R.E. Treybal, Mass Transfer Operations, 2nd ed.
McGraw-Hill, New York(1968).

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from Elroy

Equilateral-triangular coordinates

These are used extensively in the chemical literature to describe graphically the concentrations in ternary systems. It is the property of an equilateral triangle that the sum of the perpendicular distances from any point within the triangle to the three sides equals the altitude of the triangle. We may therefore let the altitude represent 100 percent composition and the distances to the three sides the percents or fractions of the three components. Refer to Fig. 10.21. Each apex of the triangle represents one of the pure components, as marked. The perpendicular distance from any point such as K to the base AB represents the percentage of C in the mixture at K, the distance to the base AC the percentage of B, and that to the base CB the percentage of A. Thus $x_K = 0.4$. Any point on a side of the triangle represents a binary mixture. Point D, for example, is a binary containing 80% A, 20% B. All points on the line DC represent mixtures containing the same ratio of A to B and may be considered as mixtures originally at D to which C has been added. If R lb of a mixture at point R is added to E lb of a mixture at E, the new mixture is shown on the straight line RE at point M, such that

$$\frac{R}{E} = \frac{\text{line } ME}{\text{line } RM} = \frac{x_E - x_M}{x_M - x_R} \qquad (10.11)$$

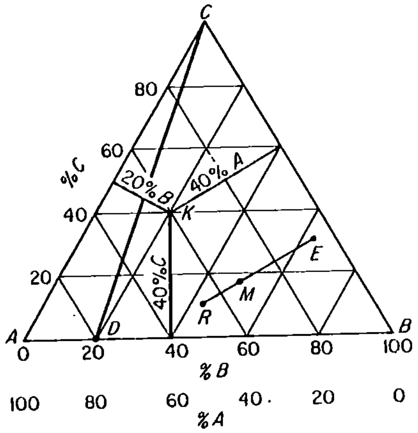


Fig. 10.21 *Equilateral-triangular coordinates.*

Alternatively the composition corresponding to point M can be computed by material balances, as will be shown later. Similarly, if a mixture at M has removed from it a mixture of composition E, the new mixture is on the straight line EM extended in the direction away from E, and located at R so that Eq. (10.11) applies.

Equation (10.11) is readily established. Refer to Fig. 10.22, which again shows R lb of mixture at R added to E lb of mixture at E. Let M represent the pounds of new mixture as well as the composition on the figure. Line RL = wt fraction C in $R = x_R$, line MO = wt fraction C in $M = x_M$, and line ET = wt fraction C in $E = x_E$. A total material balance,

$$R + E = M$$

A balance for component C,

$$R(\text{line } RL) + E(\text{line } ET) = M(\text{line } MO)$$

$$Rx_R + Ex_E = Mx_M$$

Eliminating M,

$$\frac{R}{E} = \frac{\text{line } ET - \text{line } MO}{\text{line } MO - \text{line } RL} = \frac{x_E - x_M}{x_M - x_R}$$

But line ET − line MO = line EP, and line MO − line RL = line MK = line PS. Therefore

$$\frac{R}{E} = \frac{\text{line } EP}{\text{line } PS} = \frac{\text{line } ME}{\text{line } RM}$$

The following discussion is limited to those types of systems which most frequently occur in liquid-extraction operations. For a complete consideration of the very many types of systems which may be encountered, the student is referred to one of the more comprehensive texts on the phase rule.[21]

Systems of three liquids—one pair partially soluble

This is the most commonly encountered type of system in extraction, and typical examples are water (A)–chloroform (B)–acetone (C), and benzene (A)–water (B)–acetic acid (C). The triangular coordinates are used as *isotherms*, or diagrams at constant temperature. Refer to Fig. 10.23*a*. Liquid C dissolves completely in A and B, but A and B dissolve only to a limited extent in each other to give rise to the saturated liquid solutions at L (A-rich) and at K (B-rich). The more insoluble the liquids A

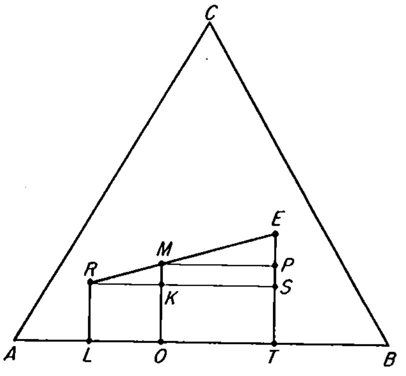


Fig. 10.22 *The mixture rule.*

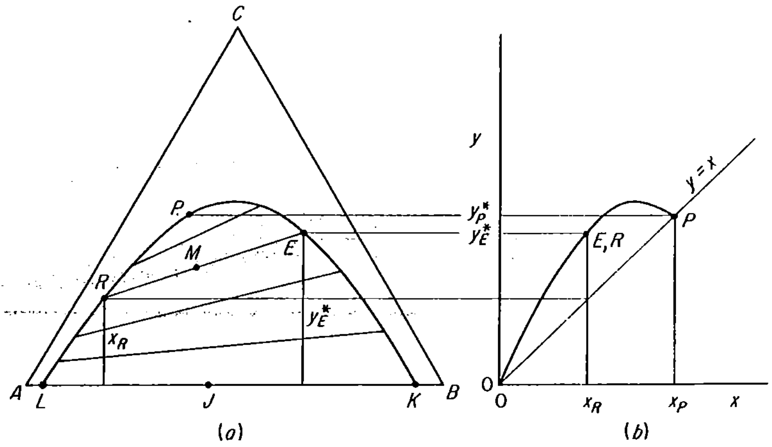


Fig. 10.23 *System of three liquids, A and B partially miscible.*

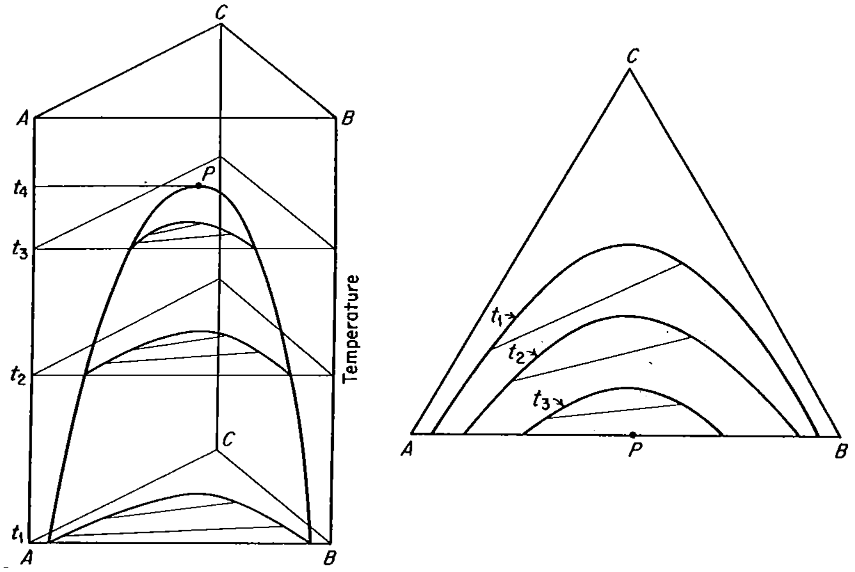
and B, the nearer the apexes of the triangle will points L and K be located. A binary mixture J, anywhere between L and K, will separate into two insoluble liquid phases of compositions at L and K, the relative amounts of the phases depending upon the position of J, according to the principle of Eq. (10.11).

