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THE APPLICATION OF SPREADING MEASUREMENTS ON OIL TESTS.

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Following a description of the method of testing the spreading value of oil, a theoretical conclusion based on experiments made proves that the measurements as such are justified and, finally, the possibilities of putting this method into practice are discussed.

INTRODUCTION.

IF a pure liquid non-volatile hydrocarbon is placed on water, this will remain there in the form of a drop. A pure mineral oil acts the same way. Should the oil, however, contain compounds which are partly hydrophile and this oil is spread out on water, then these molecules tend to accumulate in the interface while they adjust themselves in such a way that the hydrophilic part of the molecule comes into contact with the water and the hydrophobe part turns away from the water. In this manner an oil film comes into existence. This film is not monomolecular, one gets a rather thin layer of hydrocarbon almost devoid of hydrophilic substances in contact with the water via the interface described above. This is called by Langmuir a duplex film. The expanse of the surface of this oil film is a measure for the quantity of these compounds which are present. This is expressed in the spreading constant, which shows the surface occupied per unit of weight at the moment when the film just has started to exert pressure.

MEASURING APPARATUS AND METHOD OF MEASUREMENT.

The measurements are executed by the apparatus constructed by Gorter and Seeder.[1]

A barrier floats in a rectangular paraffinated glass container filled with 0·001N-hydrochloric acid, to which container it is attached by means of very thin strips of platinum, so that it can move freely within certain limits. Forces affecting the barrier are transferred to a torsion balance and compensated by the torsion of a spring, care being taken to see that the barrier always returns to zero position. The amount of torsion is registered on a scale, thus measuring the pressure on the barrier. Displacement of the barrier is indicated by means of an optical system.

The oil to be measured is dissolved in petroleum ether and blown on the water surface between a paraffinated glass slide and the barrier by means of a micro-pipette. The glass slide is driven in the direction of the barrier, and as soon as the film starts to exert a pressure on the barrier, the torsion balance is adjusted as described above and the pressure, as well as the distance from the glass slide to the barrier, is noted. After this, the glass slide is moved closer to the barrier and the measuring process repeated. In this way a pressure curve is obtained. In most instances—between wide limits—this is a straight line. By continuing this line one extrapolates to pressure zero. The surface thus found is used for the determination of the specific spreading value.

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The petroleum ether used should be purified to such an extent that it does not affect the readings. This is obtained by repeated distillation. At the same time the water surface should likewise be so purified that no interfering molecules are present. If the spreading capacity of the oil is small, 0·05 ml petroleum ether is brought on the surface, which latter contains ±15 mg of the oil. For oil which has a bigger spreading action a lesser quantity is sufficient. The determination takes three minutes. It is very fortunate that only small samples are needed.

Theoretical Considerations.

When making tests the following can be observed. After blowing the solution over the surface and moving the slide until the film exerts pressure, the major part of the surface is covered by the duplex film, there is, however, a water surface left uncovered. If the film is neither too thin nor too thick, an interference colour can be noted, indicating that the film is equally thick all over. After waiting a little, the picture changes. Holes appear in the film and the latter continues to contract, with local thickenings in it, often indicated by different interference colours. Provided one waits long enough, the film contracts to very small lenses.

Considering the problem of the duplex film thermo-dynamically, one gets various conditions of equilibrium. One is mechanical and two others physico-chemical. The mechanical equilibrium of the surface tensions and hydrostatic pressures adjust themselves immediately, unless strongly viscous liquids are concerned. In the case of solids a mechanical equilibrium is also quickly established, which equilibrium may include anisotropic tensions, which makes it difficult to make any reliable calculations. The first physico-chemical equilibrium condition stipulates a certain relationship between volume concentration of the substances with hydrophilic groups in the oil layer and the surface concentration of these substances in the interface oil-water. According to Langmuir this equilibrium is established quickly enough, which is confirmed by our own experiments. This can easily be understood when considering that diffusion only takes place across the thin oil layer. The second physico-chemical equilibrium condition establishes a relationship between the surface concentrations of the active substances in the interface air–water and oil–water. This equilibrium adjusts itself much more slowly than the other since here it is a question of diffusions along the surface. Langmuir [2] covers this in his experiments with stearic acid in petroleum. Our own experiments confirm this also, as described above.

Mechanical Equilibrium.

In the middle of the oil lense, where the interfaces show no curvature and are horizontal, the following horizontal forces work in the oil :

1. The surface tension of the surface oil–air γ_{oa} (a tensile force in dyne/cm) ;
2. That of the interface oil–water γ_{ow} (likewise a tensile force in dyne/cm).

3. The integrated lateral hydrostatic pressure, being equal at the top to the atmospheric pressure and increasing with $g\rho_0 x$ dyne/cm^2 as one descends x cm (g is the acceleration of the force of gravity in cm/sec^2, ρ_0 is the density of the oil).

If there is equilibrium, and if the oil lense is large enough, these tensions must be equal to those in the adjoining oil-free water (the surface of which, however, may possibly be occupied by active substances) at the point where the water–air interface is horizontal. At the same time they must also equal those in the pure water at the other side of the barrier plus the pressure exerted per cm by the barrier itself. This results in :

$$\gamma_{ow} + \gamma_{oa} - \tfrac{1}{2}g\,\frac{\rho_0(\rho_w - \rho_0)}{\rho_w}\,.\,t^2 = \gamma_{wa} = (\gamma_w)_p - F \quad . \quad . \quad (1)$$

t = thickness of oil lense in cm ;

$(\gamma_w)_p$ = surface tension of the pure water on the other side of the barrier in dyne/cm ;

γ_{wa} = surface tension of water–air interface adjoining the oil in dyne/cm ;

F = the surface pressure exerted by the barrier in dyne/cm.

γ_{ow} and γ_{wa} will depend on the concentrations of the active substances in the surface concerned ; γ_{oa} does not alter, according to Langmuir,[3] when the volume concentrations of the active substances in the oil vary. The thicknesses of the oil layer with which we are dealing run from 0·1 μ to several μ's, so the term :

$$\tfrac{1}{2}g\,\frac{\rho_0(\rho_w - \rho_0)}{\rho_w}\,t^2,$$

which is the difference between two integrated hydrostatic pressures

$$\tfrac{1}{2}g\rho_0 t^2 \text{ and } \tfrac{1}{2}g\rho_w\left(\frac{\rho_0}{\rho_w}t\right)^2,$$

is approximately equal to :

$$\approx \tfrac{1}{2}\,.\,1000\,.\,0{\cdot}1\,(10^{-5} \text{ till } 10^{-3})^2 \approx \tfrac{1}{2}(10^{-8} \text{ till } 10^{-4}) \text{ dyne/cm}$$

so that this term can very often be disregarded.

The above-mentioned thicknesses can be deducted either from the interference colours or by means of a simple calculation—*i.e.*, dividing the total oil volume by the surface occupied.

If the term is disregarded, it can be assumed that irrespective of the thickness of the oil-layer, the following equation applies :

$$\gamma_{ow} + \gamma_{oa} = \gamma_{wa} = (\gamma_w)_p - F \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Second Physico-chemical Equilibrium.

At a certain barrier pressure F, γ_{wa} the surface tension of the contaminated surface water–air is fixed (see equation 1). Thus also the concentration of active substances on this surface. If the second physico-chemical equilibrium holds, the concentration of active substances in the interface oil–water should also be fixed, and therefore also the interface tension and at the same time the thickness of the oil-layer.

This conflicts with observations made. For instance, if oxidized oil is diluted with the original non-oxidized oil and this mixture is spread, entirely different thicknesses of the oil layer are obtained at the same barrier surface pressure than if undiluted oxidized oil is spread.

It was also found, as has already been stated, that, provided one waits long enough, holes appear in the lense, the oil itself also changing in shape.

The interesting thing is that in all probability it is the peculiarity of the films of not attaining the second equilibrium during the measurements that renders it possible to obtain simple and comprehensible results. It is essential, however, that measurements are made quickly.

First Physico-chemical Equilibrium.

Using the described method of measurement, there is always a rather small water–air surface present between the barrier and the glass slide. The major section of the surface is, however, covered by the spread oil film. If, therefore, the water–air surfaces are disregarded, and it is assumed that there is a physico-chemical equilibrium between the surface concentration of the active substances in the interface oil–water and the volume concentration in the oil, one can easily explain theoretically the relation revealed by experiments between :

1. The surface occupied at certain barrier pressures (including that obtained by extrapolating to zero pressure);
2. Total quantity of oil spread;
3. Quantity of active substances in the oil.

This naturally gives a great deal of support to the acceptability of the suppositions.

At a certain barrier pressure F there should be a certain γ_{ow} (equation 2). This means that if there is only one active compound present, the concentration from this compound in the interface oil–water σ_{ow} (molecules per cm^2) is fixed.

Similarly the volume concentration u_0 (molecules per ml) is also fixed. But then the following formula holds independent of the original concentration of active substances in the oil.

$$A = \sigma_{ow} S + u_0 V \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which we have constants σ_{ow} and u_0, when the barrier pressure is fixed.

A = the total number of active molecules in the oil;
S = the surface in cm^2 of the oil;
V = the volume in ml of the oil.

From formula 3 it is easy to explain the seemingly paradoxical experimental results that, by adding pure oil (increasing V) to a certain quantity of impure oil (A therefore remains constant), a smaller surface is obtained with the same barrier pressure. This means, therefore, that the thickness of the oil layer increases out of proportion to the volume. The new pure oil added must also be brought up to the concentration u_0 of active molecules. These active molecules can only be obtained from the interface, which must, however, retain the same concentration, so that the surface must of necessity become smaller.

Before we discuss the results of our experiments any further, we amend the formula (3) somewhat and go on to specific quantities :

$$\frac{S}{V}=\frac{1}{\sigma_{ow}}\cdot\frac{A}{V}-\frac{u_o}{\sigma_{ow}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

$\frac{S}{V}$ is the specific spreading : Surface in cm^2 per total volume of oil in ml. We will call this s (usually the specific spreading is given in cm^2/mg oil, but for a theoretical research it is better to use the cipher cm^2 per ml).

$\frac{A}{V}$ is the total concentration of active molecules per unit of volume (thus including those present in the dividing surface). This number is unknown, and therefore we substitute a dilution x.

We started with a certain oxidized oil, which we assume had a total concentration a_u of active molecules per ml.

Spreading tests were made with this and other oils, which were obtained by mixing the latter with varying quantities of the original pure oil containing no active substances.

The relation $\frac{\text{oxidized quantity of oil}}{\text{total quantity of oil}}$ we will call dilution x.

Formula (4) thus becomes :

$$s=\frac{a_u}{\sigma_{ow}}x-\frac{u_0}{\sigma_{ow}}$$

Fig. 1 shows s as a function of x. There are three curves. The first stands for the extrapolated barrier pressure of 0 dyne/cm ; the second for a barrier pressure of 1 dyne/cm and the third for 1·5 dyne/cm. It can be seen that the points fall quite nicely along straight lines. If these lines are continued, they intersect the s axis. The section between the inter-section point and the origin should equal $\frac{u_o}{\sigma_{ow}}$. The reciprocal is a linear dimension in cm. This magnitude equals the thickness of an oil layer containing as many molecules as the corresponding interface oil–water. Corresponding means that the concentrations at the interface and in the oil are in physico-chemical equilibrium with each other at the given barrier pressure. In the case in question this thickness appears to be $\approx 10^{-4}$ cm $= 1\mu$.

When $x = 1$ (*i.e.*, the unmixed oxidized oil), the actual thickness of the oil layer at a pressure of zero is $\approx 0{\cdot}06\mu$; the major part of the active molecules is therefore present in the interface.

It is interesting to note that the lines for 0, 1 and 1·5 dyne/cm all intersect the s axis at the same point. This means that at the equilibrium there is a constant ratio between the volume and surface concentrations for these pressures, which gives strong support to the hypothesis that the active molecules in the interface are present in a two-dimensional gas state in equilibrium with non-associated molecules in solution in the oil. This hypothesis complies with Gibb's theorem, and demands a conforming with $\gamma_{oa}+\gamma_{ow}-\gamma_{w1}$ of the pure oil in the same manner as Langmuir[3] has done with stearic acid and oil. It should be remarked that Langmuir gets quantitive results different from that which we find with oxidized oils. This leads us to believe that the active molecules, which cause the previously mentioned relations, are not acids. This is also apparent from the small influence of the pH of the water shown in the result of our tests. Should such acids still be present, however, it can be understood that they would be in a condensed two-dimensional phase, and would exert a small, constant saturation pressure.

Another consequence of the constant ratio between the surface- and volume-concentration can be deduced from formula (3).

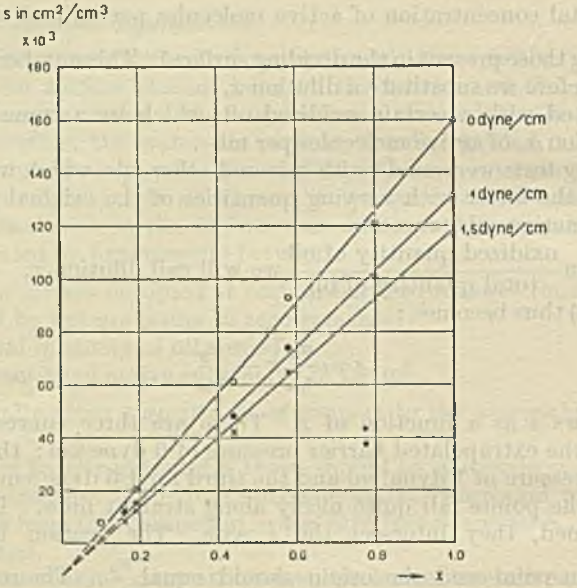

Fig. 1.

