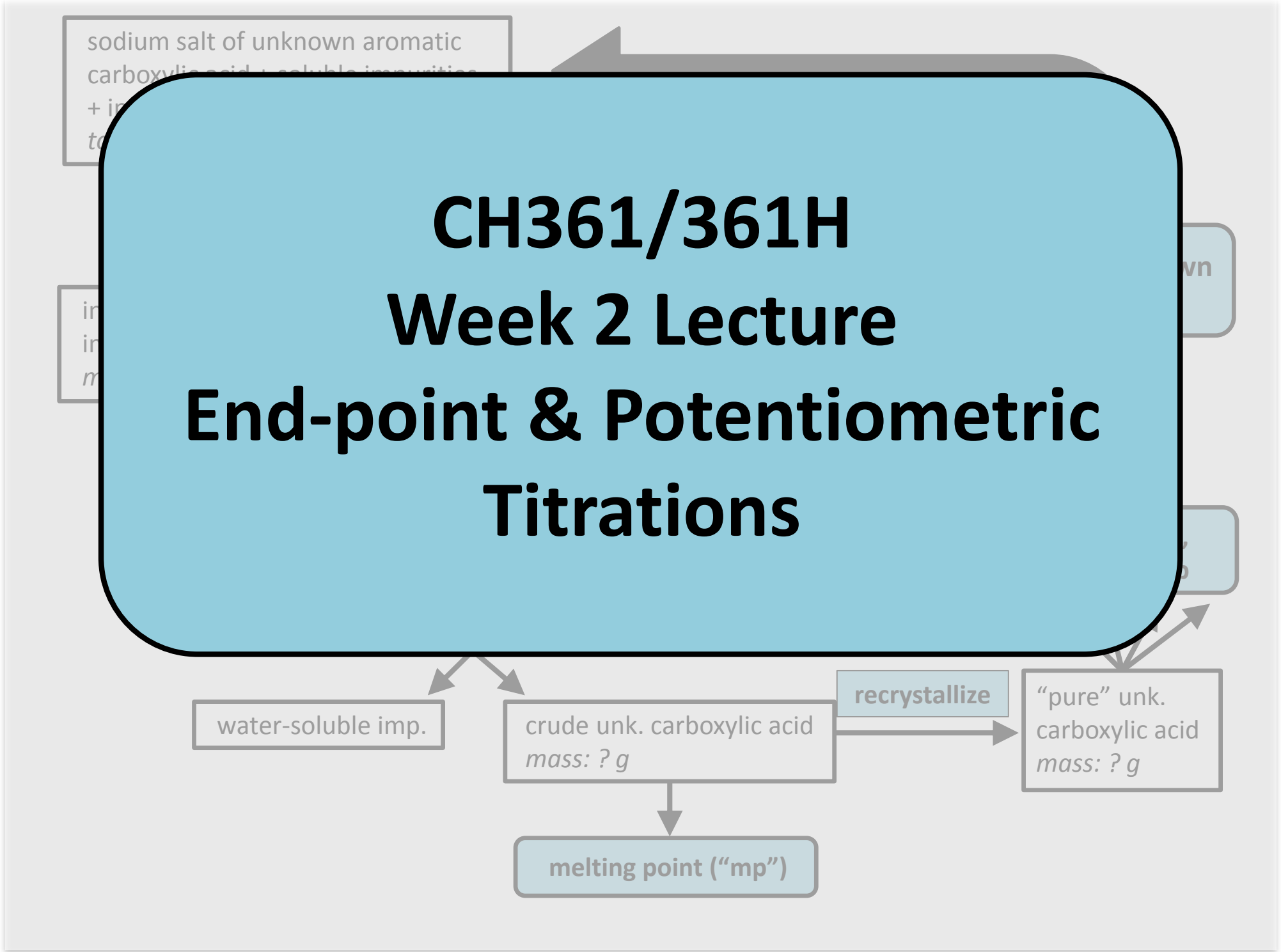
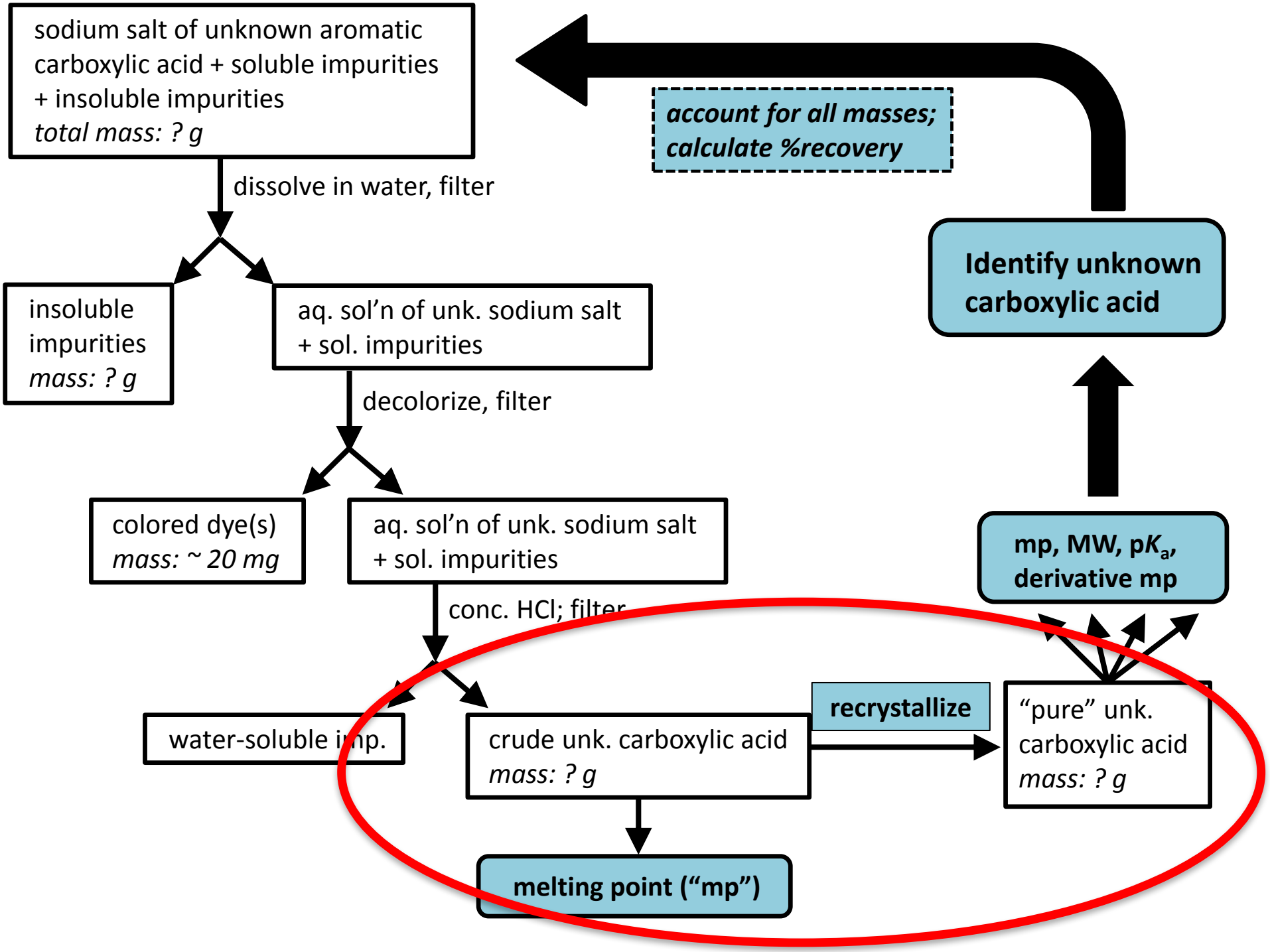


