Table 4.5 Physical properties of TBP[†]

Chemical formula	$(C_4 H_9)_3 PO_4$
Molecular weight	266
Color	Water white
Odor	Mildly sweet
Refractive index at $20°C$	1.4223
Viscosity at	
$25°C$	3.32 cP
$85°C$	0.8 cP
Boiling point at	
760 Torr	$289°C$
15 Torr	$173°C$
1 Torr	$121°C$
Density at $25°C$	0.9724
Freezing point	$-80°C$
Flash point, Cleveland open cup	$145°C$
Dielectric constant at $30°C$	7.97
Solubility in water at $25°C$	0.39 g/liter
Solubility of water in TBP at $25°C$	64 g/liter

[†]Data from J. R. Flanary [F1] and T. H. Siddall, III [S4].

solvent is held for long periods at temperatures as high as 50 to $60°C$, but it can be removed by periodically scrubbing the solvent with a basic solution [S4].

TBP can be decomposed explosively when heated to above $120°C$ in the presence of extractable nitrates [S4].

6 THEORY OF COUNTERCURRENT EQUILIBRIUM EXTRACTION

The calculation of the concentration of extractable components in a countercurrent cascade of equilibrium solvent extraction stages is first developed for the simple countercurrent extraction section of Fig. 4.3. The theory is then extended to the extracting-scrubbing system of Fig. 4.4 for fractional extraction and is illustrated by a numerical calculation for the separation of zirconium from hafnium, using TBP in kerosene as solvent.

6.1 Extracting Cascade

Here we consider an extracting cascade in which a feed solution containing one or more extractable components is contacted countercurrently with an organic solvent. Nomenclature for flow rates, concentrations, and stage numbers is shown in Fig. 4.8. It will be assumed that equilibrium is reached between the aqueous and organic phases leaving each stage. Changes in the volume flow rates of the aqueous and organic phases will be neglected. Consider the portion of the cascade below stage n. A material balance on one of the extractable components is

$$Ey_0 + Fx_n = Ey_{n-1} + Fx_1$$
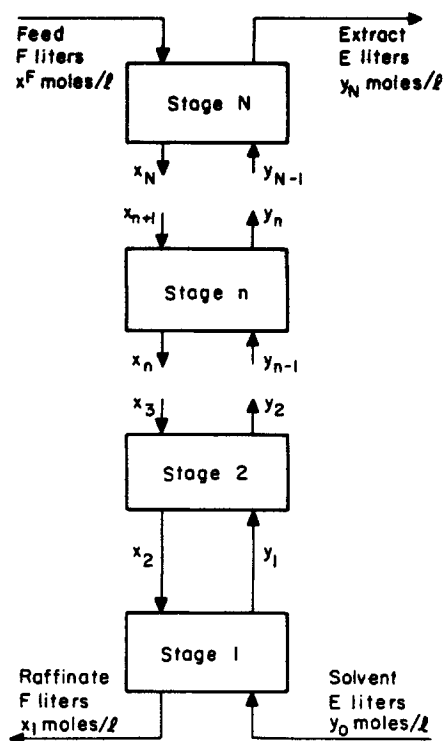
or

$$y_{n-1} - y_0 = \frac{F}{E}(x_n - x_1) \tag{4.27}$$

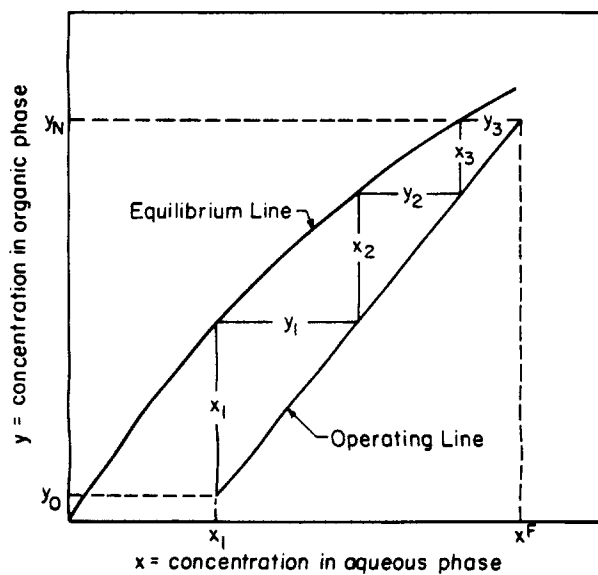**Figure 4.8** Nomenclature for cascade of solvent extraction stages.

Figure 4.9 Stage concentration diagram for solvent extraction cascade.