Curve *LRPEK* is the binodal solubility curve, indicating the change in solubility of the A- and B-rich phases upon addition of C. Any mixture outside this curve will be a homogeneous solution of one liquid phase. Any ternary mixture underneath the curve, such as M, will form two insoluble, saturated liquid phases of equilibrium compositions indicated by R (A-rich) and E (B-rich). The line RE joining these equilibrium compositions is a tie line, which must necessarily pass through point M representing the mixture as a whole. There are an infinite number of tie lines in the two-phase region, and only a few are shown. They are rarely parallel and usually change their slope slowly in one direction as shown. In a relatively few systems the direction of the tie-line slope changes, and one tie line will be horizontal. Such systems are said to be "solutropic." Point P, the *plait point*, the last of the tie lines and the point where the A-rich and B-rich solubility curves merge, is ordinarily not at the maximum value of C on the solubility curve.

The percentage of C in solution E is clearly greater than that in R, and it is said that in this case the distribution of C favors the B-rich phase. This is conveniently shown on the distribution diagram (Fig. 10.23*b*), where the point (E,R) lies above the diagonal $y = x$. The ratio y^*/x, the *distribution coefficient*, is in this case greater than unity. The concentrations of C at the ends of the tie lines, when plotted against each other, give rise to the distribution curve shown. Should the tie lines on Fig. 10.23*a* slope in the opposite direction, with C favoring A at equilibrium, the distribution curve will lie below the diagonal. The distribution curve may be used for interpolating between tie lines when only a few have been experimentally determined. Other methods of interpolation are also available.[27]

Effect of temperature. To show the effect of temperature in detail requires a three-dimensional figure, as in Fig. 10.24*a*. In this diagram, temperature is plotted vertically, and the isothermal triangles are seen to be sections through the prism. For most systems of this type, the mutual solubility of *A* and *B* increases with increasing temperature, and above some temperature t_4, the critical solution temperature, they dissolve completely. The increased solubility at higher temperatures influences the ternary equilibria considerably, and this is best shown by projection of the isotherms onto the base triangle as in Fig. 10.24*b*. Not only does the area of heterogeneity decrease at higher temperatures, but the slopes of the tie lines may also change. Liquid-extraction operations, which depend upon the formation of insoluble liquid phases, must be carried on at temperatures below t_4. Other temperature effects, which are less common, are also known.[21,27]

Effect of pressure. Except at very high pressures, the influence of pressure on the liquid equilibrium is so small that it may generally be ignored. All the diagrams shown are therefore to be considered as having been plotted at sufficiently high pressure to maintain a completely condensed system, i.e., above the vapor pressures of the solutions. However, should the pressure be sufficiently reduced so that it becomes less than the vapor pressure of the solutions, a vapor phase will appear, and the liquid equilibrium will be interrupted. Such an effect on a binary solubility curve of the type *APB* of Fig. 10.24*a* is shown in Fig. 9.8.



(*a*) (*b*)

Fig. 10.24 *Effect of temperature on ternary equilibria.*

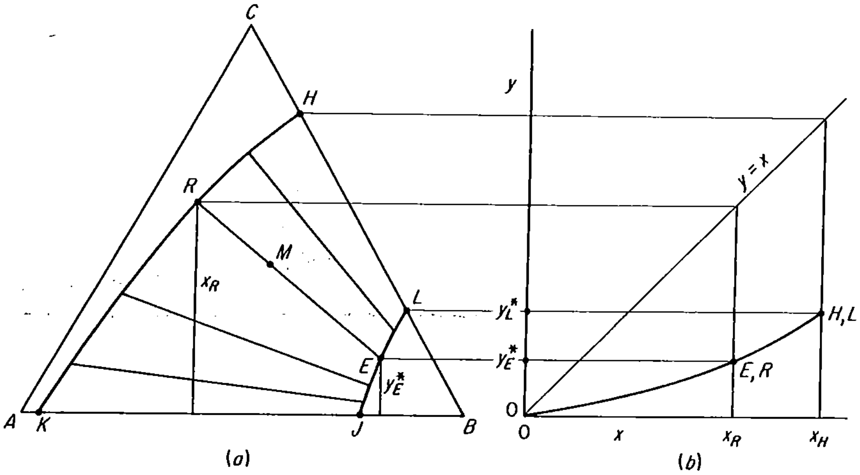


Fig. 10.25 *System of three liquids, A-B and B-C partially miscible.*

Systems of three liquids—two pairs partially soluble

This type is exemplified by the system chlorobenzene (*A*)–water (*B*)–methyl ethyl ketone (*C*), where *A* and *C* are completely soluble, while the pairs *A-B* and *B-C* show only limited solubility. Refer to Fig. 10.25*a*, a typical isotherm. At the prevailing temperature, points *K* and *J* represent the mutual solubilities of *A* and *B* and points *H* and *L* those of *B* and *C*. Curves *KRH* (*A*-rich) and *JEL* (*B*-rich) are the ternary solubility curves, and mixtures outside the band between these curves form homogeneous single-phase liquid solutions. Mixtures such as *M*, inside the heterogeneous area, form two liquid phases at equilibrium at *E* and *R*, joined on the diagram by a tie line. The corresponding distribution curve is shown in Fig. 10.25*b*.

Effect of temperature. Increased temperature usually increases the mutual solubilities and at the same time influences the slope of the tie lines. Figure 10.26 is typical of the effect that may be expected. Above the critical solution temperature of the binary *B-C* at t_3, the system is similar to the first type discussed. Other temperature effects are also possible.[21,27]

Systems of two partially soluble liquids and one solid

When the solid does not form compounds such as hydrates with the liquids, the system will frequently have the characteristics of the isotherm of Fig. 10.27, an example of which is the system naphthalene (*C*)–aniline (*A*)–isooctane (*B*). Solid *C* dissolves in liquid *A* to form a saturated solution at *K* and in liquid *B* to give the saturated solution at *L*. *A* and *B* are soluble only to the extent shown at *H* and *J*. Mixtures in the regions *AKDH* and *BLGJ* are homogeneous liquid solutions. The curves *KD* and

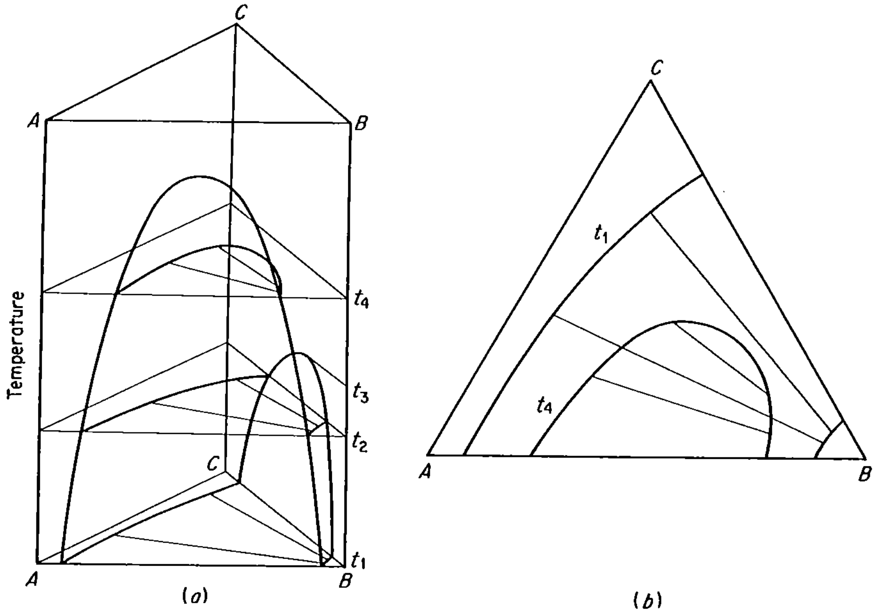


Fig. 10.26 *Effect of temperature on ternary liquid equilibria.*

GL show the effect of adding A and B upon the solubilities of the solid. In the region $HDGJ$ two liquid phases form: if C is added to the insoluble liquids H and J to give a mixture M, the equilibrium liquid phases will be R and E, joined by a tie line. All mixtures in the region CDG consist of three phases, solid C, and saturated liquid solutions at D and G. Liquid-extraction operations are usually confined to the region of the two liquid phases, which is that corresponding to the distribution curve shown.

