

Separation Methods Based on Distributions in Discrete Stages (01/30/15)

1. Chemical Separations: The Big Picture

Classification and comparison of methods

2. Fundamentals of Distribution Separations

3. Separation Methods Based on Distributions in Discrete Stages

Such as solvent extraction and distillation

4. Introduction to Distribution Separations in chromatographic

methods. The plate theory, the rate theory; van Deemter's equation.

1. Extraction Theory

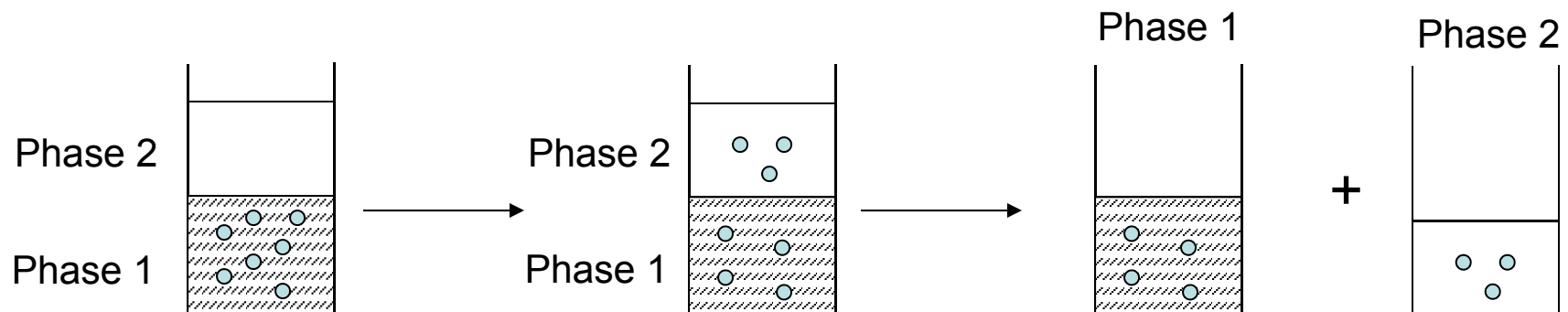
A. Definition

- (1) An extraction is a separation technique based on the distribution of solutions between two mutually insoluble phases.

- (2) The two phases are usually both liquids, but extractions can also be performed when the phases are gas-liquid, gas-solid, liquid-solid, supercritical fluid-solid.

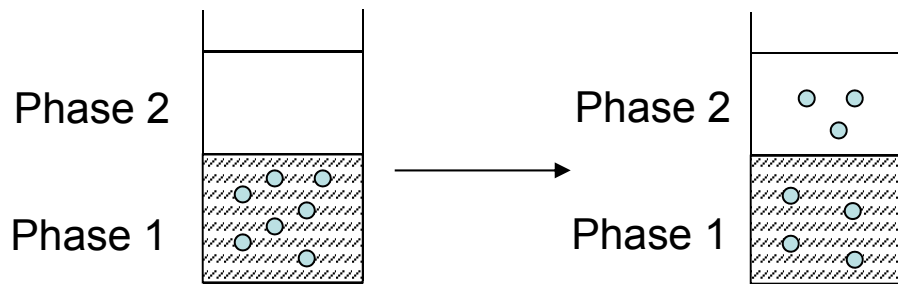
B. Extraction process

- (1) Extraction are usually based on the following procedure:
 - (a) Solute A in phase 1 is mixed with a known volume of phase 2 and allowed to distribute between the two phases.
 - (b) After equilibration, the fraction A that has gone into phase 2 is removed and saved for later use or analysis. Any A remaining in phase 1 is either further extracted or discarded.



(2) The phase that originally contains A is known as that **raffinate** (phase 1). The phase used to extract it is known as **extractant** (phase 2).

(3) If neither phase used in the extraction is a solid, solute A is said to distribute based on its ability to **partition** between the two phases.

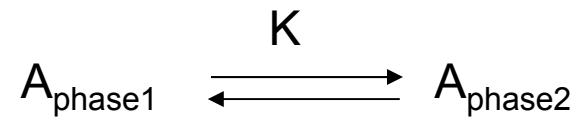


If the extractant (phase 3 is a solid, solute A is said to distribute based on **adsorption** to the extractant's surface.



