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FRACTIONAL DISTILLATION OF MULTICOMPONENT MIXTURES

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A rigorous analytical method is presented for making fractionating column calculations for multicomponent mixtures, constant molal reflux and constant relative volatilities being assumed.

It is shown that the method can be applied to take full account of the "unspecified" components, that is, those lighter than the light key component in the bottom product and heavier than the heavy key component in the top product. Attention is drawn to the possible errors that might arise if these components are neglected.

The method for determining the minimum reflux ratio, which has been presented previously, (2-3), is further extended and applied to cases where there is one or more distributed components.

In previous papers (1-3) equations were derived which give the composition on any plate in a fractionating column in which a multicomponent mixture is being separated. In particular, the method was shown to give a convenient means of determining the minimum reflux ratio. The present paper shows how the basic equations can be transformed so that calculations for the case of any reflux ratio are facilitated. It also shows how the method for determining minimum reflux ratio can be extended to cover the case of one or more distributed components. Constant molal reflux and constant relative volatilities are assumed throughout.

To facilitate the task of the reader, the method used for deriving the basic equations is briefly recapitulated here. It is illustrated with reference to a three-component mixture but, as already shown (1), it applies equally well to a mixture of any number of components.

Denoting the three components by x_1, x_2, x_3, in order of increasing volatility, the molal compositions of the liquids on any two adjacent plates (plate 1 being below plate 0) are connected by the equations

$$mx_{3,0} + a_3 = \frac{\alpha_3 x_{3,1}}{\alpha_3 x_{3,1} + \alpha_2 x_{2,1} + \alpha_1 x_{1,1}} \quad (1)$$

$$mx_{2,0} + a_2 = \frac{\alpha_2 x_{2,1}}{\alpha_3 x_{3,1} + \alpha_2 x_{2,1} + \alpha_1 x_{1,1}} \quad (2)$$

$$mx_{1,0} + a_1 = \frac{\alpha_2 x_{1,1}}{\alpha_3 x_{3,1} + \alpha_2 x_{2,1} + \alpha_1 x_{1,1}} \quad (3)$$

Where the symbol x carries two subscripts, the first subscript denotes the component in question and the second subscript denotes location. Thus $x_{3,1}$ or $x_{3,D}$ denote the mole fraction of component 3 on plate 1 and in the top product respectively.

For an enriching column,

$$m = \frac{R}{R+1}$$

where R is the reflux ratio;

$$a_3 = \frac{x_{3,D}}{R+1};\ a_2 = \frac{x_{2,D}}{R+1};$$

$$a_1 = \frac{x_{1,D}}{R+1}.$$

$\alpha_1, \alpha_2, \alpha_3$ are the relative volatilities of the components referred to any convenient standard and $\alpha_3 > \alpha_2 > \alpha_1$. In practice it is often convenient to take the least volatile component as the standard so that $\alpha_1 = 1$. For a stripping column,

$$m = \frac{S+1}{S}$$

where S is the "reboil ratio," i.e., the number of moles of vapor returned to the column by the reboiler per mole of bottom product withdrawn;

$$a_3 = \frac{-x_{3,w}}{S},\ a_2 = \frac{-x_{2,w}}{S},$$

$$a_1 = \frac{-x_{1,w}}{S}.$$

For a stripping column with an enriching column superimposed on it,

$$S = \frac{RD + qF - W}{W}.$$

For both enriching and stripping columns $a_3 + a_2 + a_1 = 1 - m$. Multiplying Equations (1), (2) and (3) by

$$\frac{\alpha_3}{\alpha_3 - \phi},\ \frac{\alpha_2}{\alpha_2 - \phi},\ \frac{\alpha_1}{\alpha_1 - \phi}$$

TABLE 1.—VALUES OF $x_{3,n}$

n	$a_1 = 10^{-5}$	$a_1 = 10^{-6}$	$a_1 = 10^{-7}$	$a_1 = 10^{-8}$	$a_1 = 10^{-9}$	$a_1 = 10^{-10}$	$a_1 = 10^{-11}$	$a_1 = 0$
5	.973	.985	.986	.986	.986	.986	.986	.986
10	.290	.700	.875	.899	.901	.902	.902	.902
15	.112	.123	.209	.469	.599	.617	.619	.619
20	.111	.111	.112	.124	.201	.344	.388	.393
25	.111	.111	.111	.111	.114	.138	.244	.342
30	.111	.111	.111	.111	.111	.112	.120	.334

TABLE 2.—VALUES OF $x_{2,n}$

n	$a_1 = 10^{-5}$	$a_1 = 10^{-6}$	$a_1 = 10^{-7}$	$a_1 = 10^{-8}$	$a_1 = 10^{-9}$	$a_1 = 10^{-10}$	$a_1 = 10^{-11}$	$a_1 = 0$
5	.0157	.0159	.0159	.0159	.0159	.0159	.0159	.0159
10	.0229	.0746	.0966	.0995	.0998	.0998	.0998	.0998
15	.0012	.0092	.0736	.2685	.3655	.379	.381	.381
20	.00036	.00062	.0032	0274	.1935	.500	.594	.607
25	.00034	.00034	.00042	.0012	.0091	.0786	.379	.659
30	.00033	.00033	.00033	.00036	.00061	.0031	.027	.665

respectively (ϕ being a quantity as yet undetermined) and adding, then

$$m\left(\frac{a_3x_{3,0}}{a_3-\phi}+\frac{a_2x_{2,0}}{a_2-\phi}+\frac{a_1x_{1,0}}{a_1-\phi}\right)+\frac{a_3a_3}{a_3-\phi}+\frac{a_2a_2}{a_2-\phi}+\frac{a_1a_1}{a_1-\phi}$$

$$=\frac{a_3x_{3,1}\cdot\dfrac{a_3}{a_3-\phi}+a_2x_{2,1}\cdot\dfrac{a_2}{a_2-\phi}+a_1x_{1,1}\cdot\dfrac{a_1}{a_1-\phi}}{a_3x_{3,1}+a_2x_{2,1}+a_1x_{1,1}} \qquad (4)$$

If ϕ is now chosen so that

$$\frac{a_3a_3}{a_3-\phi}+\frac{a_2a_2}{a_2-\phi}+\frac{a_1a_1}{a_1-\phi}=1 \qquad (5)$$

then Equation (4) reduces to

$$\frac{a_3x_{3,0}}{a_3-\phi}+\frac{a_2x_{2,0}}{a_2-\phi}+\frac{a_1x_{1,0}}{a_1-\phi}=\frac{\phi\left\{\dfrac{a_3x_{3,1}}{a_3-\phi}+\dfrac{a_2x_{2,1}}{a_2-\phi}+\dfrac{a_1x_{1,1}}{a_1-\phi}\right\}}{m(a_3x_{3,1}+a_2x_{2,1}+a_1x_{1,1})} \qquad (6)$$

Equation (5) is of the third degree and is satisfied by three values of ϕ, denoted by ϕ_1, ϕ_2, ϕ_3, it being taken that $\phi_1<\phi_2<\phi_3$. For each of these values of ϕ there is an equation corresponding to Equation (6). Dividing one such equation by one of the others gives the form

$$\frac{\dfrac{a_3x_{3,0}}{a_3-\phi_1}+\dfrac{a_2x_{2,0}}{a_2-\phi_1}+\dfrac{a_1x_{1,0}}{a_1-\phi_1}}{\dfrac{a_3x_{3,0}}{a_3-\phi_2}+\dfrac{a_2x_{2,0}}{a_2-\phi_2}+\dfrac{a_1x_{1,0}}{a_1-\phi_2}}=\frac{\phi_1}{\phi_2}\cdot\frac{\dfrac{a_3x_{3,1}}{a_3-\phi_1}+\dfrac{a_2x_{2,1}}{a_2-\phi_1}+\dfrac{a_1x_{1,1}}{a_1-\phi_1}}{\dfrac{a_3x_{3,1}}{a_3-\phi_2}+\dfrac{a_2x_{2,1}}{a_2-\phi_2}+\dfrac{a_1x_{1,1}}{a_1-\phi_2}} \qquad (7)$$

Applying this relation to successive plates gives the following relation between the composition on any plate 0 and the composition on a plate n plates below it,

$$\frac{\dfrac{a_3x_{3,0}}{a_3-\phi_1}+\dfrac{a_2x_{2,0}}{a_2-\phi_1}+\dfrac{a_1x_{1,0}}{a_1-\phi_1}}{\dfrac{a_3x_{3,0}}{a_3-\phi_2}+\dfrac{a_2x_{2,0}}{a_2-\phi_2}+\dfrac{a_1x_{1,0}}{a_1-\phi_2}}=\left(\frac{\phi_1}{\phi_2}\right)^n\cdot\frac{\dfrac{a_3x_{3,n}}{a_3-\phi_1}+\dfrac{a_2x_{2,n}}{a_2-\phi_1}+\dfrac{a_1x_{1,n}}{a_1-\phi_1}}{\dfrac{a_3x_{3,n}}{a_3-\phi_2}+\dfrac{a_2x_{2,n}}{a_2-\phi_2}+\dfrac{a_1x_{1,n}}{a_1-\phi_2}} \qquad (8a)$$

Similarly obtained are the equations:

$$\frac{\dfrac{a_3x_{3,0}}{a_3-\phi_2}+\dfrac{a_2x_{2,0}}{a_2-\phi_2}+\dfrac{a_1x_{1,0}}{a_1-\phi_2}}{\dfrac{a_3x_{3,0}}{a_3-\phi_3}+\dfrac{a_2x_{2,0}}{a_2-\phi_3}+\dfrac{a_1x_{1,0}}{a_1-\phi_3}}=\left(\frac{\phi_2}{\phi_3}\right)^n\cdot\frac{\dfrac{a_3x_{3,n}}{a_3-\phi_2}+\dfrac{a_2x_{2,n}}{a_2-\phi_2}+\dfrac{a_1x_{1,n}}{a_1-\phi_2}}{\dfrac{a_3x_{3,n}}{a_3-\phi_3}+\dfrac{a_2x_{2,n}}{a_2-\phi_3}+\dfrac{a_1x_{1,n}}{a_1-\phi_3}} \qquad (8b)$$

$$\frac{\dfrac{a_3x_{3,0}}{a_3-\phi_3}+\dfrac{a_2x_{2,0}}{a_2-\phi_3}+\dfrac{a_1x_{1,0}}{a_1-\phi_3}}{\dfrac{a_3x_{3,0}}{a_3-\phi_1}+\dfrac{a_2x_{2,0}}{a_2-\phi_1}+\dfrac{a_1x_{1,0}}{a_1-\phi_1}}=\left(\frac{\phi_3}{\phi_1}\right)^n\cdot\frac{\dfrac{a_3x_{3,n}}{a_3-\phi_3}+\dfrac{a_2x_{2,n}}{a_2-\phi_3}+\dfrac{a_1x_{1,n}}{a_1-\phi_3}}{\dfrac{a_3x_{3,n}}{a_3-\phi_1}+\dfrac{a_2x_{2,n}}{a_2-\phi_1}+\dfrac{a_1x_{1,n}}{a_1-\phi_1}} \qquad (8c)$$