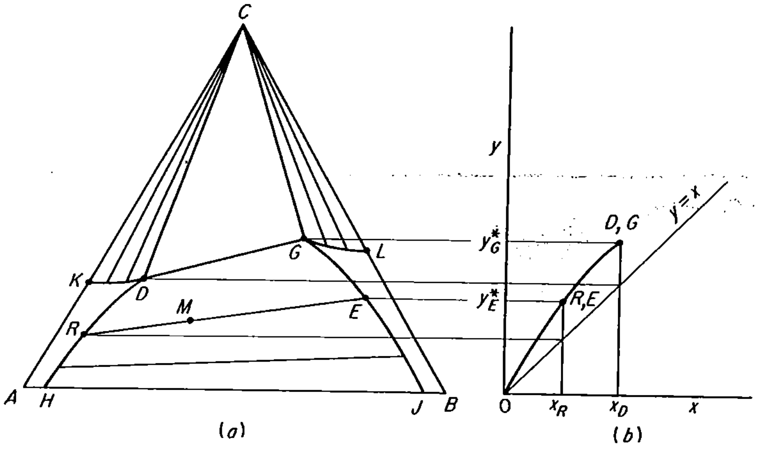


Fig. 10.27 *System of two partially soluble liquids A, B and one solid C.*

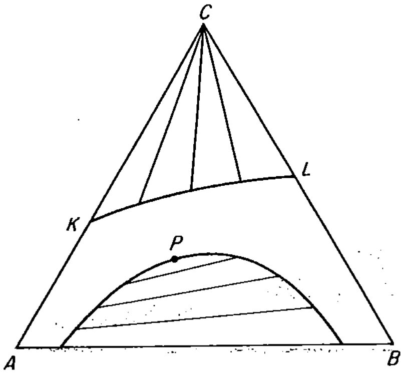


Fig. 10.28 *System of two partially soluble liquids A, B and one solid C.*

Increased temperature frequently changes these systems to the configuration shown in Fig. 10.28.

Other coordinates

Because the equilibrium relationship can rarely be expressed algebraically with any convenience, extraction computations must usually be made graphically on a phase diagram. The coordinate scales of equilateral triangles are necessarily always the same, and in order to be able to expand one concentration scale relative to the other, rectangular coordinates may be used. One of these is formed by plotting concentrations of B as abscissa against concentrations of C (x and y) as ordinate, as in Fig. 10.29*a*. Unequal scales may be used in order to expand the plot as desired. Equation (10.11) applies for mixtures on Fig. 10.29*a*, regardless of any inequality of the scales.

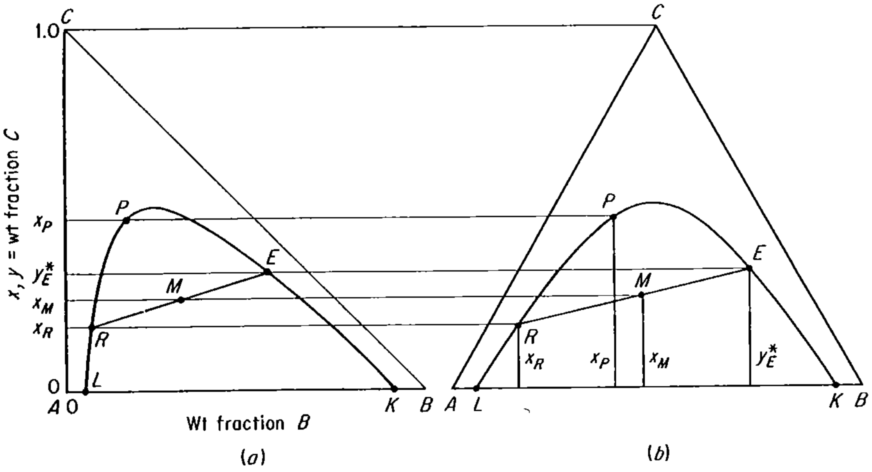


Fig. 10.29 *Rectangular coordinates.*

Another rectangular coordinate system involves plotting as abscissa the weight fraction C on a B-free basis, X and Y in the A- and B-rich phases, respectively, against N, the B-concentration on a B-free basis, as ordinate, as shown in the upper part of Fig. 10.30. This has been plotted for a system of two partly miscible pairs, such as that of Fig. 10.25.

The similarity of such diagrams to the enthalpy-concentration diagrams of Chap. 9 is clear. In extraction, the two phases are produced by addition of solvent, in distillation by addition of heat, and solvent becomes the analog of heat. This is emphasized by the ordinate of the upper part of Fig. 10.30. Tie lines such as QS can be projected to X, Y coordinates, as shown in the lower figure, to produce a solvent-free distribution graph similar to those of distillation. The mixture rule on these coordinates (see the upper part of Fig. 10.30) is

$$\frac{M'}{N'} = \frac{Y_N - Y_P}{Y_P - Y_M} = \frac{X_N - X_P}{X_P - X_M} = \frac{\text{line } NP}{\text{line } PM} \tag{10.12}$$

where M' and N' are the B-free weights of these mixtures.

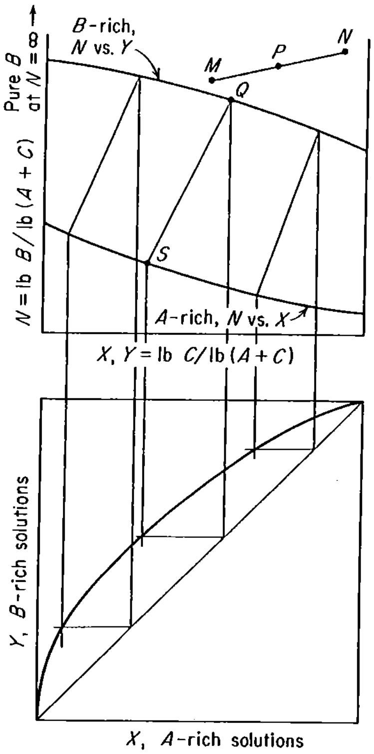


Fig. 10.30 *Rectangular coordinates, solvent-free basis, for a system of two partly miscible liquid pairs.*

Multicomponent systems

The simplest system of four components occurs when two solutes distribute between two solvents, e.g., the distribution of formic and acetic acids between the partly soluble solvents water and carbon tetrachloride. Complete display of such equilibria requires a three-dimensional graph[27] which is difficult to work with, but frequently we can simplify this to the distribution (xy) curves, one for each solute, such as that for a single solute in Fig. 10.23*b*. More than four components cannot be conveniently dealt with graphically.

