CHAPTER 7

Extraction—Organic Chemicals Processing

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The increasing diversity in the applications of liquid extraction has led to a correspondingly diverse proliferation of extraction devices that continue to be developed. This chapter focuses on those fundamental principles of diffusion, mass transfer, phase equilibrium, and solvent selection that provide a unifying basis for the entire operation. Design procedures for both stagewise and differential contactors also receive consideration, including packed and perforated plate columns and mixer-settlers. Some mechanically aided columns are discussed and an attempt is made to compare the performance of various equipment designs.

7.1 DIFFUSION AND MASS TRANSFER

First, we define concentration and flux.

7.1-1 Flux Relationships

Let the moles and mass of component A per unit volume of mixture be \( c_A \) and \( p_A \), respectively. Then the mole fraction of A is \( c_A/c \) or \( x_A \), and the mass fraction is \( p_A/p \) or \( w_A \).

Consider a nonuniform fluid mixture with \( n \) components that is experiencing bulk motion. The statistical mean velocity of component \( i \) in the \( x \) direction with respect to stationary coordinates is \( u_i \). The molal average velocity of the mixture in the \( x \) direction is defined as

\[
U = \frac{1}{c} \sum_{i=1}^{n} c_i u_i \tag{7.1-1}
\]

and the mass average velocity in the \( x \) direction is

\[
u = \frac{1}{\rho} \sum_{i=1}^{n} \rho_i u_i \tag{7.1-2}
\]

The corresponding definitions of molal fluxes in the \( x \) direction for component \( i \) are as follows:
Relative to Stationary Coordinates

\[ N_{ix} = c_i u_i \]  

(7.1-3)

Relative to the Mass Average Velocity

\[ I_{ix} = c_i (u_i - u) \]  

(7.1-4)

Relative to the Molal Average Velocity

\[ J_{ix} = c_i (u_i - U) \]  

(7.1-5)

Analogous expressions of course may be written for the mass fluxes. Relationships between the various fluxes are obtained in the following manner.

To relate molal fluxes \( I_{ix} \) and \( N_{ix} \), consider Eqs. (7.1-1), (7.1-3), and (7.1-4):

\[ I_{ix} = c_i u_i - c_i u \]
\[ = N_{ix} - \frac{c_i}{\rho} \sum_{i=1}^{n} \rho_i u_i = N_{ix} - \frac{w_i}{M_i} \sum_{i=1}^{n} n_{ix} \]  

(7.1-6)

and, for a binary mixture,

\[ I_{A_x} = N_{A_x} - w_A \left( N_{A_x} + \frac{M_B}{M_A} N_{B_x} \right) \]  

(7.1-7)

Also,

\[ \sum_{i=1}^{n} I_{ix} = c(U - u) \quad \mathrm{and} \quad \sum_{i=1}^{n} N_{ix} = cU \]  

(7.1-8)

To relate molal fluxes \( J_{ix} \) and \( N_{ix} \), consider Eqs. (7.1-2), (7.1-3), and (7.1-8):

\[ J_{ix} = c_i u_i - c_i U \]
\[ = N_{ix} - \frac{c_i}{c} \sum_{i=1}^{n} c_i u_i = N_{ix} - x_i \sum_{i=1}^{n} N_{ix} \]  

(7.1-9)

and, for a binary mixture,

\[ J_{A_x} = N_{A_x} - x_A(N_{A_x} + N_{B_x}) \]  

(7.1-10)

Also,

\[ \sum_{i=1}^{n} J_{ix} = 0 \]  

(7.1-11)

7.1-2 Steady-State Equimolal Counterdiffusion and Unimolal Unidirectional Diffusion

The kinetic theory of gases is much more developed than that of liquids. Consequently, diffusional relationships for liquids are written largely by analogy with those for gases. Relationships for the latter are therefore developed first.

When the composition of a fluid mixture varies from one point to another, each component has a tendency to flow in the direction that will reduce the local differences in concentration. If the bulk fluid is either stationary or in laminar flow in a direction normal to the concentration gradient, the mass transfer reducing the concentration difference occurs by a process of molecular diffusion. This mechanism is characterized by random movement of individual molecules.

We confine our attention here to nonreacting systems of two components A and B, for which Fick’s First Law of molecular diffusion may be written for steady one-dimensional transfer with constant \( c \) as

\[ J_{A_x} = -D_{AB} \frac{dc_A}{dz} \quad \mathrm{and} \quad J_{B_x} = -D_{BA} \frac{dc_B}{dz} \]  

(7.1-12)
where \( J_A \) and \( J_B \) are molal fluxes of A and B relative to the molal average velocity of the whole mixture, the latter with respect to stationary coordinates; \( z \) is distance in the direction of diffusion; \( c_A \) and \( c_B \) are molar concentrations of A and B; and \( D_{AB} \) and \( D_{BA} \) are molecular diffusivities of A in B and of B in A, respectively. More generally,

\[
J_A = -cD_{AB} \frac{dx_A}{dz} \quad \text{and} \quad J_B = -cD_{BA} \frac{dx_B}{dz}
\]

(7.1-13)

for which constancy of \( c \) in the \( z \) direction is not required (see Ref. 1, pp. 10-11).

Now for a perfect gas, \( c_A = p_A/RT \) and \( c_B = p_B/RT \) so that Eqs. (7.1-12) become

\[
J_A = -\frac{D_{AB}}{RT} \frac{dp_A}{dz} \quad \text{and} \quad J_B = -\frac{D_{BA}}{RT} \frac{dp_B}{dz}
\]

(7.1-14)

Consider first the general case in which a steady total or bulk flow is imposed on the fluid mixture in the direction in which component A is diffusing. The magnitude of this molal flux of the whole mixture relative to stationary coordinates will be \( N_A + N_B \). The fluxes of components A and B relative to stationary coordinates are now the resultants of two vectors, namely, the flux caused by the bulk flow and the flux caused by molecular diffusion. Whereas these two vectors are in the same direction for component A, they are clearly in opposite directions for component B. The total flux of component A relative to stationary coordinates is then the sum of that resulting from bulk flow and that due to molecular diffusion as follows for a gaseous mixture:

\[
N_A = (N_A + N_B) \frac{p_A}{P} - \frac{D_{AB}}{RT} \frac{dp_A}{dz}
\]

(7.1-15)

This relationship is clearly another expression of Eq. (7.1-10) given earlier. Then, assuming constant \( D_{AB} \),

\[
\frac{D_{AB}}{RT} \int_{p_A}^{p_A (N_A + N_B)/P} \frac{dp_A}{N_A - [(N_A + N_B)/P]} = - \int_0^z dz
\]

Integrating for constant \( N_A \) and \( N_B \), we obtain

\[
N_A = \frac{D_{AB}P}{RTz} \left( \frac{1}{1 + \gamma} \right) \ln \left[ \frac{1 - (1 + \gamma) p_A/\gamma}{1 - (1 + \gamma) p_A}/\gamma \right]
\]

(7.1-16)

where \( \gamma = N_B/N_A \).

Equation (7.1-16) reduces to two special cases of molecular diffusion which are customarily considered. In equimolal counterdiffusion, component A diffuses through component B, which is diffusing at the same molal rate as A relative to stationary coordinates, but in the opposite direction. This process is often approximated in the distillation of a binary system. In unimolal unidirectional diffusion, only one molecular species—component A—diffuses through component B, which is motionless relative to stationary coordinates. This type of transfer is approximated frequently in the operations of gas absorption, liquid—liquid extraction, and adsorption.

**Steady-State Equimolal Counterdiffusion in Gases**

In this case the total molal flux with respect to stationary coordinates is zero, so that \( N_A = -N_B \). Then from Eqs. (7.1-14) and (7.1-15),

\[
N_A = J_A = -N_B = -J_B
\]

(7.1-17)

but \( p_A + p_B = P = \text{constant} \), therefore,

\[
\frac{dp_A}{dz} = -\frac{dp_B}{dz}
\]

(7.1-18)

From Eqs. (7.1-14) and (7.1-17),

\[
D_{AB} = D_{BA} = D
\]

(7.1-19)

Application of L'Hôpital's rule to Eq. (7.1-16) for \( \gamma = -1 \) gives
where \( z \) is \( z_2 - z_1 \); \( p_{A1} \) and \( p_{A2} \) are partial pressures of A at \( z_1 \) and \( z_2 \), respectively.

Equations (7.1-14), (7.1-17), and (7.1-20) demonstrate that the partial-pressure distribution is linear in the case of steady-state equimolal counterdiffusion.

### STEADY-STATE UNIMOLAL UNIDIRECTIONAL DIFFUSION IN GASES

In this case, the flux of component B in one direction resulting from bulk flow is equal to the flux of B in the opposite direction because of molecular diffusion. Component B is therefore motionless relative to stationary coordinates and \( N_{Bc} \) equals zero. Setting \( \gamma \) equal to zero in Eq. (7.1-16) and recalling that \( P - p_A = p_B \),

\[
N_{Ac} = \frac{D}{RTz} \left( \ln \frac{p_{B2}}{p_{B1}} \right) \tag{7.1-21}
\]

which may be written

\[
N_{Ac} = \frac{DP}{RTz} \left( \frac{p_{B2} - p_{B1}}{p_{BLM}} \right) = \frac{D}{RTz} \left( \frac{P}{p_{BLM}} \right) (p_{A1} - p_{A2}) \tag{7.1-22}
\]

where

\[
p_{BLM} = \frac{p_{B2} - p_{B1}}{\ln \left( \frac{p_{B2}}{p_{B1}} \right)}
\]

The increase in transfer—by the factor \( P/p_{BLM} \)—resulting from bulk flow in the direction of diffusion of A is indicated by a comparison between Eqs. (7.1-20) and (7.1-22).

Equation (7.1-21) demonstrates that the partial-pressure distribution is nonlinear in the case of steady-state unidirectional diffusion.

