As the maximum knock spark setting for all compression ratios above 7 to 1 (octane numbers above 70) was 28°, it seemed logical to determine the effect of a fixed advance of 28° at the lower ratios. The results, as shown in Fig. 1, indicate that the effect is sufficiently small to allow this setting to be used from 40 to 120 O.N.

In the high-octane range the effect of the first increments of advance of spark from A.S.T.M. is to enable very much lower compression ratios to be employed. This becomes a rapidly diminishing effect as the spark timing approaches 28°. At 100 O.N., for instance, a 3° advance from the A.S.T.M. setting of 16° lowers the ratio by 0·5, but from 25° to 28° the ratio change is only 0·1. Beyond the optimum setting further advance causes rapid changes in performance. The above suggests that a fixed ignition setting should be adopted which is within the zone of least influence from about 24° to 28°. The guide curve resulting from tests on two engines with a fixed setting of 25° advance is shown in Fig. 1. This is reproduced in terms of micrometer setting, as in the A.S.T.M. method, in Table I.

Practical Tests in Other Engines.

In order to test the behaviour of a number of C.F.R. engines operating under the proposed 25° modifications, participants in the I.P. C.F.R. correlation scheme agreed to test fuels for several months without the throttle plate, first using the A.S.T.M. guide curve, then with 25° advance and the 25° guide curve in Fig. 1.

Eleven fuel samples of widely varying types were tested by the two methods in each of twenty engines over a period of four months, from which it was noted that there was no sensible difference in the average octane numbers in the range tested—*i.e.*, 79 to 103 O.N.—and the maximum spread and average deviation were slightly less by the 25° method. That the spread on twenty engines was less with the 25° method demonstrates that the method is acceptable to the individual engines.

It is recommended that a fixed spark setting of 25° advance be considered for the I.P. and A.S.T.M. Motor Method through the range from 40 to 120 O.N. The 17° Motor Method would then become obsolete.

It is felt that this investigation should be given prominence at the present time, as it provides a means for increasing the accuracy of rating high octane fuels.

References.

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[2] *A.S.T.M. Standards on Petroleum Products and Lubricants, October* 1942. Knock characteristics of Motor Fuels, D.357–42(T).

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FRACTIONAL DISTILLATION OF TERNARY MIXTURES. PART I.

By A. J. V. Underwood, D.Sc., M.I.Chem.E., A.M.I.Mech.E., F.R.I.C., F.Inst.F., F.Inst.Pet.

Summary.

An analytical method is presented for computations relating to the fractional distillation of ternary mixtures. It is also shown that the principle of the method can be extended to mixtures of more than three components.

For ternary mixtures with components denoted by x, y, z the compositions of the liquids on adjacent plates of a fractionating column are connected by the following relations, derived from material balances.

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

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

$$mz_0 + d = \frac{\beta_1}{\gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad . \quad (3)$$

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 returned by the reboiler to the stripping column per mole of bottom product withdrawn. For a stripping column on which a rectifying column is superimposed, $S = \frac{RP + qF - W}{W}$; $b = \frac{-x_W}{S}$; $c = \frac{-y_W}{S}$; $d = \frac{-z_W}{S}$. For both rectifying and stripping columns

$$b + c + d = 1 - m \quad . \quad . \quad . \quad . \quad (4)$$

Constant molal reflux and constant relative volatilities throughout the column are assumed.

Equations (1), (2), and (3) can be used to calculate compositions from plate to plate. It will be shown that, by suitably transforming them, the composition on any plate can be calculated without using a stepwise procedure from plate to plate. Previously such a direct calculation has been possible only for the special case of total reflux where $m = 1$ and $b = c = d = 0$.

