EXTRACTION, LIQUID-LIQUID

1. Introduction

Liquid–liquid extraction, often loosely referred to as solvent extraction, was carried out as early as Roman times when silver and gold were extracted from molten copper using lead as a solvent. The first significant industrial application of solvent extraction was in the petrochemical industry. This was followed by applications for the recovery of and the purification of penicillin, and since 1945 in the nuclear industry in the refining of uranium, plutonium, and other radioisotopes. Since 1960, solvent extraction has been applied on a large scale in the refining of other nonferrous metals, particularly copper. Most recently it has gained increasing importance as a separation technique in biotechnology.

The physical process of liquid–liquid extraction separates a dissolved component from its solvent by transfer to a second solvent, immiscible with the first, but having a higher affinity for the transferred component. The latter is sometimes called the solute component. Liquid–liquid extraction can purify a solute component with respect to other dissolved components that are not soluble in the second solvent, and often the extract solution contains a higher concentration of the solute component than the initial solution. In the process of fractional extraction, two or more solute components can be extracted and also separated if these have different distribution ratios between the two solvents.

The principle of liquid–liquid extraction, and some of the special terminology, are illustrated in Figure 1, which shows a single contacting stage. If equilibrium is fully established after contact, the stage is defined as an ideal or theoretical stage. The two resulting liquid phases are the raffinate from which most of solute C has been removed, and the extract, consisting mainly of solvent B and C.

In the simplest case, the feed solution consists of a solvent A containing a solute component C, which is brought into contact with a second solvent B. For efficient contact, there must be a large interfacial area across which component C can transfer until equilibrium is reached or closely approached. On the laboratory scale, this can be achieved in a few minutes simply by hand agitation of the two liquid phases in a stoppered flask or separatory funnel. Under continuous flow conditions it is usually necessary to use mechanical agitation to disperse one phase in the other followed by coalescence section. After sufficient time and agitation, the system approaches equilibrium that can be expressed in terms of the extraction factor ϵ for component C:

$$\epsilon = \frac{\text{quantity of C in B} - \text{rich phase}}{\text{quantity of C in A} - \text{rich phase}} = m\,\frac{\mathrm{B}}{\mathrm{A}} \tag{1}$$

where B and A refer to the quantities of the two solvents and m is the distribution coefficient.

The component C in the separated extract from the stage contact shown in Figure 1 may be separated from the solvent B by distillation, evaporation, or other means, allowing solvent B to be reused for further extraction. Alternatively, the extract can be subjected to backextraction (stripping) with solvent A under different conditions, eg, a different temperature; again, the stripped solvent B can be reused for further extraction. Solvent recovery is an important factor in the economics of industrial extraction processes.

Whereas Figure 1 assumes a physical extraction based on different solubilities as expressed by the distribution coefficient, many extractions depend on chemical changes. In such cases, the component C in the feed solvent may not itself have any solubility in the extracting solvent B, but can be made to react with an extractant to produce a compound or species that is soluble in B. Many metals can be extracted from aqueous solutions of their salts into organic carrier solvents by using organic extractants that can form organometallic compounds or complexes. Stripping of the metals from the organic to an aqueous phase can be effected by changing a chemical condition, eg, pH.

Extraction, a unit operation, is a complex and rapidly developing subject area (1–3). The chemistry of extraction and extractants has been comprehensively described (4–6). The main advantage of solvent extraction as an industrial process lies in its versatility because of the enormous potential choice of solvents and extractants. The industrial application of solvent extraction, including equipment design and operation, is a subject in itself (7). The fundamentals and technology of metal extraction processes have been described (8,9), as has the role of solvent extraction in relation to the overall development and feasibility of processes (9,10). The control of extraction columns has also been discussed (11).

The rapid development of the fundamentals and technology of solvent extraction is reflected in research papers found in chemistry, chemical engineering, and hydrometallurgical journals. Leading researchers and practitioners of solvent extraction meet regularly at the International Solvent Extraction Conferences (ISEC) whose proceedings (12–24) provide a useful indication of progress and trends. Also, journals, eg, Solvent Extraction and Ion Exchange, contain much up-to-date information on solvent extraction technology.

2. Principles

2.1. Physical Equilibria and Solvent Selection. In order for two separate liquid phases to exist in equilibrium, there must be a considerable degree of thermodynamically nonideal behavior. If the Gibbs free energy, G, of a mixture of two solutions exceeds the energies of the initial solutions, mixing does not occur and the system remains in two phases. For the binary system containing only components A and B, the condition (25) for the formation of two phases is

$$\frac{d^2G}{dx_{\mathrm{A}}^2} > 0 \qquad (2)$$

The stability criteria for ternary and more complex systems may be obtained from a detailed analysis involving chemical potentials (26). The activity of each component is the same in the two liquid phases at equilibrium, but in general the equilibrium mole fractions are greatly different because of the different activity coefficients. The distribution coefficient m', based on mole fractions, of a solute component C between solvents B and A can thus be expressed in terms of activity coefficients.

$$m' = \frac{x_{CB}}{x_{CA}} = \frac{\gamma_{CA}}{\gamma_{CB}} \tag{3}$$

If the mutual solubilities of the solvents A and B are small, and the systems are dilute in C, the ratio m' can be estimated from the activity coefficients at infinite dilution. The infinite dilution activity coefficients of many organic systems have been correlated in terms of structural contributions (27). In the more general case of nondilute systems, where there is significant mutual solubility between the two solvents, regular solution theory must be applied. Several methods of correlation and prediction have been reviewed (26,28,29). The universal quasichemical (UNIQUAC) equation has been recommended (30), which uses binary parameters to predict multicomponent equilibria.

In addition to thermodynamically based predictions of liquid–liquid equilibria, a great deal of experimental data is to be found in the research literature (28,29,31,32). A liquid–liquid equilibrium databank is also available (33).

Because of the nonideal nature of liquid–liquid systems, it is common engineering practice to quote data as mass fractions rather than mole fractions. Ternary systems can be represented graphically on a triangular diagram. The triangle can be equilateral or right angled; the latter has the advantage that ordinary graph paper can be used, and also the vertical and horizontal scales can be changed independently. Figure 2**a** shows a typical phase diagram for a system where solvents A and B are partially miscible, and the solute C is a liquid. The ordinate scale represents mass fraction x_C and the abscissa represents x_B. The composition x_A can be obtained as $(1 - x_B - x_C)$.

The triangular diagram shows the two-phase envelope that encloses regions of overall composition in which two phases exist in equilibrium. In Figure 2**a**, there is only one two-phase region; other types of systems can have two or more such regions. The equilibrium compositions of two liquid phases are connected by tie-lines. Typical tie-lines are shown. It is often convenient for a triangular diagram to be accompanied by a tie-line location curve (Fig. 2**b**), which allows any tie-line to be drawn by simple geometric construction. The procedure is shown for a given composition x_C of 0.10 in the A-rich phase. A line is drawn across from the triangular diagram to Figure 2**b**, then reflected from the equilibrium curve to the diagonal line, to give a composition y_C representing the B-rich phase. A horizontal line is then drawn back to the appropriate point on the two-phase envelope in the triangular diagram, as shown.

It is seen that as the concentration of C is increased, the tie-lines become shorter because of the increased mutual miscibility of the two phases; at the plait point, P, the tie-lines vanish. However, P does not necessarily represent the highest possible loading of C, which can exist in the system under two-phase conditions. In Figure 2**b**, the plait point lies on the diagonal because the compositions of the two phases approach each other at P.

An important use of the triangular equilibrium diagram is the graphical solution of material balance problems, eg, the calculation of the relative amounts of equilibrium phases obtained from a given overall mixture composition. As an example, consider a mixture where the overall composition is represented by point M on Figure 2**a**. If the A-rich phase is denoted by point R (raffinate) and the B-rich phase is denoted by point E (extract), it can be shown that points R, M, and E are collinear, and also

$$\frac{\text{mass of extract}}{\text{mass of raffinate}} = \frac{\text{distance MR}}{\text{distance ME}} \tag{4}$$

This is a statement of the inverse lever rule, which is the basis of techniques for graphical multistage calculations in ternary systems. Although triangular diagrams are widely used, there is the disadvantage that at low concentrations of C the tie-lines become almost horizontal and are hard to draw accurately. This problem can be overcome by plotting the compositions on a solvent-free (B-free) basis using a rectangular diagram. Detailed descriptions of this method and its application are given elsewhere (2,34).

Liquid–liquid equilibria having more than three components cannot as a rule be represented on a two-dimensional (2D) diagram. Such systems are important in fractional extraction, eg, operations in which two solute components C and D are separated by means of two solvents A and B. For the special case where A and B are immiscible, the linear distribution law can be applied to components C and D independently:

$$x_{\mathrm{CB}} = m_{\mathrm{C}} x_{\mathrm{CA}} \tag{5}$$

$$x_{\mathrm{DB}} = m_{\mathrm{D}} x_{\mathrm{DA}} \tag{6}$$

The selectivity or separation factor between the two solutes is defined as the ratio of the distribution ratios:

$$\beta_{\mathrm{CD}} = \frac{m_{\mathrm{C}}}{m_{\mathrm{D}}} = \frac{x_{\mathrm{CB}} x_{\mathrm{DA}}}{x_{\mathrm{CA}} x_{\mathrm{DB}}} \tag{7}$$

By convention, the components C and D are assigned so that the ratio β_{CD} exceeds unity. The greater the selectivity, the easier is the separation of C and D using solvents A and B. Selectivity can be defined in terms of mass ratio, mole ratio, or concentration.

The selection of solvents for a given separation depends largely on equilibrium considerations. Other important factors include cost, ease of solvent recovery by distillation or other means, safety and environmental impact, and physical properties that must permit easy phase dispersion and separation. Solvent selection is therefore a broad-based exercise that is hard to quantify (10). However, a useful quantitative approach has been proposed (25) for comparing simplified equilibrium estimations on the basis of regular solution theory. The polar- and hydrogen-bonding parameters for solutes and possible solvents are plotted as points on a solvent selection diagram. The selectivities can be approximately related to the distances between the points, providing a quick comparison between a large number of potential solvents. Computer-aided solvent selection has been developed using a molecular graphics system (35).

2.2. Chemical Equilibria. In many cases, mass transfer between two liquid phases is accompanied by a chemical change. The transferring species can dissociate or polymerize depending on the nature of the solvent, or a reaction may occur between the transferring species and an extractant present in one phase. An example of the former case is the distribution of benzoic acid [65-85-0] between water and benzene. In the aqueous phase, the acid is partially dissociated:

$$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+ \qquad (8)$$

In the organic phase, the monomer is in equilibrium with the dimer:

$$2\,C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2 \qquad (9)$$

Whereas the linear distribution law can be applied to the undissociated monomer, the interfacial distribution of total benzoic acid, as determined by analysis, is nonlinear.

Many industrial processes involve a chemical reaction between two liquid phases, eg, nitration, sulfonation, alkylation, and saponification. These processes are not always considered to be extractions because the main objective is a new chemical product, rather than separation (36). However, these processes have many features in common with extraction, eg, the need to maintain a high interfacial area with the aid of agitation and the importance of efficient phase separation after the reaction is completed.

In addition to the liquid–liquid reaction processes, there are many cases in both analytical and industrial chemistry where the main objective of separation is achieved by extraction using a chemical extractant. The technique of dissociation extraction is very valuable for separating mixtures of weakly acidic or basic organic compounds, eg, 2,4-dichlorophenol [120-83-2]; $C_6H_4Cl_2O$; and 2,5-dichlorophenol [583-78-8], which are difficult to separate by other means (37). The technique involves the use of a controlled amount of a strong base or acid in the aqueous phase, so that the overall distribution of each species is affected by its dissociation constant, as well as the distribution constant of the undissociated form (see eqs. 7 and 8). Dissociation extraction has been applied extensively to mixtures of closely similar phenols, amines, and organic acids (38).

In hydrometallurgical separations (9), a metal ion in aqueous solution can be selectively converted to an organometallic compound or complex that is soluble in an organic carrier solvent. The metal extractants may be classified (39) as: (*1*) acid and chelating acid extractants, (*2*) anion exchangers, and (*3*) solvating extractants. Acid extractants typically contain one or more long hydrocarbon chains, an example being di(2-ethyl-hexyl)phosphoric acid [298-07-7], $[C_4H_9CH(C_2H_5)CH_2]_2HPO_4$. The extractant is dissolved in an organic carrier solvent that may be a pure compound, eg, hexane, but in industry is commonly a kerosene. When the extractant in the carrier solvent is contacted using an aqueous solution of a metal cation, eg, M^{2+}, equilibria are set up that can be simplified as the overall equation:

$$M^{2+} + \overline{2\,LH} \rightleftharpoons 2\,H^{+} + \overline{ML_2} \qquad (10)$$

where the overbar denotes species in the organic phase. The control of pH is obviously an important factor in determining the degree of metal extraction and the selectivity of an extractant for two or more cations. Often, the logarithm of the distribution coefficient can be plotted as a linear function of pH (40). After a metal has been selectively extracted to the organic phase, it can be backextracted or stripped to a strongly acidic aqueous phase, giving a purer and more concentrated solution than the initial aqueous feed.

Chelating extractants owe effectiveness to the attraction of adjacent groups on the molecule for the metal. Compounds containing long hydrocarbon chains and the hydroxyoxime group, or those based on 8-quinolinol [148-24-3], C_9H_6NOH, form the basis of various commercial formulations (10,39). These extractants often show an amphoteric behavior depending on pH, changing, eg, from L^- to LH to $LH^{+}{}_{2}$ as the pH is increased; these agents can be applied in basic, as well as acidic conditions (41).

Anionic extractants are commonly based on high molecular weight amines. Metal anions, eg, $MnO^{-}{}_{4}$ or $ReO^{-}{}_{4}$, can be exchanged selectively with inorganic anions such as Cl^- or $SO^{2-}{}_{4}$. The equilibrium for a quaternary onium compound of organic radicals R for two anion species A^- and B^- might be

$$\overline{R_4N + A^-} + B^- \rightleftharpoons \overline{R_4N + B^-} + A^- \qquad (11)$$

Solvating extractants contain one or more electron-donor atoms, usually oxygen, which can supplant or partially supplant the water that is attached to the metal ions. Perhaps the best known example of such an extractant is tri-(*n*-butyl) phosphate) [126-73-8] (TBP), $C_{12}H_{27}O_4P$, which forms the basis of the PUREX process (42) for uranium extraction:

$$UO_2^{2+} + 2\,NO_3^- + \overline{2\,TBP} \rightleftharpoons \overline{UO_2(NO_3)_2 \cdot 2\,TBP} \qquad (12)$$

The TBP and nitric acid also tend to form a complex with each other, but at sufficiently high uranyl nitrate concentrations the nitric acid is mainly displaced into the aqueous phase.

2.3. Interfacial Mass-Transfer Coefficients. Whereas equilibrium relationships are important in determining the ultimate degree of extraction attainable, in practice the rate of extraction is of equal importance. Equilibrium is approached asymptotically with increasing contact time in a batch extraction. In continuous extractors, the approach to equilibrium is determined primarily by the residence time, defined as the volume of the phase contact region divided by the volume flow rate of the phases.

The rate of mass transfer depends on the interfacial contact area and on the rate of mass transfer per unit interfacial area, ie, the mass flux. The mass flux very close to the liquid–liquid interface is determined by molecular diffusion in accordance with Fick's first law:

$$N = -D \frac{\partial c}{\partial z} \tag{13}$$

where N refers to the flux in the z direction, c is the concentration of the solute component, and D is its molecular diffusivity in the solvent. It is accepted practice to use the concentration gradient as the driving force for mass transfer, although it has been suggested that the gradient of chemical potential is more appropriate (43,44). Molecular diffusivities D of solutes are commonly in the range 10^{-10}–5×10^{-9} m^2/s at ambient temperatures. Data for many systems are available in the literature or can be measured experimentally or predicted from correlations (45,46). For dilute solutions of nonelectrolytes, the correlation of Wilke and Chang (47) is recommended.

Although molecular diffusion itself is very slow, its effect is nearly always enhanced by turbulent eddies and convection currents. These provide almost perfect mixing in the bulk of each liquid phase, but the effect is damped out in the vicinity of the interface. Thus the concentration profiles at each side of a liquid–liquid interface have the appearance shown in Figure 3, with essentially uniform bulk composition, and a film on each side of the interface. The films are the regions in which there are significant concentration gradients. The equivalent film thicknesses depend on hydrodynamic conditions and are in the order of 100 μm. The film thicknesses and concentration profiles are therefore almost impossible to measure directly, and the mass fluxes are expressed by means of mass-transfer coefficients, k_{A} and k_{B}, and the concentration differences for each phase.

$$N = k_{\mathrm{A}}(c_{\mathrm{A}} - c_{\mathrm{A}i}) = k_{\mathrm{B}}(c_{\mathrm{B}i} - c_{\mathrm{B}}) \tag{14}$$

The mass-transfer coefficients are typically between 10 and 100 μm/s, depending on hydrodynamic conditions and the values of D.

