

# PRINCIPLES OF STAGewise SEPARATION PROCESS CALCULATIONS

## *A Simple Algebraic Approach Using Solvent Extraction*

BARRY D. CRITTENDEN

*University of Bath*

*Bath, BA2 7AY, United Kingdom*

Traditionally, graphical techniques such as the McCabe-Thiele and Ponchon-Savarit methods have been used to introduce undergraduate chemical engineering students to the design and analysis of multistage separation processes. While the students have quickly grasped the concepts of simultaneously solving the material balances and phase equilibrium relationships, their understanding of transforming such principles into graphical methods has often been slow to develop. A strong emphasis on the use of computers from the beginning of the first-year course at Bath has resulted in students who find it increasingly difficult to adapt their minds to solving complex problems by graphical methods.

Building on the mathematical expertise of freshmen, a simple liquid-liquid equilibrium (LLE) system has been used to demonstrate most of the essential features of multistage contacting, whether cross- or counter-current. Solutions to the material balances and phase equilibria are all algebraic and simple to derive and only an elementary knowledge of series summation is required to derive the solution for minimum solvent-to-feed ratio. The simple LLE system can then be used to introduce students to the graphical techniques which are necessary for complex equilibria.



*Barry Crittenden obtained his BSc and PhD degrees in chemical engineering from the University of Birmingham. He is a senior lecturer in the School of Chemical Engineering at the University of Bath. His teaching interests are in separation processes and heat transfer. His research and consultancy interests are in fouling of heat exchangers, novel forms of heat transfer equipment, adsorption, environmental control, and hazardous waste management.*

### BACKGROUND

At the University of Bath, lecture programs in separation processes are given in each of the three taught years in the BEng Honours degree courses in chemical engineering and chemical and bio-process engineering. Most students elect to spend their third year on industrial placement, working effectively as graduate engineers with leading process engineering companies. Thus it is important that all the core material in separation processes is given in the first two years of the BEng courses.

In the first year, students are expected to gain an understanding of the fundamental principles of phase equilibria and their application (with material and energy balances) to the design and operation of common separation processes. Examples are drawn especially from binary distillation, solvent extraction, batch adsorption, batch crystallization, *etc.*

In the second year, the principles of continuous-phase contacting are presented, using examples drawn especially from gas absorption, stripping, distillation, and solvent extraction. The selection and sequencing of separation processes, together with the principles and practices of multicomponent separations, adsorption, membrane processes, and other highly-selective separations are reserved for the final year lecture course.

Modern textbooks in chemical engineering continue to adopt the use of graphical techniques to explain stagewise separation process calculations. The main advantage of using such techniques at the outset is realized by the lecturer, who can easily create visual aids to explain concepts such as cross-current multistaging, countercurrent multistaging, minimum solvent flowrate, minimum reflux ratio, total reflux, *etc.*

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However, while some students readily understand that graphical methods are based on the fundamental material balances and phase relationships, there are many students who find the use of hypothetical pole points or difference streams to be mysterious techniques. In addition, with the advent of modern, powerful computers and supporting software, the use of graphical methods (with their inherent inaccuracies) should be discouraged for all except check calculations or for systems with complex equilibria which are difficult to model thermodynamically.

Most freshmen already appreciate the basic concepts of partitioning a solute between a solvent and a diluent. They are also mathematically competent. With these points in mind, the first-year course in separation processes now commences with a totally algebraic approach to stagewise contacting, using a simple liquid-liquid equilibrium system to illustrate a number of important aspects of stagewise contacting. For solvent extraction, these are

- the equilibrium stage model
- simultaneous solution of single-stage material balances and phase equilibria
- multistage cross-current contacting
- efficient use of solvent in multistage cross-current contacting
- multistage counter-current contacting
- advantage of counter-current contacting over cross-current contacting
- minimum solvent-to-feed ratio

The use of solvent extraction to explain important facets of stagewise contacting is particularly apt since this process is one of five which have been identified by the UK Science and Engineering Research Council as requiring special research attention under its Separation Processes Initiative. Others include membrane processes, selective adsorption, highly-selective separations, and the opportunities for exploiting centrifugal fields.