RELATION BETWEEN THE SPECIFIC SPREADING VALUES AND THE DILUTION OF AN OXIDIZED OIL WITH ITS ORIGINAL UNOXIDIZED OIL FOR DIFFERENT BARRIER PRESSURES.

This can be written :

$$A = \sigma_{ow}\left(S + \frac{u_0}{\sigma_{ow}} V\right),$$

$$\frac{u_0}{\sigma_{ow}} = \text{a constant.}$$

σ_{ow} is a function of γ_{ow}, and therefore of the barrier pressure F only. When there is an equal quantity of oxidized oil in the spread oil mixture (A = constant), and the total amount of oil V is increased from V_1 to V_2, the area S decreases by a constant amount $\frac{u_0}{\sigma_{ow}}(V_2 - V_1)$, irrespective of the barrier pressure.

So the barrier pressure area curve, staying parallel to itself, moves along the surface axis to smaller surfaces when the oil is more diluted.

This rather remarkable phenomenon was the first indication we received of the existence of the simple relationships described above.

If one examines what happens when two kinds of molecules with different surfaces are present, while the two-dimensional gas law applies, and at the same time these molecules are dissolved in non-associated condition, one obtains that the resultant theoretical relation between s and x will not be rendered by a straight line, but by a hyperbola. Over a great stretch this hyperbola cannot be distinguished from its asymptote, so that the straight line connection can still be used. (The straight line applies when the oil-layer is so thin that the major part of the active molecules are found in the surface.) The theoretical curve (the other asymptote of the hyperbola runs parallel to the x axis at a certain distance below it) likewise dips below the x axis, where x has a positive value. In fact, of course, this is not feasible. The digressions of the actual curves as compared with the theoretical ones are caused by the fact that in the case of excessive dilutions :

(1) That part of the space between the barrier and the strip occupied by the free water surface can no longer be disregarded ;

(2) The oil layer becomes so thick that the simplified equation (2) is no longer applicable.

In any case one never gets too high values when the specific spreading (surface at barrier pressure zero divided by the total quantity of oil) is taken as a measure for the content of active substances. This content is always bigger in reality and the error relatively smaller as the content increases.

APPLICATION.

Cable Research.

In such research the spreading values often give good indication as to what is happening in the insulation. The insulation of a high-tension cable consists of paper with impregnated oil. The oil used for this purpose must be of very special quality, and it is obvious that very thorough methods of investigation must be used in order to trace any changes in the oil.

The curves *a* of Fig. 2 show clearly that it is possible to point out very small differences. We are dealing here with centrifuged oil from the paper from different layers in the insulation of four pieces of cable. Of these, III and IV have been kept at an increased temperature for a certain length of time, while I and II have remained at room temperature for the same period. Furthermore, II and IV have been subjected to electrical tension tests. The spreading values are shown as a function of the number of the layer.

In addition to the spreading measurements, the power factor of the oil-impregnated paper is measured with a condenser such as described by Wyatt.[4] In curves *b* of Fig. 2 these measurements are shown. These paper tapes, after being measured at 75° C, were centrifuged too and the spreading values of the oil measured. See curves *c* of Fig. 2.

The remarkable thing is that the power factor measurements do not show the differences between the four pieces of cable in the middle of the insulation, found with the spreading measurements.

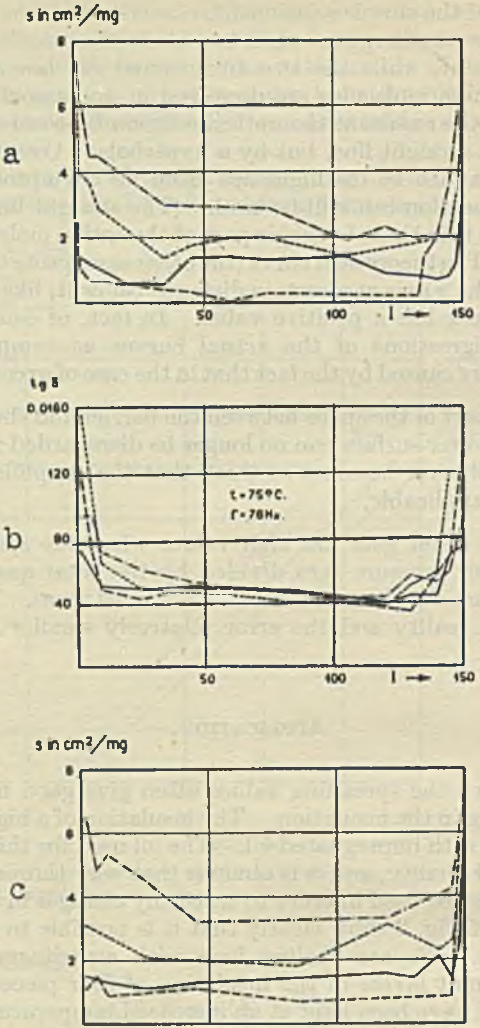

Fig. 2.

MEASUREMENTS ON FOUR DIFFERENT CABLES PLOTTED AGAINST THE NUMBER OF THE PAPER LAYERS COUNTED FROM THE LEAD SHEATH.

———— Cable kept at room temperature. No electrical tension applied.

- - - - - - - Cable kept at room temperature. Electrical tension applied 90–100 kV.

—·—·—. Cable kept at 55–75° C. No electrical tension applied.

· · · · · · · · · Cable kept at 55–75° C. Electrical tension applied 90–100 kV.

a : Specific spreading values of the oil centrifuged from the paper tapes.

b : Power factor measurements of the impregnated paper tapes at 75° C and a frequency of 76 c.p.s.

C : Specific spreading values of the oil centrifuged from the paper tapes after power factor measurements.

In addition, it is also noticeable that the oil in the condenser oxidizes slightly at a temperature of 75° C.

Oil Oxidation.

When making oxidation tests we use the specific spreading as a measure for the grade of oxidation. The top graph of Fig. 3 shows such a process

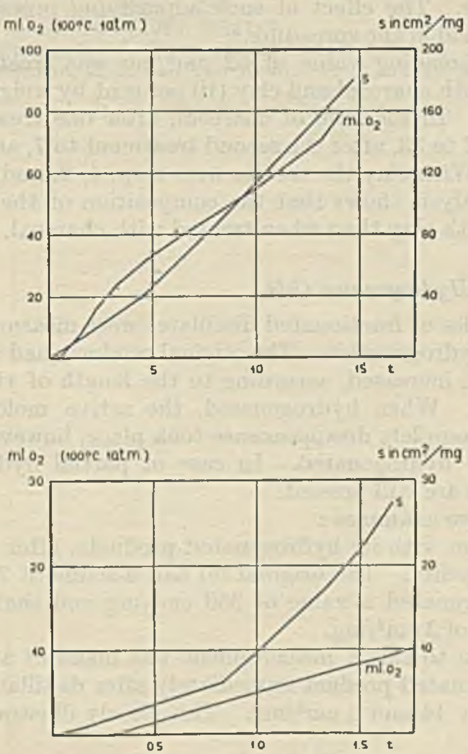

FIG. 3.

SPREADING VALUES AND OXYGEN ABSORBED AS A FUNCTION OF THE TIME IN HOURS.

with oxygen absorption plotted against the time. The way in which these oxidation tests are made has, of course, no bearing on the subject. Our test can determine the exact moment at which the oil commences to absorb oxygen, and in this particular instance the process began 15 minutes after the start of the test. It is interesting to know if anything can be noticed in the oil in this preceding induction time. Spreading measurements give an affirmative answer. When the process began, the values were measured every ten minutes; they are reproduced in the lower graph. It can be observed that the oil changes already in the induction time. Now compare these spreading measurements with the acid value. After an oxidation time of two hours the oil has a specific spreading value of 20 cm²/mg, the original oil having a zero value. This is certainly no small value for the oxidized oil. The acid value is found to be 0·07 and 0·05 mg KOH/g oil for the oxidized and non-oxidized oil respectively. This result is self-explanatory.

Purifying of Oil.

It is possible to remove oxidation products from oil by treating it with charcoal or clay. The effect of such a purifying process can easily be followed by the aid of the spreading.[5]

Oil with a spreading value of 52 cm^2/mg was treated several times consecutively with charcoal and clay (10 per cent by weight) at a temperature of 100° C. In the case of charcoal, after one treatment the value dropped from 52 to 33, after the second treatment to 7, and after the third to 3 cm^2/mg. With clay the results were resp. 4, 2, and 1 cm^2/mg. The Waterman [6] analysis shows that the composition of the oil changes less when treated with clay than when treated with charcoal.

Examination of Hydrogenated Oils.

Various samples of fractionated distillates were measured as well as the products after hydrogenation. The original products had a positive spreading value, which increased, according to the length of time the fractions had been kept. When hydrogenated, the active molecules disappear. In tests made, complete disappearance took place, however, only after the oil was entirely hydrogenated. In case of partial hydrogenation some active molecules are still present.

Here follow two examples :

First a fraction with its hydrogenated products, after having stood for a period of six years. The original oil had a value of 755 cm^2/mg; the partially hydrogenated a value of 360 cm^2/mg and that entirely hydrogenated a value of 3 cm^2/mg.

In comparison to this a measurement was made of a fraction and its entirely hydrogenated product immediately after distillation. The values were respectively 14 and 0 cm^2/mg. This clearly illustrates the influence exerted by time.

CONCLUSION.

The spreading measurements described above offer a particularly sensitive method for investigating the properties of mineral oils which are of importance for practical use from the standpoint of their oxidation stability, purity, etc. This method often enables one to show changes where other methods fail. The theoretical considerations teaches us to understand some of the formulae reached, and arouses the expectation that the method could be still further developed along the lines of what might be called differential diagnoses.

Finally we wish to pay a tribute to the memory of the late Mr. H. W. G. Van Gils, E.E., who instituted this method of research in connection with insulating oil at the laboratory. He was killed as a civilian by the Germans on May 10, 1940.

Due to the isolation caused by the war, we only learned of the papers by W. A. Zisman and by W. D. Hartins (*J. Chem. Phys.*, 1941) after the above paper had been written. We think that the interesting general investigations in these papers are supplemented from the practical viewpoint by our research.

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FRACTIONAL DISTILLATION OF TERNARY MIXTURES. PART II.

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Summary.

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

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

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

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

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

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

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

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

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

Constant molal reflux and constant relative volatilities are assumed.

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

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

$$=\frac{\gamma x_1\cdot\dfrac{\gamma}{\gamma-\phi}+\beta y_1\cdot\dfrac{\beta}{\beta-\phi}+z_1\cdot\dfrac{1}{1-\phi}}{\gamma x_1+\beta y_1+z_1}$$

Now choose ϕ so that

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

Then

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

$$=\frac{\gamma x_1\left(\dfrac{\gamma}{\gamma-\phi}-1\right)+\beta y_1\left(\dfrac{\beta}{\beta-\phi}-1\right)+z_1\left(\dfrac{1}{1-\phi}-1\right)}{\gamma x_1+\beta y_1+z_1}$$

and

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

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

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

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

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

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

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

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

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

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

and

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\begin{array}{lll}
\phi_1 = 1 - 0{\cdot}376 \times 10^{-6}; & \phi_2 = 1{\cdot}999; & \phi_3 = 3{\cdot}0015 \\
h_1 = 0{\cdot}111; & k_1 = 0{\cdot}00033; & l_1 = 0{\cdot}88867 \\
h_2 = 0{\cdot}333; & k_2 = 0{\cdot}667; & l_2 = -0{\cdot}67 \times 10^{-6} \\
h_3 = 1{\cdot}001; & k_3 = -0{\cdot}001; & l_3 = -0{\cdot}5 \times 10^{-6}
\end{array}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

we obtain

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

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

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

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

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

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

It is believed that the following analysis clarifies the position.

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

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

and

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

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

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

and

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

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

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

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

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

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

Now, from equation (4)

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

or

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

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

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

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

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

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

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

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

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

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

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

and

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

When N becomes infinite,

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

and

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

For a stripping column, equations (8) become

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

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

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

and, by difference,

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

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

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

since $z_W = 1$.

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

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

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

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

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

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

and, by difference,

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

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

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

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

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

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

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

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

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

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

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

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

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

and

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

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

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

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

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

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

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

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

and

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

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

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

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

and

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Example 4. Third component lighter than the keys.

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

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

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

The desired value of θ is that which is between 1 and 2. The solution is found to be $1{\cdot}152$.

Equation (22) then gives

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

Example 5. Third component heavier than the keys.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

With this value of θ, equation (25) becomes

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

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

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

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

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FRACTIONAL DISTILLATION OF MULTI-COMPONENT MIXTURES—CALCULATION OF MINIMUM REFLUX RATIO.

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Summary.

By extending a method which has been applied to ternary mixtures, equations are derived by which the minimum reflux ratio for multi-component mixtures can be readily calculated when the fractionation between the key components is a sharp one, relative volatilities and molal reflux being assumed constant. Numerical examples are given to illustrate the method of calculation.

The calculation of minimum reflux ratio is an important problem. Several methods of calculation have been put forward such as those of Brown and Martin,[1] Brown and Holcomb,[2] Gilliland,[3] Hogan,[4] and Colburn.[5] Some of those methods involve a considerable amount of calculation and, as has been pointed out by Colburn,[5] are open to criticism in regard to the basic assumptions made. The most convenient method for most purposes is that of Colburn,[5] but it admittedly rests on an empirical basis.

