THE THEORY AND PRACTICE OF TESTING STILLS

By A. J. V. UNDERWOOD, D.Sc. (Member).

THE testing of any kind of chemical plant is undertaken to obtain certain information concerning its performance. The nature of the information sought, and the methods employed to obtain it, depend on the purpose for which the test is undertaken. The general considerations governing any test are, therefore, the reason for undertaking it, the object aimed at in carrying it out, and the method to be employed to achieve that object.

One reason for undertaking a test is to ascertain whether certain guarantees, specified in the contract for the purchase of the plant, have been fulfilled. Another is to determine the performance of a plant in order to be able to judge whether it is capable of improvement, or how its performance compares with that of another plant performing the same function, or with that of the same plant at a previous date. The latter may be desirable in the case of a still used for corrosive liquids where the efficiency may be seriously affected by corrosion of the bubbler caps. Other important reasons for undertaking a test are the development of a new or modified design of plant and the determination of optimum operating conditions or performance of a plant for the treatment of a new product.

The object of the test, that is the nature of the information to be sought, will depend on which of the above types of test is under consideration. In the first or simplest case, in which it is desired to ascertain if certain guarantees have been fulfilled, the object will clearly have been achieved when the performance data, stated in the guarantee, have been determined. For a still these data might comprise capacity, quality of product and effluent, and consumption of heat, power and cooling water. When determined they are compared with the guarantees to decide whether the latter have been fulfilled. In such a case the plant is only regarded as an instrument for carrying out a certain operation, and no inquiry is made into why or how it does it. What is really under test is the ability or honesty of the suppliers of the plant.

In the other tests mentioned previously, information of a more fundamental nature is required. To compare the performance of plants operating under different conditions it is necessary to have some standard, usually derived by considering a theoretically perfect plant, to which the performance of any plant can be referred. The utility of such a theoretical standard lies in the fact that it affords not only a general method of comparison, but also a means of predicting performance under conditions different from those prevailing when the test is made. For instance, it may be desired to ascertain whether a still concentrating 10% alcohol to 90% could be used to concentrate 5% alcohol to 92%, or to produce 99% benzene from a mixture of 40% benzene and 60% toluene. If the plant is in commercial production under the existing conditions, it is obviously advantageous if the information required can be obtained from a test under these conditions without adopting the more direct and obvious method of altering the plant to run under the new conditions in order to determine whether it works or not.

A simple example of the use of such a theoretical standard would be a reciprocating pump which has just been installed to pump water to a given height. The simplest form of test consists in determining the quantity of water pumped per hour and the power consumed, which can then be compared with the guaranteed figures. This information is of limited utility. If, however, we consider a theoretically perfect pump, and calculate the power required under these conditions, we know the mechanical efficiency of the pump and can thus compare its performance with that of other pumps working under different conditions. It also becomes possible to foretell the power consumption of this pump if it were required to work under different conditions. From the speed of the pump and the displacement of the piston the theoretical quantity of water which would be pumped per hour can be calculated. By reference to this theoretical standard, it is possible to determine the volumetric efficiency, and so calculate the size of pump, of a similar type, which would be required for pumping a different quantity of water per hour.

In this case, two theoretical standards of reference were available from which an " energy efficiency " and a " capacity efficiency " could be derived, but this is not always so. Sometimes only one standard is available, and sometimes there is none. In a boiler test, for example, the thermal efficiency can be found, but there is no theoretical standard of reference for a capacity efficiency, as such quantities as heating surface and grate area cannot be calculated for an ideal boiler. For a filter-press neither standard is available, as there is no method of calculating from fundamental principles the amount of filtering surface or the power requirements of an ideal filter-press. In such cases one is limited to comparing empirical results.

Fractional distillation in a plate column consists in effecting a certain degree of separation between different components of the initial mixture by expending a certain amount of thermal energy. It is carried out in a definite number of stages, for on each plate there is interaction between liquid and vapour resulting in the transfer of heat and matter from one to the other. To be able to determine the relative efficacies of different columns it is necessary to know how the number of plates required in practice under certain conditions compares with the number required in an ideal column. To ascertain the effectiveness with which the heat supplied is utilised it is also necessary to know the heat requirements of an ideal column. The same considerations apply to a packed column which may be regarded as

operating with an infinite number of stages in each of which an infinitesimal change is effected. For distilling columns there are thus two theoretical standards of reference, though these are not independent. The methods of calculation for ideal columns must therefore be considered in detail in order to be able to interpret intelligently and utilise effectively any data obtained as the result of tests.

BINARY MIXTURES.

The simplest example of fractionation, that of binary mixtures, has naturally received most attention. Although mixtures in practice are usually more complex, the study of binary mixtures reveals a number of principles which are capable of application to the more general case. Among the principal contributors to the literature on the calculation of columns for binary mixtures are Sorel,[1] Hausbrand,[2] Leslie,[3] Lewis,[4] Bergström,[5] Mariller,[6] Ariis,[7] Van Nuys,[8] Gay,[9] Fouché,[10] Ponchon,[11] Savarit,[12] Rodebush,[13] Thormann,[14] McCabe and Thiele,[15] Robinson.[16] The methods of Sorel, Ponchon, and Savarit take into account variations in the heat content of the vapour and reflux due to the change in temperature from plate to plate and to the heat of mixing. In the other methods these are neglected. Those of Leslie and Lewis involve an integration based on the assumption that the change in composition from plate to plate is small and therefore the results obtained become more accurate as the number of plates increases and the actual conditions more nearly approach those assumed. Fouché, Ponchon, Savarit, Rodebush, and McCabe and Thiele employ essentially graphical methods to dispense with the labour of arithmetical calculation. A brief description of some of the above methods will facilitate a comparison of their relative utility.

Method of Sorel.[1]—A fractionating column is shown diagrammatically in Fig. 1. The following symbols are used :—

x, the mol fraction of the more volatile component in the liquid on any plate.

X, the mol fraction of the same component in the vapour given off by the liquid on any plate.

P, the mols of product per unit time.

F, the mols of feed per unit time.

W, the mols of effluent per unit time.

V, the mols of vapour per unit time.

O, the mols of reflux per unit time.

$R = \dfrac{O}{P}$ the reflux ratio.

h, the total heat of 1 mol of liquid.

H, the total heat of 1 mol of vapour.

Q, the heat absorbed in the condenser per unit time.

The position of a plate, counting from the top, in the concentrating column is denoted by the suffix n. The position of a plate, counting from the bottom, in the exhausting column is denoted by the suffix m, The suffixes p, f, and w, refer to the distillate, feed and effluent respectively. For the exhausting column, the symbols are $\overline{X}$, $\overline{O}$, $\overline{x}$, etc.

For the concentrating column, by taking balances of total material, volatile component and heat above a section between the nth and $(n+1)^{th}$ plates, the following equations are obtained :—

$$V_{n+1} = O_n + P \quad \dotfill (1)$$

$$V_{n+1} X_{n+1} = O_n x_n + P x_p \quad \dotfill (2)$$

$$V_{n+1} H_{n+1} = O_n h_n + P H_p + Q \quad \dotfill (3)$$

Putting $PH_p + Q = PQ^1$ and eliminating V_{n+1} and O_n from the above equations we obtain

$$\frac{X_{n+1} - x_n}{x_p - X_{n+1}} = \frac{H_{n+1} - h_n}{Q^1 - H_{n+1}}$$

which can also be written

$$\frac{x_p - x_n}{Q^1 - h_n} = \frac{x_p - X_{n+1}}{Q^1 - H_{n+1}} \quad \dotfill (4)$$

If x_n and consequently h_n is known, X_{n+1} can be calculated as H_{n+1} is a function of X_{n+1}. Knowing the composition of the vapour rising from the $(n+1)^{th}$
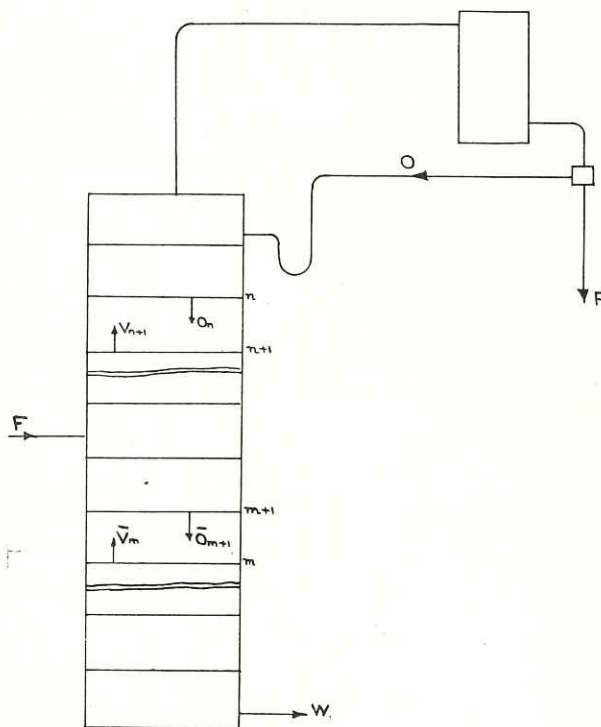

FIG. 1.

plate, and assuming the vapour and liquid to be in equilibrium the composition of the liquid on that plate can be found from the equilibrium data for the mixture. Working downwards from the top of the column the composition of the liquid on each plate can be determined. A similar equation to (4) can be obtained for the exhausting column and similar calculations made.

The minimum reflux required to effect separation at any concentration is found by assuming no change in the composition between two adjacent plates so that equation (4) becomes

$$\frac{x_p - x_n}{Q^1 - h_n} = \frac{x_p - X_n}{Q^1 - H_n} \quad \dotfill (5)$$

H

Method of Savarit.[12]—The method used by Sorel obviously involves lengthy calculations. Equation (4) represents the condition that the three points, the co-ordinates of which are (x_p, Q^1), (x_n, h_n) and (X_{n+1}, H_{n+1}) lie on a straight line. Further h_n is a function of x_n so that a curve can be drawn from this relation for all values of x and the point (x_n, h_n) must lie on this curve. Similarly H_{n+1} is a function of X_{n+1} and a second curve can be drawn on which the point (X_{n+1}, H_{n+1}) must lie. A straight line joining the point (x_p, Q^1) to a point on the (x, h) curve, the abscissa of which is x_n will thus intersect the (X, H) curve at a point the abscissa of which is X_{n+1}, thus giving a simple graphical solution of equation (4). This method originally suggested by Ponchon[11] was greatly simplified and extensively applied to the distillation of alcohol-water mixtures by Savarit.[12] The method applied to a concentrating column is illustrated in Fig. 2. The co-ordinates of A are
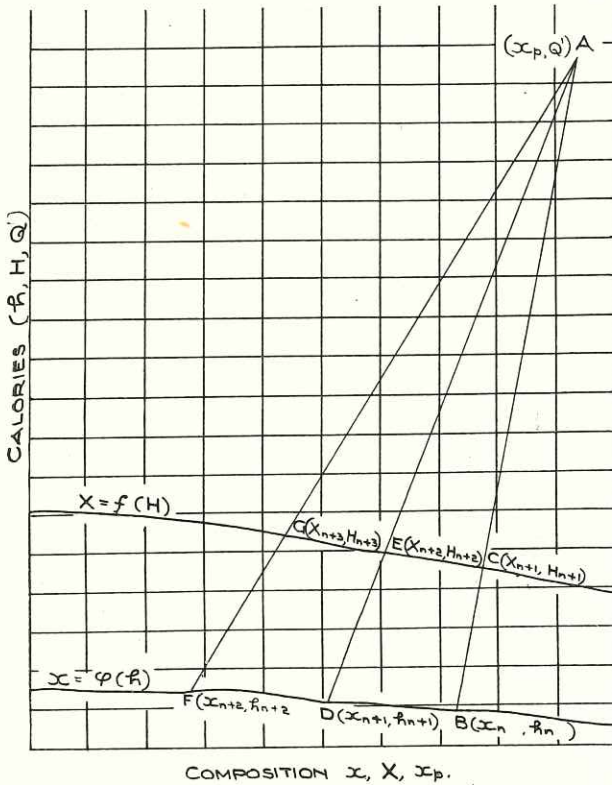

FIG. 2.

(x_p, Q^1) and the curves C E G and B D F represent relations $X = f(H)$ and $x = \phi(h)$ respectively. Joining A to B, the abscissa of which is x_n, gives a line which intersects the curve $X = f(H)$ at C the abscissa of which is X_{n+1}, given by equation (4). D represents the composition x_{n+1} of the liquid, in equilibrium with vapour of the composition X_{n+1}, found from the equilibrium relation. Joining D to A determines E on the curve $X = f(H)$ which gives the value of X_{n+2}. F represents the liquid composition x_{n+2}. and the line A F determines G which gives the value of x_{n+3}. In this way the composition of the liquid

on each plate and the number of plates required to effect a given concentration can be determined.

Both Sorel and Savarit used weight units, but molal units, which do not affect the principles, have been used above to preserve uniformity throughout this paper.

Constant Molal Reflux.—Assuming that Trouton's rule applies to the two components, and neglecting variations in the sensible heat of the liquids due to changes in temperature and composition on the different plates, then H_{n+1} can be taken as equal to H_p and equation (3) may be written :—

$$Q = (V_{n+1} - P)\, H_{n+1} - O_n h_n,$$

or substituting for V_{n+1} from equation (1) :—

$$Q = O_n\, (H_{n+1} - h_n) \ldots\ldots\ldots\ldots (6).$$

The term $(H_{n+1} - h_n)$ represents the difference between total heat of vapour and sensible heat of liquid, and is assumed equal to the constant heat of vaporisation L.

Thus $Q = O_n L$ and the reflux is constant at all points in the column. This reflux will only be equal in amount to the liquid returned from the reflux condenser to the top plate of the column if that liquid leaves the reflux condenser at its boiling point. If it is cooled below its boiling point in the reflux condenser, some condensation of vapour on the top plate will take place, to raise it to its boiling point. The molal reflux throughout the column will then be equal to that from the top plate, if losses by radiation from the surface of the column are neglected.

On these assumptions, equation (4) can be simplified as follows. Omitting the suffixes of H_{n+1}, h_n and O_n, since these are assumed constant throughout the column, then from equation (6) :—

$$Q^1 = H + \frac{Q}{P} = H + \frac{O}{P}\,(H - h)$$

$$\text{or} \quad Q^1 - h = \frac{(O+P)}{P}\,(H - h)$$

$$\text{and} \quad Q^1 - H = \frac{O}{P}\,(H - h)$$

Equation (4), $\dfrac{x_p - x_n}{Q^1 - h_n} = \dfrac{x_p - X_{n+1}}{Q^1 - H_{n+1}}$

reduces to $\dfrac{x_p - x_n}{O + P} = \dfrac{x_p - X_{n+1}}{O} \ldots\ldots\ldots\ldots (7)$

which can be derived from equations (1) and (2).

The utility of this form as a basis for a nomographic method will be shown later. Substituting $O = RP$ where R is the reflux ratio it takes the form :—

$$\frac{x_p - x_n}{R + 1} = \frac{x_p - X_{n+1}}{R} \ldots\ldots\ldots\ldots (8)$$

Method of Hausbrand.[2]—Using the equations :—

$$V_{n+1} = O_n + P \quad \text{and} \quad V_{n+1} X_{n+1} = O_n x_n + P x_p,$$

and assuming, as above, that the heat contained in the reflux is the same at all points in the column, the value of X_{n+1} corresponding to any given value of x_n is readily calculated. From this value of X_{n+1} the corresponding value of x_{n+1} is found from equilibrium data, and the calculation made through-

out the column, starting from the top. Although making this assumption regarding heat in the reflux, Hausbrand's method of calculation is unnecessarily laborious owing to the use of weight units instead of molal units, thus rendering it necessary to calculate the weight of reflux and vapour for every plate, whereas with molal units these calculations are eliminated.

Method of McCabe and Thiele.[15]—For a concentrating column, equations (1) and (2), together with the relation $O = RP$ and the assumption of constant molal reflux give :—

$$(R+1) X_{n+1} = Rx_n + x_p \dots\dots\dots\dots\dots (9)$$

This gives a linear relation between X_{n+1} and x_n, and by drawing the equilibrium curve on the same diagram as this " operating line," the value of x_{n+1}, corresponding to X_{n+1}, is found graphically by drawing a line through the point (x_n, X_{n+1}), parallel to the x axis, to meet the equilibrium curve at the point (x_{n+1}, X_{n+1}). The intersection of a line through this point parallel to the X axis with the operating line determines the point $(x_{n+1}\ X_{n+2})$, and by repetition of this construction, shown in Fig. 3, the number of plates required for a given separation, and the composition on each plate, is readily determined. From equation (9) it is seen that the operating line intersects the line $X = x$ at the point (x_p, x_p). Assuming no fractionation in the condenser, the composition of the vapour leaving the top plate is equal to x_p, and this point, D, in Fig. 3, forms the starting point for the graphical construction.

A similar method is used for the exhausting column. Considering the part of the column below a section between the mth and $(m+1)^{th}$ plates :—

$$\bar{O} = \bar{V} + W \dots\dots\dots\dots\dots\dots (10)$$

$$\bar{O}\bar{x}_{m+1} = V\bar{X}_m + Wx_w \dots\dots\dots\dots (11)$$

If the feed does not enter the column at its boiling-point then :—

$$\bar{O} = O + qF \dots\dots\dots\dots\dots\dots (12)$$

where q is the total heat required to vaporise 1 mol of feed divided by the molal heat of vaporisation.

The above equations lead to the relation :—

$$(O+qF)\bar{x}_{m+1} = (O+qF-W)\bar{X}_m + Wx_w \dots (13)$$

or $(RP+qF)\bar{x}_{m+1} = (RP+qF-W)\bar{X}_m + Wx_w \dots (14)$

which is the equation of the operating line for the exhausting column. The same step-wise graphical construction, shown in Fig. 3, can then be used for the exhausting column using this operating line. For a material balance over the whole column :—

$$F = P + W \dots\dots\dots\dots\dots\dots (15)$$

and $Fx_f = Px_p + Wx_w \dots\dots\dots\dots\dots (16)$

Using these equations to eliminate R and F from equations (9) and (14), the locus of the intersection of the operating lines for the concentrating and exhausting columns for different reflux ratios is found to be :—

$$qx - (q-1) X = x_f \dots\dots\dots\dots (17)$$

This locus, of the point C (Fig. 3), is therefore a straight line which intersects the diagonal line

$X = x$ at the point (x_f, x_f) and has a slope equal to $\frac{q}{q-1}$. When the feed is at boiling-point, $q = 1$ and the locus of intersection is the line $x = x_f$. When the feed consists of saturated vapour, $q = 0$ and the locus of intersection is the line $X = x_f$ parallel to the x axis.

The minimum reflux is found from the slope of that line through D, which makes the point C fall on the equilibrium curve or which makes the line DC tangent to the equilibrium curve where that curve has a change of curvature, as is the case for the alcohol-water curve.
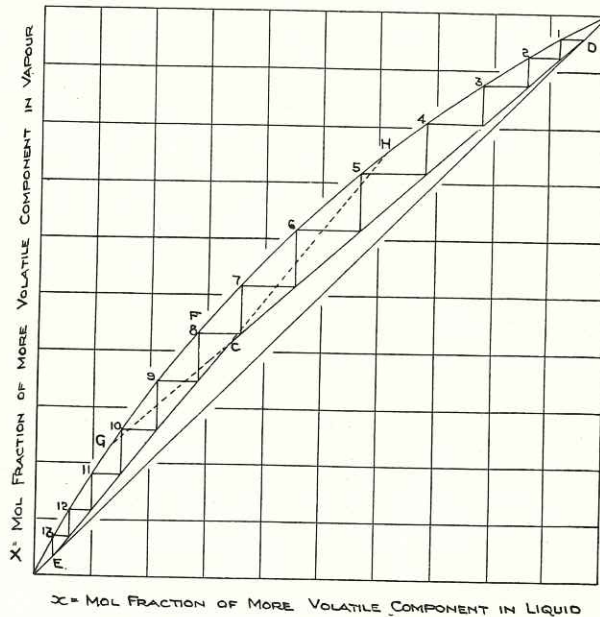
FIG. 3.

Method of Fouché.[10]—This method, originally proposed by Fouché but simplified by Thormann[14] through the introduction of molal units instead of weight units, is a graphical method, somewhat similar in principle to that of McCabe and Thiele, but using the boiling point and condensation curves instead of the equilibrium curve. Equation (9) for the concentrating column may be written in the form :—

$$X_{n+1} - x_n = \frac{x_p - x_n}{R+1} \dots\dots\dots\dots (18)$$

In Fig. 4, ATFB and AGDB are the boiling-point and condensation curves for a binary mixture. If, at any point T on the boiling-point curve, the horizontal line TV is drawn to meet the ordinate PC ($x = x_p$) at V, and the distance TV is divided by the point S so that $\frac{TS}{TV} = R+1$, then, from equation (18), the point S determines the value of X_{n+1} for the value of x_n represented by the point T. The locus of S for different values of x_n will provide an auxiliary curve, shown dotted in Fig. 4, which, as pointed out by Thormann, can also be constructed by projecting the horizontal distance QR between the

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operating line PQ and the line PR (X=x), as shown by the construction QRST, since $QR = X_{n+1} - x_n$. D (x=x_p) represents the composition of the vapour leaving the top plate of the column. From the method of construction of the auxiliary curve, the composition of the liquid on this plate is represented
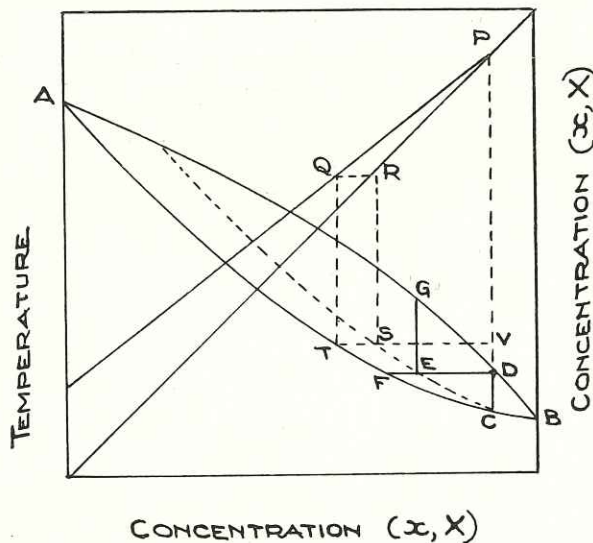

FIG. 4.

by F and the composition of the vapour below the first plate by E. The vertical line EG is drawn to intersect the condensation curve at G, and a horizontal line through G will intersect the boiling-point curve at a point representing the composition of the liquid
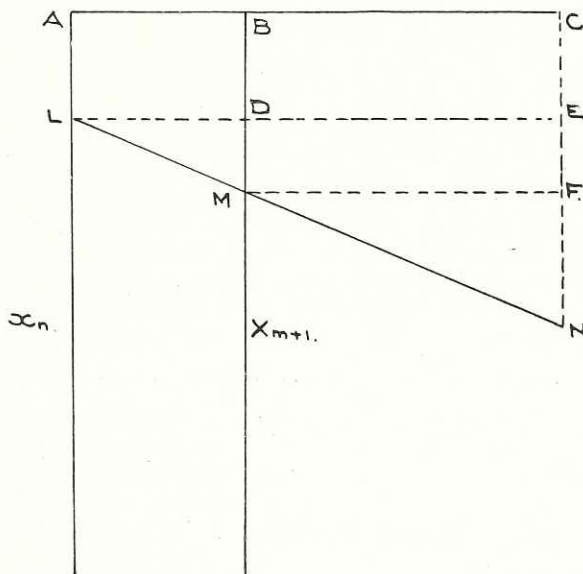

FIG. 5.

on the second plate, and the auxiliary curve at a point representing the vapour rising from the third plate. The construction is continued throughout the column. This method gives directly the temperature and composition on each plate of the column.

Nomographic Method.—If three parallel lines AL, BM and CN are drawn at right angles to the line ABC, Fig. 5, and any line LMN intersects them in L, M and N respectively, then

$$\frac{NE}{NF} = \frac{EL}{FM} = \frac{NC-AL}{NC-BM} = \frac{BC+AB}{BC}$$

If $NC = x_p$, $AL = x_n$, $BM = X_{n+1}$ and $\frac{BC}{AB} = R$, then

the above relation becomes

$$\frac{x_p - x_n}{x_p - X_{n+1}} = \frac{R+1}{R} \quad \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

which is the equation for the concentrating column. In this way the chart shown in Fig. 6 can be constructed. Any line such as LN, which joins the point representing the appropriate value of R and x_p to any given point on the x_n scale, intersects the X_{n+1} scale at the point M, which gives the value of X_{n+1} corresponding to the values of R, x_p and x_n chosen. The X_{n+1} scale can also be graduated with the corresponding values of x_{n+1}, that is to represent the equilibrium relation between liquid and vapour compositions so that the composition of the liquid on the $(n+1)^{th}$ plate is immediately read off. By repeating the process, using the value of x_{n+1} found on the left-hand scale, the corresponding value of x_{n+2} is found and this can be repeated throughout the concentrating column.

For the exhausting column, equation (14) gave

$$(RP+qF) x_{m+1} = (RP+qF-W) \bar{X}_m + W x_w$$

Putting $\frac{RP+qF-W}{W} = S$,

this becomes $(S+1) \bar{x}_{m+1} = S\bar{X}_m + x_w \quad \ldots\ldots\ldots(19)$

Comparison of this relation with equation (9) for the concentrating column, namely, $(R+1) X_{n+1} = Rx_n + x_p$, shows that the chart shown in Fig. 6 can be used for the exhausting column by substituting S for R, x_w for x_p and $\bar{X}_m$ for x_n. By graduating the left-hand scale also with the values of $\bar{x}_m$ corresponding to those of $\bar{X}_m$ the two scales can be used for reading off the composition from plate to plate as described for the concentrating column. Fig. 6 has the x_{n+1} and $\bar{x}_n$ scales graduated for alcohol-water mixtures, and is extremely simple to construct since, with the exception of the x_{n+1} and $\bar{x}_m$ scales, all the graduations are uniform so that ordinary squared paper can be used. These two scales can be drawn separately on tracing paper for any mixture under investigation and superimposed on the chart. The transversal lines, such as LMN, need not be drawn on the chart but a straight line scratched on a piece of celluloid can be used.

The method just described is somewhat similar in principle to that of Savarit, but the construction of the chart is simplified by the assumption of a constant molal reflux and the utilisation of it is made easier and more rapid by the method of carrying two sets of graduations on one scale.

The quantity S = $\left(\frac{RP+qF-W}{W}\right)$ introduced in

equation (19) is equal to $\frac{\overline{V}}{W}$ and may be termed the "revaporisation ratio." It represents the number of mols of vapour returned to the exhausting column by the kettle per mol of effluent withdrawn from it, and is thus exactly comparable with the reflux ratio R which represents the number of mols of

As uniformity is obviously desirable in the application of such a standard, it is necessary to consider which of the above methods is most suitable for the purpose. Although the methods described appear to differ substantially from each other, they fall into two groups. Each of the methods within one group will give the same result when applied to the same
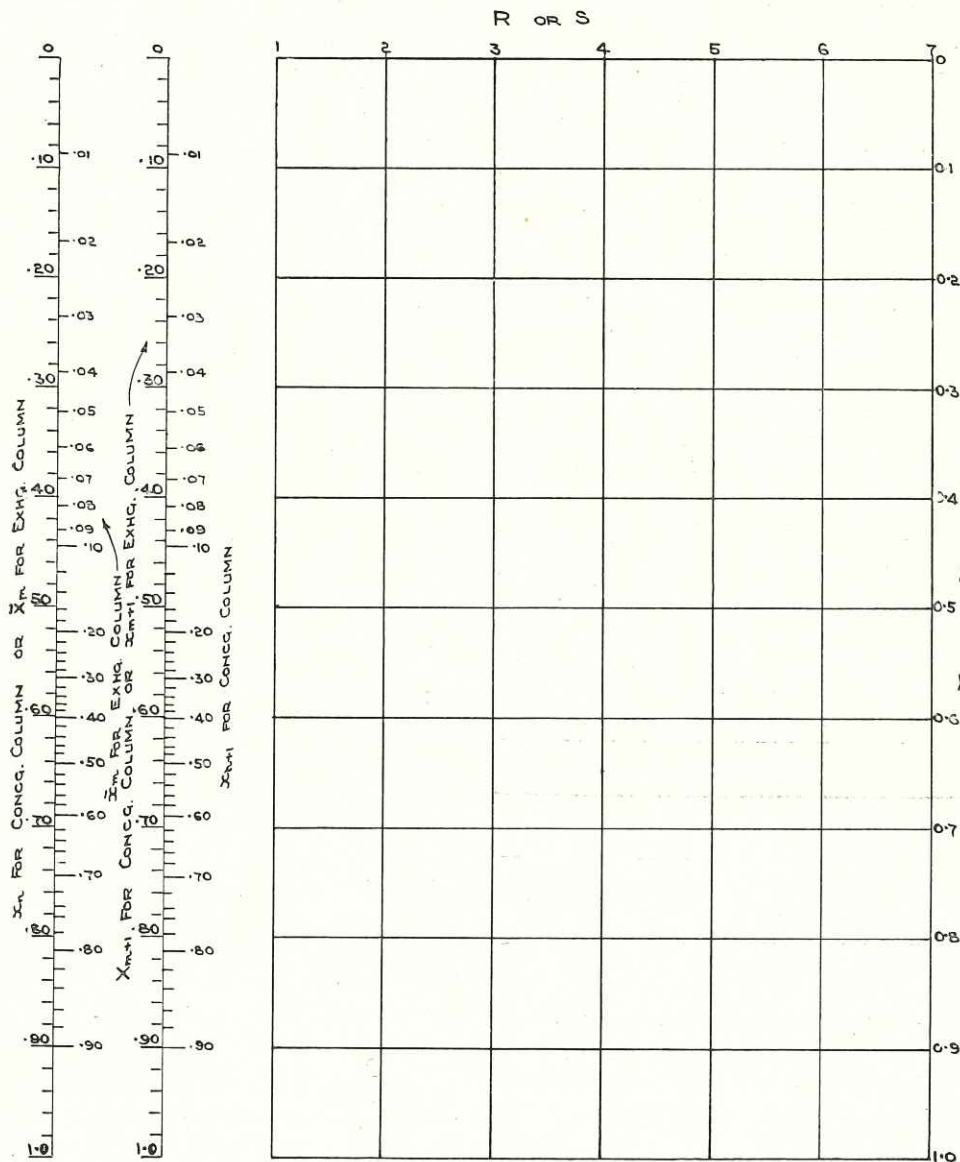

FIG. 6.

condensate returned to the concentrating column by the condenser per mol of distillate withdrawn from it.