TABLE 3.—VALUES OF $x_{1,n}$

n	$a_1=10^{-5}$	$a_1=10^{-6}$	$a_1=10^{-7}$	$a_1=10^{-8}$	$a_1=10^{-9}$	$a_1=10^{-10}$	$a_1=10^{-11}$	$a_1=0$
5	.0141	.0014	1.43×10^{-4}	1.43×10^{-5}	1.43×10^{-6}	1.43×10^{-7}	1.43×10^{-8}	0
10	.687	.227	.0294	.0030	3.04×10^{-4}	3.04×10^{-5}	3.04×10^{-6}	0
15	.887	.869	.718	.263	.0358	.0037	3.73×10^{-4}	0
20	.889	.889	.885	.851	.606	.157	.0186	0
25	.889	.889	.889	.888	.877	.784	.379	0
30	.889	.889	.889	.889	.889	.885	.853	0

The parameter ϕ was defined by Equation (5). Other relationships involving it can be deduced as follows: If the compositions of the liquids on two adjacent plates are the same, as is the case under minimum reflux conditions, denoting this composition by (c_1, c_2, c_3) and substituting these values in Equation (6), then

$$\phi=m(a_3c_3+a_2c_2+a_1c_1) \qquad (9)$$

Equations (1), (2), (3) then give

$$\frac{mc_3+a_3}{a_3c_3}=\frac{mc_2+a_2}{a_2c_2}=\frac{mc_1+a_1}{a_1c_1}=\frac{1}{a_3c_3+a_2c_2+a_1c_1}=\frac{m}{\phi}$$

and

$$c_3=\frac{a_3\phi}{m(a_3-\phi)};\ c_2=\frac{a_2\phi}{m(a_2-\phi)};\ c_1=\frac{a_1\phi}{m(a_1-\phi)} \qquad (10a)$$

or

$$c_3=\frac{x_{3,D}\phi}{R(a_3-\phi)};\ c_2=\frac{x_{2,D}\phi}{R(a_2-\phi)};\ c_1=\frac{x_{1,D}\phi}{R(a_1-\phi)} \qquad (10b)$$

For the three values of ϕ, namely, ϕ_1, ϕ_2, ϕ_3, which satisfy Equation (5) there are three corresponding values of (c_1, c_2, c_3), which will be denoted by ($c_{1,1}$, $c_{2,1}$, $c_{3,1}$) ($c_{1,2}$, $c_{2,2}$, $c_{3,2}$) and ($c_{1,3}$, $c_{2,3}$, $c_{3,3}$) respectively. Here again the first subscript denotes the component in question while the second subscript denotes the particular value of ϕ which locates the particular set of compositions. Since $c_3+c_2+c_1=1$,

$$\frac{a_3\phi}{m(a_3-\phi)}+\frac{a_2\phi}{m(a_2-\phi)}+\frac{a_1\phi}{m(a_1-\phi)}=1 \qquad (11)$$

Equation (11) is another form of Equation (5) and can be derived from it by writing Equation (5) in the form

$$\frac{a_3a_3}{a_3-\phi}-a_3+\frac{a_2a_2}{a_2-\phi}-a_2+\frac{a_1a_1}{a_1-\phi}-a_1=1-a_3-a_2-a_1$$

and noting that $1-a_3-a_2-a_1=m$. Equation (5) can also be written as

$$\frac{a_3x_{3,D}}{a_3-\phi}+\frac{a_2x_{2,D}}{a_2-\phi}+\frac{a_1x_{1,D}}{a_1-\phi}=R+1 \qquad (12)$$

For total reflux, when R becomes infinite, the solutions of this equation are $\phi_1 = \alpha_1$; $\phi_2 = \alpha_2$; $\phi_3 = \alpha_3$. Now Equation (8a) may be written as

$$\frac{(\alpha_1 - \phi_1)\left\{\dfrac{\alpha_3 x_{3,0}}{\alpha_3 - \phi_1} + \dfrac{\alpha_2 x_{2,0}}{\alpha_2 - \phi_1}\right\} + \alpha_1 x_{1,0}}{(\alpha_2 - \phi_2)\left\{\dfrac{\alpha_3 x_{3,0}}{\alpha_3 - \phi_2} + \dfrac{\alpha_1 x_{1,0}}{\alpha_1 - \phi_2}\right\} + \alpha_2 x_{2,0}}$$

$$= \left(\frac{\phi_1}{\phi_2}\right)^n \cdot \frac{(\alpha_1 - \phi_1)\left\{\dfrac{\alpha_3 x_{3,n}}{\alpha_3 - \phi_1} + \dfrac{\alpha_2 x_{2,n}}{\alpha_2 - \phi_1}\right\} + \alpha_1 x_{1,n}}{(\alpha_2 - \phi_2)\left\{\dfrac{\alpha_3 x_{3,n}}{\alpha_3 - \phi_2} + \dfrac{\alpha_1 x_{1,n}}{\alpha_1 - \phi_2}\right\} + \alpha_2 x_{2,n}}$$

Putting $\phi_1 = \alpha_1$ and $\phi_2 = \alpha_2$, this gives

$$\frac{x_{1,0}}{x_{2,0}} = \left(\frac{\alpha_1}{\alpha_2}\right)^n \cdot \frac{x_{1,n}}{x_{2,n}} \qquad (13)$$

and thus reduces to the equation for total reflux given by Fenske (4) and the writer (5).

From Equations (10) it will be seen that, when R is infinite and $\phi_1 = \alpha_1$, $c_{3,1}$ and $c_{2,1}$ equal zero and $c_{1,1}$ is indeterminate. Since $c_{3,1} + c_{2,1} + c_{1,1} = 1$, then $c_{1,1} = 1$. Similarly when $\phi_2 = \alpha_2$, $c_{3,2} = 0$, $c_{2,2} = 1$, $c_{1,2} = 0$ and when $\phi_3 = \alpha_3$, $c_{3,3} = 1$, $c_{2,3} = 0$, $c_{1,3} = 0$.

The expression

$$\left(\frac{\alpha_3 x_3}{\alpha_3 - \phi} + \frac{\alpha_2 x_2}{\alpha_2 - \phi} + \frac{\alpha_1 x_1}{\alpha_1 - \phi}\right)$$

has certain important properties. For any one of the three values of ϕ the expression becomes zero when there are substituted for (x_3, x_2, x_1) the values of (c_3, c_2, c_1) corresponding to any of the other values of ϕ. Thus

$$\left(\frac{\alpha_3 x_3}{\alpha_3 - \phi_1} + \frac{\alpha_2 x_2}{\alpha_2 - \phi_1} + \frac{\alpha_1 x_1}{\alpha_1 - \phi_1}\right)$$

becomes zero when $(c_{3,2}, c_{2,2}, c_{1,2})$ or $(c_{3,3}, c_{2,3}, c_{1,3})$ are substituted for (x_3, x_2, x_1). This is readily proved as follows:

Since both ϕ_1 and ϕ_2 are roots of Equation (5)

$$\frac{a_3\alpha_3}{\alpha_3 - \phi_1} + \frac{a_2\alpha_2}{\alpha_2 - \phi_1} + \frac{a_1\alpha_1}{\alpha_1 - \phi_1} = \frac{a_3\alpha_3}{\alpha - \phi_2} + \frac{a_2\alpha_2}{\alpha_2 - \phi_2} + \frac{a_1\alpha_1}{\alpha_1 - \phi_2} = 1$$

or

$$\frac{a_3\alpha_3(\phi_1 - \phi_2)}{(\alpha_3 - \phi_1)(\alpha_3 - \phi_2)} + \frac{a_2\alpha_2(\phi_1 - \phi_2)}{(\alpha_2 - \phi_1)(\alpha_2 - \phi_2)} + \frac{a_1\alpha_1(\phi_1 - \phi_2)}{(\alpha_1 - \phi_1)(\alpha_1 - \phi_2)} = 0$$

Dividing through by $(\phi_1 - \phi_2)$ and multiplying by $\dfrac{\phi_2}{m}$, it will be seen from Equation (10a) that the above equation becomes

$$\frac{\alpha_3 c_{3,2}}{\alpha_3 - \phi_1} + \frac{\alpha_2 c_{2,2}}{\alpha_2 - \phi_1} + \frac{\alpha_1 c_{1,2}}{\alpha_1 - \phi_1} = 0 \qquad (14a)$$

Similarly

$$\frac{\alpha_3 c_{3,3}}{\alpha_3 - \phi_1} + \frac{\alpha_2 c_{2,3}}{\alpha_2 - \phi_1} + \frac{\alpha_1 c_{1,3}}{\alpha_1 - \phi_1} = 0 \qquad (14b)$$

with corresponding equations for the other values of ϕ.

It should be noted that

$$\frac{\alpha_3 c_{3,1}}{\alpha_3 - \phi_1} + \frac{\alpha_2 c_{2,1}}{\alpha_2 - \phi_1} + \frac{\alpha_1 c_{1,1}}{\alpha_1 - \phi_1}$$

is not equal to zero.

The relation is a general one for a mixture of any number of components. The left-hand side of Equation (5) contains as many terms as there are components. The number of values of ϕ is equal to the number of components and for each value of ϕ there are corresponding values of $c_1, c_2, c_3, \ldots$. The values of $c_1, c_2, c_3, \ldots$ have been called "constant zone compositions" or "limiting compositions." A more convenient term would perhaps be "invariant compositions."

The three equations (8a), (8b), (8c) represent only two independent relations as any one of these equations can be derived from the other two. There is, however, a third relation $x_1 + x_2 + x_3 = 1$. Given the compositions $x_{1,0}, x_{2,0}, x_{3,0}$, the values of $x_{1,n}, x_{2,n}, x_{3,n}$ can be found for any value of n by solving three simultaneous equations of the first degree. If there are, say, six components in the mixture, there will be six simultaneous equations to be solved. The direct solution of the equations thus becomes increasingly laborious as the number of components increases. The basic equations can, however, be converted into other forms which facilitate the solution of problems.

Enriching Column

In Equations (8a, b and c) when $(x_{1,0}, x_{2,0}, x_{3,0})$ are put equal to $(x_{1,D}, x_{2,D}, x_{3,D})$ the left-hand side of each equation becomes unity, from Equation (12). These equations may then be written

$$\frac{\dfrac{\alpha_3 x_{3,n}}{\alpha_3 - \phi_1} + \dfrac{\alpha_2 x_{2,n}}{\alpha_2 - \phi_1} + \dfrac{\alpha_1 x_{1,n}}{\alpha_1 - \phi_1}}{\dfrac{1}{\phi_1^{\,n}}} = \frac{\dfrac{\alpha_3 x_{3,n}}{\alpha_3 - \phi_2} + \dfrac{\alpha_2 x_{2,n}}{\alpha_2 - \phi_2} + \dfrac{\alpha_1 x_{1,n}}{\alpha_1 - \phi_2}}{\dfrac{1}{\phi_2^{\,n}}} = \frac{\dfrac{\alpha_3 x_{3,n}}{\alpha_3 - \phi_3} + \dfrac{\alpha_2 x_{2,n}}{\alpha_2 - \phi_3} + \dfrac{\alpha_1 x_{1,n}}{\alpha_1 - \phi_3}}{\dfrac{1}{\phi_3^{\,n}}} \qquad (15)$$

where $x_{3,n}$, $x_{2,n}$, $x_{1,n}$ are the compositions on the nth plate from the top of the column. We now introduce three indeterminate multipliers $\lambda_1, \lambda_2, \lambda_3$, so that, for all values of n,

