HELLENIC REPUBLIC

UNIVERSITY OF CRETE

Academic English

Section: Separation Techniques
Kallia Katsampoxaki-Hodgetts
School of Sciences and Engineering

Separation Techniques

Mixture and Pure Substances

A pure substance is a single substance that is not contaminated or mixed with any other substances. A pure substance contains only one type of atoms, molecules or formula units. Most substances we encounter daily are not pure substances but mixtures. The air we breathe, the beverages we drink and the seawater are examples of mixtures. Most manufactured products are in fact mixtures. Besides the main product, excess reactants and some by-products are usually present. Preservatives, colourings, fragrances and flavourings are often added to food products to enhance their appearances, tastes and smells.

A mixture is formed when two or more substances which do not react with one another chemically are mixed together. They do not have definite properties as their compositions can vary. They do not have fixed melting points and boiling points. The mixture petrol has a boiling point between 35°C and 75°C. The candle wax is another mixture with a melting point within the range of 50°C to 60°C. The coconut oil is a mixture which has a melting point between 14°C and 22°C.

In today's world of high precision engineering, the purity of chemicals and substances cannot be compromised. Trace amount of impurities can greatly reduce the effectiveness and performance of a component. Drugs must have high degree of purity to prevent any possible detrimental side effects and poisoning. Chemists also need to work with pure substances because only pure substances retain their original properties. The highly pure quartz crystal used in quartz watches helps to ensure accurate timing. The silicon crystals used in computers, compact disc players, calculators and watches are highly pure to ensure the smooth running of the systems.

Criteria of Purity

Solids. A pure solid has a sharp and constant melting point. A pure solid will melt completely at one temperature.

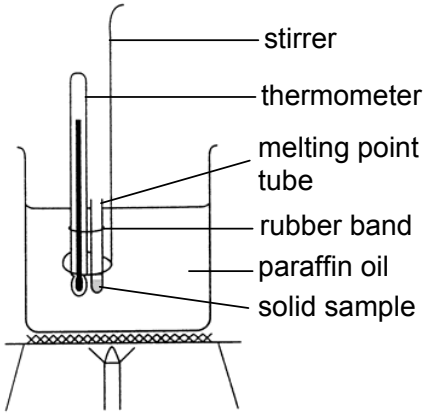
Question: How do impurities affect the melting point of a solid?

Most of the solids we encounter in our daily lives, organic or inorganic, are crystalline solids. These have molecules (for solids like sulphur, caffeine and plastics) or repeating clusters of ions (for solids like copper(II) sulphate, sodium chloride and zinc nitrate) arranged in a regular, tightly packed repeating crystal lattice. The lattice is held together by various intermolecular and/or electrostatic forces, which come about because of the chemical nature of the solid. These forces must be disrupted when a substance melts, which requires an input of energy. This in turn translates to an elevated temperature. Thus, the stronger the forces that hold the particles together in a solid, the higher its melting point. It is not difficult to understand how impurities affect the melting point. None-volatile foreign substances or impurities in a crystalline solid disrupt the repeating pattern of forces that holds the particles of the

solid together. Therefore, a smaller amount of energy is required to melt the part of the solid surrounding the impurity. This explains the melting point depression (lowering) observed from impure solids. The more impure the solid is, the more its structure is disrupted, and the greater the variation in intermolecular or electrostatic forces in different areas of the solid. The effect: the melting temperature is lowered compared to the pure solid, and the solid melts over a wider range of temperatures. Similarly, during freezing, the particles of the liquid must aligned themselves in an ordered fashion. However the presence of the impurity prevents the liquid particles from reaching this state easily. The particles need to lose more heat or become colder in order take up the orderly position and be frozen in to a solid.

The melting and boiling points of pure substances can be obtained from reference books of physical and chemical constants. No two substances have the same pair of melting and boiling points. Hence, the determination of the melting and boiling points can be used to identify a substance as well as to test the purity of a substance.

The melting point of a solid may be determined using the apparatus shown below.



A small amount of the pure solid is placed in the melting point tube. The tube is secured to the thermometer with a rubber band and place in a small beaker of paraffin oil. The oil is heated slowly with constant stirring. This ensures an even distribution of heat throughout the oil because oil is not a good conductor of heat. The temperature at which the solid melts into a liquid is noted. This temperature indicates the melting point of the solid.

Question: What is the advantage of using paraffin over water to heat the solid?

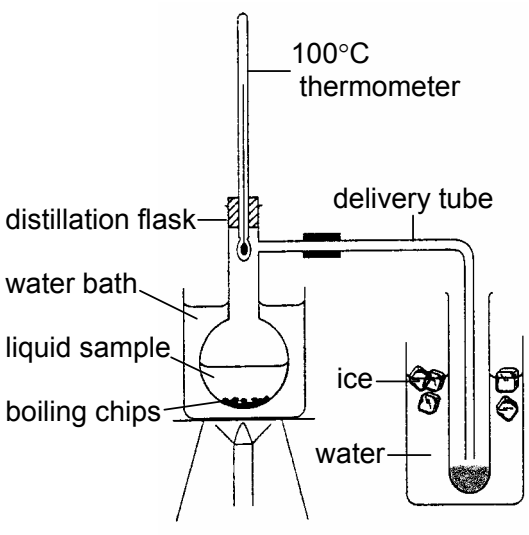
Liquids. A pure liquid has a sharp and constant boiling point. A pure liquid boils exactly at a fixed temperature.