Comparison of Methods of Calculation for Binary Mixtures.—The survey of the various methods proposed for the calculation of the number of plates and the minimum reflux required for a given separation in an ideal column indicates how these data can be obtained for use as a standard to which the performance of a column in practice can be referred.

data and differ only in ease of calculation. The methods of Sorel and Savarit take into account the variation in reflux through the column due to the changes in temperature on the plates, variations in latent heat and heat of mixing, whilst those of Hausbrand, McCabe and Thiele, Fouché and the nomographic method all assume constant molal reflux, and to this extent would appear to be somewhat less accurate. An important factor in the

choice of a standard is the ease with which it can be applied, as, however great its theoretical value may be, it loses much of its practical utility if its application is excessively laborious. Hence it was considered desirable to investigate the error involved by the assumption of constant molal reflux, which provides a very valuable simplification. The number of theoretical plates required to concentrate an alcohol-water mixture under different conditions was compared. A direct comparison of the results published by various authors was impossible owing to the variety of the data assumed for the liquid-vapour composition equilibrium for alcohol-water mixtures, and the different methods of stating the results. It was therefore decided to consider the differences in the results obtained, not only according as constant molal reflux was assumed or not but also using different physical data. Fig. 7 shows the equilibrium curves for alcohol-water mixtures, recalculated to a molal basis, given by Groening,[17] Sorel,[1] Bergstrom[5] and Lewis.[18] The differences between the curves are striking, and this uncertainty with regard to the physical data is the more remarkable in view of the age and importance of the alcohol industry and the fact that, until recent years, the theoretical study of distillation was practically confined to alcohol-water mixtures.

Table I. gives the number of theoretical plates for the concentration of an aqueous-alcohol solution of 10% strength by weight to 90%, 92% and 94·5% using different reflux ratios, and the equilibrium data given by Sorel, Bergstrom, Lewis and Groening.

TABLE I.

No. of Theoretical Plates Required to Concentrate 10% Alcohol (Figures Given to Nearest Whole Numbers).

Alcohol strength.	Reflux ratio.	Varying reflux.		Constant molal reflux.		
		Data of Sorel.	Data of Sorel.	Data of Bergstrom.	Data of Lewis.	Data of Groening.
90% wt.	∞	7	7	6	5	4
	2·5	14	14	9	7	5
92·5	∞	9	10	8	7	—
	6	15	15	11	9	—
	2·5	33	36	19	13	—
94·5	∞	16	18	15	13	—
	6	43	39	24	21	—

The differences in the results for varying and constant molal reflux, calculated from Sorel's data, are in all cases less than the differences occurring when the number of plates is calculated for constant molal reflux, but using different equilibrium data. The differences between the third and fourth columns of Table I. only becomes appreciable when the number of plates is large and the errors resulting from the use of graphical methods are then considerably greater. The error, therefore, involved by the assumption of constant molal reflux, does not seem to be of sufficient magnitude to make it worth while using the more laborious method which takes into account variations in the reflux through the column, except in special cases where the temperature difference between the top and bottom of the column is large. In any case the necessary thermal data are only available in

a few cases, so that the variation in reflux through the column cannot be calculated. Even for alcohol-water mixtures, as pointed out by Mariller,[6] the data relating to specific heat are based entirely on seven determinations by Jamin and Amaury,[19] and a considerable degree of interpolation is necessary. Quite recently Carey and Lewis [20] have published some new determinations of the liquid-vapour equilibrium data for alcohol-water mixtures which agree very closely with those of Bergstrom, so that these appear to be most reliable.

Analytical Methods for Binary Mixtures.—Although graphical methods of calculation are often the easiest to use, there are a number of cases for which equations can be derived which render arithmetical
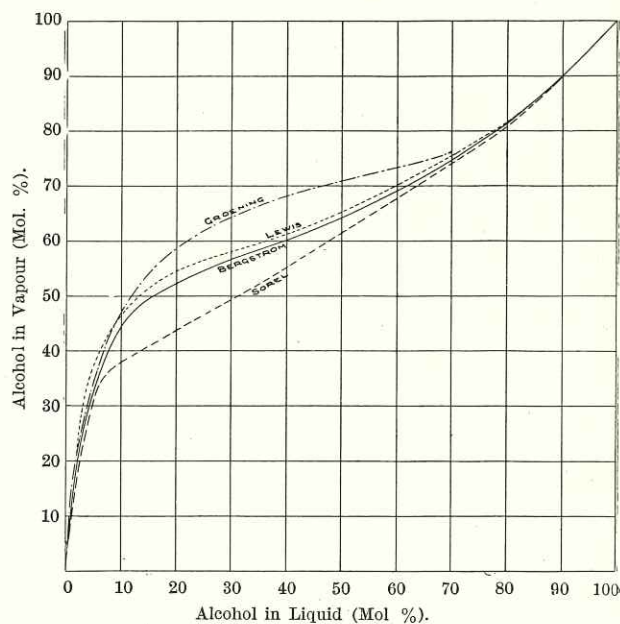

FIG. 7.

calculation simpler. The first case is when the two components of the mixture obey Raoult's Law. The relation between liquid and vapour composition for the more volatile component is then

$$X = \frac{P_1 x}{\pi}$$

where P_1 is the vapour pressure of the pure substance at the temperature of the mixture and π is the total pressure. Similarly, for the other component,

$$1 - X = \frac{P_2 (1-x)}{\pi}$$

Dividing the first of these equations by the second

$$\frac{X}{1-X} = \frac{P_1}{P_2} \cdot \frac{x}{1-x}$$

Putting $\frac{P_1}{P_2} = a$, $\therefore \frac{X}{1-X} = \frac{a x}{1-x}$ .... (20)

For such binary mixtures the term $\frac{P_1}{P_2}$ represents the "relative volatility" and is approximately constant

over a fairly wide range of temperature. It may, without serious error, be assumed constant over the temperature range in the column by taking the arithmetic mean of the values of a at the top and the bottom of the column.

The minimum reflux required for a given separation may be found as follows. Equations (9) and (14) for the concentrating and exhausting columns respectively, are

$$(R+1)\, X_{n+1} = R x_n + x_p \quad \dots \dots \dots \dots \dots \quad (9)$$

$$(R P + q\, F)\, x_{m+1} = (R\, P + q\, F - W)\, \overline{X}_m + W x_w \dots \quad (14)$$

The co-ordinates of the point of intersection of these two lines are found by using equations 15 and 16 to be

$$x = \frac{(R+1)\, x_f + (q-1)\, x_p}{R+q} \quad \text{and} \quad X = \frac{R x_f + q x_p}{R+q} \quad \dots (20\text{A})$$

The minimum reflux R_m is that value of R which causes the point of intersection to fall on the equilibrium curve. Substituting the above values of x and X in equation 20, the value of R_m is given by the quadratic equation

$$\frac{R_m x_f + q x_p}{R_m\, (1-x_f) + q\, (1-x_p)} =$$

$$\frac{a\, \{(R_m+1) x_f + (q-1) x_p\}}{(R_m+1)\, (1-x_f) + (q-1)\, (1-x_p)} \quad \dots \dots \quad (21)$$

For the two cases where the feed is composed of liquid at boiling point or entirely of vapour, the above equations reduce to very simple forms. Where the feed is liquid at boiling point, $q=1$, and equation 21 then becomes

$$\frac{R_m x_f + x_p}{R_m\, (1-x_f) + (1-x_p)} = \frac{a\, x_f}{1-x_f}$$

from which

$$R_m = \frac{1}{a-1} \left\{ \frac{x_p}{x_f} - \frac{a\,(1-x_p)}{1-x_f} \right\} \quad \dots \dots \dots \quad (22)$$

Where a fairly pure product is being separated x_p may be made equal to 1 in the above equation and then

$$R_m = \frac{1}{x_f\, (a-1)} \quad \dots \dots \dots \dots \dots \dots \dots \quad (23)$$

For example, the relative volatility of benzene and toluene is 2·55 at 80° C. and 2·33 at 110°, so that the mean value may be taken as 2·44. The minimum reflux to give a product containing 99·5 mol. per cent. of benzene from an equimolal mixture of benzene and toluene is given by

$$R_m = \frac{1}{0·5 \times 1·44} = 1·39$$

Where the feed is wholly vapour, $q=0$ and equation 21 becomes

$$\frac{x_f}{1-x_f} = \frac{a\, \{(R_m+1)\, x_f - x_p\}}{(R_m+1)\, (1-x_f) - (1-x_p)}$$

from which

$$R_m = \frac{1}{a-1} \left\{ \frac{a\, x_p}{x_f} - \frac{1-x_p}{1-x_f} \right\} \quad \dots \dots \dots \dots \quad (24)$$

For those cases where the product is fairly pure, putting $x_p=1$ gives

$$R_m = \frac{a}{(a-1)\, x_f} - 1 \quad \dots \dots \dots \dots \dots \dots \quad (25)$$

Denoting the minimum reflux where the feed is boiling liquor by R_{ml}, and the minimum reflux when the feed, of the same composition, is all vapour by R_{mv}, for a fairly pure product, equations 23 and 25 give the relation.

$$R_{mv} = a\, R_{ml} - 1 \quad \dots \dots \dots \dots \dots \dots \dots \quad (26)$$

which is independent of the composition of the feed.

The minimum number of plates in a column, with total reflux, can also be easily calculated, since the equations for the concentrating and exhausting columns then both reduce to the form

$$X_{n+1} = x_n$$

Consequently

$$1 - X_{n+1} = 1 - x_n$$

and

$$\frac{X_{n+1}}{1 - X_{n+1}} = \frac{x_n}{1 - x_n}$$

From equation 20

$$\frac{X_{n+1}}{1 - X_{n+1}} = \frac{a x_{n+1}}{1 - x_{n+1}}$$

The change in composition from plate to plate is therefore given by the equation

$$\frac{x_{n+1}}{1 - x_{n+1}} = \frac{1}{a} \cdot \frac{x_n}{1 - x_n} \dots \dots \dots \dots \dots \dots \quad (27)$$

If x_1, x_2, x_3 are the compositions on the top, second and third plates of the column respectively, then

$$\frac{x_2}{1 - x_2} = \frac{1}{a}\, \frac{x_1}{1 - x_1}; \quad x_3 = \frac{1}{a} \cdot \frac{x_2}{1 - x_2} \quad \text{or} \quad x_3 = \frac{1}{a^2} \cdot \frac{x_1}{1 - x_1}$$

The composition on the nth plate from the top is consequently

$$\frac{x_n}{1 - x_n} = \frac{1}{a^{n-1}} \cdot \frac{x_1}{1 - x_1}$$

If the nth plate is the bottom plate of the column, the liquid in the kettle has the composition x_w and

$$\frac{x_w}{1 - x_w} = \frac{1}{a} \cdot \frac{x_n}{1 - x_n}$$

Also

$$\frac{x_1}{1 - x_1} = \frac{1}{a} \cdot \frac{x_p}{1 - x_p}$$

The number of plates n in the column is thus found from the equation

$$\frac{x_w}{1 - x_w} = \frac{1}{a^{n+1}} \cdot \frac{x_p}{1 - x_p} \quad \dots \dots \dots \dots \dots \quad (28)$$

which is easily solved in the form

$$(n+1) \log a = \log \left\{ \frac{x_p\, (1 - x_w)}{(1 - x_p)\, x_w} \right\} \quad \dots \dots \dots \quad (29)$$

Where the separation of the two components is fairly close, no serious error is involved in putting $x_p = 1$ and $1 - x_w = 1$ in the numerator of the right-hand side of equation 29, so that then

$$(n+1) \log a = \log \left\{ \frac{1}{x_w\, (1 - x_p)} \right\} \quad \dots \dots \dots \quad (30)$$

For example, the minimum number of plates required to separate a mixture of benzene and toluene into 99·5 mol. per cent. benzene and 99·5 mol per cent. toluene is given by

$$(n+1) \log 2·44 = \log \left\{ \frac{1}{·005 \times ·005} \right\}$$

from which $n = 10·9$ or 11 theoretical plates are required as a minimum.

In equation 28 a mean value of a was used, whereas a varies slightly through the column. If account

were taken of these variations in a from plate to plate, equation 28 would take the form

$$\frac{x_w}{1-x_w} = \frac{1}{a_1, a_2, a_3 \dots a_n, a_w} \cdot \frac{x_p}{1-x_p} \quad \dots (31)$$

where a_1, a_2, a_3, etc., are the values of a on plates 1, 2, 3, etc., and a_w is the value for the liquid in the kettle. If equations 28 and 31 are to give the same value of n it is necessary that

$$(a_{av})^{n+1} = a_1, a_2, a_3 \dots a_n, a_w \dots \dots \dots (32)$$

where a_{av} is the mean value of a used previously, namely

$$\frac{a_1+a_w}{2}$$

As the variation of a is gradual and not large, it may be assumed approximately that the differences in the values of a from plate to plate are equal, so that $a_2 = a_1 + \delta$; $a_3 = a_1 + 2\delta$; $a_n = a_1 + (n-1)\delta$; $a_w = a_1 + n\delta$, where δ is this constant difference.

The right-hand side of equation 32 then becomes

$$a_1 (a_1+\delta)(a_1+2\delta)\dots(a_1+\overline{n-1}\cdot\delta)(a_1+n\delta)$$

which is equal to

$$a_1^{n+1}\left(1+\frac{\delta}{a_1}\right)\left(1+\frac{2\delta}{a_1}\right)\left(1+\frac{3\delta}{a_1}\right)\dots\left(1+\frac{n\delta}{a_1}\right)$$

Expanding this product and neglecting powers of the small quantity $\frac{\delta}{a_1}$ above the first, we obtain

$$a_1^{n+1}\left\{1+\frac{\delta}{a_1}+\frac{2\delta}{a_1}+\frac{3\delta}{a_1}+\dots+\frac{n\delta}{a_1}\right\}$$

or

$$a_1^{n+1}\left\{\frac{1+n(n+1)}{2}\cdot\frac{\delta}{a_1}\right\}\dots\dots\dots(33)$$

For the left-hand side of equation 32

$$(a_{av})^{n+1} = \left(\frac{a_1+a_w}{2}\right)^{n+1} = \left(\frac{2a_1+n\delta}{2}\right)^{n+1} = a_1^{n+1}\left(1+\frac{n\delta}{2a_1}\right)^{n+1}$$

Expanding the term in the bracket and neglecting powers of the small quantity $\frac{n\delta}{2a_1}$ above the first

$$(a_{av})^{n+1} = a_1^{n+1}\left\{1+\frac{n(n+1)}{2}\cdot\frac{\delta}{a_1}\right\}\dots\dots(34)$$

This is the same as expression 33, so that the condition given by equation 32 is fulfilled and the number of theoretical plates calculated by using the mean value of a is the same as the number which would be obtained by taking into account a uniform variation of a through the column.

For a binary mixture, the components of which follow Raoult's Law, convenient equations can be obtained for finite reflux ratios when the two components are being separated in a fair degree of purity, that is, when x_p is nearly equal to unity and x_w is small.

For the concentrating column

$$(R+1) X_{n+1} = Rx_n + x_p$$
or $(R+1) X_{n+1} = Rx_n + 1$ approximately
and $(R+1)(1-X_{n+1}) = R(1-x_n)$

Dividing one equation by the other gives

$$\frac{Rx_n+1}{R(1-x_n)} = \frac{X_{n+1}}{1-X_{n+1}} = \frac{a \cdot x_{n+1}}{1-x_{n+1}}$$

whence

$$\frac{R+1}{R(1-x_n)} - 1 = \frac{a}{1-x_{n+1}} - a$$

or

$$\frac{R a}{R+1}\cdot\frac{1}{1-x_{n+1}} - \frac{1}{1-x_n} = \frac{R(a-1)}{R+1}$$

For convenience putting $\dfrac{R}{R+1} = K_1$, then

$$\frac{K_1 a}{1-x_{n+1}} - \frac{1}{1-x_n} = K_1(a-1) \quad \dots\dots(35)$$

which may also be written in the form

$$\frac{(K_1 a)^{n+1}}{1-x_{n+1}} - \frac{(K_1 a)^n}{1-x_n} = K_1(a-1.)(K_1 a)^n$$

A series of equations for plates 1 to n may then be written

$$\frac{(K_1 a)^2}{1-x_2} - \frac{K_1 a}{1-x_1} = K_1(a-1)(K_1 a)$$

$$\frac{(K_1 a)^3}{1-x_3} - \frac{(K_1 a)^2}{1-x_2} = K_1(a-1)(K_1 a)^2$$

$$\frac{(K_1 a)^n}{1-x_n} - \frac{(K_1 a)^{n-1}}{1-x_{n-1}} = K_1(a-1)(K_1 a)^{n-1}$$

Adding all these equations together gives

$$\frac{(K_1 a)^n}{1-x_n} - \frac{K_1 a}{1-x_1} = K_1(a-1)\{(K_1 a)+(K_1 a)^2$$
$$+ (K_1 a)^3 + \dots + (K_1 a)^{n-1}\}$$
$$= K_1(a-1) K_1 a . \frac{(K_1 a)^{n-1}-1}{K_1 a - 1}$$

or

$$(K_1 a)^{n-1}\left\{\frac{1}{1-x_n} - \frac{K_1(a-1)}{K_1 a - 1}\right\} =$$
$$\frac{1}{1-x_1} - \frac{K_1(a-1)}{K_1 a - 1} \dots\dots\dots(36)$$

Since x_1 is nearly equal to 1, the term $\dfrac{K_1(a-1)}{K_1 a - 1}$ is usually small compared with $\dfrac{1}{1-x_1}$ and may be neglected. Also the composition of the vapour rising from plate 1 is x_p, assuming no fractionation in the condenser, so that

$$\frac{x_p}{1-x_p} = \frac{ax_1}{1-x_1}$$

Since x_p and x_1 are both nearly equal to unity

$$\frac{1}{1-x_1} = \frac{1}{a(1-x_p)}$$

Substituting in equation 36 gives

$$(K_1 a)^{n-1}\left\{\frac{1}{1-x_n} - \frac{K_1(a-1)}{K_1 a - 1}\right\} = \frac{1}{a(1-x_p)} \dots (37)$$

From this equation the number of plates required to reach a given composition x_n is easily found by taking logarithms. For the exhausting column

$$(RP+qF)\bar{x}_{m+1} = (RP-W+qF)\bar{X}_m + Wx_w \dots (14)$$

Since x_w is small the term Wx_w may be neglected and, writing

$$K_2 = \frac{RP-W+qF}{RP+qF}$$
$$K_2\bar{X}_m = \bar{x}_{m+1} \dots\dots\dots\dots\dots(38)$$

Also $\dfrac{\overline{X}_m}{1-\overline{X}_m} = \dfrac{a\overline{x}_m}{1-\overline{x}_m}$

or $\overline{X}_m = \dfrac{a\overline{x}_m}{(a-1)\overline{x}_m+1} = \dfrac{x_{m+1}}{K_2}$

or $K_2 a . \dfrac{1}{\overline{x}_{m+1}} - \dfrac{1}{\overline{x}_m} = (a-1)$

Using this relation for each plate in the exhausting column commencing with the liquid in the kettle (x_w), and multiplying both sides by a suitable power of $K_2 a$, a series of equations may be written as follows :—

$(K_2 a)\ \dfrac{1}{\overline{x}_1} - \dfrac{1}{x_w} = a-1$

$(K_2 a)^2\ \dfrac{1}{\overline{x}_2} - (K_2 a)\ \dfrac{1}{\overline{x}_1} = (a-1)\ (K_2 a)$

$(K_2 a)^3\ \dfrac{1}{\overline{x}_3} - (K_2 a)^2\ \dfrac{1}{\overline{x}_2} = (a-1)\ (K_2 a)^2$

$(K_2 a)^m . \ \dfrac{1}{\overline{x}_m} - (K_2 a)^{m-1} . \ \dfrac{1}{\overline{x}_{m-1}} = (a-1)\ (K_2 a)^{m-1}$

Adding these equations together gives

$(K_2 a)^m\ \dfrac{1}{\overline{x}_m} - \dfrac{1}{x_w} =$

$(a-1)\left\{ 1 + (K_2 a) + (K_2 a)^2 + \ldots + (K_2 a)^{m-1} \right\}$

$= (a-1)\ .\ \dfrac{(K_2 a)^m - 1}{K_2 a - 1}$

or $(K_2 a)^m\left\{ \dfrac{1}{\overline{x}_m} - \dfrac{a-1}{K_2 a - 1} \right\} = \dfrac{1}{x_w} - \dfrac{a-1}{K_2 a - 1}$

The last term is usually small compared with $\dfrac{1}{x_w}$ and can be neglected, and then

$(K_2 a)^m\left\{ \dfrac{1}{\overline{x}_m} - \dfrac{a-1}{K_2 a - 1} \right\} = \dfrac{1}{x_w}$ .... (39)

from which the number of plates required to attain a given concentration is easily found. The constant K_2 may be put in the following form.
Since $W = F - P$

$K_2 = \dfrac{RP - W + qF}{RP + qF} = \dfrac{(R+1)\ P + (q-1)F}{RP + qF}$

and $Fx_f = Px_p + Wx_w$ or approximately $Fx_f = P$ since x_p is nearly equal to 1 and x_w is small. Substituting this relation gives

$K_2 = \dfrac{(R+1)\ x_f + (q-1)}{Rx_f + q}$

As an example of the utility of the above equations, we may take the separation of a benzene-toluene mixture containing 50 mol per cent. of benzene into 99·5 mol per cent. of benzene and 99·5 mol per cent. of toluene. Assume that the feed consists of boiling liquid $(q=1)$ and that the reflux ratio is 2. Then, for the concentrating column :—

$K_1 = \dfrac{R}{R+1} = 0.667,$

and as before $a = 2.44$.

It will be shown later that, for efficient working, the composition on the feed-plate cannot exceed x_f in this case, so that x_n may be taken as 0·5 for the calculation.

Equation 37 then gives :—

$(0.667 \times 2.44)^{n-1}\left\{ \dfrac{1}{1-0.5} - \dfrac{0.667 \times 1.44}{0.667 \times 2.44 - 1} \right\} = \dfrac{1}{2.44 \times .005}$

from which $n - 1 = 10.6$ or $n = 11.6$.

For the exhausting column :—

$K_2 = \dfrac{(R+1)x_f + (q-1)}{Rx_f + q} = \dfrac{3 \times 0.5}{2 \times 0.5 + 1} = 0.75$

and equation 39 becomes :—

$(0.75 \times 2.44)^m\left\{ \dfrac{1}{0.5} - \dfrac{1.44}{0.75 \times 2.44 - 1} \right\} = \dfrac{1}{.005}$

from which $m = 10.95$.

The total number of plates in the column will be $(m + n - 1)$, since one plate is common to both parts of the calculation, so that 21·55 or 22 plates are required and the feed plate is the twelfth from the top.

Where the difference between x_p and 1 increases and tends to introduce an error in the above equations, a correction can be introduced as follows:—

The equation

$(R+1)\ X_{n+1} = Rx_n + x_p$

may be written

$(R+1)\ X_{n+1} = Rx_n + 1 - \delta,$

where δ is the small quantity $(1 - x_p)$. Dividing both sides of this equation by $(1 - \delta)$ gives

$(R + 1 + R\delta + \delta)\ X_{n+1} = R\ (1 + \delta)\ x_n + 1.$

Writing R^1 for $R\ (1 + \delta)$ this becomes

$(R^1 + 1 + \delta)\ X_{n+1} = R^1 x_n + 1.$

Neglecting the small quantity δ it takes the form :—

$(R^1 + 1)\ X_{n+1} = R^1 x_n + 1.$

This is the same form as originally assumed, but with a slightly larger reflux ratio $R^1 = R\ (1 + \delta) = R\ (2 - x_p)$.

Using this modified reflux ratio in equations 37 and 39 enables them to be used without serious error over a large range.

Advantages of Analytical Methods.—Although the above analysis was based upon a mixture of two components which follow Raoult's Law, the equations derived are not limited to these mixtures but have a much wider application. The basic assumption was that the relative volatility does not vary greatly over the range to which the various equations may be applied. So long as this is the case, all the equations derived on the basis of Raoult's Law will hold good. The relative volatility a will only be equal to the ratio of the partial pressures of the pure substances when both follow Raoult's Law. For a large number of binary mixtures, the relative volatility is constant over a small range near each end of the equilibrium curve. It is precisely over these ranges that the graphical methods are less suitable as the equilibrium curve and the operating line, in McCabe and

Thiele's method, for instance, approach each other closely. To avoid serious errors the diagram should be drawn on a large scale, which usually involves the calculation or interpolation of a number of intermediate points on the curve so that the method becomes distinctly tedious. It is much quicker, and probably more accurate, to make the calculation over these ranges by means of equations 37 and 39, and then continue from the last plate so obtained by means of one of the graphical methods on that part of the diagram where the steps are larger and the accuracy of a graphical method is not open to the same criticism.

Another approximation for the equilibrium curve to permit of the number of theoretical plates being represented analytically is that suggested by Thormann,[14] who assumes that the equilibrium curve can be represented approximately by a straight line for the part near each end of the curve. The derivation of the equation is as follows.

The equation of the operating line for the concentrating column may be written :—

$$X_{n+1} = kx_n + h,$$

$$\text{where } k = \frac{R}{R+1} \text{ and } h = \frac{x_p}{R+1}.$$

Assuming that the equilibrium curve can be represented by the equation $X = ax + b$, then

$$x_{n+1} = \frac{k}{a} x_n + \frac{h-b}{a}$$

Thus

$$x_2 = \frac{k}{a} x_1 + \frac{h-b}{a}$$

$$x_3 = \frac{k}{a} x_2 + \frac{h-b}{a} = \frac{k^2}{a^2} x_1 + \frac{k}{a} \frac{h-b}{a} + \frac{h-b}{a}$$

$$x_4 = \frac{k}{a} x_3 + \frac{h-b}{a} = \frac{k^3}{a^3} x_1 + \frac{k^2}{a^2} \cdot \frac{h-b}{a} + \frac{k}{a} \cdot \frac{h-b}{a} + \frac{h-b}{a}$$

Similarly :—

$$x_n = \left(\frac{k}{a}\right)^{n-1} x_1 + \frac{h-b}{a} \left\{ \left(\frac{k}{a}\right)^{n-2} + \left(\frac{k}{a}\right)^{n-3} + \cdots\cdots\cdots + \frac{k^2}{a^2} + \frac{k}{a} + 1 \right\}$$

$$\text{or } x_n = \left(\frac{k}{a}\right)^{n-1} x_1 + \frac{h-b}{a} \cdot \frac{\left(\frac{k}{a}\right)^{n-1} - 1}{\frac{k}{a} - 1}$$

and

$$\left(\frac{k}{a}\right)^{n-1} \left\{ \frac{b-h}{k-a} - x_1 \right\} = \frac{b-h}{k-a} - x_n$$

Since

$$x_1 = \frac{x_p - b}{a},$$

this gives

$$\left(\frac{k}{a}\right)^{n-1} \left\{ \frac{b-h}{k-a} - \frac{x_p - b}{a} \right\} = \frac{b-h}{k-a} - x_n \quad \cdots \cdots (40)$$

From this equation the value of n for a given value of x_n is readily found. A similar equation can be derived for the exhausting column.

The assumption that the equilibrium curve can be represented by a straight line does not usually give as good results as the equations based on the assumption of constant relative volatility. It is, however, useful for the particular case of alcohol-water mixtures with high alcohol content where the equilibrium curve is very nearly a straight line. For this case the writer finds that the equation

$$X = 0.8275x + 0.1542$$

gives good results over the range from 77 mol per cent. of alcohol up to the constant-boiling mixture. It is over this range that the number of plates becomes large and the graphical construction involves redrawing this portion of the curve on a scale large enough to avoid serious errors.

Plate Efficiency.—So far the assumption has been made that the vapour rising from any plate is in equilibrium with the liquid on that plate. The condition on this "theoretical plate" is, of course, never realised in practice. This difference may be allowed for in two ways. The number of theoretical plates calculated for a given separation divided by the number of plates actually used in practice under the same conditions of reflux ratio, feed temperature, etc., for the same separation gives an average value of the plate efficiency which may conveniently be termed the "overall plate efficiency."

A definition of plate efficiency, with reference to the performance of an individual plate, suggested by Murphree,[21] states the "individual plate efficiency" as the ratio of the change in composition of the vapour effected by the plate through which it passes to the change in composition which would result if the vapour, after passing through the plate, were in equilibrium with the liquid on it. This "individual plate efficiency" e is thus given by the equation

$$e = \frac{X_n - X_{n+1}}{X^1_n - X_{n+1}}$$

where X_n and X_{n+1} are the actual compositions of the vapour above and below the nth plate and X^1_n is the composition of the vapour in equilibrium with the liquid on the nth plate. In this form this definition is not very convenient for practical purposes, as its application to any given plate would involve the measurement of vapour compositions. It can, however, be put into a more suitable form involving liquid compositions, the determination of which is easier, in practice, owing to the greater ease in taking samples of liquid than of vapour.

