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FRACTIONAL DISTILLATION OF TERNARY MIXTURES. PART II.

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SUMMARY.

The basic equations derived in Part I are employed to determine the conditions for a state of minimum reflux. Equations are presented by which the minimum reflux ratio for ternary mixtures can be readily calculated when the fractionation between the key components is a sharp one.

IN Part I of this paper [1] equations were presented for computing the composition on any plate in a fractionating column for ternary mixtures. Since it appeared an alternative method of making these computations has been described by Harbert.[2]

An alternative, and rather more elegant, derivation of the basic equations presented in Part I is the following.

The compositions of the liquids on adjacent plates are given by the relations

$$mx_0 + b = \frac{\gamma x_1}{\gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$my_0 + c = \frac{\beta y_1}{\gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$mz_0 + d = \frac{z_1}{\gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As previously, for a rectifying column, $m = \frac{R}{R+1}$, where R is the reflux ratio; $b = \frac{x_D}{R+1}$; $c = \frac{y_D}{R+1}$; $d = \frac{z_D}{R+1}$. γ and β are the relative volatilities of components x and y to component z and $\gamma > \beta > 1$. For a stripping column, $m = \frac{S+1}{S}$, where S is the "reboil ratio"—*i.e.*, the number of moles of vapour produced in the reboiler per mole of bottom product withdrawn; $b = -\frac{x_W}{S}$; $c = -\frac{y_W}{S}$; $d = -\frac{z_W}{S}$. For a stripping column on which a rectifying column is superimposed, $S = \frac{RP + qF - W}{W}$.

For both rectifying and stripping columns

$$b + c + d = 1 - m.$$

Constant molal reflux and constant relative volatilities are assumed.

Now multiply equations (1), (2), and (3) by $\frac{\gamma}{\gamma - \phi}$, $\frac{\beta}{\beta - \phi}$ and $\frac{1}{1 - \phi}$, respectively (where ϕ is a quantity as yet undetermined), and Then

$$m\left(\frac{\gamma x_0}{\gamma - \phi} + \frac{\beta y_0}{\beta - \phi} + \frac{z_0}{1 - \phi}\right) + \frac{b\gamma}{\gamma - \phi} + \frac{c\beta}{\beta - \phi} + \frac{d}{1 - \phi} = \frac{\gamma x_1 \cdot \frac{\gamma}{\gamma - \phi} + \beta y_1 \cdot \frac{\beta}{\beta - \phi} + z_1 \cdot \frac{1}{1 - \phi}}{\gamma x_1 + \beta y_1 + z_1}$$

Now choose ϕ so that

$$\frac{b\gamma}{\gamma - \phi} + \frac{c\beta}{\beta - \phi} + \frac{d}{1 - \phi} = 1 \quad . \quad . \quad . \quad . \quad (4)$$

Then

$$m\left(\frac{\gamma x_0}{\gamma - \phi} + \frac{\beta y_0}{\beta - \phi} + \frac{z_0}{1 - \phi}\right) = \frac{\gamma x_1\left(\frac{\gamma}{\gamma - \phi} - 1\right) + \beta y_1\left(\frac{\beta}{\beta - \phi} - 1\right) + z_1\left(\frac{1}{1 - \phi} - 1\right)}{\gamma x_1 + \beta y_1 + z_1}$$

and

$$\frac{\gamma x_0}{\gamma - \phi} + \frac{\beta y_0}{\beta - \phi} + \frac{z_0}{1 - \phi} = \frac{\phi\left\{\frac{\gamma x_1}{\gamma - \phi} + \frac{\beta y_1}{\beta - \phi} + \frac{z_1}{1 - \phi}\right\}}{m(\gamma x_1 + \beta y_1 + z_1)} \quad . \quad (5)$$

Equation (4) is of the third degree, and gives three values of ϕ, denoted by ϕ_1, ϕ_2, ϕ_3, it being understood that $\phi_1 < \phi_2 < \phi_3$.

Substituting these values in equation (5) and applying the method used in Part I, there are obtained, for the composition on the nth plate, the three equations

$$\frac{\frac{\gamma x_0}{\gamma - \phi_1} + \frac{\beta y_0}{\beta - \phi_1} + \frac{z_0}{1 - \phi_1}}{\frac{\gamma x_0}{\gamma - \phi_2} + \frac{\beta y_0}{\beta - \phi_2} + \frac{z_0}{1 - \phi_2}} = \left(\frac{\phi_1}{\phi_2}\right)^n \cdot \frac{\frac{\gamma x_n}{\gamma - \phi_1} + \frac{\beta y_n}{\beta - \phi_1} + \frac{z_n}{1 - \phi_1}}{\frac{\gamma x_n}{\gamma - \phi_2} + \frac{\beta y_n}{\beta - \phi_2} + \frac{z_n}{1 - \phi_2}} \quad (6a)$$

$$\frac{\frac{\gamma x_0}{\gamma - \phi_2} + \frac{\beta y_0}{\beta - \phi_2} + \frac{z_0}{1 - \phi_2}}{\frac{\gamma x_0}{\gamma - \phi_3} + \frac{\beta y_0}{\beta - \phi_3} + \frac{z_0}{1 - \phi_3}} = \left(\frac{\phi_2}{\phi_3}\right)^n \cdot \frac{\frac{\gamma x_n}{\gamma - \phi_2} + \frac{\beta y_n}{\beta - \phi_2} + \frac{z_n}{1 - \phi_2}}{\frac{\gamma x_n}{\gamma - \phi_3} + \frac{\beta y_n}{\beta - \phi_3} + \frac{z_n}{1 - \phi_3}} \quad (6b)$$

$$\frac{\frac{\gamma x_0}{\gamma - \phi_3} + \frac{\beta y_0}{\beta - \phi_3} + \frac{z_0}{1 - \phi_3}}{\frac{\gamma x_0}{\gamma - \phi_1} + \frac{\beta y_0}{\beta - \phi_1} + \frac{z_0}{1 - \phi_1}} = \left(\frac{\phi_3}{\phi_1}\right)^n \cdot \frac{\frac{\gamma x_n}{\gamma - \phi_3} + \frac{\beta y_n}{\beta - \phi_3} + \frac{z_n}{1 - \phi_3}}{\frac{\gamma x_n}{\gamma - \phi_1} + \frac{\beta y_n}{\beta - \phi_1} + \frac{z_n}{1 - \phi_1}} \quad (6c)$$