The solute concentrations very close to the interface, $c_{\mathrm{A}i}$ and $c_{\mathrm{B}i}$, are assumed to be in equilibrium, in the absence of any slow interfacial reaction. According to the linear distribution law, $c_{\mathrm{B}i} = mc_{\mathrm{A}i}$ and thus from equation 14 the mass-transfer flux can be expressed in terms of an overall mass-transfer coefficient K_{A} and an overall concentration driving force:

$$N = K_{\mathrm{A}}(c_{\mathrm{A}} - c^*_{\mathrm{A}}) \tag{15}$$

where

$$c^*_{\mathrm{A}} = c_{\mathrm{B}}/m \tag{16}$$

and

$$1/K_{\mathrm{A}} = 1/k_{\mathrm{A}} + 1/(mk_{\mathrm{B}}) \tag{17}$$

This is the important rule of additivity of resistances. In practice, k_{A} and k_{B} are often of the same order of magnitude, but the distribution coefficient m can vary considerably. For solutes which preferentially distribute toward solvent B, m is large and the controlling resistance lies in phase A. Conversely, if the distribution favors solvent A the controlling mass-transfer resistance lies in phase B.

Values of the mass-transfer coefficient k have been obtained for single drops rising (or falling) through a continuous immiscible liquid phase. Extensive literature data have been summarized (46,48). The mass-transfer coefficient is often expressed in dimensionless form as the Sherwood number:

$$Sh = kd/D \tag{18}$$

The values of k, and hence Sh depend on whether the phase under consideration is the continuous phase, c, surrounding the drop, or the dispersed phase, d, comprising the drop. The notations k_c, k_d, Sh_c, and Sh_d are used for the respective mass-transfer coefficients and Sherwood numbers.

Mass-transfer coefficients are strongly affected by the degree of mobility of the drop surface. When the surface is free of adsorbed molecules it can move in response to surface shear stress, and the drops tend to circulate as they move through the continuous phase. However, even a trace of surface-active material can cause the drop surface to resist shear and the drop circulation is suppressed, resulting in greatly reduced mass transfer (49,50). Table 1 lists some of the proposed equations for mass transfer (expressed as Sh) under various conditions. Nearly a threefold variation in dispersed-phase mass transfer exists between circulating and noncirculating drops. For the continuous phase the effect of circulation is greatest at high Reynolds number. For a more detailed assessment the specialized reviews (46,48) are recommended.

Although the adsorption of surfactants tends to reduce mass-transfer coefficients by suppressing drop circulation, a sharp increase in mass transfer can occur if the transferring solute strongly reduces the interfacial tension. This effect, known as the Marangoni effect, results from interfacial turbulence induced by interfacial tension gradients (51). Extensive research in this area has been reviewed (52).

2.4. Mass-Transfer Coefficients with Chemical Reaction. Solutes exist in different chemical forms in different solvents; eg, simple carboxylic acids have been shown to exist as single molecules in an aqueous phase, but as dimmers in nonpolar solvents, eg, benzene. The transfer of a solute from one phase to another in such cases involves a reaction at the interface.

Inorganic solvent extraction systems provide frequent examples of heterogeneous reaction between metal solutes and solvent. This bonding is particularly important in hydrometallurgical extractions where the metal cations and the anions can only exist in an aqueous phase. It is therefore necessary for them to react with an appropriate organic compound to form a neutral complex before they can enter a solvent phase. Since such reagents normally have only a very slight solubility in water, the reaction generally takes place at the interface itself.

The effect of heterogeneous reaction can conveniently be described in terms of two-film theory. The result is that the concentrations of the interface are no longer in equilibrium, but can be related via an mth order forward and nth order reverse reaction with rate constants ${k_m}^+$ and ${k_n}^-$ as follows:

$$N_a = k_m^* C_x^{im} - k_n^- C_y^{in} \tag{19}$$

$$= k_m^+ \left[C_x^{im} - \frac{k_n^-}{k_m^+} C_y^{in} \right] \tag{20}$$

The parameter N_a is the flux of component through the interface and at equilibrium the net reaction rate is zero so

$$k_a^i = \frac{k_n^-}{k_m^+} = \frac{C_x^{im}}{C_y^{in}} \tag{21}$$

where k_a^i is the ratio of forward and reverse reaction rates and C_x^{im} is the concentration on the x-phase side of the interface in equilibrium with C_y^i on the y side. This can be used to derive the resistance in series to give

$$\frac{1}{k_{ax}} = \frac{1}{k_x} + \frac{1}{m_y k_y} + \frac{1}{k_m^+} \left[\frac{C_x^i - C_x^{ix}}{C_x^{im} - C_x^{imx}} \right] \tag{22}$$

This is essentially equivalent to introducing an extra resistance at the interface. In many hydrometallurgical applications, the reaction term in equation 22 can be controlling.

Chemical reaction can however occur in any of the five regions shown in Figure 3, ie, the bulk of each phase, the film in each phase adjacent to the interface, and at the interface itself. Irreversible homogeneous reaction between the solute component C and a reactant D in phase B can be described as

$$\mathrm{C} + z\ \mathrm{D} \rightarrow \text{products} \tag{23}$$

The equations of combined diffusion and reaction, and their solutions, are analogous to those for gas absorption (53). It has been shown how the concentration profiles and rate-controlling steps change as the rate constant increases (54). When the reaction is very slow and the B-rich phase is essentially saturated with C, the mass-transfer rate is governed by the kinetics within the bulk of the B-rich phase. This is defined as regime 1. Concentration profiles are shown in Figure 4**a** (54). For a slow reaction defined as regime 2, the solute component C is almost entirely depleted in the bulk of the B-rich phase (Fig. 4**b**) and the mass transfer of C between the phases controls the rate of the reaction. For a very fast reaction the depletion of C affects the concentration profile in the diffusion film. The steepening of the concentration profile as shown in Figure 4**c** for regime 3 leads to an enhancement in the film mass-transfer coefficient in the B-rich phase. Finally, the case of an instantaneous reaction (regime 4) leads to the formation of a thin reaction zone to which components C and D diffuse in stoichiometric amounts. This is shown in Figure 4**d**.

The enhanced rate expressions for regimes 3 and 4 have been presented (54) and can be applied (55,56) when one phase consists of a pure reactant, eg, in the saponification of an ester. However, it should be noted that in the more general case where component C in equation 23 is transferred from one inert solvent (A) to another (B), an enhancement of the mass-transfer coefficient in the B-rich phase has the effect of moving the controlling mass-transfer resistance to the A-rich phase, in accordance with equation 17. Resistance in both liquid phases is taken into account in a detailed model (57) that is applicable to the reversible reactions involved in metal extraction. This model, which can accommodate the case of interfacial reaction, has been successfully compared with rate data from the literature (57).

2.5. Interfacial Contact Area and Approach to Equilibrium.

Experimental extraction cells, eg, the original Lewis stirred cell (58) are often operated with a flat liquid–liquid interface the area of which can easily be measured. In the single-drop apparatus, a regular sequence of drops of known diameter is released through the continuous phase (48). These units are useful for the direct calculation of the mass flux N, and hence the mass-transfer coefficient for a given system.

In industrial equipment, however, it is usually necessary to create a dispersion of drops in order to achieve a large specific interfacial area, a, defined as the interfacial contact area per unit volume of two-phase dispersion. Thus the mass-transfer rate obtainable per unit volume is given as

$$(N \cdot a) = K_A a (c_A - c_A^*) \tag{24}$$

Drop dispersions are hardly ever uniform, and size distribution must be allowed for in calculating a. This can be done by means of the Sauter mean drop diameter, d_m, based on the average volume/area ratio for N drops.

$$d_m = \sum_{i=1}^{N} d_i^3 \Big/ \sum_{i=1}^{N} d_i^2 \tag{25}$$

The specific interfacial area based on unit volume of two-phase dispersion is given by

$$a = 6h/d_m \tag{26}$$

where h is the holdup of dispersed phase. The specific rate of interfacial mass transfer can be summarized from equations 24 and 26 as:

$$(N \cdot a) = K_A (6h/d_m)\,(c_A - c_A^*) \tag{27}$$

showing that the rate of attainment of equilibrium is proportional to the concentration difference (driving force) and to a physical rate constant $(K_A \cdot 6h/d_m)$, which has the units of s^{-1}. The extraction rate constant can be increased operationally by maintaining a high holdup and a small Sauter mean droplet diameter. Typically, in the absence of chemical effects, K_A would be on the order of 10 μm/s, h could be on the order of 0.2, and d_m could be 1 mm; hence $(K_A \cdot 6h/d_m)$ is ~0.012 s^{-1}. In a batch extraction under these conditions, the deviation from equilibrium would decay exponentially with a half-life of 0.693/0.012 s or just under 1 min.

There are certain limits to how far h can be increased and d_m can be reduced; however, if the contact time in a well-mixed extractor can be maintained at several minutes, it can usually be assumed that equilibrium between the exit phases is attained, justifying the use of the equilibrium stage concept represented by Figure 1 and equation 1.

2.6. Calculation of Equilibrium Stages.

Multistage contacting can be arranged in a cocurrent, crosscurrent, or countercurrent manner as shown in Figure 5. The sequence of stages is sometimes referred to as a cascade, referring to the early use of gravity overflow from stage to stage. Cocurrent stagewise contact (Fig. 5**a**) is not usually necessary when the stages are ideal, because equilibrium is reached between the streams after stage 1. A cross-current cascade (Fig. 5**b**) in which fresh solvent is added at each stage gives an improvement over the separation obtainable in a single stage for a given ratio of solvent to feed (7,34).

The countercurrent arrangement (Fig. 5**c**) represents the best compromise between the objectives of high extract concentration and a high degree of extraction of the solute, for a given solvent/feed ratio. The feed entering stage 1 is brought into contact with a B-rich stream that has already passed through the other stages, while the raffinate leaving the last stage has been in contact with fresh solvent. Because of the economic advantages, continuous countercurrent extraction is normally preferred for commercial-scale operations. For the case of a partially miscible ternary system, the number of ideal stages in a countercurrent cascade can be estimated graphically on a triangular diagram, using the Hunter–Nash method (59). The feed and solvent compositions and the resulting mixture point M are first located on the diagram as in Figure 2**a**. If in addition one of the exit stream (extract or raffinate) compositions is given, a point representing the composition of the net flow in the countercurrent cascade can be located. This point, called the delta point, provides the basis for construction of material balance lines and tie-lines representing a sequence of ideal stages for the countercurrent extractor. The Hunter–Nash procedure is well known and useful (7,34). For dilute systems, it is often more convenient to use the delta point construction on a diagram with solvent-free coordinates (7,34). In this case, a rectangular diagram is plotted in which the horizontal axis is the mass fraction of the solute C on a B-free basis, and the vertical axis is the mass ratio of B to $A + C$.

If the feed, solvent, and extract compositions are specified, and the ratio of solvent to feed is gradually reduced, the number of ideal stages required increases. In economic terms, the effect of reducing the solvent/feed ratio is to reduce the operating cost, but the capital cost is increased because of the increased number of stages required. At the minimum solvent/feed ratio, the number of ideal stages approaches infinity and the specified separation is impossible at any lower solvent/feed ratio. In practice the economically optimum solvent/feed ratio is usually 1.5–2 times the minimum value.

The design of countercurrent contactors is considerably simplified when the solvents A and B are not significantly miscible. The mass flows of A and B then remain constant from one stage to the next, and the material balance at any stage can be written

$$\mathrm{A}(X_0 - X) = \mathrm{B}\,(Y_1 - Y) \tag{28}$$

where A and B are the mass flows of A and B, X is the mass ratio of C to A in the feed, and Y is the ratio of C to B in the extract. The compositions X and Y, expressed as mass ratios, thus vary linearly and equation 28 can be plotted as the operating line on Figure 6. Also shown is the equilibrium curve.

The number of ideal stages can readily be found from Figure 6 by the same type of stepwise construction as used for countercurrent distillation columns. Starting at point (X_0, Y_1), the first horizontal dashed line represents the establishment of equilibrium in stage 1 to give (X_1, Y_1). The second, vertical dashed line represents the solution of the material balance (eq. 28), giving a point on the operating line relating X_1 and Y_2, and so on. The example shown in Figure 6 indicates that between three and four ideal stages are required and in practice the designer would specify four ideal stages.

Although the triangular diagram is normally used when the solvents are partially miscible, it is also possible to construct an X–Y (mass ratio) or x–y (mass fraction) operating diagram (34) and use the stepwise procedure for calculating stages. When solvents A and B are partially miscible, the operating lines are curved. An important advantage of the stepwise procedure is that it can be adapted to the case where the rate of mass transfer (eq. 27) and contact time are not sufficient to ensure equilibrium between exit streams in each contacting stage. By analogy with distillation, a Murphree stage efficiency can be defined for either phase (34). If the efficiency is <1.0, more stages are needed for a given separation than for the ideal case.

When the solvents are substantially immiscible and the equilibrium curve is linear, $Y = mX$, the number of ideal stages can be calculated without the graphical constructions (60,61). When the extraction factor ϵ (eq. 1) is not equal to unity, it can be shown that

$$N_s = \frac{\log\left[\left(\dfrac{X_0 - Y_s/m}{X_N - Y_S/m}\right)\left(1 - \dfrac{1}{\epsilon}\right) + \dfrac{1}{\epsilon}\right]}{\log \epsilon} \tag{29}$$

and for $\epsilon = 1$, denoting parallel operating and equilibrium lines,

$$N = (X_0 - X_N)/(X_N - Y_S/m) \tag{30}$$

where X_0 is the ratio C/A in the feed, X_N is the ratio C/A in the raffinate after N ideal stages, and Y_S is the ratio C/B in the entering solvent. For very dilute systems, the mass ratios X and Y in the above equations can be replaced by mass fractions or concentrations.

2.7. Fractional Extraction. Fractional extraction is the separation of two or more solute components by solvent extraction. In single solvent fractional extraction (Fig. 7**a**) the feed mixture of A and C is added at some point in a countercurrent cascade through which a solvent B is passed. The solvent B preferentially dissolves component C as it passes in the downward direction. The mixture of B and C leaving the cascade is then split into two phases, eg, by cooling. Part of the C-rich layer is removed as product and part is returned to the cascade as reflux. The B-rich layer (solvent) is sent to the other end of the cascade where it strips component C from the A + C mixture, allowing an A-rich phase to leave. The two sections of the cascade are analogous to the stripping and enriching sections in a distillation column and the design procedure for estimating the number of stages is somewhat similar (34). Single-solvent fractional extraction has been known for many years, but the range of solvents available is limited because of the requirement that the solvents must be sparingly miscible with each of the components A and C.

Dual solvent fractional extraction (Fig. 7**b**) makes use of the selectivity of two solvents (A and B) with respect to solute components C and D, as defined in equation 7. The two solvents enter the extractor at opposite ends of the cascade and the two solute components enter at some point within the cascade. Solvent recovery is usually an important feature of dual solvent fractional extraction and provision may also be made for reflux of part of the product streams containing C or D. Simplified graphical and analytical procedures for calculation of stages for dual solvent extraction are available (7) for the cases where β_{CD} is constant and the two solvents A and B are not significantly miscible. In general, the accurate calculation of stages is time-consuming (34) but a computer technique has been developed (62).

2.8. Differential Contacting. Although the equilibrium stage concept has proved extremely useful in describing the performance of mixer–settlers and plate columns having discrete stages, it is not appropriate for spray towers, packed columns, etc, in which no discrete stages can be identified. In such differential types of contactors, equilibrium between phases is never reached, and therefore the mass-transfer rate is important in the design procedure.

A differential countercurrent contactor operating with a dilute solution of the solute component C and immiscible components A and B is shown in Figure 8. Under these conditions, the superficial velocities of the A- and B-rich streams can be assumed not to vary significantly with position in the contactor, and are taken to be U_A and U_B, respectively. The concentration of C in the A-rich stream is c_A and that in the B-rich stream is c_B.

A steady-state material balance can be carried out on a small section of length dz and volume dz (on the basis of unit cross-sectional area) in the contactor:

$$U_B\,dc_B = U_A\,dc_A = K_A a(c_A - c_A)dz \tag{31}$$

Rearrangement and integration give a relationship for the contactor height in terms of the concentration change:

$$dz = \frac{U_A}{K_A a} \cdot \frac{dc_A}{(c_A - c_A^*)} \tag{32}$$

$$Z = \left(\frac{U_A}{K_A a}\right) \int_{c_{AD}}^{c_{AZ}} \frac{dc_A}{(c_A - c_A^*)} \tag{33}$$

The integral can be found graphically if the equilibrium line is curved. An analytical expression for the integral is available for the case where both the equilibrium and operating lines are linear (7):

$$\int_{c_{\mathrm{AD}}}^{c_{\mathrm{AZ}}} \frac{dc_{\mathrm{A}}}{(c_{\mathrm{A}} - c_{\mathrm{A}}^{*})} = \frac{1}{1 - 1/\epsilon} \ln\left[\left(\frac{c_{\mathrm{A0}} - c_{\mathrm{AZ}}}{c_{\mathrm{AZ}} - c_{\mathrm{AZ}}^{*}}\right)(1 - 1/\epsilon) + 1/\epsilon\right] \tag{34}$$

where $\epsilon = mU_{\mathrm{B}}/U_{\mathrm{A}}$. The integral is unitless and is known as the number of transfer units (NTU) based on the overall A-rich-phase driving force. Obviously the NTU, and hence the contactor length Z required, increase as the difference between c_{AZ} and c_{A0} is increased.