By extending to multi-component mixtures the methods previously described by the author [6, 7] in connection with ternary mixtures, the calculation of minimum reflux ratio can be made fairly simply for cases of ideal mixtures with constant relative volatilities and sharp separation between the key components. Where the relative volatilities vary in the column the same method of calculation can be used to give the minimum reflux ratio approximately.

By way of example a mixture of four components (w, x, y, z) will be considered, the relative volatilities, referred to component z, being δ, γ, β respectively. It has been shown previously [6] that an equation can be derived connecting the composition on any plate (w_0, x_0, y_0, z_0) with the composition (w_1, x_1, y_1, z_1) on the next plate below it, namely

$$\frac{\delta w_0}{\delta-\phi}+\frac{\gamma x_0}{\gamma-\phi}+\frac{\beta y_0}{\beta-\phi}+\frac{z_0}{1-\phi}=\frac{\phi\left\{\dfrac{\delta w_1}{\delta-\phi}+\dfrac{\gamma x_1}{\gamma-\phi}+\dfrac{\beta y_1}{\beta-\phi}+\dfrac{z_1}{1-\phi}\right\}}{m(\delta w_1+\gamma x_1+\beta y_1+\beta_1)} \qquad (1)$$

where ϕ is given by the equation

$$\frac{a\delta}{\delta-\phi}+\frac{b\gamma}{\gamma-\phi}+\frac{c\beta}{\beta-\phi}+\frac{d}{1-\phi}=1 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As previously, for a rectifying column, $m=\dfrac{R}{R+1}$, $a=\dfrac{w_D}{R+1}$, $b=\dfrac{x_D}{R+1}$, etc., and for a stripping column, $m=\dfrac{S+1}{S}$, where $S=\dfrac{RP+qF-W}{W}$ and $a=-\dfrac{w_W}{S}$, $b=-\dfrac{x_W}{S}$, etc.

Equation (2) gives four values of ϕ, which, in ascending order of magnitude, are denoted by ϕ_1, ϕ_2, ϕ_3, ϕ_4. These values of ϕ give four equations when substituted in equation (1). Applying these to n successive plates and dividing any one equation by any one of the others, there are obtained a set of equations such as

$$\frac{\dfrac{\delta w_0}{\delta-\phi_1}+\dfrac{\gamma x_0}{\gamma-\phi_1}+\dfrac{\beta y_0}{\beta-\phi_1}+\dfrac{z_0}{1-\phi_1}}{\dfrac{\delta w_0}{\delta-\phi_2}+\dfrac{\gamma x_0}{\gamma-\phi_2}+\dfrac{\beta y_0}{\beta-\phi_2}+\dfrac{z_0}{1-\phi_2}} = \left(\frac{\phi_1}{\phi_2}\right)^n \cdot \frac{\dfrac{\delta w_n}{\delta-\phi_1}+\dfrac{\gamma x_n}{\gamma-\phi_1}+\dfrac{\beta y_n}{\beta-\phi_1}+\dfrac{z_n}{1-\phi_1}}{\dfrac{\delta w_n}{\delta-\phi_2}+\dfrac{\gamma x_n}{\gamma-\phi_2}+\dfrac{\beta y_n}{\beta-\phi_2}+\dfrac{z_n}{1-\phi_2}} \quad . \quad . \quad (3)$$

Any two of the four values of ϕ will give an equation of this type, so that six equations are obtained in all. Denoting, for convenience, the expression

$$\frac{\delta w_0}{\delta-\phi_1}+\frac{\gamma x_0}{\gamma-\phi_1}+\frac{\beta y_0}{\beta-\phi_1}+\frac{z_0}{1-\phi_1} \text{ as } E(x_0, \phi_1) \quad . \quad . \quad . (3a)$$

the six equations, of which equation (3) is the first, are

$$\left.\begin{aligned}
\frac{E(x_0,\phi_1)}{E(x_0,\phi_2)} &= \left(\frac{\phi_1}{\phi_2}\right)^n \cdot \frac{E(x_n,\phi_1)}{E(x_n,\phi_2)}; &\quad \frac{E(x_0,\phi_1)}{E(x_0,\phi_3)} &= \left(\frac{\phi_1}{\phi_3}\right)^n \cdot \frac{E(x_n,\phi_1)}{E(x_n,\phi_3)} \\
\frac{E(x_0,\phi_1)}{E(x_0,\phi_4)} &= \left(\frac{\phi_1}{\phi_4}\right)^n \cdot \frac{E(x_n,\phi_1)}{E(x_n,\phi_4)}; &\quad \frac{E(x_0,\phi_2)}{E(x_0,\phi_3)} &= \left(\frac{\phi_2}{\phi_3}\right)^n \cdot \frac{E(x_n,\phi_2)}{E(x_n,\phi_3)} \\
\frac{E(x_0,\phi_2)}{E(x_0,\phi_4)} &= \left(\frac{\phi_2}{\phi_4}\right)^n \cdot \frac{E(x_n,\phi_2)}{E(x_n,\phi_4)}; &\quad \frac{E(x_0,\phi_3)}{E(x_0,\phi_4)} &= \left(\frac{\phi_3}{\phi_4}\right)^n \cdot \frac{E(x_n,\phi_3)}{E(x_n,\phi_4)}
\end{aligned}\right\} \quad (4)$$

These six equations represent only three independent relations. The last three can obviously be derived from the first three. The three independent relations, combined with the equation

$$w + x + y + z = 1$$

suffice to solve for the four variables, w, x, y, z.

Under certain conditions the composition on a plate may be exactly equal to the composition on the plate above or below it, and a plate-to-plate calculation leads to an infinite number of plates. For such conditions of "constant composition" or "limiting composition," denoting such a composition by (g, h, k, l), equation (1) gives

$$\phi = m(\delta g + \gamma h + \beta k + l) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

As shown previously [6]

$$g = \frac{a\phi}{m(\delta-\phi)};\ h = \frac{b\phi}{m(\gamma-\phi)};\ k = \frac{c\phi}{m(\beta-\phi)};\ l = \frac{d\phi}{m(1-\phi)} \quad . \quad (6)$$

There are four values of ϕ, and consequently four limiting compositions which may be denoted by the suffix attached to the corresponding value of ϕ. Thus g_1, h_1, k_1, l_1 are obtained by using ϕ_1 in equations (6).

The expression $E(x_n, \phi_1)$ can be shown to become zero if g_2, h_2, k_2, l_2 are substituted for w_n, x_n, y_n, z_n. The condition for this is that

$$\frac{\delta g_2}{\delta - \phi_1} + \frac{\gamma h_2}{\gamma - \phi_1} + \frac{\beta k_2}{\beta - \phi_1} + \frac{l_2}{1 - \phi_1} = 0$$

or, from equations (6),

$$\frac{a\delta}{(\delta - \phi_1)(\delta - \phi_2)} + \frac{b\gamma}{(\gamma - \phi_1)(\gamma - \phi_2)} + \frac{c\beta}{(\beta - \phi_1)(\beta - \phi_2)} + \frac{d}{(1 - \phi_1)(1 - \phi_2)} = 0 \quad . \quad (7)$$

From equation (2)

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

or

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

which is the same as equation (7).

Similarly it can be shown that $E(x_n, \phi_1)$ also becomes zero for the values g_3, h_3, k_3, l_3 and g_4, h_4, k_4, l_4. It does not become zero for the values g_1, h_1, k_1, l_1, as may be seen by putting $\phi_2 = \phi_1$ in equation (7). All the terms on the left-hand side are positive for a rectifying column and negative for a stripping column, and the sum of them can in neither case be zero.

Similar relations can be obtained for the other expressions similar to $E(x_n, \phi_1)$. The various equations are satisfied as follows. (The suffix n is here dropped for the sake of generality.)

$E(x, \phi_1) = 0$ by (g_2, h_2, k_2, l_2), (g_3, h_3, k_3, l_3) and (g_4, h_4, k_4, l_4)
$E(x, \phi_2) = 0$ by (g_1, h_1, k_1, l_1), (g_3, h_3, k_3, l_3) and (g_4, h_4, k_4, l_4)
$E(x, \phi_3) = 0$ by (g_1, h_1, k_1, l_1), (g_2, h_2, k_2, l_2) and (g_4, h_4, k_4, l_4)
$E(x, \phi_4) = 0$ by (g_1, h_1, k_1, l_1), (g_2, h_2, k_2, l_2) and (g_3, h_3, k_3, l_3)

If any three of these equations are simultaneously satisfied, they have one common solution.

Thus $$E(x, \phi_1) = E(x, \phi_3) = E(x, \phi_4) = 0$$

have (g_2, h_2, k_2, l_2) as the common solution. The suffix attached to g, h, k, l is the one which does not appear in the values of ϕ involved in the three equations.

If any two of the equations are simultaneously satisfied, they have two common solutions.

Thus $$E(x, \phi_3) = E(x, \phi_4) = 0$$

have (g_1, h_1, k_1, l_1) and (g_2, h_2, k_2, l_2) as common solutions. Here again the suffixes attached to g, h, k, l are those which do not appear in the values of ϕ.

The significance of the four limiting compositions can be shown as follows, a rectifying column being considered by way of example. It is readily shown, as in the case of ternary mixtures, that putting $w_0 = w_D$, $x_0 = x_D$, etc., makes any of the expressions on the left-hand side of equations (4) equal to (1). We then have, by selecting the three appropriate equations,

$$\frac{E(x_n, \phi_2)}{E(x_n, \phi_1)} = \left(\frac{\phi_1}{\phi_2}\right)^n; \quad \frac{E(x_n, \phi_3)}{E(x_n, \phi_1)} = \left(\frac{\phi_1}{\phi_3}\right)^n; \quad \frac{E(x_n, \phi_4)}{E(x_n, \phi_1)} = \left(\frac{\phi_1}{\phi_4}\right)^n$$

Now $\phi_1 < \phi_2 < \phi_3 < \phi_4$ and therefore, when n becomes infinite,

$$E(x_n, \phi_2) = E(x_n, \phi_3) = E(x_n, \phi_4) = 0.$$

These equations are satisfied by (g_1, h_1, k_1, l_1), which, in addition, does not make the denominator $E(x_n, \phi_1)$ zero. Thus a calculation proceeding down the column from the top finally reaches the limiting composition (g_1, h_1, k_1, l_1).

If we put $n = -N$, where N is positive, the composition can be obtained for an imaginary plate located N plates above the top of the column. From equations (4) we have

$$\frac{E(x_{-N}, \phi_1)}{E(x_{-N}, \phi_4)} = \left(\frac{\phi_1}{\phi_4}\right)^N; \quad \frac{E(x_{-N}, \phi_2)}{E(x_{-N}, \phi_4)} = \left(\frac{\phi_2}{\phi_4}\right)^N; \quad \frac{E(x_{-N}, \phi_3)}{E(x_{-N}, \phi_4)} = \left(\frac{\phi_3}{\phi_4}\right)^N$$

When n becomes infinite

$$E(x_{-N}, \phi_1) = E(x_{-N}, \phi_2) = E(x_{-N}, \phi_3) = 0$$

and the solution is (g_4, h_4, k_4, l_4), which is the limiting composition reached when a calculation is carried upwards from the top of the column.

The other two limiting compositions (g_2, h_2, k_2, l_2) and (g_3, h_3, k_3, l_3) have particular practical significance when certain components are only present in small amount in the top product.

There are three cases to be considered :—

Case I. z is the heavy key component and is present in the top product in small amount.

Case II. y is the heavy key component and both y and z are present in the top product in small amounts.

Case III. x is the heavy key component and x, y and z are present in the top product in small amounts.

For case I, since d in equation (2) is approximately zero, ϕ_1 is approximately equal to 1. Substituting this value in equations (6) gives g_1, h_1, k_1, l_1 the last of these by difference. These are the values of the limiting composition reached by calculating downwards from the top of the column with all four components in the calculation.

For case II, since both d and c in equation (2) are approximately zero, $\phi_1 = 1$ and $\phi_2 = \beta$ approximately. Using the value $\phi_1 = 1$, the values of g_1, h_1, k_1, l_1 can be calculated when the values of d and c, although very small, are specified. The method of calculation is similar to that given for

Example 3 of the previous paper.[7] Using the value $\phi_2 = \beta$ in equations (6) gives g_2, h_2, k_2, l_2. l_2 has a very small negative value which, as explained in connection with ternary mixtures,[7] may be neglected for practical purposes. k_2 is indeterminate in equation (6) when $c = 0$ and $\phi = \beta$, but can be found by difference, or by the method of approximation described in connection with ternary mixtures. This limiting composition thus contains the three components w, x, y, and is the one reached by calculating down from the top of the column using these three components. It can also be calculated by the usual method based on the small amount of the heavy key component.

For Case III, since d, c, and b are all small in equation (2), $\phi_1 = 1$, $\phi_2 = \beta$, and $\phi_3 = \gamma$ approximately. Using $\phi_3 = \gamma$ in equation (6) gives $k_3 = l_3 = 0$. After finding g_3, then h_3 is found by difference. The limiting composition contains only the two components w and x, and is the one obtained by calculating down the column from the top using these two components. It represents the limiting composition that would be reached with a binary mixture.

Thus, when making a calculation downwards from the top (g_1, h_1, k_1, l_1) is reached if z is the heavy key. If y is the heavy key, (g_2, h_2, k_2, l_2) is reached. If x is the heavy key, (g_3, h_3, k_3, l_3) is reached.

