

Analytical Solution of Equilibrium-Stage Operations—Application to Rectification with Varying Saturated Enthalpies and to Liquid-Liquid Extraction

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A complete analytical solution is developed for the number of equilibrium stages in separations processes for which operating and equilibrium lines are not necessarily straight. The resulting equations are solutions of a Riccati difference equation and are applied to liquid-liquid extraction and the distillation of a binary mixture where the liquid and vapor flows are not constant because of the variation of the saturated liquid and vapor enthalpies with concentration. A specific example is given for the separation of ethyl alcohol and water in which the equilibrium curve is highly nonlinear and where a large number of plates are required in a pinch region. Another example is given for the extraction of methylcyclopentane from its solution in n-hexane using aniline as a selective solvent.

Many problems in the design of equilibrium-stage equipment reduce to a solution of a finite difference equation that is dependent upon a so-called *operating line or function* and an equilibrium curve. Outstanding examples are the separations operations such as absorption, stripping, rectification, leaching, and extraction, and chemical reactions in a series of plates or tanks. A major objective in these operations is to determine the number of stages required to accomplish a desired separation when given specific equilibrium and operating lines. In the most general case the functional forms of these lines may be so complex that the resulting difference equation can be solved only by tedious repetitive stage-to-stage calculations. McCabe and Thiele (4), Ponchon (6), and Savarit (8) presented ingenious graphical techniques to carry out repeated stepwise balances. Kremser (3), Fenske (2), Smoker (9), and Tiller and Tour (10) developed analytical solutions for certain specialized cases; however, no general solution has been presented yet. This study essentially generalizes and extends the work of Tiller and Tour and demonstrates how a broad class of stage-wise operations can be treated effectively.

In this age of the electronic computer one might say that the stage-to-stage calculation is the proper one to use since the computer can do a multitude of these calculations in a short time. However, even with the high-speed, large-storage computer, it may be time-consuming and costly to solve a many-stage problem for a wide range of the variables. Consequently, an analytical solution of a stage-wise problem is highly desirable, as it can be programmed on the computer and then solved for many different values of the parameters. The following development yields a solution that is of general applicability to a large number of separations problems.

DEVELOPMENT OF THE ANALYTICAL SOLUTION

In many instances of stage-wise operations, the operating line that results from material and energy balances

around a given stage can be represented by an equation of the form

$$y_n = ax_{n+1} + bx_{n+1}y_n + c \quad (1)$$

Here y represents the concentration of a certain component in one phase, x is the concentration of that component in another phase, subscripts n or $n + 1$ refer to the number of the stage, and a , b , and c are constants that depend upon variables, such as liquid and gas flow rates or enthalpies, which are set by the conditions of the problem. The exceptional versatility of the functional form of Equation (1) is worth emphasizing, for although the equation appears to be relatively simple, proper specialization of the constants permits representation of a linear operating line or one that is quite curved. Furthermore, in some cases it is possible to represent an unusually shaped operating line by segmental application of Equation (1), with the various segments having the same value and slope at their junction points.

Corresponding to the operating line there is an equilibrium curve which often may be expressed by an equation of form similar to Equation (1):

$$y_n = \alpha x_n + \beta x_n y_n + \gamma \quad (2)$$

Here the variables are defined as above and α , β , and γ are arbitrary constants necessary for proper representation of the equilibrium curve. The only difference between Equations (1) and (2) is that the former involves y at the n th stage and x at the $n + 1$ th stage, whereas the latter involves y and x at the same stage whether it be n , $n + 1$, or otherwise. Again Equation (2) has the same versatility as (1), and its constants may be set to represent straight or curved lines or it may be applied piece-by-piece to fit a tortuous equilibrium curve as long as it is single-valued. A special case of the equation is the constant relative volatility function used in distillation.

Since Equation (2) holds for any given stage, it may be applied in its bilinear or linear fractional transformation form to the $n + 1$ th stage as

$$x_{n+1} = \frac{y_{n+1} - \gamma}{\alpha + \beta y_{n+1}} \quad (3)$$

Insertion of (3) into (1) yields

$$(\beta - b)y_{n+1}y_n - (a + c\beta)y_{n+1} + (\alpha + b\gamma)y_n + a\gamma - c\alpha = 0 \quad (4)$$

or when new constants are defined

$$A = -(a + c\beta)/(\beta - b), B = (\alpha + b\gamma)/(\beta - b)$$

and

$$C = (a\gamma - c\alpha)/(\beta - b)$$

Equation (4) becomes

$$y_{n+1}y_n + Ay_{n+1} + By_n + C = 0 \quad (5)$$

Equation (5) is recognized as a Riccati nonlinear difference equation whose solution (see Appendix) may be obtained in different ways. The summed or integrated forms for a total of N stages taken from $y_n = y_0$ at $n = 0$ to $y_n = y_N$ at $n = N$, are

$$N = \frac{\log \frac{(y_N + A - E_2)(y_0 + A - E_1)}{(y_N + A - E_1)(y_0 + A - E_2)}}{\log \frac{E_1}{E_2}} \quad (6)$$

$$N = \frac{E_1(y_0 - y_N)}{(y_N + A - E_1)(y_0 + A - E_1)} \quad (7)$$

and

$$N = \frac{\theta_2 - \theta_1}{\theta} \quad (8)$$

In these equations E_1 and E_2 are the roots of a discriminant equation

$$E_{1,2} = \frac{A - B}{2} \pm \sqrt{\left(\frac{A + B}{2}\right)^2 - C} \quad (9)$$

= E_1 , if the square root vanishes.