#### 7.1-3 Molecular Diffusion in Liquids

In the absence of a fully developed kinetic theory for liquids, the relationships for molecular diffusion are usually assumed to parallel those for gases, although diffusivities are often more substantially dependent on concentration of the diffusing components. In the case of equimolal counterdiffusion, the expression analogous to Eq. (7.1-20) is

\[
N_{Ac} = \frac{D}{z} \left( c_{A1} - c_{A2} \right) \tag{7.1-23}
\]

If \( c_A + c_B = c \), then \( c_A = x_A c \) and \( c_B = x_B c \), where \( x_A \) and \( x_B \) are mole fractions of A and B, respectively, and

\[
N_{Ac} = \frac{Dc}{z} \left( x_{A1} - x_{A2} \right) \tag{7.1-24}
\]

For unimolal unidirectional diffusion, the liquid-phase analog of Eq. (7.1-22) is

\[
N_{Ac} = \frac{D}{z} \left( \frac{c}{c_{BLM}} \right) (c_{A1} - c_{A2}) = \frac{Dc}{z} \left( \frac{x_{A1} - x_{A2}}{x_{BLM}} \right) \tag{7.1-25}
\]

where

\[
c_{BLM} = \frac{c_{B2} - c_{B1}}{\ln (c_{B2}/c_{B1})} \quad \text{and} \quad x_{BLM} = \frac{x_{B2} - x_{B1}}{\ln (x_{B2}/x_{B1})}
\]

In addition to variation in \( D \), the total molal concentration \( c \) also varies and a mean value of \( (c_1 + c_2)/2 \) is used when variations are not excessive.
7.1-4 Unsteady-State Diffusion in a Sphere

Many forms of extraction involve transfer between two liquid phases, one of which is dispersed as droplets in the other. Various attempts at theoretical analysis have assumed that the droplets may be regarded as spheres, in which mass transfer occurs by unsteady-state molecular diffusion. The following assumptions are made:

1. The concentration of solute (component A) is uniform at \( c_{A0} \) throughout the sphere at the start of diffusion (\( t = 0 \)).
2. The resistance to transfer in the medium surrounding the sphere is negligible, so that the surface concentration of the sphere is constant at \( c_A^* \), in equilibrium with the entire continuous phase—the latter having constant composition.
3. Diffusion is radial, there being no variation in concentration with angular position, and physical properties are constant.

The origin of coordinates is at the center of the sphere and the concentration at the spherical surface of radius \( r \) is \( c_A \) at time \( t \). At the same instant, the concentration at the spherical surface of radius \( r + dr \) is \( c_A + dc_A \). A control volume is defined between the two surfaces at \( r \) and \( r + dr \). The rate of flow of solute into the control volume is

\[-D(4\pi r^2) \frac{dc_A}{dr}\]

and the rate of flow out of the control volume is

\[-D[4\pi(r + dr)^2] \left[ \frac{dc_A}{dr} + d \left( \frac{dc_A}{r} \right) \right] \]

The difference between these two expressions, neglecting second- and third-order differentials, gives the rate of accumulation of solute in the control volume. Equating this to the rate of solute accumulation expressed as

\[(4\pi r^2 dr) \frac{dc_A}{dt}\]

leads to

\[\frac{dc_A}{dt} = D \left( \frac{\partial^2 c_A}{\partial r^2} + \frac{2}{r} \frac{\partial c_A}{\partial r} \right)\]  \hspace{1cm} (7.1-26)

The boundary conditions follow from the initial assumptions as

\[c_A(r, 0) = c_{A0}\]
\[c_A(r_s, t) = c_A^*\]
\[\lim_{r \to 0} c_A(r, t) = \text{bounded}\]

where \( r_s \) is the radius of the sphere. The solution to Eq. (7.1-26) for the local \( c_A(r, t) \) is then (Ref. 1, pp. 21-28)

\[c_A = c_A^* + \frac{2r_s}{\pi} (c_{A0} - c_A^*) \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \frac{1}{r} \sin \left( \frac{n\pi r}{r_s} \right) \exp \left( -\frac{Dn^2\pi^2t}{r_s^2} \right)\]  \hspace{1cm} (7.1-27)

The fractional extraction from the sphere at time \( t \) is as follows, where \( \bar{c}_A \) is the average concentration throughout the sphere at \( t \) (Ref. 1, pp. 21-28):

\[\frac{c_{A0} - \bar{c}_A}{c_{A0} - c_A^*} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{Dn^2\pi^2t}{r_s^2} \right)\]  \hspace{1cm} (7.1-28)

For ready solution of numerical problems Newman\(^2\) gives a graphical representation of Eq. (7.1-28) in the form of a plot of \( 1 - (c_A - \bar{c}_A)/(c_{A0} - c_A^*) \) against the dimensionless quantity \( Dt/r_s^2 \).
An individual coefficient of mass transfer for the disperse phase during free rise (or fall), \( k_{dn} \), may now be formulated. A balance on component A diffusing into a stagnant, spherical droplet rising between points 1 and 2 during time \( dt \) is

\[
k_{dn} \frac{\pi d_p^2}{6} (c_A^* - \bar{c}_A) \, dt = \frac{\pi d_p^2}{6} \, d\bar{c}_A
\]  

(7.1-29)

Integrating for constant \( c_A^* \) (at its average value) between locations 1 and 2,

\[
k_{dn} = -\frac{d_p}{6t} \ln \left( \frac{c_A^* - \bar{c}_{A1}}{c_A^* - \bar{c}_{A2}} \right) = -\frac{d_p}{6t} \ln (1 - E_f)
\]  

(7.1-30)

where \( d_p \) is the droplet diameter and \( E_f \) is the fractional extraction in time \( t \). Combining Eqs. (7.1-28) and (7.1-30), we obtain

\[
k_{dn} = -\frac{d_p}{6t} \ln \left[ \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{D_d n^2 \pi^2 t}{(d_p/2)^2} \right) \right]
\]  

(7.1-31)

The \( k_{dn} \) here is for use with a driving force expressed as \( \Delta c_A \). To obtain a \( k_{dn} \) suitable for use with \( \Delta y_A \), the right-hand side of Eq. (7.1-31) must be multiplied by \( (\rho/M)_{av} \) for the disperse phase between 1 and 2.

Equation (7.1-31) is used in the design of extraction equipment such as spray columns, perforated plate mixers, and mixer-settlers.

7.1-5 Molecular Diffusivities in Liquids

The theory of molecular diffusion has been the subject of extensive investigation because of its close relationship to the kinetic theory of gases. Detailed reviews are available \(^3 - ^8\) and a valuable critical comparison of the various correlations that have been presented for the prediction of diffusivities, including electrolytes and nonelectrolytes under a variety of conditions, is provided by Reid et al. \(^9\) Treybal (Ref. 10, pp. 150-165) reviews procedures for predicting diffusivities in liquids. Skelland (Ref. 1, Chap. 3) surveys the relationships available for estimating diffusivities for electrolytes and nonelectrolytes at low and high concentrations.

It is expected that the reader will consult the above references for a detailed understanding; the following classified relationships are presented only as an outline treatment.

**NONELECTROLYTES—DILUTE SOLUTIONS**

For dilute diffusion in organic solvents Lusis and Ratcliff \(^1\) give the following relationship:

\[
\frac{D_{AB} \mu_B}{T} = 8.52 \times 10^{-9} \left( \frac{V_{bb}}{V_{bb}} \right)^{1/3} \left[ 1.40 \left( \frac{V_{bb}}{V_{bb}} \right)^{1/3} + \frac{V_{bb}}{V_{bb}} \right]
\]  

(7.1-32)

where \( D_{AB} \) is in cm\(^2\)/s; \( \mu_B \) is viscosity of the solvent B in cP; \( T \) is in K; \( V_{bb} \) and \( V_{bb} \) are molal volumes of the solute and solvent at their normal boiling temperatures, in cm\(^3\)/mol. For water as solute it is usually necessary to evaluate \( V_{bb} \) as for four moles of water, that is, assuming water to diffuse as a tetramer. Lusis and Ratcliff \(^1\) discuss problems arising from strong solute-solvent interaction and in the diffusion of long straight-chain hydrocarbon molecules.

For diffusion in dilute aqueous solutions the following equation is provided by Hayduk and Laudie: \(^12\)

\[
D_{AB} = 13.26 \times 10^{-7} \frac{\mu_{wrf}}{V_{bb}}^{1/3} \left( \frac{V_{bb}}{V_{bb}} \right)^{1/3} + \frac{V_{bb}}{V_{bb}}
\]  

(7.1-33)

where \( \mu_{wrf} \) is the viscosity of water at \( T(K) \), in cP.

**NONELECTROLYTES—CONCENTRATED SOLUTIONS**

Leffler and Cullinan \(^13\) give

\[
(D_A \mu_{AB})_{conc} = (D_{AB} \mu_B)^{x_B} (D_{AB} \mu_A)^{x_A} \left( 1 + \frac{d \ln \gamma_A}{d \ln x_A} \right)
\]  

(7.1-34)

where \( D_{AB} \) and \( D_{AB} \) are diffusivities of very dilute A in B and B in A, respectively, in cm\(^2\)/s; \( \mu_A \), \( \mu_B \), and \( \mu_{AB} \) are viscosities of A, B, and the mixture of A and B, in cP; \( x_A \) and \( x_B \) are mole fractions of solute A and solvent B; and \( \gamma_A \) is the activity coefficient of A.
ELECTROLYTES—DILUTE SOLUTIONS

For strong (fully dissociated) electrolytes at infinite dilution, Nernst’s equation is

\[
D^\circ _A = 8.931 \times 10^{-10} T \left( \frac{l^+_A l^-_A}{l^+_A + l^-} \right) \left( \frac{z_+ + z_-}{z_+ z_-} \right) 
\]  

(7.1-35)

where \( D^\circ _A \) is diffusivity, in \( \text{cm}^2/\text{s} \); \( l^+_A \) and \( l^-_A \) are the anionic and cationic conductances at infinite dilution, in mho/equivalent; \( l^+_A + l^-_A \) is the electrolyte conductance at infinite dilution; \( z_+ \) and \( z_- \) are absolute values of the cation and anion valences; and \( T \) is the absolute temperature, in K.

ELECTROLYTES—CONCENTRATED SOLUTIONS

Gordon gives

\[
(D_{A})_{\text{conc}} = D^\circ _A \left(1 + \frac{m \ln \gamma \pm}{\partial m} \right) \left( \frac{1}{c^*_B V^*_B} \right) \left( \frac{\mu_B}{\mu_{AB}} \right) 
\]  

(7.1-36)

where \( D^\circ _A \) is calculated from Nernst’s equation (7.1-35); \( m \) is molality; \( c^*_B \) is the number of moles of water per \( \text{cm}^3 \) of solution; \( V^*_B \) is the partial molal volume of water in solution, in \( \text{cm}^3/\text{mol} \); \( \mu_B \) and \( \mu_{AB} \) are the viscosities of water and of the solution; and \( \gamma \pm \) is the mean ionic activity coefficient based on molality.

Skelland (Ref. 1, Chap. 3) illustrates the use of all these relationships.

A comprehensive tabulation of experimental diffusivities for nonelectrolytes is given by Johnson and Babb. Similar data for electrolytes are provided by Harned and Owen and Robinson and Stokes.

7.1-6 Mass Transfer Coefficients

Consider the distribution of a solute such as component A between two immiscible liquid phases in contact with each other. Under conditions of dynamic equilibrium the rate of transfer of A from the first to the second phase is equal to the rate at which A is transferred in the reverse direction. The equilibrium relationship may be represented by a plot such as Fig. 7.1-1 over a range of compositions of each phase.

