# Chapter 11
# Mass Transfer Equipment

## 11.1 Introduction

Mass transfer operations are used in several food process industries in various physical separations of components from liquids or solids for recovering valuable products, or for removing undesirable food or nonfood components. They differ from mechanical separations (Chap. 5) in the controlling transport mechanism, which is mass transfer at the molecular level, while mechanical separations are based on differences in macroscopic size, shape, and density of solid particles or pieces.

Separation of components from mixtures at the molecular level requires special devices (systems) and significant amounts of energy. Separation of, e.g., salt from seawater requires a system (evaporation, crystallization, or pressure membrane) and supply of adequate energy, while dissolving salt in water is a spontaneous process, increasing the entropy of the system, according to the second law of thermodynamics (King 1982).

Typical mass transfer operations, used in food processing, are (1) distillation, used in recovering volatile components from liquids; (2) solvent extraction or leaching, used in recovering solutes from liquids or solids; (3) gas absorption for absorption of removal of gas solutes in liquids; (4) adsorption and ion exchange for removing undesirable components from fluids; and (5) crystallization for separating dissolved salts from solutions. In all these operations, the controlling mechanism is a mass transfer within the liquid or solid phase and at the phase boundaries (Table 11.1).

In some mass transfer operations, like distillation, heat transfer is involved, but it does not constitute a rate-controlling process. In some other transfer operations, both heat and mass transfer are involved, e.g., evaporation (Chap. 7) and drying (Chap. 8), which are traditionally treated as heat transfer operations, since heat transfer is usually the rate-controlling mechanism.



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**Table 11.1** Mass transfer operations (separations) in food processing

| Operation | Basis of separation | Applications |
|---|---|---|
| Distillation | Volatility | Recovery of volatiles |
| Extraction/leaching | Solubility | Sugar from beets, oil from seeds |
| Absorption | Solubility | Absorption of $O_2$, $CO_2$ |
| Adsorption ion exchange | Sorption capacity | Removal of components |
| Crystallization from solution | Solubility | Granular sugar, salt |

In addition to the mass transfer operations listed in Table 11.1, there are some newer separation processes applied to food processing, notably membrane separations (ultrafiltration and reverse osmosis) and supercritical fluid (carbon dioxide) extraction. These operations are treated as novel food processes in Chap. 12.

Mass transfer operations are based on two fundamental physical processes, i.e., phase equilibria and mass transfer. Both processes are controlled by molecular forces, and they are evaluated and predicted by molecular dynamics or empirical correlations (Reid et al. 1987).

Phase equilibria indicate the ultimate concentrations of the components of two phases, if left long enough to reach thermodynamic equilibrium, i.e., when the activity of each component is equal in both phases. Vapor/liquid equilibria are used in the analysis of distillation, liquid/liquid and liquid/solid equilibria are needed in extraction and leaching processes, and gas/solid and liquid/solid equilibria are essential in adsorption and ion exchange operations.

Phase equilibria are calculated by equating the partial pressure of the various components in the two phases. The partial pressure of a component in ideal liquid solutions is proportional to its concentration and vapor pressure (Raoult's law). In nonideal solutions, the partial pressure is also proportional to its activity coefficient, which is usually higher than one. Aqueous solutions of volatile components have very high activity coefficients, making easier the removal of food volatiles during distillation. Empirical equations have been developed for the estimation of activity coefficients in complex mixtures, using computer techniques.

Mass transfer rates in separation processes are important for the quick attainment of thermodynamic equilibrium. Mass transfer in gases and liquids is fast, due to the molecular motion, and in liquids, it can be enhanced by mechanical mixing or high flow velocity (turbulence).

Mass transfer in solid foods is slow, and it is controlled by molecular diffusion or other transport mechanisms (Gekas 1992). The effective diffusivity of water and solutes in foods depends on the molecular, micro-, and macro-structure of the solid matrix (Aquilera and Stanley 1999; Saravacos and Maroulis 2001). Empirical models, based on regression analysis of experimental data, have been suggested to estimate the mass diffusivity in various food materials.

The equipment used in mass transfer operations has been developed mainly in the chemical and petrochemical industries. Well-designed equipment is available for mass transfer operations involving gases and liquids, e.g., distillation columns and absorption towers. Equipment for solid/fluid operations, like leaching,

adsorption, and ion exchange, has been developed from empirical and industrial experience, and it is specific for a given separation system and product (Schweitzer 1988; Walas 1988; Wankat 1990; Perry and Green 1997).

Equipment used in food mass transfer operations is basically similar to the established chemical engineering equipment, with particular attention to hygienic (sanitary) design and to corrosion, due to the presence of free water in almost all food products.

## 11.2 Distillation Equipment

Stripping or exhausting is the removal of a volatile component from a mixture by steam or gas (air), usually in a multistage column. Distillation is the recovery of a valuable component by vaporization and condensation, usually in several stages. Distillation usually combines stripping with fractionation of volatile components in a column, consisting of both stripping and fractionation sections.

The design and operation of stripping and fractionation columns requires vapor/liquid equilibrium data for the estimation of the theoretical separation stages and hydraulic and mass transfer data for the design and efficient operation of the column.

### *11.2.1 Vapor/Liquid Equilibria*

In ideal solutions, the partial pressure ($p_i$) of a component ($i$) in the liquid phase is given by the Raoult's law:

$$p_i = x_i p_i^{\circ} \tag{11.1}$$

where ($x_i$) is the mole fraction (concentration) of ($i$) and ($p_i^{\circ}$) is the vapor pressure of ($i$) at the given temperature. The ($p_i^{\circ}$) is taken from tables or is calculated from the Antoine equation as a function of the temperature (Reid et al. 1987).

#### 11.2.1.1 Activity Coefficients and Relative Volatilities

Food (aqueous) mixtures (solutions) of volatile components are highly nonideal, and the partial pressure ($p_i$) is given by the equation:

$$p_i = \gamma_\iota x_i p_i^{\circ} \tag{11.2}$$

where ($\gamma_\iota > 1$) is the activity coefficient of ($i$) in the mixture.

The vapor phase in food systems can be considered as ideal, i.e., the Dalton law is applicable:

$$p_i = y_i P \tag{11.3}$$

where ($y_i$) is the mole fraction (concentration) in the vapor phase and ($P$) is the total pressure.

The assumption of an ideal vapor phase is reasonable, since most food processing operations are carried out at the atmospheric pressure or in vacuum. Nonideal gas phases characterize high-pressure operations (e.g., $P > 10$ bar), such as supercritical fluid extraction.

At equilibrium, the partial pressure of a component ($i$) is the same in both phases, i.e.,:

$$y_i P = \gamma_\iota x_i p_i^{\circ} \tag{11.4}$$

or

$$\upsilon_\iota = \left(\gamma_\iota \pi_\iota^{\circ}/\Pi\right)\chi_\iota = K_\iota \chi_\iota \tag{11.5}$$

where ($K_i$) is the partition coefficient of component ($i$) between the two phases. It should be pointed out that, for a given system, ($K_i$) is directly proportional to the activity coefficient ($\gamma_\iota$). The activity coefficients are preferred in most distillation applications, since they can be calculated and correlated, using computer techniques.

The relative volatility of component ($i$) to component ($j$) is defined by the equation:

$$\alpha_{ij} = (y_\iota/x_i)/\left(y_j/x_j\right) = \left(y_\iota/y_j\right)\left(x_j/x_i\right) \tag{11.6}$$

For ideal mixtures,

$$\alpha_{ij} = p_i^{\circ}/p_j^{\circ} \tag{11.7}$$

For nonideal mixtures at relatively low pressures (ideal vapor phase),

$$\alpha_{ij} = \left(\gamma_i/\gamma_j\right)\left(p_i^{\circ}/p_j^{\circ}\right) = \left(K_i/K_j\right) \tag{11.8}$$

The vapor/liquid equilibrium data at a constant pressure are usually plotted in ($y$–$x$) diagrams, according to the equilibrium equation:

$$y_i = \left(\alpha_{\iota j} x_i\right)/\left[1 + \left(\alpha_{ij} - 1\right)x_i\right] \tag{11.9}$$

#### 11.2.1.2 Nonideal Mixtures and Azeotropes

The activity coefficients of the various components of a nonideal mixture are determined experimentally or correlated in semiempirical or empirical relations. Various types of equilibrium stills are used to measure the concentrations of the vapor and liquid phases ($y_i$, $x_i$) from which the activity coefficient ($\gamma_i$) is calculated, according to (11.2). The activity coefficients are strong functions of concentration of the liquid mixtures, reaching unity (1) at concentrations ($x_i = 0$) and ($x_i = 1$).

Empirical correlations, used to correlate the activity coefficients, include the Margules (two-parameter), the van Laar (two-parameter), and the Wilson (*n*-parameter) equations. The Wilson equation and its modifications (e.g., the NRTL equation) are suited for computer calculations of phase equilibria of multicomponent mixtures. A generalized correlation for multicomponent equilibrium data is the UNIQUAC (Universal Quasi-Chemical) equation. The UNIFAC (Universal Function Activity Contribution) method is based on the contributions of certain structural parameters of the components of the liquid mixture, like relative volume and surface area, which are given in thermodynamic tables (Reid et al. 1987).

Phase equilibrium data on multicomponent mixtures of chemicals and petrochemicals are available in data banks, like the DECHEMA collection (Gmehling et al. 1984).

In multicomponent liquid mixtures, like chemicals and petroleum, equilibrium data are often available in the form of the partition coefficient ($K_i = y_i/x_i$, (11.5)) in various tables and diagrams. A useful application of ($K_i$) is the estimation of the bubble and dew points for mixtures at a constant pressure. The bubble point of liquid mixture is the temperature at which the liquid begins to boil, at which the following equation applies (Perry and Green 1997):

$$\sum K_i x_i = 1 \tag{11.10}$$

By analogy, the dew point of a vapor mixture, at a constant pressure, is the temperature at which the mixture begins to condense, and the following equation applies:

$$\sum (y_i/K_i) = 1 \tag{11.11}$$

Some highly nonideal mixtures, like ethanol/water, form azeotropes, i.e., the mole fraction (concentration) of a component is identical in both vapor and liquid phases, and the equilibrium curve (11.9) crosses the diagonal ($y = x$). The ethanol/water azeotrope at atmospheric pressure is $y_i = x_i = 0.894$ (mole fraction), or 95 % ethanol by volume, with a minimum boiling point of 78.1 °C. Figure 11.1 shows a ($y$–$x$) diagram for ethanol/water.

Partially soluble components, like organic aroma compounds in water, form azeotropes, with the equilibrium line becoming horizontal and crossing the

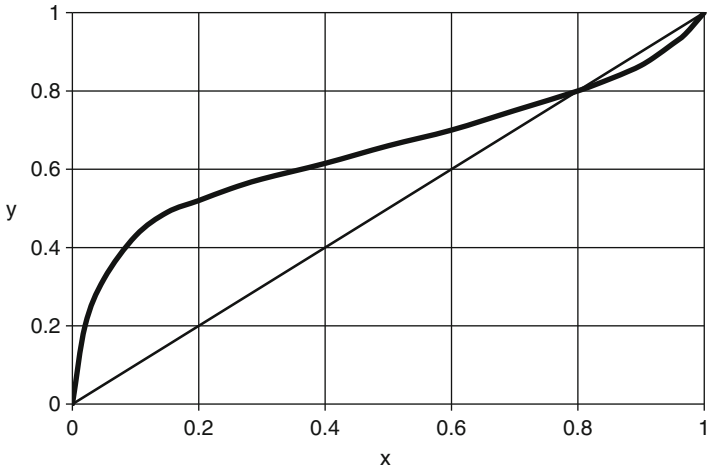


**Fig. 11.1** Vapor/liquid equilibrium diagram of ethanol/water at atmospheric pressure. Azeotrope at $y = x = 0.894$

diagonal. At low concentrations, the partially soluble components are very volatile in water, due to the strong intermolecular forces exerted. For purposes of vapor/liquid equilibria, all organic components are considered partially soluble in water, even such "insoluble" compounds like hydrocarbons.

In a partially soluble system, two liquids are formed, e.g., a lower water layer (W), saturated with the organic component (A), and an upper layer of the organic component (A), saturated with water (W). At equilibrium, the partial pressure of each component is the same in the double-layer liquid and in the vapor space above. The relative volatility of the partially soluble component (A) in the water layer can be calculated, assuming an ideal vapor phase (Dalton law, (11.3)), and that Raoult's law (11.1) is applicable to both liquid phases for the solvent, i.e., water and organic component in the lower and upper phases, respectively. Under these assumptions, the following approximate equation is derived for the relative volatility $\alpha_{AW}$ (Robinson and Gilliland 1950):

$$\alpha_{AW} = \left(x_A^A / x_A^W\right)\left(p_A^o / p_W^o\right) \tag{11.12}$$

where $(x_A^A, x_A^W)$ are the mole fractions of (A) in the phases (A) and (W), respectively, and $(p_A^o, p_W^o)$ are the vapor pressures of (pure) components (A) and (W) at the equilibrium temperature (the water temperature in very dilute mixtures).

From (11.10), it follows that the relative volatility of a partially soluble component in water (very small $x_A^W$) can be high, even for high-boiling components, i.e., compounds of vapor pressure lower than that of water ($p_A^o < p_W^o$).

### 11.2.1.3 Volatile Food Aromas

The volatile components (aromas) of foods are organic compounds, usually partially soluble in water, which form highly nonideal aqueous solutions. The high activity coefficients of these compounds in very low (ppm) concentrations (infinite dilution activity coefficients) vary widely, depending on their molecular structure and the interactions with the water and the other food components (notably sugars).

Figure 11.2 shows the activity coefficients ($\gamma_i$) of some alcohols and esters, related to food aroma, as a function of the sucrose concentration in dilute aqueous solutions. The ($\gamma_i$) values range from about 4 (ethanol) to above 1000 (ethyl butyrate). The experimental data shown in Fig. 11.2 are compared with the modified UNIFAC method (Saravacos et al. 1990).

The activity coefficients increase significantly, when the sugar concentration is increased, evidently due to a "salting-out" effect. Similar values of activity coefficients were reported by Bruin (1969) and Sancho et al. (1997).

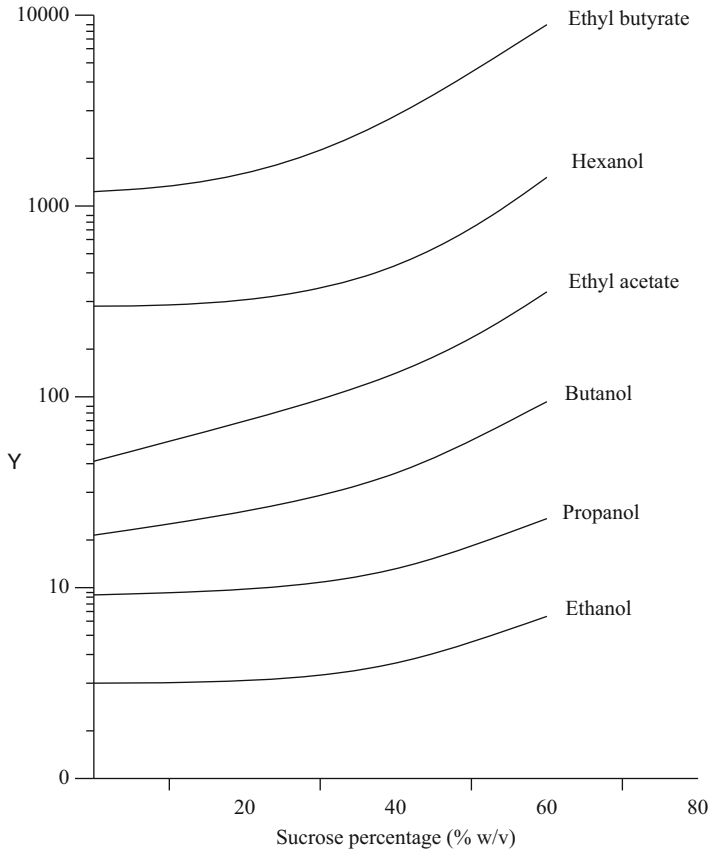


**Fig. 11.2** Activity coefficients ($\gamma$) of some fruit aroma compounds

**Table 11.2** Relative volatilities $\alpha_{AW}$ of volatile aroma compounds in water

| Component in aqueous solution | Relative volatility ($\alpha_{AW}$) | | |
|---|---|---|---|
| | Water | 15 % sucrose | 60 % sucrose |
| Ethyl anthranilate | 3.9 | 4.8 | 18.7 |
| Ethanol | 8.3 | 8.9 | 14.5 |
| *n*-Propanol | 9.5 | 10.0 | 18.5 |
| *n*-Butanol | 14.1 | 15.0 | 43.0 |
| *n*-Amyl alcohol | 23.0 | 24.7 | 105.0 |
| Hexanol | 31.0 | 34.0 | 195.0 |
| Ethyl acetate | 205 | 265 | 986 |
| Ethyl butyrate | 643 | 855 | 6500 |

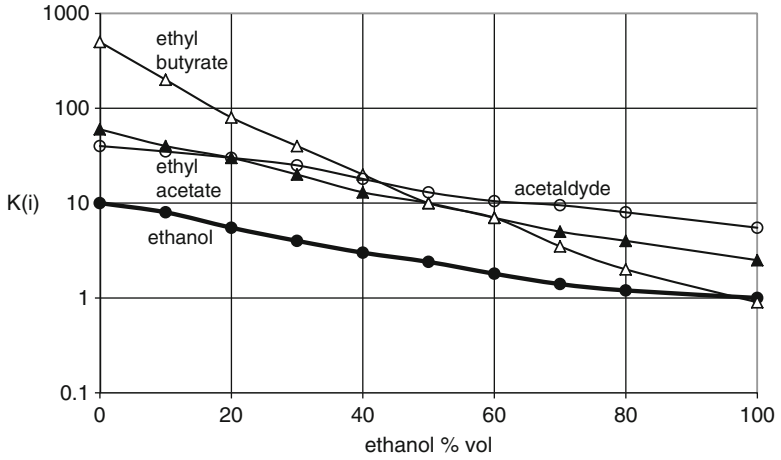


**Fig. 11.3** Partition coefficients ($K_i$) of vapor/liquid equilibria for some food volatiles in ethanol solutions

For practical applications, the relative volatilities of aroma components (A) to water (W) are more useful than the activity coefficients. Some values of the relative volatility ($\alpha_{AW}$), determined from experimental activity coefficient ($\gamma_i$) data (Marinos-Kouris and Saravacos 1974; Saravacos 1995), are shown in Table 11.2.

