

(c) If operation is at 1.12 times the minimum reflux ratio in both cases, compare the overhead-condenser cooling requirement (kilojoules per mole of feed) for 101.3 kPa column pressure with that for 506.5 kPa column pressure.

(d) Using your answer to part (c), discuss the choice between the two column pressures on the basis of minimizing energy consumption.

6-Q₂ Repeat Prob. 6-G using the MLHV method of calculation.

6-R₂ A countercurrent extraction cascade will use water as a solvent to recover acetone selectively from streams containing mixtures of acetone and methyl isobutyl ketone (MIBK). Per unit time, the two ketone feeds to the extraction will contain 11 kg acetone and 100 kg MIBK, and 20 kg acetone and 80 kg MIBK, respectively. The raffinate will be 174 kg MIBK, 4 kg water, and 1 kg acetone. The inlet water flow will be 250 kg. Extract reflux will be employed, created by a distillation column that separates 60 kg acetone and 12 kg MIBK from 246 kg water. The ketone stream from the distillation will be split exactly in half, with one half serving as extract reflux and the other half serving as product. Find the compositions for the difference points for each of the three sections of this extraction cascade and indicate where they would lie with respect to a triangular diagram representing the phase-miscibility data.

ie. if x_A/y_A is given \Rightarrow Entire composition profile of all the components is known.

PATTERNS OF CHANGE

Lecture 2

Stathis

In Chaps. 5 and 6 we discussed the application of the McCabe-Thiele graphical approach to the solution of a number of problems associated with binary separations. In these cases the graphical technique provided an efficacious solution which was at least as simple as any algebraic computational approach and in most cases simpler. Graphical methods have the unique feature of providing a *visual* representation of the separation process. (In terms of ready applicability, however, they are largely limited to situations where the entire composition of either phase is fixed through specification of the concentration of one component alone.)

Before proceeding to a consideration of various more general plans of computational attack which can be invoked for multicomponent systems, we shall pause and consider multistage separation processes from a more qualitative vantage point, analyzing the general patterns of change in flow rate, composition, and temperature which occur from stage to stage in a separation cascade. To do this, we first reconsider various types of binary multistage processes.

An understanding of the factors at play causing changes throughout a multistage separation cascade helps one select appropriate computational approaches and improve design and operating conditions. On the other hand, the patterns of change for multicomponent systems will be most fully understood after one has gained some experience with multicomponent separations. Hence the reader may find it helpful to review this chapter again after studying Chaps. 8 to 10.

BINARY MULTISTAGE SEPARATIONS

From a standpoint of interpretation the simplest multistage process is one which entails straight equilibrium and operating lines. Figure 7-1 shows an operating diagram for a dilute absorber, such as might be utilized for the removal of a small

$y_A^* = C \cdot x_A$ Henry law

$y_A = \frac{L}{G} x_A + K$

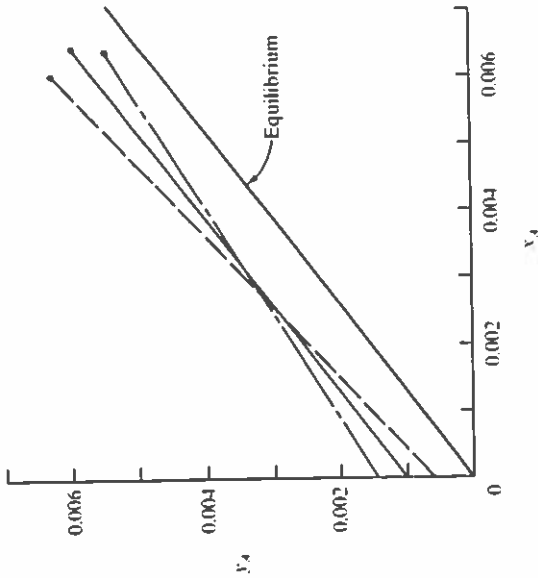


Figure 7-1 Operating diagram for dilute absorber.

amount of a single soluble constituent from a gas stream. The equilibrium line is straight if Henry's law is obeyed by the solute. The operating line is straight if total molar flows are essentially constant, and it lies above the equilibrium line since we have an absorption process where the solute is transferring from gas to liquid. Three possible operating lines are shown corresponding to the ratio of the slope of the operating line to that of the equilibrium line being greater than (dashed), equal to (solid), and less than (dot-dash) 1. Figure 7-2 shows the patterns of change resulting from the three operating lines. The numbers on the abscissa correspond to the various interstage locations (passing streams) shown in the accompanying diagram. The total flow rates are nearly constant because of the dilution. The temperatures are constant if the entering temperatures of the two phases are equal and if the system is dilute enough for the heat of absorption to be small compared with the sensible heats of the gas and liquid phases.

If the operating and equilibrium lines are parallel (solid line), the concentration of the solute in the liquid and gas changes at a uniform rate from stage to stage. If the operating line has a greater slope (dashed curve) than the equilibrium line, the solute concentrations in liquid and vapor change more rapidly at higher concentrations. On the other hand, if the operating line has a lesser slope (dot-dash curve) than the equilibrium line, the solute concentrations in both phases change more rapidly at lower concentrations. Put another way, when the operating line and equilibrium line are closer together, the phase compositions change slowly from stage to stage.

Many factors may arise to complicate the constant-flow constant-temperature straight-line situation of Figs. 7-1 and 7-2. We shall discuss several of them and assess their effects upon the patterns of change.

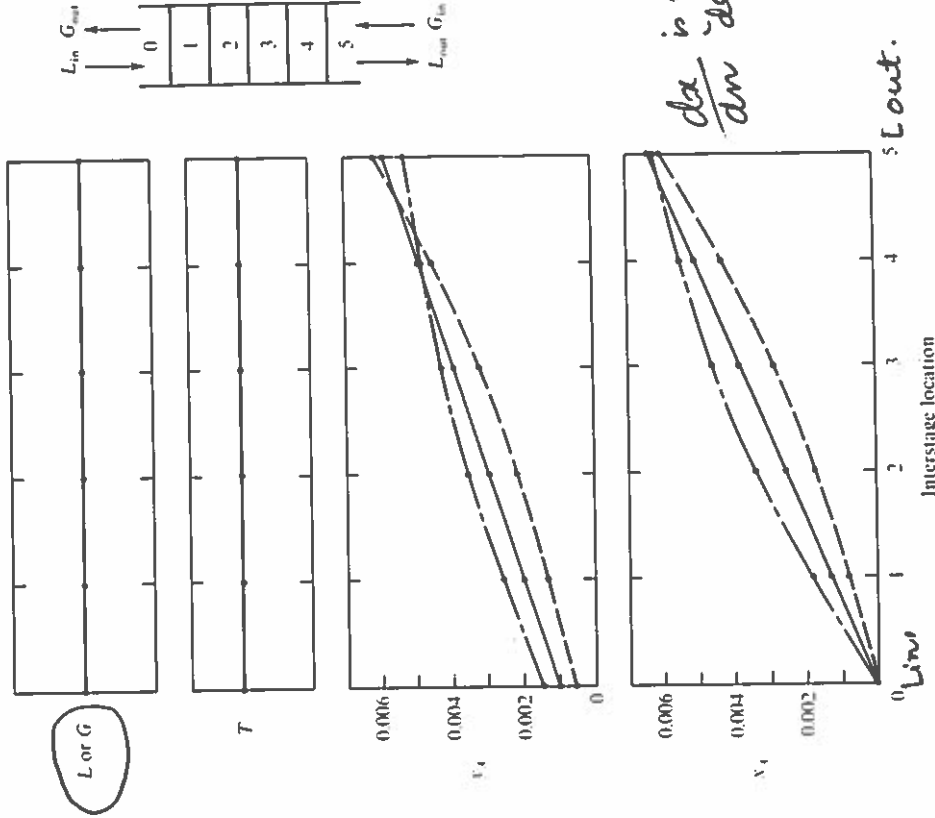


Figure 7-2 Patterns of change for dilute absorber.

Unidirectional Mass Transfer

Multistage separation processes necessarily involve the transfer of material from one counterflowing stream to the other. In a constant-molar-overflow binary distillation the two components which change phase do so in such a way as to leave the total molar flow rates between stages unchanged. The net passage of A from liquid to vapor in a stage is equal in molar rate to the net passage of B from vapor to liquid.

In the simplest absorption process only one component changes phases appreciably. The solute passes from gas to liquid; thus there must be a change in total

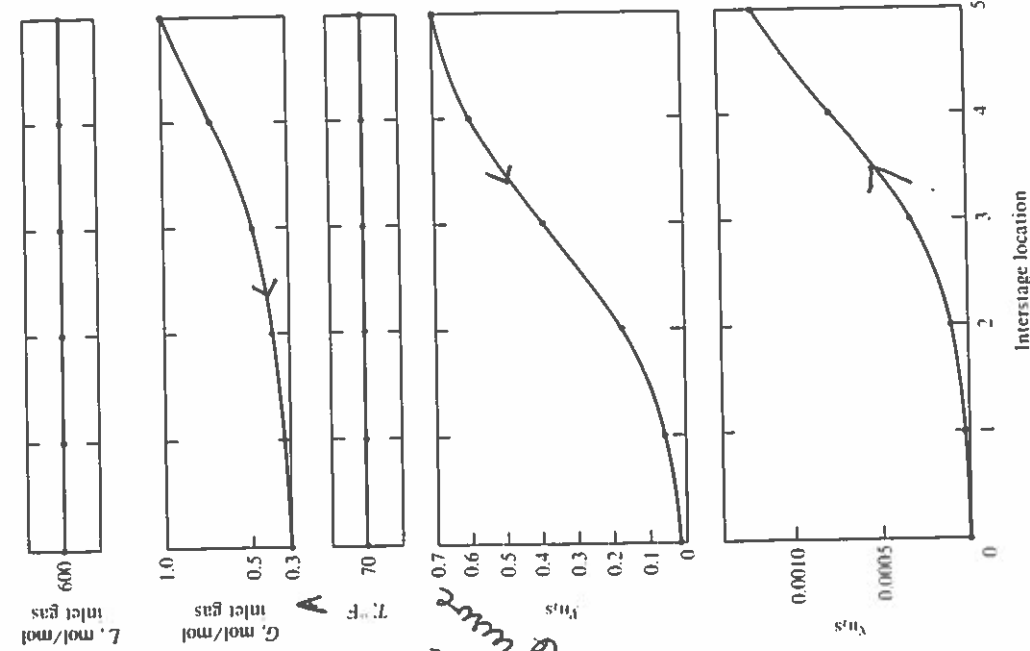


Figure 7-3 Patterns of change for absorber of Example 6-3.

molar flow rates from stage to stage. Unless the solvent has appreciable volatility, nothing returns from liquid to gas to balance the loss of solute from the gas. The absorber of Fig. 7-1 was sufficiently dilute for this change in bulk flow rates to be quite small, less than 1 percent. In Example 6-3, however, the absorber operated such that the change in bulk-gas flow rate was appreciable, as shown in Fig. 7-3. The liquid phase in Example 6-3 was highly dilute; hence the liquid-phase flow rate is nearly constant. The high ratio of liquid to gas flow also means that the liquid

sensible heat is large in comparison to the heat of absorption; thus the temperature is constant.

The composition profiles for the absorber of Example 6-3 are also shown in Fig. 7-3. The liquid composition changes most rapidly in the lower stages of the column. This behavior corresponds to the fact that the steps in the x direction shown in Fig. 6-7 are larger toward the rich end. The change in gas composition, expressed as $y_{i,s}$, is most rapid toward the middle of the column, and the change at either end is slow. This fact is not immediately obvious from Fig. 6-7. One must recall, however, that Fig. 6-7 is drawn in terms of $Y_{i,s}$ (mole ratio) instead of $y_{i,s}$ (mole fraction); y changes more rapidly per unit change in Y at low mole fractions than it does at higher mole fractions. Thus the large steps in Y at higher concentrations in Fig. 6-7 correspond to smaller steps in y .

Constant Relative Volatility

Figure 7-4 shows a McCabe-Thiele diagram for an atmospheric-pressure distillation of a saturated liquid feed containing 50 mol % benzene and 50 mol % toluene. The relative volatility is nearly constant, being 2.38 at $x_B = 0$ and 2.62 at $x_B = 1$ (Maxwell, 1950). The reflux is saturated, and the reflux ratio r/d is 1.57. There are 11 and a fraction equilibrium stages in addition to an equilibrium kettle reboiler and a

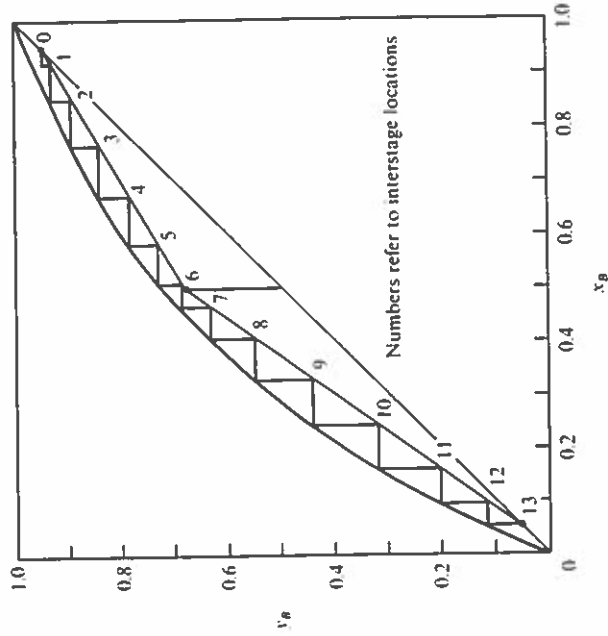


Figure 7-4 McCabe-Thiele diagram for benzene-toluene distillation.

then faster, and then slower again. The vapor composition profile is similar to that for the liquid.

Such a composition profile is common in binary distillation. With reference to Fig. 7-4, there will usually be pinches at the very top and very bottom of the column if high product purity is sought. Also, there will be pinches on either side of the feed stage if the operation is not much removed from minimum reflux. Midway in both the stripping and rectifying sections there is more distance between the equilibrium and operating curves and compositions change more rapidly.

The shape of the temperature profile closely follows that of the liquid composition profile, since the two are related through bubble-point considerations. When compositions change rapidly, temperatures also change rapidly; thus in this case temperatures change fastest midway in each of the two column sections. Operating temperatures change from stage to stage in the case of distillation not primarily because of sensible-heat effects but because of the necessity of preserving thermodynamic saturation when compositions change at the constant column pressure.

If the distillation of Fig. 7-4 were carried out at conditions closer to total reflux, the compositions would change slowly at either end and would change fastest near the feed. The pinches above and below the feed would not occur. Another possible situation is that of the acetone-water distillation of Example 6-5. The *tangent pinch* in the rectifying section of Fig. 6-15 causes the compositions and temperatures to change slowly in the middle of the rectifying section and more rapidly at the top and near the feed.

Enthalpy-Balance Restrictions

Another complicating factor in the analysis of multistage separation processes is the necessity of satisfying the first law of thermodynamics. This restriction takes the form of enthalpy balances which determine interstage flow rates and temperatures in processes such as distillation, crystallization, absorption, and stripping, which involve heat effects accompanying phase change. In distillation constant molar overflow is frequently assumed and serves as a sufficiently close approximation in many cases. However, it is important to understand at least qualitatively the factors which determine the change in flows in order to predict the systems for which constant molar flows might be expected to be too much in error. We consider the general case, where more than two components may be present.

