CONTINUOUS FLOW SYSTEMS. DISTRIBUTION OF RESIDENCE TIMES

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Summary—When a fluid flows through a vessel at a constant rate, either "piston-flow" or perfect mixing is usually assumed. In practice, many systems do not conform to either of these assumptions, so that calculations based on them may be inaccurate. It is explained how distribution-functions for residence-times can be defined and measured for actual systems. Open and packed tubes are discussed as systems about which predictions can be made. The use of the distribution-functions is illustrated by showing how they can be used to calculate the efficiencies of reactors and blenders. It is shown how models may be used to predict the distribution of residence-times in large systems.

Résumé—Quand, dans un récipient, on introduit, à vitesse constante, un fluide donné, on suppose généralement soit un mélange parfait, soit un "écoulement frontal parfait". En pratique, de nombreux systèmes s'écartent de l'une ou l'autre de ces hypothèses simplificatrices et les calculs qui en résultent sont plus ou moins inexacts. L'auteur expose, pour des systèmes réels, comment l'on peut définir et mesurer des fonctions de distribution pour la "durée de séjour": ceci peut s'appliquer à des tubes vides ou munis de garnissages. Par emploi de ces fonctions de distribution, l'auteur montre comment on peut calculer l'efficacité des réacteurs ou des mélangeurs. Des modèles peuvent être utilisés pour prévoir la répartition des "durées de séjour" dans des systèmes de grandes dimensions.

INTRODUCTION

When a stream of material flows steadily through a vessel such as a pipe or a tank, in which it takes part in some process such as chemical reaction, heat- or mass-transfer, or simple mixing, it is usual to make use of one of the following assumptions for the purposes of calculation:

(a) The fluid in the vessel is completely mixed, so that its properties are uniform and identical with those of the outgoing stream. This assumption is frequently made the basis of calculations on stirred reactors or blenders.

(b) Elements of fluid which enter the vessel at the same moment move through it with constant and equal velocity on parallel paths, and leave at the same moment. This type of behaviour will be referred to as "piston flow", and is normally assumed when considering flow through heat-exchangers, catalytic reactors, packed towers, chromatographic columns, etc.

It is clear that there are many cases in which neither type of flow corresponds exactly to the facts—for instance, fluid in laminar flow in a pipe, or gas flowing through a fluidised catalytic reactor or blast furnace. It is of some importance to investigate the discrepancies between the assumed and actual behaviour of such systems, and where necessary to allow for them in making calculations. This paper is intended to clarify some of the problems presented by steady-flow systems, and to show how their behaviour can be investigated and quantitatively specified. Some of the concepts and mathematical expressions which appear below have already been used by Gilliland and Mason [8, 9] in the course of a study of flow through fluidised beds.

F-DIAGRAMS AND AGE-DISTRIBUTION FUNCTIONS

The volume of the vessel occupied by the fluid is V, and the volumetric rate of inflow and outflow of fluid is assumed constant and equal to v. Suppose some property of the inflowing fluid undergoes a sudden change from one steady value to another; for instance, let the colour change from white to red. Call the fraction of red material in the outflow at time θ later $F(\theta)$. The plot of $F(\theta)$ vs $v\theta/V$ will be called an "F-diagram". Figure 1(a)–(d) shows F-diagrams for some representative types of system.

Perfect piston flow [Fig. 1(a)] will never occur with Newtonian fluids; there will always be some longitudinal mixing, due to viscous effects and molecular or eddy-diffusion. Figure 1(b) illustrates the departure from piston flow caused by restricted longitudinal mixing. Figure 1(c) is the diagram for perfect mixing; the equation of the curve is easily shown to be

$$F(\theta) = 1 - e^{-v\theta/V}. \tag{1}$$

It cuts the ordinate $v\theta/V = 1$ at $(1 - 1/e)$, and its initial slope is unity. Figure 1(d) shows a diagram of the type to be expected when there is a good deal of "dead water" in the system; a considerable fraction of the fluid is trapped in eddies, and spends much more than the average length of time in the vessel, while most of the flow takes place through a restricted channel.

The F-diagram of a system is easy to obtain (for instance, by injecting tracer materials into the entering stream), and its shape will clearly give a good deal

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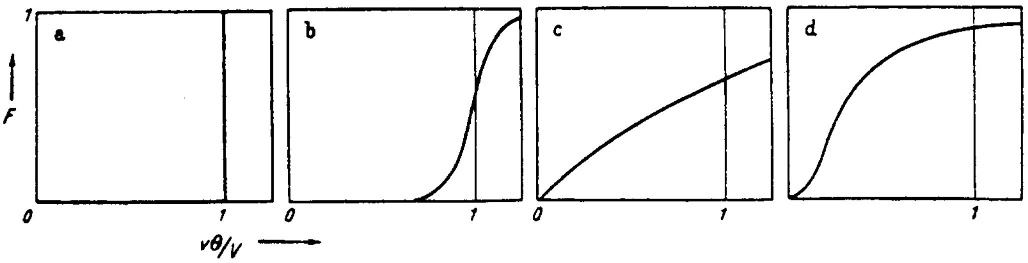

Fig. 1. F-diagrams: (a) piston flow; (b) piston flow with some longitudinal mixing; (c) complete mixing; (d) dead water.

of information about the behaviour of the fluid flowing through the vessel. As will be shown later, much of this information can be summarised by two numbers which can be derived from the F-diagram. The diagram also enables certain calculations to be made concerning the performance of the system when used, for instance, as a blender or reactor.