For a rectifying column, superimposed on a stripping column, minimum reflux conditions prevail (in the rectifying column) when a calculation made downwards from the top and a calculation made upwards from the feed-plate both meet at the appropriate limiting composition which, as shown above, depends on which are the key components. It is possible to specify what composition or range of compositions can exist at the feed-plate if the downward and upward calculations are to meet in this way.

If z is the heavy key, the composition at the feed-plate will be (g_1, h_1, k_1, l_1), and the downward and upward calculations actually meet at the feed-plate. The composition at the feed-plate is thus defined by the three equations

$$E(x, \phi_2) = 0; \quad E(x, \phi_3) = 0; \quad E(x, \phi_4) = 0 \quad . \quad . \quad . \quad (8)$$

If y is the heavy key, the limiting composition (g_2, h_2, k_2, l_2) is reached by the downward calculation. If the upward calculation is to reach this point, $E(x_n, \phi_2)$ must not be equal to zero. (Here w_n, x_n, y_n, z_n is taken to be the feed plate composition.) From equation (1) it will be seen that, if $E(x, \phi_2)$ is zero for any given plate, it will also be zero for all successive plates. From equations (4) we have, for a plate 0 which is n plates above the feed plate,

$$\frac{E(x_0, \phi_1)}{E(x_0, \phi_2)} = \left(\frac{\phi_1}{\phi_2}\right)^n \cdot \frac{E(x_n, \phi_1)}{E(x_n, \phi_2)}.$$

When n becomes infinite, $E(x_0, \phi_1)$ becomes zero. At (g_2, h_2, k_2, l_2), in addition to $E(x_0, \phi_1) = 0$ we must also have $E(x_0, \phi_3) = 0$ and $E(x_0, \phi_4) = 0$. If these two equations are satisfied by the feed-plate composition, they will also be satisfied by the compositions on all plates above it, as will be seen from equation (1). Thus, where y is the heavy key, there is a possible range of compositions at the feed-plate, and this range is defined by the equations

$$E(x, \phi_3) = 0; \quad E(x, \phi_4) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

From these equations it is also clear that the upward calculation will not pass through (g_3, h_3, k_3, l_3) or (g_4, h_4, k_4, l_4).

If x is the heavy key, the limiting composition reached by the downward calculation is (g_3, h_3, k_3, l_3). This composition must also be reached by the upward calculation. Then $E(x_n, \phi_3)$ must not be zero.

From equations (4),

$$\frac{E(x_0, \phi_1)}{E(x_0, \phi_3)} = \left(\frac{\phi_1}{\phi_3}\right)^n \cdot \frac{E(x_n, \phi_1)}{E(x_n, \phi_3)} \text{ and } \frac{E(x_0, \phi_2)}{E(x_0, \phi_3)} = \left(\frac{\phi_2}{\phi_3}\right)^n \cdot \frac{E(x_n, \phi_2)}{E(x_n, \phi_3)}.$$

When n becomes infinite, $E(x_0, \phi_1) = 0$ and $E(x_0, \phi_2) = 0$. At (g_3, h_3, k_3, l_3), we must also have $E(x_0, \phi_4) = 0$. If the feed-plate composition satisfies this equation, the upward calculation will reach (g_3, h_3, k_3, l_3). Thus, where x is the heavy key, the possible range of compositions at the feed plate is defined by the equation

$$E(x, \phi_4) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

From equations (8), (9), and (10) it will be seen that the composition at the feed-plate, for minimum reflux conditions, is defined by three, two or one equations according as z, y, or x is the heavy key.

Conditions for minimum reflux in the stripping column can be defined in a similar manner. When calculating upwards from the reboiler, the limiting composition $(\bar{g}_4, \bar{h}_4, \bar{k}_4, \bar{l}_4)$ is reached when w is the light key. When x is the light key, $(\bar{g}_3, \bar{h}_3, \bar{k}_3, \bar{l}_3)$ is reached. When y is the light key, $(\bar{g}_2, \bar{h}_2, \bar{k}_2, \bar{l}_1)$ is reached. By calculating downwards below the reboiler $(\bar{g}_1, \bar{h}_1, \bar{k}_1, \bar{l}_2)$ is reached.

For the stripping column it is convenient to write ψ instead of ϕ. Also $\psi_1 < \psi_2 < \psi_3 < \psi_4$. Let $(\bar{w}_0, \bar{x}_0, \bar{y}_0, \bar{z}_0)$ refer to the feed-plate and $(\bar{w}_n, \bar{x}_n, \bar{y}_n, \bar{z}_n)$ to a plate n plates below the feed-plate. When y is the light key, $(\bar{g}_2, \bar{h}_2, \bar{k}_2, \bar{l}_2)$ is reached by calculating upwards from the bottom, and must also be reached by calculating downwards from the feed-plate. Then $E(\bar{x}_0, \psi_2)$ is not zero.

From equations (4)

$$\frac{E(\bar{x}_n, \psi_3)}{E(\bar{x}_n, \psi_2)} = \left(\frac{\psi_2}{\psi_3}\right)^n \cdot \frac{E(\bar{x}_0, \psi_3)}{E(\bar{x}_0, \psi_2)} \text{ and } \frac{E(\bar{x}_n, \psi_4)}{E(\bar{x}_n, \psi_2)} = \left(\frac{\psi_2}{\psi_4}\right)^n \cdot \frac{E(\bar{x}_0, \psi_4)}{E(\bar{x}_0, \psi_2)}$$

When n becomes infinite, $E(\bar{x}_n, \psi_3) = 0$ and $E(\bar{x}_n, \psi_4) = 0$. For $(\bar{g}_2, \bar{h}_2, \bar{k}_2, \bar{l}_2)$ to be reached it is also necessary that $E(\bar{x}_n, \psi_1) = 0$, and this will be the case if the feed-plate composition satisfies the relation

$$E(x, \psi_1) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If x is the light key, $(\bar{g}_3, \bar{h}_3, \bar{k}_3, \bar{l}_3)$ has to be reached by calculating down from the feed-plate.

$E(\bar{x}_0, \psi_3)$ is not zero. From equations (4)

$$\frac{E(\bar{x}_n, \psi_4)}{E(\bar{x}_n, \psi_3)} = \left(\frac{\psi_3}{\psi_4}\right)^n \cdot \frac{E(\bar{x}_0, \psi_4)}{E(\bar{x}_0, \psi_3)}.$$

When n becomes infinite, $E(\bar{x}_n, \psi_4) = 0$. In addition, for $(\bar{g}_3, \bar{h}_3, \bar{k}_3, \bar{l}_3)$ it is necessary that $E(\bar{x}_n, \psi_1) = 0$ and $E(\bar{x}_n, \psi_2) = 0$. This will be the case if the feed-plate composition satisfies the relations

$$E(x, \psi_1) = 0 \text{ and } E(x, \psi_2) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

If w is the light key, the limiting composition $(\bar{g}_4, \bar{h}_4, \bar{k}_4, \bar{l}_4)$ is reached at the feed-plate and the relations to be satisfied are

$$E(x, \psi_1) = 0; \ E(x, \psi_2) = 0; \ E(x, \psi_3) = 0 \quad . \quad . \quad . \quad (13)$$

Relations have now been derived which specify the composition or range of compositions at the feed-plate if minimum reflux conditions prevail in the rectifying column or in the stripping column. If minimum reflux conditions prevail throughout the whole column, the conditions for feed-plate composition derived from the rectifying column and those derived from the stripping column must be satisfied simultaneously. Collecting together the results which have been obtained, the conditions to be satisfied for the various separations are shown in Table I.

TABLE I.

Light key.	Heavy key.	From rectifying column.	From stripping column.
y	z	$\left\{ E(x, \phi_2) = 0; \ E(x, \phi_3) = 0 \text{ and } E(x, \phi_4) = 0 \right\}$	$E(x, \psi_1) = 0$
x	y	$E(x, \phi_3) = 0; \ E(x, \phi_4) = 0$	$E(x, \psi_1) = 0; \ E(x, \psi_2) = 0$
w	x	$E(x, \phi_4) = 0$	$\left\{ E(x, \psi_1) = 0; \ E(x, \psi_2) = 0 \text{ and } E(x, \psi_3) = 0 \right\}$

In each case there are four equations to be satisfied. Each of these equations is of the type

$$\frac{\delta w}{\delta - \phi_1} + \frac{\gamma x}{\gamma - \phi_1} + \frac{\beta y}{\beta - \phi_1} + \frac{z}{1 - \phi_1} = 0$$

and involves only three independent variables such as $\frac{w}{z}$, $\frac{x}{z}$, and $\frac{y}{z}$. (In addition, there is, of course, the equation $w + x + y + z = 1$ for finding the actual values of the components from their ratios.) There must, therefore, be a relation between the four equations which reduces them to three independent equations. A relation which obviously meets this requirement is that any two of the values of ϕ or ψ involved in the equations should be equal.

From equation (2) it is readily shown that, for a rectifying column where a, b, c, d are positive

$$0 < \phi_1 < 1; \ 1 < \phi_2 < \beta; \ \beta < \phi_3 < \gamma; \ \gamma < \phi_4 < \delta.$$

Similarly for a stripping column where a, b, c, d are negative

$$1 < \psi_1 < \beta; \ \beta < \psi_2 < \gamma; \ \gamma < \psi_3 < \delta; \ \delta < \psi_4.$$

Thus none of the values of ϕ can be equal and none of the values of ψ can be equal. To satisfy the conditions for minimum reflux it is therefore necessary that one of the values of ϕ involved should be equal to one of the values of ψ involved.

For the case where y and z are the light and heavy keys respectively, ψ_1 must then be equal to ϕ_2 or ϕ_3 or ϕ_4. From the ranges of the values of

ϕ and ψ, it is obvious that the only possibility is $\phi_2 = \psi_1$. Both these lie between 1 and β—that is, between the relative volatilities of the key components y and z. The limiting composition in the rectifying column in this case is (g_1, h_1, k_1, l_1) which satisfies $E(x, \phi_2) = 0$. The limiting composition for the stripping column is $(\bar{g}_2, \bar{h}_2, \bar{k}_2, \bar{l}_2)$ which satisfies $E(x, \psi_1) = 0$. Since $\phi_2 = \psi_1$, both limiting compositions satisfy the same equation.

Where x and y are the light and heavy keys, ψ_1 or ψ_2 must be equal to ϕ_3 or ϕ_4. The only possibility is $\phi_3 = \psi_2$, as both lie between β and γ, the relative volatilities of the key components. Here again it can be shown, as before, that the limiting compositions for the rectifying and stripping columns both satisfy the same equation $E(x, \phi_3) = 0$ or $E(x, \psi_2) = 0$.

Where w and x are the light and heavy keys, ϕ_4 must be equal to ψ_1 or ψ_2 or ψ_3. Thus ϕ_4 must be equal to ψ_3, as both lie between γ and δ.

The condition for minimum reflux in both the rectifying column and the stripping column is therefore

$$\phi_{n+1} = \psi_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where n and $(n + 1)$ represent the numbers to be attached to the values of ϕ and ψ when counting up from the lowest values, and also represent the numbers to be attached to the heavy and light keys components when counting up from the least volatile component. Also ϕ_{n+1} and ψ_n have a value which lies between the relative volatilities of the key components.

When equation (14) is satisfied, a stepwise calculation starting from the reboiler will reach a limiting composition in the stripping column and an infinite number of plates will be required to pass through this composition. The calculation will then pass up through the feed plate and will reach a limiting composition in the rectifying column and an infinite number of plates will again be required to pass through this composition to reach the composition at the top of the column.

Equation (2) for the rectifying column and the corresponding equation for the stripping column thus have a common root, which will be denoted by θ. This root has a value lying between the relative volatilities of the key components. Substituting for a, b, c, d in equation (2), the appropriate values for a rectifying column and for a stripping column, there are obtained the two equations which define θ

$$\frac{\delta w_D}{\delta - \theta} + \frac{\gamma x_D}{\gamma - \theta} + \frac{\beta y_D}{\beta - \theta} + \frac{z_D}{1 - \theta} = R + 1 \quad . \quad . \quad . \quad (15)$$

and

$$\frac{\delta w_W}{\delta - \theta} + \frac{\gamma x_W}{\gamma - \theta} + \frac{\beta y_W}{\beta - \theta} + \frac{z_W}{1 - \theta} = -S \quad . \quad . \quad . \quad (16)$$

Now $\quad Pw_D + Ww_W = Fw_F; \; Px_D + Wx_W = Fx_F;$ etc.

where w_F, x_F, etc., denote the composition of the feed.

Also $SW = RP + qF - W = (R + 1)P - (1 - q)F$ since $W = F - P$. Then multiplying equation (15) by P and equation (16) by W, and adding, we obtain

$$\frac{\delta w_F}{\delta - \theta} + \frac{\gamma x_F}{\gamma - \theta} + \frac{\beta y_F}{\beta - \theta} + \frac{z_F}{1 - \theta} = 1 - q \quad . \quad . \quad (17)$$

When the feed is liquid at boiling-point, $q = 1$. When the feed is vapour at dew point, $q = 0$.

From equation (17) is found the appropriate value of θ which is the one lying between the relative volatilities of the key components. On substituting this value of θ in equation (15), the minimum reflux ratio is obtained. Similarly the minimum reboil ratio can be obtained from equation (16).

When R and S have thus been found, equations (19) and (20) can be used to find the other values ϕ and ψ required in the equations for the feed-plate composition listed in Table I. These equations can then be used to solve for the feed-plate composition.