Concentrations in the organic and aqueous phases leaving a stage are related by the equilibrium relation

$$y_n = D_n x_n \tag{4.28}$$

where D_n is the distribution coefficient at the conditions of the nth stage.

The meaning of Eqs. (4.27) and (4.28) may be visualized on a plot of y versus x, in the McCabe-Thiele diagram, Fig. 4.9. The material-balance relation (4.27) is represented by the operating line that passes through the point (x_1^E, y_0^E) and has the slope F/E. The equilibrium relation (4.28) is represented by the equilibrium line. When D is constant, the equilibrium line is a straight line, as would occur for the extraction of trace quantities of solutes in the presence of nonextractable salting agents, with constant concentration of uncombined complexing agent. More generally, as has been demonstrated in Sec. 4, D_n varies from stage to stage, resulting in a curved equilibrium line. Figure 4.9 illustrates the equilibrium line typical for the extraction of a single component in the presence of a nonextractable salting agent.

The McCabe-Thiele diagram is useful for constructing a graphic solution for the stagewise compositions. The operating line is the locus of points x_n, y_{n-1} of adjacent interstage flows. The vertical projection of any such point intersects the equilibrium line at x_n, y_n, thereby defining the compositions of the aqueous and organic phases leaving the equilibrium stage n.

Assume that the cascade is to reduce the concentration of the extractable component from x^F to x_1 by extraction with organic of relative volume E/F. The point x_1, y_0 is thereby specified. Beginning at x_1, y_0 and projecting upward in vertical and horizontal steps, the compositions for all of the other equilibrium stages are determined. The number of vertical projections between the operating line and equilibrium line necessary to step from x_1 to x^F gives the required number of equilibrium stages.

Given this number of stages, construction of a similar McCabe-Thiele diagram for other components in the feed, such as impurities, allows the calculation of the extent to which these impurities extract into the organic phase. If two or more extractable components are each in sufficient concentration to affect the distribution coefficient of the other species, e.g., TBP extraction of $UO_2(NO_3)_2$ and HNO_3, the equilibrium lines for the two components cannot be specified in advance but must be calculated by an iterative procedure, similar to that to be illustrated in Sec. 6.6 for the zirconium-hafnium separation.

From Eq. (4.27) or from the construction of Fig. 4.9 it is apparent that the ratio of organic flow rate to aqueous flow rate is given by

$$\frac{E}{F} = \frac{x^F - x_1}{y_N - y_0} \tag{4.29}$$

because x^F is the virtual aqueous effluent concentration from stage $N + 1$. If the overall fractional recovery ρ of the extractable component is specified as

$$\rho = \frac{E y_N}{F x^F} \tag{4.30}$$

and, for the simple extraction cascade,

$$1 - \rho = \frac{x_1}{x^F} \tag{4.31}$$

then Eqs. (4.29) and (4.31) combine to yield

$$\frac{E}{F} = \frac{\rho x^F}{y_N - y_0} \tag{4.32}$$

For given compositions x^F, x_1, and y_0, or for given x^F, y_0, and ρ, reducing the relative amount of organic flow brings the operating line nearer to the equilibrium line and increases
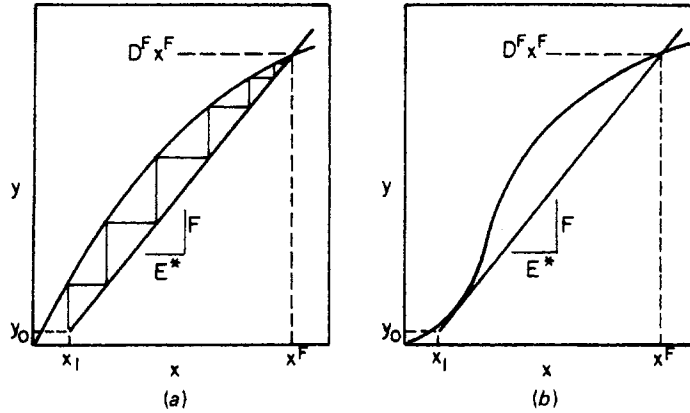
Figure 4.10 Limiting flow ratios for solvent extraction cascade.

the required number of stages. The minimum flow ratio $(E/F)_{min}$ occurs when the operating line intersects the equilibrium line at x^F, requiring an infinite number of stages as illustrated in Fig. 4.10a. In this limiting condition, denoted by asterisks, the concentration y_N^* in the organic stream leaving the cascade is

$$y_N^* = D_N x^F \tag{4.33}$$

so that (4.29) becomes

$$\left(\frac{E}{F}\right)_{min} = \frac{E^*}{F} = \frac{x^F - x_1}{D_N x^F - y_0} \tag{4.34}$$

and (4.32) becomes

$$\frac{E^*}{F} = \frac{\rho}{D_N(1 - y_0/x^F)} \tag{4.35}$$

If the equilibrium line is locally concave upward, as is possible in the extraction of a self-salting component with excess extracting agent, with sufficiently low x_1 the operating line may intersect the equilibrium at $x < x^F$. In this event Eqs. (4.33) through (4.35) are invalid unless x_1 is increased to allow intersection at x^F, as illustrated in Fig. 4.10b.

