chapter 8

Unsteady-State Stage Operations

The calculation methods developed in the previous chapters have applied to steady-state operation in which the compositions and flow rates did not vary with time. An unsteady-state or transient process involves changes of conditions with time. There are many transient operations in chemical processing. All batch mass-transfer operations involve a change in composition with time. Although the continuous stage operations are assumed to be at steady state for calculation, the question of starting the equipment naturally arises.

Start-up of Continuous Equipment. In the start-up of multistage equipment compositions and flow rates may vary with time. The length of time after start-up required to reach a steady state is an important consideration in process operation. The time depends upon the time of passage of the two phases through the equipment and upon the rate of mass transfer. The time of passage depends upon the volume of material held up in the equipment and upon the flow rates.

In the start-up of a distillation column, feed is supplied to the column, where it runs down to the still and is vaporized. The vapor rises to the condenser, where it is condensed and returned to the column. Frequently a distillation column is started up at total reflux. It is run at total reflux for a time sufficient to allow the distillate composition to approach that desired for steady-state operation. The time for this period can be predicted approximately. Once the distillate composition is achieved at total reflux, the distillate and bottom products may be withdrawn and feed added to complete the transition to steady-state operation.

There will also be a transient period at the start-up of a simple countercurrent cascade, such as in extraction or absorption. The length of this period will depend upon the flow rates of the two phases, the hold-up volume of the equipment, and the rate of approach to equilibrium. The transient period may range from minutes in small equipment to several hours in large-scale installations, to several months in some special applications.

Batch Operations. When the quantity of material to be processed is small, batch methods are often used. Although the trend in the chemical process industry is toward continuous processing wherever possible, batch operations are still very widely used.

Many batch operations can be calculated using methods developed in earlier chapters. For example, a single-stage batch operation, such as the extraction of coffee from the grounds into a hot-water phase, can be calculated assuming equilibrium between the two phases before they are separated. The two phases (initially pure water and ground coffee) are mixed and undergo composition changes with time. The time required to reach equilibrium is an important process variable. It will depend upon the rate of mass transfer and upon the degree of contact between the phases. The composition of the two product phases in any batch single-stage process can be calculated by methods developed in earlier chapters if the two phases are allowed to remain in contact until all of one phase is in equilibrium with all of the other phase. On the other hand, in some cases one phase may be added or withdrawn during the process, as in differential distillation.

Differential Distillation. In batch distillation from a single stage a liquid is vaporized, and the vapor is removed from contact with the liquid as it is formed. Each differential mass of vapor is in equilibrium with the remaining liquid. The composition of the liquid will change with time, since the vapor formed is always richer in the more volatile component than the liquid

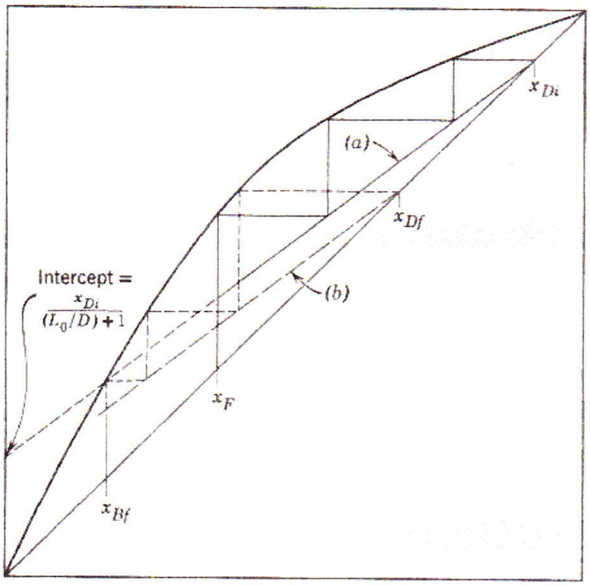


Figure 8.1. Batch distillation at constant reflux ratio. (*a*) Initial operating line. (*b*) Final operating line.

from which it is formed. This results in a continuing impoverishment of the liquid in the more volatile component.