$$\lambda_1\left(\frac{\alpha_3 x_{3,n}}{\alpha_3 - \phi_1} + \frac{\alpha_2 x_{2,n}}{\alpha_2 - \phi_1} + \frac{\alpha_1 x_{1,n}}{\alpha_1 - \phi_1}\right) + \lambda_2\left(\frac{\alpha_3 x_{3,n}}{\alpha_3 - \phi_2} + \frac{\alpha_2 x_{2,n}}{\alpha_2 - \phi_2} + \frac{\alpha_1 x_{1,n}}{\alpha_1 - \phi_2}\right) + \lambda_3\left(\frac{\alpha_3 x_{3,n}}{\alpha_3 - \phi_3} + \frac{\alpha_2 x_{2,n}}{\alpha_2 - \phi_3} + \frac{\alpha_1 x_{1,n}}{\alpha_1 - \phi_3}\right)$$

$$\equiv x_{3,n} + x_{2,n} + x_{1,n} = 1 \qquad (16)$$

$\lambda_1, \lambda_2, \lambda_3$, are then determined by the equations

$$\frac{\lambda_1\alpha_3}{\alpha_3 - \phi_1} + \frac{\lambda_2\alpha_3}{\alpha_3 - \phi_2} + \frac{\lambda_3\alpha_3}{\alpha_3 - \phi_3} = 1 \qquad (17a)$$

$$\frac{\lambda_1\alpha_2}{\alpha_2 - \phi_1} + \frac{\lambda_2\alpha_2}{\alpha_2 - \phi_2} + \frac{\lambda_3\alpha_2}{\alpha_2 - \phi_3} = 1 \qquad (17b)$$

$$\frac{\lambda_1\alpha_1}{\alpha_1 - \phi_1} + \frac{\lambda_2\alpha_1}{\alpha_1 - \phi_2} + \frac{\lambda_3\alpha_1}{\alpha_1 - \phi_3} = 1 \qquad (17c)$$

and may be found by solving these equations. Here again the solution of these equations becomes more laborious as the number of components increases.

A more convenient method of determining $\lambda_1, \lambda_2, \lambda_3$, is as follows. In Equation (16) put $(x_{3,n}, x_{2,n}, x_{1,n})$ equal to $(c_{3,1}, c_{2,1}, c_{1,1})$. As shown previously, by Equations (14a) and (14b), the coefficients of λ_2 and λ_3 become zero and Equation (16) gives

$$\lambda_1\left(\frac{\alpha_3 c_{3,1}}{\alpha_3 - \phi_1} + \frac{\alpha_2 c_{2,1}}{\alpha_2 - \phi_1} + \frac{\alpha_1 c_{1,1}}{\alpha_1 - \phi_1}\right) = 1 \qquad (18a)$$

Similarly

$$\lambda_2\left(\frac{a_3c_{3,2}}{a_3-\phi_2}+\frac{a_2c_{2,2}}{a_2-\phi_2}+\frac{a_1c_{1,2}}{a_1-\phi_2}\right)=1 \tag{18b}$$

and

$$\lambda_3\left(\frac{a_3c_{3,3}}{a_3-\phi_3}+\frac{a_2c_{2,3}}{a_2-\phi_3}+\frac{a_1c_{1,3}}{a_1-\phi_3}\right)=1 \tag{18c}$$

These equations can also be put into the following forms by substituting the values of the invariant compositions c given by Equations (10b)

$$\frac{1}{\lambda_1}=\frac{\phi_1}{R}\left\{\frac{a_3x_{3,D}}{(a_3-\phi_1)^2}+\frac{a_2x_{2,D}}{(a_2-\phi_1)^2}+\frac{a_1x_{1,D}}{(a_1-\phi_1)^2}\right\} \tag{18d}$$

$$\frac{1}{\lambda_2}=\frac{\phi_2}{R}\left\{\frac{a_3x_{3,D}}{(a_3-\phi_2)^2}+\frac{a_2x_{2,D}}{(a_2-\phi_2)^2}+\frac{a_1x_{1,D}}{(a_1-\phi_2)^2}\right\} \tag{18e}$$

$$\frac{1}{\lambda_3}=\frac{\phi_3}{R}\left\{\frac{a_3x_{3,D}}{(a_3-\phi_3)^2}+\frac{a_2x_{2,D}}{(a_2-\phi_3)^2}+\frac{a_1x_{1,D}}{(a_1-\phi_3)^2}\right\} \tag{18f}$$

We now take three other indeterminate multipliers λ_1^1, λ_2^1, λ_3^1, so that, for all values of n,

$$\lambda_1^1\left(\frac{a_3x_{3,n}}{a_3-\phi_1}+\frac{a_2x_{2,n}}{a_2-\phi_1}+\frac{a_1x_{1,n}}{a_1-\phi_1}\right)+\lambda_2^1\left(\frac{a_3x_{3,n}}{a_3-\phi_2}+\frac{a_2x_{2,n}}{a_2-\phi_2}+\frac{a_1x_{1,n}}{a_1-\phi_2}\right)+\lambda_3^1\left(\frac{a_3x_{3,n}}{a_3-\phi_3}+\frac{a_2x_{2,n}}{a_2-\phi_3}+\frac{a_1x_{1,n}}{a_1-\phi_3}\right)=x_{3,n} \tag{19}$$

Again putting ($x_{3,n}$, $x_{2,n}$, $x_{1,n}$) equal to ($c_{3,1}$, $c_{2,1}$, $c_{1,1}$), then

$$\lambda_1^1\left(\frac{a_3c_{3,1}}{a_3-\phi_1}+\frac{a_2c_{2,1}}{a_2-\phi_1}+\frac{a_1c_{1,1}}{a_1-\phi_1}\right)=c_{3,1} \tag{20}$$

or, from Equation (18a),

$$\lambda_1^1=\lambda_1c_{3,1} \tag{22a}$$

Similarly,

$$\lambda_2^1=\lambda_2c_{3,2} \tag{22b}$$

and

$$\lambda_3^1=\lambda_3c_{3,3} \tag{22c}$$

Now multiply the numerators and denominators of the three expressions in Equation (15) by λ_1, λ_2, λ_3, respectively and add the numerators and denominators. Repeat the process using λ_1^1, λ_2^1, λ_3^1 that is, $\lambda_1c_{3,1}$, $\lambda_2c_{3,2}$, $\lambda_3c_{3,3}$. Then

$$\frac{\dfrac{a_3x_{3,n}}{a_3-\phi_1}+\dfrac{a_2x_{2,n}}{a_2-\phi_1}+\dfrac{a_1x_{1,n}}{a_1-\phi_1}}{\dfrac{1}{\phi_1^n}}=\ldots\ldots\frac{1}{\dfrac{\lambda_1}{\phi_1^n}+\dfrac{\lambda_2}{\phi_2^n}+\dfrac{\lambda_3}{\phi_3^n}}=\frac{x_{3,n}}{\dfrac{\lambda_1c_{3,1}}{\phi_1^n}+\dfrac{\lambda_2c_{3,2}}{\phi_2^n}+\dfrac{\lambda_3c_{3,3}}{\phi_3^n}} \tag{23}$$

or

$$x_{3,n}=\frac{\dfrac{\lambda_1c_{3,1}}{\phi_1^n}+\dfrac{\lambda_2c_{3,2}}{\phi_2^n}+\dfrac{\lambda_3c_{3,3}}{\phi_3^n}}{\dfrac{\lambda_1}{\phi_1^n}+\dfrac{\lambda_2}{\phi_2^n}+\dfrac{\lambda_3}{\phi_3^n}} \tag{24a}$$

By an exactly similar derivation

$$x_{2,n}=\frac{\dfrac{\lambda_1c_{2,1}}{\phi_1^n}+\dfrac{\lambda_2c_{2,2}}{\phi_2^n}+\dfrac{\lambda_3c_{2,3}}{\phi_3^n}}{\dfrac{\lambda_1}{\phi_1^n}+\dfrac{\lambda_2}{\phi_2^n}+\dfrac{\lambda_3}{\phi_3^n}} \tag{24b}$$

and

$$x_{1,n}=\frac{\dfrac{\lambda_1c_{1,1}}{\phi_1^n}+\dfrac{\lambda_2c_{1,2}}{\phi_2^n}+\dfrac{\lambda_3c_{1,3}}{\phi_3^n}}{\dfrac{\lambda_1}{\phi_1^n}+\dfrac{\lambda_2}{\phi_2^n}+\dfrac{\lambda_3}{\phi_3^n}} \tag{24c}$$

By substituting in Equations (24) the values of the invariant compositions c given by Equations (10a) or (10b)

$$x_{3,n}=\frac{a_3}{m}\cdot\frac{\dfrac{\lambda_1}{\phi_1^{n-1}(a_3-\phi_1)}+\dfrac{\lambda_2}{\phi_2^{n-1}(a_3-\phi_2)}+\dfrac{\lambda_3}{\phi_3^{n-1}(a_3-\phi_3)}}{\dfrac{\lambda_1}{\phi_1^n}+\dfrac{\lambda_2}{\phi_2^n}+\dfrac{\lambda_3}{\phi_3^n}} \tag{24d}$$

or

$$x_{3,n}=\frac{x_{3,D}}{R}\cdot\frac{\dfrac{\lambda_1}{\phi_1^{n-1}(a_3-\phi_1)}+\dfrac{\lambda_2}{\phi_2^{n-1}(a_3-\phi_2)}+\dfrac{\lambda_3}{\phi_3^{n-1}(a_3-\phi_3)}}{\dfrac{\lambda_1}{\phi_1^n}+\dfrac{\lambda_2}{\phi_2^n}+\dfrac{\lambda_3}{\phi_3^n}} \tag{24e}$$

with similar equations for $x_{2,n}$ and $x_{1,n}$. Thus the compositions of the liquid on the nth plate are found by the following procedure. Values of ϕ_1, ϕ_2, ϕ_3, are obtained by solving Equation (5). Corresponding values of (c_1, c_2, c_3) are then obtained from Equation (10a) or (10b). Values of λ_1, λ_2, λ_3 are then obtained from Equations (18). Alternatively values of λ_1, λ_2, λ_3, are obtained from Equations (18d, e, f) without calculating the values of c_1, c_2, c_3. Equations (24) then give the required values of $x_{1,n}$, $x_{2,n}$, $x_{3,n}$.

Multiplying Equations (24a, b, c) by a_3, a_2, a_1, respectively and adding and using Equation (9)

$$a_3x_{3,n}+a_2x_{2,n}+a_1x_{1,n}=\frac{\dfrac{\lambda_1}{\phi_1^{n-1}}+\dfrac{\lambda_2}{\phi_2^{n-1}}+\dfrac{\lambda_3}{\phi_3^{n-1}}}{m\left(\dfrac{\lambda_1}{\phi_1^n}+\dfrac{\lambda_2}{\phi_2^n}+\dfrac{\lambda_3}{\phi_3^n}\right)} \tag{25}$$

($a_3x_{3,n}+a_2x_{2,n}+a_1x_{1,n}$) is the average volatility of the liquid on the nth plate, since it is the weighted mean obtained by multiplying the amount of each component by its relative volatility. Also for the nth plate

$$y_{1,n}=\frac{x_{1,n}}{a_3x_{3,n}+a_2x_{2,n}+a_1x_{1,n}}=K_nx_{1,n} \tag{26}$$

where $y_{1,n}$ is the mole fraction of component 1 in the vapor from the nth plate and K_n is the equilibrium constant for that component on the nth plate. Thus

$$K_n=\frac{1}{a_3x_{3,n}+a_2x_{2,n}+a_1x_{1,n}}=\frac{m\left(\dfrac{\lambda_1}{\phi_1^n}+\dfrac{\lambda_2}{\phi_2^n}+\dfrac{\lambda_3}{\phi_3^n}\right)}{\dfrac{\lambda_1}{\phi_1^{n-1}}+\dfrac{\lambda_2}{\phi_2^{n-1}}+\dfrac{\lambda_3}{\phi_3^{n-1}}} \tag{27}$$

The corresponding equilibrium constants for components 2 and 3 are obviously a_2K_n and a_3K_n.