In equations (15), (16), (17) the relative volatilities are all referred to the least volatile component. The relative volatilities can, however, be referred to any component. Thus, if y is the heavy key, and it is desired to refer the relative volatilities to it, equation (17) takes the form

$$\frac{\frac{\delta}{\beta} \cdot w_F}{\frac{\delta}{\beta} - \frac{\theta}{\beta}} + \frac{\frac{\gamma}{\beta} \cdot x_F}{\frac{\gamma}{\beta} - \frac{\theta}{\beta}} + \frac{y_F}{1 - \frac{\theta}{\beta}} + \frac{\frac{1}{\beta} \cdot z_F}{\frac{1}{\beta} - \frac{\theta}{\beta}} = 1 - q \quad . \quad . \quad . \quad (18)$$

Equations (15) and (16) can be written in the same form. The variable is now $\frac{\theta}{\beta}$, which may be written θ'. Its value lies between 1 and $\frac{\gamma}{\beta}$—*i.e.*, between the relative volatilities of the key components. The value obtained for the minimum reflux ratio is obviously the same whichever form of the equations is used.

The general equations corresponding to equations (15) and (16) for conditions other than minimum reflux are

$$\frac{\delta w_D}{\delta - \phi} + \frac{\gamma x_D}{\gamma - \phi} + \frac{\beta y_D}{\beta - \phi} + \frac{z_D}{1 - \phi} = R + 1 \quad . \quad . \quad . \quad (19)$$

and

$$\frac{\delta w_W}{\delta - \psi} + \frac{\gamma x_W}{\gamma - \psi} + \frac{\beta y_W}{\beta - \psi} + \frac{z_W}{1 - \psi} = -S \quad . \quad . \quad . \quad (20)$$

By differentiating these equations it will be seen that ϕ increases as R increases, while ψ decreases as S increases. R and S must obviously increase together. When R and S become infinite, the roots of both equations (19) and (20) are obviously 1, β, γ, δ. As R decreases from infinity to a finite value, the values of ϕ decrease and the values of ψ increase. As R is gradually decreased there will come a point when a value of ϕ and a value of ψ (lying between the relative volatilities of the key components) will become equal, and this will correspond to minimum reflux conditions.

The analysis has been given in detail for a four-component mixture. It can be made in exactly the same way for a mixture of any number of components, and equations exactly similar to equations (15), (16), (17) are then obtained. For instance, for a six-component mixture there will be six equations to be satisfied at the feed-plate for minimum reflux conditions. The ratios of the components constitute five independent variables. Two of the equations must be the same, and this condition is found to be equation (14)

$$\phi_{n+1} = \psi_n$$

where n and $(n + 1)$ refer to the heavy and light key components and the common value of ϕ and ψ lies between the relative volatilities of those components. The relation is quite a general one, and also holds good for binary mixtures.

The root of equation (17) which is normally required is the one lying between the relative volatilities of the key components. In some cases it is useful to obtain the other roots. For instance, if a mixture of four components is to be separated into the four pure substances, three fractionating columns are required. There are five different ways of using these three columns to produce the four pure substances, as illustrated diagrammatically by Thormann.[8] In such a case it is useful to calculate the heat requirements for the different ways of effecting the total separation. Equation (17) is then used to find the three values of θ corresponding to the cases where one, two, or three components are taken as the top product of the first column. Equation (15) is then used to obtain the corresponding minimum reflux ratios, it being noted that equation (15) varies with the composition of the top product, while equation (17) does not. The minimum reflux ratios for the other two columns, which may be separating either ternary mixtures or binary mixtures, are calculated similarly for the various cases.

The relative ease with which the calculation of minimum reflux ratio for multi-component mixtures can be made is illustrated by the following numerical examples.

Example 1 (from Colburn [5])

w and x are the key components

$$w_F = x_F = y_F = z_F = 0{\cdot}25;\; w_D = 1$$
$$\delta = 8;\; \gamma = 4;\; \beta = 2. \quad q = 1.$$

Equation (17) gives

$$\frac{2}{8-\theta} + \frac{1}{4-\theta} + \frac{0{\cdot}5}{2-\theta} + \frac{1}{1-\theta} = 0 \quad . \quad . \quad . \quad (21)$$

The value of θ required lies between 4 and 8. It is found by trial solution to be 5·58.

From equation (15),

$$\frac{8}{8 - 5{\cdot}58} = R + 1 \qquad \therefore\; R = 2{\cdot}31$$

Example 2 (from Colburn [5])

As in Example 1, but with x and y as key components

$$w_D = x_D = 0{\cdot}5.$$

Equation (21) is used again, the value of θ now required being that between 2 and 4. It is found to be 2·556.

From equation (15),

$$\frac{4}{8-2{\cdot}556}+\frac{2}{4-2{\cdot}556}=R+1 \quad \therefore R=1{\cdot}12$$

Example 3 (From Colburn [5]).

As in Example 1, but with y and z as key components

$$w_D = x_D = y_D = 0{\cdot}3333.$$

Equation (21) is used again, the value of θ now required being that between 1 and 2. It is found to be 1·196.

From equation (15)

$$\frac{2{\cdot}667}{8-1{\cdot}196}+\frac{1{\cdot}333}{4-1{\cdot}196}+\frac{0{\cdot}333}{2-1{\cdot}196}=R+1 \quad \therefore R=0{\cdot}698.$$

Example 4 (from Gilliland [3]).

	Feed.	Distillate.	Residue.	Relative volatility to *o*-cresol.
Phenol	0·35	0·95	0·0524	1·26
o-Cresol	0·15	0·05	0·199	1·0
m-Cresol	0·30	—	0·449	0·663
Xylenols . . .	0·15	—	0·224	0·394
Residue	0·05	—	0·075	0·087

Here there are five components. Relative volatilities are referred to *o*-cresol. Instead of recalculating them relative to the heaviest component, an equation of the type of equation (18) can be used with the variable changed to θ′. An appropriate term for the fifth component is brought into the equation. $(q = 1)$

$$\frac{1{\cdot}26\times0{\cdot}35}{1{\cdot}26-\theta'}+\frac{0{\cdot}15}{1-\theta'}+\frac{0{\cdot}663\times0{\cdot}3}{0{\cdot}663-\theta'}+\frac{0{\cdot}394\times0{\cdot}15}{0{\cdot}394-\theta'}+\frac{0{\cdot}087\times0{\cdot}05}{0{\cdot}087-\theta'}=0 \quad . \quad (22)$$

The value of θ′ required lies between 1 and 1·26. By trial solution it is found to be 1·0798. Successive approximations and interpolations are not laborious, as, when an approximate solution has been obtained, only the first two terms in the equation change appreciably with small variations in the assumed value of θ′.

The equation corresponding to equation (15) for the modified variable θ′ is

$$\frac{1{\cdot}26\times0{\cdot}95}{1{\cdot}26-1{\cdot}0798}+\frac{1\times0{\cdot}05}{1-1{\cdot}0798}=R+1 \text{ and } R=5{\cdot}02.$$

Gilliland [3] states that "detailed stepwise calculations indicate that the true minimum reflux ratio is approximately 5·2." The difference between this and the figure calculated above is thus 3–4 per cent. In this example the amounts of the heavy key in the distillate (0·05) and of the light key in the residue (0·0524), though small, are not negligible. This may affect the accuracy of the method used in this paper, which is based on negligible amounts of the heavy and light keys in the distillate and residue respectively. On the other hand, plate-to-plate calculations are not easy to carry out with a high degree of accuracy, owing to the possibility of small errors being cumulative.

This example may be used to illustrate the effect on the minimum reflux ratio of a comparatively small change in the relative volatilities of the key components when these are fairly close to each other. Assume that the relative volatility of phenol to *o*-cresol is 1·28 instead of 1·26, all other data remaining unchanged. Equation (22) then gives $\theta' = 1{\cdot}0856$ instead of 1·0798, and R is found to be 4·67 instead of 5·02. Thus a difference of about 1½ per cent in the relative volatility makes a difference of about 7 per cent in the minimum reflux ratio. This is approximately the same difference as for a binary mixture where $R = \frac{1}{(\alpha - 1)x_F}$ and the effect on R is proportional to $(\alpha - 1)$. It appears that a high degree of accuracy in the method of determining minimum reflux ratio is unwarranted unless the relative volatilities, particularly of the key components, are known to a correspondingly high degree of accuracy. Especially is this the case when the relative volatilities of the key components are not greatly different.

Example 5 (From Jenny [9]).

	Feed.	Distillate.	Bottoms.	Relative volatilities at—		
				63° F.	175° F.	300° F.
C_1	0·26	0·434	—	514·5	100	30·25
C_2	0·09	0·150	—	100·3	24·6	12·95
C_3	0·25	0·411	0·010	34·1	10	5·51
nC_4	0·17	0·005	0·417	10·69	4·85	2·96
nC_5	0·11	—	0·274	3·35	2·08	1·67
nC_6	0·12	—	0·299	1	1	1

The feed is 66 per cent vapour and 34 per cent liquid, so that $q = 0{\cdot}34$. The temperatures at the top and bottom of the column are 63° F. and 300° F. respectively. The temperature of the feed is 175° F.

Jenny gives relative volatility data for all components at the feed temperature, but only for some components at the top and bottom temperatures. The additional data used have been taken from those published by Kirkbride.[10] The relative volatilities vary considerably through the column. For the key components the variation is from 1·86 at the bottom to 3·19 at the top.

The method of calculation described in this paper is based on constant relative volatilities. To apply it to this example it appeared a reasonable approximation to take relative volatilities at a temperature midway between the top and bottom temperatures. Actually the feed temperature (175° F.) has been taken instead of the true mean (181·5° F.), owing to the data being readily available for the former temperature.

Using these data in equation (17) with two additional terms, since there are six components, we have

$$\frac{100 \times 0{\cdot}26}{100 - \theta} + \frac{24{\cdot}6 \times 0{\cdot}09}{24{\cdot}6 - \theta} + \frac{10 \times 0{\cdot}25}{10 - \theta} + \frac{4{\cdot}85 \times 0{\cdot}17}{4{\cdot}85 - \theta} \times \frac{2{\cdot}08 \times 0{\cdot}11}{2{\cdot}08 - \theta} + \frac{0{\cdot}12}{1 - \theta} = 0{\cdot}66 \quad . \quad (23)$$

The value of θ required lies between 4·85 and 10. It is found by trial solution to be 6·73. Substituting in the equation corresponding to equation (15) gives

$$\frac{100 \times 0{\cdot}434}{100 - 6{\cdot}73} + \frac{24{\cdot}6 \times 0{\cdot}150}{24{\cdot}6 - 6{\cdot}73} + \frac{10 \times 0{\cdot}411}{10 - 6{\cdot}73} = R + 1$$

from which $R = 0{\cdot}93$.

Jenny[9] obtained a value of 0·95 and Colburn a value of 0·96. The agreement with these values is quite good. The general validity of the basis assumed in the above calculation—namely, taking relative volatilities at the mean temperature in the column—requires, however, to be checked by a larger number of examples.

The limits between which the true minimum reflux must lie can be found by making two calculations, one based on the relative volatilities at the top of the column and the other based on the relative volatilities at the bottom. The first calculation assumes that the relative volatilities throughout the column are equal to the high values at the top and obviously gives too low a value for the minimum reflux ratio. Similarly, the other calculation obviously gives too high a value.

The value of R found by the first calculation is 0·53 and that found by the second calculation is 1·15. The mean of these is 0·84, compared with the true value of 0·95 or 0·96. As this mean value is obtained by averaging two substantially different values, the approximation can only be regarded as a rough one.

For many practical purposes the higher limit for the minimum reflux ratio, obtained by taking the low relative volatilities at the bottom of the column, provides a useful figure for guidance and, as shown, it can be quite readily calculated.

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THE TENDENCY TO SMOKE OF ORGANIC SUBSTANCES ON BURNING. PART I.

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Summary.

The British incendiary bomb, used in very large quantities by the R.A.F. for the bombing of German towns and cities, was essentially a 30-lb. bomb filled with a special benzol gel together with white phosphorus. The benzol gel filling produced, on burning, a large amount of black carbon smoke which obscured the target, and resulted also in an appreciable portion of the filling being wasted as unburned carbon. In addition, copious white smoke produced by the burning phosphorus increased the obscuring effect over the target. The possibility of replacing this benzol gel–phosphorus combination with a smokeless filling of a satisfactory nature was therefore investigated.

Towards this end the smoking tendency of a large number of organic compounds was assessed by flame-height measurements in a special lamp based on the I.P. smoke lamp.

A burning organic substance has a flame-height at, and above which, smoking occurs, and this height is a measure of the tendency to smoke. A new form of lamp was devised to measure flame-heights, from about 9 to 450 mm, of liquid compounds burning freely in air.

A wide range of hydrocarbons, alcohols, ketones, esters, and nitro-compounds was examined—115 compounds in all. In general, a compact molecule was found to give a smoky flame. The order for increasing tendency to smoke for hydrocarbons is: *n*-paraffins (in which increased chain length or chain branching gave increased smoke), naphthenes, olefines, and aromatics (in which appreciable aliphatic side chains on the benzene ring appeared to give no marked reduction in smoke).

In general, increased oxygen content of an organic compound resulted in decreased smoking tendency and compounds, such as methyl acetate, containing high percentages of oxygen only smoked at very large flame-heights. Some compounds, such as allyl alcohol, although having appreciable oxygen contents, had relatively high smoking tendencies, due to the nature of the carbon–hydrogen portion of the compound.

Of the aliphatic alcohols, the tertiary compounds were more smoky than the primary compounds. This also applied to nitro-paraffins. For each set of isomeric aliphatic esters, the flame-height at which smoking began increased with the chain length attached directly to the carboxylic carbon atom.

