

# Chapter 13

## Batch Distillation

### §13.0 INSTRUCTIONAL OBJECTIVES

After completing this chapter, you should be able to:

- Derive the Rayleigh equation for a simple batch distillation (differential distillation), and state the necessary assumptions.
- Calculate, by graphical and algebraic means, batch-still temperature, residue composition, and instantaneous and average distillate composition for a binary mixture as a function of time for binary batch distillation.
- Calculate, by modified McCabe–Thiele methods, residue and distillate compositions for binary batch rectification under conditions of equilibrium stages, no liquid holdup, and constant or variable reflux ratio to achieve constant distillate composition.
- Explain the importance of taking into account liquid holdup.
- Calculate, using shortcut and rigorous equilibrium-stage methods with a process simulator, multicomponent, multistage batch rectification that includes a sequence of operating steps to obtain specified products.
- Apply the principles of optimal control to optimize batch distillation.

A familiar example of a batch distillation is the laboratory distillation shown in Figure 13.1, where a liquid mixture is charged to a *still-pot* and heated to boiling. The vapor formed is continuously removed and condensed to produce a distillate. The compositions of the initial charge and distillate change with time; there is no steady state. The still temperature increases and the amount of lower-boiling components in the still pot decreases as distillation proceeds.

Batch operations can be used to advantage when:

1. The capacity of a facility is too small to permit continuous operation at a practical rate.
2. Seasonal or customer demands require distillation in one unit of different feedstocks to produce different products.
3. Several new products are to be produced with one distillation unit for evaluation by potential buyers.
4. Upstream process operations are batchwise and the compositions of feedstocks for distillation vary with time or from batch to batch.
5. The feed contains solids or materials that form solids, tars, or resin that can plug or foul a continuous distillation column.

### §13.1 DIFFERENTIAL DISTILLATION

The simple, batch distillation apparatus in Figure 13.1, which functions in an unsteady state manner, was first quantified by Lord Rayleigh [1] and is often referred to as *differential*

*distillation*. There is no reflux; at any instant, vapor leaving the still pot with composition  $y_D$  is assumed to be in equilibrium with liquid (*residue*) in the still, which is assumed to be perfectly mixed. For total condensation,  $y_D = x_D$ . The still pot is assumed to be the only equilibrium stage because there are no trays above the still pot. This apparatus is useful for separating wide-boiling mixtures.

The following nomenclature is used for variables that are a function of time,  $t$ , assuming that all compositions refer to a particular species in the multicomponent feed:

$D$  = instantaneous-distillate rate, mol/h;

$y = y_D = x_D$  = mole fraction in instantaneous distillate leaving the still pot;

$W$  = moles of liquid (residue) left in still;

$x = x_W$  = mole fraction in liquid (residue); and

$0$  = subscript referring to  $t = 0$ .

For any component in the mixture: instantaneous rate of output =  $Dy_D$ .

$$\left. \begin{array}{l} \text{Instantaneous} \\ \text{rate of depletion} \\ \text{in the still} \end{array} \right\} = -\frac{d}{dt}(Wx_W) = -W\frac{dx_W}{dt} - x_W\frac{dW}{dt}$$

Distillate rate and, therefore, liquid-depletion rate in the still, depend on the heat-input rate,  $Q$ , to the still. By component material balance at any instant:

$$\frac{d}{dt}(Wx_W) = W\frac{dx_W}{dt} + x_W\frac{dW}{dt} = -Dy_D \quad (13-1)$$

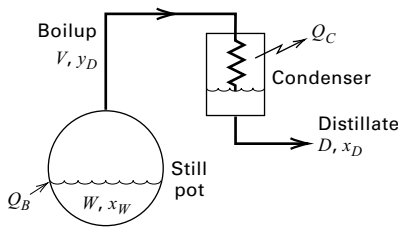


Figure 13.1 Differential (Rayleigh) distillation.