Since the liquid composition varies, so also must the equilibrium vapor composition. The original composition of the total liquid phase (L) is taken as x and of the vapor phase formed, y. By an over-all material balance for the vaporization of a differential quantity of liquid,

$$dL = -dV \tag{8.1}$$

If dV moles of average composition (y) are formed by vaporization, a material balance for the more volatile component gives

$$d(Lx) = y - dV \tag{8.2}$$

and

$$x\,dL + L\,dx = -y\,dV \tag{8.3}$$

Combination of Equations 8.1 and 8.3 gives

$$x\,dL + L\,dx = y\,dL \tag{8.4}$$

and

$$\int \frac{dL}{L} = \int \frac{dx}{y - x} \tag{8.5}$$

which is called the Rayleigh equation. Integrating over a finite change from state 1 to state 2 gives

$$\ln \frac{L_2}{L_1} = \int_{x_1}^{x_2} \frac{dx}{y - x} \tag{8.6}$$

If the equilibrium relationship between y and x is known, the right-hand side of Equation 8.6 may be integrated. If Henry's law holds, $y = Kx$, and

$$\ln \frac{L_2}{L_1} = \frac{1}{K - 1} \ln \frac{x_2}{x_1} \tag{8.7}$$

For a constant relative volatility,

$$\ln \frac{L_2}{L_1} = \frac{1}{\alpha - 1}\left(\ln \frac{x_2}{x_1} - \alpha \ln \frac{1 - x_2}{1 - x_1}\right) \tag{8.8}$$

Batch Distillation. Batch distillation is often used for separating small quantities of liquids. Often the batch still is used for a large variety of separations, and therefore it must be versatile. Since a batch distillation is usually carried out in an existing column equivalent to a known number of equilibrium stages, it is necessary to determine the reflux ratio required to give the desired distillate purity.

In the typical batch distillation the liquid to be processed is charged to a heated kettle, above which is mounted the distillation column equipped with a condenser. Once the initial liquid is charged no more feed is added. The liquid in the kettle is boiled, and the vapors pass upward through the column. Part of the liquid from the condenser is refluxed, and the remainder is withdrawn as distillate product. Nothing is withdrawn from the still pot until the run is completed.

Because the distillate which is withdrawn is richer in the more volatile component than the residue in the still pot, the residue will become increasingly depleted in the more volatile component as the distillation progresses. Since the number of equilibrium stages in the column is constant, the concentration of more volatile component in the distillate will decrease as the still-pot concentration decreases, if the reflux ratio is held constant. This is shown in Figure 8.1. F is the quantity of original charge of composition x_F, D the quantity of distillate of composition x_D, and B the residue in the still pot of composition x_B. At any time during the distillation,

$$F = D + B \tag{8.9}$$

$$Fx_F = Dx_D + Bx_B \tag{8.10}$$

Since the entire column is an enriching section, there will be only an enriching operating line. It extends initially between x_F and an initial distillate composition (x_{Di}) which is determined by the reflux ratio. The equation of the initial operating line is

$$y_{n+1} = \frac{L}{V} x_n + \frac{D}{V} x_{Di} \tag{8.11}$$

The column represented in Figure 8.1 is equivalent to three equilibrium stages. The initial distillate composition is determined by adjusting the operating line of a given slope until exactly three stages fit between x_F and x_{Di}. As the distillation continues the concentration of the more volatile component in the still-pot residue decreases to the final value x_B. The composition of the final distillate (x_{Df}) is determined by an operating line of the same slope as earlier and by the requirement of exactly three equilibrium stages.