At equal oxygen content, the general order for increasing tendency to smoke was: *n*-primary alcohols, *n*-primary nitro-paraffins, propionates, acetates, lactates, and formates, although the order varied slightly for different oxygen contents.

When an organic substance burns under fixed conditions there is a particular critical flame-height at and above which smoking occurs. It would appear that the tendency to smoke is determined by the amount of oxygen (required by the flame on the one hand and by the amount of oxygen) available to the flame on the other. At the critical flame-height the two quantities are equal.

It has been observed by Bancroft [1] that a luminous flame can be regarded as a colloidal suspension of carbon in a gaseous medium. Further, Minchin [2] suggests that through coagulation the charged carbon particles vary in size through the flame, being smallest towards the base and largest at the tip. Thus, in certain instances this coagulation may proceed to such an extent that the particles at the tip of the flame are too large to be burned in the prevailing conditions of temperature and oxygen supply, and under these conditions smoking occurs. This coagulation rate, however, depends on many factors, such as the concentration, the initial size and the initial charge of the carbon particles, the rate of loss of charge, the mean flame temperature, and the composition of the gaseous medium, which, it appears, in their turn depend on the molecular structure of the compound.

The amount of oxygen required by the flame from a compound under fixed conditions of burning and air supply will thus depend on :

(1) The molecular structure, which determines the initial state and the properties of the carbon particles when the fuel is decomposed;
(2) The rate of burning of which flame volume is a function;
(3) The flame-height, which not only influences the final particle size of the carbon, but is also intimately connected with flame volume, and hence with rate of burning.

On the other hand, the amount of oxygen available to the flame will depend on :

(*a*) The oxygen content of the compound;
(*b*) The area of flame surface in contact with the air;
(*c*) The extent of dilution of oxygen at the flame surface by gases of combustion.

Thus the flame-height at which smoking begins is intimately related to the tendency to smoke, and hence this critical flame-height can be used as a measure of the smoking tendency of the compound. Kewley and Jackson[3] have described a method of evaluating the tendency to smoke of kerosine, which is now employed as a standard method of assessing this property (I.P. Standard Method 57/45), in which the maximum height of flame that can be obtained just short of smoking is measured in millimetres. The flame-height thus obtained is, in the standard method, used as a measure of the tendency to smoke.

Minchin[4] employed with this flame-height lamp a slightly different method of expressing the value " tendency to smoke " using the formula :

$S_t = 320/h$
where S_t = smoking tendency
h = maximum flame-height in millimetres.

Further, Terry and Field[5] have described an improved form of the Davis Factor lamp in which flame-heights of up to 102 mm could be measured.

A NEW SMOKE POINT LAMP.

The maximum flame-height capable of measurement in the I.P. lamp is 50 mm, but with the improved Davis Factor lamp the maximum measurable flame-height is 102 mm, while the smoking flame-height of a good kerosine, with this lamp, exceeds 75 mm.[5]

A lamp was required for this work in which the flame-height could be varied and measured over a wide range without the use of a wick. Preliminary experiments indicated that, when a substance burned, an increase or decrease in burning area resulted in a corresponding increase or decrease in flame-height. It was felt that this principle might be used to vary the flame-height in a lamp, and the method finally adopted for changing the burning area is illustrated in Fig. 1. A shallow conical metal vessel was connected by oil-resisting rubber tubing to a liquid reservoir as shown. When liquid was introduced, the level in the reservoir determined the level in the cone, and hence the exposed liquid area in the cone. Thus, on burning the liquid in the cone, a variation in the height of the reservoir produced a corresponding variation in the burning area, and hence in the flame-height.

It was apparent that for any accurate observation of flame-height a very steady flame was essential. With the large flames that could be produced when using the cone burner, however, it was found that even in the absence of draughts, bad flickering occurred. This difficulty was overcome by enclosing the flame and using the draught from a glass chimney to draw the air necessary for the combustion through two fine copper gauzes (120 mesh) before reaching the burner (see Fig. 2). Thus the air flow was stream-lined, and a steady flame resulted.

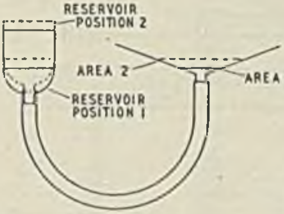

FIG. 1.

THE PRINCIPLE OF THE CONE BURNER.

As the determination of the exact point at which smoking began was somewhat difficult, it was decided to mark the position of the tip of the flame by a wire hook, which could be raised or lowered in the chimney by means of a screw. This wire passed through a hole in a copper gauze (18 mesh) at the top of the chimney, which damped any vibration set up when the wire was moved. The height of the hook was shown on a metre rule, the position of which was adjusted so that zero flame-height was indicated when the wire just touched the lowest point in the burner.

Preliminary experiments with this lamp were carried out by burning both highly inflammable substances and those substances such as cresol which burned only with difficulty. With the latter type of compound it was found that the burner had to reach a high temperature before a steady flame was produced. Thus the burner was made from thin brass (specific heat 0·092 cal/gm), which gave it a low heat capacity. This alone, however, was unsatisfactory, since substances of high volatility tended to boil and produce an irregular flame. This difficulty was overcome by fitting to the base of the burner a cold-water-circulating jacket which could be used when burning these volatile substances.

A diagram showing constructional details of the lamp finally employed is given in Fig. 2, and a photograph is shown in Fig. 3. In Fig. 2

A is the conical burner;
B is the chimney;
C is the glass collar.

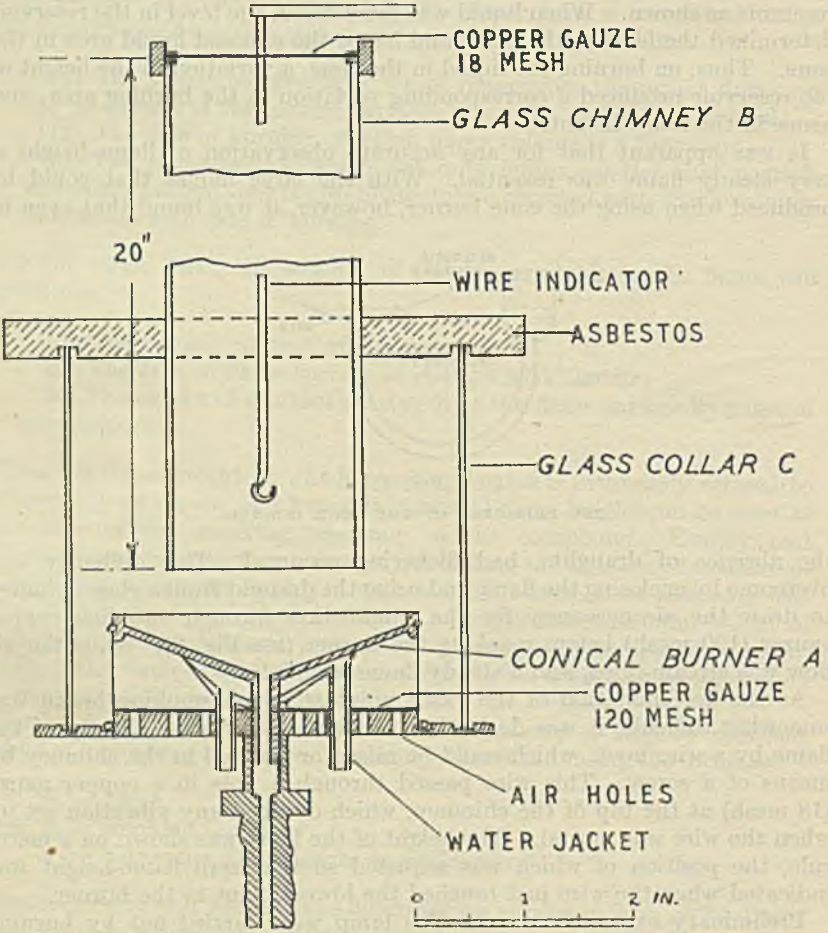

FIG. 2.

THE SMOKE-POINT LAMP.

It is important that A should be of a larger diameter than B, and the distance between the base of B and the top of A is adjustable, so that flow is in the laminar regime, and thus is steady. With this lamp flame-heights were measured over the range of 9 mm to 450 mm.

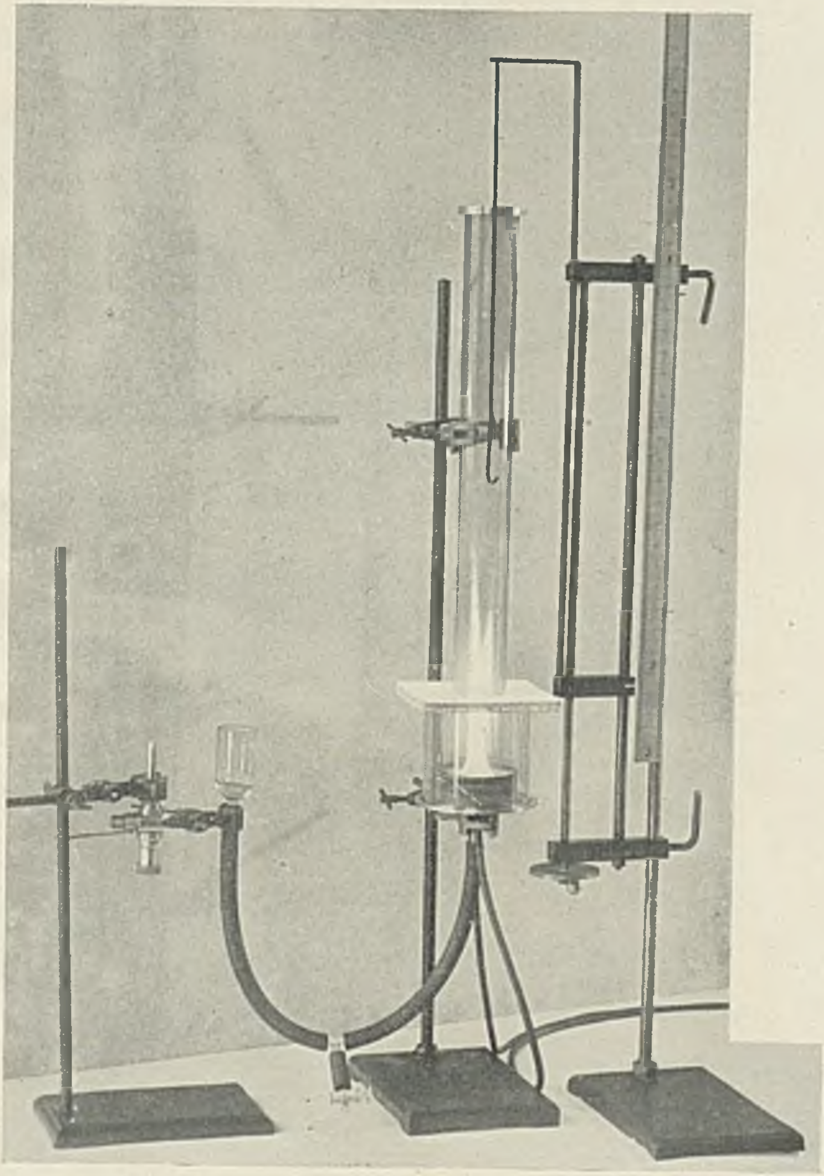

FIG. 3.

THE SMOKE-POINT LAMP.

[*To face p.* 630.

Procedure.

Having removed the chimney and glass collar, the reservoir, connection tube, and burner were washed with the liquid to be used and then filled to a suitable level. After igniting with a bunsen burner (some liquids required heating before they burned), the collar and chimney were replaced, and the liquid was allowed to burn for 3 minutes to obtain fairly steady conditions.

The flame was then raised or lowered, by movement of the reservoir, to its smoke-point, which was indicated by the movable wire. It was found that each flame formed a long red " tail " just before smoking began, and in these tests the smoke point was taken as the height at which this " tail " just disappeared. A number of observations were made for each substance, and the mean value taken. The experimental error is considered to be not greater than ±3 per cent.

The smoke points of a wide variety of organic substances (115 in all) were determined in the lamp, and were used as a measure of the tendency to smoke—a high smoke point indicating a low tendency to smoke, and a low smoke point indicating a correspondingly high tendency to smoke.

The compounds examined in the lamp were :

(1) Hydrocarbons and hydrocarbon mixtures.
(2) Oxygen containing compounds, including :
    (*a*) Alcohols.
    (*b*) Glycol and glycerol compounds.
    (*c*) Nitro compounds.
    (*d*) Ketones.
    (*e*) Esters.
    (*f*) Carboxylic acids.

Results.

(1) *Pure Hydrocarbons.*

The smoke points of pure hydrocarbons as determined in the lamp are given in Table I.

Of the three normal paraffins examined, *n*-pentane and *n*-heptane have similar flame-heights with cetane somewhat lower, showing a gradual increased tendency to smoke with increased chain length. Isopentane with a branched chain is more smoky than *n*-pentane. The flame-heights of *n*-hexane and *n*-octane must be close to those of *n*-pentane and *n*-heptane (*i.e.*, roughly 15–16 cm), and 2 : 2-dimethylbutane with a highly branched chain is much more smoky, and similarly with the branched-chain octanes. Thus the branching of the carbon chain in a compound increases the tendency to smoke, and the results suggest that more than one branch produces a greater effect. The flame-heights of the three branched-chain octanes indicate that the positions of the carbon branches have little or no effect on the smoking properties.