As previously pointed out (*1*), Equations (8) are similar to equations for total reflux if the terms such as

$$\left(\frac{a_3x_3}{a_3-\phi_1}+\frac{a_2x_2}{a_2-\phi_1}+\frac{a_1x_1}{a_1-\phi_1}\right)$$

are regarded as components and if ϕ_1, ϕ_2, ϕ_3, are regarded as relative volatilities. They may thus be described as "pseudo-components" and "pseudo-relative volatilities," terms used by Harbert (6). To make the sum of the "pseudo-components" equal to unity they should be multiplied by the appropriate value of λ as defined by Equation (16). From Equation (9),

$$\frac{\phi_1}{\phi_2} = \frac{a_3c_{3,1} + a_2c_{2,1} + a_1c_{1,1}}{a_3c_{3,2} + a_2c_{2,2} + a_1c_{1,2}} \qquad (28)$$

and the ratio of the "pseudo-relative volatilities" is thus equal to the ratio of the average volatilities at the invariant compositions.

It will be seen that Equations (24) and (28) are similar in general form to the Equations (17) and (21) of Harbert (6), which were, however, given without strict mathematical proof and which contain coefficients that have to be obtained by solving simultaneous equations, equal in number to the number of components.

A number of interesting relationships can be derived for the multipliers λ. For instance, putting $(x_{1,n}, x_{2,n}, x_{3,n})$ equal to $(x_{1,D}, x_{2,D}, x_{3,D})$ in Equation (16) and noting that $x_{1,D} = \dfrac{a_1}{1-m}$, etc., and using Equation (5), then

$$\lambda_1 + \lambda_2 + \lambda_3 = 1 - m = a_1 + a_2 + a_3 \qquad (29)$$

This equation is useful for checking the values of λ calculated by Equations (18).

Applying the same procedure to Equation (19) gives

$$\lambda_1c_{3,1} + \lambda_2c_{3,2} + \lambda_3c_{3,3} = a_3 \qquad (30a)$$

Similarly it can be shown that

$$\lambda_1c_{2,1} + \lambda_2c_{2,2} + \lambda_3c_{2,3} = a_2 \qquad (30b)$$

and

$$\lambda_1c_{1,1} + \lambda_2c_{1,2} + \lambda_3c_{1,3} = a_1 \qquad (30c)$$

Multiplying Equations (30*a, b, c*) by a_3, a_2, a_1, respectively and adding and using Equation (9) gives

$$\lambda_1\phi_1 + \lambda_2\phi_2 + \lambda_3\phi_3 = m(a_3a_3 + a_2a_2 + a_1a_1) \qquad (31)$$

An equation has been given by Edmister (7) which expresses the composition on the nth plate in terms of the equilibrium constants for the different plates.

The derivation is essentially as follows:

$$mx_{3,0} + a_3 = \frac{a_3x_{3,1}}{a_3x_{3,1} + a_2x_{2,1} + a_1x_{1,1}} = a_3K_1x_{3,1}$$

$$\therefore\ x_{3,0} = \frac{a_3K_1}{m} \cdot x_{3,1} - \frac{a_3}{m}$$

Also

$$x_{3,1} = \frac{a_3K_2}{m} \cdot x_{3,2} - \frac{a_3}{m}$$

so that

$$x_{3,0} = \frac{a_3K_1}{m} \cdot \frac{a_3K_2}{m} \cdot x_{3,2} - \frac{a_3}{m}\left(\frac{a_3K_1}{m} + 1\right)$$

Similarly

$$x_{3,0} = \frac{a_3K_1}{m} \cdot \frac{a_3K_2}{m} \cdot \ldots \frac{a_3K_n}{m} \cdot x_{3,n} - \frac{a_3}{m}\left(\frac{a_3K_1}{m} \cdot \frac{a_3K_2}{m} \cdot \ldots \frac{a_3K_{n-1}}{m} + \frac{a_3K_1}{m} \cdot \frac{a_3K_2}{m} + \frac{a_3K_1}{m} + 1\right) \qquad (32)$$

This equation can be transformed to give Equation (24*a*).

From Equation (27),

$$\frac{a_3K_n}{m} = \frac{a_3\left(\dfrac{\lambda_1}{\phi_1{}^n} + \dfrac{\lambda_2}{\phi_2{}^n} + \dfrac{\lambda_3}{\phi_3{}^n}\right)}{\dfrac{\lambda_1}{\phi_1{}^{n-1}} + \dfrac{\lambda_2}{\phi_2{}^{n-1}} + \dfrac{\lambda_3}{\phi_3{}^{n-1}}}$$

and for $n = 1$,

$$\frac{a_3K_1}{m} = \frac{a_3\left(\dfrac{\lambda_1}{\phi_1} + \dfrac{\lambda_2}{\phi_2} + \dfrac{\lambda_3}{\phi_3}\right)}{\lambda_1 + \lambda_2 + \lambda_3}$$

It is readily seen that

$$\frac{a_3K_1}{m} \cdot \frac{a_3K_2}{m} \cdot \ldots \frac{a_3K_n}{m} = \frac{a_3{}^n\left(\dfrac{\lambda_1}{\phi_1{}^n} + \dfrac{\lambda_2}{\phi_2{}^n} + \dfrac{\lambda_3}{\phi_3{}^n}\right)}{\lambda_1 + \lambda_2 + \lambda_3} = \frac{a_3{}^n}{1-m}\left(\frac{\lambda_1}{\phi_1{}^n} + \frac{\lambda_2}{\phi_2{}^n} + \frac{\lambda_3}{\phi_3{}^n}\right)$$

from Equation (29).

Substituting in Equation (32) and putting $x_{3,0} = x_{3,D} = \dfrac{a_3}{1-m}$ gives

$$\frac{a_3}{1-m} = \frac{a_3{}^n}{1-m}\left(\frac{\lambda_1}{\phi_1{}^n} + \frac{\lambda_2}{\phi_2{}^n} + \frac{\lambda_3}{\phi_3{}^n}\right)x_{3,n} - \frac{a_3}{m}\left\{\left(\frac{\lambda_1}{\phi_1{}^{n-1}} + \frac{\lambda_2}{\phi_2{}^{n-1}} + \frac{\lambda_3}{\phi_3{}^{n-1}}\right)\frac{a_3{}^{n-1}}{1-m} + \ldots + \left(\frac{\lambda_1}{\phi_1} + \frac{\lambda_2}{\phi_2} + \frac{\lambda_3}{\phi_3}\right)\frac{a_3}{1-m} + 1\right\}$$

or

$$a_3{}^n\left(\frac{\lambda_1}{\phi_1{}^n} + \frac{\lambda_2}{\phi_2{}^n} + \frac{\lambda_3}{\phi_3{}^n}\right)x_{3,n} = \frac{a_3}{m}\left\{\left(\frac{\lambda_1}{\phi_1{}^{n-1}} + \frac{\lambda_2}{\phi_2{}^{n-1}} + \frac{\lambda_3}{\phi_3{}^{n-1}}\right)a_3{}^{n-1} + \ldots + \left(\frac{\lambda_1}{\phi_1} + \frac{\lambda_2}{\phi_2} + \frac{\lambda_3}{\phi_3}\right)a_3 + 1\right\}$$

$$= \frac{a_3}{m}\left\{\lambda_1\left(\frac{a_3{}^{n-1}}{\phi_1{}^{n-1}} + \ldots + \frac{a_3}{\phi_1} + 1\right) + \lambda_2\left(\frac{a_3{}^{n-1}}{\phi_2{}^{n-1}} + \ldots + \frac{a_3}{\phi_2} + 1\right) + \lambda_3\left(\frac{a_3{}^{n-1}}{\phi_3{}^{n-1}} + \ldots + \frac{a_3}{\phi_3} + 1\right) - \lambda_1 - \lambda_2 - \lambda_3 + 1\right\}$$

$$= \frac{a_3}{m}\left\{\lambda_1 \cdot \frac{\dfrac{a_3{}^n}{\phi_1{}^n} - 1}{\dfrac{a_3}{\phi_1} - 1} + \lambda_2 \cdot \frac{\dfrac{a_3{}^n}{\phi_2{}^n} - 1}{\dfrac{a_3}{\phi_2} - 1} + \lambda_3 \cdot \frac{\dfrac{a_3{}^n}{\phi_3{}^n} - 1}{\dfrac{a_3}{\phi_3} - 1} + m\right\}$$

since, by Equation (29), $\lambda_1 + \lambda_2 + \lambda_3 = 1 - m$.

Now

$$\frac{1}{\dfrac{a_3}{\phi_1} - 1} = \frac{\phi_1}{a_3 - \phi_1} = \frac{mc_{3,1}}{a_3}$$

Making the appropriate substitutions and noting that

$$\lambda_1c_{3,1} + \lambda_2c_{3,2} + \lambda_3c_{3,3} = a_3$$

from Equation (30*a*), we get

$$\left(\frac{\lambda_1}{\phi_1{}^n} + \frac{\lambda_2}{\phi_2{}^n} + \frac{\lambda_3}{\phi_3{}^n}\right)x_{3,n} = \frac{\lambda_1c_{3,1}}{\phi_1{}^n} + \frac{\lambda_2c_{3,2}}{\phi_2{}^n} + \frac{\lambda_3c_{3,3}}{\phi_3{}^n}$$

which is Equation (24*a*). The corresponding equations for $x_{2,n}$ and $x_{1,n}$ can be derived in exactly the same way.