At any time during the distillation there are B moles of composition x_B in the still pot. If dB moles of composition x_D are removed from the column, a material balance for the more volatile component gives

$$\begin{array}{ccccc} \text{More volatile} & & \text{more volatile} & & \text{more volatile} \\ \text{component in} & = & \text{component in} & + & \text{component in} \\ \text{the original} & & \text{the } dB \text{ moles} & & \text{the } (B - dB) \\ B \text{ moles} & & \text{removed} & & \text{moles remaining} \end{array}$$

or $$Bx_B = (dB)x_D + (B - dB)(x_B - dx_B) \qquad (8.12)$$

Neglecting second-order differentials yields

$$\frac{dB}{B} = \frac{dx_B}{x_D - x_B} \qquad (8.13)$$

Integrating from the initial to final still-pot conditions (F to B) gives

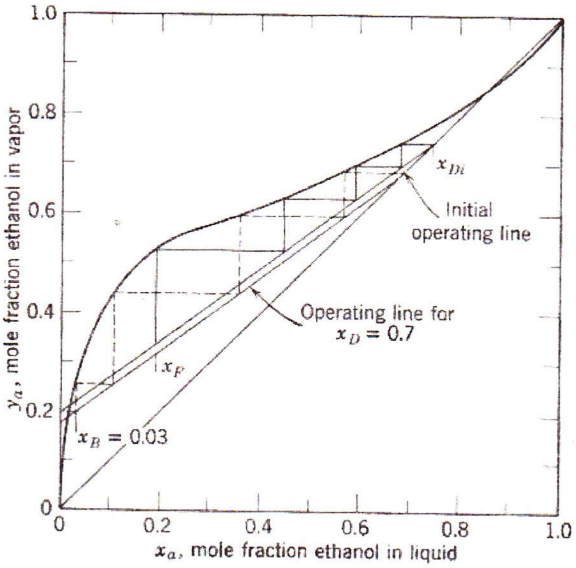
$$\int_B^F \frac{dB}{B} = \ln\frac{F}{B} = \int_{x_{Bf}}^{x_F} \frac{dx_B}{x_D - x_B} \qquad (8.14)$$

This equation is of the same form as the Rayleigh equation for differential distillation (Equation 8.6). However, a number of equilibrium stages are available so that the relationship between x_D and x_B must be determined graphically and the right-hand side of Equation 8.14 is integrated graphically, after several corresponding values of x_D and x_B have been determined. It should be noted that when only one stage is available, Equation 8.14 reduces to Equation 8.6.

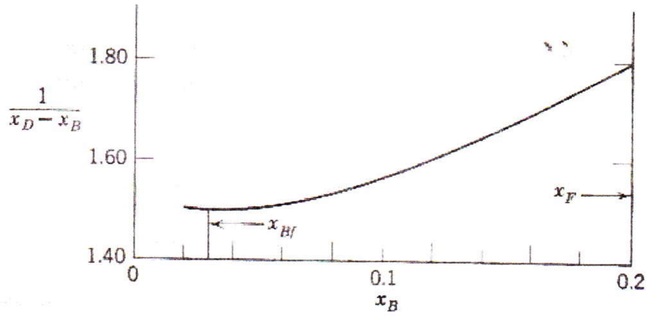
Illustration 8.1. One hundred pound moles of a mixture of 20 mole percent ethanol, 80 mole percent water is charged to the still pot of a batch distillation column equivalent to three equilibrium stages. The distillation at a reflux ratio of 3 and 1 atm is continued until the residue in the still pot reaches a composition of 0.03 mole fraction ethanol. What is the quantity and average composition of the distillate?

SOLUTION. (Figure 8.2*a*.) The slope of the operating line is 3/4. The three stages in the column plus the still pot give a total of four equilibrium stages. The initial x_D is determined by adjusting the operating line of slope 3/4 until exactly four stages fit between x_F and x_D; $x_{Di} = 0.75$. Now various values of x_D are chosen arbitrarily and x_B is determined graphically for each x_D. Then $1/(x_D - x_B)$ is plotted as a function of x_B and a graphical integration (Figure 8.2*b*) is made.

x_D	x_B	$\frac{1}{x_D - x_B}$
0.76	0.22	1.85
0.75	0.20	1.80
0.74	0.10	1.6
0.72	0.04	1.5
0.70	0.03	1.5
0.68	0.02	1.5



(*a*) Determination of x_B from x_D.



