Extraction

1.THE CHEMISTRY OF EXTRACTION

$$\mu(H) = \mu(L)$$

$$\mu^0(H) + RT\ln y = \mu^0(L) + RT\ln x$$

$$\frac{x}{y} = K = \exp\left(\frac{\mu^0(H) - \mu^0(L)}{RT}\right)$$

$$K = \frac{x}{y}$$

Changes in Solvent

$$\ln K = \frac{\mu^0(H) - \mu^0(L)}{RT}$$

$$= \frac{\overline{V_H}(\delta_A - \delta_H)^2 - \overline{V_L}(\delta_A - \delta_L)^2}{(RT\overline{V_A})}$$

TABLE. Solubility Parameters for Some Common Solvents

Solvent	δ ($cal^{1/2}$ $cm^{-3/2}$)
Amyl acetate	8.0
Benzene	9.2
Butanol	13.6
Butyl acetate	8.5
Carbon disulfide	10.0
Carbon tetrachloride	8.6
Chloroform	9.2
Cyclohexane	8.2
Hexanol	10.7
Acetone	7.5
Pentane	7.1
Perfluorohexane	5.9
Toluene	8.9
Water	9.4

Example 1. The Partition Coefficient of Weak Acid.

A partially hydrolyzed sugar believed to be monoacids is extracted from water into 1-hexanol. It has K values of 6.4 and 0.22 mol/liter at pH 4.0 and 5.8, respectively. What is the value of at pH 7.0?

Solution.

$$pH = -\log_{10} H = 7.0$$

$$H = 10^{-7}$$

$$\log_{10}\left[\left(\frac{K_i}{K}\right)-1\right] = pH - pK_a$$

$$K = \frac{K_i}{1+K_a/[H^+]_H}$$

$K_i = 11.7$ $\quad K_a = 8.3\times10^{-5}\, mol/liter$

$$K = \frac{11.7}{[1+8.3\times10^{-5}/10^{-7}]} = 0.014$$

Example 2. Seperation of Penicillins.

For the system water-amyl acetate, penicillin K and penicillin F have values of K_i of 215 and 131, respectively. They have pK_a's of 2.77 and 3.51. If penicillin F is the desired product, will an extraction at pH 3.0 give a purer product than one at pH 4.0?

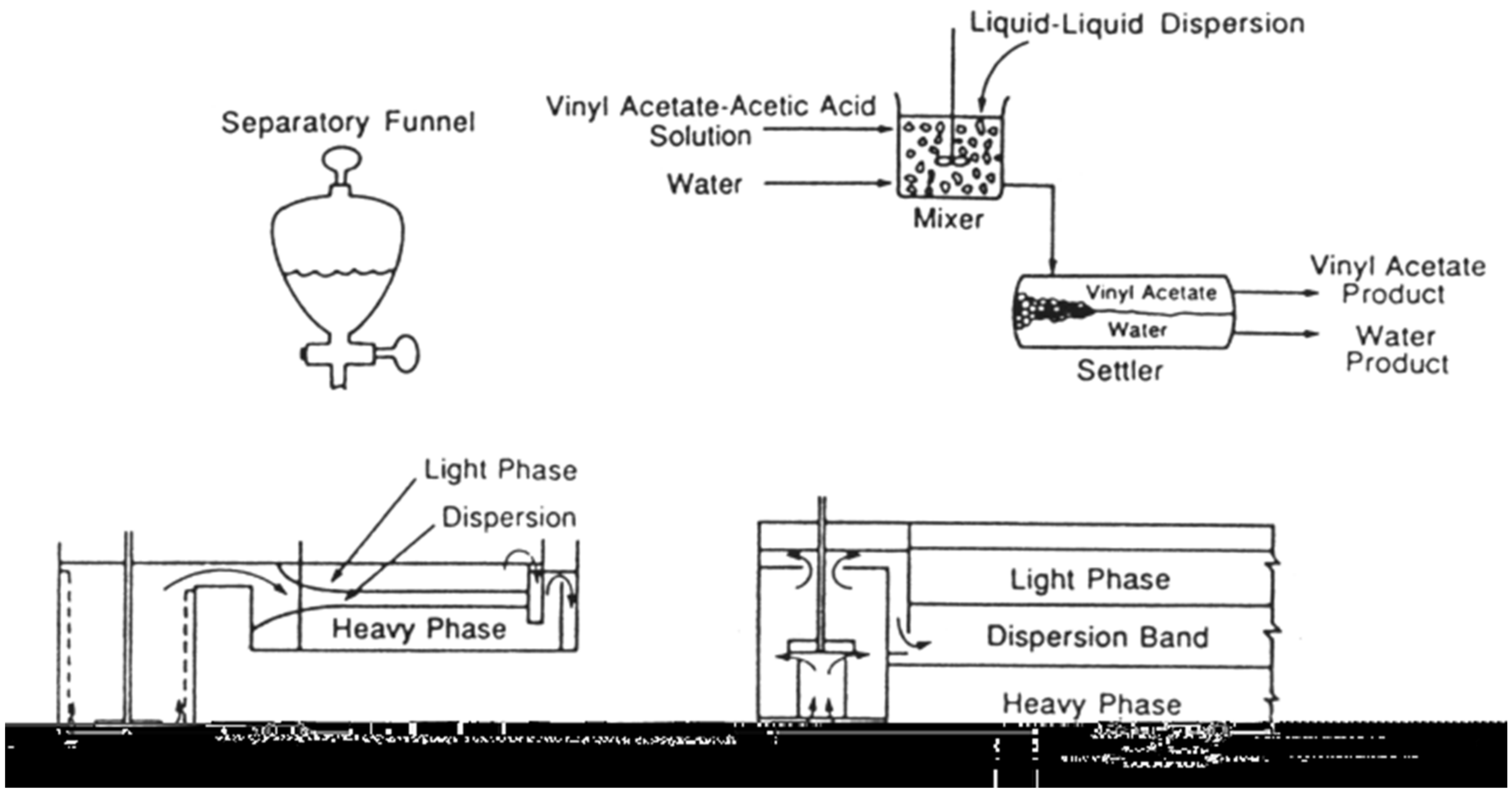
Solution.

