# Chemistry 2633
# Techniques of Organic Chemistry

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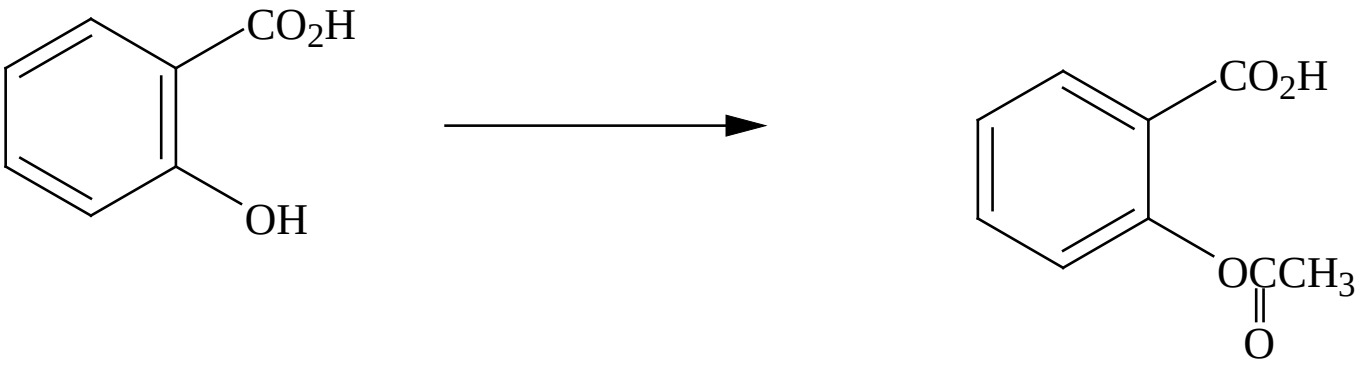
Thurs 12:00-4:30: Samira Escopy
Thurs 5:00-9:30: Mathew Queensen

Fall 2017




Salicylic acid

2-hydroxybenzoic acid

Aspirin

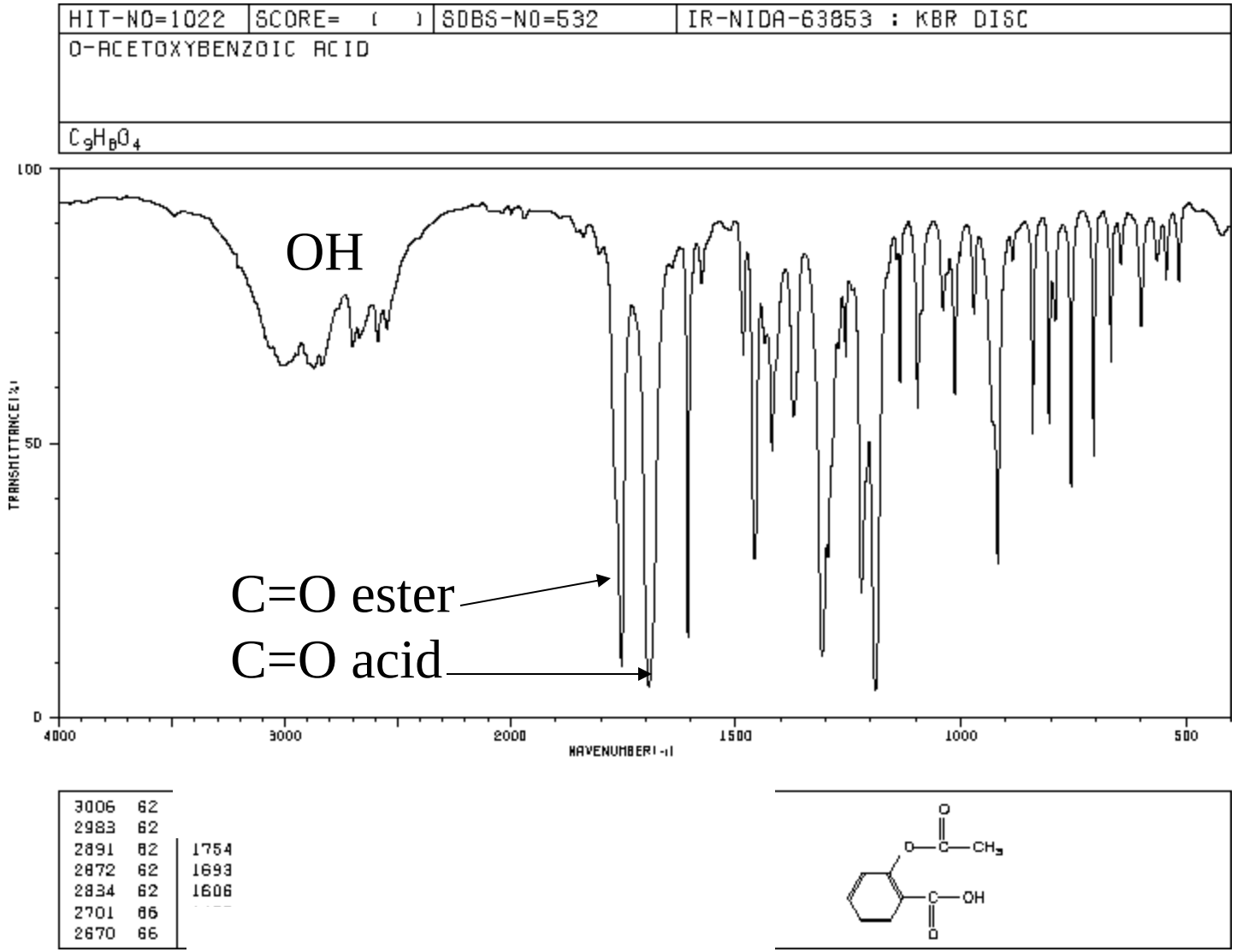
2-acetoxybenzoic acid

How do we know that what we isolated is aspirin?

1. One way is by comparing the physical properties of the material we isolated to that of pure aspirin

What physical properties?