To carry out a specified separation in an actual extracting cascade with a finite number of stages, the flow ratio E/F must be greater than the minimum ratio E^*/F given in Eq. (4.34) or (4.35). The application of these equations for the case of constant distribution coefficients will be illustrated in Sec. 6.2.

6.2 Extracting Cascade with Constant Distribution Coefficients

When the distribution coefficients are independent of stage number, an equation can be derived for analytical calculation of the number of stages.

For any extractable component with a constant distribution coefficient, Eqs. (4.27) and (4.28) can be rewritten in terms of the constant *extraction factor* β:

$$y_n = \beta(y_{n-1} - y_0) + Dx_1 \tag{4.36}$$

where

$$\beta \equiv \frac{DE}{F} \tag{4.37}$$

Equation (4.28) is again written as

$$y_n = Dx_n \tag{4.38}$$

When $n = 1$, Eq. (4.36) becomes

$$y_1 = Dx_1 \tag{4.39}$$

When $n = 2$, Eq. (4.36) becomes

$$y_2 = \beta(y_1 - y_0) + Dx_1 \tag{4.40}$$

which, with (4.39) becomes

$$y_2 = (\beta + 1)Dx_1 - \beta y_0 \tag{4.41}$$

When $n = 3$, Eq. (4. 36) becomes

$$y_3 = \beta(y_2 - y_0) + Dx_1 \tag{4.42}$$

which, with (4.41) becomes

$$y_3 = (1 + \beta + \beta^2)Dx_1 - (\beta + \beta^2)y_0 \tag{4.43}$$

Proceeding in this way to stage N, we obtain

$$y_N = (1 + \beta + \cdots + \beta^{N-1})D_1 x_1 - (\beta + \cdots + \beta^{N-1})y_0 \tag{4.44}$$

which is identical with

$$y_N = \frac{\beta^N - 1}{\beta - 1}(Dx_1 - y_0) + y_0 \tag{4.45}$$

Equation (4.45) is a form of the Kremser equation, originally derived for countercurrent gas absorption [S3].

The raffinate concentration x_1 may be eliminated by an overall material balance,

$$F(x^F - x_1) = E(y_N - y_0) \tag{4.46}$$

which combines with (4.45) to yield

$$\frac{y_N - y_0}{Dx^F - y_0} = \frac{\beta^N - 1}{\beta^{N+1} - 1} \tag{4.47}$$

Figure 4.11 provides a graphic solution of Eq. (4.47).

The overall recovery ρ of the extractable component can be expressed in terms of these variables by combining Eqs. (4.30), (4.37), and (4.47) to eliminate y_N:

$$\rho = \beta\left(\frac{\beta^N - 1}{\beta^{N+1} - 1}\right) + \beta^{N+1}\left(\frac{\beta - 1}{\beta^{N+1} - 1}\right)\frac{y_0}{Dx^F} \tag{4.48}$$

Thus, by specifying β for the cascade and the ratio y_0/Dx^F and recovery ρ for any one of the extractable components, the required number of equilibrium stages N can be calculated from (4.48).

If we have extractable components A and B in the feed to be separated in a simple extraction cascade, the constant distribution coefficients D_A and D_B result in extraction factors β_A and β_B, and the overall decontamination factor f_{AB} is obtained by applying Eq. (4.48) to each of the components, with

$$f_{AB} \equiv \frac{\rho_A}{\rho_B} \tag{4.49}$$

For the special case of $y_0 = 0$, Eqs. (4.48) and (4.49) combine to yield

$$f_{AB} = \frac{\beta_A}{\beta_B} \left(\frac{\beta_A^N - 1}{\beta_B^N - 1} \right) \left(\frac{\beta_B^{N+1} - 1}{\beta_A^{N+1} - 1} \right) \tag{4.50}$$

For a specified number of stages N and specified E/F, the decontamination factor for any two extractable components can be calculated from (4.48) and (4.49) or, for $y_0 = 0$, from (4.50).