The method of transformation which can be applied to equations (1), (2), and (3) to make them suitable for a direct calculation depends on the use of a parameter ϕ which is defined in the following manner. Let h, k, and l be the values of x, y, and z, respectively, which correspond to the compositions on two adjacent plates when there is no change in composition between these two plates. h, k, and l represent the composition at which no further fractionation takes place—that is, the composition for which minimum reflux conditions obtain with the given reflux ratio. They are defined by the equations

$$mh + b = \frac{\gamma h}{\gamma h + \beta k + l} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$mk + c = \frac{\beta k}{\gamma h + \beta k + l} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$ml + d = \frac{l}{\gamma h + \beta k + l} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Let

$$m(\gamma h + \beta k + l) = \phi \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

so that

$$\frac{1}{\phi} = \frac{mh + b}{\gamma mh} = \frac{mk + c}{\beta mk} = \frac{ml + d}{ml} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Then

$$h = \frac{b\phi}{m(\gamma - \phi)};\ k = \frac{c\phi}{m(\beta - \phi)};\ l = \frac{d\phi}{m(1 - \phi)} \quad . \quad . \quad (9)$$

Now h, k, and l are particular values of x, y, and z, and $x + y + z = 1$ for all values, so that, also, $h + k + l = 1$. Substituting from equations (9),

$$\frac{b\phi}{\gamma - \phi} + \frac{c\phi}{\beta - \phi} + \frac{d\phi}{1 - \phi} = m = 1 - b - c - d$$

or

$$\frac{b\gamma}{\gamma - \phi} + \frac{c\beta}{\beta - \phi} + \frac{d}{1 - \phi} = 1 \quad . \quad . \quad . \quad . \quad (10)$$

This is an equation of the third degree, so that there are three values of ϕ which satisfy it.

Returning to equations (1), (2), and (3), an equation can be derived in the form

$$mx_0 + b + \lambda_1(my_0 + c) + \lambda_2(mz_0 + d) + \lambda_3 = \frac{\gamma x_1 + \lambda_1\beta y_1 + \lambda_2 z_1 + \lambda_3(\gamma x_1 + \beta y_1 + z_1)}{\gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad . \quad (11)$$

This equation is obtained by multiplying equation (2) by λ_1, equation (3) by λ_2, and adding them to equation (1), and also adding λ_3 to both sides. Equation (11) is satisfied by all values of x, y, z which satisfy equations (1), (2), (3). The indeterminate multipliers λ_1, λ_2, λ_3 can be given any values desired.

Rearranging equation (11),

$$mx_0 + \lambda_1 my_0 + \lambda_2 mz_0 + b + \lambda_1 c + \lambda_2 d + \lambda_3 = \frac{\gamma(1 + \lambda_3)x_1 + \beta(\lambda_1 + \lambda_3)y_1 + (\lambda_2 + \lambda_3)z_1}{\gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad . \quad (12)$$

λ_1, λ_2, λ_3 are now chosen so that the function of x_0, y_0, z_0 on the left-hand

side of the equation becomes exactly the same function, except for a constant multiplier, as the function of x_1, y_1, z_1, which constitutes the numerator of the right-hand side of equation (12). This requires that

$$\frac{\gamma(1 + \lambda_3)}{m} = \frac{\beta(\lambda_1 + \lambda_3)}{\lambda_1 m} = \frac{\lambda_2 + \lambda_3}{\lambda_2 m} \quad . \quad . \quad . \quad . \quad (13)$$

and that

$$b + \lambda_1 c + \lambda_2 d + \lambda_3 = 0 \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Using equations (13) and (14), equation (12) becomes

$$m(x_0 + \lambda_1 y_0 + \lambda_2 z_0) = \frac{\gamma(1 + \lambda_3)(x_1 + \lambda_1 y_1 + \lambda_2 z_1)}{\gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad (15)$$