The shape of the F-diagram depends on the relative times taken by various portions of the fluid to flow through the vessel, or, in other words, on the distribution of residence-times. Those elements of the material in the vessel which have been in it for a time θ are said to have an "age" θ, and the fraction of the material in the system having at any instant ages between θ and $(\theta + \mathrm{d}\theta)$ is $I(\theta)\,\mathrm{d}\theta$. The fraction of the material having ages between θ and $(\theta + \mathrm{d}\theta)$ at the moment of leaving the system is $E(\theta)\mathrm{d}\theta$. I and E may be called the internal and exit age-distribution functions, respectively. The relationship between E, I and F can be shown by imagining the ingoing stream, as before, to change from white to red at time $\theta = 0$. At a time θ later the balance sheet for the red material is:

$$\text{entered: } v\theta$$

$$\text{still in system: } V\int_0^{\theta} I(\theta')\,\mathrm{d}\theta'$$

$$\text{left system: } v\int_{\theta''=0}^{\theta}\int_{\theta'=0}^{\theta''} E(\theta')\,\mathrm{d}\theta'\,\mathrm{d}\theta''.$$

The last follows because the rate of outflow of red material at any time θ'' after the change of colour is

$$v\int_0^{\theta''} E(\theta')\,\mathrm{d}\theta'.$$

Thus the conservation equation for red material is

$$\frac{v\theta}{V} = \int_0^{\theta} I(\theta')\,\mathrm{d}\theta' + \frac{v}{V}\int_{\theta''=0}^{\theta}\int_{\theta'=0}^{\theta''} E(\theta')\,\mathrm{d}\theta'\,\mathrm{d}\theta''. \tag{2}$$

Also, the total fraction $F(\theta)$ of red material in the outflow at time θ is

$$F(\theta) = \int_0^{\theta} E(\theta')\,\mathrm{d}\theta'. \tag{3}$$

Differentiating eq. (2) with respect to θ,

$$1 - \int_0^{\theta} E(\theta')\,\mathrm{d}\theta' = \frac{V}{v} I(\theta) \tag{4}$$

and hence from eq. (3)

$$1 - F(\theta) = \frac{V}{v} I(\theta). \tag{5}$$

Equation (4) gives the relationship between $E(\theta)$ and $I(\theta)$, while eq. (5) shows how the latter function can be determined from the F-diagram.

The same information can be obtained in a somewhat different way, which may prove more convenient under some circumstances. Suppose a quantity Q of some substance (a radioactive tracer might be chosen for ease of estimation) is injected into the entering stream virtually instantaneously—that is, within a period very short compared to V/v. As before, samples are taken at various times θ after the injection; the concentration of the injected material in the exit stream at time θ is $C(\theta)$. Then it can be shown, by methods similar to those used above, that

$$C(\theta) = \frac{Q}{v}\frac{\mathrm{d}}{\mathrm{d}\theta}\left\{F(\theta)\right\} = \frac{Q}{v}E(\theta). \tag{6}$$

Plots of $VC(\theta)/Q$ vs $v\theta/V$, which may be called C-diagrams, are shown in Fig. 2 for the systems whose F-diagrams are given in Fig. 1. Note that

$$\frac{V}{Q}\int_0^{\theta} C(\theta)\,\mathrm{d}\left(\frac{v\theta}{V}\right) = 1 \tag{7}$$

so that the area under every C-diagram is equal to unity.

It has been assumed in the foregoing that the forms of the functions I and E do not vary with time. In fact, however, instability of flow may lead to fluctuations in the internal and exit age-distributions, and cause observed values of $F(\theta)$ to oscillate about some smooth curve of the kind shown in Fig. 1. These fluctuations will generally be random in nature, and by making a number of determinations of the F-diagram and averaging, the mean form of the diagram can be obtained. The problems raised by such fluctuations will be considered on another occasion; for the moment attention will be confined to cases where they may be ignored.