The factor $(U_{\mathrm{A}}/K_{\mathrm{A}}a)$ in equation 33 is known as the height of a transfer unit (HTU). It is a characteristic of the hydrodynamic conditions, such as the flow rate A and the specific interfacial area a, but is independent of changes in c_{A}. It is important that the HTU be specified correctly in regard to the phase and driving force considered; in this case it relates to the overall mass-transfer driving force in the A-rich phase. The HTU may vary with height because of changes in drop size, etc; an average value is usually taken, assuming no variation.

Mass-transfer theory (eq. 17) indicates that the overall mass-transfer resistance $1/K_{\mathrm{A}}$ consists of contributions from each phase, so that the overall HTU is also the sum of two contributions:

$$\begin{aligned}(\mathrm{HTU})_{\mathrm{OA}} &= \frac{U_{\mathrm{A}}}{K_{\mathrm{A}}a} + \frac{U_{\mathrm{A}}}{mK_{\mathrm{B}}a} = \frac{U_{\mathrm{A}}}{K_{\mathrm{A}}a} + \left(\frac{U_{\mathrm{B}}}{K_{\mathrm{B}}a}\right)\left(\frac{U_{\mathrm{A}}}{mU_{\mathrm{B}}}\right) \\ &= (\mathrm{HTU})_{\mathrm{A}} + (\mathrm{HTU})_{\mathrm{B}}/\epsilon\end{aligned} \tag{35}$$

The heights of a transfer unit in each phase thus contribute to the overall heights of a transfer unit. Data on values of HTU for various types of countercurrent equipment have been reviewed (1). In normal operating practice, the extraction factor is chosen to be not greatly different from unity, within the range of 0.5–2.

Although the stagewise model is not physically realistic for differential contactors, it is sometimes used. The number of equivalent theoretical stages N can be determined graphically using the stepwise construction illustrated in Figure 7. For the case where both the equilibrium and operating lines are linear, it can be shown that:

$$\frac{N}{(\mathrm{NTU})_{\mathrm{OA}}} = \frac{1 - 1/\epsilon}{\ln\epsilon} \tag{36}$$

If $\epsilon = 1$, the number of theoretical stages is equal to $(\mathrm{NTU})_{\mathrm{OA}}$.

Equations 31–36 are applicable only to dilute, immiscible systems. If the amount of mass transfer is significant in comparison to the total flow rates, more complicated treatments of differential contactors are required (2,7,34).

2.9. Axial Dispersion. The development following equation 31 has assumed that the two phases move countercurrently in plug flow, ie, all the fluid in each phase has the same residence time in the equipment. In practice, this is rarely the case, because of axial mixing that arises from the action of turbulent eddies, circulation currents, or the effects of drop wakes (2,58). The effect is to flatten the axial concentration profiles within each phase. Axial mixing can lead to a reduction in the effective driving force for mass transfer that in turn reduces the NTU below that expected for the plug flow case (eq. 34). An important feature of the profile is the discontinuity or "jump" in concentration that occurs at entry to the contactor when the liquid in the feed line enters the mixed region of the column.

Two alternative approaches are used in axial mixing calculations. For differential contactors, the axial dispersion model is used, based on an equation analogous to equation 13:

$$N = -E\,\frac{\partial c}{\partial z} \tag{37}$$

which leads to a material balance similar to equation 31 as follows:

$$E_x\,\frac{d^2C_x}{dZ^2} - U_x\,\frac{dC_x}{dZ} - k_{ox}a(C_x - C_x^*) = 0 \tag{38}$$

$$E_y\,\frac{d^2C_y}{dZ^2} - U_y\,\frac{dC_y}{dZ} - k_{ox}a(C_x - C_x^*) = 0 \tag{39}$$

which can be solved with the equilibrium data and appropriate boundary conditions for a range of cases (1,2).

Values of E, several orders of magnitude greater than the molecular diffusion coefficient D, are typically in the 10^{-4}–10^{-3} m^2/s range for packed columns, and even larger for spray columns in which circulation currents are unimpeded. For contactors in which discrete well-mixed compartments can be identified, eg, sieve-plate columns, axial mixing effects are incorporated into the stagewise model by means of the backflow ratio α, which is defined as the fraction of the net interstage flow of one phase that is considered to flow in the reverse direction. For a contactor in which there are many compartments, the axial dispersion coefficient and the backflow ratio, α, are interrelated as follows:

$$E = \frac{UH}{\ln((1+\alpha)/\alpha)} \tag{40}$$

where H is the height of one compartment and U is the superficial velocity. The detailed calculations of concentration profiles and mass-transfer rates with axial mixing require the solution of a fourth-order differential equation (dispersion model) or the equivalent difference equation (backflow model) along with appropriate boundary conditions. The methodology was developed in the 1950s and early 1960s, and has been concisely reviewed (63). Pratt (64,65) has shown how the profile solutions can be rearranged to give a direct calculation of column height. In the case of the dispersion model, the relative effect of axial mixing is a function of the axial Peclet number, defined as

$$Pe = UZ/E \tag{41}$$

The Peclet numbers are different for each phase because U and E are different. Axial mixing effects are usually greater in the continuous phase than in the dispersed phase. Plug flow conditions can be assumed only if Pe exceeds ~ 50. Experimentally measured values of E or a are widely available for laboratory-scale columns with a diameter of up to 15 cm (1). Typically at low agitation rates, circulation effects (hydrodynamic nonuniformity) can lead to large values of E. The circulation effects are mainly a result of the motion of the dispersed-phase droplets, but unstable axial density gradients may also contribute to increased mixing (66,67). Circulation effects are reduced by mechanical agitation that promotes radial uniformity, but at high levels of agitation the increased turbulence leads to an overall increase in E, resulting in a minimum in the plotted curve of E versus agitation.

The effect of increasing column diameter in some types of columns is to increase the tendency for circulation, and hence to increase the axial mixing (68,69). However, extremely few measurements of axial mixing at the industrial scale are available, so large-scale contactor design must still rely quite heavily on empirical experience with the particular type of equipment.

2.10. Drop Diameter. In extraction equipment, drops are initially formed at distributor nozzles; in some types of plate column the drops are repeatedly formed at the perforations on each plate. Under such conditions, the diameter is determined primarily by the balance between interfacial forces and buoyancy forces at the orifice or perforation. For an ideal drop detaching as a hemisphere from a circular orifice of diameter d_0 and then becoming spherical:

$$d = (6\sigma d_0/g\Delta\rho)^{1/3} \tag{42}$$

Equation 42 must be corrected for changes in the drop shape and for the effects of the inertia of liquid flowing through the orifice, viscous drag, etc (70). As the orifice or aperture diameter is increased, d_0 has less effect on the drop diameter and the mean drop size then tends to become a function only of the system properties:

$$d_m \simeq (\sigma/g\Delta\rho)^{1/2} \tag{43}$$

This type of equation has been found useful in correlating drop diameters in packed columns where the packing size exceeds the drop diameter (71).

In many types of contactors, eg, stirred tanks, rotary agitated columns, and pulsed columns, mechanical energy is applied externally in order to reduce the drop size far below the values estimated from equations 42 and 43 and thereby increase the rate of mass transfer. The theory of local isotropic turbulence can be applied to the breakup of a large drop into smaller ones (72), resulting in an expression of the form

$$d_m = K'\sigma^{0.6}\rho_m^{-0.06}\Psi^{-0.4} \tag{44}$$

In this equation, Ψ represents the rate of energy dissipation per unit mass of fluid. In pulsed and reciprocating plate columns the dimensionless proportionality constant K' in equation 44 is on the order of 0.3. In stirred tanks, the proportionality constant has been reported as $0.024(1 + 2.5h)$ in the holdup range 0–0.35 (73). The increase of drop size with holdup is attributed to the increasing tendency for coalescence between drops as the concentration of drops increases. A detailed survey of drop size correlations is given by the literature (71).

The value of d_m is a mean value, based on a broad distribution of sizes. In a mass-transfer situation the smallest drops, because of the very high specific surface area, quickly come to equilibrium; conversely the largest drops, which typically have a diameter of $\sim 2\ d_m$, are much slower to come to equilibrium with the continuous phase. The effects of drop size distribution on extractor performance are being studied (74–76), although the single parameter d_m is still widely in use for design work.

2.11. Holdup and Flooding. The volume fraction of the dispersed phase, commonly known as the holdup h, can be adjusted in a batch extractor by means of the relative volumes of each liquid phase added. In a continuously operated well-mixed tank, the holdup is also in proportion to the volume flow rates because the phases become intimately dispersed as soon as they enter the tank.

$$h = Q_d/(Q_c + Q_d) \tag{45}$$

However, in a countercurrent column contactor as sketched in Figure 8, the holdup of the dispersed phase is considerably less than this, because the dispersed drops travel quite fast through the continuous phase, and therefore have a relatively short residence time in the equipment. The holdup is related to the superficial velocities U of each phase, defined as the flow rate per unit cross-section of the contactor, and to a slip velocity U_s (77,78):

$$U_s = U_d/h + U_c/(1-h) \tag{46}$$

In the case of a packed column, the terms on the right-hand side should each be divided by the voidage, ie, the volume fraction not occupied by the solid packing (77). In unpacked columns at low values of h, the slip velocity U_s approximates the terminal velocity of an isolated drop, but the slip velocity decreases with holdup and may also be affected by column internals, eg, agitators and baffle plates. The slip velocity can generally be represented by (79):

$$U_s = U_k(1-h)^{\beta} \tag{47}$$

where the characteristic velocity U_k is a function of drop size and system properties and the exponent β relates to system properties and the degree of flow uniformity in the contactor.

In many columns and systems, $\beta = 1$ and equation 47 can be expressed as follows:

$$\frac{U_d}{h} + \frac{U_c}{1-h} = U_k\epsilon(1-h) \tag{48}$$

Thus a plot of $\dfrac{U_d}{z} + [hU_c/(1-h)] vs h\epsilon(1-h)$ gives a straight line of slope $U_k\epsilon$, which is independent of flow rates and only varies with physical properties and pulsation rates. This is useful for interpreting column performance.

As the throughput in a contactor represented by the superficial velocities U_c and U_d is increased, the holdup h increases in a nonlinear fashion given by equation 48. A flooding point is reached at which the countercurrent flow of the two liquid phases cannot be maintained. The flow rates at which flooding occurs depend on system properties, in particular density difference and interfacial tension, and on the equipment design and the amount of agitation supplied (46,71).

The nonuniformity of drop dispersions can often be important in extraction. This nonuniformity can lead to axial variation of holdup in a column even though the flow rates and other conditions are held constant. For example, there is a tendency for the smallest drops to remain in a column longer than the larger ones, and thereby to accumulate and lead to a localized increase in holdup. This phenomenon has been studied in reciprocating-plate columns (80). In the process of drop breakup, extremely small secondary drops are often formed (70). These drops, which may be only a few micrometers in diameter, can become entrained in the continuous phase when leaving the contactor. Entrainment can occur well below the flooding point.

2.12. Coalescence and Phase Separation. Coalescence between adjacent drops and between drops and contactor internals is important for two reasons. It usually plays a part, in combination with breakup, in determining the equilibrium drop size in a dispersion, and it can therefore affect holdup and flooding in a countercurrent extraction column. Second, it is an essential step in the disengagement of the phases and the control of entrainment after extraction has been completed.

The role of coalescence within a contactor is not always obvious. Sometimes the effect of coalescence can be inferred when the holdup is a factor in determining the Sauter mean diameter (73). If mass transfer occurs from the dispersed (d) to the continuous (c) phase, the approach of two drops can lead to the formation of a local surface tension gradient that promotes the drainage of the intervening film of the continuous phase (81), and thereby enhances coalescence. It has been observed that d-to-c mass transfer can lead to the formation of much larger drops than for the reverse mass-transfer direction, c to d (82,83).

Phase disengagement occurs at a layer or wedge in which the holdup of the drop phase is very high, providing good opportunities for close contact between drops (71). Coalescence between drops occurs by a mechanism of drainage of the intervening film of the continuous phase. This process is favored by low viscosity, high interfacial tension, and a relatively large difference in density between the liquid phases. For difficult systems that do not have these properties, various types of mesh-packing coalescence enhancers have been developed (84). These provide a large surface that is preferentially wetted by the drop phase. Another effective technique for enhancing coalescence and phase separation is the application of pulsed electrical fields (85).

2.13. Membrane Extraction. An extraction technique that uses a thin liquid membrane or film has been introduced (86,87). The principal advantages of liquid-membrane extraction are that the inventory of solvent and extractant is extremely small and the specific interfacial area can be increased without the problems that accompany fine drop dispersions.

Figure 9**a** shows an early form of liquid-membrane extraction in which the solute is transferred from the continuous phase to a thin spherical film of an immiscible phase; within this film there is a quantity of strip solution that preferentially removes the solute from the membrane. Thus the membrane is analogous to a selective filter for the diffusional transport of the solute. The spherical film can be stabilized by surfactants, but a more convenient arrangement is the emulsion globule as shown in Figure 9**b**, in which the strip solution is dispersed as very small drops within a globule of solvent. This technique lends itself particularly to chemically driven extraction stripping, eg, hydrometallurgical extractions according to equation 10 (88–90). In this case, the extractant acts as a carrier to transport the metal complex across the membrane.

In order to maintain a definite contact area, solid supports for the solvent membrane can be introduced (91). Those typically consist of hydrophobic polymeric films having pore sizes between 0.02 and 1 μm. Figure 9**c** illustrates a hollow fiber membrane where the feed solution flows around the fiber, the solvent–extractant phase is supported on the fiber wall, and the strip solution flows within the fiber. Supported membranes can also be used in conventional extraction, where the supported phase is continuously fed and removed. This technique is known as dispersion-free solvent extraction (92,93). Pilot-scale studies of treatment of metal waste streams by liquid membrane extraction have been reported (94). The developments in membrane technology have been reviewed (95). Despite the research interest and potential, membranes have yet to be applied at an industrial production scale (96).

2.14. Supercritical Extraction. The use of a supercritical fluid, eg, carbon dioxide as extractant, is growing in industrial importance, particularly in the food-related industries. The advantages of supercritical fluids as extractants include favorable solubility and transport properties, and the ability to complete an extraction rapidly at moderate temperature. Whereas most of the supercritical extraction processes are solid–liquid extractions, some liquid–liquid extractions are of commercial interest also. For example, the removal of ethanol from dilute aqueous solutions using liquid carbon dioxide (97,98) or a supercritical hydrocarbon solvent (99–101) is under active investigation and several potential applications in food technology have also been reported (99–101).

2.15. Two-Phase Aqueous Extraction. Liquid–liquid extraction usually involves an aqueous phase and an organic phase, but systems having two or more aqueous phases can also be formed from solutions of mutually incompatible polymers such as poly(ethylene glycol) (PEG) or dextran. A system having as many as 18 aqueous phases in equilibrium has been demonstrated (102). Two-phase aqueous extraction, particularly useful in purifying biological species, eg, proteins and enzymes, can also be carried out in combination with fermentation so that the fermentation product is extracted as it is formed (103).

Because of the growth in biotechnology, two-phase aqueous extraction is becoming more important industrially. Two-phase aqueous systems have low interfacial tension, low interphase density difference, and high viscosity in comparison with most aqueous–organic systems. Although interfacial contact is very efficient, the separation of the phases after contact can be slow, requiring centrifugation. The performance of a spray column for two-phase aqueous extraction has also been reported (104).

3. Equipment and Processing

The earliest large-scale continuous industrial extraction equipment consisted of mixer-settlers and open-spray columns. The vertical stacking of a series of mixer-settlers was a feature of a patented column in 1935 (105) in which countercurrent flow occurred because of density difference between the phases, avoiding the necessity for interstage pumping. This was a precursor of the agitated column contactors that have been developed and commercialized since the late 1940s. There are several texts (1,2,8,106,107) and reviews (108,109) available that describe the various types of extractors.

The unique ability of solvent extraction to achieve separation according to chemical-type rather than physical characteristics, eg, vapor pressure, enables a great variety of processes ranging from nuclear-fuel enrichment and reprocessing to fertilizer manufacture, and from petroleum refining to biochemical and food processing. Probably more types of contactors have been developed for solvent extraction than for any other chemical engineering unit operation. Contactors have been developed for specific processes with which they then tend to become associated. As a result, selection of extractors for a new process application is not necessarily simple, and the choice of a contactor remains both an art and a science, largely based on practical experience.

The following criteria should be considered when selecting a contactor for a particular application: (*1*) stability and residence time, (*2*) settling characteristics of the solvent system, (*3*) number of stages required, (*4*) capital cost and maintenance, (*5*) available space and building height, and (*6*) throughput. The preliminary choice of an extractor for a specific process is primarily based on consideration of the system properties and number of stages required for the extraction. A qualitative chart of the economic operating range of various classes of extractors is shown in Figure 10 (110). A useful selection chart is also available (111) (Table 2). The vendor's experience, pilot-testing procedures, scaling-up methods, costs for capital equipment and maintenance, and reliability of operation should be considered and evaluated at an early stage, before the pilot-plant tests are committed. Although cost ought to be a primary balancing consideration, in many cases previous experience and practice are the deciding factors.

An extraction plant should operate at steady state in accordance with the flow-sheet design for the process. However, fluctuation in feed streams can cause changes in product quality unless a sophisticated system of feed-forward control is used (112). Upsets of operation caused by flooding in the column always force shutdowns. Therefore, interface control could be of utmost importance. The plant design should be based on (*1*) process control decisions made by trained technical personnel, (*2*) off-line analysis or limited online automatic analysis, and (*3*) control panels equipped with manual and automatic control for motor speed, flow, interface level, pressure, temperature, etc.