In general, partially water-soluble compounds, like ethyl acetate and ethyl butyrate, are more volatile than water-soluble components, like ethanol. Methyl anthranilate, an aroma component of Concord grapes, has a low relative volatility (but higher than one), due to its low vapor pressure (boiling point of 266.5 °C at atmospheric pressure), compared to the vapor pressure of water (11.10).

In the distillation of wine and ethanol-fermented products, the volatility of aroma components decreases, in general, as the ethanol concentration is increased. Figures 11.3 and 11.4 show the change (decrease) of the partition coefficient ($K_i$) at increasing ethanol concentrations. These changes in volatility are important in the

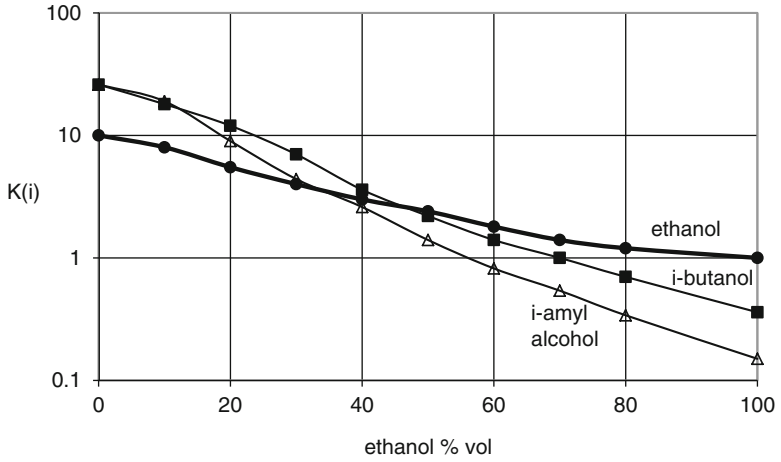


**Fig. 11.4** Partition coefficients ($K_i$) of some alcohols in ethanol solutions

distillation of ethanol-fermented liquids for the production of brandy and other alcoholic drinks (Saravacos 1970).

Of particular importance is the volatility of the higher alcohols of the fermented liquids, like propanol, butanol, amyl alcohol, and their isomers (known as "fusel oils"), which must be separated from the distilled product in the distillation column.

The volatility ($K$-value) of aroma compounds is high at low ethanol concentrations, i.e., when water is the main component of the mixture. These compounds are more soluble in ethanol, which reduces their activity coefficients and relative volatilities. At higher ethanol concentrations, e.g., above 50 % mole fraction, the partition coefficient ($K$) drops below (1), i.e., the compound is less volatile than water in the liquid mixture.

### *11.2.2 Determination of Equilibrium Stages*

The separation of volatile components of liquid mixtures is usually achieved in a series or equilibrium stages, operated countercurrently in distillation columns. Single-stage separators can separate partially a component, because of equilibrium limitations. Single-stage or flash units are used to separate some components from food liquids, e.g., off-flavors from milk in a HTST (aseptic) sterilization process.

Most stripping (removal) and fractionation (enrichment) of volatile components in a mixture is carried out in columns, using various types of trays (plates), each one of which acts as a vapor/liquid equilibrium stage. Since thermodynamic equilibrium is not possible to be reached in a tray liquid/vapor contactor, the number of trays, for a given separation, is always greater than the number of theoretical stages.

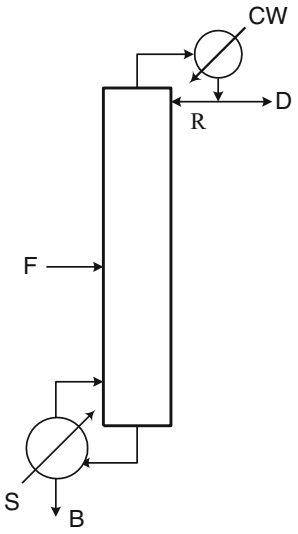


**Fig. 11.5** Diagram of a continuous distillation column

Some distillation columns, usually of low capacity, operate in continuous vapor/liquid contact, without discrete separation stages (trays). These units are known as packed columns or towers, and they are discussed in Sect. 4.3 of this chapter.

Most of the industrial distillation columns are operated as continuous units, although there are some batch columns, used in small-scale operations. Distillation systems, used in separating complex mixtures in the chemical and petrochemical industries, consist of a number of continuous distillation columns, operated and controlled by computers. The food processing industry uses limited distillation processes of medium to small size, some of them batch operated.

Figure 11.5 shows diagrammatically a simple continuous distillation column. The unit consists of a long vertical column, containing the required number of trays, made up of the stripping (lower) and the fractionating (upper) sections. The trays (perforated, bubble cups, or valves) allow the counterflow of liquid and vapors, after thorough mixing to approach equilibrium. The column is equipped with a reboiler at the bottom, which produces the required vapor flow upward, and a condenser at the top, which supplies the required liquid flow downward.

Feed (F) is introduced near the middle of the column, while a distillate (D) is received from the top and a residue (B) is obtained from the bottom. Steam (S) is used to heat the liquid in the reboiler, and cooling water (CW) is used in the condenser. The column is designed to separate a component from the feed of concentration ($x_F$) to a distillate ($x_D$) and a residue ($x_B$).

In most distillation columns, a total condenser is used, i.e., all the vapors coming out of the first (top) tray are condensed, and the liquid condensate is split into two streams, the distillate product and the reflux, which is returned to the column. In some columns, a partial condenser may be used, with the vapors coming out of the condenser as a product in equilibrium with the liquid condensate, which is returned

to the column as the reflux. In this case, the condenser acts as an additional separation stage of 100 % efficiency.

The number of theoretical stages in a distillation column is estimated either graphically or by analytical methods. In both methods, vapor/liquid equilibria of the system are required. These methods were developed for the distillation of binary mixtures, but they have been modified and extended to be used for multicomponent systems.

#### 11.2.2.1 Graphical Methods

The McCabe–Thiele diagram is the most common graphical method used for the calculation of the theoretical (equilibrium) stages of distillation. It is also used in the calculation of separation stages of absorption and extraction processes (King 1982; Perry and Green 1997).

Figure 11.6 shows a McCabe–Thiele diagram for the separation of an ethanol/water mixture. Vapor/liquid equilibrium ($y_n$, $x_n$) data in graphical form (Fig. 11.1) at the given pressure (usually atmospheric) are used. The basic assumption of the McCabe–Thiele method is the constant molar flow of liquid (L) and vapor (V) in the two sections of the column, which results in straight-line operating lines.

The operating lines of the fractionating and stripping sections of a column are given by the following equations, respectively:

$$y_n = (L/V)x_{n-1} + (D/V)x_D \tag{11.12}$$

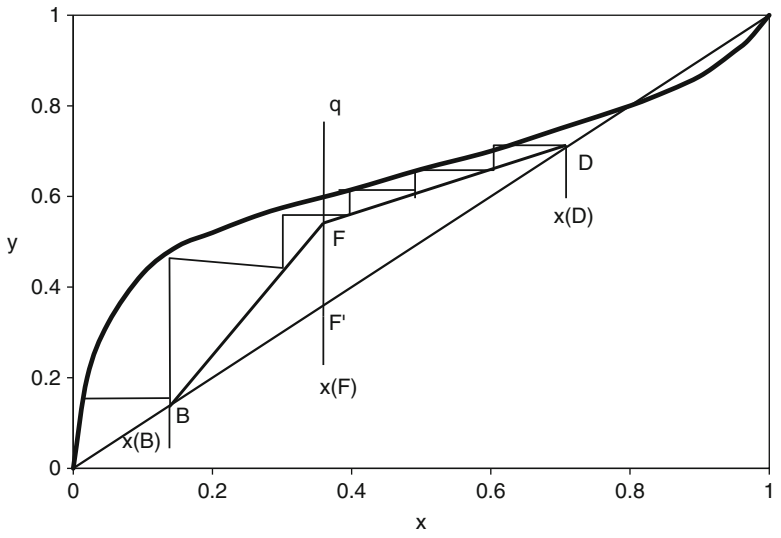


**Fig. 11.6** McCabe–Thiele diagram for distillation of ethanol/water

$$y_m = \left(L^{'}/V^{'}\right)x_{m-1} - \left(B/V^{'}\right)x_{\mathrm{B}} \tag{11.13}$$

where ($L$, $V$) and ($L'/V'$) are the liquid/vapor flow rates of the fractionating and stripping sections and $D$, $B$ are the flow rates of the distillate and the residue (bottoms), respectively.

In the operating lines, the composition of the vapors leaving a stage ($n$ or $m$) is related by material balances to the composition of the liquid coming from the previous (above) stage ($n-1$) or ($m-1$), and the compositions of the distillate ($x_{\mathrm{D}}$) or residue ($x_{\mathrm{B}}$).

The operating lines of the two sections of the column are straight lines with slopes ($L/V$) and ($L'/V'$), respectively, if the molar flows are constant. The stripping line is plotted from the bottom point (B), defined from the given bottom concentration ($x_{\mathrm{B}}$), with a slope of ($L'/V'$). Similarly, the fractionating line is plotted from the top point (D), defined by the given concentration ($x_{\mathrm{D}}$), with a slope of ($L/V$).

The two operating lines intersect at point (F), which corresponds to the feed concentration ($x_{\mathrm{F}}$). The line (F′F) is known as the "$q$-line," and it represents the thermal condition of the feed. It is plotted from point (F′) with a slope of $[q/(q-1)]$. The values of $q$ are the following: $q=1$ (saturated liquid, i.e., liquid at its boiling point), $q=0$ (saturated vapors), and $0<q<1$ (vapor/liquid mixture). In the example of Fig. 11.6, the feed is assumed to enter the column as a saturated liquid, i.e., $q=1$, and the "$q$-line" has a slope $[q/(q-1)]=\infty$, i.e., it is a vertical line drawn from point (F′). It should be noted that the "$q$-line" becomes horizontal when the slope is $[q/(q-1)]=0$, i.e., when $q=0$ or when the feed is saturated vapors.

The number of theoretical stages ($N$) is determined graphically by constructing rectangular steps between the operating and the equilibrium lines, starting from the top (point D) and ending at the bottom (point B). In the example of Fig. 11.6, the number of theoretical stages is nearly $N=5$ (3.5 fractionation and 1.5 stripping). The separation of ethanol in the stripping section is easier (less stages needed) because of the high volatility of ethanol at low concentrations. The actual trays of the distillation column of Fig. 11.6 would be equal to the theoretical stages divided by the column efficiency (11.17). Thus, for an efficiency of 60 %, the required plates will be equal to $[5/0.6]=8.3$. The number of plates should be rounded off, e.g., in this case (9) distillation plates. The theoretical stages can be a fractional number.

Adding theoretical stages to the top of the ethanol/water distillation column will increase slightly the ethanol concentration of the distillate ($x_{\mathrm{B}}$), which will approach asymptotically the concentration of the azeotrope ($y=x=0.896$). This azeotrope can be broken, and nearly pure ethanol can be produced by operating the distillation column in vacuum (pressure lower than 130 mbar), or by azeotropic distillation, i.e., adding a compound to the mixture, like benzene, which increases the volatility of ethanol in the aqueous solution.

The reflux ratio ($R$) in a distillation column is defined as the liquid ratio $R = (L/D)$, which returns to the column from the condenser. If ($R$) is known, the operating line of the fractionating section (11.12) can be written as follows:

$$y_n = [R/(R+1)]x_{n-1} + [1/(R+1)]x_D \tag{11.14}$$

When the two operating lines intersect on the equilibrium ($y_n$, $x_n$) line, the number of theoretical stages becomes infinite, i.e., the mixture cannot be separated by the particular column arrangement. This limiting operating condition is known as the minimum reflux ratio ($R_{min}$). The opposite condition is the total reflux ($R_\infty$), in which the slope of the operating line becomes equal to (1), i.e., it coincides with the diagonal line. In the total reflux operation, the number of stages becomes minimum ($N_{min}$). For economic reasons, the distillation columns are operated between the two extremes of total reflux and minimum reflux, usually at $R = (1.1–1.5)R_{min}$.

The McCabe–Thiele diagram is a relatively simple graphical method, which is applicable when the operating lines are straight lines (equal molar flows). However, in many nonideal mixtures, including the system ethanol/water, significant differences in the enthalpy of the mixtures result in variable molar flows, i.e., nonlinear operating lines. For such systems, analytical stage-to-stage methods or the Ponchon–Savarit graphical method can be used.

The Ponchon–Savarit diagram is an enthalpy–concentration diagram for both the liquid and the vapor phases. A typical diagram, resembling the equilibrium enthalpy ($H$, $h$) concentration ($y$, $x$) data for ethanol/water, is shown in Fig. 11.7. The two enthalpy lines (vapor and liquid) are joined by the "tie lines" (AB), which represent the enthalpy of the liquid ($h$) and the vapor ($H$), which are in thermodynamic equilibrium ($y_n$, $x_n$). The number of theoretical stages, required to affect a given separation, is determined graphically by applying repeatedly material balances between the two phases (King 1982).

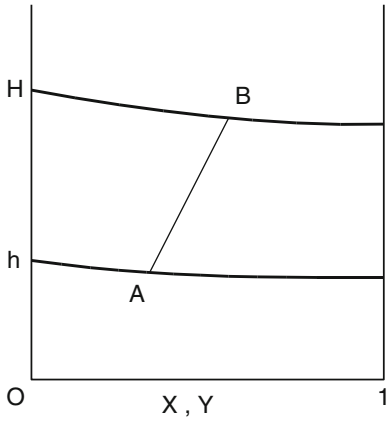


**Fig. 11.7** Ponchon–Savarit diagram. ($H$, $h$) molar enthalpies of saturated vapors and liquid, respectively. AB equilibrium "tie" line

#### 11.2.2.2 Analytical Methods

Analytical methods are used in approximate calculations of the theoretical stages in distillation and other separation processes. They are particularly useful when a large number of stages are involved, such as when the operating lines are very close to the equilibrium lines, and in calculations of multicomponent systems, where the graphical methods are difficult to be applied. The analytical calculations can be included in computer calculation packages.

The most common analytical method is the Fenske–Underwood–Gilliland calculation method, which involves the determination of the minimum number of theoretical stages ($lN_{min}$) at total reflux, the minimum reflux ratio ($R_{min}$) with infinite number of theoretical stages, and the number of stages or theoretical plates ($N$) for the given finite reflux ratio ($R$). This method is used in binary and multicomponent mixtures for the separation of two "key" components, i.e., the light and heavy "keys" (Perry and Green 1997).