To illustrate the use of these equations, consider the extraction of zirconium from an aqueous solution of zirconium and hafnium nitrates, as shown in Fig. 4.12. Although the distribution coefficients do, in fact, depend on the concentration of zirconium and hafnium, as shown later in Sec. 6.6, constant distribution coefficients are assumed here for the purpose of this illustration. The specified feed composition and the specified recovery to be obtained are listed in Table 4.6.

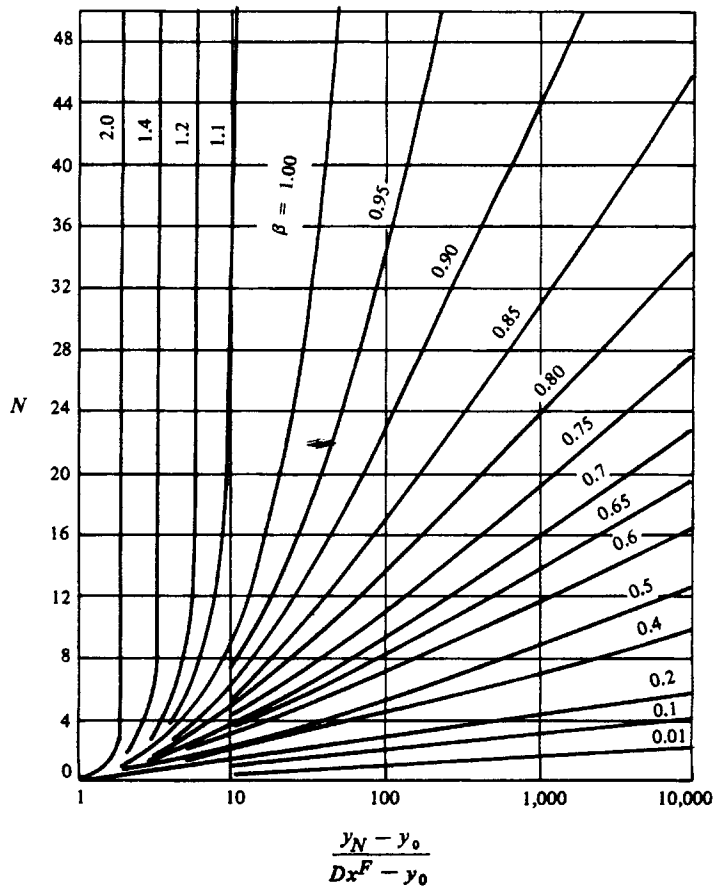The distribution coefficients assumed above are those observed by Huré and Saint James

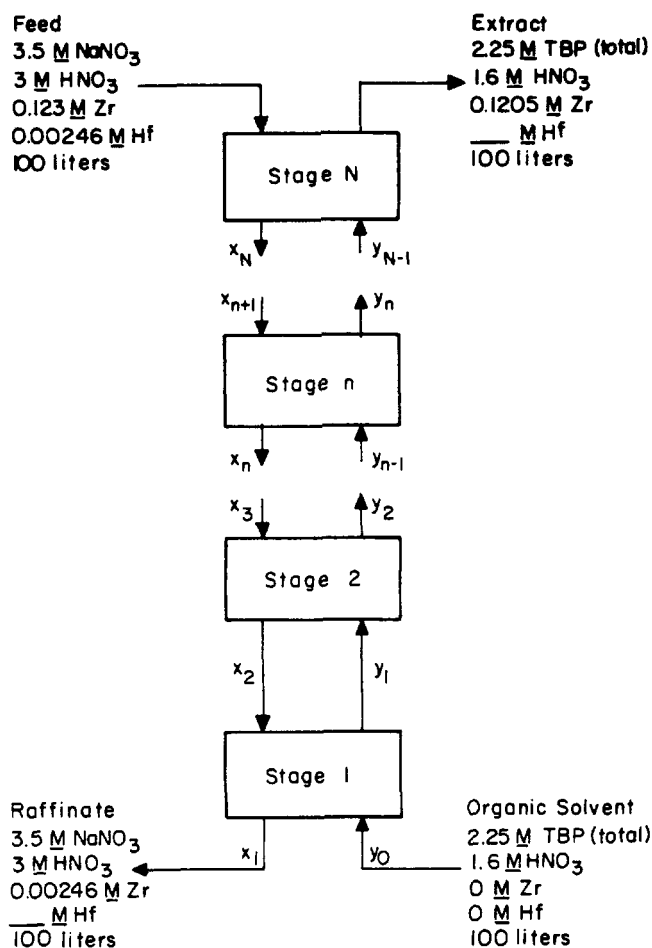Figure 4.11 Number of equilibrium stages in an extraction cascade. (*Adapted from Sherwood et al. [S3]*.)

