*Melting point → Solid الصهر نقطة
*Boiling point → liquid الغليان نقطة

→ Indicator of purity

physical property ← <mark>BOILING POINTS AND DISTILLATION</mark>

Identity and Purity of Liquid Organic Compounds
Distillation as a Method for the Separation of Liquids

INTRODUCTION

If a liquid is kept in a sealed container, equilibrium is eventually established between the liquid and gaseous molecules. The pressure exerted by these gaseous molecules is called the <mark>vapor pressure and it increases with increasing temperature of the liquid</mark> (Figure 7).

التعريف The <mark>boiling point of a liquid</mark> is defined as the temperature at which the

for Capillary ← <mark>(vapor pressure) of the liquid equals the external pressure (usually 1 atmosphere).</mark> <mark>It is also defined as the temperature at which vapor and liquid are in equilibrium at a given pressure.</mark> كابت فيزيائي

The boiling point, like the melting point, is a <mark>physical constant</mark> and may be

المعرفة ← <mark>used to identify unknown organic liquids.</mark>
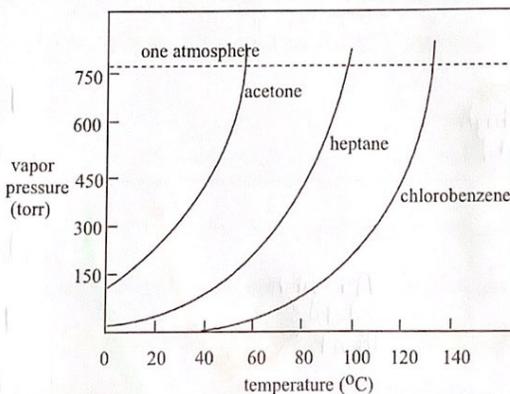
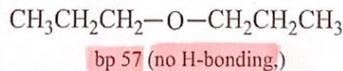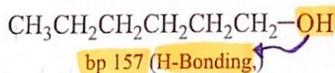Figure 7. Vapor pressure-temperature curves.
للسوائل النقية

<mark>Boiling Points of **Pure Liquids**.</mark> The boiling point of a pure liquid depends on the following variables: الأقوى → Polar covalent

a) <mark>Nature of intermolecular attractive forces:</mark> H-bonding, dipole-dipole, or

القوة ← London forces. ↘ Non-polar

$CH_3CH_2CH_2CH_2CH_2CH_2$—<mark>OH</mark> $CH_3CH_2CH_2$—O—$CH_2CH_2CH_3$
<mark>bp 157 (H-Bonding.)</mark>   <mark>bp 57 (no H-bonding,)</mark>

22   London-force

note: نبتأتد على ال H
intermolecular forces | intramolecular forces   والكثافة الولية
قوة الترابط بالركب المجاور | قوة ذرات المركب داخل المركب   في المركبين
و مع قوة ال | قوة الإلكتروي

علاقة طردية b) **Molar mass**: boiling point increases with molar mass.

c) **Shape of molecules**: among isomeric compounds, having the same
functional group, straight chain molecules have higher boiling points
than the corresponding branched ones (less molecular surface area).
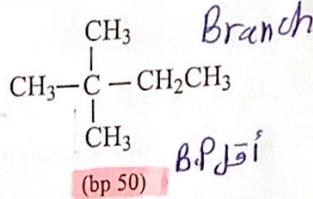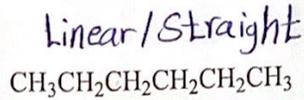
شكل الحركبات متشابهة حيث كلما كان متفرع أكثر قلّ الـ B.P وكلما كان متماسك أكثر تزداد الـ B.P

كلما كان متفرع أكثر قل الـ B.P والـ Surface area

Linear/Straight
$CH_3CH_2CH_2CH_2CH_2CH_3$

Branch
$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2CH_3$

أعلى B.P (bp 68)

أقل B.P (bp 50)

