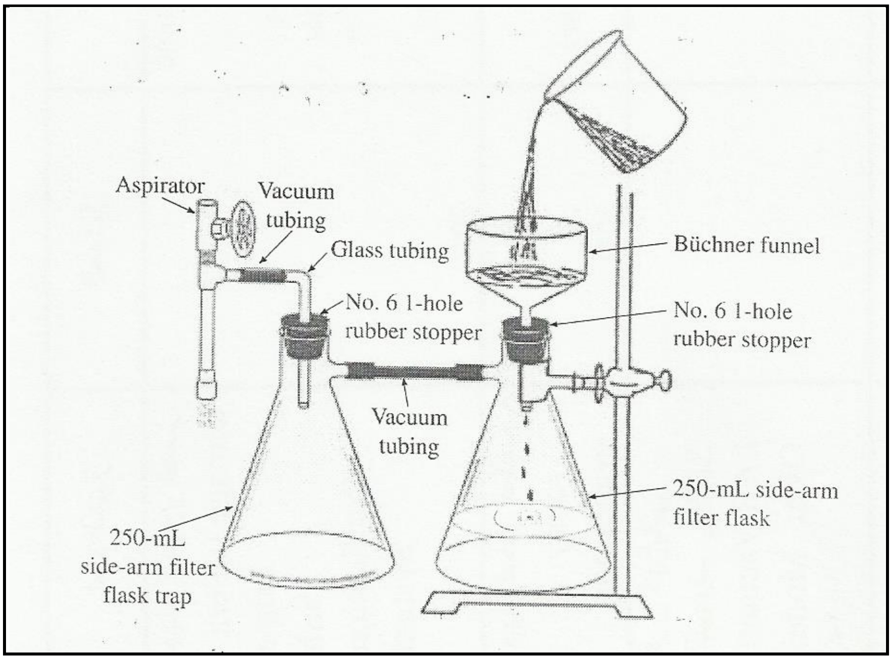




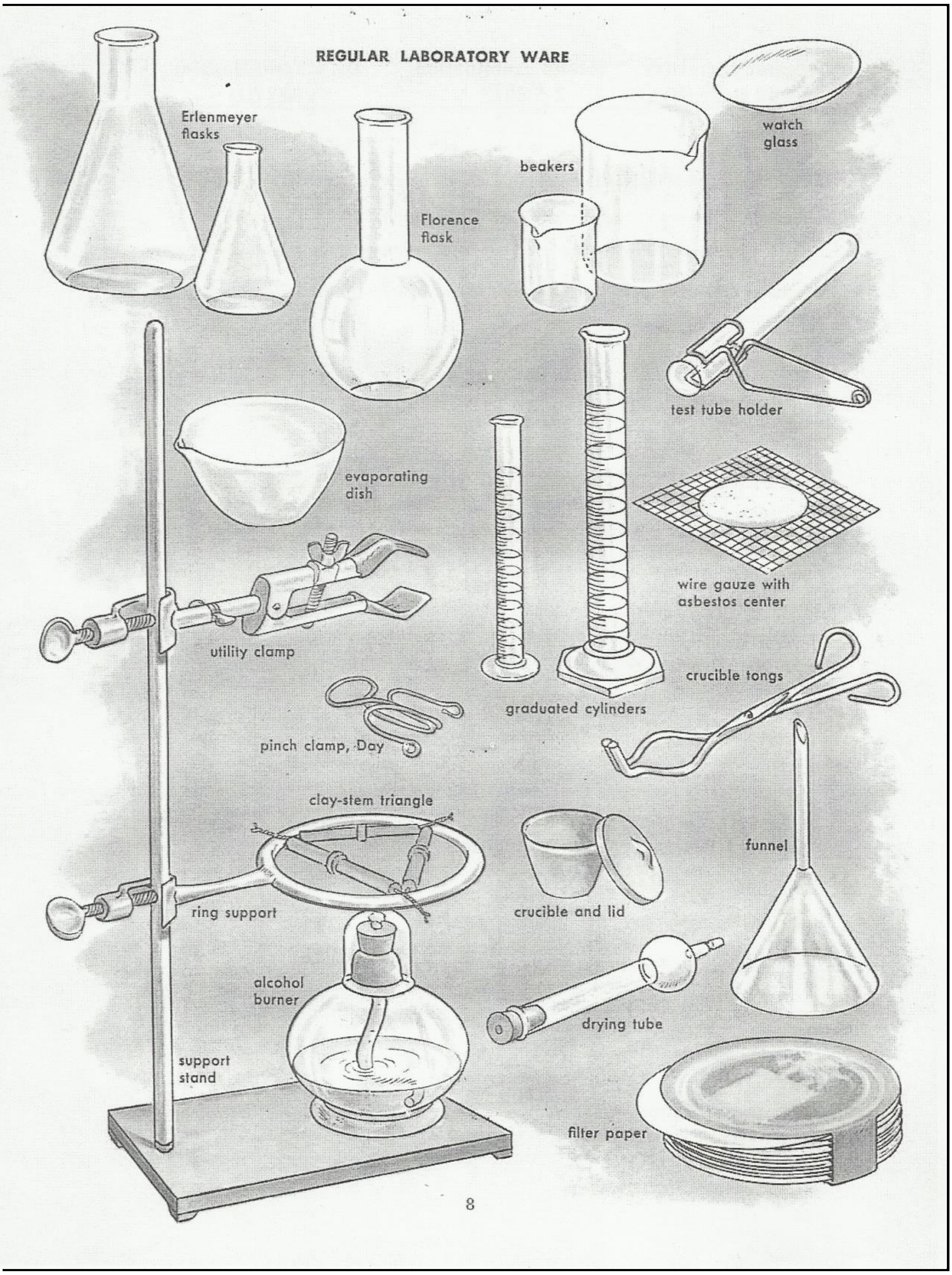
Simple distillation at atmosphere pressure

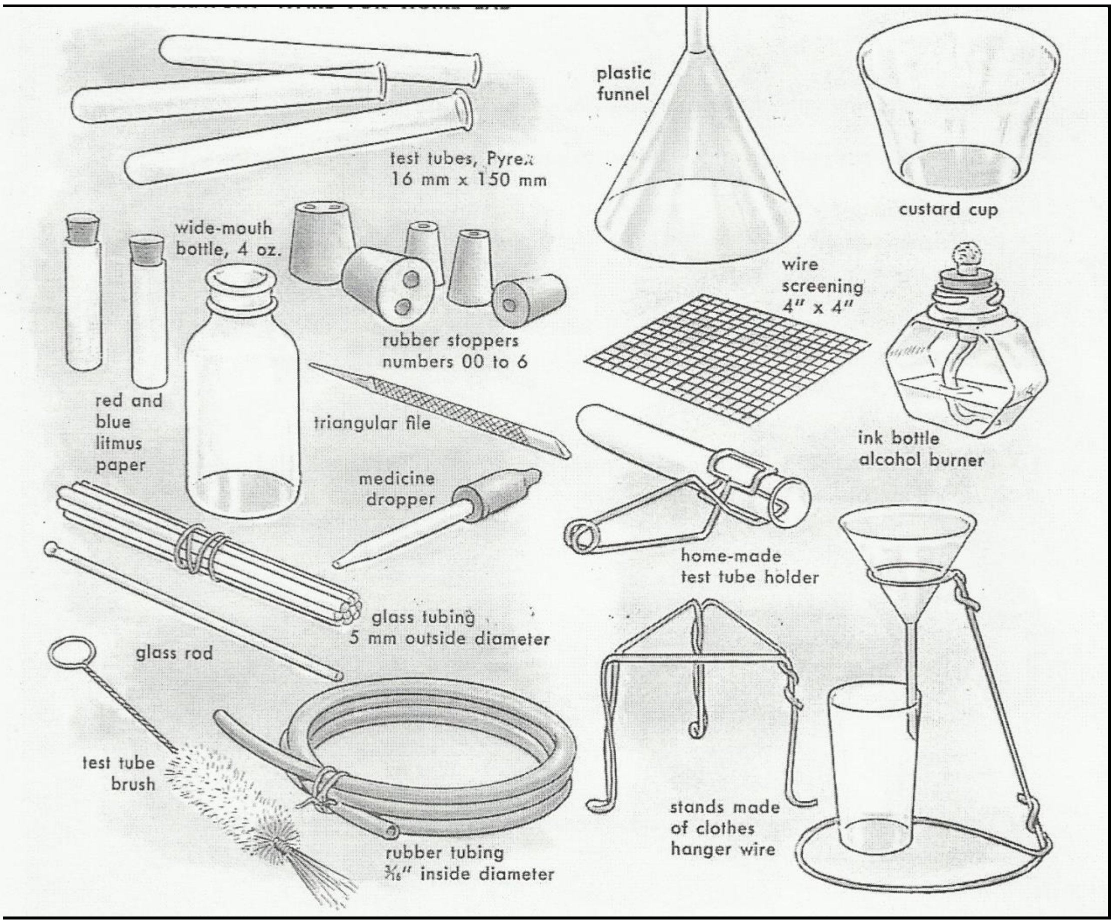


Steam distillation



Vacuum filtration setup using the Buchner funnel


REGULAR LABORATORY WARE


test tubes, Pyrex
16 mm x 150 mm
plastic funnel
custard cup
red and blue litmus paper
wide-mouth bottle, 4 oz.
rubber stoppers numbers 00 to 6
wire screening 4" x 4"
ink bottle alcohol burner
triangular file
medicine dropper
home-made test tube holder
glass tubing
5 mm outside diameter
glass rod
test tube brush
rubber tubing
3/16" inside diameter
stands made of clothes hanger wire

Melting Point

Purpose of experimental

1) To determine melting point of unknown compounds.
2) To identify a solid unknown.
3) To determine the purity of organic compound.

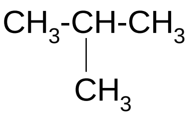
Theory part of experimental

The melting point of a compound is the temperature at which the solid phase is in equilibrium with the liquid phase. A solid compound changes to a liquid when the molecules acquire enough energy to overcome the forces holding them together in an orderly crystalline lattice. For most organic compounds, these intermolecular forces are relatively weak. **The melting point range** is defined as the span of temperature from the point at which the crystals first begin to liquefy to the point at which the entire sample is liquid. Most pure organic compounds melt over a narrow temperature range of 1-2 °C. The presence of a soluble impurity almost always causes a decrease in the melting point expected for the pure compound and a broadening of the melting point range.

Melting points can also be used to assess compound purity. Purification of the compound causes the melting point range to narrow and the melting point to increase.

The branched chain compounds have lower melting points than the corresponding straight chain isomers. For example, n- butane has a melting points of (- 138 ^{o}C) and isobutene (- 159 ^{o}C), This is due to the fact that branching of the chain makes the molecule more compact and thereby decreases the surface area. Therefore, the intermolecular attractive forces which depend upon the surface area, also become small in magnitude on account of branching. Consequently, *the boiling points of the branched chain alkanes are less than the straight chain isomers.*

$CH_3CH_2CH_2CH_3$



$CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_3$

n- butane , M.P. = (- 138 ^{o}C)

B.P. = (O ^{o}C)

isobutane , M.P. = (- 159 ^{o}C)

B.P. = (- 12 ^{o}C)

Properties of oil bath:

1) Oil must have a high temperature (> 300 ^{o}C)
2) Oil vapor is not toxic
3) Oil must be transparent

Factors affecting the melting point

1) The nature of the organic compound (aliphatic or aromatic or salt)
2) Molecular weight organic compound
3) Geometric shape of the organic compound (branched chain or straight chain)
4) Composite purity

Chemical and Apparatus

Capillary tubes (about 1 mm bore, about 8 cm length), thermometer (-10 - 110^{o} C), rubber band, glass rod, stand and clamp, burner, 250 cm^3 beaker, food oil or paraffin oil , chemical compound (powder).

Experimental No. (1) Melting Point

Procedure of Experimental

1) Obtain a sample from your instructor. Record sample ID.
2) Put the sample into a capillary tube (about 1-2 mm in height).
3) Measure the melting point using the apparatus as shown in Figure 4. Attach the capillary tube to a thermometer with sewing thread. Place 25-30 mL of paraffin oil or glycerol in a 50 mL beaker.
4) Turn on the hotplate and observe the melting point. Use a clean glass rod to stir the oil to ensure a uniform heat distribution.
5) Record the melting point range (for example 70-73°C)

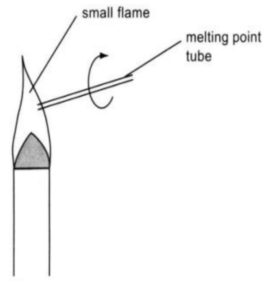


Figure 1

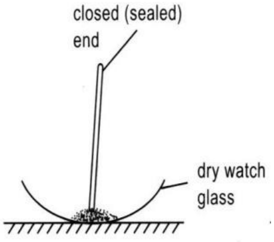


Figure 2

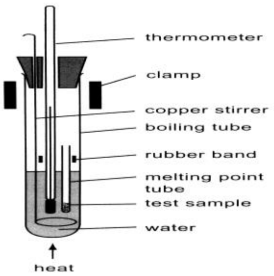


Figure 4

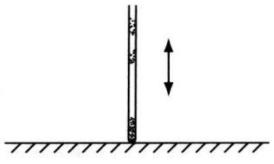


Figure 3

Question for discussion

1. What is the melting point range of pure compound?
2. Is the melting point sharp?
3. How is the melting point of a solid defined?
4. How is the melting point of a solid used to identify the solid?
5. How is the melting point of a solid used to assess the purity of the solid?

Boiling point

Purpose of experimental

1) To determine boiling point of unknown compounds.
2) To identify a liquid unknown.
3) To determine the purity of organic compound.

Theory part of experimental

Boiling points are also useful physical properties for indicating the purity of an organic compound. Boiling point is the temperature at which the vapor pressure of a liquid equals atmospheric pressure or some other applied pressure. A boiling point is commonly measured during a distillation, in which a liquid is heated to form vapor, and then the vapor is condensed and collected in another container. The boiling temperature is measured as distillation vapor covers the bulb of a thermometer suspended above the boiling liquid. Typically, the most accurate boiling point measurement is the relatively constant temperature achieved during a distillation.

Factors affecting the boiling point

1. The nature of the organic compound
2. Molecular weight organic compound
3. External pressure
4. Composite purity
5. Geometric shape of the organic compound (branched chain or straight chain)

Experimental No. (2) Boiling Point

Chemical and Apparatus

Capillary tubes, boiling tube, thermometer(-10 - 110^{o} C) , rubber band, glass rod, stand and clamp, burner, 250 cm^3 beaker, food oil or paraffin oil , chemical compound (liquid).

Procedure of Experimental

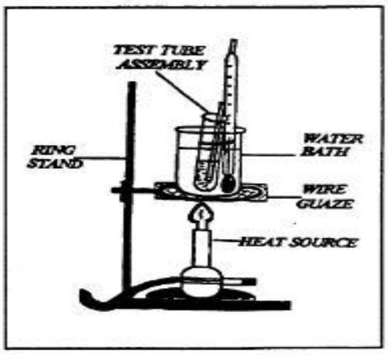
1) Obtain a liquid unknown from your instructor. Record the sample number.

2) Attach a clean and empty test tube to a thermometer with sewing thread. Put an empty capillary tube in the test tube so that the open end of capillary is down. Set up the apparatus as in

3) Ensure that the temperature of the paraffin oil is below 50 °C. Place 2-3 mL of sample in the test tube.

4) Turn on the hot plate and use a clean glass rod to stir the paraffin oil to ensure a uniform heat distribution.

5) Record the temperature when rapid air bubbles come out from the capillary. At this stage, the vapor pressure of the unknown inside the capillary is higher than the atmospheric pressure.



Heating Assembly↑

Solubility and solution

Purpose of experimental

1) Preparation of different solutions in concentrate and to show how temperature affects solubility.
2) To show how the nature of the solute and the solvent affects solubility.

Theory part of experimental

The solubility of a solute is the maximum quantity of solute that can dissolve in a certain quantity of solvent or quantity of solution at a specified temperature. The substance to be dissolved is called as **solute** and the dissolving fluid in which the solute dissolve is called as **solvent**, which together form a solution. The process of dissolving solute into solvent is called as **solution** or hydration if the solvent is water. Solubility definitions are; The process of **solubilisation** involves the breaking of inter-ionic or intermolecular bonds in the solute, the separation of the molecules of the solvent to provide space in the solvent for the solute, interaction between the solvent and the solute molecule .

One generalization which can be used for determining solubility is **“like dissolves like.”** This means that the more similar the polarity of a solute is to the polarity of the solvent, the more likely the two will form a homogeneous solution. A polar solvent, such as water, will dissolve a polar compound. Nonpolar solvents such as naphtha or turpentine will dissolve nonpolar material, such as grease or oil. On the other hand, oil and water do not mix because of their different polar, If it will not mix it is **immiscible**. The rate at which it can dissolve can be influenced by three methods: **heating**, **stirring**, and **grinding**. Each of these will increase the rate at which a solute will dissolve.

