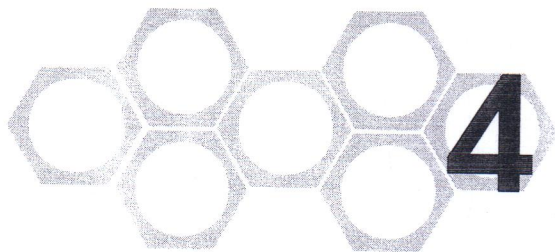# Extraction

One of the main concerns of experimental organic chemistry is the separation of mixtures and the isolation of compounds in as pure a form as needed for subsequent use. Crystallization is a useful method for purification and isolation, but it is restricted to solids, and as indicated in Chapter 3, it is a relatively inefficient way to separate a mixture of very similar compounds.

Several more general separation methods are described in this and the following chapters. All depend in some way on the *partitioning* of the compounds to be separated *between two distinct phases*. By choosing the phases so that the different compounds are *unequally distributed* between them, **fractional separation** of the compounds is effected. The various methods are mechanically quite different, but they all depend on this common principle, and it should be thoroughly understood. The principle is most easily illustrated by the general method of extraction, and this method is therefore covered in some detail in this chapter.

THEORY OF EXTRACTION

Extraction is the general term for the recovery of a substance from a mixture by bringing it into contact with a solvent that preferentially dissolves the desired material. The initial mixture may be a solid or liquid, and various techniques and apparatus are required for different situations. After an organic reaction, the reaction product is frequently obtained as a solution or a suspension in water along with inorganic and other organic by-products and reagents. By shaking the aqueous mixture with a water-immiscible organic solvent, the product is transferred to the solvent layer and may be recovered from it by evaporation of the organic solvent.

The extraction of a compound from one liquid phase into another is an equilibrium process governed by the solubilities of the substance in the two solvents. The ratio of the solubilities is called the *distribution coefficient,* $K_d = C_1/C_2$, and is an equilibrium constant with a characteristic value for any compound and pair of solvents at a given temperature.
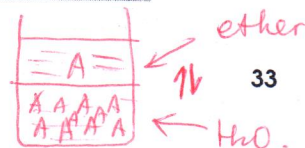
Let us consider the following situation: A 100-mL aqueous solution contains 1 g each of compounds A and B, the solubilities of which in water and ether are given below.

COMPOUND	SOLUBILITY IN WATER C_{Water}	SOLUBILITY IN ETHER C_{Ether}	$K_{Ether/Water}$
A	10 g/100 mL	1 g/100 mL	$\frac{1}{10} = 0.1$
B	2 g/100 mL	10 g/100 mL	$\frac{10}{2} = 5.0$

Solute A $\rightleftharpoons$ Solute A
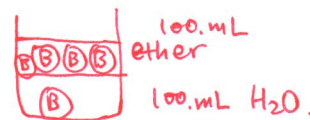in H₂O   in ether

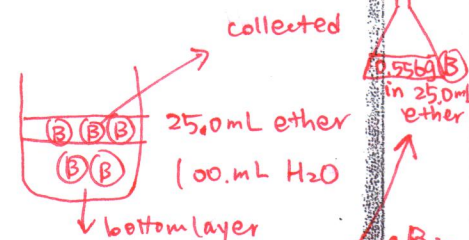$$K_{dA} = \frac{[A]_{\text{in ether}}}{[A]_{\text{in H}_2\text{O}}} = \frac{1 g/100 mL}{10 g/100 mL} = 0.1$$

By the foregoing definition, the distribution coefficients of A and B (C_{ether}/C_{water}) are 0.1 and 5, respectively. If the aqueous solution is shaken with 100 mL of ether, the amount of each compound transferred to the ether phase, X, can be calculated as follows:

Compound A

$$\frac{C_{ether}}{C_{water}} = \frac{X_A/100}{(1 - X_A)/100} = 0.1$$

$X_A = 0.091$ g in ether
$1 - X_A = 0.909$ g in water

Compound B

$$\frac{C_{ether}}{C_{water}} = \frac{X_B/100}{(1 - X_B)/100} = 5$$

$X_B = 0.833$ g in ether
$1 - X_B = 0.167$ g in water

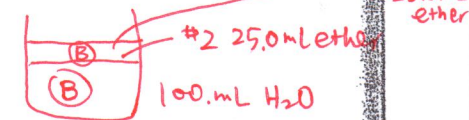*[handwritten: 100.mL ether / BBBB B / 100.mL H₂O]*

If the same aqueous solution is extracted with the same amount of ether, but in four 25-mL portions, we have for the first extraction:

$$\frac{X_A/25}{(1 - X_A)/100} = 0.1$$

(1) $X_A = 0.0244$ g in ether, leaving 0.9756 g in water

$$\frac{X_B/25}{(1 - X_B)/100} = 5$$

$X_B = 0.556$ g in ether and 0.444 g in water

[handwritten: #1]

[handwritten: collected / 0.556 B in 25.0mL ether / BBB BB 25.0mL ether / 100.mL H₂O / bottom layer]

For the second 25-mL extraction:

$$\frac{X_A/25}{(0.9756 - X_A)/100} = 0.1$$

(2) $X_A = 0.0238$ g in ether, leaving 0.9518 g in water

$$\frac{X_B/25}{(0.444 - X_B)/100} = 5$$

$X_B = 0.247$ g in ether and 0.197 g in water

[handwritten: #2]

[handwritten: 0.247 g B in 25.0mL ether / B B #2 25.0mL ether / 100.mL H₂O]

After the third and fourth extractions:

(3) $X_A = 0.0232$ g in ether
(4) $X_A = 0.0226$ g in ether

$X_B = 0.109$ g in ether   *[handwritten: #3]*
$X_B = 0.049$ g in ether   *[handwritten: #4]*

Totals:

$X_A = 0.094$ g A in ether
$1 - X_A = 0.906$ g A in water

$X_B = 0.961$ g B in ether   *[handwritten: total]*
$1 - X_B = 0.039$ g B in water

It can be seen from these values that even with a relatively small distribution coefficient ($K_d = 5$) virtually complete extraction of compound B can be effected and that several extractions with small volumes of extractant are more efficient than a single extraction with the same total volume in one portion.

In the extractions described above, a significant amount of compound A was also transferred to the ether layers. If the ether were removed from the solution at this point, the residue would be 1.055 g of material that is only 92% pure B. However, if the ether is shaken (back-extracted) with 50 mL of water before evaporation, the amounts (Y) of A and B removed from the ether solution can be calculated as follows:

$$\frac{C_{ether}}{C_{water}} = \frac{(0.094 - Y_A)/100}{Y_A/50} = 0.1$$

$Y_A = 0.078$ g in water, leaving 0.016 g in ether

$$\frac{(0.961 - Y_B)/100}{Y_B/50} = 5$$

$Y_B = 0.087$ g in water and 0.874 g in ether

Evaporation of the ether now leaves a residue of 0.890 g that is more than 98% pure B. Some B was lost in this process, to be recovered by subsequent extractions, but that which remains may be pure enough for its intended use.

What is K$_d$ of a substance X if 25 ml of a 0.015 M aqueous solution of X is extracted with 10.0 ml of ether? The entire 25 ml of water (aqueous solution) is titrated and it is found that the concentration of X after extraction is 0.0050 M. The molar mass of X is 162 g/mol.

Using the K$_d$ you determined above calculate the total amount of X would be extracted by two 5.00 ml portions of ether.