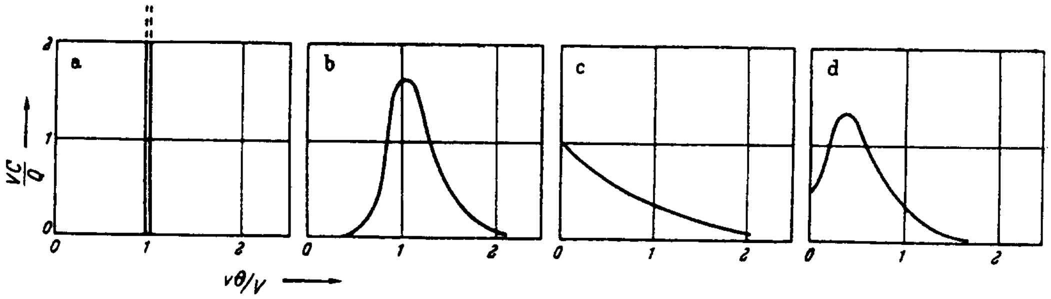

Fig. 2. C-diagrams: (a) piston flow; (b) piston flow with some longitudinal mixing; (c) complete mixing; (d) dead water.

It will be noted that

$$\int_0^\infty I(\theta)\,\mathrm{d}\theta \equiv \frac{v}{V}\int_0^\infty \{1 - F(\theta)\}\,\mathrm{d}\theta = 1 \tag{8}$$

and

$$\int_0^\infty E(\theta)\,\mathrm{d}\theta = 1 \tag{9}$$

[because the integrals in eqs (8) and (9) represent the total fractions of material, in the vessel and at the exit, respectively, having ages between 0 and ∞—namely, *all* the material in each case]. Equation (8) implies that the area between the curve $F(\theta)$ vs $v\theta/V$ and the line $F(\theta) = 1$ is equal to unity. It can be seen immediately that the two shaded areas are equal in Fig. 3, whatever the shape of the curve.

The average age $\bar{\theta}_E$ of the material leaving the vessel is always V/v. This can be shown as follows:

$$\bar{\theta}_E = \int_0^\infty \theta \cdot E(\theta)\,\mathrm{d}\theta. \tag{10}$$

Hence, from eq. (3)

$$\frac{v\bar{\theta}_E}{V} = \int_0^\infty \frac{v\theta}{V}\frac{\mathrm{d}F(\theta)}{\mathrm{d}\theta}\,\mathrm{d}\theta = \int_{F=0}^1 \frac{v\theta}{V}\,\mathrm{d}F(\theta). \tag{11}$$

It can be seen from Fig. 3 that the last integral is equal to 1.

The average age of the material in the system at any time is $\bar{\theta}_I$, where

$$\bar{\theta}_I = \int_0^\infty \theta \cdot I(\theta)\,\mathrm{d}\theta = \frac{v}{V}\int_0^\infty \theta\{1 - F(\theta)\}\,\mathrm{d}\theta. \tag{12}$$

Integrating by parts we have

$$\bar{\theta}_I = \frac{v}{2V}\int_{F=0}^1 \theta^2\,\mathrm{d}F(\theta). \tag{13}$$

The integral in eq. (12) or eq. (13) can be evaluated graphically with the help of the F-diagram.

HOLD-BACK AND SEGREGATION

The systems illustrated in Fig. 1(a)–(d) show in progressively greater degree a quality which will be called "hold-back". In a system which displays hold-back, some elements of fluid spend more, others less, than the average time, V/v, in the vessel. In a system with piston-flow [Fig. 1(a)], there is no hold-back. Quantitatively, the magnitude of the hold-back will be denoted by H, and can be conveniently defined as the area under the F-diagram between $v\theta/V = 0$ and $v\theta/V = 1$ (area A in Fig. 3):

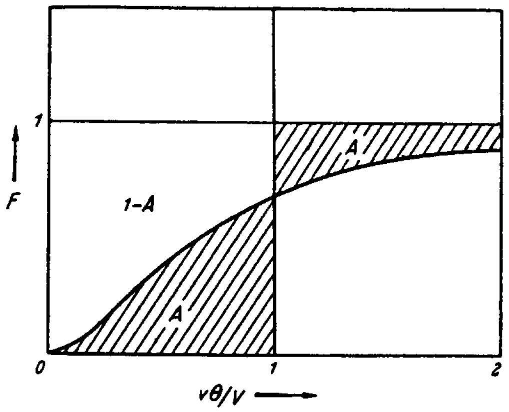

Fig. 3.

$$H = \frac{v}{V}\int_{\theta=0}^{V/v} F(\theta)\,\mathrm{d}\theta. \tag{14}$$

H varies from 0 for piston-flow to values approaching 1 when most of the space in the vessel is dead water. For the completely mixed vessel [Fig. 1(c)], $H = 1/e$. The magnitude of H is a measure of the deviation from piston-flow. Its significance is most easily visualised as follows: if the colour of the inflowing stream changes suddenly from white to red, H is equal to the fraction of the vessel which will still be occupied by white fluid after a volume of red fluid equal to the volume of the vessel has flowed in.