From the equations

$$(R+1) X_n = Rx_{n-1} + x_p$$
$$(R+1) X_{n+1} = Rx_n + x_p$$
$$(R+1) X^1_n = Rx^1_{n-1} + x_p$$

we have $\dfrac{X_n - X_{n+1}}{X^1_n - X_{n+1}} = \dfrac{x_{n-1} - x_n}{x^1_{n-1} - x_n} = e \quad \cdots\cdots (42)$

Here x^1_{n-1} is the composition which the liquid on the $(n-1)^{th}$ plate would have if the liquid on the plate below and the vapour rising from it were in equilibrium. The "individual plate efficiency" may thus be defined as the ratio of the enrichment between a plate and the plate above it to the enrichment which would be effected if the lower plate were an ideal one.

The identity of the two definitions is clear from Fig. 8, in which A B C shows the stepwise construction for a given plate and A D E that for an ideal plate. By Murphree's definition the efficiency of this plate is $\frac{AB}{AD}$. By the definition in terms of liquid composition given above it is $\frac{BC}{DE}$, and these two ratios are obviously equal.

To take into account the individual plate efficiency in calculating column data, the method suggested by Baker and Stockhardt[22] may be used. This consists in drawing a " modified equilibrium curve " which is the locus of the point B in Fig. 8. The

CO-ORDINATES OF

A ARE x_n, X_{n+1}

B " x_n, X_n

C " x_{n-1}, X_n
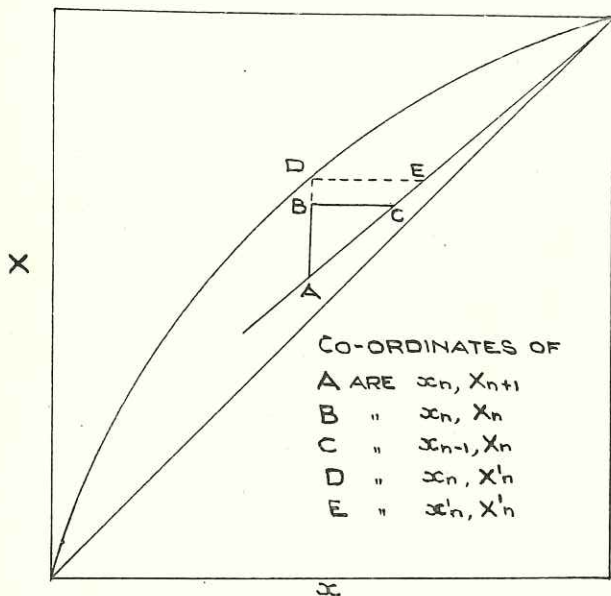
D " x_n, X'_n

E " x'_n, X'_n

FIG. 8.

ratio of the vertical distance between this modified equilibrium curve and the operating line to the distance between the true equilibrium curve and the operating line is equal to the " individual plate efficiency." This modified equilibrium curve can then be used instead of the true equilibrium curve for calculation by the graphical method of McCabe and Thiele, but it involves the construction of a new modified equilibrium curve for each operating line. For binary mixtures where Raoult's Law applies the method of Lewis and Wilde,[26] which is described later, may also be used.

For most practical purposes the " overall plate efficiency," denoted by E, is the most convenient criterion of the performance of a column. In general, therefore, the ideal column is considered in this paper, so that results of tests are related to it by the overall efficiency. The use of individual plate efficiency introduces considerable complications into the calculations and, as there is really no information available regarding the variation of this efficiency through the column as the composition and temperature vary, the use of this individual efficiency really involves the assumption of an average value for the column. The conception of individual plate efficiency as defined above is, however, useful in dealing with certain distillation problems.

The factors affecting plate efficiency in actual operation will be considered after mixtures of more than two components have been dealt with.

The minimum reflux for a given separation is not affected by plate efficiency. For minimum reflux the point of intersection of the operating lines, C in Fig. 3, falls on the equilibrium curve and then the true equilibrium curve and the modified equilibrium curve touch at this point. This is also true for mixtures such as alcohol-water, for which the minimum reflux may be determined by the tangency of the concentrating operating line and the equilibrium curve.

Composition of Liquid on the Feed-plate.—For a column to function at its highest efficiency the feed must be introduced at the appropriate point. The composition of the liquid on the feed-plate provides a valuable means of judging whether a given column has the feed correctly placed and is being utilised most efficiently. Thormann[14] has investigated this question by assuming that the composition on the feed-plate is the average composition resulting from the mixing of the feed and the reflux from the plate above. This assumption is only true if the vapour rising to the feed-plate and the vapour leaving it are identical in composition and amount, that is when the feed is introduced at boiling-point and the column is operating with minimum reflux. It does not hold in other cases, since the vapour rising to the feed-plate interacts with the liquid on that plate and leaves that plate in an enriched condition. The following method shows how the question can be treated for any condition of the feed and any reflux ratio.

In the graphical method shown in Fig. 3, assuming the step-wise construction to be started at D and continued downwards, the change from the operating line for concentration to the operating line for exhaustion must be made at the feed-plate. In Fig. 3 this change has been made at the point of intersection of the two lines and the composition on the feed-plate is given by 8. Fig. 9 shows where the feed is introduced too high in the column and the composition on the feed-plate is then given by 5, and Fig. 10 shows where the feed is introduced too low in the column and the composition on the feed-plate is then given by 12. In both of these cases the number of plates required is greater than that shown in Fig. 3. The plates of a column will be utilised most efficiently when the change from one operating line to the other is made at the point of intersection, for if the change were made at this point in Fig. 9 the increase in composition from plate 11 to plate 10 would be greater than that shown, and similarly for the plates above. In Fig. 10 also, if the change from one operating line to the other were made at the point of intersection, the change in composition from plate 8 to plate 9 would be greater than that shown, and similarly for the plates below. The highest possible concentration on the feed-plate for the given separation is, from

Fig. 9, that represented by H, the intersection of the exhausting operating line with the equilibrium curve. To attain this concentration an infinite number of plates would be required in the exhausting column. Similarly, the lowest possible concentration on the feed-plate is, from Fig. 10, that represented by G, the intersection of the concentrating operating line with the equilibrium curve, and to attain this concentration an infinite number of plates would be required in the concentrating column. Hence if the feed is introduced at too high a point the number of plates required in the exhausting column is increased, while if it is introduced at too low a point the number of plates required in the concentrating column is increased. It can easily be shown by constructing diagrams similar to Figs. 9 and 10 that, for a column with a fixed number of plates with the same feed and reflux ratio and producing a product of the same concentration, the concentration of more volatile product in the effluent from the column will be too high when the feed is introduced either at too high or too low a point. In such a case, to raise the point at which the feed enters would be the wrong thing to do if the feed is already too high. It is not possible to tell whether the feed is too high or too low merely from the fact that the product is too low in strength or the effluent is too rich as a column in which the feed is wrongly placed may be operated in such a way as to give either result.

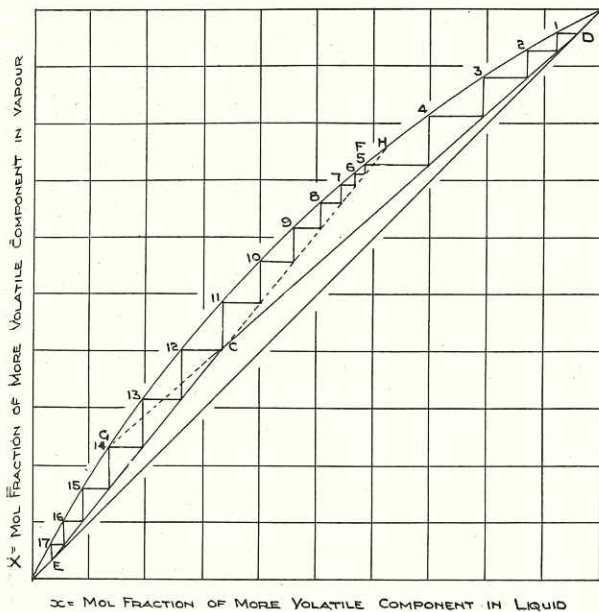X = MOL FRACTION OF MORE VOLATILE COMPONENT IN LIQUID

FIG. 9.

Figs. 3, 9 and 10 show that, as the reflux ratio increases so that C approaches the diagonal line and the angle between the two operating lines becomes smaller, the effect of the feed entering at the wrong place becomes less. For total reflux, when the two operating lines coincide with the diagonal line, it is practically immaterial where the feed is introduced. As the reflux increases in amount for a fixed amount of feed the change in composition on any plate due to the introduction of the feed on that plate decreases,

and consequently the effect on the whole system of altering the feed-plate becomes less. It is possible therefore to mask the bad effect of a feed incorrectly introduced by working the column with a large reflux. The effect would be more apparent with a smaller reflux ratio, but in practice this might never be observed, as working a column with a smaller reflux

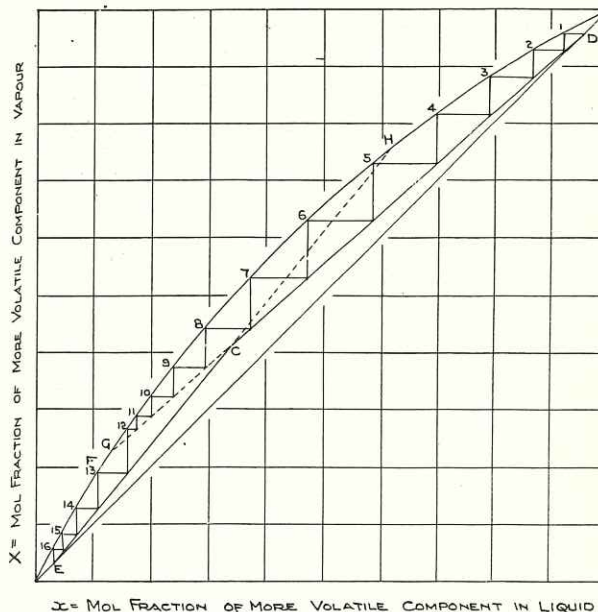x = MOL FRACTION OF MORE VOLATILE COMPONENT IN LIQUID

FIG. 10.

would fail to give the required separation and this would usually be ascribed to insufficient reflux, whereas it might be possible to effect the required separation with a smaller reflux if the position of the feed were altered. If the position of the feed is wrong the plate efficiency determined from any test will appear to be lower than is actually the case.

It is therefore extremely important to have some reliable method of judging whether the feed enters at the correct point in any column. One possible way is to calculate the number of plates required in the concentrating column and the exhausting column and compare the ratio of the two with the ratio in the actual column. This ratio should be the same in both cases if it is assumed that the plate efficiency in both columns is the same. This is not necessarily so, and consequently the method given below, in which the composition of the liquid on two plates is used to determine if the feed is correctly placed, is preferable, and has the advantage that it is applicable to cases where the equilibrium curve is not known.

If the feed is correctly placed for most efficient operation, the change over from the concentrating to the exhausting operating line takes place at the point of intersection of these two lines and the composition of the liquid on the feed-plate and the vapour rising from it, assuming equilibrium, are given by the abscissa and ordinate respectively of the corresponding point (8 in Fig. 3), on the equilibrium curve. The position of this point can vary to a certain extent, as it depends on how the stepwise construction fits in

between the equilibrium curve and the operating lines. This variation can only take place between certain limits, and the limiting positions are shown in Fig. 11. Where the change over from one operating line to the other takes place by means of a step such as G H K, the composition of the liquid on the feed-plate, H, will be a maximum; where it takes place by means of a step as B D E, the composition of the liquid on the feed-plate, D, will be a minimum. In these limiting positions B and K practically coincide with C, the point at which the two operating lines intersect. In the maximum position the abscissæ of H and C are equal and in the minimum position the ordinates of D and C are equal. From equation 20a, the co-ordinates of C are

$$x_c = \frac{(R+1)x_f+(q-1)x_p}{R+q} \text{ and } X_c = \frac{Rx_f+qx_p}{R+q}$$

Consequently the highest possible composition of the liquid on the feed-plate is x_c and the lowest possible composition is a liquid which is in equilibrium with vapour of the composition X_c where x_c and X_c have the values given above. If a horizontal line is drawn through C to meet the equilibrium curve in D the abscissæ of these two points represent the limits between which the composition of the liquid on the feed-plate must lie if the column is being utilised most efficiently. It may be emphasised here that these are the limits for the composition of the liquid on the feed-plate for the most effective utilisation of the column. As pointed out previously, the limits of possible composition with a wrongly placed feed, Figs. 9 and 10, are much wider.

When the liquid on the feed-plate has its minimum composition for efficient operation, as shown by D, Fig. 11, the composition of the liquid on the plate above the feed-plate will be given by the abscissa of B, that is of C, and this will represent the minimum composition for the liquid on that plate. Consequently the liquid on that plate must have a composition greater than x_c. We thus have the following rule, which can be applied when the equilibrium curve is not known, that the composition of the liquid on the feed-plate must not exceed $\dfrac{(R+1) x_f + (q-1) x_p}{R+q}$ and the composition of the liquid on the plate above the feed-plate must not be less than that quantity. Where the feed is all liquid at its boiling point, $q=1$ and the quantity $\dfrac{(R+1) x_f + (q-1) x_p}{R+q}$ is equal to x_f. The liquid on the feed-plate cannot then have a composition above that of the feed, and the liquid on the plate above the feed-plate cannot have a composition below that of the feed.

Fig. 11 also shows that the composition of the vapour rising from the feed-plate must be greater than X_c and the composition of the vapour rising from the plate below the feed-plate must be less than X_c. Where the feed is all vapour, $q=0$ and then

$$X_c = \frac{Rx_f + qx_p}{R + q} = x_f.$$

In this case the vapour rising from the feed-plate must be richer than the feed vapour, and the vapour rising from the plate below the feed-plate must be poorer than the feed vapour. This condition, like that derived for the case where the feed is all boiling liquid, is independent of reflux ratio and composition of product.

As the reflux ratio decreases C moves along the line M C L towards the equilibrium curve. The limits within which the composition of the liquid on the feed-plate can vary, represented by the abscissæ of C and D, approach each other and ultimately coincide when C and L coincide, that is, for minimum reflux. The composition of the liquid on the feed-plate is then definitely given by the abscissa of L. The difference between the limits within which the composition can vary is greatest for total reflux that is when C coincides with M.
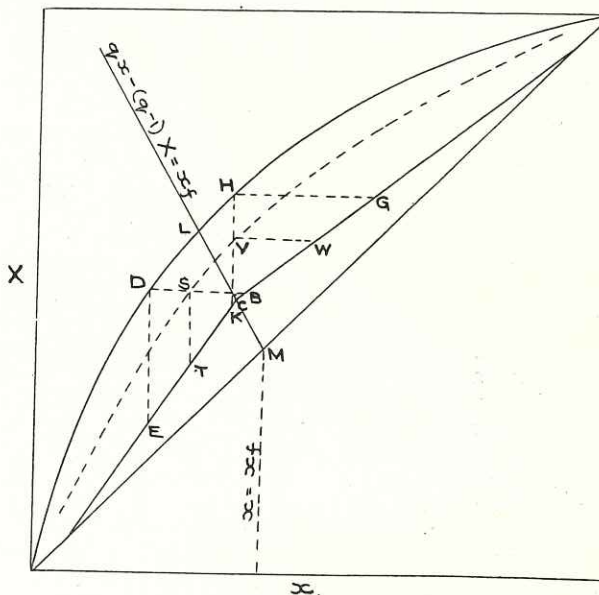

FIG. 11.

With minimum reflux, when C and L coincide, with a feed composed partly of liquid and partly of vapour, $q<1$, the composition of the liquid on the feed-plate must be the same as the composition of the liquid portion of the feed. Since q is the total heat required to vaporise 1 mol of feed divided by the molal heat of vaporisation, 1 mol of feed is made up of q mols of liquid and $(1-q)$ mols of vapour. If x_g is the composition of the liquid portion of the feed and X_h is the composition of the vapour portion, then $q x_g + (1-q) X_h = x_f$, that is the point (x_g, X_h) lies on the line $q x + (1-q) X = x_f$, which is the locus of the intersection of the two operating lines for the concentrating and exhausting columns, the line M C L. Since there is equilibrium between the liquid and the vapour portions of the feed, the point (x_g, X_h) must also lie on the equilibrium curve, so that this point is given by the intersection of the line M C L with the equilibrium curve. For minimum reflux, therefore, the composition of the liquid on the feed-plate, which is given by the abscissa of L is the same as the composition of the liquid portion of the feed. Incidentally this gives a convenient graphical construction for determining the composition of liquid and vapour when a liquid of given

composition is partly vaporised or a vapour of given composition is partly condensed, equilibrium vaporisation or condensation being assumed in both cases. All that is necessary is to draw the line M C L and note its intersection with the equilibrium curve. Conversely the fraction of a liquid which must be vaporised to attain a given concentration in the residual liquid or vapour is easily found by joining the appropriate point on the equilibrium curve to M and observing its slope which is equal to $\frac{q}{q-1}$.

If the feed is liquid below its boiling-point, $q > 1$, the line M C L has a positive slope and the upper limit for the possible composition on the feed-plate will be somewhat greater than x_f, as will be also the lower limit for the possible composition on the plate above the feed.

In the above discussion of the composition of the liquid on the feed-plate, ideal plates were assumed with equilibrium between liquid and vapour. As pointed out, the "individual plate efficiency" can be taken into account by drawing a modified equilibrium curve as shown dotted in Fig. 11. The limiting positions for the feed-plate step in the graphical construction will then be given by B S T and W V K instead of B D E and G H K. It is clear from the diagram that in this case also the composition of the liquid on the feed-plate cannot exceed x_c, and the composition of the vapour rising from it must be greater than X_c where x_c and X_c are the co-ordinates of C ; also the composition of the liquid on the plate above the feed-plate must be greater than x_c. This method for determining, by analyses of the liquid on the feed-plate and the liquid on the plate above it, whether the feed is correctly placed in any column can thus be applied in practice to any binary mixture without any knowledge of the equilibrium curve or the plate efficiency. Where the feed is all liquid at its boiling-point, it is not even necessary to determine the reflux ratio or the composition of the product. This also applies to the case where the feed is all vapour, if analyses are made of the vapour rising from the feed-plate and the vapour rising from the plate below.

If a feed, consisting partly of liquid and partly of vapour, is separated into the liquid and vapour portions before entering the column and these are introduced separately, then the operating line for the section of the column between the two feeds is given by D E where D is the intersection of the concentrating operating line with a horizontal line through L, and E is the intersection of the exhausting operating line with the vertical line through L. The operating lines for the column will then be P D E W instead of P C W, where the whole feed is introduced at one point. The new arrangement will result in a slight saving, somewhat less than one theoretical plate. If, however, the feed is first passed through a preliminary column to effect a separation into liquid and vapour portions, with compositions wider apart than those corresponding to equilibrium, the operating lines for the main column will then be P K N W instead of P C W. K is a point on the concentrating operating line which has an ordinate equal to the

composition of the vapour portion of the feed and N lies on the exhausting operating line and has an abscissa equal to the composition of the liquid portion of the feed. The main column will thus be able to effect a better separation with the same number of plates, or to effect the same separation with a lower reflux. In certain cases, particularly where it is desired to increase the capacity of an existing column or to effect a better separation where local conditions render it inconvenient to add to the height of the column, this method of effecting a comparatively crude preliminary separation in a small column placed before the main column may be useful.*

Rectification.—A subject which may be conveniently considered under the heading of binary mixtures, although strictly it does not fall into this classification, is the rectification of alcohol, that is the removal of impurities such as aldehydes, esters and higher alcohols from alcohol-water mixtures. In his treat-
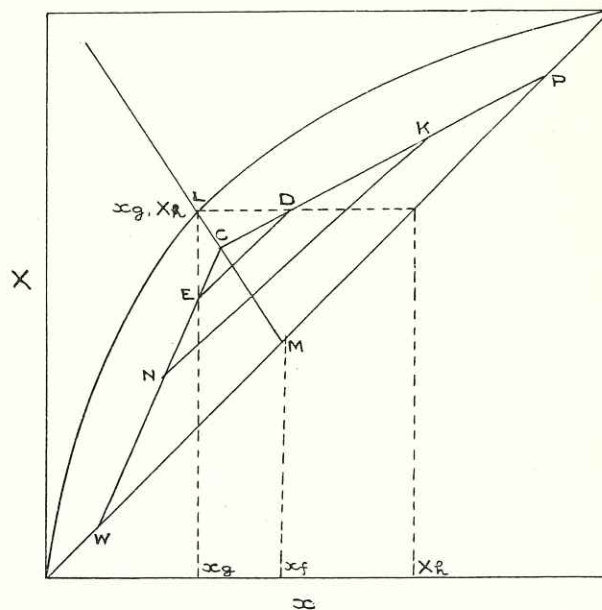

Fig. 12.

ment of rectification, Sorel[1] uses a relation $Z = Kz$ where Z is the fractional concentration of the impurity in the vapour and z its fractional concentration in the liquid, and gives the name "coefficient of solubility" to the term K. The value of K varies with the alcoholic strength of the liquid, and was determined for various compounds by Sorel[1] over a range of alcohol concentrations. The concentration of the impurity was less than 2% in all the determinations. Barbet[23] used a "coefficient of purification" which is Sorel's "coefficient of solubility" modified by referring concentrations to the alcohol present in liquid and vapour and not to the total amounts of alcohol and water in each.

For a part of the rectifying column over which the concentration of alcohol does not vary greatly, the coefficient of solubility K may be assumed to be

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* Patent application pending.

constant. A material balance across the nth plate from the top of the column gives

$$VZ_{n+1} + Oz_{n-1} = VZ_n + Oz_n$$

or, since $Z_{n+1} = Kz_{n+1}$ and $Z_n = Kz_n$

$$z_n - z_{n+1} = \frac{O}{KV}(z_{n-1} - z_n) \cdots \cdots \cdots (43)$$

For the sake of uniformity molal units are used, and, as weight units were used by Sorel, the values of K are assumed to be modified accordingly.

Applying equation 43 to the first plate of the column

$$z_1 - z_2 = \frac{O}{KV}(z_p - z_1)$$

since z_p is the composition of the reflux from the condenser.

For successive plates

$$z_2 - z_3 = \frac{O}{KV}(z_1 - z_2) = \left(\frac{O}{KV}\right)^2 (z_p - z_1)$$

$$z_3 - z_4 = \frac{O}{KV}(z_2 - z_3) = \left(\frac{O}{KV}\right)^3 (z_p - z_1)$$

$$z_{n-1} - z_n = \left(\frac{O}{KV}\right)^{n-1} (z_p - z_1)$$

Adding these equations

$$(z_1 - z_2) + (z_2 - z_3) + (z_3 - z_4) + \ldots (z_{n-1} - z_n) = z_1 - z_n$$

$$= (z_p - z_1)\left\{ \frac{O}{KV} + \left(\frac{O}{KV}\right)^2 + \left(\frac{O}{KV}\right)^3 + \ldots + \left(\frac{O}{KV}\right)^{n-1} \right\}$$

and adding $(z_p - z_1)$ to both sides of this equation

$$z_p - z_n = (z_p - z_1)\left\{ \frac{\left(\frac{O}{KV}\right)^n - 1}{\left(\frac{O}{KV}\right) - 1} \right\} \cdots \cdots \cdots (43a)$$

But $kz_1 = z_p$ and putting $\lambda = \frac{O}{KV} = \frac{R}{K(R+1)}$, the relation

becomes $z_n = z_p \left\{ \frac{\lambda^n(1-K) + K\lambda - 1}{K(\lambda - 1)} \right\} \cdots \cdots \cdots (44)$

It may be remarked here that the equation corresponding to equation 43a as given by Sorel has $\frac{KV}{O}$ instead of $\frac{O}{KV}$. This error has been copied by subsequent writers, and it would therefore appear that many of their deductions drawn from the incorrect equation require reconsideration.

By means of equations 43a or 44, the variation in the concentration of an impurity from plate to plate can be calculated. It should, however, be pointed out that Sorel's determinations were limited to solutions containing less than 2% of an impurity, and may consequently give erroneous results when applied to higher concentrations. The influence of various impurities on each other in a mixture is also obscure. In view of this paucity of physical data relating to liquid-vapour equilibria for aqueous alcohol and the impurities commonly associated with it, the method of calculation outlined above must be

regarded as providing useful guidance in the examination of the rectification process rather than a strictly quantitive treatment. At the present time the element of uncertainty involved renders it unsuitable as a theoretical standard of performance to which test results can be related, more particularly so as the criteria in practice of the performance of a rectifying still are frequently such qualities in the product as "flavour," "body," "harshness" rather than the concentration of any particular impurity determined by analysis.

MIXTURES OF MORE THAN TWO COMPONENTS.

Some of the methods of calculation described for the separation of binary mixtures can be used with certain modifications for mixtures containing a larger number of components. There is, however, one fundamental difference between the two cases. If the concentration of one component of a binary mixture in the liquid or the vapour phase of an equilibrium mixture of the two is given, then for a given total pressure the system is defined, that is the composition of the other phase and the temperature are fixed. The system has two phases and two components, and therefore two degrees of freedom. In a mixture of three components the fixing of the total pressure and the concentration of one component in the liquid does not fix the concentration of that component in the vapour. The concentration of a second component must be fixed before the system is defined. There are two phases and three components and consequently three degrees of freedom. The relation between the concentration of a given component in the liquid and its concentration in the vapour in equilibrium with that liquid depends, in a ternary or more complex mixture, on the concentration of the other components. There is consequently no unique equilibrium curve for these more complex mixtures such as was used in the calculations for binary mixtures.

The following additional symbols will be used in the discussion of mixtures of more than two components.

$a, b, c, d, e.$ The mol. fractions of the different components in the liquid at any point. The boiling-points of the pure substances rise from a to e.

$A, B, C, D, E.$ The mol. fractions of the different components in the vapour at any point.

$P_n{}^a, P_n{}^b, P_n{}^c, P_n{}^d, P_n{}^e.$ The vapour pressures of the pure components at the temperature on the nth plate.

π The total pressure in the column.

$a, \beta, \gamma, \delta.$ The relative volatilities of components a and b, b and c, c and d, d and e respectively.

The other symbols used have the same significance as before.

For that portion of the concentrating column above a section between the nth and $(n+1)^{th}$ plates, taking

balances for the total material and for each component gives the following equations :—

$$V_{n+1} = O_n + P$$
$$V_{n+1}\,A_{n+1} = O_n a_n + P a_p$$
$$V_{n+1}\,B_{n+1} = O_n b_n + P b_p$$
$$V_{n+1}\,C_{n+1} = O_n c_n + P c_p$$
$$V_{n+1}\,D_{n+1} = O_n d_n + P d_p$$
$$V_{n+1}\,E_{n+1} = O_n e_n + P e_p.$$

Assuming constant molal reflux and $O = RP$.

$$\left.\begin{array}{l}(R+1)\,A_{n+1} = R a_n + a_p \\ (R+1)\,B_{n+1} = R b_n + b_p \\ \text{and similar equations for c, d and e.}\end{array}\right\} \dots\dots\dots (45)$$

For the exhausting column, in exactly the same way as for binary mixtures, an equation can be obtained for each component, giving :—

$$\left.\begin{array}{l}(O+qF)\,\bar{a}_{m+1} = (O+q\,F-W)\,\bar{A}_m + W a_w \\ (O+qF)\,\bar{b}_{m+1} = (O+qF-W)\,\bar{B}_m + W b_w\end{array}\right\} \quad (46)$$

These equations may also be written :—

$$\left.\begin{array}{l}(RP+qF)\,\bar{a}_{m+1} = (RP+qF-W)\bar{A}_m + W a_w \\ (RP+qF)\,\bar{b}_{m+1} = (RP+qF-W)\bar{B}_m + W b_w\end{array}\right\} \quad (47)$$
and similar equations for c, d, e.

From equations 45 the composition of the vapour from the $(n+1)^{th}$ plate can be found when the composition of the liquid on n^{th} plate is known. If the equilibrium relations between liquid and vapour compositions are known, the composition of the liquid on the $(n+1)^{th}$ plate can be found. The calculation can thus be made for each plate in the concentrating column starting from the top. A similar calculation can be made for the exhausting column starting at the bottom. The two calculations come together at the feed-plate. Although this method is simple in principle it is quite otherwise in practice. Equilibrium data are known for very few complex mixtures, and for mixtures of more than three components even the graphical representation of such data is difficult. The equilibrium relations are known for mixtures, the components of which can be assumed without serious error to follow Raoult's Law, and this is true for the industrially important case of mixtures of petroleum hydrocarbons.

Thormann[14] has described a graphical method for calculating the composition of the liquid on each plate of a column for a mixture of three components to which Raoult's Law applies. This method which uses the usual trilinear co-ordinates cannot be applied to mixtures of more than three components.

Lewis and Matheson[24] give a method for applying equations 45 and 47 to the fractionation of natural gasoline. Applying Raoult's Law for the partial pressure of each component :—

$$A_{n+1} = \frac{P^a_{n+1}\,a_{n+1}}{\pi}; \quad B_{n+1} = \frac{P^b_{n+1}\,b_{n+1}}{\pi}; \quad \text{etc.} \dots \dots (48)$$

From the values of A_{n+1}, B_{n+1}, etc., found from equations 45 the corresponding values of a_{n+1}, b_{n+1}, etc., can be found from equations 48. In the latter equations, the vapour pressures are functions of the temperature on the $(n+1)^{th}$ plate which is not known. This temperature must be found by assuming various temperatures until one is found which gives values of a_{n+1}, b_{n+1}, etc., in equation 48 which satisfy the relation

$$a_{n+1} + b_{n+1} + c_{n+1} + d_{n+1} + e_{n+1} = 1.$$

In this way the calculations are made from plate to plate for the concentrating and exhausting columns until both calculations give approximately the same plate composition at the middle of column. One important difference may here be mentioned between this type of calculation for binary mixtures and for more complex mixtures. For a binary mixture, specifying the concentration of one component in the product and the residue automatically fixes the other, and the plate to plate calculations made from the top of the concentrating column and the bottom of the exhausting columns obviously include both components. For mixtures of more than two components the two calculations do not always take into account the same components. As an example we may consider a mixture of five components, a, b, c, d, e, which has to be fractionated so that the distillate contains the components a and b with a small amount of c, while the residue is to contain components c, d, e with a small amount of b. The plate to plate calculation from the top of the column will only contain components a, b, c as the amounts of components d and e in the distillate are not specified, and cannot be predicted before making the calculation. The calculation would not show the presence of components d and e for any plates above the feed-plate. Similarly the calculation from the bottom of the column would not show the presence of component a below the feed-plate. This result is obviously not correct, but usually the amounts of d and e above the feed-plate, and of a below the feed-plate, are small, and corrections can be introduced as shown by Lewis and Matheson or by another method which will be described later.