Molarity is a way of expressing how concentrated a solution is. This molarity is expressed in moles of solute per liter of solution (solution being solute plus solvent). It is give the symbol, **M**.

Type of solutions

Saturated solution: A solution with solute that dissolves until it is unable to dissolve anymore, leaving the un dissolved substances at the bottom.

Saturated Solution

Figure 1.1 Figure 1.2 Figure 1.3

Unsaturated Solution: A solution (with less solute than the saturated solution) that completely dissolves, leaving no remaining substances.

Unsaturated Solution

Figure 2.1 Figure 2.2 Figure 2.3

Supersaturated Solution : A solution (with more solute than the saturated solution) that contains more undissolved solute than the saturated solution because of its tendency to crystallize and precipitate.

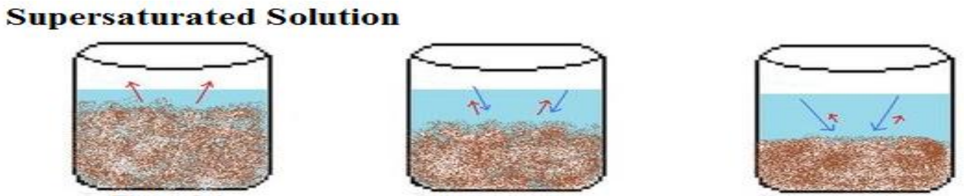


Figure 3.1 Figure 3.2 Figure 3.3

Chemical and Apparatus

$KMnO_4$, NaCl , Naphthalene, Iodine, Ethanol (ethyl alcohol), Acetone, hexane, Hot plate, Wash bottle, test tubes

Procedure of Experimental (preparation of solutions)

1. Place 10 mL of distilled water into a 50-mL beaker, while stirring with a glass rod, add NaCl salt to the water in 2-g portions; keep
2. adding until no more NaCl dissolves. The solution should be saturated.
3. Heat the solution on a hot plate to 50 ^{o}C; maintain this temperature. Again add to the solution, while stirring, salt in 2-g portions until no more NaCl dissolves.
4. Heat the solution above 50 C until all of the solid dissolves. With beaker tongs, remove the beaker from the hot plate and set it on the bench top.
5. Observe what happened to the solution when it cooled to room temperature. Offer an explanation for what has taken place (5).

Procedure of Experimental (Solubility – Solids in Liquids)

1- Clean and dry 12 test tubes.

2. Place approximately 0.1 g of the following solids into test tubes numbered as indicated (your instructor will weigh exactly 0.1 g of solid as a demonstration; use your spatula to estimate the 0.1g sample):

a. No. 1: table salt, NaCl

b. No. 3: naphthalene, $C_{10}H_8$

c. No. 4: iodine, I_2

d. No. 4: potassium permanganate , $KMnO_4$

3. Add 3 mL of distilled water to each test tube and shake the mixture (simply tapping the test tube with your fingers will agitate the contents enough).

4. Record on the Report Sheet whether the solid dissolved completely (soluble), partially (slightly soluble), or not at all (insoluble).

5. With new sets of labeled test tubes containing the solids listed above, repeat the solubility tests using the solvents ethanol (ethyl alcohol), C_2H_5OH, and hexane. Record your observations.

6. Discard your solutions in waste containers provided. *Do not discard into the sink*

Solute	**Solvent**		
	water	**hexane**	**ethanol**
NaCl			
$KMnO_4$			
I_2			
Naphthalene			

Experimental No. (3) Solubility and solution

Procedure of Experimental (Miscibility – Liquids in Liquids)

Set up three test tubes in your test tube rack. Put 20 drops of water into each of them. Add 20 drops of acetone, C_3H_6O, to the first test tube, 20 drops of hexane, C_6H_{14}, to the second test tube, and 20 drops of ethanol,

CH_3CH_2OH, to the third test tube. Shake gently and note whether the liquids are miscible or immiscible.

Solvent (liquid)	**Solvent (liquid)**		
	Acetone	**Hexane**	**Ethanol**
Water			

Questions for discussion

1) What is meant by the following terms?

Soluble, Miscible, Undersaturated, saturated, and supersaturated, Molarity,“like dissolves like”

2) Indicate whether each of these solute/solvent pairs is soluble or insoluble:

Solute	**Solvent**	
	Water	**Hexane**
Ionic Solid		
Polar Solid		
Nonpolar Solid		
Sugar		
KCl		

3) Indicate which of the liquid pairs is miscible or immiscible:

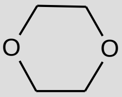
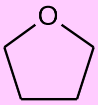
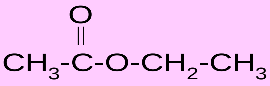
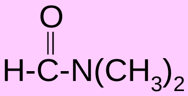
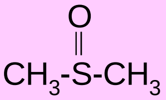
1st Liquid	2nd Liquid	Miscible/Immiscible
Water	Alcohol	
Hexane	Alcohol	
Water	Oil	
Oil	Gasoline	

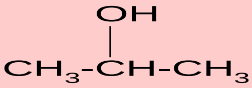
4) What are the three ways to increase the rate of dissolving?

Which appears to affect the rate the most?

Table of polar and non polar solvents

Dipolar	**Density**	**Dielectric constant**	**Bioling points**	**Chemical formula**	**Solvent**
Non-polar solvents					
0.00 D	0.626 g/ml	1.84	36 °C	$CH_3-CH_2-CH_2-CH_2-CH_3$	Pentane
0.00 D	0.751 g/ml	1.97	40 °C	C_5H_{10}	Cyclopentane
0.00 D	0.655 g/ml	1.88	69 °C	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$	Hexane
0.00 D	0.779 g/ml	2.02	81 °C	C_6H_{12}	Cyclohexane

0.00 D	0.879 g/ml	2.3	80 °C	C_6H_6	Benzene
0.36 D	0.867 g/ml	2.38	111 °C	$C_6H_5\text{-}CH_3$	Toluene
0.45 D	1.033 g/ml	2.3	101 °C		1,4 - Dioxane
1.04 D	1.498 g/ml	4.81	61 °C	$CHCl_3$	Chloroform
1.15 D	0.713 g/ml	4.3	35 °C	$CH_3CH_2\text{-}O\text{-}CH_2\text{-}CH_3$	Diethyl ether
Polar aprotic solvents					
1.60 D	1.3266 g/ml	9.1	40 °C	CH_2Cl_2	Dichloromethane (DCM)
1.75 D	0.886 g/ml	7.5	66 °C		Tetrahydrofuran (THF)
1.78 D	0.894 g/ml	6.02	77 °C	 $CH_3\text{-}\overset{\overset{O}{\Vert}}{C}\text{-}O\text{-}CH_2\text{-}CH_3$	Ethyl acetate
2.88 D	0.786 g/ml	21	56 °C	 $CH_3\text{-}\overset{\overset{O}{\Vert}}{C}\text{-}CH_3$	Acetone
3.82 D	0.944 g/ml	38	153 °C	 $H\text{-}\overset{\overset{O}{\Vert}}{C}\text{-}N(CH_3)_2$	Dimethylform-amide (DMF)
3.92 D	0.786 g/ml	37.5	82 °C	$CH_3\text{-}C\equiv N$	Acetonitrile (MeCN)
3.96 D	1.092 g/ml	46.7	189 °C	 $CH_3\text{-}\overset{\overset{O}{\Vert}}{S}\text{-}CH_3$	Dimethyl sulfoxide (DMSO)

Polar protic solvents					
1.41 D	1.21 g/ml	58	101 °C	H-COOH	Formic acid
1.63 D	0.810 g/ml	18	118 °C	CH_3-CH_2-CH_2-CH_2-OH	*n*-Butanol
1.66 D	0.785 g/ml	18	82 °C	 $CH_3\text{-}\overset{OH}{\overset{\vert}{C}}H\text{-}CH_3$	Isopropanol (IPA)
1.68 D	0.803 g/ml	20	97 °C	CH_3-CH_2-CH_2-OH	*n*-Propanol
1.69 D	0.789 g/ml	24.55	79 °C	CH_3-CH_2-OH	Ethanol
1.70 D	0.791 g/ml	33	65 °C	CH_3-OH	Methanol
1.74 D	1.049 g/ml	6.2	118 °C	CH_3-COOH	Acetic acid
1.85 D	1.000 g/ml	80	100 °C	H_2O	Water

Recrystallization

Purpose of experimental

To separate organic compounds (solid) from impurities by recrystallization.

Theory part of experimental

Recrystallization is an important technique for purifying solid organic compounds. **It is based on the principle that solids are more soluble in hot solvents than in cold solvents**. The compound is dissolved in the smallest possible amount of boiling solvent and then the solvent is allowed to cool, and the compound precipitates out. Hopefully, the impurities remain in the cold solvent, and only the pure compound precipitates out.

The most important factors in a recrystallization are:

a) choosing a good solvent

b) using the right amount of solvent.

If the solvent polarity is too similar, the compound will dissolve. If the solvent polarity is too different, the compound won’t dissolve at all. If the solvent polarity is moderately different, then temperature will have a big impact on the solubility, allowing the compound to dissolve in boiling solvent but crystallize out when the solvent is cooled. Getting the right amount of solvent is a matter of proper technique.

Characteristics of a Good Recrystallization Solvent:

1. The recrystallization solvent should NOT dissolve the substance to be purified at room temperature, but it should dissolve it well at the solvent's boiling point
2. The solvent should dissolve soluble impurities well at room temperature.
3. The solvent should not dissolve insoluble impurities even at the solvent's boiling point. These insoluble impurities can then be removed by gravity filtration.
4. The solvent must not react with the substance to be purified.
5. The solvent should be volatile.
6. The solvent should be inexpensive.

Note : Characteristics 1, 2, 3, and 4 are essential for a good recrystallization solvent. Characteristics 5 and 6 are desirable, but not essential.

Commonly Used Solvents

Solvent	**B.P.**	**Dielectric Constant***	**Safety Concerns**
Water	100	78.4	None
Ethanol	78	24.5	Flammable; irritating to the eyes, respiratory system, and skin
Acetone	56	20.6	Flammable; Irritating to the eyes; Vapors may cause drowsiness or dizziness

Commonly Used Solvents

Solvent	**B.P.**	**Dielectric Constant***	**Safety Concerns**
Tetrahydrofuran	66	7.58	Flammable; Harmful if swallowed; Irritating to the eyes, skin, and respiratory system
Ethyl acetate	78	6.02	Flammable; Irritating to the eyes; Vapors may cause drowsiness or dizziness
Cyclohexane	81	1.89	Flammable; May damage lungs if swallowed; Vapors may cause drowsiness or dizziness

*The dielectric constant is a measure of the solvent's ability to separate ions. In general, ionic compounds are more soluble in solvents with high dielectric constants.

Chemical and Apparatus

Erlenmeyer flask (125 mL), short-stemmed funnel, hot plate, boiling chips, benzoic acid.

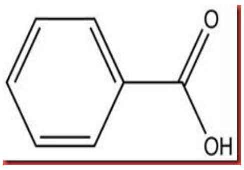
Procedure of Experimental

1. To perform a recrystallization, heat about 10 ml of the recrystallization solvent to boiling in a beaker in your hot plate – use a stir bar to keep it from bumping.
2. Add the boiling solvent slowly to the (0.5 g) impurity benzoic acid (in a separate beaker) with a pipet, stirring it with a spatula and heating it on the hot plate until the solid has dissolved and the solvent is still boiling.
3. Filter the hot solution by gravity filtration using filter paper.

4. Cool the solution to room temperature and then place the flask in ice water.
5. Wait more minutes and then collect the crystals using a vacuum filter apparatus. Wash the crystals with a very small amount of ice cold solvent.
6. Allow the crystals to dry with the vacuum on for several minutes. During this time, crystals may be observed forming in the mother liquor.
7. Determine the weigh the DRY crystals of recovered benzoic acid.

Calculate the percent recovered using the following *written* formula and determine the melting point of your recrystallized benzoic acid.

$$\textbf{\% Recovered} = \frac{\textbf{Weight of benzoic acid obtained after recrystallization}}{\textbf{Weight of benzoic acid before recrystallization}} \times \textbf{100}$$

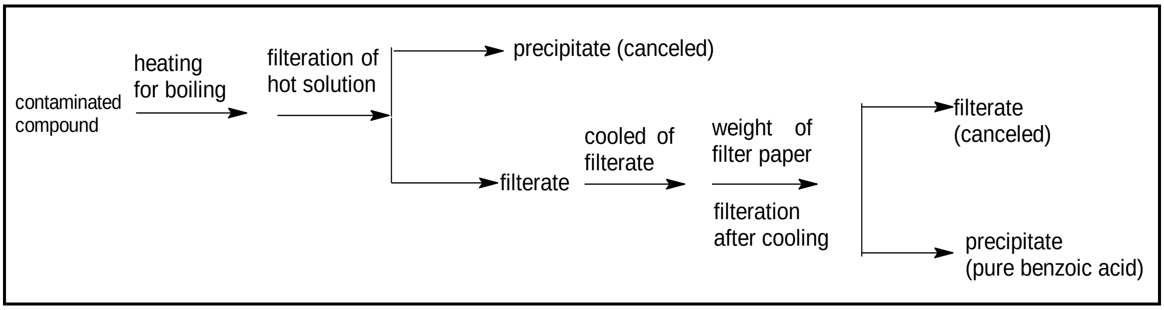


(Structure of benzoic acid)

Questions for discussion

1. What is the ideal solvent for crystallization of a particular compound? What is the primary consideration in choosing a solvent for crystallizing a compound?
2. What is the purpose of recrystallization?

Plan of work



Experimental No. (5) Sublimation

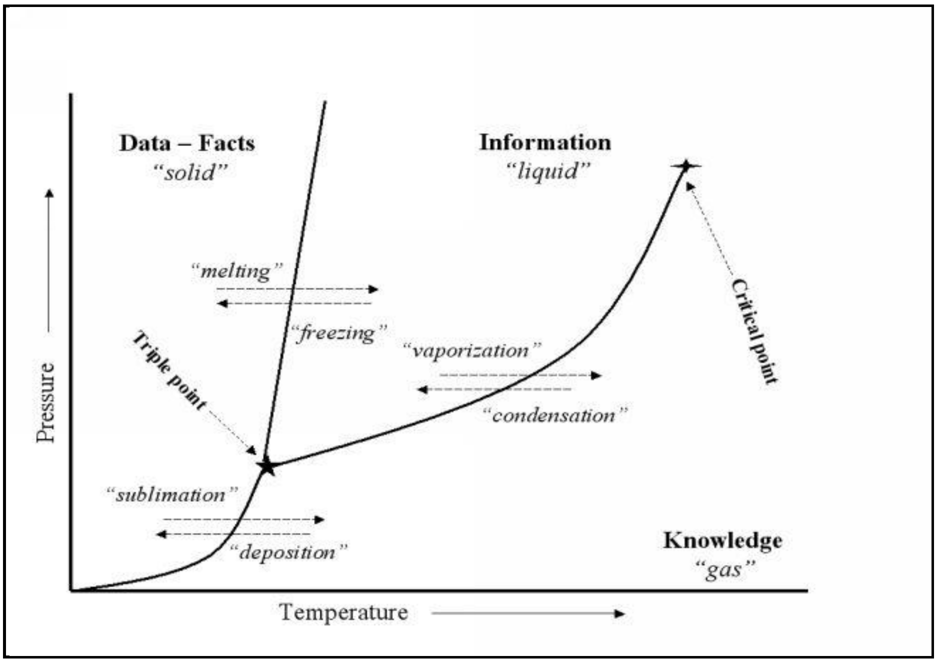
Sublimation

Purpose of experimental

Purification of solid sublimed substances (naphthalene)

Theory part of experimental

Sublimation is the transition of a substance directly from the solid to the gas phase without passing through the intermediate liquid phase. Sublimation is an endothermic phase transition that occurs at temperatures and pressures below a substance's triple point [In thermodynamics, the **triple point** of a substance is the temperature and pressure at which the three phases (gas, liquid, and solid) of that substance coexist in thermodynamic equilibrium] as in its phase diagram.



Phase diagram thermodynamic equilibrium

The reverse process of sublimation is desublimation or deposition, in which a substance passes directly from a gas to a solid phase. At normal pressure , most chemical compounds and elements possess three different states at different temperatures. In these cases, the transition from the

solid to the gaseous state requires an intermediate liquid state. So, all solids that possess an appreciable vapor pressure at a certain temperature usually can sublimate in air (e.g. water ice just below 0 °C).Sublimation is much easier than evaporation from the melt, because the pressure of their triple point is very high, and it is difficult to obtain them as liquids. Sublimation requires additional energy and is an endothermic change.