Question: How do impurities affect the boiling point of a liquid?

A liquid boils at the temperature when its vapour pressure equals the surrounding or external pressure. When a non-volatile impurity is added into a liquid, the vapour pressure of the system is equivalent to the sum of the vapour pressures exerted by both the solvent liquid and impurity. For the solvent liquid, the presence of the impurity decreases or depresses its vapour pressure by dilution. A non-volatile impurity has a vapour pressure of zero; so the vapour pressure of the solution is the

same as the vapour pressure of the solvent. Thus, a higher temperature is needed for the depressed vapour pressure of the system to reach the surrounding pressure, and the boiling point is elevated.

The boiling point of a liquid may be determined using the apparatus shown below. If the liquid has relatively low boiling point and is highly flammable, direct heating should be avoided. A water bath or sand bath should be used.



A small volume of the liquid is placed in a distillation flask. A few boiling chips were added into the liquid to suppress the vigorous bubbling due to the boiling so as to obtain the smooth boiling of the liquid. The distillation flask is lowered into a beaker of water. The thermometer is fixed so that the bulb of thermometer is situated beside the sidearm. This measures the temperature of the vapour entering the sidearm. The water is heated gently with continuous stirring. The maximum temperature registered by the thermometer for the vapour of the liquid is noted. The temperature indicates the boiling point of the liquid. This is possible because temperature does not change during the change of state.

Question: Ethyl benzene has a boiling point of 136°C. Why is the above apparatus not suitable to measure the boiling point of ethyl benzene?
How would you modify the apparatus so as to measure the boiling point of ethyl benzene?

Oil bath is not suitable for very high temperatures because the hot oil may catch fire.

Mixtures are formed by physical changes only. They may be separated into their individual components by physical methods such as dissolving, filtration, evaporation, crystallisation, distillation, fractional distillation and chromatography. The methods used to separate the mixtures depend on the properties, the solubilities and physical states of the constituents of a mixture. These separation techniques enable chemists to separate and purify substances.

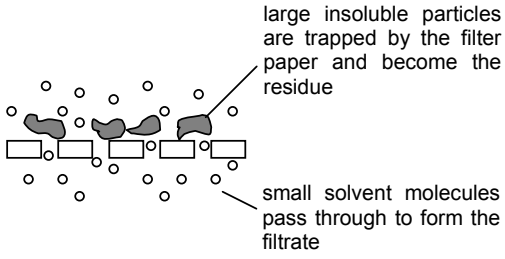
Dissolving or Dissolution

When a solid is dissolved into a liquid to form a homogeneous solution, the solid is known as the solute and the liquid is known as the solvent. The sugar solute dissolves in the water solvent to form the homogeneous sugar solution. It is interesting to note that sugar is soluble in water but not in organic solvents.

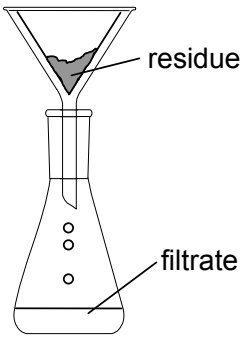
Suitable solvents must be used to dissolve different solutes. Water is the most common solvent used to dissolve most ionic compounds to form aqueous solution of the substances. Some ionic compounds such as calcium sulphate, barium sulphate, lead(II) sulphate, silver chloride, lead(II) chloride and lead(II) iodide and most carbonates however are insoluble in water. Lead(II) chloride and lead(II) iodide are soluble only in hot water. (Please refer to the section on solubility of compounds) Most organic compounds are insoluble in water but are highly soluble in organic solvents such as chloroform, tetrachloromethane and 1,1,1-trichloroethane.

Filtration

Filtration is suitable for separating mixtures whose solid components behave differently in a particular solvent – one component must be soluble and the other insoluble in it. A liquid which contains insoluble solid particles is called a suspension.

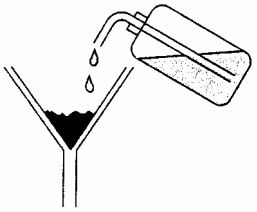


The solid mixture is first dissolved in a suitable solvent and the suspension poured through a filter which is usually made of paper. The filter paper has tiny holes through which the smaller molecules of the liquid are able to pass through as filtrate. The particles of the solid are large. They cannot pass through the holes and are trapped by the filter paper as residue.



The residues (insoluble solids) are trapped in the filter paper. The filtrate (liquid) passes through the filter paper and collects in the flask. The filtrate may be evaporated to obtain crystals of the solute in the filtrate. The solution may also be saturated by heating to half volume and allowing it to cool for crystals to form. The crystals are recovered via filtration.

Question: Explain why it is necessary to wash the residue with a little solvent?

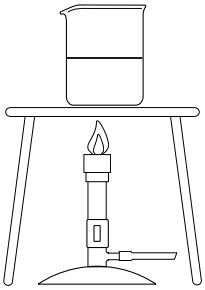


Filtration is employed in the purification of water. All solid impurities are first removed by filtration before the water is treated for harmful micro-organisms and

viruses. Some special filters can filter biological cells. The antibiotic penicillin is made from yeast. The penicillin is separated from the yeast by filtration. While the small penicillin molecules pass through the filter the big yeast cells are trapped.

