Appl. sci. Res.   Section A, Vol. **3**

THE DEFINITION AND MEASUREMENT OF SOME CHARACTERISTICS OF MIXTURES

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Summary

The systematic study of mixing processes requires a quantitative method of expressing "goodness of mixing", based on conveniently-made measurements. In this paper, mixtures of mutually soluble liquids, fine powders, or gases are considered. It is shown that the important features of such mixtures can be expressed by two statistically-defined quantities, the scale and the intensity of segregation, and methods of measuring these are suggested. The discussion also throws light on some of the factors which affect the efficiency of mixing processes.

Notation

a = Concentration (volume-fraction) of component A.
$\bar{a}$ = Mean concentration of A in mixture.
b = Concentration (volume-fraction) of component B.
$\bar{b}$ = Mean concentration of B in mixture.
c = $a - \bar{a}$.
d = Diameter (of circle, strip, sphere or pipe).
D = Diffusivity.
I = Intensity of segregation (defined by eqn. (14)).
J = Content of A in line sample (eqn. (5)).
k = Reaction-velocity constant.
K = Content of A in volume sample.
l = Length of section of pipe.
m = Concentration of reactant M in solution A (moles per unit volume).
n = Concentration of reactant N in solution B.
r = Distance apart of two points in mixture.
$R(r)$ = Correlation coefficient between points in mixture distance r apart.

S = Linear scale of segregation (defined by eqn. (3)).
t = Time.
T = See eqn. (12).
u = Velocity of flow.
v = Volume of sample.
V = Volume scale of segregation (defined by eqn. (4)).
x = Distance from one end of line-sample, or general space-coordinate.
X = Length of line-sample.
ξ = Value of r for which $R(r)$ falls to 0.
ϱ = Mean reaction rate per unit volume of mixture.
σ^2 = Variance of quantity denoted by subscript.

§ 1. *Introduction.* The study of mixing processes suffers at the present time from the lack of any quantitative method of expressing "goodness of mixing". To be of practical value, such a quantitative description must fulfil certain conditions: (*a*) It must be related as closely as possible to the properties of the mixture which we assess qualitatively when we judge it to be well or badly mixed; (*b*) It must be possible to make the required measurements conveniently; (*c*) The method of classification should be applicable without modification to as many different types of mixture as possible; (*d*) It should not depend on purely arbitrary tests, leading to quantities of doubtful physical significance.

The following notes suggest a system of describing mixtures which seems to go some way towards fulfilling the above requirements. The treatment is suitable chiefly for mixtures in which the ultimate particles (i.e. the smallest capable of independent movement in the mixture) are very small compared to the size of the portions which will normally be taken for use or for analysis. Under these conditions it is possible to speak of the "concentration at a point", and a series of samples taken from a "completely mixed" mixture will have the same composition. The discussion will refer mainly to a mixture of two mutually soluble liquids (which may be a solution and a pure solvent respectively), but many of the conclusions are applicable to gases, powders and pastes, and to multi-component systems. Mixtures of coarse particles, which are not extremely small compared to the samples taken, present a problem which must be approached in a different way [1]). It will also be assumed that the mixture is uniform in texture; that is to say, it cannot be divided into two parts of equal size in which the mean concentration or the scale or intensity of segregation (as defined later) differ significantly. This is the most important limitation on the practical value of the definitions and tests which will be proposed. Large-scale segregation caused, for instance, by sedimentation, or by dead space in a mixer, is of great practical importance, but its study cannot conveniently be combined with that of the small-scale characteristics, or texture, which are the subject of the present discussion. The subject of large-scale segregation in continuous-flow systems will be dealt with on another occasion.

Three different situations have been borne in mind: (*a*) we may be confronted with a mass of material already mixed, and desire to investigate its texture; (*b*) we may desire to determine the effectiveness of a continuous mixer, from which a stream of material is issuing; (*c*) we may desire to follow the progress of the mixing of a batch of material.

§ 2. *The mixing process.* If two mutually soluble liquids are mixed together two things happen. In the first place the liquids are broken up into "clumps", which are intermingled (this will happen even if the liquids are not mutually soluble). The shape of the clumps will depend on the mechanism of the mixing-process; they may, for instance be compact, or in the form of long streaks. Up to a point, at least, the average size of these clumps will continue to decrease as mixing is continued.