It is assumed that local equilibrium prevails at the interface between phases, where the compositions are \( Y_A \) and \( X_A \). If transfer of A takes place from the lighter liquid to the heavier liquid, the individual coefficients \( k_Y \) and \( k_X \) for the light and heavy phases, respectively, are defined as follows:

\[
N_A A = k_Y A(Y_A - Y^*_A) = k_X A(X^*_A - X_A) 
\]  

(7.1-37)

\( A \) is the area of the interface, where the flux is \( N_A \), and \( Y_A \) and \( X_A \) are concentrations of component A in the bulk of the light- and heavy-liquid phases. Equation (7.1-37) shows that

\[
\frac{Y_A - Y^*_A}{X_A - X^*_A} = \frac{k_X}{k_Y} 
\]  

(7.1-38)

This relationship is plotted in Fig. 7.1-2 on the assumption of interfacial equilibrium.

Interfacial concentrations \( (X^*_A, Y^*_A) \) are often unknown at a given location within a two-phase system and it is then more convenient to use overall coefficients \( K_Y \) and \( K_X \), defined in terms of overall concentration differences or "driving forces," as shown below.

\[
N_A A = K_Y A(Y_A - Y_{AL}) = K_X A(X_{AG} - X_A) 
\]  

(7.1-39)

![FIGURE 7.1-1 Equilibrium distribution of component A between two conjugate phases.](image-url)
FIGURE 7.1-2 Individual and overall concentration "driving forces" for a two-phase system with distributed component A. Bulk concentrations of the two phases are $X_A$ and $Y_A$, respectively, and interfacial equilibrium is assumed.

where $Y_{AL}$ is the light liquid concentration that would be in equilibrium with the existing heavy liquid concentration; $X_{AG}$ is the heavy liquid concentration that would be in equilibrium with the existing light liquid concentration. The location of these quantities is shown in Fig. 7.1-2. The relationships between the individual coefficients of Eq. (7.1-37) and the overall coefficients of Eq. (7.1-39) can be shown to be the following (Ref. 1, pp. 91-93).

$$\frac{1}{K_Y} = \frac{1}{k_Y} + \frac{m}{k_X}, \quad \frac{1}{K_X} = \frac{1}{k_X} + \frac{1}{m'k_Y}, \quad \frac{1}{K_X} = \frac{1}{m''K_Y} \quad (7.1-40)$$

where the first two relationships express the overall resistance to transfer (in terms of the light and heavy liquids, respectively) as equaling the sum of the individual (or single-phase) resistances to mass transfer. The final expression relates the two forms of overall resistance to mass transfer, $1/K_X$ and $1/K_Y$ (note that constancy of $K$ over a given concentration range requires constant $k_X$, $k_Y$, and $m$).

The interfacial area $A$ is often unknown in many types of mass transfer equipment. In such cases mass transfer rates frequently are based on unit volume of the equipment, instead of unit interfacial area. The rate equations (7.1-37) and (7.1-39) are then modified to the following form:

$$N_A A = k_Y a(Y_A - Y_A^*)_m V_0 = k_X a(X_A - X_A^*)_m V_0 = k_Y a(Y_A - Y_{AL})_m V_0 = K_X a(X_{AG} - X_A)_m V_0 \quad (7.1-41)$$

where subscript $m$ denotes a suitable mean, $V_0$ is the contacting volume of the equipment, $a$ is the interfacial area per unit volume, and the combined quantities $k_Y a$, $k_Y a$, $K_X a$, and $K_Y a$ are called volumetric or capacity coefficients. Dividing Eq. (7.1-40) by $a$, we obtain

$$\frac{1}{k_Y a} = \frac{1}{k_Y a} + \frac{m}{k_X a'}, \quad \frac{1}{k_X a} = \frac{1}{k_X a} + \frac{1}{m'k_Y a'}, \quad \frac{1}{k_X a} = \frac{1}{m''K_Y a} \quad (7.1-42)$$

7.1-7 The Two-Film Theory

This theory, developed by Lewis and Whitman, supposes that motion in the two phases dies out near the interface and the entire resistance to transfer is considered as being contained in two fictitious films on either side of the interface, in which transfer occurs by purely molecular diffusion. It is postulated that local equilibrium prevails at the interface and that the concentration gradients are established so rapidly in the films compared to the total time of contact that steady-state diffusion may be assumed.

Individual or single-phase mass transfer coefficients ($k$) are defined customarily as follows for a mechanism involving bulk molal flow:

**Light Phase**

$$N_A = k_x \Delta y_A = k_x \Delta c_A \quad (7.1-43)$$
Heavy Phase

\[ N_A = k_i \Delta c_A = k_i \Delta x_A = k_i \left( \frac{\rho}{M} \right) \Delta x_A \quad (7.1-44) \]

In the important case of unimolal unidirectional diffusion, Eqs. (7.1-25) and (7.1-43) show the following relationship:

\[ k_r = \frac{D_G c}{z_G(1 - y_A)_{LM}} = \frac{D_G c}{z_G y_{BLM}} \quad (7.1-45) \]

where \( D_G \) is the solute diffusivity in the light phase, which has a fictitious film thickness \( z_G \); \( k_r \) is the individual light-phase coefficient of mass transfer for use with \( \Delta x_A \).

Similarly, for the heavy liquid phase, from Eqs. (7.1-25) and (7.1-44),

\[ k_s = \frac{D_L c}{z_L(1 - x_A)_{LM}} = \frac{D_L c}{z_L x_{BLM}} \quad (7.1-46) \]

where \( D_L \) is the solute diffusivity in the heavy phase, which has a fictitious film thickness \( z_L \); \( k_s \) is the individual heavy-phase coefficient of mass transfer for use with \( \Delta x_A \).

Equations (7.1-45) and (7.1-46) show that the two-film theory predicts that the mass transfer coefficient is directly proportional to the molecular diffusivity to the power unity. The complexity of flow normally prevents evaluation of \( k_r \), but it will decrease with increasing turbulence.

7.1-8 Other Theories

In the general relationship

\[ k \propto D^n \quad (7.1-47) \]

the value of \( n \) was seen to be unity according to the two-film theory. In contrast to this, a variety of theories have been developed on the basis of some form of surface-renewal mechanism, which often show \( n = \frac{1}{2} \), but which include \( 0 \leq n \leq 1 \).

The work of Higbie\(^{21}\) in 1935 provided the foundation for the penetration theory, which supposes that turbulence transports eddies from the bulk of the phase to the interface, where they remain for a short but constant time before being displaced back into the interior of the phase to be mixed with the bulk fluid. Solute is assumed to "penetrate" into a given eddy during its stay at the interface by a process of unsteady-state molecular diffusion, in accordance with Fick's Second Law and appropriate boundary conditions:

\[ \frac{\partial c_A}{\partial t} = D \frac{\partial^2 c_A}{\partial z^2} \quad (7.1-48) \]

The solution yields \( k = 2 \left( D/\pi t_r \right)^{1/2} \), where \( t_r \) is the (constant) time of exposure of the eddy at the interface.

Danckwerts\(^{22}\) theory of penetration with random surface renewal modifies this picture by proposing an "infinite" range of ages for elements of the surface. The probability of an element of surface being replaced by a fresh eddy is considered to be independent of the age of that element. Danckwerts\(^{22}\) introduced this modification by defining a surface age distribution function, \( \phi(t) \), such that the fraction of surface with ages between \( t \) and \( t + dt \) is \( \phi(t) dt \). If the probability of replacement of a surface element is independent of its age, Danckwerts showed that \( k = (s D)^{1/2} \), where \( s \) is the fractional rate of surface renewal.

The film-penetration theory, presented by Toor and Marchello,\(^{23}\) represents a combination of the three earlier theories reviewed above. The entire transfer resistance is considered to lie in a laminar surface layer of thickness \( z_L \), where \( c_A \) is uniform at \( c_{A_{\infty}} \) for all \( z \) greater than \( z_L \). Surface renewal occurs by eddies that penetrate the surface from the bulk of the phase. Thus, transfer through young elements of surface obeys the penetration theory \( (k \propto D^{1/2}) \), transfer through old elements follows the film theory \( (k \propto D) \), and transfer through elements of intermediate age is characterized by both mechanisms.

In a series of papers between 1949 and 1954 Kishinevskii and coworkers\(^{24-27}\) proposed a surface-renewal mechanism which, in contrast to the theories described above, postulates that transfer into an eddy at the interface occurs predominantly by convective mass flow and not by molecular diffusion. The authors also dispute the suggestion that the probability of replacement of a surface element is independent of its age.

King\(^{28}\) has proposed another general model for turbulent liquid-phase mass transfer to and from a free
gas-liquid interface. The model requires the evaluation of three parameters and involves concepts of surface
renewals in which surface tension exerts a damping effect on the smaller eddies. Allowance is made for a
continuous eddy diffusivity profile near the free interface, thereby avoiding the postulate of a "film" or
 discontinuity in transport properties as required by the film-penetration theory.

Harriott29 presents a model that incorporates the penetration mechanism, but which includes thin,
laminar, interfacial films that are stabilized by interfacial tension and are therefore excluded from inter-
mittent mixture with the bulk fluid. The penetration theory has been extended by Angelo et al.30 to allow
for "stretching" surfaces, such as those that occur, for example, in large, oscillating droplets. Ruckenstein31
has further refined the penetration theory to accommodate the effects of velocity distributions within the
eddies during solute penetration.

Skelland (Ref. 1, p. 106) gives the results of a theory of penetration with surface renewal in which it
is assumed that the fractional rate of surface renewal s is related to the age of the surface through the
constants ± and n as s = ±n, where (±, n + 1) > 0. A theory of penetration with periodically varying
rates of surface renewal has been developed by Skelland and Lee32 for two-phase dispersions in turbine-
agiteted vessels. This attempts to allow for the varying degrees of turbulence encountered by bubbles or
drops as they circulate through all regions of the vessel.

Comparisons between experimental observation and the predictions of the film theory on the one hand
and various forms of surface-renewal theory on the other are reviewed briefly in Ref. 33 (Chap. 5). It is
interesting that, although the evidence generally appears to favor the surface-renewal mechanisms, the two-
film theory contributes to the design of complex processes in a manner that continues to be very useful.
An example of this will be given later in the formulation of transfer unit relationships for packed column
design.

Although application of some of the theories outlined above is hampered by lack of knowledge of some
essential components (such as ±, t, ±, or ±, as appropriate), they are nevertheless valuable in indicating
limits on n between 0 and 1 in Eq. (7.1-47). Empirical correlations of data which show an exponent on D
outside this range should probably be rejected.