A graphical method of solution of equations 45 and 48 or 47 and 48 has been described by Cope and Lewis.[25] Consider, for instance, the exhausting column. Then for any component an operating line can be drawn for equation 47 to represent the relation between vapour and liquid composition between any two plates as was done for binary mixtures. Such an operating line can be drawn for each component, and equation 47 shows that they will all be parallel. The equilibrium relation between liquid and vapour, corresponding to the equilibrium curve for binary mixtures, will be a series of straight lines through the origin having slopes equal to different values of $\dfrac{P}{\pi}$. For each temperature a line can be drawn with a slope $\dfrac{P}{\pi}$ where P is the vapour pressure of the pure component at that temperature. The composition from plate to plate is then determined by a step-wise construction between the operating line and the equilibrium lines, a different equilibrium line being used for each plate. The principle of the method is shown in Fig. 13. In passing from one plate to the next the equilibrium line to be used is unknown, since the temperature is not known. This temperature must be found by trial and error by assuming various temperatures

and using the corresponding equilibrium lines to determine the amount of every component on the next plate. The correct temperature is that which gives the sum of the values found for the various components equal to unity. By repeating this process from plate to plate for both the exhausting and the concentrating column, the composition on each plate and the number of plates required can be found.

Lewis and Wilde [26] derive equations taking into account the individual plate efficiency and a factor f to correct for deviation from Raoult's Law, as suggested by Brown and Caine.[27]
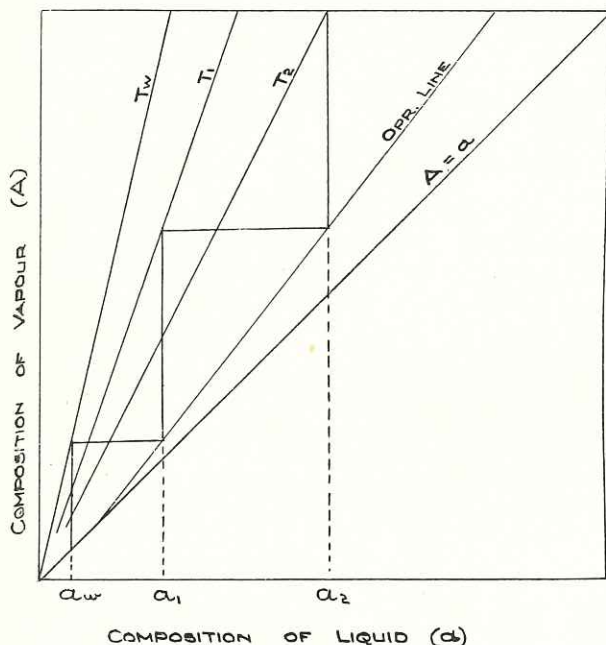

FIG. 13.

For the concentrating column, considering component a,

$$(R+1) A_{n+1} = Ra_n + a_p$$

If the theoretical composition, assuming equilibrium, of the vapour rising from plate n is denoted by A^1_n

then $A^1_n = f \dfrac{a_n P_n^a}{\pi}$.

From the definition of individual plate efficiency

$$(A_n - A_{n+1}) = e (A^1_n - A_{n+1})$$

If A^1_n and a_n are eliminated from the above equations, the relation between the compositions of the vapours rising from successive plates becomes

$$A_n = A_{n+1} - e\left[A_{n+1} - f\frac{P_n^a}{\pi R}\left\{(R+1) A_{n+1} - a_p\right\}\right] (49)$$

A corresponding equation can be derived for the exhausting column.

These equations, modified to allow for varying reflux, have been used by Lewis and Wilde to determine the plate efficiency of a column from actual operating data. To calculate the number of plates required for a given separation the equations would be used in the same way as in Lewis and Matheson's method.

The methods described above, although comparatively simple in theory, are distinctly laborious when applied to a practical problem, because the correct plate temperature has to be determined by trial and error. A modified method will be described in which this disadvantage is eliminated, and it will be shown that certain very important data for any fractionation problem, namely, the minimum reflux, the minimum number of plates, and the limits of composition of the liquid on the feed-plate, for efficient operation, can be obtained from very simple equations.

As a concrete illustration, the methods will be applied to the fractionation of a mixture containing 25% by weight of hexane, 25% of heptane, 20% of octane, 15% of nonane and 15% of decane, to produce a distillate containing the hexane and heptane and not more than 0·5% by weight of octane, whilst the residue is to contain the octane, nonane, and decane with not more than 0·1% of heptane. The feed enters the column half as liquid and half as vapour ($q = 0·5$), and the fractionation is carried out at atmospheric pressure. Converting weight compositions into mol. fractions, the following figures are obtained, the components hexane to decane being denoted by a, b, c, d, e respectively.

	a Hexane.	b Heptane.	c Octane.	d Nonane.	e Decane.
Feed (1·731 mols.)	0·310	0·266	0·187	0·125	0·112
Distillate (1 mol.)	0·536	0·460	0·00406	—	—
Residue (0·731 mol.)	—	0·00126	0·437	0·296	0·266

Minimum Number of Plates.—For total reflux, R becomes infinite and equations 45 become

$$A_{n+1} = a_n ; \quad B_{a+1} = b_n ; \quad C_{n+1} = c_n ; \quad D_{n+1} = d_n ;$$
$$E_{n+1} = e_n \quad \ldots\ldots\ldots \quad (50)$$

Dividing each equation by the next gives a series of equations

$$\frac{A_{n+1}}{B_{n+1}} = \frac{a_n}{b_n} ; \quad \frac{B_{a+1}}{C_{n+1}} = \frac{b_n}{c_n} ; \quad \frac{C_{n+1}}{D_{n+1}} = \frac{c_n}{d_n} ; \quad \frac{D_{n+1}}{E_{n+1}} = \frac{d_n}{e_n} \quad ..(51)$$

From equations 48 a similar series can be derived, namely,

$$\frac{A_{n+1}}{B_{a+1}} = \frac{P_{n+1}^a}{P_{n+1}^b} \cdot \frac{a_{n+1}}{b_{n+1}} ; \quad \frac{B_{a+1}}{C_{a+1}} = \frac{P_{n+1}^b}{P_{n+1}^c} \cdot \frac{b_{n+1}}{c_{n+1}} \quad \ldots . \text{ etc.}$$

As pointed out in dealing with binary mixtures, the ratio of the vapour pressures at the same temperature for substances following Raoult's Law can be assumed constant by taking an average value for the column. Introducing the relative volatilities a, β, γ, δ gives

$$\frac{A_{n+1}}{B_{a+1}} = a \cdot \frac{a_{n+1}}{b_{n+1}} ; \quad \frac{B_{n+1}}{C_{n+1}} = \beta \cdot \frac{b_{n+1}}{c_{n+1}} ;$$
$$\frac{C_{n+1}}{D_{n+1}} = \gamma \cdot \frac{c_{n+1}}{d_{n+1}} ; \quad \frac{D_{n+1}}{E_{n+1}} = \delta \cdot \frac{d_{n+1}}{e_{n+1}} \quad \ldots . \quad (52)$$

From these equations and equations 51

$$\frac{a_{n+1}}{b_{n+1}} = \frac{1}{a} \cdot \frac{a_n}{b_n} ; \quad \frac{b_{n+1}}{c_{n+1}} = \frac{1}{\beta} \cdot \frac{b_n}{c_n} ;$$
$$\frac{c_{n+1}}{d_{n+1}} = \frac{1}{\gamma} \cdot \frac{c_n}{d_n} ; \quad \frac{d_{n+1}}{e_{n+1}} = \frac{1}{\delta} \cdot \frac{d_n}{e_n} \quad \ldots . \quad (53)$$

These equations give the variation in the ratio of any two components from plate to plate. The two

I

components to consider are those between which the cut is being made, in this case b and c, since b goes into the distillate and c into the residue. For plates 1, 2, 3, etc., the successive application of of equation 53 gives

$$\frac{b_2}{c_2} = \frac{1}{\beta} \cdot \frac{b_1}{c_1}, \quad \frac{b_3}{c_3} = \frac{1}{\beta} \cdot \frac{b_2}{c_2} = \frac{1}{\beta^2} \cdot \frac{b_1}{c_1}$$

and

$$\frac{b_n}{c_n} = \frac{1}{\beta^{n-1}} \cdot \frac{b_1}{c_1} \quad \dots \dots \dots \dots (53\text{A})$$

If there are n plates in the column, the relation for the nth plate and the kettle is

$$\frac{b_w}{c_w} = \frac{1}{\beta} \cdot \frac{b_n}{c_n}$$

If there is no fractionation in the condenser, the vapour from the top plate has the same composition as the distillate, and therefore

$$\frac{b_p}{c_p} = \beta \cdot \frac{b_1}{c_1} \cdot$$

Combining these equations gives

$$\frac{b_w}{c_w} = \frac{1}{\beta^{n+1}} \cdot \frac{b_p}{c_p} \quad \dots \dots \dots \dots \dots \dots (54)$$

and the number of plates required is given by

$$n+1 = \frac{\log\left\{ \frac{b_p}{c_p} \cdot \frac{c_w}{b_w} \right\}}{\log \beta} \quad \dots \dots \dots \dots (55)$$

This is similar to equation 29 for a binary mixture, and the number of plates required is the same as that required for the separation of a binary mixture, in which b and c are present in the same proportion, into two fractions having the same ratios of b and c as those in the complex mixture. For the example given

$$\beta = 2 \cdot 22 \text{ and } n+1 = \frac{\log\left\{ \frac{\cdot 460}{\cdot 00406} \times \frac{\cdot 437}{\cdot 00126} \right\}}{\log 2 \cdot 22}$$

from which n=12·3, that is, 13 plates are required, and will give a slightly smaller amount of c in the residue than that specified. Similar calculations can be made for any two other components : for example, a and b or c and d ; but it will be found that the number of plates required is much less than that found above, and the minimum number required is that which will effect the separation of the two components between which the cut is made.

It can be shown, exactly as for a binary mixture, that the number of plates calculated by assuming an average value for the relative volatility is the same as would be obtained by taking it as varying uniformly down the column.

The composition on each plate of the column can be calculated by using equations similar to 53A to find the ratio of each pair of components for each plate of the column. These being known, the actual amount of each component is easily calculated. Although the assumption of an average value for the relative volatility does not affect the number of plates, it will give slightly different values for the compositions on each plate. If these are required more accurately, they can be found by a method,

described later, which allows for change in relative volatility. The composition on each plate can be found in the following manner, which also assumes constant relative volatility.

By multiplying successively equations 53 we obtain

$$\frac{a_{n+1}}{b_{n+1}} = \frac{1}{a} \cdot \frac{a_n}{b_n}; \quad \frac{a_{n+1}}{c_{n+1}} = \frac{1}{a\beta} \cdot \frac{a_n}{c_n}; \quad \frac{a_{n+1}}{d_{n+1}} = \frac{1}{a\beta\gamma} \cdot \frac{a_n}{d_n}$$

and

$$\frac{a_{n+1}}{e_{n+1}} = \frac{1}{a\beta\gamma\delta} \cdot \frac{a_n}{e_n}$$

Substituting in the equation

$$a_{n+1} + b_{n+1} + c_{n+1} + d_{n+1} + e_{n+1} = 1,$$

$$a_{n+1}\left(1 + a\frac{b_n}{a_n} + a\beta\frac{c_n}{a_n} + a\beta\gamma\frac{d_n}{a_n} + a\beta\gamma\delta\frac{e_n}{a_n}\right) = 1$$

or

$$a_{n+1} = \frac{a_n}{a_n + ab_n + a\beta c_n + a\beta\gamma d_n + a\beta\gamma\delta e_n} \quad \dots \dots (56)$$

Also

$$b_{n+1} = \frac{ab_n}{a_n + ab_n + a\beta c_n + a\beta\gamma d_n + a\beta\gamma\delta e_n}$$

$$c_{n+1} = \frac{a\beta c_n}{a_n + ab_n + a\beta c_n + a\beta\gamma d_n + a\beta\gamma\delta e_n}$$

with corresponding equations for d_{n+1} and e_{n+1}. Thus when the composition on the nth plate is known, the composition on the $(n+1)^{th}$ plate can be found directly without the necessity for trial and error determinations.

In the example considered, the amounts of d and e in the distillate are not specified, but they can be found from the equations similar to equation 54. The amounts found by calculation are

$$d_p = 9 \cdot 7 \times 10^{-8} \text{ and } e_p = 3 \cdot 3 \times 10^{-12},$$

which are extremely small quantities. Similarly the amount of hexane in the residue is found to be $2 \cdot 1 \times 10^{-8}$. Fig. 14 shows the variation in the amounts of each component through the column.

Minimum Reflux.—Consider, again, the two components b and c. Dividing the corresponding equations 45 gives

$$\frac{B_{n+1}}{C_{n+1}} = \frac{Rb_n + b_p}{Rc_n + c_p}$$

Since

$$\frac{B_{n+1}}{C_{n+1}} = \beta \cdot \frac{b_{n+1}}{c_{n+1}}$$

therefore

$$\beta \cdot \frac{b_{n+1}}{c_{n+1}} = \frac{Rb_n + b_p}{Rc_n + c_p}.$$

For minimum reflux the change in composition between the two plates is negligible, so that we may put $b_{n+1} = b_n$ and $c_{n+1} = c_n$, so that

$$\beta \cdot \frac{b_n}{c_n} = \frac{Rb_n + b_p}{Rc_n + c_p}$$

The value of R given by this equation is

$$R(\beta - 1) = \frac{b_p}{b_n} - \beta \cdot \frac{c_p}{c_n} \quad \dots \dots \dots \dots (57\text{A})$$

and is the minimum value necessary to attain given values of b_n and c_n in the concentrating column. It increases as b_n decreases and c_n increases, that is, as we descend the column from the top. The minimum value of R for the given separation is obtained from the lowest value of b_n and the highest value of c_n found on any plate in the concentrating column.

For the exhausting column, equations 47 give

$$\frac{(RP+qF)\,\overline{b}_{m+1}-Wb_w}{(RP+qF)\,\overline{c}_{m+1}-Wc_w}=\frac{\overline{B}_m}{\overline{C}_m}=\beta\,\frac{\overline{b}_m}{\overline{c}_m}$$

When the change in composition from plate to plate is negligible, this equation gives

$$\frac{(RP+qF)\,\overline{b}_m-Wb_w}{(RP+qF)\,\overline{c}_m-Wc_w}=\beta\,\frac{\overline{b}_m}{\overline{c}_m}\quad\ldots\ldots\ldots\ldots (58)$$

and the value of R is given by

$$(RP+qF)\,(\beta-1)=W\left(\beta\cdot\frac{c_w}{\overline{c}_m}-\frac{b_w}{\overline{b}_m}\right)\ldots\ldots(58a)$$

The value of R given by this equation increases as $\overline{b}_m$ increases and $\overline{c}_m$ decreases, that is, as we ascend the column from the bottom, and the minimum value of R for the given separation is determined by the

Substituting these values of b_n and c_n in either of the equations 57 or 58 gives

$$\beta\left\{\frac{(R+1)\,b_f+(q-1)\,b_p}{(R+1)\,c_f+(q-1)\,c_p}\right\}=\frac{Rb_f+qb_p}{Rc_f+qc_p}\quad\ldots (59)$$

This equation determines the minimum reflux R required for the given separation. It is similar to equation 21 for a binary mixture, so the minimum reflux for the complex mixture is the same as that required for the equivalent binary mixture. This generalisation has only been proved for substances which follow Raoult's Law, and cannot be applied without question to other mixtures.

Equation 59 is of the second degree but reduces to one of the first degree for the two important cases where the feed is boiling liquid, $q=1$, and where
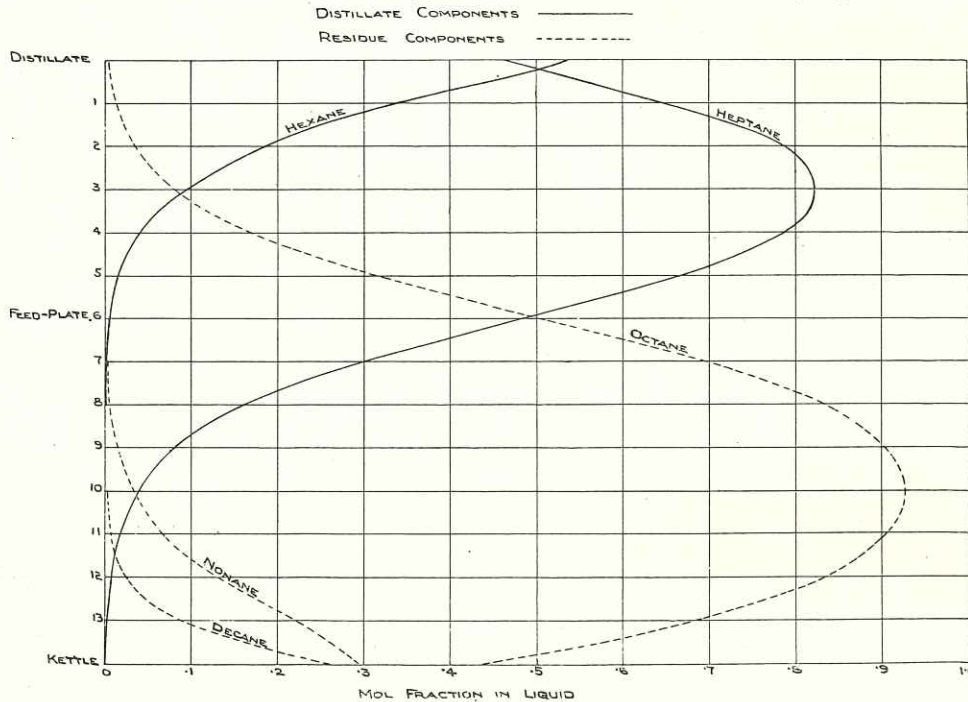

FIG. 14.

highest value of $\overline{b}_m$ and the lowest value of $\overline{c}_m$ on any plate in the exhausting column. From equations 57A and 58A the minimum reflux for the given separation is seen to be determined by the fractionation required for the plates just above and below the feed-plate. With this minimum reflux the compositions on these plates will be approximately equal. In this case we can write equation 45 for the concentrating column and equation 47 for the exhausting column for component b,

$$(R+1)\,B_n=Rb_n+b_p$$

and $\quad(RP+qF--W)\,B_n=(RP+qF)\,b_n-Wb_w$

Solving these two equations for b_n gives

$$\left.\begin{array}{l}b_n=\dfrac{(R+1)\,b_f+(q-1)\,b_p}{R+q}\\[2mm]\text{and similarly}\\[2mm]c_n=\dfrac{(R+1)\,c_f+(q-1)\,c_p}{R+q}\end{array}\right\}\quad\ldots (58B)$$

the feed is all vapour, $q=O$. Where the feed is all liquid, putting $q=1$ gives

$$R_{min}=\frac{1}{\beta-1}\left(\frac{b_p}{b_f}-\beta\frac{c_p}{c_f}\right)\ldots\ldots\ldots (60)$$

Generally c_p is small and can be neglected so that

$$R_{min}=\frac{b_p}{b_f\,(\beta-1)}\ldots\ldots\ldots\ldots\ldots (60A)$$

Where the feed is all vapour putting $q=O$ gives

$$R_{min}=\frac{1}{\beta-1}\left(\beta\,\frac{b_p}{b_f}-\frac{c_p}{c_f}\right)-1\ldots\ldots (61)$$

Where c_p is small this gives

$$R_{min}=\frac{\beta\,b_p}{b_f\,(\beta-1)}-1\ldots\ldots\ldots\ldots (61A)$$

Denoting the minimum reflux for liquid feed by R_{ml} and that for vapour feed by R_{mv} then

$$R_{mv}=\beta\,R_{ml}-1\ldots\ldots\ldots\ldots\ldots (62)$$

Equations 60 to 62 correspond to equations 22 to 26 for a binary mixture.

An inspection of equations 60 and 61 shows that a higher value for the minimum reflux is obtained by considering components b and c than for any other two components. For any two components in the distillate, the term corresponding to $\frac{c_p}{c_f}$ will be much larger, and for any two components in the residue the term corresponding to $\frac{b_p}{b_f}$ will be much smaller so that lower values of R would be obtained in both cases.

Substituting in the example given the values for b_f, c_f, b_p, c_p, and putting $q = 0.5$ and $\beta = 2.22$ gives the equation

$$R^2 - 1.255\,R - 0.698 = O$$

which has one positive solution $R = 1.68$.

If the feed were all liquid at its boiling point, equation 60 would give

$$R = \frac{1}{1.22}\left(\frac{.460}{.266} - \frac{2.22 \times .00406}{.187}\right)$$
$$= 1.42 - .04 = 1.38.$$

If the feed were all vapour, equation 61 would give

$$R = \frac{1}{1.22}\left(2.22 \times \frac{.460}{.266} - \frac{.00406}{.187}\right) - 1$$
$$= 3.15 - .02 - 1 = 2.13.$$

Obviously, no appreciable error is involved in putting $c_p = O$ in equations 60 and 61; and the ratio $\frac{b_p}{b_f}$ is equal to $\frac{F}{P}$ where the amount of component b in the residue is small. When the feed is partly liquid and partly vapour, instead of using the more complicated equation 59, it may be assumed to be all vapour and the minimum reflux calculated from equations 61 or 61a. This value will be higher than the true one but a reflux ratio, substantially above the minimum, is employed in practice.

Equation 59 can be interpreted geometrically. If the operating lines for components b and c are drawn according to the method of Cope and Lewis[25] as shown in Fig. 15, the point of intersection L of the operating lines for component b, namely HL and ML, has the co-ordinates b_L, B_L where

$$b_L = \frac{(R+1)\,b_f + (q-1)b_p}{R+q} \text{ and } B_L = \frac{Rb_f + qb_p}{R+q}$$

corresponding to equations 20A. Similarly for component c,

$$c_G = \frac{(R+1)\,c_f + (q-1)c_p}{R+q} \text{ and } C_G = \frac{Rc_f + qc_p}{R+q}$$

Equation 59 may therefore be put in the form

$$\beta \cdot \frac{b_L}{c_G} = \frac{B_L}{C_G} \text{ or } \frac{B_L}{b_L} = \beta \cdot \frac{C_G}{c_G}$$

$\frac{B_L}{b_L}$ is the slope of the line joining L to the origin and $\frac{C_G}{c_G}$ is the slope of the line joining G to the origin. The slope of any equilibrium line for component b, which has the equation $B = \frac{P^b}{\pi} \cdot b$ and the slope of the

equilibrium line for the same temperature for component c, which has the equation $C = \frac{P^c}{\pi} \cdot c$ are in the ratio $\frac{P^b}{P^c} = \beta$. The points of intersection L and G thus lie on equilibrium lines for b and c, corresponding to the same temperature, and this condition determines the minimum reflux. When this condition is fulfilled, the equilibrium lines for b, for a lower temperature, will lie to the right of point L, and those for C for a higher temperature will lie to the left of point G and the separation will be impossible.
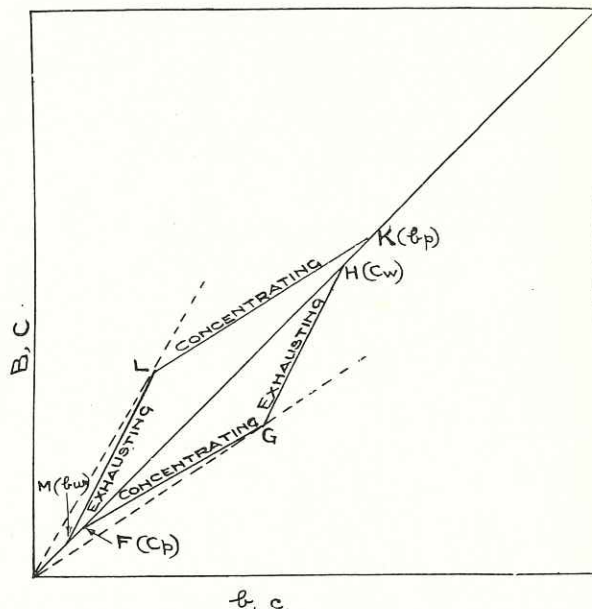

FIG. 15.

Composition of Liquid on Feed-Plate.---If the feed is introduced at the correct point in the column, say on the nth plate, as shown in Fig. 16 (Case I.), then raising the feed to the one above, the $(n-1)^{th}$ plate, or lowering it to the one below, the $(n+1)^{th}$ plate, will give inferior fractionation in both cases. This principle can be used to derive two conditions which ensure that the feed is neither too low nor too high in the column.

For Case I., as shown in Fig. 16,

$$(R+1)\,B_n = R\,b_{n-1} + b_p \text{ and } (R+1)\,C_n = Rc_{n-1} + c_p$$

so that

$$\frac{B_n}{C_n} = \frac{Rb_{n-1} + b_p}{Rc_{n-1} + c_p}$$

For Case II. the composition of the liquid on the $(n-1)^{th}$ plate will not be altered, but the composition of the vapour rising from the nth plate will be different. Denoting the new composition by B^1_n and C^1_n, we have

$$(RP + qF - W)\,B^1_n = (RP + qF)\,b_{n-1} - Wb_w$$

and $(RP + qF - W)\,C^1_n = (RP + qF)\,c_{n-1} - Wc_w$

and $\dfrac{B^1_n}{C^1_n} = \dfrac{(RP + qF)b_{n-1} - Wb_w}{(RP + qF)c_{n-1} - Wc_w}$

If the fractionation is better in Case I. than in Case II. then $\frac{B_n}{C_n} < \frac{B^1_n}{C^1_n}$ since the component b is being taken off as distillate and the component c as residue.

Using the above equations this condition gives
$$\frac{Rb_{n-1}+B_p}{Rc_{n-1}+c_p} < \frac{(RP+qF)b_{n-1}-Wb_w}{(RP+qF)c_{n-1}-Wc_w}$$
Substituting $Wb_w=Fb_f-Pb_p$ and $Wc_w=Fc_f-Pc_p$, this condition reduces to
$$\frac{Rb_{n-1}+b_p}{Rc_{n-1}+c_p} > \frac{Rb_f+qb_p}{Rc_f+qc_p} \quad \dots \dots \dots \dots \dots (63)$$

Similarly considering Cases I. and III. (Fig. 16), where the feed is lowered to the $(n+1)^{th}$ plate, for the section between the nth and $(n+1)$th plate, we have
$$\frac{B_{n+1}}{C_{n+1}} = \frac{(RP+qF)b_n-Wb_w}{(RP+qF)c_n-Wc_w}$$
and
$$\frac{B^1_{n+1}}{C^1_{n+1}} = \frac{Rb_n+b_p}{Rc_n+c_p}$$

it becomes
$$\frac{b_n}{c_n} > \frac{1}{\beta} \cdot \frac{Rb_f+qb_p}{Rc_f+qc_p} \quad \dots \dots \dots (65)$$

The liquid on the feed plate must then have a composition between the limits given by relations 64 and 65.

For minimum reflux, the two limits coincide, since b_{n-1} is then equal to b_n and c_{n-1} to c_n, so that relations 63 and 64 give
$$\frac{Rb_n+b_p}{Rc_n+c_p} > \frac{Rb_f+qb_p}{Rc_f+qc_p} \text{ and } \frac{Rb_n+b_p}{Rc_n+c_p} < \frac{Rb_f+qb_p}{Rc_f+qc_p}$$

These relations must then be satisfied by the limiting case
$$\frac{Rb_n+b_p}{Rc_n+c_p} = \frac{Rb_f+qb_p}{Rc_f+qc_p} \quad \dots \dots \dots \dots (66)$$

Relation 65 in this case becomes
$$\beta \cdot \frac{b_n}{c_n} = \frac{Rb_f+qb_p}{Rc_f+qc_p} \quad \dots \dots \dots \dots \dots (67)$$

The values of b_n and c_n for minimum reflux given by equation 58B satisfy equation 66. On substituting
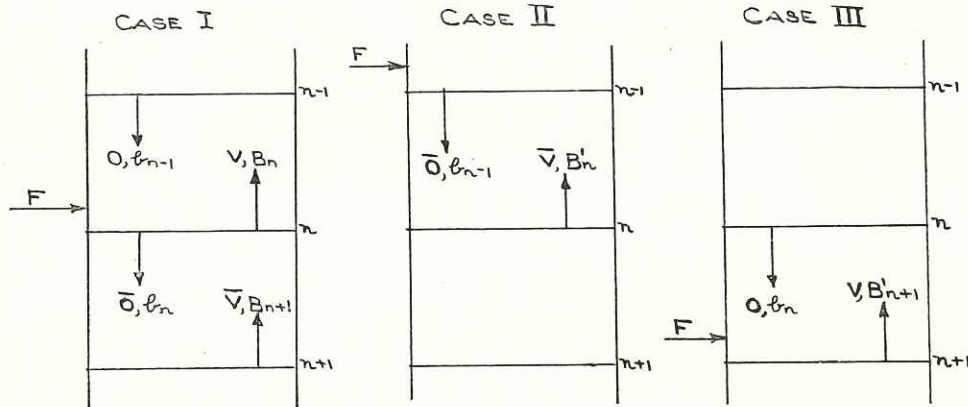

CASE I   CASE II   CASE III

FIG. 16.

If the fractionation is better in Case I., then
$$\frac{B_{n+1}}{C_{n+1}} < \frac{B^1_{n+1}}{C^1_{n+1}}$$
$$\therefore \frac{(RP+qF)b_n-Wb_w}{(RP+qF)c_n-Wc_w} < \frac{Rb_n+b_p}{Rc_n+c_p}$$

As before this reduces to
$$\frac{Rb_n+b_p}{Rc_n+c_p} < \frac{Rb_f+qb_p}{Rc_f+qc_p} \quad \dots \dots \dots \dots (64)$$

These two relations 63 and 64 give an upper limit for the composition of the liquid on the feed-plate and a lower limit for the composition of the liquid on the plate above the feed-plate. They are independent of any assumptions regarding liquid-vapour equilibria and can therefore be applied to determine whether the feed is correctly placed in any column without knowing the equilibrium relations of the mixture being treated or the plate efficiency. For mixtures to which Raoult's Law applies, relation 63 can be put in a different form.