Evaporation to Dryness

When sodium chloride (table salt) is dissolved into the solvent water it cannot be separated and recovered by filtration. Instead, the solution must be heated until all the solvent liquid evaporates away leaving the solid solute behind. Evaporation to dryness is employed to recover solutes such as sodium chloride which solubility do not change much with temperature.



Many substances decompose when they are heated strongly. For example, sugar will decompose to give water and carbon when heated. Most crystals, including hydrated copper(II) sulphate crystals, lose their water of crystallisation and collapsed into powders when heated. For such substances, evaporation to dryness is not a good method of purification. Furthermore, when all the water is driven off during evaporation any soluble impurity present will be deposited together with the required solid. In this respect crystallisation is induced to obtain the solute crystals.

Question: A sample of salt has been found to be contaminated with some dirt particles.
Outline the method to separate the salt crystals from the dirt particles.

Question: Lead(II) iodide may be prepared by the following reaction.

$$2KI\,(aq) + Pb(NO_3)_2\,(aq) \rightarrow PbI_2\,(s) + 2KNO_3\,(aq)$$

Describe how you would obtain pure lead(II) iodide from the mixture.

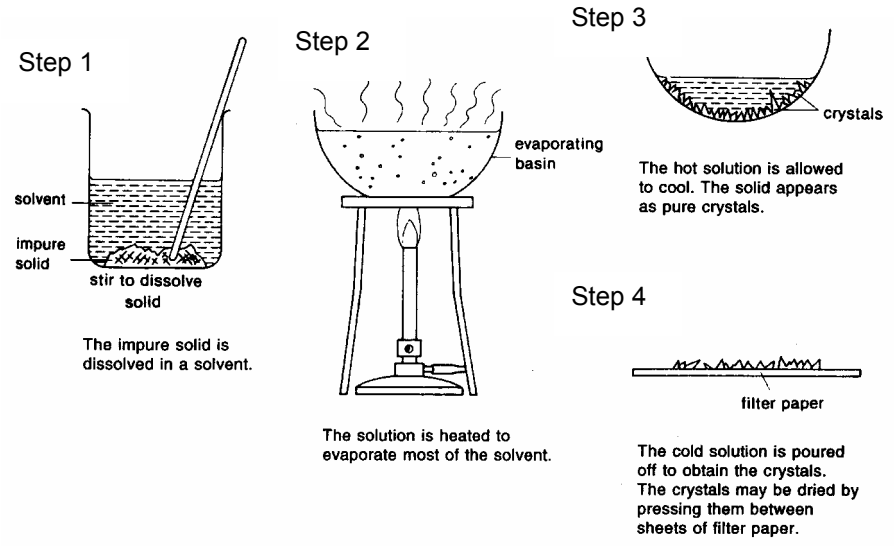
Crystallisation

The best method of obtaining a pure solid sample from its solution is by crystallisation. When the solution is heated evaporation occurs. The heating is stopped at the stage when a hot saturated solution is formed. Because the solubility of most solids decreases with decreasing temperature, lesser solid will be able to dissolve in the solvent at a lower temperature. Hence, if the resulting hot saturated solution is allowed to cool to room temperature, the excess dissolved solid will be precipitated out as pure crystals. The process is generally known as crystallisation.

Question: What is a saturated solution?

Question: How could you test if a boiling solution is saturated?

The crystallisation process is useful when the non-volatile impurities of the substance are soluble in the solvent even when it is cooled. The soluble impurity will remain in the solution and only the required substance crystallises out. Impure solids may also contain impurities which are insoluble in the solvent. These insoluble impurities are removed by first filtering the mixture before evaporating the solvent.



Question: A sample of copper(II) sulphate crystals was recklessly contaminated with sand.
Outline the procedures to obtain pure crystals of copper(II) sulphate back.

Crystallisation is employed for substances which solubility differs appreciably with temperature. It is used to purify sugar and fertilisers like potassium nitrate. Some impure solids may be purified by melting and recrystallizing them from their

molten state. The melt (hot liquid) is cooled slowly and crystals are formed slowly. The first crystals to form are very pure. These are collected before the rest of the substance freezes completely. This method is applied on a small scale to produce metals with an extremely high degree of purity. Very pure germanium and silicon obtained by this method are used as semiconductors in transistors.

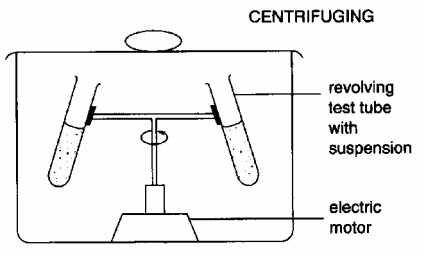
Question: Given the following reaction,

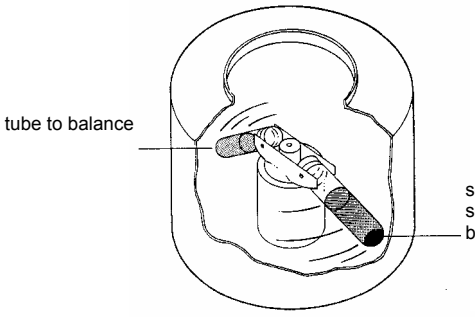
$$Ba(NO_3)_2\,(aq) + K_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + 2KNO_3\,(aq)$$

Outline the methods to obtain pure sample of the products.