Distillation The molecular weight usually changes throughout a distillation column as a result of the fractionation, the average molecular weight generally decreasing upward through the column, since high volatility of a compound generally corresponds to low molecular weight. Since the latent heat of vaporization per mole is usually less for a lower-molecular-weight material, the vapor rising and entering a typical stage when condensed will produce a vapor leaving the stage that has a greater number of moles. Because of this factor the flows usually will tend to increase upward in a column. If the system being fractionated is composed of only two components, the difference in molar latent heats of the pure species is large, or the

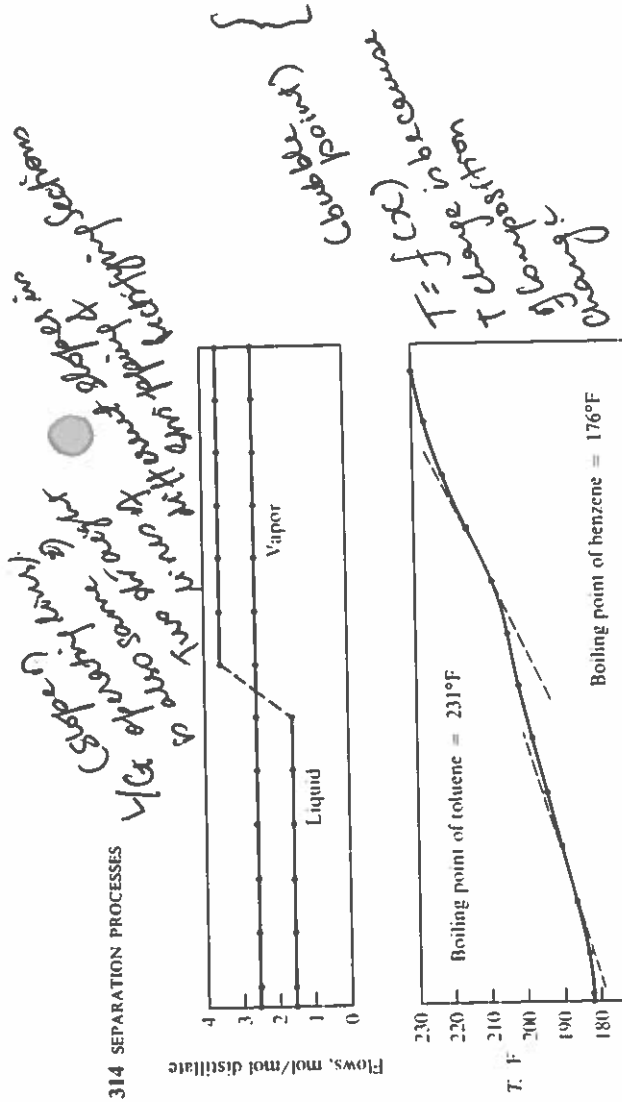


Figure 7-5 Patterns of change for benzene-toluene distillation of Fig. 7-4.

total condenser. The feed is introduced so as to provide maximum separation, which corresponds to a distillate containing 95 mol % benzene and a bottoms product containing 5 mol % benzene.

In Fig. 7-5 the flows, temperatures, and compositions for this distillation are shown as a function of interstage location. The molar flow rates are essentially constant except for the change in liquid flow at the feed plate. This is the case of nearly constant molar overflow. The profile of liquid compositions shows two points of inflection denoted by the dashed tangent lines. The liquid composition changes slowly at the very top of the column, then more rapidly and then more slowly again as the feed stage is approached. The same process is repeated below the feed: slow,

slowly approach section
downward
composition
latent heat
effect
downward
composition
constant molar
overflow assumed
be
latent
heat
effect

volatility spread of the feed is small, this effect will tend to predominate. In some cases the higher-boiling component will have the lower heat of vaporization and the latent-heat effect will tend to make flows increase downward.

Second, as the vapor flows upward through a column it must be cooled, since the temperature is decreasing upward. This cooling must be done at the expense of either sensible heat of the liquid or vaporization of the liquid, resulting in flows which increase upward if liquid is vaporized. Third, the liquid flows must be heated as they proceed down through the column, and this heating is done at the expense of either sensible heat or condensation of the vapor, resulting in flows which increase downward if vapor is condensed.

The last two factors can predominate if there are large amounts of components in the feed which are very light or very heavy relative to the components being fractionated or, more generally, if the temperature span from tower top to tower bottom is large.

In order to determine the combined effects of the sensible-heat factors it is necessary to consider a typical plate in each section. Consider first a typical plate in the stripping section. The liquid flow necessarily exceeds the vapor flow, and its heat capacity is greater. Thus heating of the liquid outweighs cooling of the vapor, resulting in condensation of the vapor and increasing flows downward. If the typical stage is in the rectifying section, the vapor flow is larger than the liquid flow, the opposite reasoning holds, and flows tend to increase upward.

It is apparent that the total effect of these three factors is complicated, and no completely general rule can be formulated. However, it is also apparent that the factors are often compensating to a large extent and this is borne out in the usefulness of the assumption of constant molar flows.

Interstage flows are linked together by the overall material balance. Therefore, if the vapor flow increases in a certain direction through the section, the liquid flow will also increase in that direction. Further, since the fractionation is mainly dependent on the ratio L/V , considerable changes can occur in flows without greatly disturbing L/V , and hence the fractionation, from stage to stage. The more nearly equal the two interstage flows, i.e., the closer the operation to total reflux, the less the effect on fractionation caused by changes in the flows.

One example of the effect of varying molar flow rates in a distillation process is the acetone-water separation of Example 6-5. Acetone is the more volatile component and has a lower latent heat of vaporization than water. As a consequence the latent-heat effect is dominant, and the flow rates tend to be higher on the upper stages of the column. This is reflected in the fact that the rectifying-section operating curve of Fig. 6-17 is concave upward and the chord to (x_d, y_d) has a slope that is farther removed from 1.0 on the lower stages.

If molar flows increase upward, the result (as shown in Fig. 6-17) is that the fractionation is poorer (slower changes in temperature and composition) compared with the constant-molar-overflow case at the same overhead reflux ratio r/d . On the other hand, the fractionation is better than that for constant molar overflow when compared at the same bottoms boil-up ratio V'/b .

Absorption and stripping Heat effects are also important in absorption and stripping processes. The temperature will change from stage to stage unless the system is dilute enough for heats of absorption and desorption to be small in comparison with sensible heats of the counterflowing streams. In absorption the unidirectional transfer of solute from gas to liquid brings about a heating effect since the heat of condensation of the solute must be dissipated. This will usually lead to temperatures which increase downward in the column since the liquid generally has a greater sensible-heat consumption than the gas. In absorbers the liquid is sometimes passed through water-cooled heat exchangers, called *intercoolers*, at intermediate points in the column in order to hold the liquid temperature down, preventing absorbent vaporization and loss of favorable equilibrium for absorption.

Conversely, in stripping operations there is a tendency for the liquid to be cooled as it passes downward. The reasons for this are wholly analogous to those developed for absorbers.

If the absorbent liquid has appreciable volatility, it can vaporize partially on the lower stages of the column, so as to bring the inlet gas toward an equilibrium content of vaporized solvent. This phenomenon has been analyzed by Bourne et al. (1974) in the context of absorption of ammonia from air into water at atmospheric pressure. They show that the competing effects of liquid heating from absorption and liquid cooling from solvent evaporation serve to produce a temperature maximum midway along the column.

When the heat capacities (specific heat times flow rate) of the counterflowing streams have roughly equal magnitudes, there is another effect which can cause a temperature maximum. Such a case is shown by Kohl and Riesenfeld (1979) in the form of actual test data for an acid-gas absorber using ethanalamine solution to treat a gas at 3.7 MPa containing 4% CO_2 and 0.8% H_2S . As shown in Fig. 7-6, this absorber operates with inlet and effluent amine temperatures of 40 and 79°C, respectively, while developing an internal maximum temperature of 112°C at a point a few plates above the bottom. Here the hot downflowing liquid loses heat by preheating the incoming gas, and the hot upflowing gas loses heat by preheating the incoming liquid. The preheated gas and preheated liquid both flow away from the ends of the column, serving to reinforce the rise in temperature due to release of the heat of absorption in the middle of the column. This phenomenon has also been noted for countercurrent isotope-exchange towers (Pohl, 1962) and for counterflow heat exchangers where there is generation of heat due to chemical reaction in one of the streams (Grens and McKean, 1963).

It is interesting to observe that in Fig. 7-6 the gas-phase content of H_2S actually undergoes an internal maximum because of the higher equilibrium partial pressures associated with the temperature maximum. The CO_2 content, which is much farther from equilibrium, does not show such behavior.

The high gas pressure in the example of Fig. 7-6 serves to give the counterflowing streams roughly equal heat capacity. In the more usual situation, the liquid heat capacity exceeds that of the gas, tending to make the liquid temperature increase continually down the column. In some ethanalamine absorbers for gases with very

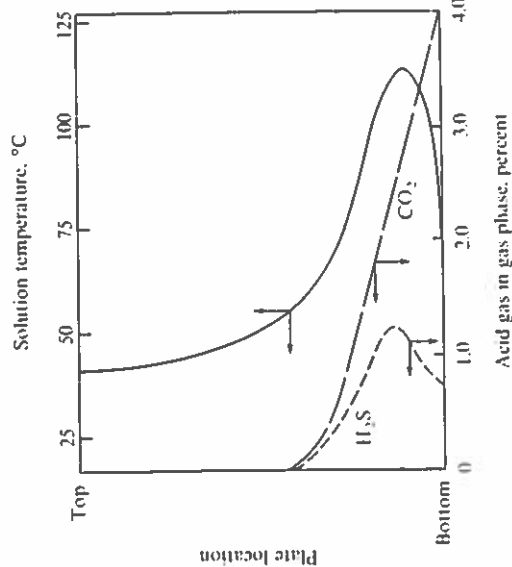


Figure 7-6 Temperature bulge in acid-gas absorber. (Adapted from A. L. Kohl and F. C. Rosenfeld, *Gas Purification*, 3d ed., Copyright © 1979 by Gulf Publishing Co., Houston, Texas, p. 62; used by permission. All rights reserved.)

low CO_2 and H_2S contents the liquid-gas ratio is low enough for the heat of absorption to go primarily to the gas and cause temperatures to increase upward.

The development of an internal temperature maximum complicates the design and analysis of absorbers in two ways: (1) there tends to be an internal pinch which increases the required solvent-to-gas ratio, and (2) there is a strong interaction between the enthalpy balances and the composition changes, which depend upon the equilibrium as influenced by the temperature. Methods of handling such situations are discussed in Chap. 10. Stockar and Wilke (1977) present a method for estimating the temperature profile in packed gas absorbers.

Contrast between distillation and absorber-strippers It is important to note that temperature profiles in ordinary *distillation* columns primarily reflect the compositions of the streams, while total interstage flow profiles primarily reflect enthalpy-balance restrictions. In *absorbers* and *strippers*, on the other hand, the situation is reversed: temperature profiles primarily reflect enthalpy-balance restrictions and interstage flow profiles primarily reflect stream compositions. This distinction will be of considerable use in setting up convergence loops for computer calculations in Chap. 10.

Phase-Miscibility Restrictions; Extraction

In staged liquid-liquid extraction processes there is usually no substantial heat effect accompanying the transfer of solute from one liquid to the other; consequently operation is usually nearly isothermal. In dilute extraction systems the interstage flow rates will remain essentially constant as long as there is no appreciable miscibility of the extract and raffinate phases. When the solvent and the unextracted component are totally immiscible but the solute concentration is high enough, there will

be an increase in interstage flows in the direction of extract flow because of unidirectional mass transfer. In still more concentrated extraction systems, however, all components will necessarily become appreciably miscible and the interstage flows will vary to satisfy the phase-equilibrium relationships. This effect again causes flows to increase in the direction of extract flow, as is shown in the following discussion.

Example 6-6 covered a case of extraction involving appreciable miscibility between the phases. The ketones and water in the acetone-MIBK-water system are substantially soluble in each other, and at high enough acetone concentrations total miscibility is reached. Figure 6-24 gives an operating diagram for an acetone-MIBK-water extraction, plotted on a weight-fraction solvent-free basis. The operating curve is not a straight line; hence the mass flow rates of the combined ketones (acetone + MIBK) vary from stage to stage. Similarly, flow rates defined in any other way are not constant from stage to stage.

Figure 7-7 shows the interstage flow rates for the operation, expressed as total mass flow rates of the extract and raffinate phases, and as mass flows of the combined ketones, the two species which are being separated. The interstage flow of combined ketones is greatest at the left-hand, or acetone-rich, end of the cascade. At low acetone concentrations the solubility of *total ketones* in the water-rich (extract) phase is quite small (see Fig. 6-20), but as the acetone concentration increases toward the rich end of the cascade, the solubility of total ketones in the water-rich phase increases. The water-rich and ketone-rich phases become more nearly alike in composition as the acetone content increases. In fact, the compositions of the phases become identical at the plait point. The difference in flows of any of the components between raffinate and extract interstage streams must be constant from stage to stage since the operation is at steady state. As the streams become more alike in composition at higher acetone contents, greater interstage flows of all components—and hence of combined ketones—become necessary in order to preserve the constant difference in flows of those components between streams.

The total flow rates follow suit. The flow of the raffinate phase is nearly equal to the flow of combined ketones in that phase, since the solubility of the water solvent in that phase is always comparatively small. Therefore the raffinate flow is still greatest at the acetone-rich end, being increased somewhat by the higher solubility of water in ketones at that end. Since the difference in total flows of raffinate and extract must remain constant at all interstage positions, the total extract flow must also be higher at the acetone-rich end.

This behavior is characteristic of three-component extraction processes. The main transferring solute (acetone in Example 6-6) will be the component which is relatively soluble in both phases. In many cases the solute will produce complete miscibility when present above some particular concentration. Since presence of the solute promotes miscibility of the phases and similarity of composition of the two phases, the foregoing reasoning leads one to expect higher interstage flow rates at the solute-rich end of the cascade as a general rule.

There is an analogy to be drawn between the governing effect of enthalpy balances on interstage flows in distillation, on the one hand, and the governing effect of miscibility relationships on interstage flows in extraction, on the other. In each case

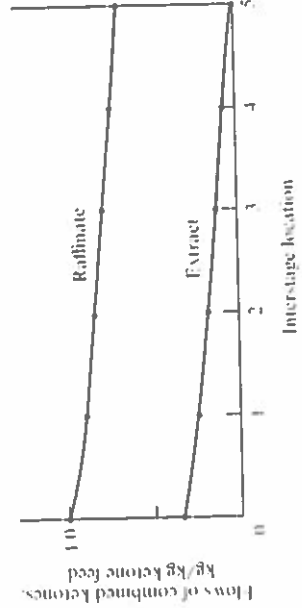
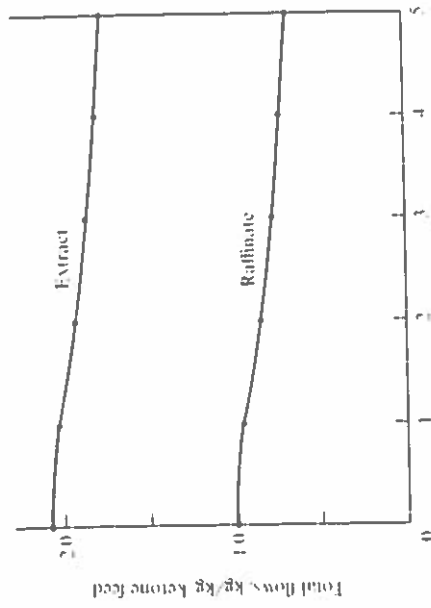
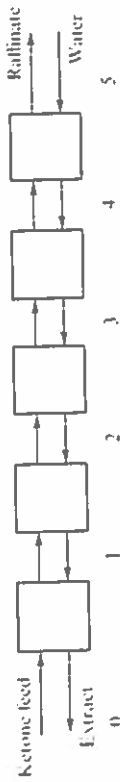


Figure 7-7 Interstage flows in acetone-MIBK-water extraction process of Example 6-6.

the restriction involves conservation of the separating agent—heat or enthalpy in distillation, and solvent in extraction. In distillation, interstage flows are determined from a knowledge of the specific enthalpy content of the appropriate saturated vapor and liquid phases. In extraction, interstage flows are determined from a knowledge of the specific solvent content of the appropriate saturated extract and raffinate phases. In both processes, interstage flows increase when the difference in separating agent content between saturated phases becomes smaller. In distillation, interstage flows increase in the direction of compositions where the difference in enthalpy content per kilogram or mole between vapor and liquid is smaller corresponding to a smaller

latent heat. In extraction, interstage flows increase in the direction of compositions where the difference in solvent content per kilogram or mole between the two phases is smaller. This corresponds to the direction of increased miscibility between phases.

MULTICOMPONENT MULTISTAGE SEPARATIONS

The separations we have considered in Chaps. 5 and 6 have been binary, and as a consequence there have been relatively few components present whose properties and behavior had to be considered individually. When more components are present in a separation process, calculational procedures necessarily become more involved because it is not possible to specify as much about the process in a problem description. Graphical computation approaches are of limited usefulness when it is not possible to fix an entire phase composition uniquely by specifying the concentration of a single component on an operating diagram.

In spite of the increased computational difficulties, the qualitative understanding of multicomponent separation processes involves little added complexity beyond an understanding of binary separation processes. The following sections consider published solutions to three different multicomponent separation processes and explore the nature of the patterns of change in temperature, composition, and total flow rates. The computational procedures involved in solving all the various equations describing these processes need not concern the reader at this point: they form much of the subject matter of Chaps. 8 to 10.

Absorption

Horton and Franklin (1940) present a detailed solution to an oil-refinery absorption problem. A schematic of the process is shown in Fig. 7-8. A heavy lean-oil absorbent

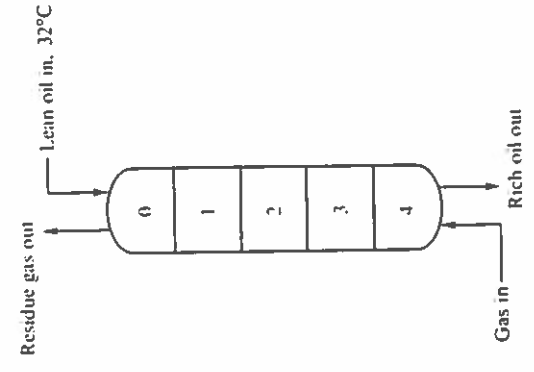


Figure 7-8 Schematic of multicomponent absorption process.