## SIMPLE LIQUID-LIQUID EQUILIBRIUM

The algebraic analyses are restricted to the simplest case of extraction of a solute from a diluent by means of a solvent which is immiscible with the diluent even in the presence of the solute. The distribution coefficient  $K$  for the solute is constant and is given by

$$K = \frac{Y}{X} = \frac{\text{mass of solute per unit mass of solvent in extract}}{\text{mass of solute per unit mass of diluent in raffinate}}$$

***In the first year, students are expected to gain an understanding of the fundamental principles of phase equilibria and their application (with material and energy balances) to the design and operation of common separation processes.***

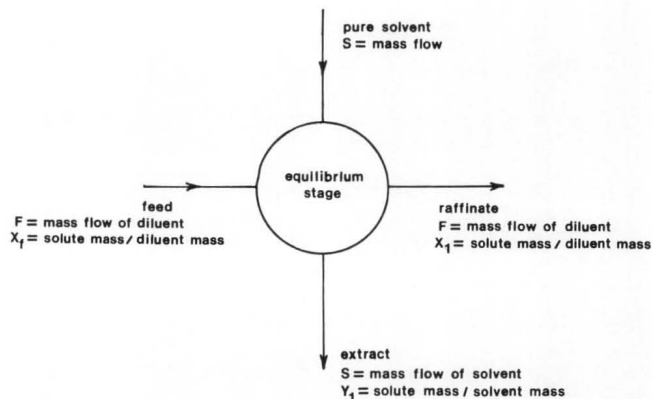


FIGURE 1. Single equilibrium stage with pure solvent.

The use of mass ratios in place of mass fractions is readily understood by the students. The simple conversions are given later in this article.

## SINGLE EQUILIBRIUM STAGE

Students are encouraged to read about discrete stage solvent extraction equipment such as the mixer-settler. A single equilibrium stage is shown schematically in Figure 1. To keep the problem as simple as possible, a feedstock containing only solute and diluent is contacted with a pure solvent. The performance of the unit is calculated as a function of the following parameters:

$S$  = mass flow of solvent

$F$  = mass flow of diluent in feedstock

$X_f$  = mass of solute per unit mass of diluent in feedstock

$X_1$  = mass of solute per unit mass of diluent in raffinate

The material balances for diluent and solvent are trivial because these two components are immiscible. The solute material balance is

$$X_f F = X_1 F + Y_1 S \quad (1)$$

The assumption that the stage behaves as an equilibrium stage means that the phases leaving are in equilibrium, i.e.,

$$Y_1 = KX_1 \quad (2)$$

Hence the performance of the single stage is given

by the simultaneous solution of Eqs. (1) and (2)

$$\frac{X_1}{X_f} = \frac{1}{(r+1)} \quad (3)$$

where

$$r = KS / F \quad (4)$$

It is readily seen from Eq. (3) that the amount of solute extracted can be improved by one or a combination of the following:

- increasing the solvent-to-feed ratio
- increasing  $K$  either by changing the temperature or by using another solvent
- passing the raffinate as the feedstock to second and further equilibrium stages, *i.e.*, cross-current extraction shown schematically in Figure 2.

### MULTISTAGE CROSS-CURRENT EXTRACTION

Provided that an equal flowrate of pure solvent  $S$  is fed to each stage, the solute balance for the general stage  $n$  is

$$X_{n-1}F = X_nF + Y_nS \quad (5)$$

Applying the equilibrium relationship yields

$$\frac{X_n}{X_{n-1}} = \frac{1}{(r+1)} \quad (6)$$

Hence for a battery of  $N$  equilibrium stages

$$\frac{X_N}{X_f} = \frac{1}{(r+1)^N} \quad (7)$$

From Eq. (7) it can be seen that  $X_N/X_f$  tends to zero as  $N$  tends to infinity.