In the above derivation the only property assumed for the parameter ϕ is that it should satisfy equation (4). The other properties of this parameter, stated in Part I, can be readily deduced. Assume the composition of the liquids on any two adjacent plates in the column to be the same, as is the case under minimum reflux conditions. If this composition is denoted by (h, k, l), then, from equation (5)

$$\phi = m(\gamma h + \beta k + l) \qquad (7)$$

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

$$\frac{mh + b}{\gamma h} = \frac{mk + c}{\beta k} = \frac{ml + d}{l} = \frac{1}{\gamma h + \beta k + l} = \frac{m}{\phi}$$

and

$$h = \frac{b\phi}{m(\gamma - \phi)}; \quad k = \frac{c\phi}{m(\beta - \phi)}; \quad l = \frac{d\phi}{m(1 - \phi)} \qquad (8)$$

For the three values of ϕ—*i.e.*, ϕ_1, ϕ_2, ϕ_3—which satisfy equation (4) there are three values of (h, k, l) which will be denoted by (h_1, k_1, l_1), (h_2, k_2, l_2) and (h_3, k_3, l_3), respectively.

For a rectifying column b, c, d are positive, and it has been shown in Part I that, in this case,

$$0 < \phi_1 < 1; \quad 1 < \phi_2 < \beta; \quad \beta < \phi_3 < \gamma.$$

For ϕ_1, equation (8) will give positive values for h_1, k_1, and l_1. For ϕ_2, h_2 and k_2 will be positive and l_2 will be negative. For ϕ_3, h_3 will be positive and k_3 and l_3 will be negative.

For a stripping column, it will be convenient to write $\bar{b}, \bar{c}, \bar{d}$ instead of b, c, d and ψ instead of ϕ and $\bar{h}, \bar{k}, \bar{l}$ instead of h, k, l. In this case $\bar{b}, \bar{c}, \bar{d}$ are negative and it can be readily shown that

$$1 < \psi_1 < \beta; \quad \beta < \psi_2 < \gamma; \quad \gamma < \psi_3.$$

For ψ_1, equation (8) will give $\bar{h}_1$ and $\bar{k}_1$ negative and $\bar{l}_1$ positive. For ψ_2, $\bar{h}_2$ will be negative and $\bar{k}_2$ and $\bar{l}_2$ positive. For ψ_3, $\bar{h}_3$, $\bar{k}_3$, and $\bar{l}_3$ will all be positive.

For both a rectifying column and a stripping column there are thus three cases where compositions on adjacent plates are the same, and each of these cases will correspond to minimum reflux conditions. Equation (4), applied to a rectifying column, can be written in the form

$$\frac{\gamma x_D}{\gamma - \phi} + \frac{\beta y_D}{\beta - \phi} + \frac{z_D}{1 - \phi} = R + 1 \qquad (9)$$

For any given value of R, equation (9) gives the corresponding value of ϕ, and those of h, k, l are then obtained from equation (8). These values of h, k, l represent the limiting compositions which can be attained with the given reflux ratio when the number of plates is infinite.

The various types of cases which arise can be illustrated by the following three examples which all deal with a rectifying column. In all three examples $\gamma = 4$, $\beta = 2$, $R = 3$.

Example 1. All three components are present in substantial amounts in the top product. $x_D = 0{\cdot}4$; $y_D = 0{\cdot}4$; $z_D = 0{\cdot}2$. Equation (9) gives $\phi_1 = 0{\cdot}9267$; $\phi_2 = 1{\cdot}774$; $\phi_3 = 3{\cdot}649$. Equation (8) gives

$$\begin{aligned} h_1 &= 0{\cdot}040; & k_1 &= 0{\cdot}115; & l_1 &= 0{\cdot}843 \\ h_2 &= 0{\cdot}106; & k_2 &= 1{\cdot}046; & l_2 &= -0{\cdot}153 \\ h_3 &= 1{\cdot}386; & k_3 &= -0{\cdot}295; & l_3 &= -0{\cdot}092. \end{aligned}$$

Example 2. The heaviest component is present in only a small amount in the top product. $x_D = 0{\cdot}599$; $y_D = 0{\cdot}400$; $z_D = 0{\cdot}001$.

Then

$$\begin{aligned} \phi_1 &= 0{\cdot}999583; & \phi_2 &= 1{\cdot}729; & \phi_3 &= 3{\cdot}473 \\ h_1 &= 0{\cdot}0664; & k_1 &= 0{\cdot}1333; & l_1 &= 0{\cdot}8003 \\ h_2 &= 0{\cdot}152; & k_2 &= 0{\cdot}850; & l_2 &= -0{\cdot}000791 \\ h_3 &= 1{\cdot}315; & k_3 &= -0{\cdot}3145; & l_3 &= -0{\cdot}000468 \end{aligned}$$

Example 3. The two heavier components are present in only small amounts in the top product. $x_D = 0{\cdot}999$; $y_D = 0{\cdot}001$; $z_D = 0{\cdot}000001 = 1 \times 10^{-6}$. An extremely small amount of the heaviest component is here included. In any fractionation of a ternary mixture all three components will be present in the top product. Where the second heaviest component (y) is present in small amount in the product, the amount of the heaviest component in the product is quite negligible for all practical purposes and is not normally taken into account. The effect of including it in the calculation will be discussed later.

Then

$$\begin{aligned} \phi_1 &= 1 - 0{\cdot}376 \times 10^{-6}; & \phi_2 &= 1{\cdot}999; & \phi_3 &= 3{\cdot}0015 \\ h_1 &= 0{\cdot}11\;; & k_1 &= 0{\cdot}00033; & l_1 &= 0{\cdot}88867 \\ h_2 &= 0{\cdot}333; & k_2 &= 0{\cdot}667; & l_2 &= -0{\cdot}67 \times 10^{-6} \\ h_3 &= 1{\cdot}001; & k_3 &= -0{\cdot}001; & l_3 &= -0{\cdot}5 \times 10^{-6} \end{aligned}$$

The results for Examples 2 and 3 have been calculated to a degree of accuracy which is obviously greater than would be required in any practical problem. The many decimal places shown in some of the results do not, however, mean that the calculations require an accuracy in computation greater than that of a slide-rule. When any of the components are present in the product in small amount the calculations are considerably simplified.