The Fenske equation estimates the ($lN_{min}$) for the separation of a binary mixture of relative volatility ($\alpha$) into a distillate (top) product ($x_D$) and a residue (bottom) product ($x_B$) at total reflux ($R = \infty$):

$$N_{min} = \log[x_D(1 - x_B)/x_B(1 - x_D)]/\log(\alpha) \tag{11.13}$$

The Underwood equations estimate the minimum reflux ratio ($R_{min}$), for the same separation:

$$\alpha x_F/(\alpha - \theta) + (1 - x_F)/(1 - \theta) = 1 - q \tag{11.14}$$

$$R_{min} + 1 = \alpha x_D/(\alpha - \theta) + (1 - x_D)/(1 - \theta) \tag{11.15}$$

where ($x_F$) is the mole fraction of the feed and ($\theta$) is an empirical parameter ($1 < \theta < \alpha$), connecting (11.14) and (11.15). The Underwood equations can be extended to $n$ components (multicomponent systems).

The limiting operating conditions ($N_{min}$, $R_{min}$) are used in the empirical Gilliland diagram $\{(N - N_{min})/(N + 1)$ versus $(R - R_{min})/(R + 1))$ to estimate the number of stages ($N$) at a given reflux ratio ($R$). The Gilliland diagram is expressed by the empirical equation:

$$\left(N - N_{\mu\nu}\right)/(N + 1) = 1 - \varepsilon\chi\pi\left\{\left[(1 + 54.1\Psi)/(1 + 117.2\Psi)\right]\left[(\Psi - 1)/\Psi^{0.5}\right]\right\} \tag{11.16}$$

where $\Psi = (R - R_{min})/(R + 1)$.

Economic analysis shows that the optimum reflux ratio is in the range of $(1.1–1.5)R_{min}$, and the corresponding optimum number of stages (plates) is in the range of $(1.5–2)N_{min}$.

Detailed (rigorous) calculations of the theoretical separation stages in multicomponent mixtures can be made by numerical, computer, and simulation

methods, like the Lewis–Mathieson and Thiele–Geddes stage-to-stage computation methods (Perry and Green 1997; Holland 1981). These complex methods are applied to the design, operation, and control of continuous distillation systems, used in large-scale chemical, petrochemical, and petroleum processing.

#### 11.2.2.3 Column Efficiency

The actual number of trays ($N_T$) in a distillation column is estimated from the number of theoretical stages or plates ($N$) according to the equation

$$N_T = N/E_o \tag{11.17}$$

where ($E_o$) is the overall column efficiency, which for distillation columns varies from 0.50 to 0.70.

The overall column efficiency depends primarily on the tray or Murphree efficiency, defined by the equation

$$E_M = (\upsilon_\nu - \upsilon_{\nu+1})/(\upsilon_{\nu\varepsilon} - \upsilon_{\nu+1}) \tag{11.18}$$

where ($y_n$, $y_{n+1}$) are the mole fractions of the vapors coming out of the ($n$) and ($n + 1$) stages, respectively, and ($y_{ne}$) is the mole fraction of the vapors in equilibrium with the liquid ($x_n$), coming out of the ($n$) stage.

The Murphree efficiency of distillation columns is determined by detailed mass transfer and flow analysis of the vapor/liquid mixture in a tray (AIChE 1958).

The efficiency of distillation columns can be estimated from the empirical correlation and diagram of o'Connell (Perry and Green 1997). The efficiency is inversely proportional to the product of the liquid viscosity and the relative volatility of the key component. The viscosity is known to have a negative effect on mixing, while high relative volatilities increase the escaping tendency of the volatile components, reducing the residence time and the efficiency.

The distillation trays are the most important column component, since they must provide enough residence time and mixing for the liquid and the vapors to approach thermodynamic equilibrium, and subsequently separate the two phases effectively for the next vapor/liquid stage contact. Bubble cup and sieve (perforated) trays are commonly used, with valve trays and other specialized designs applied to some distillations. Sieve trays are preferred in the distillation of fermented food liquids, particularly in the stripping section of the column, because they can handle better the food suspensions, without being fouled and plugged.

Figure 11.8 shows diagrammatically the operation of a distillation sieve tray. The liquid (L) flowing down through the downcomers from tray to tray spreads on each (sieve) tray, and it comes in intimate contact with the vapors, rising from the bottom through the main body of the column. The liquid is held on the sieve by the vapors up-flowing through the tray perforations. In large diameter columns

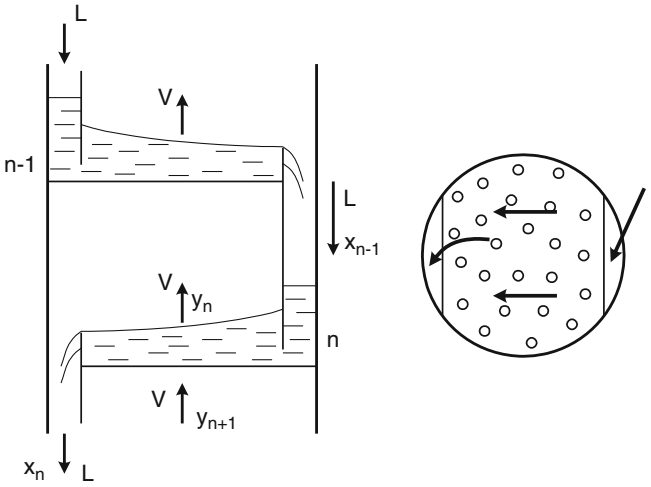


**Fig. 11.8** Diagram of a simple distillation tray

(above 1.5 m), the active tray area is divided into smaller sections, which are connected to appropriate downcomers.

Bubble cap and valve trays can hold the liquid, without flowing through (dripping), even without upward vapor flow. Tray hydraulics, i.e., flow conditions for vapors and liquids in the column (normal operation, flooding, etc.), are discussed in Perry and Green (1997) and in specialized distillation books (Kirschbaum 1969; Billet 1973; van Winkle 1967).

## *11.2.3 Food Distillation Equipment*

### 11.2.3.1 Ethanol Distillation

Distillation is used in the production of brandy and other alcoholic beverages from wine and other ethanol-fermented liquids. Traditional brass (copper) stills of small capacity are used to separate the ethanol and other volatiles in simple one-stage distillations. Partial fractionation of ethanol is obtained by partial reflux in the piping of the still, obtaining distillates of about 50 % ethanol by volume.

Fractional distillation of alcoholic beverages in medium to large-scale operations is carried out in batch or continuous distillation columns made of stainless steel. Figure 11.9 shows the diagram of a continuous distillation column, producing ethanol of high concentration, about 95 % by volume (190° proof), used in the preparation of alcoholic beverages and spirits. The column produces a mixture of "fusel oils" as a side cut between the feed and the condenser. The stripping section in this column is heated by live steam directly at the bottom, instead of the usual reboiler heat exchanger.

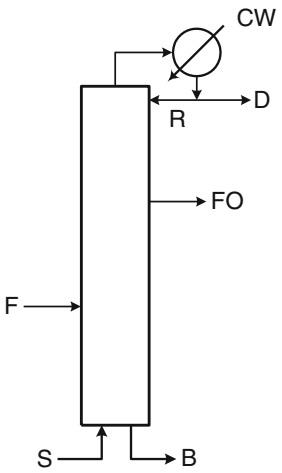


**Fig. 11.9** Diagram of a simple distillation tray

The fusel oils are mixtures of higher alcohols (propanol. butanol, amyl alcohol, and some of their isomers), which, due to their volatility (Fig. 11.4), are concentrated at an ethanol concentration of about 50 % on trays located between the feed and the overhead condenser. Their presence in the alcoholic beverages is undesirable, because of the adverse effect on the quality (flavor) of the product.

A three-column distillation system may be used for the production of 95 % ethanol by volume, free of fusel oils, aldehydes, and other oxygenated compounds: (1) a stripping column heated with live steam; (2) a fractionating column, which produces ethanol 95 % plus aldehydes at the top, water residue at the bottom, and a fusel oil side cut; and (3) an aldehyde column, producing ethanol 95 % at the bottom and an aldehyde-rich product at the top.

Ethanol distillation for the production of alcoholic beverages and spirits is governed by strict regulations, concerned with taxation, like the US Bureau of Alcohol and Cigarettes.

#### 11.2.3.2 Essence Recovery Units

Recovery of aroma or volatile components is practiced in the processing of fruit juices and other fluid foods, usually in connection with evaporation and dehydration processes.

The fruit aroma consists normally of volatile organic compounds, such as esters, alcohols, and oxygenated compounds, which are lost or changed during evaporation, drying, and other physical and thermal processing operations. These compounds are partially soluble in water, and therefore, they have high activity coefficients and high relative volatilities. Concentration of fruit juices by evaporation or drying of aroma-containing foods results in considerable losses of most aroma components from the concentrated or dehydrated product (Saravacos 1995; Karlsson and Tragardh 1997).

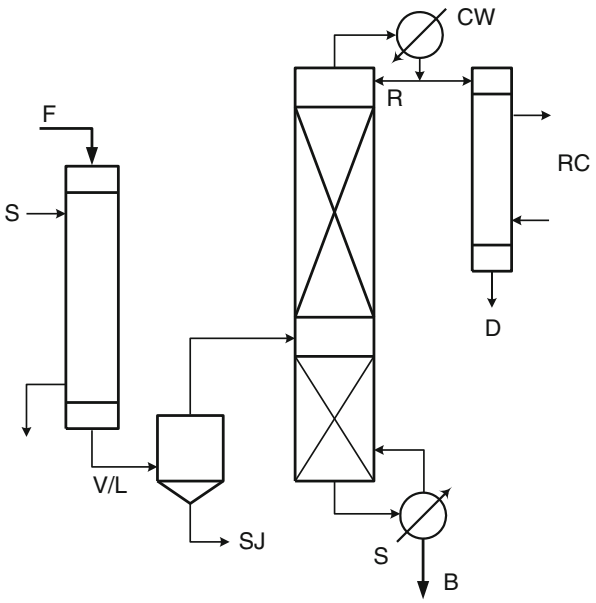


**Fig. 11.10** Simplified diagram of an essence recovery unit at atmospheric pressure. *F* feed, *S* steam, *V/L* vapor/liquid, *SJ* stripped juice, *R* reflux, *CW* cooling water, *RC* refrigerated condenser, *D* distillate, *B* aqueous residue

Aroma recovery is accomplished mainly by stripping/distillation processes, but some novel food processes, like supercritical fluid extraction and pervaporation, can also be applied (Chap. 14). Solvent extraction and solid/fluid adsorption can also be used, as discussed briefly later in this chapter.

The design and operation of essence (aroma) recovery equipment is based on vapor/liquid equilibria of aroma components/water and on distillation techniques (Roger and Turkot 1965; Moyer and Saravacos 1968; Sulc 1984; Lazarides et al. 1990).

Figure 11.10 shows a simplified diagram of a classical essence recovery unit, operated at atmospheric pressure. The principle of the classical system is to strip the fruit juice of most volatile components and concentrate them by fractional distillation into an aqueous solution of about 100–200 times the original concentration in the juice (Moyer and Saravacos 1968).

The essence recovery system consists of a flash evaporator, e.g., a falling film tubular or plate unit, which evaporates between 10 and 30 % of the juice. The evaporator is heated with steam (S) and the vapors are separated from the liquid in the (V/L) separator. The vapors are introduced into the stripping section of the distillation column (DC), which is heated by steam (S) in a reboiler, from which the bottom residue (B) is removed. An overhead condenser, cooled with cold water (CW), provides the required reflux ratio (R), and the distillate is further cooled in a refrigerated condenser (RC).

Compared to normal distillations of nonpolar mixtures, the stripping and distillation of aqueous volatile compounds present some problems, which are discussed briefly below.

### Stripping of Aromas

The stripping of the various aroma components depends primarily on their relative volatility in the fruit juices. Although the activity coefficients and relative volatilities in aqueous solutions of sugars are high, a significant fraction of volatiles may be retained in the concentrate, due to a diffusion-controlled trapping mechanism (Chap. 8; Saravacos and Maroulis 2001). Thus, while in food dehydration the objective is high aroma retention (fast drying), in essence recovery the aroma components should be allowed to approach thermodynamic equilibrium (better mixing, longer residence time).

Very volatile aroma components, like esters, are easily stripped by evaporating a relatively small portion of the juice, e.g., 10 %. Thus, most aroma components in some fruit juices, like apple juice, can be recovered in the condensate of the first effect of an evaporator, which may be up to 25 % of the original water in the juice. However, higher boiling aroma components, like methyl anthranilate (Concord grape juice) and some carboxylic acids, may require removal of about 40 % water for substantial stripping (Saravacos and Moyer 1968).

In some cases, stripping of volatile components from food liquids, without further food concentration, may be required in order to remove undesirable components from the product. For instance, high-boiling methyl anthranilate, the characteristic aroma in Concord grape, may be undesirable in wines prepared from this grape juice. In this case, a stripping column, with about ten trays may be used to strip by steam about 90 % of the methyl anthranilate (Saravacos et al. 1969).

Vacuum stripping of aromas from heat-sensitive food liquids, like orange juice, requires special vacuum pumps, which can collect most of the volatiles in the liquid ring of the pump (Bomben et al. 1967, 1973). Sealing liquids, used in the vacuum pumps, include water and ethanol solutions and should be refrigerated during operation at about 2 °C to prevent loss of volatiles in the exhaust gases. Vacuum stripping is carried out at temperatures 45–80 °C, and an inert gas stream (nitrogen or air) may be injected in the bottom of the column to increase the stripping capacity. Condensing of the stripped volatiles from the carrier gas requires low-temperature condensers and cold traps.

### Fractionation of Aromas

The fractionation of aroma components is carried out in distillation columns, using packed columns for small- and medium-size capacities and trays (sieve, bubble cap, or valve) for large capacities. The packed columns are discussed in Sect. 4.3.

The number of theoretical stages is estimated on the basis of separation of two key components, one of which is water and the other a flavor characteristic component of the particular food product. The key aroma component should have a relative volatility lower than the very volatile compounds, so that its recovery by

distillation will ensure that all other components are recovered. Graphical or analytical methods can be used for the estimation of the required separation stages.

In the essence recovery from food liquids, the concentration of the volatile components is generally low (ppm range), and therefore, water is the major component in the distillation column. The column efficiency ($E_o$) in water-rich distillations is relatively low (about 50–60 %), due to the difficulty of mixing water/vapors effectively. This is caused by the high surface tension of pure water, which retards effective mass transfer between phases.

Typical columns of essence recovery contain about ten trays of 1 m diameter and 5 m high (distance between trays is about 0.5 m).

Fractionation of high-boiling flavor compounds requires high-vacuum columns and other specialized distillation equipment (see Sect. 2.3.4).

#### 11.2.3.3 Spinning Cone Stripping Column

The spinning cone stripping column (SCSC) is a special distillation column, developed in Australia, capable of recovering aromas and removing undesirable volatile components from fruit juices and other food liquids. It is operated at low temperatures and short residence times with effective vapor/liquid mixing and high mass transfer rates, distinct advantages over the conventional plate columns, which are operated at atmospheric pressure (high temperatures) with long residence time and high-pressure drops, damaging the quality of sensitive products.

The basic SCSC unit consists of a column, about 1 m diameter and 3 m high, with alternating stationary and rotating truncated cones, which act as contacting stages for liquid and vapors flowing countercurrently (Fig. 11.11). The preheated liquid is fed at the top of the column, while live steam is injected at the bottom, acting as a stripping medium. The volatile components are condensed in refrigerated condensers at the top, and the stripped product is obtained at the bottom.

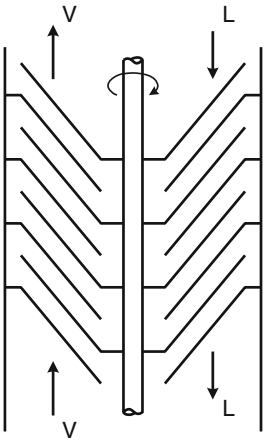


**Fig. 11.11** Principle of spinning cone stripping column

The system operates at a relatively high vacuum (boiling temperatures 25–35 °C), maintained by a special vacuum pump, equipped with a cold liquid ring, which traps any volatiles from the exhaust air (Casimir and Craig 1990; Gray 1993).

The capacity of a standard (1 m × 4 m) SCSC unit is 10,000 L/h, and the residence time is less than 1 min. The moving cones are attached to a shaft, which rotates at 250–550 RPM. The rotating finned cones and the centrifugal force develop turbulence and high heat and mass transfer rates for the falling liquid film and the rising vapors. The estimated separation efficiency of the SCSC units is about 20 NTU/m, much better than the approximate 6 NTU/m in conventional packed columns (see Sect. 4.3 in this chapter).

