

IMPROVED ACCURACY OF C.F.R. MOTOR METHOD TEST FOR HIGH OCTANE RATING; WITH CONTINUOUS SCALE FROM 40 TO 120 O.N.

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INTRODUCTION.

THE desirability of an uninterrupted scale of octane numbers from the lowest to the highest anti-knock values in current use has always been evident, and it was in order to fill this need that the "17° Motor Method" was introduced and standardized by the Institute of Petroleum in 1941.¹ This method has been in use in the United Kingdom up to the present time in conjunction with the C.F.R. Motor Method, employing a carefully set bouncing-pin for determining standard knock intensity.

About two years ago the A.S.T.M. approved the following somewhat drastic alterations to the Motor Method.

- (a) Removal of the carburettor throttle plate.
- (b) Use of "Guide Tables for Micrometer setting (compression ratio) for Standard Knock Intensity."

The fact that these modifications rendered the 17° method extension of the octane scale non-linear, prompted the work described in this report. Now that the Institute of Petroleum Motor Method has been brought into line with the A.S.T.M. regarding (a) and (b) above, the work will be of general interest.

SUMMARY.

1. Ratings were obtained on twenty-one engines on two Institute of Petroleum monthly correlation samples by the old and the new A.S.T.M. Motor Method. The results indicated no appreciable change in ratings, but there was a reduction in "spread" of half an octane number by the new method.

2. A brief examination of the 17° Motor Method without the throttle plate led to the finding that there was a break in continuity of test conditions at 100 O.N. The Guide Tables for micrometer setting for standard knock intensity below 100 O.N. could not be extrapolated to cover ratings in the higher octane range because excessively high compression ratios and knock intensity would be encountered.

3. An investigation has been made on the relationship of octane number to compression ratio at standard knock intensity with various ignition settings.

It was established that the A.S.T.M. ignition setting at high compression ratios creates unstable conditions of engine operation, with the result that slight fluctuations in spark timing have a very marked effect on the knock intensity. This condition probably accounts for much of the rough-running and difficulty of octane rating which are experienced on fuels of

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100 O.N. and over. This can be overcome by setting the spark for maximum knock, as this allows a considerably lower compression to be used with standard knock intensity. A smooth curve then relates octane number and compression ratio from 40 to 120 O.N., and a separate method above 100 O.N. is not necessary.

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

DETAILS OF TEST.

In the absence of data from America to show the effect of the changes in the A.S.T.M. Motor Method on the rating of fuels, members of the I.P. monthly correlation scheme agreed to test the two samples for November 1942 by the existing and the modified A.S.T.M. Motor Method, so that a comparison of ratings could be made. A summary of the results obtained from tests on twenty-one engines is as follows :—

| No. of C.F.R. engines 21. | Sample No. 67. | | Sample No. 68. | |
|-----------------------------|----------------------|-------------------------|----------------------|-------------------------|
| | With throttle plate. | Without throttle plate. | With throttle plate. | Without throttle plate. |
| Average O.N. | 78.2 | 78.2 | 99.5 | 99.6 |
| Spread O.N. | 2.3 | 1.8 | 2.1 | 1.7 |
| Average deviation | 0.55 | 0.47 | 0.42 | 0.37 |

When the A.S.T.M. Guide Table² figures of octane number and compression ratio for standard knock intensity are plotted, a curve is obtained (Fig. 1) which is very flat in the high-octane range and extrapolation above 100 O.N. suggests impossibly high compression ratios for fuels up to 120 O.N. A study of the data on the development work of the 17° Method (*i.e.* with the throttle plate) indicated that lower compression ratios should be employed for standard knock intensity.

Preliminary tests without the throttle plate on one engine confirmed that there was a decided kink in the curve at 100 O.N. when extrapolating it to cover the 17° Method. A fixed setting of 19° advance above 90 O.N. showed an improvement in the shape of the curve. This is shown graphically in Fig 1, and it will be observed that changing the ignition advance from 17° to 19° at 100 O.N. alters the compression ratio requirement for standard knock intensity from 8.5 to 8.07 : 1.