### EFFICIENT USE OF SOLVENT

Equation (7) can be used to show that a greater extraction of solute can be obtained if the total flow of solvent is split between a number of equilibrium stages rather than all the solvent being used in a single equilibrium stage. This general result is most easily demonstrated by the example of splitting the solvent equally between two equilibrium stages. For

this case

$$\frac{X_2}{X_f} = \frac{1}{\left\{\frac{r}{2} + 1\right\}^2} = \frac{1}{\left\{\frac{r}{2}\right\}^2 + r + 1} \quad (8)$$

Comparison of Eq. (8) with Eq. (3) confirms the improvement in the extraction of solute, but at the additional expense of providing an extra equilibrium stage. The general result for splitting a total flow of solvent  $S$  equally into  $N$  stages is

$$\frac{X_N}{X_f} = \frac{1}{\left\{\frac{r}{N} + 1\right\}^N} \quad (9)$$

### MULTISTAGE COUNTER-CURRENT EXTRACTION

The counter-current extraction scheme is shown in Figure 3. A solute balance across stage 1 gives

$$X_fF + Y_2S = X_1F + Y_1S \quad (10)$$

but

$$Y_1 = KX_1 \quad \text{and} \quad Y_2 = KX_2$$

Hence

$$X_1 - X_f = r(X_2 - X_1) \quad (11)$$

Applying solute balances across each stage in turn yields

$$X_2 - X_1 = r(X_3 - X_2) \quad (12)$$

$$X_n - X_{n-1} = r(X_{n+1} - X_n) \quad (13)$$

$$X_N - X_{N-1} = r(X_{N+1} - X_N) \quad (14)$$

Eliminating  $X_1$  from Eqs. (11) and (12) gives

$$X_2 - X_f = \{r + r^2\}(X_3 - X_2) \quad (15)$$

With further eliminations of intermediate raffinate compositions, it can be shown that

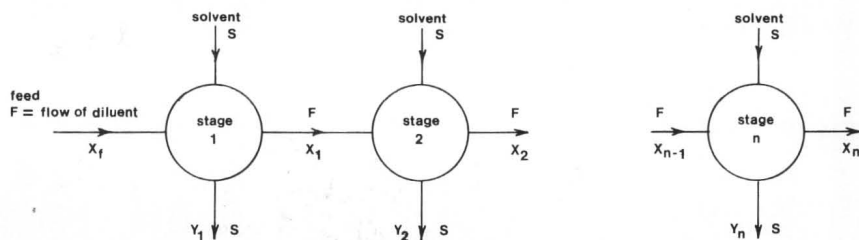


FIGURE 2. Multistage cross-current extraction with pure solvent.

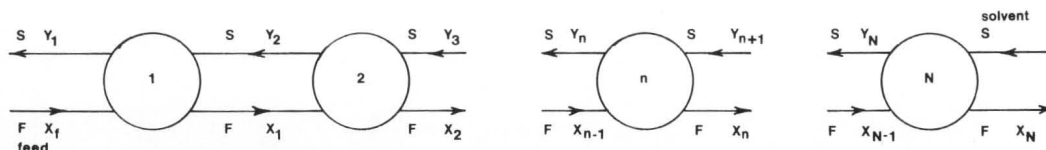


FIGURE 3. Multistage counter-current extraction with pure solvent.

$$X_n - X_f = \{r + r^2 + r^3 + \dots r^n\}(X_{n+1} - X_n) \quad (16)$$

$$\text{i.e.,} \quad X_n - X_f = \{X_{n+1} - X_n\} \sum_{i=1}^n r^i \quad (17)$$

and hence

$$X_N - X_f = \{X_{N+1} - X_N\} \sum_{i=1}^N r^i \quad (18)$$

Since  $X_{N+1}$  would be nominally in equilibrium with a pure solvent stream S,

$$X_{N+1} = 0 \quad (19)$$

Hence from Eq. (18)

$$\frac{X_N}{X_f} = \frac{1}{1 + \sum_{i=1}^N r^i} = \frac{1}{\sum_{i=0}^N r^i} \quad (20)$$

The performance of a battery of counter-current extractors (Eq. 20) is compared with that of a battery of cross-current extractors in which the solvent is split equally between all N stages (Eq. 9) in Figure 4. It should be noted that for the same total solvent flowrate S and the same number of stages, the performance of the counter-current battery is always superior to that of the cross-current battery. Figure 4 can be used to demonstrate that the amount of separation that can be achieved on each successive stage decreases as the number of stages increases.