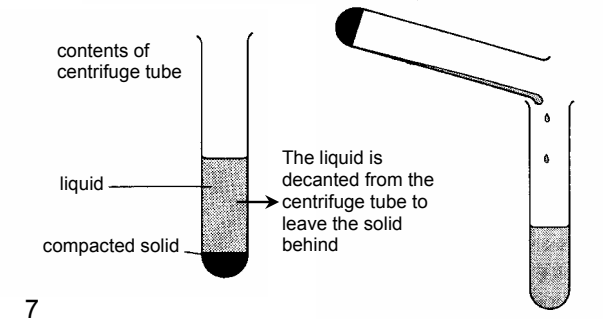
Question: After crystallizing an aqueous solution of potassium nitrate, the crystals are collected via filtration. Explain why the residue is washed with a little cold deionized water and not with copious amount of water in this case?

Centrifuging (optional)





Centrifuging and decanting are employed as alternative methods to filtration. A centrifuge is a high speed, rotating apparatus that separates substances of varying densities through centrifugal forces.

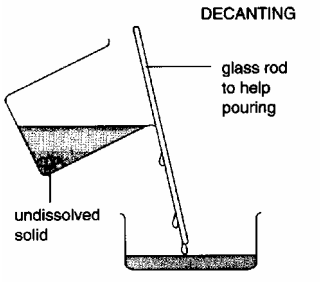


Centrifuging is the separation of solid or liquid particles of different densities by rapidly rotating the material in a suitable container in a horizontal circle. Spin-drying, to remove water from washed clothes, is an example of centrifuging. Centrifuging is used to achieve good separation of two mutually insoluble liquids, and as a form of filtration of a solid product. Intermediate chemicals in pharmaceutical and dyestuff production are often filtered by centrifuging.

Centrifuging is a quicker and efficient technique for separating fine insoluble solid particles from a liquid. These fine solid particles are very light, and they will take a long time to sink to the bottom. In the centrifuge, an electric motor causes the test tubes containing the suspension to revolve at high speed. The centrifugal force will fling the solids to the bottom of the test tube. The clear liquid is then decanted off.

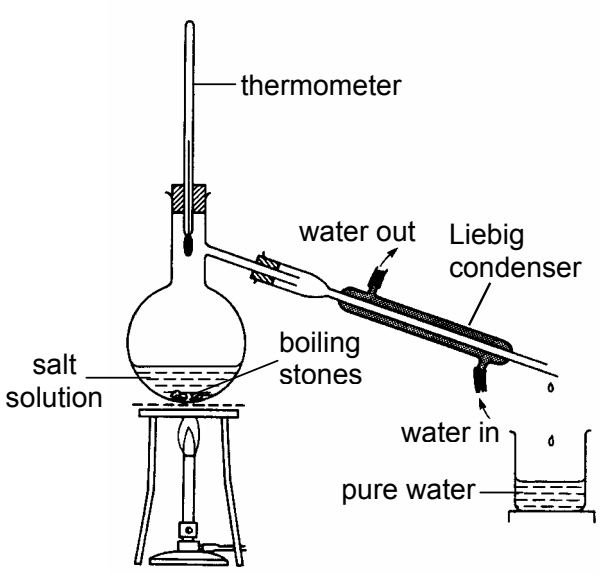
Centrifuging is used in winemaking to remove yeast cells from a wine before it completes the fermentation process. It is also used instead of other processes (such as filtering) to remove particles from wine.

Decanting (optional)



Decanting implies pouring off the liquid and leaving the insoluble solid at the bottom of the container. The liquid is slowly led down the stirring rod to another container. It is quicker than filtration but the separation may not be effective. Decanting does not completely separate the suspension into its individual constituents but it removes most of one component so that complete separation is easier and faster later.

Simple Distillation



Simple distillation is employed to recover the solvent from a solution, e.g. water from salt solution. The flask is heated and when the solution boils, steam is given off. The steam is cooled down and condensed in a Liebig condenser. It consists of a jacket of cold water with the coldest water entering at the bottom of the jacket and circulating out through the top. This way it ensures that the coldest part of the condenser is just before the vapour escapes. The condensed water is called the distillate and is collected in a receiver. The salt solute is left behind in the flask.

The water which collects in this way is very pure as all its impurities are left behind in the flask. It is called distilled water. The thermometer indicates the temperature of the water vapour and hence the boiling point of the solvent water that

distils over (100°C). It is positioned with its bulb next to the side arm, so that it records the temperature of the steam as it enters the Liebig condenser. The thermometer should register 100°C which shows pure water is being distilled over. In order to achieve even boiling, with not too much frothing and bubbling in the flask, 'anti-bumping granules' or 'boiling chips' could be added to the salt water.