The SCSC unit can be used for the removal of undesirable volatiles from fruit juices, e.g., sulfur dioxide from grape juice, and in the recovery of valuable volatiles from sensitive food liquids, which are damaged by high-temperature stripping.

The spinning cone distillation column is particularly suited for the preparation of alcohol-free or nonalcoholic wines, which contain less than 0.5 % ethanol (Mermelstein 2000). Wine de-alcoholization can be carried out by evaporating a relatively large portion of wine, e.g., 30–40 %, in a falling (tubular or plate) film or agitated-film evaporator at atmospheric pressure. Stripping of ethanol requires evaporation of higher portions of liquid than stripping of volatile esters and other aromas, because of its lower relative volatility (Saravacos 1974).

The SCSP de-alcoholization process involves first the recovery of the volatile aromas (esters, etc.) in a low-temperature column ($T < 30$ °C) and, second, the stripping of ethanol at a higher temperature (about 35 °C), resulting in a stripped wine. The volatile aromas, recovered in the first stripping, are returned to the stripped wine, obtaining a full-flavored nonalcoholic product.

The SCSC unit can be used to enrich the ethanol content of weak wines or alcoholic spirits to desirable levels for better flavor and quality, without the need to add distilled alcohol.

Nonalcoholic wine can be produced by membrane separation processes, like reverse osmosis and pervaporation, as discussed briefly in Chap. 12.

#### 11.2.3.4 Molecular Distillation

Molecular or short-path distillation is applied to the separation of high-boiling and heat-sensitive food components, such as flavors, vitamins, and monoglycerides. The mixture is first separated from the volatile components by normal vacuum evaporation or distillation.

Molecular distillation is an expensive process, requiring very high vacuum (about 0.01 mbar), which is achieved by special vacuum pumps. For small, laboratory-size applications, an oil rotary (ballast) pump, followed by an oil diffusion pump, may be used. For pilot plant and industrial applications, a rough vacuum pump, e.g., steam jets or liquid ring pump, is used to reach a vacuum (absolute pressure) of about 10 mbar (see Appendix D). The very high vacuum

required is obtained by using a rotary dry pump, followed, if necessary, by an oil diffusion pump.

The molecular still consists basically of a film evaporator, which is surrounded by a condenser. The high-boiling compounds are evaporated and condensed very fast on the condenser surface, which is located very closely to the evaporator. The short distance (short path) between evaporator and condenser is smaller than the mean free path of the molecules at the prevailing pressure and temperature of the still.

## 11.3 Solvent Extraction/Leaching Equipment

The analysis and design of solvent extraction and leaching is similar to the procedures used in distillation processes. Empirical correlations are used for liquid/liquid equilibria, while experimental data are essential for solid/liquid systems. Approximate methods are used for the estimation of equilibrium stages, and the extraction/leaching equipment is more specialized than the generalized distillation systems.

### *11.3.1 Liquid/Liquid and Liquid/Solid Equilibria*

Liquid/liquid extraction is based on the thermodynamic equilibrium between two partially soluble phases, the extract and the raffinate (Fig. 11.12): In a simple three-component system, the two liquid phases consist of the following: (1) the raffinate, containing mainly the residue (A), the solute (B), and small amount of solvent (S), and (2) the extract, containing mainly the solvent (S), part of the solute (B), and small amount of residue (A).

The equilibrium is expressed by the empirical equation

$$Y = KX \tag{11.19}$$

The concentrations of the solute in the extract ($Y$) and raffinate ($X$) phases are usually expressed as mass fractions of the mixture. The partition or distribution coefficient ($K$) is analogous to the volatility coefficient of vapor/liquid equilibria, and it is related to the activity coefficients of the solute in the raffinate ($\gamma_r$) and extract ($\gamma_e$):

$$K = \gamma_r/\gamma_e \tag{11.20}$$

The activity coefficients of various liquid systems are correlated in various empirical relations, like the Wilson and UNIFAC equations (Reid et al. 1987). Liquid/liquid mixtures, used in solvent extraction, are nonideal systems, facilitating the separation in a relatively small number of stages.

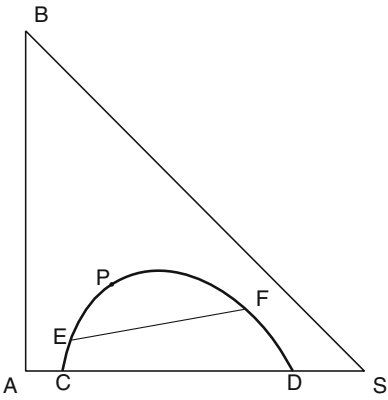


**Fig. 11.12** Right-triangular liquid/liquid equilibrium diagram. *A* residue, *B* solute, *S* solvent, *P*, plait point; (EF), tie line

The liquid/liquid equilibrium data are presented in right-triangular diagrams (Fig. 11.20), or modified McCabe–Thiele and Ponchon–Savarit diagrams (Fig. 11.21).

The Orthogonal triangle diagram of Fig. 11.12 shows a typical liquid/liquid extraction system in which the solvent (S) is partially soluble with the residue (A), e.g., water. The solute to be extracted is completely soluble in both (S) and (A). The two phases are confined within the curve (CPD) of the diagram, with the "plait" point (P) representing the common composition of both extract (DP) and raffinate (CP) phases. The "tie" line (EF) connects two equilibrium points of the raffinate (E) and the extract (F).

The modified McCabe–Thiele diagram for liquid/liquid extraction uses as coordinates the mass fractions $Y$ (extract) and $X$ (raffinate) of the solute ($B$), defined by the equations

$$Y = B/(A+B) \text{ extract phase}, \quad X = B/(A+B) \text{ raffinate phase} \qquad (11.21)$$

It should be noted that the amount of solvent ($S$) does not enter the McCabe–Thiele diagram.

The common equilibrium point of the two phases or "plait" point is represented by point (P) on the modified McCabe–Thiele diagram (Fig. 11.13).

The role of solvent in extraction is analogous to the enthalpy (heat content) in distillation, which enters quantitatively into the Ponchon–Savarit diagram, as shown in Fig. 11.7.

The ordinates of the Ponchon–Savarit diagram for liquid/liquid equilibria are $Z = S/(A+B)$ for the extract (line ZP) and $z = S/(A+B)$ for the raffinate (line zP). Equilibrium ("tie") lines connect the solvent (V) and the raffinate (L) phases.

Solid/liquid equilibria are determined experimentally, assuming that the solute is completely soluble in the solvent and that it is not sorbed on the inert solid. Under these conditions, equilibrium is expressed by the simple equation

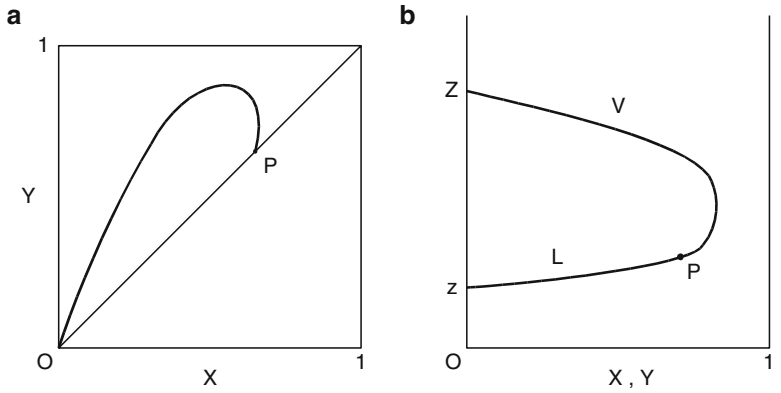


**Fig. 11.13** McCabe–Thiele (**a**) and Ponchon–Savarit (**b**) diagrams for liquid/liquid extraction for a partially soluble (two-phase) system. *P* plait point

$$Y_e = X \tag{11.22}$$

where ($Y_e$) is the mass fraction of the solute (B) in the extract and ($X$) is the concentration of solute in the liquid remaining in the pores of the solids, after reaching equilibrium.

The solubility of solids in liquids is discussed by Reid et al. (1987).

The solid/liquid equilibrium data can be plotted on modified Ponchon–Savarit and McCabe–Thiele diagrams, in a similar manner with the liquid/liquid equilibria. The ordinates of the modified Ponchon–Savarit diagram for solid/liquid equilibria are the concentrations of the inert solid ($A$) in the solid (underflow) and in the extract (overflow), defined by the equations

$$z = A/(B + S) \quad \text{underflow} \tag{11.23}$$

$$z = A/(B + S) \quad \text{overflow} \tag{11.24}$$

where $A$, $B$, and $S$ are the amounts (kg) of inert solid, solute, and solvent, respectively.

For the normal extraction case of an inert solid that is completely insoluble in the solvent, the overflow line coincides with the $X$-axis, i.e., $Z = 0$ (Fig. 11.14). The equilibrium "tie" lines, e.g., line (AB) are vertical lines, which facilitate the graphical construction of the equilibrium stages between the equilibrium and the operating lines.

In the modified McCabe–Thiele diagram for leaching, the coordinates are the mass fractions of the solute ($B$) in the extract ($Y$) and the residue ($X$), respectively, as defined in liquid/liquid equilibria (11.21).

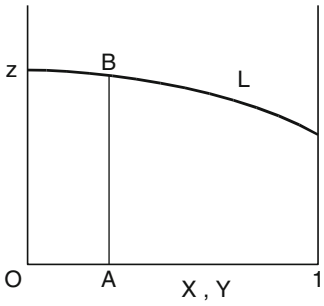


**Fig. 11.14** Modified Ponchon–Savarit diagram for liquid/solid leaching. AB, tie (*vertical*) line

## *11.3.2 Determination of Equilibrium Stages*

Liquid/liquid (L/L) extraction is carried out usually in a countercurrent operation of extract (solvent) and raffinate (residue), either in a series of mixing tanks or in a column, similar to distillation columns. Although fractionating columns for enriching the solute have been proposed, in most practical applications only the stripping section is utilized. Solute purification and solvent recovery are obtained by other separation processes, notably distillation, if the solvent is volatile (the usual case).

The number of theoretical stages in an (L/L) extraction is determined using the modified McCabe–Thiele or Ponchon–Savarit diagrams. The equilibrium line is plotted, using literature or experimental data, and the operating line is constructed from material balances of the given system, in analogy with distillation. In extraction, the solvent ($V$) and raffinate ($L$) flows are taken as mass flow rates (kg/h) and the concentrations ($Y, X$) as mass fractions. In concentrated solutions, the operating lines of the McCabe–Thiele diagram are nonlinear.

In dilute (low-concentration) solutions, straight equilibrium and operating lines facilitate the graphical constructions. The equilibrium line ($Y = KX$) is plotted from the origin of the coordinates with a slope of ($K$). The operating line, representing the overall material balance in a countercurrent column, takes the form of a straight line with a slope of ($L/V$):

$$Y_1 - Y_{n+1} = (L/V)\,(X_0 - X_n) \tag{11.25}$$

where ($X_0$, $X_n$) are the solute concentrations in the raffinate and ($Y_1$, $Y_{n+1}$) are the solute concentrations of the extract at the entrance (stage 1) and exit (stage $n$) of the column, respectively. For pure solvent, entering the last stage ($n$), $Y_{n+1} = 0$, and the operating line goes through the origin of the coordinates.

In multistage separations ($K$ approaching unity), graphical construction of the (theoretical) stages is difficult near the origin of the equilibrium and operating lines, and a log–log plot can improve the numbering of stages. An alternative is to use the Kremser equation, discussed in Sect. 4.3, which, for extraction, becomes

$$N = \log[R(1-E)+E]/\log(E) \tag{11.26}$$

where $E = (KV)/L$, extraction factor, and $R = (X_n - Y_{n+1}/K)/(X_0 - Y_1/K)$, extraction ratio.

The number of (theoretical) extraction stages ($N$) can also be determined from the graphical solution of the Kremser equation (Perry and Green 1997).

The (L/L) extractors have lower efficiencies (20–30 %) than the distillation columns, because of the difficulties in mixing the liquid phases, i.e., inefficient mass transfer. The efficiency can be improved by thorough mixing, using agitation, vibration, etc.

Solid/liquid extraction (leaching) is usually carried out in fixed beds of solids, contained in a series (battery) of vessels. A leaching operation can be visualized as a series of stages, with the extract ($V$) flowing countercurrently with the liquid (usually water) residue ($L$), while the inert solids remain fixed in the beds. The solvent removes gradually the solute from the liquid residue, reaching equilibrium at each stage (thorough mixing, sufficient residence time).

The number of stages can be determined graphically, using the modified McCabe–Thiele or Ponchon–Savarit diagrams. Graphical construction of the stages is facilitated by the assumption that the equilibrium line coincides with the diagonal line ($Y = X$).

For low concentrations of the solute in the inert solid and in the extract, a straight operating line similar to the (L/L) extraction (11.25) is obtained, assuming constant flows of liquid underflow ($X$) and extract ($V$). The number of (theoretical) stages ($N$) can be calculated from the Kremser equation (11.26) or the Kremser diagram of the literature.

The efficiency of the solid/liquid extractors is very high, about 90–95 %, due to the thorough mixing and the relatively long residence time in each stage.

### *11.3.3 Mass Transfer Considerations*

Solvent extraction of liquids and leaching of solids are controlled by mass transfer of the solutes from the material to the transfer interface. Although other mechanisms may be involved, mass transfer within liquid and solid materials is usually assumed to take place through molecular diffusion, and the transport rate is expressed by an effective or apparent diffusivity ($D$), which is an overall transport coefficient, based on the diffusion (Fick) equation (Saravacos and Maroulis 2001). In some cases, other transport mechanisms, like capillary and hydrodynamic flow, are prevalent and they should be taken into consideration.

Diffusivity data of solutes in liquids are presented by Cussler (1997) and Reid et al. (1987). Diffusivity ($D$) in liquids is related to the molecular (particle) size of the solute and the viscosity of the mixture (Stokes–Einstein equation), or the molecular solute/solvent interactions (Wilke–Chang equation). Typical values

of ($D$) of solutes in dilute water solutions (25 °C) are sodium chloride, $12 \times 10^{-10}$ m$^2$/s; sucrose, $5 \times 10^{-10}$ m$^2$/s; and lactalbumin, $0.7 \times 10^{-10}$ m$^2$/s.

Diffusivity data in solids are more variable, depending strongly on the microscopic and macroscopic structure (homogeneous, porous, fibrous, etc.) of the material. Prediction and correlation of ($D$) in solids is difficult, and experimental data are required for each material at given conditions (Saravacos and Maroulis 2001). Data on ($D$) of importance to leaching are given by Schwartzberg and Chao (1982) and Schwartzberg (1987), e.g., oil (soybean flakes)/hexane, $1 \times 10^{-10}$ m$^2$/s, and coffee solubles (coffee beans)/water, $1 \times 10^{-10}$ m$^2$/s. The ($D$) of solutes increases when the porosity of the solid is increased. Large molecules, like lipids and proteins, have smaller diffusivities than smaller molecules, like sugars.

Various mechanical and hydrothermal pretreatments of the solid foods are used to increase the transport rate of solutes and improve leaching efficiency, e.g., slicing, flaking, and steam injection. Slicing of beets and fruits and flaking reduce the thickness (diffusion path) of the material, without serious damage of the cells, which would release cell components into the solution and make difficult the solid/liquid separation. Heating by steam or water modifies the cellular structure (e.g., denaturation of proteins) increasing the solute diffusivity.

Recovery of oil from oilseeds containing above 22 % oil is accomplished by mechanical expression, usually screw presses (Chap. 5), followed by leaching with an organic solvent, e.g., hexane. Mechanical pressing can remove up to 90 % of the oil in the seeds. Direct solvent leaching is applied to oilseeds containing less than 22 % oil, e.g., soybeans.

The oilseeds are prepared for leaching by cleaning, cracking, dehulling, heat/water conditioning, and flaking (Aquilera and Stanley 1999). Heat (steam) conditioning of oilseeds at 70–75 °C denatures the proteins, facilitates flaking, and reduces the viscosity of the oil. Flakes about 0.5 mm thick are prepared by pressing the conditioned seeds in rotating smooth cylinders. Solvents used include hexane, chlorinated hydrocarbons, and alcohols. Oil is removed from the seed flakes by a combination of mechanisms, including washing of surface oil, and diffusion through the cellular components and the pores of the material.

Sugar beets are cut into long, thin slices (cossettes), which are heated to 50–60 °C to denature the proteins and increase the diffusivity of sucrose, without leaching of nonsugar components.