(*b*) Graphical integration of Equation 8.14.

Figure 8.2. Solution to Illustration 8.1.

$$\int_{x_{Bf}}^{x_F} \frac{dx_B}{x_D - x_B} = 0.275$$

$$\ln\frac{100}{B} = 0.275$$

$$B = 76.2, \qquad D = 23.8$$

$$\text{Average distillate composition} = \frac{Dx_D}{D} = \frac{Fx_F - Bx_B}{D}$$

$$= \frac{(100)(0.2) - (76.2)(0.03)}{23.8}$$

$$= 0.745$$

In this case the average composition of the distillate is close to its initial value since the change during the distillation was small. In other cases the average distillate composition may be considerably less than the initial value.

It is possible to maintain a constant distillate composition in batch distillation if the reflux ratio is continuously increased during the run. Calculations in this case are

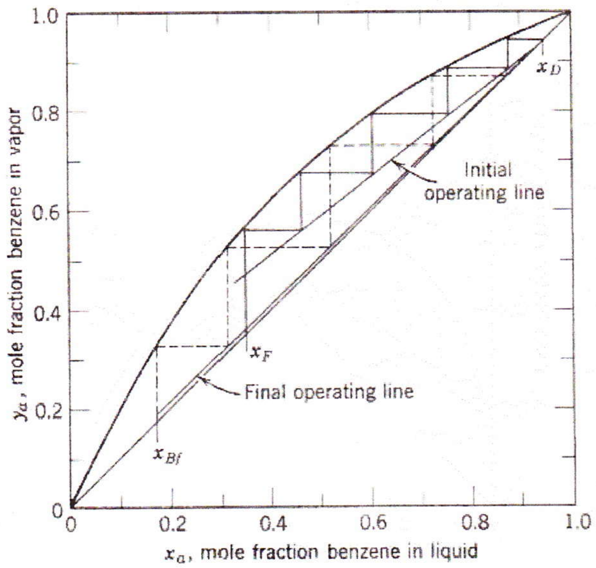


Figure 8.3. Solution to Illustration 8.2.

identical with those illustrated previously, except that x_D remains constant and the slope of the operating line (L/V) must change to maintain a constant number of equilibrium stages between x_D and x_B.

Illustration 8.2. A mixture of 35 mole percent benzene and 65 mole percent toluene is to be fractionated at 1 atm pressure in a batch column to recover 60 per cent of the benzene in a distillate of composition 0.95 mole percent benzene. The column is equivalent to four equilibrium stages.

(*a*) What is the initial reflux ratio?

(*b*) What is the final reflux ratio?

SOLUTION. (*a*) The initial reflux ratio is determined by adjusting the slope of the operating line through $x_D = 0.95 = y$ until exactly five stages fit between x_F and x_D. From Figure 8.3, the slope is 0.8, so that the initial reflux ratio is $L_0/D = 0.8/(1 - 0.8) = 4$.

(*b*) One hundred pound moles charged: 35 lb moles benzene, 65 lb moles toluene.

Benzene recovered in distillate $= (0.60)(35) = 21$

$$\text{Toluene in distillate} = \frac{0.05}{0.95}(21.0) = 1.1$$

Final still-pot composition: Benzene = 14.0
Toluene = 63.9

$$x_{Bf} = \frac{14.0}{63.9 + 14.0} = 0.18$$

The operating line is pivoted around $x_D = 0.95 = y$ until exactly five stages fit between $x_{Bf} = 0.18$ and $x_D = 0.95$. The slope is 76/77, and the reflux ratio is $(76/77)/(1 - 76/77) = 76$. This value is close to total reflux. Operation at such a high reflux ratio would require a large quantity of heat per unit of product and would be economically unjustifiable. More benzene could be recovered, but the purity of the distillate product would have to be reduced.