Multiplying (13-1) by  $dt$ :

$$Wdx_W + x_WdW = y_D(-Ddt) = y_DdW$$

since by total balance,  $-Ddt = dW$ . Separating variables and integrating from the initial charge condition of  $W_0$  and  $x_{W_0}$ ,

$$\int_{x_{W_0}}^{x_W} \frac{dx_W}{y_D - x_W} = \int_{W_0}^W \frac{dW}{W} = \ln\left(\frac{W}{W_0}\right) \quad (13-2)$$

This is the well-known Rayleigh equation, which was first applied to batch distillation of wide-boiling mixtures such as  $\text{HCl-H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ , and  $\text{NH}_3\text{-H}_2\text{O}$ , where one stage is sufficient to get the desired separation. Without reflux,  $y_D$  and  $x_W$  are assumed to be in equilibrium, and (13-2) simplifies to

$$\int_{x_0}^x \frac{dx}{y - x} = \ln\left(\frac{W}{W_0}\right) \quad (13-3)$$

where  $x_{W_0}$  is replaced by  $x_0$ .

Equation (13-3) is easily integrated when pressure is constant, temperature change in the still pot is relatively small (close-boiling mixture), and  $K$ -values are composition-independent. Then  $y = Kx$ , where  $K$  is approximately constant, and (13-3) becomes

$$\ln\left(\frac{W}{W_0}\right) = \frac{1}{K - 1} \ln\left(\frac{x}{x_0}\right) \quad (13-4)$$

For a binary mixture, if the relative volatility  $\alpha$ , instead of  $K$ , is assumed constant, substitution of (4-8) into (13-3), followed by integration and simplification, gives

$$\ln\left(\frac{W_0}{W}\right) = \frac{1}{\alpha - 1} \left[ \ln\left(\frac{x_0}{x}\right) + \alpha \ln\left(\frac{1 - x}{1 - x_0}\right) \right] \quad (13-5)$$

If the equilibrium relationship  $y = f\{x\}$  is graphical or tabular, integration of (13-3) can be performed graphically or numerically, as in the following three examples, which illustrate use of the Rayleigh equation for binary mixtures.

**EXAMPLE 13.1 Constant Boilup Rate.**

A batch still is loaded with 100 kmol of a binary mixture of 50 mol% benzene in toluene. As a function of time, make plots of: (a) still temperature, (b) instantaneous vapor composition, (c) still-pot composition, and (d) average total-distillate composition. Assume a constant boilup rate, and, therefore, constant  $D$  of 10 kmol/h, and a constant  $\alpha$  of 2.41 at a pressure of 101.3 kPa (1 atm).

**Solution**

Initially,  $W_0 = 100$  kmol and  $x_0 = 0.5$ . Solving (13.5) for  $W$  at values of  $x$  from 0.5 in increments of 0.05, and determining corresponding values of time in hours from  $t = (W_0 - W)/D$ , the following table is generated:

$t, \text{h}$	2.12	3.75	5.04	6.08	6.94	7.66	8.28	8.83	9.35
$W, \text{kmol}$	78.85	62.51	49.59	39.16	30.59	23.38	17.19	11.69	6.52
$x = x_W$	0.45	0.40	0.35	0.30	0.25	0.20	0.15	0.10	0.05

The instantaneous-vapor composition,  $y$ , is obtained from (4-8), which is  $y = 2.41x/(1 + 1.41x)$ , the equilibrium relationship for constant  $\alpha$ . The average value of  $y_D$  or  $x_D$  over the time interval 0 to  $t$  is related to  $x$  and  $W$  at time  $t$  by combining overall component and total material balances to give

$$(x_D)_{\text{avg}} = (y_D)_{\text{avg}} = \frac{W_0x_0 - Wx}{W_0 - W} \quad (13-6)$$

Equation (13-6) is much easier to apply than an equation that integrates the distillate composition.