C. Simple Extraction

- (1) The distribution of a simple solution A between two phases, 1 and 2, is described by:

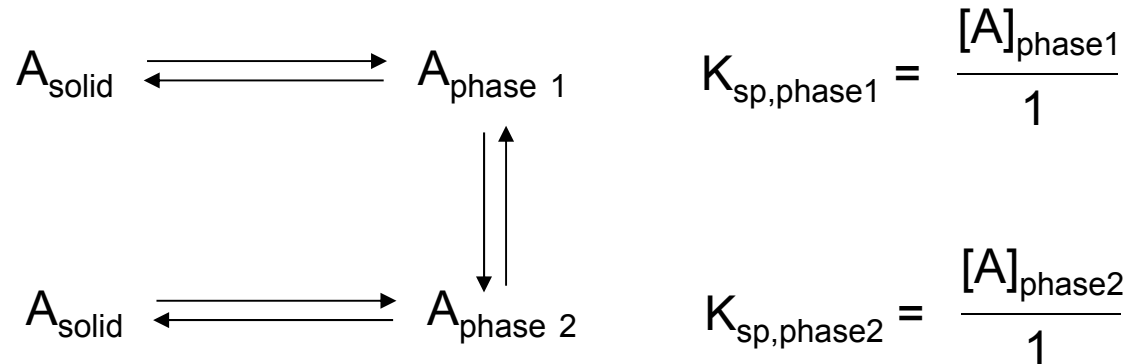


$$K_D = \frac{[A]_{\text{phase2}}}{[A]_{\text{phase1}}}$$

- (2) By convention, the above reaction and equilibrium expression are written so that Phase 1 is the more polar solvent (usually aqueous) and phase 2 is the more non-polar solvent (usually organic).

- (3) K_D is commonly known as the ***distribution constant***. It is constant for a given solute, set of phase, and temperature under ideal condition.

(4) K_D can be estimated based on the solubility of A in the two phase.

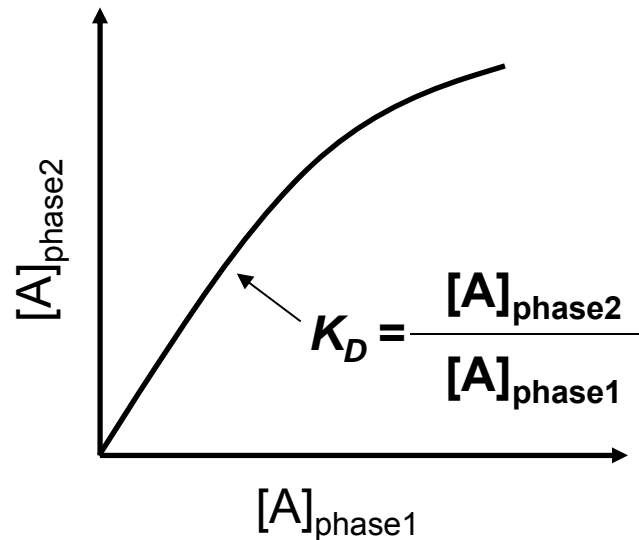


$$K_D = \frac{[A]_{\text{phase2}}}{[A]_{\text{phase1}}} = \frac{K_{\text{sp,phase2}}}{K_{\text{sp,phase1}}}$$

(5) K_D can be also be predicted using the *Hildebrand solubility parameters* for phase 1, Phase 2, and solution A.

$$\ln (K_D) = - \frac{\bar{V}_i}{RT} (\delta_1 - \delta_2)(\delta_1 + \delta_2 - 2\delta_A)$$

(6) For non-ideal (i.e. non-dilute) solution, the degree of distribution of A between phase 1 and 2 is no longer constant, but varies with [A].



(7) The graph of $[A]_{\text{phase1}}$ vs. $[A]_{\text{phase2}}$ at a given temperature is known as a distribution isotherm.

(8) Since the ration of $[A]_{\text{phase2}}/[A]_{\text{phase1}}$ (i.e., K_D , or the slope of the distribution isotherm) is not constant at higher temperature. In this region ***K is called distribution coefficient.***

(9) The condition used in lower end of the above curve (where K_D is constant) are referred to as *linear conditions*. The conditions at the upper end of the cure (where K_D varies with the amount of A) is referred to as *non-linear conditions*.

D. Extraction for solutions with multiple forms

(1) Many solutes exist in multiple forms in solution

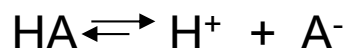
Examples: acid and bases (HA and A⁻), solutes that complex with other compounds (A, AL, AL₂), and solute that dimerize (A, A₂).