# Infrared Spectroscopy




conjugated acid: 1693 $cm^{-1}$; non-conjugated ester: 1754 $cm^{-1}$

Common Organic Functional Groups in IR

C-H

O-H

N-H

C=O

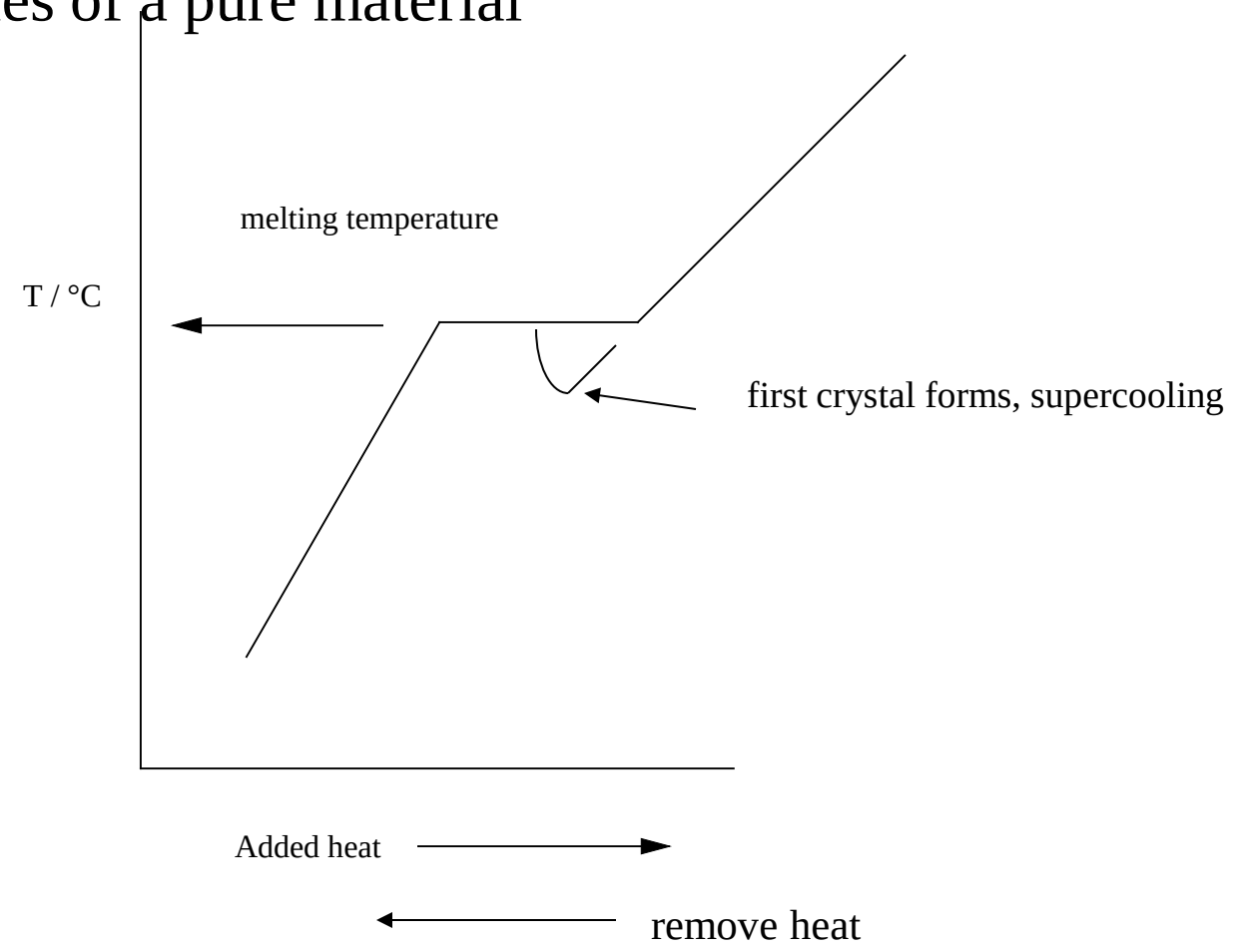
C=C

C≡C

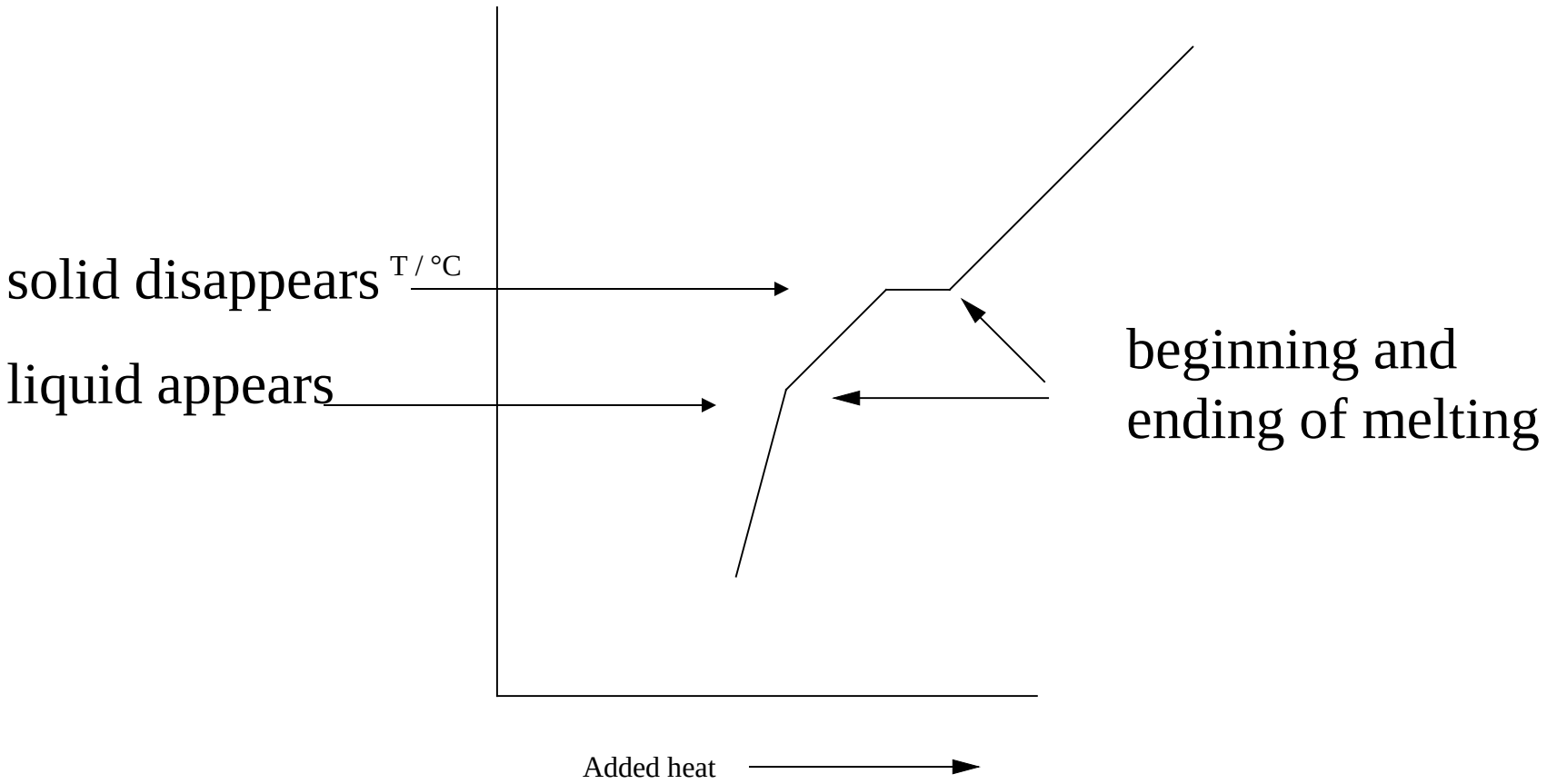
C ≡N

# Other Physical Properties

## Melting properties of a pure material

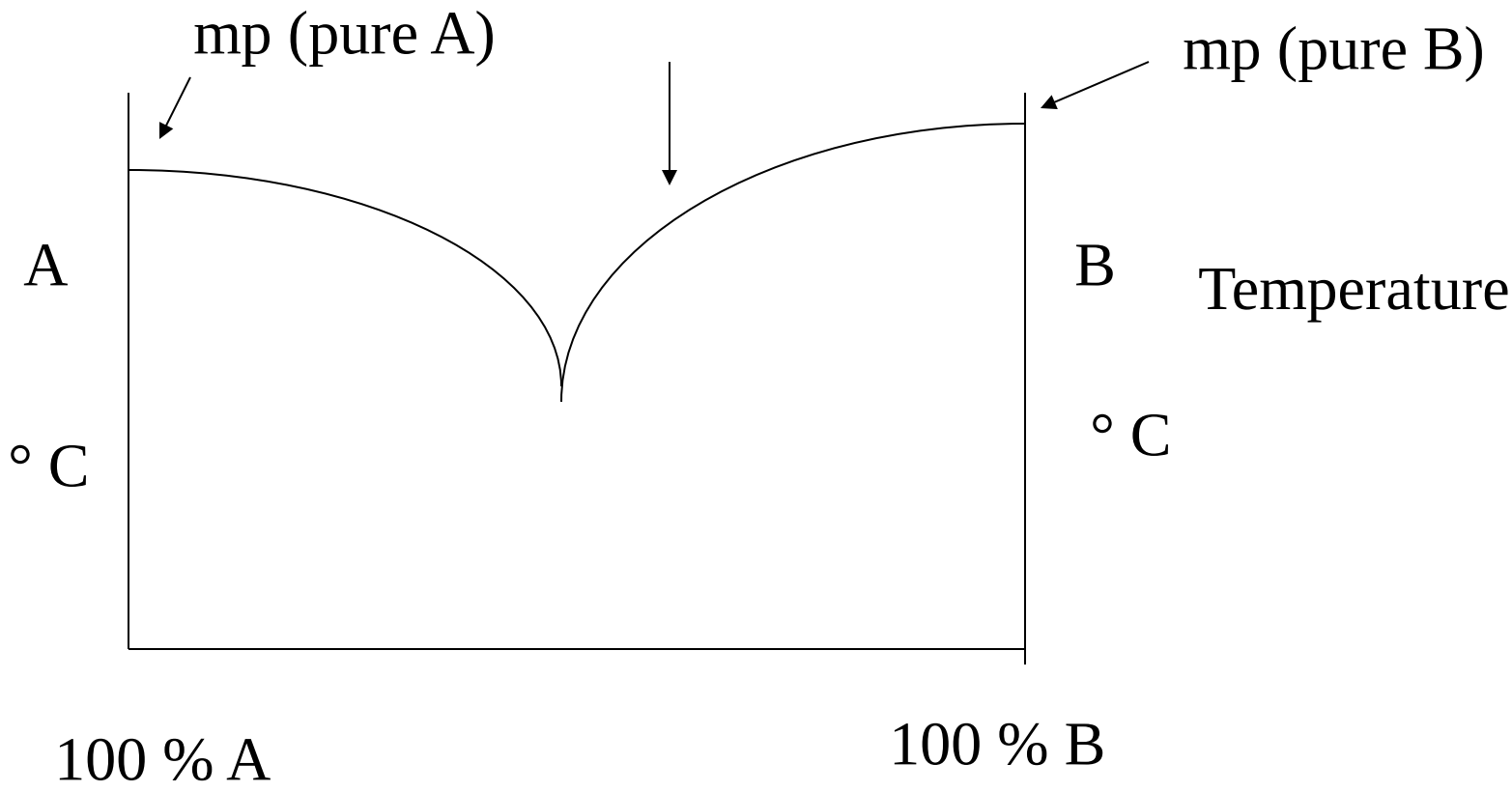


