EXPERIMENT 2: RECRYSTALLIZATION

A Purification Technique for Solids

INTRODUCTION

Crystallization may be defined as the process in which a solid compound precipitates from a saturated solution in the form of crystals. Saturation is usually affected through cooling or evaporation. In certain cases, ***recrystallization*** may be used for the **separation** of a solid mixture and **purification** of a desired impure crystalline substances (fractional recrystallization). Impure crystalline substances can be purified by recrystallization from a suitable solvent.

This process depends on two facts:

a. Different solids have different solubilities in a given solvent (impurities have solubilities different from those of the desired compound).

b.Most solids are more soluble in hot than in cold solvents.

When the impure solid is dissolved in a minimum volume of a suitable hot solvent and the resulting solution is gradually cooled, saturation and eventual crystallization of the pure compound occurs.

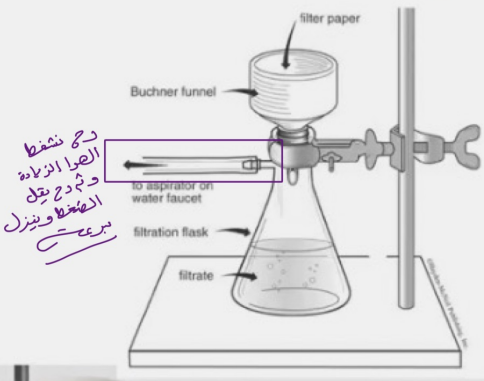
Impurities in a solid are of two kinds: soluble and insoluble and recrystallization involves the removal of both to purify a solid. Insoluble impurities are first removed by gravity filtration of the hot solution. While soluble impurities remain dissolved in the cold saturated solution (mother liquor) after precipitation of the desired compound. The pure crystals are separated from the supernatant liquid by suction filtration. After drying, the purity is checked by a melting point determination.

نوعين من الفلتره

Gravity filtration

تعتمد على قوة الجاذبية

Suction /vacuum filtration



ملخص

Solid Mix → Desired compound + soluble impurities + insoluble impurities

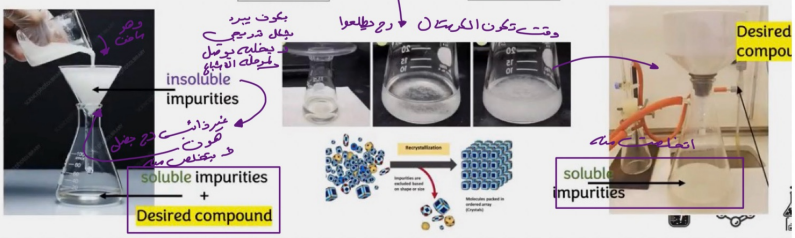
Impurities

Insoluble

Soluble

Gravity Filtration

Suction Filtration



التبلور عملية انتقائية لأن جزيئات نفس المادة فقط تدخل في الشبكة البلورية، أما الشوائب فلا تدخل وتبقى في المحلول.

Crystal formation is a selective process and only molecules of the same substance can fit into the crystal lattice, excluding foreign molecules (impurities) which remain in solution (Figure 14).