To obtain the still temperature,  $T$ - $x$ - $y$  data are required for benzene-toluene at 101.3 kPa, as given in Table 13.1. Temperature and compositions as a function of time are shown in Figure 13.2.

Table 13.1 Vapor-Liquid Equilibrium Data for Benzene (B)-Toluene (T) at 101.3 kPa

$x_B$	$y_B$	$T, ^\circ\text{C}$
0.100	0.208	105.3
0.200	0.372	101.5
0.300	0.507	98.0
0.400	0.612	95.1
0.500	0.713	92.3
0.600	0.791	89.7
0.700	0.857	87.3
0.800	0.912	85.0
0.900	0.959	82.7
0.950	0.980	81.4

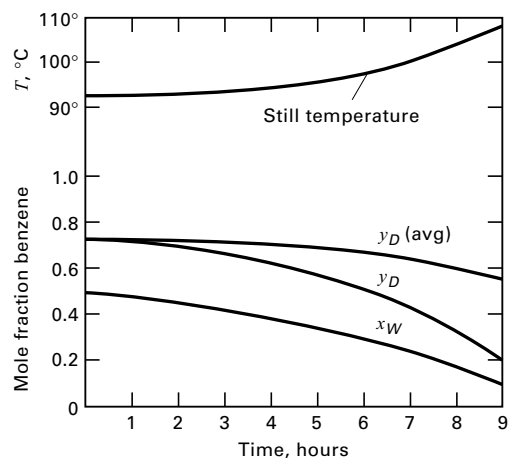


Figure 13.2 Distillation conditions for Example 13.1.

**EXAMPLE 13.2 Using Tabular Data.**

Repeat Example 13.1, except instead of using  $\alpha = 2.41$ , use the vapor–liquid equilibrium data in Table 13.1 for benzene–toluene at 101.3 kPa to solve the problem graphically or numerically with (13-3) rather than (13-5).

**Solution**

Equation (13-3) is solved by graphical integration by plotting  $1/(y-x)$  versus  $x$  with a lower limit of  $x_0 = 0.5$ . Using the data of Table 13.1 for  $y$  as a function of  $x$ , points for the plot in terms of benzene are as follows:

$x$	0.5	0.4	0.3	0.2	0.1
$1/(y-x)$	4.695	4.717	4.831	5.814	9.259

The area under the curve from  $x_0 = 0.5$  to a given value of  $x$  is equated to  $\ln(W/W_0)$ , and  $W$  is computed for  $W_0 = 100$  kmol. In the region from  $x_0 = 0.5$  to 0.3,  $1/(y-x)$  changes only slightly; thus a numerical integration by the trapezoidal rule is readily made:

$x_0 = 0.5$  to 0.4:

$$\begin{aligned}\ln\left(\frac{W}{W_0}\right) &= \int_{0.5}^{0.4} \frac{dx}{y-x} \approx \Delta x \left[ \frac{1}{y-x} \right]_{\text{avg}} \\ &= (0.4 - 0.5) \left( \frac{4.695 + 4.717}{2} \right) = -0.476\end{aligned}$$

$$W/W_0 = 0.625, \quad W = 0.625(100) = 62.5 \text{ kmol}$$

$x = 0.5$  to 0.3:

$$\begin{aligned}\ln\left(\frac{W}{W_0}\right) &= \int_{0.5}^{0.3} \frac{dx}{y-x} \approx \Delta x \left[ \frac{1}{y-x} \right]_{\text{avg}} \\ &= (0.3 - 0.5) \left[ \frac{4.695 + 4.717 + 4.717 + 4.831}{4} \right] = -0.948\end{aligned}$$

$$W/W_0 = 0.388, \quad W = 0.388(100) = 38.8 \text{ kmol}$$

These two values of  $W$  are in good agreement with those in Example 13.1. A graphical integration from  $x_0 = 0.4$  to  $x = 0.1$  gives  $W = 10.7$ , which is approximately 10% less than the result in Example 13.1, which uses a constant value of the relative volatility.