Example of compounds that are purification by sublimation: camphor, benzoic acid, naphthalene, salicylic acid and the quinines.

Conditions of sublimation

1. The chemical has a triple point
2. Heating should be quiet

Chemical and Apparatus

Beaker , watch glass, hotplate, glass rod, filter paper, cold water or ice, naphthalene contaminated with sand, balance

Procedure of experimental

1. Place a mixture of 1 gm. of one of the sublimed substances (impurity naphthalene with sand) in a 200 ml. beaker, covered with a round bottomed flask filled with cold water or ice .
2. The beaker is placed on a hotplate or a low flame.
3. The sublimed substance (i, e. the naphthalene) will collect on the bottom of the cold flask and on the side walls of the beaker in pure, crystallic form .

4. Scrap the sample of sublimed material from the flask and beaker.
5. Collect in a small flask , weigh, and determine the M.P. of the pure substance . Compare to the original sample .

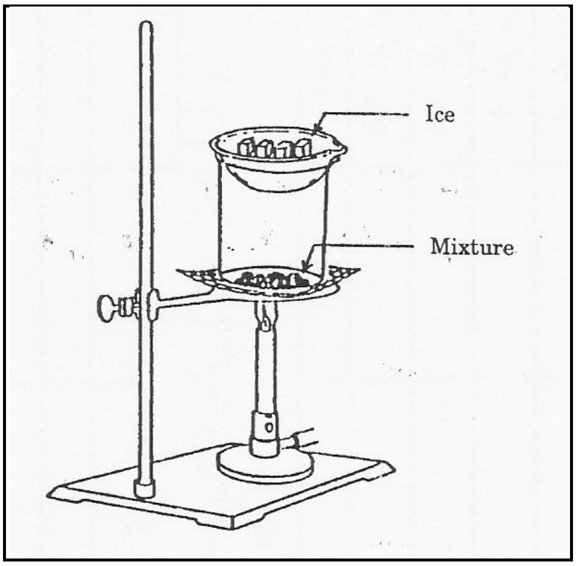


Figure shows the experience of sublimation

Calculations

$$\% \text{ Yield} = \frac{\text{Weight of product}}{\text{Weight of sample}} \times 100$$

Questions for discussion

1- Define the following: sublimation, triple point

2- What is the different between sublimation and desublimation or deposition

3- What is the compounds which purification by sublimation

4- Draw the Phase diagram thermodynamic equilibrium

5- Why we using the ice in the sublimation experimental

Extraction

Purpose of experimental

To purify samples of organic compounds that are solids at room temperature

Theory part of experimental

Extraction is a method often used by organic chemists for the rapid crude separation of mixtures containing acidic and/or basic compounds often in the presence of neutral materials. The separation uses acid-base chemistry and two mutually insoluble layers of solvent (water and t-butylmethylether).

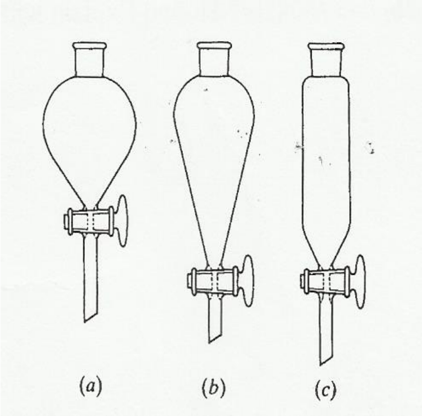
Extraction is the recovery of a substance from a mixture by bringing it into contact with a solvent, which dissolves the desired material.

Like recrystallization and distillation, **extraction** is a separation technique frequently employed in the laboratory to isolate one or more components from a mixture. **Unlike** recrystallization and distillation, it does not yield a pure product; thus, the former techniques may be required to purify a product isolated by extraction. In the technical sense **extraction is based on the principle of the equilibrium distribution of a substance (solute) between two immiscible phases, one of which is usually a solvent**. The solvent need not be a pure liquid but may be a mixture of several solvents or a solution of some chemical reagent that will react with one or more components of the mixture being extracted to form a new substance soluble in the solution. The material being extracted may be a liquid, a solid, or a mixture of these.

Extraction is accomplished by shaking the solution in a **separatory funnel** with a second solvent that is immiscible with the one in which the compound is dissolved, but dissolves the compound more readily. Sometimes not the entire product is extracted in a single operation and the process must be repeated once or twice more to assure a clean separation. It has been found that when two immiscible solvents are shaken together, the solute distributes itself between them in a ratio roughly proportional to its solubility in each. The ratio of the concentration of the solute in each solvent at equilibrium is a constant called the **distribution ratio(d) or partition coefficient (Kd).**

$$\mathbf{Kd = [solute]_{org.} / [solute]aq. = C_{org.} / C_{aq.}}$$

The larger the value of Kd, the more solute will be transferred to the ether with each extraction, and the fewer portions of ether will be required for essentially complete removal of the solute.



seperatory funnel

Properties of an organic extraction solvent :

(1) It must readily dissolve the substance being extracted but must not dissolve to any appreciable extent in the solvent from which desired substance is being extracted.

(2) It should extract neither the impurities nor other substances present in the original mixture.

(3) It should not react with the substance being extracted.

(4) It should be readily separated from the desired solute after extraction. Some of the solvents commonly used for extracting aqueous solutions or mixtures include diethyl ether, methylene chloride, chloroform, carbon

tetrachloride, benzene, n-pentane, n-hexane, and various mixtures of saturated hydrocarbons from petroleum (petroleum ether, ligroin, etc.). Each of these has a relatively low boiling point so that it may be fairly easily separated from the solute by evaporation or distillation. Methanol and ethanol are not good solvents for extracting aqueous solutions or mixtures because of their solubility in water; however, if an aqueous solution can be saturated with potassium carbonate without affecting the solute, ethanol can be used to extract polar solutes from the solution.

Chemical and Apparatus

benzoic acid, CH_2Cl_2 (dichloromethane), water, separatory funnel , beaker, $CaCl_2$, boiling chip, hotplate, balance, filter paper, funnel

Procedure of experimental

Part A

1- Weigh out 0.5 mg of benzoic acid and dissolve it in separatory funnel containing 1.6 mL CH_2Cl_2.

2- Add 1.6 mL distilled water and mix thoroughly.

3- Alternatively, you may shake the separatory funnel after sealing with a stopper.

4- Set the separatory funnel aside and allow the layers to separate.

5- Remove the aqueous layer without removing any organic layer.

6- Add anhydrous $CaCl_2$ to the CH_2Cl_2 layer

7- After 5 minutes of drying time, remove the organic layer and place in a clean, dry, pre-weighed 10 mL Erlenmeyer flask with a boiling chip. 8-Evaporate the solvent on a hotplate in the hood to dryness.

9- Weigh the flask with boiling chip and benzoic acid. Use this mass to determine the weight of benzoic acid.

Questions for discussion

1- Why must you remove the stopper from the separatory funnel before draining?

2- What is the purpose of $CaCl_2$?

3- What is the purpose of the boiling chips?

Part B

1- Place 5 mL of CCl_4 contamination with acetic acid in separatory funnel .

2- Add 15 mL of (15%) sodium carbonate solution and mix thoroughly.

3- Alternatively, you may shake the separatory funnel after sealing with a stopper.

4- Set the separatory funnel aside and allow the layers to separate.

5- Remove the aqueous layer without removing any organic layer.

6- After 5 minutes of time, remove the organic layer and place in a clean, dry, pre-weighed 10 mL Erlenmeyer flask

7- Measure the volume of organic layer and calculate the percentage volume

$$\text{The percentage volume \%} = \frac{\text{practical volume}}{\text{theoretical volume}} \times 100$$

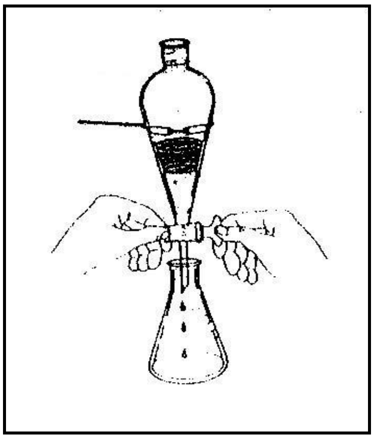
Experimental No. (6) Extraction

$$CCl_4+CH_3COOH+NaHCO_3 \longrightarrow (CH_3COONa+H_2O)+CCl_4+CO_2$$

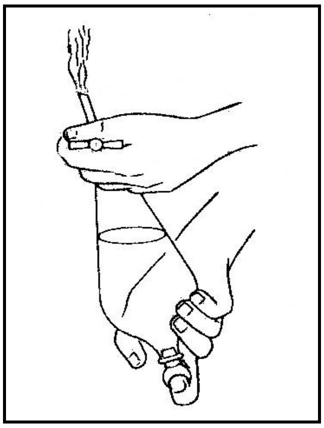
Questions for discussion

1. Why we added sodium carbonate solution ?
2. Define the extraction
3. What is the principle of extraction

Separating the bottom layer



Opening the stopper to let out the gas



Experimental No. (7) Extraction of caffeine from tea

Extraction of caffeine from tea

Purpose of experimental

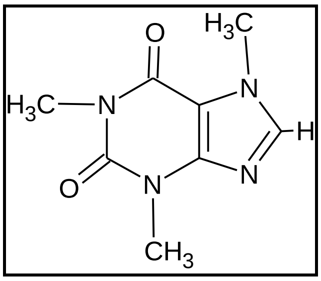
1. To demonstrate the isolation of a natural product.
2. To learn the techniques of extraction.

Theory part of experimental

Many organic compounds are obtained from natural sources through extraction. This method takes advantage of the solubility characteristics of a particular organic substance with a given solvent. In the experiment here, caffeine is readily soluble in hot water and is thus separated from the tea leaves. Caffeine is one of the main substances that make up the water solution called tea. Besides being found in tea leaves, caffeine is present in coffee, kola nuts, and cocoa beans. As much as 5% by weight of the leaf material in tea plants consists of caffeine.

The caffeine structure is shown below. It is classed as an alkaloid, meaning that with the nitrogen present, the molecule has base characteristics (alkali-like). In addition, the molecule has the purine ring system, a framework which plays an important role in living systems.

Caffeine is the most widely used of all the stimulants.



Structure of Caffeine

Experimental No. (7) Extraction of caffeine from tea

Tea leaves consist primarily of cellulose; this is the principle structural material of all plant cells. Fortunately, the cellulose is insoluble in water, so that by using a hot water extraction, more soluble caffeine can be separated. Also dissolved in water are complex substances called tannins. These are colored phenolic compounds of high molecular weight (500 to 3000) that have acidic behavior. If a basic salt such as Na_2CO_3 is added to the water solution, the tannins can react to form a salt. These salts are insoluble in organic solvents, such as chloroform or dichloromethane, but are soluble in water.

Although caffeine is soluble in water (2 g/100 g of cold water), it is more soluble in the organic solvent dichloromethane (14 g/100 g). Thus caffeine can be extracted from the basic tea solution with dichloromethane, but the sodium salts of the tannins remain behind in the aqueous solution. Evaporation of the dichloromethane yields crude caffeine; the crude material can be purified by sublimation.

Chemical and apparatus

Boiling chips, Cold finger condenser, Filter paper, fast flow

Hot plate, 125-mL separatory funnel with stopper, Melting point capillaries, adapter, Tea leaves, rubber stopper, Anhydrous sodium sulfate Na_2SO_4, Anhydrous sodium carbonate Na_2CO_3, Dichloromethane CH_2Cl_2,

Procedure of experimental

1. Into a 150-mL beaker, place the tea leaves so that they lie flat on the bottom. Add 30 mL of distilled water and 2.0 g of anhydrous Na2CO3; heat the contents with a hot plate, keeping a *gentle* boil, for 20 min. While the mixture is boiling, keep a watch glass on the beaker.

2. Decant the hot liquid into a 50-mL Erlenmeyer flask, carefully pressing the tea bag with a glass rod; add this wash water to the tea extract. (If any solids are present in the tea extract, filter them by gravity to remove.) Cool the combined tea extract to room temperature. Transfer the cool tea extract to a 125-mL separatory funnel that is supported on a ring stand with a ring clamp.
3. Carefully add 5.0 mL of dichloromethane to the separatory funnel. Stopper the funnel and lift it from the ring clamp By holding the stopper in place with one hand, invert the funnel.
4. Return the separatory funnel to the ring clamp, remove the stopper, and allow the aqueous layer to separate from the dichloromethane layer. You should see two distinct layers form after a few minutes, with the dichloromethane layer at the bottom. Sometimes an emulsion may form at the juncture of the two layers. The emulsion often can be broken by gently swirling the contents or by gently stirring the emulsion with a glass rod. Separation of the aqueous layer and the dichloromethane layer in the separatory funnel.
5. Carefully drain the lower layer into a 25-mL Erlenmeyer flask. Try not to include any water with the dichloromethane layer.
6. Repeat the extraction with an additional 5.0 mL of dichloromethane. Combine the separated bottom layer with the dichloromethane layer obtained from step no. 5.
7. Add 0.5 g of anhydrous Na_2SO_4 to the combined dichloromethane extracts. Swirl the flask. The anhydrous salt is a drying agent and will remove any water that may still be present.
8. Weigh a 25-mL side-arm filter flask containing one or two boiling stones. Record this weight (2). By means of a gravity filtration, filter

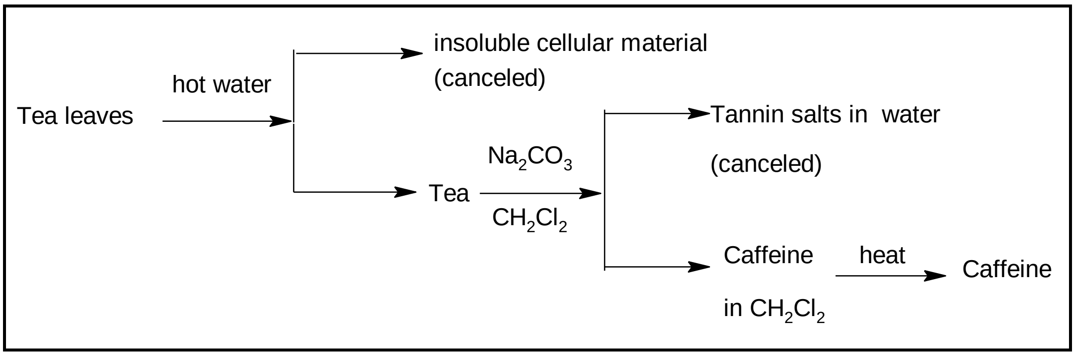
the dichloromethane–salt mixture into the pre-weighed flask. Rinse the salt on the filter paper with an additional 2.0 mL of dichloromethane.

9. Remove the dichloromethane by evaporation *in the hood*. Be careful not to overheat the solvent, since it may foam over. The solid residue which remains after the solvent is gone is the crude caffeine. Reweigh the cooled flask (3). Calculate the weight of the crude caffeine by subtraction (4) and determine the percent yield (5).
10. Take a melting point of your solid. First, scrape the caffeine from the bottom and sides of the flask with a microspatula and collect a sample of the solid in a capillary tube. Pure caffeine melts at 238 ^{o}C. Compare your melting point to the literature value.

Calculation

$$\textbf{\% Yield} = \frac{\textbf{Weight of product}}{\textbf{Weight of sample}} \textbf{ x100}$$

Plan of work



Experimental No. (7) Extraction of caffeine from tea

Questions for discussion

1. Is methylene chloride more or less dense than water? What evidence do you have to support your answer?
2. Was your melting point the same as the reported melting point? If not, why not?
3. Why was sodium carbonate added to the coffee solution?
4. Explain why the caffeine that you obtained in this experiment may not have been white in color.
5. What method is used to obtain caffeine for tea leaves?
6. Why is caffeine classed as an alkaloid?
7. Why might an individual use a product containing caffeine?
8. Besides caffeine, what other compounds are found in tea leaves?