Since this equation is satisfied by all values of x_0, y_0, z_0 and x_1, y_1, z_1, which satisfy equations (1), (2), (3), it is also satisfied by $x_0 = x_1 = h$; $y_0 = y_1 = k$; $z_0 = z_1 = l$, which are particular solutions as defined by equations (5), (6), (7). Substituting these values in equation (15), therefore

$$m(h + \lambda_1 k + \lambda_2 l) = \frac{\gamma(1 + \lambda_3)(h + \lambda_1 k + \lambda_2 l)}{\gamma h + \beta k + l}$$

and $\dfrac{\gamma(1 + \lambda_3)}{m} = \gamma h + \beta k + l = \dfrac{\phi}{m}$ from equation (7a). Each of the three terms in equation (13) is therefore equal to $\dfrac{\phi}{m}$ and, solving for λ_1, λ_2 and λ_3,

$$\lambda_3 = \frac{\phi}{\gamma} - 1;\ \lambda_1 = \frac{\dfrac{\phi}{\gamma} - 1}{\dfrac{\phi}{\beta} - 1};\ \lambda_2 = \frac{\dfrac{\phi}{\gamma} - 1}{\phi - 1} \quad . \quad . \quad . \quad (16)$$

These values of λ_1, λ_2, λ_3 also satisfy equation (14) for

$$b + \lambda_1 c + \lambda_2 d + \lambda_3 = b + c \,.\, \frac{\dfrac{\phi}{\gamma} - 1}{\dfrac{\phi}{\beta} - 1} + d \,.\, \frac{\dfrac{\phi}{\gamma} - 1}{\phi - 1} + \frac{\phi}{\gamma} - 1$$

$$= \left(1 - \frac{\phi}{\gamma}\right)\left\{\frac{b\gamma}{\gamma - \phi} + \frac{c\beta}{\beta - \phi} + \frac{d}{1 - \phi} - 1\right\}$$

$$= 0 \text{ from equation (10)}$$

Substituting the values of λ_1, λ_2, λ_3 in equation (15) gives

$$x_0 + \frac{\dfrac{\phi}{\gamma} - 1}{\dfrac{\phi}{\beta} - 1} \,.\, y_0 + \frac{\dfrac{\phi}{\gamma} - 1}{\phi - 1} \,.\, z_0 = \frac{\phi}{m}\left[x_1 + \frac{\dfrac{\phi}{\gamma} - 1}{\dfrac{\phi}{\beta} - 1} \,.\, y_1 + \frac{\dfrac{\phi}{\gamma} - 1}{\phi - 1} \,.\, z_1\right]$$

or

$$\frac{\gamma x_0}{\gamma - \phi} + \frac{\beta y_0}{\beta - \phi} + \frac{z_0}{1 - \phi} = \frac{\dfrac{\phi}{m}\left\{\dfrac{\gamma x_1}{\gamma - \phi} + \dfrac{\beta y_1}{\beta - \phi} + \dfrac{z_1}{1 - \phi}\right\}}{\gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad (17)$$

There are three values of ϕ given by equation (10). Denoting these by ϕ_1, ϕ_2, ϕ_3, there are three equations corresponding to equation (17), namely,

$$\frac{\gamma x_0}{\gamma-\phi_1}+\frac{\beta y_0}{\beta-\phi_1}+\frac{z_0}{1-\phi_1}=\frac{\frac{\phi_1}{m}\left\{\frac{\gamma x_1}{\gamma-\phi_1}+\frac{\beta y_1}{\beta-\phi_1}+\frac{z_1}{1-\phi_1}\right\}}{\gamma x_1+\beta y_1+z_1} \quad . \quad (18a)$$

$$\frac{\gamma x_0}{\gamma-\phi_2}+\frac{\beta y_0}{\beta-\phi_2}+\frac{z_0}{1-\phi_2}=\frac{\frac{\phi_2}{m}\left\{\frac{\gamma x_1}{\gamma-\phi_2}+\frac{\beta y_1}{\beta-\phi_2}+\frac{z_1}{1-\phi_2}\right\}}{\gamma x_1+\beta y_1+z_1} \quad . \quad (18b)$$

$$\frac{\gamma x_0}{\gamma-\phi_3}+\frac{\beta y_0}{\beta-\phi_3}+\frac{z_0}{1-\phi_3}=\frac{\frac{\phi_3}{m}\left\{\frac{\gamma x_1}{\gamma-\phi_3}+\frac{\beta y_1}{\beta-\phi_3}+\frac{z_1}{1-\phi_3}\right\}}{\gamma x_1+\beta y_1+z_1} \quad . \quad (18c)$$