# Melting properties of an impure material

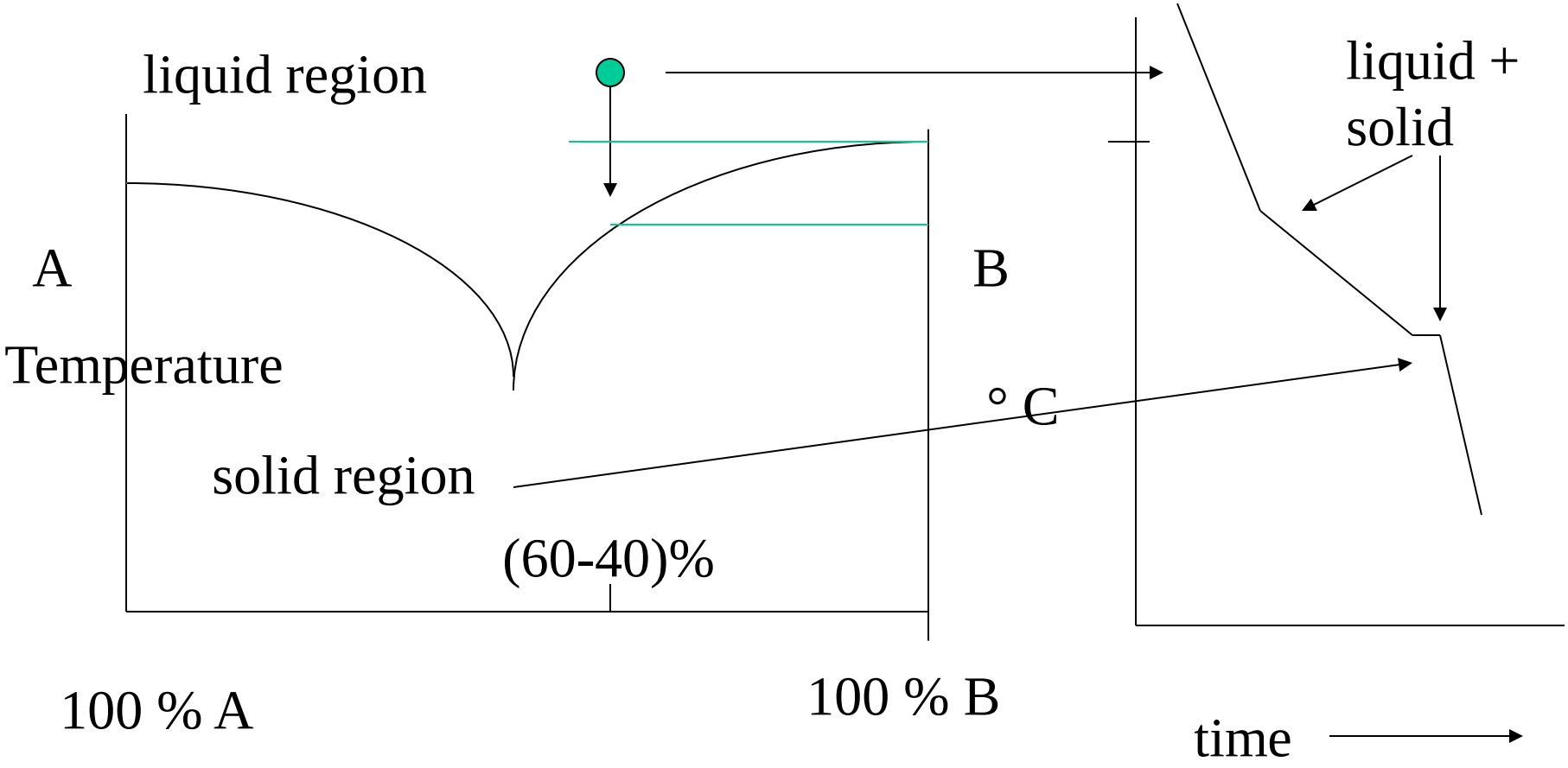


1. Melting point of a known material should melt within 1-2 °C of the value reported previously.
2. Melting point of a pure material melts sharply;

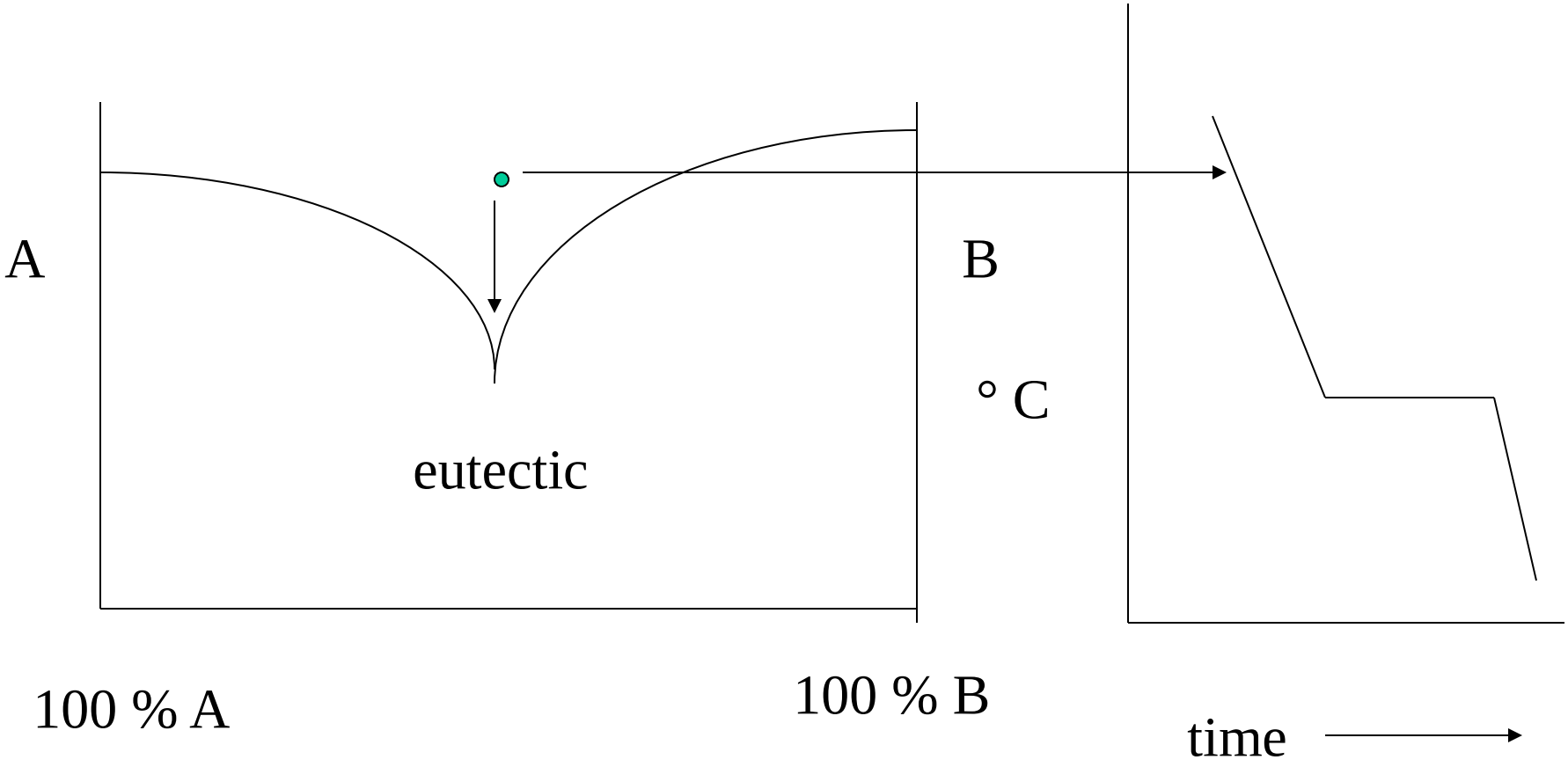
If a compound melts sharply, is it necessarily a pure material?