## MINIMUM SOLVENT FLOWRATE

For the counter-current system, Eq. (20) may be simplified by summation of the series to give

$$\frac{X_N}{X_f} = \frac{1-r}{1-r^{N+1}} \quad \text{for } r \neq 1 \quad (21)$$

When KS/F is greater than unity, the term  $r^{N+1}$  tends

to infinity as N tends to infinity, and therefore  $X_N/X_f$  tends to zero. Thus complete extraction of the solute is possible with an infinite number of stages. This is clearly shown in Figure 4.

Reducing the solvent flowrate reduces the value of KS/F. When KS/F becomes less than unity,  $r^{N+1}$  tends to zero as N tends to infinity, and hence Eq. (21) becomes

$$\frac{X_N}{X_f} = 1 - r \quad (22)$$

It is clear from Eq. (22) that complete extraction of the solute is not possible (even with an infinite number of stages) when KS/F is less than one. The limiting performance is given by Eq. (22), and this result is also clearly shown in Figure 4. The highest flowrate, at which the limiting performance expressed by Eq. (22) occurs, is given by

$$r = 1 \quad (23)$$

i.e., by

$$S = \frac{F}{K} \quad (24)$$

Solvent flowrates in excess of this value would allow  $X_N/X_f$  to tend to zero as N tends to infinity. The concept of minimum solvent-to-feed ratio for a given specification, i.e., to reduce a solute concentration from  $X_f$  to  $X_N$ , is thus clearly demonstrated by the simple LLE system.

## USE OF THE SIMPLE SYSTEM AS AN INTRODUCTION TO GRAPHICAL METHODS

The above algebraic analyses enable the principal features of multistage contacting to be demonstrated quickly, although the liquid-liquid equilibrium system is hypothetical. The equilibria for real systems are more complex, particularly when the solute concentrations are high. The above LLE system can be used to introduce students to the graphical solution methods. For convenience, the solute ratios Y and X should be converted to mass fractions. Thus, since the solvent and all extracts contain no diluent, the mass fraction of solute is given by

$$y = \frac{Y}{1+Y} \quad (25)$$

Similarly, since the feed and all raffinates contain no solvent, the mass fraction of solute is given by

$$x = \frac{X}{1+X} \quad (26)$$

The locus of extracts (solute and solvent only) is clearly the hypotenuse of the right-angled diagram shown in Figure 5, while the locus of raffinates (solute and diluent) is clearly the abscissa.

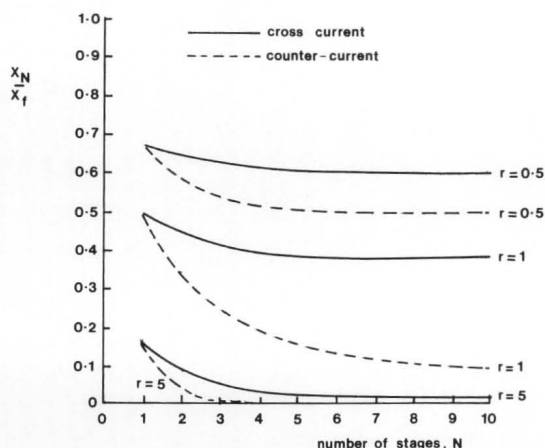


FIGURE 4. Comparison of multistage cross- and counter-current extraction.