In order to obtain some further data on the effect of spark-timing, some investigational work was carried out on three engines, one of which was arranged for power output readings, to determine :—

(a) The ignition setting for *maximum knock* at maximum knock mixture strength and standard knock intensity on fuels ranging from 40 to 120 O.N.

(b) The ignition setting for *maximum power* at maximum knock mixture strength at various compression ratios from 4.5 to 1 up to the highest ratio possible without detonation.

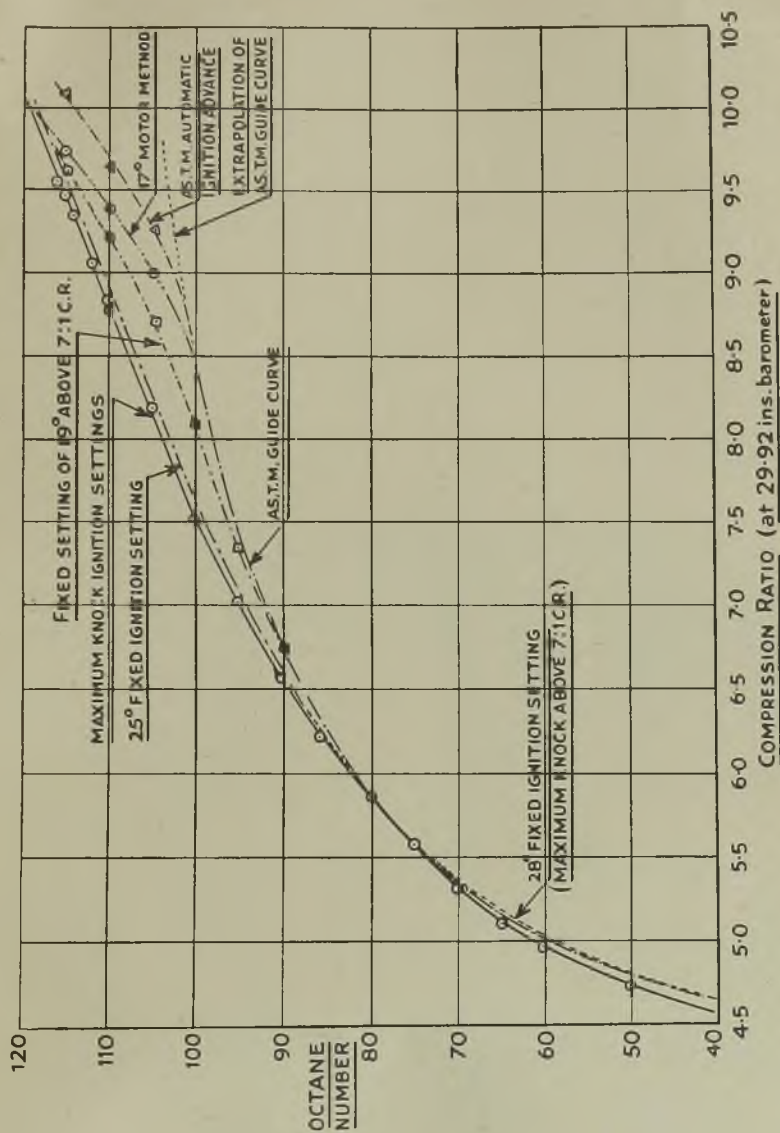


FIG. 1.

C.F.R. MOTOR METHOD (WITHOUT THROTTLE PLATE), COMPRESSION RATIO-OCTANE NUMBER GUIDE CURVES FOR STANDARD KNOCK INTENSITY AT VARIOUS IGNITION SETTINGS.