CH361/361H
Week 2 Lecture
End-point & Potentiometric Titrations


sodium salt of unknown aromatic carboxylic acid + soluble impurities + insoluble impurities
total mass: ? g
dissolve in water, filter
insoluble impurities
mass: ? g
aq. sol'n of unk. sodium salt + sol. impurities
decolorize, filter
colored dye(s)
mass: ~ 20 mg
aq. sol'n of unk. sodium salt + sol. impurities
conc. HCl; filter
water-soluble imp.
crude unk. carboxylic acid
mass: ? g
recrystallize
"pure" unk. carboxylic acid
mass: ? g
melting point ("mp")
mp, MW, pKa, derivative mp
Identify unknown carboxylic acid
account for all masses; calculate %recovery

Recrystallization – *practical considerations*

Progressive approach:

1) solvent selection on micro-scale (~20 mg)
2) medium batch (~100 – 200 mg)
3) large batch (~3 – 5 g) – also involves hot filtration

Solvent selection

- *sample must be completely **dry**!*
- *careful, detailed observations are crucial!*
- *begin with 20 mg in ~0.1 mL solvent; incrementally add more solvent*
- *if > 1.0 mL solvent required, solvent is not suitable*

Solvent choices

- *water*
- *ethanol (CH_3CH_2OH)*
- *hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$)*
- *toluene (methylbenzene)*

Mixed solvent systems

water/ethanol

hexane/toluene

Recrystallization – *practical considerations*

Common "pitfalls":

1) crystals do not form

seed crystal
"scratching"
too much solvent?

2) crystals are of insufficient purity

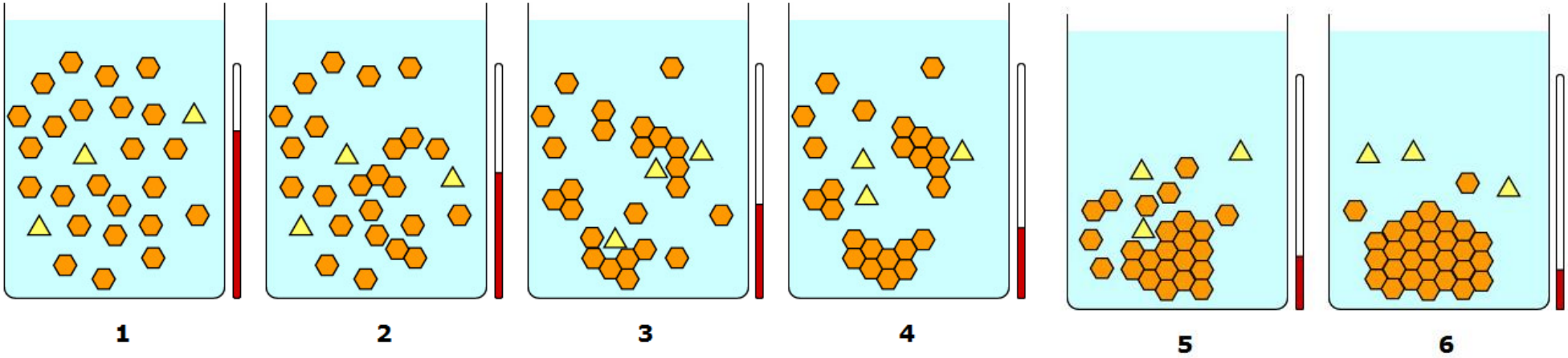
was solution cooled slowly?
inappropriate solvent
sample "melting" at boiling point of recrystallization solvent