For numerical computation of the values of λ, Equations (18) are the most convenient. Equations (17) can, however, be solved in the usual way and the following expressions for λ are obtained.

$$\lambda_1 = \frac{\phi_2\phi_3(a_3-\phi_1)(a_2-\phi_1)(a_1-\phi_1)}{a_1a_2a_3(\phi_1-\phi_2)(\phi_1-\phi_3)} \qquad (33a)$$

$$\lambda_2 = \frac{\phi_1\phi_3(a_3-\phi_2)(a_2-\phi_2)(a_1-\phi_2)}{a_1a_2a_3(\phi_2-\phi_1)(\phi_2-\phi_3)} \qquad (33b)$$

$$\lambda_3 = \frac{\phi_1\phi_2(a_3-\phi_3)(a_2-\phi_3)(a_1-\phi_3)}{a_1a_2a_3(\phi_3-\phi_1)(\phi_3-\phi_2)} \qquad (33c)$$

It has been shown (*1*) that $\phi_1\phi_2\phi_3 = ma_1a_2a_3$ so that Equation (33*a*) can also be written

$$\lambda_1 = \frac{m(a_3-\phi_1)(a_2-\phi_1)(a_1-\phi_1)}{\phi_1(\phi_1-\phi_2)(\phi_1-\phi_3)} \qquad (34)$$

Stripping Column

For a stripping column ψ will be used instead of ϕ and a'_3, a'_2, a'_1 instead of a_3, a_2, a_1 and c'_3, c'_2, c'_1 instead of c_3, c_2, c_1. Also μ will be used instead of λ and m' instead of m. Equations (8) give the relation between the composition on plate 0 and the composition on plate n, which is n plates below plate 0. For a stripping column the plates will be counted upwards from the reboiler. The composition on the sth plate above the reboiler will be given by $x_{3,0} = x_{3,s}$, etc., and $x_{3,n} = x_{3,w}$, etc. Then

$$\frac{\dfrac{a_3x_{3,s}}{a_3-\psi_1}+\dfrac{a_2x_{2,s}}{a_2-\psi_1}+\dfrac{a_1x_{1,s}}{a_1-\psi_1}}{\dfrac{a_3x_{3,s}}{a_3-\psi_2}+\dfrac{a_2x_{2,s}}{a_2-\psi_2}+\dfrac{a_1x_{1,s}}{a_1-\psi_2}} = \left(\frac{\psi_1}{\psi_2}\right)^s$$

and two similar equations, so that

$$\frac{\dfrac{a_3x_{3,s}}{a_3-\psi_1}+\dfrac{a_2x_{2,s}}{a_2-\psi_1}+\dfrac{a_1x_{1,s}}{a_1-\psi_1}}{\psi_1^s} = \frac{\dfrac{a_3x_{3,s}}{a_3-\psi_2}+\dfrac{a_2x_{2,s}}{a_2-\psi_2}+\dfrac{a_1x_{1,s}}{a_1-\psi_2}}{\psi_2^s} = \frac{\dfrac{a_3x_{3,s}}{a_3-\psi_3}+\dfrac{a_2x_{2,s}}{a_2-\psi_3}+\dfrac{a_1x_{1,s}}{a_1-\psi_3}}{\psi_3^s} \qquad (35)$$

Equations exactly similar to Equations (16)-(22) can be derived for the indeterminate multipliers μ. Thus

$$\mu_1\left(\frac{a_3c'_{3,1}}{a_3-\psi_1}+\frac{a_2c'_{2,1}}{a_2-\psi_1}+\frac{a_1c'_{1,1}}{a_1-\psi_1}\right) = 1, \text{ etc.}$$

Then, by the same procedure as was used for an enriching column, is obtained:

$$x_{3,s} = \frac{\mu_1c'_{3,1}\psi_1^s+\mu_2c'_{3,2}\psi_2^s+\mu_3c'_{3,3}\psi_3^s}{\mu_1\psi_1^s+\mu_2\psi_2^s+\mu_3\psi_3^s} \qquad (36a)$$

$$x_{2,s} = \frac{\mu_1c'_{2,1}\psi_1^s+\mu_2c'_{2,2}\psi_2^s+\mu_3c'_{2,3}\psi_3^s}{\mu_1\psi_1^s+\mu_2\psi_2^s+\mu_3\psi_3^s} \qquad (36b)$$

$$x_{1,s} = \frac{\mu_1c'_{1,1}\psi_1^s+\mu_2c'_{1,2}\psi_2^s+\mu_3c'_{1,3}\psi_3^s}{\mu_1\psi_1^s+\mu_2\psi_2^s+\mu_3\psi_3^s} \qquad (36c)$$

Comparing Equations (36) with Equations (24) it will be seen that ψ appears instead of $\dfrac{1}{\phi}$. This inversion does not appear in the equations for λ and μ which merely contain ψ instead of ϕ and c' instead of c. Thus

$$\frac{1}{\lambda_1} = \frac{a_3c_{3,1}}{a_3-\phi_1}+\frac{a_2c_{2,1}}{a_2-\phi_1}+\frac{a_1c_{1,1}}{a_1-\phi_1} \qquad (18a)$$

and

$$\frac{\mu_1}{1} = \frac{a_3c'_{3,1}}{a_3-\psi_1}+\frac{a_2c'_{2,1}}{a_2-\psi_1}+\frac{a_1c'_{1,1}}{a_1-\psi_1} \qquad (37a)$$

The equation for the average volatility or equilibrium constant, similar to Equations (25) and (27) is

$$\frac{1}{K_s} = a_3x_{3,s}+a_2x_{2,s}+a_1x_{1,s} = \frac{\mu_1\psi_1^{s+1}+\mu_2\psi_2^{s+1}+\mu_3\psi_3^{s+1}}{m'(\mu_1\psi_1^s+\mu_2\psi_2^s+\mu_3\psi_3^s)} \qquad (38)$$

The values of λ are all positive and the values of μ are all negative. This is readily shown as follows.

$$c_{3.1} = \frac{a_3\phi_1}{m(a_3-\phi_1)} = \frac{x_{3.D}\phi_1}{R(a_3-\phi_1)}$$

$$\text{and } c'_{3.1} = \frac{a'_3\psi_1}{m'(a_3-\psi_1)} = \frac{-x_{3.w}\psi_1}{(S+1)(a_3-\psi_1)}$$

Equations (18*a*) and (37*a*) become, with these substitutions,

$$\frac{1}{\lambda_1} = \frac{\phi_1}{R}\left\{\frac{a_3x_{3.D}}{(a_3-\phi_1)^2}+\frac{a_2x_{2.D}}{(a_2-\phi_1)^2}+\frac{a_1x_{1.D}}{(a_1-\phi_1)^2}\right\} \qquad (39)$$

and

$$\frac{1}{\mu_1} = \frac{-\psi_1}{S+1}\left\{\frac{a_3x_{3.w}}{(a_3-\psi_1)^2}+\frac{a_2x_{2,w}}{(a_2-\psi_1)^2}+\frac{a_1x_{1.w}}{(a_1-\psi_1)^2}\right\} \qquad (40)$$

From Equation (12),

$$\frac{a_3x_{3.D}}{a_3-\phi}+\frac{a_2x_{2.D}}{a_2-\phi}+\frac{a_1x_{1,D}}{a_1-\phi} = R+1 \qquad (12)$$

On differentiation, with R and ϕ as variables, this gives

$$\frac{a_3x_{3.D}}{(a_3-\phi)^2}+\frac{a_2x_{2.D}}{(a_2-\phi)^2}+\frac{a_1x_{1.D}}{(a_1-\phi)^2} = \frac{dR}{d\phi}$$

so that

$$\frac{1}{\lambda_1} = \left(\frac{\phi}{R}\cdot\frac{dR}{d\phi}\right)_{\phi=\phi_1} \qquad (41)$$

The equation for the stripping column corresponding to Equation (12) is

$$\frac{a_3x_{3.w}}{a_3-\psi}+\frac{a_2x_{2.w}}{a_2-\psi}+\frac{a_1x_{1.w}}{a_1-\psi} = -S$$

and, similarly,

$$\frac{1}{\mu_1} = \left(\frac{\psi}{S+1}\cdot\frac{dS}{d\psi}\right)_{\psi=\psi_1} \qquad (42)$$

Enriching Column with Stripping Column

For the case of an enriching column superimposed on a stripping column a calculation would be made in the following way. Using Equations (24), the number of plates, n, required to give a certain composition ($x_{3,n}$, $x_{2,n}$, $x_{1,n}$) at the bottom of the enriching column would be found. Using this composition in Equations

(36), the number of plates, s, in the stripping column would be found. The composition at the bottom of the enriching column and the top of the stripping column is the composition on the feed-plate. The optimum location of the feed-plate to give the smallest number of plates for a given reflux ratio can be determined if the feed-plate composition can be calculated. Alternatively a number of calculations can be made to determine which composition gives the smallest value of $(n+s)$.

The practical application of this procedure is quite straightforward if the amounts of all components are specified in both the top product and the bottom product, a case which is practically limited to binary mixtures. It will be seen from Equations (39) and (40) that all components enter into the expressions for λ and μ and the amounts of all components in the top product and the bottom product need to be known for calculating the values of λ and μ. Not all the values of λ and μ are affected equally when there are some unspecified components, that is, components heavier than the heavy key component, which would be unspecified in the enriching column, or components lighter than the light key component, which would be unspecified in the stripping column. Consider, for instance, Equation (39), assuming x_3 and x_2 to be the key components so that $x_{1,D}$ is unspecified. Although $x_{1,D}$ will be very small, $(\alpha_1 - \phi_1)$ is also very small as ϕ_1 is very nearly equal to α_1. The term $\frac{x_{1,D}}{(\alpha_1-\phi_1)^2}$ will therefore not be negligible. On the other hand, the corresponding term $\frac{x_{1,D}}{(\alpha_1-\phi)^2}$ appearing in the expression for λ_2 will be quite negligible and the value of λ_2 will not be affected by the uncertainty as to the value of $x_{1,D}$.

The particular values of λ and μ that are affected by the values of the unspecified components are the ones which relate to those particular components. Thus, in the example given above, λ_1 is the value of λ related to ϕ_1, which in turn is the smallest value of ϕ, that is, the one related to the heaviest component, which is the unspecified one. In a ternary mixture with x_2 and x_1 as key components, x_3 would be unspecified in the bottom product and the value of μ which would be affected by variations in $x_{3,w}$ would be μ_3 corresponding to ψ_3.

Equations (24) or (36) contain all values of λ (or μ) in the expressions for x_3, x_2, x_1, and uncertainty regarding any one value of λ (or μ) will affect the values of all components x_3, x_2 and x_1 as found from these equations. This is not a special defect in the method of calculation presented in this paper. It is merely the analytical expression of the basic fact that a negligible amount of an unspecified component in the product leaving an enriching column or a stripping column may correspond to a substantial amount of that component at some other point in the column and that variations in the amount of the component at the point where it is negligible will cause variations at the point where the amount is substantial. The extent of these variations is illustrated by the following example (enriching column). $x_{3,D} = 0.999$; $x_{2,D} = 0.001$; $x_{1,D}$ is small and unspecified. $R = 3$; $\alpha_3 = 4$; $\alpha_2 = 2$; $\alpha_1 = 1$. Then $m = 0.75$.

The equation for finding ϕ is

$$\frac{\alpha_3 a_3}{\alpha_3-\phi}+\frac{\alpha_2 a_2}{\alpha_2-\phi}+\frac{\alpha_1 a_1}{\alpha_1-\phi}=1$$

$$\alpha_3 a_3 = \frac{0.999\times 4}{3+1} = 0.999;$$

$$\alpha_2 a_2 = \frac{0.001\times 2}{3+1} = 0.0005$$

Since a_1 is very small, the term $\frac{\alpha_1 a_1}{\alpha_1-\phi}$ can be neglected when finding ϕ_2 and ϕ_3, which are found to be 1.999 and 3.0015 respectively. Since ϕ_1 is very nearly equal to α_1,

$$\frac{\alpha_3 a_3}{\alpha_3-\alpha_1}+\frac{\alpha_2 a_2}{\alpha_2-\alpha_1}+\frac{\alpha_1 a_1}{\alpha_1-\phi_1}=1$$

or

$$\frac{0.999}{3}+0.0005+\frac{a_1}{1-\phi_1}=1$$

from which $\frac{a_1}{1-\phi_1} = 0.6665$

Although both a_1 and $(1-\phi_1)$ may be extremely small, the ratio of these two quantities is not so. We also find $c_{3,1} = 0.111$; $c_{2,1} = 0.0003333$ and $c_{1,1} = 0.88867$.

$$\frac{1}{\lambda_1} = \frac{\alpha_3 c_{3,1}}{\alpha_3-\phi_1}+\frac{\alpha_2 c_{2,1}}{\alpha_2-\phi_1}+\frac{\alpha_1 c_{1,1}}{\alpha_1-\phi_1}$$

$$= \frac{4\times 0.111}{3}+\frac{2\times 0.00033}{1}$$

$$+\frac{c_{1,1}}{1-\phi_1} = 0.1487+\frac{c_{1,1}}{1-\phi_1}$$

From Equation (10a),

$$\frac{c_{1,1}}{1-\phi_1} = \frac{a_1\phi_1}{m(1-\phi_1)^2}$$

$$= \frac{\phi_1}{m}\left(\frac{a_1}{1-\phi_1}\right)^2\cdot\frac{1}{a_1}$$

$$= \frac{1}{0.75}(0.6665)^2\cdot\frac{1}{a_1}$$

$$= \frac{0.5923}{a_1}$$

$$\therefore \frac{1}{\lambda_1} = 0.1487+\frac{0.5923}{a_1}$$

Since a_1 is very small, the term 0.1487 is negligible in comparison with $\frac{0.5923}{a_1}$ so that $\lambda_1 = 1.690a_1$, which gives the value of λ_1 for any assumed value of a_1. In finding λ_2 and λ_3, the term involving a_1 will be found to be negligible and $\lambda_2 = 0.00075$ and $\lambda_3 = 0.2496$.