Distillation

Purpose of experimental

1. Separate a liquid solvent mixture using both simple and fractional distillation.
2. Determine the boiling point of the purified solvent

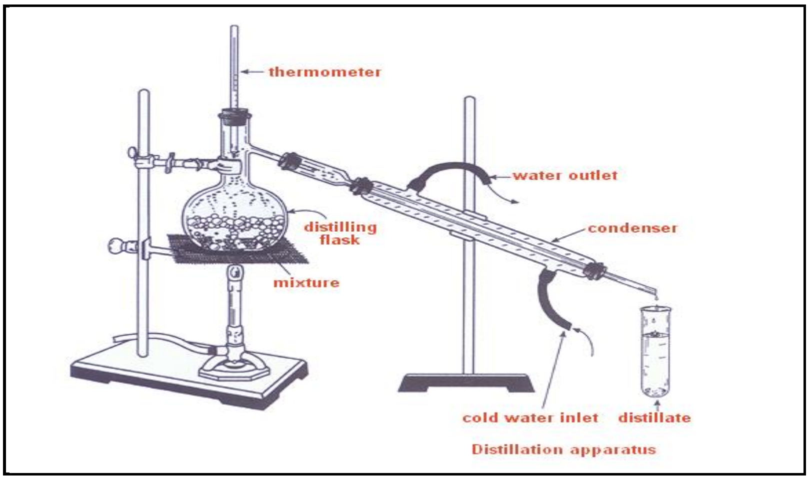
Theory part of experimental

Distillation is the most common method used to separate and purify liquids. **The process consists of** heating a liquid to its boiling point and conducting the vapors to a cooling device where they are condensed. The condensate is then collected. The vapor pressure of a liquid is defined as the pressure that is exerted by a liquid at a given temperature. This force is due to the molecules escaping from the liquid's surface into the gas phase. The vapor pressure of a liquid increases with increasing temperature. The boiling point of a liquid is that temperature at which the vapor pressure is equal to the pressure of the surroundings. If a flask is open to the air, the vapor pressure at the boiling point is equal to the atmospheric pressure. The boiling points of many liquids are listed in the literature referenced to 760 mm Hg (standard pressure).

The boiling point of a liquid is determined by placing a thermometer in the vapor. The temperature of the vapor will remain constant throughout the distillation if the vapor is pure. The boiling point at a given pressure is a characteristic property of the pure compound just as the melting point of a pure crystalline compound. If a mixture of two miscible liquids with different boiling points is heated to boiling, the vapor will not have the same composition as the liquid; it will be richer in the more volatile component. In order to obtain pure components, the now enriched mixture must be redistilled. A **fractionating column** is a device for increasing the efficiency of the distillation process. It consists of a vertical column packed with inert materials or with indentations which increase the surface area of the column. As the hot vapors of the liquid rise, they condense on the greater surface area. As the condensate flows back down to the boiling flask, the liquid is revaporized as it comes in contact with the hotter portion of the lower column. This is repeated many times, until the final distillate is nearly pure. By using select columns, liquids with boiling points just 2° C apart can be separated. Some liquid mixtures do not form nearly.

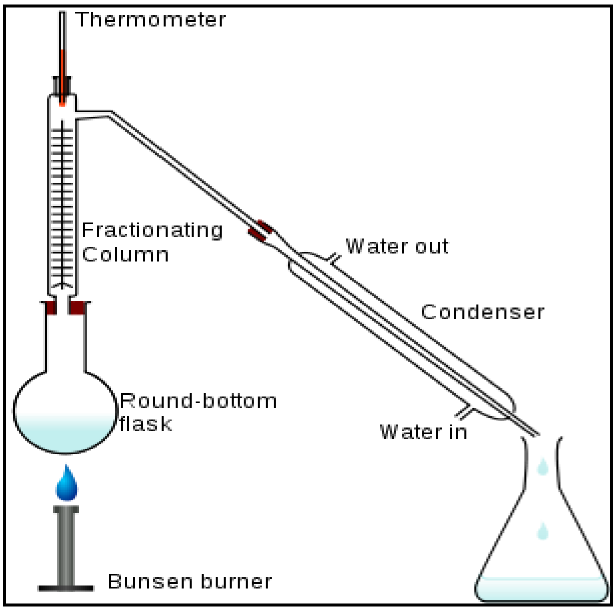
Types of distillation

1- **Simple distillation**: in simple distillation, the vapor is immediately channeled into a condenser. Consequently, the distillate is not pure but rather its composition is identical to the composition of the vapors at the given temperature and pressure. If the difference in boiling points is greater than 25°C, a simple distillation is used.



Simple distillation apparatus

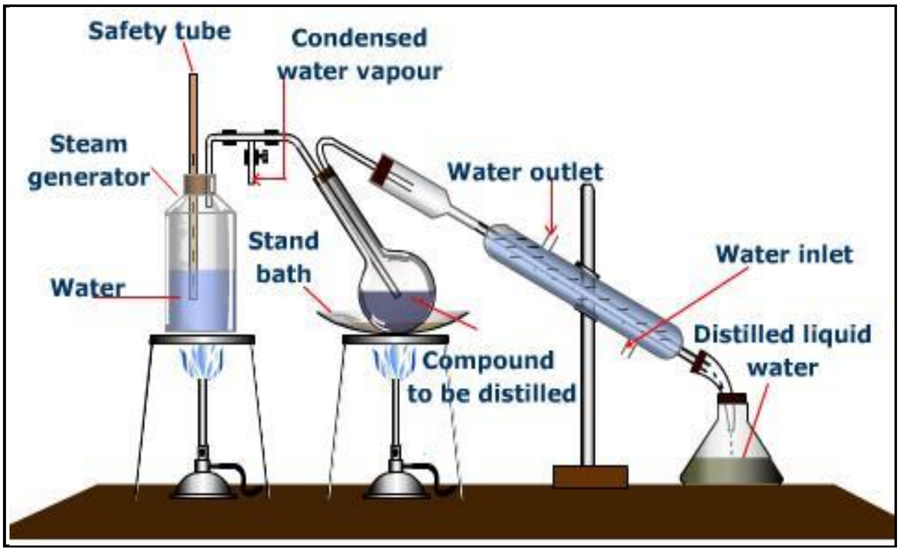
2- Fractional distillation: fractional distillation is the separation of a mixture into its component parts, or fractions, such as in separating chemical compounds by their boiling point by heating them to a temperature at which several fractions of the compound will evaporate. It is a special type of distillation. Generally the component parts boil at less than 25°C from each other under a pressure of one atmosphere (atm).



Fractional distillation apparatus

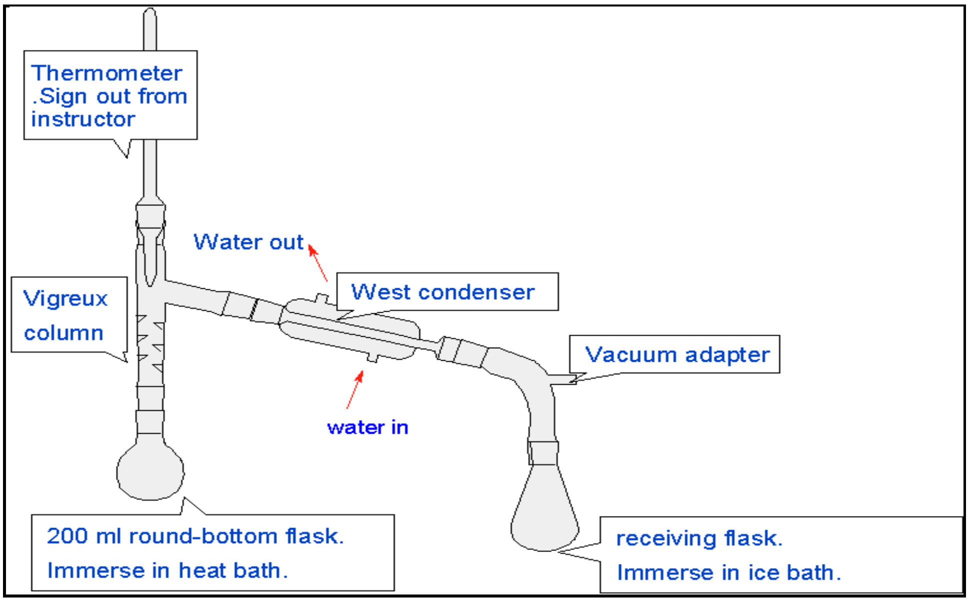
3- Steam distillation: steam distillation is a method for distilling compounds which are heat-sensitive. The temperature of the steam is easier to control than the surface of a heating element, and allows a high rate of heat transfer without heating at a very high temperature. This process involves bubbling steam through a heated mixture of the raw material. The vapor mixture is cooled and condensed, usually yielding a layer of oil and a layer of water.

Steam distillation of various aromatic herbs and flowers can result in two products; an essential oil as well as a watery herbal distillate.



Steam distillation apparatus

4- Vacuum distillation: vacuum distillation Some compounds have very high boiling points. To boil such compounds, it is often better to lower the pressure at which such compounds are boiled instead of increasing the temperature. Once the pressure is lowered to the vapor pressure of the compound (at the given temperature). This technique is also very useful for compounds which boil beyond their decomposition temperature at atmospheric pressure and which would therefore be decomposed by any attempt to boil them under atmospheric pressure.



Vacuum distillation apparatus

Pieces of distillation apparatus

- heat source, such as a hot plate with a bath
- distilling flask, typically a round-bottom flask
- receiving flask, often also a round-bottom flask
- fractionating column (Vigreux column)
- distillation head
- thermometer
- condenser
- boiling chips

Boiling chips: are small, insoluble, porous **stones** made of calcium carbonate or silicon carbide. These **stones** have pores inside which provide cavities both to trap air and to provide spaces where bubbles of solvent vapor can form.

Experimental No. (8) Distillation

Application of distillation

The application of distillation can roughly be divided in four groups: laboratory scale, industrial distillation, distillation of herbs for perfumery and medicinals (herbal distillate), and food processing.

Commercially, distillation has a number of uses. It is used to separate crude oil into more fractions for specific uses such as transport, power generation and heating. Water is distilled to remove impurities, such as salt from seawater.

Chemical and apparatus

$KMnO_4$ solution, boiling chips, thermometer, distillation head, hot plate , distilling flask (typically a round-bottom flask),receiving flask (often also a round-bottom flask).

Procedure of experimental (simple distillation)

1- Place 50 mL your unknown mixture ($KMnO_4$ solution) with boiling chips in a 100 mL round-bottom flask equipped with a hot plate

2- Distill the mixture slowly to obtain the best result, increase the temperature very gradually.

3- Even though your heating mantle is heating, the temperature that the thermometer displays doesn’t change much until after the liquid boils. Why?

4- As the distillation proceeds, record the temperature and the total volume of the distillate collected in your laboratory notebook.

Calculation

$$\% \text{ Yield} = \frac{\text{Volume of product}}{\text{Volume of sample}} \times 100$$

Questions for discussion

1. What is the purpose of the boiling chips?
2. In this lab you will separate a mixture of organic liquids by two methods; simple and fractional distillation. In theory, which method should give the better separation? Briefly explain why?
3. What effect is produced on the boiling point of a solution by a soluble, non-volatile substance? What is the effect produced on the boiling point of a liquid by an insoluble substance? What is the vapor temperature above the surfaces of these to liquids?
4. Why doesn’t a pure liquid distill all at once when the boiling point is reached?
5. Why is a packed column more efficient than an unpacked column for fractional distillation?
6. Why does slow distillation result in better separation of two liquids than fast distillation?
7. Why is it dangerous to attempt a distillation in a completely closed system?

Experimental No. (9) Identification of hydrocarbons

Identification of hydrocarbons

Purpose of experimental

1. To investigate the physical properties, solubility and density, of some hydrocarbons.
2. To compare the chemical reactivity of an alkane, an alkene, and an aromatic compound.
3. To use physical and chemical properties to identify an unknown.

Theory part of experimental

Hydrocarbons are organic compounds that contain only carbon and hydrogen. **Hydrocarbons** can be classified into two main types which are: 1) aliphatic hydrocarbons and, 2) aromatic hydrocarbons. **Aliphatic hydrocarbons** are further divided into three major groups which are: 1) alkanes, 2) alkenes and 3) alkynes. **Aromatic hydrocarbons** are hydrocarbons that have at least one aromatic ring. They are known as **arenes**. Some examples of aromatic hydrocarbonsinclude benzene (C_6H_6) and methylbenzene ($C_6H_5CH_3$).These **hydrocarbons** can also be classified into: 1) saturated and, 2) unsaturated hydrocarbons. If ahydrocarbon contains only carbon-carbon single bonds (C-C) and has no multiple bonds(double or triple bonds), it is said to be **saturated** because it has the maximum number of bonded hydrogen atoms. If a hydrocarbon contains multiple bonds, it is said to be **unsaturated**. That means that alkanes and cycloalkanes are classified as saturated hydrocarbons while alkenes, alkynes and aromatic hydrocarbons are known as unsaturated hydrocarbons. **Alkanes** are the simplest family of hydrocarbons that contain carbon – hydrogen bonds and carbon – carbon single bonds. The general formula for alkane is **CnH_2n+1** where **n** can be either 1, 2, 3 and so on.

Experimental No. (9) Identification of hydrocarbons

The Alkanes are only very slightly polar. Alkanes have a fairly restricted set of reactions that in which are combustion, halogenations and cracking process. Alkanes are not very reactive and have little biological activity. **Cycloalkanes** or cyclic alkanes are a type of hydrocarbon just like alkanes but contain one or more rings such as cyclopropane, cyclobutane, cyclopentane, cyclohexane and so on. The larger cycloalkanes with greater than 20 carbon atoms are typically called paraffins. Cycloalkanes have the same general formula as alkenes ($\mathbf{CnH_2n}$). Cycloalkanes are similar to alkanes in their general physical properties, but they have higher boiling points, melting points, and densities than alkanes.

Some of the observed **physical properties of hydrocarbons** result from the nonpolar character of the compounds. **A-**In general, hydrocarbons do not mix with polar solvents such as water or ethyl alcohol. **B-**On the other hand, hydrocarbons mix with relatively nonpolar solvents such as carbon tetrachloride, or dichloromethane. **C-**Since the density of most hydrocarbons is less than that of water. Crude oil and crude oil products (home heating oil and gasoline) are mixtures of hydrocarbons; these substances, when spilled on water, spread quickly along the surface because they are insoluble in water. The chemical reactivity of hydrocarbons is determined by the type of bond in the compound. Although saturated hydrocarbons (alkanes) will burn (undergo *combustion*), they are generally unreactive to most reagents.

Alkanes do undergo a substitution reaction with halogens but require ultraviolet light.) Unsaturated hydrocarbons, **alkenes and alkynes**, not only burn, but also react by *addition* of reagents to the double or triple bonds. The addition products become saturated, with fragments of the reagent becoming attached to the carbons of the multiple bond.

Experimental No. (9)   Identification of hydrocarbons

Aromatic compounds burn with a sooty flame as a result of unburned carbon particles being present. These compounds undergo *substitution* in the presence of catalysts rather than an addition reaction.

Chemical and Apparatus

1% aqueous KMnO4, 1% Br_2, Concentrated H_2SO_4, Cyclohexene, Hexane, Test tubes, Toluene, Watch glasses, Ice, distilled water

Procedure of Experimental

A- Physical Properties of Hydrocarbons

1- melting and boiling points

2. *Water solubility and density of hydrocarbons*.

Solubility: Add about 2 ml. of water in a small test tube and add 2 or 3 drops of the hydrocarbon (hexane, cyclohexene, toluene) to be tested. Shake the mixture to determine whether the hydrocarbon is soluble (a colorless second layer may be hard to see). Is there any separation of components? Which component is on the bottom; which component is on the top. Record your results.?

Relative Density: Mix the contents as described above. What do you conclude about the density of the hydrocarbon? Is the hydrocarbon *more* dense than water or *less* dense than water? Record your observations.

B- Chemical Properties of Hydrocarbons

1. *Combustion*. Place 5 drops of each hydrocarbon on separate watch glasses. Carefully ignite each sample with a match. Observe the flame and color of the smoke for each of the samples.

Record your observations on the Report Sheet.

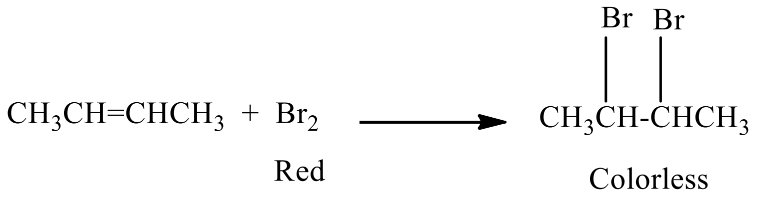
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

$$CH_3CH_2CH_3 + 5O_3 \longrightarrow 3CO_2 + 4H_2O$$

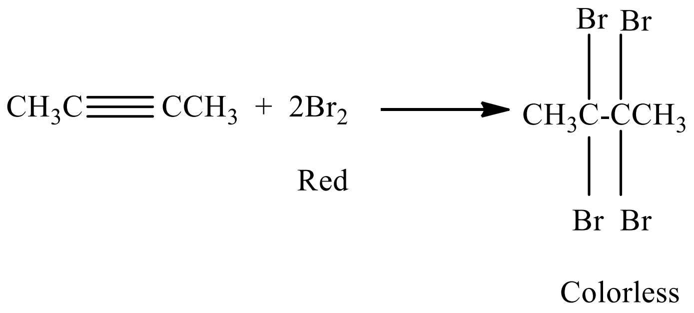
The major component in “natural gas” is the hydrocarbon methane. Other hydrocarbons used for heating or cooking purposes are propane and butane. The products from combustion are carbon dioxide and water (heat is evolved, also).

