Principles of Extraction

S343

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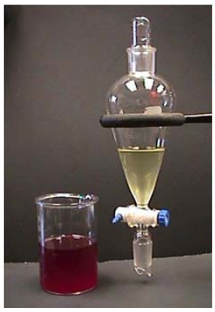
Separatory Funnel





Separation of immiscible liquids

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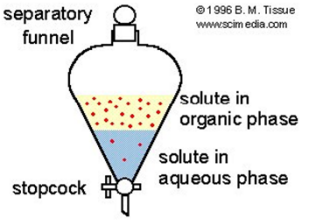
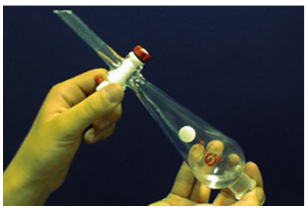
Extraction

- To <u>pull out</u> a compound from one layer into another
- A compound partitions more toward where it is more soluble (equilibrium)
- Partition coefficient
- Multiple extractions may be needed to completely extract a substance





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Partition coefficient (K)

Any organic compound with K>1.5 can be separated from water by an organic solvent.

$K = C_1/C_2$

C_1 = solubility of your compound in organic solvent

C_2 = solubility in water (aqueous)

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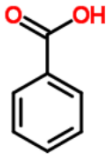
Example: Benzoic Acid



Goal – extract benzoic acid from water into an organic solvent.
Which solvents can we cross out immediately?
Which solvent will give the most optimal partition coefficient?
What is the partition coefficient in this solvent?

Solvent	(M)	Mole Fraction (X)	pph (g/100g)
acetone	1.35	0.11	24.77
acetonitrile	0.76	0.04	13.37
benzene	0.48	0.04	7.06
chloroform	1.8	0.15	17.95
ethanol	2.52	0.17	53.18
methanol	2.84	0.15	64.89
THF	3.37	0.29	69.27
toluene	0.65	0.07	9.81
water	0.03	0.00	0.37

Bradley, et al. Open Notebook Science Challenge: Solubilities of Organic Compounds in Organic Solvents. Available from Nature Precedings <http://dx.doi.org/10.1038/npre.2010.4243.3> (2010)

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Extraction Calculation

- If the partition coefficient between water and chloroform is about 49 for benzoic acid, how would 1.00 g of benzoic acid be distributed between 100 mL of water and 100 mL of chloroform?
- 49 = (*X* g/100mL)/(*Y* g/100mL) and X+Y = 1.00
- 49 = ((1.00-Y)/100)/(Y/100) = (1.00-Y)/Y
- Y = 0.020g in water and X = 0.980g in chloroform

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Multiple Extractions

1 g of compound dissolved in 50 mL H_2O
Partition coefficient = 5
45 mL ether

Question: What is better, one 45 mL extraction, or three 15 mL extractions?

$$\frac{(Final\ mass\ of\ solute)_{water}}{(Initial\ mass\ of\ solute)_{water}} = \left(\frac{V_2}{V_2 + V_1 K}\right)^n$$

Mohrig p. 145

V_1 = volume of organic solvent used in each extraction
V_2 = original volume of water
n = number of extractions
K = partition coefficient

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Example Extraction Continued

$$\frac{(Final\ mass\ of\ solute)_{water}}{(Initial\ mass\ of\ solute)_{water}} = \left(\frac{V_2}{V_2 + V_1 K}\right)^n$$

n = 1
K = 5
Initial mass = 1 g
Final mass = x
V_1 = 45 mL ether
V_2 = 50 mL water

Final mass of compound in water =

n = 3
K = 5
Initial mass = 1 g
Final mass = x
V_1 = 15 mL ether
V_2 = 50 mL water

Final mass of compound in water =

Takeaway message?

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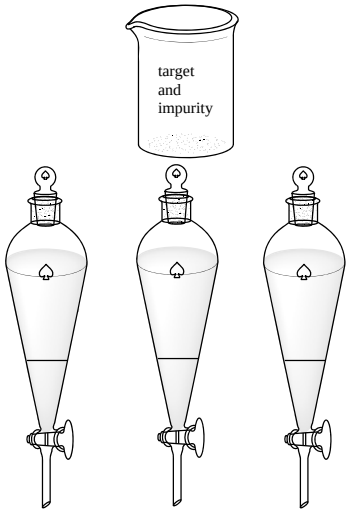
Separation Using Extraction

- What if our solid sample contains two substances?
- When the solids dissolve and partition, there are three possibilities—which would be effective for a purification technique?



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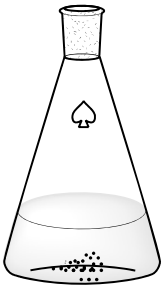
Flowchart

Extract → Separate → Dry → Evaporate



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Solubility

- To plan for an extraction, must be able to choose proper solvents to separate impurities from target
- Partitioning is based on relative solubility
- Is the compound more organic soluble or more aqueous soluble?