(miscible يعني ممتزجة) not pure

قابل للامتزاج

Boiling Points of Solutions. For solutions the boiling point is defined as
the temperature at which the total vapor pressure is equal to the external
(atmospheric) pressure. The effect of any solute, A, on the boiling point of a
liquid B, will depend on the nature of A (Figure 8). If A is less volatile than
B, then the total vapor pressure of the solution is lower at any given
temperature, and its boiling point is higher than that of pure B (e.g., a
solution of sugar in water). If, on other hand, solute A is more volatile than
B, then the total vapor pressure of the solution, at any given temperature, is
higher and its boiling point is lower than that of pure B (e.g., a solution of

تعريف الـ B.P للـ Solution

Total (high B.P) ← solution of sugar in water

Total (low B.P) ← (acetone and water)
→ very high volatile

note: Solution يعني

* Solid + Liquid
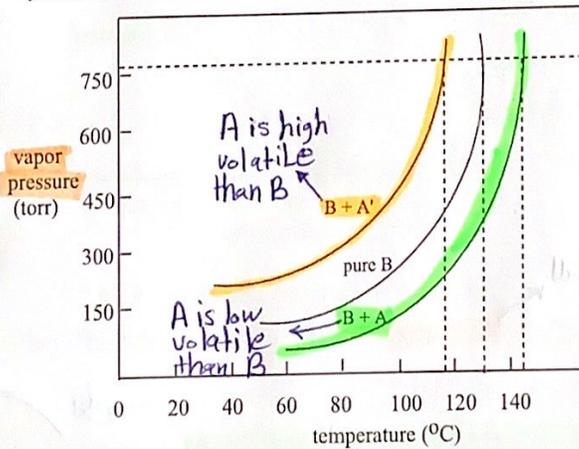(Sugar in water)

* Liquid + Liquid
(miscible to each other)

Figure 8. Vapor pressure-temperature diagram for a pure liquid and different
solutions.

Figure labels:
vapor pressure (torr): 750, 600, 450, 300, 150
A is high volatile than B, B + A'
pure B
A is low volatile than B, B + A
temperature (°C): 0, 20, 40, 60, 80, 100, 120, 140

لو خفضنا المادة A على السائل B وكانت المادة A أقل تطاير (Less volatile) من B بالتالي الـ B.P يرفع مع (total) يكون (solution) كأن أقل من الـ B.P للـ B لوحده وأيضاً الـ (Total Vapor Pressure) تكون أقل من والعكس صحيح.

Ⓐ more volatile than Ⓑ So the B.P of total solution is Lower than Ⓑ

والـ total Vapor Pressure يكون أكثر.

23

علاقة عكسية بين الـ B.P والـ Vapor Pressure

Pure إذا كانت القاطة
فقط A لوحدها
$\boxed{X_A = 1}$
mole fraction
فيبح الفانون
$P_A = P_A^\circ$

The behavior of a solution of two miscible liquids, A and B, is best explained by referring to Raoult's law which states that the partial pressure of liquid A (p_A) in a mixture is equal to the vapor pressure of pure liquid A (P°_A) multiplied by the mole fraction of A in the mixture (X_A). The same applies to liquid B. Therefore:

mole fraction ←
partial pressure ← $p_A = X_A \cdot P^\circ_A$ → Vapor pressure and $\quad p_B = X_B \cdot P^\circ_B$

From Dalton's law, the total vapor pressures of the solution (P_T) is the sum of the partial pressures of A and B:

$$P_T = p_A + p_B = X_A \cdot P^\circ_A + X_B \cdot P^\circ_B \qquad (X_A + X_B = 1)$$

A vapor pressure-composition diagram for the ideal two-component mixture is shown below (Figure 9).
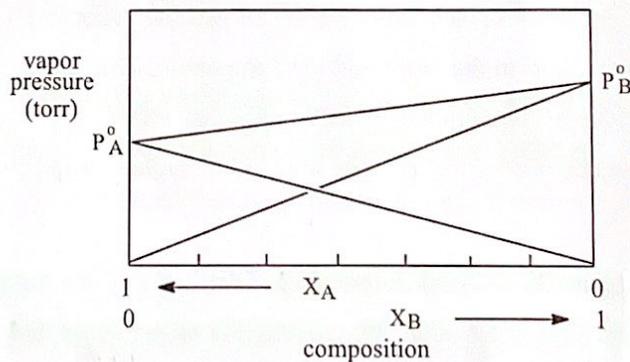

Figure 9. Vapor pressure-composition diagram for two miscible liquids

atmospheric ←
Pressure

A solution of A and B will boil when the total vapor pressure (P_T) equals the external pressure. This occurs at a temperature which is intermediate between the boiling points of the two pure liquids (lower curve in Figure 10).