Since $\quad \frac{R\,b_{n-1}+b_p}{c_{n-1}+c_p} = \frac{B_n}{C_n} = \beta \cdot \frac{b_n}{c_n}$

them in equation 67 the result is equation 59 for determining the minimum reflux.

For total reflux relations 63 and 64 reduce to
$$\frac{b_{n-1}}{c_{n-1}} > \frac{b_f}{c_f} \text{ and } \frac{b_n}{c_n} < \frac{b_f}{c_f} \quad \dots \dots \dots \dots (68)$$
while relation 65 becomes
$$\frac{b_n}{c_n} > \frac{1}{\beta} \cdot \frac{b_f}{c_f} \quad \dots \dots \dots \dots \dots \dots (69)$$

It will be seen that these relations are independent of q, b_p or c_p. In the example under consideration, illustrated in Fig. 14, the feed-plate is thus determined as the 6th plate from the top.

Brown, Souders and Nyland,[29] in dealing with the fractionation of a mixture of propane, butane and pentane under total reflux, make the assumption that the liquid on the feed-plate has the same composition as the feed for all components. Relations 68 and 69 show that this assumption is unjustified, as the ratio of components b and c in the liquid on the feed-plate can vary from that in the feed down to this divided by β.

The discordant results reported by these writers can be attributed to this cause.

General Case for any Reflux Ratio.—For many practical problems the simple calculation, by means of equation 55, of the minimum number of plates required with total reflux provides a useful method of comparison. When comparing two columns dealing with similar substances and working at approximately the same reflux ratio, the ratio of the number of plates required will be approximately equal to the ratio of the numbers required for total reflux in the two cases. Data obtained from one column may thus be applied to predict approximately the number of plates required for another column. A similar proposal has been made by Keyes, Soukup and Nichols[28] for binary mixtures, the method suggested being to calculate the number of plates required for total reflux and to multiply by a suitable safety factor to give the number of plates required in practice for a given separation. The safety factor has to take into account the overall plate efficiency and the difference in the number of plates required for total reflux and for the reflux ratio actually used, the assumption being that for a given binary mixture approximately the same reflux ratio is generally used. For many purposes the methods of calculation described for total reflux could be usefully applied where the reflux ratio is lower. Where it is necessary to know how the composition varies on different plates of a column, or which components, such as b and c in Fig. 14, reach a maximum composition in the column, with a view to taking off a sidestream, the calculation described for total reflux will provide useful information, since the general distribution will usually be similar when the reflux ratio is reduced. From the compositions on the plates, calculated for total reflux, the plate temperatures can be calculated and a similar temperature distribution assumed for a lower reflux ratio.

Where the above methods are insufficiently exact for a given purpose, the number of plates required for a given separation with a given reflux ratio can be calculated in the following way. If the composition of the liquid on the nth plate, $a_n, b_n, \ldots e_n$, is known, then by equations 45 the values of A_{n+1}, $B_{n+1} \ldots E_{n+1}$ are obtained, and the values of $a_{n+1}, b_{n+1} \ldots e_{n+1}$ can be determined from equation 48 using the relation :—

$$a_{n+1} + b_{n+1} + c_{n+1} + d_{n+1} + e_{n+1} = 1.$$

Substituting from equations 48 gives :—

$$\frac{\pi \cdot A_{n+1}}{P^a_{n+1}} + \frac{\pi B_{n+1}}{P^b_{n+1}} + \frac{\pi C_{n+1}}{P^c_{n+1}} + \frac{\pi D_{n+1}}{P^d_{n+1}} + \frac{\pi E_{n+1}}{P^e_{n+1}} = 1 .. (70)$$

In the method of Lewis and Matheson[24] this is solved by assuming various values for the temperature and substituting the corresponding vapour pressures in equation 70 until the correct solution is obtained, but by the following method the necessity for trial and error is eliminated.

Using the relative volatilities a, β, γ, δ which are given by the equations :—

$$\frac{P^a_{n+1}}{P^b_{n+1}} = a ; \quad \frac{P^b_{n+1}}{P^c_{n+1}} = \beta ; \quad \frac{P^c_{n+1}}{P^d_{n+1}} = \gamma ; \quad \frac{P^d_{n+1}}{P^e_{n+1}} = \delta$$

and substituting for P^b_{n+1}, P^c_{n+1}, etc., in terms of P^a_{n+1} in equation 70 gives :—

$$P^a_{n+1} = \pi (A_{n+1} + aB_{n+1} + a\beta C_{n+1} + a\beta\gamma D_{n+1} + a\beta\gamma\delta E_{n+1}) \ldots (71)$$

so that the value of P^a_{n+1}, and consequently the temperature, is obtained by a direct calculation. The values of a_{n+1}, b_{n+1}, etc., are then found from the equations :—

$$a_{n+1} = \frac{\pi A_{n+1}}{P^a_{n+1}} ; \quad b_{n+1} = \frac{\pi B_{n+1}}{P^b_{n+1}} = \frac{a\pi B_{n+1}}{P^a_{n+1}} ; \quad c_{n+1} =$$
$$\frac{a\beta\pi C_{n+1}}{P^a_{n+1}} \quad \ldots (72)$$

The calculation is thus continued from plate to plate.

If it is desired to take into account variations in the relative volatilities with temperature, in cases where the temperatures at the top and bottom of the still are very different, this may be done by taking new values of a, β, γ, δ every few plates. The values of a, β, γ, δ, or of $a, a\beta, a\beta\gamma, a\beta\gamma\delta$, can be plotted against temperature and the appropriate values taken as the temperature changes. As these quantities vary so slowly with temperature no appreciable error is involved in the solution of equation 71 if the values taken do not correspond exactly to the temperature determined by the value of P^a_{n+1} found from this equation. For instance, with the mixture of hexane, heptane, etc., which has been discussed, the relative volatility of heptane and octane varies only from 2·37 at 85° C., the temperature of the top plate, to 2·07 at 140° C., the temperature in the kettle, while the vapour pressure of heptane varies from 500 mm. to 2320 mm. and that of octane from 210 mm. to 1120 mm.

If a " correction factor " for deviations from Raoult's Law is used, as suggested by Brown and Caine,[27] this will not affect the calculation of the compositions, but will only affect the temperature determined for each plate.

Obviously, if equations 48 are written

$$A_{n+1} = f \cdot \frac{P^a_{n+1} \cdot a_{n+1}}{\pi} ; \quad B_{n+1} = f \cdot \frac{P^b_{n+1} b_{n+1}}{\pi}, \text{ etc.,}$$

the relation

$$\frac{A_{n+1}}{B_{n+1}} = \frac{P^a_{n+1}}{P^b_{n+1}} \cdot \frac{a_{n+1}}{b_{n+1}} = a \cdot \frac{a_{n+1}}{b_{n+1}}$$

is independent of the value of f.

The calculation of the values of a_{n+1}, b_{n+1}, etc., by equations 71 and 72 will not be affected by the value of f. The only difference will be that $f \cdot P^a_{n+1}$ will appear instead of the term P^a_{n+1}, and the temperature thus determined will be different.

For the exhausting column the calculation is similar. If the composition on the mth plate is known, the composition of the vapour rising from that plate is known, that is, the values of $\bar{A}_m, \bar{B}_m$, etc. From equations 47 the values of $\bar{a}_{m+1}, \bar{b}_{m+1}$, etc., are found. The next step is to find the composition of the vapour rising from the $(m+1)^{th}$ plate, the temperature of which is unknown. Since

$$\bar{A}_{m+1} + \bar{B}_{m+1} + \bar{C}_{m+1} + \bar{D}_{m+1} + \bar{E}_{m+1} = 1,$$

substituting from equations 48 gives

$$\frac{P^a_{m+1} \bar{a}_{m+1}}{\pi} + \frac{P^b_{m+1} \bar{b}_{m+1}}{\pi} + \frac{P^c_{m+1} \bar{c}_{m+1}}{\pi} + \frac{P^d_{m+1} \bar{d}_{m+1}}{\pi}$$
$$+ \frac{P^e_{m+1} \bar{e}_{m+1}}{\pi} = 1 \ldots (73)$$

Instead of solving this equation by assuming different temperatures and substituting the corresponding vapour pressures in equation 73 until the correct solution is obtained, we may introduce the relative volatilities as before.

This gives

$$\frac{P^a_{m+1}}{\pi}\left(\bar{a}_{m+1}+\frac{\bar{b}_{m+1}}{\alpha}+\frac{\bar{c}_{m+1}}{\alpha\beta}+\frac{\bar{d}_{m+1}}{\alpha\beta\gamma}+\frac{\bar{e}_{m+1}}{\alpha\beta\gamma\delta}\right)=1$$

$$\dots\dots\dots(74)$$

from which P^a_{m+1} is found directly.

By another method the composition from plate to plate can be calculated for both the concentrating and the exhausting columns without the intermediate steps of calculating the vapour compositions, as was done in the above method.

From the equations for the concentrating column

$$\frac{R\,a_n+a_p}{R\,b_n+b_p}=\frac{A_{n+1}}{B_{n+1}}=a.\frac{a_{n+1}}{b_{n+1}}\;;\quad\frac{R\,b_n+b_p}{R\,c_n+c_p}=\beta.\frac{b_{n+1}}{c_{n+1}},$$

etc.,

we obtain a series of relations

$$\frac{R\,a_n+a_p}{R\,b_n+b_p}=a.\frac{a_{n+1}}{b_{n+1}}\;;\quad\frac{R\,a_n+a_p}{R\,c_n+c_p}=a\beta.\frac{a_{n+1}}{c_{n+1}}\;;$$

$$\frac{R\,a_n+a_p}{R\,d_n+d_p}=a\beta\gamma.\frac{a_{n+1}}{d_{n+1}},\text{ etc.}$$

These values of b_{n+1}, c_{n+1}, etc., are then substituted in the equation

$$a_{n+1}+b_{n+1}+c_{n+1}+d_{n+1}+e_{n+1}=1$$

Then $a_{n+1}=$

$$\frac{R\,a_n+a_p}{(R\,a_n+a_p)+a\,(R\,b_n+b_p)+a\beta\,(R\,c_n+c_p)+a\beta\gamma\,(R\,d_n+d_p)+a\beta\gamma\delta\,(R\,e_n+e_p)}$$

or

$$a_{n+1}=\frac{R\,a_n+a_p}{R\,\Sigma_n+\lambda}$$

where $\quad\Sigma_n=a_n+a\,b_n+a\beta\,c_n+a\beta\gamma\,d_n+a\beta\gamma\delta\,e_n$

and $\quad\lambda=a_p+a\,b_p+a\beta\,c_p+a\beta\gamma\,d_p+a\beta\gamma\delta\,e_p$

Similarly, $\quad b_{n+1}=\dfrac{a\,(R\,b_n+b_p)}{R\,\Sigma_n+\lambda}$

$$c_{n+1}=a\beta\,\frac{(R\,c_n+b_p)}{R\,\Sigma_u+\lambda}\dots\dots\dots(74A)$$

Etc., etc.

From these equations the composition on the $(n+1)^{th}$ plate is found when the composition on the nth plate is given. From the values of a_{n+1}, b_{n+1}, etc., thus found, the new value of Σ_{n+1} is obtained and the calculation repeated for the next plate. The term λ is a constant.

For the exhausting column the equations are

$$(R\,P+q\,F)\,\bar{a}_{m+1}-W\,a_w=(R\,P+q\,F-W)\,\bar{A}_m$$

$$(R\,P+q\,F)\,\bar{b}_{m+1}-W\,b_w=(R\,P+q\,F-W)\,\bar{B}_m$$

and $\quad\dfrac{\bar{A}_m}{\bar{B}_m}=a.\dfrac{\bar{a}_m}{\bar{b}_m}=\dfrac{(R\,P+q\,F)\,a_{m+1}-W\,a_w}{(R\,P+q\,F)\,\bar{b}_{m+1}-W\,b_w}$

Denoting the constant quantitiy

$$\frac{W}{R\,P+q\,F}$$

by μ, then

$$\frac{\bar{a}_{m+1}-\mu\,a_w}{\bar{b}_{m+1}-\mu\,b_w}=a.\frac{\bar{a}_m}{\bar{b}_m}.$$

Similarly

$$\frac{\bar{b}_{m+1}-\mu\,b_w}{\bar{c}_{m+1}-\mu\,c_w}=\beta.\frac{\bar{b}_m}{\bar{c}_m}\text{ , etc.}$$

and

$$\frac{\bar{a}_{m+1}-\mu\,a_w}{\bar{c}_{m+1}-\mu\,c_w}=a\beta\frac{\bar{a}_m}{\bar{c}_m}$$

Now $(\bar{a}_{m+1}-\mu\,a_w)+(\bar{b}_{m+1}-\mu\,b_w)+\dots.(\bar{e}_{m+1}-\mu\,e_w)$

$$=1-\mu$$

since $\quad\bar{a}_{m+1}+\bar{b}_{m+1}+\dots.+\bar{e}_{m+1}=1$

and $\quad a_w+b_w+\dots.+e_w=1$

Substituting in the above equation for all the other components in terms of component a, gives

$$\bar{a}_{m+1}-\mu a_w=\frac{\bar{a}_m(1-\mu)}{\bar{a}_m+\dfrac{\bar{b}_m}{a}+\dfrac{\bar{c}_m}{a\beta}+\dfrac{\bar{d}_m}{a\beta\gamma}+\dfrac{\bar{e}_m}{a\beta\gamma\delta}}$$

or $\quad\bar{a}_{m+1}=\dfrac{a\beta\gamma\delta(1-\mu)\bar{a}_m}{\Sigma^1_m}+\mu a_w\;\;\dots\;(75)$

where $\quad\Sigma^1_m=a\beta\gamma\delta\bar{a}_m+\beta\gamma\delta\bar{b}_m+\gamma\delta\bar{c}_m+\delta\bar{d}_m+\bar{e}_m$

Similarly

$$\bar{b}_{m+1}=\frac{\beta\,\gamma\,\delta\,(1-\mu)\,\bar{b}_m}{\Sigma^1_m}+\mu\,b_w\;\dots\dots\dots(75)$$

$$\bar{c}_{m+1}=\frac{\gamma\,\delta\,(1-\mu)\bar{c}_m}{\Sigma^1_m}+\mu\,c_w\;\dots\dots\dots(75)$$

Etc., etc.

From these equations the composition on the $(m+1)^{th}$ plate is found when the composition on the mth plate is known. The application of the above equations to a numerical example is not so laborious as might appear, for, at different parts of the column, various components are present only in negligible quantities and may be neglected.

In making the above calculations, those high-boiling constituents, not specified in the distillate, will not appear in the calculations relating to the concentrating column. Similarly, those low-boiling constituents, not specified in the residue, will not appear in the calculations for the exhausting column. The manner in which these can be allowed for is as follows. In the example of hexane, heptane, etc., taken it was found, using a reflux ratio of 3, and calculating from the top of the column in the manner described, that the compositions for the 6th and 7th plates from the top were as follows :—

Plate.	a	b	c	d	e
6th from top ..	0·091	0·610	0·299	—	—
7th from top ..	0·079	0·492	0·429	—	—
10th from bottom ..	—	0·481	0·377	0·082	0·060

The 7th plate from the top is the feed-plate, since the value of b and c for that plate satisfy relations 64 and 65.

Calculating from the bottom gives the composition on the 10th plate from the bottom as shown. The ratios of b to c, found from the two calculations, are approximately equal, so that the 10th plate from the bottom is the feed-plate and the column has 16 plates in all. The ratio of b to c does not exactly coincide in the two calculations, which only means that a slightly different reflux ratio would be required to

give the separation specified, or that the reflux ratio of 3 which was chosen would actually give a slightly better separation than that specified when 16 plates are used. The liquid on the feed-plate, found by calculation from the top of the column, should contain components d and e in the amounts 0·082 and 0·060 respectively. Reducing the other components proportionately to allow for these amounts would give as the composition of the liquid on the feed-plate : a=0·068, b=0·422, c=0·368, d=0·082, e=0·060. This method of reduction is justified as the relative proportions of a, b, c in the vapour will remain substantially unchanged when their relative proportions in the liquid remain the same.

Now for two adjacent plates in the concentrating column we have

$$\gamma \cdot \frac{c_{n+1}}{d_{n+1}} = \frac{Rc_n + c_p}{Rd_n + d} \text{ and } \delta \cdot \frac{d_{n+1}}{e_{n+1}} = \frac{Rd_n + d_p}{Re_n + e_p}$$

Since c_p, d_p and e_p are all small, these equations may be written

$$\gamma \cdot \frac{c_{n+1}}{d_{n+1}} = \frac{c_n}{d_n} \text{ and } \delta \cdot \frac{d_{n+1}}{e_{n+1}} = \frac{d_n}{e_n}$$

Using these equations to find the values of d_n and e_n on the 6th plate from the top gives $d_6 = 0·032$ and $e_6 = 0·011$. Reduction of the amounts of a, b, c, previously found to make the sum of all components equal to unity gives $a_6 = 0·087$, $b_6 = 0·584$, $c_6 = 0·286$, $d_6 = 0·032$, $e_6 = 0·011$. This method may also be used to allow for the presence of component a in the exhausting column.

For this part of the column

$$\alpha \cdot \frac{\bar{a}_m}{\bar{b}_m} = \frac{(RP + qF)\bar{a}_{m+1} - Wa_w}{(RP + qF)\bar{b}_{m+1} - Wb_w}$$

or, since a_w and b_w are both small

$$\alpha \frac{\bar{a}_m}{\bar{b}_m} = \frac{\bar{a}_{m+1}}{\bar{b}_{m+1}}$$

When the number of plates has been calculated for a given reflux ratio and the minimum reflux and minimum number of plates have been found, the number of plates for any other reflux ratio can be calculated with fair accuracy by the following method. If a series of results for the number of plates is plotted against the corresponding reflux ratios, a curve is obtained which has two asymptotes, namely,

$$R = R_m \text{ and } N = N_m$$

where R_m is the minimum reflux and N_m is the minimum number of plates.

Assuming this curve to be a rectangular hyperbola, its equation is

$$(R - R_m)(N - N_m) = c^2$$

If one value of R and N has been found the constant, c^2 is determined and the value of N for any other value of R is known.

Since the above was written, the writer finds that equations similar to 53A, for the minimum number of plates, and 60, for the minimum reflux, have been published by Fenske.[44] Fenske makes equation 60 applicable to all conditions of the feed, but it has been shown that it only holds when the feed is all liquid and that for other cases equations 59 or 61 must be used. The same author gives equations for calculating the number of plates required with a given reflux R, which are derived as follows.

The equations for the concentrating column for components b and c, between which the cut is made, are

$$(R+1) B_{n+1} = Rb_n + b_p \text{ and } (R+1) C_{n+1} = Rc_n + c_p$$

The first of these may be written

$$1 - \frac{b_p}{(R+1) B_{n+1}} = \frac{Rb_n}{(R+1)b_{n+1}} = \theta$$

It is assumed that θ is approximately a constant quantity, which is equivalent to assuming B_{n+1} constant throughout the column. θ will obviously vary less as R is greater, and the assumption will then be more justifiable.

Since

$$(R+1) C_{n+1} = Rc_n + c_p$$

$$\therefore \frac{C_{n+1}}{B_{n+1}} = \frac{Rc_n + c_p}{(R+1)B_{n+1}} = \frac{Rb_n}{(R+1)B_{n+1}} \cdot \frac{c_n}{b_n} + \frac{b_p}{(R+1)B_{n+1}} \cdot \frac{c_p}{b_p}$$

or

$$\frac{1}{\beta} \cdot \frac{c_{n+1}}{b_{n+1}} = \theta \cdot \frac{c_n}{b_n} + (1-\theta) \cdot \frac{c_p}{b_p}$$

This gives a linear relationship between $\frac{c_{n+1}}{b_{n+1}}$ and $\frac{c_n}{b_n}$ and by applying this equation to successive plates

$$\frac{c_n}{b_n} = (\beta\theta)^{n-1} \frac{c_1}{b_1} + \frac{\beta(1-\theta)}{\beta\theta - 1} \left\{ (\beta\theta)^{n-1} - 1 \right\} \frac{c_p}{b_p}$$

The composition of the liquid on the nth plate is thus found in terms of that on the top plate. A similar equation can be derived for the exhausting column.

These equations are admittedly convenient for calculation, but to assume generally that θ is constant appears open to question. A modification of this method, which would eliminate this objection, would be to apply it to the other component c, which is usually present in the product in small amount only.

Then

$$\frac{Rc_n}{(R+1)C_{n+1}} = 1 - \frac{c_p}{(R+1)C_{n+1}} = \phi$$

Since c_p is small, the quantity ϕ will be nearly equal to unity for all plates except the top two or three of the column, where C_{n+1} is also quite small.

Then

$$\frac{B_{n+1}}{C_{n+1}} = \frac{Rb_n + b_p}{(R+1)C_{n+1}} = \frac{Rc_n}{(R+1)C_{n+1}} \cdot \frac{b_n}{c_n} + \frac{c_p}{(R+1)C_{n+1}} \cdot \frac{b_p}{c_p}$$

or

$$\beta \cdot \frac{b_{n+1}}{c_{n+1}} = \phi \cdot \frac{b_n}{c_n} + (1-\phi) \frac{b_p}{c_p}$$

from which

$$\frac{b_n}{c_n} = \left(\frac{\phi}{\beta}\right)^{n-1} \frac{b_1}{c_1} + \frac{1-\phi}{\phi - \beta} \left\{ \left(\frac{\phi}{\beta}\right)^{n-1} - 1 \right\} \frac{b_p}{c_p}$$

This equation would give a good approximation except for the top two or three plates, for which the

calculation should be made by one of the more accurate methods.

In either case it is necessary to use an average value of θ or ϕ for the column. Fenske suggests determining the value at the top of the column and at the feed-plate, on the assumption that the composition of the liquid on that plate is the same as that of the feed. How incorrect this assumption may be is shown by the calculations given for the mixture of hexane, heptane, etc. The actual figures are

	a	b	c	d	e
Feed	0·310	0·266	0·187	0·125	0·112
Liquid on feed-plate (R=3)	0·068	0·422	0·368	0·082	0·060
Liquid on feed-plate (R=∞)	0·005	0·483	0·511	0·001	—

Fenske states that a complex mixture can be treated as a binary mixture of the two components between which the cut is made. For a binary mixture the equations for the concentrating column for the two components are

$$(R+1)\, X_{n+1} = R\, x_n + x_p \text{ and}$$
$$(R+1)\,(1 - X_{n+1}) = R\,(1-x_n) + (1-x_p).$$

Dividing one equation by the other gives

$$\frac{X_{n+1}}{1-X_{n+1}} = \frac{R\, x_n + x_p}{R\,(1-x_n)+(1-x_p)}$$

For a mixture of more than two components the corresponding relation for components b and c is

$$\frac{B_{n+1}}{C_{n+1}} = \frac{R\, b_n + b_p}{R\, c_n + c_p}$$

or

$$\frac{\dfrac{B_{n+1}}{B_{n+1}+C_{n+1}}}{1-\dfrac{B_{n+1}}{B_{a+1}+C_{n+1}}}$$

$$= \frac{\left(\dfrac{b_n+c_n}{b_p+c_p}\right) R.\, \dfrac{b_n}{b_n+c_n} + \dfrac{b_p}{b_p+c_p}}{\left(\dfrac{b_n+c_n}{b_p+c_p}\right) R \left(1-\dfrac{b_n}{b_n+c_n}\right) + 1 - \dfrac{b_p}{b_p+c_p}}.$$

In the equivalent binary mixture of b and c, the ratio of the two components being the same, we should have

$$X_{n+1} = \frac{B_{u+1}}{B_{n+1}+C_{n+1}}, \quad x_n = \frac{b_n}{b_n+c_n} \text{ and } x_p = \frac{b_p}{b_p+c_p}$$

The complex mixture could thus be treated as a binary mixture, but with a varying reflux ratio equal to $\dfrac{R\,(b_n+c_n)}{b_p+c_p}$ and this reflux ratio would vary from plate to plate and would depend on the other components present. The comparison between the binary mixture and the more complex mixture cannot be justified as a generalisation, and is only legitimate for total reflux and minimum reflux.

SIDESTREAMS.

In the methods of calculation described it has been assumed that the material entering the column is all drawn off as distillate or residue, but with complex mixtues certain components reach maximum concentrations on certain plates, as shown in Fig. 14, and by drawing off liquid from these plates as sidestreams, products can be obtained which contain a large proportion of such components. The purity of the product so obtained depends on the mixture being fractionated, and sometimes high concentrations can be attained. Fig. 14 shows that a product containing 93% of octane could be drawn off at the tenth plate from the top.

For total reflux $b_n = B_{n+1} = \dfrac{P^b_{n+1} \cdot b_{n+1}}{\pi}$. If $P^b_{n+1} > \pi$, then $b_n > b_{n+1}$ and if $P^b_{n+1} < \pi$, then $b_n < b_{n+1}$, and if $P^b_{n+1} = \pi$, then $b_n = b_{n+1}$. Each component will therefore reach a maximum concentration on a plate, the temperature of which is equal to the boiling point of that component at the
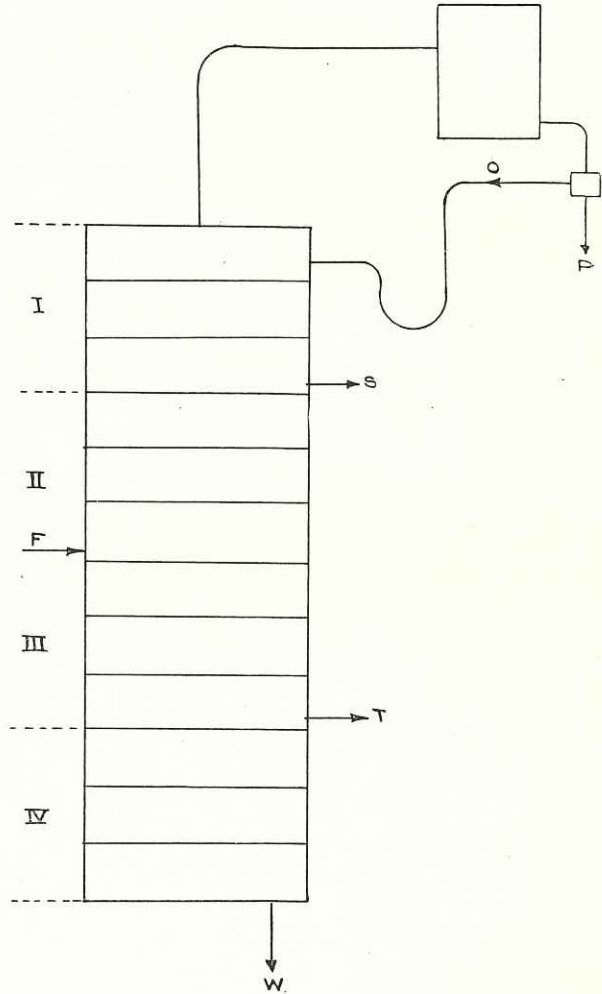

FIG. 17.

pressure in the column. Every component which has a boiling point between the boiling points of the distillate and the residue will reach such a maximum.

A sidestream draw-off is widely used industrially. For example, in the petroleum industry. The methods already described can be applied to such cases with very slight modification.

Fig. 17 shows diagrammatically a column with two sidestreams, one in the exhausting column and one

in the concentrating column. For the four portions of the column shown in Fig. 17, the following equations can be derived by taking material balances across a suitable section for each portion of the column. The equations are given only for component a but exactly similar equations apply for each of the other components. The amounts of the sidestreams are denoted by S and T and their compositions by a_s, b_s, etc., and a_t, b_t, etc.

For Part I of the column

$$(O+P) A_{n+1} = Oa_n + Pa_p$$
$$\text{or } (R+1) A_{n+1} = Ra_n + a_p \quad \ldots\ldots\ldots\ldots(76)$$

where R is the reflux in the top portion of the column.

For Part II of the column,

$$(O + P) A_{n+1} = (O-S) a_n + Sa_s + Pa_p$$

Writing this equation in the form

$$\left(\frac{O-S}{S+P} +1\right)A_{n+1} = \frac{O-S}{S+P}\cdot a_n + \frac{Sa_s+Pa_p}{S+P} \quad \ldots\ldots(77)$$

and comparing it with the standard form $(R+1)A_{n+1}$ $=Ra_n+a_p$ it is obvious that this is the same as the equation for a concentrating column with a reflux ratio of $\frac{O-S}{S+P}$ giving a product of composition $\frac{Sa_s+Pa_p}{S+P}$ which is the average composition of the total material taken off above this part of the column.

For part III. of the column

$$(O-S + qF)a_{m+1} = (O-S+qF-T-W) A_m + Ta_t + Wa_w$$

Putting this equation in the form

$$\left\{\frac{O-S}{S+P}\cdot (S+P) + qF\right\}a_{m+1} = \left\{\frac{O-S}{S+P}\cdot (S+ P)+\right.$$

$$\left. qF-(T+W)\right\}A_m+(T+W)\cdot \frac{Ta_t+Wa_w}{T+W}$$

and comparing this with the standard equation for the exhausting column

$$(RP+qF) a_{m+1}=(RP+qF-W)A_m+Wa_w$$

shows that it represents an exhausting column producing a residue equal to (T+W) with a composition $\left(\frac{Ta_t+Wa_w}{T+W}\right)$ which is the average composition of the total material taken off below this portion of the column. The reflux ratio in the corresponding concentrating column is $\frac{O-S}{S+P}$ and the distillate (S+P).