The melting point behavior of a simple binary mixture

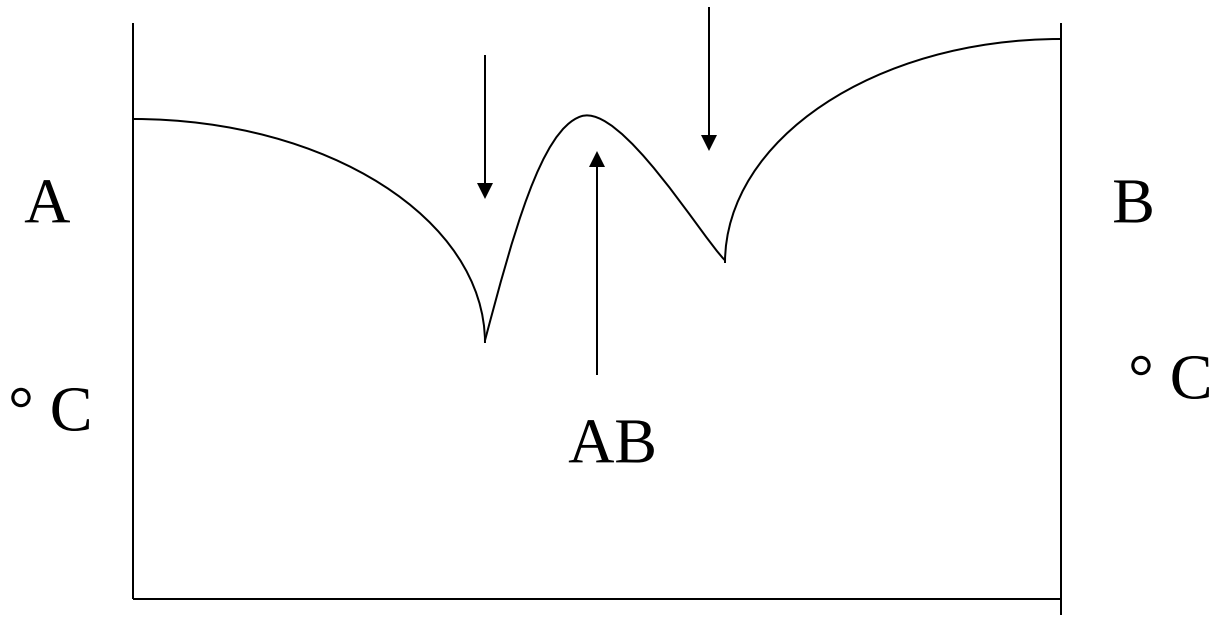



The melting point behavior of a simple binary mixture

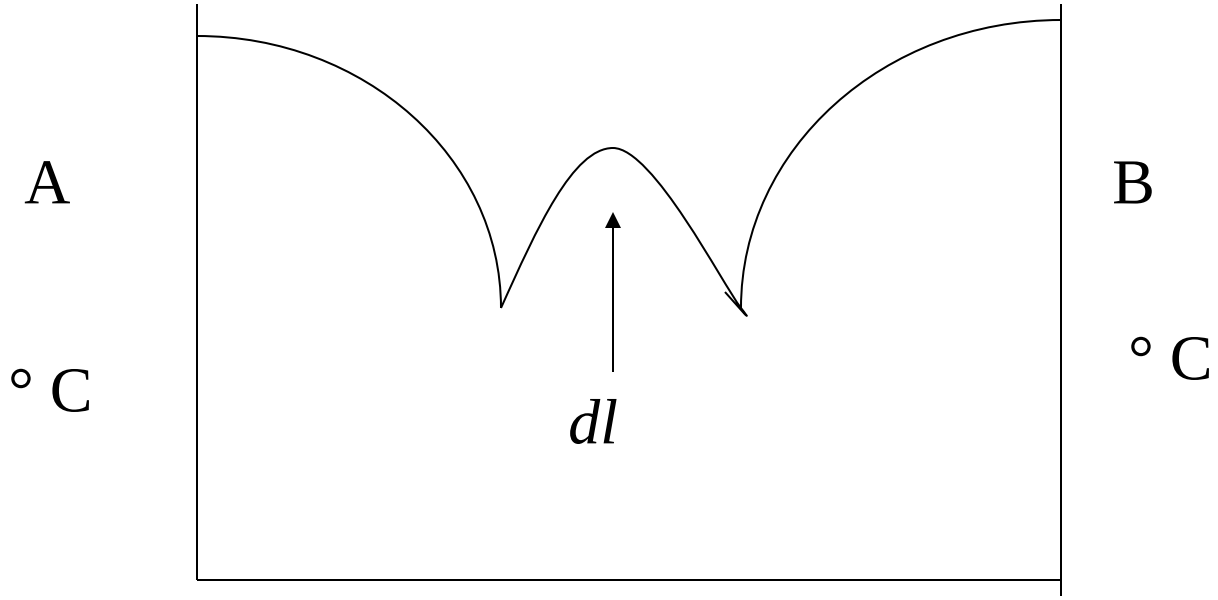



The melting point behavior of a simple binary mixture at the eutectic composition

The eutectic point is the lowest temperature solid and liquid exists in equilibrium




The melting point behavior of a more complex mixture




100 % *d*-menthol

100 % *l*-menthol

The melting point of a chiral system

Many chiral systems exhibit this type of behavior

(for example: *dl* menthol)