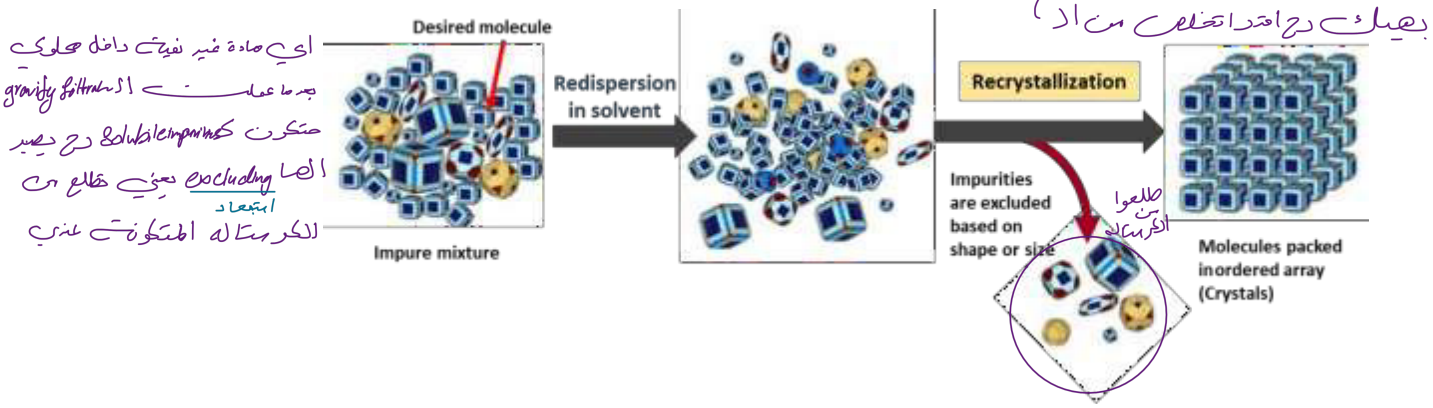


Figure 14. The crystallization process.

The solubility of a solid solute in a solvent is determined by two factors:

a. The relative polarities of the solvent and solute. "Like dissolves like" is the best summary of solubility behavior.

Polar solvents dissolve polar solutes and non-polar solvents dissolve non-polar solutes. For example, solutes that contain polar groups like OH, NH_2, and COOH dissolve in polar solvents like water, methanol, and ethanol while hydrocarbons and their halogenated derivatives are non-polar and dissolve in non-polar solvents like chloroform, carbon tetrachloride, hexane, and petroleum ether.

b. The lattice energy of the crystalline solute. The crystal lattice, holding solute molecules together in the solid state, is broken down upon dissolution.

The necessary energy is provided through "*solvation*" of the solute bysolvent molecules. The stability of a crystal lattice is roughly reflected by the melting point: a high melting point indicates a high lattice energy, and *vice versa*. For a given set of isomers, *the higher the melting point, the less soluble the substance is in a given solvent.*

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	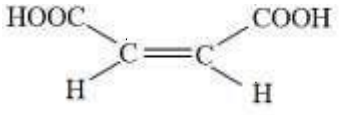	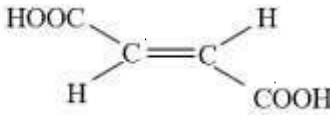
Melting point ^{o}C	130	288
Solubility (g/100 mL water)	78.8	0.70

A suitable solvent for recrystallization should possess the following important properties:

a. Dissolve a large amount of the solid to be purified at high temperatures, but very little at room temperature.

b. Dissolve impurities readily at low temperatures or not at all even atthe boiling point.

c. Not react with the substance to be purified.

d. Evaporate readily from the crystals, i.e., be relatively volatile.

If two or more solvents appear to be equally suitable, it is preferable tochoose a solvent which is non-flammable, non-toxic, and cheap.

GENERALIZED EXPERIMENTAL PROCEDURE

Recrystallization involves the following sequence of steps:

1. *Selection of a suitable solvent.*
2. *Preparation of the hot solution and "decolorization" if necessary.*
3. *Filtration of the hot solution to remove insoluble impurities (and charcoal).*
4. *Cooling to effect crystallization.*
5. *Collection (cold filtration), washing, and drying of the crystals.*

Each step will now be discussed more fully.

1. ***Selection of the Solvent.*** The suitable solvent is determined experimentally through solubility tests.

This is done by shaking about 0.1 g of the powdered solid with 2 mL of the given solvent in a dry test tube. If all the solid has nearly dissolved in the cold solvent, the solvent is considered unsuitable.

If not, the mixture is heated gently to the boiling point with stirring (water bath for flammable solvents). If most of the solid did not dissolve, the solvent is also unsuitable.