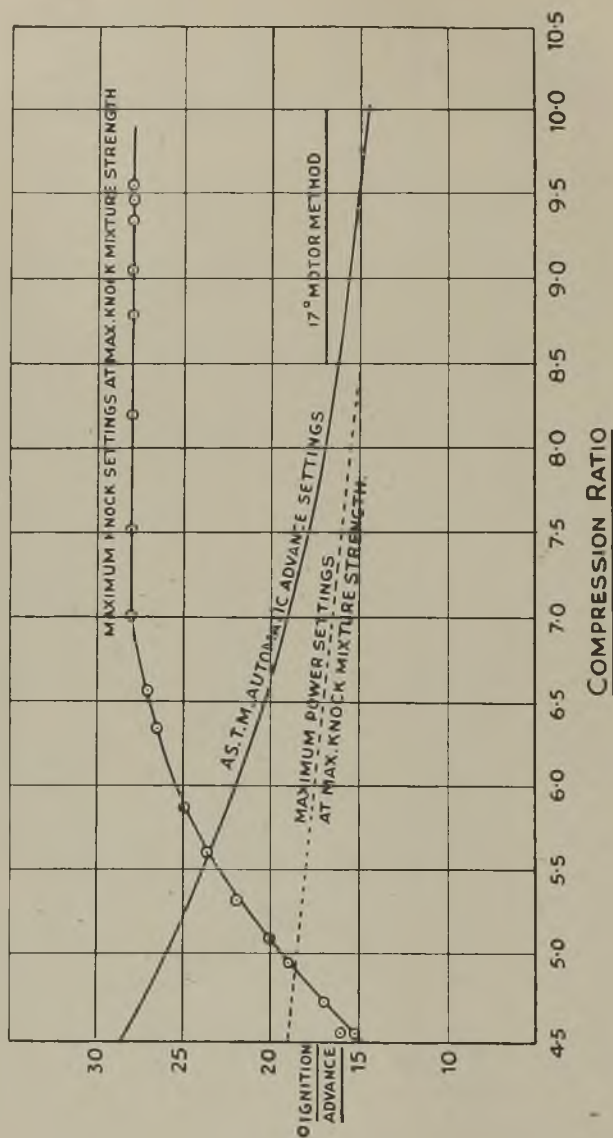


Fig. 2.

C.F.R. MOTOR METHOD (WITHOUT THROTTLE PLATE). COMPRESSION RATIO-IGNITION ADVANCE FOR A.S.T.M. MAXIMUM KNOCK AND MAXIMUM POWER.

The standard knock intensity was obtained throughout the tests by setting the compression ratio for the O.N. of the fuel according to the A.S.T.M. Guide Table and obtaining a mid-scale knock-meter reading. When alterations in the spark advance changed the knock-meter reading, the compression ratio was adjusted to re-establish a midscale reading. On high-octane fuels advance of spark-timing from A.S.T.M. towards the maximum knock point caused heavy detonation, which was beyond the recording limit of the knock-meter.

The results of the work on (a) and (b) are shown graphically in Fig. 2, and it will be noticed that there is a very wide discrepancy not only between the maximum knock and the maximum power ignition settings, but also between these settings and the Motor Method ignition timing. In the high-octane range the standard and the maximum-power ignition settings are similar, and it is here that the operation of the engine is decidedly unsteady. This is very apparent when using a dynamometer unit, but it is partly obscured on a synchronous motor unit.

In order to check the effect of using maximum knock ignition setting, four sensitive types of fuel were tested on one engine using this setting, and the ratings were similar to those obtained by the latest A.S.T.M. Motor Method.

TABLE I.

Micrometer Setting for Standard Knock Intensity for Barometric Pressure of 29.92 in. of Mercury and $\frac{1}{2}$ in. Venturi.