Choice of solvent

There is usually a wide choice among liquids to be used as solvents for extraction operations. It is unlikely that any particular liquid will exhibit all the properties considered desirable for extraction, and some compromise is usually necessary. The following are the quantities to be given consideration in making a choice:

1. *Selectivity.* The effectiveness of solvent B for separating a solution of A and C into its components is measured by comparing the ratio of C to A in the B-rich phase to that in the A-rich phase at equilibrium. The ratio of the ratios, the separation factor, or selectivity, β, is analogous to the relative volatility of distillation. If E and R are the equilibrium phases,

$$\beta = \frac{(\text{wt fraction } C \text{ in } E)/(\text{wt fraction } A \text{ in } E)}{(\text{wt fraction } C \text{ in } R)/(\text{wt fraction } A \text{ in } R)} = \frac{y_E^*(\text{wt fraction } A \text{ in } R)}{x_R(\text{wt fraction } A \text{ in } E)} \qquad (10.13)$$

For all useful extraction operations the selectivity must exceed unity, the more so the better. If the selectivity is unity, no separation is possible.

Selectivity usually varies considerably with solute concentration, and in systems of the type shown in Fig. 10.23 it will be unity at the plait point. In some systems it passes from large values through unity to fractional values, and these are analogous to azeotropic systems of distillation.

2. *Distribution coefficient.* This is the ratio y^*/x at equilibrium. While it is not necessary that the distribution coefficient be larger than 1, large values are very desirable since less solvent will then be required for the extraction.

3. *Insolubility of solvent.* Refer to Fig. 10.31. For both systems shown, only those A-C mixtures between D and A can be separated by use of the solvents B or B', since mixtures richer in C will not form two liquid phases with the solvents. Clearly the solvent in Fig. 10.31*a*, which is the more insoluble of the two, will be the more useful. In systems of the type shown in Figs. 10.25*a* and 10.27*a*, if the solubility of C in B is small (point L near the B apex), the *capacity* of solvent B to extract C is small, and large amounts of solvent are then required.

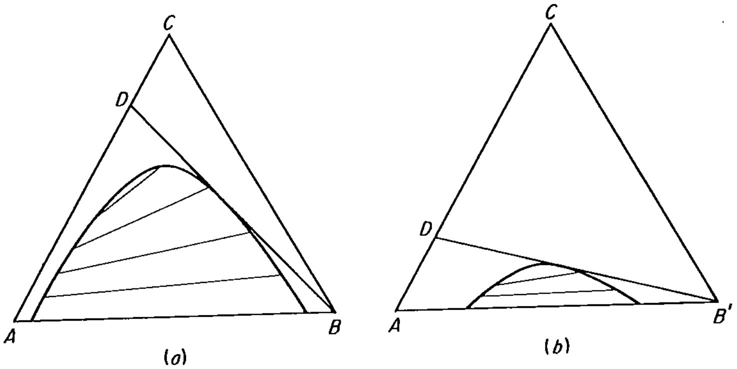


Fig. 10.31 *Influence of solvent solubility on extraction.*

4. *Recoverability.* It is always necessary to recover the solvent for reuse, and this must ordinarily be done by another of the mass-transfer operations, most frequently distillation. If distillation is to be used, the solvent should form no azeotrope with the extracted solute, and mixtures should show high relative volatility for low-cost recovery. That substance in the extract, either solvent or solute, which is present as the lesser quantity should be the more volatile in order to reduce heat costs. If the solvent must be volatilized, its latent heat of vaporization should be small.

5. *Density.* A difference in densities of the saturated liquid phases is necessary, both for stagewise and continuous-contact equipment operation. The larger this difference the better. In systems of the type shown in Fig. 10.23, the density difference for equilibrium phases will become less as C concentrations increase and will be zero at the plait point. It may reverse in sign before reaching the plait point, in which case continuous-contact equipment cannot be specified to operate at the concentrations at which the density difference passes through zero.

6. *Interfacial tension.* The larger the interfacial tension, the more readily will coalescence of emulsions occur, but the more difficult will the dispersion of one liquid in the other be. Coalescence is usually of greater importance, and interfacial tension should therefore be high. Interfacial tension between equilibrium phases in systems of the type shown in Fig. 10.23 falls to zero at the plait point.

7. *Chemical reactivity.* The solvent should be stable chemically and inert toward the other components of the system and toward the common materials of construction.

8. *Viscosity, vapor pressure, and freezing point.* These should be low for ease in handling and storage.

9. The solvent should be *nontoxic*, *nonflammable*, and of *low cost*.

STAGEWISE CONTACT

Extraction in equipment of the stage type may be carried on according to a variety of flow sheets, depending upon the nature of the system and the extent of separation desired. In the discussion which follows it is to be understood that each stage is a *theoretical* or *ideal* stage, such that the effluent extract and raffinate solutions are in equilibrium with each other. Each stage must include facilities for contacting the insoluble liquids and separating the product streams. A combination of a mixer and a settler may therefore constitute a stage, and in multistage operation these may be arranged in cascades as desired. In the case of countercurrent multistage operation, it is also possible to use towers of the multistage type, as described earlier.

Single-stage extraction

This may be a batch or a continuous operation. Refer to Fig. 10.32. The flow sheet shows the extraction stage. Feed F lb (if batch) or F lb/hr (if continuous) contains substances A and C at x_F weight fraction C. This is contacted with S_1 lb (or lb/hr) of a solvent, principally B, containing y_S weight fraction C, to give the equilibrium extract E_1 and raffinate R_1, each measured in pounds or pounds per hour. Solvent recovery then involves separate removal of solvent B from each product stream (not shown).

The operation may be followed in either of the phase diagrams as shown. If the solvent is pure B ($y_S = 0$), it will be plotted at the B apex, but sometimes it has been recovered from a previous extraction and therefore contains a little A and C as well, as shown by the location of S. Adding S to F produces in the extraction stage a mixture M_1 which, on settling, forms the equilibrium phases E_1 and R_1 joined by the tie

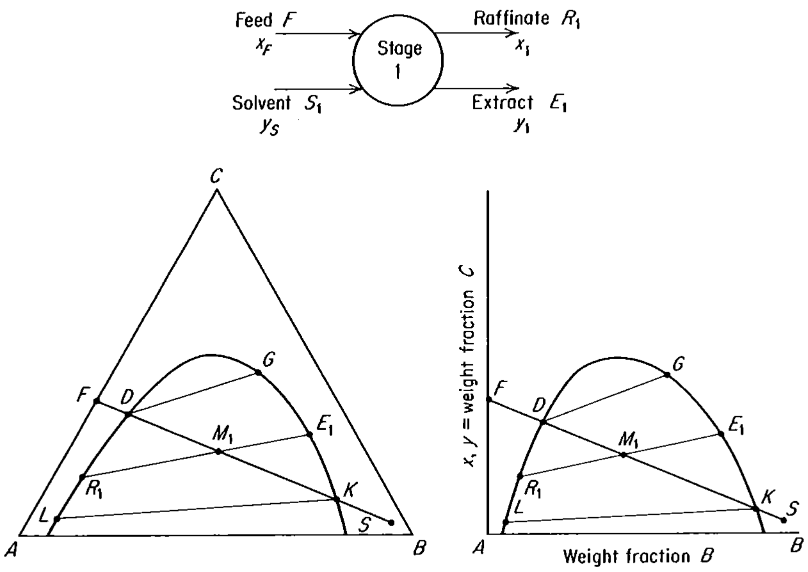


Fig. 10.32 *Single-stage extraction.*

line through M_1. A total material balance is

$$F + S_1 = M_1 = E_1 + R_1 \tag{10.14}$$

and point M_1 may be located on line FS by the mixture rule, Eq. (10.11), but it is usually more satisfactory to locate M_1 by computing its C concentration. Thus, a C balance provides

$$Fx_F + S_1y_S = M_1x_{M1} \tag{10.15}$$

from which x_{M1} may be computed. Alternatively, the amount of solvent to provide a given location for M_1 on the line FS may be computed:

$$\frac{S_1}{F} = \frac{x_F - x_{M1}}{x_{M1} - y_S} \tag{10.16}$$

The quantities of extract and raffinate may be computed by the mixture rule, Eq. (10.11), or by the material balance for C:

$$E_1y_1 + R_1x_1 = M_1x_{M1} \tag{10.17}$$

$$E_1 = \frac{M_1(x_{M1} - x_1)}{y_1 - x_1} \tag{10.18}$$

and R_1 can be determined through Eq. (10.14).