For part IV. for the column

$$(O-S-T+qF)a_{m+1}=(O-S-T+qF-W)A_m+Wa_w$$

This may be written in the form

$$\left\{\frac{O-S-T}{P+S+T}\cdot (P+S+T)+qF\right\}a_{m+1}= \left\{\frac{O-S-T}{P+S+T}\cdot\right.$$

$$\left. (P+S+T)+qF-W\right\}A_m+Wa_w\ldots\ldots(79)$$

Comparing this with the standard equation for an exhausting column shows that this is the same as the equation for an exhausting column giving a residue W with a composition a_w, the corresponding concentrating column producing a product of the amount (P+S+T) and having a reflux ratio of $\left(\frac{O-S-T}{P+S+T}\right)$.

All the above equations are thus reducible to the standard forms. For a concentrating column with a number of sidestreams, the equation at any section is the same as that for a concentrating column without sidestreams, but giving a distillate equal in amount to the sum of the distillate and all sidestreams above that point, this distillate having the average composition of all the material taken off as distillate or sidestreams above that point. The reflux is equal to the reflux at the top of the column less the amount of the sidestreams. Similarly, for an exhausting column, the equation at any section is the same as that for an exhausting column without sidestreams, giving a residue equal in amount to the sum of the residue and all sidestreams below this point, and having a composition equal to the average composition of all material taken off as residue or sidestreams below that point. All sidestreams taken off above this point, whether in the exhausting or concentrating column, are to be reckoned with the distillate to give an equivalent distillate of the same total amount and average composition. The equivalent reflux ratio R to be used in equations 47 is obtained by subtracting from the reflux at the top of the column the amount of all the sidestreams above the point in question and dividing this by the sum of the distillate and all the sidestreams above this point.

With these modifications the methods described for a column producing only distillate and residue can be applied to a column where sidestreams are drawn off. The minimum number of plates required with total reflux is not affected by any sidestreams and depends only on the compositions of the distillate and residue. All the equations 76 to 79 given above for the different parts of the column reduce in this case to $A_{n+1}=a_n$, and the number of plates required is obtained from equation 54 or 55. The minimum reflux ratio determined from equations 59, 60 or 61 will be the minimum reflux ratio required at the feed section of the column. The reflux required at the top of the column will be the reflux at this section plus the amount of all the sidestreams above it. The values of b_p and c_p to be taken in equations 59, 60 and 61 will be the average values for the distillate plus all the sidestreams above the feed.

With the same modification, equations 63 to 65 for the composition of the liquid on the feed-plate can be used.

When making a test on a column in operation the amount and composition of each sidestream is known and equations similar to equations 76 to 79 are then available for calculating the theoretical number of plates required. When designing a column the amount and composition of the sidestreams which it would be possible to obtain have to be calculated. A general idea of the type of product will be given by the calculation of plate compositions for total reflux, but with any lower reflux ratio the fractionation will be less effective and the separation of the different components less sharp. The actual calculation is made by starting from the top of the column and the bottom of the column and by assuming values of P and W and taking off a sidestream where a suitable

composition is reached. The amounts and compositions of these sidestreams must satisfy the equations

$$F = P + W + S + T + \ \ldots\ldots\ldots\ldots\ldots$$
$$Fa_f = Pa_p + Wa_w + Sa_s + Ta_t + \ \ldots\ldots\ldots$$
$$Fb_f = Pb_p + Wb_w + Sb_s + Tb_t + \ \ldots\ldots\ldots$$
$$Fc_f = Pc_p + Wc_w + Sc_s + Tc_t + \ \ldots\ldots\ldots$$

and similar equations for all the components of the mixture.

MIXTURES CONTAINING A VERY LARGE NUMBER OF COMPONENTS.

In the treatment of complex mixtures given above, it has been assumed that the mixture consisted of a definite number of components in definite proportions. Where the number of components becomes very large with a small variation in boiling-point between one component and the next, as in the mixtures treated in the petroleum industry, with the exception of natural gasoline, the composition is then usually expressed by the " true boiling point curve." This curve represents the relation between the boiling-point of the instantaneous distillate and the total amount distilled when the mixture is distilled with efficient fractionation and corresponds to a mixture containing an infinite number of components, the boiling-points of which vary infinitesimally. The amount of a component of a given boiling-point in the mixture is proportional to the slope of the tangent to the curve at that temperature. The fractionation of such mixtures can be dealt with by the methods described by dividing the true boiling-point curve into a number of small sections, and assuming that each of these sections is an individual component with a boiling-point equal to the average boiling-point for that section.

Where steam is used in the distillation of such mixtures, its effect is to reduce the pressure under which the distillation is taking place. As the relative volatility of two components varies very slightly with this reduction in pressure, the calculations by the methods described will not be affected by this modification, except that slightly different values for the relative volatilities might have to be taken. The composition of the liquids on the various plates, the number of plates required for a given reflux ratio, the minimum reflux ratio and the minimum number of plates will only be affected to this slight extent. The temperatures on the plates will, of course, be affected materially, and the necessary allowance is easily made when the partial pressure of the steam is known.

FACTORS AFFECTING PLATE EFFICIENCY.

The interaction between the vapour passing through a plate and the liquid on that plate, involves transfer of material and heat between the vapour and liquid, and this may take place in two ways. With an alcohol-water mixture we may imagine alcohol diffusing from the liquid into the vapour and water diffusing from the vapour into the liquid. Alternatively we may imagine a part of the vapour containing both alcohol and water condensing, and part of the liquid, containing both alcohol and water,

evaporating. In the latter case the amount of material and heat to be transferred would be greater than in the former case. The extent to which either of these mechanisms is actually involved in practice is almost entirely a matter of conjecture. All that can be said with certainty is that the second mechanism, involving condensation and evaporation of both components must take place where heat is transferred through the plate from the vapour below it to the liquid on it.

The interaction between liquid and vapour will thus depend on the physical properties of the mixture being fractionated as well as on the constructional details of the column. For this reason the published results of determinations of plate efficiency vary considerably. Without entering into the question of plate design, a brief summary of some of the published results may indicate these variations. In all cases " overall plate efficiency " is meant unless otherwise mentioned. Peters[30] found, for the same column, an efficiency of 45% for a mixture of acetic acid and water, and 70% for a mixture of alcohol and water containing less than 90% alcohol by weight, the efficiency decreasing as the strength of the alcohol increased. For perforated plates or bubbler-cap plates the efficiency was about the same with equal depths of liquid and equal areas of slots and perforations. Thormann,[14] by calculation from the experiments of Lühder and Kilp[31] on an alcohol still, found individual plate efficiencies of about 70%, 80% and 100% for the upper, middle and lower plates of the exhausting column respectively, and from 30 to 50%, 70 to 90% and 90 to 100% for the lower, middle and upper plates of the concentrating column. These results are in contradiction to those of Peters for the higher strengths of alcohol. In both cases the results are probably affected by the accumulation of fusel oil on the lower plates of the concentrating column. Shirk and Montonna[32] found that the plate efficiency decreased almost linearly as the rate of distillation increased with the reflux ratio constant, and that the plate efficiency increased almost linearly with the reflux ratio, when the rate of distillation remained the same. On the other hand, Badger and McCabe[33] state that " the plate efficiency diminishes to a substantially constant quantity as the vapour velocity increases, but is apparently independent of reflux ratio." Robinson,[34] in a test on an alcohol still, found plate efficiencies varying from 24 to 56%, but points out that these figures were based on an assumed value of 0·0001 mol. fraction of alcohol in the effluent. Kirschbaum[35] found plate efficiencies of 19 to 23% for plates of a somewhat unusual design. Lewis and Wilde,[26] using the method previously mentioned, for testing a petroleum still found an average figure of 65% for the " individual plate efficiency " in the concentrating column. The corresponding figure for the exhausting column was 80%, but the authors regard this figure as less reliable than that given for the concentrating column. Lewis and Smoley,[36] using the same method found plate efficiencies of between 85 and 95% for petroleum mixtures, and state that more complex mixtures appear to give higher plate

efficiencies than binary mixtures. Thus the same column, which gave 59% for a benzol-toluol mixture, gave 75% for a mixture of benzol, toluol and xylol. Robinson[16] quotes some results of Carey, which show that the plate efficiency increases with the depth of liquid on the plate and is practically independent of the design of the slots in the bubber-cap except at very low velocities. Practically none of the above authors state what equilibrium data were assumed in calculating the plate efficiency, so that it is impossible to tell how comparable the different results are. For mixtures of more than two components it is possible that the plate efficiency may be different for different components. As there is no information on this point it is customary to assume the same plate efficiency for all components of a mixture.

One factor affecting the plate efficiency, which hardly appears to have been investigated, is the entrainment of liquid from one plate to another. Obviously any such entrainment will affect the plate efficiency both by reducing the actual amount of reflux and by diluting the liquid on the upper plate. Some experiments made by the writer on a 9 in. dia. column with rectangular bubber-caps indicate that this factor may be an appreciable one even at moderate vapour velocities. The method used was to blow air through the column and to run in water at the top to represent the vapour and reflux respectively in a fractionation and to run a salt solution on to one of the plates of the column. From determinations of the concentration of salt on plates above the feed the amount of entrainment can be easily calculated, since the salt can only be present on these plates through entrainment of the liquid from the plates below. These experiments are being continued, and it is hoped to publish the results in due course.

The influence of entrainment on plate efficiency may be seen from the following analysis for total reflux.

Equation 49 given by Lewis and Wilde[26] gives, for total reflux, with an "individual plate efficiency" e

$$B_n - B_{n+1}(1-e) = \frac{efP_n^b}{\pi} \cdot B_{n+1}$$

$$C_n - C_{n+1}(1-e) = \frac{efP_n^c}{\pi} \cdot C_{n+1}$$

Dividing one equation by the other,

$$\frac{B_n - B_{n+1}(1-e)}{C_n - C_{n+1}(1-e)} = \frac{P_n^b}{P_n^c} \cdot \frac{B_{n+1}}{C_{n+1}} = \beta \cdot \frac{B_{n+1}}{C_{n+1}}$$

For total reflux

$$B_n = b_{n-1}, \quad C_n = c_{n-1}, \quad B_{n+1} = b_n, \quad C_{n+1} = c_n,$$

so that $\quad \dfrac{b_{n-1} - b_n(1-e)}{c_{n-1} - c_n(1-e)} = \beta \cdot \dfrac{b_n}{c_n}$ ....(81)

Considering the case where equilibrium is reached on each plate, but an amount of liquid ψ is entrained in unit time from one plate to the next, material balances at a section between the $(n-1)^{th}$ and the nth plates give, V being the amount of vapour and O the reflux per unit time,

$$V + \psi = O$$
$$VB_n + \psi b_n = Ob_{n-1}$$
$$VC_n + \psi c_n = Oc_{n-1}$$

or $\quad \dfrac{B_n}{C_n} = \dfrac{Ob_{n-1} - \psi b_n}{Oc_{n-1} - \psi c_n}$

i.e., $\quad \beta \cdot \dfrac{b_n}{c_n} = \dfrac{b_{n-1} - \dfrac{\psi}{O} \cdot b_n}{c_{n-1} - \dfrac{\psi}{O} \cdot c_n}$ .... (82)

Comparison of equations 81 and 82 shows that both equations will be the same if :—

$$1 - e = \frac{\psi}{O}$$

or $\quad e = 1 - \dfrac{\psi}{O}$ .... (83)

A perfect plate where entrainment occurs will thus show a loss of efficiency equal to the ratio of the amount of liquid entrained to the amount of reflux. The experiments referred to above showed that this ratio might easily reach the order of from 10 to 20%, so that the question of entrainment would appear to be one requiring serious consideration in plate design. The effect of entrainment will obviously decrease as the reflux ratio and consequently the enrichment from plate to plate decrease until finally with minimum reflux the effect will be zero as the composition on two adjacent plates is then the same. The minimum reflux ratio required would be increased by the amount of entrainment.

PACKED COLUMNS.

The theory of packed columns has not been generally investigated to the same extent as the theory of plate columns. A commonly used criterion of the fractionating efficiency of a packed column is that suggested by Peters,[30] namely, "the height equivalent to one theoretical plate."

This is obtained by dividing the height of the column required to effect a given separation by the number of theoretical plates which would be required for the same separation. With the same packing, this figure varies greatly according to the substances fractionated, and must therefore be specified with reference to a given fractionation. Thus Peters found that the height equivalent to one theoretical plate, using $\frac{1}{4}$ in. Raschig rings, varied from 3·7 in. for an alcohol-water mixture to 10 in. for a benzene-toluene mixture. Thormann[14] uses a similar conception and gives an equation,

$$\frac{dX}{dh} = \frac{X^1 - X}{k}$$ .... (84)

where X is the composition of the vapour at any point in the column,

X^1 is the composition of the vapour which would be in equilibrium with the liquid at the same point in the column,

h is the height of the column,

and k is a constant equivalent to the height equivalent to one theoretical plate.

The height of column required for a given separation is found by graphical integration between the appropriate limits of the equation

$$h = k \int \frac{dX}{X^1 - X}.$$

Kirschbaum[37] has made an interesting analysis of the fractionation in a packed column on the assumption that it depends entirely on heat transfer between liquid and vapour. The increase in concentration up the column is assumed to be brought about by a combination of partial condensation of the vapour and partial evaporation of the liquid at each section of the column. This leads to the equation

$$h = \frac{VL}{K} \int \frac{1}{X^1 - x^1} \cdot \frac{1}{\delta} \cdot \frac{1}{a} \cdot dX$$

In this equation V is the mols of vapour passing per unit time, L the molal latent heat, K a constant expressing the surface area of the packing per unit height of column, X is the composition of the vapour at any point in the column, x^1 is the composition of the liquid with which it would be in equilibrium, and X^1 is the composition of the vapour which would be in equilibrium with the liquid at the same point in the column, δ is the temperature difference between liquid and vapour at that point, and a is the coefficient of heat transfer between liquid and vapour. This equation can be integrated graphically using the equilibrium curve and the boiling-point and condensation curves. As it is based on the assumption that the fractionation is effected by equilibrium condensation of the vapour and equilibrium vaporisation of the liquid, its validity will depend on the extent to which this mechanism predominates over diffusion between liquid and vapour as a means of fractionation. Lack of experimental evidence renders a decision on this point impossible.

The influence on the fractionating efficiency or the height equivalent to one theoretical plate of such factors as size of packing, vapour velocity and reflux ratio has only been investigated to a very limited extent. Peters[30] found that for Raschig rings the height equivalent to one theoretical plate varied directly as the diameter of the packing. On the other hand, Jantzen[38] found a smaller variation than this, the ratio for 10·6 mm. and 4·5 mm. packing being only 1:1·59 while, on the basis of Peters' results it should have been 1:2·36. Jantzen also found that the efficiency of a packed column decreased slightly with increasing vapour velocity and increasing reflux.

One extremely important factor in reducing the efficiency of a packed column is the tendency for the liquid to flow outwards from the centre and collect in the region adjoining the shell of the column. This point has been investigated by Kirschbaum[35], who found that the efficiency could be substantially increased by returning the liquid from the outer to the central portion of the column. This factor will be particularly important in tall columns of large diameter, and insufficient appreciation of it is probably responsible for numerous cases of inferior performances of such columns.

Data for different kinds of packing have been given by Zeisberg[39] and Butcher.[40] A very interesting type of packing is that recently designed by Prof. E. Berl.[41] This so-called "saddle-packing" has many advantages over the commonly used hollow cylinders, for example, larger surface per unit volume, lower resistance to gas or vapour flow, and more intimate contact between liquid and vapour.

DISCONTINUOUS DISTILLATION.

Continuous distillation only has been treated in this paper as it represents the most important industrial aspect of the subject. All the methods of calculation described can obviously be applied to discontinuous distillation, making the necessary allowances for changes in the composition of the distillate and the residue in the kettle as the distillation progresses.

REFLUX CONDENSER.

So far it has been assumed that no fractionation takes place in the condenser, and all the methods of calculation given have been based on this assumption. Considerable discussion, and even controversy, has taken place during the last half century about the part played by the condenser as a fractionating device. Where a single condenser is used to liquefy all the vapour from the column and return part as reflux to the column, the remainder being taken away as distillate, obviously there can be no difference in composition between reflux and product. Where two condensers are used in series, one to effect partial condensation of the vapour and provide reflux for the column and the other to condense the remaining vapour as distillate, the product might be richer than the reflux. Various results have been put forward at different times showing very large differences in composition between the liquid and vapour resulting from partial condensation, but none of these have been expressed on the only logical basis, namely, the number of theoretical plates required to effect the change in composition. For "simple condensation," that is, condensation in which the condensed liquid and the remaining vapour are in equilibrium, the enrichment is only equivalent to one theoretical plate. For a column in which no fractionation takes place in the condenser, at the section between the first and second plates

$$(R+1)\, X_2 = Rx_1 + x_p$$

where x_p is the composition of the vapour in equilibrium with the liquid of composition x_1. If the top plate is now removed and simple condensation takes place in the condenser, R mols. of vapour being condensed for each mol. of vapour passing away as product, then if x_1^1 and x_p^1 are the compositions of the liquid and the vapour thus obtained

$$(R+1)\, X_2 = Rx_1^1 + x_p^1$$

Since equilibrium between vapour and liquid is assumed, the compositions x_1^1 and x_p^1 must be in equilibrium and, comparing the two equations, x_1^1 must equal x_1 and x_p^1 must equal x_p. The reflux to the column and the product will be exactly the same as before. Simple condensation is thus exactly equal to the action of one theoretical plate and, if it is

assumed that the condenser has this effect, one plate less will be required in the column. For " differential condensation," where the liquid is removed from contact with the vapour as soon as it is formed, the difference in composition between the condensate and the remaining vapour will be greater. The relation is then given by the equation

$$\log_e \frac{G_2}{G_1} = -\int_{X_1}^{X_2} \frac{dX}{X-x}$$, where G_1 and G_2 are the

initial and final amounts of liquid and X_1 and X_2 are the initial and final compositions of the vapour. Kirschbaum[42] gives the results of laboratory experiments, which show that partial condensation gave the same results for alcohol-water mixtures as were obtained by calculation from the above equation. The same author gives the results of a test on an industrial condenser, which support this view, but as the condenser in question was a counter-current condenser of the type containing perforated plates it does not appear justifiable to ascribe the fractionation obtained in this condenser to condensation alone. Experiments on the partial condensation of alcohol-water mixtures on a laboratory scale have also been reported by Dehnicke[43], who found that the difference between the compositions of liquid and vapour resulting from partial condensation, expressed as a percentage of the difference in composition between the condensed liquid and the vapour which would be in equilibrium with it, averaged 62%, 56% and 50% in three series of experiments. Dehnicke used the inaccurate equilibrium data of Grœning and recalculating the results using the more accurate data of Bergström gives 77%, 71% and 66%. These figures express the efficiency of the condenser considered as one plate. The differences in results which may be obtained in the laboratory and on the industrial scale can probably be ascribed to the fact that relatively larger quantities of cooling water are usually used in laboratory experiments so that the condensate has a lower temperature and is less likely, once it is formed, to interact with the vapour. Lower vapour velocities would have the same effect. It might, therefore, be possible to approximate to differential condensation, in laboratory experiments. In industrial condensers, where the vapour velocity and the temperature of the condensate would be higher, conditions are more likely to resemble those of simple condensation. It is extremely unlikely that this degree of fractionation is exceeded in any industrial condenser, and is probably only attained when condensing weak mixtures or mixtures of several components so that the condenser at its best will never be equivalent to more than one theoretical plate.

PRACTICAL POINTS IN THE TESTING OF DISTILLATION PLANT.

Before commencing a test it is essential that a definite plan be made covering the objects and conditions of the test, and that this plan be adhered to throughout the test. A test, made on a new plant to ascertain if the manufacturer's guarantees have been fulfilled, will generally be made in the presence of representatives of both the manufacturers and the purchaser of the plant. The procedure should be agreed before commencing the test, and it should be definitely arranged that only one person gives instructions to the personnel operating the plant during the test. With a new type of plant, unfamiliar to the factory personnel, the operating directions would generally be given by the maker's representative, and possibly the actual operators might be temporarily supplied by the makers of the plant if this has been specified in the purchase contract. The function of the factory staff would then be limited to obtaining necessary data during the test, though the men who were to run the plant later would at the same time be on the plant to receive instruction in operating it. Where the plant is one with which the factory staff is already familiar, the maker's representative would normally be present merely as an observer.

The duration of the test should be fixed with regard to local circumstances so that any periodic variations in operating conditions are included in the test period—for example, possible variations in steam or water supply, composition of feed, etc. The actual test should not commence until steady conditions have been attained unless the time required for starting up is one of the factors under guarantee. Where a plant is to be run for limited periods, for example, on account of Excise regulations, the time required for starting-up and shutting-down may be an important point. For stills heated by steam the time required to attain steady operation may be 4–6 hours. For stills heated by direct firing the time required would generally be greater and would be determined mainly by the time required for heating up the brickwork, etc., rather than for bringing the distilling plant proper into operation. A period of 6–8 hours should be regarded as a minimum for the duration of the test. Where automatic control is used to a considerable extent for operating the plant, the test period should be as long as possible in order to test the response of the automatic controls to varying conditions. Before attempting to commence the test, water, steam, etc., should be circulated through the whole system to test all joints, valves and connections, and to make sure that sufficient " breathers " are provided to prevent the possibility of air-locks. All meters, thermometers, pressure gauges, etc., which are to be used during the test should be checked or calibrated beforehand.

If it is desired to test the plant under different sets of conditions, a period of sufficient length should be allowed before altering the conditions so that each period can be regarded as a separate test. For instance, it might be desired to test the plant not only at its normal output, but also to force it to its maximum possible output to determine what losses then take place. In a time of heavy production it is often an economic advantage to obtain additional output at the cost of some loss. In a methanol concentrating still, for example, the feed and output can be increased by reducing the reflux ratio so as to maintain the same permissible vapour velocity. To maintain the same quality of product with the lower reflux ratio necessitates lengthening the concentrating column, that is, lowering the feed, thus

reducing the exhausting column and causing some loss of methanol in the effluent. Up to a certain limit this procedure may be profitable and the limit may be determined by actual test or by calculation, once the plate efficiency is known. Such tests must obviously be carried out separately from tests on normal operation.

The data to be obtained during the test should be sufficient to furnish complete material and heat balances for the plant. It is unsatisfactory to determine important data by difference. Any result deduced in this way will include all the errors of the results used to obtain it. For instance, in a distilling plant producing three products, from the amount of the feed and two of the products the amount of the third product might be obtained by difference, but this figure would be liable to the total errors of the three figures from which it was obtained, there would be no check on the accuracy of those results, and there would be no measurement of the loss of material during the distillation. A balance is necessary not only to show if serious errors exist, but also to indicate the order of the errors involved in the measurements.

For a complete material balance the quantities and compositions of the feed or feeds to the still and all products obtained from it must be determined, a worthless residue such as water being also designated as a product in this sense. Material balances for each component present in the mixture can thus be drawn up. Where live steam is used as a heating medium, its amount will also appear in the material balance. The method used for measuring these quantities will depend on circumstances. Usually storage vessels are available from which the feed is drawn or in which the products are collected, and the weights of these can be obtained from the calibrations of the vessels and the specific gravities. Where one of the products—for example, water—is run to waste this method is not usually available, and a weir or notch or a small collecting tank fitted with an orifice might be used. Any device, such as an orifice or a Venturi meter, which would cause back-pressure on the column, would be inadmissible. Where the effluent runs away hot, precautions must be taken when measuring it to prevent excessive loss by evaporation. The measurement of the effluent is sometimes difficult where there is only a small difference in level between the column outlet and the drain. In addition to determining the total quantities of the feed and products for the test period as described above, it is also desirable to determine the rates of flow at frequent intervals, not only as a check on the measurements, but also to provide an indication of the variations from the average rate. For the products this can usually be done by finding the weight or volume collected in a suitable measuring vessel over a short period. For the feed this will not generally be possible, and the only method would be to use a meter on the feed-pipe. It is important that the product be drawn off at the correct rate ; if too much is drawn off its strength will fall, and if too little is drawn off the concentration of the more volatile component in the residue will ultimately rise. Both cases might lead to the erroneous conclusion that the

fractionation was inadequate. Thermometers placed at suitable points in the column show whether the product is being taken off at the correct rate. The amounts of the different components are obtained from the analyses of the feed and products. Where the products are of high purity the analytical methods may not be sufficiently exact to determine those components present in small amounts with the degree of accuracy required in such cases for the calculation of the plate efficiency of the column. The number of theoretical plates required for any separation increases rapidly with comparatively small changes in composition of a product which contains only a small amount of one of the components. Thus Robinson[34], in a test on an alcohol still, obtained figures of 24%, 40% and 50% for the plate efficiency, assuming the alcohol in the effluent to be 0·0001 mol. fraction, and pointed out that the figure of 70%, which was to be expected from the type of plate used, would require 0·000002 mol. fraction of alcohol in the effluent. As both these quantities are too small to determine by analysis, the data required for calculating plate efficiency would have to be obtained by taking samples from plates some distance away where the amounts present can be determined with reasonable accuracy. This applies also to complex petroleum products, where one of the components at the point of cut is present in small amount, and its amount is estimated by the true boiling-point analysis. For the analysis of the feed and products samples may be taken from the storage vessels, adequate mixing being ensured, or a continuous sample may be drawn throughout the test. Check samples should also be taken at frequent intervals and analysed separately to ascertain the amount of variation from the average.

The thermal balance is made between the heat supplied to the bottom of the column and the following items : the heat used for providing the reflux, the heat carried away by the vapour forming the distillate, the heat required to raise the feed to the temperature of the feed-plate, the heat required to raise the effluent from the feed-plate temperature to its boiling-point, the heat lost by radiation. The reflux heat and the heat of the distillate are obtained by measuring the cooling water used in the respective condensers and observing the rise in temperature. The cooling water is measured by any convenient method such as collecting it over a given time in a storage vessel, using a meter, notch or weir or a tank fitted with an orifice. Where the reflux and the distillate are both obtained from one condenser, the reflux heat is obtained by difference, knowing the amount of the distillate and the heat given up in condensing and cooling to the temperature at which it leaves the condenser. Usually it is not convenient to measure the amount of reflux, and this is obtained by calculation from the heat absorbed in the condenser. If the reflux is measured and it leaves the condenser below its boiling-point, the actual reflux in the column will be greater by the amount of vapour condensed on the top plate in heating the reflux to its boiling-point. This correction is easily made when the amount, temperature and composition of the reflux are known. The reflux as measured by the heat absorbed in the condenser gives the true

reflux in the column, regardless of the temperature at which the reflux actually leaves the condenser. The heat required to raise the feed to its boiling-point is obtained from the amount and temperature of the feed. When the feed enters the column partly as vapour, this amount is negative. Alternatively the heat contained in the feed above its boiling point may be brought in on the other side of the balance as a source of supply of heat. The heat used in raising the effluent from the feed-plate temperature to its boiling-point is obtained from the known temperatures and amount. Radiation losses can only be estimated approximately by calculation or by the difference in the balance. It is desirable to make the calculation, even though approximate, in order to have a check on the other figures. If appreciable, radiation losses should be allowed for in the reflux by adding to the reflux actually found an amount equivalent in latent heat to half the radiation loss. Heat recovered by preheating the feed in the reflux condenser or by heat interchange with the boiling effluent will not appear as a separate item in the heat balances. It is automatically allowed for by the smaller amount of heat required to raise the feed from the temperature at which it enters the column to its boiling-point than would be required without preheating. The amount of heat recovered by such heat interchangers can be reported as a separate item as a criterion of the efficiency of this part of the plant. It can appear implicitly or explicitly in the final figure given for the heat or fuel consumption of the plant per unit weight of product or feed treated.

For a column heated by steam, the steam consumption is obtained by measurement of the condensate when coil heating is used or by metering where live steam is used. When the effluent from the column is water, it is seldom sufficiently accurate to measure the live steam used by the increase in quantity of effluent compared with that calculated from the amounts and compositions of the feed and distillate. When the steam passes into the distillate and is not miscible with it, the amount used can be found by measuring the water condensed and allowing for any water dissolved in the product. In all cases it is essential to measure the dryness fraction of the steam entering the column, using a separating calorimeter or, if the wetness is small, a throttling calorimeter. The sample is best taken on a vertical pipe, not a horizontal one. Neglect to measure the quality of the steam may introduce a serious error. The common assumption that steam which is super-heated at the boiler remains superheated until it enters the column is not always justified.

Where the plant is heated by direct firing, the heat supplied to the column, and not the heat supplied to the furnace unit, is to be taken for the distillation heat balance. For instance, for a tube still, the heat in the material leaving the furnace unit is the relevant figure for the fractionation process. The heat supplied to the furnace unit is important only for the efficiency of that unit, which should be calculated separately. The two figures may be combined to give an overall heat consumption for the whole plant.

The reflux ratio being known from the amounts of the reflux and the product, the number of theoretical plates required for the given separation can be calculated by the methods already described. The actual number of plates divided by this figure gives the "overall plate efficiency." As pointed out previously, it may be desirable to take samples from plates below the top and above the bottom of the column in cases where the product or residue contains only a small amount of a component which is to be used in the calculation. Samples taken at other points in the column are useful as additional checks in the calculations, and indicate whether the plate efficiency varies appreciably in the column. Such samples should be drawn off into the collecting vessel through a small cooler, otherwise the sampling may be vitiated through excessive loss of the more volatile components by evaporation.

When the reflux ratio approaches the minimum for the particular separation, the number of theoretical plates required increases very rapidly with very small changes in the reflux ratio. A small error in the measurement of the reflux ratio would then lead to a much larger error in calculating the plate efficiency. In such a case it would be better to calculate the theoretical reflux ratio required for the actual number of plates, considering them as ideal plates, and take the quotient of this theoretical reflux ratio divided by the actual reflux ratio as an indication of the efficiency of the column. This case occurs rarely in practice. A column cannot be operated satisfactorily with a reflux ratio too near to the minimum, as it would be too sensitive to a small reduction in the reflux ratio.