In order to understand the separation of a pair of miscible liquids A and B by simple and fractional distillation, a boiling point diagram is helpful (Figure 10).
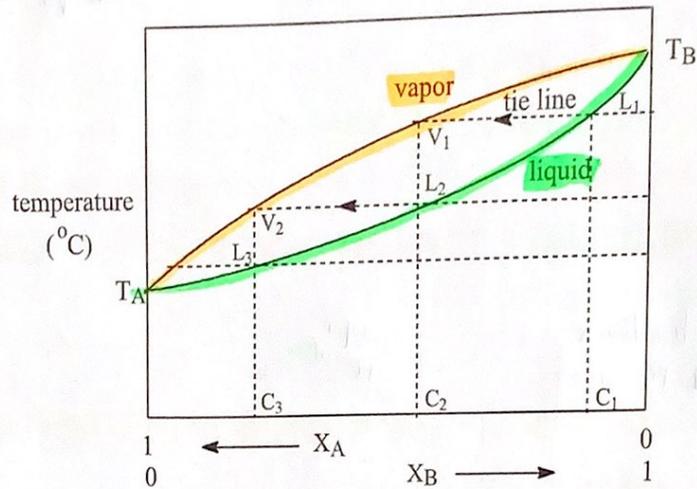
Figure 10. Temperature-composition diagram of two miscible liquids.

This diagram shows the temperature at which mixtures of A and B of various composition boil (lower curve). The composition of the vapor in equilibrium with the liquid is given by the tie line connecting the liquid and vapor curves. It is clear from Figure 10 that the vapor will always be richer than the liquid in the more volatile component. This makes sense, since the molecules of the component with the higher vapor pressure (more volatile) will escape more readily, and thus be in higher proportion in the vapor phase.

Simple and Fractional Distillation. Distillation is the process of heating a liquid to its boiling point, condensing the vapor by cooling, and collecting the liquid distillate. It is a technique for the purification of liquids and for the separation of liquid mixtures. The principles involved in distillation (simple / fractional) may be explained by referring to Figure 10.

If a liquid mixture of A and B with composition C_1 ($X_A = 0.2$) is heated to boiling (L_1), then the vapor in equilibrium with it (V_1) will have the composition C_2 ($X_A = 0.4$), i.e., the vapor will contain more of the volatile component A, than the original liquid. If this vapor is condensed (L_2) and redistilled, the distillate ($V_2 \rightarrow L_3$) will be much richer in A (composition C_3). As the distillation progresses, the mixture will gradually have less of

the more volatile component and its boiling point will gradually rise. Consequently the distillate will contain a continually decreasing proportion of the more volatile component until finally all has been collected and the less volatile component is left as a residue.

In practice, separation of a liquid mixture into its components by a single distillation (simple distillation) is possible only when the boiling points of the components are 80 degrees or more apart. For mixtures of liquids having boiling points much less than 80 degrees apart, separation can be achieved only by fractional distillation. Such a distillation is equivalent to several repeated simple distillations. It uses a fractionating column which provides a large surface area for continuous heat exchange between the hot ascending vapor and the cooler descending liquid, thus resulting in a series of evaporations and condensations leading to separation of the two components.

Vacuum distillation is a technique for the distillation of high boiling liquids, and for compounds that decompose at atmospheric pressure. At the low pressures employed, those compounds distil at much lower temperatures.