2. *Reaction with bromine*.

In a small test tube, add (1 ml) of hydrocarbon (hexane, cyclohexene, toluene) to (3-4 ml) of 2% bromine in carbon tetrachloride (Br_2/CCl_4). Shake well and observe after two or three minutes. If the bromine is not decolorized prepare a second similar tube and place on tube in your laboratory locker and the other in bright sunlight. Allow both tubes to stand for ten to fifteen minutes and compare them. Observe the color of each tube, and whether or not hydrogen bromide was evolved and record the results. Record your observations.

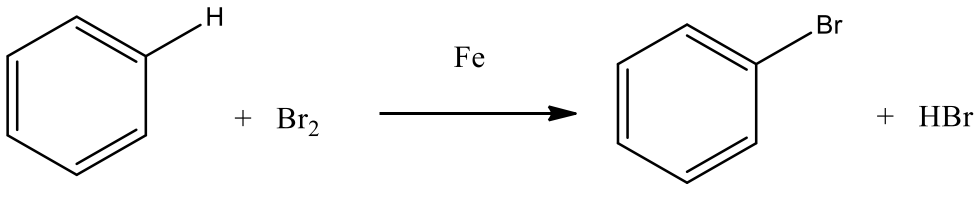


$$CH_3CH{=}CHCH_3 + \underset{\text{Red}}{Br_2} \longrightarrow \underset{\text{Colorless}}{CH_3\overset{Br}{\overset{|}{C}}H\text{-}\overset{Br}{\overset{|}{C}}HCH_3}$$



$$CH_3C{\equiv}CCH_3 + \underset{\text{Red}}{2Br_2} \longrightarrow CH_3\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}\text{-}\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}CH_3$$

Colorless

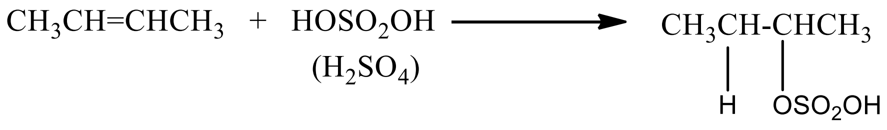


Unsaturated hydrocarbons react rapidly with bromine in a solution of carbon tetrachloride. The reaction is the addition of the elements of bromine to the carbons of the multiple bonds.

The bromine solution is red; the product that has the bromine atoms attached to carbon is colorless. Thus a reaction has taken place when there is a loss of color from the bromine solution and a colorless solution remains. Since **alkanes**, no reaction with bromine is observed; the red color of the reagent would persist when added. **Aromatic compounds** resist addition reactions because of their "aromaticity": *the possession of a closed loop (sextet) of electrons*. These compounds react with bromine in the presence of a catalyst such as iron filings or aluminum chloride. Note that a substitution reaction has taken place and the gas HBr is produced.

4. ***Reaction with concentrated sulfuric acid***.

In a small test tube add 1 ml. of hydrocarbon (hexane, cyclohexene, toluene), cautiously and with gentle shaking, to about 3 ml. of concentrated sulfuric acid. Shake the tubes well and note the results. Observe whether heat evolved and whether the hydrocarbon dissolves. Discard the contents by pouring them into a beaker containing at least 50 mL of water. Although alkanes are inert to cold, concentrated sulfuric acid, alkenes react by addition. The product, alkyl hydrogen sulfate, is soluble in concentrated sulfuric acid. Record your observations.

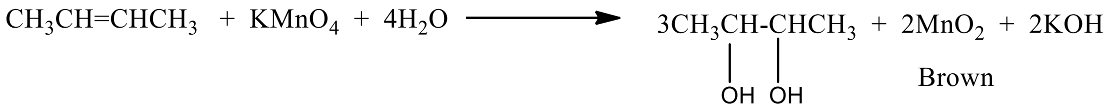


$$CH_3CH{=}CHCH_3 + \underset{(H_2SO_4)}{HOSO_2OH} \longrightarrow CH_3\underset{H}{CH}\text{-}\underset{OSO_2OH}{CH}CH_3$$

Alkenes react with cold concentrated sulfuric acid by addition. Alkyl sulfonic acids form as products and are soluble in H_2SO_4. Saturated hydrocarbons are unreactive (additions are not possible); alkynes react slowly and require a catalyst ($HgSO_4$); aromatic compounds also are unreactive since addition reactions are difficult.

4. ***Reaction with potassium permanganate (Baeyer's Test)***

In a small test tube, add (1 ml) of hydrocarbon (hexane, cyclohexene, toluene) to a mixture of (3 ml) of dilute potassium permanganate solution (0.5 % $KMnO_4$ solution) and (3 ml) of dilute sodium carbonate solution (10% Na_2CO_3 solution) and shake the tube for 1-2 minutes, and note the results. (Note -Dilute sulfuric acid may be substituted for sodium carbonate. This substitution gives a better test reagent for certain purpose since manganese dioxide is not precipitated in the acid solution)



$$CH_3CH{=}CHCH_3 + KMnO_4 + 4H_2O \longrightarrow 3CH_3\underset{OH}{C}H\text{-}\underset{OH}{C}HCH_3 + \underset{\text{Brown}}{2MnO_2} + 2KOH$$

Dilute or alkaline solutions of $KMnO_4$ oxidize unsaturated compounds. Alkanes and aromatic compounds are generally unreactive. Evidence that a reaction has occurred is observed by the loss of the purple color of $KMnO_4$ and the formation of the brown precipitate manganese dioxide, MnO_2.

5. ***Unknowns***. By comparing the observations you made for your unknowns with that of the known hydrocarbons, you can identify unknowns A, B, and C. Record their identities on your Report Sheet.

Experimental No. (9) Identification of hydrocarbons

Table of tests

No.	Name of hydrocarbone	*Combustion*	Test with water		Test with $KMnO_4$	Test with H_2SO_4
			solubility	*Density		
1-						
2-						
3-						
4-						

*Relative densities (L = low, H = high)

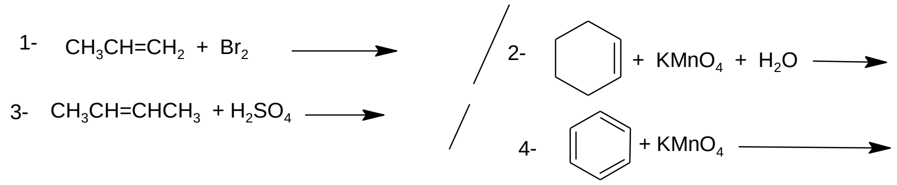
Questions for discussion

1- Distinguish between *saturated* and *unsaturated* hydrocarbons.

2- Show the structural feature that distinguishes whether a hydrocarbon is an alkane, alkene, alkyne, aromatic

3- Hydrocarbons do not mix with water, and they float. Explain these characteristics.

4- Write the structure of the major organic product for the following reactions; if no reaction, write NR.



5- Octane isunbranched alkane of formula C_8H_{18}. Based on your observations in this experiment, predict the following:

a. Solubility in water, b. Combustion characteristics, c. Density versus water.

6- 1-Hexene is alkene. Based on your observations in this experiment, what should you expect to see for this compound in the following tests:

a. Bromine test, b. $KMnO_4$ test, c. Combustion.

Nitration of benzene

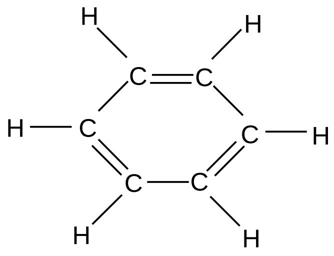
Purpose of experimental

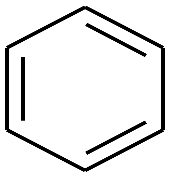
To learn nitration of benzene and preparation of nitrobenzene

Theory part of experimental

Benzene, C_6H_6 is the simplest member of the class of hydrocarbon called aromatic hydrocarbons or arenes. It is a colourless liquid with a characteristic smell.

These aromatic compounds contain a ring of sp^2 carbon atoms, with a delocalized system of π electrons. Aromatic compounds (including aromatic hydrocarbons) are stabilized by the π electron delocalization.



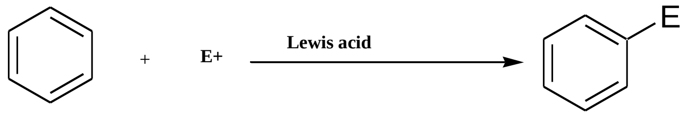


Reactions of benzene

As benzene contains carbon-carbon double bonds, it might be expected to undergo addition reactions readily. This is not the case, however, and benzene will not decolorise bromine water. Neither will benzene readily undergo any other addition reactions. The reason for this is that the delocalized system in benzene is stable, and any reactions, such as addition reactions, which break up the delocalized system will not be favoured. Benzene thus tends to undergo substitution, rather than addition reactions.

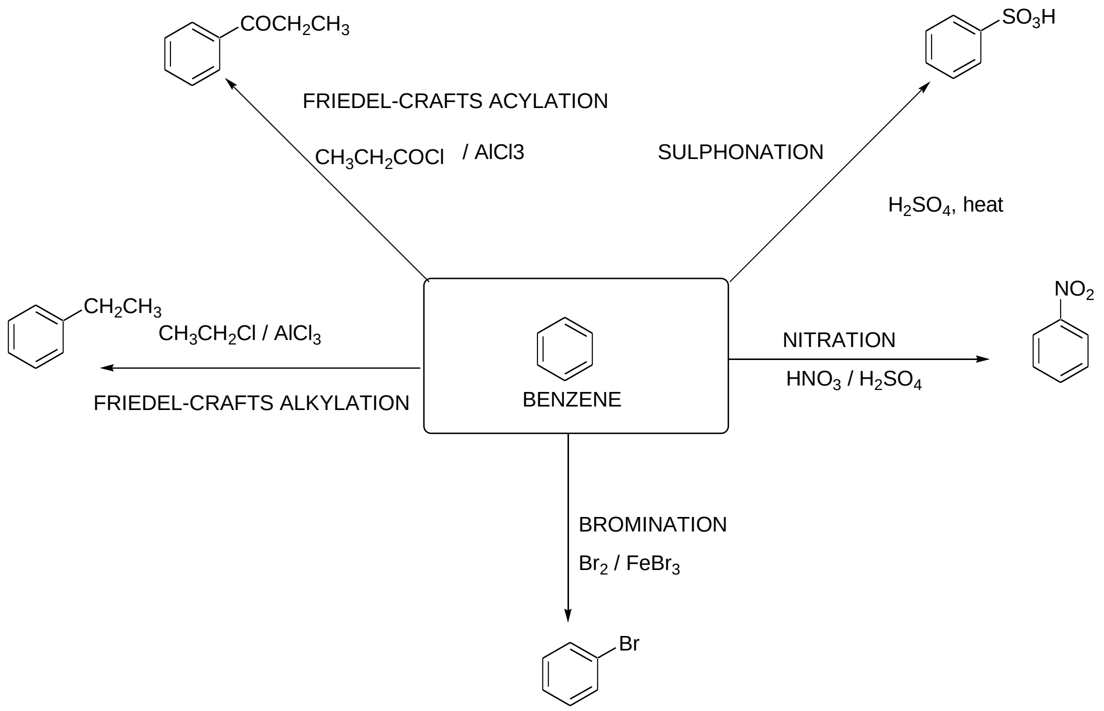
Experimental No. (10) Nitration of benzene

The delocalized electrons constitute an electron-rich area, and they are thus susceptible to attack by electrophiles. Benzene tends to undergo electrophilic substitution.



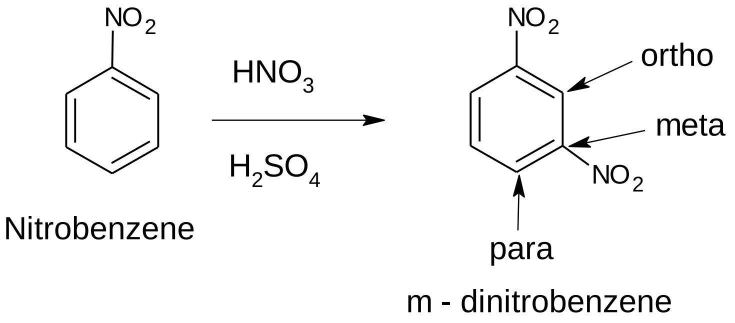
Where E+ is an electrophile (electron deficient species)

There are a variety of substitution reactions undergone by nearly all aromatic rings; these include reactions such as nitration, sulphonation, halogenation, and Friedel-Crafts alkylations and acylations.

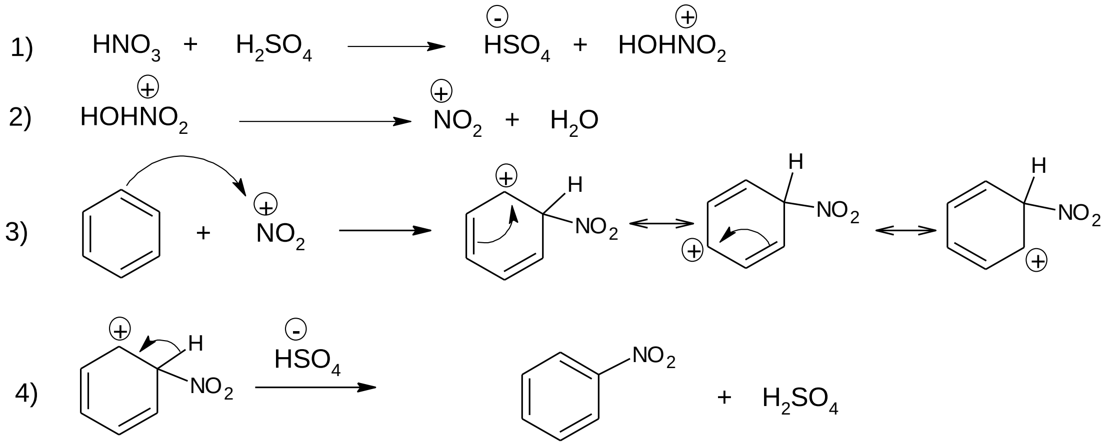


The nitro group (NO_2) is electron withdraw, deactivation of benzene ring and direction the attack on the benzene to meta position

Experimental No. (10) Nitration of benzene



The nitration mechanism of benzene :



Chemical and Apparatus

Benzene, conc.HNO_3, conc.H_2SO_4, cold distilled water, ethanol, ice path, Round bottom, condenser, funnel, electric heater, beaker, balance, filter paper, oven,

Safety Note

Caution: Avoid contact with the acids used in this experiment and the reaction product. Prevent contact with the skin, eyes, and clothing; work in the hood. An acid spill is neutralized using solid sodium carbonate or bicarbonate. The reaction is highly exothermic.

Concentrated nitric acid and concentrated sulfuric acid are both strong oxidizers, and strongly corrosive--wear gloves while handling them, and avoid breathing their vapors.

Experimental No. (10) Nitration of benzene

Procedure of Experimental

1- In hood, prepare a mixture of (4 mL) conc. HNO_3 and (4 mL) conc. H_2SO_4 in a beaker. Cool beaker to room temperature (30^0C) by means of a ice bath, , remove the beaker from the ice bath, wipe off the outside of the conical flask, and clamp it to hotplate .

2- To the conical flask, add (0.5 mL) benzene **DROPWISE** over a period of about 5-10 min; gently swirling the tube to mix the contents after each addition. Keep the reaction mixture between 50 - 55 ^oC. **DO NOT ALLOW THE REACTION MIXTURE TO EXCEED 60 ^{o}C.**

3- After the addition is completed and the exothermic reaction has subsided, put the mixture in the round bottom with condenser and heat the round for (45 min) in a hot water bath, maintaining the temperature in the reaction below 90 ^{o}C during this period.

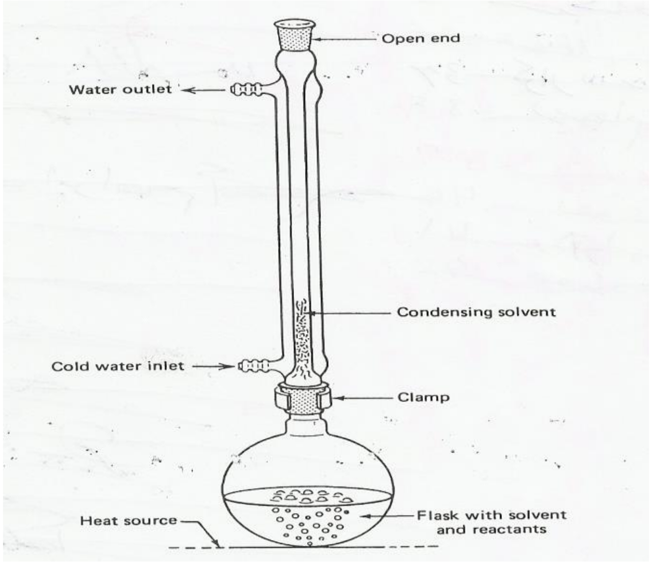


Figure show the reflux of reaction mixture

4- Cool the conical flask in an ice bath to room temperature.