Micrometer settings up to 70 O.N. as for A.S.T.M. Motor Method.

| 25° Motor method octane number. | Micrometer setting, in. | 25° Motor method octane number. | Micrometer setting, in. | 25° Motor method octane number. | Micrometer setting, in. |
|---------------------------------|-------------------------|---------------------------------|-------------------------|---------------------------------|-------------------------|
| 70 | 0.533 | 90 | 0.303 | 110 | 0.068 |
| 71 | 0.523 | 91 | 0.290 | 111 | 0.059 |
| 72 | 0.513 | 92 | 0.277 | 112 | 0.051 |
| 73 | 0.503 | 93 | 0.264 | 113 | 0.043 |
| 74 | 0.492 | 94 | 0.251 | 114 | 0.034 |
| 75 | 0.482 | 95 | 0.238 | 115 | 0.026 |
| 76 | 0.471 | 96 | 0.226 | 116 | 0.018 |
| 77 | 0.460 | 97 | 0.214 | 117 | 0.011 |
| 78 | 0.449 | 98 | 0.201 | 118 | 0.004 |
| 79 | 0.436 | 99 | 0.189 | 119 | -0.003 |
| 80 | 0.424 | 100 | 0.177 | 120 | -0.010 |
| 81 | 0.412 | 101 | 0.165 | | |
| 82 | 0.400 | 102 | 0.154 | | |
| 83 | 0.388 | 103 | 0.143 | | |
| 84 | 0.376 | 104 | 0.132 | | |
| 85 | 0.364 | 105 | 0.121 | | |
| 86 | 0.352 | 106 | 0.110 | | |
| 87 | 0.340 | 107 | 0.099 | | |
| 88 | 0.328 | 108 | 0.088 | | |
| 89 | 0.316 | 109 | 0.078 | | |

Barometric correction. For each 0.1 in. mercury add or subtract 0.003 in. to the micrometer setting. Add for high barometer, subtract for low barometer. As for A.S.T.M. Motor Method.

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.

- ¹ Knock-Rating of Fuels over 100 O.N.—the 17° Motor Method. The Institute of Petroleum. *Standard Methods for Testing Petroleum and its Products*, fourth edition, 1942, I.P. 43/42(T), p. 158.
- ² A.S.T.M. *Standards on Petroleum Products and Lubricants*, October 1942. Knock characteristics of Motor Fuels, D.357-42(T).

FRACTIONAL DISTILLATION OF TERNARY MIXTURES. PART I.

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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.

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

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

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

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

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

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

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

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

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

Let $m(\gamma h + \beta k + l) = \phi \dots \dots \dots (7a)$

so that $\frac{1}{\phi} = \frac{mh + b}{\gamma m h} = \frac{mk + c}{\beta m k} = \frac{ml + d}{ml} \dots \dots \dots (8)$

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

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

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

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

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),

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

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

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

and that $b + \lambda_1 c + \lambda_2 d + \lambda_3 = 0 \dots \dots \dots (14)$

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

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

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 $\frac{\gamma(1 + \lambda_3)}{m} = \gamma h + \beta k + l = \frac{\phi}{m}$ from equation (7a). Each of the

three terms in equation (13) is therefore equal to $\frac{\phi}{m}$ and, solving for λ_1, λ_2 and λ_3 ,

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

These values of $\lambda_1, \lambda_2, \lambda_3$ also satisfy equation (14) for

$$\begin{aligned} b + \lambda_1 c + \lambda_2 d + \lambda_3 &= b + c \cdot \frac{\frac{\phi}{\beta} - 1}{\frac{\phi}{\beta} - 1} + d \cdot \frac{\frac{\phi}{\beta} - 1}{\frac{\phi}{\beta} - 1} + \frac{\phi}{\gamma} - 1 \\ &= \left(1 - \frac{\phi}{\gamma}\right) \left\{ \frac{b\gamma}{\gamma - \phi} + \frac{c\beta}{\beta - \phi} + \frac{d}{1 - \phi} - 1 \right\} \\ &= 0 \text{ from equation (10)} \end{aligned}$$

Substituting the values of $\lambda_1, \lambda_2, \lambda_3$ in equation (15) gives

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

or

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

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,

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

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

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

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

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

Applying this relation to successive pairs of plates, there is readily obtained for the n th 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
$$x_D = \frac{b}{1-m}, y_D = \frac{c}{1-m}, z_D = \frac{d}{1-m}$$