Table 7-1 Composition of residue gas and K_i values (data from Horton and Franklin, 1940)

| Component | Composition, mole fraction | | | K_i |
|-----------------------------|----------------------------|---------|-------------|-------|
| | Lean oil | Wet gas | Residue gas | |
| Methane (C_1) | | 0.286 | 0.499 | 51 |
| Ethane (C_2) | | 0.157 | 0.250 | 13 |
| Propane (C_3) | | 0.240 | 0.214 | 3.1 |
| <i>n</i> -Butane (C_4) | | 0.169 | 0.025 | 0.85 |
| <i>n</i> -Pentane (C_5) | 0.05 | 0.148 | 0.012 | 0.26 |
| Heavy oil | 0.93 | | | ~ 0 |
| | 1.00 | 1.000 | 1.000 | |

is employed to recover roughly 60 percent of the propane, and most of the heavier hydrocarbons from a gaseous feed stream. A tower providing four equilibrium stages is used. Operating conditions are

Lean oil inlet temperature = 32°C Tower pressure = 405 kPa

Lean-oil feed rate = 1.104 mol/mol gas fed

In the four-equilibrium-stage column, 44.8 percent of the gas is absorbed, and the residue-gas composition is shown in Table 7-1. The patterns of change in flows and temperature are shown in Fig. 7-9. The changes in molar flows of the individual components in the gas and liquid phases are also shown ($v_i = y_i V$ and $l_i = x_i L$), along with the gas-phase mole fractions (y_i). The process is similar to the absorption of a single component except that now several individual species are being absorbed.

Some idea of the relative solubilities of the five gas-phase components can be obtained from the values of the equilibrium ratio K_i ($= y_i/x_i$ at equilibrium) at 38°C, also shown in Table 7-1. The total flow rates of both the gas and liquid phases increase downward in the column, in the direction of high-solute contents in the liquid phase (Fig. 7-9a). This increase in flows is the result of unidirectional mass transfer; the components pass from the gas to the liquid without any comparable amount of material passing back the other way.

Temperatures increase downward in the column (Fig. 7-9b); the cause is the heat of absorption released by the phase change of solutes passing from gas to liquid. The heat released serves to increase the sensible heat of the liquid stream, which receives most of the heat released at the interface.

Methane and ethane are sufficiently volatile to remain relatively unabsorbed by the oil. The flow rates of methane and ethane in the vapor are therefore essentially

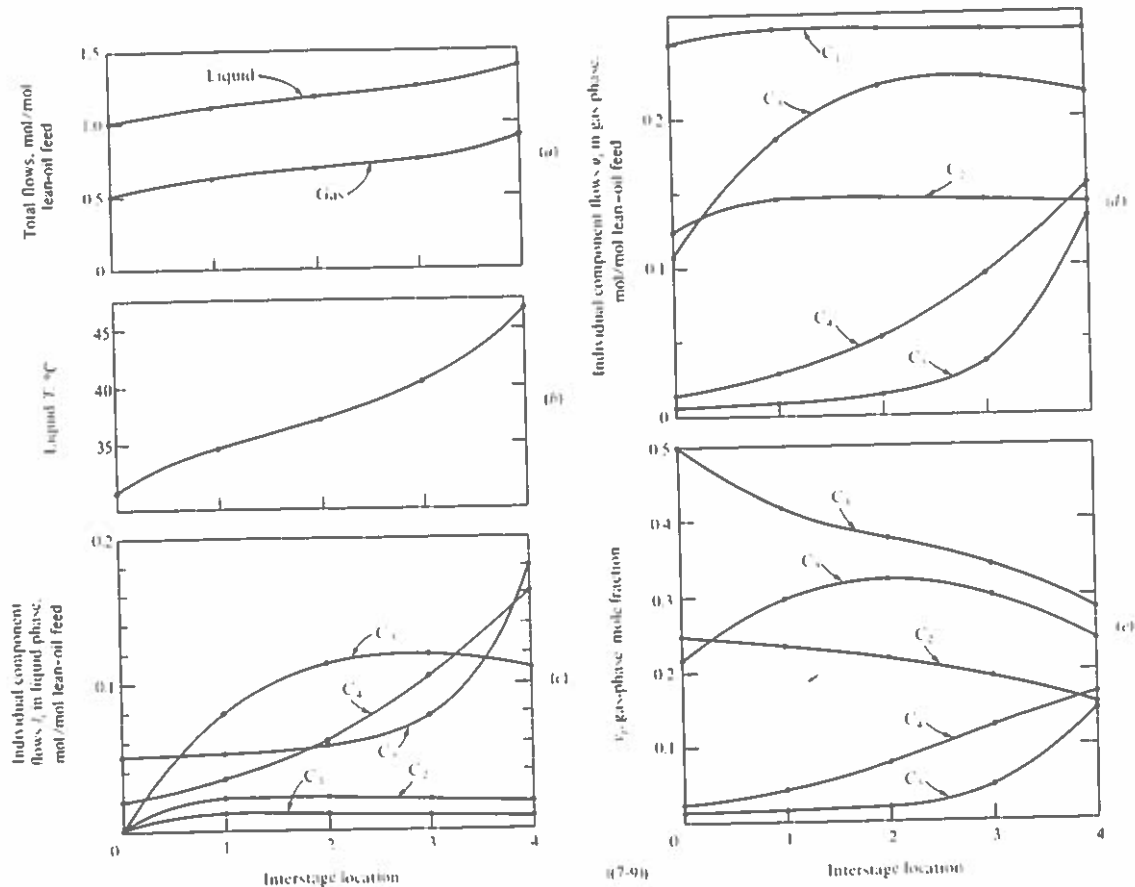


Figure 7-9 Patterns of change for multicomponent absorption process: (a) total flows; (b) liquid temperature; (c) liquid-component flows; (d) gas-component flows; (e) gas composition. (Results from Horton and Franklin, 1940.)

constant (Fig. 7-9d). The small depletion in the vapor means that the liquid equilibrates nearly completely with those components in one stage, with little change in l_i thereafter.

Pentane has the least volatility of any component in the gas. As a result it is rapidly absorbed in the lower stages of the column soon after the gas feed enters (Fig. 7-9d). There is little pentane remaining in the gas reaching the upper stages; hence not much pentane enters the liquid on the upper stages. As a result, the pentane flow in the liquid on the upper stages remains constant at the level present in the lean-oil feed until the liquid reaches the lower stages, where rapid absorption of pentane occurs. Butane is the next least volatile component; it also absorbs rapidly on the lower stages but not as rapidly as pentane.

Because of the large absorption of butane and pentane on the lower stages, the mole fractions of these two components fall in the gas phase as the gas passes to higher stages (Fig. 7-9e). Methane and ethane are relatively unabsorbed, and the total gas flow rate decreases upward; as a result the mole fractions of methane and ethane continually rise in the gas as it comes to stages higher in the column.

The amounts of methane and ethane absorbed in the liquid, although small, actually pass through a maximum on an intermediate stage (Fig. 7-9c). This is the result of the changes in temperature and in gas-phase mole fraction. The equilibrium concentration of a solute in the liquid phase is given by $x_i = y_i/K_i$. On the upper stages the mole fractions y_i of methane and ethane are higher in the gas phase. The temperature is also lower on the upper stages, which tends to make K_i lower. As a consequence the equilibrium x_i for methane and ethane is highest on the top stage and becomes progressively lower on lower stages. On the lower stages, methane and ethane tend to absorb to the equilibrium amount, accounting for maxima in the amounts of methane and ethane absorbed. No maxima occur for butane and pentane since they are readily absorbed on the lower stages, reducing y_i for those components on the upper stages.

Propane is a component which is intermediate in volatility. About half the propane in the wet gas is ultimately absorbed (Fig. 7-9d), whereas most of the butane and pentane and very little of the methane and ethane are absorbed. An appreciable amount of propane remains in the gas reaching the upper stages, where it encounters a more favorable equilibrium for absorption in terms of temperature. Thus the maximum of propane in the liquid occurs for much the same reasons as the maxima in amounts of methane and ethane absorbed. Propane is absorbed most readily on the upper stages (Fig. 7-9d) because the combination of high gas-phase mole fraction and low temperature is more effective at that point. Butane and pentane can be absorbed readily on the lower stages because their already low volatility offsets the higher temperature on the lower stages.

The reader should realize that one could not absorb more propane by removing the bottom stage from the column, even though the amount of propane absorbed in the liquid is higher at location 3 than at location 4. The maximum in propane absorption occurs as a direct result of the large absorption of pentane and butane on the bottom stage, which reduces the total gas flow and increases y_{C_3} . This phenomenon will occur no matter what the number of stages.

Table 7-2 Feed and products for depropanizer example (data from Edmister, 1948)

| Component | mol % | | mol/(100 mol feed) | | α_i (rel. to C_3) |
|-----------------------------|-------|------------|--------------------|------------|-----------------------------|
| | Feed | Distillate | Bottoms | Distillate | |
| Methane (C_1) | 26 | 43.5 | | 26 | 10.0 |
| Ethane (C_2) | 9 | 15.0 | | 9 | 2.47 |
| Propane (C_3) | 25 | 41.0 | 1.0 | 24.6 | 1.0 |
| <i>n</i> -Butane (C_4) | 17 | 0.5 | 41.7 | 0.3 | 0.49 |
| <i>n</i> -Pentane (C_5) | 11 | | 27.4 | | 0.21 |
| <i>n</i> -Hexane (C_6) | 12 | | 29.9 | | 0.10 |
| | 100 | 100 | 100 | 59.9 | 40.1 |

Distillation

Edmister (1948) presents a detailed stage-to-stage solution for a depropanizer distillation column. The column operates at an average total pressure of 2.17 MPa and receives a feed with the composition shown in Table 7-2. The thermal condition of the feed is such that it is 66 mol % vapor at tower pressure. The column is equipped with a kettle-type reboiler and a partial condenser, which allows the manufacture of reflux at 2.17 MPa total pressure while using water for cooling. The product compositions are also given in Table 7-2. The overhead reflux rate r is 0.90 mol per mole of feed.

The example is worked assuming constant molal overflow; 15 equilibrium stages within the tower are required for the separation, the feed being introduced between the ninth and tenth equilibrium stages from the bottom of the tower proper.

The total flow rates are shown as a function of interstage location in Fig. 7-10. The flows are constant above and below the feed, in line with the assumption of constant molal overflow. The changes in total flow of vapor and liquid at the feed point are governed by the fact that the feed is two-thirds vapor.

Figure 7-11 shows the changes of vapor composition from stage to stage for all six of the components present; Fig. 7-12 shows the composition profile in the liquid. In both figures the left- and right-hand sides correspond to the bottoms and distillate, respectively. Values of α_i at 96°C (feed-plate temperature) are also given in Table 7-2.

Key and nonkey components The separation is being achieved primarily between propane and butane, since, as shown in Table 7-2, most of the propane and essentially all the more volatile components appear in the distillate, while most of the butane and essentially all the less volatile components appear in the bottoms. Propane and butane are therefore called the *key components*. The key components, or *keys*, appear to a significant extent in both products, while the other components (called *nonkeys*) are merely "along for the ride," being relegated almost exclusively to

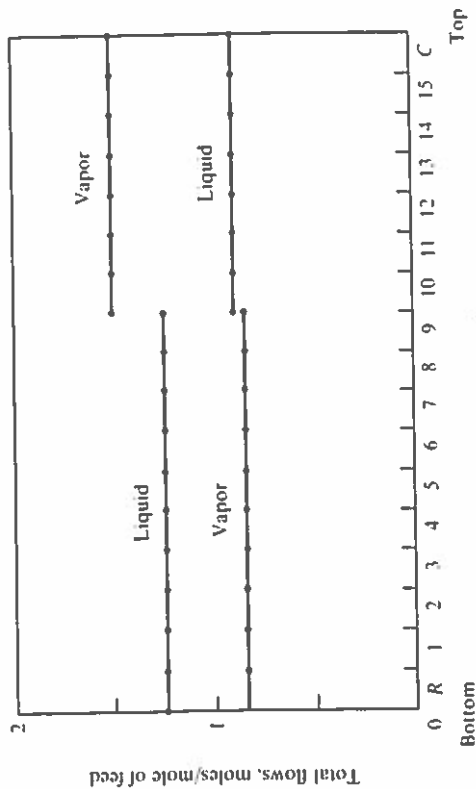


Figure 7-10 Total vapor and liquid flows in depropanizer. (Results from Edmister, 1948.)

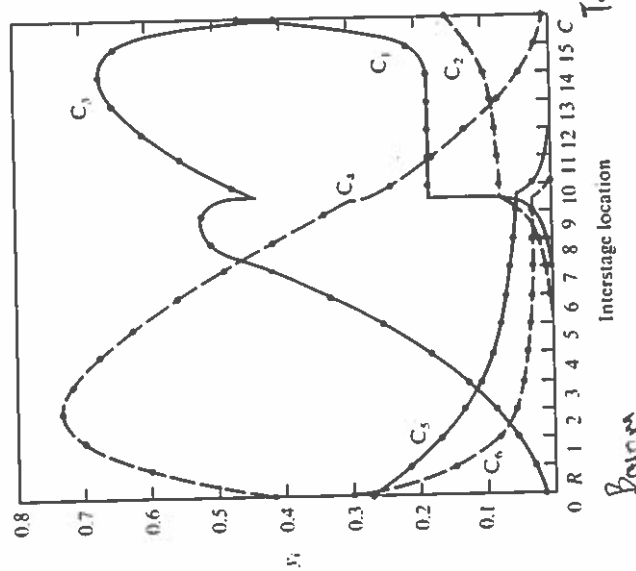


Figure 7-11 Vapor-composition profile in depropanizer. (Results from Edmister, 1948.)

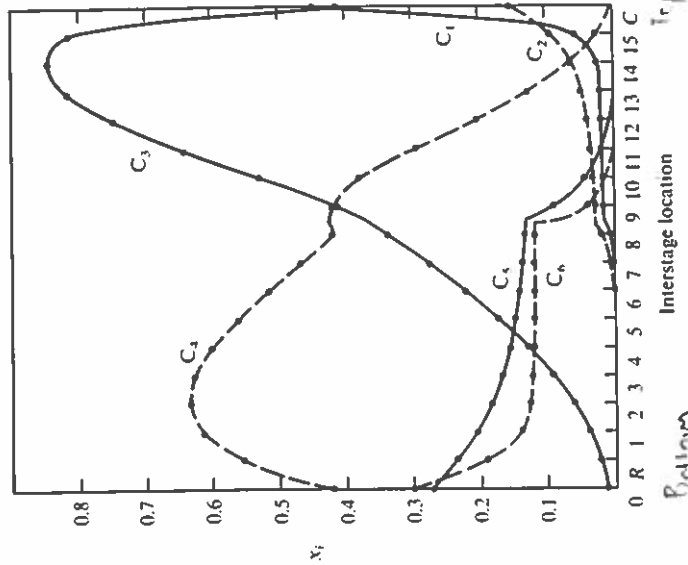


Figure 7-12 Liquid-composition profile in depropanizer. (Results from Edmister, 1948.)

one product or the other. Hexane and pentane are called *heavy* nonkeys since they are less volatile than the keys, while methane and ethane are *light* nonkeys since they are more volatile than the keys.

Considering Figs. 7-11 and 7-12, it is apparent that all components are present to a significant amount at the feed stage.† This is logical since all components are present in the feed which is introduced at that point. Above the feed the heavy nonkeys (C_5 and C_6) in both liquid and vapor die out rapidly. Because of their low relative volatility with respect to all the other components present, these two components do not enter the upflowing vapor on the stages above the feed to any large extent and thus are not able to pass upward in the column far above the feed. A few stages suffice to reduce the mole fractions of pentane and hexane to a very low value. Since pentane is more volatile than hexane, it persists for a greater number of stages.

Entirely analogous reasoning applies to the light nonkeys, methane and ethane, below the feed point. These components are so volatile that they do not enter the liquid to any great extent and thus are unable to flow down the column in any

† In Fig. 7-11 the vapor between stages 9 and 10 is arbitrarily taken to be that leaving stage 9 before being mixed with the feed vapor. In Fig. 7-12 the liquid between stages 9 and 10 is that leaving stage 10 before being mixed with the feed liquid.