If the roots are real and unequal, Equation (6) is to be used. If the roots are equal, Equation (7) applies, and if the roots are complex, Equation (8) is required with

$$\theta = \arctan \frac{2p}{A - B} \quad (10)$$

$$\theta_2 = \arctan \frac{p}{y_N + (A + B)/2} \quad (11)$$

$$\theta_1 = \arctan \frac{p}{y_0 + (A + B)/2} \quad (12)$$

and

$$ip = \sqrt{\left(\frac{A + B}{2}\right)^2 - C} \quad (13)$$

One further special case needs to be noted. If in Equation (4) the term, $\beta - b$, vanishes, such as if both β and b are either zero or equal, the resulting difference equation will be of the form

$$-(a + c\beta)y_{n+1} + (\alpha + b\gamma)y_n + a\gamma - c\alpha = 0 \quad (14)$$

This is readily recognized as a first-order linear difference equation whose solution is obtained by similar procedures as

$$N = \frac{\log \frac{y_N(a + c\beta - \alpha - b\gamma) - a\gamma + c\alpha}{y_0(a + c\beta - \alpha - b\gamma) - a\gamma + c\alpha}}{\log \frac{\alpha + b\gamma}{a + c\beta}} \quad (15)$$

or if b and β vanish and $a = \alpha$

$$N = \frac{y_N - y_0}{\gamma - c} \quad (16)$$

In summary, Equations (6), (7), (8), (15), and (16) will give the number of stages in any process for which equilibrium and operating curves are of the form of Equations (1) and (2) or any modification thereof. These summed or integrated forms have been obtained for the case of specified values of y_0 and y_N . If a special material or energy balance applies to the first and last stages, so that they are different from the others, it may be necessary to utilize y_1 and y_{N-1} instead of y_0 and y_N . This is easily done by following exactly the same procedure as given in the Appendix, but introducing y_1 at $n = 1$ and y_{N-1} at $N - 1$. The solutions to the difference equations before introduction of the limits are precisely the same.

Of the many possible applications of the equations which have been developed, two have been selected to illustrate the procedure and utility of the analytical method. The first is in the field of distillation and the second in liquid-liquid extraction.

RECTIFICATION OF AN ALCOHOL-WATER MIXTURE

Problem

A 61 wt. % ethyl alcohol—39 wt. % water mixture is to be enriched to 92 wt. % alcohol in a rectifying column operating at atmospheric pressure. The feed is a saturated vapor while the product (and reflux) removed from a total overhead condenser is to be saturated liquid. With a reflux ratio (defined as the ratio of liquid reflux returned to the top plate from the condenser to the vapor stream from the top plate to the condenser) of 0.6, calculate the number of equilibrium plates required for the separation. Take into account the variation of liquid and vapor flow from plate to plate owing to the enthalpy-composition effects. The column may be assumed to operate adiabatically.

Solution

In the usual and well-known way, material and energy balances are taken around a section from just above the n th plate to and including the N th plate at the top of the column. These are straightforward and are given here only to present the complete analysis.

The overall material balance is

$$V_n + L_r = V_N + L_{n+1} \quad (17)$$

where V is the vapor flow rate, L the liquid flow rate, subscripts n , $n + 1$, and N are plate numbers as defined earlier, and r refers to the reflux. The balance on the more volatile component is

$$V_n y_n + L_r x_D = V_N x_D + L_{n+1} x_{n+1} \quad (18)$$

where x and y refer to concentrations in mass fractions of the more volatile component in liquid and vapor streams, respectively, and subscript D refers to the distillate product. The enthalpy balance is

$$V_n h_n + L_r h_D = V_N H_N + L_{n+1} h_{n+1} \quad (19)$$

where h and H are the specific enthalpies of the liquid and vapor, respectively. When V_n/V_N is eliminated from (17) and (18) and the conventional reflux ratio is defined

$$R = L_r/V_N \quad (20)$$

one obtains

$$\frac{L_{n+1}}{V_N} (y_n - x_{n+1}) + y_n + (x_D - y_n) R = x_D \quad (21)$$

When the same procedure is followed with Equations (17) and (19)

$$\frac{L_{n+1}}{V_N} (H_n - h_{n+1}) + H_n + (h_0 - H_n) R = H_N \quad (22)$$

When L_{n+1}/V_N is eliminated from (21) and (22)

$$(x_D - y_n)(1 - R)(H_n - h_{n+1}) = [H_N - H_n - (h_D - H_n)R](y_n - x_{n+1}) \quad (23)$$

Linear expressions for the enthalpies as functions of composition with arbitrary constants, b_v , m_v , b_l , and m_l , are now employed in the forms

$$H_n = b_v + m_v y_n \quad (24)$$

and

$$h_n = b_l + m_l x_n \quad (25)$$

When these are put into (23), the result is

$$(x_D - y_n)(1 - R)(b_v + m_v y_n - b_l - m_l x_{n+1}) = [H_N - b_v - m_v y_n - (h_D - b_l - m_l x_{n+1})R](y_n - x_{n+1}) \quad (26)$$

This is the equation of the operating curve which can be rearranged to

$$(x_D m_v - R x_D m_v + b_l - R b_l - H_N + R h_D) y_n = (x_D m_l - R x_D m_l - H_N + b_v - R b_v + R h_D) x_{n+1} + (m_v - R m_v - m_l + R m_l) y_n x_{n+1} + x_D b_l - x_D b_v + R x_D b_v - R x_D b_l \quad (27)$$

Comparison of (27) with Equation (1) shows the two forms are identical if

$$a = \frac{x_D m_l - R x_D m_l - H_N + b_v - R b_v + R h_D}{x_D m_v - R x_D m_v + b_l - R b_l - H_N + R h_D} \quad (28)$$

$$b = \frac{m_v - R m_v - m_l + R m_l}{x_D m_v - R x_D m_v + b_l - R b_l - H_N + R h_D} \quad (29)$$

and

$$c = \frac{x_D b_l - x_D b_v + R x_D b_v - R x_D b_l}{x_D m_v - R x_D m_v + b_l - R b_l - H_N + R h_D} \quad (30)$$

The curve represented by (27) is usually not straight unless $m_v = m_l$, as noted in (29), in which case the non-linear term, $b y_n x_{n+1}$, of Equation (1) vanishes. This is the well-known McCabe and Thiele (4) assumption which results in a straight operating line.