For instance, in Example 2, z_D is small. The root ϕ_1 of equation (9) is therefore very nearly equal to 1. Equations (8) can be written in the form

$$h = \frac{\phi \, . \, x_D}{R(\gamma - \phi)}; \quad k = \frac{\phi \, . \, y_D}{R(\beta - \phi)}; \quad l = \frac{\phi \, . \, z_D}{R(1 - \phi)} \qquad (10)$$

As ϕ_1 is very nearly equal to 1, the values of h_1 and k_1 become $\frac{x_D}{R(\gamma - 1)}$ and $\frac{y_D}{R(\beta - 1)}$. Since $h_1 + k_1 + l_1 = 1$, the value of l_1 can be found by difference.

Alternatively, putting $\phi_1 = 1$ in the first two terms of equation (9), we have

$$\frac{\gamma x_D}{\gamma - 1} + \frac{\beta y_D}{\beta - 1} + \frac{z_D}{1 - \phi_1} = R + 1.$$

This gives the value of the small quantity $(1 - \phi_1)$ and also the value of $\frac{z_D}{1 - \phi_1}$, which can then be used to find l_1 from equation (10). For this example the other two roots ϕ_2 and ϕ_3 are found by neglecting the term $\frac{z_D}{1-\phi}$ in equation (9) and solving the resulting quadratic equation.

In Example 3 both y_D and z_D are small. In this case ϕ_1 is very nearly equal to 1 and ϕ_2 is very nearly equal to β. For finding ϕ_1 and h_1, k_1, l_1 the same procedure is used as for Example 2. For ϕ_2 a second approximation is made as follows. Since ϕ_2 is very nearly equal to β, the term $\frac{z_D}{1-\phi_2}$ can be neglected, and equation (9) can be written (with β for ϕ_2 in the first term) as

$$\frac{\gamma x_D}{\gamma-\beta}+\frac{\beta y_D}{\beta-\phi_2}=R+1.$$

This gives the small quantity $(\beta-\phi_2)$ and the value of $\frac{y_D}{\beta-\phi_2}$ required for finding k_2 from equation (10). It has been shown in Part I of this paper that $\phi_1\phi_2\phi_3 = m\beta\gamma$, and when $\phi_1 = 1$ and $\phi_2 = \beta$ approximately, then $\phi_3 = m\gamma = \frac{R\gamma}{R+1}$ approximately. A second approximation for ϕ_3 can be found by a similar procedure to that already described for ϕ_2 by writing

$$\frac{\gamma x_D}{\gamma-\phi_3}+\frac{\beta y_D}{\beta-\frac{R\gamma}{R+1}}=R+1$$

Most discussions of calculations for minimum reflux conditions have dealt with the case of a rectifying column superimposed on a stripping column. This is obviously the most important type of case in practice, but certain important principles can be illustrated more clearly by considering a rectifying column or a stripping column alone. For the following discussion a rectifying column alone is considered, and is assumed to be mounted on a still kettle containing liquid of composition (x_F, y_F, z_F). We now have to find the limiting kettle composition for a given reflux ratio when the number of plates is infinite.

A method which has been used by Colburn,[3] by Gilliland [4] and by the author [5] for the case where the top product contains one component in small amount is the following. If the compositions on two adjacent plates are the same, equations (2) and (3) give

$$\frac{my_F+c}{mz_F+d}=\beta\cdot\frac{y_F}{z_F}$$

and if d is negligible, then $y_F = \frac{c}{m(\beta-1)} = \frac{y_D}{R(\beta-1)}$. Similarly $x_F = \frac{x_D}{R(\gamma-1)}$. This method obviously gives the values (h_1, k_1, l_1) obtained by putting $\phi_1 = 1$ in equations (10).

If y_D is small as well as z_D, the usual procedure has been to neglect z_D altogether—a very natural thing to do, as z_D must be very small indeed, and, if a small value y_D is specified in the product, the value of z_D cannot also be specified *ab initio*. Neglecting z_D and also neglecting c in the equation

$$\frac{mx_F+b}{my_F+c}=\frac{\gamma x_F}{\beta y_F}$$

we obtain

$$x_F=\frac{b}{m\left(\frac{\gamma}{\beta}-1\right)}=\frac{x_D}{R\left(\frac{\gamma}{\beta}-1\right)}=\frac{1}{R\left(\frac{\gamma}{\beta}-1\right)}.$$

(It is obvious that this represents the limiting composition under minimum reflux conditions for the binary mixture of components x and y.) It is then assumed that, with this value of x_F, a " pinched-in region " occurs in which z_F is negligible and $y_F = 1 - x_F$. The values so obtained are those of (h_2, k_2, l_2) obtained by putting $\phi_2 = \beta$ in equations (10) and neglecting the small value of l_2. The calculation can be carried farther by adding in a small amount of component z and carrying out a plate-to-plate calculation down the column.

It would, however, be equally legitimate to base the calculation on z_D instead of y_D, and there would then be obtained the limiting compositions (h_1, k_1, l_1) corresponding to ϕ_1. As will be seen from the results of Example 3, where $z_D = 1 \times 10^{-6}$, the final effect of including it in the calculation is very marked. The values of h_1, k_1, l_1 calculated for this example can, of course, also be arrived at by making a plate-to-plate calculation down the column, including the component z in the calculation.

The method just described does not give a correct conception of minimum reflux. It fails to provide answers to the following questions :—

(1) In the apparently straightforward case where only z_D is small the limiting compositions are given by $x_F = \frac{x_D}{R(\gamma-1)}$ and $y_F = \frac{y_D}{R(\beta-1)}$. The ratio of x_F to y_F is $\frac{x_D(\beta-1)}{y_D(\gamma-1)}$ which is independent of R. It therefore depends only on the composition of the product and the relative volatilities of components x and y, and is the same for any reflux ratio. If the still kettle contains a charge in which the ratio of these components is other than $\frac{x_D(\beta-1)}{y_D(\gamma-1)}$, how does this method of calculation apply ?

(2) If both y_D and z_D are small, very different results are obtained for the limiting compositions, according as z_D is omitted from or included in the calculation. Which of these results is correct ?

It is believed that the following analysis clarifies the position.