3.1. Laboratory Extractors, Pilot-Scale Testing, and Scale-Up. Miniature mixer–settler assemblies set up as continuous, bench-scale, multistage, countercurrent, liquid–liquid contactors (113) are particularly useful for the preliminary laboratory work associated with flow-sheet development and optimization because these give a known number of theoretical stages. Laboratory-scale columns are typified by the 5-cm diameter reciprocating-plate extraction column, in which a minimum height of an equivalent theoretical stage (HETS) of 7.1 cm and high volumetric efficiencies were achieved employing a methyl isobutyl ketone (MIBK)–acetic acid–water system (114).

Because the factors relating to mass transfer and fluid dynamics of the systems in an extractor are extremely complex, particularly for mixed solvents and feedstocks of commercial interest, pilot-scale testing remains an almost inevitable preliminary to a full-scale contactor design. These tests provide (*1*) total throughput and agitation speed; (*2*) HETS or HTU; (*3*) stage efficiency; (*4*) hydrodynamic conditions, such as droplet dispersion, phase separation, flooding, emulsion layer formation, etc; (*5*) selection of direction of mass transfer; (*6*) solvent/feed ratio; (*7*) material of construction and its wetting characteristics; and (*8*) confirmation of the desired separation in cases where equilibrium data are not available.

For design of a large-scale commercial extractor, the pilot-scale extractor should be of the same type as that to be used on the large scale. Reliable scale-up for industrial-scale extractors still depends on correlations based on extensive performance data collected from both pilot- and large-scale extractors covering a wide range of liquid systems. Only limited data for a few types of large commercial extractors are available in the literature.

3.2. Commercial Extractors. Extractors can be classified according to the methods applied for interdispersing the phases and producing the countercurrent flow pattern. Figure 11 summarizes the classification of the principal types of commercial extractors; Table 3 summarizes the main characteristics.

Unagitated Columns. Because of the simplicity and low cost, unagitated columns are widely used in industry despite low efficiency, particularly for processes requiring few theoretical stages and for corrosive systems, where absence of mechanical moving parts is advantageous (Table 3). Three types of unagitated column extractors are shown in Figure 12. Spray columns (Fig. 12**a**) are the simplest in construction mechanically, but have very low efficiency because of poor phase contacting and excessive backmixing in the continuous phase. These generally provide one or, at the most, two equilibrium stages. For example, a baffled spray tower, 2.7 m in diameter and 24 m in height for propane deasphalting of residue was reported to have only 3–3.5 theoretical stages (115). Because of the simple construction, however, spray columns are used for industrial operations requiring only a few stages.

Packed columns (Fig. 12**b**) have better efficiency because of improved contacting and reduced backmixing; it is important that the packing material should be wetted by the continuous phase to avoid coalescence of the dispersed phase. To reduce the effects of channeling, redistribution of the liquids at fixed intervals is normally required in the taller columns. Packed columns should not be used if the ratio of the phase-flow rates is beyond the range 0.5–2.0 because of probable flooding when suitable holdup and interfacial area are provided (116). Normally, a packed column is preferred over a spray column because the reduced flow capacity is less important than the improved mass transfer. Sulzer static mixers have been reported as a packing in liquid–liquid extraction. The overall values of height of a transfer unit range from 0.6 to 1.6 m depending on the system and direction of mass transfer (117,118). Sulzer static mixers have also been used in a column for multistage supercritical fluid extraction. A description of high efficiency packing for liquid–liquid extraction has been reported (117,118).

Perforated-plate columns (Fig. 12**c**) are operated semistagewise and are reasonably flexible and efficient. If the light phase is dispersed, the light liquid flows through the perforations of each plate and is dispersed into drops that rise through the continuous phase. The continuous phase flows horizontally across each plate and passes to the plate beneath through a downcomer. If the heavy phase is dispersed, the column is reversed and upcomers are used for the continuous phase. A perforated-plate tower 2.13 m in diameter and 24.38 m in height used for extraction of aromatics was reported to have the equivalent of 10 theoretical stages (119). Mass-transfer data obtained in various types of perforated-plate columns up to 230 mm in diameter using different extraction systems have been summarized (120). The data are generally correlated in terms of overall heights of transfer units versus flow velocities of the phases for a specific column and system. There are many variations of basic designs for perforated-plate (sieve-plate) columns and detailed information is given in the literature (120).

Mixer–Settlers. Mixer–settlers are widely used in the chemical process industry because of reliability, flexibility, and high capacity. These extractors are particularly economical for operations that require high throughput and few stages. Mixer–settlers having capacity up to 22.7 m^3/min (6000 gal/min) have been used in the mining industry. The main disadvantages of mixer–settlers are size and the inventory of material held up in the equipment. Considerable development work has been done to improve mixer–settler design, and many newer devices have been reported. Figure 13 shows some of these extractors.

The simple box-type mixer–settler (121) has been used extensively in the United Kingdom for the separation and purification of uranium and plutonium (122). In this type of extractor, interstage flow is handled through a partitioned box construction. Interstage pumping is not needed because the driving force is provided by the density difference between solutions in successive stages.

A widely used type of pump–mixer–settler, developed by Israeli Mining Industries (IMI) (123), is shown in Figure 13**a**. A unit having capacity 8.3 m^3/min (2000 gal/min) has been used in phosphoric acid plants (124). The unique feature of this design is that the pumping device is not required to act as the mixer, and the two phases are dispersed by a separate impeller mounted on a shaft running coaxially with the drive to the pump.

The General Mills mixer–settler (125), shown in Figure 13**b**, is a pump–mix unit designed for hydrometallurgical extraction. It has a baffled cylindrical mixer fitted in the base and a turbine that mixes and pumps the incoming liquids. The dispersion leaves from the top of the mixer and flows into a shallow rectangular settler designed for minimum holdup.

In the Davy–Powergas unit (126–128), shown in Figure 13**c**, the liquids run through a draft tube and are pumped by an impeller running directly above the draft tube. The dispersion flows out from the top of the mixer and down through a channel into a rectangular settler. Large units of this type are used for copper extraction (9).

The development of the novel Davy–McKee combined mixer–settler (CMS) has been described (129). It consists of a single vessel (Fig. 13**d**) in which three zones coexist under operating conditions. A detailed description of units used for uranium recovery has been reported (130), and the units have also been studied at the laboratory scale (131). Application of the Davy combined mixer electrostatically assisted settler (CMAS) to copper stripping from an organic solvent extraction solution has been reported (132).

The Lurgi contactor (133), developed in Germany, consists of stacked mixer–settler units. Mixing and interphase transfer take place in pumps attached to the side of the settling column. It has a capacity of 1600 t/h and columns up to 3 m in diameter have been used for aromatic extractions. The Holmes and Narver mixer–settler (134) incorporates a multicompartment mixer and has many other special features. The Kemira mixer–settler (135) developed in Finland also uses the pump–mix concept, in which the phase to be mixed is drawn from a point in line with mixing impeller. Only the heavy phase is pumped into the mixer, and the light phase is allowed to flow freely from the settler. A large auxiliary space is provided between the mixer and the settler. The unit has been successfully used in extraction of the rare earths and nitrophosphate fertilizer processes (136,137) and found to be particularly flexible when there are great variations in flow rate from stage to stage. A type of mixer–settler (EC-D) having a delta-type pump–mixing impeller has been developed in China (138). The delta impeller is reported to have the advantages of developing high flow velocities in both the axial and radial directions (139), resulting in high efficiency and relatively low energy consumption. Applications in a large rare-earth extraction plant have been reported (140).

Motionless inline mixers obtain energy for mixing and dispersion from the pressure drops developed as the phases flow at high velocity through an array of baffles or packing in a tube. Performance data on the Kenics (141) and Sulzer (142) types of motionless mixer have been reported.

The scale-up and design of mixer–settlers is relatively reliable because they are practically free of interstage backmixing and stage efficiencies are high, typically 80–90%. Various studies (142–145) have shown that (*1*) the rate of extraction is a function of power input, and (*2*) mixers can be reliably scaled up by geometric similitude at constant power input per unit mixer volume, up to a 200-fold factor of throughput (146,147). The processes taking place in the settler are complex. In large industrial mixer–settlers, the settlers usually represent at least 75% of the total volume of the units. The flow capacity of a settler depends on the behavior of a band of dispersion at the interface. The thickness of the band is a measure of the approach to flooding (106). The thickness increases exponentially with increasing flow per unit interfacial area, and settlers can be scaled up by factors of up to 1000 on this basis. A practical means to increase the throughput per unit settler area is needed so that the size of the settler can be reduced and the inventory of solvent lowered. The efficiency of the settler can be enhanced by minimizing turbulence and the formation of small drops, and maintaining low values of the linear velocity along the settler to avoid entrainment of small drops from the dispersion band.

Pulsed Columns. The efficiency of sieve-plate disk and doughnut or packed columns is increased by the application of sinusoidal pulsation to the contents of the column. The well-distributed turbulence promotes dispersion and mass transfer while tending to reduce axial dispersion in comparison with the unpulsed column. This leads to a substantial reduction in HETS or HTU values.

The pulsed-plate column is typically fitted with horizontal perforated plates or sieve plates that occupy the entire cross-section of the column. The total free area of the plate is ∼20–25%. The columns are generally operated at frequencies of 1.5–4 Hz with amplitudes 0.63–2.5 cm. The energy dissipated by the pulsations increases both the turbulence and the interfacial areas and greatly improves the mass-transfer efficiency compared to that of an unpulsed column. Pulsed-plate columns in diameters of up to 1.0 m or more are widely used in the nuclear industry (148,149).

Figure 14 shows that several regions of operation in the pulsed-plate column can be distinguished, depending on the flow rate and intensity of pulsation (150). At low pulsation velocities (expressed as amplitude × frequency), a discrete layer of liquid appears between plates during each reversal of the pulse cycle. At higher velocities, there is little or no layer formation and the column then behaves as a differential contactor. Extensive studies have been made on flooding, mass transfer, and the development of empirical correlations for the column design (151–153), and on the hydrodynamics and performance of columns of various sizes in uranium extraction (152).

Pulsed-packed columns consist of vertical cylindrical vessels filled with packing. The light and dense liquids passing countercurrently through the packing are acted on by pulsations transmitted hydraulically to form a dispersion of drops. The pulsation device is connected to the side of the column, usually at the base, through a pulse leg. Mechanical difficulties with the generation of the pulse formerly limited pulsed columns to comparatively small diameters, but the installation of pulsed-packed columns up to 2.74 m in diameter has been reported (154,155). The generation of pulses by compressed air has received increasing attention (156). A detailed model of pulsed-packed column behavior has been developed (156). The controlled cycling column (157) has a high throughput, but no large-scale application has been reported.

3.3. Mechanically Agitated Columns. *Rotary Agitated Columns.* Because of the mechanical advantages of rotary agitation, most modern differential contactors employ this method. The best known of the commercial rotary agitated contactors are shown in Figure 15. Features and applications of these columns are given in Table 3.

In the Scheibel column, developed in 1948 (158), every alternate compartment is agitated by an impeller, and the unagitated compartments are packed with open woven wire mesh. Capacity and mass-transfer data are given in the literature (158–161). A newer type of Scheibel column (Fig. 15**a**) using horizontal baffles with or without wire mesh packing was developed in 1956 (162). Performance data for a 30.5-cm column, with or without wire mesh packing, have shown that the HETS varies as the square root of diameter. A third design (163) is basically similar, but a pumping impeller instead of a turbine is used in the mixing stage.

Scale-up and performance of a 1.47-m Scheibel column have been reported (107,164,165), as have detailed description and design criteria for the Scheibel column (166) and scale-up procedures (167).

The rotating-disk contactor (RDC), developed in the Netherlands (168) in 1951, uses the shearing action of a rapidly rotating disk to interdisperse the phases (Fig. 15**b**). These contactors have been used widely throughout the world, particularly in the petrochemical industry for furfural [98-01-1] and SO_2 extraction, propane deasphalting, sulfolane [126-33-0] extraction for separation of aromatics, and caprolactam [105-60-2] purification. Columns up to 4.27 m in diameter are in service. An extensive study (169) has provided an excellent theoretical framework for scale-up. A design manual has also been compiled (170). Detailed descriptions and design criteria for the RDC may also be found (171).

The Oldshue–Rushton column (Fig. 15**d**) was developed (172) in the early 1950s and has been widely used in the chemical industry. It consists essentially of a number of compartments separated by horizontal stator-ring baffles, each fitted with vertical baffles and a turbine-type impeller mounted on a central shaft. Columns up to 2.74 m in diameter have been reported in service (172–177). Scale-up is reported to be reliably predictable (178) although only limited performance data are available (179). A detailed description and review of design criteria are available (180).

The asymmetric rotating disk (ARD) contactor (Fig. 15**c**) was developed in Czechoslovakia (170,181–184) and has been increasingly used in western Europe. Its design aims at retaining the efficient shearing and dispersing action of the RDC while reducing backmixing by means of the coalescence-redispersion cycle produced in the separate transfer and settling zones. The ARD extractor is used for extraction of petrochemicals, pharmaceuticals, and caprolactam, as well as for propane deasphalting, phenol removal from wastewater, furfural refining of oils, etc. Columns up to 2.4 m in diameter are in service and a detailed description and review of design procedures are given in the literature (185).

Kuhni contacters (Fig. 15**e**) have gained considerable commercial application. The principal features are the use of a shrouded impeller to promote radial discharge within the compartments, and a variable hole arrangement to allow flexibility of design for different process applications. Columns up to 5 m in diameter have been constructed (186). Description and design criteria for Kuhni extraction columns have been reported (187,188).

The RTL contactor, formerly known as the Graesser raining bucket contactor (182), is a horizontal design having the phases interdispersed by slowly rotating waterwheel-type impellers. This unit, which has the feature of dispersing each phase into the other, was developed for handling the difficult settling systems found in the coal-tar industry. It is also suitable for solid–liquid systems (190) and data on mass transfer and axial mixing have been reported (191,192). Units have been built from 100 mm (4 in.)–1.8 m (6 ft) in diameter. There are many other types of rotary agitated contactors (193) that have been less widely used.

Reciprocating-Plate Columns. Phase dispersion can also be achieved by reciprocating or vibrating of plates in a column. Improvement of extraction efficiency in a perforated-plate column by pulsing the liquid contents or by reciprocating the plates was proposed in 1935 (194). A reciprocating-plate column (RPC) was later developed (195) and scale-up was shown to be effectively accomplished by adding fixed baffles to the column (196). Many different types of column employing reciprocating plates or packing have been described (197–205) (Fig. 15**f**).

Reciprocation of plates requires less energy than pulsing the entire volume of liquid in a column, and has the same effect in terms of mixing patterns and uniform dispersion. This is a considerable advantage in large-scale commercial extractors (107). The main difference between the different types of RPC that have been built for industrial use lies in the plate design, as shown in Figure 16. Table 2 outlines the general features and industrial applications of the different types of RPC. Also available are reviews (205,206) and a more detailed description of the design criteria (207).

The open-type (Karr) RPC plate (196) has relatively large (12−15 mm) diameter perforations and free area of ∼58% (Fig. 16**a**). It operates only in the emulsion regime. A minimum HETS of 50.8 cm has been measured in a 0.91-m diameter column using the relatively difficult (high interfacial tension) system *o*-xylene−acetic acid−water. Empirical correlations for scale-up have been proposed (106,115,196,208–210). Hydrodynamics and axial mixing have also been studied (211,212). As well as being operated countercurrently, the Karr RPC can be operated in cocurrent flow. This type of column has gained increasing industrial application in the pharmaceutical, petrochemical, and hydrometallurgical industries, and in wastewater treatment (106,206,208); the Karr RPCs are in service in North America and Europe in diameters up to 1.7 m (213).

The RPCs having perforated plates and downcomers (Fig. 16**b**) have been developed industrially in the former Czechoslovakia (214,215) under the trademark VPE (vibrating plate extractor). For large columns a segmental downcomer is used instead of a tubular downcomer. The downcomers permit a much higher throughput than would be possible using perforations alone. The largest units for phenol [108-95-2] extraction have a diameter of 1.2 m and plate stack height 9.1 m. These have a capacity of 80 m^3/h for phenolic wastewater (106,208).

The KRIMZ and GIAP types of RPC (204,205) (Figs. 16**c** and **d**, respectively) were developed in the former USSR and the plate designs feature rectangular punched perforations, where the displaced metal strips remain attached as inclined vanes. The purpose of the vanes is to deflect the liquid and give it radial motion, which can be beneficial in reducing axial mixing in larger diameter columns. The modeling, design, and scale-up (216) have been based on theoretical principles (217). Industrial applications of KRIMZ and GIAP plates in RPCs up to 1.5 m in diameter have been reported (206,218).

Other types of RPC have been proposed, but are not in industrial use. These include a reciprocated wire-mesh packing (202), a reciprocating screen-plate (219), and the multistage vibrating disk column (MVDC) developed in Japan (203,220,221). These types of RPC may be useful for gas−liquid contact as well as liquid−liquid contact.

Centrifugal Extractors. In centrifugal extractors, contact time between the phases is reduced and phase separation is accelerated by the application of centrifugal forces that greatly exceed gravitational forces. The units are compact and a relatively high throughput per unit volume can be achieved. Centrifugal extractors are particularly useful for systems that are chemically unstable, eg, extraction of antibiotics, or for systems in which the phases are slow to settle.