$$K = \frac{K_i}{1 + K_a/[H^+]_H}$$

$$\beta = \left(\frac{K_i(A)}{K_i(B)}\right)\left(\frac{1 + K_a(B)/[H^+]}{1 + K_a(A)/[H^+]}\right)$$

	K_K	K_F	β
pH 3	80	100	1.3
pH 4	12	32	2.7

2. BATCH EXTRACTIONS



Example 3. A Batch Steroid Extraction.

Water containing 6.8 mg/liter of a steroid is extracted with initially pure methylene dichloride. The equilibrium constant for the steroid is 170 and ratio of water to solvent is 82. What is the concentration in the organic after the extraction? What fraction of the steroid has been removed?

Solution. extraction factor E

$$E = \frac{KL}{H} = \frac{170}{82} = 2.07$$

$$x = \frac{Ky_F}{1+E} = \frac{170(6.8)}{1+2.07} = 377 mg/liter$$

fraction extracted p

$$p = \frac{E}{1+E} = \frac{2.07}{1+2.07} = 0.67$$

Example 4. Amino Acid Stripping

For a nonessential amino acid, the equilibrium relation between toluene and pure water is

$$x^2 = (0.001 mol / liter) y$$

We plan to contact 4.7 liters of toluene containing 0.006 M amino acid with 1 liter of water. What fraction of the amino acid can we extract?

Solution.

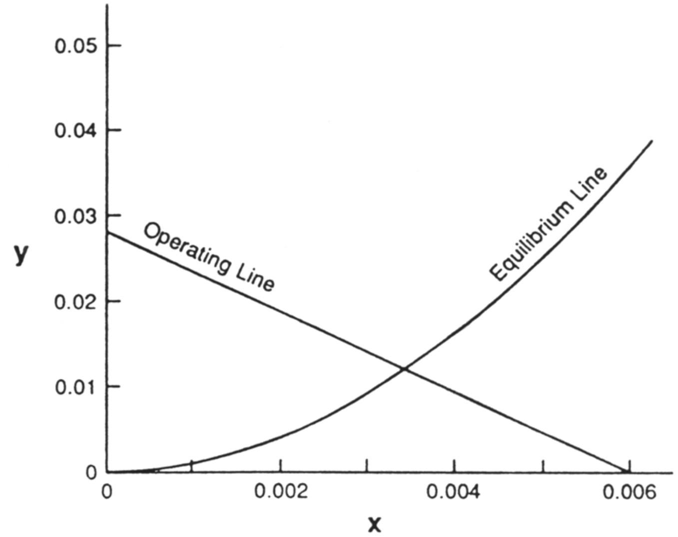
equilibrium relation $x^2 = (0.001 mol / liter) y$