At the same time, molecular interdiffusion of the two liquids occurs across the boundaries of the clumps. This process is spontaneous and will continue even if the mechanical mixing is stopped. Diffusion will ultimately reduce any mixture of mutually soluble liquids to complete uniformity, but the process is slow unless the liquids have first been broken up into small clumps. Unless diffusion (or some analogous process) occurs, continuous stirring will not produce a homogeneous mixture; the composition at any point will be that of one of the pure components, and it will vary discontinuously from one region to another. In the case of powders, independent motion of the ultimate particles will produce an effect similar to molecular diffusion, but only so long as some kind of mechanical agitation is continued.

The breaking-up and the interdiffusion are, in the case of liquids, largely independent processes which produce distinguishable results. The former reduces the size of the clumps, while the latter tends to obliterate differences of concentration between neighbouring regions of the mixture. It therefore seems desirable to use two quantities to describe the degree of mixing — namely the *scale of segregation* and the *intensity of segregation*. Owing to the lack of geometrical regularity in the mixture, both quantities must be defined and determined by statistical methods.

§ 3. *The scale of segregation.* The measure of the scale of segregation adopted here is analogous to the "scale of turbulence" used in the statistical theory of turbulence [5]). Considering a mixture of two liquids, A and B, let their concentrations (volume-fractions) at any point be a and b respectively, and their mean concentrations in the mixture as a whole be $\bar{a}$ and $\bar{b}$. Then

$$a + b = 1, \quad \bar{a} + \bar{b} = 1. \tag{1}$$

Suppose the concentrations (a_1, a_2) are measured at two points in the mixture a distance r apart. The deviations of the two concentrations from the mean are multiplied together to give the product $(a_1 - \bar{a}).(a_2 - \bar{a})$. If a large number of such pairs are taken, the points in each pair being the same distance r apart, we can find the mean value, $\overline{(a_1 - \bar{a})\,(a_2 - \bar{a})}$, of the corresponding products of the deviations, and also the mean square deviation, $\overline{(a - \bar{a})^2}$, of all the concentrations from the mean. The quantity

$$R(r) = \frac{\overline{(a_1 - \bar{a})\,(a_2 - \bar{a})}}{\overline{(a - \bar{a})^2}} \equiv \frac{\overline{(b_1 - \bar{b})\,(b_2 - \bar{b})}}{\overline{(b - \bar{b})^2}} \tag{2}$$

derived from these measurements is called the *coefficient of correlation* between values of a (or b) at points separated by a distance r. The denominator is usually called the *variance* of a (or b), and may be written σ_a^2 or σ_b^2 (the two are of course equal).

$R(r)$ may have any value from 1 to 0. (Negative values will only be encountered when there is some form of long-range segregation present, or some regularity in the pattern of the mixture. Such cases are not considered here, and attention is confined to systems for which $R(r) \geqslant 0$ for all values of r). $R(0)$, the value when $r = 0$, is identically equal to 1, and in general a value close to 1 means that a concentration much above the average at a given point is likely to be associated with an above-average concentration a distance r away, or that below-average concentrations are similarly related. A value of 0 means that there is only a random relationship between the concentrations at points distant r apart. In an imperfect mixture, $R(r)$ will be greater than 0 for small values of r, because points close together will often be in the same clump. However, when r exceeds a certain value the relationship between the two concentrations will become a random one (provided there is no large-scale segregation or regular periodicity in the mixture) and $R(r)$ will fall to 0, whatever the proportions of A and B in the mixture. $R(r)$ will therefore vary with r somewhat in the manner of fig. 1, although the shape of the curve will differ from case to case.

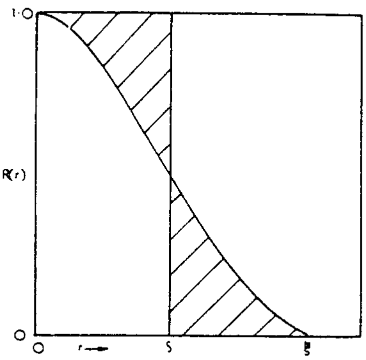

Fig. 1. Shaded areas are equal.

The curve is known as the *correlogram* of the mixture. (It is shown in Appendix C that the slope of the curve is always zero at $r = 0$ in systems in which diffusion occurs). Figs. 2 and 3 show correlograms for two two-dimensional models of mixtures. (The slopes of these curves are not zero at $r = 0$, because the "clumps" have sharp edges).

The value of r for which $R(r)$ falls to zero will be called ξ. (If $R(r)$ approaches zero asymptotically, ξ is assigned a value such that $\int_0^\xi r^2\, R(r)\, \mathrm{d}r$ differs from $\int_0^\infty r^2\, R(r)\, \mathrm{d}r$ by a fraction which is small enough to be ignored in evaluating V — see (4)).