It has been shown in Part I that if we put x_0, y_0, z_0 equal to x_D, y_D, z_D, respectively, the left-hand side of equations (6*a*), (6*b*) and (6*c*) becomes unity. From equations (6*a*) and (6*c*) the composition on the nth plate below the top of the column is given by

$$\frac{\frac{\gamma x_n}{\gamma-\phi_2}+\frac{\beta y_n}{\beta-\phi_2}+\frac{z_n}{1-\phi_2}}{\frac{\gamma x_n}{\gamma-\phi_1}+\frac{\beta y_n}{\beta-\phi_1}+\frac{z_n}{1-\phi_1}}=\left(\frac{\phi_1}{\phi_2}\right)^n \quad . \quad . \quad . \quad (11a)$$

and

$$\frac{\dfrac{\gamma x_n}{\gamma - \phi_3} + \dfrac{\beta y_n}{\beta - \phi_3} + \dfrac{z_n}{1 - \phi_3}}{\dfrac{\gamma x_n}{\gamma - \phi_1} + \dfrac{\beta y_n}{\beta - \phi_1} + \dfrac{z_n}{1 - \phi_1}} = \left(\frac{\phi_1}{\phi_3}\right)^n \quad . \quad . \quad . \quad (11b)$$

Since $\phi_1 < \phi_2$ and $\phi_1 < \phi_3$, when n becomes infinite

$$\frac{\gamma x_n}{\gamma - \phi_2} + \frac{\beta y_n}{\beta - \phi_2} + \frac{z_n}{1 - \phi_2} = 0 \quad . \quad . \quad . \quad . \quad (12a)$$

and

$$\frac{\gamma x_n}{\gamma - \phi_3} + \frac{\beta y_n}{\beta - \phi_3} + \frac{z_n}{1 - \phi_3} = 0 \quad . \quad . \quad . \quad . \quad (12b)$$

It is necessary that the values of x_n, y_n, z_n which satisfy equations (12*a*) and (12*b*) should not make the denominator $\dfrac{\gamma x_n}{\gamma - \phi_1} + \dfrac{\beta y_n}{\beta - \phi_1} + \dfrac{z_n}{1 - \phi_1}$ equal to zero. The values of x_n, y_n, z_n which meet these requirements are h_1, k_1, l_1.

The condition that h_1, k_1, l_1 should satisfy equation (12*a*) is

$$\frac{\gamma h_1}{\gamma - \phi_2} + \frac{\beta k_1}{\beta - \phi_2} + \frac{l_1}{1 - \phi_2} = 0 \quad . \quad . \quad . \quad . \quad (13)$$

From equations (8), $h_1 = \dfrac{b\phi_1}{m(\gamma - \phi_1)}$, $k_1 = \dfrac{c\phi_1}{m(\beta - \phi_1)}$, $l_1 = \dfrac{d\phi_1}{m(1 - \phi_1)}$ and equation (13) becomes

$$\frac{b\gamma}{(\gamma - \phi_2)(\gamma - \phi_1)} + \frac{c\beta}{(\beta - \phi_2)(\beta - \phi_1)} + \frac{d}{(1 - \phi_2)(1 - \phi_1)} = 0 \ . \quad (14)$$

Now, from equation (4)

$$\frac{b\gamma}{\gamma - \phi_1} + \frac{c\beta}{\beta - \phi_1} + \frac{d}{1 - \phi_1} = \frac{b\gamma}{\gamma - \phi_2} + \frac{c\beta}{\beta - \phi_2} + \frac{d}{1 - \phi_2} = 1$$

or

$$\frac{b\gamma(\phi_1 - \phi_2)}{(\gamma - \phi_2)(\gamma - \phi_1)} + \frac{c\beta(\phi_1 - \phi_2)}{(\beta - \phi_2)(\beta - \phi_1)} + \frac{d(\phi_1 - \phi_2)}{(1 - \phi_2)(1 - \phi_1)} = 0$$

which is the same as equation (14), so that h_1, k_1, l_1 satisfy equation (12*a*). In exactly the same way it can be shown that they satisfy equation (12*b*). Also

$$\frac{\gamma h_1}{\gamma - \phi_1} + \frac{\beta h_1}{\beta - \phi_1} + \frac{l_1}{1 - \phi_1} = \frac{b\gamma\phi_1}{m(\gamma - \phi_1)^2} + \frac{c\beta\phi_1}{m(\beta - \phi_1)^2} + \frac{d\phi_1}{m(1 - \phi_1)^2}$$

All three terms in this expression are positive for a rectifying column or negative for a stripping column, and therefore their sum cannot be zero.

It can similarly be shown generally that the three equations of the type of (12*a*) are satisfied as follows :—

$$\frac{\gamma x}{\gamma - \phi_1} + \frac{\beta y}{\beta - \phi_1} + \frac{z}{1 - \phi_1} = 0 \text{ by } h_2, k_2, l_2 \text{ and } h_3, k_3, l_3.$$

$$\frac{\gamma x}{\gamma - \phi_2} + \frac{\beta y}{\beta - \phi_2} + \frac{z}{1 - \phi_2} = 0 \text{ by } h_1, k_1, l_1 \text{ and } h_3, k_3, l_3$$

$$\frac{\gamma x}{\gamma - \phi_3} + \frac{\beta y}{\beta - \phi_3} + \frac{z}{1 - \phi_3} = 0 \text{ by } h_1, k_1, l_1, \text{ and } h_2, k_2, l_2$$

If any two of the equations are satisfied simultaneously the solution is the values of h, k, l, which correspond to the value of ϕ, which does not appear in the two equations.