3) low recovery

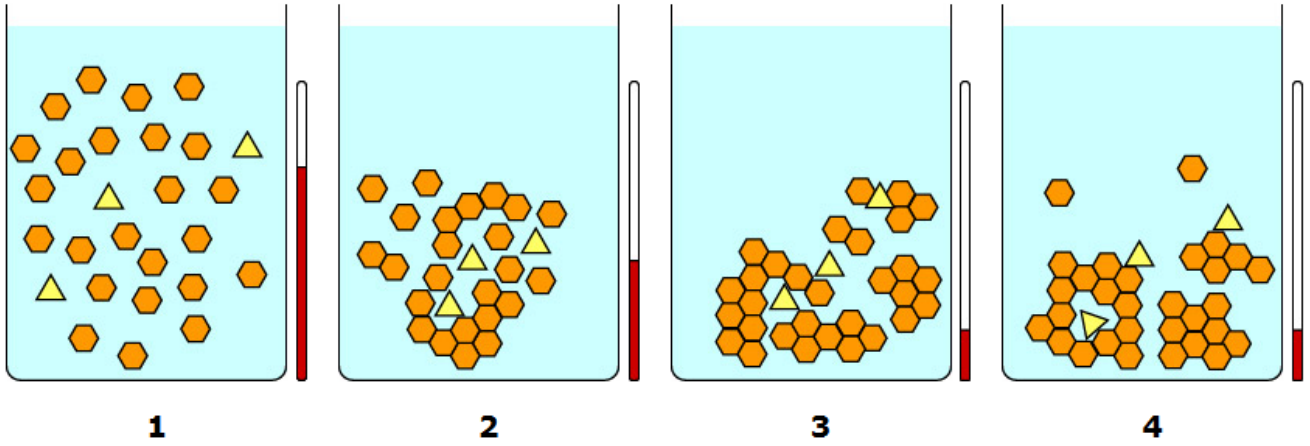
filtrate (mother liquor) contains compound of interest
too much solvent?
insufficient cooling

Recrystallization

Crystallization that occurs with slow cooling:



Crystallization that occurs with fast cooling:



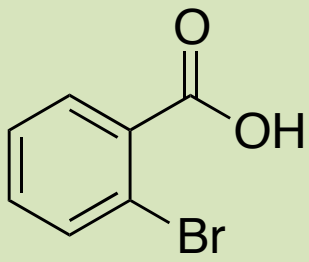
Images downloaded from:
http://orgchem.colorado.edu/Technique/Procedures/Crystallization/Crystallization.html

sodium salt of unknown aromatic carboxylic acid + soluble impurities + insoluble impurities
total mass: ? g

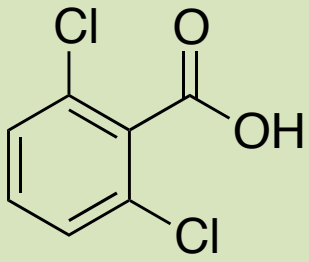
account for all masses; calculate %recovery