A most important point in testing a column, but one which is commonly overlooked, is to determine whether the feed is correctly placed in the column. The only satisfactory method of doing this is to take samples of the liquid on the feed-plate and on the plate above it and determine whether their compositions satisfy the conditions for most efficient operation given by relations 63 to 65 or the corresponding ones for binary mixtures. If the liquid-vapour equilibrium data are known for the mixture being treated, a sample of the liquid on the feed-plate alone is sufficient to determine the position of the feed as has already been shown. The other methods of testing whether the position of the feed is correct, namely, altering the feed and noting the effect on the operation of the column or assuming that the ratio of the number of plates in the concentrating column to the number in the exhausting column should be the same as in an ideal column, are more laborious and less accurate. If the feed is wrongly placed, an incorrect result will be obtained for the plate efficiency and the capacity of the column will be reduced on account of the higher reflux ratio required. The common assumption that the liquid on the feed-plate has approximately the same composition as the feed may lead to serious error, particularly where the feed is partly vapour and where a mixture of more than two components is being fractionated.

During the test, observations should be made and recorded of any points bearing on the practical

working or control of the plant. For instance, the arrangement of the controls should be such that steam, water, feed, draw-off, etc., can be controlled

ladders, and sufficient illumination should be provided to render them visible. All important parts of the plant should be readily accessible so that they can
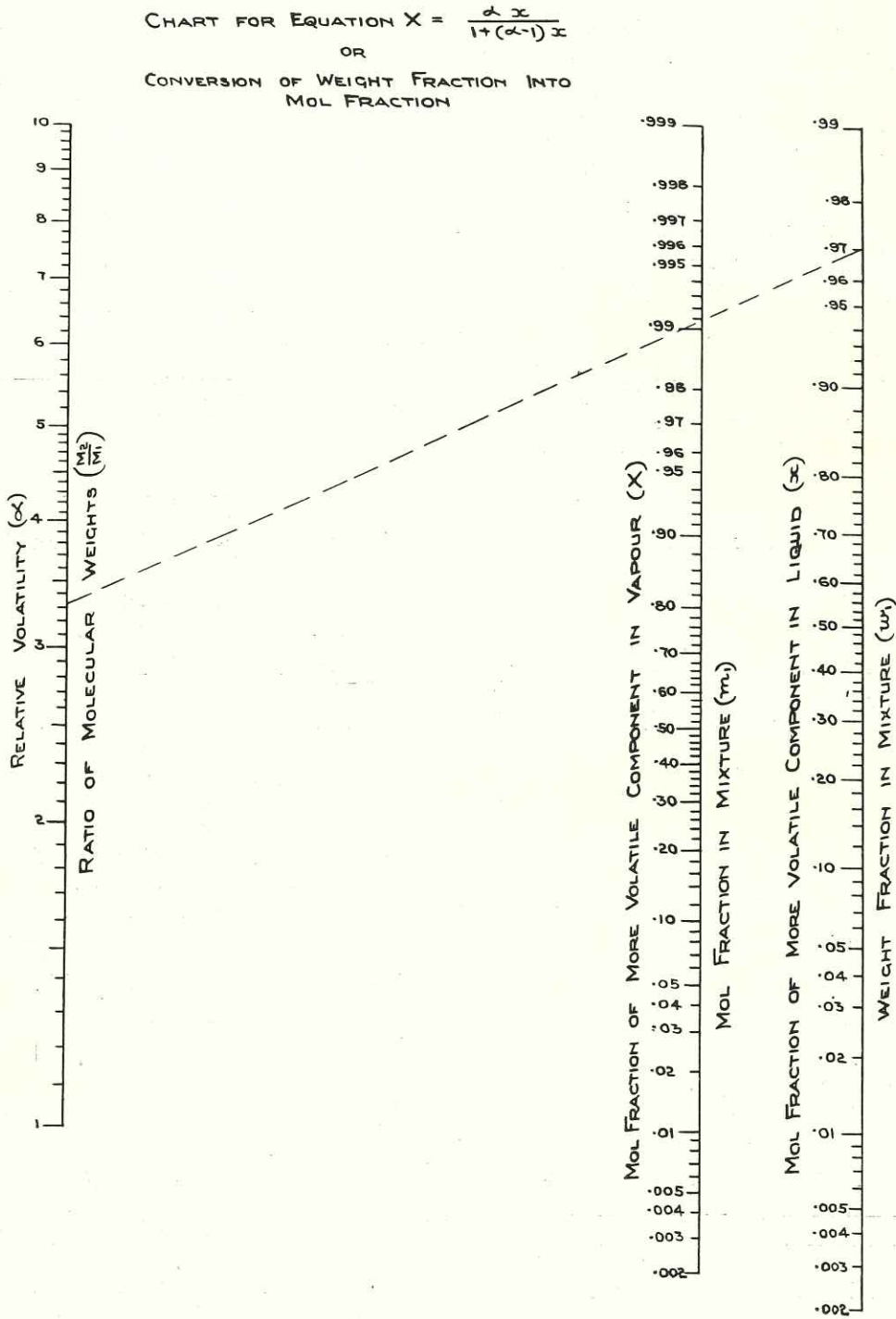
CHART FOR EQUATION $X = \dfrac{\alpha x}{1+(\alpha-1)x}$

OR

CONVERSION OF WEIGHT FRACTION INTO MOL FRACTION

RELATIVE VOLATILITY (α)

RATIO OF MOLECULAR WEIGHTS ($\frac{M_2}{M_1}$)

MOL FRACTION OF MORE VOLATILE COMPONENT IN VAPOUR (X)

MOL FRACTION IN MIXTURE (m.)

MOL FRACTION OF MORE VOLATILE COMPONENT IN LIQUID (x)

WEIGHT FRACTION IN MIXTURE (w.)

FIG. 18.

from one point without the necessity of the operator running about from one floor to the other. Thermometers and pressure gauges should be installed in positions where they can be seen without climbing

be got at without performing gymnastic feats. Where frequent cleaning of the plates or condensers is necessary, the suitability of the arrangements provided for this purpose is important. Variations

K

in the pressure drop through the column during the test may be very important in vacuum distillation. The sensitivity of the plant to small changes in conditions, for example, steam pressure or composition of feed, should be carefully noted. The sensitivity decreases with increasing depth of liquid on the plates and with decreasing vapour velocity. A higher vapour velocity gives a larger throughput relative to to the amount of liquid held in the column, which consequently has a smaller stabilising effect. Where fluctations in conditions are unavoidable, the choice of a column of smaller diameter with higher vapour velocity for reasons of economy may necessitate providing additional plates to ensure efficient separation in all circumstances. If the sensitivity of the plant is too great, the control will be unduly affected by minor fluctuations, and, if it is too small, the time required to effect any change in operation will be unduly great.

Carefully carried out tests on the industrial scale are of great value in elucidating fundamental principles and rendering possible the extension of these principles to practical problems. A more liberal attitude regarding the publication of test results would do much for the progress of distillation by furthering its development as a science based on rational principles, rather than as an art based mainly on tradition and what Sorel aptly terms "*raisonnements alambiqués.*"

Appendix.

In this appendix are given some charts which the writer has found useful for facilitating calculations in various distillation problems. The charts are all constructed on the nomographic principle, which is preferable to the use of rectilinear co-ordinates as the nomographic charts are easier to construct, easier to read and interpolation is more accurate, since it is made along a scale instead of between curves.

Fig. 18 is a chart for the equation $X = \dfrac{ax}{1+(a-1)\,x}$ which represents the relation between the compositions of the vapour and the liquid for a binary mixture where the relative volatility of the two components is a. The same chart can be used for a mixture of two components to convert weight fractions or percentages into mol. fractions. If w_1 is the weight fraction of one component, m_1 its mol. fraction M_1 is its molecular weight and M_2 is the molecular weight of the other component, then :—

$$m_1 = \frac{\dfrac{w_1}{M_1}}{\dfrac{w_1}{M_1} + \dfrac{1-w_1}{M_2}} = \frac{\dfrac{M_2}{M_1} \cdot w_1}{1 + \left(\dfrac{M_2}{M_1} - 1\right) w_1}$$

This equation has exactly the same form as the equation

$$X = \frac{ax}{1+(a-1)x},$$

reading m_1 for X, w_1 for x, and $\dfrac{M_2}{M_1}$ for a. The same chart can therefore be used for both cases. A

line is drawn joining the value of w_1 or x on the right hand scale to the value of $\dfrac{M_2}{M_1}$ or a on the left hand scale. The intersection on the centre scale gives the value of m_1 or X. The dotted line in Fig. 18 shows the construction for a mixture containing 97% by weight of water and 3% of acetic acid. The ratio of the molecular weights is 3·33. From the reading on the centre scale the mol fraction of water in the mixture is 0·9908. The same construction shows that, in a mixture of two components having a relative volatility of 3·33, a liquid containing 0·97 mol fraction of the more volatile component will be in equilibrium with vapour containing 0·9908 mol fraction of that component. The chart is easily constructed by putting the equation $X = \dfrac{ax}{1+(a-1)x}$ in the form :—

$$\log \frac{X}{1-X} = \log a + \log \frac{x}{1-x}.$$

Fig. 19 shows a chart for calculating the minimum number of plates, with total reflux, from equation 54

$$\frac{b_w}{c_w} = \frac{1}{\beta^{n+1}} \cdot \frac{b_p}{c_p}$$

or the corresponding equation 28 for a binary mixture. The equation is charted by the usual method in the form $(n+1)\log \beta = \log \dfrac{r_p}{r_w}$ where $r_p = \dfrac{b_p}{c_p}$ is the ratio of the two components in the product and $r_w = \dfrac{b_w}{c_w}$ is the ratio of the two components in the residue. The dotted line in Fig. 19 shows the construction for the mixture of hexane, heptane, etc., discussed previously. For that case $\beta = 2\cdot22$, the ratio of heptane to octane in the distillate is 113·2 and the ratio in the residue is ·00288, so that $\dfrac{r_p}{r_w} = 39{,}300$. The reading on the "n" scale shows that 12·3 theoretical plates are required for this separation. The zero point on the "n" scale, that is no plates at all, corresponds to simple distillation and refers to the ratios in the residual liquid and the vapour given off by it.

Fig 20 shows a chart for the equation $X = \dfrac{xP}{\pi}$ which represents the relation between liquid and vapour composition for substances following Raoult's Law. Instead of the pressure P, the corresponding temperature is plotted as this is the quantity which is usually given or has to be found. The method of construction is to mark off two uniform scales at right-angles to each other for x and X, and two uniform scales of pressure parallel to the first two as shown for m-xylene. One pressure scale is then graduated with the corresponding temperatures as shown. Any number of substances can be charted on the same diagram, using the same "x" and "X" scales and the same diagonal. Fig. 20 shows such scales for m-xylene, toluene and benzene. The moduli of the "P" and "π" scales can be given any suitable value to give readings over particular pressure or temperature ranges, so long as the

moduli are equal. Any point on the diagonal line can be taken for the starting point of these scales. The dotted line in Fig. 20 shows the construction for a liquid containing 0·32 mol. fraction of toluene boiling at 104° C. under a pressure of 760 mm. The mol. fraction of toluene in the vapour is found to

of X and dertemining whether the sum of these values for all the components is unity. From the numerical example given above it will be seen that a series of values of X for different temperatures is very quickly read off, using the same point of inter-section of the x line with the diagonal.

MINIMUM NUMBER OF PLATES (TOTAL REFLUX)
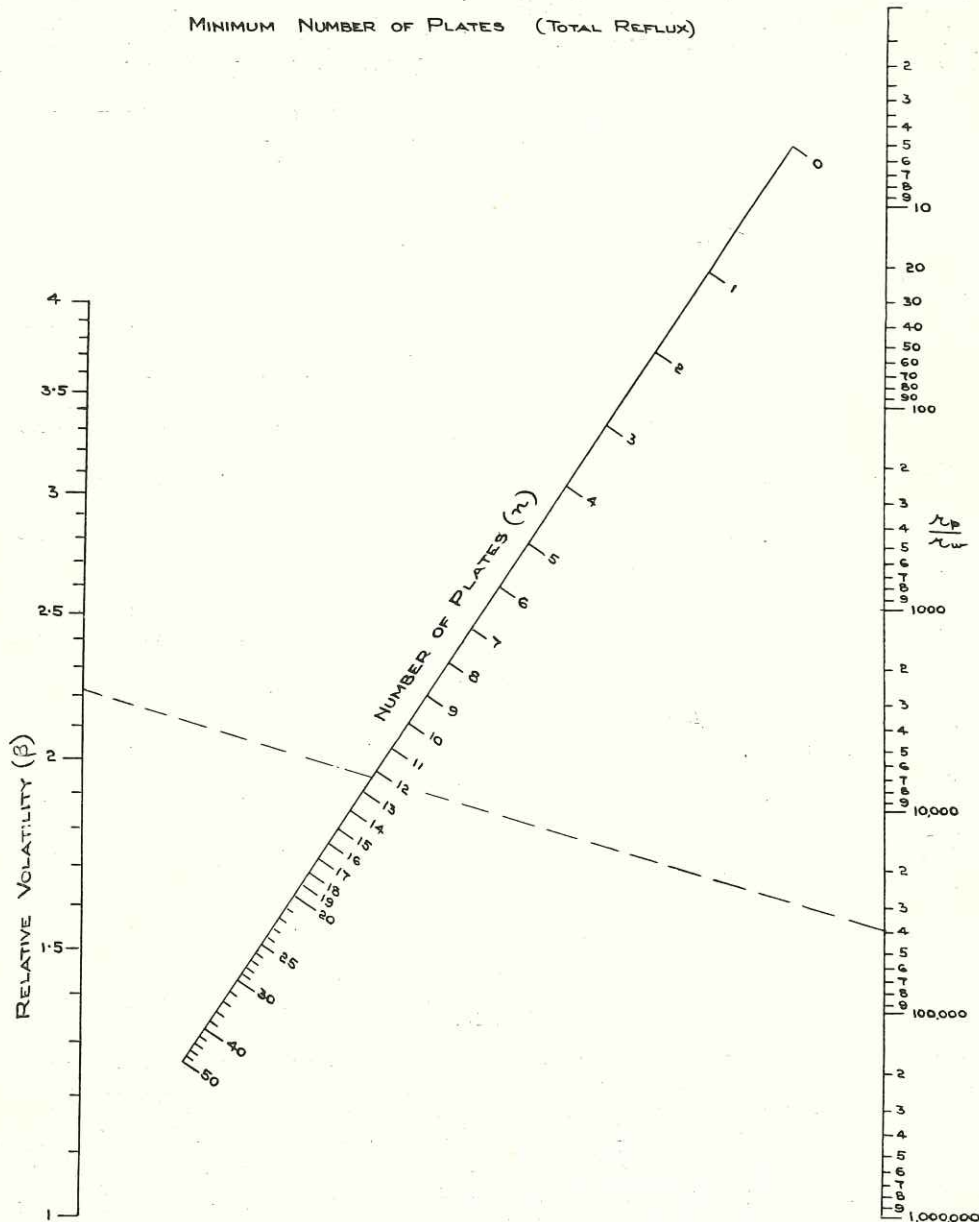
FIG. 19.

be 0·27 by joining the points x = 0·32 and π = 760 and, through the intersection of this line with the diagonal, drawing a line from the point 104° C. on the temperature scale to meet the X scale, where the value of X is seen to be 0·27. The chart can obviously be used to calculate the boiling point of a given mixture under a given pressure by assuming a temperature and finding the corresponding value

Fig. 21 shows a vapour pressure chart based on Dühring's rule. In this case hexane has been used as the reference substance. Two uniform parallel temperature scales are marked off, and one of them is graduated also with the corresponding vapour pressure of hexane. For any substance to which Dühring's rule applies, all lines joining corresponding values of temperature on the left-hand scale, and of

K 2

pressure on the right-hand scale, will intersect at one point. The points shown in Fig. 21 are determined by drawing a few such lines for each substance. To find the vapour pressure of any substance at any given temperature, a line is drawn from that value on the temperature scale through the appropriate point for that substance to meet the pressure scale. At the same time the temperature at which hexane has the same vapour pressure can be read off if it is required —for example, if it is required for the determination

which is a modification of Ramsay and Young's rule :

$$\frac{t_a + 273}{t_b + 273} = \frac{t_a^1 + 273}{t_b^1 + 273}.$$

Substances to which Ramsay and Young's rule applies give points which lie on the dotted line drawn in Fig. 21. If the vapour pressure of a substance is known for only one temperature, the corresponding point can be located by drawing a line joining these temperatures and pressure values and finding its
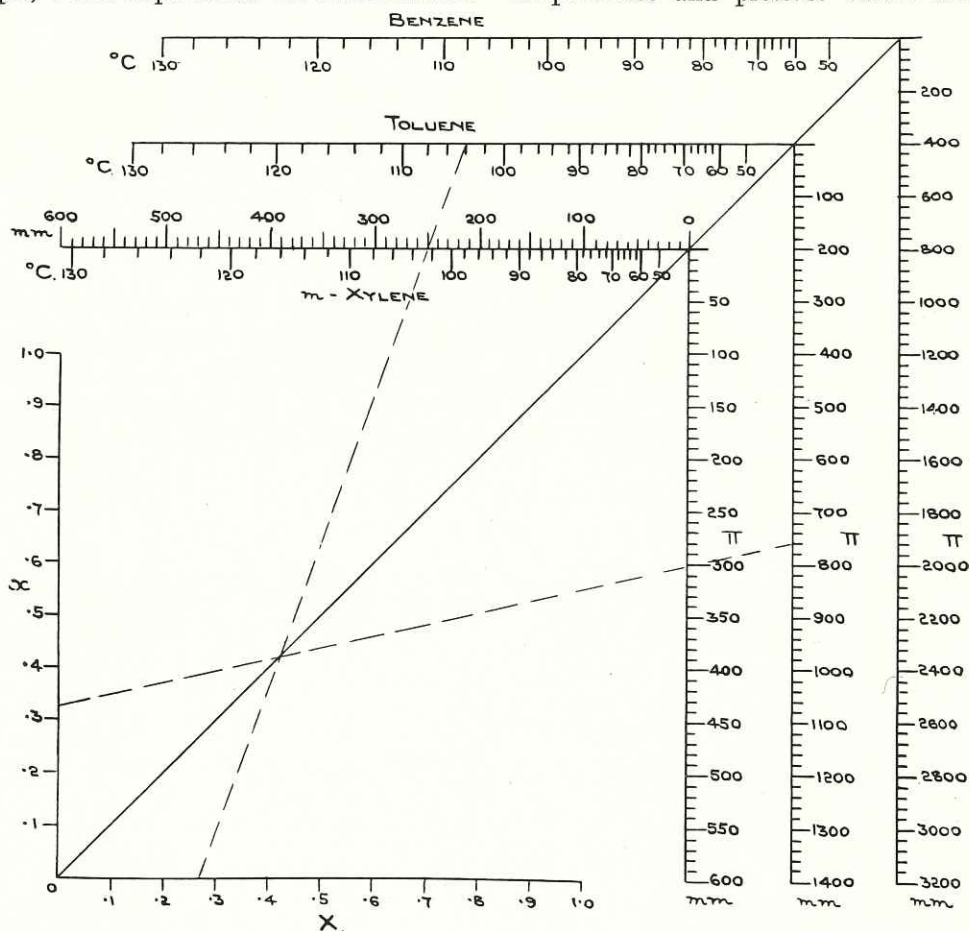

FIG. 20.

of the latent heat by the method of Lewis and Weber[45] or of Schultz.[46] The ratio of the distances of any of the individual points from the two scales is equal to the slope of the Dühring line in rectilinear co-ordinates. Twenty-seven different substances have been charted in Fig. 21, using the data given by Rechenberg.[47] The chart is quite clear and easy to use, but if the same number of substances were charted in rectilinear co-ordinates the diagram would be too confused for practical use. The points representing the normal paraffin hydrocarbons lie very close to a straight line as shown in Fig. 21. This line passes through the point –364° C. on the tempera-ture scale so that the boiling points of such substances are connected by the relation

$$\frac{t_a + 364}{t_b + 364} = \frac{t_a^1 + 364}{t_b^1 + 364}$$

intersection with the Ramsay and Young line or the line for the normal paraffins, according to the category to which the substance belongs.

It is obvious that a chart constructed in the same way as Fig. 21 can be used for expressing any other physical properties to which Dühring's rule applies— e.g., for vapour pressures of mixtures (Leslie and Carr)[48] for steam distillation temperatures (Baker and Pettibone),[49] for vapour pressures of salt solu-tions (Baker and Waite),[50] and for solubilities of inorganic salts (Harris).[51]

A nomographic chart for the vapour pressures of the normal paraffins can also be constructed on the basis of the method suggested by White[52] and Maxwell[53] who, using rectilinear co-ordinates, found a linear relation between the reciprocals of the absolute boiling-points of two related substances at

the same pressure. Using hexane as the reference substance this relation is $\dfrac{1}{T_x} = \dfrac{k}{T_6} + 1$ where T_6

scales are plotted, using reciprocals of absolute temperature, and one of these scales is graduated with the corresponding vapour pressures of hexane.
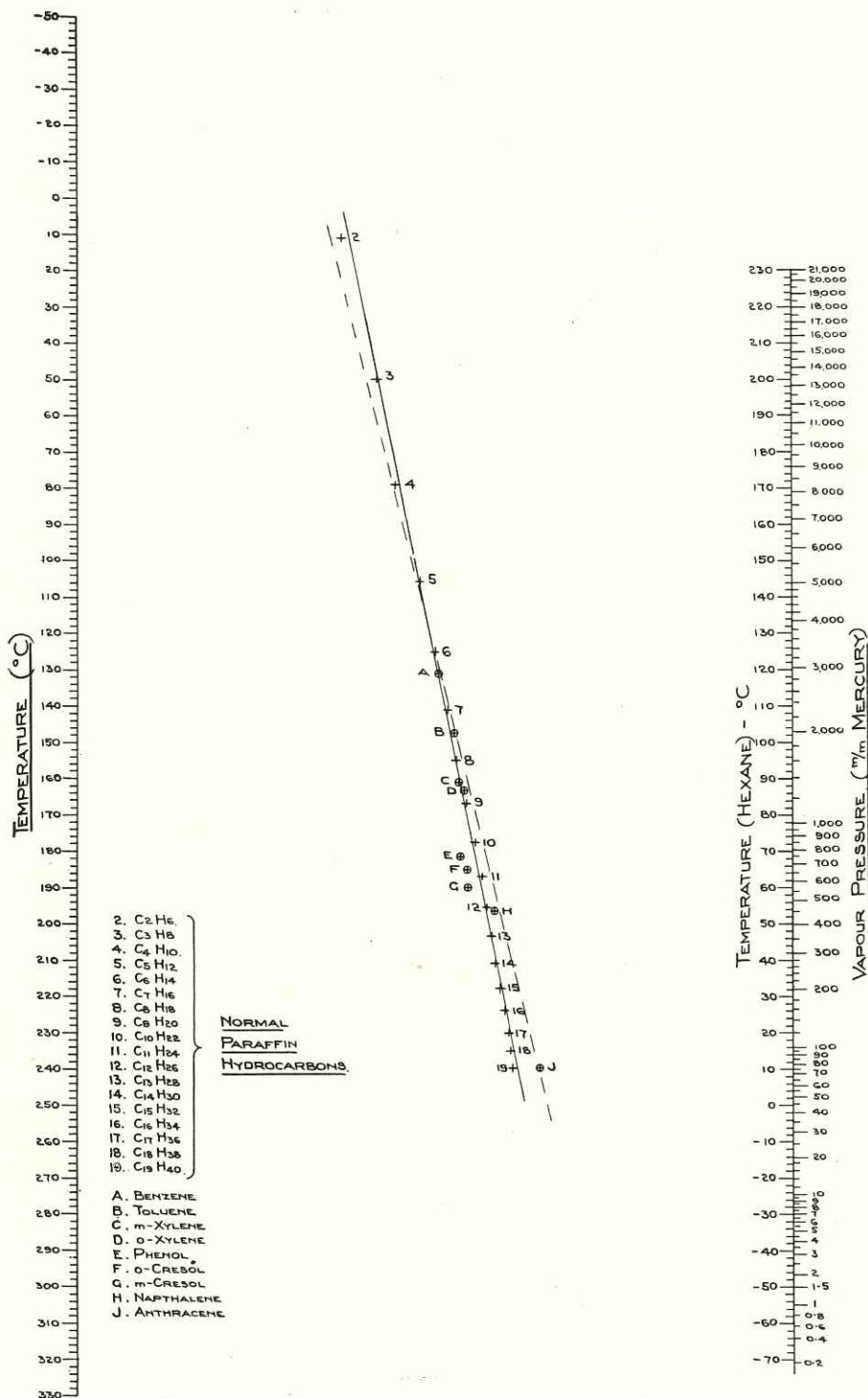

Fig. 21.

and T_x are the absolute boiling-points of hexane and the other substance. This method has been used to construct Fig. 22. Two parallel temperature

If the above temperature relation holds, the lines joining corresponding points on the temperature and pressure scales for any one substance must intersect at

a common point. In this way the points for the normal paraffins with 4 to 18 carbon atoms were plotted. These points lie on a straight line, which corresponds to the condition that the lines for

only slightly in their slopes pass through a distant common point. The line on which the points lie in Fig. 22 would meet the two temperature scales at a point corresponding to 2090° abs. or 1817° C. This
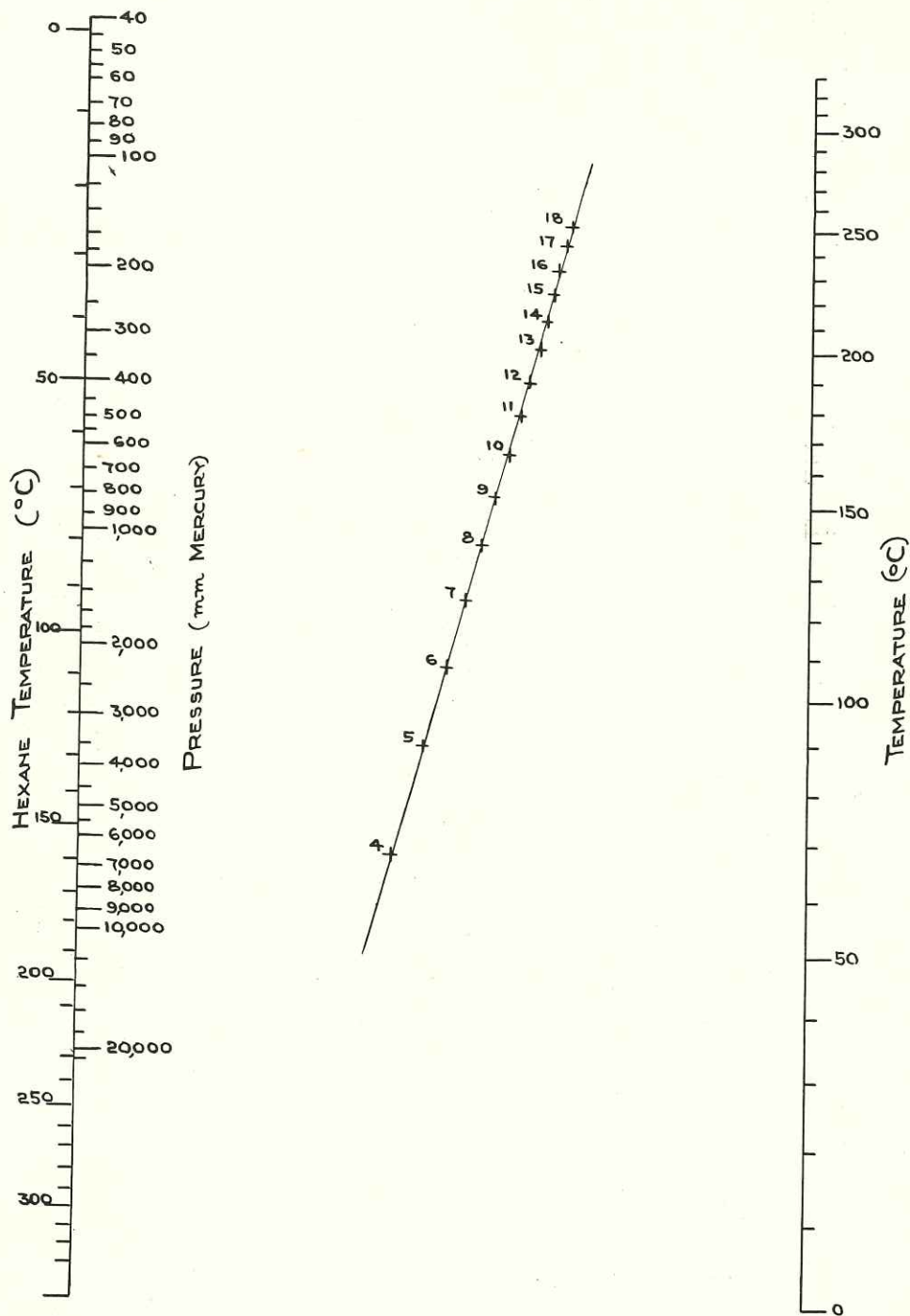

FIG. 22.

different substances plotted in rectilinear co-ordinates intersect at a point. It is, however, easier to see from charts such as Figs. 21 or 22 whether a series of points lie on a straight line than to decide whether, using rectilinear co-ordinates, a series of lines differing

temperature is approximate, as the graduations at that part of the scale would be so close that a very small graphical error would affect the result greatly. For practical purposes, however, it would be quite accurate enough to locate the points representing
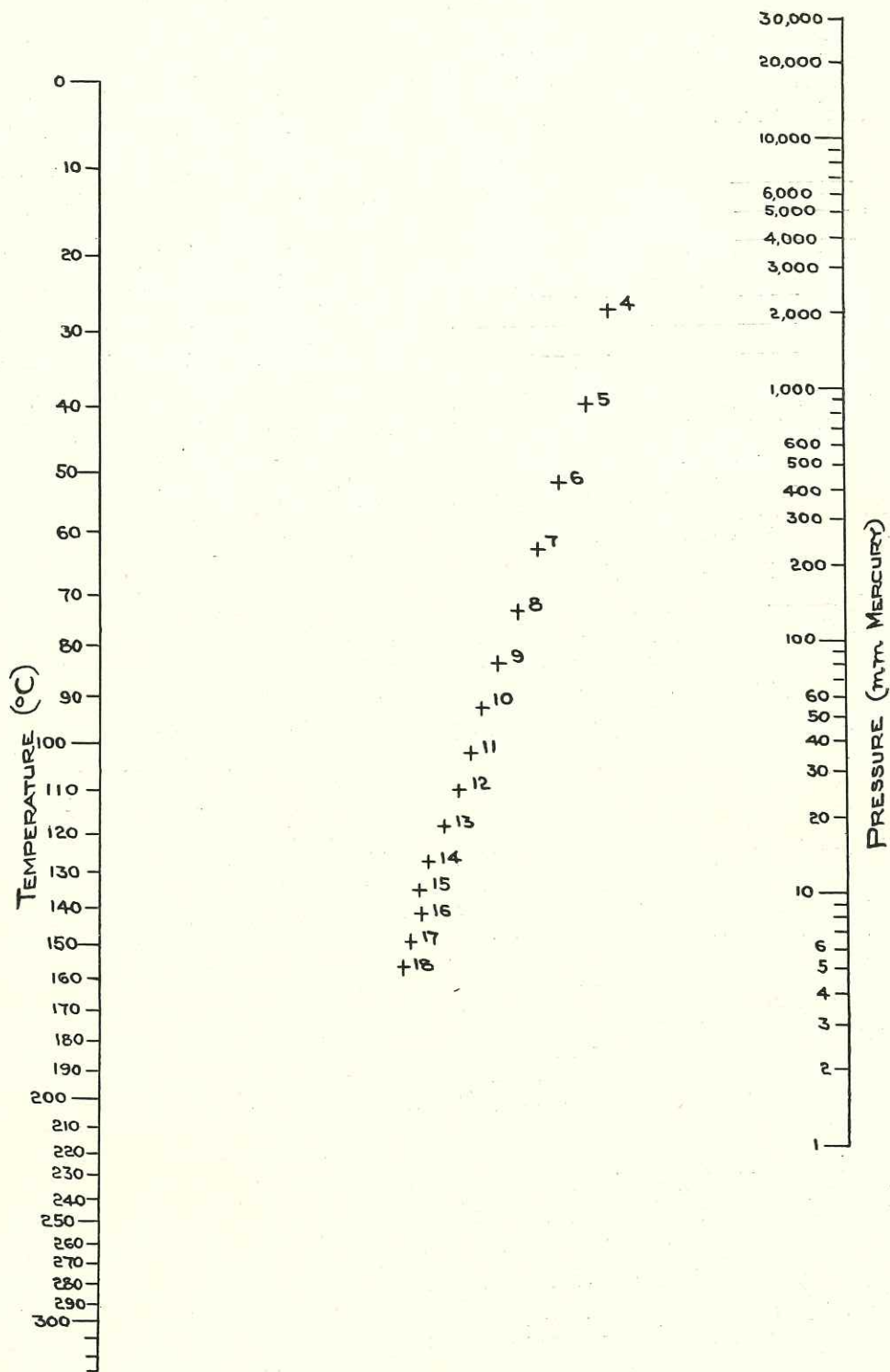
Fig. 23.

different substances on the chart by drawing the line which would meet the two temperature scales at 1817° C., and then using one temperature and pressure value for each substance to determine the position of that point on the line so drawn. From the method of construction of the chart it follows that the boiling-point of any two normal paraffins at two different pressures are connected by the relation :—

$$\frac{\frac{1}{T_a} - \frac{1}{2090}}{\frac{1}{T_b} - \frac{1}{2090}} = \frac{\frac{1}{T_a{}^1} - \frac{1}{2090}}{\frac{1}{T_b{}^1} - \frac{1}{2090}} \text{ or}$$

$$\frac{\frac{1}{T_a} - \cdot000478}{\frac{1}{T_b} - \cdot000478} = \frac{\frac{1}{T_a{}^1} - \cdot000478}{\frac{1}{T_b{}^1} - \cdot000478}$$

The constant ·000478 was determined graphically. For greater accuracy it should be determined by statistical methods.