operating line $y = 4.7(0.006 - x)$

interaction $y = 0.012 mol / liter$

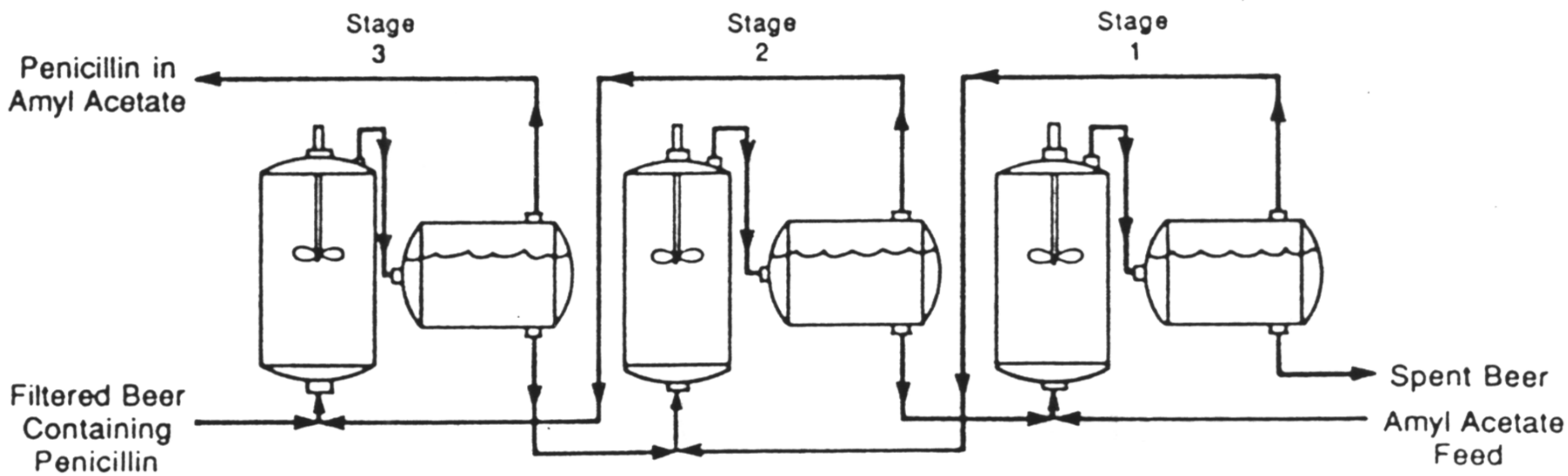
fraction extracted p

$$p = \frac{Hy}{Lx_F} = \frac{1.0(0.012)}{4.7(0.006} = 0.43$$

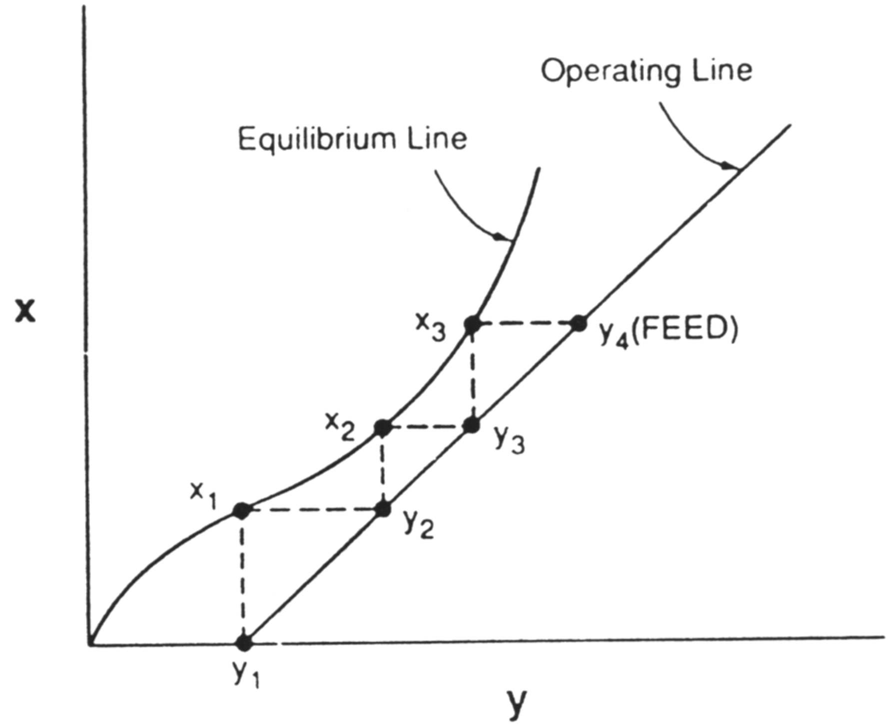


3. STAGED EXTRACTIONS

Equipment



Staged Extraction: Graphical Methods



Example 5. Stages for Actinomycin D Extraction.

A clarified fermentation beer H containing 260 mg/liter of this antibiotic is to be extracted using butyl acetate L. Because the beer's pH is 3.5, the equilibrium constant K is 57. You plan to let H equal 450 liters/hr and L equal 37 liters/hr; you hope to recover 99% of the antibiotic in the feed. How many stages will you need to accomplish this separation?