Since two insoluble phases must form for an extraction operation, point M_1 must lie within the heterogeneous liquid area, as shown. The minimum amount of solvent is thus found by locating M_1 at D, which would then provide an infinitesimal amount of extract at G, and the maximum amount of solvent is found by locating M_1 at K, which provides an infinitesimal amount of raffinate at L. Point L represents also the raffinate with the lowest possible C concentration, and if a lower value were required, the recovered solvent S would have to have a lower C concentration.

Computations for systems of two insoluble liquid pairs, or with a distributed solute which is a solid, are made in exactly the same manner, and Eqs. (10.14) to (10.18) all apply.

All the computations may also be made on a solvent-free basis, as in the upper part of Fig. 10.33, if the nature of this diagram makes it convenient. If solvent S is pure B, its N value is infinite, and the line FS is then vertical. Products E_1 and R_1 lie on a tie line through M_1 representing the entire mixture in the extractor. Material balances for use with this diagram must be made on a B-free basis. Thus,

$$F' + S' = M_1' = E_1' + R_1' \tag{10.19}$$

where the primes indicate B-free weight (the feed is normally B-free, and $F = F'$). A balance for C is

$$F'X_F + S'Y_S = M_1'X_{M1} = E_1'Y_1 + R_1'X_1 \tag{10.20}$$

and for B,

$$F'N_F + S'N_S = M_1'N_{M1} = E_1'N_{E1} + R_1'N_{R1} \tag{10.21}$$

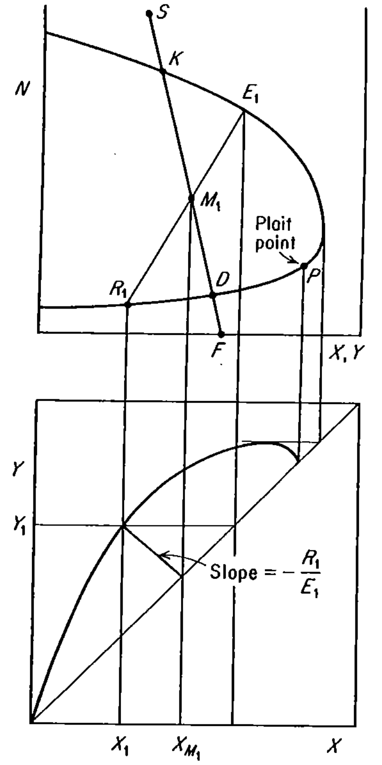


Fig. 10.33 *Single-stage extraction, solvent-free coordinates.*

(ordinarily, $N_F = 0$ since the feed contains no B). The coordinates of M_1' may be computed, point M_1 located on line FS, the tie line located, and the B-free weights, E_1' and R_1', computed:

$$E_1' = \frac{M_1'(X_{M1} - X_1)}{Y_1 - X_1} \tag{10.22}$$

and R_1' is obtained through Eq. (10.19). The total weights of the saturated extract and raffinate are then

$$E_1 = E_1'(1 + N_{E1}) \qquad R_1 = R_1'(1 + N_{R1}) \tag{10.23}$$

If the solvent is pure B, whence $N_S = \infty$, these equations still apply, with the simplification that $S' = 0$, $Y_S = 0$, $S'N_S = B$, and $F' = M_1'$. Minimum and maximum amounts of solvent correspond to putting M_1 at D and K on the figure, as before.

Equations (10.19) and (10.20) lead to

$$\frac{R_1'}{E_1'} = \frac{Y_1 - X_{M1}}{X_{M1} - X_1} \tag{10.24}$$

When the equilibrium extract and raffinate are located on the lower diagram of Fig. 10.33, Eq. (10.24) is seen to be that of the operating line shown, of slope $-R_1'/E_1'$.

The single stage is seen to be analogous to the flash vaporization of distillation, with solvent replacing heat. If pure B is used as solvent, the operating line on the lower figure passes through the 45° line at X_F, which completes the analogy (see Fig. 9.14).

Multistage crosscurrent extraction

This is an extension of single-stage extraction, wherein the raffinate is successively contacted with fresh solvent, and may be done continuously or in batch. Refer to Fig. 10.34, which shows the flow sheet for a three-stage extraction. A single final raffinate results, and the extracts may be combined to provide the composited extract, as shown. As many stages may be used as desired.

Computations are shown on triangular and on solvent-free coordinates. All the material balances for a single stage of course now apply to the first stage. Subsequent stages are dealt with in the same manner, except of course that the "feed" to any stage is the raffinate from the preceding stage. Thus, for any stage n,

Total balance: $$R_{n-1} + S_n = M_n = E_n + R_n \tag{10.25}$$

C balance: $$R_{n-1}x_{n-1} + S_n y_S = M_n x_{Mn} = E_n y_n + R_n x_n \tag{10.26}$$

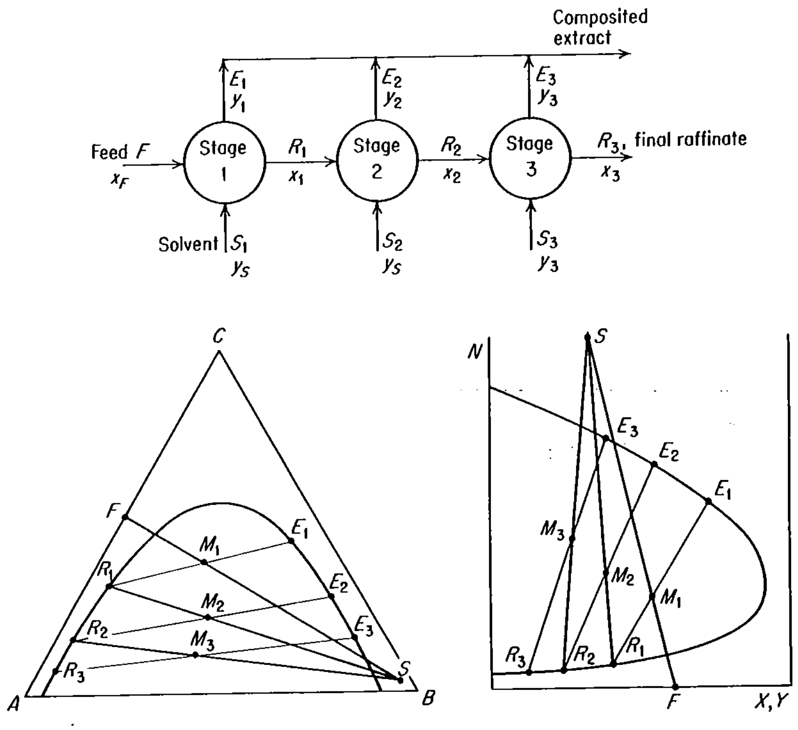


Fig. 10.34 *Crosscurrent extraction.*

For the solvent-free coordinates,

$$A + C \text{ balance:} \qquad R'_{n-1} + S'_n = M'_n = E'_n + R'_n \qquad (10.27)$$

$$C \text{ balance:} \qquad R'_{n-1}X_{n-1} + S'_n Y_S = M'_n X_{Mn} = E'_n Y_n + R'_n X_n \qquad (10.28)$$

$$B \text{ balance:} \qquad R'_{n-1}N_{R,n-1} + S'_n N_S = M'_n N_{Mn} = E'_n N_{En} + R'_n N_{Rn} \qquad (10.29)$$

from which the quantities can be calculated for either type of graph.