Dividing equation (18a) by equation (18b),

$$\frac{\frac{\gamma x_0}{\gamma-\phi_1}+\frac{\beta y_0}{\beta-\phi_1}+\frac{z_0}{1-\phi_1}}{\frac{\gamma x_0}{\gamma-\phi_2}+\frac{\beta y_0}{\beta-\phi_2}+\frac{z_0}{1-\phi_2}}=\frac{\phi_1}{\phi_2}\cdot\frac{\frac{\gamma x_1}{\gamma-\phi_1}+\frac{\beta y_1}{\beta-\phi_1}+\frac{z_1}{1-\phi_1}}{\frac{\gamma x_1}{\gamma-\phi_2}+\frac{\beta y_1}{\beta-\phi_2}+\frac{z_1}{1-\phi_2}} \quad . \quad (19)$$

Applying this relation to successive pairs of plates, there is readily obtained for the nth plate the equation

$$\frac{\frac{\gamma x_0}{\gamma-\phi_1}+\frac{\beta y_0}{\beta-\phi_1}+\frac{z_0}{1-\phi_1}}{\frac{\gamma x_0}{\gamma-\phi_2}+\frac{\beta y_0}{\beta-\phi_2}+\frac{z_0}{1-\phi_2}}=\left(\frac{\phi_1}{\phi_2}\right)^n\cdot\frac{\frac{\gamma x_n}{\gamma-\phi_1}+\frac{\beta y_n}{\beta-\phi_1}+\frac{z_n}{1-\phi_1}}{\frac{\gamma x_n}{\gamma-\phi_2}+\frac{\beta y_n}{\beta-\phi_2}+\frac{z_n}{1-\phi_2}} \quad (20a)$$

By following the same procedure with the other pairs of equations (18a), (18b), (18c) there are also obtained the equations

$$\frac{\frac{\gamma x_0}{\gamma-\phi_2}+\frac{\beta y_0}{\beta-\phi_2}+\frac{z_0}{1-\phi_2}}{\frac{\gamma x_0}{\gamma-\phi_3}+\frac{\beta y_0}{\beta-\phi_3}+\frac{z_0}{1-\phi_3}}=\left(\frac{\phi_2}{\phi_3}\right)^n\cdot\frac{\frac{\gamma x_n}{\gamma-\phi_2}+\frac{\beta y_n}{\beta-\phi_2}+\frac{z_n}{1-\phi_2}}{\frac{\gamma x_n}{\gamma-\phi_3}+\frac{\beta y_n}{\beta-\phi_3}+\frac{z_n}{1-\phi_3}} \quad (20b)$$

and

$$\frac{\frac{\gamma x_0}{\gamma-\phi_3}+\frac{\beta y_0}{\beta-\phi_3}+\frac{z_0}{1-\phi_3}}{\frac{\gamma x_0}{\gamma-\phi_1}+\frac{\beta y_0}{\beta-\phi_1}+\frac{z_0}{1-\phi_1}}=\left(\frac{\phi_3}{\phi_1}\right)^n\cdot\frac{\frac{\gamma x_n}{\gamma-\phi_3}+\frac{\beta y_n}{\beta-\phi_3}+\frac{z_n}{1-\phi_3}}{\frac{\gamma x_n}{\gamma-\phi_1}+\frac{\beta y_n}{\beta-\phi_1}+\frac{z_n}{1-\phi_1}} \quad (20c)$$

Equations (20a), (20b), (20c) provide a means for calculating the compositions on plate n when the compositions on plate 0 are given. When given values of x_0, y_0, z_0 are substituted, there are obtained three simultaneous equations of the first degree in x_n, y_n, z_n. These three equations are only equivalent to two independent equations, as any one of equations (20a), (20b), (20c) can be obtained from the other two by division. There

is, however, also the equation $x_n + y_n + z_n = 1$, so that three equations are available for solving for the three unknowns x_n, y_n, z_n.

The left-hand side of equations (20a), (20b), (20c) becomes unity when $x_0 = x_D$, $y_0 = y_D$, $z_0 = z_D$.