Rearranging, we find

$$y_{HNSK, \text{lim}} = \frac{N_{HNSK, b}/V''}{(L/V''K_{HNSK}) - 1} \quad (7-4)$$

To a first approximation K_{LKA} , the equilibrium ratio of the light key, is equal to L/V'' in the stripping section in this zone of constant heavy nonkey mole fraction. † Since $x_{LKA} - H_{NSK} = K_{LKA}/K_{HNSK}$, we have

$$y_{HNSK, \text{lim}} \approx \frac{N_{HNSK, b}/V''}{x_{LKA} - H_{NSK}} - 1 \quad (7-5)$$

where $\alpha_{LKA} - H_{NSK}$ is the relative volatility of the light key with respect to the heavy nonkey (a value greater than 1.0), taking $\alpha_{HNSK} = 0.12$ below the feed (see Table 8-2).

Substituting for hexane in our example,

$$x_{C_6, \text{lim}} \approx \frac{(0.299)(40.184)}{(1.0)(0.12)} - 1 \approx 0.0191$$

and from Eq. (7-2)

$$x_{C_6, \text{lim}} = \frac{0.0191}{K_{C_6}} \approx \frac{0.0191 V'' x_{LKA} - H_{NSK}}{L} \approx \frac{(0.0191)(84)(1.0)}{(124)(0.12)} \approx 0.108$$

Figures 7-11 and 7-12 verify these estimates.

The same reasoning can be applied to the behavior of the light nonkeys, methane and ethane, above the feed. All the light nonkeys in the feed must appear in the overhead product and hence must appear in the upflowing vapor leaving each stage above the feed. Fractionation between the light nonkeys and the keys is effective on the top few stages, which serve to reduce the mole fraction of light nonkeys toward the constant limiting values. A lesser, also nearly constant, amount of light nonkeys must appear in the liquid above the feed because of the equilibrium relationship. A derivation similar to that carried out for the heavy nonkeys shows that

$$y_{LNA, \text{lim}} = \frac{y_{LNA, b} D/L}{(V'K_{LNA}/L) - 1} \quad (7-6)$$

and

$$y_{LNA, \text{lim}} = K_{LNA} y_{LNA, \text{lim}} \quad (7-7)$$

† For a relatively sharp separation y_{LKA} is relatively small compared with y_{LNA} in the zone of constant heavy nonkey mole fraction. Hence the y_{LKA} term is small compared with the y_{LNA} and y_{LNA} terms in a mass-balance equation. If the mole fraction of the light key is changing slowly from stage to stage, an approximate equation is

$$y_{LKA} L = y_{LKA} V'' = K_{LKA} y_{LKA} V'' \quad \text{or} \quad K_{LKA} = \frac{L}{V''}$$

In Chap. 8 we see that there is a method for estimating K_{HNSK} more accurately from the Underwood equations (8-106) and (8-107)

substantial amount; thus they drop to very low concentrations a few stages below the feed. Ethane persists longer than methane since ethane is less volatile.

Next it should be noted that the heavy nonkeys, pentane and hexane, have relatively constant mole fractions in the liquid and vapor below the feed until a point some three or four stages from the bottom of the column is reached. These two components make up a sizable portion of the bottoms product. The lowest stages of the column are necessarily devoted to a fractionation between these heavy nonkey components and the two keys, propane and butane. The two keys are more volatile than the two heavy nonkeys; hence the keys concentrate in the vapor and increase in mole fraction going upward from the bottom at the expense of the heavy nonkeys.

It is important, however, to realize that the mole fractions of the heavy nonkeys cannot be reduced to zero before the feed point is reached. There must be some certain quantity of these materials in the liquid passing downward from the feed stage below the feed must at the very least equal the amount of that component flowing out in the bottoms product. Thus the relatively constant amount of pentane and hexane in the liquid on the stages just below the feed is associated with the necessity of transporting the pentane and hexane downward toward the bottoms product. Proceeding up the tower from the bottom, the mole fractions of the two heavy nonkeys reach values corresponding to these limiting constant flows after the fractionation on the bottom stages has depleted these components as much as possible.

Figure 7-11 reveals that there is also an appreciable, but lesser, constant mole fraction of pentane and hexane in the vapor in the zone where there is a constant liquid mole fraction for these materials. The presence of these components in all vapors below the feed is logical in view of the fact that the downflowing heavy nonkeys in the liquid do have some volatility, and hence the vapor mole fractions of heavy nonkeys correspond to equilibrium with the relatively constant mole fraction in the liquid. In fact, this concept allows us to derive in simple fashion an expression for the limiting mole fraction reached by a heavy nonkey in a zone where it has constant mole fraction below the feed. If mole fractions of heavy nonkeys are constant,

$$N_{HNSK, \text{lim}} L = N_{HNSK, b} + y_{HNSK, \text{lim}} V'' \quad (7-1)$$

$$y_{HNSK, \text{lim}} = \frac{y_{HNSK, \text{lim}}}{K_{HNSK}} \quad (7-2)$$

where the subscript "lim" refers to the heavy nonkey component in the zone where it has constant mole fraction and the subscript b corresponds to the same heavy nonkey in the bottoms product. Hence

$$y_{HNSK, \text{lim}} \left(\frac{L}{K_{HNSK}} - 1 \right) = N_{HNSK, b} \quad (7-3)$$

To a first approximation K_{HK} , the equilibrium ratio of the heavy key, is equal to L/V in the rectifying-section zone of constant light nonkey mole fraction.[†] Therefore

$$x_{LNK, \text{lim}} \approx \frac{y_{LNK, D} D/L}{\alpha_{LNK-HK} - 1} \quad (7-8)$$

and

$$y_{LNK, \text{lim}} \approx \frac{\alpha_{LNK-HK} L}{V} x_{LNK, \text{lim}} \quad (7-9)$$

The mole-fraction curves for the two keys, propane and butane, in Figs. 7-11 and 7-12 can be understood in the light of the foregoing discussion of the monkey behavior. The keys must adjust in mole fraction so as to accommodate fractionation against the nonkeys as well as against each other. Thus, the mole fraction of propane does tend to increase upward and the mole fraction of butane tends to increase downward in the column as a simple reflection of the fractionation between the two keys. At the very bottom of the tower the mole fractions of both keys decrease downward. This is the result of fractionation of the keys against the heavy nonkeys. The heavy nonkeys grow rapidly at the bottom at the expense of both the keys, and especially at the expense of the heavy key since it is the more plentiful of the keys. This is the cause of the maximum in butane mole fraction below the feed.

At the very top of the column there is fractionation of the light nonkeys against the keys. The light nonkeys grow on the top few plates at the expense of the keys, especially the more plentiful light key. This is the cause of the maximum in propane mole fraction above the feed in Figs. 7-11 and 7-12.

Just above the feed tray the heavy nonkeys die down from their limiting mole fractions below the feed toward zero. This fractionation is again accomplished against the lighter components, and there is a tendency for mole fractions of the keys and the light nonkeys to rise somewhat more rapidly in the first few stages, proceeding upward away from the feed. Thus we have the slight hump in butane mole fraction in the liquid above the feed (Fig. 7-12). The effect is more marked in the liquid since there is a higher heavy nonkey mole fraction in the liquid. Similarly, the dying out of the light nonkeys in the few stages below the feed is reflected in a slight increase in propane mole fraction in the vapor, as shown in Fig. 7-11.

The temperature profile for the depropanizer column shown in Fig. 7-13 should be compared with the profile shown for a typical binary distillation in Fig. 7-6. In most binary distillations the temperature changes most sharply in the midsections of the rectifying and stripping sections if the operation is near minimum reflux. This reflects the bigger steps in these regions on the McCabe-Thiele diagram, and the corresponding larger changes in mole fraction from stage to stage. As shown in Fig. 7-13, the temperature changes most rapidly at the very top and very bottom of

[†] For a relatively sharp separation, $y_{HK, D}$ is small compared with x_{HK} in the zone of constant light nonkey mole fraction. Neglecting the $y_{HK, D}$ term in a mass balance and assuming that x_{HK} changes slowly from stage to stage gives $x_{HK} L = y_{HK} V = K_{HK} x_{HK} V$ or $K_{HK} = L/V$. Again a more accurate value of K_{LNK} is available through the Underwood equations (8-104) and (8-105).

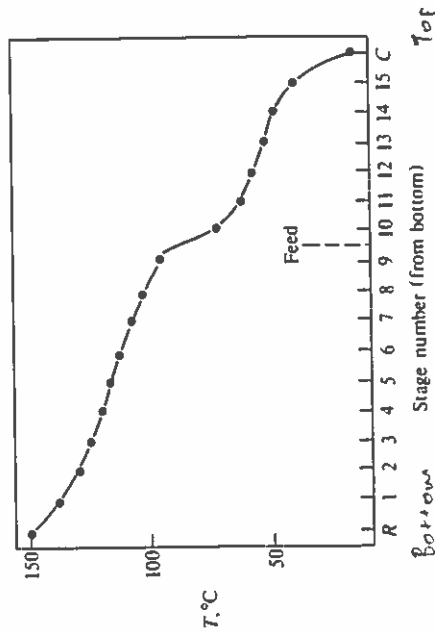


Figure 7-13 Temperature profile for depropanizer. (Results from Edmister, 1948.)

the column and in the vicinity of the feed point for the multicomponent distillation. These are the regions where compositions are changing the fastest, but to a large extent it is the nonkey components that are changing. At the top the light nonkey components die out rapidly in the liquid, and the bubble-point temperatures for the individual stage liquids are highly sensitive to the amount of light species present. Below the feed the light nonkeys again die down rapidly in the liquid and again change the bubble-point temperatures markedly. The reduction of heavy nonkeys in the vapor has a similar effect on dew-point temperatures of the vapor at the bottom and just above the feed.

The reader should also note that the presence of nonkey components serves to widen the span of temperature across a column.

Equivalent binary analysis Hengstebeck (1961) has suggested that the performance of a multicomponent distillation column be analyzed in terms of an equivalent binary distillation based upon the keys alone. This procedure has the feature of providing a familiar graphical representation of the distillation process which assists in understanding through visualization.

A multicomponent distillation can be treated as a binary involving the keys if the flows and compositions are placed on a basis of the two keys alone. Thus we could use $y'_C = y_C/(y_C + y_{C'})$ and $x'_C = x_C/(x_C + x_{C'})$ as effective mole fractions and express the flow as $V'(y'_C + y_{C'})$ for the vapor with similar expressions for liquid, feed, and product flows. The total flows of combined keys in the vapor and the liquid at various interstage locations are shown in Fig. 7-14 for our depropanizer example. The flows are, of course, less than the total flows of vapor and liquid (Fig. 7-10) and show maxima midway along the stripping and rectifying sections. From our previous discussion there is obviously a limit on the flows of combined keys. Below the feed this will correspond to the light nonkeys being absent and the heavy nonkeys being

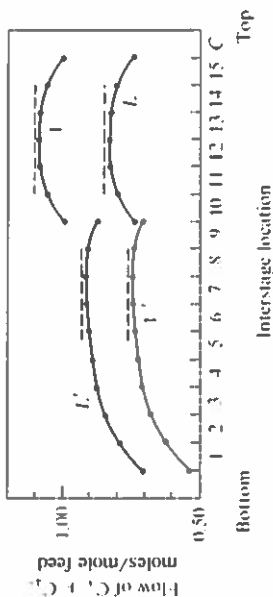


Figure 7-14 Flows of combined keys in depropanizer.

at their limiting mole fractions. Above the feed the situation is reversed, and the limit on the flow of combined keys corresponds to the heavy nonkeys being absent and the light nonkeys being at their limiting mole fractions. These limits on the flows of combined keys can be computed for the depropanizer example and are represented by dashed lines in Fig. 7-14.

Figure 7-15 shows a McCabe-Thiele diagram for the equivalent binary system in the depropanizer. The steps represent the actual changes in propane and butane mole

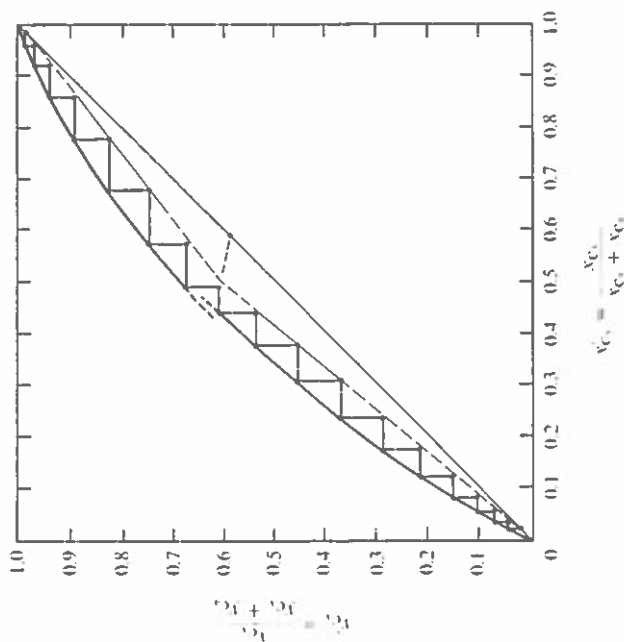


Figure 7-15 McCabe-Thiele diagram for equivalent binary system in depropanizer example.

fractions taken from Figs. 7-11 and 7-12. The equilibrium curve through the stage-exit-stream points forms smooth curves above and below the feed. Readers should verify for themselves that the equilibrium curve can be calculated from Eq. (1-12) using the relative volatility of propane to butane at the temperature of each stage. If this relative volatility were constant, the equilibrium curve would not undergo a sudden shift at the feed; however, in our case $\alpha_{C_2-C_3}$ is a function of temperature, and temperature changes rapidly near the feed because of the rapid changes in nonkey mole fractions. Thus there is a sharp change in $\alpha_{C_2-C_3}$ near the feed.

The operating lines in Fig. 7-15 are drawn for the limiting combined-key flow conditions shown by the dashed lines in Fig. 7-14. The flows of combined keys are always below these upper limits, and the liquid flows and vapor flows of combined keys always differ from each other by a constant amount equal to the amount of keys in the distillate (above the feed) or the bottoms (below the feed). Where flows are less than the upper limits, the point for passing stream compositions necessarily lies above the limiting operating line in Fig. 7-15. This follows since lesser total flows and a constant difference between flows necessarily produce an effective value of L/V farther removed from 1.0.

The combined-key flows fall below the limits by the greatest amounts at points where the nonkeys are dying down in mole fraction, namely, at the top, just above the feed, just below the feed, and at the bottom. The operating points fall most within the limiting operating lines in these regions. Thus we can conclude that in our depropanizer example the equivalent binary separation resembles that of an ordinary binary distillation, but there are added factors causing pinches at the very top, at the very bottom, and near the feed.

The limiting-flow operating lines approximate the separation well in Fig. 7-15. The success of a limiting-flow equivalent binary analysis is not always this good, but it is generally a good first approximation. The equivalent binary analysis, assuming that the nonkeys are at their limiting mole fractions on all stages, often can be used as an effective first analysis of a multistage multicomponent separation. It is also useful as a means of visualizing the stage-to-stage behavior of a separation. It should be noted, though, that the equivalent binary analysis necessarily underestimates the stage requirement for a given degree of separation.

Minimum reflux It is also instructive to consider the behavior of a multicomponent distillation under conditions of minimum reflux. At minimum reflux there must be at least one zone of constant composition of all components. Otherwise the addition of more stages must change the separation characteristics, and such a result is contrary to the concept of infinite stages at minimum reflux. If there is one zone of constant composition for all components above the feed, we can convince ourselves that there must be another such zone below the feed unless there is the equivalent of the tangent pinch of binary distillation above the feed or unless the feed is misplaced. If there is not a zone of constant composition below the feed, it must be possible to alter the separation characteristics by shifting some of the stages from the zone of constant composition above the feed to a point below the feed.

There are two possible locations for the zones of constant composition within

OK
 EXPT when the non keys are nondistributing → zone of constant comp migration from the feed to the center sections

the rectifying section and within the stripping section. The particular location depends upon the relative volatilities of the nonkey components. It should be recalled that for a binary distillation the zones of constant composition lie adjacent to the feed stage immediately above and immediately below. If there are no heavy nonkey components in a multicomponent distillation, the zone of constant composition above the feed will still be adjacent to the feed. Similarly, if there are no light nonkey components, the zone of constant composition below the feed will still be adjacent to the feed.

When heavy nonkey components are present, the zone of constant composition above the feed may move to a position higher in the rectifying section, partly between the feed and the distillate. Whether or not the zone will move to this new location depends upon whether the heavy nonkeys are *distributing* or *nondistributing* between the products at minimum reflux (Shiras et al. 1950). If one or more of the heavy nonkey components are nondistributing, they will appear at zero mole fraction in the distillate product, and the zone of constant composition above the feed will move away from the feed stage in order to allow the nondistributing heavy nonkey to die down toward zero mole fraction in the stages immediately above the feed. A distributing heavy nonkey will appear to a finite mole fraction in the distillate. If all heavy nonkeys are distributing, the zone of constant composition above the feed will remain immediately adjacent to the feed stage.