Suppose now that a plate-to-plate calculation is made starting from the top and proceeding *upwards*. This can be done by putting $n = -N$ (where N is positive) to give the composition on the nth plate *above* the top. From equation (6*a*), (6*b*), and (6*c*) the following equations can be derived in the same way as equations (11*a*) and (11*b*).

$$\frac{\dfrac{\gamma x_{-N}}{\gamma - \phi_1} + \dfrac{\beta y_{-N}}{\beta - \phi_1} + \dfrac{z_{-N}}{1 - \phi_1}}{\dfrac{\gamma x_{-N}}{\gamma - \phi_3} + \dfrac{\beta y_{-N}}{\beta - \phi_3} + \dfrac{z_{-N}}{1 - \phi_3}} = \left(\frac{\phi_1}{\phi_3}\right)^N \quad . \quad . \quad . \quad (15a)$$

and

$$\frac{\dfrac{\gamma x_{-N}}{\gamma - \phi_2} + \dfrac{\beta y_{-N}}{\beta - \phi_2} + \dfrac{z_{-N}}{1 - \phi_2}}{\dfrac{\gamma x_{-N}}{\gamma - \phi_3} + \dfrac{\beta y_{-N}}{\beta - \phi_3} + \dfrac{z_{-N}}{1 - \phi_3}} = \left(\frac{\phi_2}{\phi_3}\right)^N \quad . \quad . \quad . \quad (15b)$$

When N becomes infinite,

$$\frac{\gamma x_{-N}}{\gamma - \phi_1} + \frac{\beta y_{-N}}{\beta - \phi_1} + \frac{z_{-N}}{1 - \phi_1} = 0 \quad . \quad . \quad . \quad . \quad (16a)$$

and

$$\frac{\gamma x_{-N}}{\gamma - \phi_2} + \frac{\beta y_{-N}}{\beta - \phi_2} + \frac{z_{-N}}{1 - \phi_2} = 0 \quad . \quad . \quad . \quad . \quad (16b)$$

The solution of these equations is then (h_3, k_3, l_3).

Thus, if a plate-to-plate calculation is started at the top (including all components) and continued downwards, the limiting composition finally reached is (h_1, k_1, l_1). If the calculation is made upwards, the limiting composition finally reached is (h_3, k_3, l_3).

We now have to consider how the limiting composition (h_2, k_2, l_2) can be reached. Suppose now that the values of (x, y, z) on any plate are such that they satisfy the equation

$$\frac{\gamma x}{\gamma - \phi_3} + \frac{\beta y}{\beta - \phi_3} + \frac{z}{1 - \phi_3} = 0 \quad . \quad . \quad . \quad . \quad (17)$$

but do not satisfy the other two equations, so that these values of (x, y, z) do not represent limiting compositions. From equation (5) it is seen that, if equation (17) holds good for a plate it will also hold good for the next plate above or below it, and therefore for all plates above or below it. From equation (6a) it will be seen that, as n increases, the left-hand side of the equation continuously decreases, and finally becomes zero when n is infinite. This requires that $\frac{\gamma x}{\gamma - \phi_1} + \frac{\beta y}{\beta - \phi_1} + \frac{z}{1 - \phi_1} = 0$. As equation (17) is also satisfied, this means that the limiting composition (h_2, k_2, l_2) is reached as the calculation is made up the column. Note that h_2, k_2, l_2 do not make the denominator of the left-hand side of equation (6a) zero. In exactly the same way it can be shown that the limiting composition (h_1, k_1, l_1) is reached as the calculation is made down the column.

Thus, if the composition of the charge in the still kettle is such that it satisfies equation (17), a plate-to-plate calculation up the column, starting from the kettle, will finally reach the limiting composition (h_2, k_2, l_2). A slight increase in the reflux ratio will result in an increase in the values of ϕ which satisfy equation (9), for, differentiating this equation, we have

$$\left\{\frac{\gamma x_D}{(\gamma - \phi)^2} + \frac{\beta y_D}{(\beta - \phi)^2} + \frac{z_D}{(1 - \phi^2)}\right\}\delta\phi = \delta R.$$

With an increase in the value of ϕ_3 the expression $\frac{\gamma x}{\gamma - \phi_3} + \frac{\beta y}{\beta - \phi_3} + \frac{z}{1 - \phi_3}$ will no longer be zero, but will have a positive value. The plate-to-plate calculation up the column will then no longer pass into and remain stuck at the limiting composition (h_2, k_2, l_2), but will be capable of being continued until the composition corresponding to the top product is reached. Thus any composition of the kettle charge which satisfies the equation (17) will be a composition for which the reflux ratio used in calculating the values of ϕ from equation (9) is the minimum reflux ratio. The two limiting compositions (h_1, k_1, l_1) and (h_2, k_2, l_2) are merely particular values which satisfy the general equation (17). This conception of minimum reflux appears to answer satisfactorily the two questions which were stated earlier in this paper.

Examples 1, 2, and 3 show that the value of l_2 is always negative. Although a slight increase in the reflux ratio to make $\frac{\gamma x}{\gamma - \phi_3} + \frac{\beta y}{\beta - \phi_3} + \frac{z}{1 - \phi_3}$ positive will permit of a plate-to-plate calculation being continued to the top of the column, it does not necessarily follow that this calculation will not pass through a negative value of z when plate compositions approaching h_2, k_2, l_2 are reached in the calculation. A plate-to-plate calculation which passes through a negative value of one of the components obviously does not represent a practical case. In a case like Example 1, where all three components are present in substantial amounts in the top product, l_2 has a substantial negative value, and when the reflux is increased slightly over the minimum, a plate-to-plate calculation could still pass through a negative value of z. This case is, however, an unusual one. In the normal cases, such as Examples 2 and 3, where one or two of the components are only present in small amount in the top product, l_2, although negative, is very small. A quite minute increase in the reflux ratio above the minimum will ensure that the plate-to-plate calculation does not pass through a negative value. In other words, the theoretically correct minimum reflux ratio is that which will give a value of z (at the appropriate point in the column) of $-0{\cdot}000791$ in Example 2 or $-0{\cdot}67 \times 10^{-6}$ in Example 3. The minimum reflux ratio for practical purposes is that which gives a value of zero instead. The difference is obviously outside the range of normal calculations.

It is to be noted that, as in the case of a binary mixture, as long as the amount of a component in the product is small, the actual amount does not affect the minimum reflux ratio appreciably, as the limiting compositions do not occur in the neighbourhood of the product composition. If, however, a calculation is made for a finite number of plates, the actual amount of a component present in small quantity will appreciably affect the number of plates required for a given separation.