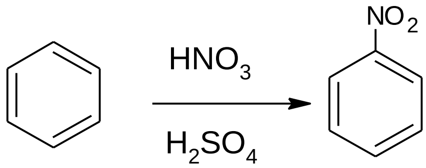
5- Pour the reaction mixture into 100 mL of distilled water which is in a 150 mL beaker.

6- Isolate the crude product by filtration.

7- Wash the filter cake thoroughly with cold (0-10°C) distilled water and dry the filter in the oven.

8- The crude product may be purified by recrystallization by hot ethanol, then determine the weight, melting point, and percentage yield.

Calculation



M.Wt =

Wt. = gm

M.Wt =

Wt. = ?

$$\textbf{Theoritical weight of nitobenzene} = \frac{\text{Wt of benzene} \times \text{M.Wt of nitrobenzene}}{\text{M.Wt of benzene}}$$

Experimental weight = weight of product with filter paper – weight of filter paper

of nitrobenzene

$$\text{\% of nitrobenzene} = \frac{\textbf{Experimental weight}}{\textbf{Theoritical weight}} \text{ X } 100$$

Questions for discussion

1. Which is nitrated faster? toluene or nitrobenzene, toluene or phenol ? Explain.
2. List three combinations of reagents used for nitration of aromatic compounds?
3. Why is concentrated sulfuric acid employed in this reaction? What is the electrophile that is produced by the reaction of sulfuric acid and nitric acid/
4. Why is it important to maintain the reaction temperature low and the addition of nitric acid-sulfuric acid mixture carried out slowly?
5. Explain why concentrated H_2SO_4, not concentrated HCl, was used in this experiment?

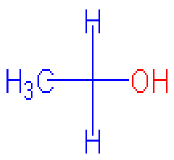
Alcohols

Purpose of experimental

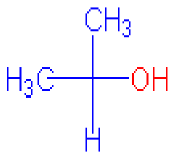
1. To characterization of alcohols
2. To learn some of characteristic chemical reactions of alcohols

Theory part of experimental

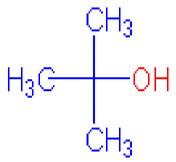
Alcohols and Phenols contain the functional group, OH. In a phenol, the OH group is connected to a carbon on a benzene ring where as in alcohols, the OH group is connected to a sp^3 hybridized carbon atom. Alcohols are classified as 1^0, 2^0 and 3^0, depending on the number of carbon atoms connected to the carbon bearing the OH group. Representative examples of a phenol, and three types of alcohols are shown below.



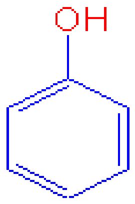
A primary alcohol



A secondary alcohol



A tertiary alcohol



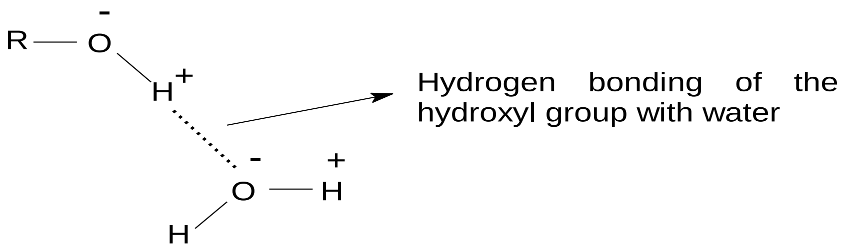
Phenol

Phenols are more acidic than alcohols. Alcohols as well as phenols find a variety of industrial, pharmaceutical, and even household applications. Derivatives of alcohols and phenols are found in medicines, alcohols are used as common industrial solvents etc.

Physical Properties

- Since the hydroxyl group is present in alcohols and phenols, these compounds are polar because of the hydroxyl group.
- The polar side and hydrogen bonding allows them to dissolve in water.

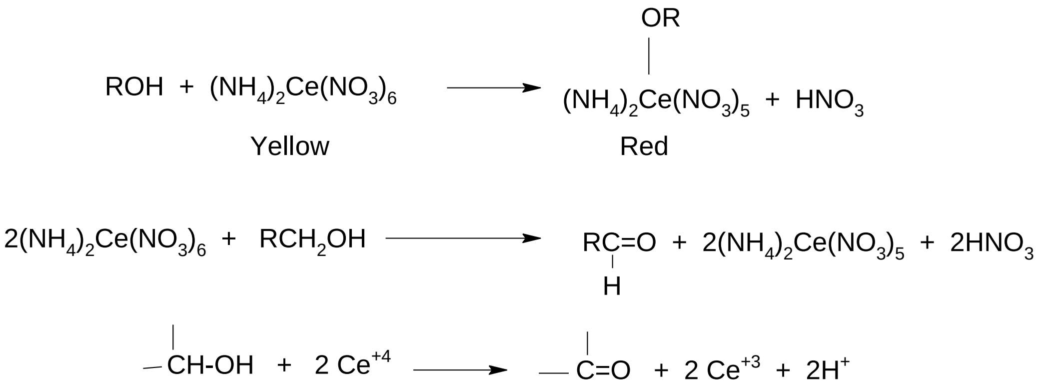
- The non-polar side allows them to dissolve in certain organic solvents, such as dichloromethane and diethyl ether.
- Alcohols are not acidic Phenols are acidic



Chemical Properties

1. **General test for alcohols by addition of Ceric ammonium nitrate $(NH_4)_2Ce(NO_3)_6$**

Ceric ammonium nitrate (yellow soluion) is an oxidizing agent that reacts with alcohols to give a red complex and with phenols to give a brown to greenish brown precipitate.



$$\underset{\text{Yellow}}{ROH + (NH_4)_2Ce(NO_3)_6} \longrightarrow \underset{\text{Red}}{(NH_4)_2\overset{\overset{OR}{|}}{Ce}(NO_3)_5} + HNO_3$$

$$2(NH_4)_2Ce(NO_3)_6 + RCH_2OH \longrightarrow R\underset{\underset{H}{|}}{C}{=}O + 2(NH_4)_2Ce(NO_3)_5 + 2HNO_3$$

$$-\overset{|}{C}H\text{-}OH + 2\,Ce^{+4} \longrightarrow -\overset{|}{C}{=}O + 2\,Ce^{+3} + 2H^{+}$$

2. **Lucas test**: This test is used to distinguish between water-soluble primary, secondary, and tertiary alcohols. Lucas reagent is a mixture of zinc chloride, $ZnCl_2$, in concentrated HCl. Upon addition of this reagent, a tertiary alcohol reacts rapidly and immediately gives an insoluble white layer. A secondary alcohol reacts slowly and, after heating slightly, gives the white layer within 15-20 min. A primary

alcohol does not react. Any formation of a heterogeneous phase or appearance of an emulsion is a positive test. The reaction depends on the formation of a stable carbonium ion. The more stable the carbonium ion formed, the faster the reaction is.

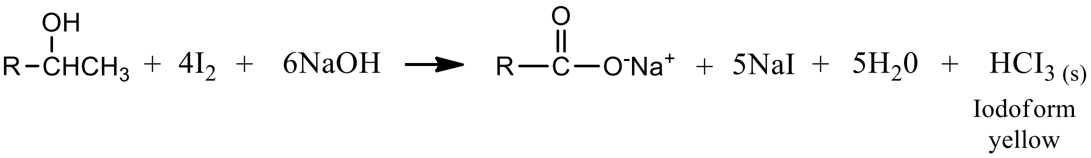
$$\underset{\text{Primary alcohol}}{CH_3CH_2{-}OH} + HCl + ZnCl_2 \longrightarrow \text{No reaction}$$

$$\underset{\text{Secondary alcohol}}{(CH_3)_2CH{-}OH} + HCl + ZnCl_2 \longrightarrow \underset{\text{Insoluble}}{(CH_3)_2CH{-}Cl} + H_2O \ \text{(10 min. heat)}$$

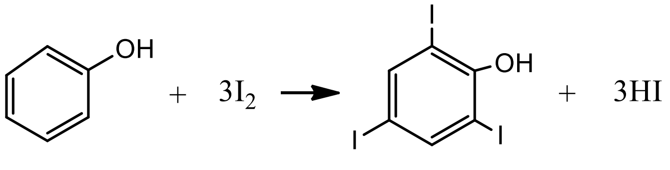
$$\underset{\text{Tertiary alcohol}}{(CH_3)_3C{-}OH} + HCl + ZnCl_2 \longrightarrow \underset{\text{Insoluble}}{(CH_3)_3C{-}Cl} + H_2O \ (< 5 \text{ min.})$$

3- Iodoform test

This test is used to distinguish alcohols with the partial structure R-CH(OH) CH_3 from other alcohols. Phenols also react.



$$R{-}\overset{OH}{\overset{|}{C}}HCH_3 + 4I_2 + 6NaOH \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}O^-Na^+ + 5NaI + 5H_20 + \underset{\substack{\text{Iodoform}\\ \text{yellow}}}{HCI_{3\,(s)}}$$



Triiodophenol
yellow precipitate

The mechanism of this reaction involves many steps, the first of which is the formation of the oxidizing agent sodium hypoiodate (NaOI).

$$I_2 + 2NaOH \longrightarrow NaOI + NaI + H_2O$$

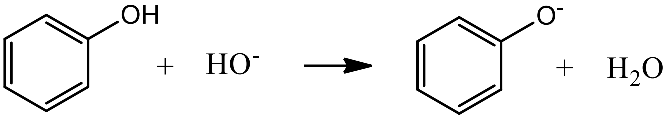
The next steps are: Oxidation of the alcohol to the corresponding aldehyde or ketone by sodium hypoiodate .

$$RCH_2\text{-}OH + NaOI \longrightarrow RCHO + NaI + H_2O$$

Both ethanol and sec-butanol give positive iodoform test and they can be differentiated only by testing their solubility in water; sec-butanol is less soluble in water than ethanol.

4-Acidity

Phenols are acidic and dissolve in a basic solution. Alcohols are not acidic and will not dissolve in a basic solution.



Chemical and Apparatus

Different alcohols, ceric ammonium nitrate solution, H_2O, 10% NaOH,

iodine (I_2) solution, test tube

Procedure of Experimental

1- General test

In test tube mix (1 ml) of the alcohol with one drop of ceric ammonium nitrate solution(reagent). A red complex indicates a positive test.

2- Lucas test

Mix (3 ml) of the alcohol with (1 ml) of Lucas reagent & observe the results: **Tertiary alcohols** give two phases that separate within 2-3 minutes. **Secondary alcohols** give two phases that separate after 15-

20 minutes (giving a cloudy solution). In **primary alcohols** one layer appears

3- Iodoform test :

- In test tube mix (3 drops) of alcohol and (1 mL) of H_2O.
- Add about (1 ml) of 10% NaOH solution.
- Add iodine (I_2) solution drop wise with shaking until either a yellow iodoform precipitate is formed(test is positive and is completed) or the dark colour of the iodine solution is present. Allow the solution to stand for (3 minutes) during which period check for the appearance of the yellow precipitate at the bottom of the test tube. If there is no precipitate , warm the solution in water bath (60˚C) for (3 minutes) with shaking from time to time and check for the yellow precipitate. Finally if no precipitate is formed after the 10 minutes-standing period, dilute the solution with an equal volume of distilled water to obtain the iodoform precipitate.

Results:

Record the results in the following table

No.	Name of alcohol	General test	Lucas test	Iodoform test
1- 2- 3-				

Questions for discussion

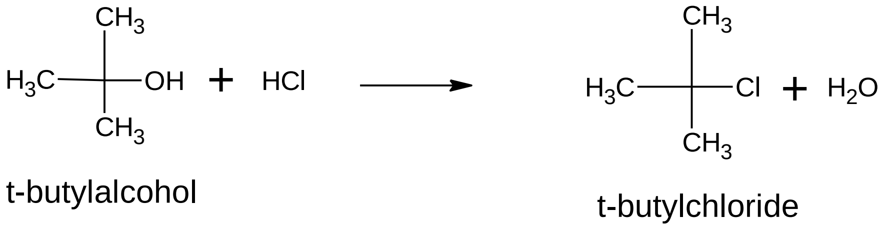
1- Explain , why the rate of the reaction among different alcohols with lucas reagent is shown below:

tert– alcohol > sec–alcohol > primary alcohol (–ve)

2- Write the mechanism of iodoform test reaction

Experimental No. (12) Alkyl halides

Preparation of t-butylchloride



Purpose of experimental

To convert t-butylalcohol to butylchloride using an S_N1 reaction with HCl.

Theory part of experimental

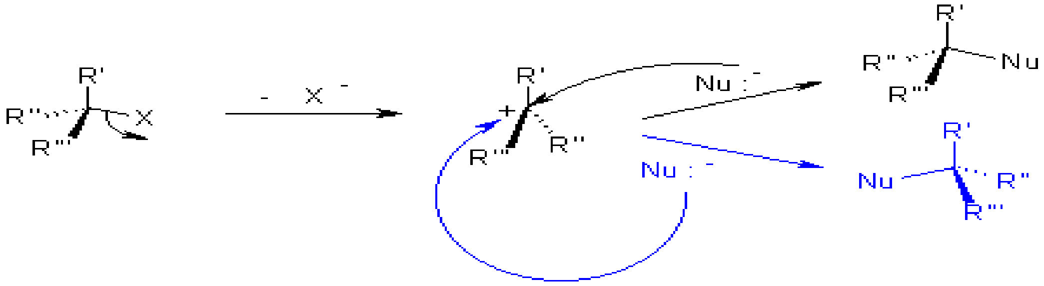
The most common of the variety of methods available for preparing alkyl halides is the replacement of the hydroxyl group of an alcohol. This type of reaction is representative of an important class of reactions in organic chemistry called *nucleophilic aliphatic substitution reactions*. In this experiment you will convert an alcohol to an alkyl halide by reaction with a hydrohalic acid. The overall reaction is shown in equation (1); however the mechanism of the reaction depends on the structure of the alkyl group bearing the functional group being replaced.

$$\text{R-OH} + \text{H-X} \rightarrow \text{R-X} + H_2O \quad \ldots\ldots\ldots\ldots(1)$$

The reaction may occur by one of two mechanisms designated S_N1 or S_N2. Which mechanism operates depends on the structure of the R group and the reaction conditions.

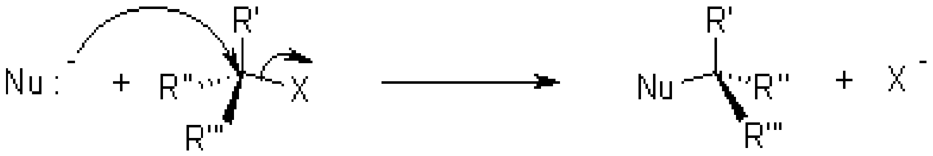
When (R) is a tertiary alkyl group and is called S_N1 (substitution, nucleophilic, unimolecular).

S_N1 Mechanism:



If (R) is a primary alkyl group, then substitution occurs generally without formation of the carbocation by an S_N2 mechanism (why no carbocation? Because 1° carbocations are generally unstable). When (R) is a secondary group, an S_N1 or an S_N2 mechanism may be involved, depending on the reaction conditions.

S_N2 Mechanism:



Methods for preparation of alkyl halides

1. From alcohols : R-OH + HX $\longrightarrow$ R-X
2. Halogenation of hydrocarbons : R-H + X_2 $\longrightarrow$ R-X
3. Addition of HX to alkenes : $CH_2{=}CH_2$ + HX $\longrightarrow$ CH_3-CH_2-X

Experimental No. (12) Alkyl halides

Physical properties of alkyl halides

1. Haloalkanes have higher boiling points than alkanes with the same number of carbons.
2. The boiling point increases with increasing atomic weight of the halogen and carbon number.
3. Haloalkanes have low polarity, and are soluble in the typical organic solvents of low polarity, like benzene, ether, chloroform. They are insoluble in water, probably because of their inability to form hydrogen bonds.

Chemical and Apparatus

t-butyl alcohol, conc.HCl, 5% Na_2CO3 , beaker, seperatory funnel, cylinder

Procedure of Experimental

1. Place (6.0 mL) of *t*-butyl alcohol in seperatory funnel
2. Cautiously add (12 mL) of conc.HCl and shaking the mixture and allow the mixture to separate completely into two layers, cancel the lower aqueous layer.