Extraction (leaching) of solubles (sugars) from apple pomace with water, following mechanical expression (Chap. 5), can improve juice recovery and process economics.

Water extraction of soluble solids from roasted coffee beans is facilitated by the high porosity of the beans, developed during thermal treatment (roasting). In the processing of decaffeinated soluble coffee, the diffusion of caffeine in water is controlling the process.

Leaching of soluble solids from ground malt and adjuncts into water is an important step in beer processing. The malt is treated with water at 63–68 °C for 1–2 h. The fermentable solutes are obtained by a combined extraction–filtration process (lautering). The leaching efficiency is increased by optimum combination of particle size, bed depth, temperature, and water content.

### 11.3.4 Food Extraction and Leaching Equipment

The simplest extraction and leaching equipment is the mixing/settling tank, in which the solvent is mixed thoroughly with the liquid or solid to be extracted until equilibrium is reached, and then the two phases are separated mechanically into the extract and the raffinate (residue). The stage efficiency of mixer/settlers increases substantially, when the agitation power (kW) is increased (Perry and Green 1997).

For more efficient and economical separation, multistage extraction (leaching) systems are used. Multistage countercurrent extraction in liquid/liquid (L/L) systems is performed in extraction columns, which are similar to the stripping section of a standard distillation column. The solvent (extract) flow is similar to the vapor flow (V), while the raffinate flow resembles the flow of the liquid (L) in the stripping column. It is assumed that (L/L) equilibrium is reached in each (theoretical) stage, which can be approached by thorough mechanical mixing of the two phases.

Equipment used in liquid/liquid extraction is discussed by Walas (1988) and Perry and Green (1997). Most of this (L/L) extraction equipment is used in the chemical and petroleum industries, with a few applications to food processing. Countercurrent extraction columns are generally used with the heavy phase fed at the top and the light at the bottom. The columns are analyzed either as plate (tray) or packed tower systems. Their efficiency depends mainly on the mass transfer between the two phases, and various types of mixing and agitation are used to increase the efficiency. Instead of a column efficiency value, the height of an equivalent theoretical plate (HETP) or the height of a theoretical unit (HTU) are used. Typical values of these heights vary, depending on the column, from 0.125 to 1 m, i.e., there are from 1 to 8 equilibrium stages per meter of column height.

Industrial (L/L) solvent extraction columns include the sieve tray, the rotating disk (RTC), the Oldshue (paddle agitation), the Scheidel (packing and agitation), the pulsed columns, the Graesser rotary raining cup extractor, and the centrifugal extractor, used in the extraction of sensitive products (short residence time), like antibiotics (Walas 1988).

The RTC column (Fig. 11.15) consists of a vertical cylindrical vessel with circular baffles (rings) on the walls and a series of rotating flat discs, mounted on a shaft in the center of the column. The liquid (e.g., water solution) is fed from the top, while the (lighter) solvent is fed countercurrently from the bottom. The extract is received at the top, while the raffinate is removed from the bottom. The RTC is used in the solvent extraction of caffeine from aqueous solutions in the manufacture of decaffeinated soluble coffee.

The capacity of RTC columns varies from 100 to 500 $m^3$/h, maximum loads of 40 $m^3/m^2$ h, and diameters in the range of 1–4 m.

Leaching of solutes from solids is usually carried out in static (fixed) beds of particulate material, prepared to the appropriate size and physicochemical condition and to facilitate mass (diffusion) transport of the solute. The bed of material,

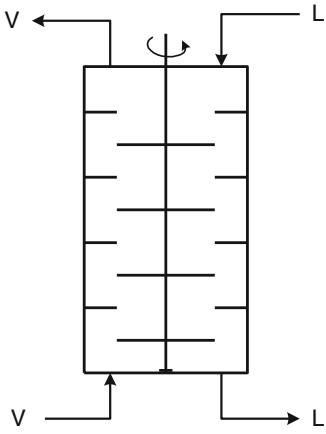


**Fig. 11.15** Diagram of a rotating disk L/L extraction column. *L* aqueous solution, *V* organic (insoluble) solvent

resting on a false bottom, is enclosed in vertical cylindrical vessels, which can stand high-pressure operation of volatile solvents. The solvent is fed to a distributor at the top, while the extract can be recirculated through the solids, before it is removed from the system.

For better efficiency, multistage equipment is used for the leaching of solids. In a true multistage countercurrent operation, the solid particles should be moved from stage to stage by special (slurry) pumps, in counterflow with the stage-to-stage flow of the solvent (extract). Such systems are difficult to use in food processing, and the multistage countercurrent static-bed system is commonly used (Walas 1988; Brennan et al. 1990).

The static-bed system is operated semicontinuously as follows: A series of static-bed cells (vessels) are leached with solvent flowing from cell to neighboring cell until the extract is nearly saturated with the solute. The first cell, containing the spent (leached) residue, is taken off and discharged, while the solvent feed is switched to the next (second) cell. The solvent flows from stage to stage until the recently filled last cell, from which it is taken off as concentrated extract. The first cell, after emptying, washing, and loading with the particulate solids, becomes the last cell of the series, from which the enriched extract is removed. The cycle is repeated when the second cell is exhausted and the spent residue is discharged.

In the leaching of sugar beets with water, 10–14 extraction cells are used, each with a volume of 4–12 $m^3$ and height to diameter ratio of 1.5. Leaching time is 60–100 min, and 110 kg of sugar solution 12–16 °Brix is produced per 100 kg beets. The extraction efficiency (mass transport rate) is increased considerably by heating the solution between the cells.

Similar multistage countercurrent static-bed systems are used for the leaching of oil from oilseeds with organic solvents and soluble solids from ground roasted coffee and tea. In the processing of instant coffee and tea, 5–8 extraction cells are used with cycle time ½ to 1 h. Ratios of water/solids are 7/2 to 5/1, and the extracts contain 25–30 % soluble solid.

Moving-bed (continuous) leaching equipment is described by Walas (1988) and Brennan et al. (1990).

Examples of continuous leaching equipment are the following:

1. The Bollmann bucket elevator with perforated buckets carrying each about 40 kg of particulate material in solvent bath, contained in a closed vessel. The residence time of the solids in the extractor is about 1 h, and the solvent (extract) is recirculated through the top of the vessel, and it is removed from the bottom, after approaching equilibrium, into the next stage of extraction.
2. The Hildebrand extractor, in which the solids are transported with screw conveyors through three sections (two vertical and one horizontal) in countercurrent flow with the solvent/extract (Fig. 11.16).
3. The Bonotto multi-tray tower extractor, in which the trays rotate, while the solid particles are scraped and discharged from tray to tray (similar to the agitated tray pan dryer (Fig. 8.24).
4. The Rotocell extractor, which consists of about 18 wedge-shaped cells in a rotating shell, enclosed in a stationary tank. Fresh solvent is charged to the last cell and the drained solutions are pumped countercurrently to each cell in series. The Rotocell is used in the leaching of sugar beets and oilseeds.

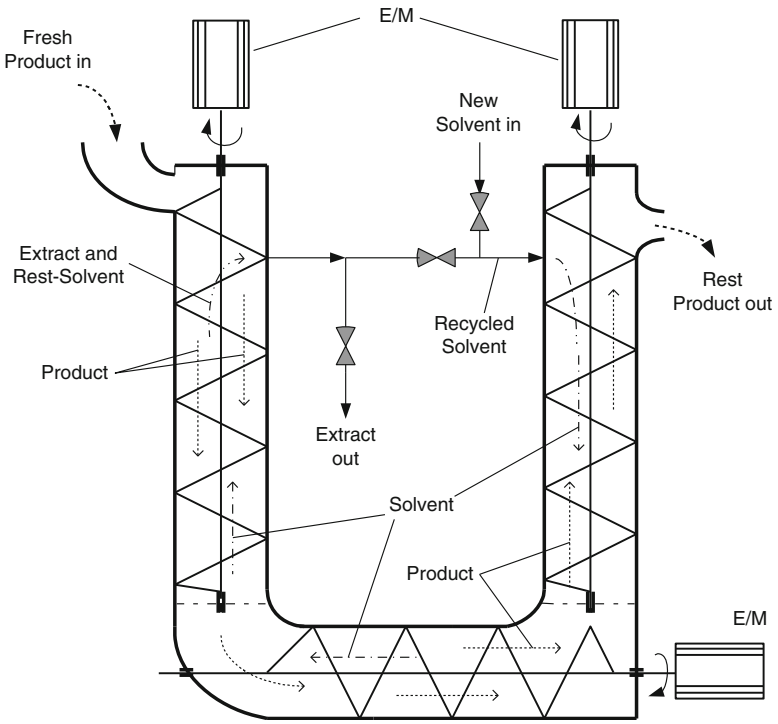


**Fig. 11.16** Hilderbrand extractor

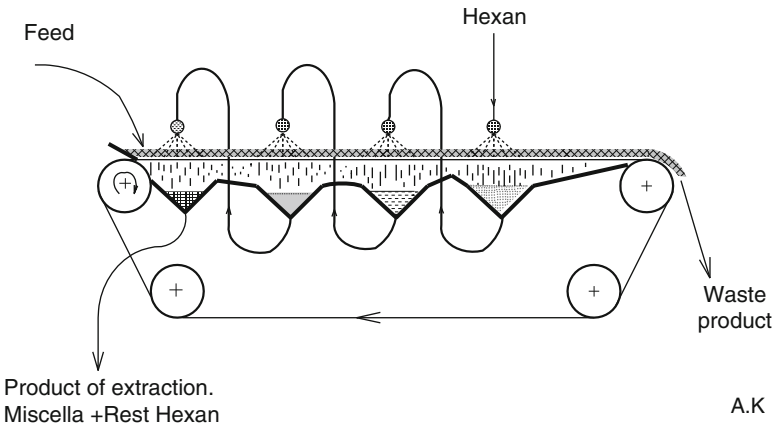


**Fig. 11.17** DeSmet extractor

5. The screw extractor, similar to the screw expression equipment, used in the expression of fruit juices (Chap. 5). Such equipment can be used in the leaching of sugar beets, where the cossette pieces move countercurrently at a slope against the hot water solution.
6. The DeSmet, in which the solids are carried by a band, while the solvent flows countercurrently (Fig. 11.17).

## *11.3.5 Curing*

### 11.3.5.1 Introduction

Curing is a preservation process which improves the sensory characteristics of certain foods. It is used mainly in the treatment of meat, poultry, and fish with salt and other additives, and it covers also processes such as smoking and drying. *Marination* is a curing process, when seasonings and spices are added to the food material. Curing involves the diffusion of solid or liquid substances in solid foods. When applied to meat, curing may include also substances such as nitrates, nitrites, ascorbates, sugars, and several other chemicals or substances that improve its color, taste, and flavor. Curing is a diffusion process, but its theoretical interpretation is more complicated than the simple liquid or gas diffusion process.

In curing, besides the solvent, the composition and the macro- and microscopic structure of the cured food are very important. Therefore, engineering estimations in curing processes are based mainly on empirical knowledge.

The curing rate of meat increases when the moisture content, the temperature, the salt concentration, and the acidity of the meat are increased. The size or thickness and the fat content of the meat have a negative effect on the curing rate.

The nitrate content and bacteria in the meat contribute to the conversion of nitrate to nitrite, enhance the color, and act as a preservative. The activity of bacteria has an optimum of pH 5.8–6.0

#### 11.3.5.2 Curing Processes

Fast curing is an economic process, but in some products, the high speed of curing may reduce the quality of foods. This is when the high diffusion rate (fast curing) is related to a higher processing temperature, which reduces the food flavor and the preservation time. Cooked ham, a popular cured pig meat product, is cooled down to 4 °C, before injected with brine. The ham is then tumbled, placed in metallic forms, and soaked in hot water or steamed until the temperature in the center of the product is about 68–75 °C. Subsequently, the product is cooled as fast as possible, packed, and stored at 0–2 °C.

The main curing processes are dry and wet curing and soaking, wet curing, muscle injection, artery injection, combination methods (e.g., dry and wet curing combinations with vacuum or/and warm brine application), tenderizing, and smoking.

##### Dry and Wet Curing and Soaking

*Dry curing*. The product is covered with additives such as salt and other curing ingredients, and it is stored in more or less controlled temperature until a certain amount of the curing additives is absorbed. Covering of the product with salt and ingredients may be repeated during a long period of storage. Usually in such processes, the form of food influences the rate of curing. For equal weight of products, the diffusion of curing medium lasts longer in a thicker cubic product than in a thinner slab one.

*Wet curing* is carried out with brine of pH about 6.0. The addition of dextrose, lactose, or maltose helps to increase the product acidity. The acidity of the product is relatively low. But if it exceeds, e.g., pH 7.0, spoilage of the brine and product may be evident. The relation (brine quantity)/meat may be from 1/2 to 1/3.

*Soaking* in brine may last for more than 24 h. Methods such as dry and wet curing and soaking give products of good quality, but it must be pointed out that the end quality of the products, besides curing processing, depends also on the initial quality of the raw material.

##### Muscle Injection

Brine is injected in meat through fine needles (Fig. 11.18). There is equipment having more than 180 hypodermic needles, which sometimes are set in diversified

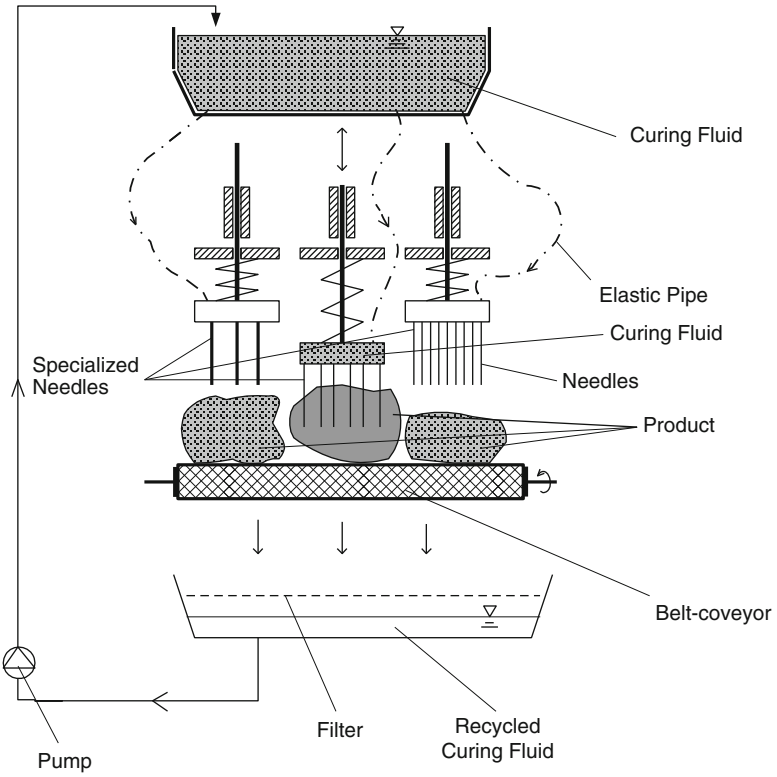


**Fig. 11.18** Needle curing injection

small groups according to the types of products that have to be processed (fat content, bones, toughness of the cured product). In this case, there is a specialization of each group of needles of the equipment, for meeting the specific requirements of the food product. There are also machines constructed to fit to a modular system that increases their versatility. The method using needles for the brine injection reduces the required time of curing, as the injected ingredients start diffusion initially deeper in the product. The thinner the needles, the less are the damages of fibers. The temperature of the injected brine solution must be almost equal to that of the meat (4–8 °C). Usually, the injected quantity is approximately 12–15 % of the fresh product weight. The injection process is performed in two steps, applying a relatively low overpressure (1.5–2.0 bars). This way, the fibers of the product are damaged minimally and less material is required, due to less losses. In case the meat pieces are relatively thick (>10 cm), curing injection is often preferably done before tendering. Tenderizing in this case helps to a subsequent more even distribution of the already injected substances.

### Artery Injection

Artery injection is applied to fresh meat, injecting the curing solution through the arteries of larger meat parts. This way, a thorough distribution is achieved and the brine leaches away the remaining blood as well.

### Combined Methods of Curing

In case of vacuum application, the exit of air facilitates diffusion of salt and other ingredients into meat fibers, as meat expands and the curing operation is faster. Usually, a time of 10 min is required to load and empty the vacuum curing equipment and another 20 min for the processing of meat. Furthermore, the application of vacuum contributes to the increase of the absorption of marinade, reduces oxidation of the product, and reduces weight lose in subsequent cutting and cooking operations. Vacuum also improves the color and flavor of the products and extends their shelf life. Warm brining (temperature 36–38 °C) helps in the loosening of fibers and the increase of chemical reactions. It is often used in manufacturing products that do not stay for a long time in cold storage.