The Rayleigh equation, (13-1), for differential distillation applies to any two components,  $i$  and  $j$ , of a multicomponent mixture. Thus, if  $M_i$  is the moles of  $i$  in the still pot,

$$\frac{dM_i}{dt} = \frac{d}{dt}(Wx_{w_i}) = -Dy_{D_i}$$

$$\text{Then,} \quad dM_i/dM_j = y_{D_i}/y_{D_j} \quad (13-7)$$

For constant  $\alpha_{i,j} = y_{D_i}x_{w_j}/y_{D_j}x_{w_i}$ , (13-7) becomes

$$dM_i/dM_j = \alpha_{i,j}(x_{w_i}/x_{w_j}) \quad (13-8)$$

Substitution of  $M_i = Wx_{w_i}$  for both  $i$  and  $j$  into (13-8) gives

$$dM_i/M_i = \alpha_{i,j}dM_j/M_j \quad (13-9)$$

Integration from the initial-charge condition gives

$$\ln(M_i/M_{i_0}) = \alpha_{i,j} \ln(M_j/M_{j_0}) \quad (13-10)$$

The following example shows that (13-10) is useful for determining the effect of relative volatility on the separation achievable by differential distillation.

**EXAMPLE 13.3 Effect of Relative Volatility.**

The charge to a simple batch still consists of an equimolar, binary mixture of A and B. For values of  $\alpha_{A,B}$  of 2, 5, 10, 100, and 1,000 and 50% vaporization of A, determine the mole fraction and % vaporization of B in the total distillate.

**Solution**

For  $\alpha_{A,B} = 2$  and  $M_A/M_{A_0} = 1 - 0.5 = 0.5$ , (13-10) gives  $M_B/M_{B_0} = (M_A/M_{A_0})^{1/\alpha_{A,B}} = (0.5)^{(0.5)} = 0.7071$ . % vaporization of B =  $(1 - 0.7071)(100) = 29.29\%$ .

For 200 moles of charge, the amounts in the distillate are  $D_A = (0.5)(0.5)(200) = 50$  mol and  $D_B = (0.2929)(0.5)(200) = 29.29$  mol. Mole fraction of B in the total distillate =  $\frac{29.29}{50 + 29.29} = 0.3694$ .

Similar calculations for other values of  $\alpha_{A,B}$  give:

$\alpha_{A,B}$	% Vaporization of B	Mole Fraction of B in Total Distillate
2	29.29	0.3694
5	12.94	0.2057
10	6.70	0.1182
100	0.69	0.0136
1,000	0.07	0.0014

These results show that a sharp separation between A and B for 50% vaporization of A is achieved only if  $\alpha_{A,B} \geq 100$ . Furthermore, the purity achieved depends on the % vaporization of A. For  $\alpha_{A,B} = 100$ , if 90% of A is vaporized, the mole fraction of B in the total distillate increases from 0.0136 to 0.0247. For this reason, as discussed §13.6, it is common to conduct a binary, batch-distillation separation of LK and HK in the following manner:

1. Produce a distillate LK cut until the limit of impurity of HK in the total distillate is reached.
2. Continue the batch distillation to produce an intermediate (slop) cut of impure LK until the limit of impurity of LK in the liquid remaining in the still is reached.
3. Empty the HK-rich cut from the still.
4. Recycle the intermediate (slop) cut to the next still charge.

For desired purities of the LK cut and the HK cut, the fraction of intermediate (slop) cut increases as the LK–HK relative volatility decreases.

### §13.2 BINARY BATCH RECTIFICATION

For a sharp separation and/or to reduce the intermediate-cut fraction, a trayed or packed column is added between the still and the condenser, and a reflux drum is added after the condenser, as shown in Figure 13.3. In addition, one or more drums are provided to collect distillate cuts. For a column of a given diameter, the molar vapor-boilup rate is usually fixed at a value safely below the column flooding point.