General features and fields of application are given in Table 3 and a detailed review including design criteria is available (222).

The first differential centrifugal extractor to be used in industry was the Podbielniak extractor which was introduced in the 1950s (223,224) and can be regarded as a perforated-plate column wrapped around a rotor shaft. Rotation creates a centrifugal force that results in a great reduction in the equivalent height and contact time that would be needed in a conventional perforated-plate column.

The behavior of drops in the centrifugal field has been studied (225) and the residence times and mass-transfer rates have been measured (226,227). Podbielniak extractors have been widely used in the pharmaceutical industry, eg, for the extraction of penicillin, and are increasingly used in other fields as well. Commercial units having throughputs of up to 98 m^3/h (26,000 gal/h) have been reported.

The Alfa-Laval extractor (228) can give up to 20 theoretical stages in one unit. Depending on the system being handled, the capacity of the standard unit ranges between 5.7 and 21.2 m^3/h (1500–5600 gal/h). Antibiotic extractions and petrochemical processing are typical applications.

A countercurrent continuous centrifugal extractor developed in the former USSR (229) has the feature that mechanical seals are replaced by liquid seals with the result that operation and maintenance are simplified; the mechanical seals are an operating weak point in most centrifugal extractors. The operating units range between 400 and 1200 mm in diameter, and a capacity of 70 m^3/h has been reported in service. The extractors have been applied in coke-oven refining, erythromycin production, lube oil refining, etc.

The class of discrete stage centrifugal extractors includes the Westfalia centrifugal extractor (230,231), which rotates about a vertical axis and is available with up to three contact stages. Its advantage is that the light phase does not have to be introduced under pressure. The capacity of the largest model is reported as ranging from 7.6 m^3/h (2000 gal/h) for three stages, to 49.2 m^3/h (13,000 gal/h) for a single stage. Another important member of this class is the Robatel extractor that consists of a series of mixer–settlers stacked on their sides with the mixing in each stage being provided by a stationary disk attached to the shaft while the chamber rotates. Typical units provide three to eight stages, and throughputs up to 6.2 m^3/h (1600 gal/h) have been reported. Robatel extractors have found general application in the chemical, pharmaceutical, and petrochemical industries, and particularly the nuclear industry. Technical and economic comparisons of the Robatel extractor with mixer–settlers and pulsed columns have been made (232). Research and development on other nondispersive forms of contactors, eg, Hi-Gee solvent extractors that give a high efficiency per unit volume, and contactors effective with very short residence times, eg, improvement on the centrifugal extractor, has been reported (233,234).

3.4. Economics of Extraction. Economic considerations for solvent extraction include both capital and operating costs. Capital cost is made up of the installed cost of equipment and the cost of the inventory of material (including solvent and extractant) held within the plant. Operating costs include the cost of extractor operation, solvent recovery, and solvent losses. Solvent recovery is often the dominant factor because of the high energy consumption involved.

Process economy can often be improved by increasing the number of stages, which reduces the solvent recovery despite increasing the capital cost.

4. Organic Processes

4.1. Petroleum and Petrochemical Processes. The first large-scale application of extraction was the removal of aromatics from kerosene [8008-20-6] to improve its burning properties. Jet fuel kerosene and lubricating oil, which require a low aromatics content, are both in demand. Solvent extraction is also extensively used to meet the growing demand for the high purity aromatics, eg, benzene, toluene, and xylene (BTX), as feedstocks for the petrochemical industry. Additionally, the separation of aromatics from aliphatics is one of the largest applications of solvent extraction.

Lubricating Oil Extraction. Aromatics are removed from lubricating oils to improve viscosity and chemical stability. The solvents used are furfural, phenol, and liquid sulfur dioxide. The latter two solvents are undesirable owing to concerns over toxicity and the environment and most newer plants are adopting furfural processes. A useful comparison of the various processes is available (235,236).

Separation of Aromatic and Aliphatic Hydrocarbons. Aromatics extraction for aromatics production, treatment of jet fuel kerosene, and enrichment of gasoline fractions is one of the most important applications of solvent extraction. The various commercial processes are summarized in Table 4.

The Udex process (237) was popular in the United States in the 1970s. The original process produced high purity gasoline by removing aromatics using diethylene glycol as a solvent. The process has also been used for the manufacture of BTX; aqueous tetraethylene glycol [112-60-7] appears to be the best solvent (238). The sulfolane process (239–241), introduced by the Shell Co. in 1962 (Fig. 17), is used in many large units all over the world. Sulfolane [126-33-0] [(tetrahydrothiophene)-1,1-dioxide], is a strongly polar compound that is highly selective for aromatic hydrocarbons and has much greater solvent capacity for hydrocarbons than glycol systems. Additional features in its favor are high density, heat capacity, and chemical stability. The sulfolane process uses the rotating-disk contactor (RDC) (242). The Lurgi Arosolvan process (243) has been used in over a dozen commercial installations. Two process arrangements are available, using as solvent either a mixture of *N*-methyl-2-pyrrolidinone [872-50-4] (NMP) and water or a mixture of NMP and ethylene glycol [107-21-1]. The polar mixing component (water or ethylene glycol) increases the selectivity of the solvent for aromatics. The Lurgi multistage mixer–settler is used with towers up to 6 m in diameter and 35 m high. The NMP (Arosolvan) process for BTX separation has been described (244). A DMSO [67-68-5] process, which employs two separate extraction steps, has been developed (245). The selectivity and low viscosity of the solvent (DMSO plus a few percent water) allow the extraction to take place entirely at ambient temperatures. In addition, DMSO is nontoxic and relatively inexpensive. The process uses the Kuhni column (Fig. 15**e**) in diameters up to 2.7 m. In the Union Carbide process (246), the solvent (tetraethylene glycol) is recovered by a second extraction step rather than from the extract by distillation. However, it is necessary to distill the raffinate from the first extractor in order to recover the dissolved process solvents. A useful description of the Union Carbide TETRA process is available (247). The Formex process (248) which employs *N*-formylmorpholine [4394-85-8] and a few percent water as solvent, has the flexibility to handle different feedstocks and product ranges. Either distillation or secondary extraction may be used to regenerate the solvent, depending on the range of aromatics that is to be produced. The Redox process (249) (recycle extract dual extraction) improves the octane number of diesel fuels by extracting an aromatic concentrate. The solvents include furfural–furfuryl alcohol–water mixtures, aqueous tetrahydrofurfuryl alcohol, and aqueous dimethylformamide (DMF).

Desulfurization. The sulfur compounds in petroleum oil include hydrogen sulfide, mercaptans, thiophenols, and thioethers in amounts ranging from a few tenths to several percent. Sulfur compounds have objectionable odors and adversely affect the stability of light distillate and the antiknock and oxidation characteristics of gasoline. Sulfurs are generally removed by multistage countercurrent extraction using a relatively large volume of dilute alkali solution.

Butadiene Separation. Solvent extraction is used in the separation of butadiene [106-99-0] from other C4 hydrocarbons in the manufacture of synthetic rubber. The butadiene is produced by catalytic dehydrogenation of butylene and the liquid product is then extracted using an aqueous cuprammonium acetate solution with which the butadiene reacts to form a complex. Butadiene is then recovered by stripping from the extract. Distillation is a competing process.

Caprolactam Extraction. A high degree of purification is necessary for fiber-grade caprolactam, the monomer for nylon-6. Crude aqueous caprolactam is purified by solvent extractions using aromatic hydrocarbons, eg, toluene, as the solvent (250). Many of the well-known types of column contactors have been used; a detailed description of the process is available (251).

Extraction of C8 Aromatics. The Japan Gas Chemical Co. developed an extraction process for the separation of *p*-xylene [106-42-3] from its isomers using $HF{-}BF_3$ as an extraction solvent and isomerization catalyst (252). The highly reactive solvent imposes its own restrictions, but this approach is claimed to be economically superior to more conventional separation processes.

Anhydrous Acetic Acid. In the manufacture of acetic acid by direct oxidation of a petroleum-based feedstock, solvent extraction has been used to separate acetic acid [64-19-7] from the aqueous reaction liquor containing significant quantities of formic and propionic acids. Isoamyl acetate [123-92-2] is used as solvent to extract nearly all the acetic acid, and some water, from the aqueous feed (253). The extract is then dehydrated by azeotropic distillation using isoamyl acetate as water entrainer. It is claimed that the extraction step in this process affords substantial savings in plant capital investment and operating cost. A detailed description of various extraction processes is available (254).

Synthetic Fuel. Solvent extraction has many applications in synthetic fuel technology, eg, the extraction of the Athabasca tar sands and Irish peat using *n*-pentane [109-66-0] (255) and a process for treating coal using a solvent under hydrogen (256). In the latter case, coal reacts with a minimum amount of hydrogen so that the solvent extracts valuable feedstock components before the solid residue is burned. Solvent extraction is used in coal liquefaction processes (257) and synthetic fuel refining.

4.2. Pharmaceutical Processes. The pharmaceutical industry is a principal user of extraction because many pharmaceutical intermediates and products are heat-sensitive and cannot be processed by methods, eg, distillation. A useful broad review can be found in the literature (258).

Antibiotics. Solvent extraction is an important step in the recovery of many antibiotics, eg, penicillin [1406-05-9], streptomycin [57-92-1], novobiocin [303-81-1], bacitracin [1405-87-4], erythromycin, and the cephalosporins. A good example is in the manufacture of penicillin (259) by a batchwise fermentation. Amyl acetate [628-63-7] or *n*-butyl acetate [123-86-4] is used as the extraction solvent for the filtered fermentation broth. The penicillin is first extracted into the solvent from the broth at pH 2.0–2.5 and the extract treated with a buffer solution (pH 6) to obtain a penicillin-rich solution. Then the pH is again lowered and the penicillin is reextracted into the solvent to yield a pure concentrated solution. Because penicillin degrades rapidly at low pH, it is necessary to perform the initial extraction as rapidly as possible; for this reason centrifugal extractors are generally used.

Fractional extraction has been used in many processes for the purification and isolation of antibiotics from antibiotic complexes or isomers. A 2-propanol–chloroform mixture and an aqueous disodium phosphate buffer solution are the solvents (260). A reciprocating-plate column is employed for the extraction process (164).

Vitamins. The preparation of heat-sensitive natural and synthetic vitamins involves solvent extraction. Natural vitamins A and D are extracted from fish liver oils and vitamin E from vegetable oils; liquid propane [74-98-6] is the solvent. In the synthetic processes for vitamins A, B, C, and E, solvent extraction is generally used either in the separation steps for intermediates or in the final purification.

Miscellaneous Pharmaceutical Processes. Solvent extraction is used for the preparation of many products that are either isolated from naturally occurring materials or purified during synthesis. Among these are sulfa drugs, methaqualone [72-44-6], phenobarbital [50-06-6], antihistamines, cortisone [53-06-5], estrogens and other hormones, and reserpine [50-55-5] and alkaloids. Common solvents for these applications are chloroform, isoamyl alcohol, diethyl ether, and methylene chloride.

4.3. Food Processing. Food processing makes use of solvent extraction in several ways. Industrial refining of fats and oils using propane is known as the Solexol process (262). Vegetable oils are refined by extraction using furfural as solvent (263). Solvent extraction is used in many protein refining processes, eg, the extraction of fish protein from ground fish using *i*-propyl alcohol (264). Recovery of lactic acid by an extractive fermentation has been reported (265). The applications of extraction in the food industry have been reviewed (266).

4.4. Other Organic Processes. Solvent extraction has found application in the coal-tar industry for many years, as, eg, in the recovery of phenols from coal-tar distillates by washing with caustic soda solution. Solvent extraction of fatty and resimic acid from tall oil has been reported (267). Dissociation extraction is used to separate *m*-cresol from *p*-cresol (268) and 2,4-xylenol from

2,5-xylenol (269). Solvent extraction can play a role in the direct manufacture of chemicals from coal (270).

Treatment of Industrial Effluents. Solvent extraction appears to have great potential in the field of effluent treatment, both for the economic recovery of valuable materials and for the removal of toxic materials to comply with environmental requirements.

The Phenox process (271,272) removes phenol from the effluent from catalytic cracking in the petroleum industry. Extraction of phenols from ammoniacal coke-oven liquor may show a small profit. Acetic acid can be recovered by extraction from dilute waste streams (273). Oils are recovered by extraction from oily wastewater from petroleum and petrochemical operations. Solvent extraction is employed commercially for the removal of valuable by-products from wool industry effluents (274) and is applied in the same way in the pharmaceutical industry. A successful extraction process to recover *p*-nitrophenol [100-02-7] from a waste solution containing 8000 ppm has been developed (275). A combination of solvent extraction and wet air oxidation is used in the treatment of toxic pharmaceutical effluent prior to discharge for biological treatment. Several schemes for organic industrial wastewater treatment have been reported (276). Amphiphilic polymer solutions have high capacity for trace organics and can be used with hollow fiber membrane extractors to treat contaminated aqueous streams for environmental applications (276).

Biopolymer Extraction. Research interests involving new techniques for separation of biochemicals from fermentation broth and cell culture media have increased as biotechnology has grown. Most separation methods are limited to small-scale applications but recently solvent extraction has been studied as a potential technique for continuous and large-scale production and the use of two-phase aqueous systems has received increasing attention (278,279). A range of enzymes have favorable partition properties in a system based on a PGE–dextran–salt solution (106):

Enzyme	Industrial application
α-amylase	glues–food ingredients
glucoamylase	cornstarch–glucose conversion; starch–glucose conversion
α-glucosidase	maltose–glucose conversion
glucose-6-phosphate dehydrogenase	medicinal indicator
formate dehydrogenase	oxalate–formate determination
formaldehyde dehydrogenase	aldehyde–alcohol conversion
catalase	cold milk sterilization
pullunanase	starch–maltose conversion
glucose isomerase	glucose–fructose conversion
β-glucosidase	food processing
interferon	pharmaceutical applications

In many cases, rapid and effective removal of contaminants and undesirable products, eg, nucleic acids and polysaccharides is achieved.

Difficult Separations. Difficult separations, characterized by separation factors in the range 0.95–1.05, are frequently expensive because these involve high operating costs. Such processes can be made economically feasible by reducing the solvent recovery load (280); this approach is effective, for example, in the separation of *m*- and *p*-cresol, linoleic and abietic components of tall oil, and the production of heavy water.

5. Inorganic Processes

The first significant application of liquid–liquid extraction in inorganic chemical technology was the separation of uranium and plutonium from nuclear reactor fission products in the late 1940s (228). A few years later, extraction was successfully applied at the front end of the nuclear fuel cycle in separating uranium from ore leach liquors as an alternative to ion exchange. Since then, many other hydrometallurgical applications of liquid–liquid extraction have been developed (1,2,9,282), as well as a number of applications involving nonmetallic inorganic products (283).

Most inorganic compounds are insoluble or sparingly soluble in organic solvents, whereas metal ions in aqueous solution are stable because water has a high dielectric constant and because of the solvation of ions by water molecules. Aqueous affinity must be overcome usually by an extractant that can react with the metal ion to displace the solvated water and form an uncharged species having significant solubility in the organic solvent, as illustrated in equations 10–12. The organic carrier solvent, or diluent, is usually regarded as being chemically inert although the relative aliphatic–aromatic content of the diluent can affect the extraction rates and equilibria (284). Physical properties of the carrier solvent should include a low viscosity, low flash point, and low vapor pressure to minimize evaporative losses (10). The interfacial tension between the extractant–diluent phase and the aqueous phase should preferably be high in order to provide good phase separation and minimize entrainment losses. For reasons of cost, the carrier solvent is usually a cut from petroleum distillation having flash points in the 40–80°C range.

As metal extraction into a diluent–extractant solution proceeds, there is sometimes a tendency for formation of two organic phases in equilibrium with the aqueous phase. A third phase is highly undesirable and its formation can be prevented by adding to the organic phase a few percent of a modifier that is typically a higher alcohol or tri-*n*-butyl phosphate (TBP) (9).

5.1. Nuclear Fuel Reprocessing. Spent fuel from a nuclear reactor contains ^{238}U, ^{235}U, ^{239}Pu, ^{232}Th, and many other radioactive isotopes (fission products). Reprocessing involves the treatment of the spent fuel to separate plutonium and unconsumed uranium from other isotopes so that these can be recycled or safely stored (281,284,285).

The spent fuel is dissolved in nitric acid and the solution is extracted by an appropriate solvent. The Purex process (284–286) uses a 30% solution of tri-*n*-butyl phosphate (TBP) as extractant, in an aliphatic diluent, eg, a kerosene. The uranium and plutonium are present in the aqueous phase in the hexavalent state as $UO_2(NO_3)_2$ and $PuO_2(NO_3)_2$ and are selectively extracted (see eq. 12).

Fission products remain in the aqueous raffinate. The organic extract is treated with an aqueous strip solution containing nitric acid and a cationic reducing agent which converts Pu to its trivalent state, which is preferentially stripped to the aqueous phase. Finally, the uranium is stripped from the organic phase by contact with a dilute aqueous solution of nitric acid. The aqueous raffinate from the Purex process contains actinides and rare-earth fission products that are long lived and radiotoxic. Bifunctional extractants of the carbamoylmethylphosphoryl family have been developed with the capability to remove many of these substances and thus improve the economics of safe disposal of the bulk raffinate (285,287). This objective can also be achieved by *n,n*-dialkyl amides (288,289). The various alternative approaches to fuel reprocessing have been critically reviewed (288,289).