There are two ways in which the correlogram of a mixture can be used to define a scale of segregation. The *linear scale*, S, is defined as the area under the correlogram:

$$S = \int_0^\infty R(r)\,\mathrm{d}r = \int_0^\xi R(r)\,\mathrm{d}r. \tag{3}$$

The *volume scale*, V, is defined as 2π times the area under the curve $r^2\,R(r)$ vs. r:

$$V = 2\pi \int_0^\infty r^2\,R(r)\,\mathrm{d}r = 2\pi \int_0^\xi r^2\,R(r)\,\mathrm{d}r. \tag{4}$$

The relationship between S and V depends on the shape of the clumps and hence of the correlogram. If the latter were linear, for example, V would be equal to $4\pi S^3/3$, i.e. to the volume of a sphere of radius S. In general, mixtures having equal S may have different V, and the ratio of S^3 to V in a given system may change during the course of mixing. When the clumps are not extremely elongated (i.e. when the mixture is mottled rather than streaky) V will be of the same order of magnitude as $4S^3$. S and V will both normally diminish during the mixing process. The ease with which each can be measured is likely to determine whether S or V is used as a measure of the scale of segregation in a given situation.

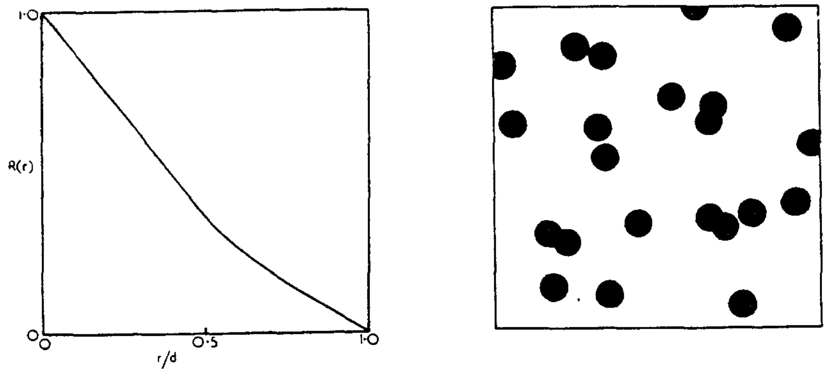

Fig. 2. Correlogram. Diameter of circles d, $S/d = 0.42$.

The clumps in a mixture may vary widely in size and shape, and both will generally be indeterminate because the boundaries will be diffuse. It is not possible, therefore, to refer with any precision to an "average diameter" or an "average volume" of the clumps. S and V, on the other hand, are precisely-defined quantities and their magnitudes vary in the same sense as the size of the clumps. For this reason it is convenient to use them as unambiguous measures of the scale of segregation, even though their significance is not easily visualised.

Fig. 2 illustrates the point that if clumps of component A are scattered in an excess of B, S will indicate the size of the clumps of A. Fig. 3 shows the effect of elongation of the clumps on the shape of the correlogram and the value of S. The latter would increase indefinitely as the rectangles were lengthened. Provided the black elements are scattered at random, the shapes of the correlograms and the values of S do not depend on the ratio of black areas to white.

A random collection of spheres of diameter d, analogous to fig. 2, will give $S/d = 0{\cdot}38$, $V/S = 4{\cdot}7$.

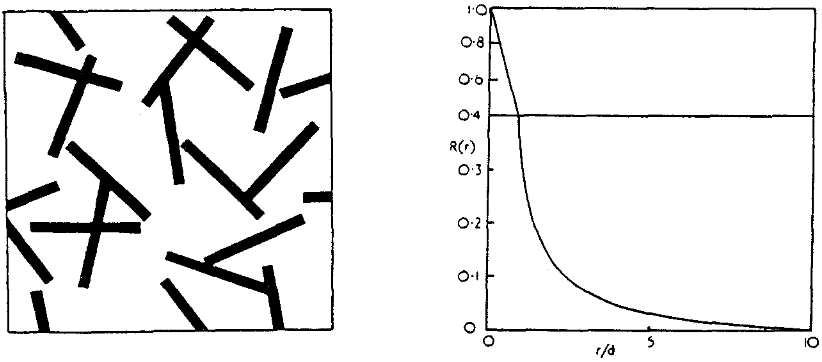

Fig. 3. Correlogram. Width of strips d, length of strips $10d$, $S/d = 1.1$.

§ 4. *Measurement of the scale of segregation.* There are a number of ways in which S and V can be determined. The method used in any given situation will depend on the circumstances.

(a) By measuring the concentration at a large number of points in the mixture, $R(r)$ can be determined as a function of r, and hence S and V found. Even if practicable, such a method is likely to be laborious.