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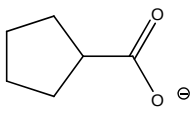
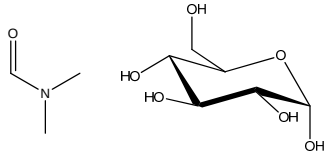
Solubility Rules of Thumb

- Water soluble
  - Ionic
  - Organic ions of < 7-8 carbons
  - Small polar molecules
  - Organic compounds with one H-bond donor per 3-4 carbons

NaCl





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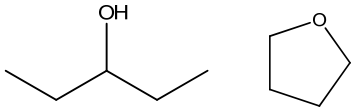
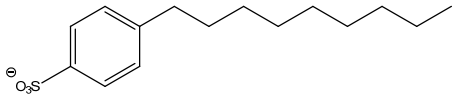
Water Insolubility Spectrum

- Somewhat soluble



- Insoluble

- Detergents



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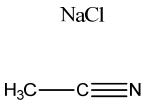
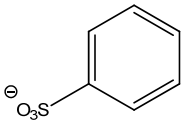
Organic Solvent Solubility

- Organic Soluble
  - Other organic molecules unless extremely different polarity
- Organic insoluble
  - Ionic

These are not organic soluble:





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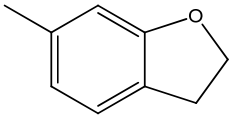
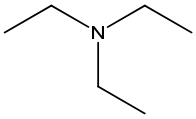
Planning an Extraction

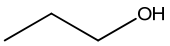
- You want to separate the following two impurities from your target with extraction. You dissolve the mixture in water/ether in a separatory funnel.
  - Will the purification work?
  - In which layer is your target (top or bottom)?



target compound



impurity 1



impurity 2

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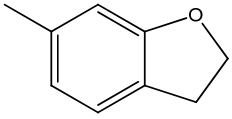
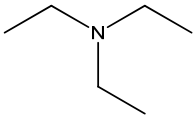
Acid/Base Extractions

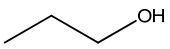
- Rather than neutral water, extract with aqueous acid or aqueous base
- What happens in our example case if we extract with aqueous NaOH instead of water? Where are the compounds? What about aqeuous HCl?



target compound



impurity 1



impurity 2

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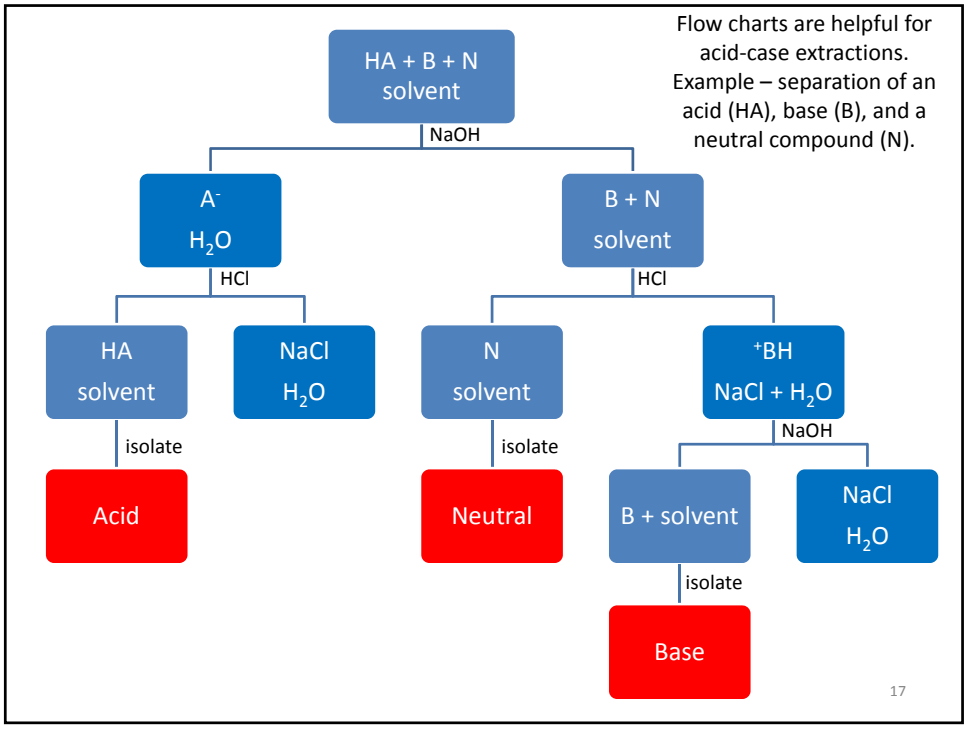
Flow charts are helpful for acid-case extractions. Example – separation of an acid (HA), base (B), and a neutral compound (N).
HA + B + N solvent
NaOH
A⁻ H2O
B + N solvent
HCl
HCl
HA solvent
NaCl H2O
N solvent
⁺BH NaCl + H2O
isolate
isolate
NaOH
Acid
Neutral
B + solvent
NaCl H2O
isolate
Base
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