Crystallization & Filtration

Purification of Salicyclic Acid and Sodium Chloride

Separation processes

- Liquid-liquid extraction
- Adsorption
- Filtration
- Solid-liquid extraction (leaching)
- Elution chromatography
- Membrane separation processes
- Distillation
- Affinity separation processes
- Drying and evaporation
- Freeze-drying
- Precipitation
- Crystallization
- Electrophoresis
- Centrifugation
- Mechanical sieving

Dr. Zerong Wang at UHCL

Recrystallization

- Recrystallization is a *purification technique* which consists of dissolving the impure substance in a minimal volume of a solvent near its boiling point, then allowing the solution to cool slowly to crystallize the substance (ideally, leaving the impurities dissolved.)

Recrystallization and Filtration

- Solid compounds synthesized in the organic laboratory usually need to be purified before final confirmation tests are performed
- One of the most commonly used techniques to purify a sample is recrystallization followed by vacuum filtration.

Recrystallization

- Solid organic compounds produced in the laboratory usually need to be purified.
- The most common technique involves recrystallizing the sample from an appropriate Solvent.
- The recrystallization process is a relatively slow and selective formation of crystals from a solvent.
- Precipitation is a rapid and nonselective process; thus not used to purify samples.

Recrystallization Procedure

- Dissolve sample in a minimal amount of an appropriate solvent.
- Sample should be insoluble in solvent at room temperature, but soluble at elevated (boiling point) temperature.
- If solution is colorized, it is sometimes necessary to add a decolorizing agent (activated charcoal - Norite)
- Colorized solutions are first filtered through a fluted filter or a column containing alumina or silica gel.

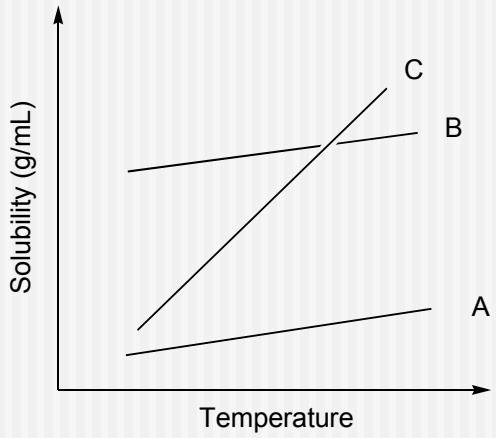
Recrystallization Procedure

- The hot solution is cooled slowly to room temperature. As the temperature changes the solute particles begin to come out of solution, leaving the more soluble impurities in solution.
- After crystallization, place beaker in water/ice bath.
- Collect crystals by vacuum filtration.
- Rinse the crystals with small portion of cold solvent.
- Dry the crystals in air in your drawer.
- Determine melting point of dried sample.

The Appropriate Solvent

- The solute particles are generally insoluble in cold solvent, but soluble in hot solvent.
- The solvent (or mixed solvent) should have a steep solubility vs temperature curve.
- Solute sparingly soluble at room temperature
- Solute very soluble at elevated temperature
- The solvent should be volatile enough to be removed by evaporation.
- The solvent should not react with the substance to be purified.

The Appropriate Solvent



The Appropriate Solvent

- **Solubility of organic compounds is a function of the polarities of both the solvent and the solute:**
  - "Like Dissolves Like"
  - Polar solvents dissolve polar solutes
  - Nonpolar solvents dissolve nonpolar solutes
- **The stability of the solute crystal lattice affects the solubility. The higher the melting point (higher stability), the less soluble the solute.**

The Appropriate Solvent

- The boiling point of the solvent must be less than the Melting Point of the solute.
- If the boiling point of the solvent is higher than the melting point of the solute, the solute will "Melt" instead of "Dissolving" in the solvent at the elevated temperature.
- Upon cooling, the "Melted" solute will "Oil" out forming an insoluble mass that is not purified.
- solvent temperature - solubility increases with temperature {stirring will increase the rate of dissolving, but not the degree of solubility}
- Compounds with functional groups that can form hydrogen bonds (-OH, -NH-, -COOH, -CONH-) will be more soluble in hydroxylic (polar) solvents such as Methanol and Water.

The Appropriate Solvent

- Sometimes the best recrystallization solvent is a mixture of two miscible solvents, one which dissolves the compound readily, the other which does not.
- For example, aspirin is very soluble in ethanol but quite insoluble in water, even hot water.

Solvent Polarity

Polarity Index	Common Name of Solvent	Structure	
0.0	hexane	$CH_3(CH_2)_4CH_3$	(least polar)
1.7	carbon tetrachloride	CCl_4	
2.3	toluene	$C_6H_5CH_3$	
2.9	diethyl ether	$(CH_3CH_2)_2O$	
3.0	benzene	C_6H_6	
3.4	methylene chloride	CH_2Cl_2	
4.2	tetrahydrofuran (THF)		
4.3	ethyl acetate	$CH_3CO_2CH_2CH_3$	
4.3	chloroform	$CHCl_3$	
5.2	ethanol	CH_3CH_2OH	
5.4	acetone	$(CH_3)_2C=O$	
6.2	acetonitrile	CH_3CN	
6.2	acetic acid	CH_3CO_2H	
6.4	dimethylformamide (DMF)	$(CH_3)_2NCH=O$	
6.5	dimethyl sulfoxide (DMSO)	$(CH_3)_2S=O$	
6.6	methanol	CH_3OH	
9.0	water	H_2O	(most polar)