(b) In a batch mixing-process, the concentrations at two fixed points a distance r apart might be measured continuously while the mixture moved past them (electrical or optical methods suggest themselves). $R(r)$ could be calculated from records of the readings from each point, or by a modification of one of the methods devised for measuring the scale of turbulence ³). The value of $R(r)$ for a number of values of r must be found by employing a number of pairs of measuring points at various distance apart.

(c) A different and more convenient type of method can be used for finding S if a means can be found for measuring the total "content" of one of the components along a straight line joining two points. The content, J, of component A in a line-sample of length X is defined by

$$J = \int_0^X a \, \mathrm{d}x \tag{5}$$

where a is the concentration of A at a point distance x from one end of the line. For instance, if both the components are transparent, one being coloured and one colourless, the content of the coloured material in a path of length X is proportional to the colour-density of this thickness of the mixture. In this case the content could conveniently be measured by setting up a light-source and photo-cell a distance X apart, both immersed in the mixture. The method seems particularly suitable for following a batch mixing-process.

Suppose that J is determined for a large number of such line-samples in different regions of the mixture. (In a batch-process this would probably be done by letting the mixture flow across a fixed line during the mixing process. The observations must then be confined to a period short enough so that the scale S does not alter appreciably). If the mixture is imperfect, the content J will fluctuate, and the scale of segregation, S, is related to the magnitude of the fluctuations by the expression (derived in Appendix A)

$$S = \frac{\sigma_J^2}{2X\,\sigma_a^2}, \tag{6}$$

where σ_J^2, σ_a^2 are the variances of J and a respectively and are defined by

$$\sigma_J^2 = \overline{(J - \bar{a}X)^2} \equiv \overline{J^2} - (\bar{a})^2\,X^2; \tag{7}$$

$$\sigma_a^2 = \overline{(a - \bar{a})^2} \equiv a^2 - (\bar{a})^2. \tag{8}$$

$\bar{a}$ is the mean concentration of a, which is assumed to be known. $\overline{J^2}$ and $\overline{a^2}$ are the mean square values of J and a respecively. The former can be determined in various ways from the output of the instrument which measures J. Hot-wire ammeters or other instruments capable of measuring root-mean-square voltages directly would probably provide the most convenient method.

$\overline{a^2}$ might be derived from the output of a simular instrument with a value of X very much smaller than S or by any method by which point-concentrations could be conveniently and continuously measured. Methods of determining $\overline{a^2}$ by following the progress of a chemical reaction are discussed in § 6.

Equation (6) is approximate, the error being of the order ξ/X. Assuming that ξ has the same order of magnitude as S, this implies that X must be considerably greater than S if this method of measuring the latter is to be used. On the other hand, a large value of X means a small value of the *fractional* fluctuations of J, with consequent difficulty in determining σ_J^2 accurately. The value of X most suitable in given circumstances must de betermined by trial and experience. If two substantially different values of X give the same value of S, it may be concluded that the latter contains no serious error.

This method is likely to be more convenient than (*b*), because it does not require independent measurement of $R(r)$ for a number of different values of r, and because the computation, automatic or otherwise, leading from the output of the measuring instruments to S will be simpler.

(*d*) In some cases it may be preferable to determine V, using a method based on the analysis of samples. Suppose a number of samples of volume v are taken from the mixture, and the content, K, of A found in each sample. The variance of K among the samples is related to V by the expression (derived in Appendix B)

$$V = \frac{\sigma_K^2}{2v\,\sigma_a^2}, \tag{9}$$

where

$$\sigma_K^2 = \overline{(K - v\bar{a})^2} \equiv \overline{K^2} - v^2(\bar{a})^2 \tag{10}$$

and σ_a^2 is defined by (8). $\overline{a^2}$ might be determined by taking a number of samples much smaller than V, or by one of the methods mentioned in (*c*) above. Equation (9) is an approximation; its use is justifiable only if $v \gg V$, and if the the samples are of a reasonably compact shape (e.g. cubes, spheres, short cylinders).