As the only olefines available were probably mixtures, no reliable conclusion can be drawn, except that the introduction of the double bond, and probably some branching, make these compounds very smoky.

Benzene, having a high C/H ratio, is very smoky indeed, and the building up of this effect may be traced from *n*-hexane through *cyclo*hexane to *cyclo*hexene and benzene. A similar effect may be noted with decalin and tetralin. Results 14–17 for toluene, xylene, di-isopropyl benzene and *p*-cymene indicate that the introduction of aliphatic side-chains in the benzene nucleus has little effect on the smoky nature of the benzene flame.

It is interesting to compare these results with those obtained by Minchin.[4] This investigator was able to show that the flame volume was related to the molecular volumes of combusted products and of oxygen required for combustion by the formula :

TABLE I.

Hydrocarbons.

Substance.	Boiling point, ° C.	C/H ratio.	Smoke point flame height, cm.
1. *n*-Pentane	36	0·42	15·5
2. Isopentane	30	0·42	11·8
3. 2 : 2-Dimethyl butane	49·5	0·43	6·9
4. *n*-Heptane	98	0·44	15·9
5. Iso-octane (2 : 2 : 4-trimethyl pentane)	100	0·44	6·3
6. 2 : 2 : 3-Trimethyl pentane (84%)	—	0·44	6·6
7. 2 : 3 : 4-Trimethyl pentane (82%)	—	0·44	6·7
8. Cetane	m. pt. 17	0·47	12·5
9. Pentene	,, 42	0·50	4·8
10. Hexene	,, 65	0·50	5·1
11. Heptene	,, 94	0·50	6·4
12. Decene	,, 167	0·50	7·0
13. Benzene	,, 80	1·00	0·9
14. Toluene	110	0·88	1·0
15. " Xylene "	135–142	0·80	0·9
16. *m*-Di-isopropyl benzene	200	0·67	1·2
17. *p*-Cymene	175	0·71	1·3
18. *cyclo*Pentane	49	0·50	6·2
19. *cyclo*Hexane	81	0·50	7·7
20. *cyclo*Hexene	84	0·60	4·3
21. Methyl*cyclo*hexane	101	0·50	7·0
22. Di*cyclo*hexyl	—	0·55	5·2
23. Pinene	156	0·63	2·1
24. Tetralin	206	0·83	1·2
25. Decalin	192	0·56	3·5

$$\frac{1}{V} = k_1\frac{y}{x} + k_2$$

where V = flame volume;
y = molecular volume of oxygen required for complete combustion;
x = molecular volume of combusted products;
K_1 and K_2 = constants.

Since the flame, in the lamp he employed, was conical, then $\frac{1}{V} = \frac{1}{h} \times$ a constant, and hence h (the smoke point flame-height), for any substance, could be calculated if K_1 and K_2 were evaluated. By burning various substances in his lamp and measuring flame-heights and radii at their smoke points by means of a travelling microscope, he evaluated K_1 and K_2 and calculated h for several homologous series. From these calculated values of h the "tendency to smoke" was obtained from the equation :

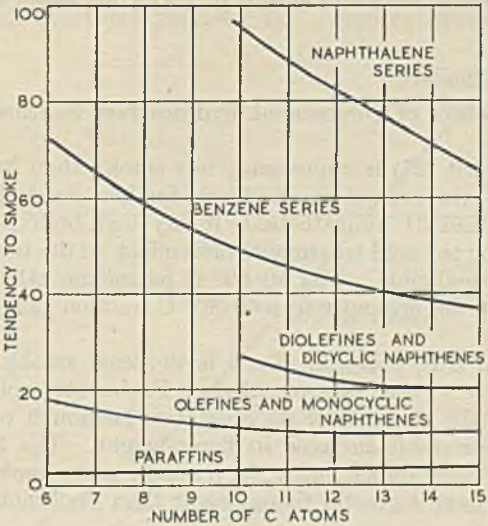

Fig. 4.

$$S_t = 320/h$$

His results are shown in Fig. 4.

Table II.

Hydrocarbon Mixtures.

Substance.	Smoke point flame-height, cm.
26. Benzole (sp. gr. 0·88)	0·9
27. Pool motor spirit (sp. gr. 0·738, aromatics 25%) . . .	5·1
28. Aromatic-free Pool motor spirit	9·3
29. Pool motor spirit distilled	5·4
30. Pool motor spirit distilled and freed from aromatics . . .	9·5
31. Aromatic-free Pool motor spirit distilled over the same range as 29	9·5
32. Petroleum ether 40–60° C.	11·7
32a. Aromatic-free petroleum ether 60–80° C.	8·9
33. Special B.P. Solvent No. 1	9·0
33a. ,, ,, ,, No. 1 (aromatic-free)	10·3
34. ,, ,, ,, No. 2	7·5
35. ,, ,, ,, No. 4	7·4
36. ,, ,, ,, No. 5	6·4

One of the most interesting features of these curves is the fact that the tendency to smoke of the hydrocarbon series investigated decreased with increase in the number of carbon atoms or boiling point, with the exception of the paraffins, which show an increased tendency to smoke with increase in molecular weight. In the other series examined the increase in molecular weight is brought about largely by the addition of paraffinic side-chains, and the influence of the nucleus is thus progressively offset by the increased paraffinicity.

Hydrocarbon Mixtures.

The smoke points of commercial hydrocarbon mixtures are listed in Table II.

Pool motor spirit (27) is appreciably less smoky than benzole (26), and the removal of its aromatics produces further marked improvement. Results 29, 30, and 31 indicate that, if any high-boiling-point polymers are formed during the acid treatment, their effect on the tendency to smoke of the spirit is negligible. The 40–60° C petroleum ether (32) produces little smoke, but the aromatic-free 60–80° C fraction (32*a*) is rather more smoky.

Of the Special B.P. Solvents, No. 1 is the least smoky (33), its flame-height being close to that of aromatic-free Pool motor spirit, while result 33*a* shows that the removal of its aromatics (although only 3 per cent) produces an appreciable increase in flame-height. The flame-heights of Nos. 2 and 4 are very similar, with No. 5 a little more smoky. All of these special solvents have a greater flame-height than Pool motor spirit.

OXYGEN-CONTAINING COMPOUNDS.

(a) *Alcohols.*

TABLE III.

Alcohols.

Substance.	Boiling point, ° C.	Oxygen in compound as a percentage of the total required for complete combustion.	Smoke point flame-height, cm.
37. Methyl alcohol	65	25·0	Blue flame
38. Ethyl alcohol	78	14·3	37·7
39. *n*-Propyl alcohol	97	10·0	27·7
40. Isopropyl alcohol	83	10·0	17·9
41. *n*-Butyl alcohol	116	7·7	23·6
42. Isobutyl alcohol	108	7·7	18·4
43. Secondary butyl alcohol	99	7·7	19·1
44. Tertiary butyl alcohol	83	7·7	10·6
45. *n*-Amyl alcohol	136	6·3	19·7
46. Isobutyl carbinol	131	6·3	16·5
47. Secondary butyl carbinol	128	6·3	16·2
48. Methyl propyl carbinol (secondary amyl)	119	6·3	16·7
49. Dimethyl-ethyl-carbinol (tertiary amyl)	101	6·3	10·8
50. *n*-Hexyl alcohol	156	5·3	16·9
51. 1 : 3-Dimethyl butyl alcohol	131	5·3	11·2
52. 2-Ethyl butyl alcohol	147	5·3	12·8
53. Allyl alcohol	97	11·1	8·3
54. Benzyl alcohol	205	5·6	1·3
55. *cyclo*Hexanol	160	5·6	9·3
56. Cresylic acid	—	5·6	1·2

With the straight-chain primary alcohols the tendency to smoke increases with increasing chain length, the flame-heights of the lower members showing a straight-line relationship with their oxygen content expressed as a percentage of the total required for complete combustion (Fig. 5).

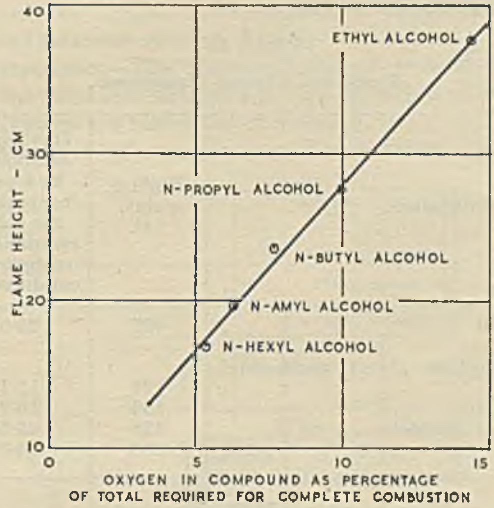

FIG. 5.

Further, for these compounds the inverse of flame-height shows a straight-line relationship with the boiling point (Fig. 6). The secondary alcohols are in all cases more smoky than the corresponding primary compounds,

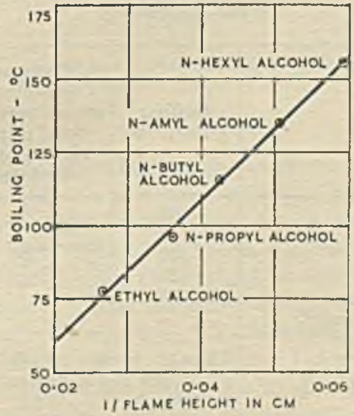

FIG. 6.

which indicates that the shifting of the –OH group from the end of the chain to some other position increases the tendency to smoke. As in the case of the hydrocarbons, the branching of the chain increases the smoke, and it is interesting to note that a primary alcohol with a single-carbon branch has roughly the same flame-height as the corresponding secondary alcohol; results for isobutyl carbinol (46) and secondary butyl carbinol (47) suggest that the position of the branch relative to the primary –OH group has little or no effect on the smoking properties.

(b) *Glycol and Glycerol Compounds.*

TABLE IV.

Glycol and Glycerol Compounds.

Substance.	Boiling point, ° C.	Oxygen in compound as a percentage of the total required for complete combustion.	Smoke point flame-height, cm.
57. Ethylene glycol	197	28·6	Semi-luminous
58. Cellosolve (ethylene glycol mono-ethyl ether)	127	15·4	38·5
59. Cellosolve acetate	156	16·7	28·2
60. Ethylene glycol diacetate . . .	188	23·5	29·2
61. Triacetin	258	24·0	26·1

The importance of the C/H ratio in these compounds is stressed by a comparison of *n*-propyl alcohol (39) and allyl alcohol (53), since allyl alcohol, although having a higher oxygen content, is far more smoky than *n*-propyl alcohol. Also *cyclo*hexanol has a greater tendency to smoke than *n*-hexyl alcohol, although in this case ring formation may be an additional effect. Benzyl alcohol and cresylic acid, being essentially aromatic, are very smoky, in spite of their oxygen content.

TABLE V.

Nitro-compounds.

Substance.	Boiling point, ° C.	Oxygen in Compound as a percentage of the total required for complete combustion.	Smoke point flame-height, cm.
62. Nitro-methane . . .	101	assuming $N \rightarrow NO_2$ 36·4	Semi-luminous
63. Nitro-ethane . . .	114	23·5	44 (approx.)
64. 1-Nitro-propane . . .	132	17·4	36·6
65. 2-Nitro-propane . . .	120	17·4	20·3
66. Tertiary-nitro-isobutane .	128	13·8	7·9
67. Nitrated Pool motor spirit .	—	—	5·2
68. Nitrated aviation spirit . .	—	—	4·3
69. Nitrated spirit 100 flat . .	Much brown "oil" on burner made measurement difficult.		4–5
70. Nitrated spirit 90 flat . .			4–5

When the flame-height of cellosolve (58) is plotted against oxygen content in Fig. 8, the point lies close to the normal primary alcohol line, suggesting that the introduction of an oxygen atom into the carbon chain does not greatly modify the flame-height/oxygen content relationship. A comparison of cellosolve (58) with cellosolve acetate (59) indicates that the presence of the acetate group increases the tendency to smoke and this receives some support from the comparison between ethylene glycol diacetate (60) and triacetin (61) (cf. Fig. 8).

(c) *Nitro Compounds.*—The flame-heights of several pure nitro-compounds and of the products obtained by the nitration of some commercial hydrocarbon mixtures are tabulated in Table V.

As in the case of aliphatic alcohols, the tertiary nitro-compound is relatively smoky in spite of its high oxygen content. Also 2-nitro-propane (secondary) is more smoky than 1-nitro-propane (primary).

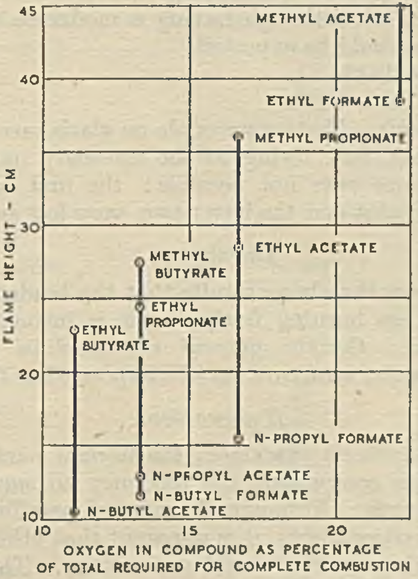

Fig. 7.

Acetone and methyl ethyl ketone appear to have very similar smoking properties, although they differ in oxygen content. The flame-height of diacetone alcohol is much higher than might be expected, since it contains a tertiary alcohol grouping. Also the flame-height of *cyclo*hexanone (which is very close to that of *cyclo*hexanol—9·8 cm) suggests that the substitution of O for H_2 in *cyclo*hexane (7·7 cm) reduces the smoke. Phenyl-*n*-butyl ketone, although it contains a *n*-butyl chain, shows that the benzene ring is still strongly influencing the smoking tendency.