### Tenderizing

Tenderizing is done in tumbling or, in case of heavy duty applications, in massaging equipment. The main reason is to minimize the toughness of the connecting fibers of muscles, which result in a negative eating experience. A tumbler consists of a drum, with some fittings in it (Fig. 11.19). The tenderizing of the product such as

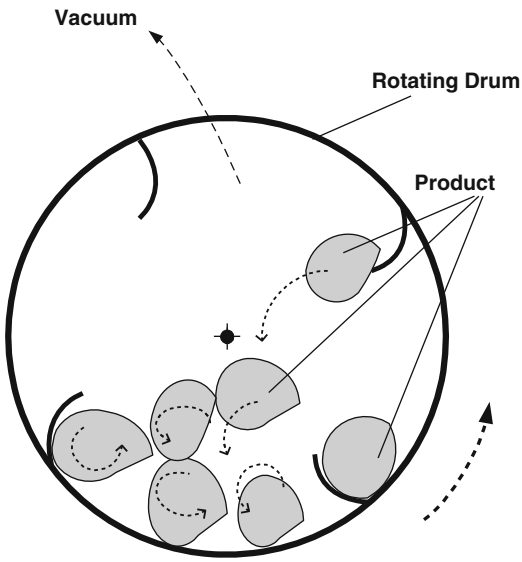


**Fig. 11.19** Tumbling drum

meat, bone-in and boneless poultry, or low profile products such as fish is carried up as the kettle drum rotates. The entrained product falls down, in the lower part inside the drum after about a half rotation. When it falls, it hits products that are already in the lower part of the drum, waiting to be carried up. The process is repeated continuously. This way a reaction between the protein of the products and the added brine solution is speeded up, providing a tendered product of better sensory characteristics. Both methods, tumbling and massaging, are similar. In massaging in the drum, instead of fittings, there are special small blades intensifying the tendering process. In tumbling, the drum rotates at 8–12 RPM along its axis. The entire tumbling operation lasts about 10–20 h. Each tumbling of the product lasts 15 min per hour. In the remaining 45 min, the product rests, until tumbling restarts for another 15 min. A tumbling process may also last for 1–4 continuous hours in a total tumbling period of 10–20 h. The tumbling equipment operates in rooms of about 10 °C. The temperature during processing is kept under control by additional measures, such as the use of tumbling equipment that can be cooled by glycol systems. The tenderizing process is enhanced when it is performed in vacuum. A large drum of 10 $m^3$ may tumble about 15 ton a day.

### Automation of Curing Processes

For practical reasons, equipment that combines tenderizing with other curing process may be used, reducing the processing time. In addition to modular systems, automation is important in curing processes, especially for products that are designated to be consumed in not too long time. In such systems, the steady temperature and the pH value control of the processed material are important. Furthermore, they are provided with special filters for cleaning recycled processing curing liquids, and the equipment is provided with a CIP (Clean in Place) system.

### Smoking

Smoking in food is applied for sensory and, nowadays less, for preservation reasons. Besides meat and fish that were among the first foods preserved by smoking, some other products are smoked, such as peppers, cheese, eggs, and fruits, and even some drinks such as beer and Scottish whiskey. The characteristic odor and taste of smoked foods depend to a significant extend on the kind of smoke and the method of smoking. The kind of smoke depends very much on the wood used. Generally, hard wood is better than soft wood (e.g., beech, hickory, apples). Wood shavings, saw dust, or wood chips are normally used (Fig. 11.20). The influence of the type of wood is reduced, when the size of the wood pieces becomes smaller. When larger pieces of wood are used, the heated wood is continuously rubbed against a rotating disc, producing smoke and serving to maintain the fire on wood alive (Fig. 11.21). There are more than 200–300 substances in the smoke of wood. In food preservation, substances such as phenols and formaldehyde are

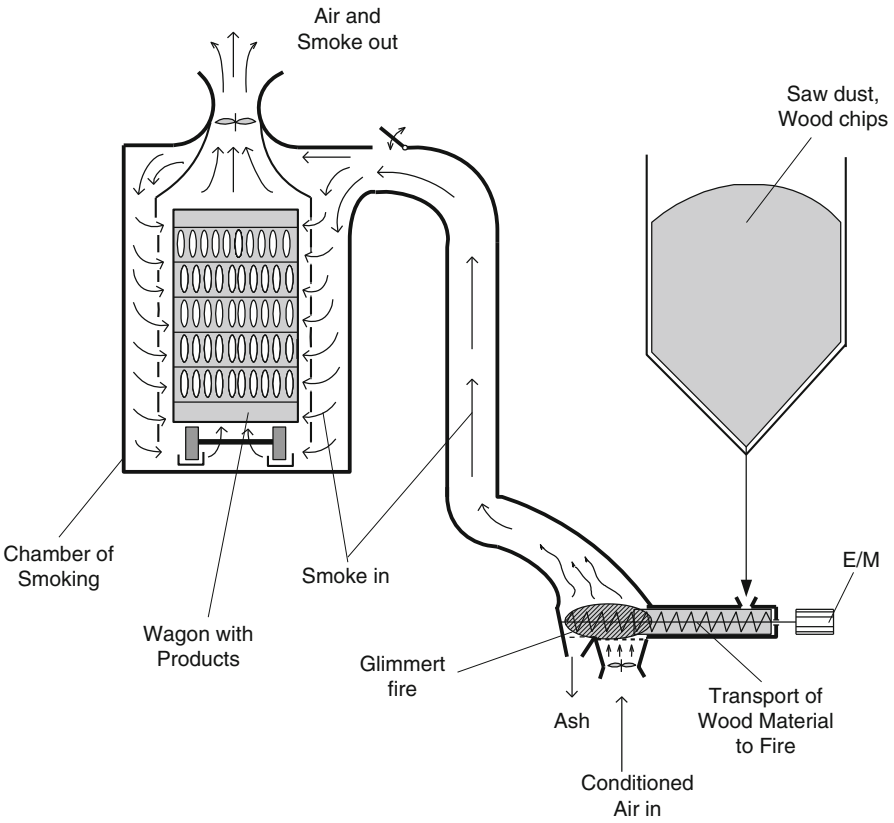


**Fig. 11.20** Chamber-hot smoking

important. The first acts against microorganisms and the second against yeasts and molds. In sensory aspects, smoke may influence the color, the taste, the odor, and the texture of products.

Sensory changes caused by smoke include the following: color (product*s* become brown), taste (reduced palatability), texture (firmer due to partial drying), and flavor (aroma influenced by carboxylic acid and polycyclic reactions). However, recently, as in smoke there are carcinogenic substances (e.g., polycyclic aromatic hydrocarbons such as benzopyrene), the smoke is filtered out.

Three methods of smoking can be distinguished as cold smoking, warm drying, and water smoking.

*Cold smoking* process is applied to products that must be preserved longer. It lasts several hours or even days, and it is performed at temperatures 8–26 °C. In some cases, higher temperatures may be applied (e.g., 30–55 °C). The air humidity varies between 60 and 100 %, and smoke prevents molding of the surface of the food products in the first days of the product input, when the product (e.g., sausages) is still wet. The method is rather a traditional drying process, accomplished in smoke chambers by using hard wood for producing smoke. The high salt

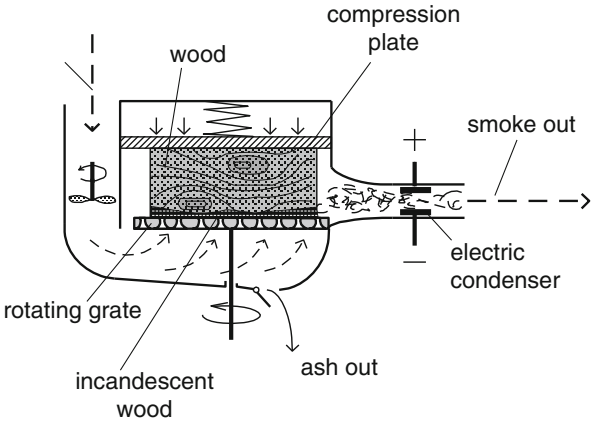


**Fig. 11.21** Electrostatic accretion of smoke

content of the meat and the reduced water content discourage the invasion of molds and microorganisms in the food. The products are hanged above glowing fire, which must be maintained steady by slow agitation.

*Warm drying*. In this process, temperatures at about 60 °C are used. According to the type of meat and the desired quality of the final product, this process may last from hours up to several days. The heating in the smoking chamber is mainly induced by installed heat exchangers which are part of other heating sources, serving a better control of the overall temperature.

*Hot smoking*. This kind of smoking is also called "water smoking." Heating is independent of smoking. The products are hanging in small wagons (about $1 \times 1 \times 2$ m) that get in full air-conditioned tunnel chambers (Fig. 11.20). In the case of a continuous process, more wagons may follow each other in a tunnel. When curing meat, the product is washed up, pre-dried, smoked, cooked, water cooled, and air cooled before exiting the tunnel. In another case, the products are put in small baskets being moved (circulating) in a smoked chamber (Fig. 11.22).

The fish hot smoking process in tunnels is similar to that of meat products. Here, the processing is as follows: washing, pre-salting, splitting, pre-drying with warm air, smoking, refined cooking, cooling with air, and packaging.

For a better control of smoking, smoke may pass through electric condensers, ionizing its particles which successively adhere on the products that have to be smoked (Fig. 11.21). Hot smoking is prevailing nowadays, because preservation is not the prime objective of the consumers.

## 11.4 Gas/Liquid Absorption Equipment

Gas absorption and desorption (stripping) are physical separation processes, in which a gas component of a mixture is absorbed or desorbed in a liquid, using single- or multistage absorption equipment, in a similar operation with distillation

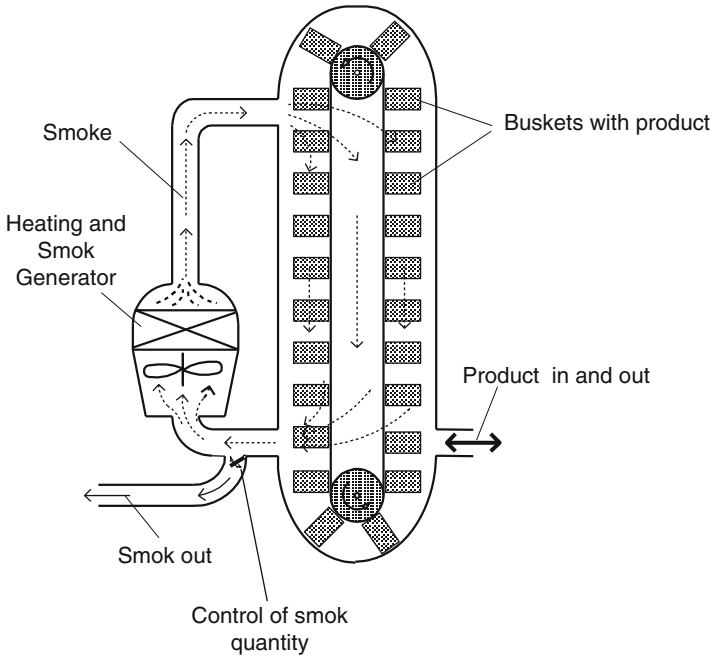


**Fig. 11.22** Continuous smoking

and liquid/liquid extraction. In food processing, absorption and desorption (stripping) of oxygen and carbon dioxide in aqueous solutions/liquid foods are the most important systems (aerobic fermentations, deaeration of liquid foods, carbonation of beverages). In addition, absorption/desorption of sulfur dioxide in some fluid food systems (fruit juices, wine) is of interest.

### *11.4.1 Gas/Liquid Equilibria*

Most of the gas/liquid operations in food processing involve dilute aqueous solutions, which simplify the analysis of gas/liquid equilibria and the design of separation equipment.

In dilute solutions, the gas/liquid equilibria are expressed by the Henry law:

$$p_i = H_i x_i \tag{11.27}$$

where ($p_i$, $x_i$) are the partial pressure (bar) and mole fraction of component ($i$) and ($H_i$) is the Henry law constant (bar/mole fraction). Equilibrium or solubility of gases in liquids is expressed either as the Henry law constant ($H_i$) or, more appropriately, by its inverse ($1/H_i$) in units of mole fraction/bar. Typical solubility

data for gases/water at 25 °C of interest to food processing (Perry and Green 1997) are as follows:

Oxygen, $1/H_i = 2.3 \times 10^{-5}$ mole fraction/bar $= 2.3 \times 32 \times 10^{-5}/18 = 4 \times 10^{-5}$ g/g water bar or 40 ppm/bar. The solubility of oxygen in air at atmospheric pressure ($P \approx 1$ bar) in water is about $40/5 = 8$ ppm.

Carbon dioxide, $1/H_i = 8 \times 10^{-4}$ mole fraction/bar $= 8 \times 44 \times 10^{-4}/18 = 19.6 \times 10^{-4}$ g/g water bar or 1960 ppm/bar $= 0.2$ % by weight.

Nitrogen, $1/H_i = 1.2 \times 10^{-5}$ mole fraction/bar $= 1.2 \times 28 \times 10^{-5}/18 = 1.8 \times 10^{-5}$ g/g water bar $= 18$ ppm/bar.

For atmospheric air at I bar, the solubility of nitrogen in water becomes $18 \times (4/5) = 14.4$ ppm.

In food processing, the gas phase is considered as ideal (relatively low pressures), and the Dalton law is applicable ($p_i = y_i P$), where ($y_i$) is the mole fraction of component ($i$) in the gas phase and ($P$) is the total pressure. Thus, the equilibrium relationship of (11.27) becomes

$$y_i = m_i x_i \tag{11.28}$$

where $m_i = H_i/P$.

The gas/liquid equilibrium constant ($m_i$) is equivalent to the distribution coefficient ($K_i$) of the vapor/liquid- and liquid/liquid-phase equilibria.

## *11.4.2 Determination of Equilibrium Stages*

Absorption and desorption (stripping) of gases in solutions can be carried out in agitated vessels and in columns/towers. In the agitated vessels, equilibrium (one stage) is approached by vigorous mixing. Agitated vessels are used for the transfer of oxygen in aerobic fermentations, and their construction and power requirements are discussed in Chap. 5 (mixing). Multistage countercurrent absorption is carried out either in tray columns or in packed towers.

### 11.4.2.1 Tray Columns

Design of tray columns is similar to the design of distillation and liquid/liquid tray columns, discussed earlier in this chapter. For dilute solutions, common in food applications, the gas ($G$) and liquid ($L$) flow rates in countercurrent columns are considered constant, and overall material balance in the column yields a straight operating line:

$$y_1 - y_2 = (L/G)(x_1 - x_2) \tag{11.29}$$

where ($y_1$, $y_2$) are the mole fractions of the component in the gas at the inlet (bottom) and outlet (top) of the column, respectively, and ($x_1$, $x_2$) are the corresponding mole fractions in the liquid.

The number of equilibrium stages ($N$) can be determined graphically, using the McCabe–Thiele diagram, in which both equilibrium and operating lines are straight lines with slopes ($m$) and ($L/G$), respectively. The number of stages can also be calculated analytically, in analogy to extraction, using the Kremser equation:

$$N = \log[R_a(1 - 1/A) + 1/A]/\log(A) \tag{11.30}$$

where $R_a = (y_1 - mx_2)/(y_2 - mx_2)$, absorption ratio and $1/A = (mG/L)$, absorption factor.

If pure liquid is used at the top of the column ($x_2 = 0$), the absorption ratio is $R_a = (y_1/y_2)$.

An equation similar to (11.30) can be used for the calculation of ($N$) of a stripping column, substituting ($R_a$) with $R_s = (x_2 - y_1/m)/(x_1 - y_1/m)$, stripping ratio, and ($1/A$) with $A = (L/mG)$, stripping factor.

The efficiency of the tray columns, used for absorption and stripping operations, is generally lower than the efficiency of the distillation and extraction columns (about 10–15 %), due to the poor mixing of the gas with the liquid and inefficient mass transfer.

#### 11.4.2.2 Packed Towers

Absorption of gases in liquids in the chemical process industries is usually carried out in packed towers, which use various packing materials to affect gas/liquid contact and mass transfer, instead of the tray columns, used in distillation and extraction. Packed towers are continuous separation systems, the separating capacity of which is measured by the number of theoretical transfer units (NTU) instead of the number of theoretical stages ($N$) of the multistage systems.