(*e*) When it is desired to measure the scale of segregation in a stream of material flowing continuously from a mixer through a pipe, method (*c*) above may be used if the diameter d of the pipe is much greater than S. Method (*d*) may also be used, subject to the same condition, if it is possible to measure continuously the content K of component A in a length l of the pipe. The volume v of liquid in this "sample" is $\pi d^2 l/4$, and hence, substituting in equation (9),

$$V = 2\sigma_K^2/\pi d^2 l \sigma_a^2, \tag{11}$$

(*f*) A case which is perhaps more likely to be encountered in practice is that in which a continuous stream of liquid leaves a mixer through a pipe whose diameter is very much less than S. The concentration will then be virtually uniform at all points at a given cross-section at a given moment, and the mixture will display segregation only in a longitudinal direction. Suppose a method is available for measuring continuously the concentration, a, of component A at a given cross-section; let the velocity of flow be u. Then the quantity

$$J = u \int_0^T a\,.\mathrm{d}t \tag{12}$$

is the content of A in a line-sample of length uT, the line being directed along the axis of the flow. The linear scale of segregation in this direction is thus seen from (6) to be

$$S = \sigma_J^2/2uT\sigma_a^2. \tag{13}$$

If a record of a is obtained as a function of the time t, the variance of J (as defined by (12)) can be found by integrating over a number of periods of length T (a convenient method of doing this has been described elsewhere [2]) and σ_a^2 can easily be computed from the same record. Hence S can be obtained from (13). The method described will not generally be applicable unless the velocity-profile across the pipe is nearly flat. In the case, for instance, of fully-developed laminar flow a given cross-section will not be uniform in composition, but will display ring-shaped zones of varying concentration due to the passage of successive clumps down the pipe; ostensible values of S found by the above method will then have little or no significance. On the other hand the method can be used if the fluid is in well-developed turbulent flow (Reynold's number $>$ 10,000), or if it displays the phenomenon of "Bingham flow" (e.g. extrusion of a plastic material), or even when it is in laminar flow, provided in the last case that the measurements are made close to the pipe-entry. It must be remembered that flow through a pipe, and subsequent discharge into a vessel, will themselves promote mixing, so that the scale of segregation measured at a given point in a pipe has only a local significance. Its value may nevertheless be a useful indication of the effectiveness of a mixer.

§ 5. *The intensity of segregation.* The intensity, I, of segregation is conveniently defined by the following mathematically identical expressions

$$I = \frac{\sigma_a^2}{\bar{a}.\bar{b}} \equiv \frac{\sigma_b^2}{\bar{a}.\bar{b}} \equiv \frac{\sigma_a^2}{\bar{a}(1-\bar{a})} \equiv \frac{\sigma_b^2}{\bar{b}(1-\bar{b})}\,. \tag{14}$$

Thus defined, I has the value 1 when segregation is complete (i.e. when the concentration of A or B at every point is either 1 or 0), and the value 0 when the concentration is uniform. In general I reflects not the relative amounts of A and B nor the size of the clumps, but the extent to which the concentration in the clumps departs from the mean. If B is present in large excess, the value of I will depend primarily on the extent to which the clumps of A in the mixture have become diluted by B.

When two miscible liquids are mixed, the value of I is progressively reduced. However, as previously mentioned, this reduction is not caused directly by the mechanical process of mixing, but depends on molecular interdiffusion of the two components. In the absence of diffusion the mixture would remain "grainy", as when immiscible liquids are emulsified. It is shown in Appendix C that the fractional rate of decay of I is given by the relationship:

$$-\frac{1}{I}\cdot\frac{\mathrm{d}I}{\mathrm{d}t} = -6D\left[\frac{\mathrm{d}^2R}{\mathrm{d}r^2}\right]_{r=0} \tag{15}$$

Now $-[\mathrm{d}^2R/\mathrm{d}r^2]_{r=0}$ is a measure of the sharpness with which the correlogram bends over from its initially flat top. Circumstances which emphasize this change of slope therefore favour the rapid production of a homogeneous mixture. These are: (*a*) A small scale of segregation. If two mixtures are geometrically similar — that is, identical in pattern, but different in geometrical scale — the respective rates of decay of I will be proportional to D/S^2. This illustrates the importance of designing mixers so as to reduce the scale of segregation as quickly as possible. (*b*) Steep average concentration gradients at the boundaries of the clumps. These will generally be produced by the same processes which progressively decrease the scale of segregation — that is, by flattening or elongating the clumps, or by subdividing them by "slicing" action or by the dispersal of material in eddies.

If the purpose of mixing A and B is to enable them to react with one another, I represents an inverse measure of the effectiveness of the mixing. It is shown in Appendix D that if the local rate of reaction is proportional to the concentrations of both A and B, the total rate of reaction in the mixture will be greatest when $I = 0$. When $I \neq 0$, there is a linear relationship between I and the total reaction rate, which may be used as described in the next section to determine I.