Feed
3.5 $\underline{M}$ NaNO$_3$
3 $\underline{M}$ HNO$_3$
0.123 $\underline{M}$ Zr
0.00246 $\underline{M}$ Hf
100 liters

Extract
2.25 $\underline{M}$ TBP (total)
1.6 $\underline{M}$ HNO$_3$
0.1205 $\underline{M}$ Zr
___ $\underline{M}$ Hf
100 liters

Stage N

x_N y_{N-1}

x_{n+1} y_n

Stage n

x_n y_{n-1}

x_3 y_2

Stage 2

x_2 y_1

Stage 1

Raffinate
3.5 $\underline{M}$ NaNO$_3$
3 $\underline{M}$ HNO$_3$
0.00246 $\underline{M}$ Zr
___ $\underline{M}$ Hf
100 liters

x_1 y_0

Organic Solvent
2.25 $\underline{M}$ TBP (total)
1.6 $\underline{M}$ HNO$_3$
0 $\underline{M}$ Zr
0 $\underline{M}$ Hf
100 liters

Figure 4.12 Flow sheet for zirconium-hafnium extraction example.

[H4] for an aqueous solution of the feed of concentration 3.5 N in NaNO$_3$ and 3.0 N in HNO$_3$, in contact with 60 percent TBP in kerosene. Distribution coefficients will be higher at the bottom of the cascade, where the aqueous zirconium concentration is lower; this will be neglected in the present treatment, but will be taken into account in Sec. 6.6.

By applying Eqs. (4.37) and (4.48) to zirconium,

$$\beta_{Zr} = 1.2$$

and

$$0.98 = \frac{1.2^{N+1} - 1.2}{1.2^{N+1} - 1}$$

from which $N = 12.2$.

The zirconium-hafnium decontamination factor is obtained from (4.48) and (4.49) with $\beta_{Hf} = 0.12$:

$$f_{\text{Zr-Hf}} = 0.98 \, \frac{0.12^{13.2} - 1}{0.12^{13.2} - 0.12} = 8.17$$

The McCabe-Thiele diagrams for this example are shown in Fig. 4.13.

It is interesting to compare the decontamination obtainable for $\rho_{\text{Zr}} = 0.98$ and $E/F = 1.0$ with that obtainable with an infinite number of stages, corresponding to operation at the same zirconium recovery but at $(E/F)_{\text{min}}$. From Eq. (4.35):

$$\frac{E}{F_{\text{min}}} = \left(\frac{E^*}{F}\right) = \frac{0.98}{1.20} = 0.817$$

and with $N = \infty$, Eq. (4.50) yields

$$\lim_{N \to \infty} f_{\text{Zr-Hf}} = \frac{1}{\beta_{\text{Hf}}} = 8.33$$

A more effective way to use an increased number of stages in a simple extracting cascade would be to increase the zirconium recovery. This would occur by allowing the slope of the operating line to approach D_{Zr}. In the limit of $N \to \infty$, $x_{\text{Zr},1} \to 0$ and $\rho_{\text{Zr}} \to 1$. Because $D_{\text{Hf}} \ll D_{\text{Zr}}$, the operating line for hafnium can intersect the hafnium equilibrium line only at $x > x_{\text{Hf}}^F$ and not at $x_{\text{Hf}} = 0$. In this limit of

$$\frac{F}{E} \to D_{\text{Zr}}$$

$$N \to \infty$$

$$\rho_{\text{Zr}} \to 1$$

Table 4.6 Specifications for zirconium-hafnium separation example in an extracting cascade

Given	
Aqueous feed concentration	
Zirconium	$x_{\text{Zr}}^F = 0.123$ mol/liter
Hafnium	$x_{\text{Hf}}^F = 0.00246$ mol/liter
Solvent feed concentration	
Zirconium	$y_{\text{Zr},0} = 0$
Hafnium	$y_{\text{Hf},0} = 0$
Zirconium recovery	$\rho_{\text{Zr}} = 0.98$
Distribution coefficients, assumed to be constant for all stages	
Zirconium	$D_{\text{Zr}} = 1.20$
Hafnium	$D_{\text{Hf}} = 0.12$
Flow ratio	$E/F = 1.0$
Required	
Number of stages N	
Zr-Hf decontamination factor f	

Source: Adapted from J. Huré and R. Saint James, "Process for Separation of Zirconium and Hafnium," *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, vol. 8, United Nations, New York, 1956, p. 551.