Analytical expressions that fit the enthalpy-composition data given by Brown (1) with excellent precision are

$$H = 1,150 - 692y \quad (31)$$

and

$$h = 156 - 66x \quad (32)$$

where H is the enthalpy of the saturated vapor in British thermal units per pound, h is the saturated liquid enthalpy in British thermal units per pound, and x and y are mass fractions of alcohol in the liquid and vapor, respectively. Since the vapor-liquid equilibrium curve (1, 5, 7) inflects at about $x = 0.5$, the relative volatility equation

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \quad (33)$$

cannot be used. Two equations covering the respective ranges from $x = 0$ to 0.5 and $x = 0.5$ to 1.0 were obtained simply by passing them through two points, including the 0.5 point, and giving them equal slopes at this point. The resulting equations are

$$y = \frac{11.689x}{1 + 13.21x} \text{ for } 0 < x < 0.5 \quad (34)$$

and

$$y = \frac{0.702 - 0.408x}{1 - 0.704x} \text{ for } 0.5 < x < 1.0 \quad (35)$$

Equation (35) for the upper range predicts the azeotrope at a composition of 0.9467 , and both equations predict $y = 0.76851$ at the junction point, $x = 0.5$.

The numerical calculations may now be made. The constants for Equations (28), (29), and (30) must first be assembled. When one compares Equations (31) and (32) with (24) and (25), it is seen that $b_v = 1,150$, $m_v = -692$, $b_l = 156$, and $m_l = -66$. From the statement of the problem $x_D = 0.92$, $R = 0.6$. When $x_D = 0.92$ is put into (24) and (25) one obtains $H_N = 1,150 - 692(0.92) = 513.36$, $h_D = 156 - 66(0.92) = 95.28$. The a , b , and c may now be calculated from (28), (29), and (30). When Equation (34) is compared with (2), the equilibrium equation constants for the part of the column where y is less than the junction point y of 0.76851 are $\alpha = 11.689$, $\beta = -13.21$, $\gamma = 0$. The constants in Equation (5) are calculated from the relations preceding that equation, namely

$$A = \frac{a + c\beta}{\beta - b} \quad (36)$$

$$B = \frac{\alpha + b\gamma}{\beta - b} \quad (37)$$

and

$$C = \frac{\alpha\gamma - c\alpha}{\beta - b} \quad (38)$$

The results are $A = -0.5457594$, $B = -0.8597285$, $C = 0.4849761$. These numbers are introduced into Equation (9) to obtain the roots, $E_{1,2} = 0.1569845 \pm 0.0941962i$ so that $E_1 = 0.2511807$ and $E_2 = 0.0627883$. Since the roots are real and different, the number of plates in this section is given by Equation (6). When this equation is applied, the limiting values of y are $y_0 = 0.61$ and $y_N = 0.76851$. One can describe the feed composition of 0.61 as y_0 only because the feed is saturated vapor which gives the first plate the same energy and mass balances as all the other plates that follow the general operating line. If the feed condition had been other than a saturated vapor, it would have been necessary to write a special balance around the first plate, calculate y_1 , and use that as a limit in the summed Equation (7A*). Equation (6) gives for the part of the column below $y = 0.76851$, $N = 4.75$. For the part of the column above $y = 0.76851$, one uses the same values of a , b , and c calculated before from Equations (28), (29), and (30). When (35) is compared with (2), the equilibrium equation constants for the part of the column where y is greater than 0.76851 are $\alpha = -0.408$, $\beta = 0.704$, $\gamma = 0.702$. Equations (36), (37), and (38) may now be used to obtain for the upper section of the column, $A = -1.3488353$, $B = -0.4307754$, $C = 0.7938584$. When these numbers are inserted into Equation (9) one obtains the roots $E_1 = -0.4590300 + 0.045879i$, $E_2 = -0.4590300 - 0.045879i$. Because these roots are complex the number of plates in this section is given by Equation (8). In order to calculate the angles, θ , θ_1 , and θ_2 , it is noted that for this section of the column $y_0 = 0.76851$, $y_N = 0.92$. From Equations (9) and (13) it is seen that $p = 0.045879$. Thus, it is found from (10), (11), and (12) that $\theta = \arctan(-0.0999477) = -5^\circ - 42'$, $\theta_2 = \arctan(1.5194403) = 56^\circ - 39'$, $\theta_1 = \arctan(-0.3782421) = 159^\circ - 17'$. From Equation (8) the number of plates in the upper section is $N = \frac{56^\circ - 39' - 159^\circ - 17'}{-5^\circ - 42'}$

* A refers to the Appendix to this paper.