§ 6. *Measurement of the intensity of segregation.* Any method of measuring $\overline{a^2}$ (such as those already mentioned) will enable I to be found from (8) and (14). Alternatively a method based on the measurement of the rate of a chemical reaction might prove more convenient when it is desired to follow the progress of mixing in a batch process. Its use would normally be limited to circumstances in which the liquids A and B could be chosen to suit the investigator. The reaction chosen must have a rate which is either proportional to the square of the concentration of one component, or to the products of the concentrations of the two components. The components A and B will normally be relatively dilute solutions of the actual reagents, so that changes in temperature and physical properties as a result of the reaction will be small. It is necessary to choose reaction systems such that the *fractional* rate of reaction is relatively slow, so that the mean concentration of the various reactants do not change appreciably during the period over which I is to be observed.

(*a*) Reaction between A and B. Solution A contains m moles per unit volume of reactant M; solution B, n of reactant N. The local rate of reaction between A and B at a point where the volume-fraction of A is a, is $[kmna(1 - a)]$ moles of M per unit volume per unit time, where k is the reaction-velocity constant. Then, as shown in Appendix D

$$I = 1 - \varrho/kmn\bar{a}(1 - \bar{a}), \tag{16}$$

where ϱ is the mean rate of reaction per unit volume of the mixture.

(*b*) Second-order reaction of A. Solution A contains m moles per unit volume of M, and is destroyed at a local rate of km^2a^2 moles of M per unit volume per unit time. Then

$$I = \frac{\varrho}{km^2\bar{a}(1 - \bar{a})} - \frac{\bar{a}}{(1 - \bar{a})}. \tag{17}$$

The choice of suitable reactions for the determination of I offers scope for considerable ingenuity. (Data on the kinetics of a large number of reactions in solution are given by Moelwyn-Hughes[4]). It must be possible either to measure the mean concentration of one of the reactants with great accuracy, or to measure the concentration of a product of the reaction (a lower standard of accuracy is permissible in this case) or to measure the reaction-rate directly. Reactions of which the progress can be followed by optical methods may prove useful, because of the ease and accuracy of the measurements. The following types of system are worth consideration.

(*a*) Polarimetric methods, in combination with mutarotation or racemisation reactions.

(*b*) Colorimetric methods, in combination with reactions giving coloured products.

(*c*) Photometric methods, in combination with chemiluminescent reactions. This method has the attraction that it is the reaction rate itself which is measured and not the integral extent of the reaction. For this reason it might be particularly suited to cases where I changed very rapidly.

An optical method of judging the extent of a reaction by sighting through the mixture (as in (*a*) or (*b*) above) will generally give information about the "content" of reactant or product in a "line-sample" of the mixture. The mean value of the content of the line-sample will change progressively as the reaction proceeds. However, superimposed on this steady change will be fluctuations due to segregation in the mixture, which may make it difficult to determine the rate of reaction. This difficulty can be overcome by taking a line-sample sufficiently large in relation to the scale of segregation to display only small fractional variations in content. Under some circumstances (depending on the rate of movement of the mixture, the rate of reaction and the rates of change of I and S) it may be possible to determine both the mean value and the variance of the content of the line-sample from readings taken over a period of time too short to allow the extent of the reaction or the degree of mixing to change appreciably. This would enable both I and S to be calculated as functions of the time of mixing from a single series of readings.

§ 7. *Conclusions.* A knowledge of the scale and intensity of segregation in a mixture will provide a good deal of information about its texture, in a quantitative form which allows different degrees of mixing to be compared. The two quantities are virtually independent and represent aspects of "goodness of mixing" which cannot be defined by a single quantity.

The determination of the scale and intensity, even by the simplest methods suggested, involves in effect making a considerable number of measurements and averaging them. This is inevitable, as the only useful information which can be given about the degree of mixing is of a statistical nature. It seems unlikely that any simpler programme of measurements than those suggested here would yield quantities which would be of any value in a systematic investigation of mixing processes. However, simplified procedures could probably be devised for specific industrial purposes. For instance, the continuous measurement of $\overline{J^2}$ or $\overline{K^2}$ alone might be used to monitor the texture of a stream of constant mean composition, without the additional determination of $\overline{a^2}$. An increase in $\overline{J^2}$ or $\overline{K^2}$ would indicate an increase in either the scale or intensity of segregation, and hence a general decrease in the efficiency of the mixing process.

It is suggested that the statistical treatment of mixtures advocated in this paper may be useful in developing a general theory of mixing processes. For instance, if turbulence is used to bring about mixing it seems likely that power is most economically applied in producing turbulence with a scale comparable to the scale of segregation.