It has been shown that, for a rectifying column, if the composition at any point in the column satisfies the equation $\frac{\gamma x}{\gamma - \phi_3} + \frac{\beta y}{\beta - \phi_3} + \frac{z}{1 - \phi_3} = 0$ there is a possible range of compositions between (h_1, k_1, l_1) and (h_2, k_2, l_2). It can be similarly shown that, if the equation $\frac{\gamma x}{\gamma - \phi_2} + \frac{\beta y}{\beta - \phi_2} + \frac{z}{1 - \phi_2} = 0$ is satisfied, there is a possible range of compositions between (h_1, k_1, l_1) and (h_3, k_3, l_3), and that if the equation $\frac{\gamma x}{\gamma - \phi_1} + \frac{\beta y}{\beta - \phi_1} + \frac{z}{1 - \phi_1} = 0$ is satisfied there is a possible range of compositions between (h_2, k_2, l_2) and (h_3, k_3, l_3). It appears, however, that these other two cases are not significant for practical problems of fractionation.

The analysis has been given in detail for a rectifying column. It can be made in exactly the same way for a stripping column. For a stripping column, equation (4) becomes (writing ψ instead of ϕ)

$$\frac{\gamma x_W}{\gamma - \psi} + \frac{\beta y_W}{\beta - \psi} + \frac{z_W}{1 - \psi} = -S \quad . \quad . \quad . \quad . \quad (18)$$

Here also $\psi_1 < \psi_2 < \psi_3$.

For a stripping column, the limiting composition ($\bar{h}_3$, $\bar{k}_3$, $\bar{l}_3$) corresponding to ψ_3 is the one reached by calculating up the column from the reboiler, using all three components in the calculation. The limiting composition ($\bar{h}_1$, $\bar{k}_1$, $\bar{l}_1$) corresponding to ψ_1 is the one reached by calculating downwards below the reboiler. The limiting composition ($\bar{h}_2$, $\bar{k}_2$, $\bar{l}_2$) is the intermediate one, and corresponds to that reached by calculation upwards from the reboiler when two of the components are present in small amount in the reboiler and the lightest component is not taken into account in the calculation.

For any given value of S in equation (18) minimum reflux conditions will obtain in the stripping column if the composition at any point satisfies the equation

$$\frac{\gamma x}{\gamma - \psi_1} + \frac{\beta y}{\beta - \psi_1} + \frac{z}{1 - \psi_1} = 0 \quad . \quad . \quad . \quad . \quad (19)$$

and this equation represents a range of compositions between ($\bar{h}_3$, $\bar{k}_3$, $\bar{l}_3$) and ($\bar{h}_2$, $\bar{k}_2$, $\bar{l}_2$). Similar relations can be obtained for the other equations, but, as in the case of a rectifying column, they do not correspond to practical cases.

It should be noted that equation (17) for a rectifying column contains ϕ_3, the value of which lies between β and γ, while equation (19) for a stripping column contains ψ_1, the value of which lies between 1 and β.

For a stripping column, equations (8) become

$$\bar{h} = -\frac{\psi x_W}{(S+1)(\gamma-\psi)}; \bar{k} = -\frac{\psi y_W}{(S+1)(\beta-\psi)}; \bar{l} = -\frac{\psi z_W}{(S+1)(1-\psi)} \quad (20)$$

For ordinary purposes it is not necessary to calculate compositions to several decimal places, as was done in Examples 2 and 3, and this results in considerable simplification. When $x_W = 0$, equation (18) gives $\psi_3 = \gamma$. Then, from equations (20),

$$\bar{k}_3 = \frac{\gamma y_W}{(S+1)(\gamma-\beta)}, \bar{l}_3 = \frac{\gamma z_W}{(S+1)(\gamma-1)}$$

and, by difference,

$$\bar{h}_3 = 1 - \frac{\gamma y_W}{(S+1)(\gamma-\beta)} - \frac{\gamma z_W}{(S+1)(\gamma-1)}.$$

If, in addition, $y_W = 0$, then equation (18) gives $\psi_2 = \beta$ and $\bar{h}_2 = 0$,

$$\bar{l}_2 = \frac{\beta z_W}{(S+1)(\beta-1)} = \frac{\beta}{(S+1)(\beta-1)}$$

since $z_W = 1$.

By difference, $$\bar{k}_2 = 1 - \frac{\beta}{(S+1)(\beta-1)}.$$

If both x_W and y_W are zero, equation (18) gives

$$\frac{z_W}{1-\psi_1} = -S \text{ or } \psi_1 = \frac{S+1}{S}.$$

and $h_1 = 0$, $k_1 = 0$, and $l_1 = 1$.

Similarly for a rectifying column, if $z_D = 0$, equation (9) gives $\phi_1 = 1$ and equations (10) give

$$h_1 = \frac{x_D}{R(\gamma-1)}, k_1 = \frac{y_D}{R(\beta-1)}$$

and, by difference,

$$l_1 = 1 - \frac{x_D}{R(\gamma-1)} - \frac{y_D}{R(\beta-1)}.$$

If, in addition, $y_D = 0$, equation (9) gives $\phi_2 = \beta$ and, from equations (10), $h_2 = \frac{\beta}{R(\gamma-\beta)}$, $l_2 = 0$ and, by difference, $k_2 = 1 - \frac{\beta}{R(\gamma-\beta)}$. Also, for this case, equation (9) gives

$$\frac{\gamma x_D}{\gamma-\phi_3} = \frac{\gamma}{\gamma-\phi_3} = R+1 \text{ and } \phi_3 = \frac{\gamma R}{R+1}.$$

Then $h_3 = 1$, $k_3 = 0$, $l_3 = 0$.

When a rectifying column is superimposed on a stripping column, true minimum reflux conditions obtain for the system when minimum reflux conditions obtain in both the rectifying column and the stripping column. With a mixture of three components, of which two are " key " components, one component will be small in the top product and two components will be small in the bottom product or vice versa. (The following analysis is limited to such sharp separations.)