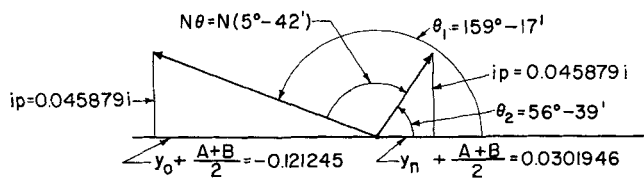


Fig. 1. Vectors in complex plane for upper part of distillation problem.

= 18.01 plates. The total number of equilibrium plates in the column is, therefore, $N = 4.75 + 18.01 = 22.76$.

The calculation of the number of plates in the upper region of the complex solution requires further explanation because the arc tangent of a number is a multiple-valued angle. This will give those uninitiated in complex numbers considerable difficulty, and, indeed, a lack of full understanding of this problem delayed the publication of this paper almost ten years. The angle θ_1 is determined by a vector in the complex plane as given by Equations (22A) and (23A). The position of this vector is shown in Figure 1. Because the real part of the complex number is negative, the vector must lie in the second quadrant rather than in the fourth, even though in both cases $\tan \theta_1 = -0.3782421$. This vector is called the *lower limit vector* because its position is specified by the lower limit of summation of the difference equations, y_0 . Correspondingly, the upper limit vector is determined by y_N in Equations (20A) and (21A). It is seen in Figure 1 that the positive value of the real part of the complex number here places the vector in the first quadrant rather than the third even though in both cases $\tan \theta_2 = 1.5194403$.

Now the process of passing from the lower limit at θ_1 to the upper limit at θ_2 merely involves rotation of a vector clockwise from $159^\circ-31'$ back to $56^\circ-31'$. The incremental angle passed through for each stage in this rotation is θ which is determined by the stage modulus which is defined as $\log (E_1/E_2)$ or $\log \{[(A-B)/2 + ip]/[(A-B)/2 - ip]\}$. Since the rotation is in a negative direction, it is necessary that the stage modulus be negative in order to end up with a positive number of stages, since a negative number would have no real significance. Consequently, θ is taken as a negative angle in the fourth quadrant. If $(A-B)/2$, which is the real part of the vector in the stage modulus, is negative as it is in this example problem $[(A-B)/2 = -0.45903]$, one would be tempted to argue that the stage modulus vector given as angle θ must lie in the second quadrant. A simple device showing the alternate possibility that it may lie in the fourth quadrant is to multiply numerator and denominator of the stage modulus by -1 , so that in Equation (42A) the lefthand side would be $\{[(B-A)/2 - ip]/[(B-A)/2 + ip]\}^N$. The complex number may be defined as

$$re^{i\theta} = (B-A)/2 + ip \quad (39)$$

It will be seen that if one follows the procedure used in Equations (17A) through (25A), the resulting equation for N is

$$N = \frac{\theta_2 - \theta_1}{-\theta} \quad (40)$$

where θ is the positive angle $5^\circ-42'$. Thus, the answer is the same as it would be if the angle θ were $-(5^\circ-42')$ in the first place; the negative sign arises automatically to account for negative rotation of the vector from the lower limit position to the upper limit position.

The problem of handling the vectors in the complex solution has its exact counterpart in the real solution. In Equation (6), $\log (E_1/E_2)$ is the stage modulus, as before, showing just how much advance will take place

along the real axis per stage. The total range along the real axis to be covered is the range from the lower limit number, $(y_0 + A - E_1)/(y_0 + A - E_2)$, to the upper limit number, $(y_N + A - E_2)/(y_N + A - E_1)$. Handling these real numbers usually offers no difficulty, but experience with many students has shown that the interpretation of complex numbers requires the above explanation.

A number of other important features of the method as illustrated by the alcohol-water problem should be mentioned. Figure 2 shows the graphical solution. The operating line is merely a plot of Equation (1) with the values of a , b , and c from the problem. The number of plates stepped off between the operating line and the equilibrium curve agrees well with the calculated number, but it required a much larger graph and a sharp pencil to get this number precisely. Carrying eight or ten significant figures in the analytical solution is equivalent to using an extremely large piece of graph paper. This problem is even worse on a Ponchon diagram. Consequently, the proposed analytical solution offers a considerable advantage when many plates are to be counted in a pinch region where the operating and equilibrium curves are close together. When the numbers in the problem that determine the discriminant are studied, it may also be shown that it is necessary to carry several significant figures or one cannot ascertain correctly whether to use Equation (6), (7) or (8). The number of figures to use depends directly on the closeness of the equilibrium and operating lines.

It is noted that the operating curve intersects the equilibrium curve at a point just below the inlet feed composition. This point can easily be obtained by simultaneous solution of Equations (1) and (2) by letting the x_{n+1} of (1) be the same as the x_n of (2). The point is also determined by letting y_0 be a variable and solving for its value in the lower limit number that makes this number go to infinity. This happens when $E_2 - y_0 - A = 0$, or for this problem

$$y_0 = E_2 - A = 0.0627883 + 0.5457594 = 0.6085477$$

If y_0 is taken less than this value, a logarithm of a negative number will appear in the solution to show that there is an impossible situation, for the plates cannot be counted