Special safety constraints apply to equipment selection, design, and operation in nuclear reprocessing (290). Equipment should be reliable and capable of remote control and operation for long periods with minimal maintenance. Pulsed columns and remotely operated mixer–settlers are commonly used (291). The control of criticality and extensive monitoring of contamination levels must be included in the process design.

Uranium Extraction from Ore Leach Liquors. Liquid–liquid extraction is used as an alternative or as a sequel to ion exchange in the selective removal of uranium [7440-61-1] from ore leach liquors (9,285,292). These liquors differ from reprocessing feeds in that they are relatively dilute in uranium and only slightly radioactive, and contain sulfuric acid rather than nitric acid.

In the Amex process, the feed typically containing 5 g/L uranium and 100 g/L sulfuric acid is first filtered and treated to remove interfering anions, eg, molybdates and vanadates. The extractant is a commercially available formulation containing tertiary amines having C8–C12 alkyl chains. A kerosene diluent is used, and the extractant is at a concentration of ~5%, plus ~2% of a higher alcohol, eg, decanol as a modifier. The extracted species is an amine uranyl sulfate. Mixer–settler extractors are commonly used; stripping of the uranium can be carried out under acidic, basic, or neutral conditions. The alternative Dapex process employs alkyl phosphoric acids such as di-(2-ethylhexyl) phosphoric acid [298-07-7] (D2EHPA) as extractants. Although the feed pretreatment requirements are less rigorous than for the Amex process, the extractant is somewhat less selective for uranium (292).

Uranium is present in small (50–200 ppm) amounts in phosphate rock and it can be economically feasible to separate the uranium as a by-product from the crude black acid (30% phosphoric acid) obtained from the leaching of phosphate for fertilizers. The development and design of processes to produce 500 t U_3O_8/year at Freeport, Louisiana have been detailed (293).

5.2. Copper. The recovery of copper [7440-50-8], Cu, from ore leach liquors as a stage in the hydrometallurgical route to the pure metal is one of the largest applications of liquid–liquid extraction (9,212,223).

The most common type of copper feed entering a liquid–liquid extraction plant is produced by dilute sulfuric acid leaching and contains between 1 and 10 g/L Cu. This concentration is too low for electrowinning and the purpose of solvent extraction is to raise the concentration as well as to purify the copper solution. A typical extraction circuit for acid leach liquors is shown in Figure 18

(294). Extraction is carried out at a pH 2–4 using an aliphatic kerosene diluent containing chelating extractants based on hydroxyoximes or quinolinol derivatives. These extractants effectively exchange cupric ions and hydrogen ions in the aqueous phase as in the case of acid extractants (eq. 10), so the equilibrium is pH dependent. Stripping is effected by a strongly acid solution having zero or negative pH, as shown in Figure 18. Only a few stages are needed for extraction and stripping, so mixer–settlers rather than columns are used. Rapid and efficient phase separation in the settlers is an important element of the plant design (9,295).

5.3. Nickel and Cobalt. Often present with copper in sulfuric acid leach liquors are nickel [7440-02-0] and cobalt [7440-48-4]. Extraction using an organophosphoric acid, eg, D2EHPA at a moderate (3–4) pH can readily take out the nickel and cobalt together, leaving the copper in the aqueous phase, but the cobalt–nickel separation is more difficult (295) other processes for the separation of nickel and cobalt involve the use of orgonophosphorus acid extractants, eg, Cyanex 272, and oxines, eg, LIX84. In the case of chloride leach liquors, separation of cobalt from nickel is inherently simpler because cobalt, unlike nickel, has a strong tendency to form anionic chloro complexes. Thus cobalt can be separated by amine extractants, provided the chloride content of the aqueous phase is carefully controlled. A successful example of this approach is the Falcon-bridge process developed in Norway (295).

5.4. Other Metals. Because of the large number of chemical extractants available, virtually any metal can be extracted from its aqueous solution. In many cases, extraction has been developed to form part of a viable process (296). A review of more recent developments in metal extraction including those for precious metals and rare-earths is also available (282). In China, a complex extraction process employing a cascade of 600 mixer–settlers has been developed to treat leach liquor containing a mixture of rare earths (140).

There is a growing interest in the use of extraction for recovery of metals from effluent streams, for example the wastes from pickling plants and electroplating plants (292,298). Recovery of metals from liquid effluent has been reviewed (299), and an AM–MAR concept for metal waste recovery has recently been reported (300). Possible applications exist in this area for liquid membrane extraction (94), as well as conventional extraction. Other schemes proposed for effluent treatment are a wetted fiber extraction process (301) and the use of two-phase aqueous extraction (302).

5.5. Extraction of Nonmetallic Inorganic Compounds. Phosphoric acid is usually formed from phosphate rock by treatment with sulfuric acid, which forms sparingly soluble calcium sulfate from which the phosphoric acid is readily separated. However, in special circumstances it may be necessary to use hydrochloric acid:

$$Ca_3(PO_4)_2 + 6\,HCl \rightleftharpoons 3\,CaCl_2 + 2\,H_3PO_4 \tag{49}$$

A process developed in Israel (283) uses solvent extraction using a higher alcohol or other solvating solvent. This removes phosphoric acid and some hydrochloric acid from the system driving the equilibrium of equation 49 to the right. The same principle can be applied in other salt–acid reactions of the form

$$\mathrm{MX + HY \rightleftharpoons MY + HX} \tag{50}$$

where M is a metal cation and X and Y are anions. An organic solvent is chosen to remove HX, again driving the equilibrium to the right. Examples of this type of reaction are (*1*) the production of potassium nitrate from potassium chloride and nitric acid and (*2*) the production of alkali metal phosphates from the alkali chloride and phosphoric acid (283).

A number of processes for the recovery of mineral acids for recycling have been proposed (303) that are based on phosphate or amine extraction chemistry. These offer the potential to economically reduce the environmental impact of many existing hydrometallurgical and metal plating processes.

6. Nomenclature

a = specific interfacial area	m^{-1} or cm^{-1}
A = quantity or flow of component A	kg or kg/s
B = quantity or flow of component B	kg or kg/s
c = concentration	kg/m^3 or g/cm^3
D = molecular diffusivity	m^2/s or cm^2/s
d = drop diameter	m or cm
d_m = Sauter mean drop diameter	m or cm
d_o = orifice diameter	m or cm
E = axial dispersion coefficient	m^2/s or cm^2/s
Figs. 1 and 5 extract flow	kg/s or g/s
F = feed flow	kg/s or g/s
g = acceleration owing to gravity	m/s^2 or cm/s^2
G = molar Gibbs free energy	J/mol
H = height of a compartment	m or cm
HTU = height of a transfer unit	m or cm
h = holdup of dispersed phase	
k = mass-transfer coefficient	m/s or cm/s
K = overall mass-transfer coefficient	m/s or cm/s
K' = dimensionless constant in equation 44	
m = distribution ratio based on mass fraction	
m' = distribution ratio based on mole fraction	
N = flux of solute (eq. 25) number of drops	$kg/(m^2{\cdot}s)$ or $g/(cm^2{\cdot}s)$
N_s = number of stages	
NTU = number of transfer units	
Q = volume flow rate	m^3/s or cm^3/s
R = raffinate flow	kg/s or g/s
Re = Reynolds number	
S = solvent flow	kg/s or g/s
Sc = Schmidt number	
Sh = Sherwood number	
U = superficial velocity	m/s or cm/s

U_s = slip velocity	m/s or cm/s
U_K = characteristic velocity	m/s or cm/s
X = mass ratio of C to A	
x = mole fraction	
Y = mass ratio of C to B	
Z = contactor height	m or cm
z = distance (eq. 18) stoichiometric factor	m or cm
α = backflow ratio	
β = selectivity or (eq. 48) exponent	
$\Delta\rho$ = density difference	kg/m^3 or g/cm^3
γ = activity coefficient	
ϵ = extraction factor	
σ = interfacial tension	N/m
Φ = fractional open area, perforated plate	
Γ = specific energy dissipation rate	W/kg

Subscripts

A = component A
B = component B
C = component C
CA = component C in solvent A
CB = component C in solvent B
c = continuous phase
D = component D
DA = component D in solvent A
DB = component D in solvent B
d = dispersed phase
i = at the interface or (eq. 25) identity of drop
N = exit from stage N
O = overall
0 = feed stream
1 = exit from stage 1
2 = exit from stage 2, etc

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Table 1. **Equations for Liquid–Liquid Mass Transfer in Single Drops**[a]

	Sherwood numbers	
Type of drop	Dispersed phase, Sh_d	Continuous phase, Sh_c
noncirculating	6.58	$2 + 0.6\,Re_e^{0.5}\,Sc_c^{0.333}$
circulating	17.9[b]	$1.13(Re_c \cdot Sc_c)^{0.5}$

[a] Ref. 46.

[b] For laminar conditions.

Table 2. **Extractor Selection Chart**[a,b]

	Gravity-separated extractors																			
						Discontinuous contact														
	Continuous contact					Without interstage settling		With settling					Mixer-settlers				Centrifugally separated			
	Non-mechanical		Mechanical			Mechanical		Non-mechanical		Mechanical			Horizontal		Vertical		Continuous contact		Mixer-settler	
Design requirements	Spray column	Baffle-plate column	Packed column	Pulsed-packed column	Raining-bucket contractor	Rotary-agitated columns	Reciprocating-plate column	Pulsed-plate column	Perforated-plate column	Scheibel column	ARDC column	Rotary film contractor	Pump–settler	Agitated mixer–settler	Pump–settler	Agitated mixer–settler	Perforated plate	Film-flow type (de Laval)	Luwesta	Rotabal
total throughput, m^3/h																				
<0.25	3	3	3	3	3	3	3	3	3	3	3	1	0	1	0	1	3	1	0	0
0.25–2.5	3	3	3	3	3	3	3	3	3	3	3	3	1	3	1	3	3	3	1	1
2.5–25	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
25–250	3	1	3	3	1	3	1	1	3	1	1	1	3	3	3	1	0[c]	0[c]	0[c]	0[c]
>250	1	0	1	1	0	1	0	1	1	0	0	1	5	5	1	1	0[c]	0[c]	0[c]	0[c]
number of stages																				
<1.0	5[d]	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
1–5	1,[e]0	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	5[f]	3
5–10	0	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	1[c]	1	0[c]	3
10–15	0	1	1	3	1	1	3	3	1	3	1	1	3	3	1	1	0[c]	0[c]	0[c]	0[c]
>15	0	1	1	1	1	1	1	1	1	1	1	0	3	3	1	1	0[c]	0[c]	0[c]	0[c]
physical properties[g]																				
$(\sigma/\rho g)^{1/2} > 0.60$	1	1	1	3	1	3	3	3	1	3	3	3	3	3	3	3	5	5	5	5

density difference, g/cm^3																				
$0.05 > \Delta p > 0.03$	3	3	3	0	3	0	0	0	1	0	1	3	1	1	1	1	5	5	5	5
viscosity[e], mPa·s(= cP)																				
μ_c or $\mu_d > 20$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
slow heterogeneous reaction																				
$k_t < 4 \times 10^{-5}$ m/s	0	1	1	3	1	3	3	3	1	3	3	0	0	3	0	3	3	3	3	3
slow homogeneous reaction																				
$t_{1/2} = 0.5–5$ min	1	1	1	1	3	1	1	1	3	1	1	1	3	5	3	3	0	0	1	1
>5 min	0	0	0	0	1	0	0	0	1	0	0	0	3	5	3	3	0	0	0	0
extreme phase ratio																				
$F_d/F_f < 0.2$ or >5	1	1	1	1	3	1	1	1	3	1	1	3	1	5[h]	1	5[h]	3	3	3	3
short residence time	0	0	0	1	0	1	1	1	0	0	0	0	0	0	0	0	5	5	3	3
ability to handle solids																				
trace (<0–0.1% in feed)	3	3	1	1	5	3	3	3	1	1	1	5	3	3	3	3	1	1	1	1
appreciable (0.1–1% in feed)	1	1	1	1	3	3	3	3	0	0	0	5	1	1	1	1	1	1	1	1
heavy (>1% in feed)	1	1	0	0	1	1	1	1	0	0	0	5	1[i]	1[i]	1[i]	1[i]	0	0	1	1
tendency to emulsify																				
slight	3	3	1	1	3	1	1	1	3	1	1	3	1	1	1	1	5	5	5	5
marked	1	1	1	0	1	0	0	0	1	0	0	1	0	0	0	0	3	3	3	3
limited space available																				
height	0	1	1	1	5	1	1	1	1	1	1	3	5	5	0	0	5	5	5	5
floor	5	5	5	5	0	5	5	5	5	5	5	0	0	0	5	5	5	5	5	5
special materials required																				
metals (stainless steel, Ti, etc)	5	3	5	5	3	3	3	3	3	3	3	3	3	3	3	3	5	5	5	5
nonmetals	5	3	5	1	1	0	0	1	1	0	0	1	1	5	1	1	0	0	0	0
radioactivity present																				
weak (mainly α, β)	5	5	5	3	1	1	1	3	3	1	1	1	3	5	3	1	1	1	1	1
strong γ	5	5	5	3	0	0	0	3	3	0	0	0	3	5	1	0	0	0	0	0
ease of cleaning	5	3	1	1	3	3	3	3	1	1	3	5	3	3	3	3	1	3	3	1
low maintenance	5	5	5	3	3	3	3	3	5	3	3	3	3	3	3	3	1	1	1	1

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[a] Ref. 102.

[b] Rating of 5, very strongly recommended; 3, satisfactory; 1, may be used; and 0, not suitable.

[c] Multiple units in series or parallel can be used.

[d] For immeasurably fast homogeneous reaction.

[e] For diameters <15 cm.

[f] Two or three stages only in single machine.

[g] See text for effect of direction of transfer.

[h] With recirculation of separated phases to mixer.

[i] Requires provision for solids removal from settler.

Table 3. **Summary of Commercial Extractors**

Types of extractor	General features[a]	Fields of industrial application
unagitated columns	low capital cost, low operating and maintenance cost, simplicity in construction, handles corrosive material	petrochemical, chemical
mixer–settlers	high stage efficiency, handles wide solvent ratios, high capacity, good flexibility, reliable scale-up, handles liquids with high viscosity	petrochemical, nuclear, fertilizer, metallurgical
pulsed columns	low HETS, no internal moving parts, many stages possible	nuclear, petrochemical, metallurgical
rotary agitation columns	reasonable capacity, reasonable HETS, many stages possible, reasonable construction cost, low operating and maintenance cost	petrochemical, metallurgical, pharmaceutical, fertilizer
reciprocating-plate columns	high throughput, low HETS, great versatility and flexibility, simplicity in construction, handles liquids containing suspended solids, handles mixtures with emulsifying tendencies	pharmaceutical, petrochemical, metallurgical, chemical
centrifugal extractors	short contacting time for un-stable material, limited space required, handles easily emulsified material, handles systems with little liquid density difference	pharmaceutical, nuclear, petrochemical

[a] Height of an equivalent theoretical stage = HETS.

Table 4. **Extractive Processes for the Separation of Benzene–Toluene–Xylene Mixture from Light Feedstocks**[a]

Process	Solvent	Solvent additives and reflux conditions	Operating temperature, °C	Contacting equipment	Comments
Shell process, Universal Oil Products	sulfolane	sulfolane selectivity and capacity insensitive to water content caused by steam-stripping during solvent recovery; heavy paraffinic countersolvent use	120	rotating-disk contactor, up to 4 m in diameter	the high selectivity and capacity of sulfolane leads to low solvent-feed ratios, and thus smaller equipment
Udex process, Universal Oil Products	glycol–water mixture	solvent can be diethylene glycol and water, or mixture of diethylene and dipropylene glycols and water, or tetraethylene glycol and water; light hydrocarbon reflux	150 for diethylene glycol and water	sieve-tray extractor	tetraethylene glycol and water mixtures are claimed to increase capacity by a factor of 4 and also require no antifoaming agent; the extract requires a two-step distillation to recover BTX
Union Carbide Corp.	tetraethylene glycol (TETRA)	the solvent is free of water; a dodecane reflux is used which is later recovered by distillation	100	reciprocating-plate extractor	the extract leaving the primary extractor is essentially free of feed aliphatics, and no further purification is necessary; two-stage extraction uses dodecane as a displacement solvent in the second stage

Table 4. (*Continued*)

Process	Solvent	Solvent additives and reflux conditions	Operating temperature, °C	Contacting equipment	Comments
Institut Français du Pétrole	dimethyl sulfoxide (DMSO)	solvent contains up to 2% water to improve selectivity; reflux consist of aromatics and paraffins	ambient	rotating-blade extractor, typically 10–12 stages	low corrosion allows use of carbon steel equipment; solvent has a low freezing point and is nontoxic; two-stage extraction has displacement solvent in the second stage
Arosolvan process, Lurgi	*N*-methyl-2-pyrrolidinone (NMP)	a polar mixing component, either water or monoethylene glycol (40–50 wt%) must be added to the NMP to increase the selectivity and to decrease the boiling point of the solvent; the NMP–water processes use pentane countersolvent	NMP–glycol, 60; NMP–water, 35	vertical multistage mixter–settler, 24–30 stages, up to 8 m in diameter	the quantity of mixing component required depends on the aromatics content of the feed
Formex process, Snamprogetti	*N*-formylmorpholine (FM)	water is added to the FM to increase its selectivity and also to avoid high reboiler temperatures during solvent recovery by distillation	40	perforated-tray extractor, FM density at 1.15 aids phase separation	low corrosion allows use of carbon steel equipment

[a] Ref. 180.