Unequal amounts of solvent may be used in the various stages, and even different temperatures, in which case each stage must be computed with the help of a phase diagram at the appropriate temperature. For a given final raffinate concentration, less total solvent will be used the greater the number of stages.

Illustration 10.3. One hundred pounds of a solution of acetic acid (C) and water (A) containing 30% acid is to be extracted three times with isopropyl ether (B) at 20°C, using 40 lb of solvent in each stage. Determine the quantities and compositions of the various streams. How much solvent would be required if the same final raffinate concentration were to be obtained with one stage?

Solution. The equilibrium data at 20°C are listed below [*Trans. AIChE*, **36**, 628 (1940), with permission]. The horizontal rows give the concentrations in equilibrium solutions. The system is of the type shown in Fig. 10.29, except that the tie lines slope downward toward the B apex. The rectangular coordinates of Fig. 10.29a will be used, but only for acid concentrations up to $x = 0.30$. These are plotted in Fig. 10.35.

Water layer			Isopropyl ether layer		
Wt % acetic acid $100x$	Water	Isopropyl ether	Acetic acid $100y^*$	Water	Isopropyl ether
0.69	98.1	1.2	0.18	0.5	99.3
1.41	97.1	1.5	0.37	0.7	98.9
2.89	95.5	1.6	0.79	0.8	98.4
6.42	91.7	1.9	1.93	1.0	97.1
13.30	84.4	2.3	4.82	1.9	93.3
25.50	71.1	3.4	11.40	3.9	84.7
36.70	58.9	4.4	21.60	6.9	71.5
44.30	45.1	10.6	31.10	10.8	58.1
46.40	37.1	16.5	36.20	15.1	48.7

Stage 1. $F = 100$ lb, $x_F = 0.30$, $y_S = 0$, $S_1 = B_1 = 40$ lb.

Eq. (10.14): $\qquad M_1 = 100 + 40 = 140$ lb

Eq. (10.15): $\qquad 100(0.30) + 40(0) = 140x_{M1} \qquad x_{M1} = 0.214$

Point M_1 is located on line FB. With the help of a distribution curve, the tie line passing through M_1 is located as shown, and $x_1 = 0.258$, $y_1 = 0.117$ wt fraction acetic acid.

Eq. (10.18): $$E_1 = \frac{140(0.214 - 0.258)}{0.117 - 0.258} = 43.6 \text{ lb}$$

Eq. (10.14): $\qquad R_1 = 140 - 43.6 = 96.4$ lb

Stage 2. $S_2 = B_2 = 40$ lb.

Eq. (10.25): $$M_2 = R_1 + B_2 = 96.4 + 40 = 136.4 \text{ lb}$$

Eq. (10.26): $$96.4(0.258) + 40(0) = 136.4x_{M2} \qquad x_{M2} = 0.1822$$

Point M_2 is located on line R_1B and the tie line R_2E_2 through M_2. $x_2 = 0.227$, $y_2 = 0.095$. Eq. (10.18) becomes

$$E_2 = \frac{M_2(x_{M2} - x_2)}{y_2 - x_2} = \frac{136.4(0.1822 - 0.227)}{0.095 - 0.227} = 46.3 \text{ lb}$$

Eq. (10.25): $$R_2 = M_2 - E_2 = 136.4 - 46.3 = 90.1 \text{ lb}$$

Stage 3. In a similar manner, $B_3 = 40$, $M_3 = 130.1$, $x_{M3} = 0.1572$, $x_3 = 0.20$, $y_3 = 0.078$, $E_3 = 45.7$, and $R_3 = 84.4$. The acid content of the final raffinate is $0.20(84.4) = 16.88$ lb.

The composited extract is $E_1 + E_2 + E_3 = 43.6 + 46.3 + 45.7 = 135.6$ lb, and its acid content $= E_1y_1 + E_2y_2 + E_3y_3 = 13.12$ lb.

If an extraction to give the same final raffinate concentration, $x = 0.20$, were to be done in one stage, the point M would be at the intersection of tie line R_3E_3 and line BF of Fig. 10.35, or at $x_M = 0.12$. The solvent required would then be, by Eq. (10.16), $S_1 = 100(0.30 - 0.12)/(0.12 - 0) = 150$ lb, instead of the total of 120 required in the three-stage extraction.

Insoluble liquids. When the extraction solvent and feed solution are insoluble and remain so at all concentrations of the distributed solute which are encountered in the operation, the computations may be simplified. For this purpose, the equilibrium

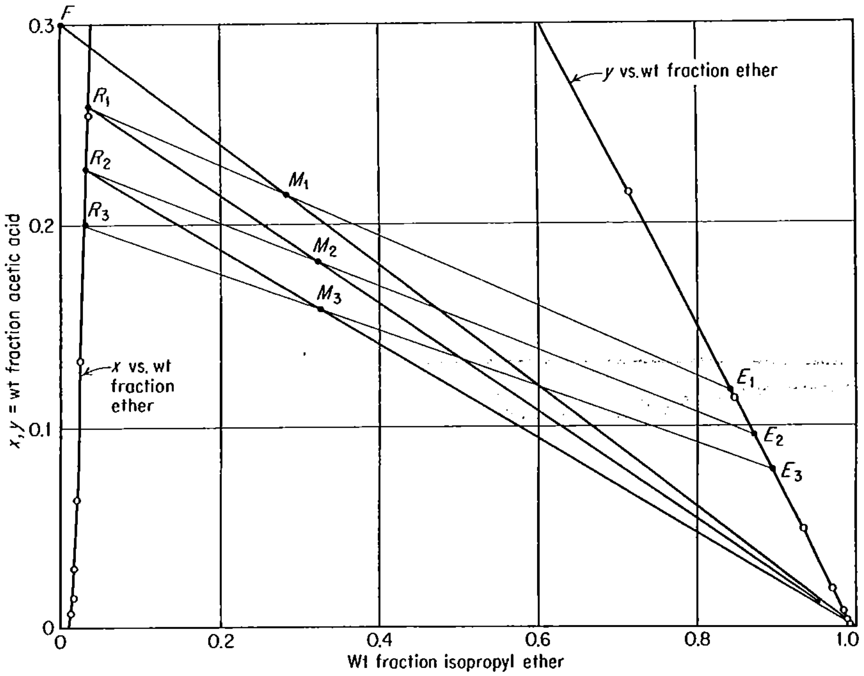


Fig. 10.35 *Solution to Illustration* 10.3.