Identify unknown carboxylic acid

mp, MW, pK_a, derivative mp



mp = 148 °C

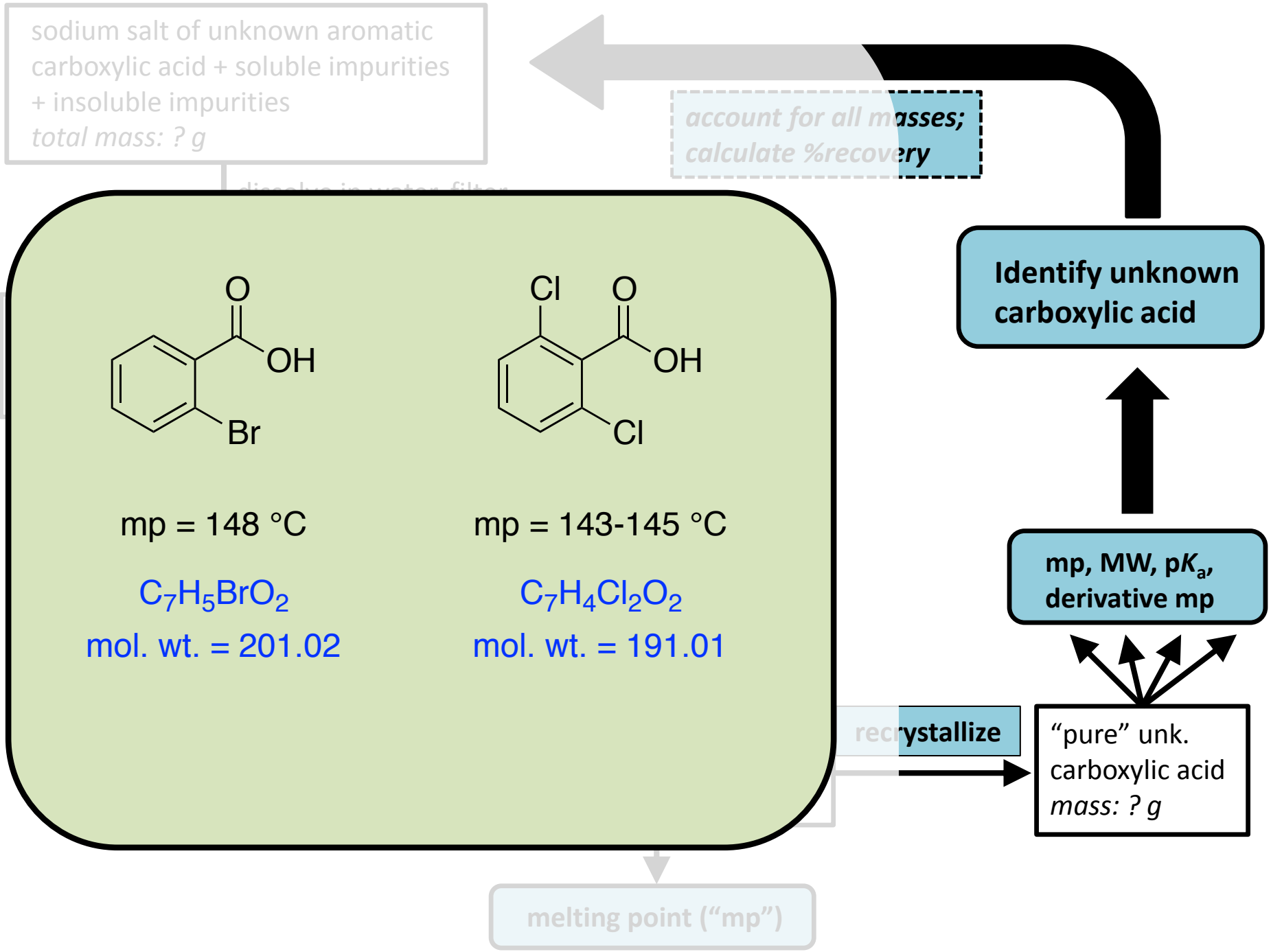


mp = 143-145 °C

recrystallize

"pure" unk. carboxylic acid
mass: ? g

melting point ("mp")

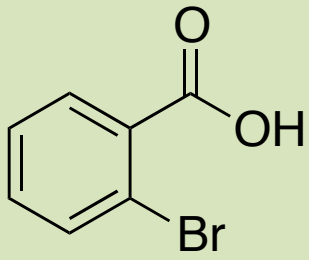

sodium salt of unknown aromatic carboxylic acid + soluble impurities + insoluble impurities
total mass: ? g
account for all masses; calculate %recovery
Identify unknown carboxylic acid
O
OH
Br
mp = 148 °C
C7H5BrO2
mol. wt. = 201.02
Cl
O
OH
Cl
mp = 143-145 °C
C7H4Cl2O2
mol. wt. = 191.01
mp, MW, pKa, derivative mp
recrystallize
“pure” unk. carboxylic acid
mass: ? g
melting point (“mp”)

sodium salt of unknown aromatic carboxylic acid + soluble impurities + insoluble impurities
total mass: ? g

account for all masses; calculate %recovery

Identify unknown carboxylic acid

mp, MW, pK_a, derivative mp

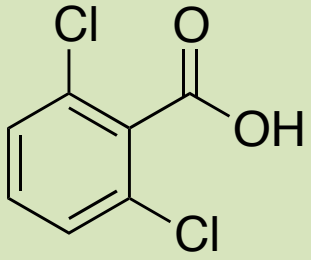


mp = 148 °C

$C_7H_5BrO_2$

mol. wt. = 201.02

pK_a = 2.85



mp = 143-145 °C

$C_7H_4Cl_2O_2$

mol. wt. = 191.01

pK_a = 1.82

recrystallize

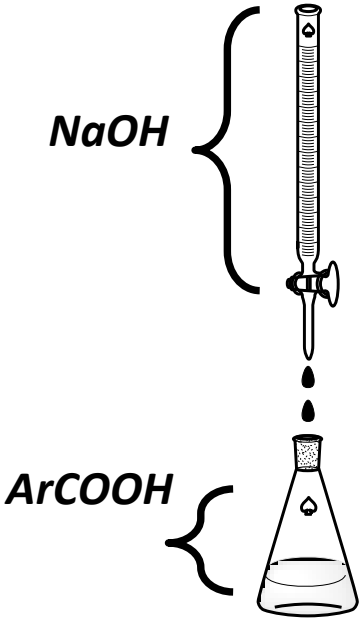
"pure" unk. carboxylic acid
mass: ? g

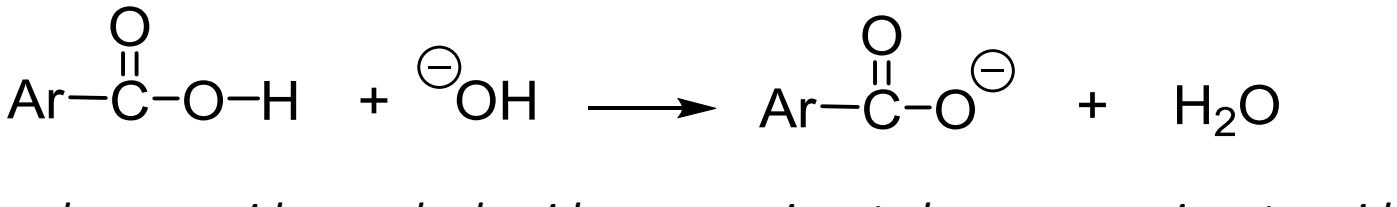
melting point ("mp")