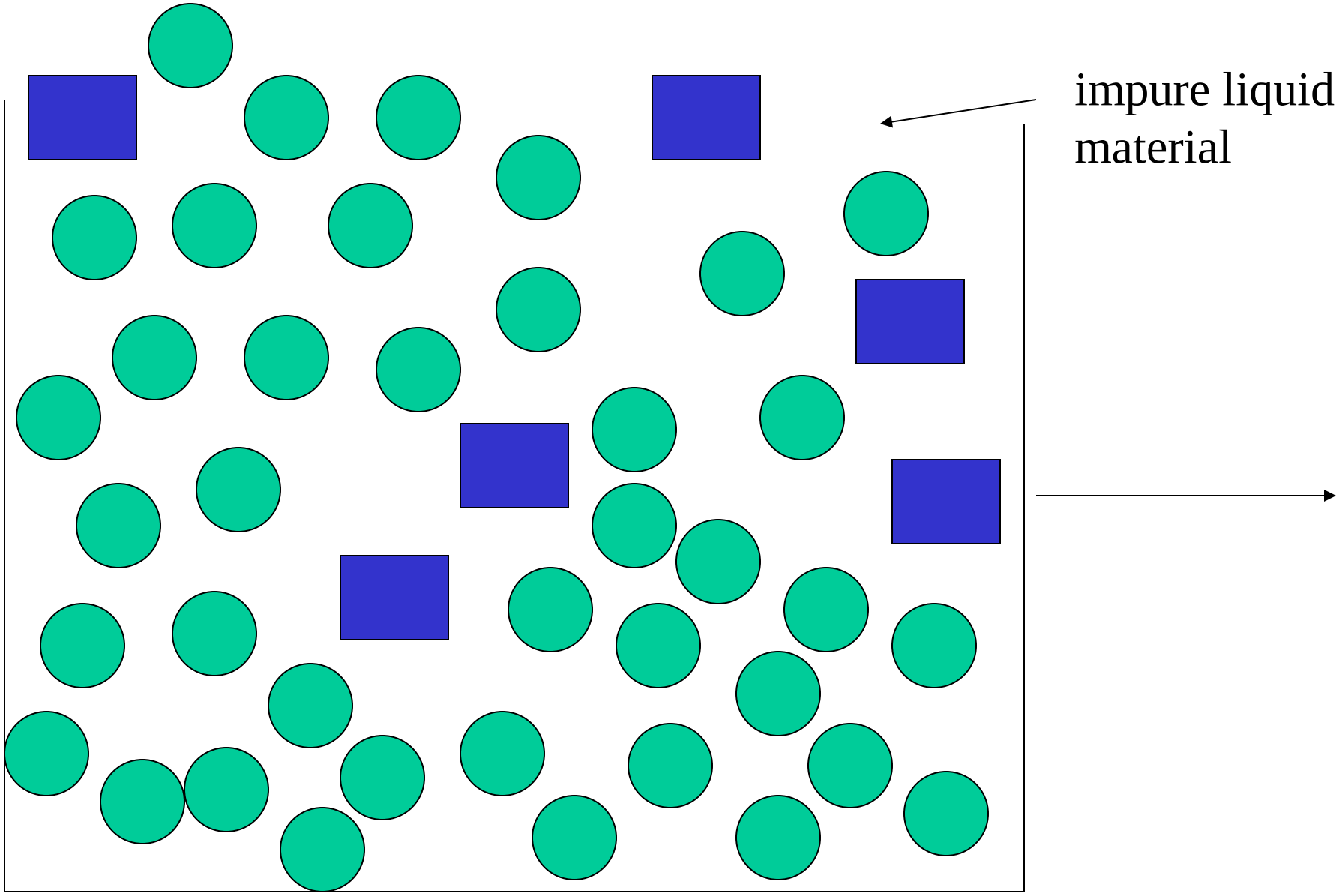
How do we purify an impure material?