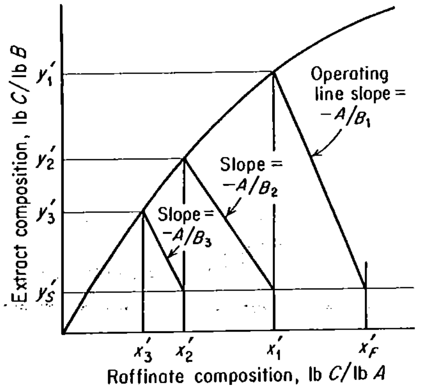


Fig. 10.36 *Crosscurrent extraction with an insoluble solvent.*

concentrations are plotted as in Fig. 10.36, $x' = x/(1 - x)$ against $y' = y/(1 - y)$. Since the liquids A and B are insoluble, there are A lb of this substance in all raffinates. Similarly, the extract from each stage contains all the solvent B fed to that stage. A solute-C balance about any stage n is then

$$Ax'_{n-1} + B_n y'_S = B_n y'_n + Ax'_n \tag{10.30}$$

$$-\frac{A}{B_n} = \frac{y'_S - y'_n}{x'_{n-1} - x'_n} \tag{10.31}$$

This is the operating-line equation for stage n, of slope $-A/B_n$, passing through points (x'_{n-1}, y'_S) and (x'_n, y'_n). The construction for a three-stage extraction is shown in Fig. 10.36, where for each stage a line is drawn of slope appropriate to that stage. Each operating line intersects the equilibrium curve at the raffinate and extract compositions. No raffinate of concentration smaller than that in equilibrium with the entering solvent is possible.

Solute concentrations for these cases are sometimes also conveniently expressed as mass/volume. Equations (10.30) and (10.31) then apply with x' and y' expressed as mass solute/volume, and A and B as volume/time (or volumes for batch operations).

Illustration 10.4. Nicotine (C) in a water (A) solution containing 1% nicotine is to be extracted with kerosene (B) at 20°C. Water and kerosene are essentially insoluble. (a) Determine the percentage extraction of nicotine if 100 lb of feed solution is extracted once with 150-lb solvent. (b) Repeat for three ideal extractions using 50-lb solvent each.

Solution. Equilibrium data are provided by Claffey et al., *Ind. Eng. Chem.*, **42**, 166 (1950), and expressed as lb nicotine/lb liquid, they are as follows:

$x' = \dfrac{\text{lb nicotine}}{\text{lb water}}$	0	0.001011	0.00246	0.00502	0.00751	0.00998	0.0204
$y'^* = \dfrac{\text{lb nicotine}}{\text{lb kerosene}}$	0	0.000807	0.001961	0.00456	0.00686	0.00913	0.01870

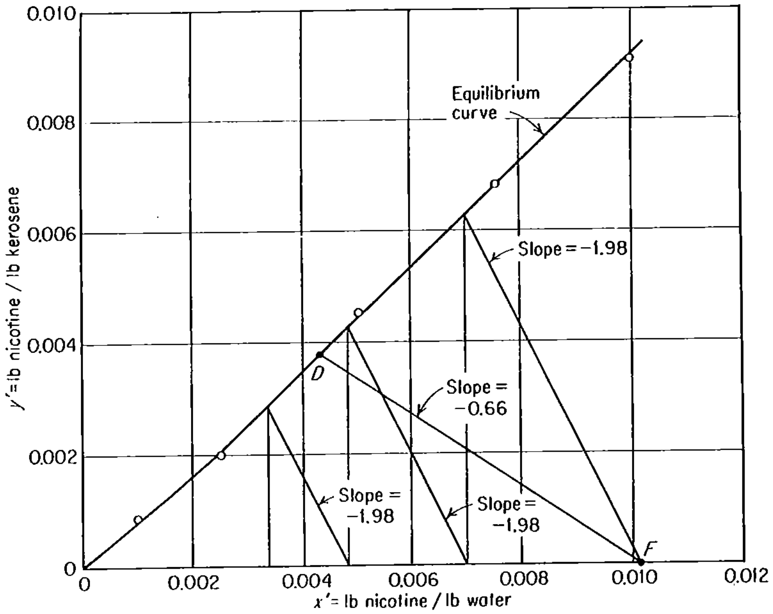


Fig. 10.37 *Solution to Illustration* 10.4.

a. $x_F = 0.01$ wt fraction nicotine, $x'_F = 0.01/(1 - 0.01) = 0.0101$ lb nicotine/lb water. $F = 100$ lb. $A = 100(1 - 0.01) = 99$ lb water. $A/B = 99/150 = 0.66$.

Refer to Fig. 10.37, which shows the equilibrium data and the point F representing the composition of the feed. From F, line FD is drawn of slope -0.66, intersecting the equilibrium curve at D, where $x'_1 = 0.00425$ and $y'_1 = 0.00380$ lb nicotine/lb liquid. The nicotine removed from the water is therefore $99(0.0101 - 0.00425) = 0.580$ lb, or 58% of that in the feed.

b. For each stage, $A/B = 99/50 = 1.98$. The construction is started at F, with operating lines of slope -1.98. The final raffinate composition is $x'_3 = 0.0034$, and the nicotine extracted is $99(0.0101 - 0.0034) = 0.663$ lb, or 66.3% of that in the feed.

Continuous countercurrent multistage extraction

The flow sheet for this type of operation is shown in Fig. 10.38. Extract and raffinate streams flow from stage to stage in countercurrent and provide two final products, raffinate R_{N_p} and extract E_1. For a given degree of separation, this type of operation requires fewer stages for a given amount of solvent, or less solvent for a fixed number of stages, than the crosscurrent methods described above.

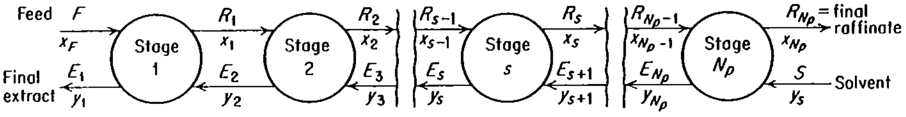


Fig. 10.38 *Countercurrent multistage extraction.*

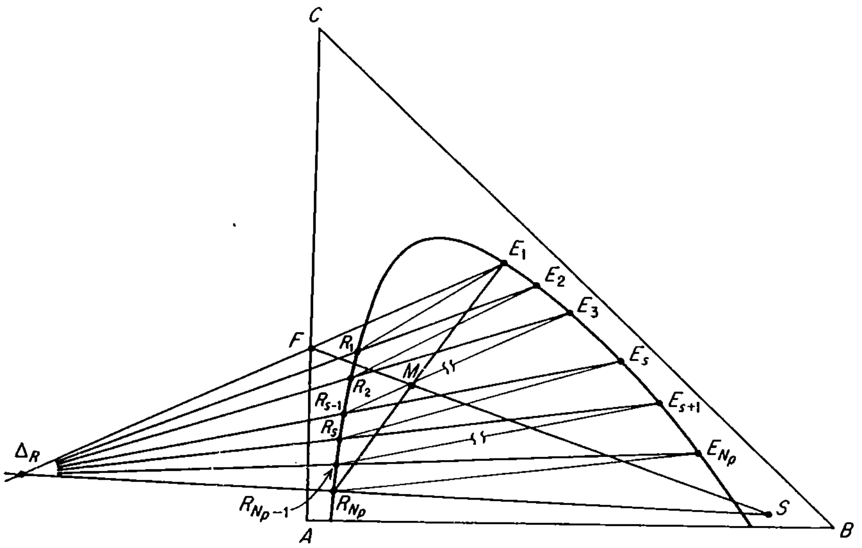


Fig. 10.39 *Countercurrent multistage extraction.*

The graphical treatment is developed in Fig. 10.39 on rectangular coordinates. Construction on the equilateral triangle is identical with this. A total material balance about the entire plant is