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 n th plate from the top of a rectifying column or the n th 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

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

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

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

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

$$\begin{aligned} \text{when } \phi = 0, E &= \beta\gamma(b + c + d - 1) = -m\beta\gamma, \text{ i.e. negative,} \\ \phi = 1, E &= d\beta\gamma, \text{ i.e. positive,} \\ \phi = \beta, E &= -c\beta(\beta - 1)(\gamma - \beta), \text{ i.e. negative,} \\ \phi = \gamma, E &= b\gamma(\gamma - \beta)(\gamma - 1), \text{ i.e. positive.} \end{aligned}$$

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,

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

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

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

If we now assume as approximate solutions,

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

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,

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

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

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

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

Using the indeterminate multipliers $\lambda_1, \lambda_2, \lambda_3, \lambda_4$, 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 $\lambda_1, \lambda_2, \lambda_3, \lambda_4$ so that

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

and

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

ϕ is now defined by the equations

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

where g is the corresponding value for component w and

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

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

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

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 $\frac{\phi}{m}$.

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

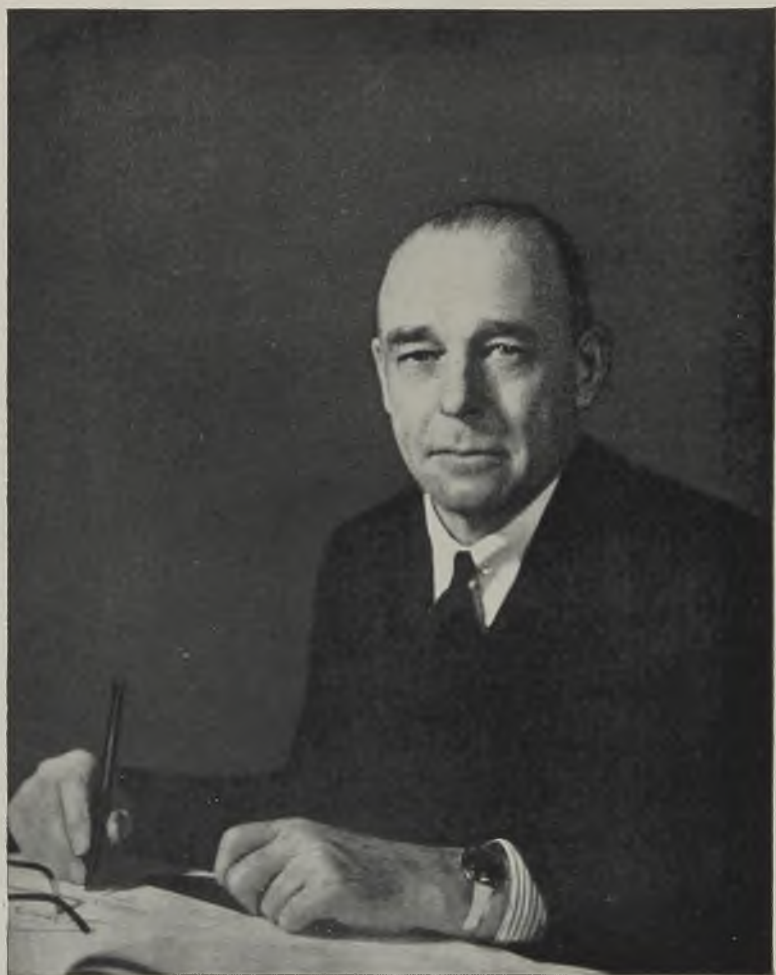
These values of $\lambda_1, \lambda_2, \lambda_3, \lambda_4$ will be seen to satisfy equation (33).

Equation (31) becomes

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

There are four of these equations corresponding to the four values of ϕ . From them can be derived four equations similar to equations (20a), (20b), (20c) 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.



ALEXANDER DUCKHAM,
1877-1945.

OBITUARY.