7.2 EQUILIBRIUM CONSIDERATIONS

Both liquid-liquid and vapor-liquid equilibria are important for the recovery of organic chemicals by solvent
extraction. The former equilibria determine the required liquid-liquid contacting equipment sizes and op-
erating conditions while the latter usually determine similar requirements for the solvent regeneration and
product recovery system. Although other flowsheet configurations are possible, it is common to follow the
liquid-liquid extraction step by solvent and product recovery to minimize the solvent inventory in the
process and the sizes of subsequent equipment. Also, the chosen solvent, or mass separating agent (MSA),
generally will affect the vapor-liquid equilibria of the solute-diluent binary as well as determine the liquid-
liquid equilbrium properties. Hence, a solvent that is added to effect the solute-diluent separation via
formation of a liquid-liquid mixture may be useful in a subsequent azeotropic or extractive distillation step
to achieve further solute-diluent separation.

Clearly, the accurate determination and correlation of these equilibrium properties are of paramount
importance in the rational design of extraction operations. In general, it is desirable to use computer-aided
design techniques for the modeling of such a system. The more attractive correlation techniques for multi-
component systems include the UNIQUAC and UNIFAC methods, which are described in Chapter 1 of
this handbook and are not discussed here. These techniques are suitable for computer-based computations.

On the other hand, it is often useful to complete simple hand calculations, especially during the initial
screening of alternative solvents. When experimental data are available, the distribution coefficients for
both diluent and solute can be correlated effectively using equations with the form:

\[ \ln D_A = b_0 + b_1 W_A + b_2 V_M + b_3 W_D + b_4/T \]  \hspace{1cm} (7.2-1)

where \( D_A \) is the distribution coefficient of \( A \), \( W_A \) and \( W_D \) are weight fractions, \( V_M \) is a volume fraction, T
is temperature, and the \( b \)'s are empirical parameters.

Similarly, it is often useful to correlate solute and diluent vapor-liquid equilibria over the solvent with
an equation of the form:

\[ \ln K_A = b_0 + b_1 X_A + b_2 X_B + b_3/T \]  \hspace{1cm} (7.2-2)

where \( K_A \) is a vapor-liquid distribution coefficient, \( X_A \) and \( X_B \) are mole fractions, and the \( b \)'s are again
empirical parameters. The liquid-liquid distribution coefficients usually are expressed as weight fraction
ratios, while the vapor-liquid equilibria are expressed more often in terms of the mole fraction ratios.

Although these equations are quite useful with experimental data in the range of low solute concen-
trations, Eq. (7.2-1) is limited by the fact that it cannot be used to predict the mutual solubility curve.
Consequently, it can lead to extrapolation beyond the two-phase region and therefore its use must be
constrained.
On the other hand, the simplicity of Eqs. (7.2-1) and (7.2-2) and their accuracy over the intended range favor their use for preliminary calculations. They permit consideration of the effects of inextractable materials (e.g., salts or dissolved solids) on the liquid-liquid equilibrium and the temperature with the introduction of relatively few adjustable parameters. In addition, they can be expanded into a polynomial form to account for situations where the logarithm of the apparent distribution coefficient is not a linear function of one of the important variables. Several examples are given in Fig. 7.2-1, which is taken from Tawfik.\(^1\)

The typical forms of Type 1 and Type 2 liquid-liquid systems are shown in Figs. 7.2-2\(^1\) and 7.2-3\(^2\). Also illustrated in Fig. 7.2-2 is the effect of temperature on the mutual solubility curve, which may be so pronounced in some cases as to cause transition from one type of system to the other.

During the extraction of organic species, it may be desirable to modify the solvent. An inert paraffinic compound or mixture may be blended with a suitable modifier (e.g., a species that hydrogen bonds) to enhance the solvent properties. Such properties might include viscosity, density, surface tension, or attraction for the solute. In these cases, the mutual solubility curve may appear as in Fig. 7.2-4 when the solvent mixture is plotted at one vertex. Reasons for solvent blending may include improved solvent selectivity, interfacial tension, reduced solvent phase viscosity, and increased density differences between the two phases. A solvent that forms stable emulsions when mixed with the diluent phase, for example, may be suitable for use when it is modified with a suitable inert paraffinic material.

Other representations of equilibrium data are in common use. For example, a Hand\(^3\) plot is often attractive as well as distribution diagrams and the use of other coordinate systems (e.g., rectangular or Janecke coordinates). Since the use of these systems has been described in detail elsewhere,\(^4-6\) they simply are mentioned here.

### 7.3 STAGEWISE AND DIFFERENTIAL CONTACTING CALCULATION METHODS

Sections 7.3-7.5 deal with mass transfer between two liquid phases in countercurrent flow through packed and plate columns and in agitated vessels. In such cases the details of velocity distribution in the two phases
FIGURE 7.2-2 Effect of temperature on the mutual solubility curve of ethanol–water–20% tridecyl alcohol in Norpar 12.¹

FIGURE 7.2-3 Equilibrium data for the system n-heptane, methylcyclohexane, and aniline at 25°C. (Data from Ref. 2).
are unknown, so that the convective contribution to transfer cannot be formulated quantitatively. Therefore, one must resort to empirical correlations of mass transfer rates with operating conditions, physical properties, and system geometry in the manner to be described.

Continuous-contact or packed columns are usually filled with Raschig rings, Pall rings, Berl saddles, Lessing rings, or other types of packing to promote intimate contact between the two phases. Continuous contact is maintained between the two countercurrent streams throughout the equipment, which necessitates a treatment based on a differential section of packing.

In contrast, stagewise contactors feature intermittent, rather than continuous, contact between the phases. The stages often take the form of plates or trays of varied design, arranged vertically above each other in a column. Alternatively, stagewise contactors can be constructed from a series of mixer-settlers. The two phases enter a stage from opposite directions in countercurrent flow, mix together to facilitate transfer, then separate and leave the stage. When the two phases leave in a state of equilibrium, the stage is said to be an "ideal" or "theoretical" one. This concept has been extended to packed columns by defining the height (of packing) equivalent to a theoretical stage (HETS), such that the streams leaving this section are in equilibrium.

7.3-1 The Operating Line

The relationship giving the composition of the two phases passing one another at a given location in the system is obtained by material balance and is called the operating line. Consider the column sketched in Fig. 7.3-1. Note carefully the locations of sections 1 and 2, which are directionally the same as that used by some authors and the reverse of that used by others.

A balance on component A over the differential volume $S \, dH$ gives

$$d(Gy_A) = d(Lx_A) \tag{7.3-1}$$

Integrating between section 1 and any section within the column leads to

$$y_A = \frac{L}{G}x_A + \frac{G_1y_{A1} - L_1x_{A1}}{G} \tag{7.3-2}$$

This is the equation for the operating line; it is valid for either packed or stagewise contactors and it relates $y_A$ to $x_A$ at any section within the column. In the general case, $L$ and $G$ may vary with location, giving a curved operating line. Equation (7.3-2) is effectively linear, however, in those cases of very dilute streams for which composition changes due to mass transfer have a negligible effect on $L$ and $G$. Graphical representation of the operating line is also readily possible when phases $G$ and $L$ each consist only of inert
FIGURE 7.3-1 Terminology for a continuous column. \( A \), total interfacial area; \( G, L \), flow rates of phases \( G \) and \( L \) (moles/time); \( H \), column height; \( S \), cross-sectional area of empty column; \( x_A, y_A \), concentration of component \( A \) in phases \( L \) and \( G \) (mole fraction). \( G \) is the raffinate phase and \( L \) is the extract phase.

(nontransferring) material and component \( A \). Thus, if \( G' \) and \( L' \) are flow rates of nontransferring components in phases \( G \) and \( L \) (in moles/time), then

\[
G' = G(1 - y_A) = G_1(1 - y_{A1}) = G_2(1 - y_{A2}) \tag{7.3-3}
\]
\[
L' = L(1 - x_A) = L_1(1 - x_{A1}) = L_2(1 - x_{A2}) \tag{7.3-4}
\]

Substituting for \( L, L_1, G, \) and \( G_1 \) in Eq. (7.3-2) and rearranging,

\[
\frac{y_A}{1 - y_A} = C_1 + C_2 \frac{x_A}{1 - x_A} \tag{7.3-5}
\]

where

\[
C_1 = \frac{y_{A1}}{1 - y_{A1}} - C_2 \frac{x_{A1}}{1 - x_{A1}} \tag{7.3-6}
\]
\[
C_2 = \frac{L'}{G'} \tag{7.3-7}
\]

The quantities \( x_{A1}, x_{A2}, y_{A1}, y_{A2}, G_2, \) and \( L_1 \) are normally known or can be calculated, so that \( L' \) and \( G' \) can be determined from Eqs. (7.3-3) and (7.3-4). The operating line is plotted readily from Eq. (7.3-5), with the terminal points \((x_{A1}, y_{A1})\) and \((x_{A2}, y_{A2})\).

When conditions required for the two simple cases just described are not met, the operating curves may be located on the \( x_A-y_A \) diagram by appropriate use of the triangular diagram, as described below.

7.3-2 Triangular Diagrams and the Line Ratio Principle

Ternary systems are often represented on equilateral or right triangular coordinates, as sketched in Fig. 7.3-2a.

Any point on one of the sides of the triangle represents a binary mixture of the components at each end of that side. For example, mixture \( J \) contains (line length \( CJ \)/line length \( AC \)) 100% of \( A \), with the remainder being \( C \).
A point inside the triangle, such as S, represents a ternary mixture. The perpendicular distance of the point S from a given side of the equilateral triangle gives the percentage (or fraction) of the component represented by the apex opposite that side. The vertical height of the equilateral triangle represents 100% (or 1.0). In the right triangle—which need not be isosceles—the composition of a ternary mixture S is identified conveniently in terms of the scales of axes AB and BC. A point outside the triangle represents an imaginary mixture, of negative composition.

The right-triangular diagram is more convenient since it may be constructed readily to any scale, with enlargement of any particular region of interest. Accordingly, this representation will be used here.

Liquid extraction exhibits at least two common forms on the triangular diagram. Figure 7.3-2b shows both type I and type II systems, the former being characterized by the plait point. In type I systems, the tie lines linking equilibrium phases shrink to a point at the plait point, so that the two conjugate phases become identical.

When reflux, which is discussed later in more detail, is used in a type II system the feed is theoretically separable into pure A and B after solvent removal. This contrasts with type I systems for which, even with the use of reflux, a feed mixture is theoretically separable only into pure B at one end of the unit and a mixture of A and B at the other end—after removal of solvent. Thus, the most concentrated extract obtainable is E*.

Any point in the two-phase region of Fig. 7.3-2b represents an overall mixture that separates into two phases linked, at equilibrium, by a tie line.