Consider the former case, in which the third component is lighter than the key components y and z. The top product contains component x and component y with a small amount of component z. For minimum reflux conditions in the rectifying column, by calculating downwards, the limiting composition h_1, k_1, l_1 is reached. For the stripping column, the bottom product is component z with a negligible amount of x and a small amount of y. If on any plate below the feed-plate the equation

$$\frac{\gamma x}{\gamma-\psi_1} + \frac{\beta y}{\beta-\psi_1} + \frac{z}{1-\psi_1} = 0$$

is satisfied, minimum reflux conditions will obtain in the stripping column. If, at the feed plate, the values h_1, k_1, l_1 for the rectifying column satisfy the equation

$$\frac{\gamma x}{\gamma-\psi_1} + \frac{\beta y}{\beta-\psi_1} + \frac{1}{1-\psi_1} = 0$$

for the stripping column, then minimum reflux conditions will obtain in both columns. The condition for minimum reflux is therefore

$$\frac{\gamma h_1}{\gamma-\psi_1} + \frac{\beta h_1}{\beta-\psi_1} + \frac{l_1}{1-\psi_1} = 0$$

Now it has been shown previously that h_1, k_1, l_1 is a solution of two equations for the rectifying column—namely,

$$\frac{\gamma h_1}{\gamma-\phi_2} + \frac{\beta k_1}{\beta-\phi_2} + \frac{l_1}{1-\phi_2} = 0$$

and

$$\frac{\gamma h_1}{\gamma-\phi_3} + \frac{\beta k_1}{\beta-\phi_3} + \frac{l_1}{1-\phi_3} = 0$$

There are thus three equations to be satisfied, and there are actually only two variables in these equations—namely, $\frac{h_1}{l_1}$ and $\frac{k_1}{l_1}$. The condition that the three equations are satisfied simultaneously is that the determinant

$$\begin{vmatrix} \frac{\gamma}{\gamma-\psi_1} & \frac{\beta}{\beta-\psi_1} & \frac{1}{1-\psi_1} \\ \frac{\gamma}{\gamma-\phi_2} & \frac{\beta}{\beta-\phi_2} & \frac{1}{1-\phi_2} \\ \frac{\gamma}{\gamma-\phi_3} & \frac{\beta}{\beta-\phi_3} & \frac{1}{1-\phi_3} \end{vmatrix} = 0 \quad . \quad . \quad . \quad (21)$$

This determinant becomes zero if any two rows are the same, and this occurs if $\psi_1 = \phi_2$ or $\psi_1 = \phi_3$ or $\phi_2 = \phi_3$. Now, ϕ_2 cannot equal ϕ_3 because ϕ_2 lies between 1 and β and ϕ_3 lies between β and γ. Also ψ_1 cannot equal ϕ_3 because ψ_1 lies between 1 and β and ϕ_3 lies between β and γ. But ψ_1 and ϕ_2 both lie between 1 and β, so that $\psi_1 = \phi_2$ is the only possible solution. This, therefore, is the condition for minimum reflux in the case where the third component is lighter than the key components. It is to be noted that ϕ_2 is the root corresponding to the light key component in the rectifying column, the components being regarded in the order of increasing volatility and the values of ϕ in the order of increasing magnitude. In the same way, ψ_1 is the root corresponding to the heavy key component in the stripping column.

The other case to be considered is that in which the third component is heavier than the key components. In this case the key components are x and y. The top product is component x with a small amount of component y and a negligible amount of component z. The bottom product is components y and z, with a small amount of component x. For a stripping column the limiting composition, proceeding upwards, is reached at $\bar{h}_3$, $\bar{k}_3$, $\bar{l}_3$. For the rectifying column, minimum reflux conditions obtain if the equation

$$\frac{\gamma x}{\gamma - \phi_3} + \frac{\beta y}{\beta - \phi_3} + \frac{z}{1 - \phi_3} = 0$$

is satisfied, and this equation must be satisfied by $\bar{h}_3$, $\bar{k}_3$, $\bar{l}_3$ for minimum reflux conditions to obtain in both sections of the column. Now, $\bar{h}_3$, $\bar{k}_3$, l_3 is given by the equations

$$\frac{\gamma x}{\gamma - \psi_1} + \frac{\beta y}{\beta - \psi_1} + \frac{z}{1 - \psi_1} = 0$$

and

$$\frac{\gamma x}{\gamma - \psi_2} + \frac{\beta y}{\beta - \psi_2} + \frac{x}{1 - \psi_2} = 0.$$

By the same reasoning as before, the condition that all three equations are satisfied is $\psi_2 = \phi_3$. Here again the value of ϕ corresponds to the light key component in the rectifying column and the value of ψ to the heavy key component in the stripping column.

The general condition for both cases is that equation (9) for the rectifying column and equation (18) for the stripping column have a common root. Denoting this common root by θ, then

$$\frac{\gamma x_D}{\gamma - \theta} + \frac{\beta y_D}{\beta - \theta} + \frac{z_D}{1 - \theta} = R + 1 \quad . \quad . \quad . \quad . \quad (22)$$

and

$$\frac{\gamma x_W}{\gamma - \theta} + \frac{\beta y_W}{\beta - \theta} + \frac{z_W}{1 - \theta} = -S \quad . \quad . \quad . \quad . \quad (23)$$

Multiplying the first equation by P and the second equation by W and noting that

$$Px_D + Wx_W = Fx_F;\ Py_D + Wy_W = Fy_F;\ Pz_D + Wz_W = Fz_F$$

where x_F, y_F, z_F are the composition of the feed, then

$$\frac{\gamma F x_F}{\gamma - \theta} + \frac{\beta F y_F}{\beta - \theta} + \frac{F z_F}{1 - \theta} = (R + 1)P - SW \quad . \quad . \quad (24)$$

Now, $SW = RP + qF - W = (R + 1)P - (1 - q)F$
since $W = F - P$.
Equation (24) then becomes

$$\frac{\gamma x_F}{\gamma - \theta} + \frac{\beta y_F}{\beta - \theta} + \frac{z_F}{1 - \theta} = 1 - q \quad . \quad . \quad . \quad . \quad (25)$$

If the feed is liquid at boiling point, $q = 1$ and equation (25) reduces to a quadratic. If the feed is all vapour, $q = 0$. In this case equation (25) obviously has one solution $\theta = 0$ since $x_F + y_F + z_F = 1$ and equation (25) again reduces to a quadratic.