Using Equations (24), values of $x_{3,n}$, $x_{2,n}$, $x_{1,n}$, were calculated for $n = 5, 10, 15, 20, 25, 30$ with different assumed values of a_1 (equal to $\frac{x_{1,D}}{4}$) ranging from 1×10^{-5} to 1×10^{-11} and also for $a_1 = 0$, which would represent the binary mixture of x_3 and x_2. The values of $x_{3,n}$, $x_{1,n}$ and also of $\frac{x_{2,n}}{x_{3,n}}$, the ratio of the key components, are shown in Tables 1-4.

Tables 1-4 show clearly how great can be the variations in $x_{1,n}$ and in $\frac{x_{2,n}}{x_{3,n}}$, the ratio of the key components, with variations in the value of a_1 even though a_1 or $x_{1,D}$ is so very small. In Table 3, for instance, it is noted how $x_{1,20}$ varies from .851 to .0186 as a_1 varies from 10^{-8} to 10^{-11} and, in Table 4, how $\frac{x_{2,20}}{x_{3,20}}$ varies from .222 to 1.533 with the same variations of a_1. This is readily understandable. For a binary mixture, with $a_1 = 0$, an infinite number of plates gives $x_{3,\infty} = .3333$, $x_{2,\infty} = .6667$ and $\frac{x_{2,\infty}}{x_{3,\infty}} = 2.0$. When the third component is taken into account, however small $x_{1,D}$ may be as long as it is finite, an infinite number of plates gives $x_{3,\infty} = c_{3,1} = .111$; $x_{2,\infty} = .000333$; $x_{1,\infty} = c_{1,1} = .8887$ and $\frac{x_{2,\infty}}{x_{3,\infty}} = .003$.

In view of such variations it is essential to bear in mind the possibilities of appreciable errors arising when calculations for multicomponent mixtures are made in which are neglected the unspecified components, that is, the components heavier than the heavy key component in the enriching column and the components lighter than the light key component in the stripping column.

Equations derived in this paper do permit of an exact analytical determination of the number of plates, even where there are unspecified components, though the solution may appear somewhat involved. Consider a mixture of four components x_4, x_3, x_2, x_1, the key components being x_3 and x_2. Then x_1 is unspecified in the top product and x_4 is unspecified in the bottom product. There are four equations, similar to Equations (24) for $x_{4,n}$, $x_{3,n}$, $x_{2,n}$, $x_{1,n}$. Denoting the invariant compositions by c_4, c_3, c_2, c_1, etc., and using the summation sign Σ for convenience, the equations for the enriching column are

$$x_{4,n} = \frac{\dfrac{\lambda_1 c_{4,1}}{\phi_1^{\,n}} + \dfrac{\lambda_2 c_{4,2}}{\phi_2^{\,n}} + \dfrac{\lambda_3 c_{4,3}}{\phi_3^{\,n}} + \dfrac{\lambda_4 c_{4,4}}{\phi_4^{\,n}}}{\dfrac{\lambda_1}{\phi_1^{\,n}} + \dfrac{\lambda_2}{\phi_2^{\,n}} + \dfrac{\lambda_3}{\phi_3^{\,n}} + \dfrac{\lambda_4}{\phi_4^{\,n}}} = \frac{\sum_{r=1}^{4} \dfrac{\lambda_r c_{4,r}}{\phi_r^{\,n}}}{\sum_{r=1}^{4} \dfrac{\lambda_r}{\phi_r^{\,n}}} \tag{43a}$$

$$x_{3,n} = \frac{\sum_{r=1}^{4} \dfrac{\lambda_r c_{3,r}}{\phi_r^{\,n}}}{\sum_{r=1}^{4} \dfrac{\lambda_r}{\phi_r^{\,n}}} \tag{43b}$$

$$x_{2,n} = \frac{\sum_{r=1}^{4} \dfrac{\lambda_r c_{2,r}}{\phi_r^{\,n}}}{\sum_{r=1}^{4} \dfrac{\lambda_r}{\phi_r^{\,n}}} \tag{43c}$$

$$x_{1,n} = \frac{\sum_{r=1}^{4} \dfrac{\lambda_r c_{1,r}}{\phi_r^{\,n}}}{\sum_{r=1}^{4} \dfrac{\lambda_r}{\phi_r^{\,n}}} \tag{43d}$$

Similarly for the stripping column, the equations similar to Equations (36) are

$$x_{4,s} = \frac{\sum_{r=1}^{4} \mu_r c'_{4,r} \psi_r^{\,s}}{\sum_{r=1}^{4} \mu_r \psi_r^{\,s}} \tag{44a}$$

$$x_{3,s} = \frac{\sum_{r=1}^{4} \mu_r c'_{3,r} \psi_r^{\,s}}{\sum_{r=1}^{4} \mu_r \psi_r^{\,s}} \tag{44b}$$

$$x_{2,s} = \frac{\sum_{r=1}^{4} \mu_r c'_{2,r} \psi_r^{\,s}}{\sum_{r=1}^{4} \mu_r \psi_r^{\,s}} \tag{44c}$$

$$x_{1,s} = \frac{\sum_{r=1}^{4} \mu_r c'_{1,r} \psi_r^{\,s}}{\sum_{r=1}^{4} \mu_r \psi_r^{\,s}} \tag{44d}$$

At the point in the column, taken as the feed-plate, $x_{4,n} = x_{4,s}$, $x_{3,n} = x_{3,s}$, etc. For the four components, this gives four equations similar to

$$\frac{\sum_{r=1}^{4} \dfrac{\lambda_r c_{3,r}}{\phi_r^{\,n}}}{\sum_{r=1}^{4} \dfrac{\lambda_r}{\phi_r^{\,n}}} = \frac{\sum_{r=1}^{4} \mu_r c'_{3,r} \psi_r^{\,s}}{\sum_{r=1}^{4} \mu_r \psi_r^{\,s}} \tag{45}$$

These four equations, however, represent only three independent relations as the fixing of three components automatically fixes the fourth component. Now x_1 is unspecified in the top product and x_4 is unspecified in the bottom product so that λ_1 and μ_4 are not known. Using the three independent equations of the type of Equation (45), the two unknowns λ_1 and μ_4 can be eliminated and there would be obtained an equation containing n and s together with the known quantities ϕ_1, ϕ_2, ϕ_3, ϕ_4; ψ_1, ψ_2, ψ_3, ψ_4; λ_2, λ_3, λ_4; μ_1, μ_2, μ_3. This final equation gives a relation between n and s and there are an infinite number of solutions corresponding to all possible locations of the feed-plate. If the feed-plate is to be located at the optimum point so that $(n+s)$ is a minimum, this gives another relation and n and s are then determined. The condition that $(n+s)$ is a minimum could be applied by the usual mathematical method or, alternatively, the values of s could be calculated for a number of values of n to determine when $(n+s)$ was a minimum.

Although the principle of the method for an exact determination of the number of plates required has been illustrated for a case of four components, the method applies equally to the general case of any number of components. If the number of components is Z, the number of independent relations corresponding to Equations (45) will be $(Z-1)$. The number of values of λ and μ which are not known will be equal to the sum of the number of components heavier than the heavy key component in the enriching column and the number of components lighter than the light key component in the stripping column and will be equal to $(Z-2)$, where the heavy and light key components are adjacent ones. The $(Z-2)$ unknowns can be eliminated from the $(Z-1)$ equations to give a final equation involving only known quantities in addition to n and s.

There is a method of eliminating the unknowns corresponding to the unspecified components and obtaining the final equation for n and s, which is somewhat more convenient than using Equations (45). Take again the four-component example for which Equations (43) and (44) have been given. As before, x_1 is unspecified in the top product and x_4 in the bottom product. For the enriching column the equations corresponding to Equations (15) are

$$\frac{\dfrac{a_4 x_{4,n}}{a_4-\phi_1} + \ldots + \dfrac{a_1 x_{1,n}}{a_1-\phi_1}}{\dfrac{1}{\phi_1^{\,n}}} = \frac{\dfrac{a_4 x_{4,n}}{a_4-\phi_2} + \ldots + \dfrac{a_1 x_{1,n}}{a_1-\phi_2}}{\dfrac{1}{\phi_2^{\,n}}} = \frac{\dfrac{a_4 x_{4,n}}{a_4-\phi_3} + \ldots + \dfrac{a_1 x_{1,n}}{a_1-\phi_3}}{\dfrac{1}{\phi_3^{\,n}}} = \frac{\dfrac{a_4 x_{4,n}}{a_4-\phi_4} + \ldots + \dfrac{a_1 x_{1,n}}{a_1-\phi_4}}{\dfrac{1}{\phi_4^{\,n}}} \tag{46}$$

As x_1 is unspecified in the top product, $(a_1 - \phi_1)$ will be small and unknown. The three expressions involving ϕ_2, ϕ_3, ϕ_4, in Equations (46) give two equations

$$\frac{\dfrac{a_4 x_{4,n}}{a_4-\phi_2} + \ldots + \dfrac{a_1 x_{1,n}}{a_1-\phi_2}}{\dfrac{a_4 x_{4,n}}{a_4-\phi_3} + \ldots + \dfrac{a_1 x_{1,n}}{a_1-\phi_3}} = \left(\frac{\phi_3}{\phi_2}\right)^n \tag{47a}$$

and

$$\frac{\dfrac{a_4 x_{4,n}}{a_4 - \phi_2} + \ . \ . \ . \ + \dfrac{a_1 x_{1,n}}{a_1 - \phi_2}}{\dfrac{a_4 x_{4,n}}{a_4 - \phi_4} + \ . \ . \ . \ + \dfrac{a_1 x_{1,n}}{a_1 - \phi_4}} = \left(\frac{\phi_4}{\phi_2}\right)^n \tag{47b}$$

If there are substituted in these equations the values of $x_{1,s}$, $x_{2,s}$ . . . . for the stripping column as given by Equations (44), there are obtained two equations containing one unknown, μ_4, in addition to n and s. It can then be eliminated to give the final equation involving n and s. It will be seen that this procedure renders it unnecessary to compute the indeterminate multipliers λ for the enriching column. The procedure can, of course, be reversed, using the equations for the stripping column corresponding to Equations (46) and substituting the values of $x_{1,n}$, $x_{2,n}$ . . . , from Equations (43). In practice there would obviously be chosen the procedure which gave the least number of unknowns for the final elimination.