ALEXANDER DUCKHAM.

IT is with great regret that we have to record the death of Mr. Alexander Duckham, which occurred on February 1st, in a London nursing home, following an operation.

Although not a Founder Member, Duckham was one of the oldest members of the (then) Institution of Petroleum Technologists, having joined at its inception in 1914. He gave many years of useful service to the Institution as a Member of Council (1919-1934) and as a Vice-President (1925-1934), and his passing will be felt keenly by all the older members who were associated with him in those vital early days of the Institution.

More particularly is the Institute indebted to Duckham's foresight in having first suggested that the work of Standardization of Tests should be undertaken. In 1917, at the Twenty-fourth General Meeting, the then President, Mr. Charles Greenway (later Lord Greenway) read a letter from Duckham in which he said :—

“ My suggestion is that the Institution should appoint a Standardization Committee, whose reference should be to investigate methods of testing and to recommend Standards for adoption in this country.”

The first meeting of the Standardization Committee was held on 17th June, 1921, and a few months later Mr. Duckham was elected Chairman (in succession to Mr. James Kewley, who had resigned), and with his accustomed energy he presided over the many meetings of the Committee preparatory to the publication of the first Report on the Standardization of Tests. In 1925 he had to resign the Chairmanship owing to illness following an operation. All the members of this first Committee and its several Panels will remember the wholehearted support the work received from Mr. Duckham.

During the first World War he was busily engaged with the Ministry of Munitions, being successively Director of Small Arms Supply, Controller of National Aircraft Factories, and of American Aircraft Assembly in this country, in much of the work being closely associated with a Past President of the Institution, the late Sir Frederick Black.

From the beginning of aviation Duckham took the keenest interest in the new venture, and this led to an intimate friendship with Bleriot. He provided a memorial stone near Dover Castle to mark the spot where Bleriot landed after the first successful Channel flight. This interest was maintained throughout his life in his activities on behalf of the R.A.F. Benevolent Fund, to which he was a generous contributor, and moreover was the means of collecting considerable sums. In addition to financial support, Duckham gave his house, Vanbrugh Castle, Blackheath, as a home for R.A.F. orphan boys and, later, his charming residence, Rooks Hill, near Sevenoaks, with a generous endowment towards upkeep.

Alexander Duckham was born on March 11th, 1877, the son of Frederick Duckham, Manager and Engineer of the Millwall Dock Company. His younger brother, Sir Arthur Duckham, was well-known as a prominent figure in the gas industry. Alexander was educated at the old Blackheath School, and after matriculating studied under Ramsay at University College, where he won the Goldsmiths Scholarship, the Exhibition of the Clothworkers Company, and the Senior Gold Medal. His start in a career was largely influenced by his godfather, Alfred Yarrow (later Sir Alfred), the well-known shipbuilder, who, appreciating the coming importance of oil, especially as a naval fuel, suggested to Duckham that here he might find a practical application of his chemical knowledge, and in 1899, working almost single-handed, he laid the foundation of the well-known firm bearing his name.

A few years later he became interested in the important question of oil supplies from within the Empire, an interest stimulated by the clearly forthcoming change to oil as the naval fuel, and in 1905 he founded Trinidad Central Oilfields, Ltd., of which he was Chairman and Managing Director.

Initiative, an exceptional ability to grasp new ideas, with energy and "drive" to put them into practice and obtain the co-operation of his staff in carrying them to a successful issue were the outstanding characteristics of Alexander Duckham. Nor must his generosity be forgotten. As Viscount Trenchard wrote :—

"You do wonderful work, and I must say you are the most generous man I know to the R.A.F. Benevolent Fund."

A Memorial Service was held on 12th February at St. Michael's, Cornhill, when a large number of friends, representatives of the R.A.F. Benevolent Fund (including Lord Trenchard), and employees of the firm, paid a last tribute to Alexander Duckham, the Institute being represented by the Secretary, Mr. F. H. Coe.

J. S. S. B.