A. solid

B. liquid

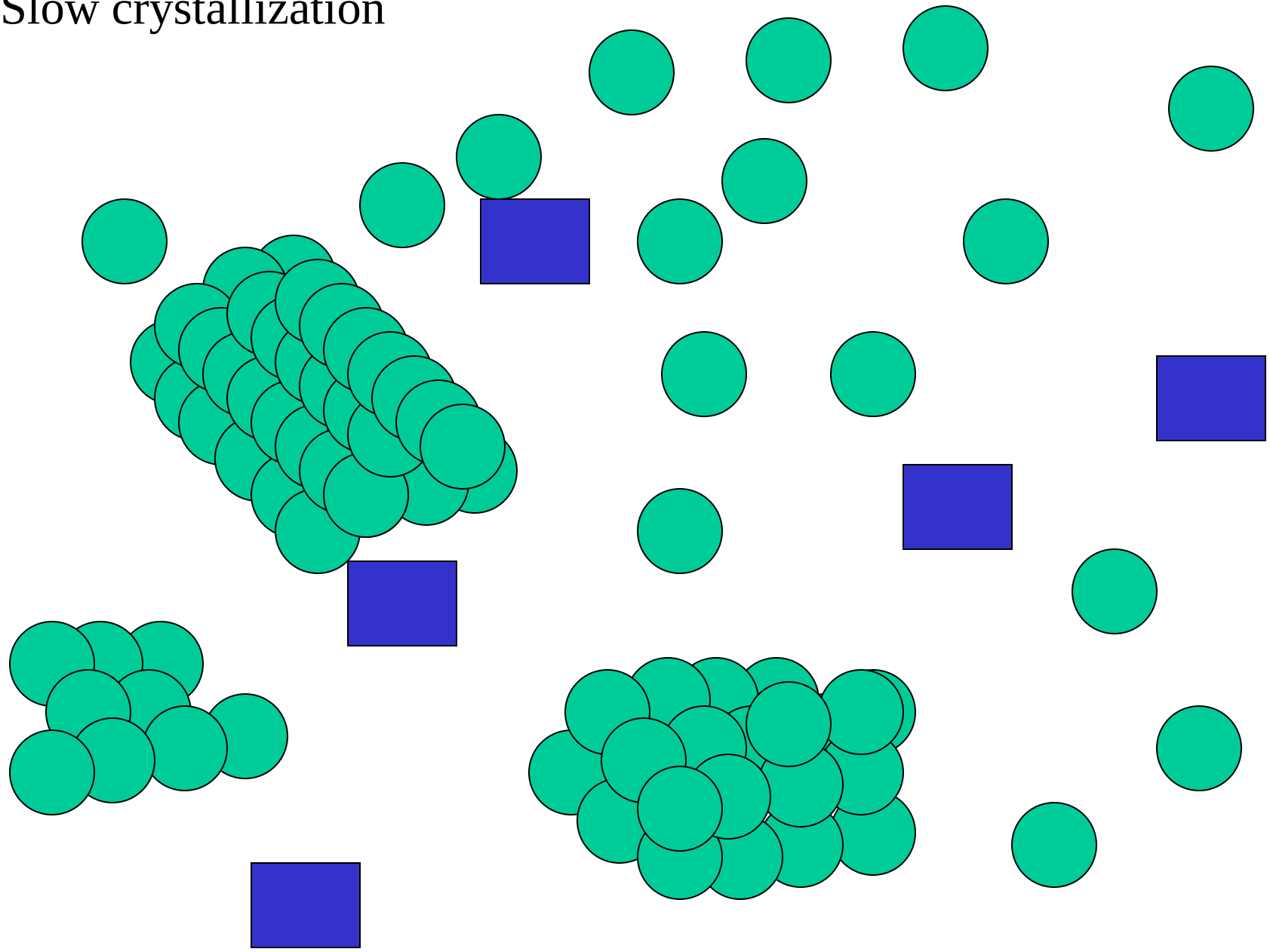
C. gas

1. Solids: recrystallization



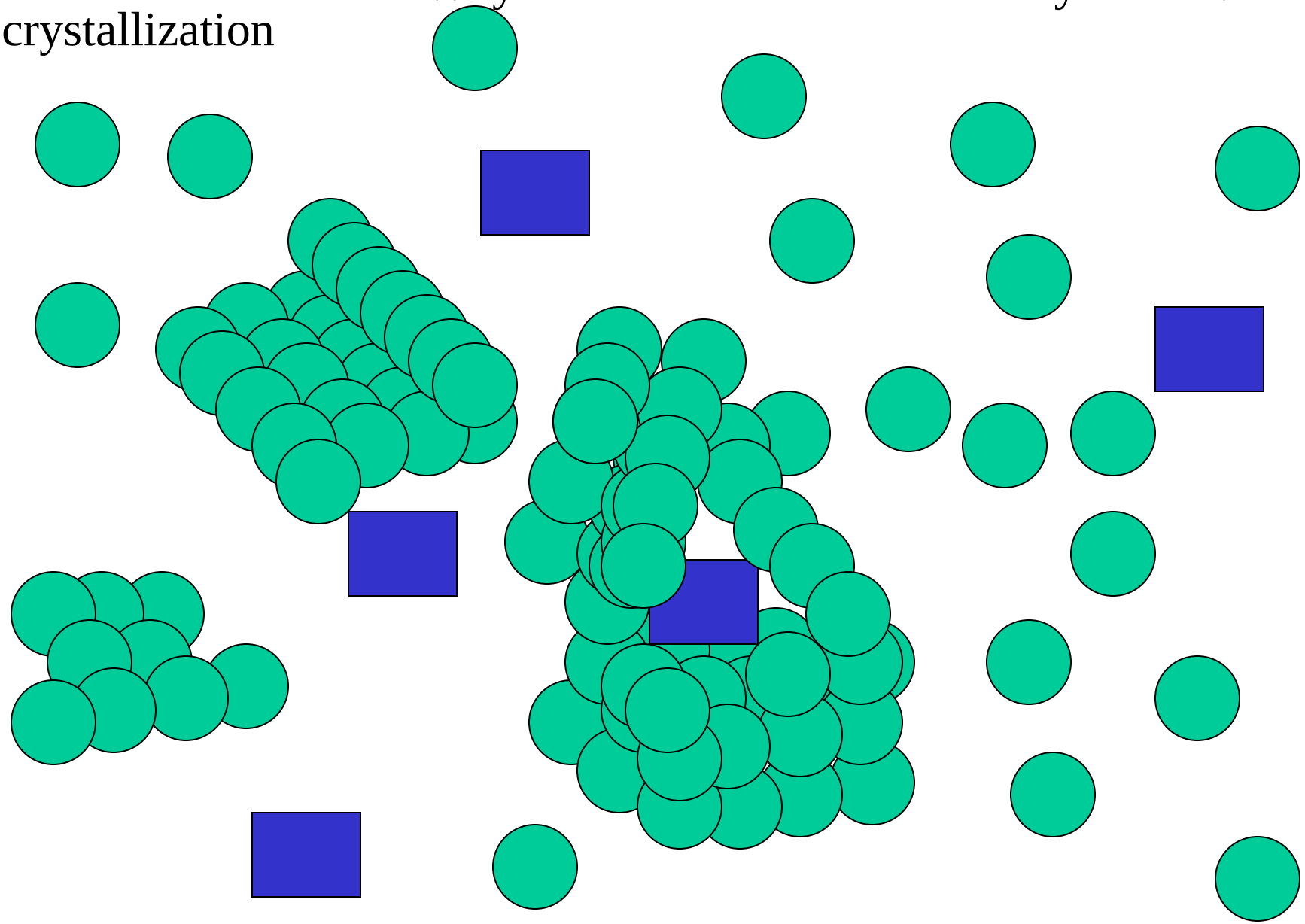

Solvent molecules not shown

Slow crystallization

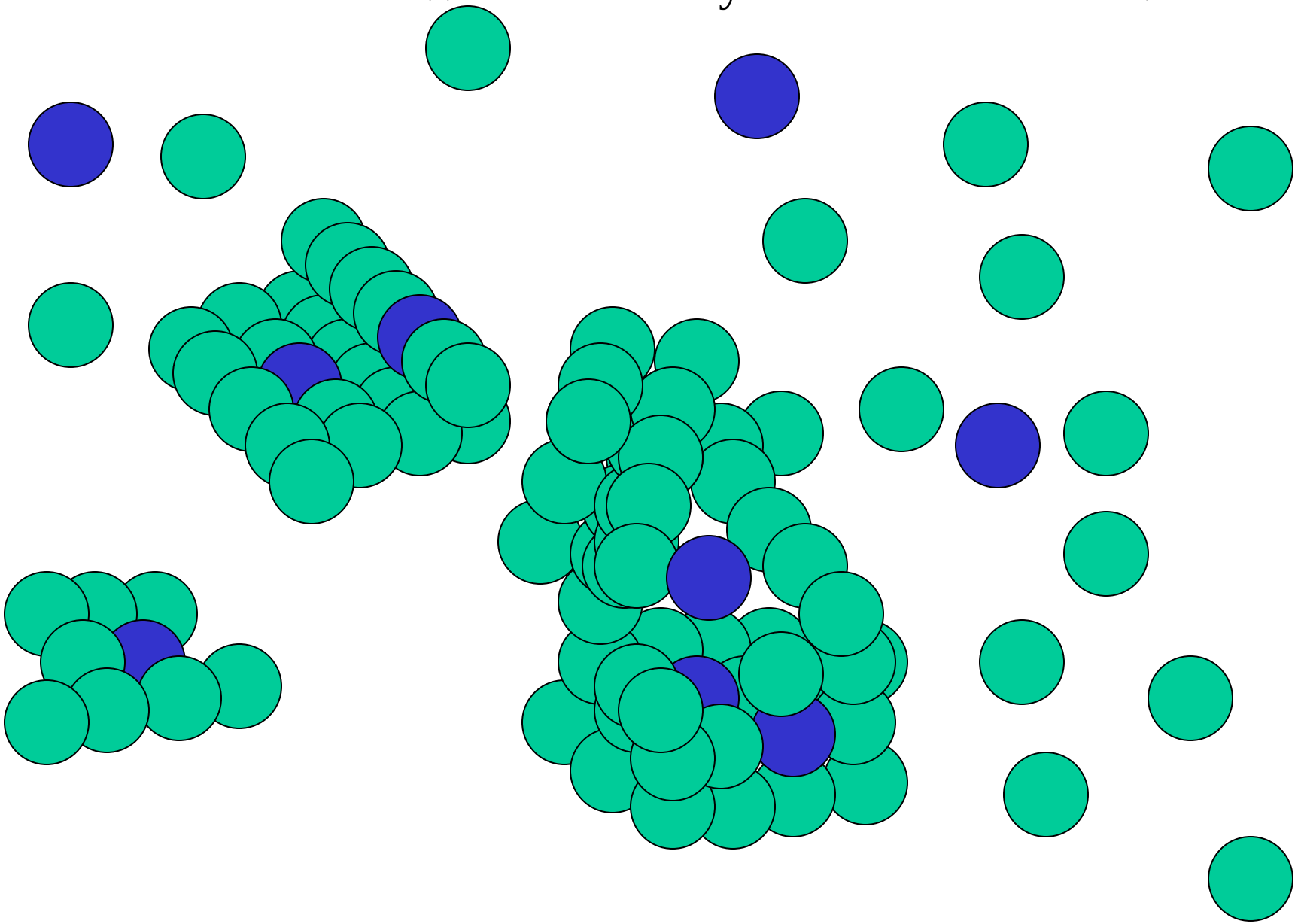


Fast crystallization

Why doesn’t the blue material crystallize?



# When does recrystallization not work?



What are the factors affecting the quality of the crystal obtained?

1. rate of crystal growth
2. nature of the solvent and of the impurity

Factors affecting the amount of the crystal obtained:

1. solubility of materials in the solvent
2. temperature

How to choose a solvent for recrystallization?

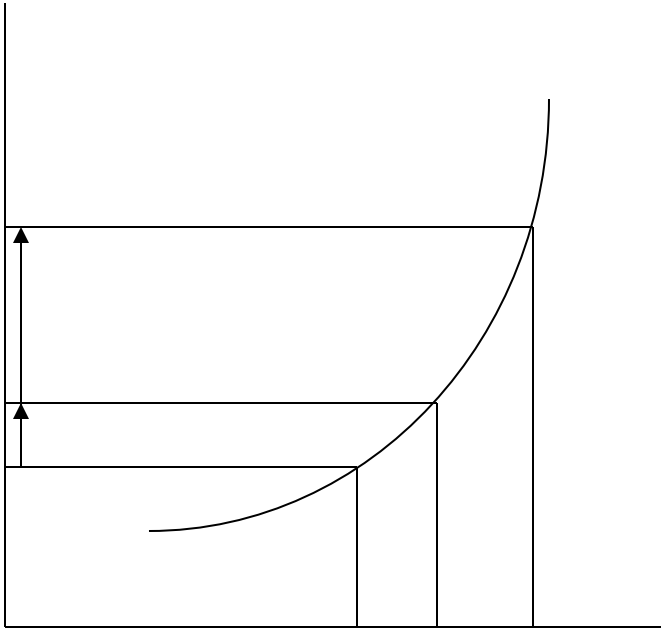
1. Choose a solvent similar in polarity to the compounds being recrystallized -like dissolves like- polar solvents dissolve polar substrates; non-polar substrates dissolve non polar substrates

2. Choose a solvent with a reasonable boiling point

Why?