Two modes of operating a batch rectification are cited most frequently because they are the most readily modeled. The first is operation at a constant reflux rate or ratio (same as a constant distillate rate), while the second is operation at a constant distillate composition. With the former, the distillate composition varies with time; with the latter, the reflux ratio or distillate rate varies with time. The first mode is easily implemented because of the availability of rapidly responding flow sensors. For the second mode, a rapidly responding composition sensor is required. In a third mode, referred to as the optimal-control mode, both reflux ratio (or distillate rate) and distillate composition vary with time to maximize the amount of distillate, minimize operation time, or maximize profit. Constant reflux is discussed first, followed by constant composition. Optimal control is deferred to §13.8.

#### §13.2.1 Constant Reflux Operation

If  $R$  or  $D$  is fixed, instantaneous-distillate and still-bottoms compositions vary with time. Assume a total condenser, negligible holdup of vapor and liquid in the condenser and column, phase equilibrium at each stage, and constant molar overflow. Then, (13-2) applies with  $y_D = x_D$ . The analysis is facilitated by a McCabe–Thiele diagram using the method of Smoker and Rose [2].

Initially, the composition of the LK in the liquid in the still is the charge composition,  $x_{W_0}$ , which is 0.43 in the McCabe–Thiele diagram of Figure 13.4. If there are two theoretical stages (the still-pot and one equilibrium plate), the initial distillate composition,  $x_{D_0}$ , at time 0 can be found by constructing an operating line of slope  $L/V = R/(R+1)$ , such that exactly two stages are stepped off to the right from  $x_{W_0}$  to the  $y = x$  line in Figure 13.4. At an arbitrary later time, say, time 1, at still-pot composition  $x_W < x_{W_0}$ , e.g.,  $x_W = 0.26$  in Figure 13.4, the instantaneous-distillate

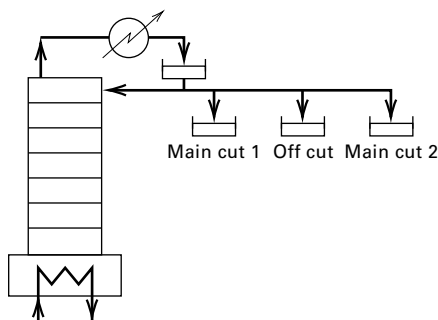


Figure 13.3 Batch rectification.

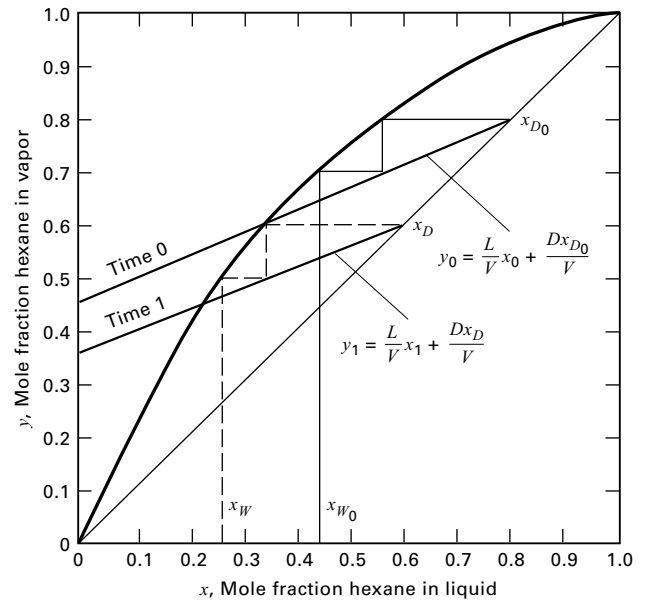


Figure 13.4 Batch binary distillation with fixed  $L/V$  and two theoretical stages.

composition is  $x_D$ . In this manner, a time-dependent series of points for  $x_D$  as a function of  $x_W$  is established, with  $L/V$  and the number of stages held constant.