Similar reasoning holds for distributing and nondistributing light nonkeys and the location of the zone of constant composition below the feed.

The question of finding whether nonkey components are distributing or nondistributing at minimum reflux is explored further in Chap. 9. By far the most common situation is for the nonkeys to be nondistributing. A nonkey component may be distributing if it has a volatility very close to that of one of the keys or if the specified separation of the keys is not very sharp. A nonkey with a volatility intermediate between the keys also will be distributing.

Figure 7-16 shows a typical vapor-composition profile for a distillation such as our depropanizer example under conditions of minimum reflux. This is a case of nondistributing light and heavy nonkeys. The four zones correspond to those marked on the schematic of the column in Fig. 7-17. If there are nondistributing heavy and light nonkeys, the nature of the distillation dictates that the various nonkeys must necessarily be changing in mole fraction at the top, at the bottom, and on both sides of the feed point. Therefore, the zones of constant mole fraction of all components corresponding to a condition of minimum reflux and infinite stages can only occur midway in the rectifying and stripping sections.

Figure 7-18 displays the minimum reflux condition qualitatively on an equivalent binary McCabe-Thiele diagram. In zone A the heavy nonkeys decrease to their limiting mole fractions, the two keys increase, and there is also effective fractionation between the keys on an equivalent binary basis. Proceeding on upward in the tower past the zone of constant composition to zone B, the nondistributing light nonkeys begin to appear below the feed and the mole fractions of both keys decrease. This turns out to correspond to *reverse* fractionation, for as we proceed upward, the fraction of light key in the combined keys actually decreases. The operating points in

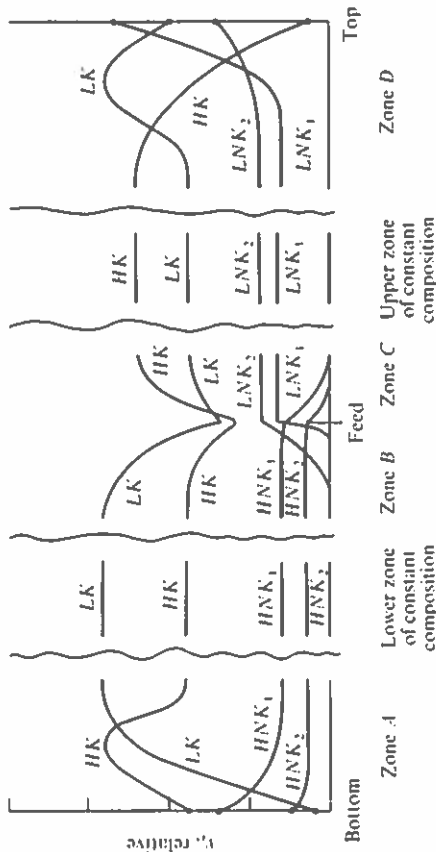


Figure 7-16 Typical vapor-composition profile for multicomponent distillation at minimum reflux.

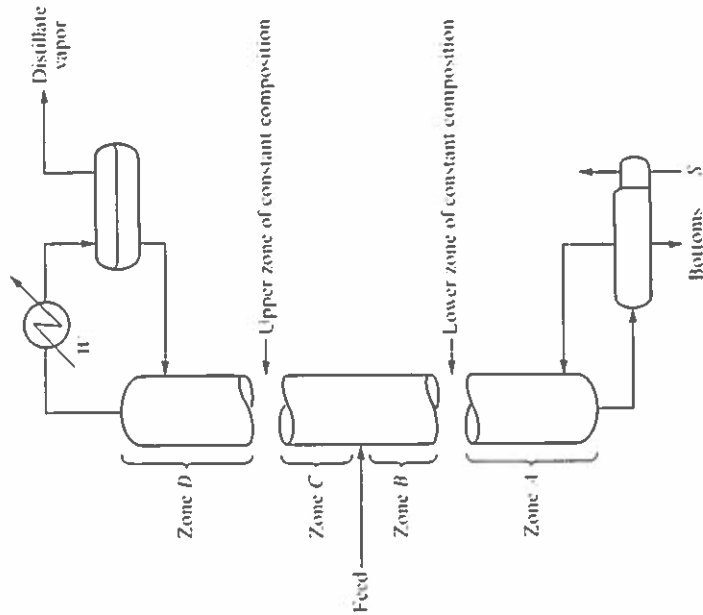


Figure 7-17 Operation of multicomponent distillation at minimum reflux.

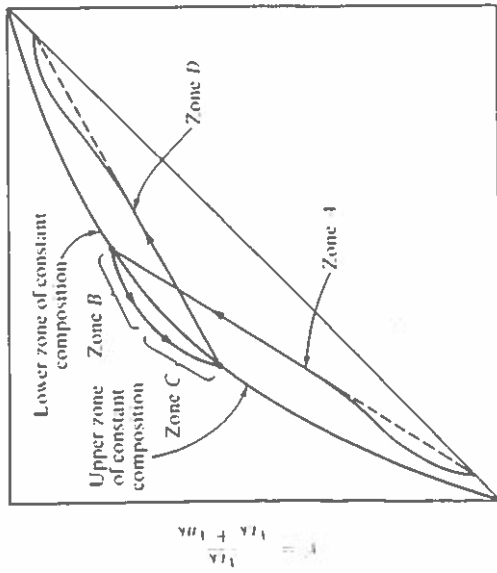


Figure 7-18 Equivalent binary fractionation at minimum reflux.

reverse distillation

zone B must lie to the upper left of the limiting operating line for the stripping section. This follows since the flow of combined keys has become less as the feed stage is approached from below, and L/V for the combined keys has therefore become more removed from 1.0. As a result the operating curve for zone B necessarily lies outside the equilibrium curve. Since the operating curve is above the equilibrium curve, the steps in zone B necessarily proceed downward. This situation is shown schematically in Fig. 7-19.

Analogous reasoning applies to zone C, where the nondistributing heavy nonkeys die out as we proceed upward and the fractionation continues in the reverse direction. We next reach the zone of constant composition above the feed, which corresponds to less light key on a binary basis than the zone of constant composition below the feed. From there we pass to zone D, where the light nonkeys increase upward and there is once again effective fractionation in the desired direction.

Extraction

Hanson et al. (1962) present a detailed solution for an isothermal extraction cascade which serves to separate acetone from ethanol by using two different solvents, chloroform and water, as the prime components of the two countercurrent liquid phases. The operation is shown schematically in Fig. 7-20, where it is postulated that equilibrium-staged contactings occur in a plate tower. The two solvents enter at

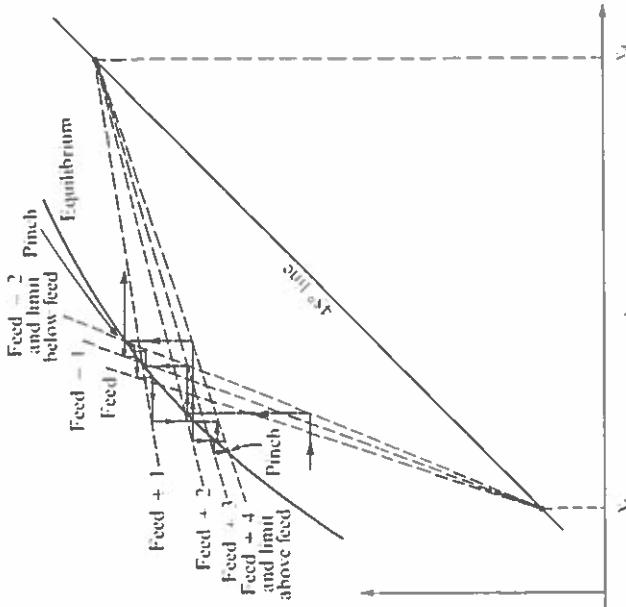


Figure 7-19 Example of "reverse distillation" of keys near feed stage at minimum reflux.

either end of the column, and the feed enters at a point such that there are five equilibrium stages above it and ten below it. The chloroform-rich phase flows downward, since the density of chloroform is greater than that of water. The solvent flow rates are high in comparison with the feed rate of acetone and ethanol on either side of the point and also to preserve a high degree of immiscibility between the phases with a consequent high separation factor for acetone and ethanol. As noted in Chap. 4, we can look upon one of the solvents as a substitute for extract reflux in an extraction process of the type more commonly encountered.

The behavior of the fractional-extraction process shown in Fig. 7-20 for separating ethanol from acetone can be understood in terms of a few qualitative facts concerning the phase equilibrium in this four-component system. In binary solutions preference for the two components correspond to a tendency toward immiscibility and a lack of high activity coefficients at infinite dilution for the various binary systems which can be formed from the four components in the present example.

Several facts are apparent from Table 7-3. First, there is obviously a strong "liking" of acetone and chloroform for each other. Activity coefficients less than 1.0 mean that there are negative deviations from Raoult's law and vapor pressures are

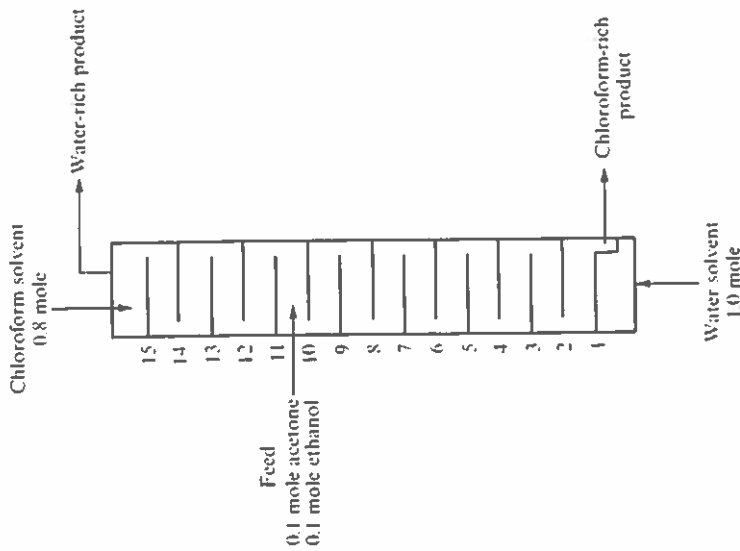


Figure 7-20 Fractional-extraction example.

less than predicted by ideal-solution theory. This is the result of hydrogen bonding between acetone and chloroform



while neither molecule hydrogen-bonds appreciably to itself.

The highest activity coefficients are between water and chloroform, indicating almost total immiscibility between those species. Thus water and chloroform serve effectively as prime components of each of the two counterflowing streams, which should be relatively immiscible in order to facilitate the operation of this process.

The next highest activity coefficients belong to the acetone-water binary. Thus acetone will tend to dissolve preferentially in a phase containing ethanol or, especially, chloroform rather than in a phase containing a large amount of water. Ethanol, on the other hand, shows roughly the same activity coefficients in either solvent, water or chloroform. Thus acetone will tend to concentrate in the chloroform phase, and ethanol will be left behind more than acetone in the water phase. Ethanol does show somewhat more preference for acetone than for either of the solvents, which is why there is a separation problem in the first place.

The composition profiles for the extraction column are shown in Fig. 7-21 for the chloroform-rich phase and in Fig. 7-22 for the water-rich phase. The stage numbering corresponds to Fig. 7-20; hence the left-hand sides of Figs. 7-21 and 7-22 refer

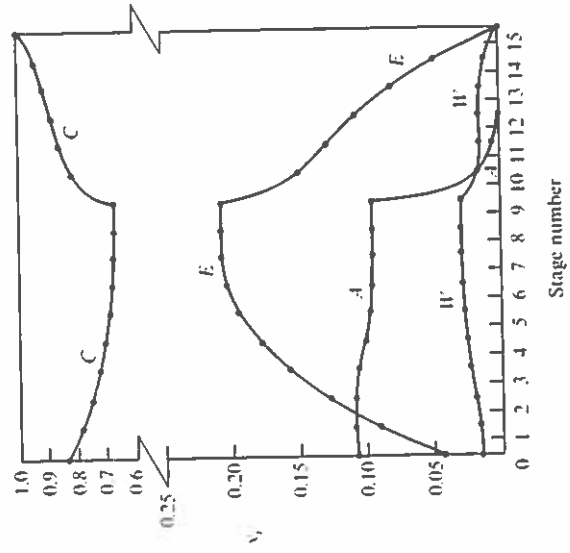


Figure 7-21 Composition profile for chloroform-rich phase. (Results from Hanson et al., 1962.)

Table 7-3 Activity coefficients at infinite dilution for binary solutions represented in fractional-extraction example

| Binary solution | Activity coefficient† | Binary solution | Activity coefficient |
|-----------------------|-----------------------|-----------------------|----------------------|
| Acetone in chloroform | 0.39 | Chloroform in acetone | 0.51 |
| Acetone in ethanol | 1.72 | Ethanol in acetone | 1.82 |
| Ethanol in chloroform | 5.0 | Chloroform in ethanol | 1.65 |
| Ethanol in water | 4.3 | Water in ethanol | 2.4 |
| Acetone in water | 6.5 | Water in acetone | 3.8 |
| Chloroform in water | 370 | Water in chloroform | 118 |

† Referred to Raoult's law.

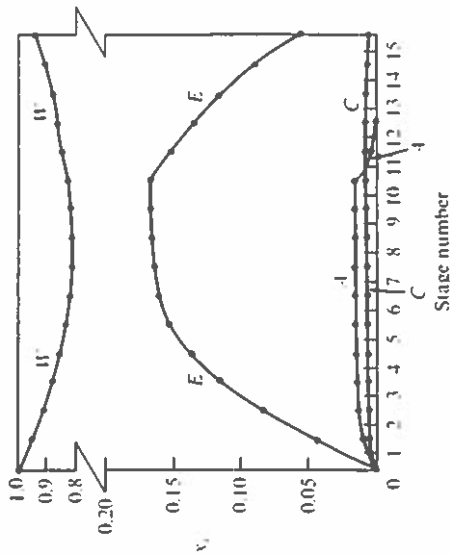


Figure 7-22 Composition profile for water-rich phase. (Results from Hanson et al., 1962.)

to the bottom, or acetone-rich, end of the column. The chloroform-rich phase flows from right to left on the composition diagrams, and the water-rich phase flows from left to right. The compositions shown in either diagram refer to points on a multidimensional four-component thermodynamic saturation envelope since we have postulated equilibrium between exit streams from a stage. In accord with Table 7-3, the solubility of acetone and chloroform in the water phase is low, while that of water in the chloroform phase is also low. The solubility of ethanol in both phases is about equal, as already noted, although ethanol does show some preference for the chloroform phase when there is a sizable acetone concentration in it. Both solvents constitute 60 percent or more of their respective phases; this is the result of the high solvent-to-feed ratio.

The solutes are carried up the column by the water phase. Acetone does not enter the water phase to any large extent; hence above (or to the right of) the feed, acetone quickly dies down to a very small concentration. This behavior is completely analogous to the dying out of a heavy nonkey above the feed in the previous multicomponent-distillation example. The heavy nonkey does not enter the upflowing vapor appreciably because of its low volatility, as reflected by a K value much less than 1.0; the acetone does not enter the water stream appreciably because of its low solubility in water compared with its solubility in chloroform.

Below (or to the left of) the feed, the acetone behavior is also similar to that of a heavy nonkey. Since more than 99 percent of the acetone must leave in the chloroform product, there must be a significant amount of acetone in the chloroform phase on all stages below the feed, and since acetone does have some solubility in water, albeit small, there must also be some acetone in the water phase on all stages below the feed. Because a mass separating agent (water) creates the counterflowing stream at the bottom, the flow rate of the chloroform-rich product is close to the flow rate of that phase within the column. There is no need for the acetone to build up to a higher

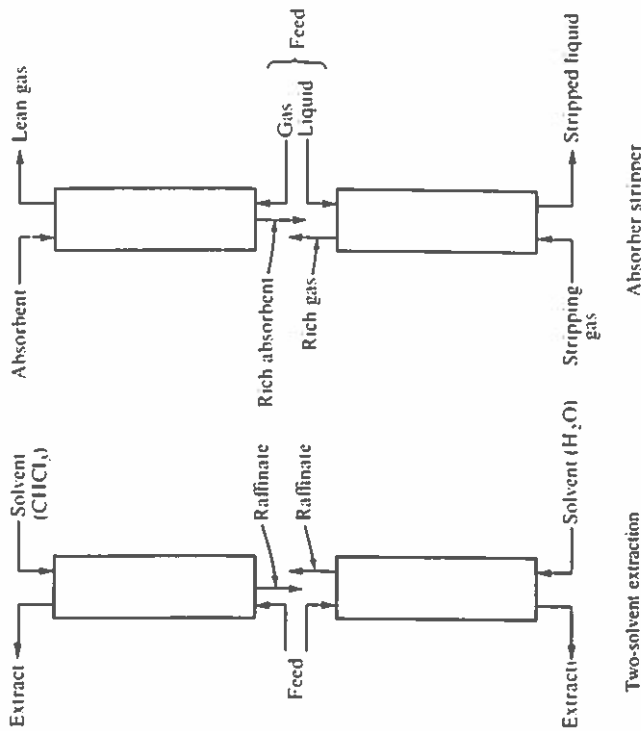


Figure 7-23 Analogy between two-solvent extraction and absorber-stripper.

concentration in the bottom raffinate product, as occurs for a heavy nonkey in distillation where $b < L$. Thus the acetone fraction does not curve upward on the bottom stages, as a heavy nonkey does in distillation.