In dilute solutions, which are characteristic of gas/liquid absorption in food systems, the height of absorption or stripping towers ($Z$) is equal to the product of the number of theoretical transfer units (NTU) times the height of transfer unit (HTU):

$$Z = (\text{NTU})(\text{HTU}) \tag{11.31}$$

For absorption towers, $(\text{NTU}) = \int[dy/(y - y_e)]$ and $\text{HTU} = G/K_g\alpha P$.

The integral $\int[dy/(y - y_e)]$ is estimated graphically or analytically from ($y_2$) to ($y_1$), where ($y_1$, $y_2$) are the mole fractions of the gas component being transferred at the inlet (bottom) and outlet (top) of the column, respectively, and $y_e$ is the mole fraction of the gas in equilibrium with the liquid entering the column at the top ($y_e = mx$). For clean absorption liquid, $x_2 = 0$ and $y_e = 0$ at the top of the column. ($G$) is the gas flow rate (kmol/m$^2$ s), ($K_g$) is the mass transfer coefficient

(kmol/m$^2$ s Pa), ($\alpha$) is the specific surface of the packing (m$^2$/m$^3$), and ($P$) is the total pressure (Pa).

For stripping (desorption) towers, the following analogous relationships are used:

$$\text{NTU} = \int [dx/(x_e - x)] \quad \text{and} \quad \text{HTU} = L/K_1 \alpha \rho_M \tag{11.32}$$

The integral $\int[dx/(x_e - x)]$ is estimated graphically or analytically from ($x_2$) to ($x_1$), where ($x_2$, $x_1$) are the liquid mole fractions of the component at the inlet (top) and outlet (bottom) of the stripping tower, respectively, and ($x_e$) is the mole fraction in the liquid which is in equilibrium with the gas phase ($x_e = y/m$). For clean stripping gas, $y_2 = 0$ and $x_e = 0$ at the bottom of the tower. ($L$) is the liquid flow rate (kmol/m$^2$ s), ($K_l$) is the liquid overall mass transfer coefficient (m/s), ($\alpha$) is the specific surface of the packing (m$^2$/m$^3$), and ($\rho_M$) is the molar liquid density (kmol/m$^3$).

The overall mass transfer coefficients ($K_g$) and ($K_l$), based on the gas and liquid phase, respectively, are characteristic parameters of the mass transfer system, related to the geometry and flow conditions of the equipment and to the physical and transport properties of the materials involved (Perry and Green 1997; Saravacos and Maroulis 2001).

For dilute solutions, the number of theoretical transfer units in a countercurrent absorption tower can be estimated by the Colburn equation, which is analogous to the Kremser equation:

$$\text{NTU} = \ln[R_a(1 - A) + A]/[1 - (1/A)] \tag{11.33}$$

where the absorption ratio ($R_a$) and the absorption factor ($A$) are defined as in the Kremser equation for absorption columns (11.30). The same equation (11.33) can be used for estimating the (NTU) of packed stripping towers, substituting ($R_a$) with the stripping ratio ($R_s$) and ($A$) with the stripping factor ($1/A$), as defined in the Kremser equation (11.30).

An alternative method of determining the height of a packed tower ($Z$) is the equation

$$Z = N(\text{HETP}) \tag{11.34}$$

where $N$ is the number of theoretical stages of a multistage countercurrent column of equivalent separating capacity with the absorption tower and HETP is the height of an equivalent theoretical plate ($m$). The number ($N$) is more easily determined with methods developed in distillation, and it can replace NTU, provided that data on HETP are available. In some systems, NTU and HTU may coincide with N and HETP.

Experimental and operating data on HTU and HETP of various packing materials have been correlated empirically with the flow conditions of absorption and stripping equipment (Perry and Green 1997; Walas 1988).

## *11.4.3 Gas Absorption and Stripping Equipment*

Gas absorption or desorption (stripping) equipment is carried out in agitated vessels, absorption towers, or gas scrubbers.

### 11.4.3.1 Agitated Vessels

Agitated vessels are used for simple, one-stage operations, like absorption of oxygen in aerobic fermentations. The design and operation (power requirements) of the agitated vessels are discussed in Chap. 5 (mixing). Special impellers (turbines) and baffles are required for efficient dispersion and absorption of gases in liquids (Perry and Green 1997).

Absorption of oxygen in water and aqueous solutions presents certain difficulties, due to its very low solubility. High power (kW) is required for dispersing and absorbing oxygen gas in water (increasing the mass transfer coefficient). The optimum mass transfer rate is about 2.2 kg $O_2$/kWh.

Surface agitators are used in the aerobic treatment of wastewater, transferring oxygen from the atmosphere to the liquid biomass. Oxygen can also be supplied to liquid media by gas spargers (distributors), installed at the bottom of the treatment tanks.

Removal of air, oxygen, and other dissolved gases from food liquids is usually accomplished by vacuum stripping in single-stage equipment. For efficient operation, large specific surface of the liquid is required, obtained by spraying the product into the vacuum vessel.

Absorption of carbon dioxide in liquid foods, e.g., carbonated beverages, is easier than oxygen absorption, due to the higher solubility of the gas in water. According to Henry law, the solubility of carbon dioxide increases linearly with the partial pressure, and this explains the need for pressurized packaging of the carbonated beverages.

### 11.4.3.2 Multistage Columns and Packed Towers

Tray columns and packed towers are used, when relatively large numbers of stages are needed. The simplest multistage system for gas absorption is the bubble column, which consists of a column, with the liquid flowing downward and the gas bubbling through the liquid from the bottom and exiting at the top. The bubble columns have a relatively low separation efficiency (high HTU or HETP values). Spray towers

operate in a similar manner, with the liquid falling from the top in the form of sprays (droplets) and the gas introduced at the bottom of the tower.

More efficient absorption is achieved in tray columns and absorption towers, operated in countercurrent flow of liquid and gas. Sieve trays are commonly used in columns, similar to the distillation and liquid/liquid extraction equipment, but with lower efficiencies (10–15 %).

Packed towers are preferred for smaller operations (diameter less than 1.5 m) and in systems where high-pressure drop is not accepted, e.g., in vacuum operation. Porcelain, metal, and plastic materials in the form of rings, cylinders, and saddles are used (Perry and Green 1997). The effectiveness of the packing materials depends on their specific surface ($\alpha$, $m^2/m^3$) and the packed porosity ($\varepsilon$), expressed by the packing factor $F = \alpha/\varepsilon^3$ in units ($m^2/m^3$). The HETP values of packed materials range from 0.3 to 0.5 m.

#### 11.4.3.3 Gas Scrubbers

Gas scrubbers are used to remove small particles and undesirable gases from industrial exhaust gases, for the primary purpose of reducing environmental pollution (Perry and Green 1997). They are usually installed after the mechanical cyclone collectors, which are efficient for removing particles larger than 1–5 μm (Chap. 5, Mechanical Separations).

Cyclone scrubbers are mechanical cyclones in which an absorbing liquid (water or aqueous solutions) is sprayed from several nozzles in a central manifold. The gas comes into intimate contact with the liquid, and it leaves the cyclone near equilibrium (one-stage operation).

The ejector-venturi scrubbers use high-velocity jets of water to create a suction and absorb the gas, in a parallel-flow operation. Large quantities of water are required, which should be disposed in the environment without creating pollution problems.

Scrubbers are necessary to reduce air pollution in some food processing plants. Certain food processing operations produce undesirable gases and volatiles, which cause air pollution (mainly offensive odors) in the area surrounding the food plant. Food processes, involved in air pollution, include air drying, solvent extraction and refining of edible oils, coffee processing, fermentation, and baking. Air scrubbers, usually installed after dust collection equipment (cyclones or air filters), operating with water or dilute alkaline solutions, can remove most of the offensive gases from the exhaust streams (see Chap. 5).

## 11.5 Adsorption and Ion Exchange Equipment

Adsorption and ion exchange equipment is used to adsorb solute components from liquids or gases with the purpose of clarifying the fluid of unwanted materials or recovering valuable components. The separation is affected by physical adsorption on solid adsorbents or ion exchange resins, which are regenerated for repeated use.

Commercial adsorbents include activated carbon, silica gel, activated alumina, and molecular sieves, while ion exchangers include cation and anion exchange resins. Batch adsorption and ion exchange equipment (fixed beds) is used in most applications. Desorption of the adsorbed components is accomplished by washing the fixed bed or by increasing the temperature. Regeneration of the ion exchange beds is achieved by washing with salt or alkali solutions.

### *11.5.1 Adsorption Equilibria and Mass Transfer*

The adsorption capacity of a solid adsorbent is determined by measuring the amount of the solute component as a function of its partial pressure or concentration in the fluid phase. Various empirical equations are used to express this relationship, the simplest of which is the Freundlich equation, which for a gas/solid system becomes (Perry and Green 1997)

$$w_i = K p_i^n \tag{11.35}$$

where ($w_i$) is the amount of adsorbed component (kg/kg adsorbent), ($p_i$) is the partial pressure of the solute component in the gas phase (Pa), and ($K$, $n$) are characteristic constants of the system. For systems favoring adsorption, $n < 1$. For liquid/solid adsorption, the partial pressure is replaced by the concentration ($C$) of the solute component in the liquid phase (kg/m$^3$).

More complex sorption relationships, such as the Langmuir, the BET, and the GAB equations, have been used to express the fluid/solid equilibria in food systems.

Fluid/solid equilibrium data are usually presented as component mass fraction ($w_i$) versus relative pressure ($p_i/p_o$), where ($p_o$) is the vapor pressure of component ($i$) at the given temperature of the system. These plots are known as the sorption isotherms of the solute component/solid adsorption system, and they are used extensively in food science and engineering.

The separating specificity and capacity of solid adsorbents depends primarily on the physical and chemical structure of the material. Special processes are used to prepare efficient adsorbents for a specific application, e.g., activated carbon is prepared by burning some of its liquid components, increasing the porous structure and specific surface area. Molecular sieves (special aluminosilicate compounds), due to their pore structure, have a much higher sorption capacity at lower partial pressures than silica gel, making them more effective in removing small amounts of solutes from the fluid phase, e.g., a better desiccating agent.

The volumetric mass transfer rate from a gas or liquid phase to a solid adsorbent ($J$, kg/m$^3$ s) is given by the equation

$$J = k_g \alpha (p_i - p_{ie}) \tag{11.36}$$

where ($p_{ie}$, Pa) are the equilibrium concentration of component ($i$), ($k_g$) is the mass transfer coefficient of the gas phase (kg/m$^2$ s Pa), and ($\alpha$) is the interfacial area (m$^2$/m$^3$).

For liquid-phase volumetric mass transfer, the rate equation becomes

$$J = k_L \alpha (C_i - C_{ie}) \tag{11.37}$$

where ($C_i$, $C_{ie}$) are the concentrations of component ($i$) in the liquid and at equilibrium, respectively (kg/m$^3$) and ($k_L$) is mass transfer coefficient in the liquid phase (m/s).

The mass transfer coefficients can be estimated from empirical correlations of the mass transfer factor ($j_M$):

$$j_M = aRe^m \tag{11.38}$$

Regression analysis of published data on mass transfer coefficients in food systems (Saravacos and Maroulis 2001) has yielded the following average values of the constants of (11.37): ($a = 1.11$, $m = -0.54$). The Reynolds number is defined as $Re = dG/\eta$ or $Re = dL/\eta$, where ($d$) is the particle diameter (m) and ($\eta$) is the fluid viscosity (Pa s).

The mass transfer factor is defined by the equations

$$j_M = k_G P/G \quad \text{or} \quad j_M = k_L \rho/L \tag{11.39}$$

where ($G$, $L$) are the gas or liquid flow rates (kg/m$^2$s), respectively, $P$ is the total pressure (Pa), and ($\rho$) is the liquid density (kg/m$^3$).

Physical properties of the adsorbents, which affect mass transfer and adsorption capacity, are the particle diameter ($d$), bulk density ($\rho_b$), bulk porosity ($\varepsilon$), and specific surface area ($\alpha$). Typical values of these properties for commercial adsorbents are $d = 1$–$4$ mm; $\rho_b = 500$–$800$ kg/m$^3$; $\varepsilon = 0.25$–$0.35$; and $\alpha = 1000$–$3000$ m$^2$/m$^3$.

### 11.5.2 Adsorption Equipment

Adsorption of components from fluids is accomplished in fixed vertical beds of porous granular adsorbents. The fluid flows usually from the top down through the bed, while regeneration is carried out by upward flow of the regenerant solution.

Figure 11.23 shows diagrammatically the operation of an adsorption bed with the characteristic breakthrough curve.

A fluid of initial solute concentration ($Y_o$) is fed from the top through the bed, and the concentration of the effluent ($Y$) is recorded. Initially, all the adsorbent in the bed is active, and the effluent concentration is nearly zero. However, after some time of operation, the concentration ($Y$) starts to rise sharply, e.g., at the "break" point (B). After all the adsorbent is saturated with the solute, the effluent concentration reaches asymptotically the initial solute concentration ($Y_o$).

The fixed adsorption bed is designed on the basis of material balances and equilibrium relationships, in a similar manner with the design of packed absorption towers. The resulting design equation is

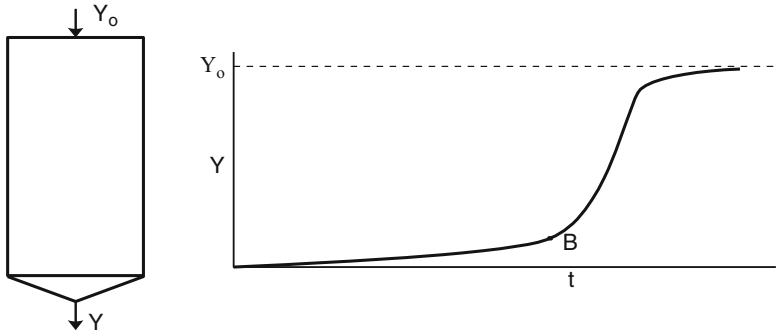


**Fig. 11.23** Breakthrough curve in an adsorption column

$$\partial Y/\partial z = (1/\mathrm{HTU})(Y - Y_e) \tag{11.40}$$

where ($Y$, $Y_e$) are the concentrations of the solute in the bed at bed depth $z$ and at equilibrium, respectively, and (HTU) is the height of one transfer unit, defined by the equation: for the gas phase, (HTU) $= G/k_G\alpha$ and for the liquid phase, (HTU) $= L/k_L\rho$ (11.41), where ($\rho$) is the liquid density (kg/m$^3$).

The height of the adsorption bed ($Z$) is calculated from (11.41), e.g., from a graphical solution (Walas 1988), using appropriate parameters.

### *11.5.3 Ion Exchange Equipment*

Ion exchange separations are based on the exchange of cations and anions from a solution or food liquid with the ions of an ion exchange resin. Synthetic polymer resins are designed to separate specific ions from various liquids.

Commercial ion exchange columns range up to 4 m diameter and bed heights of 1–3 m. Sufficient free space above the bed should be allowed for bed expansion during operation and regeneration, which can exceed 50 %. The particle size of the ion exchange resins ranges from 0.3 to 0.8 mm and 18 to 04 mm. The resin beds are supported by a layer of about 0.2 m at the bottom. Construction details of the ion exchange columns are given by Walas (1988).

The ion exchange rate is affected by the mass transfer resistances of the resin particulate system. At low solute concentrations, which is the case of most food applications, film diffusion is the controlling mechanism.

The capacity of ion exchange resin is about 2 meq/g of resin, which corresponds to the removal of about 0.2 kg of calcium carbonate/kg of resin (softening or demineralization of hard water). The bulk density of the ion exchange resins varies from 600 to 900 kg/m$^3$. Liquid flow rates in the ion exchange beds range from 14 to 18 m$^3$/m$^2$ h.

Regeneration of the cation exchange resins is usually accomplished by upward flow of sodium chloride solutions, while alkali solutions are used to regenerate the anion exchange resins. Mixed beds, consisting of two layers of cation and anion exchange resins of differing bulk densities, are regenerated by salt and alkali solutions, introduced from the top and the bottom, with the waste solutions removed from the middle of the bed.

The operating cycle of an ion exchange system includes the following: (1) passing of the process stream through the bed for the proper time, (2) rinsing the bed and recovering any occluded valuable solution, (3) backwashing of the bed to remove accumulated materials and reclassify the particle size distribution, (4) regeneration of the bed for the proper time, and (5) rinsing of the bed to remove any occlude regenerant.

## *11.5.4 Food Applications*

### 11.5.4.1 Water Treatment

Removal of odors, chlorine, and other undesirable compounds from drinking and process water can be accomplished by adsorption in activated carbon beds. Regeneration of the spent adsorbent is usually achieved by controlled burning in special furnaces.