Consider the steady flow of two ternary streams into the mixer shown in Fig. 7.3-3. The streams enter at the rates of $M$ and $N$ mol/h and a third stream leaves at $P$ mol/h. In representing this process on the triangular diagram it can be shown that, when streams $M$ and $N$ are mixed, the resultant stream $P$ lies on the line $MN$ such that

$$\text{moles (or mass) of } N/\text{hour} = \frac{N}{M} \times \text{(length of) line } MP$$

$$\text{moles (or mass) of } M/\text{hour} = \frac{M}{P} \times \text{(length of) line } PN$$

Since the triangle used in Fig. 7.3-3 is neither equilateral nor isosceles, it follows that graphical addition of streams and the line ratio principle are independent of the shape of the triangle.
FIGURE 7.3-3 Mixing of streams and the line ratio principle.

7.3-3 Use of Triangular Diagrams to Locate Operating Curves on Distribution Diagrams

Whereas the determination of the number of theoretical stages required for a prescribed separation can usually be performed by appropriate construction on the triangular diagram, the number of transfer units (used to establish the necessary height of a packed column) is evaluated most readily via the distribution \( x_A - y_A \) diagram. The latter may also be applied to stagewise evaluation using the usual McCabe-Thiele-type stepwise construction procedure. To facilitate both stagewise and packed column design, therefore, the location of the operating and equilibrium curves on the distribution diagram are outlined, via appropriate construction on the triangular diagram. This procedure is generally useful in cases where the simplified conditions for location of the operating line, given earlier, do not apply.

EXTRACTION WITHOUT REFLUX

Consider the countercurrent extraction of solute A from solution in B using pure solvent C. The operation is performed in the column shown in Fig. 7.3-1, which may be either continuous-contact (packed) or stagewise.

To obtain the operating curve on the \( x_A - y_A \) distribution diagram, the terminal streams, raffinate \( G_t \), solvent \( L_1 \), and feed \( G_2 \), are located on the triangular diagram of Fig. 7.3-4. This diagram shows the solubility or binodal curve for a type I system.

A material balance around the column in Fig. 7.3-1 gives

\[
G_2 + L_1 = G_1 + L_2 = \Sigma
\]

so that from the line ratio principle,

\[
\frac{G_2}{G_2 + L_1} = \frac{\text{length of line } L_1 \Sigma}{\text{length of line } L_1 G_2}
\]

This enables the location of \( \Sigma \) on Fig. 7.3-4; the point \( L_2 \) — the extract product — then lies at the intersection of the binodal curve and the extended line \( G_1 \Sigma \). Next, consider the net flow of material in the \( G \) direction in Fig. 7.3-1: \( G_1 - L_1 = G - L = G_2 - L_2 = \Delta \). The lines \( L_2 G_2 \) and \( L_1 G_1 \) are extended to intersect at the difference point \( A \) in accordance with the graphical addition (or subtraction) of streams principle demonstrated in Fig. 7.3-3.

The fixed location of \( \Delta \) for the entire column is readily demonstrated by successive balances on any two of the three components involved. Random lines from \( \Delta \) intersect the binodal curve at \( w_{AB} \) on the B-rich side and at \( w_{AC} \) on the C-rich side. These intersections, when converted to mole fractions, give points \( (x_A, y_A) \) on the operating curve of Fig. 7.3-5. (Note: \( w_{AB} = \text{mass fraction of } A \text{ in the B-rich phase.} \) It is also acceptable to construct a \( W_{AB} \) versus \( W_{AC} \) diagram and perform calculations similar to those that will be described for the \( x-y \) diagram.

The equilibrium curve is plotted in Fig. 7.3-5 from the terminal points or each experimentally determined tie line on the triangular diagram. The use of Fig. 7.3-5 in determining either the number of theoretical stages needed (for stagewise contact) or the number of transfer units needed (for packed column contact) will be discussed shortly.

Tie lines, of course, cannot cross in the two-phase region within the binodal curve of Fig. 7.3-4. Furthermore, a line from \( \Delta \) must not coincide with a tie line in the region between lines \( L_1 \Delta \) and \( L_2 \Delta \), since this would cause contact (pinch) between the operating and equilibrium curves of Fig. 7.3-5, signifying zero driving force for the transfer of A. Such coincidence occurs in the use of a minimum solvent-to-feed ratio. The condition is avoided by using solvent in excess of the minimum solvent-to-feed ratio for the prescribed separation, which is established as follows with reference to Fig. 7.3-6.
FIGURE 7.3-4 Triangular diagram for extraction without reflux.

All tie lines to the left of—and including—the one that extends through \( G_2 \) are extrapolated to intersect the extended line \( L_1G_1 \). The farthest intersection (if below the triangle) or the nearest (if above the triangle) gives \( A_w \) corresponding to the minimum solvent-to-feed ratio. The line \( A_nG_2 \) then locates \( L_{1n} \), at its intersection with the binodal curve. \( E_m \) is found at the intersection of lines \( L_xG_2 \) and \( G_1L_{2n} \), so that

\[
L_{1,\text{min}} = \frac{\text{line length } G_2E_m}{\text{line length } L_1E_m}
\]

An operable solvent flow rate will exceed \( L_{1,\text{min}} \).

FIGURE 7.3-5 Distribution diagram for extraction without reflux, as in Fig. 7.3-1, showing both the operating and equilibrium curves.
Extraction with Reflux

Reflux can be employed in countercurrent columns or in a series of mixer-settlers in liquid-liquid extraction. This allows the solute-rich stream leaving the unit to attain a higher concentration of solute than that which would be in equilibrium with the feed. In considering the separation of a binary mixture it must be realized, however, that reflux does not enhance the degree of separation between components of the feed unless they both transfer significantly into the phase that extracts the solute. (The proportions in which the two components transfer must be different from that in the feed for the separation to be feasible.)

The operation is shown in flowsheet form on the left side of Fig. 7.3-7, while the right side of the same figure identifies some of the terminology to be used. The C remover may be a distillation column, an evaporator, or another liquid extraction unit. It withdraws sufficient C from phase $L$ to convert it to a G phase.

Material Balances in Fig. 7.3-7

A balance around the C remover results in

$$L - G_0 = L_0 + G_p = \Delta_1$$

A similar balance around the C remover plus any portion of the column above the feed plane gives

$$L - G_0 = L - G = \Delta_1$$

Converting Eq. (7.3-11) into component B and C balances,

$$L(x_B)_{L_1} - G_0(y_B)_{G_0} = L(x_B) - G(y_B) = \Delta_1(x_B)_{\Delta_1}$$

$$L(x_C)_{L_1} - G_0(y_C)_{G_0} = L(x_C) - G(y_C) = \Delta_1(x_C)_{\Delta_1}$$

Equations (7.3-11)-(7.3-13) demonstrate that the differences between adjacent streams in the column section above the feed plane are constant in amount and composition. These differences therefore may be represented by the single point $\Delta_1$ on the triangular diagram. The "difference point" $\Delta_1$ is located in Fig. 7.3-8 from the following development in terms of the reflux ratio, $G_0/G_p$.

Streams $G_0$, $G_p$, and $G_0$ in Fig. 7.3-7 are identical in composition and are represented by a common
A = Solute
B = Diluent solvent
C = Extracting solvent

Solute transfer is from $G$ to $L$ throughout

**FIGURE 7.3-7** Liquid–liquid extraction with extract reflux $G_0$.

point in Fig. 7.3-8. The compositions of $L_0$ and $G_p$ typically are specified and Eq. (7.3-10) shows that the points representing streams $L_0$, $G_p$, $G_0$, $L_1$, and $\Delta_1$ all lie on the same straight line because of the graphical addition of streams and the line ratio principle. Then from Eq. (7.3-10),

$$\frac{G_p}{\Delta_1} = \frac{\text{line } L_0 \Delta_1}{\text{line } L_0 G_p} \quad \text{and} \quad \frac{G_0}{\Delta_1} = \frac{\text{line } L_1 \Delta_1}{\text{line } L_1 G_0}$$

The reflux ratio typically is specified and since

$$\frac{G_0}{G_p} = \frac{\Delta_1}{\Delta_1} \cdot \frac{\text{line } L_1 \Delta_1}{\text{line } L_1 G_0} \cdot \frac{\text{line } L_0 G_p}{\text{line } L_0 \Delta_1} \quad (7.3-14)$$

$\Delta_1$ can be located from the readily measurable line lengths $L_1 G_0$, $L_0 G_p$, and $L_0 L_1$ or from the projections of these lines onto the appropriate axes of the graph.

A material balance over the lower portion of the column below the feed plane in Fig. 7.3-7 shows that

$$\bar{G} - \bar{L} = G_2 - L_2 = \Delta_2 \quad (7.3-15)$$

This equation may be converted into component B and C balances analogous to Eqs. (7.3-12) and (7.3-13), to demonstrate that the difference between adjacent streams in the column section beneath the feed is constant in amount and composition. This quantity can therefore be represented by a second single difference point $\Delta_2$ on the triangular diagram. Location of $\Delta_2$ requires the following material balance about the feed plane:

$$F + \bar{L} + G = L + \bar{G}$$

$$F = L - G + \bar{G} - \bar{L}$$

$$= \Delta_1 + \Delta_2 \quad (7.3-16)$$
The problem specifications will enable points F, G₂, and L₀ to be located in Fig. 7.3-8. Equations (7.3-15) and (7.3-16) show that Δ₂ lies at the intersection of the extended lines L₂G₂ and Δ₁F, in accordance with the graphical addition of streams principle. It is clear that whether Δ₂ lies above or below the triangle merely depends on the relative positions of points L₂, G₂, F, and Δ₁. Thus, when Δ₂ lies above the diagram, Eq. (7.3-16) [together with Eq. (7.3-15)] shows that Δ₁ − F = −Δ̂₂. If L₀ or L₂ contains no A or B the corresponding point coincides with apex C.

The operating line on the distribution diagram (y_A versus x_A) may now be obtained from the triangular diagram of Fig. 7.3-8 in the following manner. Corresponding x_A and y_A values for the two phases at a given column cross-section are obtained from the intersection of random lines from the appropriate difference point (Δ₁ or Δ₂) with the upper and lower boundaries, respectively, of the two-phase region. Where reflux is used, as in Fig. 7.3-7, two difference points are required and a discontinuity will occur between the two operating curves representing the two sections of the column. The discontinuity will appear at the point on the distribution diagram corresponding to the intersection of the line FA with the upper and lower boundaries of the two-phase region on the triangular diagram. The procedure is sketched in Fig. 7.3-9.

The equilibrium curve on the distribution diagram may be obtained from the values of y_A and x_A read from the terminals of tie lines on the triangular diagram. One such point (L*, G*) is shown on the equilibrium curve in Fig. 7.3-9. The distribution diagram is now ready for the evaluation of either the number of theoretical stages or the NTU, as described later.