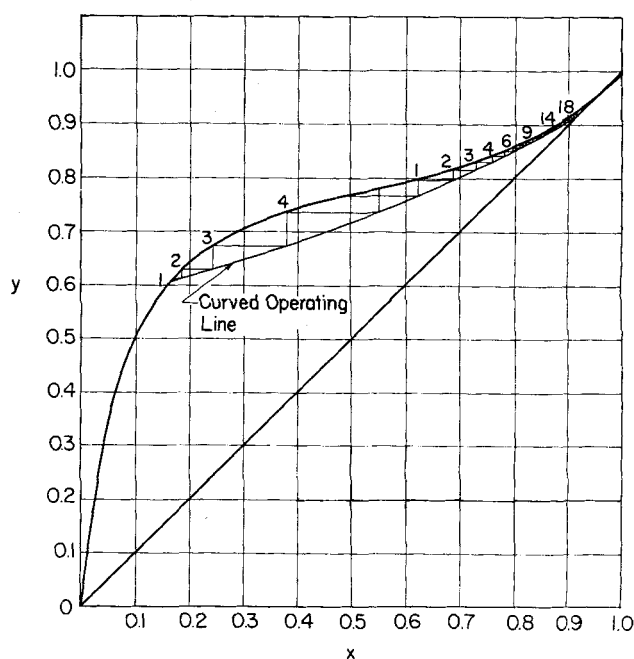


Fig. 2. Graphical solution of distillation problem.

in a pinch past an intersection point of the operating and equilibrium curves.

If total reflux is used, it will be found that the roots of the discriminant equation are real and different. If the reflux is left a variable in the discriminant and the square root term is set equal to zero, the special case will be determined where the roots are equal and the solution will be given by Equation (7). It will be found that R occurs in a quadratic equation at this condition and will take on two values. These values are $R = 0.898$ and $R = 0.543$. At the first value an operating line will be determined which is tangent to the equilibrium curve at a point outside the range of interest (that is, for $x \gg 0.92$), but at the second value the operating curve becomes tangent to the equilibrium curve at $x = 0.83$. This value of 0.543 is, therefore, the minimum reflux based on the upper portion of the diagram. If $R = 0.543$ is used, the operating line will intersect the equilibrium curve at a point above the feed concentration of 0.61. Therefore the minimum reflux for the case of a feed fixed at 0.61 is just a bit under the 0.6 given in the problem, since the intersection point at 0.61 is the limiting condition rather than the tangency point at 0.83.

For reflux ratios between 0.898 and 1.0, the operating line intersects the equilibrium curve (when only the upper portion above 0.76351 is considered), the roots of the discriminant are real, and the solution is given by Equation (6). At $R = 0.898$, the solution is given by Equation (7). Between $R = 0.898$ and 0.543, the equilibrium curve and the operating line never intersect, the roots are complex, and the solution is given by Equation (8). At $R = 0.543$, the solution is given by Equation (7), but it will yield an infinite number of plates, since this is the point at which the equilibrium and operating curves are tangent at 0.83. For any $R < 0.543$, logarithms of negative numbers will occur and the solutions are meaningless.

LIQUID-LIQUID EXTRACTION

Problem*

A mixture of 0.4 mole fraction methylcyclopentane and 0.6 mole fraction n-hexane is to be contacted with an aniline solvent in a liquid-liquid extraction battery to extract the methylcyclopentane. The extract is to be distilled to recover the solvent as 0.995 mole fraction aniline and 0.005 mole fraction methylcyclopentane. This solution is combined with a small amount of makeup solvent of the same concentration and introduced into the first stage as the extracting solvent. The methylcyclopentane-rich stream from the distillation column is to contain 0.700 mole fraction methylcyclopentane, 0.184 mole fraction n-hexane, and 0.116 mole fraction aniline. A portion of this stream will be taken as the product and the rest returned to the extraction system as reflux. The ratio of reflux to product is to be 10 to 1. The raffinate stream is to contain 0.150 mole fraction methylcyclopentane. Determine the number of ideal contact stages above and below the entry point for the feed.

Solution

It is simpler to solve this problem by converting all concentrations from mole fractions to mole ratios. This has been done with the simple relations

$$Y_A = \frac{y_A}{y_A + y_B} \quad (41)$$

$$Y_B = \frac{y_B}{y_A + y_B} \quad (42)$$

* This problem is taken from Brown (1).

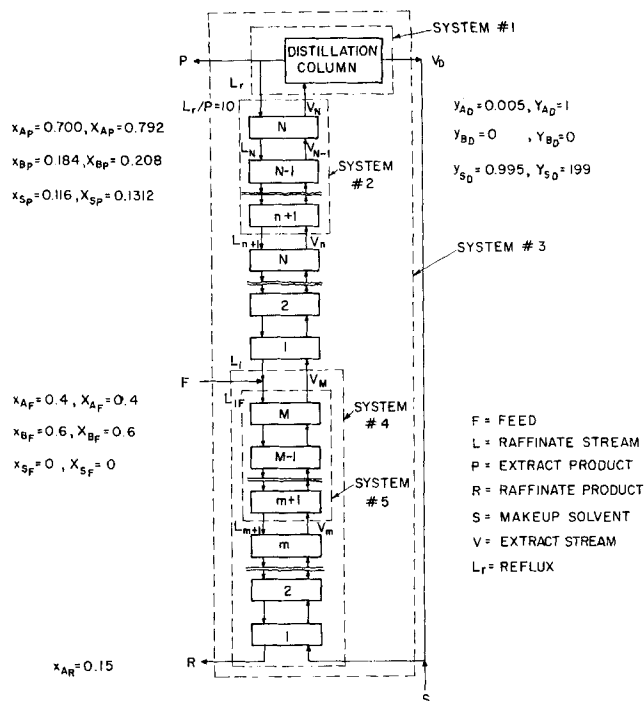


Fig. 3. Liquid-liquid extraction system with extract reflux.

$$Y_S = \frac{y_S}{y_A + y_B} \quad (43)$$

Y is the ratio in the extract phase of moles of a given component to the moles of two other components, A and B , where A refers to the methylcyclopentane, B to the n-hexane, and S to the solvent, aniline; the y 's are mole fractions. The same relations hold for X 's and x 's which designate concentrations in the raffinate phase. Consequently, the specified concentrations of the problem may be converted to mole ratio units and the flows may be expressed in moles of A and B . Figure 3 shows the concentrations specified by the problem in both mole fractions and mole ratios.