Ethanol behaves more like a key component of a multicomponent distillation, but the other key against which it fractionates is the chloroform in one phase and the water in the other.

The ethanol composition profile below the feed is analogous to that for the solute in a single-section extraction column or in a stripping operation, as shown in the lower portion of Fig. 7-23. Stripping agent or solvent (water) is introduced at the bottom and serves to lower continuously the solute concentration in the liquid feed entering the top. The ethanol composition profile above the feed is analogous to the single-section extraction cascade or to the absorber shown in the upper portion of Fig. 7-23. Fresh absorbent or solvent (chloroform) enters the top and serves to lessen the solute concentration in the upflowing feed which enters at the bottom.

The acetone profile can, of course, be interpreted in the same way. The difference between the ethanol and acetone profiles is the result of the different distribution coefficients for these two solutes between the two solvents. Acetone has a greater preference for the chloroform phase and is highly nonvolatile in the absorber-

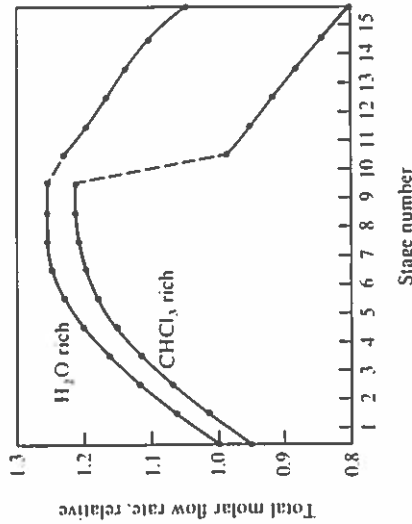


Figure 7-24 Total-flow-rate profile for extraction process. (Results from Hanson *et al.*, 1962.)

stripper analogy. Thus acetone is rapidly absorbed or extracted above the feed and dies down to a very low concentration, but below the feed it is not stripped out or extracted to any great extent; therefore the concentration of acetone in the downflowing phase is relatively unaffected. On the other hand, since ethanol has no strong preference for either phase, it is extracted appreciably but less rapidly than acetone above the feed and more than acetone below the feed.

The result of these phenomena is to give a water product out the top which contains about half the ethanol and very little acetone. Thus this acetone-ethanol separation produces a highly pure ethanol product, but there is only 58 percent recovery of ethanol.

Figure 7-24 shows the variation in total flow rates of the two phases with respect to the stage location. There is a trend producing higher flow rates near the feed and lower flows at either end of the column. This result is logical in view of our earlier conclusion regarding the effect of the degree of miscibility on total interstage flows. Ethanol tends to create miscibility in this system; indeed, the ternary system chloroform-ethanol-water probably exhibits a plait point at sufficiently high concentrations of ethanol. The degree of miscibility increases at high ethanol concentrations, the phase compositions become more similar, there is less discrepancy in the amount of any one component per unit amount of any other component in the two phases, and—since the net product flow of any component must be constant in either section of the column—total flows increase toward regions of high ethanol concentration.

One should also note from Fig. 7-24 that most of the feed enters the chloroform phase rather than the water phase. Again, the selective solubility of acetone in chloroform exerts itself and the presence of acetone in the chloroform phase creates a more favorable medium for ethanol in that phase.

This fractional extraction can also be interpreted on an equivalent binary operating diagram. Figure 7-25 is an equivalent binary operating diagram on which the fraction of acetone in the combined acetone + ethanol in the chloroform phase is

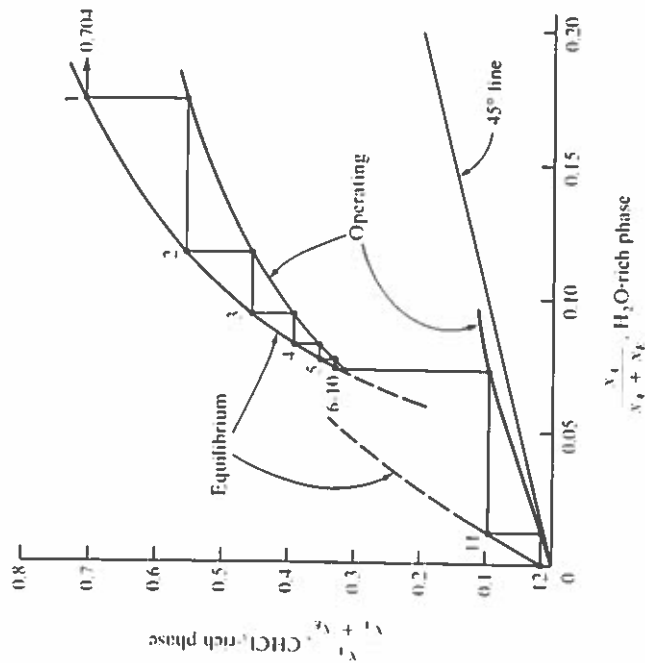


Figure 7-25 Equivalent binary operating diagram for extraction process, rectilinear coordinates.

plotted against the fraction of acetone in the combined acetone + ethanol in the water phase. Figure 7-26 is the same plot on logarithmic coordinates, which serve to expand the low-concentration region.

The equilibrium curves in Figs. 7-25 and 7-26 are smooth above and below the feed, but the abrupt changes in slopes of the composition profiles at the feed point cause a discontinuity in the equilibrium curve. This was also noted for the multicomponent distillation example (Fig. 7-15). The upper operating curve (bottom column section) in Fig. 7-25 is concave downward since the intersection with the 45° line is at the upper end of the plot ($x_A = 0.704$) and combined flows of acetone and ethanol increase toward the feed. The lower operating curve (top column section) is also concave downward since the intersection with the 45° line is at the lower end of the plot, and the combined flows of acetone and ethanol increase toward the feed. The lower operating curve lies closer to the 45° line than the upper operating curve does. This is the result of the higher combined solubility of acetone and ethanol in chloroform than in water which gives a higher reflux ratio $[(A + E \text{ in downflowing chloroform}) / (A + E \text{ in chloroform product})]$. There are enough stages in the bottom column section to produce a severe pinch near the feed. Lowering the feed-injection stage would produce a still more acetone-free ethanol product without lessening the ethanol recovery significantly.

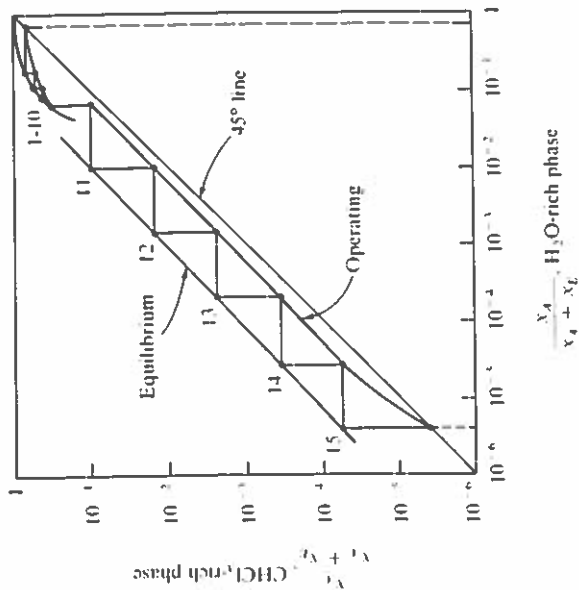


Figure 7-26 Equivalent binary operating diagram for extraction process, logarithmic coordinates.

Extractive and Azeotropic Distillation

Azeotropic and extractive distillations involve the addition of a third component to a binary system to facilitate the separation of the system by distillation. The added component modifies liquid activity coefficients and hence the vapor-liquid equilibria of the other two components in a favorable direction. The third component and the energy input to the reboiler are two different separating agents in these processes.

A typical extractive distillation process is shown in Fig. 7-27. The added component (or *solvent*) is relatively nonvolatile and is present to a high concentration (typically 65 to 90 mole percent) in the liquid within each stage. It is necessary to add the solvent near the top of the column since its lack of volatility will not produce a sufficient solvent concentration to modify the equilibrium in the desired way above the point of introduction. A few stages above the solvent entry point serve to reduce the contaminant level of solvent in the distillate product. The solvent is separated from the bottoms product in a second distillation tower.

The system shown in Fig. 7-27 accomplishes the separation of isobutane from 1-butene using furfural as a solvent (Zdonik and Woodfield, 1950). The relative volatility of isobutane to 1-butene in the presence of 80 mol % furfural is 2.0 at 52°C, as opposed to a relative volatility of 1.16 at the same temperature in the absence of the solvent. Furfural is a polar molecule

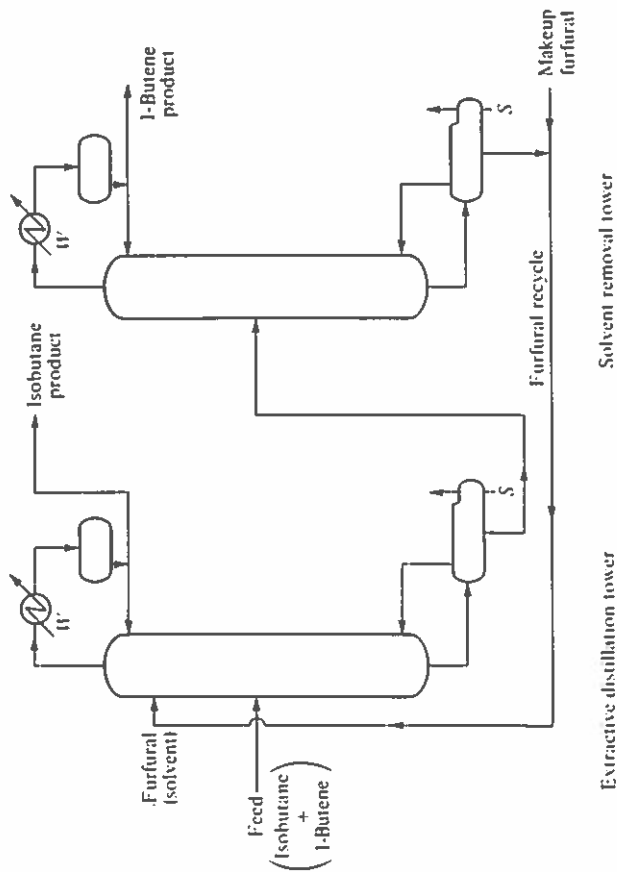
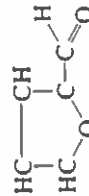


Figure 7-27 Extractive distillation for separation of isobutane from 1-butene using furfural as solvent. (Adapted from Zdonik and Woodfield, 1950, p. 647, used by permission.)

the C—O—C and C=O bonds being dipoles. The furfural molecule exerts a selective attraction on 1-butene through dipole-induced dipole interaction with the olefinic bond. In the absence of solvent, the activity coefficients of isobutane and 1-butene are nearly equal to 1.0, and the relative volatility simply represents the ratio of the vapor pressures of these species, which are also not very different from each other. At high dilution in furfural, isobutane at 52°C has an activity coefficient of 1.2, while 1-butene has an activity coefficient of only 6.2. Thus the addition of a high concentration of furfural increases the volatilities of both hydrocarbons since the polar furfural is a different type of molecule, but it increases the volatility of 1-butene the least because the polar group preferentially polarizes the double bond.

The solvent in extractive distillation is often chosen to be much less volatile than the species being separated in order to facilitate recovery of the solvent in the solvent-removal tower. Furfural, for example, is over two orders of magnitude less volatile than isobutane and 1-butene. As a result, very little furfural appears in the vapor phase, and the furfural molar flow in the liquid is effectively constant at some high value from stage to stage below the point of solvent feed. The other two components take up the difference and would give a composition profile the same as that for a binary distillation (Fig. 7-5), except that the mole fractions add up to $1 - x_{\text{furf}}$. Above the solvent feed, the furfural would die out rapidly.

A typical azeotropic distillation process is shown in Fig. 7-28. The added com-

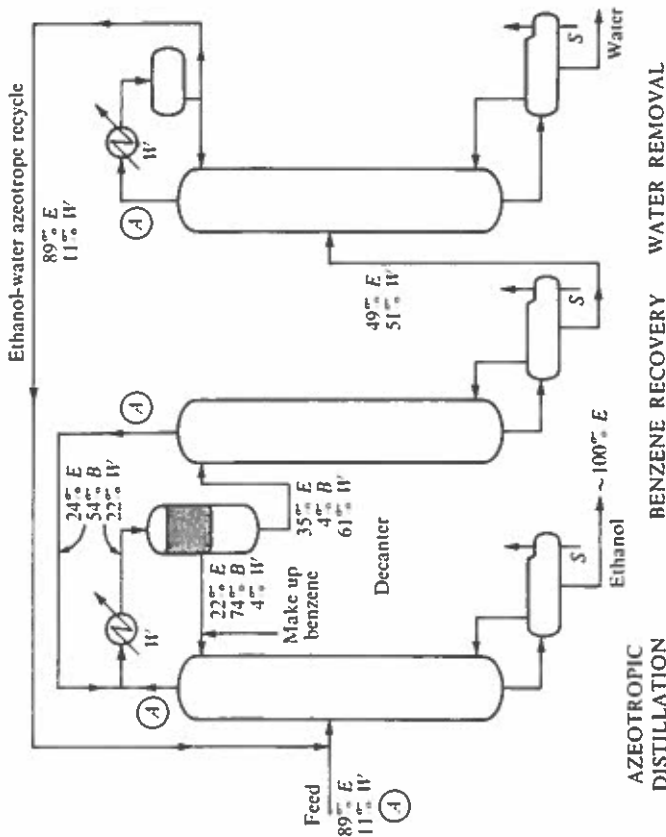


Figure 7-28 Azeotropic distillation for separation of ethanol from water using benzene as entrainer. Compositions are given in mole percent. (Adapted from Zdonik and Woodfield, 1950, p. 652; used by permission.)

ponent (or entrainer) in this case is relatively volatile and forms an azeotrope with the component to be taken overhead. The entrainer modifies the activity coefficients of the compounds being separated and thereby makes it possible to separate a feed that was originally a close-boiling mixture or a binary azeotrope. The entrainer emerges overhead from the column but must enter the liquid phase sufficiently to affect the equilibria of the other components; hence it must have a volatility comparable to that of the feed mixture. The azeotrope formed by the entrainer is frequently heterogeneous; i.e., it is composed of two immiscible liquid phases when condensed. The heterogeneous nature of the azeotrope facilitates separation of the products from the entrainer.