For any number of components it is also possible to use Equations (46) and the similar equations for the stripping column, neglecting those expressions which contain unknown values of $(a - \phi)$ or $(a - \psi)$ due to unspecified components. Then there will be a sufficient number of equations to eliminate the compositions x_1, x_2 . . . , (noting that $x_{1,n} = x_{1,s}$, etc.) to give the final equation for n and s. The composition at the feed-plate can also be found from these equations when appropriate values of n and s have been determined.

The elimination of the unknown values of λ and μ is rather laborious and the procedure may be shortened by adopting the approximation frequently used in making plate-to-plate calculations, that is, neglecting the unspecified components. This, in effect means putting $\lambda_1 = 0$ in Equations (43) and $\mu_4 = 0$ in Equations (44) for the four-component example just discussed. Dividing Equation (43b) by Equation (43c) gives the ratio of the key components for the enriching column and similarly Equations (44b) and (44c) give this ratio for the stripping column. Fixing this ratio for the feed-plate enables n and s to be calculated. The ratio of the key components on the feed-plate may be taken as the ratio of these components in the feed as discussed by Gilliland (8). It may be pointed out that Gilliland's method gives essentially the same result as assuming that the ratio on the feed-plate is the same as it would be under total reflux with optimum location of feed point, as may be seen by comparing Gilliland's equation with equations presented elsewhere (5).

TABLE 4.—VALUES OF $\dfrac{x_{2,n}}{x_{3,n}}$

n	$a_1 = 10^{-5}$	$a_1 = 10^{-6}$	$a_1 = 10^{-7}$	$a_1 = 10^{-8}$	$a_1 = 10^{-9}$	$a_1 = 10^{-10}$	$a_1 = 10^{-11}$	$a_1 = 0$
5	.0161	.0161	.0161	.0161	.0161	.0161	.0161	.0161
10	.0789	.1066	.1105	.1106	.1108	.1108	.1108	.1108
15	.0110	.0750	.3525	.572	.611	.614	.614	.614
20	.0033	.0055	.0281	.222	.963	1.455	1.533	1.545
25	.0030	.0030	.0038	.0110	.0797	.568	1.555	1.932
30	.0030	.0030	.0030	.0032	.0055	.0277	.225	2.000

It should be realized that the adoption of such "short-cut" methods inevitably involves some loss of accuracy. The magnitude of the inaccuracy thus introduced is at present almost entirely a matter of guesswork. It is clear that an examination of this question would be valuable.

For many practical problems of column design the calculation of the minimum number of plates and the minimum reflux ratio will provide adequate data, using for instance the approximations for the actual number of plates and actual reflux ratio suggested by Crosley (9). As has already been mentioned, the minimum reflux ratio can be readily calculated by equations published in previous papers (2, 3) and derived by the basic mathematical analysis used in this paper. The basic equations are Equation (12) and the equation

$$\frac{a_3 x_{3,F}}{a_3 - \phi} + \frac{a_2 x_{2,F}}{a_2 - \phi} + \frac{a_1 x_{1,F}}{a_1 - \phi} = 1 - q \tag{48}$$

where $x_{1,F}$, $x_{2,F}$, $x_{3,F}$, represent the composition of the feed and q represents the thermal condition of the feed, that is, the total heat required to vaporize one mole of feed divided by the latent heat of vaporization. Equation (48) is solved for that value of ϕ which lies between the relative volatilities of the key components and the value of ϕ so found is substituted in Equation (12) to give a value of R which is the minimum reflux ratio.

In the original presentation of this method for determining minimum reflux ratio (3) it was pointed out that it assumes constant molal reflux and constant relative volatilities, though methods of approximation were indicated for the case where relative volatilities are not constant. It was originally stated that the application of the basic equations was limited to cases of sharp separation between adjacent key components. Further examination shows that this limitation may be removed. The basic equations of the type of (48) and (12) can be applied equally well where the separation between adjacent key components is not sharp, that is, the amount of the heavy key component in the top product and the amount of the light key component in the bottom product are not small.

They can also be applied, using a slightly modified procedure, to cases where there are one or more distributed components between the key components. The derivation is similar in principle to that given for the simpler cases (3) and will be only briefly described here. Equation (48) was derived by showing that, for minimum reflux conditions, a value of ϕ for the enriching column must be equal to a value of ψ for the stripping column. This resulted from the fact that a stepwise calculation upwards from the feed-plate and a stepwise calculation downwards from the feed-plate must lead to the appropriate invariant compositions, and consequently the feed-plate composition must satisfy a certain number of equations of the type

$$\frac{a_4 x_4}{a_4 - \phi} + \frac{a_3 x_3}{a_3 - \phi} + \frac{a_2 x_2}{a_2 - \phi} + \frac{a_1 x_1}{a_1 - \phi} = 0$$

and a certain number of similar equations with ψ instead of ϕ. The number of equations to be satisfied being greater than the number of unknowns (x_1, x_2, . . .) necessitated that a value of ϕ must be equal to a value of ψ.

If a similar process of reasoning is followed out for the case of a distributed component between the key components, it will be found that two values of ϕ must be equal to two values of ψ. Thus two solutions of Equation (48) are used and these are the two values of ϕ lying between the relative volatilities of the key components. These two values of ϕ are substituted in the equation corresponding to (12) to give two equations which contain two unknowns, namely, the minimum reflux ratio and the distribution of the intermediate component. Where there are two distributed components between the key components, three values of ϕ from the equation similar to (48) are used to give three equations similar to (12) containing three unknowns, the minimum reflux ratio and the distributions of the two intermediate components. The method is quite generally applicable to any number of distributed components.

The various cases will be illustrated by a numerical example for a mixture containing six components, with the following data.

$$x_{1,F} = 0.2;\ x_{2,F} = x_{3,F} = x_{4,F} =$$

$$= x_{5,F} = 0.15;\ x_{6,F} = 0.2$$

$$\alpha_1 = 1;\ \alpha_2 = 2;\ \alpha_3 = 3;\ \alpha_4 = 4;$$

$$\alpha_5 = 5;\ \alpha_6 = 6;\ q = 0.$$

The equation similar to (48) is

$$\frac{(6)(0.2)}{6-\phi} + \frac{(5)(0.15)}{5-\phi} + \frac{(4)(0.15)}{4-\phi} + \frac{(3)(0.15)}{3-\phi} + \frac{(2)(0.15)}{2-\phi} + \frac{0.2}{1-\phi} = 1 \qquad (49)$$

Case 1.

Separation between adjacent components, x_3 as heavy key component and x_4 as light key component. $x_{3,D} = 0.0001 = x_{4,w}$.

The root of Equation (49) which is required is the one lying between α_3 and α_4, i.e., ϕ_4, which has a value between 3 and 4. By trial solution of Equation (49), $\phi_4 = 3.50$. As the top product contains only negligible amounts of x_1, x_2, x_3, its composition is $x_{6,D} = 0.4$; $x_{5,D} = 0.3$; $x_{4,D} = 0.3$.

The equation corresponding to (12) is

$$\frac{(6)(0.4)}{6-3.50} + \frac{(5)(0.3)}{5-3.50} + \frac{(4)(0.3)}{4-3.50} = R_m + 1 \qquad (50)$$

Then $R_m = 3.36$.

Case 2.

One distributed component x_4. Key components x_5 and x_3. $x_{3,D} = x_{5,w} = 0.0001$.

Two solutions of Equation (49) are required, lying between α_3 and α_5. These are ϕ_4 and ϕ_5. The value of ϕ_4 has already been found as 3.50. The value of ϕ_5, which lies between 4 and 5, is similarly found to be 4.559. The composition of the top product is not yet known. The top product contains all of x_5 and x_6 present in the feed and in the same ratio as in the feed. In addition it contains an unknown amount of x_4. Then $x_{4,D} + x_{5,D} + x_{6,D} = 1$ and $\frac{x_{5,D}}{x_{6,D}} = \frac{0.15}{0.2}$ so that $x_{5,D} = 0.429(1 - x_{4,D})$ and $x_{6,D} = 0.571(1 - x_{4,D})$.

There are then two equations corresponding to (12), namely,

$$\frac{(6)(0.571)(1-x_{4,D})}{6-\phi_4} + \frac{(5)(0.429)(1-x_{4,D})}{5-\phi_4} + \frac{(4)(x_{4,D})}{4-\phi_4} = R_m + 1 \qquad (51a)$$

and

$$\frac{(6)(0.571)(1-x_{4,D})}{6-\phi_5} + \frac{(5)(0.429)(1-x_{4,D})}{5-\phi_5} + \frac{(4)(x_{4,D})}{4-\phi_5} = R_m + 1 \qquad (51b)$$

Subtracting one equation from the other, dividing through by $(\phi_4 - \phi_5)$ and substituting the numerical values of ϕ_4 and ϕ_5 found above, gives $x_{4,D} = 0.2266$. Then, from either of the equations, $R_m = 2.978$.

The composition of the top product is then found as $x_{6,D} = 0.4416$; $x_{5,D} = 0.3318$; $x_{4,D} = 0.2266$; $x_{3,D} = 0.0001$.

Now

$$\frac{D}{F} = \frac{x_{5,F} + x_{6,F}}{x_{5,D} + x_{6,D}} = 0.4526$$

and

$$\frac{W}{F} = 0.5474.$$

The composition of the bottom product is then found as $x_{5,w} = 0.0001$; $x_{4,w} = 0.0866$; $x_{3,w} = x_{2,w} = 0.274$; $x_{1,w} = 0.3655$.

Case 3.

Two distributed components, x_3 and x_4. Key components x_5 and x_2. $x_{2,D} = x_{5,w} = 0.0001$. Three solutions of Equation (49) are required, lying between α_2 and α_5. These are ϕ_3, ϕ_4, ϕ_5. The two latter have already been found. The value of ϕ_3, which lies between 2 and 3, is similarly found as 2.441.

For the composition of the top product, $x_{3,D} + x_{4,D} + x_{5,D} + x_{6,D} = 1$ and $\frac{x_{5,D}}{x_{6,D}} = \frac{0.15}{0.2}$ so that $x_{5,D} = 0.429(1 - x_{3,D} - x_{4,D})$ and $x_{6,D} = 0.571(1 - x_{3,D} - x_{4,D})$.

There are then three equations corresponding to (12), namely

$$\frac{(6)(0.571)(1-x_{3,D}-x_{4,D})}{6-\phi_3} + \frac{(5)(0.429)(1-x_{3,D}-x_{4,D})}{5-\phi_3} + \frac{4x_{4,D}}{4-\phi_3} + \frac{3x_{3,D}}{3-\phi_3} = R_m + 1 \qquad (52a)$$

and two similar equations with ϕ_4 and ϕ_5 instead of ϕ_3. Subtracting the first equation from the second, and the second from the third gives two equations for $x_{3,D}$ and $x_{4,D}$ from which $x_{3,D} = 0.1608$ and $x_{4,D} = 0.2235$. Then $x_{5,D} = 0.2642$ and $x_{6,D} = 0.3516$. Then, from Equation (52a), $R_m = 1.548$. Also $\frac{D}{F} = 0.4526$ and $\frac{W}{F} = 0.5474$.

The composition of the bottom product is $x_{1,w} = 0.463$; $x_{2,w} = 0.3472$; $x_{3,w} = 0.1358$; $x_{4,w} = 0.0534$; $x_{5,w} = 0.0001$.