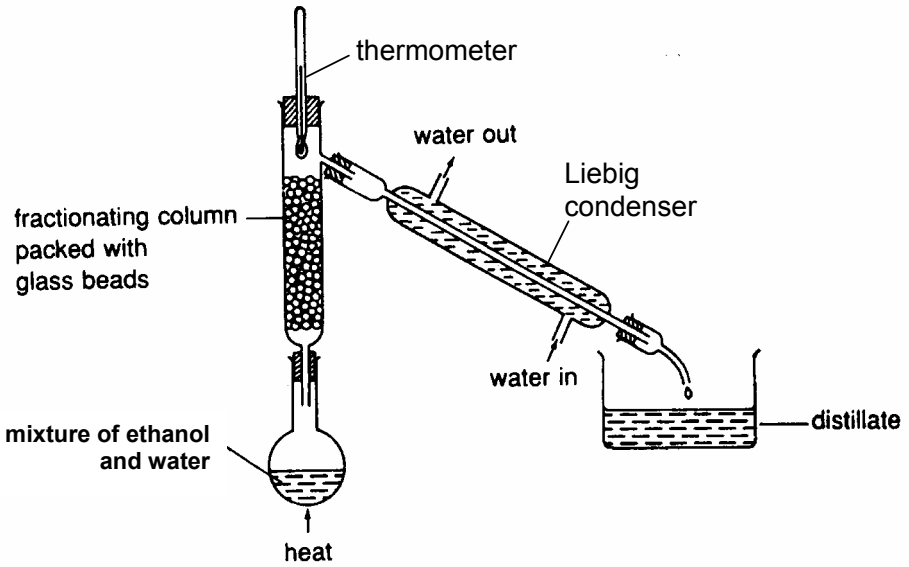
Simple distillation is generally employed in hot and arid countries such as Saudi Arabia to obtain pure water for drinking. This process is carried out in a desalinating plant which removes salt and other dissolved substances and chemicals from the water. This technique however is expensive because a lot of fuels are needed to boil the water.

Separating Funnel

Separating funnel is used to separate two liquids which are **immiscible**, e.g. organic compounds like oil and water. The mixture is poured into the funnel and the layers allowed to separate out. The less dense liquid collects above the denser liquid. The lower and denser layer is run off by opening the tap. The tap is closed as the last drop of the denser layer runs out. The tap is then opened again to drain the lighter layer into another beaker.

Question: Why are simple distillation and fractional distillation not appropriate methods to separate immiscible liquids with different boiling points?

Fractional Distillation



Fractional distillation is a technique used to separate two liquids which dissolve in one another. They are said to be miscible liquids as they mix completely in any proportion to form a homogenous layer. The separation relies on the difference in boiling points of the two liquids. The liquid with the lowest boiling point

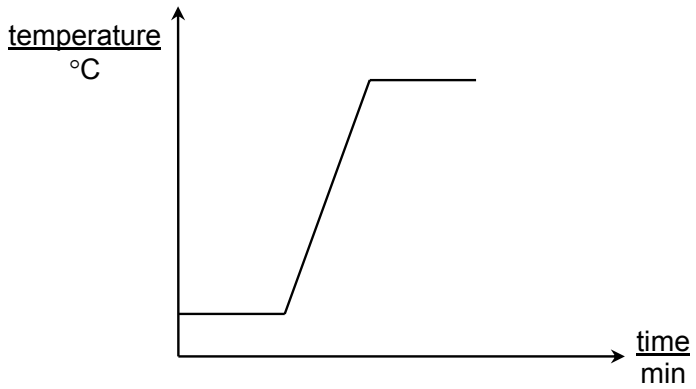
is distilled first. The liquid with the highest boiling point is distilled last. A mixture of ethanol (boiling point 78°C) and water (boiling point 100°C) may be separated using fractional distillation because both liquids are miscible and have very different boiling points.

The fractionating column used is normally packed with glass bead or some other unreactive substance. This provides a large surface area for condensation. When the flask is heated, the vapour coming from the mixture will contain both ethanol and water molecules. However, it will be richer in ethanol molecules as these have the lower boiling point of the two.

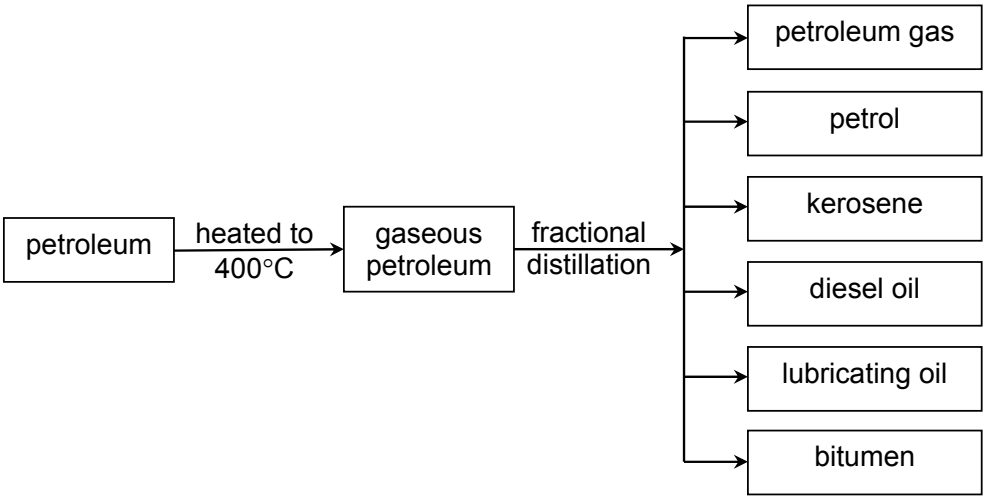
At first, both vapours simply condense in the cold fractionating column and flow down into the distillation flask, at the same time imparting some heat to the glass beads in the fractionating column. As the fractionating column is warmed by the hot vapours, the vapours may rise further up before condensing. As we go up the fractionating column, the temperature becomes lower and the vapour with the lower boiling point (ethanol) may survive as a vapour while the vapour with the higher boiling point (water) will condense into liquid and flows down back into the distillation flask.