Fig. 23 shows a similar chart for the normal paraffins based on the method used by Cox[54] with rectilinear co-ordinates, which, as shown by Calingaert and Davis[55], is equivalent to using a pressure scale graduated with log p and a temperature scale graduated with $\frac{1}{t+230}$ where t is the Centigrade temperature. In Fig. 23 two parallel scales are constructed with these graduations, and the positions of the points representing the different substances are determined as described previously. Here, also, the various points lie approximately on a straight line.

Any of the temperature or pressure scales in Figs. 21, 22 or 23 can be used to carry two sets of graduations, which is a further advantage of the nomographic method. Thus the temperature scale can be graduated for both Centigrade and Fahrenheit temperatures, and the pressure scale for mm. of mercury, and lbs./sq. in., or atmospheres. The scales marked " hexane temperature " in Figs. 21 and 22 would normally be used only for constructing the charts and need not be retained if two sets of graduations for pressure are required on that scale. Any of the above charts can be easily extended if they are required to cover a greater range or can be made to cover a smaller range if greater accuracy is desired over such a range.

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DISCUSSION.

Mr. E. A. ALLIOTT said that ten or eleven years ago, when the Institution was first formed, it would probably have been said that such a meeting as this was one of the ideals to be looked forward to but which had a very remote chance of achievement. The Institution was therefore performing the function for which it was formed with 100% efficiency or effectiveness. The papers were an important contribution to the work of the Institution, and would be of great help to all those who had anything to do with the testing of chemical plant. The first paper dealt with the general problem in a scientific and philosophical manner, and was followed by the particular example of an evaporator and the far more complicated problem of distillation. On behalf of his colleagues in the British Chemical Plant Manufacturers' Association he offered sincere appreciation of the papers and the encouragement of the Association, because they would like to see more work of this nature done in the general interests of chemical engineering.

Mr. J. H. WEST particularly thanked Dr. Under-wood for the work he had done in looking up the literature, re-calculating the various authors' work on a common basis, and comparing them, in addition to his own mathematical contribution to the subject. In practice the designer worked out the number of plates according to the best of his ability, and then he added a number of plates to take care of poor plate efficiency. Then, if the firm had to guarantee the steam consumption, a few more were added to make quite sure. Feed connections were made to three plates, and the user of the still was left to find out which was the best. Extra plates were very ex-pensive for both large and small stills and, with a large column, might increase the cost by more than £100. Plate efficiency was very important and had been very much neglected. Indeed, plate design was a subject on which very little work had been done, and upon which very few patents had been taken out during the last 30 or 40 years. Dr. Underwood had stated that little information had been published on why plates were inefficient and it certainly was a wonder that they worked so well. When one considered the plate as an apparatus for scrubbing vapour and liquid, it seemed a very poor thing, because with vertical slots in the bubblers the vapour leaving the top had a very short path whilst that leaving lower down had a longer path. On the liquid side there were either two drop pipes on opposite sides of the plate, which meant that probably the liquid was flowing straight across, leaving the sides more or less stagnant, or there were inlet pipes side by side with a baffle down the middle, and then some of the bubblers were surrounded by liquid fresh from the plate above, whereas bubblers on the opposite side were getting liquid through which vapour had passed.

The design of bubbler plates and plate efficiency generally was an almost untouched subject so far as research was concerned. Some of our still manu-facturers would no doubt provide two or three plates, which were all that were needed to enable experi-mental work to be carried out.

Another aspect of chemical plant testing which he would like to mention was the need for checking drawings before plant was ordered, particularly when the designers were the makers of the plant, because they were naturally inclined to protect themselves. A foreign maker supplied a discontinuous still under guarantee, and it worked very well for about a year. When the time came for the coil to be repaired it was decided to replace the original coil by one made in this country. The continental makers had provided a coil with a surface of $19\frac{1}{2}$ sq. m., but when the area was calculated, allowing a reasonable heat trans-mission coefficient, it was found to be about 6 sq. m., and a coil with an area of 7 sq. m. was actually put into the still and gave a perfectly satisfactory result. The maker, in this case, had sold to the consumer a coil having an area about three times greater than was required.

If the user asked for a guarantee he had to leave the plant more or less in the hands of the maker, but in considering the economic efficiency of a plant, cost was a considerable factor and an excessive

protection of the maker in regard to the guarantee, such as the case he had mentioned, required careful attention.

Mr. S. G. M. URE said the object of the conference was to get data from which a testing code could be devised. It was thought the best method of doing this was to get three papers of a theoretical nature and follow them with others giving figures from actual tests. The work of arranging this conference had been undertaken by Mr. Norman Swindin, who had carried out the task with great zest and thorough-ness. Whether the makers and users of plants were in favour of disclosing data or not he could not say, but no one came forward to complete the present series with papers giving practical results. He mentioned this fact in the presence of Mr. Alliott in the hope that the British Chemical Plant Manu-facturers' Association might be able to assist.

Dr. R. LESSING said that the papers certainly indicated the manner in which chemical engineering in this country was progressing. He wished to refer to a practical point particularly applicable to the plant maker and to a certain extent to the plant user. In practice it was often difficult, and in some cases impossible, to adhere to the standard or code of testing laid down. He had sometimes to test chemical plant which was not provided with the wherewithal to carry out tests. In some cases it was impossible to make the most rudimentary measure-ments upon which the cycle of tests so clearly out-lined by Mr. Bloomfield could be completed. The user must make it necessary for the plant manu-facturer to devote sufficient expenditure to the plant that not only could it be shown to conform to the guaranteed requirements of output and efficiency and effectiveness, but also to allow tests to be made which would permit both the manufacturer and the user to do better next time. From that point of view a very great deal was to be desired at the present time.

Very little was known about the theory of packed columns; the difficulty, in the first place, was the impossibility of sub-dividing a packed column into sections as could be done with a plate column. He was interested in the experiment referred to by Dr. Underwood in which he had endeavoured to show a packed fractionating column by the simple analogy of running water down and passing air up the column. Ten years ago he had read a paper before the Society of Chemical Industry in which the suggestion was put forward that a fractionating column should be regarded as a simple scrubber. He was convinced that this was the way to consider such a fractionating column; the only difference from the ordinary scrubber in which a gas was washed with a liquid was the heat to be introduced, into both the liquid and the vapour, in the various zones of the column. If that was determined, preferably by mathematical treatment, then the fractionating column could be treated like a scrubber, and the reflux ratio and vapour then became apparent and comparatively simple. Therefore he suggested to those in the

position to carry out the theoretical treatment of the problem that this aspect should be investigated.

Dr. W. R. ORMANDY remarked that the fact discovered by Dr. Underwood that some workers had inverted their equations might account for some of the peculiarities met with in actual stills. He knew of fractionating columns which worked very well for a year or more with apparently constant efficiency. Suddenly they ceased to function adequately, and on dismantling it was found that more than 90% of the bells on the plates were corroded away. Apparently the columns as designed were much too large. He had also noticed that plants supplied by different makers for the same duty differed greatly in dimensions. If Dr. Underwood had found a simple method of determining where the feed pipe ought to be inserted, he had performed a really valuable service. The work on entrainment was valuable and he hoped that it would be continued.

Mr. NORMAN SWINDIN said this conference was intended to obtain practical information from the makers and users of plant. He was the fourth Chairman of the Institution's sub-committee on Testing, which comprised Dr. Sinnatt, Mr. Bloomfield and Mr. Riley. It was decided that chemical plant was too big a subject, and so the present papers were limited to the evaporator and still, which were simple but very important pieces of apparatus. Mr. Bloomfield had given the fundamental principles of testing, and Prof. Gibbs had applied them to an evaporator, whilst the application to the still had been in the hands of Dr. Underwood, who was a mathematician and believed all mathematics to be true. On the whole he felt three very interesting papers had been prepared, and it was to be hoped those who made the plants, and those who used them, would supply data relating to their working from which it might be possible to determine some standard of performance by which such experiences as Dr. Ormandy had mentioned of three different firms supplying three different types of plant to do the same work and putting in plants many times larger than they should be could be avoided.

He was once called in to test a caustic soda recovery plant in connection with a law case. There was not a single piece of apparatus on it which could be used for making the tests and no provision made for taking readings. The guarantee was for 2% caustic soda solution to be concentrated to 55° Tw., and when he was prevented from seeing certain things he became suspicious. Eventually he managed to find out that the raw liquor was only 0·2% caustic, one-tenth of the guarantee figure. He thereupon told those concerned that it was impossible to make soda from water, and went home.

Mr. F. RUMFORD said that Mr. Parrish's book on ammonia stills gave detailed particulars of experiments carried out on entrainment. Several patents dealing with certain motor fuels had been taken out recently which claimed that these fuels were efficient in their evaporation in the carburetter, because they were mixtures of compounds with stepped boiling points. Perhaps the higher efficiency of columns dealing with mixtures of benzene, toluene and xylene might be due to this cause. Information on that point would be valuable.

He had hoped to hear comments on the flow-sheets in Mr. Bloomfield's paper, because the system advocated in the paper left out a very important item, labour, which surely should appear in testing any plant. The number of man-hours put into a plant affected its efficiency considerably, and should be taken into account in the flow-sheets.

Mr. E. A. ALLIOTT said he knew the British Chemical Plant Manufacturers' Association would be very pleased to consider helping in the production of papers relating to actual tests on chemical plant based on the scientific and theoretical proposals outlined that evening. The plant manufacturer, however, could not be expected to put forward tests which would contain the highly scientific results outlined in the three papers, for the plant manufacturer seldom had a real opportunity to carry out such tests on his plant. Usually, as soon as the plant turned out a product of the required quality, the user was satisfied, and if suggestions were made to alter the flow or temperature they were regarded as a nuisance. Any tests or experiments had to be subordinated to the general operation of the plant. The user had to produce a certain amount in a given time, and anything which interfered with production could not be tolerated during working hours. Small quantities could be treated easily in a works or testing laboratory, but it was difficult to find an opportunity for full-scale tests.

Once arrangements were made for a test of eight hours on a full sized drier to which all operations in the works were to be subsidiary, the object being to show whether another product could be handled. At the end of the first half-hour the people concerned, seeing the product being turned out satisfactorily, said they were satisfied and went away. After they had gone the product changed completely, and it took two or three hours to put it right. The difficulties were ultimately overcome, but the instance illustrates the lack of interest in tests taken by users.

If a maker were asked to give a guarantee he must choose his own conditions, and the Chairman would agree with him that it was not always the plant which had to be guaranteed, but sometimes also the customer.

Dr. F. S. SINNATT said that the Director of Fuel Research had been empowered to undertake an exhaustive test on any low temperature carbonisation plant which had reached a stage of development in which a unit was available for examination. The first test was made in 1924, and since that time about ten separate low temperature carbonisation plants had been examined. These tests had given quite satisfactory balances of products obtained and the coal carbonised. In carrying out these tests it had been necessary for the staff of the Fuel Research Station to take much of their own measuring apparatus, while the products had been sampled and examined at the Fuel Research Station. In

certain cases the whole of the tar had been transported to the Fuel Research Station in order to be able to obtain an average sample for examination.

There had been suggestions that the testing of distillation plants was a difficult matter, but there was now available a mass of information upon the testing of low temperature carbonisation plants, and the examination of such plants was not in quite the same position as the testing of the plants dealt with during the discussion.

The CHAIRMAN associated himself with everything that Mr. Alliott had said about the desire of the manufacturer of chemical plant and processes to get complete tests of their apparatus, but the buyer, having paid a large sum of money for an installation, naturally wanted to get uninterrupted production as soon as possible, so that it might begin to earn a return on his capital.

The buyers of plant were very seldom willing to allow full particulars of their plant and processes to be published, a point of view with which one could sympathise. All would sympathise with the dearth of published tests of chemical plant, but the testing of chemical plant bore no relation to the testing of boilers, or engines, because the users of the plant had definite reasons for keeping the information to themselves.

The great difficulty which both the manufacturers and users of chemical plant had to contend with was that often there was considerable variation in raw material brought to a process so that there had to be enough elasticity in the plant to meet these variations.

In considering the testing of chemical plant, all the facts of the particular cases, both in relation to the user and the manufacture, should be remembered.

Mr. BLOOMFIELD, in reply, expressed his appreciation of the sympathetic way in which the papers had been received. The discussion had centred mainly round testing of plants in works, and, from a user's point of view, his sympathies were with the manufacturer. The flow-sheet described in the paper dealt only with the actual components in the plant, whether of energy or of material, and labour did not enter as a component into the product at any stage. It entered, however, in the economic aspect of the question. There was a section of the paper which dealt to some extent with the economic side in which it was suggested that a flow-sheet could be constructed on the basis of costs. If that were done, then labour would appear as a subsidiary raw material.

Prof. GIBBS only wished to say two things. The first was that the discussion indicated that it was high time that men were trained in chemical engineering. The second was that for the last eighteen months his department had been carrying out intensive research into the mechanism of the bubbler plate, and a paper on that work would be published shortly.

Dr. UNDERWOOD said that there was still a lot to be learned about the efficiency of bubbler plates and much research to be done. The present type had been developed empirically and served its purpose fairly well. The overall efficiency was about 70%, quite a good figure. Although there was at present no definite evidence, he believed that the action of a bubbler plate was not so much due to the scrubbing which took place as the vapour passed through the liquid as to the action between the liquid and the vapour in the space between the plates where the liquid was sprayed. There the interfacial surface between the liquid and the vapour was so much greater that it was conceivable that the greater part of the reaction took place there. Probably the bubbler plate was a device for spraying liquid into the vapour rather than a scrubbing device.

The experiments mentioned in the paper concerning entrainment did not relate to packed but to plate columns. The analogy between the distillation column and a scrubber was true to a certain extent, and had been employed by Lewis and Wilde in their paper. There was a difference between the two cases because in scrubbing only one constituent was removed from a gas, whereas in a distilling column some constituents were being removed from the gas and other constituents were being put into it, so that there were two actions going on at the same time.

It would have been very interesting if Dr. Ormandy had given some data for the steam consumption with a curve showing the increase of steam consumption with age for the still which functioned after the disappearance of several of the bubblers. As long as the number of plates was greater than the minimum required for total reflux, plates could be removed until the minimum was reached. There would still be fractionation as long as the reflux was increased, and the steam coils and reflux condenser were large enough. In these circumstances the plant would continue to work, but with ever increasing steam consumption, until the minimum was reached.

The experiments by Mr. Parrish were interesting, but the method used did not appear to be as easily applied to quantitative measurement as the method described in the paper. Mr. Rumford also referred to motor fuels made up of components with stepped boiling points. He would not comment on that subject in view of the number of experts present, but he would mention that any patents regarding the remarkable effects of adding various substances to motor fuels should be subjected to careful examination. The fact that efficiency increased when dealing with complex mixtures compared with a binary mixture seemed to be substantiated by experiments carried out by Lewis and Smoley, but he did not think anybody had put forward an explanation.

The difficulties of the manufacturers in making tests under commercial conditions were real, because the user invariably desired to get the plant into production at the earliest possible moment. The manufacturer could only make such tests in the user's works, and the user ought to make these tests, if possible, in conjunction with the manufacturer. Clearly the manufacturer was interested in making

these tests because he desired to get as much informa-tion as possible with a view to improving the design of future plants. The user should also be interested in such information, though he might not be quite so ready to disseminate it. In normal times the making of such tests might involve interference with the works' operations, but at the present moment many works were not operating at full capacity and therefore these tests would not seriously interfere with production. Special efforts, therefore, should be made to get full-scale tests carried out now, and if the users of chemical plant would undertake such tests and arrange for the results to be published and discussed, they would render a considerable service to chemical engineering.

In a written communication, Mons. R. SAVARIT said that he had read Dr. Underwood's paper with much interest. It was the most complete study he had read on a subject which had interested him greatly. He was therefore very pleased to have this opportunity to offer his congratulations on this important work and at the same time to submit his own views on the subject.

He would explain that his point of view was essentially and exclusively a practical one. The study of the physical laws governing the compositions of the liquid and vapour phases was one thing and the calculation of distilling columns was another. For the latter object, it was sufficient to know the vapour composition curve, and the specific and latent heats of the constituents of the mixture. In certain somewhat rare cases, the curve could be drawn by applying Raoult's Law. More frequently, the curve must be obtained experimentally, as was the case with mixtures of ethyl alcohol and water. He regarded it as a mistake to use " mol fractions " in distillation questions. A chemist, who dealt with reactions, legitimately reasoned in terms of mole-cules. An industrialist, whether a manufacturer of alcohol or a refiner of petrol, only recognised weights.

It was justly remarked, on page 117, that there were two methods of calculation—those derived from Sorel, which were exact, and those which assume a constant molal reflux, which were approximate. The method of Sorel, using the graphical construction of Ponchon, was as simple to apply as the second method. The conception of " mol fraction," intro-duced as a simplification but to the detriment of clarity and precision, was therefore not justified.

Whatever the method employed, he thought it was very important to keep clearly in mind and to treat separately the two principal types of columns, the exhausting column, below the feed, and the concentrating column, above the feed.

For each type of column there were four funda-mental characteristics :—

(a) The minimum quantity of heat to be supplied, exhausting column or to be absorbed, con-centrating column, for a given separation, however great the number of plates.

(b) The minimum number of plates for a given separation, however great the heat consumption.

(c) For a given separation, the amount of heat to be supplied or absorbed according to the number of plates and, conversely, the number of plates required with a given amount of heat.

(d) The limiting composition in each case. For example, a mixture of water and ethyl alcohol, there was for the exhausting column, if the number of plates and the heat consumption were specified, a concentration of alcohol on the top plate which could not be exceeded. Similarly, for the concentrating column, if the number of plates and the heat consumption were specified, there would be on the lowest plate a concentration of alcohol below which it was impossible to pass.

The conception of reflux was secondary as well as being inexact when working with weight units. In the concentrating column the reflux was liquid, and in the exhausting column the reflux was vapour. The only thing practically constant from the bottom to the top of the column was the flow of heat.

If the problem were treated in the manner which had been indicated, there would no longer be the slightest difficulty in finding the composition of the liquid on the feed plate as the diagram showed it immediately. Nor would there be any difficulty in determining the point at which the feed was to be introduced which was at the junction of the two columns.

Plate efficiency affected not only the number of plates necessary for a given separation, but also the consumption of heat. This followed from the fundamental conceptions set out above. Further-more, a simple glance at the diagram allowed of it being taken into account. Most authors had made erroneous statements on this subject.

As far as the ethyl alcohol-water mixture was concerned, fermented wash from beet, molasses, etc., experience showed that the efficiency was very near to 100%, even with plates of rudimentary construc-tion. This fact was verified by the operation of numerous installations. In fact, the majority of French agricultural beet distilleries distilled a wash containing 5%, by weight of alcohol, to obtain a product of 86% strength, using columns which operated according to Fig. 24, and in which the wash was used as the sole cooling agent. These columns generally comprised 20 exhausting plates and 5 to 10 concentrating plates.

In such an installation it was easy to draw up the heat balance since the calories brought in by the heating steam could only be absorbed by the wash or lost by radiation.

Investigation showed that the consumption of heat was very close to that determined by using the data of Bergström. That implied a plate efficiency very nearly 100%.

The study of distilling columns for binary mixtures by the Sorel-Ponchon method, permitting the solution of simple practical cases such as the separa-tion of mixtures of water-ethyl alcohol, acetic acid-water, water-acetone, etc., also offered the valuable advantage of demonstrating the fundamental

principles which govern the operation of columns in the most general case of 3 or more components.

For such mixtures there was no simple and exact general rule as there was for binary mixtures. An experimental study in each case served to determine the method of operation. Nevertheless, the experience obtained from the study of columns treating

A. Steam inlet.

B. Spent wash, 103° C.

C. 5% Alcohol wash, 25° C.

D. Product, 86% Alcohol.

E. Alcohol inlet, 75° C.

FIG. 24.

Diagrammatic sketch of column for the treatment of a Wash containing 5% Alcohol.

binary mixtures was of great assistance. He had many examples at the Melle factories such as the dehydration of alcohol, manufacture of esters, rectification of the complex mixtures resulting from the acetone-butyl alcohol fermentation, etc.

In reply to M. Savarit, Dr. UNDERWOOD wrote that it was quite logical to deal separately with the exhausting and concentrating columns as M. Savarit remarked. The paper dealt mainly with the case,

most common in industrial practice, of the concentrating column superimposed on the exhausting column. Other cases such as an exhausting or concentrating column used alone or the double column type of still, used in the German alcohol industry, had not been specifically treated in the paper from considerations of space. The methods described could be applied also to these cases.

The use of mol fractions as units had little physical significance. It was to be regarded as a convenient mathematical transformation. Where the molal latent heats were not equal, as in the case of acetic acid and water, fictitious molecular weights were assumed so as to give units of "equal latent heat." The argument could be illustrated algebraically as follows for a binary mixture.

Let V_n be the weight of vapour rising from the nth plate per unit time, W_n the weight fraction of one component, and L_1 and L_2 the latent heats, per unit weight, of the two components. Neglecting changes in the heat content of the liquid through the column, the amount of heat passing any point in the column per unit time was constant, so that

$$V_n W_n L_1 + V_n (1-W_n) L_2 = \text{constant.}$$

If m_1 and m_2 were the molecular weights of the two components, assuming Trouton's Rule to hold and neglecting changes in temperature through the column, then $m_1 L_1 = m_2 L_2 = \text{constant}$ and

$$\frac{V_n W_n}{m_1} + \frac{V_n (1-W_n)}{m_2} = \text{constant.}$$

If V_n^1 denoted the amount of vapour per unit time in mols, that is, the sum of the number of mols of each component, then
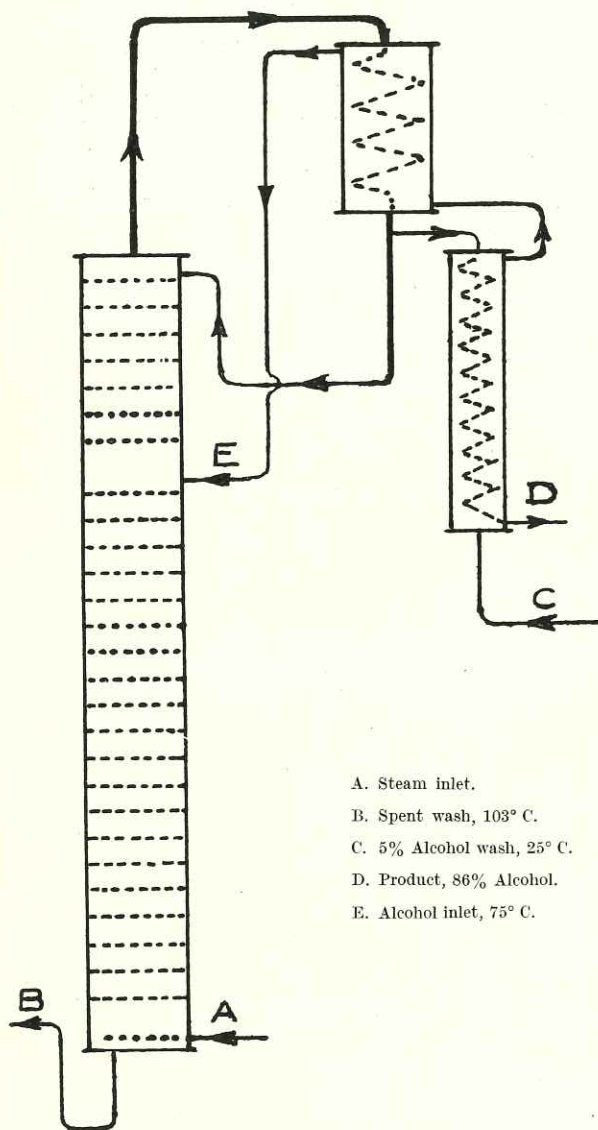
$$V_n^1 = \frac{V_n W_n}{m_1} + \frac{V_n (1-W_n)}{m_2}$$

and from the previous equation V_n^1 was constant through the column.

This held good for any system of units, apart from molal units, so long as the relation $m_1 L_1 = m_2 L_2 = \text{constant}$ was satisfied—that is, so long as the latent heats of the two components were constant through the column and m_1 and m_2 were chosen so that $\frac{m_1}{m_2} = \frac{L_2}{L_1}$. So long as this ratio $\frac{m_1}{m_2}$ had the appropriate value, any suitable values of m_1 and m_2 could be taken so that an infinite number of systems of units was available. The choice of molal units was simply a matter of convenience, because Trouton's Rule applied to a large number of substances.

Regarded geometrically, referring to Fig. 2 of the paper, it meant that the scales of the X, H axes were transformed so that the curve $X = f (H)$ became the straight line $H = \text{constant}$, parallel to the X axis. By this derivation, with some modifications, we arrived at the nomographic form given in Fig. 6.

The Savarit-Ponchon method was certainly more accurate, since it took into account variations in latent heat and variations in the sensible heat of the liquid. These were generally small in comparison with the latent heat, and, if they were taken into account, allowance should also be made for radiation losses. For most purposes the approximation was

a legitimate one, particularly as accurate physical data for latent heats, heats of mixing, etc., were lacking for many important problems. When making any kind of approximation it was desirable to realise this fact and to know the degree of approximation involved. For this reason the Savarit-Ponchon method had a fundamental place in the study of distillation. The conception of constant molal reflux was of particular value when dealing with mixtures of more than two components where Raoult's Law applied, as was approximately the case with petroleum hydrocarbons. The use of any method other than one which assumed constant molal reflux would involve complicated calculations.

A lot of conflicting information had been published on plate efficiency. The efficiency quoted of nearly 100% was higher than was usually found. As pointed out on pages 139 and 143 of the paper, it was difficult to ascertain accurately the theoretical number of plates required where the amount of one component in the product or effluent was very small. In such cases samples should be taken at other points in the column.

As M. Savarit pointed out, there was no difficulty in determining the correct position for introducing the feed if the calculations were made for the exhausting and concentrating columns. The methods given in the paper for determining whether the feed was in the correct position in any column in operation did not require any such calculations and could be applied to cases where the liquid-vapour equilibrium data were not known. They could also be applied to any number of components, whether they obeyed Raoult's Law or not.