An Ideal Recrystallization Solvent

- **should dissolve all of the compound when the solvent is hot (boiling).**
- **should dissolve none of the compound when the solvent is at room temperature.**
- **should have different solubilities for the compound and the impurities.**
- **should have a lower boiling point than the melting point of the compound.**
- **should have a fairly low boiling point**
- **should be cheap, non-toxic, non-reactive, and non-smelly**

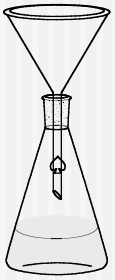
Filtration

- Separate purified solid from the soluble impurities in the solution from which it was recrystallized.
- Remove solid impurities from a liquid
- Two types of filtration: gravity and vacuum filtration

Filtration

- Porosity: measure of the size of the holes in filter paper than can pass through the particles.
- Retentivity: opposite of porosity; measure of the size of particles that can be retained on the filter paper.

Gravity Filtration



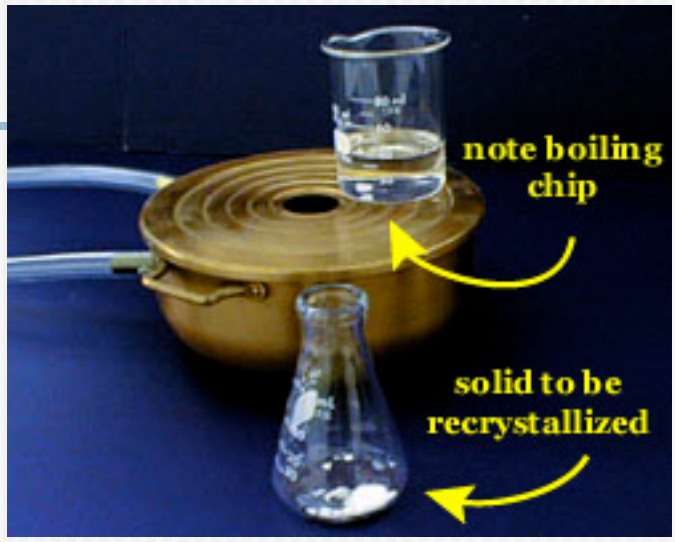
- **Filter Cones: folded paper filter inserted into a glass funnel with stem extending into a receiving flask. Applicable volume > 10 mL.**
- **Fluted Filters: specially folded (many creases) filter paper inserted into a glass funnel with stem extending into a receiving flask. Applicable volume > 10 mL**
- **Filtering Pipettes: microscale technique used with Pasteur Pipets. A piece of cotton is inserted into the top of the lower constriction. Applicable volume < 10mL**
- **Decantation: careful pouring of supernatant liquid into another vessel leaving solids particles behind**

Vacuum Filtration
A Rapid Process

- **Buchner Funnels: primarily used to filter large volumes of liquid from solids, such as crystals from the recrystallization process. Applicable volume > 10 mL.**
- **Hirsch Funnels: similar, but smaller than Buchner Funnel, with sloping sides. Used in microscale techniques. Applicable volume < 10 mL.**

Demo of Recrystallization Process

Dr. Zerong Wang at UHCL



Pour a small amount of the hot solvent into the flask containing the solid.

Swirl the flask to dissolve the solid.

Dr. Zerong Wang at UHCL

Place the flask on the hot plate to keep the solution warm.

Dr. Zerong Wang at UHCL

If the solid is still not dissolved, add a tiny amount more solvent and swirl again.

Dr. Zerong Wang at UHCL

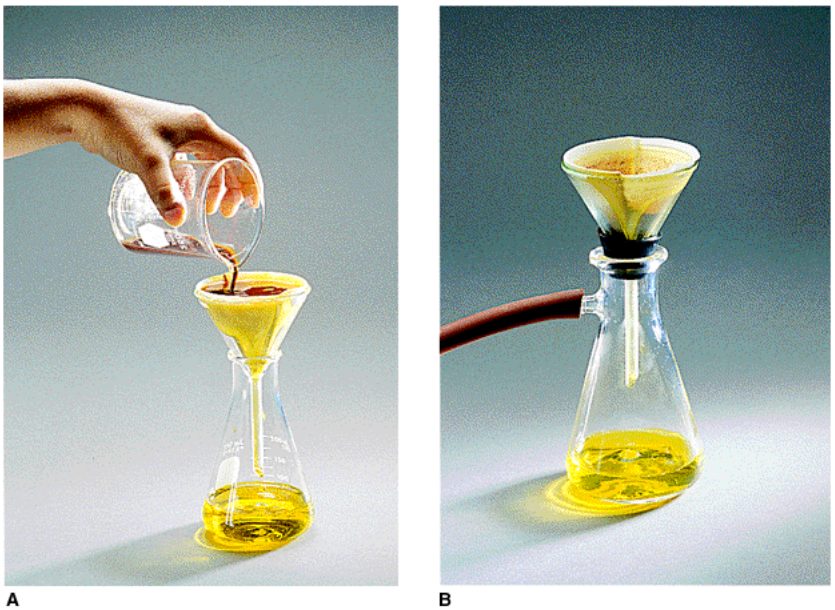
When the solid is all in solution, set it on the bench top. Do not disturb it!

Dr. Zerong Wang at UHCL

After a while, crystals should appear in the flask.

You can now place the flask in an ice bath to finish the crystallization process.

Dr. Zerong Wang at UHCL



A B

Dr. Zerong Wang at UHCL

Suction Filtration Apparatus.

Dr. Zerong Wang at UHCL