Appendix A. *Determination of S from variance of content of line-samples.* Put $c = a - \bar{a}$. The content, J, of a line-sample of length X is then given by

$$J = \int_0^X a \, \mathrm{d}x = \bar{a}X + \int_0^X c \, . \, \mathrm{d}x, \qquad (18)$$

from which follows

$$(J - \bar{J})^2 = [\int_0^X c \, . \, \mathrm{d}x]^2 \equiv 2 \int_{r=0}^{X} \int_{x=0}^{X-r} c(x) \, . \, c(x+r) \, . \, \mathrm{d}x \, . \, \mathrm{d}r, \qquad (19)$$

$c(x)$, $c(x + r)$ being the values of c at points distant x, $(x + r)$ from one end of the line. So

$$\sigma_J^2 = \overline{(J - \bar{J})^2} = 2 \int_{r=0}^{X} \int_{x=0}^{X-r} \overline{c(x).c(x + r)}.\mathrm{d}x.\mathrm{d}r. \tag{20}$$

But $\overline{c(x).c(x + r)}$ is independent of x, and equal to $\sigma_a^2\, R(r)$ (see (2)). Hence

$$\sigma_J^2 = 2\sigma_a^2 \int_{r=0}^{X} (X - r)\, R(r)\, \mathrm{d}r \tag{21}$$

Now $R(r)$ falls to zero at some value $r = \xi$; if $X \gg \xi$, (21) becomes

$$\sigma_J^2 \approx 2\sigma_a^2\, X \int_0^{\infty} R(r)\, \mathrm{d}r = 2\sigma_a^2\, XS, \tag{22}$$

which leads to (6).

The error is

$$2\sigma_a^2 \int_0^{X} r\, R(r)\, \mathrm{d}r = 2\sigma_a^2 \int_0^{\xi} r\, R(r)\, \mathrm{d}r < 2\sigma_a^2\, \xi S. \tag{23}$$

Appendix B. *Determination of V from variance of content of volume samples.* The content, K, of the sample is given by

$$K = \iiint a\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z, \tag{24}$$

where the integral is taken over the volume, v, of the sample. Putting $c = a - \bar{a}$:

$$K = \bar{a}v + \iiint c\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z; \tag{25}$$

but $\bar{K} = \bar{a}v$, hence

$$K - \bar{K} = \iiint c\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z. \tag{26}$$

For a large number, n, of samples of volume v:

$$n\sigma_K^2 = n\overline{(K - \bar{K})^2} = \iiint_{x,y,z} \iiint_{x',y',z'} \Sigma\, c(x,y,z).c(x',y',z').\mathrm{d}x\mathrm{d}y\mathrm{d}z.\mathrm{d}x'\mathrm{d}y'\mathrm{d}z', \tag{27}$$

where $c(x, y, z)$, $c(x', y', z')$ are the values of c at the points (x, y, z), and (x', y', z') respectively, and both sets of integrals are taken over the whole volume. However, the value of the sum $\Sigma\, c(x, y, z).c(x', y', z')$ will be independent of x, y, z, x', y', z' and equal to $n\overline{c^2}\, R(r)$ for a given value of r, where $r = \sqrt{\{(x - x')^2 + (y - y')^2 + (z - z')^2\}}$, and will be zero for $r > \xi$. Integrating over x', y', z' about any point (x, y, z) gives therefore:

$$4\pi n\overline{c^2} \int_{r=0}^{\xi} r^2\, R(r)\, \mathrm{d}r.\mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z, \text{ or } 2nV\overline{c^2}.\mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z.$$

Equation (27) therefore becomes:

$$\sigma_K^2 \approx 2V\overline{c^2}\iiint dx\, dy\, dz = 2Vv\overline{c^2} \tag{28}$$

and since $\overline{c^2} = \sigma_a^2$, we have

$$V \approx \sigma_K^2/2v\sigma_a^2. \tag{29}$$

The integral in (28) has been taken over all the points (x, y, z) in the sample. Since we have previously integrated over a radius ξ about each of these points, it is clear that the expression given in (28) actually "overlaps" the surface of the sample, and should be corrected by an additional term analogous to that in equation (23). The fractional error introduced into (29) by ignoring this correction will be less than $\xi A/V$, where A is the area of the surface of the sample. Assuming that the value of ξ is of the same order of magnitude as $V^{\frac{1}{3}}$ and that the sample is, for example, cubical in shape, the error will be of the order $(V/v)^{\frac{1}{3}}$.The error will be increased if the shape of the sample is not reasonably compact.