When the temperature at the top of the fractionating column reaches 78°C, molecules of ethanol can survive as vapour and these pass over into the Liebig condenser and condensed into liquid ethanol flows down and collect in the beaker. Water molecules with the higher boiling point condense and fall back into the flask. This continues until a large proportion of the ethanol is boiled off. When all the ethanol has distilled over, the temperature reading on the thermometer rises steadily to 100°C, indicating that the steam is now entering the condenser. At this point the receiver should be changed so that the condensing water may be collected. In this technique, complete separation is not effected. The ethanol distillate will contain largely ethanol; traces of water may be found. The first distillate may contain about 95.6% of ethanol and 4.4% of water. The trace amount of water can only be removed by chemical means such as filtering through a bed of magnesium sulphate.

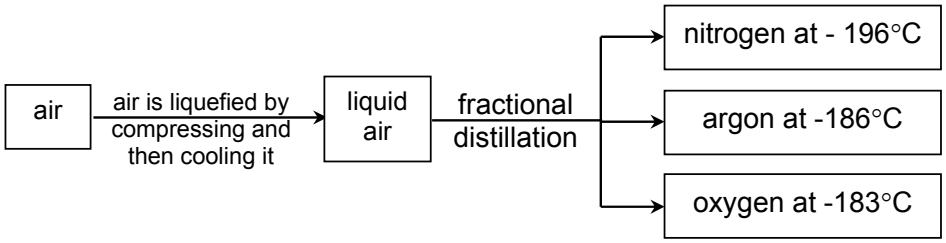
Question: Sketch the graph of temperature against time for the fractional distillation process.



Fractional distillation is used in the petroleum industry. Petroleum (or crude oil) is a mixture of very useful miscible liquid fuels such as petrol, paraffin and diesel. Fractional distillation is used to separate the useless mixture of petroleum into its useful fractions.



Fractional distillation is employed to obtain pure oxygen and nitrogen from air. The air is liquefied by first cooling it to about -200°C. The liquid air is then distilled by gently warming up the liquid air. Nitrogen has a lower boiling point (-196°C) distils out first. The oxygen with a higher boiling point (-183°C) distils next. This produces nitrogen and oxygen separately.



Another industrial application of fractional distillation is in the extraction of ethanol from the fermentation of glucose. During fermentation, glucose is broken down by yeast to form ethanol and carbon dioxide.

$$\text{glucose} \xrightarrow[37°C]{\text{yeast}} \text{ethanol} + \text{carbon dioxide}$$

$$C_6H_{12}O_6\,(aq) \xrightarrow[37°C]{\text{yeast}} 2C_2H_5OH\,(aq) + CO_2\,(g)$$

The resulting mixture is a solution of dilute ethanol (15 – 20%) in glucose solution. The ethanol may be separated from the mixture by fractional distillation.

Paper Chromatography

Chromatography is a technique engaged extensively in researches, experiments, and investigations due to its sensitivity and ability to pick up minute traces of impurities and drugs. The principle involved depends upon the *relative solubilities* of the solutes (in the mixture) between the stationary phase (the paper or plate) and mobile phase (the solvent).

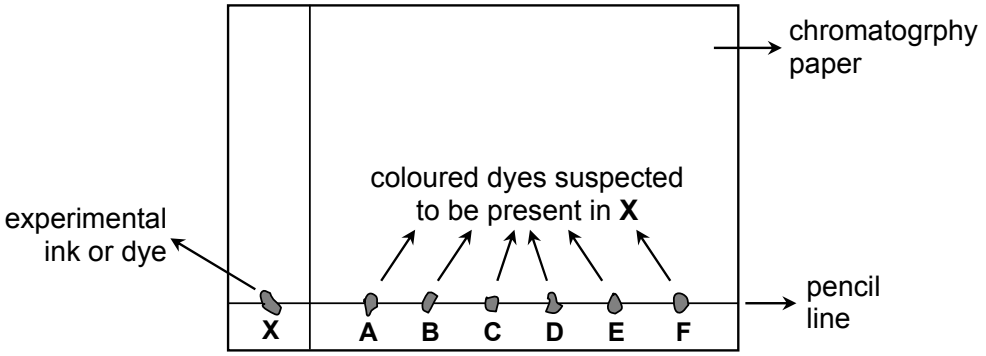
The paper used in paper chromatography contains water loosely combined with the cellulose of the paper. This water constitutes the stationary (non-moving) phase. When a dye is placed at the bottom of the paper, and another solvent (mobile phase) is soaked up the paper, the solutes present in the dyes dissolve to different extents between the two phases. Solutes which are more soluble in the

mobile phase travel upward with the solvent. Solutes which dissolve better in the water (stationary phase) on the paper will be trapped in the paper and therefore do not travel very far up the paper. This difference in solubility between the two phases enables the different pigments of a dye to be separated. The chromatography paper with the separated components is called a chromatogram.