For $$x_D = \frac{b}{1-m},\quad y_D = \frac{c}{1-m},\quad z_D = \frac{d}{1-m}.$$

Then

$$\frac{\gamma x_D}{\gamma-\phi_1}+\frac{\beta y_D}{\beta-\phi_1}+\frac{z_D}{1-\phi_1}=\frac{1}{1-m}\left(\frac{b\gamma}{\gamma-\phi_1}+\frac{c\beta}{\beta-\phi_1}+\frac{d}{1-\phi_1}\right)$$

$$=\frac{1}{1-m}\text{ from equation (10).}$$

The same relation holds good for all three values of ϕ. A similar simplification is obtained for a stripping column by putting $x_n = x_w$, $y_n = y_w$, $z_n = z_w$, and the right-hand side of equations (20a), (20b), (20c) then reduces to unity. The simplified equations facilitate calculation of the composition on the nth plate from the top of a rectifying column or the nth plate from the bottom of a stripping column.

Constant molal reflux and constant relative volatility have been assumed. Variations in them can be taken into account by applying equations (20a), (20b), (20c) successively to sections of the column in which appropriate values are used.

Equations (20a), (20b), (20c) are similar in type to the equations for the usual calculation in the special case of total reflux. In that case, equations (1), (2), (3) give

$$\frac{x_0}{y_0}=\left(\frac{\gamma}{\beta}\right)^n\cdot\frac{x_n}{y_n}\quad\text{and}\quad\frac{y_0}{z_0}=\beta^n\cdot\frac{y_n}{z_n}$$

Equations (20a), (20b), (20c) correspond, therefore, to a case of total reflux in which the components are

$$\left(\frac{\gamma x}{\gamma-\phi_1}+\frac{\beta y}{\beta-\phi_1}+\frac{z}{1-\phi_1}\right),\ \left(\frac{\gamma x}{\gamma-\phi_2}+\frac{\beta y}{\beta-\phi_2}+\frac{z}{1-\phi_2}\right)\ \text{and}$$

$$\left(\frac{\gamma x}{\gamma-\phi_3}+\frac{\beta y}{\beta-\phi_3}+\frac{z}{1-\phi_3}\right)\ \text{respectively}$$

and the relative volatilities are ϕ_1, ϕ_2, ϕ_3 respectively.

Equations (20a), (20b), (20c) can also be written in another form. Denoting by h_1, k_1, l_1 the values corresponding to ϕ_1 and similarly for ϕ_2 and ϕ_3, the use of equations (9) in equation (20a) gives

$$\frac{\frac{\gamma h_1}{b}\cdot x_0+\frac{\beta k_1}{c}\cdot y_0+\frac{l_1}{d}\cdot z_0}{\frac{\gamma h_2}{b}\cdot x_0+\frac{\beta k_2}{c}\cdot y_0+\frac{l_2}{d}\cdot z_0}=\left(\frac{\phi_1}{\phi_2}\right)^n\cdot\frac{\frac{\gamma h_1}{b}\cdot x_n+\frac{\beta k_1}{c}\cdot y_n+\frac{l_1}{d}\cdot z_n}{\frac{\gamma h_2}{b}\cdot x_n+\frac{\beta k_2}{c}\cdot y_n+\frac{l_2}{d}\cdot z_n} \quad (21)$$

together with two similar equations.

It has been mentioned that h, k and l represent the limiting composition for which the reflux ratio represents conditions of minimum reflux. There are three such limiting compositions corresponding to the three sets of values of h, k and l. The significance of these three compositions will be discussed in the second part of this paper.