The graph of smoke point flame-height against oxygen content for the straight-chain esters (Fig. 7) reveals an interesting relationship. For each set of isomers (members having equal oxygen content and similar boiling points in this case) there is a decrease in flame-height in the order butyrate, propionate, acetate, formate. Thus for each oxygen content the flame-height at which smoking begins, increases with the chain length attached directly to the carboxylic carbon atom. Results for *n*- and iso-butyl acetate (86) and (87), for *n*- and iso-butyl propionate (94) and (95), and for *n*- and iso-butyl butyrate (100) and (101) indicate that, as with other compounds, the branching of a carbon chain tends to increase the smoke from these esters. Again results for ethyl formate and oxylate (80) and (103), and for ethyl acetate and malonate (84) and (104) suggest that the ethyl esters of dibasic acids have a greater tendency to smoke than the ethyl esters of mono-basic acids of similar oxygen content. A comparison of ethyl carbonate (110) and ethyl lactate (105) gives further evidence that the introduction of an oxygen atom into a carbon chain does not affect the flame-height/oxygen content relationship.

Ethyl benzoate (108), although having a moderate oxygen content, is still very smoky, as would be expected.

(d) *Ketones.* See Table VI.

(e) *Esters.* See Table VIII.

(f) *Carboxylic Acids.*—Tests were made on glacial acetic acid, oleic acid, and naphthenic acid, but, owing to the unsteady nature of the flame, reliable measurements were not possible: the first named appeared to have a high smoke point and the latter two, very low smoke points.

DISCUSSION.

It is apparent from the above results that the tendency to smoke of an organic compound on burning freely in air is intimately related to its molecular structure. Certain general relationships between smoking tendency and molecular structure may be expressed as follows.

Hydrocarbons.

Of all the hydrocarbons examined, the normal paraffins are the least smoky. With these compounds the tendency to smoke increases with increasing chain length. Although the normal paraffins have the lowest C/H ratios of the hydrocarbons, it is apparent that other factors also have an important bearing on the smoking tendency. Thus branched-chain paraffins are more smoky than their normal isomers, although they have the same C/H ratios. Indeed, the more highly branched the carbon chain, the more smoky does the paraffin become, while the relative positions of the branches appear to have little effect.

Although the olefines examined were probably mixtures, the results suggest that unsaturation in a hydrocarbon produces an appreciable increase in the tendency to smoke. It seems probable, however, that an increase in chain length of an olefine results in a decreased smoking tendency, since the effect of the double bond is progressively offset by increased paraffinicity.

The tendency to smoke of the naphthenes, although relatively high in comparison with the normal paraffins, is approximately equal to that of those paraffins having two or three branches in the carbon chain. There is insufficient evidence to show the effect of the number of carbon atoms in the naphthene ring on the smoking tendency, but a comparison of *cyclo*pentane and *cyclo*hexane suggests that the effect is not pronounced. As with other hydrocarbons, the introduction of one double bond in a napthene produces a marked increase in the tendency to smoke.

TABLE VI.

Ketones.

Substance.	Boiling point, ° C.	Oxygen in compound as a percentage of the total required for complete combustion.	Smoke point flame-height, cm.
71. Acetone	56	11·1	26·3
72. Methyl-ethyl ketone . .	80	8·3	26·2
73. Di-acetone alcohol . .	164	11·1	26·4
74. *cyclo*Hexanone . . .	155	5·9	10·0
75. Phenyl-*n*-butyl ketone . .	246	3·4	1–2

TABLE VIII.

Esters.

Substance.	Boiling point, ° C.	Oxygen in Compound as a percentage of the total required for complete combustion.	Smoke point flame-height, cm.
80. Ethyl formate	54	22·2	38·5
81. *n*-Propyl formate	81	16·7	15·6
82. *n*-Butyl formate	107	13·3	11·6
83. Methyl acetate	57	22·2	About 45
84. Ethyl acetate	77	16·7	28·6
85. *n*-Propyl acetate	101	13·3	13·0
86. *n*-Butyl acetate	126	11·1	10·5
87. Isobutyl acetate	116	11·1	9·2
88. Amyl acetate	131–135	9·5	10·0
89. *cyclo*Hexyl acetate . . .	175	8·7	9·2
90. Octyl acetate (2-ethyl-hexyl acetate)	196	6·7	9·6
91. Ethyl acetoacetate . . .	181	17·6	21·6
92. Methyl propionate . . .	79	16·7	36·0
93. Ethyl propionate	98	13·3	24·5
94. *n*-Butyl propionate . . .	146	9·5	13·7
95. Isobutyl propionate . . .	137	9·5	10·3
96. Amyl propionate	156	8·3	10·5
97. Methyl butyrate	102	13·3	27·5
98. Ethyl butyrate	120	11·1	22·9
99. Propyl butyrate	143	9·5	14·4
100. *n*-Butyl butyrate	165	8·3	13·3
101. Isobutyl butyrate	157	8·3	11·3
102. Ethyl laurate	269	4·8	18·4
103. Ethyl oxalate	186	23·5	29·0
104. Ethyl malonate	198	20·0	25·7
105. Ethyl lactate	154	20·0	32·1
106. Butyl lactate	187	14·3	19·0
107. Amyl lactate	198	12·5	15·4
108. Ethyl benzoate	213	8·7	2·5
109. Ethyl nitrate	87	35·3	Semi-luminous
110. Ethyl carbonate	126	20·0	33·0

Benzene, having three double bonds in its ring and a correspondingly high C/H ratio, is very smoky, and the building up of this effect may be traced from *n*-hexane through *cyclo*hexane to *cyclo*hexene and benzene. Further, the results obtained with this lamp indicate that aliphatic side-chains on the benzene ring have little effect on its tendency to smoke.

In the naphthalene series the effect of unsaturation (or C/H ratio) is shown, since decalin (C/H ratio 0·56) is appreciably less smoky than tetralin (C/H ratio 0·83).

The Compactness of a Hydrocarbon Molecule and the Tendency to Smoke.

It seems likely that when a hydrocarbon is decomposed in a flame, the more compact the molecule, the greater will be the initial size of the carbon particles. This in its turn will probably produce a greater tendency to smoke. Thus a branched-chain paraffin, having a more compact molecule, is more smoky than its straight chain isomer, although they have the same C/H ratio. Ring formation also produces a compact molecule, and these substances, even when saturated, are more smoky than the corresponding straight chain compounds.

Oxygen-Containing Compounds.

The effect of the structure of oxygen-containing organic compounds on the tendency to smoke on burning may be resolved into three factors:

(1) The structure of the hydrocarbon portion of the molecule;
(2) The structure of the oxygen-containing group or groups;
(3) The oxygen content as a percentage of that required for complete combustion.

The structure of the hydrocarbon portion of the molecule is of primary importance, and largely determines the tendency to smoke of the compound. It would appear that the relationships between the structure of the hydrocarbon portion and the smoking tendency of the substance are largely the same as for the hydrocarbon compounds. In general, increased oxygen content results in a decreased tendency to smoke, but this effect may be offset by the influence of the hydrocarbon portion.

With the straight-chain primary alcohols the tendency to smoke increases with increasing chain length, the flame-heights of the lower members showing a straight-line relationship with their oxygen contents expressed as a percentage of the total required for complete combustion. Further, for these compounds the inverse of flame-height shows a straight-line relationship with the boiling points. Tertiary alcohols are more smoky than the corresponding secondary alcohols, which are in turn more smoky than the primary compounds.

The importance of the hydrocarbon structure in alcohols is apparent in several instances. Firstly an alcohol with a branched chain is more smoky than the corresponding straight-chain compound, although they have the same oxygen content. Also an alcohol having an unsaturated carbon chain is, in spite of its higher oxygen content, far more smoky than the corresponding saturated alcohol. Further, a saturated cyclic alcohol has a greater tendency to smoke than the straight-chain compound, and an aromatic alcohol shows the pronounced influence of the aromatic ring in spite of its oxygen content.

With the straight-chain aliphatic esters the tendency to smoke is influenced by the carbon chain length attached to the carboxylic carbon atom and to the hydroxyl oxygen atom respectively. For each set of isomers (members having equal oxygen content and similar boiling points in this case) there is a variation in the smoke point flame-height, and the order of decreasing tendency to smoke is: formate, acetate, propionate, butyrate. Thus for equal oxygen content the flame-height at which smoking begins increases with the chain length attached directly to the carboxyl carbon atom.

As with the other types of compounds, the branching of a carbon chain tends to increase the smoke from these esters. Also the results suggest that the ethyl esters of dibasic acids are more smoky than the ethyl esters of monobasic acids of similar oxygen content. Aromatic esters are again very smoky.

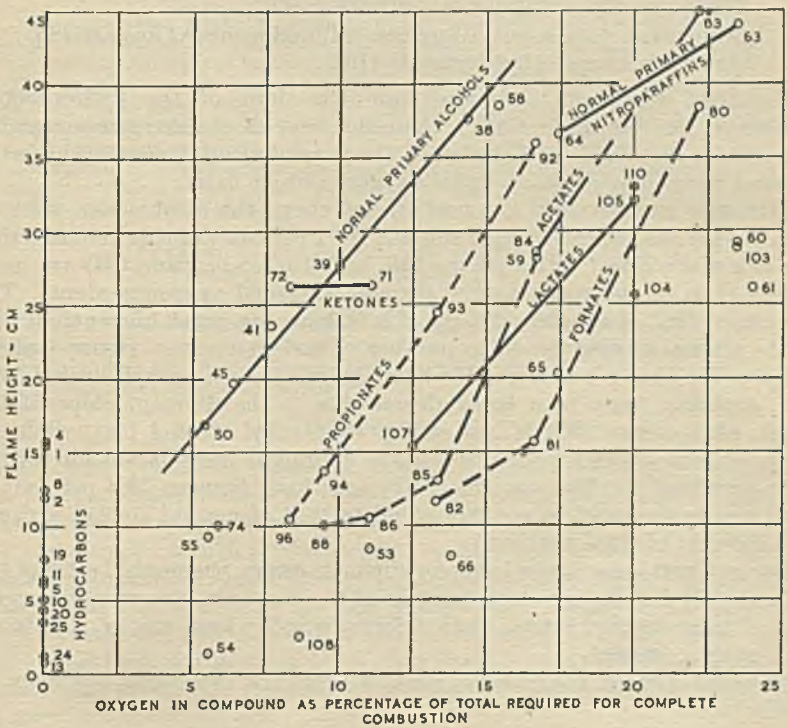

Fig. 8.

It would appear from the few aliphatic nitro-compounds examined that the tertiary compound is more smoky than the corresponding secondary compound, which is in turn more smoky than the primary compound.

It is interesting to note that with several substances the introduction of one or two oxygen atoms into the carbon chain appears to have little or no effect on the flame-height/oxygen content relationship.

The relative smokiness of the various types of organic compounds may be observed from Fig. 8. The introduction of an oxygen atom into *n*-

pentane (1) to form *n*-amyl alcohol (45) produces a marked increase in flame-height. If, however, the flame-heights of *n*-hexane and *n*-heptyl alcohol are obtained by extrapolation, the results suggest that the increase from *n*-hexane to *n*-hexyl alcohol (50) is less marked than for the above 5-carbon compounds and that the conversion of *n*-heptane (4) into *n*-heptyl alcohol produces no increase in flame-height. It is interesting to note that, due to their structures, a number of compounds containing fairly high percentages of oxygen are more smoky than hydrocarbons, such as *n*-pentane (1) and *n*-heptane (4). Examples of such substances are :

Unsaturated aliphatic alcohol–allyl alcohol (33);
Nitro-paraffin–tertiary nitro-*iso*butane (66);
Aliphatic esters–*n*-butyl formate (82) and *n*-propyl acetate (85);
Aromatic esters–ethyl benzoate (108).

However, *n*-pentane and *n*-heptane (the best of the hydrocarbons examined) are far more smoky than the best of the oxygen-containing compounds examined. Of the latter, the normal primary alcohols have the greatest flame heights on an equal oxygen content basis.

Although methyl ethyl ketone (72) lies above the alcohol line, acetone (71), having the highest oxygen content (11·1 per cent) of this ketone series, lies below the line. Nitro-ethane (63) and 1-nitro-propane (64) are more smoky than the normal primary alcohols for equal oxygen content. The oxygen content of a mono-nitro paraffin is, however, much higher than that of the alcohol having the same number of carbon atoms. Hence 1-nitro-propane (64) has a much greater flame-height than *n*-propyl alcohol (39), and, similarly (only to a lesser degree due to the different slope of the lines), nitro-ethane (63) is less smoky than ethyl alcohol (38), while by extrapolation (assuming for this purpose a straight-line relationship for the nitro-paraffins) the flame-height of nitro-methane (oxygen 36·4 per cent of total required) would be roughly equal to that of methyl alcohol (oxygen 25·0 per cent of total required).

For any particular set of isomeric aliphatic esters, the methyl ester of the highest acid has the greatest flame-height. However, the results suggest that of these methyl esters, methyl formate is the least smoky, due to its high oxygen content.

At equal oxygen content the general order for increasing tendency to smoke is :

(1) Normal primary alcohols;
(2) Normal primary nitro-paraffins;
(3) Propionates;
(4) Acetates;
(5) Lactates;
(6) Formates;

although this order will vary slightly for different oxygen contents.

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