To separate the coloured components in coloured inks or food dyes using paper chromatography, the following procedures are used.

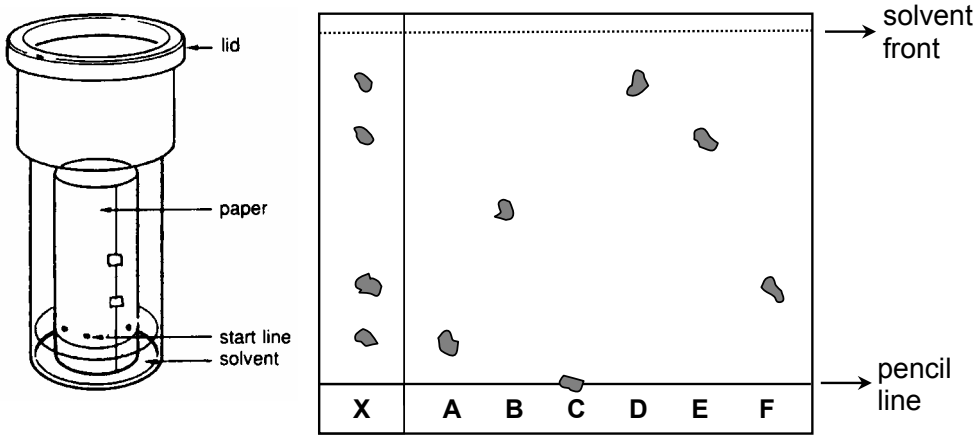
(a) Draw a pencil line on a piece of chromatography paper about 2 cm from one end of the paper.

(b) Place a small spot of the experimental ink or dye on the pencil line. Then place small drops of other coloured inks or dyes on the pencil line. These coloured inks or dyes are the ones which are suspected to be present in the experimental ink or dye. Repeat dripping the inks or dyes 2 to 3 times on the same spots. This is to make the spots more concentrated so that they will show up more distinctly on the chromatogram.



(a) Roll the chromatography paper into a cylinder and secure it with tapes or staple. Immerse the chromatography paper in a beaker with a suitable solvent such as ethanol or water. Cover the beaker with a lid.

(b) The solvent will travel up the chromatography paper. When the solvent almost reaches the top of the paper, take the paper out of the beaker. Note down the height of the solvent front by drawing a line with pencil. Allow the chromatogram to dry.



Question: How many dyes are found in **X**? List the dyes found in **X**.

Question: Which dye does not move with the solvent? What modification may be made to this separation technique to improve the separation of this dye?

Question: Why must the applied spot be as small as possible?

Question: Why must the starting line be drawn with a pencil and not a pen?

Question: Why must the starting line be drawn above the solvent?

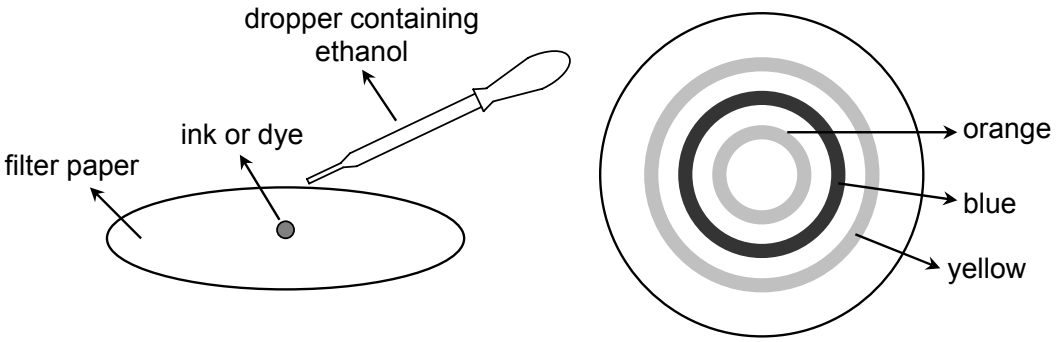
Question: Give two reasons why should the jar be covered with a lid?

Question: Explain why should the solvent front be as high as possible?

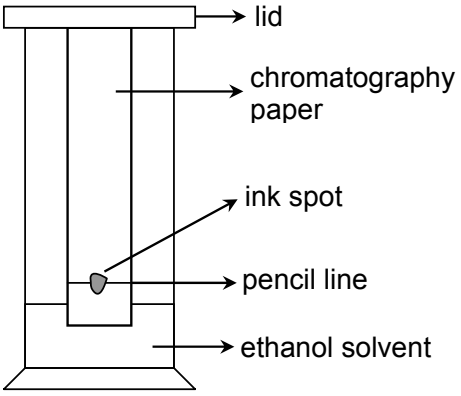
Question: Explain why the solvent front must never reach the top of the chromatogram?

Question: How should the chromatogram be treated if the substances are colourless such as amino acids.