The method which has been outlined requires the solution of the cubic equation (10) to find ϕ_1, ϕ_2, ϕ_3. The process of solution is facilitated by the following considerations. Equation (10) can be written

$$b\gamma(\beta - \phi)(1 - \phi) + c\beta(1 - \phi)(\gamma - \phi) + d(\gamma - \phi)(\beta - \phi) - (\gamma - \phi)(\beta - \phi)(1 - \phi) = 0 \quad . \quad . \quad (22)$$

Denoting the expression on the left-hand side of the equation by E and giving to ϕ the values 0, 1, β, γ successively it is seen that

when $\phi = 0$, $E = \beta\gamma\,(b + c + d - 1) = -\,m\beta\gamma$, *i.e.* negative,
$\phi = 1$, $E = d\beta\gamma$, *i.e.* positive,
$\phi = \beta$, $E = -\,c\beta(\beta - 1)(\gamma - \beta)$, *i.e.* negative,
$\phi = \gamma$, $E = b\gamma(\gamma - \beta)(\gamma - 1)$, *i.e.* positive.

Thus E must become zero for a value of ϕ between 0 and 1, for a value between 1 and β and for a value between β and γ. Denoting these values by ϕ_1, ϕ_2 and ϕ_3 respectively then

$$0 < \phi_1 < 1\,;\; 1 < \phi_2 < \beta\,;\; \beta < \phi_3 < \gamma$$

This gives a ready indication of the values of ϕ which satisfy equation (10). A further indication can also be obtained. If equation (22) is multiplied out, it becomes

$$\phi^3 - \phi^2\{(1 - d) + \beta(1 - c) + \gamma(1 - b)\} + \phi\{\beta + \gamma + \beta\gamma - b(\gamma + \beta\gamma) - c(\beta + \beta\gamma) - d(\beta + \gamma)\} - (1 - b - c - d)\beta\gamma = 0 \quad (23)$$

Since ϕ_1, ϕ_2, ϕ_3 are the roots of this equation,

$$\phi_1 + \phi_2 + \phi_3 = (1 - d) + \beta(1 - c) + \gamma(1 - d) \quad . \quad . \quad . \quad . \quad (24)$$

$$\phi_1\phi_2 + \phi_2\phi_3 + \phi_3\phi_1 = \beta + \gamma + \beta\gamma - b(\gamma + \beta\gamma) - c(\beta + \beta\gamma) - d\,(\beta + \gamma) \quad . \quad . \quad (24a)$$

and $$\phi_1\phi_2\phi_3 = (1 - b - c - d)\beta\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

If we now assume as approximate solutions,

$$\phi_1 = 1 - d\,;\; \phi_2 = \beta(1 - c)\,;\; \phi_3 = \gamma(1 - b) \quad .. \quad . \quad (26)$$

these values satisfy equation (24). They also approximately satisfy equation (25) since, to a first approximation,

$$(1 - d)(\beta(1 - c)\gamma(1 - d) = \beta\gamma(1 - b - c - d)$$

as b, c and d are fairly small compared with unity and, for a first approximation, powers above the first may be neglected. With the same approximation, equation (24a) is also satisfied. The procedure for solving equation (10) or (22) is therefore to assume the values given by equations (26) as a first approximation and then to obtain a closer approximation by any of the usual methods.

In many cases the process of solution is facilitated through one or more of the coefficients b, c, d in equation (10) being approximately zero when the component in question is present in very small amount in the product.

In the second part of this paper it is planned to show the application of the methods here presented to numerical cases.

Mixtures of More than Three Components.

The method of transforming the basic equations which has been described can also be applied to mixtures of more than three components and this application is briefly indicated below. Consider a four-component mixture. Using the same symbols as before, let w be the fourth component, more volatile than x and having a relative volatility of δ referred to z. Then, as before,

$$mw_0 + a = \frac{\delta w_1}{\delta w_1 + \gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad . \quad . \quad (27)$$

$$mx_0 + b = \frac{\gamma x_1}{\delta w_1 + \gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad . \quad . \quad (28)$$

$$my_0 + c = \frac{\beta y_1}{\delta w_1 + \gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad . \quad . \quad (29)$$

$$mz_0 + d = \frac{z_1}{\delta w_1 + \gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad . \quad . \quad (30)$$