As noted earlier, reflux will only be of value in increasing the degree of separation between the feed components when the transfer of A into the C-rich phase is accompanied by significant transfer of B. Consequently, the single-phase region near the C apex of Fig. 7.3-8 will always be present to a significant extent in such cases. (In other words, the upper boundary of the two-phase region will not coincide with line AC when reflux will enhance separation.) The construction is unchanged if the lower boundary of the two-phase region is indistinguishable from the AB axis of the triangle.

**EVALUATION OF TERMINAL STREAM FLOW RATES IN FIG. 7.3-7**

In the general case, streams F, L₂, L₀, G_p, and G₂ will each contain all three components, A, B, and C, and the composition of these five streams will be specified. Also given will be the flow rate of F and the reflux ratio G₀/G_p to be used. It is then necessary to estimate the flow rates of streams G_p, G₂, L₂, and L₀, the latter determining the size of the C remover needed for the operation. Estimation of these flow rates is performed conveniently on the triangular diagram.

An overall material balance around the extraction unit in Fig. 7.3-7 gives

\[ F + L₂ = G₂ + G_p + L₀ = G₂ + Δ₁ = Σ \]  

\[ \text{(7.3-17)} \]

This enables location of Σ and other relevant points in Fig. 7.3-10. Application of the line ratio principle then allows evaluation of both L₂ and Σ, since

\[ L₂ = F \left( \frac{\text{line } ∑F}{\text{line } ∑L₂} \right) \]
FIGURE 7.3-9 Construction of the operating lines on the distribution diagram via random lines from $\Delta_1$ and $\Delta_2$ on the triangular diagram. The operation portrayed is that in Fig. 7.3-7.

Next, let

\[
\frac{G_2}{\Delta_1} = N_1 \text{ so } \Delta_1(1 + N_1) = \Sigma
\]

where $N_1 = (\text{line } \Sigma \Delta_1)/(\text{line } G_2 \Sigma)$ is known from Fig. 7.3-10; hence, we can evaluate $\Delta_1$ and $G_2$. From Eq. (7.3-10),

\[
L_0 + G_p = \Delta_1 = \text{known}
\]

\[
\frac{L_0}{G_p} = \frac{\text{line } \Delta_1 G_p}{\text{line } \Delta_1 L_0} = N_2 = \text{known}
\]

\[
L_p = N_2 G_p \quad \therefore G_p(1 + N_2) = \Delta_1
\]

hence, we can evaluate $G_p$ and $L_0$.

FIGURE 7.3-10 Construction to evaluate flow rates of terminal streams in Fig. 7.3-7.
A limiting condition in column operation is that of total reflux, in which the flow rates of feed and product streams \( G_2 \) and \( G_p \) are all zero and \( L_2 = L_0 = \Delta \) in amount and composition. The result on triangular coordinates is shown in Fig. 7.3-11. The intersection of random lines from \( \Delta \) with the upper and lower bounds of the two-phase region would provide points on the single operating curve on an \( x_A-y_A \) diagram. No discontinuity would appear in the curve since \( F = 0 \).

In the special case of \( L_2 \) and \( L_0 \) consisting of pure \( C \), these points coincide with apex \( C \). This condition corresponds to the conventional definition of total reflux. However, there is an infinite number of operating lines corresponding to total reflux, depending on the particular identical composition of \( L_2 \) and \( L_0 \) and the consequent location of \( \Delta \).

**MINIMUM REFLUX RATIO IN FIG. 7.3-7**

Suppose that, on the distribution diagram of Fig. 7.3-9, the operating curve intersects or becomes tangent to the equilibrium curve at some point between the terminals of the column. At such a pinch point the two adjacent phases have attained a state of equilibrium, and the driving force causing mass transfer \((y_A - y_{AI})\) has become zero. This, however, requires an infinitely tall column: borrowing from Eq. (7.3-30) developed later in this section, the \( NTU_{DG} \) needed to reach this condition is infinite. Referring to the triangular diagram of Fig. 7.3-9, the condition just described evidently corresponds to coincidence between a tie line and a random line from \( \Delta_1 \) or \( \Delta_2 \). This amounts to location of \( \Delta_1 \) or \( \Delta_2 \) such that some tie line above or below the feed will extrapolate through the difference point appropriate to that section of the column. The situation must be avoided as follows to ensure a column of finite dimensions.

Equation (7.3-14) shows that \( \Delta_1 \) approaches \( L_0 \) on the diagram as the reflux ratio increases. Thus the minimum reflux ratio corresponds to \( \Delta_1 \) located at the closest intersection to \( L_0 \) of all extended tie lines in the column section above the feed with line \( L_0G_p \). ("Above the feed" is in the sense of the right-hand side of Fig. 7.3-7; this could be the lower part of the column in a liquid extraction operation in which the extract phase is more dense than the raffinate phase.) The point \( \Delta_{1m} \) located in this manner is then used to find \( \Delta_{2m} \) at the intersection of lines \( F\Delta_{1m} \) and \( G_2L_2 \) extended, as shown in Fig. 7.3-12.

If, however, any extended tie lines in the column section below the feed intersect extended line \( G_2L_2 \) between \( \Delta_{2m} \) and \( L_2 \), then the intersection closest to \( L_2 \) finally determines \( \Delta_{2m} \). In this case, the intersection of the line \( \Delta_{2m}F \) with line \( L_0G_p \) finally determines \( \Delta_{1m} \), at a point farther from \( L_1 \) than found earlier by extension of tie lines between \( G_p \) and \( F \).

The minimum reflux ratio is then obtainable from Eq. (7.3-14) and Fig. 7.3-12 as

\[
\frac{G_0}{G_{p, \min}} = \frac{\text{line } L_1\Delta_{1m}}{\text{line } L_1G_0} \cdot \frac{\text{line } L_0G_p}{\text{line } L_0\Delta_{1m}}
\]

(7.3-18)

The corresponding minimum ratio of solvent to feed is found from the relationship

\[
\left( \frac{L_2}{F} \right)_{\min} = \frac{\text{line } \Sigma_mF}{\text{line } \Sigma_mL_2}
\]

(7.3-19)

This follows from Eq. (7.3-17).
Figure 7.3-12 Construction to evaluate the minimum reflux ratio and the minimum solvent-to-feed ratio in Fig. 7.3-7.

7.3-4 Stagewise Contact Calculations

Suppose that the extraction in Figs. 7.3-1 and 7.3-5 is occurring in an extraction unit with stagewise contacting. If the feed stage, labeled "2" in Fig. 7.3-1, is symbolized by a horizontal line, the streams entering and leaving it may be sketched as in Fig. 7.3-13a. If the stage is ideal, $y_{A2}$ and $x_{A2}$ are in equilibrium and therefore constitute a point on the equilibrium curve in Fig. 7.3-13b.

Furthermore, as explained when deriving the operating line earlier, the points $(x_{A2}, y_{A2})$ and $(x'_{A2}, y'_{A2})$ lie on the operating line. Thus, the feed stage (2) may be represented by the shaded "step" between the operating and equilibrium curves of the distribution diagram in Fig. 7.3-13c.

The use of these principles in solving mass balances and equilibrium relationships in sequence leads to a determination of the number of ideal stages required for a specified separation. An example illustrating the graphical solution of component mass balances and equilibrium relationships is given by the broken line construction in Fig. 7.3-5, which shows the need for approximately 3.6 ideal stages. The procedure for determination of the stage requirements in an extraction unit with reflux is entirely analogous to that just described. Considering the $x$-$y$ diagram in Fig. 7.3-9, the ideal stage at which the stagewise calculations move from one operating line to the other (at the point $L_c$, $G_c$) is the stage at which the feed is to be introduced.

7.3-5 Differential Contact in Packed Columns

The continuous contact between phases provided by packed columns requires a differential treatment for a horizontal "slice" of the column, followed by integration over the column height.

Transfer Units in Extraction

The transfer of component $A$ from one phase to the other is not accompanied by significant transfer in the reverse direction, so that $L$ and $G$ are not constant between sections 1 and 2 of Fig. 7.3-1. The rate equations (7.1-41) are written in differential form in terms of $x_A$ and $y_A$ as follows:

\[
\frac{d(N_A)}{S} = k_r a(y_A - y_A^*)dH = k_r a(x_A^* - x_A)dH
\]

\[
= K_r a(y_A - y_A^*)dH = K_r a(x_{AC} - x_A)dH
\]  

(7.3-20)

where $dV_0 = S \, dH$. Now

\[
d(N_A) = d(Gy_A) = -d(Lx_A)
\]  

(7.3-21)
If it is assumed either that the solute \((A)\) is the only component being transferred or that the solute transfer is accompanied by an equimolal countertransfer of the respective solvents (non-\(A\)) between phases, then

\[
dG = d(Gy_A) = G \frac{dy_A}{1 - y_A} \quad \text{(7.3-22)}
\]

and

\[
dL = d(Lx_A) = \frac{L \, dx_A}{1 - x_A} \quad \text{(7.3-23)}
\]

Combining Eqs. (7.3-20)-(7.3-23) and integrating,

\[
\int_{y_A}^{y_{A2}} \frac{dy_A}{1 - y_A} = \int_{x_A}^{x_{A2}} \frac{dx_A}{1 - x_A} = \int_{y_{A1}}^{y_{A2}} \frac{G}{SK_a (1 - y_A)(y_A - y_{A1})} \, dy_A = \int_{x_{A1}}^{x_{A2}} \frac{L}{SK_a (1 - x_A)(x_A - x_{A1})} \, dx_A \quad \text{(7.3-24)}
\]

If the process is interpreted in terms of the two-film theory, Eqs. (7.1-45) and (7.1-46) show that the mass transfer coefficients are dependent on the concentration of component \(A\) because of the term \((1 - y_{A1})LM\) or \((1 - x_{A1})LM\) in the denominator of the right-hand side of each equation. Accordingly, from Eqs. (7.1-45) and (7.1-46), if \(D_G\) and \(D_L\) do not vary, the quantities \(k_r(1 - y_{A1})L\), \(k_r(1 - x_{A1})L\), \(K_r(1 - y_{A1})L\), and \(K_r(1 - x_{A1})L\) should be independent of concentration (assuming constant \(m\) in the case of the overall mass transfer coefficients), where

\[
k_r(1 - y_{A1})L = \frac{k_r(y_A - y_{A1})}{\ln [(1 - y_{A1})(1 - y_A)]} \quad \text{(7.3-25)}
\]

\[
k_r(1 - x_{A1})L = \frac{k_r(x_{A1}^* - x_A)}{\ln [(1 - x_{A1})(1 - x_{A1}^*)]} \quad \text{(7.3-26)}
\]

\[
K_r(1 - y_{A1})L = \frac{K_r(y_A - y_{A1})}{\ln [(1 - y_{A1})(1 - y_A)]} \quad \text{(7.3-27)}
\]

\[
K_r(1 - x_{A1})L = \frac{K_r(x_{A1}^* - x_A)}{\ln [(1 - x_{A1})(1 - x_{A1}^*)]} \quad \text{(7.3-28)}
\]
Equation (7.3-24) may now be multiplied and divided throughout by either \((1 - y_A)_{LM}\) or \((1 - x_A)_{LM}\), to obtain

\[
H = \int_{y_A}^{y_{2A}} \frac{G/S}{k_A(a(1 - y_A))_{LM}} \frac{(1 - y_A)_{LM} dy_A}{(1 - y_A)(y_A - y_A)}
\]

\[
= \int_{x_A}^{x_{2A}} \frac{L/S}{k_A(a(1 - x_A))_{LM}} \frac{(1 - x_A)_{LM} dx_A}{(1 - x_A)(x_A - x_A)}
\]

\[
= \int_{y_A}^{y_{2A}} \frac{G/S}{K_A(a(1 - y_A)_{0,LM}} \frac{(1 - y_A)_{0,LM} dy_A}{(1 - y_A)(y_A - y_A)}
\]

\[
= \int_{x_A}^{x_{2A}} \frac{L/S}{K_A(a(1 - x_A)_{0,LM}} \frac{(1 - x_A)_{0,LM} dx_A}{(1 - x_A)(x_A - x_A)}
\]