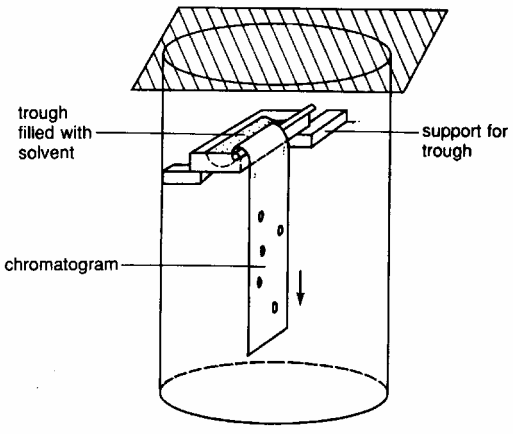
Chromatography may also be performed on round chromatographic paper as shown below.



Question: An alternative set of apparatus for the above experiment is shown below. In this set-up, a strip of filter paper is used and the filter paper is dipped in a glass jar containing ethanol solvent. Draw and state the colour of the spot.

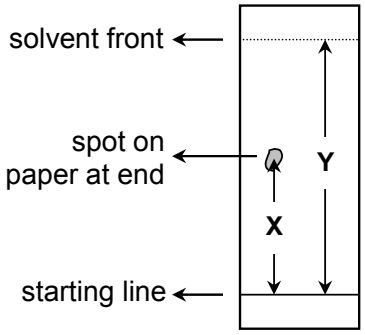


Paper chromatography is better carried out with the solvent running down the paper. This descending method of paper chromatography works better for longer pieces of paper as the solvent does not have to move against gravity, and thus flows more quickly. This means that the solutes which are separated can travel further and thus the separation between the spots is greater.



R_f Values

Given the same conditions, i.e. the same solvent, temperature, pressure and nature of stationary phase (paper), a particular substance will always move at the same rate relative to the solvent. In another word, the ratio of the distance travelled by the substance to the distance travelled by the solvent is constant. This ratio is called the R_f value of the substance.



Numerical measurements known as R_f values can be obtained from the chromatogram. The R_f value, which is typical for each solute, may be calculated from the equation:

$$R_f = \frac{\text{distance travelled by the solute}}{\text{distance moved by the solvent}} = \frac{X}{Y}$$

The distances are measured from the starting pencil line.

When stating the R_f value for a particular substance, it is necessary to cite the solvent used, temperature at which the measurement was taken as well as the type of paper used for the chromatogram.

sugar	R_f value
fructose	0.86
glucose	0.57
maltose	0.40
sucrose	0.20
galactose	0.69

The identity of a substance may be determined from its R_f value by comparing it with standard literature. The R_f values for some sugars in a certain solvent are tabulated. The R_f value is characteristic for a given paper, solvent combination and temperature. Because of slight variation in papers, it is always a good idea to determine the R_f value on each set of papers.

Chromatography can be used to separate and identify complicated substances such as dyes and drugs. It is employed to detect unauthorised artificial dyes and additives in food. Chromatography can be qualitatively and quantitatively employed to detect traces of pesticides and herbicides in vegetables and fruits. It has also been used extensively in the separation of pigments from plants, dyes from ink and amino acids from proteins.

The sole advantage of chromatography is its ability to detect minute quantity of impurities present in the sample. This is particularly valuable for biochemistry, where small and complex samples are often found.

Chromatography is an extremely accurate and precise technique that has been used

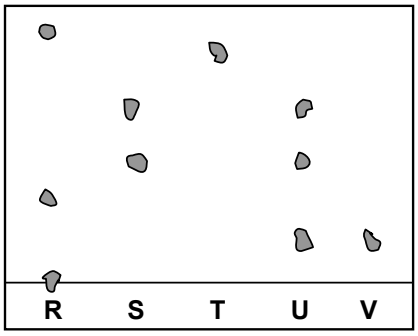
(a) to separate the components in a sample and, hence to identify the number of substances in it;

(b) to identify the substances present in a sample; and

(c) to determine if the sample is pure.

Question: State and briefly explain three ways to test the purity of a substance.

Question: With reference to the following chromatogram, answer the questions that follow.



Question: How many dyes are there in colour **R**?

Question: Which dyes may be combined to form colour **U**?

Question: Which colours are pure?

ϕϕϕϕϕϕϕ End of Chapter ϕϕϕϕϕϕϕ

Notes

Reference Note

Licensing Note

[1] http://creativecommons.org/licenses/by-nc-nd/4.0/

As Non-Commercial is defined the use that:

- Does not involve direct or indirect financial benefits from the use of the work for the distributor of the work and the license holder
- Does not include financial transaction as a condition for the use or access to the work
- Does not confer to the distributor and license holder of the work indirect financial benefit (e.g. advertisements) from the viewing of the work on website

- The copyright holder may give to the license holder a separate license to use the work for commercial use, if requested.

Preservation Notices

Any reproduction or adaptation of the material should include:

- the Reference Note
- the Licensing Note
- the declaration of Notices Preservation
- the Use of Third Parties Work Note (if is available)

together with the accompanied URLs.

Financing

- The present educational material has been developed as part of the educational work of the instructor.

- The project “Open Academic Courses of the University of Crete” has only financed the reform of the educational material.
- The project is implemented under the operational program “Education and Lifelong Learning” and funded by the European Union (European Social Fund) and National Resources