It is frequently found most feasible to maintain a constant distillate composition at the beginning of batch distillation. When the reflux ratio has increased to an economic or physical limit, it is held constant for the remainder of the run, and the distillate composition is allowed to decrease until it reaches a predetermined limit, at which time distillation is stopped.

In many batch distillation columns the liquid held up on each plate of the column is appreciable. This must be taken into account when predicting the yield and composition of distillate.

PROBLEMS

8.1. Derive Equations 8.7 and 8.8.

8.2. A liquid mixture of 65 mole percent benzene and 35 mole percent toluene is distilled with the vapor continuously withdrawn as it is formed.

(*a*) What is the composition of the liquid after 25 mole percent of the original liquid has been vaporized?

(*b*) How much of the original liquid will have vaporized when the equilibrium vapor has a composition of 65 mole percent benzene?

8.3. A vapor mixture of 40 mole percent hexane and 60 mole percent heptane is slowly condensed at 1 atm and the equilibrium liquid is withdrawn as it is formed.

(*a*) What is the composition of the vapor after 50 mole percent of it has condensed?

(*b*) If all the liquid formed were allowed to remain in contact with the vapor what would be the composition of the vapor after 50 mole percent had condensed?

8.4. An equimolar mixture of benzene and toluene is charged to the still pot of a batch distillation tower which is equivalent to six equilibrium stages. The distillation is carried out at 1 atm at a constant reflux ratio of 3 until the concentration of benzene in the still pot is reduced to 5 mole percent.

(*a*) What is the average composition of the distillate?

(*b*) What is the over-all percentage recovery of benzene in the distillate?

(*c*) What is the temperature in the still pot at the beginning and at the end of the run?

8.5. 95 per cent of the ethylene glycol in a 20 mole percent ethylene glycol–80 mole percent water mixture must be recovered in the residue from a batch distillation tower equivalent to three equilibrium stages (including the still pot) operating at 228 mm Hg.

EQUILIBRIUM DATA:* ETHYLENE GLYCOL–WATER AT 228 mm Hg

Mole percent ethylene glycol

Liquid	0	10	20	30	40	50	60	70	80	90	92	95	97	99	100
Vapor	0	0.2	0.4	0.7	1.1	1.8	2.8	5.0	10.0	21.4	25.5	35.0	46.5	69.0	100
Temperature, °C	69.5	72.8	75.6	78.8	82.9	87.7	93.1	100.5	111.2	127.5	132.0	139.5	145.1	152.4	160.6

* Trimble and Potts, *Ind. Eng. Chem.*, **27**, 66 (1935).

An over-all distillate composition of 5 mole percent ethylene glycol is desired.

(*a*) If the distillate composition is held constant, what must be the initial and final reflux ratios?

(*b*) If the reflux ratio is held constant, what must be its value?

8.6. A mixture of 36 mole percent chloroform and 64 mole percent benzene is to be separated using a batch distillation tower equivalent to ten equilibrium stages operating 760 mm Hg. The distillate composition will be held constant at 96 mole percent chloroform during the run.

(*a*) Plot the reflux ratio as a function of the percentage of original charge distilled.

(*b*) What is the theoretical maximum recovery of chloroform in the 96 per cent distillate?

EQUILIBRIUM DATA:[*] CHLOROFORM–BENZENE

Mole percent chloroform

Liquid	0	8	15	22	29	36	44	54	66	79	100
Vapor	0	10	20	30	40	50	60	70	80	90	100
Temperature, °C	80.6	79.8	79.0	78.2	77.3	76.4	75.3	74.0	71.9	68.9	61.4

[*] *International Critical Tables*, McGraw-Hill Book Company, New York (1926).