(7.3-29)

Various experimental correlations for mass transfer coefficients show that \(k_y\) or \(k_x\) is proportional to \(G^{0.8}\) or \(L^{0.8}\) and this relationship—at least in terms of mass velocities—has been extended to include the capacity coefficients \(k_{yA}\) and \(k_{xA}\). It is therefore customary to consider the capacity coefficients as varying roughly with the first power of flow rate of the corresponding phase between sections 1 and 2. The considerations following Eq. (7.3-24) to the present point provide some justification for regarding quantities such as \(G/k_y\) or \(L/k_x\) as constant for a particular situation—generally at an average of the values at sections 1 and 2. These quantities are therefore removed from the integral signs in Eq. (7.3-29) to give

\[
H = \left[ \frac{G/S}{k_A(a(1 - y_A))_{LM}} \right] \int_{y_A}^{y_{2A}} \frac{(1 - y_A)_{LM} dy_A}{(1 - y_A)(y_A - y_A)}
\]

\[
= \left[ \frac{L/S}{k_A(a(1 - x_A))_{LM}} \right] \int_{x_A}^{x_{2A}} \frac{(1 - x_A)_{LM} dx_A}{(1 - x_A)(x_A - x_A)}
\]

\[
= \left[ \frac{G/S}{K_A(a(1 - y_A)_{0,LM}} \right] \int_{y_A}^{y_{2A}} \frac{(1 - y_A)_{0,LM} dy_A}{(1 - y_A)(y_A - y_A)}
\]

\[
= \left[ \frac{L/S}{K_A(a(1 - x_A)_{0,LM}} \right] \int_{x_A}^{x_{2A}} \frac{(1 - x_A)_{0,LM} dx_A}{(1 - x_A)(x_A - x_A)}
\]

(7.3-30)

If the correction factors \((1 - y_A)_{LM}/(1 - y_A)\) or \((1 - x_A)_{LM}/(1 - x_A)\) are neglected for conceptual purposes, then the integrals represent the total change in composition of a given phase between sections 1 and 2 divided by the available driving force causing the transfer. Each integral is therefore a measure of the difficulty of separation and has been defined by Chilton and Colburn as the number of transfer units (NTU). Clearly, the ratio \(H/NTU\) may be called the height of a transfer unit (HTU) and is given by the quantity outside each integral in Eq. (7.3-30). The latter relationship shows that there is an individual and an overall NTU expression for each of the \(G\) and \(L\) phases, combined with corresponding HTU expressions as follows:

\[
H = (HTU)_G(NTU)_G = (HTU)_L(NTU)_L = (HTU)_OC(NTU)_OC
\]

(HTU)_OL(NTU)_OL

(7.3-31)

By setting the NTU equal to unity, and with the simplification noted below Eq. (7.3-30), it is evident from that equation that the HTU is the column height necessary to effect a change in phase composition equal to the average driving force in the region under consideration. The evaluation of NTU and HTU to determine the column height needed to obtain a specified separation will be considered shortly.

It may be noted that, although the rate equations (7.3-20) could be integrated to obtain \(H\) using mass transfer coefficients, the procedure in terms of transfer units is preferable. This is because the coefficients are strongly dependent on flow rate and composition and therefore would vary with position. In contrast, the HTU has been shown to be less dependent on both flow rate and composition changes in a given application, and this greater stability renders it more suitable for design.

**APPORXIMATE EXPRESSIONS FOR NTU IN UNIMOLAL UNIDIRECTIONAL DIFFUSION**

In many cases the evaluation of the integrals in Eq. (7.3-30) is facilitated by the use of the arithmetic mean in place of the logarithmic mean \((1 - y_A)_{LM}\) or \((1 - x_A)_{LM}\), incurring only a small error. Thus, in the case of \((NTU)_G\),

\[
(1 - y_A)_{LM} \approx \frac{(1 - y_A^*)+(1 - y_A)}{2}
\]

(7.3-32)
Insertion in the first integral of Eq. (7.3-30) leads to

\[(NTU)_G = \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{y_A - y_A^*} + \frac{1}{2} \ln \frac{1 - y_{A1}}{1 - y_{A2}} \] (7.3-33)

The acceptability of Eq. (7.3-32) must be considered in any given case. Application of this approximation to the remaining three integrals in Eq. (7.3-30) results in

\[(NTU)_L = \int_{y_{A1}}^{y_{A2}} \frac{dx_A}{x_A - x_A^*} + \frac{1}{2} \ln \frac{1 - x_{A2}}{1 - x_{A1}} \] (7.3-34)

\[(NTU)_{OG} = \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{y_A - y_{AL}} + \frac{1}{2} \ln \frac{1 - y_{A1}}{1 - y_{A2}} \] (7.3-35)

\[(NTU)_{OL} = \int_{x_{A1}}^{x_{A2}} \frac{dx_A}{x_A - x_A^*} + \frac{1}{2} \ln \frac{1 - x_{A2}}{1 - x_{A1}} \] (7.3-36)

The reader should perhaps be cautioned regarding the incorrect forms of Eqs. (7.3-34) and (7.3-36) which are often seen in the literature, where the logarithmic terms are erroneously inverted.

**EVALUATION OF THE NTU**

The integrals in Eqs. (7.3-30) and (7.3-33)-(7.3-36) are usually evaluated numerically, for example, by graphical integration. Information for this procedure is obtained from the equilibrium curve–operating line plot on \((x_A, y_A)\) coordinates, as sketched in Fig. 7.3-14 for unimolal unidirectional diffusion (liquid extraction).

It is often inconvenient to determine interfacial compositions \((x_A^*, y_A^*)\) corresponding to each point on the operating line, so that overall NTU values are frequently determined in preference to the individual ones. In evaluating the number of G-phase transfer units, values of \(1 - y_A\) and \(y_A - y_{AL}\) are readily obtained to enable evaluation of the integrand for a series of \(y_A\) values between \(y_{A1}\) and \(y_{A2}\). (The quantity \(y_{AL} - y_{A}\) is evidently the vertical distance between the operating line and the equilibrium curve at a given \(y_A\).) The quantity \((1 - y_A)\) is used in \((NTU)_{OG}\) defined by Eq. (7.3-27). A plot such as that sketched in Fig. 7.3-15 is then prepared and the \((NTU)_{OG}\) is given by the area under the curve between the limits of integration.

It should be noted that, in the case of operation with reflux, the change in \(L\) and \(G\) below the feed plate necessitates the determination of separate NTU values for the column segments above and below the feed—namely, above and below point \((L_c, G_c)\) in Fig. 7.3-9b.

The evaluation of \((NTU)_{OL}\) may be performed in an analogous manner, noting that \(x_{AG} - x_A\) is the horizontal distance between the operating line and the equilibrium curve at a given \(x_A\).

**FIGURE 7.3-14** Evaluation of components in the expressions for NTU. The operation is shown in Fig. 7.3-1.
The selection of an NTU expression for computation is arbitrary, but normally it is considered appropriate to use the relationships corresponding to the phase offering the greater resistance to mass transfer.

**Relationship Between Overall and Individual HTUs**

In the case of unimolal unidirectional diffusion, the HTU expressions in Eq. (7.3-30) may be rearranged to give

\[
\frac{1}{K_r} = (\text{HTU})_{OC} \frac{a(1 - y_{A0,LM})}{G/S}
\]  
\[
\frac{1}{k_r} = (\text{HTU})_G \frac{a(1 - y_{A1,LM})}{G/S}
\]  
\[
\frac{1}{k_r} = (\text{HTU})_L \frac{a(1 - x_{A1,LM})}{L/S}
\]

Inserting these expressions in the first part of Eq. (7.1-40) and multiplying throughout by \(G\alpha(1 - y_{A0,LM})S\), we obtain

\[
(\text{HTU})_{OC} = (\text{HTU})_G \frac{(1 - y_{A1,LM})}{(1 - y_{A0,LM})} + \frac{mG}{L} (\text{HTU})_L \frac{(1 - x_{A1,LM})}{(1 - y_{A0,LM})}
\]  
\[
(\text{HTU})_{OC} = (\text{HTU})_L \frac{(1 - x_{A1,LM})}{(1 - x_{A0,LM})} + \frac{L}{mG} (\text{HTU})_G \frac{(1 - y_{A1,LM})}{(1 - x_{A0,LM})}
\]

A parallel development using the second part of Eq. (7.1-40) will yield

\[
(\text{HTU})_{OL} = (\text{HTU})_L \frac{(1 - x_{A1,LM})}{(1 - x_{A0,LM})} + \frac{L}{mG} (\text{HTU})_G \frac{(1 - y_{A1,LM})}{(1 - x_{A0,LM})}
\]

When the controlling resistance to transfer lies in the \(G\) phase,

\[1 - y_{A1,LM} \approx 1 - y_{A0,LM}\]

If the solutions are also dilute,

\[1 - x_{A1,LM} \approx 1 - y_{A0,LM}\]

Similarly, when the \(L\) phase is controlling,

\[1 - x_{A1,LM} \approx 1 - x_{A0,LM}\]

If the solutions are also dilute,

\[1 - y_{A1,LM} \approx 1 - x_{A0,LM}\]

Equations (7.3-40) and (7.3-41) reduce to obviously simple forms in such cases.