Equation (13-2) cannot be integrated analytically because the relationship between  $y_D = x_D$  and  $x_W$  depends on  $L/V$ , the number of theoretical stages, and the phase-equilibrium relationship. However, (13-2) can be integrated graphically with pairs of values for  $x_W$  and  $y_D = x_D$  obtained from the McCabe–Thiele diagram, as in Figure 13.4, for a series of operating lines of the same slope.

The time  $t$  required for this batch rectification can be computed by a total material balance based on a constant boilup rate  $V$ , to give an equation due to Block [3]:

$$t = \frac{W_0 - W_t}{V \left(1 - \frac{L}{V}\right)} = \frac{R+1}{V} (W_0 - W_t) \quad (13-11)$$

With a constant-reflux policy, instantaneous-distillate purity is above specification at the beginning and below specification at the end of the run. By an overall material balance, the average mole fraction of LK in the accumulated distillate at time  $t$  is given by

$$x_{D,\text{avg}} = \frac{W_0 x_0 - W_t x_{W_t}}{W_0 - W_t} \quad (13-12)$$

#### EXAMPLE 13.4 Constant Reflux Operation.

A three-stage batch rectifier (first stage is the still-pot) is charged with 100 kmol of a 20 mol%  $n$ -hexane in  $n$ -octane mixture. At a constant-reflux ratio of 1 ( $L/V = 0.5$ ), how many moles of charge must be distilled for an average product composition of 70 mol%  $n$ C<sub>6</sub>? The phase-equilibrium curve at column pressure is given in Figure 13.5. If the boilup rate is 10 kmol/h, calculate distillation time.

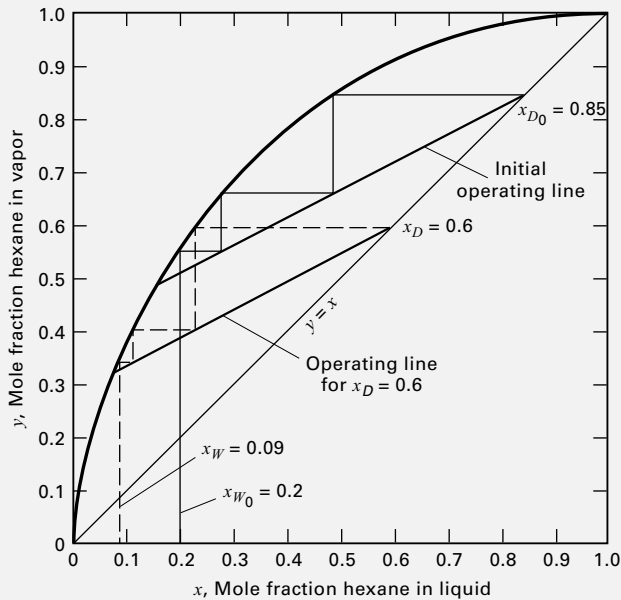


Figure 13.5 Solution to Example 13.4.

### Solution

A series of operating lines and values of  $x_W$  are located by the trial-and-error procedure described earlier, as shown in Figure 13.5 for  $x_{W_0} = 0.20$  and  $x_W = 0.09$ . Using Figure 13.5, the following table is developed:

$y_D = x_D$	0.85	0.60	0.5	0.35	0.3
$x_W$	0.2	0.09	0.07	0.05	0.035
$\frac{1}{y_D - x_W}$	1.54	1.96	2.33	3.33	3.77

The graphical integration is shown in Figure 13.6. Assuming a final value of  $x_W = 0.1$ , for instance, integration of (13-2) gives

$$\ln \frac{100}{W} = \int_{0.1}^{0.2} \frac{dx_W}{y_D - x_W} = 0.162$$

Hence,  $W = 85$  and  $D = 15$ .