Softening and demineralization of drinking, process, and steam boiler water are the most important applications of ion exchange separations. Softening and removal of carbonates can be accomplished using two cation exchange beds, one weak acid, and a second strong acid resin. Complete demineralization of water with simultaneous removal of silicates can be accomplished with four columns, in the following order: strong acid, weak alkali, strong alkali, and mixed bed. Regeneration is accomplished with acid (hydrochloric acid) and alkali (sodium hydroxide).

Fouling of the ion exchange beds with suspended particles can be prevented by pre-filtration of the water through carbon beds or other filters. Some macroporous resins can handle suspended materials during operation, which are rejected from the resins by vigorous backwashing, before regeneration.

Special ion exchangers are used to remove from drinking and process water some specific mineral ions, which may be toxic or radioactive, such as nitrates, lead, barium, strontium, and cesium.

Figure 11.24 shows a system of cation/anion exchange columns used in water softening.

### 11.5.4.2 Recovery of Valuable Components

Recovery of valuable proteins from food and biotechnological solutions/suspensions can be accomplished with special ion exchange resins. A typical application is

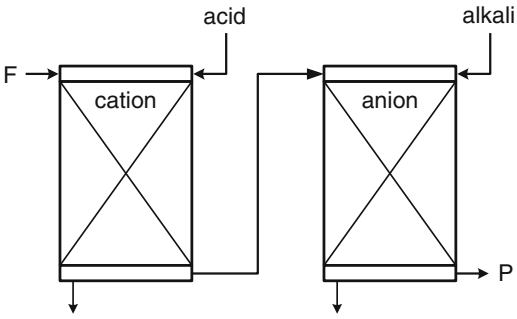


**Fig. 11.24** Diagram of a cation/anion exchange column system. *F* feed water, *P* product (deionized) water

the recovery of proteins from cheese whey. Depending on the pH of the liquid, the proteins behave either as cation or anion components, and thus anion or cation exchange resins are used for their recovery. Elution of the adsorbed proteins is affected either by altering the pH or increasing the ionic strength (Grandison and Lewis 1996).

Industrial enzymes (e.g., amylase) can be recovered from fermentation liquids or from food materials with special ion exchange resins (combinations of strong anion and strong cation exchangers).

#### 11.5.4.3 Removal of Undesirable Components

Adsorption and ion exchange beds are used for the removal of various undesirable components from food liquids, either as a pretreatment step during further processing or a final step for improving the quality of the food product. Typical applications are decolorizing of sugar solutions and liquid foods, decaffeination of soluble coffee, demineralization of dairy products and fruit juices, and debittering of citrus juices.

Demineralization of food liquids (e.g., cheese whey) with ion exchangers can remove undesirable ions, such as Na, K, Mg, Cl, phosphate, citrate, and lactate. A system of strong cation, followed by a weak anion exchanger, may be used, followed by regeneration with strong acid and alkali.

Demineralization of cane, beet, and hydrolyzed sugar solutions with ion exchangers is applied in clarifying and preparing sugar solutions for further processing by evaporation, followed by crystallization.

Bitter components of citrus (grapefruit and navel orange) juices, like limonin and naringin, should be removed, particularly when present in considerable concentrations (Nagy et al. 1993; Kimball 1999). The juices are first clarified by centrifugation or membrane ultrafiltration (UF) and then debittered in beds of special ion exchange resins, made of divinylbenzene polymer (Cheryan 1998). The bed removes practically all the limonin and about 90 % of the naringin, and it is regenerated with a weak alkali solution. The saturated bed is regenerated after about 20 h of operation. The operating cycle includes 2 h of debittering and 4 h of

regeneration. The debittered clear juice is combined with the separated fruit pulp to make the regular cloudy citrus juice (see also Chap. 12).

Simultaneous debittering and deacidification of citrus juices can be achieved with special ion exchange resins. Ion exchange resins and adsorption materials, used in food processing, must be nontoxic and approved by national food authorities, such as the FDA in the USA.

## 11.6 Crystallization from Solution Equipment

Commercial crystallization from solution is used to separate and recover various solutes from solutions, by cooling or evaporating the solvent. Crystallization of ice in freeze concentration and fat fractionation by crystallization from melt are treated in Chap. 12.

Like the other mass transfer operations, crystallization from solution is based on phase equilibria (solubilities) and mass transfer rates.

### *11.6.1 Solubility Considerations*

In food processing, most crystallizations take place from aqueous solutions, e.g., sugar and salt. The solubility of a solute in water ($C$) is expressed in crystallization calculations as a mass ratio, i.e., kg solute/kg of water, and it increases significantly with the temperature, as shown in Fig. 11.25.

Below the saturation line (AB), the solution is undersaturated. By cooling a solution from point (E) at constant concentration C (no evaporation), the solution can cross the supersaturation line (CD) and reach an unstable state (F), where fast crystallization may start.

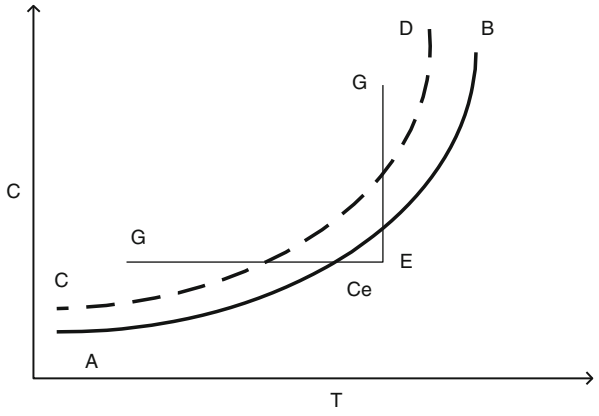


**Fig. 11.25** Solubility–temperature diagram. AB, saturation; CD, supersaturation

A similar condition may be created by concentrating the solution at constant temperature ($T$), e.g., by evaporation, when a supersaturation point (G) may be reached, starting fast crystallization. The area between saturation and supersaturation is the unstable state.

The supersaturation of a solute is expressed by the difference $\Delta C = C - C_e$, where $C_e$ is the equilibrium concentration (on the saturation line).

### *11.6.2 Nucleation and Mass Transfer*

Crystallization from solution starts with nucleation, followed by crystal growth. Nucleation (formation of several microscopic nuclei) is either heterogeneous (foreign particles) or homogeneous (particles of the same material).

The rate of homogeneous nucleation ($N$, nuclei/m$^3$ s) is given by reaction-rate kinetics, which is simplified to the empirical equation

$$N = k(\Delta C)^i \tag{11.41}$$

The nucleation constants ($k$, $i$) depend on the geometry of the system and the agitation rate.

The nucleation can be enhanced by adding small crystals (about 1 μm size) to the saturated solution, as in the seeding of sugar crystallizers.

Crystal growth of the nuclei of the solution is limited by the mass transfer from the bulk of the solution to the surface of the growing crystals (molecular or turbulent diffusion). The growth rate of crystals is usually expressed as the rate of increase of a linear dimension ($L$) of the crystal (d$L$/d$t$), which is related linearly to the supersaturation ($\Delta C$), according to the McCabe law:

$$(dL/dt), = (K/\rho)(\Delta C) \tag{11.42}$$

where ($K$) is the mass transfer coefficient (m/s) and ($\rho$) is the density of the crystals.

The crystal growth rate is a function of the mass transfer coefficient ($K$), which increases at high agitation rates and lower viscosity of the solution. The growth of crystals is affected by the presence of foreign substances in the solution, resulting in the production of crystals of special sizes and shapes, e.g., in the crystallization of sodium chloride.

The crystallization kinetics (nucleation and crystal growth) is investigated in the laboratory and the pilot plant, using the mixed suspension mixed product removal (MSMPR) continuous crystallizer (Mullin 1993; Nyvlt 1971). In analyzing the operation of the MSMPR crystallizer, in addition to the usual material balances and mass transfer rates, the population balances of the system should be considered (Randolph and Larson 1971).

### 11.6.3 Industrial Crystallizers

The industrial crystallizers are classified according to the method of obtaining supersaturation, i.e., by cooling, evaporation, or mixed operation. The crystallizing suspension is called "magma," while the saturated solution, remaining after removing the crystals, is known as "mother liquor."

The yield of a crystallizer ($Y$, kg) is given by the simplified material balance equation:

$$Y = W[C_1 - C_2(1 - V)] \tag{11.43}$$

where $W$ is the initial mass of the solvent (water), ($C_1$, $C_2$) are the concentrations of the solute before and after crystallization, and ($V$) is the fraction of water evaporated (kg water/kg initial solution).

Cooling crystallizers consist of a cooling/separation system, resembling the forced circulation evaporator (Chap. 7), with the heater replaced by a cooling (shell and tube) heat exchanger. In the draft tube baffled (DTB) crystallizers, the recirculation is carried out in a draft tube, which is installed in the crystallizer. Crystallization by cooling of viscous solutions is accomplished in scraped surface heat exchangers (Chap. 6), e.g., in margarine and ice cream production.

Evaporative crystallizers are similar to the forced circulation evaporators (Chap. 7) with an additional crystallization vessel below the vapor/liquid separator for the growth of the crystals (Oslo crystallizer). Simultaneous evaporation and cooling crystallizers operate without external heat exchangers, with the cooling effect provided by vacuum evaporative cooling of the saturated solution (Walas 1988).

Production of large crystals can be obtained by recirculation of the magma within the crystallizer and removal of the small crystals by dissolving in an outside vessel. Large crystals are produced in a crystallization column at the bottom of the crystallizer (elutriation leg).

*Example 11.1* Design a distillation column to recover the ethanol from a fermentation solution, containing 5 % of ethanol, using the simplified method. The composition of the distillate and the bottom products will be 89 % and 0.1 % ethanol res.

**Data and Assumptions**

The column is assumed to operate at atmospheric pressure with steam heating the reboiler and water cooling the total condenser. The mean relative volatility of ethanol/water in the column is taken $\alpha = 4$.

The feed is assumed to enter the column as saturated liquid ($q = 1$). The molar flow rates of liquid and vapors in the stripping and enriching sections of the column are assumed constant, although the ethanol/water system is highly nonideal. A more accurate analysis of the ethanol/water distillation can be made using numerical stage-to-stage calculations or the Ponchon–Savarit graphical method.

It should be noted that the maximum concentration of the distillate in an atmospheric distillation is 0.896 mole ethanol, i.e., the azeotrope of ethanol/water (95 % ethanol by volume).

**Theoretical Stages and Trays**

The minimum number of stages ($N_{min}$) at total reflux will be, for $x_D = 0.89$, $x_B = 0.001$ (11.13):

$$N_{min} = \log\{(0.89)(0.999)/(0.001)(0.11)\}/\log(4) = 6.5$$

The minimum reflux ratio ($R_{min}$) for infinite number of stages will be given by the Underwood equations (11.14) and (11.15), for $x_F = 0.05$, $q = 1$, and $\alpha = 4$:

$$(4 \times 0.05)/(4 - \theta) + (1 - 0.05) = 0 \quad \text{and} \quad R_{min} + 1 = (4 \times 0.89)/(4 - \theta)$$

from which $\theta = 3.13$ and $R_{min} = 3.04$.

Assume that the reflux ratio is $R = 1.2R_{min} = 1.2 \times 3.04 = 3.65$. Then $(R - R_{min})/(R + 1) = (3.65 - 3.04)/4.65 = 0.131$. From the Gilliland diagram (Perry and Green 1997) or from the Gilliland correlation (11.16), $(N - N_{min})/(N + 1) = 0.46$. For $N_{min} = 6.5$, $N = 12.9$.

Assuming a column efficiency of 65 %, the number of trays of the column will be $N_T = 12.9/0.65 = 19.83$ or $N_T = 20$.

**Column Sizing**

The column diameter and height are estimated as follows: material balances in the column, $F = D + B = 500$ kmol/h and $x_D D + x_B B = x_F F$. For $x_D = 0.89$, $x_B = 0.001$, and $x_F = 0.05$, $D = 27.6$ kmol/h and $B = 472.4$ kmol/h. In terms of mass flow, considering the molecular weights of ethanol (46) and water (18), $D = 1184$ and $B = 8517$ kg/h.

The column diameter is calculated on the basis of vapor flow in the upper (enriching) section, which is usually higher than in the lower (stripping) section. For the reflux ratio $R = L/D = 3.65$, the liquid flow in the enriching section will be $L = 3.65 \times 27.6 = 100$ kmol/h. The liquid/vapor ratio in this section (slope of the operating line) will be $L/V = R/(R + 1) = 3.65/4.65 = 0.78$ and $V = 100.74/0.78 = 129.15$ kmol/h.

Assume that the mean molar concentration of ethanol in the enriching section is 50 % with a corresponding mean molecular weight of $0.5 \times 46 + 0.5 \times 18 = 32$. Therefore, the mass flow of the vapors will be $V = 129.15 \times 32 = 4133$ kg/h.

The vapor density in the enriching section at a mean temperature of 90 °C will be approximately 0.4 kg/m$^3$. Therefore, the volumetric flow rate of vapors will be $V = 4133/0.4 = 10{,}332$ m$^3$/h or $V = 10{,}332/3600 = 2.87$ m$^3$/s.

The vapor velocity in distillation columns is selected on the basis of flooding (maximum) velocity, which for this system can be taken as 1.5 m/s. The vapor velocity is taken as $0.8 \times 1.5 = 1.2$ m/s.

Therefore, the column cross section (for vapor flow) will be $A = 2.87/1.2 = 2.39$ m$^2$, and the column diameter will be $d = (4A/\pi)^{1/2} = (4 \times 2.39/3.14)^{1/2} = 1.74$ m.

Sieve (perforated) trays are selected, since they are inexpensive and they can be cleaned more easily than the complex tray arrangements. The distance between the trays is taken empirically for this system as equal to 50 cm. Therefore, the column height will be equal to $20 \times 0.5 = 10$ m.

Summarizing, a column 1.74 m diameter and 10 m height will be suitable for the proposed separation.

Note
The design of the reboiler and the condenser of the column is carried out with the conventional procedure of designing shell and tube heat exchangers (see Example 6.1).

*Example 11.2* Estimate the height of a countercurrent liquid/liquid extraction column to remove 90 % of the caffeine from an aqueous solution of 3 % caffeine, using an immiscible organic solvent.

**Data and Assumptions**
Assume a partition coefficient for solvent/solution $K = 2.5$ and a constant mass flow rate ratio liquid/solvent $(L/V) = 1.5$.

Use both the graphical (McCabe–Thiele) and the analytical (Kremser) methods.

**Graphical Method**
For such a dilute system, straight equilibrium and operating lines can be assumed: $Y_e = KX$ or $Y_e = 2.5X$ and $Y = 1.5X$. Feed $X_2 = 0.03$, product $X = 0.003$ (mass fractions).

The following graphical representation (McCabe–Thiele diagram) of the extraction process is easily constructed:

Since this is a dilute system, constant flow rates can be assumed, i.e., the operating line is a straight line, $Y = 1.5X$. The equilibrium line is also a straight line, $Y = 2.5X$.

Graphical construction between the operating and equilibrium lines, starting from $X2 = 0.03$ and stopping at $X = 0.003$, yields number of stages $N \approx 3.5$.

Kremser equation:

The absorption factor $A = L/KV = 1.5/2.5 = 0.6$ and the shipping factor $1/A = 1/0.6 = 1.67$.

Kremser equation (11.26):

$$N = \log\{10(1 - 0.6) + 0.6\}/\log(1.67) = 0.663/0.223 = 3$$

The efficiency of the extraction column depends on the mass transfer between the immiscible phases, and it can be increased by agitation, e.g., the RTC column (Fig. 11.26). Assuming an efficiency of 30 %, the number of plates will be $3/0.3 = 10$. If the distance between the plates is taken as 30 cm, the height of the column will be $10 \times 0.3 = 3$ m.

The diameter of the column will depend on the mass flow rate (kg/h) of the solution (L).

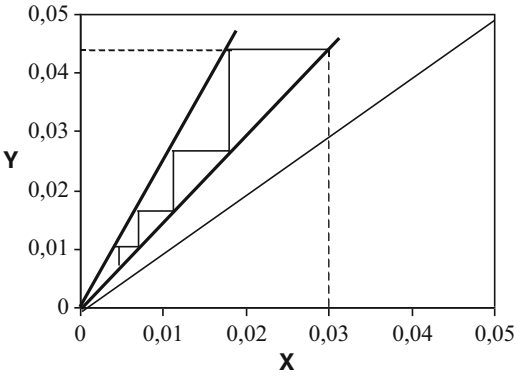


**Fig. 11.26** McCabe–Thiele diagram for extraction of Example 11.2

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