An azeotropic distillation process (Zdonik and Woodfield, 1950) for the separation of the water from 89 mol % (pure-component basis) ethyl alcohol using benzene as entrainer is shown in Fig. 7-28. The 89 mol % ethanol corresponds to the azeotrope in the ethanol-water binary system and is the highest ethanol enrichment that can be achieved by ordinary distillation. Near-azeotropic compositions are present at points marked A in Fig. 7-28. All towers operate at atmospheric pressure. The presence of the relatively nonpolar benzene entrainer serves to volatilize water (a

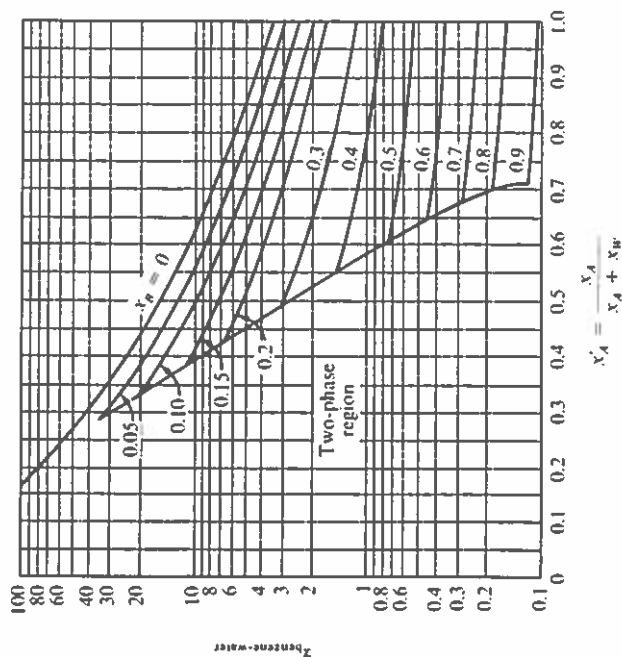
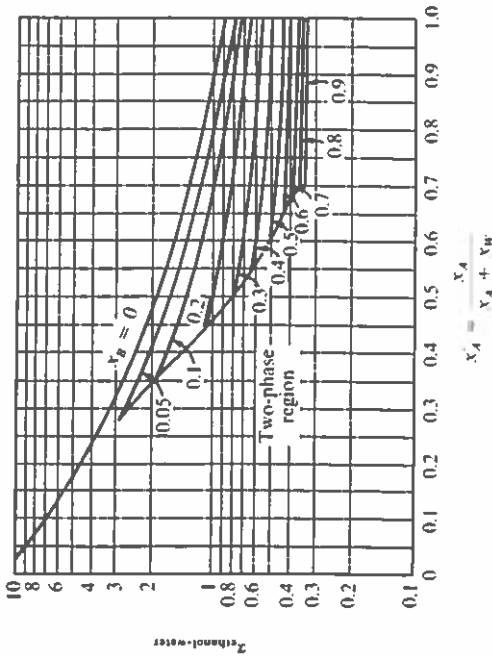


Figure 7-29 Vapor-liquid equilibrium data for ethanol-water-benzene. (Adapted from Robinson and Gilliland, 1950, pp. 314, 315; used by permission.)

highly polar molecule) more than it volatilizes ethanol (a moderately polar molecule). Because benzene volatilizes water preferentially, it enables us to obtain a pure ethanol product that cannot be obtained from a binary distillation because of the binary azeotrope. Benzene forms a ternary minimum-boiling azeotrope with water and alcohol at atmospheric pressure.

Figure 7-29 shows the relative volatility of alcohol to water as a function of composition and the relative volatility of benzene to water as a function of composition, as reported by Robinson and Gilliland (1950). The composition parameter is the equivalent binary mole fraction of ethanol in the total ethanol + water. Curves are plotted for different levels of benzene in the liquid. Note that two immiscible liquid phases are formed at low ethanol contents. Ethanol promotes miscibility since it is the component of intermediate polarity. The presence of benzene decreases the ethanol-water relative volatility, and the presence of ethanol reduces the benzene-water relative volatility.

The first tower in Fig. 7-28 forms the ternary azeotrope as an overhead vapor. Nearly pure alcohol issues from the bottom. The ternary azeotrope is condensed and splits into two liquid phases in the decanter. The benzene-rich phase from the decanter serves as reflux, while the water-ethanol-rich phase passes to two towers, one for benzene recovery and the other for water removal. The azeotropic overheads from these succeeding towers are returned to appropriate points of the primary tower.

Figure 7-30 shows a composition profile for the azeotropic distillation column in the process of Fig. 7-28. For the situation they considered, the feed to the azeotropic distillation tower was 89 mol ethanol and 11 mol water per hour, the reflux rate 345 mol/h, and the bottoms rate 82.7 mol/h. Benzene enters the tower by means of the reflux. In the presence of the high concentration of benzene in the rectifying section, the relative volatility of ethanol to water is substantially less than 1, and so the ethanol grows at the expense of water as we go lower in the column toward the feed. Benzene, in the rectifying section, has a relative volatility intermediate between those of water and ethanol. Hence it increases downward where it is fractionating primarily against water and decreases downward where it is fractionating primarily against ethanol.

On the bottom stages of the column there is virtually no water. From Fig. 7-29 (ratio of the two α 's) the relative volatility of benzene to ethanol in the absence of water is 1.6 at 40 mol % benzene, 2.8 at 20 mol % benzene, and 4.1 near 0 mol % benzene. Hence, as far as benzene and ethanol are concerned, the behavior in the stripping section is equivalent to that in a binary distillation, benzene being the more volatile component. Thus the benzene dies out and ethanol grows as we go downward toward the bottom of the column.

The behavior of benzene and ethanol below the feed in Fig. 7-30 is characteristic of a binary distillation with a misplaced feed. It appears at first glance that there are many more stages below the feed than are needed, since from stage 10 through stage 21 the benzene and ethanol concentrations change hardly at all. This would correspond to these stages being located in a *pinch* zone at the intersection of the lower operating line and the equilibrium curve in a binary distillation. In the binary distillation we would gain by lowering the feed stage.

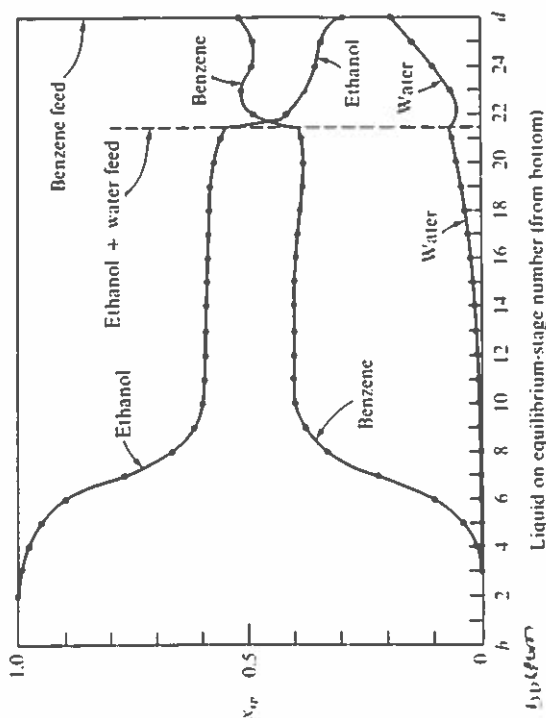


Figure 7-30 Composition profile for azeotropic distillation of ethanol and water with benzene as entrainer. (Results from Robinson and Gilliland, 1950.)

In azeotropic distillation having this pinch zone for the ethanol and benzene concentrations is very useful, however, and is in fact necessary for obtaining nearly pure alcohol in the column under consideration. In the pinch zone (stages 10 to 21) the water concentration drops markedly. As can be seen in Fig. 7-29, the relative volatility of ethanol to water is 0.5 at the pinch-zone composition, whereas it is 0.9 or higher (much closer to unity) in the absence of benzene. Hence water can be stripped out of the product ethanol in a reasonable number of stages only in the presence of a high benzene mole fraction. The stages in the ethanol-benzene pinch zone all necessarily have a high benzene concentration. Thus providing the pinch zone is necessary in this tower in order to give an opportunity for stripping water out of the high-purity (99.9 mol %) product ethanol.

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PROBLEMS

- 7-A₁ In Fig. 7-11 y_{C_1} is greater than y_{C_2} on the stages above the feed, but x_{C_1} is less than x_{C_2} on most of the stages above the feed in Fig. 7-12. Why?
- 7-B₁ Draw qualitatively an equivalent binary McCabe-Thiele diagram, a temperature-profile, and a composition-profile diagram for a multicomponent distillation in which there are no light monkey components.
- 7-C₂ Sketch the vapor or liquid mole fraction profile of a trace amount of a sandwich component, intermediate in volatility between the two main key components in a multicomponent distillation. Explain the shape of the profile. *Note:* One approach to this problem is to derive the K 's for the two key components as a function of position from Figs. 7-11 and 7-12 and then use the fact that the K of the sandwich component is intermediate between those of the keys.
- 7-D₂ Often a multicomponent distillation tower is operated to provide one or more sidestream products in addition to the usual overhead distillate and bottoms products. Consider cases where the sidestreams are withdrawn directly from the column, with no sidestream stripper or sidestream rectifier. A sidestream will contain a high fraction of one of the intermediate-boiling components, and it will be desirable to provide for a high purity of that component in the sidestream. For maximum sidestream purity, should the sidestream be withdrawn as liquid or as vapor? Does your answer depend upon whether the sidestream is withdrawn from a plate above or below the feed? Explain briefly.
- 7-E₂ Smith (1963, pp. 424-438) presents a stage-to-stage solution of an extractive distillation process separating methylcyclohexane from toluene using phenol as a solvent. This is interesting as a case of extractive distillation where the solvent has an appreciable volatility, albeit one that is still lower than the volatilities of the keys. Equilibrium data for this system are shown in Fig. 7-31, which gives the relative volatilities of methylcyclohexane to toluene and the relative volatility of phenol to toluene as functions of the equivalent binary mole fraction of methylcyclohexane and the mole fraction of the solvent phenol. The solution is derived for an extractive distillation tower of 20 equilibrium stages plus a reboiler and a total condenser, with a feed of 50 mol % methylcyclohexane and 50 mol % toluene entering above the seventh stage from the bottom and a 99 mol % phenol solvent feed entering above the twelfth stage from the bottom; 2.3 mol of phenol is fed per mole of hydrocarbon feed and the overhead reflux ratio r/d is 8.1. The mole fraction of each component in the liquid phase leaving each stage is shown in the composition profile of Fig. 7-32.
- (a) Which component is preferentially volatilized by the phenol solvent and why?
- (b) Considering the three different sections of the column—below both feeds, between feeds, and above both feeds—indicate the function of each section in relation to the overall process objectives.
- (c) Contrast the amount of separation of methylcyclohexane from toluene occurring above the top

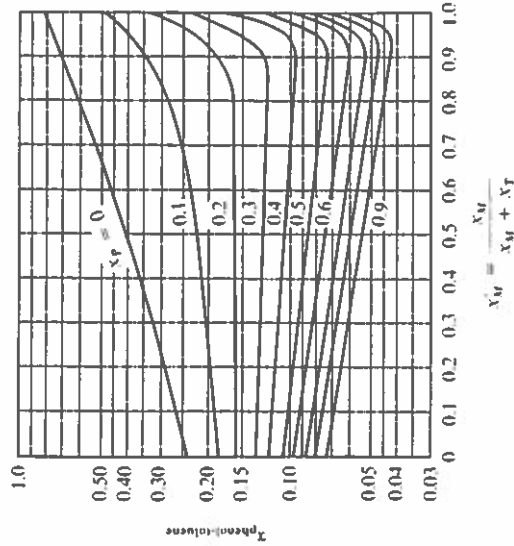
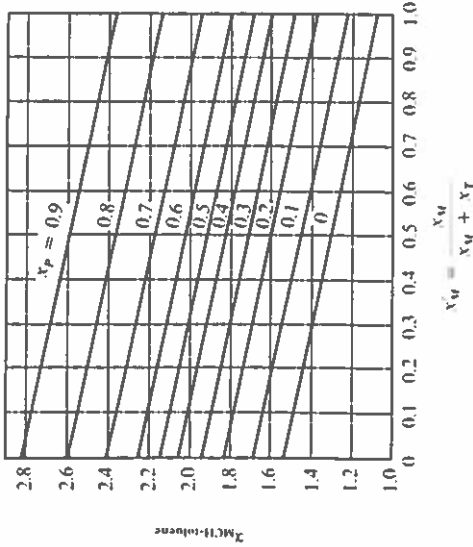


Figure 7-31 Vapor-liquid equilibrium data for methylcyclohexane-toluene-phenol. (Adapted from Smith, 1963, pp. 428, 429, used by permission.)

feed with the amount of separation of these components occurring below the top feed. Explain the difference. Why is there a relatively large number of stages above the top feed?

(d) For each of the three column sections indicate whether phenol behaves like a key component, a light monkey, or a heavy monkey. Why is there an abrupt change in the mole fraction of phenol in the liquid at the hydrocarbon feed point even though the phenol mole fraction does not change much in the adjoining stages?

(e) What change in column design would you make if you wanted to obtain a higher-purity overhead methylcyclohexane product?

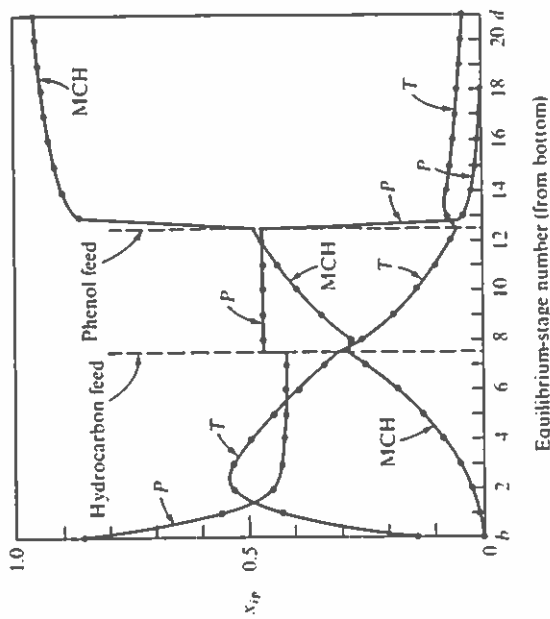


Figure 7-32 Composition profile in extractive distillation of methycyclohexane and toluene with phenol as solvent. (Results from Smith, 1963.)

7-F₂ Smith (1963, pp. 408-420) presents a detailed stage-10-stage calculation for an azeotropic distillation of *n*-heptane and toluene, using methyl ethyl ketone (MEK) as the entrainer. The entrainer-to-hydrocarbon feed molar ratio is 1.94, half of the entrainer being introduced with the feed above the tenth equilibrium stage from the bottom and the other half being introduced above the sixth equilibrium stage from the bottom. Equilibrium data for this system as presented by Smith are shown in Fig. 7.33 and are plotted as relative volatilities of heptane to toluene and of MEK to toluene as functions of the mole fraction of toluene and the mole fraction of MEK. This system does not form two immiscible liquid phases in the reflux drum, as the water-ethanol-benzene did. The tower contains 16 equilibrium stages, a total condenser, and a reboiler. The overhead reflux ratio r/d is 1.50. The composition profile for this situation is shown in Fig. 7-34.

- (a) Which component is preferentially volatilized by the MEK entrainer and why?
 - (b) Considering the three different sections of the column—below both feeds, between feeds, and above both feeds—indicate the function of each section in relation to the overall process objectives.
 - (c) In the water-ethanol-benzene system (Figs. 7-28 and 7-30) the benzene entrainer entered the column only through the reflux stream to the azeotropic distillation column. Would that form of adding MEK be suitable in the present system? Explain.
 - (d) Why is a portion of the MEK added to the column as a second feed below the point of the main hydrocarbon feed? Why could the water-ethanol-benzene azeotropic distillation be operated without such a second feed of entrainer?
 - (e) The mole fraction of MEK in the liquid falls going from stage to stage upward in the zone between the feeds, while the mole fraction of MEK rises going from stage to stage upward in the zone above the feeds. Explain this difference.
- 7-G₂ The Solvay process, developed to economic fruition by Ernest and Alfred Solvay in 1861 to 1872, has for many years been the source of most of the soda, Na_2CO_3 , produced in the world. The process is an excellent example of the recovery and recycle of materials in order to minimize requirements for makeup reactants.

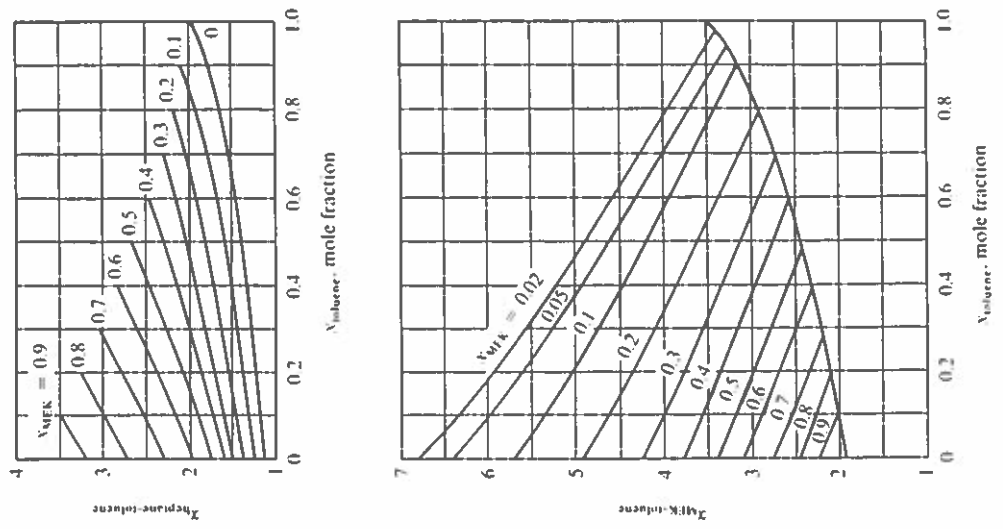


Figure 7-33 Vapor-liquid equilibrium data for *n*-heptane-toluene-methyl ethyl ketone. (Adapted from Smith, 1963, pp. 414, 415; used by permission.)