If $q = 1$, equation (25) becomes

$$(\gamma x_F + \beta y_F + z_F)\theta^2 - \{\gamma(\beta + 1)x_F + \beta(\gamma + 1)y_F + (\gamma + \beta)z_F\}\theta + \beta\gamma = 0 \quad . \quad (25a)$$

If $q = 0$, equation (25) becomes

$$\theta^2 - \{(\beta + 1)x_F + (\gamma + 1)y_F + (\gamma + \beta)z_F\}\theta + \beta x_F + \gamma y_F + \beta\gamma z_F = 0 \quad . \quad (25b)$$

We thus have a simple method of calculating the minimum reflux ratio. Equation (25) is used to find θ, and this value of θ is then substituted in equation (22) to find R, which is the required minimum reflux ratio. Alternatively, S, the minimum reboil ratio, can be found from equation (23). Where y and z are the key components, $\theta = \psi_1 = \phi_2$ and lies between 1 and β. Where x and y are the key components, $\theta = \psi_2 = \phi_3$ and lies between β and γ. In both cases the value of θ required from equation (25) is the one which lies between the relative volatilities of the key components.

The method of calculation is illustrated by the following examples taken from the paper by Colburn.[3]

Example 4. Third component lighter than the keys.

$x_F = 0{\cdot}6$; $y_F = 0{\cdot}2$; $z_F = 0{\cdot}2$; $q = 1$.
$x_D = 0{\cdot}75$; $y_D = 0{\cdot}25$; $z_D = 0$; $x_W = 0$; $y_W = 0$; $z_W = 1$.
$\gamma = 4$; $\beta = 2$.

Equation (25) or (25*a*) becomes

$$\frac{2{\cdot}4}{4 - \theta} + \frac{0{\cdot}4}{2 - \theta} + \frac{0{\cdot}2}{1 - \theta} = 0 \text{ or } 3\theta^2 - 10{\cdot}4\theta + 8 = 0$$

The desired value of θ is that which is between 1 and 2. The solution is found to be 1·152.

Equation (22) then gives

$$\frac{3}{4 - 1{\cdot}152} + \frac{0{\cdot}5}{2 - 1{\cdot}152} = R + 1 \text{ and } R = 0{\cdot}643.$$

Example 5. Third component heavier than the keys.

$x_F = 0{\cdot}2$; $y_F = 0{\cdot}2$; $z_F = 0{\cdot}6$; $q = 0$.
$x_D = 1$; $y_D = 0$; $z_D = 0$; $x_W = 0$; $y_W = 0{\cdot}25$; $z_W = 0{\cdot}75$.
$\gamma = 10$; $\beta = 2$.

Equation (25) or (25*b*) becomes

$$\frac{2}{10-\theta} + \frac{0{\cdot}4}{2-\theta} + \frac{0{\cdot}6}{1-\theta} = 1 \text{ or } \theta^2 - 10\theta + 14{\cdot}4 = 0.$$

The desired value of θ lies between 2 and 10, and is found to be 8·255. Then from equation (22),

$$\frac{10}{10-8{\cdot}255} = R + 1 \text{ and } R = 4{\cdot}73.$$

In a paper by Mayfield and May [6] a method was given for calculating minimum reflux ratio which was based on the hypothesis that the minimum reflux ratio of a ternary mixture was the same as the minimum reflux ratio of two binary mixtures into which the ternary mixture was resolved. The hypothesis was not proved, but was demonstrated to give results corresponding to the results obtained by other methods for a number of examples in which the condition of the feed was $q = 1$ or $q = 0$. It can, however, be proved correct for the general case by means of the equations which have been derived in this paper.

Consider the case where the third component is heavier than the key components, which are x and y. The feed composition is x_F, y_F, z_F. Let the ternary mixture be divided into two binary mixtures. The first binary mixture contains part of component x, say x_F', and all of component y. The second binary mixture contains the rest of component x, say x_F'' and all of component z.

The feed composition for the first binary mixture is $\frac{x_F'}{x_F' + y_F}, \frac{y_F}{x_F' + y_F}$.

The relative volatility of the two components is $\frac{\gamma}{\beta}$. Applying equation (25) to this binary mixture, the term $\frac{z_F}{1-\theta}$ corresponding to the third component, disappears. The equation becomes

$$\frac{\frac{\gamma}{\beta} \cdot x_F'}{\frac{\gamma}{\beta} - \theta} + \frac{y_F}{1-\theta} = (1-q)(x_F' + y_F) \quad . \quad . \quad . \quad . \quad (26)$$

For this binary mixture, with $x_D = 1$, equation (22) becomes $\frac{\frac{\gamma}{\beta}}{\frac{\gamma}{\beta} - \theta} = R' + 1$, and substituting this value of R' in equation (26) gives

$$x'_F(R'+1) + \frac{\beta y_F(R'+1)}{\beta - (\gamma-\beta)R'} = (1-q)(x'_F + y_F) \quad . \quad . \quad (27)$$

Similarly for the other binary mixture, with relative volatility γ, there is obtained the equation

$$x_F''(R''+1) + \frac{z_F(R''+1)}{1-(\gamma-1)R''} = (1-q)(x_F'' + z_F) \quad . \quad (28)$$

Now, by the hypothesis, if the minimum reflux ratios for the two binary mixtures are made equal to each other, they should also be equal to the minimum reflux ratio for the ternary mixture.

Putting $R' = R'' = R$ in equations (27) and (28) and adding them, we have, since $x'_F + x''_F = x_F$ and $x_F + y_F + z_F = 1$,

$$x_F(R+1) + \frac{\beta y_F(R+1)}{\beta-(\gamma-\beta)R} + \frac{z_F(R+1)}{1-(\gamma-1)R} = 1 - q \quad . \quad (29)$$

For the ternary mixture, the minimum reflux ratio is given by equations (25) and (22). From the latter equation we have, since $x_D = 1$,

$$\frac{\gamma}{\gamma - \theta} = R + 1 \text{ or } \theta = \frac{\gamma R}{R+1}.$$

With this value of θ, equation (25) becomes

$$x_F(R+1) + \frac{\beta y_F(R+1)}{\beta-(\gamma-\beta)R} + \frac{z_F(R+1)}{1-(\gamma-1)R} = 1 - q$$

which is the same as equation (29) derived from the two binary mixtures.

A similar proof can be given for the case where the third component is lighter than the key components. For this case it is more convenient to use equation (23) with equation (25) to give the final result in terms of the minimum reboil ratio.

It will be noted that equation (29) can be used to give a direct solution for R, instead of following the procedure previously described of first finding θ from equation (25) and then finding R from equation (22). This latter procedure is the more convenient one, as it readily permits of the correct value of θ, and therefore of R, being selected. The use of equation (29) involves finding the various values of R which satisfy it and then deciding which value correctly represents minimum reflux conditions.

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