$$F + S = E_1 + R_1 = M \tag{10.32}$$

Point M may be located on line FS through a balance for substance C,

$$Fx_F + Sy_S = E_1y_1 + R_{N_p}x_{N_p} = Mx_M \tag{10.33}$$

$$x_M = \frac{Fx_F + Sy_S}{F + S} \tag{10.34}$$

Equation (10.32) indicates that M must lie on line $R_{N_p}E_1$, as shown. Rearrangement of Eq. (10.32) provides

$$R_{N_p} - S = F - E_1 = \Delta_R \tag{10.35}$$

where Δ_R, a difference point, is the net flow outward at the last stage N_p. According to Eq. (10.35), the extended lines E_1F and SR_{N_p} must intersect at Δ_R, as shown in Fig. 10.39. This intersection may in some cases be located at the right of the triangle. A material balance for stages s through N_p is

$$R_{s-1} + S = R_{N_p} + E_s \tag{10.36}$$

or

$$R_{N_p} - S = R_{s-1} - E_s = \Delta_R \tag{10.37}$$

so that the difference in flow rates at a location between any two adjacent stages is constant, Δ_R. Line E_sR_{s-1} extended must therefore pass through Δ_R, as on the figure.

The graphical construction is then as follows. After location of points F, S, M, E_1, R_{N_p}, and Δ_R, a tie line from E_1 provides R_1 since extract and raffinate from the first ideal stage are in equilibrium. A line from Δ_R through R_1 when extended provides E_2, a tie line from E_2 provides R_2, etc. The lowest possible value of x_{N_p} is that given by the A-rich end of a tie line which, when extended, passes through S.

As the amount of solvent is increased, point M representing the overall plant balance moves toward S on Fig. 10.39 and point Δ_R moves farther to the left. At an amount of solvent such that lines E_1F and SR_{N_p} are parallel, point Δ_R will be at an infinite distance. Greater amounts of solvent will cause these lines to intersect on the right-hand side of the diagram rather than as shown, with point Δ_R nearer B for increasing solvent quantities. The interpretation of the difference point is, however, still the same: a line from Δ_R intersects the two branches of the solubility curve at points representing extract and raffinate from adjacent stages.

If a line from point Δ_R should coincide with a tie line, an infinite number of stages will be required to reach this condition. The maximum amount of solvent for which this occurs corresponds to the minimum solvent/feed ratio which may be used for the specified products. The procedure for determining the minimum amount of solvent is indicated in Fig. 10.40. All tie lines below that marked JK are extended to line SR_{N_p}, to give intersections with line SR_{N_p} as shown. The intersection farthest from S (if on the left-hand side of the diagram) or nearest S (if on the right) represents the difference point for minimum solvent, as at point Δ_{Rm} (Fig. 10.40). The actual position of Δ_R must be farther from S (if on the left) or nearer to S (if on the right) for a finite number of stages. The larger the amount of solvent, the fewer the number of stages. Usually, but not in the instance shown, the tie lines which when extended pass through F, i.e., tie line JK, will locate Δ_{Rm} for minimum solvent.

When the number of stages is very large, the construction indicated in Fig. 10.41 may be more convenient. A few lines are drawn at random from point Δ_R to intersect the two branches of the solubility curve as shown, where the intersections do not now necessarily indicate streams between two actual adjacent stages. The C

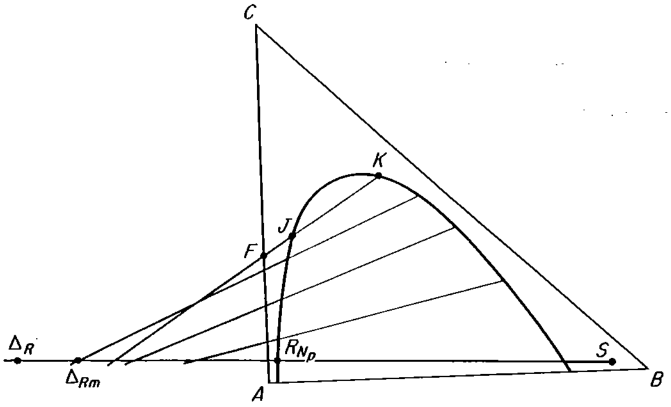


Fig. 10.40 *Minimum solvent for countercurrent extraction.*

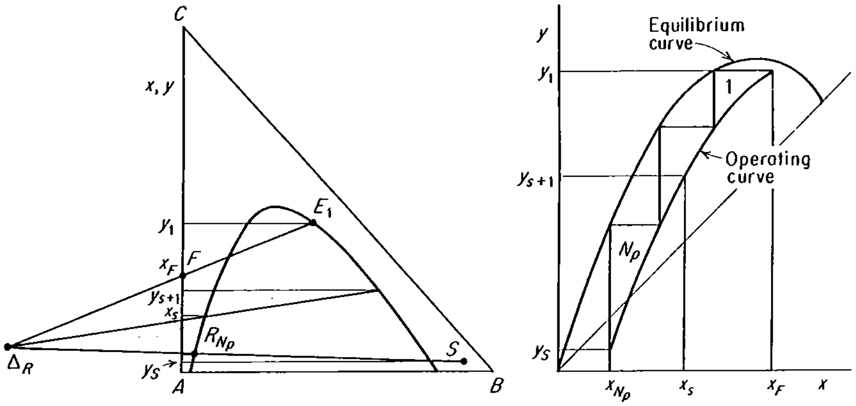


Fig. 10.41 *Transfer of coordinates to distribution diagram.*

concentrations x_s and y_{s+1} corresponding to these are plotted on x, y coordinates as shown to provide an operating curve. Tie-line data provide the equilibrium curve y^* vs. x, and the theoretical stages are stepped off in the manner used for gas absorption and distillation.

Figure 10.42 shows the construction for solvent-free coordinates. The B-free material balance for the entire plant is

$$F' + S' = E_1' + R_{N_p}' = M' \tag{10.38}$$

where ordinarily $F = F'$ since the feed is usually B-free. M' is therefore on the line FS at X_M calculated by a C balance

$$F'X_F + S'Y_S = M'X_M \tag{10.39}$$

If pure B is used as solvent, $S' = 0$, $S'Y_S = 0$, $F' = M'$, $X_M = X_F$, and point M is vertically above F.

Line $E_1R_{N_p}$ must pass through M. Then

$$R_{N_p}' - S' = F' - E_1' = \Delta_R' \tag{10.40}$$

The balance for stages s through N_p is

$$R_{N_p}' - S' = R_{s-1}' - E_s' = \Delta_R' \tag{10.41}$$

where Δ_R' is the difference in solvent-free flow, out — in, at stage N_p, and the constant difference in solvent-free flows of the streams between any two adjacent stages. Line E_sR_{s-1} extended, where s is any stage, must therefore pass through Δ_R on the graph.

The graphical construction is then as follows. After locating points F, S, M, E_1, R_{N_p}, and Δ_R, a tie line from E_1 provides R_1, line $\Delta_R R_1$ extended locates E_2, etc. If the solvent is pure B ($N_S = \infty$), line $R_{N_p}\Delta_R$ is vertical.