Using the indeterminate multipliers λ_1, λ_2, λ_3, λ_4, then

$$(mw_0 + a) + \lambda_1(mx_0 + b) + \lambda_2(my_0 + c) + \lambda_3(mz_0 + d) + \lambda_4 = \frac{\delta w_1 + \lambda_1\gamma x_1 + \lambda_2\beta y_1 + \lambda_3 z_1 + \lambda_4(\delta w_1 + \gamma x_1 + \beta y_1 + z_1)}{\delta w_1 + \gamma x_1 + \beta y_1 + z_1}$$

or

$$mw_0 + \lambda_1 mx_0 + \lambda_2 my_0 + \lambda_3 mz_0 + a + \lambda_1 b + \lambda_2 c + \lambda_3 d + \lambda_4 = \frac{\delta(1 + \lambda_4)w_1 + \gamma(\lambda_1 + \lambda_4)x_1 + \beta(\lambda_2 + \lambda_4)y_1 + (\lambda_3 + \lambda_4)z_1}{\delta w_1 + \gamma x_1 + \beta y_1 + z_1} \quad (31)$$

Choose λ_1, λ_2, λ_3, λ_4 so that

$$\frac{\delta(1 + \lambda_4)}{m} = \frac{\gamma(\lambda_1 + \lambda_4)}{\lambda_1 m} = \frac{\beta(\lambda_2 + \lambda_4)}{\lambda_2 m} = \frac{\lambda_3 + \lambda_4}{\lambda_3 m} \quad . \quad . \quad (32)$$

and

$$a + \lambda_1 b + \lambda_2 c + \lambda_3 d + \lambda_4 = 0 \quad . \quad . \quad . \quad . \quad (33)$$

ϕ is now defined by the equations

$$\frac{mg + a}{\delta mg} = \frac{mh + b}{\gamma mh} = \frac{mk + c}{\beta mk} = \frac{ml + d}{ml} = \frac{1}{\phi} \quad . \quad . \quad (34)$$

where g is the corresponding value for component w and

$$\phi = m(\delta g + \gamma h + \beta k + l) \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Since $g + h + k + l = 1$, the equation for ϕ corresponding to equation (10) is

$$\frac{a\phi}{\delta - \phi} + \frac{b\phi}{\gamma - \phi} + \frac{c\phi}{\beta - \phi} + \frac{d\phi}{1 - \phi} = m = 1 - a - b - c - d$$

or

$$\frac{a\delta}{\delta - \phi} + \frac{b\gamma}{\gamma - \phi} + \frac{c\beta}{\beta - \phi} + \frac{d}{1 - \phi} = 1 \quad . \quad . \quad . \quad (36)$$

This is an equation of the fourth degree giving four values of ϕ.

As before it can be shown that each of the terms in equation (32) is equal to $\frac{\phi}{m}$.

Then $\lambda_4 = \frac{\phi}{\delta} - 1$; $\frac{\lambda_4}{\lambda_1} = \frac{\phi}{\gamma} - 1$; $\frac{\lambda_4}{\lambda_2} = \frac{\phi}{\beta} - 1$; $\frac{\lambda_4}{\lambda_3} = \phi - 1$.

These values of λ_1, λ_2, λ_3, λ_4 will be seen to satisfy equation (33).

Equation (31) becomes

$$\frac{\delta w_0}{\delta - \phi} + \frac{\gamma x_0}{\gamma - \phi} + \frac{\beta y_0}{\beta - \phi} + \frac{z_0}{1 - \phi} = \frac{\frac{\phi}{m}\left\{\frac{\delta w_1}{\delta - \phi} + \frac{\gamma x_1}{\gamma - \phi} + \frac{\beta y_1}{\beta - \phi} + \frac{z_1}{1 - \phi}\right\}}{\delta w_1 + \gamma x_1 + \beta y_1 + z_1} \quad . \quad . \quad (37)$$

There are four of these equations corresponding to the four values of ϕ. From them can be derived four equations similar to equations (20*a*), (20*b*), (20*c*) and they are equivalent to three independent equations. The fourth equation required is $w + x + y + z = 1$, and the final solution involves the solution of four linear simultaneous equations.

The general procedure can obviously be applied similarly to mixtures of more than four components.