It is also convenient to develop analytical expressions for the equilibrium data given by Brown, using the mole ratio units. In the extract phase it is desirable to relate the concentration of aniline to that of the methylcyclopentane. The data are correlated well over the range of concentrations of the problem by the linear equation

$$Y_S = m_Y Y_A + b_Y = -8.4 Y_A + 11.6 \quad (44)$$

Correspondingly, in the raffinate phase another linear expression relates the aniline concentration to that of the methylcyclopentane:

$$X_S = m_X X_A + b_X = 0.09 X_A + 0.06 \quad (45)$$

The phase equilibrium data for the methylcyclopentane form a smooth uninflected curve and are fitted well over the desired concentration range by an equation of the form of Equation (2). With the constants evaluated this is

$$Y_A = \frac{\alpha X_A + \gamma}{1 - \beta X_A} = \frac{1.42 X_A + 0.033}{1 + 0.44 X_A} \quad (46)$$

The usual material balances around portions of an extraction system are made as shown in Figure 3. Around system no. 1, the distillation column, the total material balance is

$$V_N = V_D + L_r + P \quad (47)$$

where V_N is the extract stream from the N th stage, V_D

is the recovered solvent from the distillation column, L_r is the reflux, and P is the product, all in moles of A and B per unit time. A material balance for methylcyclopentane gives

$$V_N Y_{AN} = V_D Y_{AD} + L_r X_{AP} + P X_{AP} \quad (48)$$

The material balance on the aniline is

$$V_N Y_{SN} = V_D Y_{SD} + L_r X_{SP} + P X_{SP} \quad (49)$$

From the problem statement, $L_r/P = 10$, $X_{AP} = 0.792$, $X_{SP} = 0.1312$, $Y_{AD} = 1$, and $Y_{SP} = 199$, as shown in Figure 3, and one may combine (47), (48), and (49) and employ (44) to obtain $V_N/P = 11.27056$, $V_D/P = 0.27056$, $Y_{AN} = 0.797$, $Y_{SN} = 4.905$. Material balances around system no. 2 are

$$V_n + L_r = V_N + L_{n+1} \quad (50)$$

$$V_n Y_{An} + L_r X_{AP} = V_N Y_{AN} + L_{n+1} X_{An+1} \quad (51)$$

and

$$V_n Y_{Sn} + L_r X_{SP} = V_N Y_{SN} + L_{n+1} X_{Sn+1} \quad (52)$$

These three equations may be combined in the same manner as (17), (18), and (19). Also (44) and (45) may be utilized to eliminate the aniline concentration terms. The result is

$$Y_{An} = a X_{An+1} + b Y_{An} X_{An+1} + c \quad (53)$$

where

$$a = \frac{Y_{An} m_X - r X_{AP} m_X - Y_{SN} - (r-1) b_Y + r X_{SP}}{m_Y Y_{AN} - r X_{AP} - (r-1) b_X - Y_{SN} + r X_{SP}} \quad (54)$$

$$b = \frac{(r-1) m_X + (r-1) m_Y}{m_Y Y_{AN} - r X_{AP} m_Y - (r-1) b_X Y_{SN} + r X_{SP}} \quad (55)$$

$$c = \frac{r X_{AP} b_Y - b_Y Y_{AN} + b_X Y_{AN} - r X_{AP} b_X}{m_Y Y_{AN} - r X_{AP} m_Y - (r-1) b_X Y_{SN} + r X_{SP}} \quad (56)$$

and the reflux ratio is defined as

$$r = \frac{L_r}{V_N} \quad (57)$$

Equations (46) and (53) may be combined by eliminating Y_A to yield

$$X_{n+1} X_n + A X_{n+1} + B X_n + C = 0 \quad (58)$$

with

$$A = -\frac{a + \gamma b}{a\beta - ab} \quad (59)$$

$$B = \frac{\alpha + c\beta}{a\beta - ab} \quad (60)$$

$$C = \frac{\gamma - c}{a\beta - ab} \quad (61)$$

Clearly Equation (58) is the same form as Equation (5) with X 's in place of y 's. Consequently, the solution Equations (6), (7), (8), (15), and (16) are directly applicable. The following constants are readily noted from the data to be $X_{AP} = 0.792$, $X_{SP} = 0.1312$, $r = 0.88727$, $m_Y = -8.4$, $b_Y = 11.6$, $m_X = 0.09$, $b_X = 0.06$, $\alpha = 1.42$, $\beta = -0.44$, $\gamma = 0.033$. From Equations (54), (55), (56), (59), (60), and (61), the values of A , B , and C are found to be $A = 1.21378$, $B = -2.57579$, $C = 0.31315$. Insertion of these values into Equation (9) gives $E_1 = 2.28288$, $E_2 = 1.50670$. Since these roots are real and unequal, the solution is given by Equation (6) in the form

$$N - 1 = \frac{\log \left(\frac{X_{AN} + A - E_2}{X_{AN} + A - E_1} \right) \left(\frac{X_{A1} + A - E_1}{X_{A1} + A - E_2} \right)}{\log \left(\frac{E_1}{E_2} \right)} \quad (62)$$

This form is obtained from (6A) by taking the definite summation between $X_A = X_{A1}$ at $n = 1$, and $X_A = X_{AN}$ at $n = N$. The value of X_{AN} is found from Equation (46) by putting in $Y_{AN} = 0.797$, so that $X_{AN} = 0.71446$. The value of X_{A1} is just that of the feed or $X_{A1} = 0.4$. The upper and lower limit numbers may now be calculated from (62) to give $N = 5.83$. This is the number of equilibrium stages above feed.