Solution

extraction factor E

$$E = \frac{KL}{H} = \frac{57(37 liters/hr)}{450 liters/hr} = 4.69$$

$$y_{n+1} = \left(\frac{E^{n+1}-1}{E-1}\right) y_1 = \left(\frac{E^{n+1}-1}{E-1}\right) 0.01 y_{n+1}$$

$$100 = \frac{4.69^{n+1}-1}{4.69-1}$$

$$n = 2.8$$

Example 6. Actinomycin D Extraction by Graphical Methods.

Repeat the preceding example using graphical methods.

Solution.

Equilibrium line

$$x_n = x_n(y_n)$$

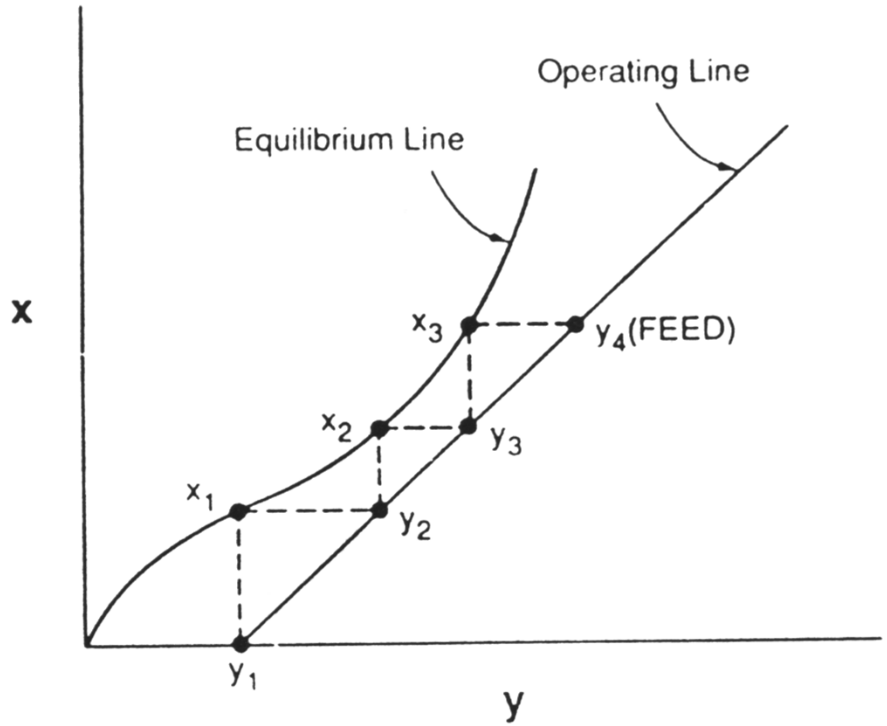
$$x_n = Ky_n = 57y_n$$

Operation line

$$x_n = \frac{H}{L}(y_{n+1} - y_1)$$

$$= \frac{450}{37}(y_{n+1} - 260 \times 0.01)$$

$$= 12.2y_{n+1} - 32mg / liter$$



Example 7. Actinomycin D Stripping.

The butyl acetate extract in the previous problems contains 3.13 g/liter of the antibiotic and is produced at 37 liters/hr. We plan to wash this extract with water at pH 6, for which K=0.11. We will use the same three stage extractor as before, but will be satisfied with 95% recovery.
What water flow should we use?

Solution

$$y_{n+1} = \left(\frac{E^{n+1} - 1}{E - 1} \right) y_1 \qquad x_{n+1} = \left[\frac{(1/E)^{n+1} - 1}{1/E - 1} \right] x_1$$

$$3.13 g/liter = \frac{(1/E)^4 - 1}{1/E - 1} 0.05(3.13 g/liter)$$

$$E = 0.44 = \frac{KL}{H} = \frac{(37 liters/hr)(0.11)}{H}$$

$$H = 9.2 liters/hr$$

Example 8. Glucose Isomerase Purification.

The extractions of proteins cannot often be accomplished with organic solvents, for these solvents often denature the proteins. However, such extractions can be accomplished by "two-phase aqueous extraction," using immiscible aqueous solutions of polyethylene glycol 1550 (L)/aqueous potassium phosphate (H), the distribution constant K (= x/y) for the enzyme glucose isomerase is 3.0. The enzyme is fed in the heavy phosphate phase.

We have a four stage extractor with which we hope to isolate this enzyme. If we set the flow ratio H/L = 2, what percent of the enzyme can we recover in the light phase?

Solution.

Entering conc. y_5

$$p = \frac{Lx_n}{Hy_{n+1}} = \frac{E(E^n - 1)}{E^{n+1} - 1}$$

Fraction extracted p

$$= \frac{Lx_4}{Hy_5} = \left(\frac{E(E^4 - 1)}{E^5 - 1} \right) = 0.92$$

$$E = \frac{LK}{H} = \frac{3}{2}$$

Experiment

p = 0.86