(2) Since the concentration of the individual forms of A may not be known, its total or *analytical concentration* (C_A) is used

$$C_A = [A]_{\text{form1}} + [A]_{\text{form2}} + [A]_{\text{form3}} + [A]_{\text{form4}} + \dots$$

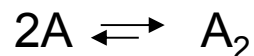
Examples:

(a) For a compound A that undergoes an acid-base reaction:



$$C_A = [\text{HA}] + [\text{A}^-]$$

(b) For a compound A that undergoes an dimerization:



$$C_A = [\text{A}] + 2[\text{A}_2]$$

(3) The distribution of a multiple-form solute (A) is described by using the ration of its analytical concentrations in phases 1 and 2. **This value (D_c) is known as the *concentration distribution ratio*.**

$$D_c = C_{A, \text{ phase 2}} / C_{A, \text{ phase 1}}$$

(4) Note that for a solute that exists in only one form in either phase, $D_c = K_D$

E. Extraction Theory:

(1) Single Extraction

a. For the extraction of A in phase 1 with phase 2, the fraction of A remaining in phase 1 after a single extraction ($f_{\text{phase1,1}}$) is

$$f_{\text{phase1,1}} = \frac{1}{(1 + D_c V_2/V_1)}$$

Where: V_1 and V_2 = volume of phases 1 and 2.

D_c = concentration distribution ratio for A

The value of V_2/V_1 is also known as phase ratio (β).

b. The fraction of A extracted into phase 2 is

$$f_{\text{phase2,1}} = 1 - f_{\text{phase1,1}}$$

(2) Multiple extractions:

- a. A problem in extraction many solutes is that D_c may be small. This results in only small amount of A being extracted.
- b. One way to increase the amount of **A** extracted is to perform multiple extractions of phase 1 and combine the amounts of A obtained in phase 2 with each extraction.
- c. For multiple extraction of A in phase 1 with fresh portions of phase 2, the fraction remaining in phase 1 after n extractions with equal volumes of phase 2 is


$$f_{\text{phase1},n} = \left(\frac{1}{1 + D_c V_2/V_1} \right)^n$$

- d. The total fraction of A extracted into phase 2 after n extractions ($f_{\text{phase2},n}$) is


$$f_{\text{phase2},n} = 1 - f_{\text{phase1},n}$$

(3) Multiple extractions:

- a. To remove A from other solution in a mixture using extraction, the recovery of A as well as its purity should be considered. The purity of A (**Purity_A**) in a given phase may be defined as.

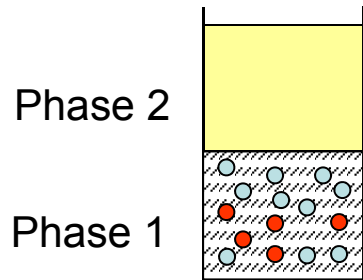

$$\text{Purity}_A = \frac{\text{Moles of A}}{\text{Total moles of all solutes in the phase}}$$

- b. The purification yield of A express how relative amount of A in a phase has increased as a results of a separation. This is determined by comparing the purity of A in the final vs. initial sample mixture.


$$\text{Purification Yield}_A = \frac{\text{Purity}_{A,\text{phase2}}}{\text{Purity}_{A,\text{phase1}}}$$

- c. To get a good separation of A from other solutions requires that their values of D_c (or K_D) be significantly different (usually 100-fold differences or greater). The Lager the difference, the better the separation.
- d. One problem with doing multiple extraction of multi-component mixture is that the purification yield and purity of A decreases as more extractions are performed even through recovery of A increases. This is due to the increased extraction of other components.

One-Step Extraction



- [A] = 0.01 M
- [B] = 1 M
- $V_1 = V_2 = 10 \text{ mL}$
- $D_{cA} = 10, D_{cB} = 0.1$

$$f_{\text{phase1},1} = \frac{1}{(1 + D_c V_2/V_1)}$$

$$f_{\text{phase1},A} = \frac{1}{(1 + D_{c,A} V_2/V_1)} = 0.091; f_{\text{phase2},A} = 1 - f_{\text{phase1},A} = 0.909$$

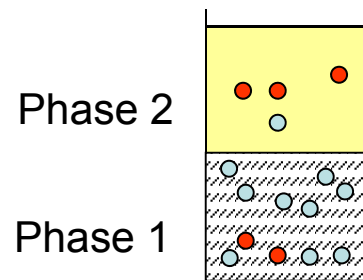
$$f_{\text{phase1},B} = \frac{1}{(1 + D_{c,B} V_2/V_1)} = 0.909; f_{\text{phase2},B} = 1 - f_{\text{phase1},B} = 0.091$$

Results:

Recovery of A in phase 2 = 0.909 = 90.9%

$$\begin{aligned} \text{Final purity of A in phase 2} &= \frac{\text{Total Moles of A in phase 2}}{\text{Total Moles of (A + B) in phase 2}} \\ &= \frac{(0.909)(0.01 \text{ M})(0.01 \text{ L})}{(0.909)(0.01 \text{ M})(0.01 \text{ L}) + (0.091)(1.00 \text{ M})(0.01 \text{ L})} \\ &= 0.091 \text{ (9.1\%)} \end{aligned}$$

$$\text{Purification yield of A} = \frac{\text{Final purity of A in phase 2}}{\text{Initial purity of A in phase 1}} = \frac{0.091}{0.0099} = 9.2$$



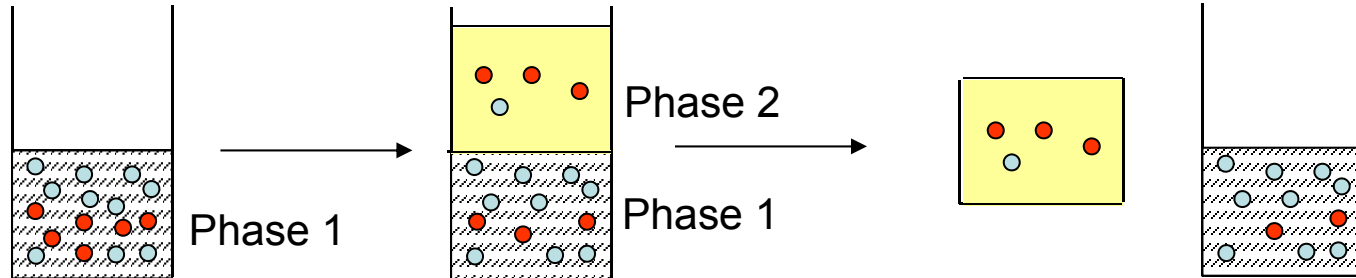
Two-Step Extraction

● [A] = 0.01 M

○ [B] = 1 M

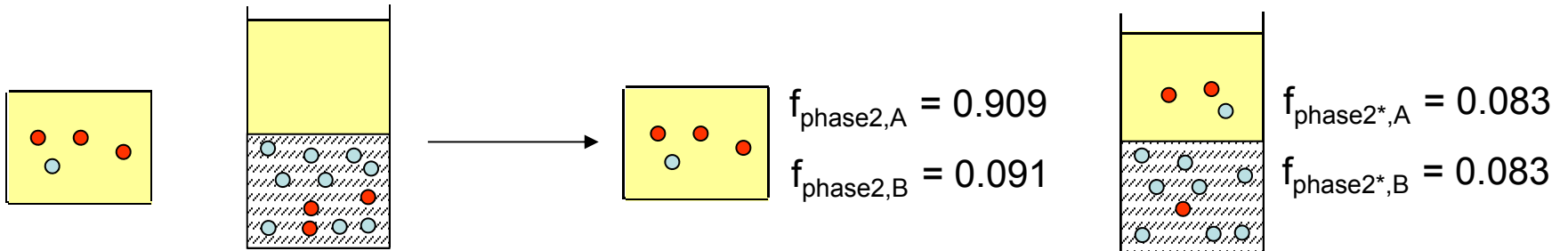
$V_1 = V_2 = 10 \text{ mL}$

$D_{cA} = 10, D_{cB} = 0.1$



Extraction 1

Separation of phases



Addition of fresh phase 2

Extraction 2

Total fraction A in phase 2 = $0.909 + 0.083 = 0.992$

Total fraction B in phase 2 = $0.091 + 0.083 = 0.174$

Recovery of A in phase 2 = $0.992 = 99.2\%$

Final purity of A in phase 2 = $\frac{(0.992) \cdot (0.01 \text{ M}) \cdot (0.01 \text{ L})}{(0.992) \cdot (0.01 \text{ M}) \cdot (0.01 \text{ L}) + (0.174) \cdot (1.00 \text{ M}) \cdot (0.01 \text{ L})} = 0.054 = 5.4\%$

Purification yield of A = $\frac{\text{Final purity of A in phase 2}}{\text{Initial purity of A in phase 1}} = \frac{0.054}{0.0099} = 5.45$

Comparison of the Results in One- and Two-Step Extraction

	One-step	Two-step
Recovery of A in phase 2 = 0.909 = 90.9%		99.2%
Final purity of A in phase 2 = 0.091 (9.1%)		5.4%
Purification yield of A = 9.2		5.45

The purification yield and purity of A decreases as more extractions are performed even through *recovery of A increases*. This is due to the increased extraction of other components.