Titration

Method to determine the concentration of an analyte, through the slow, incremental addition of a known concentration of another reagent

Acid-Base Titration:

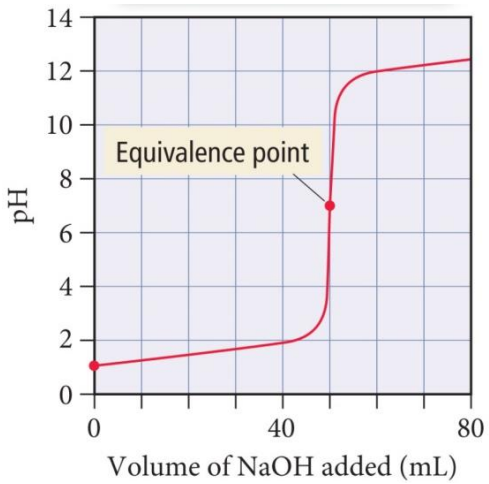




unknown acid (weak) *hydroxide (strong base)* *conjugate base* *conjugate acid*

Determining the Equivalence Point:

- pH vs. vol. NaOH added *(potentiometric)*
- Color change of pH indicator *(end-point)*



Figures from *"Principles of Chemistry: A Molecular Approach, 2nd Edition"* by N. Tro (Pearson)

End-Point Titration

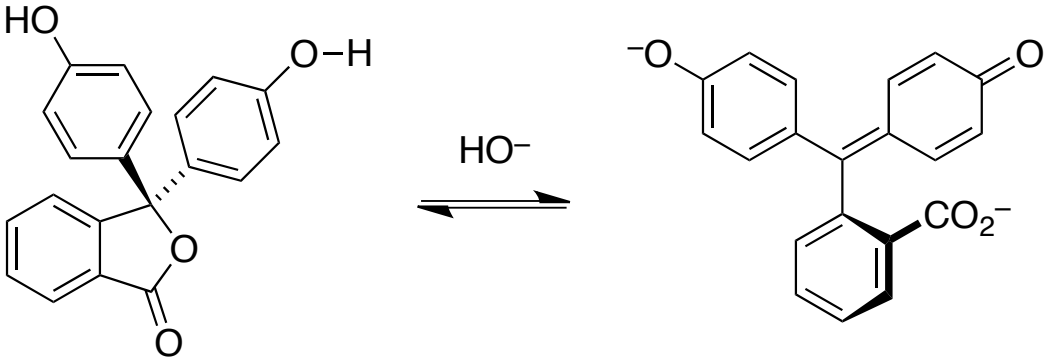
- data allows calculation of equivalent weight of unknown acid

  (for a monoprotic acid, equivalent weight = molecular weight)

- Phenolphthalein is the end-point indicator you will use

  *** unless you are colorblind to red ***

  (if so, inquire about alternative indicators)



phenolphthalein
colorless: pH 0 to 8.2

phenolphthalein: dianion form
pink: pH 8.2-12.0

(phenolphthalein)

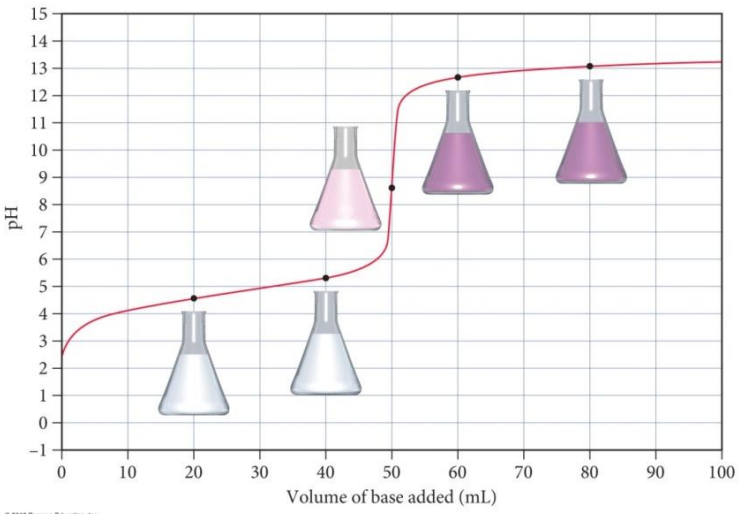
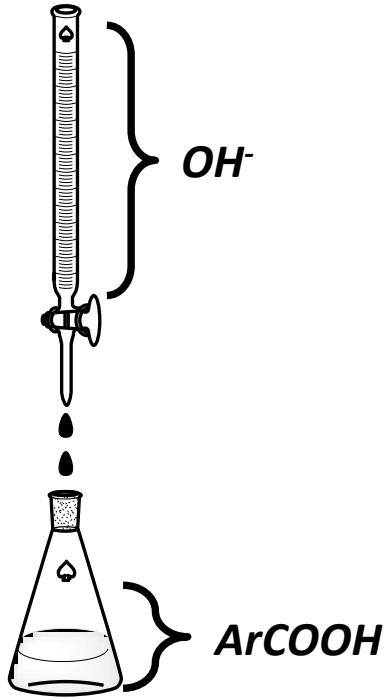


Figure from *"Principles of Chemistry: A Molecular Approach, 2nd Edition"* by N. Tro (Pearson)

End-Point Titration: *Practical Considerations*

Titrations must be carried out carefully!