GENERAL PROCEDURE

A typical set-up for simple and fractional distillation is given in Figures 11 and 12, respectively.
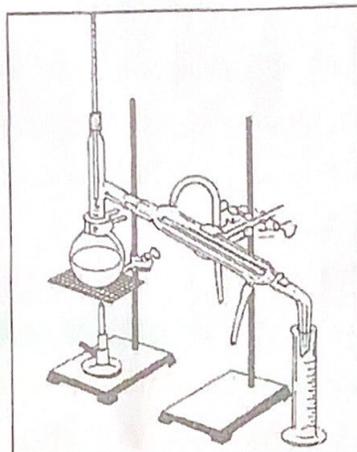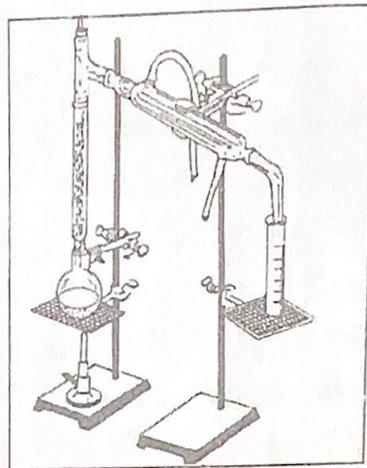
Figure 11. Simple distillation apparatus   Figure 12. Fractional distillation apparatus.

When carrying out a distillation, the following practical points should be observed:

round

a. The boiling flask should not be more than half full. ⟶

b. Boiling stones are added to the liquid to prevent bumping.

c. Each ground joint should be greased to ensure a completely sealed system.

d. Cooling water in the condenser should enter at the lower end and exit at *hot water* the upper end. This ensures that the condenser jacket is always full of water.

e. The (bulb of the thermometer) should be below the opening of the side arm so as to measure the temperature at which liquid and vapor are in equilibrium.

f. Heat sources used depend on the nature of the liquid. A water bath is used to distil low-boiling and flammable liquids, while a burner with a wire gauze is used for higher boiling and less flammable liquids.

very volatile

neek الـ نهية
round flask الـ

OBJECTIVES

1. Distilling a pure liquid (acetone) and determining its boiling point.

2. Separating a mixture of acetone and water by simple distillation.

27

3. Separating a mixture of acetone and water by fractional distillation. Having done this experiment you should be able to compare the efficiency of each type of distillation.

EXPERIMENTAL

MATERIALS NEEDED	Glassware: Round-bottomed flasks (50 and 100 mL), distillation head, adapter, condenser, 2 Erlenmeyer flasks (50 mL), fractionating column, 2 stands, wire gauze, 2 clamps, 2 clamp holders, large beaker for water bath, graduated cylinder (10 mL).
	Chemicals: 30 mL acetone, boiling stones, grease

DETERMINATION OF BOILING POINT OF PURE ACETON

Arrange a simple distillation apparatus as shown in Figure 11 using a water bath as a heat source. Introduce about 20 mL of a liquid (e.g. acetone) and a few boiling stones in a 50 mL round-bottomed flask. Heat gently so that the distillate collects in the receiver drop by drop. Make sure that there is a drop of liquid hanging from the bulb of the thermometer to ensure that the thermometer is reading the correct boiling point. Absence of this drop indicates superheating. Wait until 1-2 mL of the distillate have been collected before recording the temperature. Continue the distillation until about 2 mL of residue are left in the distillation flask, and record the temperature again. Keep the acetone for the following part.

SEPARATION OF A MIXTURE

1. **Simple Distillation.** Make a mixture of two liquids (e.g. acetone-water) 20 mL each and pour it into a 100 mL round-bottomed flask. Carry out a simple distillation as before and collect five fractions in the following boiling ranges: 50-62, 62-72, 72-82, 82-95 plus the fifth

28

fraction which is the residue. Measure the volume of each fraction and record the results in the report sheet.

2. **Fractional Distillation.** Combine the five fractions and pour into a 100 mL round-bottomed flask, attach the fractionating column and proceed as for simple distillation. Measure the volume of each fraction as before and record your results.

إذا كانت المادتين
للمزوجات معاً
الفرق لل B.P لهم
أعل من 50
(دليل)
نستخدمها