The term corresponding to the heavy key component has been omitted from Equations (50-52) as it is negligible. If the amount of the heavy key component in the top product were appreciable, an appropriate term would appear in the equations.

The case of three or more distributed components can be treated in exactly the same way. The number of equations similar to (51) and (52) will be one more than the number of distributed components.

Notation

a = intercept of operating line

m = slope of operating line

c = "limiting" or "invariant" composition

q = thermal condition of feed, i.e., total heat required to vaporize 1 mole divided by latent heat of vaporization

x = mole fraction of component in liquid

D = moles of top product per unit time

F = moles of feed per unit time

R = reflux ratio

S = reboil ratio

W = moles of bottom product per unit time

α = relative volatility

λ = multiplier for enriching column

μ = multiplier for stripping column

ϕ = parameter for enriching column

ψ = parameter for stripping column

n, s = subscripts referring to position of a plate in enriching column and stripping column respectively

a', c', m', etc. = indicate stripping column

Subscripts 1, 2, 3, etc., are used to identify a component and also to indicate location. Where two subscripts are used, the first one identifies the component. Thus $x_{3,1}$ denotes the mole fraction of component 3 on plate 1. Similarly $c_{3,1}$ denotes the amount of component 3 at the invariant composition corresponding to ϕ_1. The components are numbered in order of increasing volatility, x_1 being the least volatile.

Literature Cited

1. Underwood, A. J. V., *J. Inst. Petroleum*, 31, 111-118 (1945).
2. Underwood, A. J. V., *J. Inst. Petroleum*, 32, 598-613 (1946).
3. Underwood, A. J. V., *J. Inst. Petroleum*, 32, 614-626 (1946).
4. Fenske, M. R., *Ind. Eng. Chem.*, 24, 482-485 (1932).
5. Underwood, A. J. V., *Trans. The Inst. Chem. Engrs. (London)*, 10, 112-152 (1932).
6. Harbert, W. D., *Ind. Eng. Chem.*, 37, 1162-1167 (1945).
7. Edmister, W. C., *Trans. Am. Inst. Chem. Engrs.*, 42, 15-32 (1946).
8. Gilliland, E. R., *Ind. Eng. Chem.*, 32, 918-920 (1940).
9. Crosley, S., *Chem. Met. Eng.*, 48, 10, 92 (1941).

Written Discussion

D. E. Holcomb (Purdue University, Lafayette, Ind.): Dr. Underwood has presented an excellent mathematical analysis of the fractional distillation of multicomponent mixtures. However, I believe that for practical application in the design of a distillation column the equations as presented are somewhat limited in their usefulness, particularly when the feed to the column contains a large number of components.

The equations in this paper have been derived on the assumption of constant molal reflux over the rectifying section and over the stripping section of a distillation column. In many cases this assumption is not true for the entire section of the column; however, a reasonably accurate value for the reflux may be determined by making plate-to-plate calculations and heat balances down from the top of the tower and up from the bottom of the tower until more or less constant values are obtained for the reflux. These values may then be used in conjunction with the equations presented in this paper to give more accurate results than those obtained when the assumption of constant molal reflux over the entire sections of the tower is used.

The method of determining the minimum reflux ratio is of real value to the design engineer, and it is perhaps the most rapid method available at the present time. The main difficulty in using this method lies in selecting the correct temperature at which to evaluate the relative volatilities. I have checked this method with the rigorous method for a column operating on a feed stream containing eight components and found that the minimum reflux ratio agrees within about 5% with the true value when evaluating the relative volatilities at the average tower temperature. A closer check can, of course, be obtained by using a more nearly correct temperature for evaluating the relative volatilities.

A. J. V. Underwood: Some contributors to the discussion have commented on the nomenclature used in the original manuscript. The nomenclature has therefore been altered in the published version and will, it is hoped, be found more acceptable. In a method which takes account of all components, the equations and nomenclature must inevitably appear more complicated than in methods which take account of two key components only. Attention is drawn to the errors which may arise in this paper when the unspecified components are neglected.

Dr. Holcomb, commenting on the limitation in the method of calculating minimum reflux ratio, states that constant relative volatility is assumed. This is undoubtedly a limitation at present if an accurate calculation is required. Approximations which might be used in cases of varying relative volatility were indicated in the original description of the method (*3*).

Manson Benedict (Hydrocarbon Research, Inc., New York, N. Y.): One of the most valuable aspects of Underwood's method for solving the equations of multicomponent distillation is the insight it gives into the factors controlling the change in composition from plate to plate in the fractional distillation of multicomponent mixtures. It does this by showing that the familiar Fenske-Underwood equation for total reflux distillation may be used for partial reflux distillation by an appropriate transformation of composition variables.

For a three-component mixture, this transformation has a simple geometric representation. In Figure 1, the equilateral triangle made up of full lines gives the coordinate axes used when composition is expressed in terms of mole fractions (x_1, x_2, and x_3) of actual components 1, 2, and 3 with relative volatilities (α_1, α_2, and α_3). For total reflux distillation these mole fractions and relative volatilities are used in Fenske's equation.

In partial reflux distillation, Underwood's method is equivalent to representation of composition by means of mole fractions of three pseudo-components whose coordinates are those of the three pinch points. The coordinate system referred to these components is given by the (usually) nonequilateral triangle made up of the broken lines. The mole fraction of each of these pseudocomponents in a mixture at point 0 is determined by drawing lines parallel to each of the sides of the broken-line triangle connecting the pairs of pseudocomponents. These parallel lines cut each side of the triangle into three lengths which are proportional to the mole fractions w_1, w_2 and w_3 of the pseudocomponents 1, 2, and 3, respectively, as indicated in the figure. These three mole fractions are the number of moles of each of the pseudocomponents needed

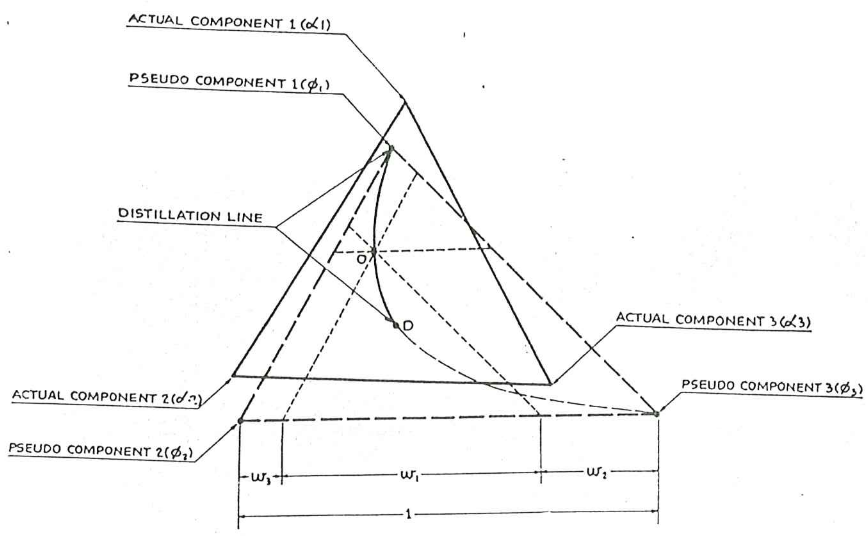

Fig. 1. Transformation of Composition Vairables in Ternary Mixture.

to make up the mixture of interest at the Point 0. The transformation from mole fractions of actual components (w_1, w_2, and w_3) is given by the system of equations

$$w_1 = \lambda_1 \left[\frac{a_1 x_1}{a_1 - \phi_1} + \frac{a_2 x_2}{a_2 - \phi_1} + \frac{a_3 x_3}{a_3 - \phi_1} \right]$$

$$w_2 = \lambda_2 \left[\frac{a_1 x_1}{a - \phi_2} + \frac{a_2 x_2}{a_2 - \phi_2} + \frac{a_3 x_3}{a_3 - \phi_2} \right]$$

$$w_3 = \lambda_3 \left[\frac{a_1 x_1}{a_1 - \phi_3} + \frac{a_2 x_2}{a_2 - \phi_3} + \frac{a_3 x_3}{a_3 - \phi_3} \right]$$

The scale factors, λ, are defined in Underwood's paper.

The distillation line representing the change in composition from plate to plate in a ternary mixture under partial reflux, is obtained by applying Fenske's total reflux equations, with pseudorelative volatilities ϕ_1, ϕ_2, and ϕ_3, to compositions w_1, w_2, and w_3 expressed in terms of mole fraction of the three pseudocomponents. This distillation line passes through the point *D*, representing the overhead composition and may be extended, in a column with an infinite number of plates, to the pinch point for the least volatile pseudocomponent (1). Theoretically, the distillation line might be extended in the other direction to the pinch point for the most volatile pseudocomponent (3), but this part of the line has no physical significance. The course of the distillation line for partial reflux from the most volatile pseudocomponent to the least volatile is analogous to the course of the distillation line for total reflux from the most volatile actual component to the least volatile. It will be observed that the distillation line for partial reflux does not usually pass through the points representing actual components.

A. J. V. Underwood: Dr. Benedict has given a graphical representation of the transformation to pseudocomponents. If one of the components is unspecified so that $(1-\phi_1)$, for instance, is not known, the same indeterminacy will be present in the graphical method as in the analytical method.

J. F. Middleton (Foster Wheeler Corp., New York, N. Y.): The method of solution for problems in distillation of multicomponent mixtures presented in Dr. Underwood's paper is unquestionably a noteworthy achievement in this field of study. The minimum reflux calculation will be particularly useful. It seems probable that any further improvement in these methods of calculation will depend heavily on the ingenious derivations reported by Dr. Underwood.

Among the problems requiring further development are:

1. Means of obtaining solutions based on actual reflux ratios instead of the constant values usually assumed
2. Means of allowing for variations in relative volatilities of components
3. An improved approach to the trial and error procedure required for the solution of distillation problems in which a large number of components are common to both product streams

Problems 1 and 2 can be taken care of to some extent by considering separately the two tower sections when choosing average temperatures for estimation of the relative volatilities, and by using separate heat balances to determine the refluxes above and below the feed trays. These, however, are stop-gap expedients that do not give completely satisfactory results.

Problem 3 has generally been ignored, partly because solutions to this type of problem are not so important commercially as those involving "sharp" separations, and probably also because no solution is possible except by trial-and-error calculations. This difficulty arises because the calculations usually employed cannot be started without first assuming a "split" of the feed into product compositions, and the actual "split" cannot be determined until the number of trays and reflux rates have been established. What is required is a way of assuming an approximately correct "split" that would avoid the need of making more than one complete calculation. This particular problem is perhaps more important than is generally believed, since it is the general case of multicomponent distillation, whereas the "sharp" separation is really a special case in which the product compositions may be correctly assumed before calculation. It differs somewhat from the calculation of "sharp" separations in its objective, since the determination of the number of trays and reflux rates is less critical and the part of the solution of greatest interest is the determination of the compositions of the products.

A. J. V. Underwood: Mr. Middleton has defined three important problems. As far as the first two are concerned, the most feasible method of attack seems at present to be on the lines he has indicated. Any rigid analytical solution would presumably have to include relative volatilities, latent heats and specific heats as functions of temperature or composition and would then be extremely complicated.

The third problem—that of distributed components—certainly requires further elucidation. The determination of the minimum reflux ratio and the distribution under these conditions is dealt with in this paper. The distribution under total reflux conditions is also readily determined. The case of a distributed component with partial reflux is considered in another paper to be published later.

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