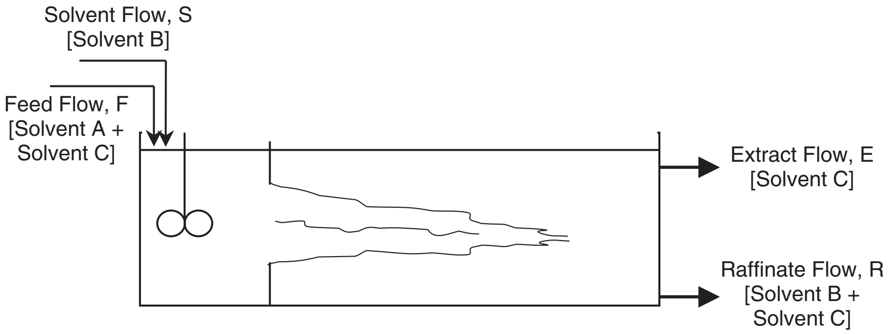
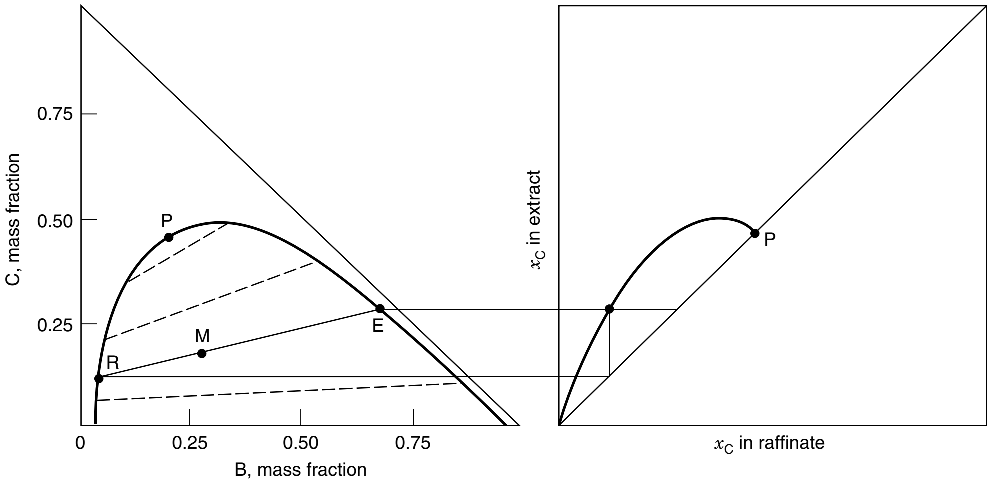


Fig. 1. Single contacting stage.



(**a**) (**b**)

Fig. 2. (**a**) Triangular diagram, where the dashed lines represent tie-lines, and (**b**) tie-line location curve. Terms are defined in the text.

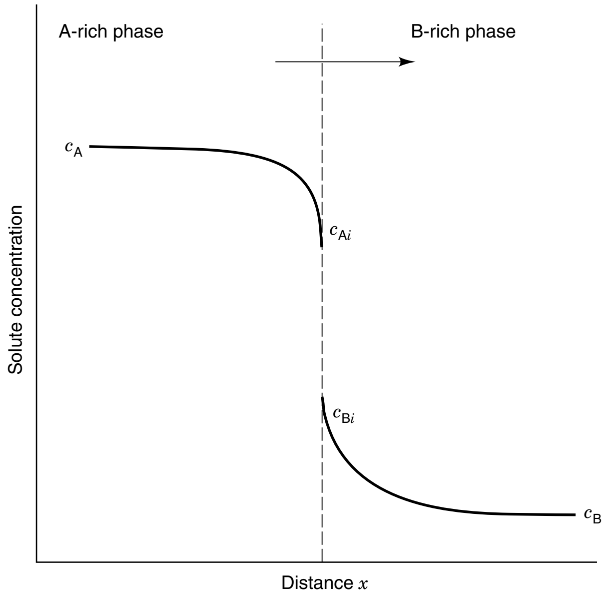


Fig. 3. Concentration profiles near an interface where the arrow represents the direction of mass transfer, c_A = concentration of C in A-rich phase, c_B = concentration of C in B-rich phase, and the subscript i denotes the interface.

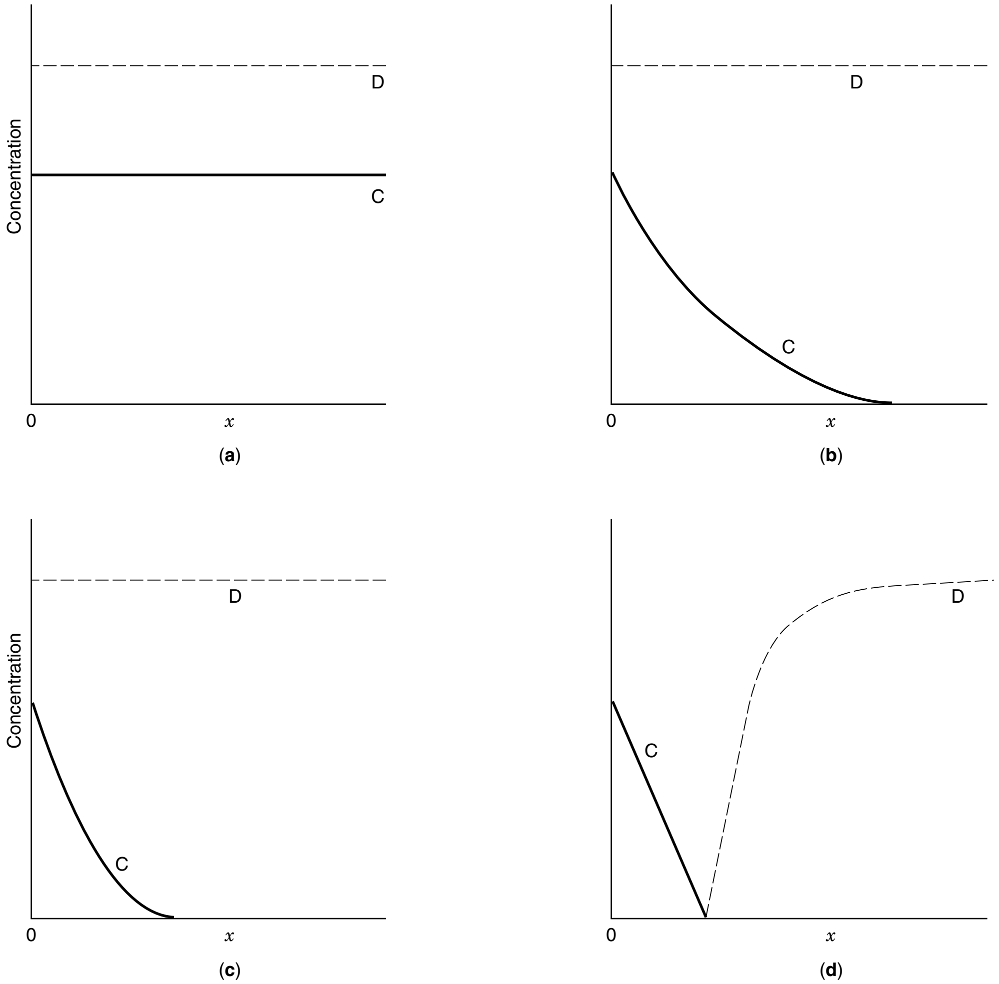


Fig. 4. Concentration profiles for the reaction of equation (4) where (—) is the concentration of C; (—) the concentration of D; and x is the distance from the interface. (**a**) Regime 1; (**b**) regime 2; (**c**) regime 3; and (**d**) regime 4, as described in the text.

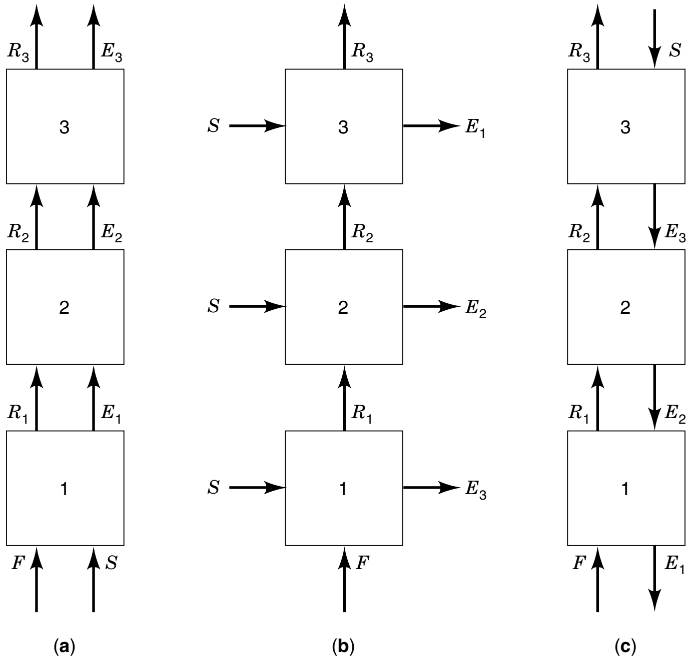


Fig. 5. Arrangement of multistage contactors where F = feed flow (A-rich), R = raffinate flow, S = solvent flow (B-rich), and E = extract flow. (**a**) Cocurrent; (**b**) crosscurrent; and (**c**) countercurrent.

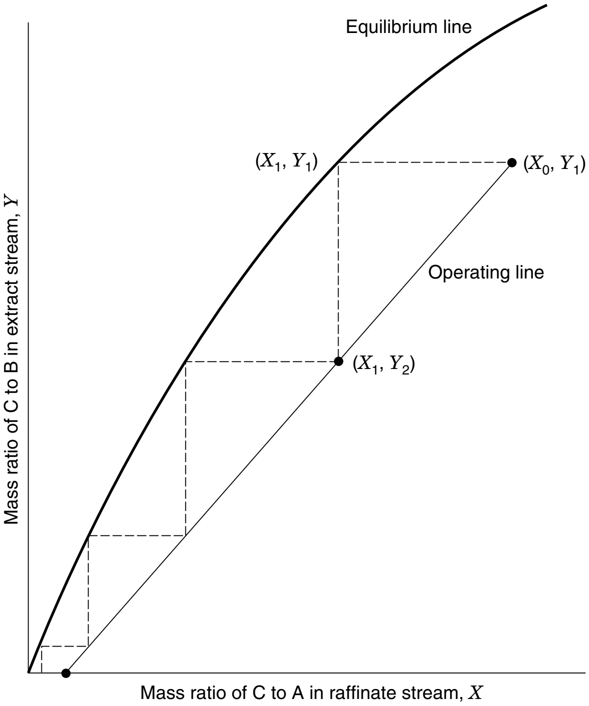


Fig. 6. Countercurrent extraction showing the equilibrium stages (horizontal dashed lines) where A and B are immiscible.

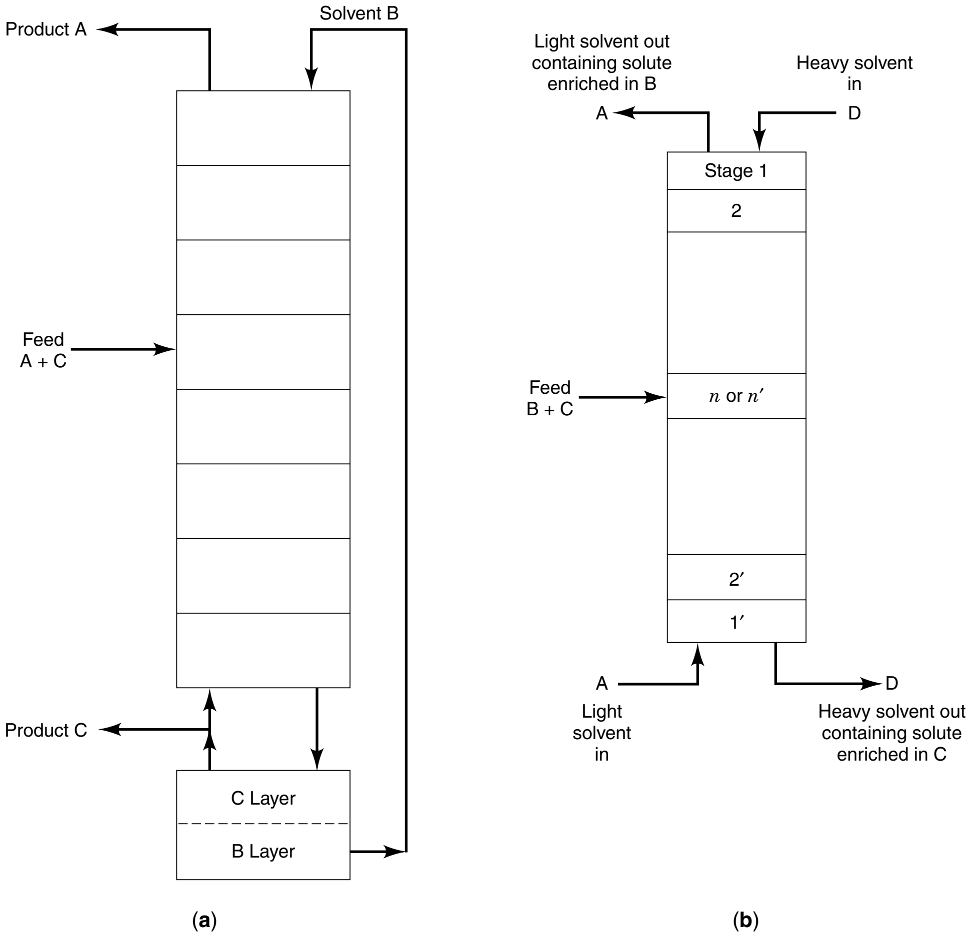


Fig. 7. Fractional extraction: (**a**) one solvent; (**b**) two solvents.

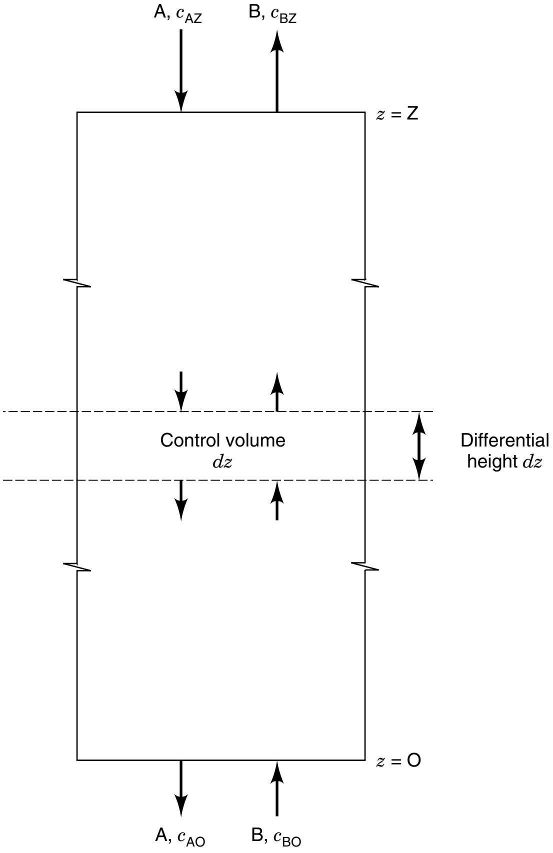


Fig. 8. Mass transfer in a differential contactor. Terms are defined in the text.

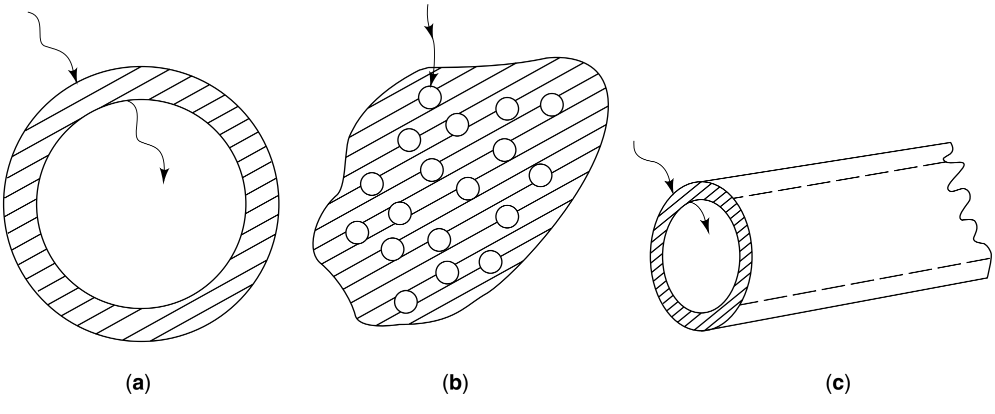


Fig. 9. Membrane extraction where the solvent phase is represented by hatched lines and the arrows show the direction of mass transfer. (**a**) Spherical film; (**b**) emulsion globule where the strip solution is represented by circles; and (**c**) hollow fiber support.