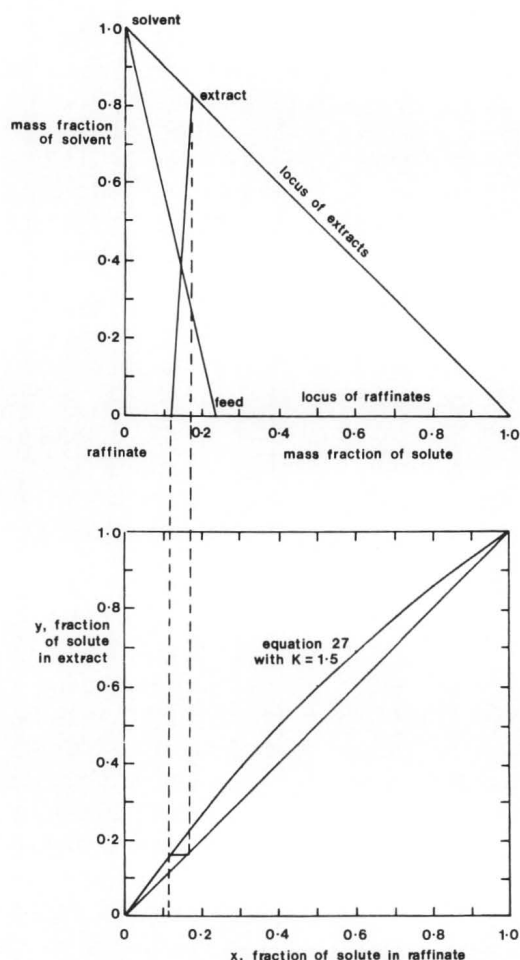


FIGURE 5. Single stage extraction with simple LLE system.

A single stage calculation of the extraction by a pure solvent of a solute from a mixture with only the diluent is shown in Figure 5. The value of the partition coefficient used in this example is  $K = 1.5$ . When written in terms of mass fractions rather than solute ratios, the equilibrium relationship is no longer in linear form. Substituting Eqs. (25) and (26) in the equilibrium relationship  $Y = KX$  gives the revised form of the equation

$$\left\{ \frac{y}{1-y} \right\} = K \left\{ \frac{x}{1-x} \right\} \quad (27)$$

Students are encouraged to derive the inverse lever arm rule from the material balances and to apply the rule to the single stage calculation. Analyses of cross- and counter-current extractions, including minimum solvent-to-feed ratio, can also be studied using the system shown in Figure 5. However, at this point in the first-year course, students would be expected to be using real chemical systems in which either one pair or two pairs of the three components are partially miscible, and the corresponding graphs

would show the extract and raffinate loci not to be the sides of the triangle.

## CONCLUSION

A simple liquid-liquid equilibrium system involving a constant partition coefficient, which is based on solute ratios, is used to develop an understanding of multistage contacting in the first-year separation processes course of BEng degrees at Bath. The algebraic solutions are used to demonstrate the advantage of counter-current operation over cross-current operation, to demonstrate the effectiveness of splitting the solvent in cross-current operation, and to demonstrate the problem of minimum solvent-to-feed flow ratio in counter-current operation.

## NOTATION

- $F$  = mass flowrate of diluent in feedstock
- $K$  = distribution or partition coefficient expressed in mass ratio units
- $N$  = number of stages in solvent extraction battery
- $r$  = parameter defined by Eq. (4)
- $S$  = mass flowrate of pure solvent
- $x$  = mass fraction of solute (in feed or raffinate)
- $X$  = mass of solute per unit mass of diluent
- $y$  = mass fraction of solute (in extract)
- $Y$  = mass of solute per unit mass of solvent

## Subscripts

- $f$  = feed
- $n$  = phase leaving stage  $n$
- $N$  = phase leaving stage  $N$
- $1$  = phase leaving stage 1
- $2$  = phase leaving stage 2 □

## ChE books received

*Organic Reactions*: Volume 38, edited by Beak et al.; John Wiley & Sons, 1 Wiley Dr., Somerset, NJ 08875-1272; 805 pages, \$89.95 (1990)

*CAE: Computer Modeling for Polymer Processing*, by Charles L. Tucker, III; Oxford University Press, 2001 Evans Road, Cary, NC 27513; 623 pages, \$99 (1990)

*Biotechnology Focus 2*, by R. K. Finn and P. Prave; Oxford University Press, 2001 Evans Road, Cary, NC 27513; 543 pages, \$79 (1990)

*Fermentation: A Practical Approach*, edited by McNeil and Harvey; Oxford University Press, 2001 Evans Road, Cary, NC 27513; 226 pages, \$65.00 (1990)

*Polymer Characterization*, by Schröder, Müller, Arndt; Oxford University Press, 2001 Evans Road, Cary, NC 27513; 344 pages, \$47.50 (1989)