Packed column design is often effected by the use of HTU measurements made in a pilot plant in which the system, packing, and flow rates are the same as those to be used on the full scale.
Alternatively, interfacial areas per unit volume, \( a \), and individual mass transfer coefficients are estimated from some existing correlations, leading to formulation of the overall HTU via Eqs. (7.3-37)-(7.3-41). These procedures are described at length by Skelland and Culp (Ref. 4, Chap. 6), who also outlines the correction methods available to allow for axial mixing. The latter results in an increase in the number of transfer units required to achieve a given separation compared to the number expected on the assumption of plug flow of both phases. This assumption is often invalidated by convective mixing currents, channeling effects, recirculation, and entrainment behind the disperse-phase drops.

### 7.4 STAGEWISE CONTACT IN PERFORATED PLATE COLUMNS

Two partially miscible liquid phases may be contacted for extraction purposes in a discontinuous or stage-wise manner in columns where the stages take the form of perforated plates, fitted with downcomers to facilitate flow of the continuous phase. Bubble-cap plates have been found ineffective in extraction, because of the lower density difference, lower interfacial tension, and higher viscosity of the disperse phase, compared to gas-liquid systems.

Skelland and co-workers\(^1\)–\(^6\) have developed a procedure for the design of perforated plate extraction columns. This eliminates the need for experimentally measured stage efficiencies, which are usually costly and troublesome to obtain. Additionally, the validity of such efficiencies in scaled-up application is frequently uncertain. Currently, the procedure involves use of rate equations for mass transfer during drop formation either at the perforations or at the end of jets issuing from the perforations, during free rise or fall of the drops, and during coalescence beneath each plate, to locate a pseudo-equilibrium curve. The latter is employed instead of the actual equilibrium curve on the \( x_A - y_A \) distribution diagram in a stepwise construction between the operating and pseudo-equilibrium curves to obtain the number of real stages needed for a given separation.

When flow rates of the disperse phase are low, drop formation and detachment occur at the perforations on each plate. At higher flow rates, however, drops form at the tips of jets emerging from the perforations. Either form of operation is accommodated by the design procedure, but the jetting mode is the more desirable, since throughputs are higher and plate efficiency increases up to 2.5-fold.\(^7\)

The original presentation of the design procedure, in FORTRAN IV computer language and for nonjetting conditions,\(^1\)\(^,\)\(^3\) has been both revised and expanded to incorporate jetting operation. The computer printout gives the column diameter needed, the cross-sectional area of the downcomers, the number of perforations per plate, and the number of actual plates needed to achieve a specified separation. Good agreement was obtained with published measurements.\(^6\) The structure of the design procedure will now be outlined.

In contrast to Section 7.3, where the two phases were symbolized by \( G \) and \( L \) without regard to which was the disperse phase, it is now convenient to identify the continuous and disperse phases as \( C \) and \( D \), respectively, denoting the flow rates of each phase through the column cross section in moles/time.

Figure 7.4-1 shows the \( n \)th stage of a perforated plate extraction column, where transfer is from the continuous phase to the disperse phase. Drop formation is taking place under jetting conditions and the agitation resulting from motion of the droplets ensures constancy of \( y^*_{An} \) for a given stage. The mass transfer rate in stage \( n \) can be written in terms of the disperse phase (subscript \( d \)) as

\[
q = K_{df}A_j(y^*_{An} - y_A)_LM + K_{df}A_j(y^*_{An} - y_{df})LM + K_{dr}A_c(y^*_{An} - y_A)_LM + K_{dr}A_c(y^*_{An} - y_{Ac})LM
\]

(7.4-1)

This is the sum of the mass transfer rates to the jets (subscript \( j \)), during drop formation at the tip of each jet (subscript \( f \)), during free rise (subscript \( r \)), and during coalescence (subscript \( c \)) beneath plate \( n + 1 \). But

\[
(y^*_{An} - y_A)_LM = (y^*_{An} - y_{df})LM = (y^*_{An} - y_{Ac})LM
\]

(7.4-2)

\[
(y^*_{An} - y_A)_LM = (y^*_{An} - y_{An + 1})
\]

(7.4-3)

and if the variation in \( D \) over stage \( n \) is slight,

\[
(y^*_{An} - y_A)_LM = \frac{(y^*_{An} - y_{An}) - (y^*_{An} - y_{An + 1})}{\ln \left(\frac{y^*_{An} - y_{An}}{y^*_{An} - y_{An + 1}}\right)}
\]

(7.4-4)

Insertion in Eq. (7.4-1) results in

\[
q = (K_{df}A_j + K_{df}A_j)(y^*_{An} - y_{An}) + K_{dr}A_c\left(\frac{y_{An + 1} - y_{An}}{\ln \left(\frac{y^*_{An} - y_{An}}{y^*_{An} - y_{An + 1}}\right)}\right) + K_{dr}A_c(y^*_{An} - y_{An + 1})
\]

(7.4-5)
FIGURE 7.4-1 Plates \( n + 1 \) and \( n \) in a perforated plate liquid-liquid extraction column.

Next, the assumption is made either that solute transfer is accompanied by equimolal countertransfer of solvents between phases or that only solute (A) is transferred. Then

\[
q = D_{n+1} y_{An+1} - D_n y_{An} \quad (7.4-6)
\]

If the inlet for \( D \) is at section 2 of the column, a material balance on non-A gives

\[
D_n = \frac{D_2(1 - y_{A2})}{1 - y_{An}} \quad (7.4-7)
\]

\[
D_{n+1} = \frac{D_2(1 - y_{A2})}{1 - y_{An+1}} \quad (7.4-8)
\]

A trial-and-error process will yield \( y_{An+1} \) corresponding to a given pair of \( y_{An} \) and \( y_{An}^* \) values in the following way, if \( A_j, A_f, A_r, A_c, K_{dj}, K_{df}, K_{dr}, \) and \( K_{dc} \) are all predictable:

1. A value of \( y_{An+1} \) is assumed, corresponding to a given pair of \( y_{An} \) and \( y_{An}^* \) values in Fig. 7.4-2.
2. \( D_n \) and \( D_{n+1} \) corresponding to \( y_{An} \) and the assumed \( y_{An+1} \) are calculated next from Eqs. (7.4-7) and (7.4-8).
3. Values of \( q \) are computed from Eqs. (7.4-5) and (7.4-6).

The value assumed for \( y_{An+1} \) is correct when these two estimates of \( q \) coincide. This enables construction of the pseudoequilibrium curve, which is then used with the operating curve to step off the number of real plates needed to accomplish the desired change in \( D \)-phase composition from \( y_{A2} \) to \( y_{A1} \).

The original references give details of the methods of estimation of \( A_j, A_f, A_r, A_c, K_{dj}, K_{df}, K_{dr}, \) and \( K_{dc} \). An outline is given here, assuming that there are \( n_0 \) nozzles or perforations on each plate:

\[
A_j = n_0 \pi \left( \frac{d_n + d_e}{2} \right) L_j \quad (7.4-9)
\]

FIGURE 7.4-2 Location of the pseudoequilibrium curve and determination of actual stages.
where $d_{jc}$ is the diameter of the contracted jet at breakup, $d_n$ is the nozzle or perforation diameter, and $L_j$ is the length of the jet. The latter may be predicted with reasonable success.\(^5\)\(^6\) Also,

\[ A_j = n_0 \pi d_p^2 \]  

(7.4-10)

in which $d_p$ is the predictable diameter\(^5\)\(^6\) of the formed drops; $A_j$ is for use with coefficients based on the drop surface at detachment. Next,

\[ A_r = \frac{(A_0 - A_D) (H_p - h_c) \phi_d}{\text{volume per drop}} \]  

(7.4-11)

where the coalesced layer thickness $h_c$ and the disperse-phase holdup $\phi_d$ are predictable.\(^5\) Finally,

\[ A_r = A_0 - A_D \]  

(7.4-12)

The overall mass transfer coefficients based on the disperse phase during jetting, drop formation, free rise, and coalescence are assembled from the corresponding individual coefficients for the disperse and continuous phases, in accordance with Eq. (7.1-40), as

\[ \frac{1}{k_{d,f,r., \alpha \sigma c}} = \frac{1}{k_{d,f,r., \alpha \sigma c}} + \frac{m}{k_{d,f,r., \alpha \sigma c}} \]  

(7.4-13)

During free rise or fall, drops may be stagnant, internally circulating due to the drag of the surrounding continuous phase, or oscillating, depending on drop size, physical properties, and the presence of trace amounts of surface-active contaminants.

The correlations currently preferred for predicting the individual mass transfer coefficients in Eq. (7.4-13) are listed in Table 7.4-1 for systems nominally free from surface-active contamination. Criteria are available\(^5\) for detecting whether drops of a given system are stagnant, circulating, or oscillating.

Reductions in mass transfer rates due to the presence of trace amounts of surface-active contaminants may be substantial. These effects have been measured\(^8\) for each of the two phases during drop formation, free fall, and coalescence and, although correlation was not achieved, at least those existing relationships that came closest to the data in each case were identified. These observations were systematized by Skelland and Chadha,\(^9\) who also developed criteria for selection of the disperse phase in spray and plate extraction columns both in the presence and the absence of surface-active contamination.

### 7.5 STAGEWISE CONTACT IN MIXER-SETTLERS

Mixer-settlers have been used extensively in liquid–liquid extraction; nevertheless, they have received little theoretical or experimental attention until recently. This was perhaps due to the fact that increased stage efficiency was often attainable merely by increasing the agitator speed, without concern for the corresponding increase in energy consumption. Recent escalation of energy costs has rendered this solution less appealing, so that a closer understanding of the process is needed.

#### 7.5-1 Mixers

Hydrodynamic aspects of the operation include the minimum impeller speed needed to ensure complete dispersion of one liquid phase in the other, and the size of droplets produced under a given set of conditions, preferably during the process of mass transfer.

Skelland and Seksaria\(^1\) and Skelland and Ramsay\(^2\) showed that in some cases an impeller speed of 1000 rpm is insufficient to ensure complete dispersion. Skelland and Ramsay\(^2\) combined their own measurements with those from two other published sources to obtain the following correlation for the minimum impeller speed needed to ensure complete dispersion in a batch unit:

\[ (N_{Fr})_{\text{min}} = C^2 \left( \frac{I}{D} \right)^2 \phi^{0.106} (Ne_{c}N_{Bo})^{-0.064} \]  

(7.5-1)

$C$ and $\alpha$ are tabulated in their paper for flat- and curved-blade turbines, disk turbines, three-bladed propellers, and pitched-blade turbines as a function of position in the vessel. The average absolute deviation between Eq. (7.5-1) and experimental values was 12.7%, and the lowest value of $N_{\text{min}}$ was provided by the six-flat-blade turbine located centrally in the vessel.

Skelland and Lee\(^3\) showed that gross uniformity of dispersion was obtained with values of $N$ that exceeded $N_{\text{min}}$ by an average of about 8%. Furthermore, it was found by Skelland and Moeti\(^4\) that Eq.