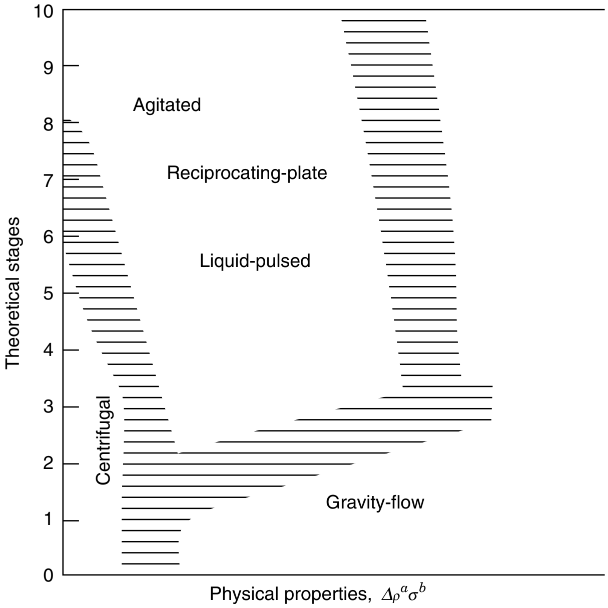


Fig. 10. Economic operating range of extractors. Superscripts *a* and *b* are constants. (Courtesy of Luwa AG (10)).

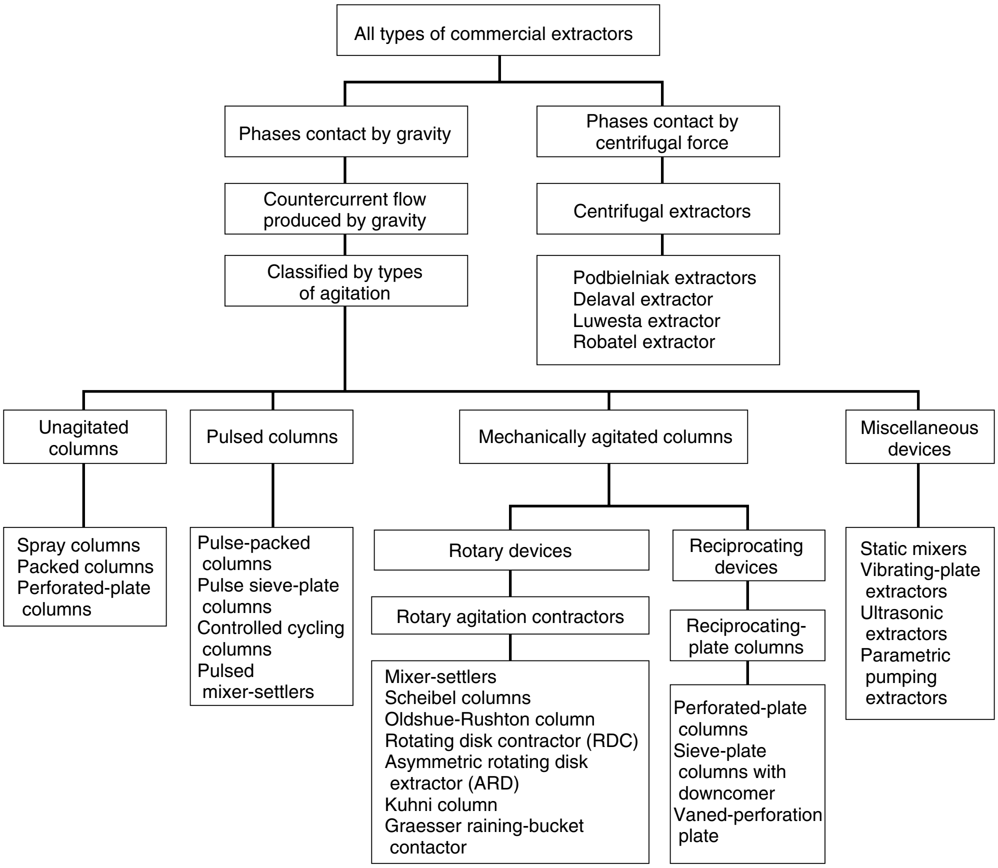


Fig. 11. Classification of commercial extractors.

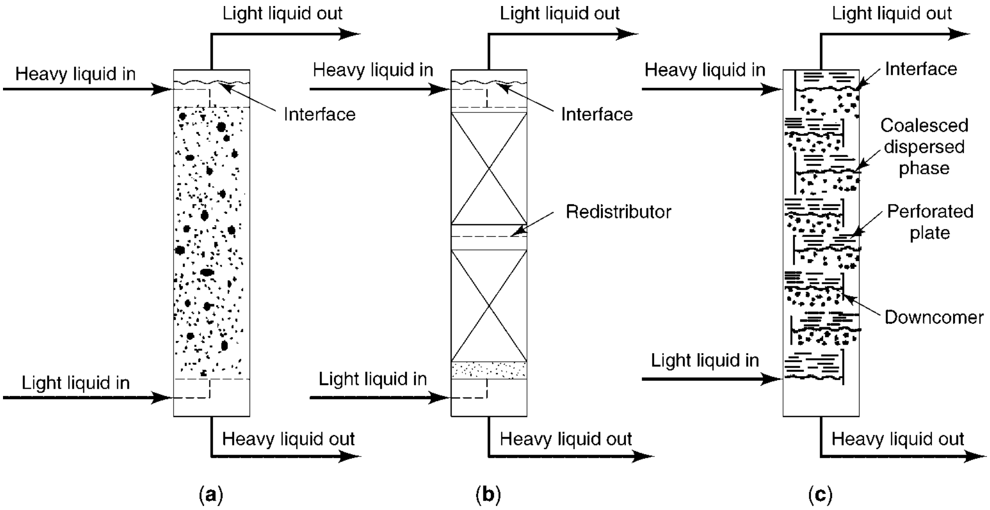
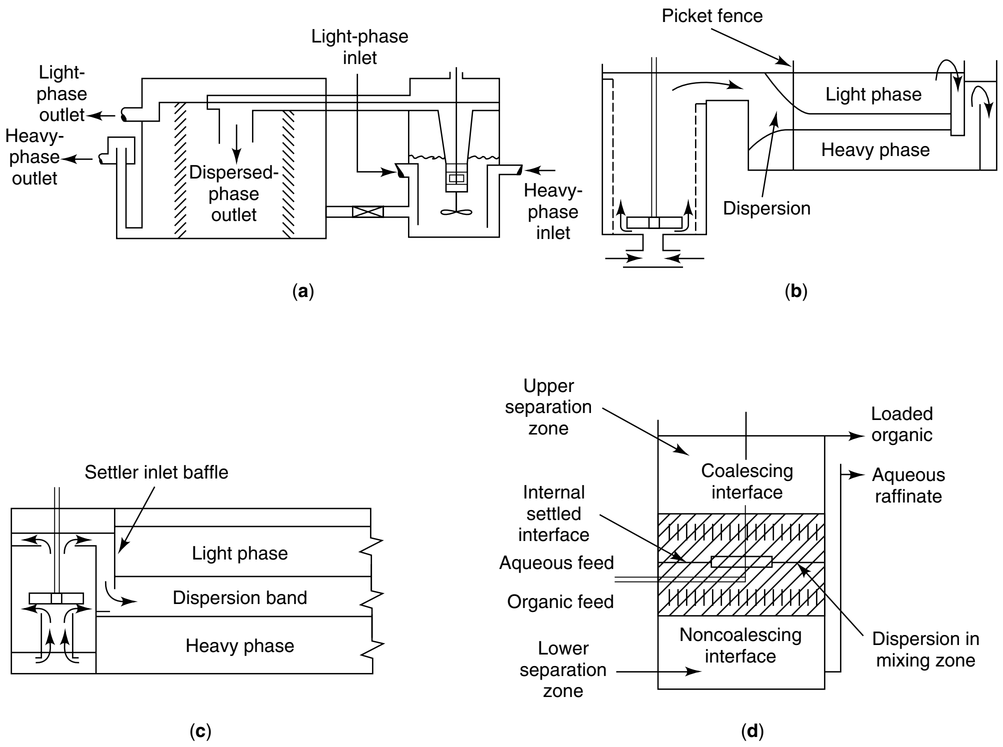


Fig. 12. Unagitated column extractors: (**a**) spray column; (**b**) packed column; and (**c**) perforated-plate column.



(**a**) (**b**)

(**c**) (**d**)

Fig. 13. Mixer–settlers: (**a**) IMI;(**b**) General Mills; (**c**) Davy-McKee; and (**d**) CMS.

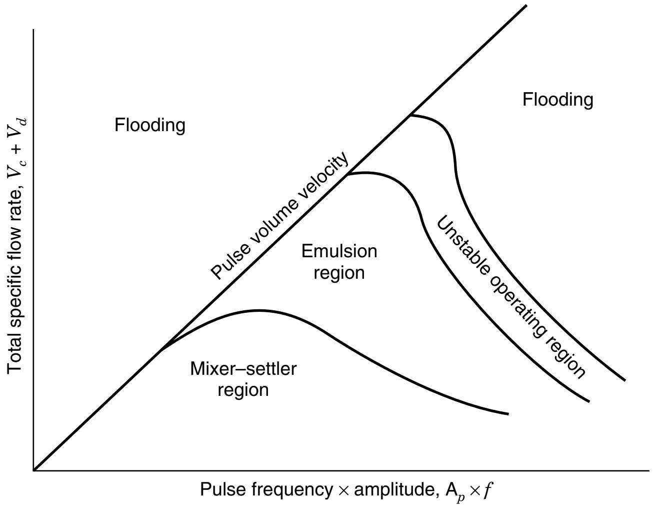


Fig. 14. Regions of operation of a pulsed, perforated-plate column (50).

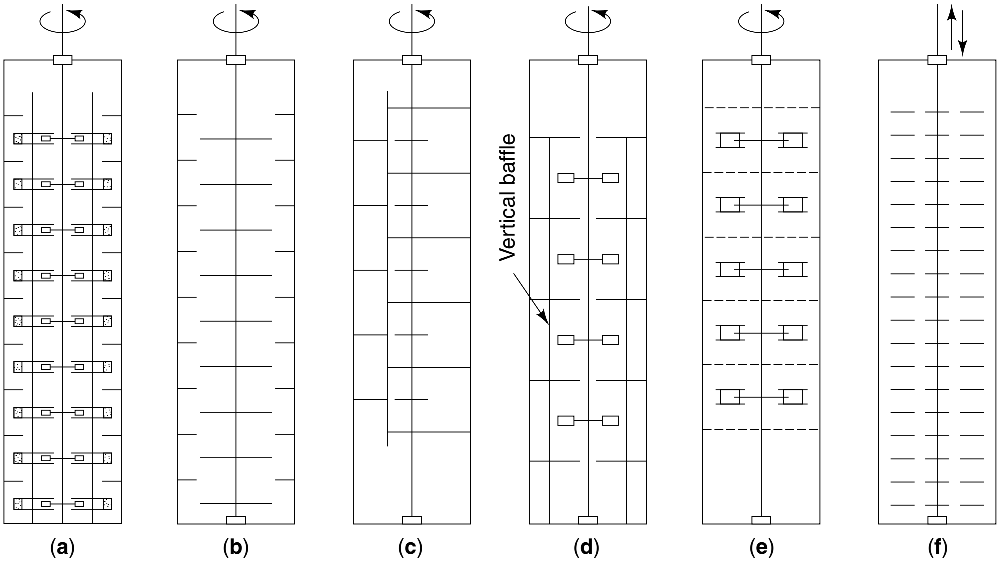


Fig. 15. Mechanically agitated columns: (**a**) Scheibel column; (**b**) rotating-disk contactor (RDC); (**c**) asymmetric rotating-disk (ARD) contactor; (**d**) Oldshue–Rushton multiple-mixer column; (**e**) Kuhni column; and (**f**) reciprocating-plate column.

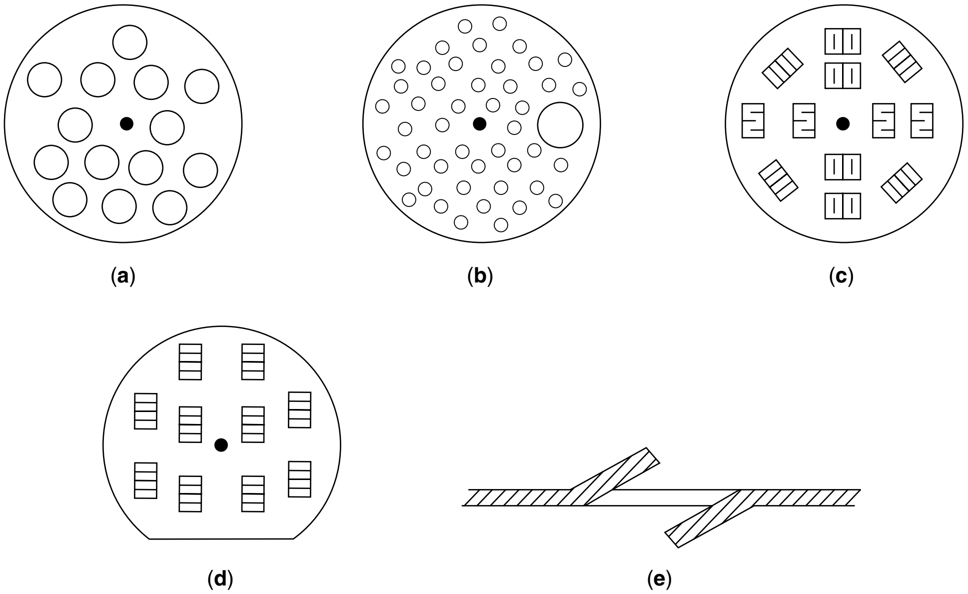


Fig. 16. Types of RPC plate in industrial use: (**a**) Karr RPC plate, $\phi = 0.5–0.6$, $d_o = 10–16$ mm; (**b**) Prochazka RPC plate, $\phi = 0.04–0.3$ (excluding (○) downcomer), $d_o = 2–5$ mm; (**c**) KRIMZ RPC plate, $\phi \approx 0.45$, which has vaned rectangular perforations; (**d**) GIAP II RPC plate, $\phi \approx 0.05–0.15$; and (**e**) sectional view of rectangular perforations for (**d**).

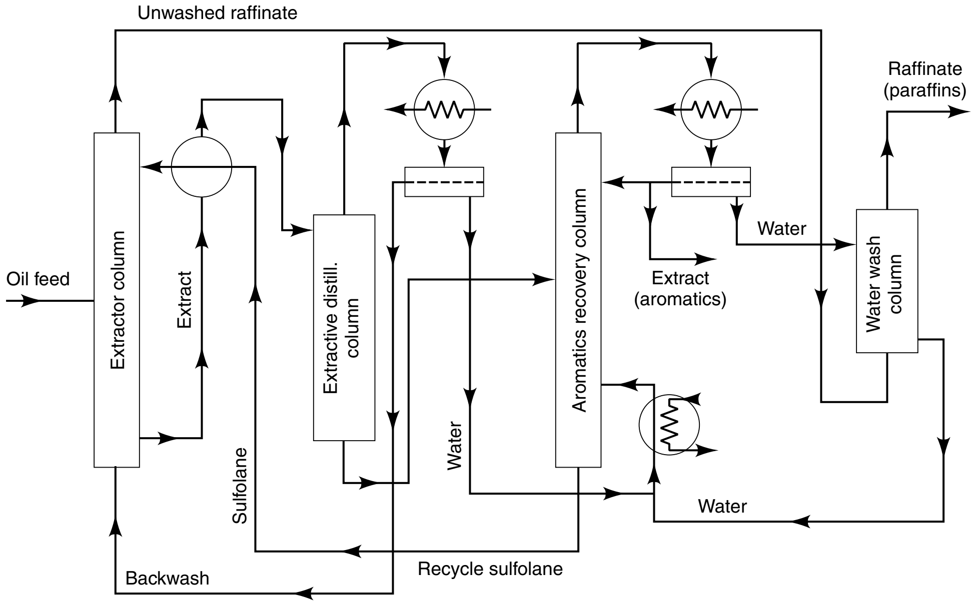


Fig. 17. Aromatic separation, sulfolane process (239–241).

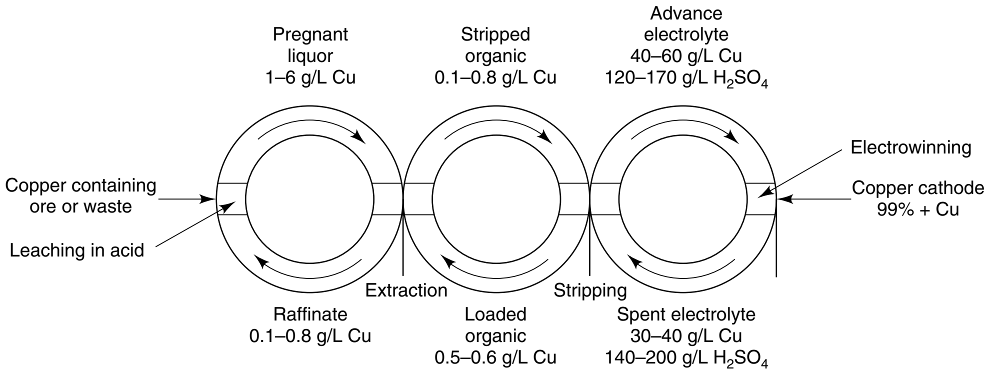


Fig. 18. Diagrammatic representation of copper extraction using solvent extraction (94).