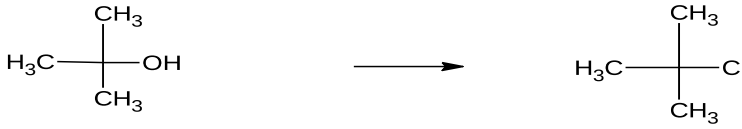
Note : to verify that t-butyl chloride should be the upper layer, add a few drops of water and observe. The water should not dissolve in the upper layer.

3. Add (10 mL) of 5% Na_2CO3 to the *t*-butyl chloride layer (in seperatory funnel) and shaking the mixture for separate completely to two layers, cancel the lower aqueous layer and measure the volume the upper layer (t-butyl chloride) by cylinder.
4. Add a minute amount of anh.Na_2SO_4 to upper layer (to drying) and swirl the solution. Filter the solution and distillation the solution to get pure t-butyl chloride.

5. **Test for *t*-butyl chloride with $AgNO_3$**: Place a few drops of the *t*-butyl chloride in test tube and Add (2 drops) of 0.1M $AgNO_3$ and mix.

If no reaction is observed in 5 minutes at room temperature, warm the mixture and observe any change. The appearance of a white precipitate indicates that a reaction has taken place between the alkyl halide and silver nitrate.

Calculation



M.Wt =
Wt =

M.Wt =
Wt =

Wt. = density x volume

$$\text{Theoritical weight of t- butyl chloride} = \frac{\text{Wt. of R - OH} \times \text{M.Wt. of R -Cl}}{\text{M.Wt of R - OH}}$$

$$\text{\% of t- butyl chloride} = \frac{\text{Experimental weight of t- butyl chloride}}{\text{Theoritical weight of t- butyl chloride}} \times 100$$

Questions for discussion

1. Why is the *t*-butyl chloride phase the upper layer?
2. What was the purpose of addition Na_2CO_3 solution? Give equations.
3. Why is it undesirable to add aqueous NaOH (instead of Na_2CO_3 solution) to the t-butyl chloride solution (in the step 3) ?
4. Write the mechanism of reaction t-butyl alcohol with HCl for prepare t-butyl chloride.

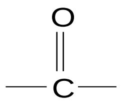
Aldehydes and ketones

Purpose of experimental

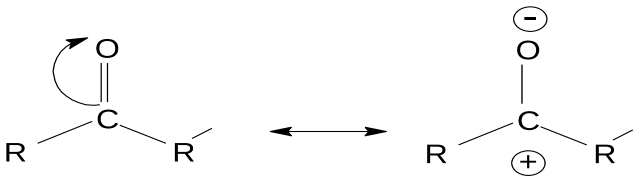
To learn identification of aldehydes , ketones and investigate the chemical properties of aldehydes and ketones.

Theory part of experimental

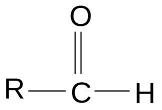
Aldehydes and ketones are representative of compounds which possess the carbonyl group. The carbonyl group (C=O), found in aldehydes and ketones, is a very important functional group that is involved in several common reactions. This particular functionality is unique because of the polarization (dipolar resonance) between the carbon-oxygen π bond.



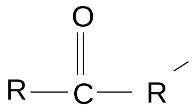
The carbonyl group



Aldehydes have at least one hydrogen attached to the carbonyl carbon; in ketones, no hydrogens are directly attached to the carbonyl carbon, only carbon containing R-groups:



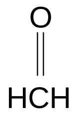
aldehyde



ketone

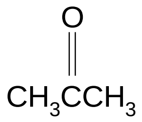
(R and R′ can be alkyl or aromatic)

Aldehydes and ketones of low molecular weight have commercial importance. Many others occur naturally. Examples :



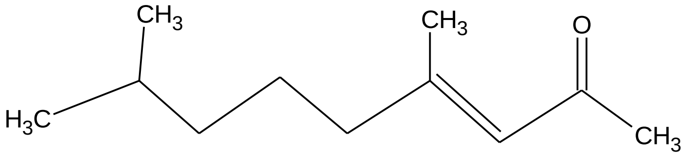
$H\overset{O}{\overset{\|}{C}}H$

formaldehyde



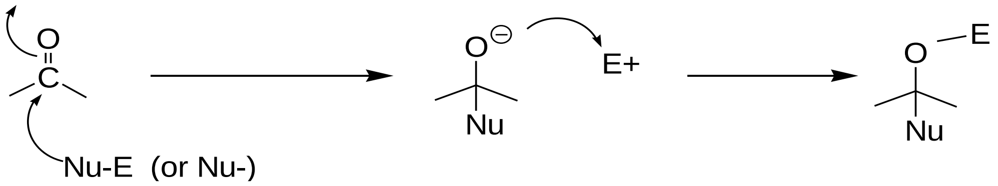
$CH_3\overset{O}{\overset{\|}{C}}CH_3$

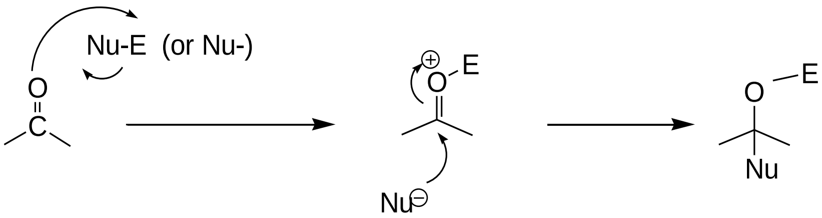
acetone



citral (lemongrass oil)

Due to the resonance of the C-O bond, there are a variety of reactions where the electrophilic carbon is attacked by nucleophiles (Lewis bases) and the oxygen reacts with corresponding electrophiles (Lewis acids). The result of the reaction is the addition of a Nu-E to the π bond of the carbonyl group. The two most common mechanisms are outlined below, although they may vary based on the reagent and reaction conditions.



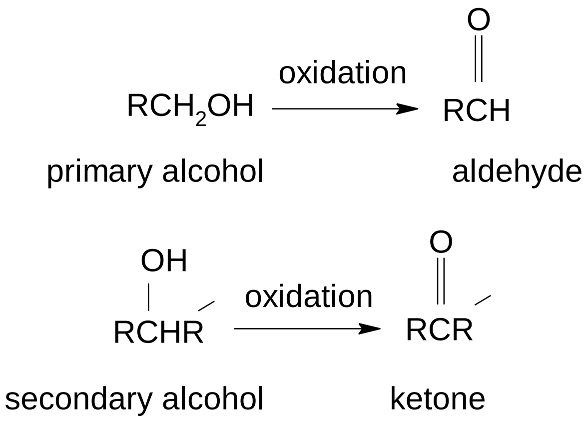


The carbonyl groups in both aldehydes and ketones will be examined in this experiment. Although the two groups often react similarly, aldehydes commonly react faster than ketones (with the same reagent) due to less steric hindrance at the carbonyl group. Aldehydes are also more easily oxidized than ketones. You will examine the similarities and differences between ketones and aldehydes and then use those skills to accurately identify an unknown compound containing a carbonyl group.

Experimental No. (13) Aldehydes and ketones

Physical properties and preparation

Aldehydes and ketones are polar compounds soluble in water and polar solvents. **Aldehydes** prepare by oxidation primary alcohols, while **ketones** prepare by oxidation secondary alcohols.



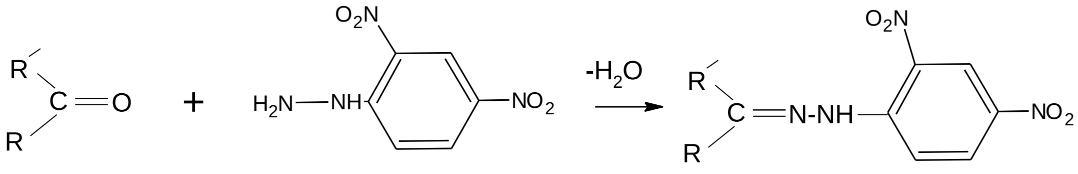
Chemical and Apparatus

Tollen’s reagent (prepare from mixing (1ml) of 5% $AgNO_3$, (3 drops) of 5% NaOH), 2,4-dinitrophenylhydrazine, 10% NaOH, iodine (I_2) solution, aldehyde compound, ketone compound

Procedure of Experimental

1- General test for aldehydes and ketones- by reaction with nitrogen nucleophiles (2,4- Dinitrophenylhydrazine (DNP) Test), Brady’s Test

2,4-dinitrophenylhydrazine can be used to qualitatively detect the carbonyl group functionality of an aldehyde or ketone functional group. A positive test is signaled by a yellow/red precipitate, known as a dinitrophenylydrazone. The solid derivatives are more stable than the original liquid compound.



Aldehyde : R = alkyl or aryl, R' = hydrogen

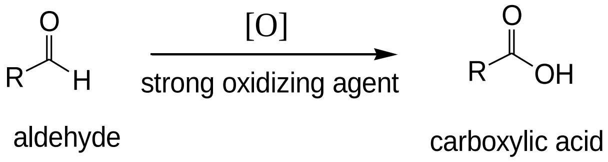
Ketone : R = alkyl or aryl, R' = alkyl or aryl

Procedure :

- Place 5 drops of aldehyde or ketone into separately labeled clean, dry test tubes and add (1ml) of the 2,4-dinitrophenylhydrazine reagent to each. If no precipitate forms immediately, heat for 5 min. in a warm water bath (60 °C), cool.
- A positive test is denoted by a yellow→orange/red→red crystalline precipitate of the 2,4-dinitrophenylhydrazone derivative within a few minutes.
- Record your observations.

2- Oxidation

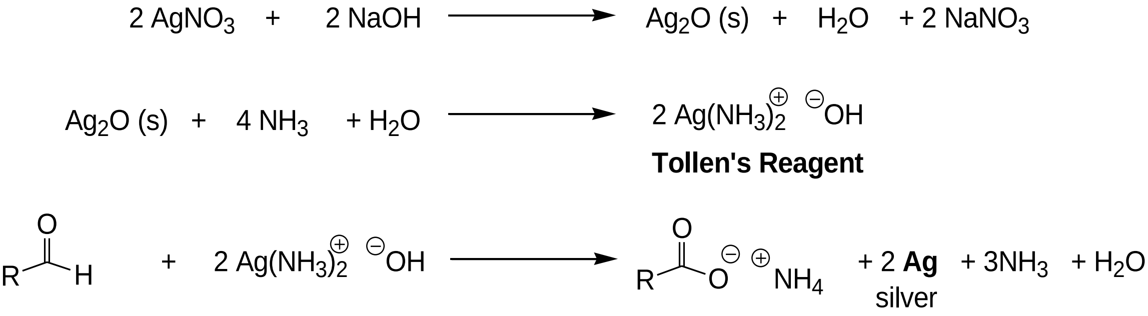
Aldehydes are more rapidly oxidized than ketones due to the hydrogen atom bonded to the α-carbon. Aldehydes are oxidized to carboxylic acids.



Ketones are not readily oxidized, which makes the two functional groups easily distinguishable. Only under extreme conditions (strong reagents and high temperature) can ketones be oxidized since the reaction requires the cleavage of a carbon-carbon bond.

Tollen's Test

Commonly known as the Silver Mirror Test, this distinctive qualitative test involves the oxidation of *aldehydes* to their corresponding carboxylic acid. The oxidizing agent is a silver complex ion [$Ag(NH_3)^+_2$] which is reduced to a metallic silver which remains on the walls of the test tube as a mirror. Otherwise, the silver is deposited as a black precipitate. Tollen's reagent is prepared by dissolving silver oxide in ammonia:



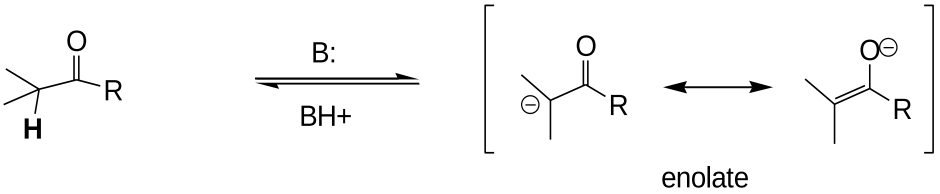
Procedure :

- Place 5 drops of aldehyde or ketone into separately labeled clean, dry test tubes Then, add (2 ml) of the prepared Tollens' reagent and mix.
- Place the test tube in a 60 °C water bath for 5 min. Remove the test tubes from the water and look for a silver mirror. If the tube is clean, a silver mirror will be formed; if not, a black precipitate of finely divided silver will appear.

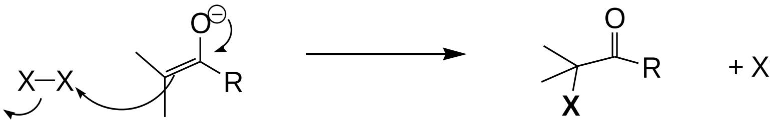
- Record your results on the report sheet.
- Clean your test tubes with 1 M HNO_3 and discard the solution in a waste container designated by your instructor.

3- The Haloform Reaction

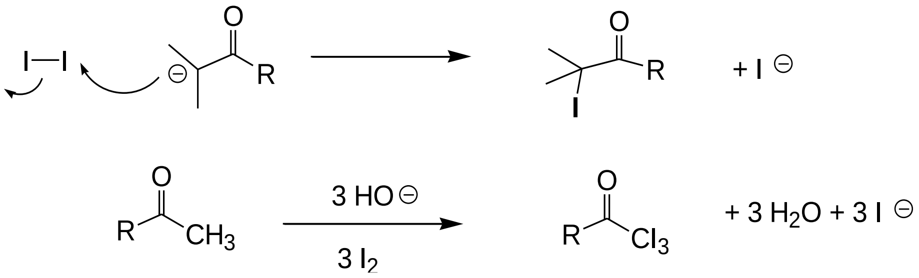
The haloform reaction is unique in the way that it occurs at the α-carbon of the carbonyl group. This reaction arises due to the increased acidity of the α-hydrogens and the resonance stabilization of the conjugate base (enolate anion).



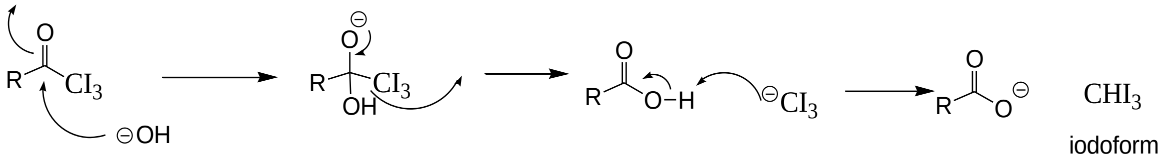
This reactive enolate anion acts as a nucleophile with halogens, generating an α-halo substitution product. Halogenation occurs to produce α-halocarbonyl compounds:



The first substituting halogens cause an electron withdrawing effect which makes any remaining hydrogens even more acidic. These hydrogens are then replaced quickly by other halogens. As seen below, a methyl group (α) to a carbonyl group is converted to a trihalomethyl group in a stepwise fashion.



With the addition of excess base, the electron withdrawing trihalo compound is cleaved, and the iodoform is generated.



Only carbonyl compounds with α-methyl groups undergo the carbon-carbon cleavage that produce the haloform and the corresponding carboxylic acid. This is due to the weakened bond that *only* results when three halogens are attached to the carbon (making it a sufficient leaving group).

When bromine or chlorine is used instead of iodine, the products are bromoform and chloroform, respectively. Most commonly, this reaction is used to test for the presence of methyl ketones, which uses iodine because it is safer and iodoform is a highly insoluble crystalline yellow solid that has a medicinal odor.

Procedure :

- Obtain two clean test tubes (not rinsed with acetone) and add 2-4 drops of aldehyde or ketone and Add about 2.5 mL of the base solution provided (NaOH) and then about 0.75 mL of the iodine solution. Shake well.

- Shake well and put into an ice bath if necessary.
- Record your observations.

Table of results

Compound	General test	Tollen’s Test	Haloform test
Aldehyde			
Ketone			

Questions for discussion

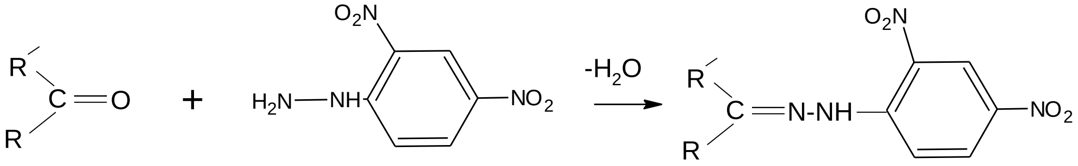
1. How can Tollens’ reagent be used to distinguish between an aldehyde and a ketone?
2. Explain, why Aldehydes are more active than ketones in oxidation?
3. Write the reaction of haloform reaction for ketone

Experimental No. (14) Derivatives of carbonyl compounds

Derivatives of carbonyl compounds

Purpose of experimental

Preparation of 2,4-dinitrophenylhydrazone



Aldehyde : R = alkyl or aryl, R′ = hydrogen

Ketone : R = alkyl or aryl, R′ = alkyl or aryl

Theory part of experimental

carbonyl compounds (aldehydes and ketones) react with ammonia derivatives such as 2,4-Dinitrophenyl hydrazine, semicarbazide and hydroxylamine, etc. to form orange-red coloured stable products which have well defined melting points. These compounds are useful in identification and characterization of carbonyl compounds. The reaction catalyzed by protonic acids such as HCl, H_2SO_4, CH_3COOH etc. involves nucleophilic addition of the ammonia derivatives to the carbonyl carbon followed by elimination of water molecule. pH of the reaction should be maintained around 5 to 6.