Appendix C. *Effect of Diffusion. Rate of Decay of I.* Let $c = a - \bar{a}$. $c(p)$ is the value of c at some point p in the mixture. $\overline{c(p + r)}$ is the mean value of c at all points distant r from p. Then (2), the definition of $R(r)$, can be put in the form

$$\overline{c^2}\, R(r) = \overline{c(p) . \overline{c(p + r)}}, \tag{30}$$

the product $c(p). \overline{c(p + r)}$ being averaged over all points p in the mixture. Differentiating (30) with respect to r (at constant t) and putting $r = 0$ gives

$$\overline{c^2}\left[\frac{\partial R}{\partial r}\right]_{r=0} = \overline{c(p)\left[\frac{\partial \overline{c(p + r)}}{\partial r}\right]_{r=0}}. \tag{31}$$

Now $[\partial\, \overline{c(p + r)}/\partial r]_{r=0}$ is the average, at any instant, of the values of $\partial c/\partial r$ measured in all directions from the point p. Provided there are no discontinuities in $\partial c/\partial r$, this average will be zero, because the value of $\partial c/\partial r$ measured from the point in any direction will be equal and opposite in sign to that measured in the opposite direction. Now it is easily shown that in a system in which diffusion occurs, discontinuities in the concentration-gradient cannot persist for a finite length of time (unless the diffusivity D is a discontinuous function of c). For such systems, therefore

$$[dR/dr]_{r=0} = 0, \tag{32}$$

and the correlogram will have a flat top.

Consider a small spherical element of the mixture, centre p, radius δr. Equating the rate of inflow of component A by diffusion to the rate of rise of concentration, we have

$$\frac{4}{3}\pi(\delta r)^3 \frac{\partial c(p)}{\partial t} = 4\pi(\delta r)^2 D \left[\frac{\partial \overline{c(p+r)}}{\partial r}\right]_{r=\delta r}. \tag{33}$$

Using equations ((31) and (32) we have

$$\left[\frac{\partial \overline{c(p+r)}}{\partial r}\right]_{r=\delta r} = \delta r \left[\frac{\partial^2 \overline{c(p+r)}}{\partial r}\right]_{r=0} \tag{34}$$

Differentiating (30) twice with respect to r, and putting $r = 0$ we have

$$\overline{c^2}\left[\frac{\partial^2 R}{\partial r^2}\right]_{r=0} = \overline{c(p)\left[\frac{\partial^2 \overline{c(p+r)}}{\partial r^2}\right]_{r=0}}. \tag{35}$$

Substituting (34) and (35) in (33) we find

$$\overline{c(p)\,\frac{\partial c(p)}{\partial t}} = 3D\,\overline{c^2}\left[\frac{\partial R^2}{\partial r^2}\right]_{r=0}. \tag{36}$$

Whence

$$\frac{1}{\overline{c^2}} \cdot \frac{\mathrm{d}\overline{c^2}}{\mathrm{d}t} = 6D\left[\frac{\mathrm{d}^2 R}{\mathrm{d}r^2}\right]_{r=0} \tag{37}$$

and from the definition of I (equation (2)):

$$-\frac{1}{I}\,\frac{\mathrm{d}I}{\mathrm{d}t} = -6D\left[\frac{\mathrm{d}^2 R}{\mathrm{d}r^2}\right]_{r=0}. \tag{38}$$

Appendix D. *Determination of I from reaction-rate.*

(*a*) 2nd-order reaction between A and B. The local rate of reaction per unit volume is

$$k\,m\,n\,a\,(1 - a)$$

The total reaction rate in the system is therefore

$$\varrho v = kmn \int\!\!\int\!\!\int a(1 - a)\,\mathrm{d}x\,\mathrm{d}y\mathrm{d}z \tag{39}$$

the integral being taken over the whole volume v, and ϱ being the mean rate of reaction per unit volume. But

$$\frac{1}{v}\int\!\!\int\!\!\int a(1 - a)\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = \bar{a} - \overline{a^2}, \tag{40}$$

from which

$$\bar{a} - \overline{a^2} = \varrho/kmn, \tag{41}$$

and using (7)

$$\bar{a} - (\bar{a})^2 - \sigma_a^2 = \varrho/kmn \tag{42}$$

whence

$$I = 1 - \varrho/kmn\bar{a}(1 - \bar{a}). \tag{43}$$

(*b*) 2nd-order reaction of A. The local rate per unit volume is km^2a^2. The total reaction-rate in the system is therefore

$$\varrho v = km^2 \int\int\int a^2 \, dx \, dy \, dz \tag{44}$$

so

$$\varrho/km^2 = \overline{a^2}. \tag{45}$$

Using (7)

$$\sigma_a^2 = \overline{a^2} - (\bar{a})^2 \equiv \varrho/km^2 - (\bar{a})^2, \tag{46}$$

$$I = \varrho/km^2\bar{a}(1 - \bar{a}) - \bar{a}/(1 - \bar{a}). \tag{47}$$

Received 28th March, 1952.

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