- **obtain accurate mass of unknown**
- **acid must be completely dissolved**
  (~0.3 g/50 mL; can add some ethanol if needed)
- **proper buret reading**
- **may need to add fraction of a drop of NaOH solution**
- **must obtain 2 measurements within 0.5% of each other**
- **do not "overshoot" the end-point**

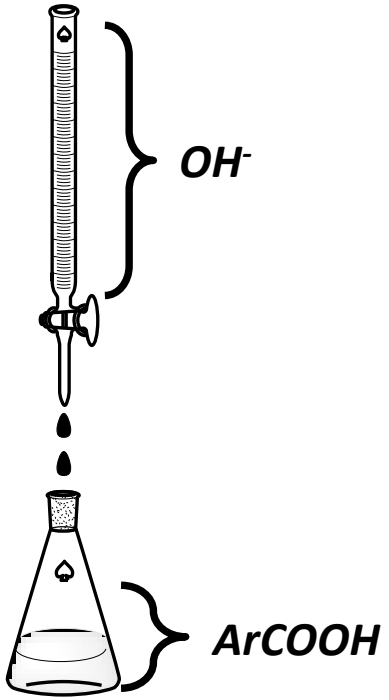


- **make all measurements to 4 significant figures**

Figures from *"Principles of Chemistry: A Molecular Approach, 2nd Edition"* by N. Tro (Pearson)

End-Point Titration: *Practical Considerations*

Example calculation and consequences of errors



- **254.2 mg** of dry purified acid titrated with **0.1033 N** aq. NaOH

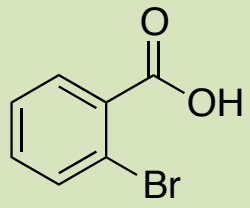
⇨ end-point reached upon addn. of **12.24 mL** of base

⇨ # mmols of base = 0.1033 mmol mL^{-1} x 12.24 mL

= **1.264 mmol**

⇨ mol. wt. of acid = 254.2 mg / 1.264 mmol

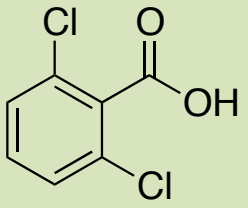
= **201.11 g mol^{-1}**



mp = 148 °C

$C_7H_5BrO_2$

mol. wt. = 201.02



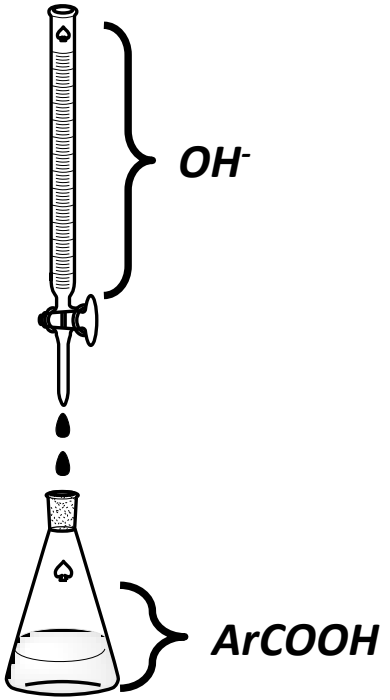
mp = 143-145 °C

$C_7H_4Cl_2O_2$

mol. wt. = 191.01

End-Point Titration: *Practical Considerations*

Example calculation and consequences of errors



- **254.2 mg** of dry purified acid titrated with **0.1033 N** aq. NaOH

⇒ end-point reached upon addn. of **12.24 mL** of base

⇒ # mmols of base = 0.1033 mmol mL^{-1} x 12.24 mL

= **1.264 mmol**

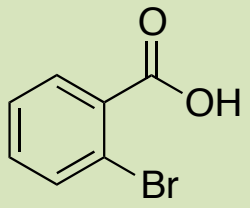
⇒ mol. wt. of acid = 254.2 mg / 1.264 mmol