From (13-12):  $(x_D)_{\text{avg}} = \frac{100(0.20) - 85(0.1)}{(100 - 85)} = 0.77$

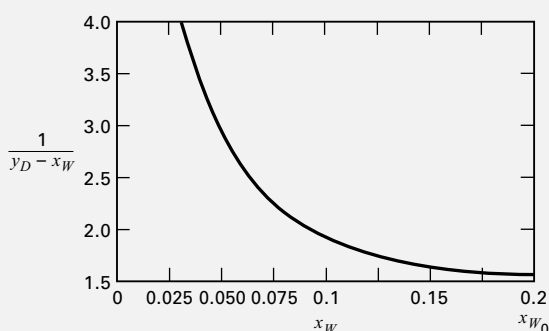


Figure 13.6 Graphical integration for Example 13.4.

The  $(x_D)_{\text{avg}}$  is higher than the desired value of 0.70; hence, another  $x_W$  must be chosen. By trial, the correct answer is found to be  $x_W = 0.06$ , with  $D = 22$ , and  $W = 78$ , corresponding to a value of 0.25 for the integral. From (13-11), distillation time is  $t = \frac{(1+1)}{10}(100 - 78) = 4.4$  h. When differential distillation is used, Figure 13.5 shows that 70 mol% hexane distillate is not achievable because the initial distillate is only 56 mol% hexane.

### §13.2.2 Constant Distillate Composition

The constant-reflux-ratio policy described in the previous section is easy to implement. For small batch-rectification systems, it may be the least expensive policy. A more optimal policy is to maintain a constant  $V$  but continuously vary  $R$  to achieve a constant  $x_D$  that meets the specified purity. This requires a more complex control system, including a composition sensor on the distillate, which may be justified only for large batch-rectification systems. Other methods of operating batch columns are described by Ellerbe [5].

Calculations for the policy of constant  $x_D$  can also be made with the McCabe–Thiele diagram, as described by Bogart [4] and illustrated in Example 13.5. The Bogart method assumes negligible liquid holdup and constant molar overflow. An overall material balance for the LK, at any time  $t$ , is given by a rearrangement of (13-12) at constant  $x_D$ , for  $W$  as a function of  $x_W$ .

$$W = W_0 \left[ \frac{x_D - x_{W_0}}{x_D - x_W} \right] \quad (13-13)$$

Differentiating (13-13) with respect to  $t$  for varying  $W$  and  $x_W$  gives

$$\frac{dW}{dt} = W_0 \frac{(x_D - x_{W_0}) dx_W}{(x_D - x_W)^2 dt} \quad (13-14)$$

For constant molar overflow, the distillation rate is given by the rate of loss of charge,  $W$ :

$$-\frac{dW}{dt} = (V - L) = \frac{dD}{dt} \quad (13-15)$$

where  $D$  is now the amount of distillate, not the distillate rate. Substituting (13-15) into (13-14) and integrating:

$$t = \frac{W_0(x_D - x_{W_0})}{V} \int_{x_{W_0}}^{x_0} \frac{dx_W}{(1 - L/V)(x_D - x_W)^2} \quad (13-16)$$

For fixed values of  $W_0$ ,  $x_{W_0}$ ,  $x_D$ ,  $V$ , and the number of stages, the McCabe–Thiele diagram is used to determine values of  $L/V$  for a series of values of still composition between  $x_{W_0}$  and the final value of  $x_W$ . These values are then used with (13-16) to determine, by graphical or numerical integration, the time for rectification or the time to reach any still composition. The required number of stages can be estimated by assuming total reflux for the final value of  $x_W$ . While rectification is proceeding, the instantaneous-distillate rate varies according to (13-15), which can be expressed in terms of  $L/V$  as

$$\frac{dD}{dt} = V(1 - L/V) \quad (13-17)$$