The Solvay process uses as feeds (1) a sodium chloride-rich brine (natural brine, dissolved rock salt, or even concentrated seawater) and (2) limestone rock, CaCO_3 . The process focuses on the reaction of ammonium bicarbonate with the sodium chloride of this brine in concentrated aqueous solution. Of the various compounds which can be formed from the various ions present (sodium, ammonium, chloride, bicarbonate), the least soluble is sodium bicarbonate. The sodium bicarbonate is made to precipitate out of solution, is filtered and washed, and is then calcined (heated) to cause it to decompose into sodium carbonate, with the release of carbon dioxide and water vapor.

The main contribution of the Solvays to the process was to cause the ammonium bicarbonate to be formed in place in a highly concentrated brine solution by the successive absorption of ammonia and then carbon dioxide into the solution. It was also economically necessary to provide for a high degree of

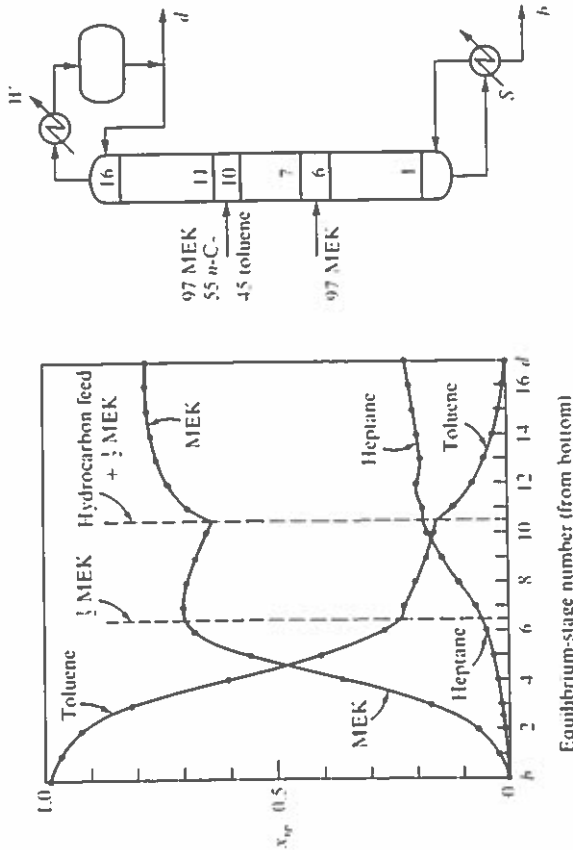


Figure 7-34 Composition profile for azeotropic distillation of *n*-heptane and toluene with MEK as entrainer. (Results from Smith, 1963.)

recovery of the ammonia for recycle, to minimize purchases of relatively expensive ammonia as fresh feed. Ammonia recovery is accomplished by calcining the limestone to form lime, CaO, and carbon dioxide:



The ammonium chloride-rich solution remaining after the precipitation of sodium bicarbonate is treated with the lime to free ammonia, which can then be recovered. The by-product of this step is CaCl₂, which is either sold or discarded with unreacted NaCl:



The carbon dioxide from the limestone calcination is used as a portion of the carbon dioxide required as carbonating agent to form ammonium bicarbonate in the ammoniated NaCl brine. Additional carbon dioxide comes from the calcination of sodium bicarbonate.

If there were to be more complete ammonia recovery and pure feeds, the overall stoichiometry of the process would correspond to



The heart of the process is the two countercurrent gas-liquid contacting towers shown in Fig. 7-35. The carbonating tower receives as feed an ammoniated sodium chloride-rich brine, known as *green liquor*. This feed typically contains about 5 mol/L NH₃, 4.5 mol/L NaCl, and 1 mol/L CO₂. The CO₂ in the ammoniated brine entered with some of the ammonia-rich gases returned from various places to the ammonia absorber. The carbonating gas typically contains 56 mol % CO₂, the remainder being mostly nitrogen. The carbonating tower is equipped with cooling coils on the bottom stages to remove the heat of the reaction forming ammonium carbonate and bicarbonate. The cooling-water flow and the area of the coil are adjusted to give a temperature profile like that shown in Fig. 7-36. The pressure is maintained at

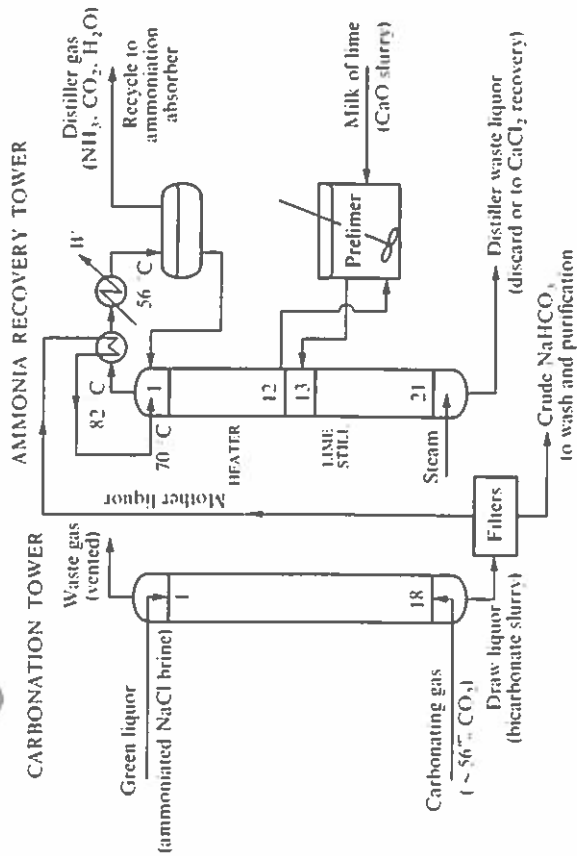


Figure 7-35 Brine-carbonation tower and ammonia-recovery tower in the Solvay process.

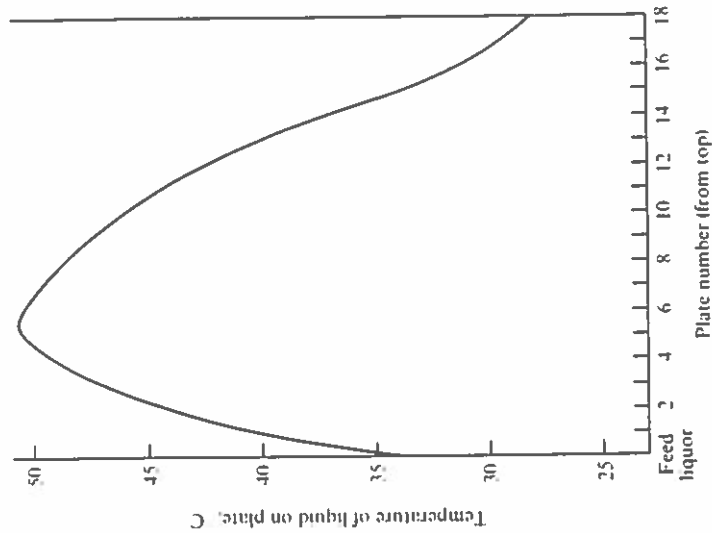


Figure 7-36 Temperature profile for brine-carbonation tower. (Data from How, 1942.)

about 340 kPa. As the carbon dioxide is absorbed, it first reacts with ammonia to form ammonium carbonate



The ammonium carbonate reacts with additional CO₂ to form bicarbonate



The ammonium bicarbonate then precipitates the less soluble sodium bicarbonate by reaction with the brine



The solubility of sodium bicarbonate is about 1.2 mol/L, so an appreciable amount of it remains in solution. The reactions forming ammonium carbonate, ammonium bicarbonate, and sodium bicarbonate all take place in the carbonating tower, and precipitated NaHCO₃ emerges as a slurry in the bottoms liquid. Figure 7-37 shows a liquid-phase composition profile for the carbonation tower. The diagram is based upon actual plates, not equilibrium stages, and the data are real plant data.

The ammonia-recovery tower is generally run at atmospheric pressure and consists of two portions called the *heater* and the *lime still*. The feed liquor enters the top heater section and passes down the tower. At a point approximately halfway down the tower (plate 12 in Fig. 7-35) all the downflowing liquid is drawn off to a large agitated vessel, known as the *prelimer*, where it is mixed with milk of lime (an aqueous slurry of the CaO produced in the lime kiln) and is held until the reaction of NH₃Cl with CaO (see above) occurs substantially to completion. The overflow liquid from the prelimer reenters the tower and flows downward through the lime still. Live steam is introduced at the bottom, and the vapors rise through both

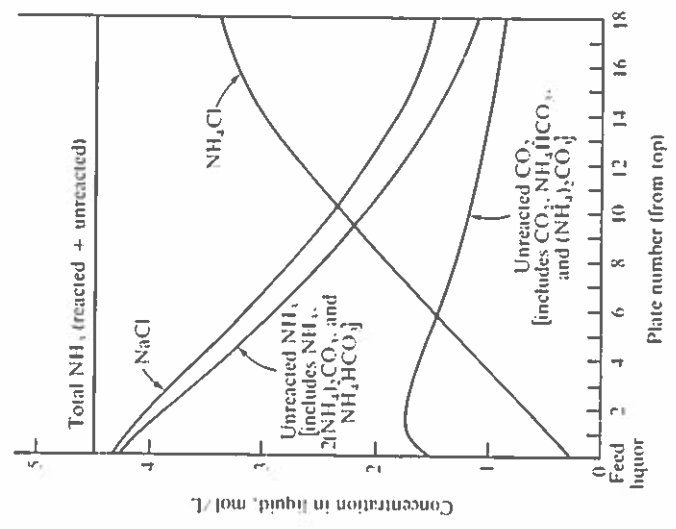


Figure 7-37 Liquid composition profile for brine-carbonation tower. (Data from Hou, 1942.)

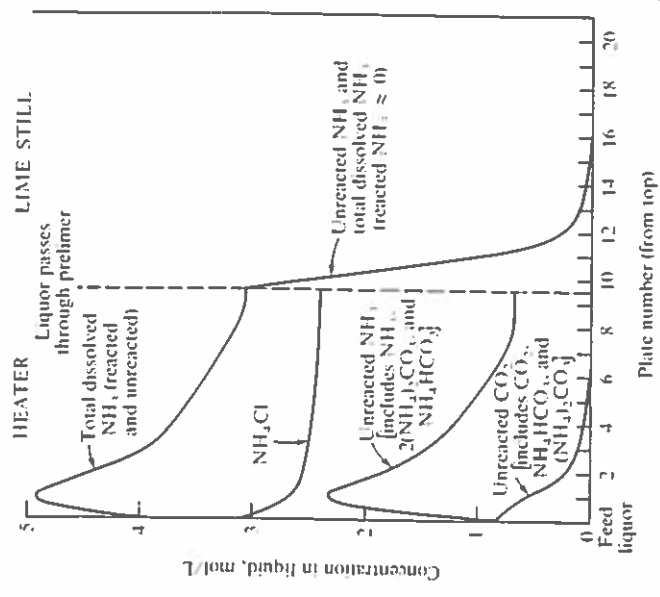


Figure 7-38 Composition profile for ammonia-recovery tower. (Data from Hou, 1942.)

sections of the column to a partial condenser overhead, which produces a gas (containing NH₃, CO₂, and water vapor) and a reflux stream. The gaseous product is the main gas stream fed to the absorbers for ammoniating the original brine. Figure 7-38 shows a liquid-phase composition profile for the ammonia recovery tower. Again, the diagram is based upon real plant data.

Figure 7-39 shows vapor-liquid equilibrium data for partial pressures of NH₃ and CO₂ over solutions of these gases in water. The equilibrium would be altered considerably by the high content of other salts in the Solvay process solutions, but the qualitative trends should remain the same.

- Make a simple schematic flow scheme of the entire Solvay process on the basis of the description given.
- In the Solvay process it is important that the brine be ammoniated first and then subsequently be carbonated. Why isn't the reverse procedure, absorbing the CO₂ into the brine first and then absorbing the NH₃ second, workable?
- What is the main function of the heater section of the ammonia-recovery tower (consider your answer carefully)? What is the main function of the lime-still section?
- What are effectively the key components in the heater section of the ammonia-recovery tower? In the lime-still section?
- Is the sodium bicarbonate precipitated out primarily in the top or the bottom portion of the carbonating tower, or is it formed to about the same amount on each stage?
- What specifically is the main benefit to the process of the countercurrent operation of the carbonating tower? Of the countercurrent operation of the ammonia-recovery tower?
- Why is the total NH₃ (reacted + unreacted) concentration in the carbonating tower essentially constant from plate to plate? Suggest a specific cause for the decrease in NH₄Cl concentration from plate to plate downward in the heater section of the ammonia-recovery tower.
- In most countercurrent absorbers the concentration of the transferring solute in the liquid phase

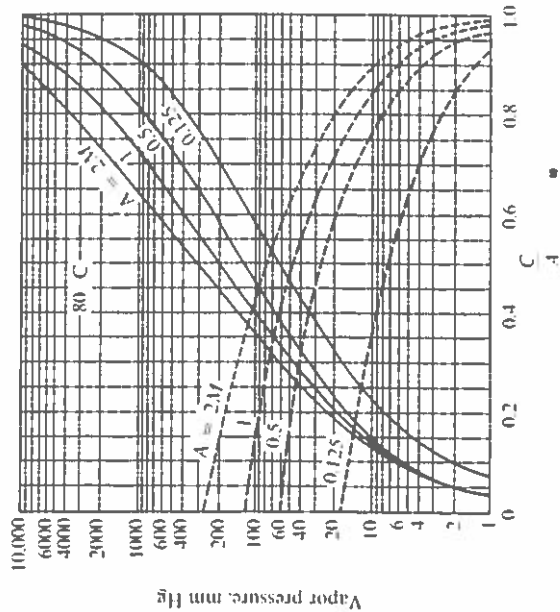


Figure 7-39 Vapor-liquid equilibrium data for solutions of CO_2 and NH_3 dissolved in water at 80°C ; solid curves = CO_2 partial pressure; dashed curves = NH_3 partial pressure, A = moles per liter of NH_3 in solution, and C = moles per liter of CO_2 in solution. (Adapted from Kreyerlein, 1949, p. 205, used by permission.)

decreases from plate to plate going upward in the column. This is not the case for the carbonating tower. Explain why the CO_2 concentration increases from plate to plate going upward in this column.

- (j) The unreacted NH_3 concentration in the liquid of the ammonia recovery tower is higher in the liquid leaving the top plate than it is in the feed liquor. How can this be?
- (j) The unreacted ammonia concentration in the liquid seems to drop asymptotically to a finite lower limit in the lower part of the heater section. What factor would set this lower limit?
- (k) Sketch operating diagrams for each of the towers.
- (l) A serious water-pollution problem results from Solvay plants. This, plus the increased availability of mined natural trona, has led to the closing of several Solvay-process plants in recent years. What is the source of the water-pollution problem from the Solvay process?

7-11 The trays and downcomers of a distillation column are usually metallic and are therefore good conductors of heat. Suppose that heat transfer occurs across the metal wall of the downcomers of a column between the vapor rising up toward a plate and the liquid leaving that plate. Neglecting any effects on tower capacity (tendencies toward flooding, etc.), will this heat transfer have any effect on the degree of separation of a given feed provided by a fixed number of plates at a fixed reflux ratio? If so, will it serve to improve the degree of separation or to lessen it? Why? Will the same conclusions apply to heat transfer across the metal of a plate itself between the vapor rising to the plate and the liquid on the plate? Why?

7-12 Multicomponent distillation columns from which sidestreams are withdrawn frequently use sidestream strippers, of the sort shown in Fig. 7-40. This is common practice, for example, in the primary fractionation of crude oil. What is the purpose of the sidestream strippers? Why can't this purpose be accomplished by the main column?

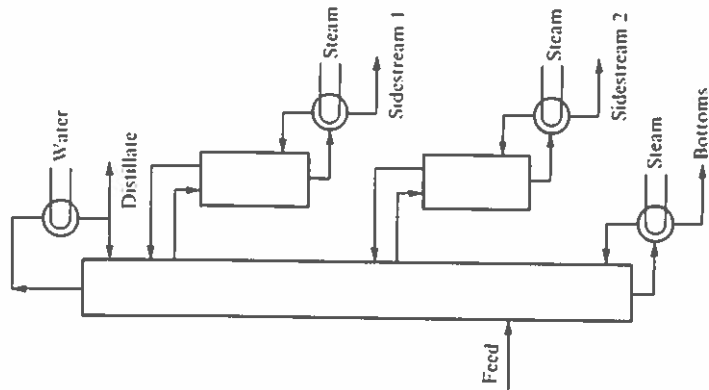


Figure 7-40 Multicomponent distillation column with sidestream strippers.

7-13 Draw a qualitative yx diagram for a single-solute absorber developing an internal temperature maximum. Assume that the isothermal equilibrium relationship is relatively linear. What factor sets the minimum flow of absorbent liquid to accomplish a given separation?