If a substance is found to be too soluble in one solvent and insoluble in another, then a mixture of both solvents (solvent pair) may be used. In such cases the two solvents must be completely miscible. The compound to be recrystallized is first dissolved in the solvent in which itis very soluble, then the other solvent is added gradually, with heating,until a slight turbidity occurs. The solution is then allowed to stand at room temperature to effect slow crystallization before chilling in ice.

Table 2. Common solvents for recrystallization.

Solvent	b.p	Particulars of Solvent
Water	100	to be used whenever suitable
Methanol	65	flammable; toxic
Ethanol	78	flammable
Acetone	56	flammable
Ethyl acetate	78	flammable
Chloroform	61	non-flammable; vapor toxic
Benzene	80	flammable; vapor highly toxic
Cyclohexane	81	flammable

2. ***Preparation of the Solution.*** To prepare the hot solution, the solid is placed in an Erlenmeyer flask and the selected solvent is added in small portions. The mixture is stirred and heated to boiling after each addition, until the solid dissolves completely. A slight excess of the solvent is usually added to compensate for any losses (through evaporation) during filtration.

Decolorizing charcoal may be added at this stage if the solution is colored due to colored impurities. The flask should be removed from the heat source before adding charcoal to it, otherwise bumping will occur.

3. ***Hot Filtration (Gravity Filtration).*** Filtration of the hot solution is necessary to remove insoluble impurities. A fluted filter paper and a short-stem funnel (Figure 15) allow rapid filtration and avoidpremature crystallization inside the stem and on the filter paper.

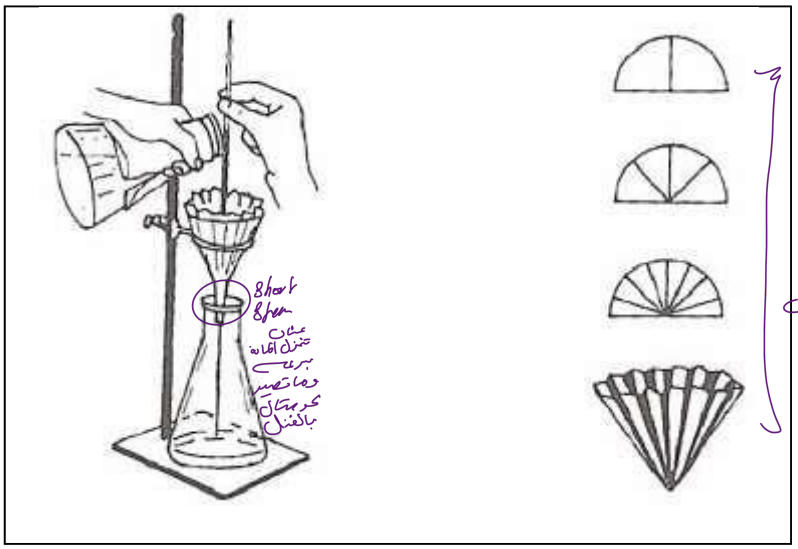

Figure 15. Rapid filtration of a hot solution using a fluted filter paper.

4. ***Cooling***. To induce crystallization, the clear, hot filtrate is allowed to cool down to room temperature, undisturbed, until a large number of crystals has formed. The mixture is finally chilled in ice to complete crystallization.

5. ***Collecting and Drying of Crystals.*** The crystals are collected by suctionfiltration (cold filtration) using a Buchner funnel to ensure rapid and complete removal of the solvent. The crystals are then washed with a few milliliters of fresh, ice-cold solvent to get rid of the last traces of mother liquor. The crystals are finally dried in an oven or allowed to air-dry, in case the melting point is low, by spreading them over a sheet of paper.

$$\%\ Yield = \frac{mass\ of\ purified\ products}{mass\ of\ crude\ sample} \times 100\%$$

NOTE

The value should be less than 100%. If it is greater, your recrystallized material is wet or impure.