Solubility

g/mL



25 °C

Temperature

When will crystallization work?

1. If the material is reasonably pure to begin with ~90+%.

2. The impurities have different properties including polarity, solubility, structure

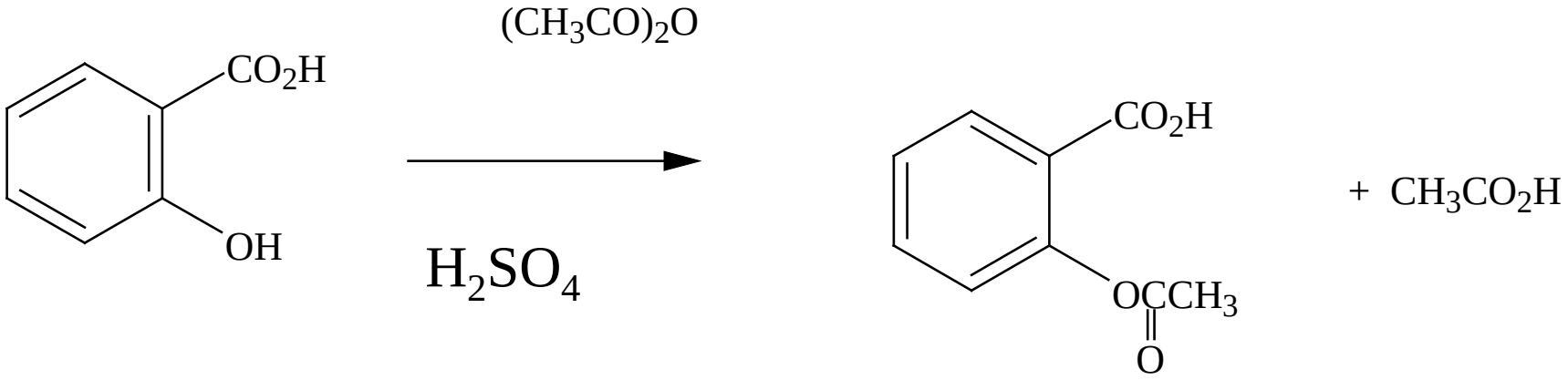
Typical Solvents in Organic Laboratory (~in decreasing polarity)

**Green Solvents**
water, methanol, ethanol, 1, and 2-propanol, 1-butanol, t-butanol
acetone, 2-butanone, ethyl acetate

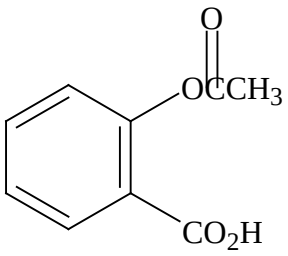
**Usable solvents**
acetic acid, dimethyl sulfoxide, acetonitrile, tetrahydrofuran,
toluene, xylenes, cyclohexane, heptane, isooctane

**Undesirable**
dimethylformamide, pyridine, dioxane, **diethyl ether**, di-
isopropyl ether, chloroform, **dichloromethane**, carbon
tetrachloride benzene, pentane**, hexane**

end

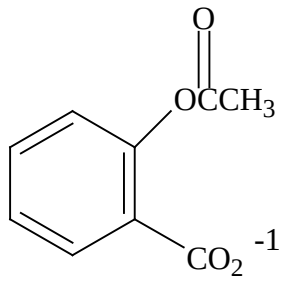



1. Mix the appropriate reagents and heat on a water bath;
2. Cool in ice and scratch until solid forms;
3. Add cold water and break up solid;
4. Filter and wash with cold water;
5. Dissolve the wet aspirin in $NaHCO_3$;