= **201.11 g mol^{-1}**

BUT, what if acid was not dry?
e.g., only 95 wt.% pure

true mol. wt. of acid = 241.5 mg / 1.264 mmol

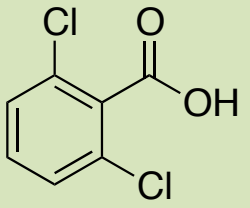
= **191.05 g mol^{-1}**



mp = 148 °C

$C_7H_5BrO_2$

mol. wt. = 201.02



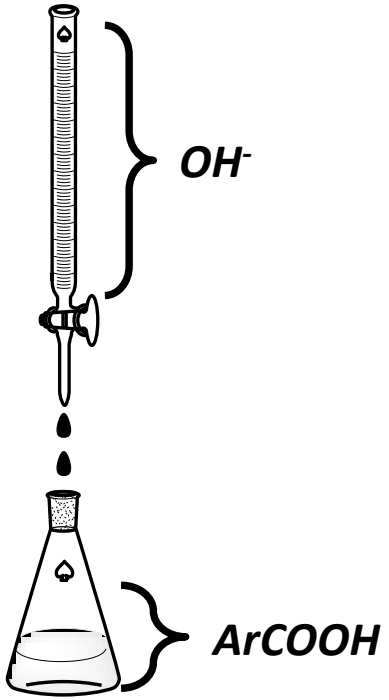
mp = 143-145 °C

$C_7H_4Cl_2O_2$

mol. wt. = 191.01

End-Point Titration: *Practical Considerations*

Example calculation and consequences of errors



- **254.2 mg** of dry purified acid titrated with **0.1033 N** aq. NaOH

⇨ end-point reached upon addn. of **12.24 mL** of base

⇨ # mmols of base = 0.1033 mmol mL^{-1} x 12.24 mL

= **1.264 mmol**

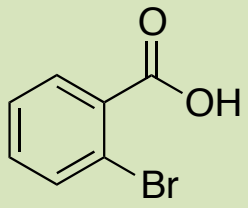
⇨ mol. wt. of acid = 254.2 mg / 1.264 mmol