Chemical and Apparatus

Benzaldehyde, 2,4-dinitrophenylhydrazine, ethanol, sulphuric acid, beaker, heater, filter paper, funnel,

Experimental No. (14) Derivatives of carbonyl compounds

Procedure of Experimental

Part A: Preparation the 2,4-dinitrophenylhydrazine test reagent.

1. Weigh out 0.5 g of 2,4-dinitrophenylhydrazine and dissolve in 10 mL of concentrated sulphuric acid in a beaker.
2. Add this solution carefully to a solution of 15 mL of ethanol and 5 mL of deionised water. This gives the yellow-brown stock solution. The solution can be used for about 10 days but it gradually deteriorates as a precipitate forms

Part B: Preparation of Benzaldehyde 2,4-Dinitrophenyl hydrazone

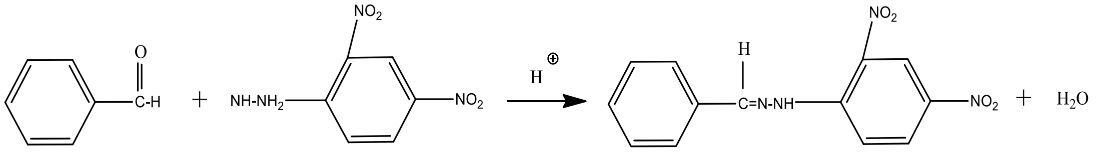
1- In a clean and dry test tube or beaker take 2 ml of benzaldehyde. Add 10 ml of 2,4-dinitrophenylhydrazine reagent

2- Warm the contents of tube or beaker on water bath for 5 minutes and allow the tube or beaker to stand at room temperature for 5 minutes.

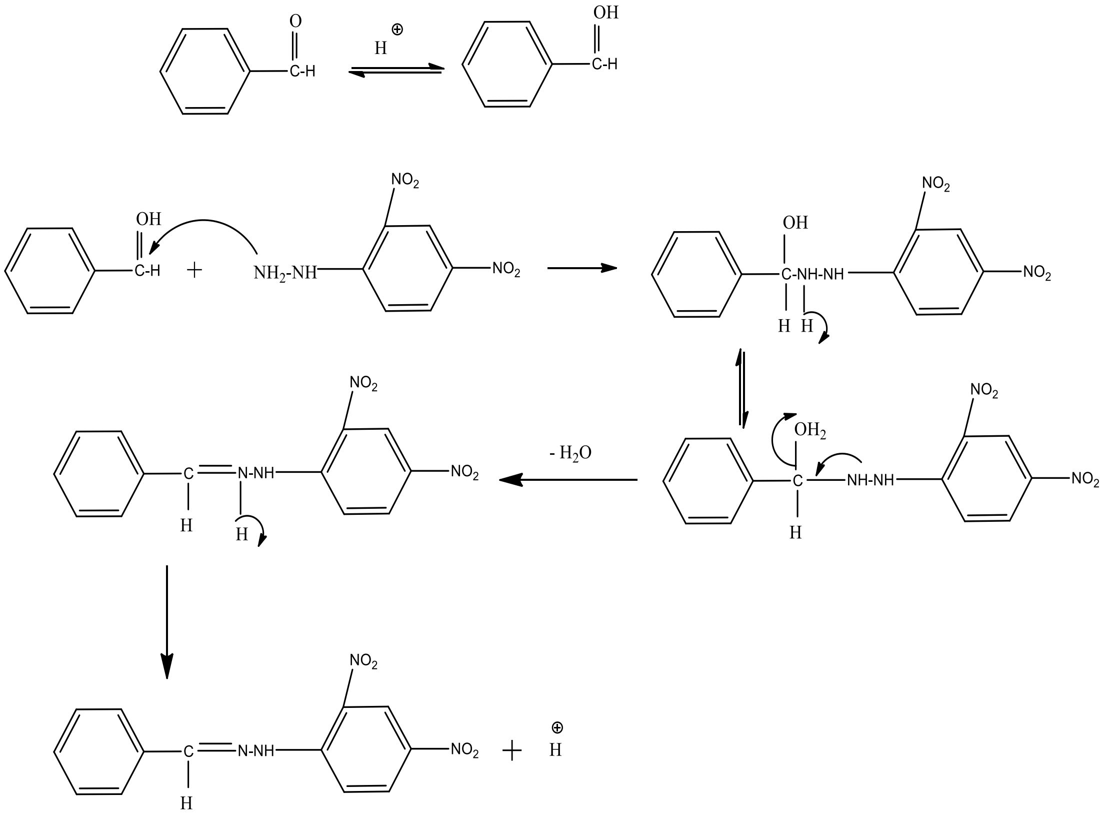
3- Cool the contents of tube or beaker in ice water bath when an orange-coloured precipitate of Benzaldehyde 2,4-Dinitrophenyl hydrazone will separate out.

4- Filter the product and dry it.

5- Record the yield of the product and determine the melting point of the product, (lit. 237 ^{o}C).

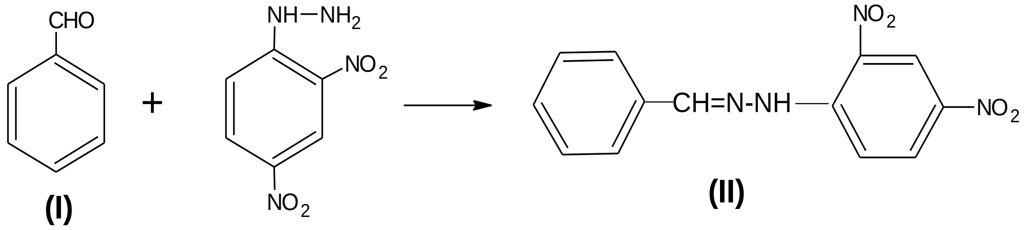

O
C-H
NH-NH₂
NO₂
NO₂
H⊕
H
C=N-NH
NO₂
NO₂
H₂O

Mechanism:


O
C-H
H⊕
OH
C-H
OH
C-H
NH₂-NH
NO₂
NO₂
OH
C-NH-NH
H H
NO₂
NO₂
OH₂
C
NH-NH
H
NO₂
NO₂
- H₂O
C
N-NH
H
H
NO₂
NO₂
C
N-NH
H
NO₂
NO₂
H⊕

Experimental No. (14) Derivatives of carbonyl compounds

Calculation



M.Wt =

Wt. =

M.Wt =

Wt. =

weight = density x volume

$$\text{Theoritical weight of } \mathbf{(II)} = \frac{\text{Wt. of } \mathbf{(I)} \ \mathbf{X} \ \text{M.Wt of } \mathbf{(II)}}{\text{M.Wt of } \mathbf{(II)}}$$

$$\text{\% of benzaldehyde 2,4-dinitrophenylhydrazone} = \frac{\text{Experimental weight of } \mathbf{(II)}}{\text{Theoritical weight of } \mathbf{(II)}} \text{ X } 100$$

Questions for discussion

1. Can you write equations for any reactions occurring?
2. What is the purpose of making derivatives of unknowns?
3. Why we added the sulphuric acid in preparation of Benzaldehyde 2,4-Dinitrophenyl hydrazone
4. Which method use to purification of yield (Benzaldehyde 2,4-Dinitrophenyl hydrazone)

Chromatography

Purpose of experimental

1- Determine the number of components in a mixture via paper chromatography
2- Verify a substance's identity
3- Monitor the progress of a reaction

Theory part of experimental

The name *chromatography* (Greek "color") comes from a technique used by the Russian botanist Michael Tswett in 1903 to separate plant pigments from green leaves. Chromatography is the separation of two or more compounds or ions by the distribution between two phases, one which is moving and the other which is stationary. These two phases can be solid-liquid, liquid-liquid or gas-liquid. Chromatography divided into :

1) plate Chromatography , 2) column Chromatography.

The plate Chromatography divided into:

A) Paper Chromatography, B) Thin Layer Chromatography (TLC).

TLC is normally done on a small glass or plastic plate coated with a thin layer of a solid — the most common are *silica* (SiO_2) or *alumina* (Al_2O_3), this is the stationary phase. TLC, is a solid-liquid form of chromatography where the stationary phase is normally a polar absorbent and the mobile phase (the eluent) can be a single solvent or solvent mixture.

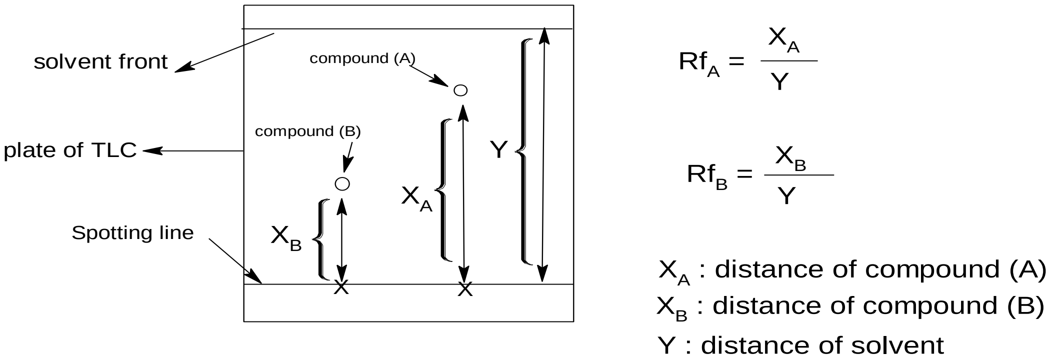
For silica gel-coated TLC plates, the solvent (eluent) polarity strength increases in the following order: perfluoroalkane **(weakest)**, hexane ,

pentane, carbontetrachloride, benzene/toluene, dichloromethane, diethyl ether, ethyl acetate, acetonitrile, acetone, 2-propanol/*n*-butanol , water , methanol, triethylamine, acetic acid, formic acid **(strongest)**.

Polar compounds are adsorbed strongly and therefore move along the plate slowly, while non-polar compounds are absorbed only weakly and are therefore carried along the plate more quickly. Of course, solvent polarity also affects how fast compounds travel. Polar compounds are carried along quickly by polar solvents, but move slowly or not at all with non-polar solvents. Because non-polar compounds don't adhere strongly to the silica, they tend to move more quickly in most solvents.
The sample mixture is applied near the bottom of the plate as a small spot, then placed in a jar containing a few ml of solvent. A solvent (the moving phase) is allowed to travel across the paper by capillary action. As the solvent front moves, the components of the mixture separate.. Each compound in the mixture moves at a different rate, depending on it’s : a) solubility in the mobile phase and, b) the strength of its absorption to the stationary phase. The ratio of the distance a compound moves to the distance the solvent moves is the **Rf** value (retention factor). This value is characteristic of the compound, the solvent, and the stationary phase.

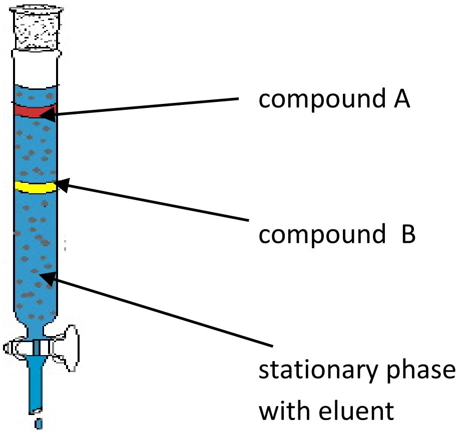
$$R_f = \frac{\text{distance traveled by a component of the mixture}}{\text{distance traveled by the solvent}}$$

Experimental No. (15) Chromatography



{Figure of paper chromatography}

Column chromatography is used most conveniently for preparative purposes, when one deals with a relatively large amount of the mixture and the components need to be isolated in milligrams or grams quantities.



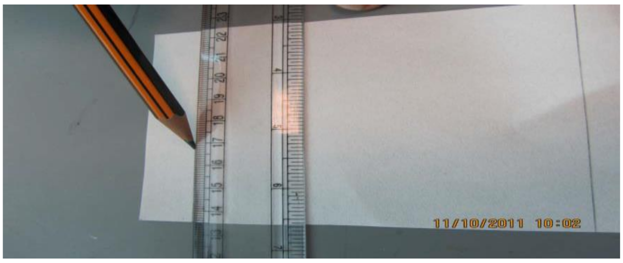
{ figure of column chromatography }

Chemical and Apparatus

Gar or beaker , watch glass, solvents

Procedure of Experimental

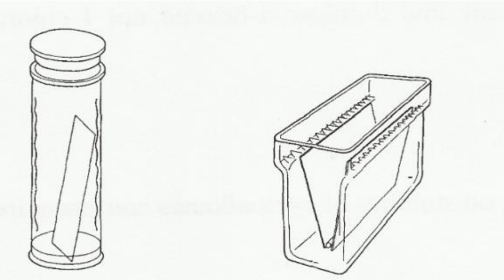
1- Draw a light pencil line 1-2cm from the bottom of the paper.



2- Place a single drop of compound at intervals 2cm.

3- Dry with hair dryer.

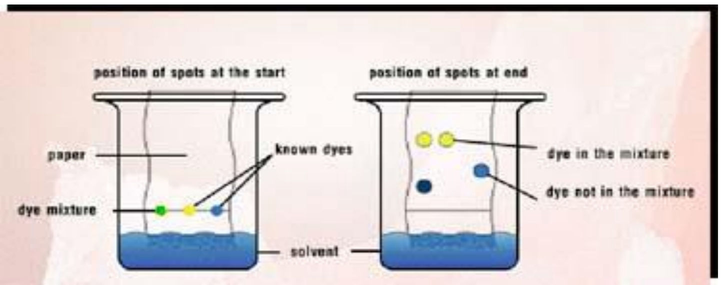
4- Dip the paper in the jar. Do not disturb the beaker while the chromatograms are developing.

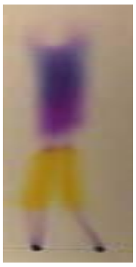


{Figure of Gar}

5- Allow to run until the solvent has nearly reached the top of the paper.

Experimental No. (15) Chromatography

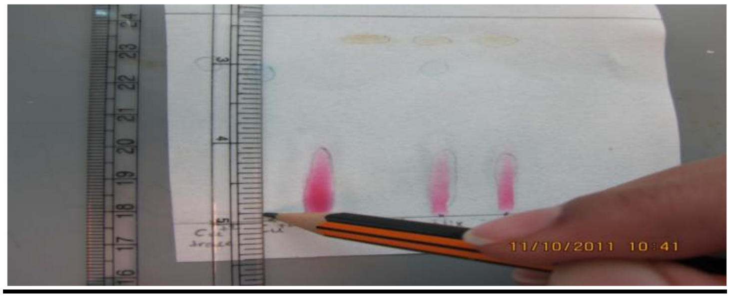




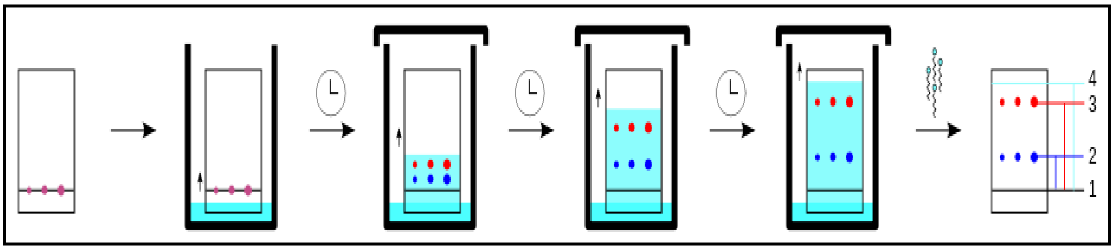
6- Remove the paper.

7- Dry the paper.

8- Measure distances from the start line to the solvent front and to the middle of each spot.(Rf) Write down results in your work sheet.



Steps of paper chromatography



Questions for discussion

1- Why use a pencil and not a pen to mark where to put the compound coloring spots?
2- Why do you think some pigments moved farther than others?

References

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4- Sonia Ratnani and Shriniwas Gurjar, Experimental organic chemistry, New Delhi, 2012

5- Supawan Tantayanon, Small Scale Laboratory:Organic Chemistry at University Level, Department of Chemistry, Faculty of Science Chulalongkorn University, Bangkok, THAILAND, 2010