To calculate the number of stages below the feed, the limiting conditions must be determined. Using Equation (41) in the X form and Equation (45) with $X_{AR} = 0.15$, one finds $X_{AR} = 0.1612$ and $X_{SR} = 0.0745$. When the same three material balances used for the other systems are formed around system no. 3, it is determined that $F/P = 2.63707$, $R/P = 1.63834$, and $V/P = 0.27183$. The same three material balances around system no. 4 show that $V_M/P = 7.18408$, $L_1/P = 5.91352$, $Y_{AM} = 0.47716$. When L_1/P and F/P are combined one obtains

$$L_1 F = 8.55059 \text{ so that } r = \frac{L_1 F}{V_M} = 1.190214. \text{ Since } X_{A1}$$

and X_{AF} are both 0.4, $X_{A1F} = 0.4$ which inserted into (45) makes $X_{S1F} = 0.06639$. When $Y_{AM} = 0.47716$ is put into (44) one obtains $Y_{SM} = 7.59184$. The material balances around system no. 5 yield the same difference equation as (58) with

$$a = \frac{Y_{AM} - r X_{A1F} - Y_{SM} - (r-1) b_Y + r X_{S1F}}{m_Y Y_{AM} - r X_{A1F} m_Y - (r-1) b_X - Y_{SM} + r X_{S1F}} \quad (63)$$

$$b = \frac{(r-1) m_X + (r-1) m_Y}{m_Y Y_{AM} - r X_{A1F} m_Y - (r-1) b_X - Y_{SM} + r X_{S1F}} \quad (64)$$

$$c = \frac{r X_{A1F} b_Y - b_Y Y_{AM} + b_X Y_{AM} - r X_{A1F} b_X}{m_Y Y_{AM} - r X_{A1F} m_Y - (r-1) b_X - Y_{SM} + r X_{S1F}} \quad (65)$$

When these three equations are used with (59), (60), (61), and (9) and the previous values of m_X , b_X , m_Y , b_Y , α , β , and γ , as given for the upper section, one may calculate $A = 4.873726$, $B = -5.396501$, $C = -0.13161$, $E_1 = 5.58225$, $E_2 = 4.68797$. These values are put into (62) with M replacing N , and with $X_A = X_{AR} = 0.1612$ at $m = 1$, and $X_A = X_{AM} = 0.36706$ at $m = M$, where the latter value is obtained by insertion of $Y_{AM} = 0.47716$ into (46), to give $M = 6.37$. This is the number of equilibrium stages below the point of entry of the feed. The total number of stages in the whole system is $N + M = 5.83 + 6.37 = 12.2$. Brown (1) gives 12.7 stages as the result of a graphical analysis; however, a high precision graph was drawn, and it appears that the answer is much closer to 12.2 as calculated. This points up one of the advantages of the analytical method: one obtains precise results which can be obtained graphically only with large graph paper and a sharp pencil, which is actually comparable to carrying a number of figures in the calculation procedure. With either electronic computers or desk calculators, it is easy to carry six to ten figures in all the calculations so precise results are easily obtainable. Furthermore, if the variables are changed a little, it is simple to change the feed input to an electronic computer program and obtain a new answer in a very short time, whereas the graphical technique becomes very tedious and difficult. If stage-to-stage calculations are carried out on the computer, far more storage and computer time will be required to solve a problem with many variations in the input parameters.

SUMMARY

The analytical method developed here for solving stage-to-stage operation problems should have broad applica-

bility. The real power of the method lies in the ability of Equations (1) and (2) to fit highly nonlinear data either directly or piece by piece. Problems which previously seemed to require graphical treatment or stage-to-stage calculations because of nonlinear equilibrium and operating lines may now be handled in a direct analytical way. Examples have been given to demonstrate the versatility of the method.

NOTATION

a	= constant in operating line equation
A	= constant in Riccati equation
b	= constant in operating line equation and in concentration equations
B	= constant in Riccati equation
c	= constant in operating line equation
C	= constant in Riccati equation
e	= base of natural logarithms, 2.71828
$E_{1,2}$	= roots of discriminant equation
F	= feed stream rate
h	= specific enthalpy of liquid
H	= specific enthalpy of vapor
i	= $\sqrt{-1}$
L	= liquid flow rate
m	= constant in concentration or enthalpy equations
M	= number of stages
N	= number of stages
p	= $\sqrt{C - \left(\frac{A+B}{2}\right)^2}$
P	= extract product
R	= reflux ratio, L_r/V_N in distillation, raffinate in extraction
S	= makeup solvent
V	= vapor flow rate or extract stream
x	= concentration as mole or mass fraction
X	= mole ratio in n-hexane layer
y	= concentration as mole or mass fraction
Y	= mole ratio in aniline layer
$\theta, \theta_1, \theta_2$	= angles in complex root solution
α	= constant in equilibrium equation
β	= constant in equilibrium equation
γ	= constant in equilibrium equation

Subscripts

A	= methylcyclopentane
B	= n-hexane
D	= distillate or overhead product
F	= feed
l	= liquid
M	= top or last stage
$n, n+1$	= nth or n+1 th stage
N	= top or last stage
O	= condition just before first stage
P	= extract product
r	= reflux stream
R	= reflux stream
S	= solvent, aniline
v	= vapor
X	= raffinate phase
Y	= extract phase

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APPENDIX

Solution of Riccati Equation

The solution of the Riccati Equation (5)

$$y_{n+1}y_n + Ay_{n+1} + By_n + C = 0 \quad (1A)$$

may be obtained by the usual procedures as

$$y_n = \frac{cE_1^{n+1} + E_2^{n+1}}{cE_1^n + E_2^n} - A \quad (2A)$$

where

$$E_{1,2} = \frac{A-B}{2} \pm \sqrt{\left(\frac{A+B}{2}\right)^2 - C} \quad (3A)$$

and c is the constant of summation. If the two roots $E_{1,2}$ are equal, the solution is

$$y_n = \frac{n+1+c}{n+c} E_1 - A \quad (4A)$$

where E_1 is the single root.