= **201.11 g mol^{-1}**

BUT, what if we over shot end-point?
e.g., true value 12.00 mL

true mol. wt. of acid = 254.2 mg / 1.240 mmol

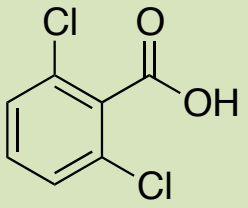
= **205.00 g mol^{-1}**



mp = 148 °C

$C_7H_5BrO_2$

mol. wt. = 201.02



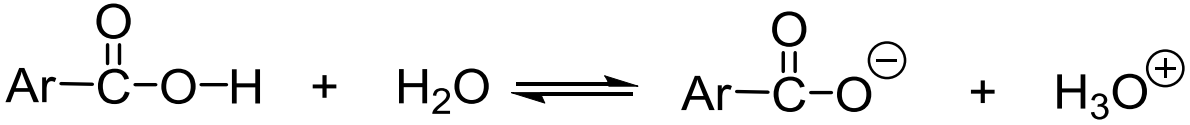
mp = 143-145 °C

$C_7H_4Cl_2O_2$

mol. wt. = 191.01

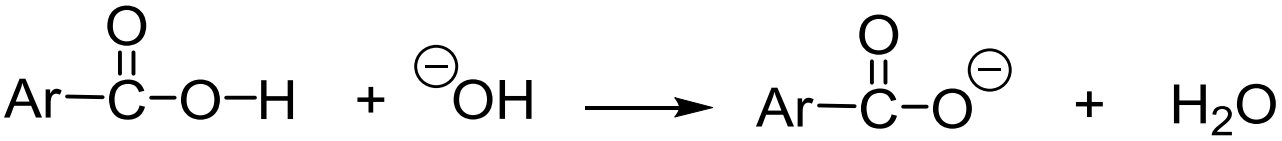
Potentiometric Titration

- data allows determination of pK_a of unknown acid



$$K_a = \frac{[ArCOO^-][H_3O^+]}{[ArCOOH]} \qquad pK_a = -log(K_a)$$

- as hydroxide is added, a buffer system develops



$$pH = pK_a + log\left(\frac{[ArCOO^-]}{[ArCOOH]}\right)$$

- when [ArCOO$^-$] = [ArCOOH], pH is equal to the pK_a of the unknown acid

Potentiometric Titration

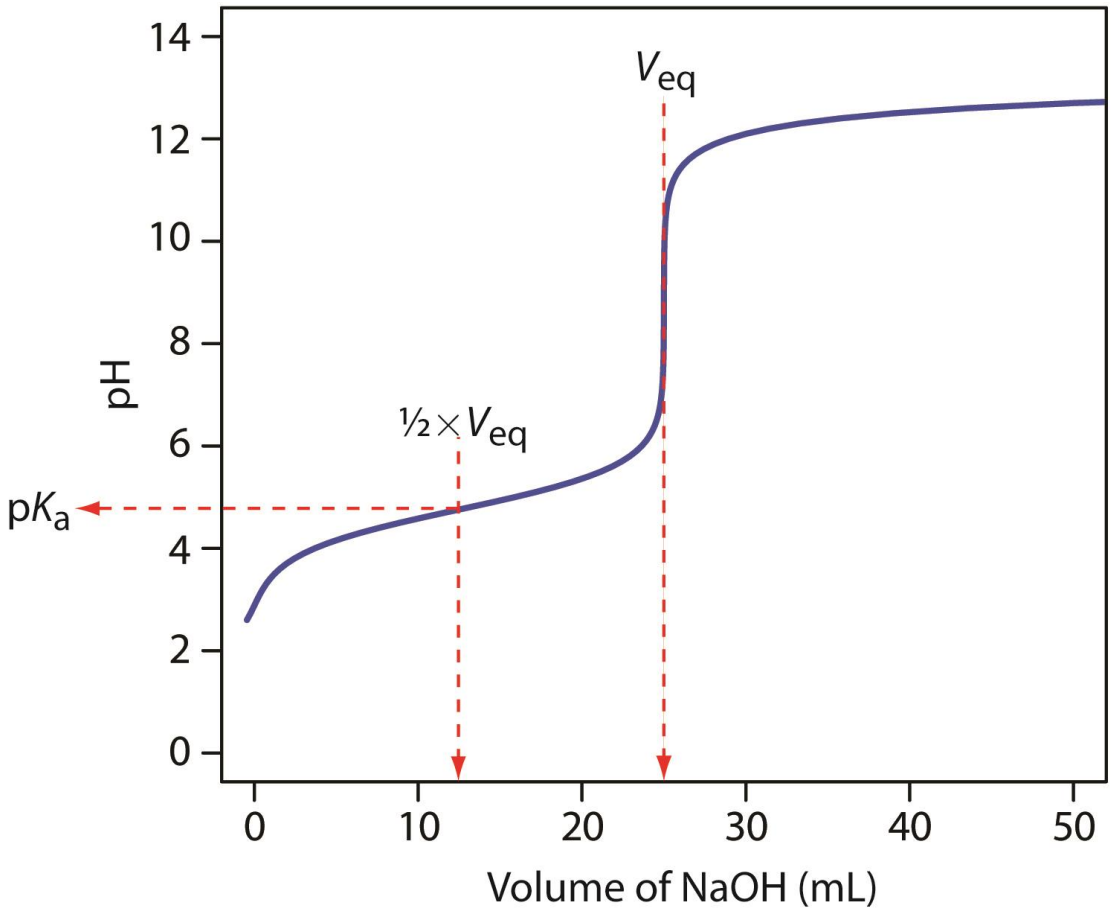
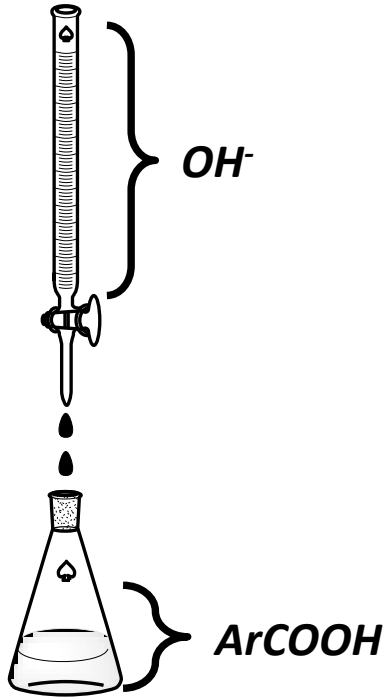


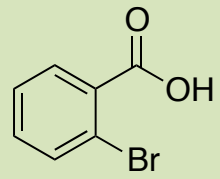
Figure downloaded from UC Davis ChemWiki website

Potentiometric Titration: *Practical Considerations*



- **prepare a solution of ~100 mg in 100-150 mL**
- **acid must be completely dissolved**
  (ethanol will obscure results – use only if needed)
- **heat solution to aid dissolution**

  do not begin titration until solution has cooled to 25°C
- **interpret pK_a data with caution**

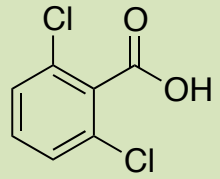


mp = 148 °C

$C_7H_5BrO_2$

mol. wt. = 201.02

pK_a = 2.85



mp = 143-145 °C

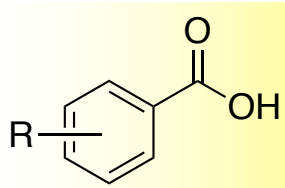
$C_7H_4Cl_2O_2$

mol. wt. = 191.01

pK_a = 1.82

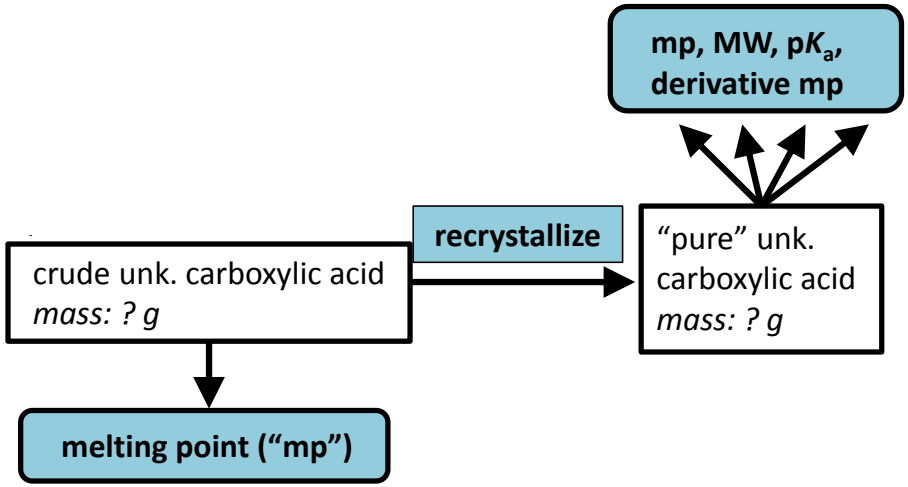
Tasks for Week 2: Trial, Medium, and Large Batch Recrystallizations

- *polar non-ionic compound*
- *sparing solubility in H_2O*



+ related impurities

precipitate (solid)



Wednesday	• conclude trial recrystallizations and apply selected solvent to medium batch – check % recovery, if ca. ≥75%, solvent system OK for large batch (rest of material)
Wed./ Fri.	• large batch recrystallization, collect and dry material (oven), need ca. 4 g (after drying to constant weight), accurrately determine melting point of pure acid
(Friday)	• TIME ALLOWING – begin end-point titrations