solid

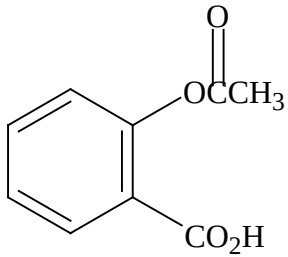
$NaHCO_3$




+ $CO_2$

in aqueous solution

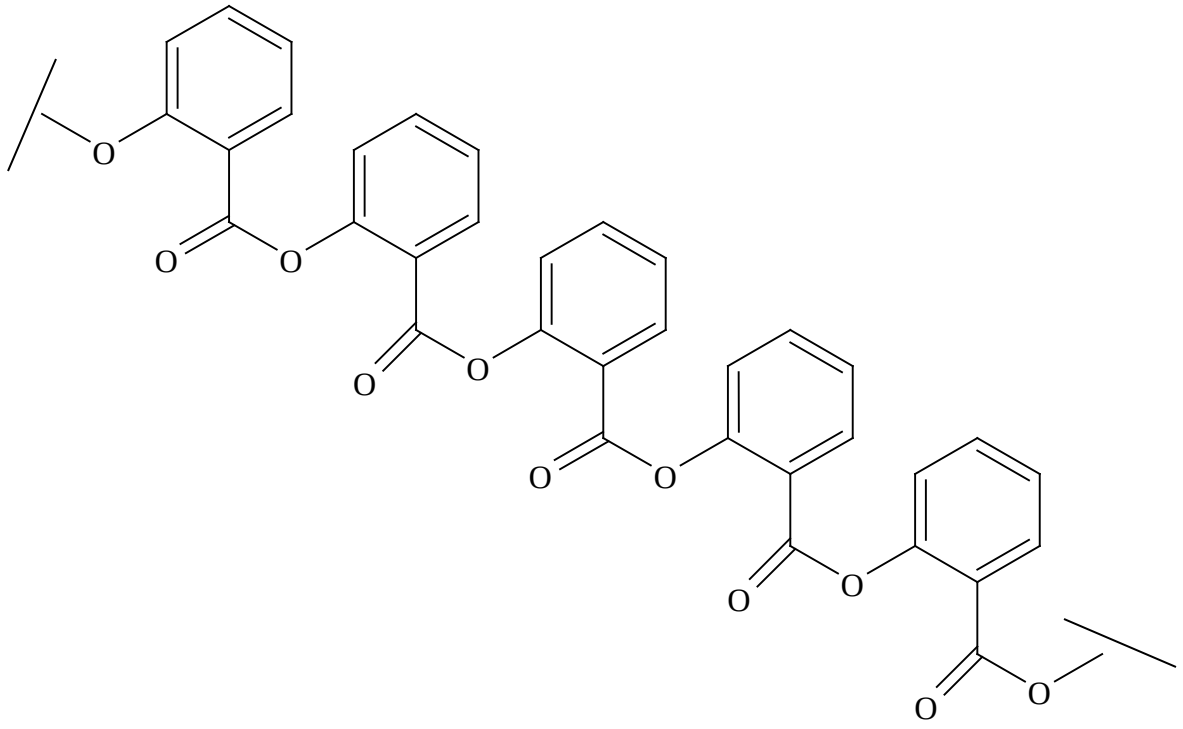
HCl pH 1

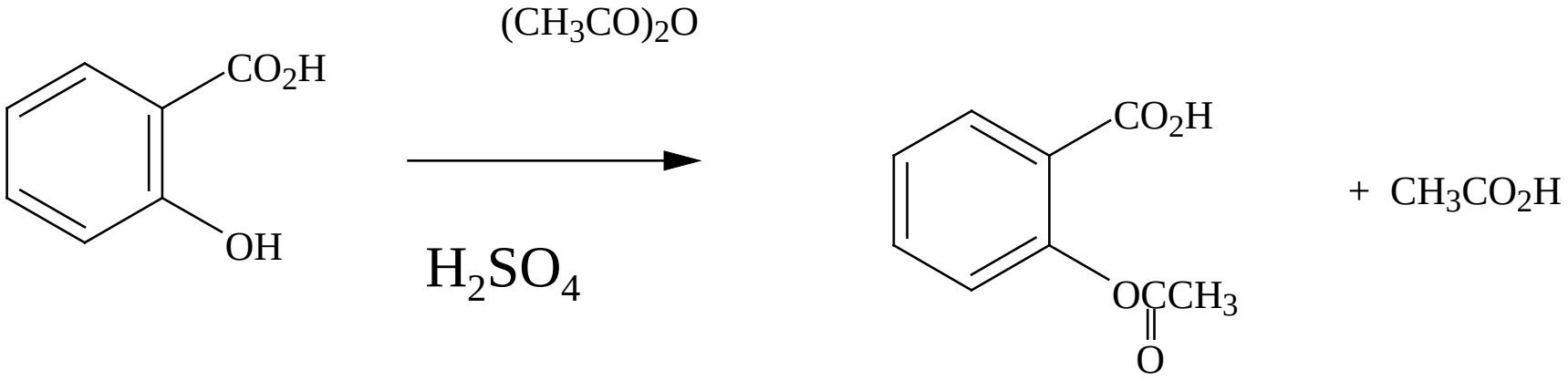



+ $CO_2$

solid

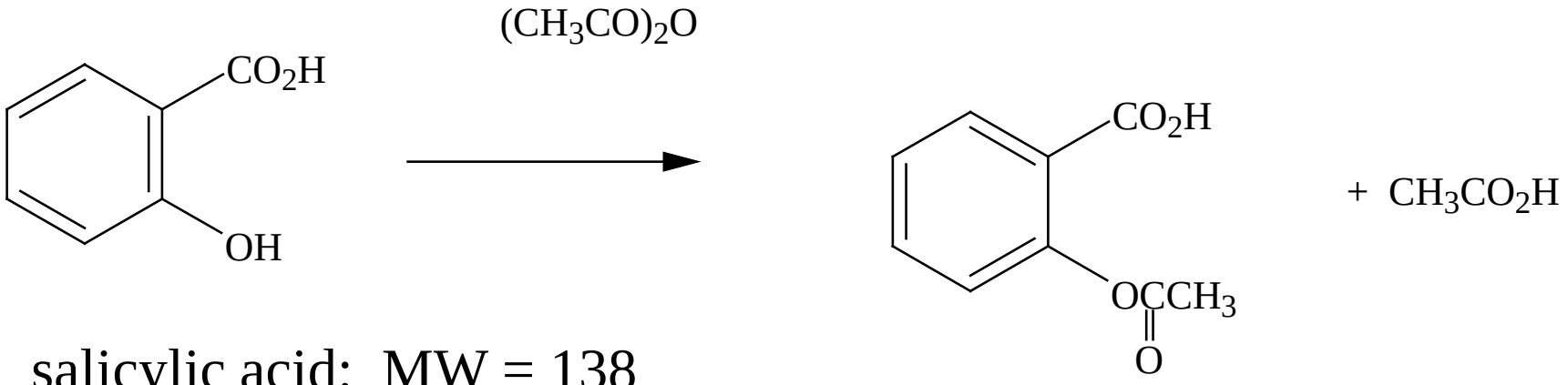
# A likely structure of the tacky polymer






1. Mix the appropriate reagents and heat on a water bath (> 90 °C).
2. Cool in ice and scratch until solid forms;
3. Add cold water and break up solid;
4. Filter and wash with cold water;
5. Dissolve the wet aspirin in $NaHCO_3$;
6. Filter to remove polymer (tacky insoluble material); (save liquid)
7. Acidify to pH ~ 1, filter (suction filtration)
8. Allow to dry until next week.

# Typical Calculations in Organic Chemistry Laboratory

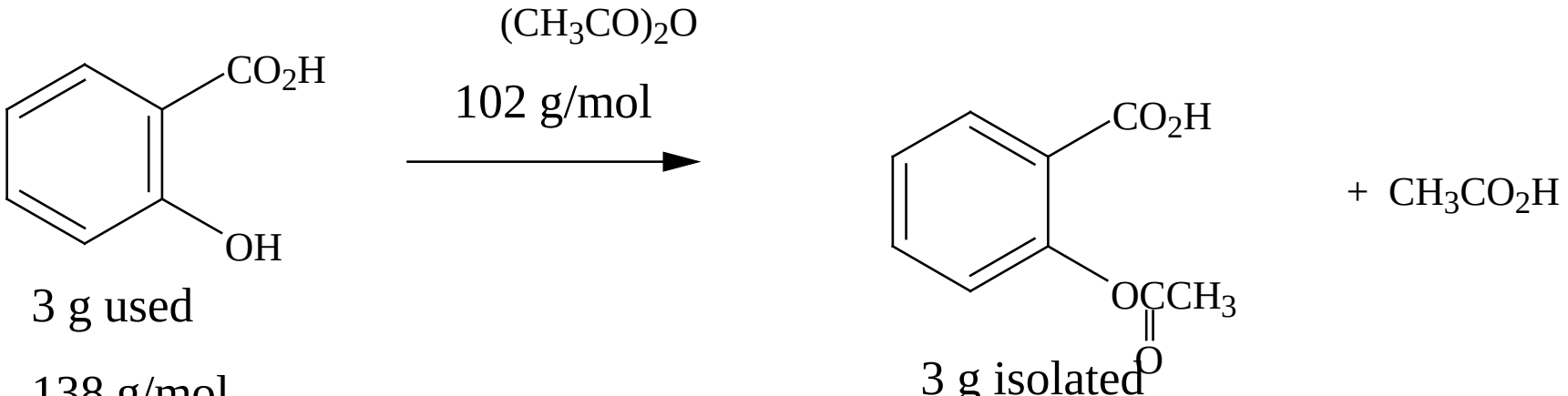



salicylic acid: MW = 138
material used: 3.0 g

acetic anhydride: MW =102
material used: 5.0 mL
density: 1.10 g/mL

aspirin isolated: 3.0 g

What is the limiting reagent?
What is the yield?




3 g used

138 g/mol

3 g isolated

180 g/mol

3g/138g/mol = 0.0217 mol SA

5 mL*1.10 g/mL = 5.5 g/102 = 0.0539 mol AA

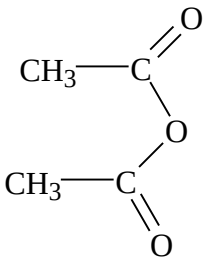
The limiting reagent is SA;

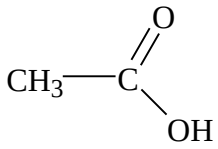
Why is SA made the limiting reagent and not AA?

The theoretical yield is?

0.0217 mol *180 g/mol = 3.906 g Aspirin

% Yield: 3.0/3.906 = 0.768*100 = 76.8 %




$H_2SO_4$

Acetic anhydride: irritating liquid

Acetic acid: also irritating (vinegar is a ~5% solution of acetic acid in water)

Sulfuric acid: concentrated sulfuric acid is a strong dehydrating liquid

Work in Hood!

Why is the yield less than 100%?

1. Loss due to transfers
2. assume 100 % reaction
3. assume limiting reagent is 100 % pure
4. solubility of aspirin in water
5. Competing side reactions

If solid A has a solubility of 1 g /100mL of solvent at 25 °C and 15 g /100mL at the solvent's boiling temperature, how much can you recover by recrystallization of 167 g of this material if it is 90% pure? Lets assume the impurity has a similar solubility.

If we use a minimum amount of boiling solvent to dissolve this material, how much solvent must we use?

167g *0.9 = 150.3 g of A requires 1000 mL of boiling solvent

At 25 °C, 10 g of A will remain in solution along with the impurity. Thus 140 g will be recovered.

In order to achieve good separation, the solid and liquid should be separated as quantitatively as possible. Any solvent that evaporates on the solid will deposit dissolved materials.

Note: 16.7 g of impurity/1000mL or 1.67g/100mL