Equations (2A) and (4A) are solutions to (1A) for the cases of unequal roots and equal roots, respectively, of (3A). Usually one wishes to solve for the number of steps, n , rather than for a concentration, y_n , so these equations are rearranged accordingly. If the roots are real (that is, not complex), the rearrangement is straightforward. For example, Equation (2A) may be written

$$(y_n + A)(cE_1^n + E_2^n) = cE_1^{n+1} + E_2^{n+1} = cE_1E_1^n + E_2E_2^n \quad (5A)$$

When the E 's are factored out one obtains

$$\left(\frac{E_1}{E_2}\right)^n = \frac{E_2 - y_n - A}{c(y_n + A - E_1)} \quad (6A)$$

from which

$$n = \frac{\log \frac{E_2 - y_n - A}{c(y_n + A - E_1)}}{\log \left(\frac{E_1}{E_2}\right)} \quad (7A)$$

If y_n is known as y_0 at $n = 0$, Equation (6A) yields

$$c = \frac{E_2 - y_0 - A}{y_0 + A - E_1} \quad (8A)$$

When this is put into (7A) and $y_n = y_N$ at $n = N$, the total number of stages

$$N = \frac{\log \frac{(y_N + A - E_2)(y_0 + A - E_1)}{(y_N + A - E_1)(y_0 + A - E_2)}}{\log \left(\frac{E_1}{E_2}\right)} \quad (9A)$$

For the case of equal roots, Equation (4A) may be solved for n as

$$n = \frac{E_1}{y_n + A - E_1} - c \quad (10A)$$

From $y_n = y_0$ at $n = 0$

$$c = \frac{E_1}{y_0 + A - E_1} \quad (11A)$$

When (10A) and (11A) are combined with $n = N$ at $y_n = y_N$

$$N = \frac{E_1(y_0 - y_N)}{(y_N + A - E_1)(y_0 + A - E_1)} \quad (12A)$$

If the roots of the discriminant (3A) are complex, a case which often arises in practical applications, one may write (3A) in two forms:

$$E_1 = \frac{A - B}{2} + ip \quad (13A)$$

and

$$E_2 = \frac{A - B}{2} - ip \quad (14A)$$

where

$$ip = \sqrt{\left(\frac{A + B}{2}\right)^2 - C} \quad (15A)$$

When (6A) and (8A) are combined

$$\left(\frac{E_1}{E_2}\right)^n = \frac{(E_2 - y_n - A)(y_0 + A - E_1)}{(E_2 - y_0 - A)(y_n + A - E_1)} \quad (16A)$$

When (13A) and (14A) are inserted, the equation may be rearranged to obtain, at $n = N$ and $y_n = y_N$

$$\left[\frac{\frac{A - B}{2} + ip}{\frac{A - B}{2} - ip} \right]^N$$

$$= \frac{\left(y_N + \frac{A + B}{2} + ip\right)\left(y_0 + \frac{A + B}{2} - ip\right)}{\left(y_N + \frac{A + B}{2} - ip\right)\left(y_0 + \frac{A + B}{2} + ip\right)} \quad (17A)$$

The complex numbers may then be represented as follows:

$$re^{i\theta} = \frac{A - B}{2} + ip \quad (18A)$$

where

$$\arctan \frac{2p}{A - B} = \theta \quad (19A)$$

$$r_2 e^{i\theta_2} = y_N + \frac{A + B}{2} + ip \quad (20A)$$

where

$$\arctan \frac{p}{y_N + (A + B)/2} = \theta_2 \quad (21A)$$

$$r_1 e^{i\theta_1} = y_0 + \frac{A + B}{2} + ip \quad (22A)$$

where

$$\arctan \frac{k}{y_0 + (A + B)/2} = \theta_1 \quad (23A)$$

When these are inserted into (17A) one obtains

$$e^{2iN\theta} = e^{2i\theta_2} \cdot e^{-2i\theta_1} \quad (24A)$$

When logarithms are taken

$$N = \frac{\theta_2 - \theta_1}{\theta} \quad (25A)$$

Thermal Diffusion of Liquids in Columns

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A number of studies of the operating variables of the thermal diffusion column have been made since the war. Most of these show that the early theory is essentially correct, but that certain irregularities may prevail. The purpose of the present work is to continue the study of the theory of the column in transient batchwise operation and in continuous flow. The work was limited to liquids in annular columns without end reservoirs.

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PREVIOUS WORK

The early studies of thermal diffusion were made in the single-stage, convection-free apparatus in which separations are very small. In 1938 Clusius and Dickel (1) devised the thermal diffusion column which acts as a multistage device and thus greatly magnifies the possible separations. In 1939 Furry, Jones, and Onsager (2) and, independently, Debye (3) published theories to explain the behavior of the column. A number of investigations followed which demonstrated the approximate validity of the theory of the column for gases.