The hold-back is of importance in connection with chemical reactors and the successive flow of fluids through pipes and other vessels. In the former case it will usually be true to say that if the reactants are adequately mixed before or shortly after entering the vessel, the output of the reactor will be greatest when the hold-back is least (although the reverse may be true for autocatalytic reactions). A high hold-back means that much of the volume of the reactor is occupied by material which has already undergone reaction, while much reactant passes rapidly through the vessel by a "short-circuit" route. The magnitude of the hold-back gives only a general idea of the behaviour of the system, however; the whole F-diagram (and possibly other information) is needed if the actual performance of the reactor is to be calculated. This subject is discussed in a later section.

An indication of the efficiency of mixing in a system can be given by a single quantity, S, which will be called the "segregation", and can be derived from the F-diagram as follows. If one superimposes the F-diagrams for a perfectly mixed system [eq. (1)] and for an imperfectly mixed system such as that represented in Fig. 1(b), the result will be similar to Fig. 4.

The degree of departure of the system from perfect mixing will be indicated by the size of the shaded area $(A_1 + A_2)$. However, since the area between each curve, and the line $F(\theta) = 1$ is the same, the two shaded regions have the same area $(A_1 = A_2)$. It is thus convenient to define the segregation S quantitatively as the area A_1 between the F-diagram of the system and the curve $F(\theta) = 1 - e^{-v\theta/V}$, up to the point (at $\theta = T$) where the curves cross; it is thus equal to half the total shaded area.

When there is dead water in the system the positions of the curves may be inverted, as in Fig. 5.

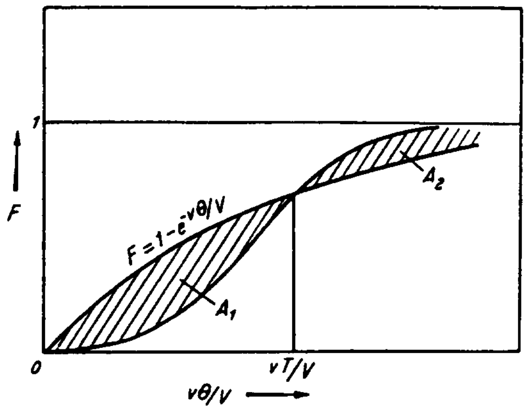

Fig. 4.

The segregation is then given the negative value $-A_1$ to indicate the nature of the departure from perfect mixing. In a case such as that illustrated in Fig. 1(b), the two curves may cut twice, as indicated in Fig. 6.

In such cases $A_1 + A_3 = A_2$, and the segregation is equal to $-A_2$. S varies from $+1/e$ for piston-flow to values approaching -1 when most of the space in the system is dead water.

The sense in which the word "mixing" has been used here should be clearly understood. We are not concerned with homogeneity, but with the age-distribution of material in the vessel and in the outgoing stream. If these distributions are the same, the system is said to be perfectly mixed, although there might, in the experiment described, be a perceptible non-uniformity of colour. On the other hand, when a fluid flows through a pipe with a high degree of turbulence, the segregation as defined above may approach that for piston-flow, although mixing in directions at right-angles to the axis of flow may be very efficient, ensuring that at any given moment the composition will be uniform across each cross-section and in the outflowing fluid.

As pointed out by Gilliland and Mason [9], although the F-diagram for a fluidised bed may be quite close to that for perfect mixing, other tests show that longitudinal mixing is in fact not very efficient, and moreover a considerable proportion of the gas passes through the bed in the form of bubbles.

Under some circumstances, when the fluid concerned is a gas, molecular diffusion between neighbouring elements of fluid may play a material part in determining the shape of the F-diagram. In liquids, however, diffusion coefficients are so small that only hydrodynamic effects will usually be of significance.

FLOW THROUGH BEDS OF SOLIDS

A very large number of chemical engineering operations involve the flow of a fluid through beds of stationary solid particles. Calculations are usually based on the assumption that piston-type flow occurs in such systems. This is certainly not exactly true,

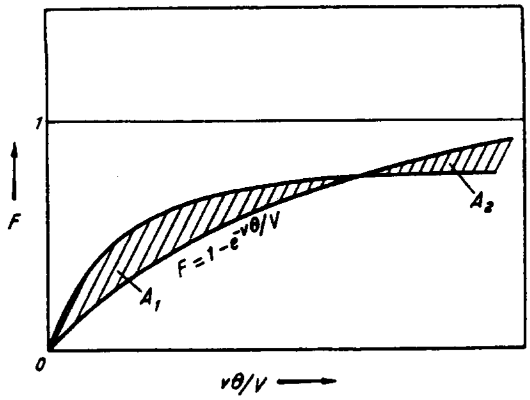

Fig. 5.

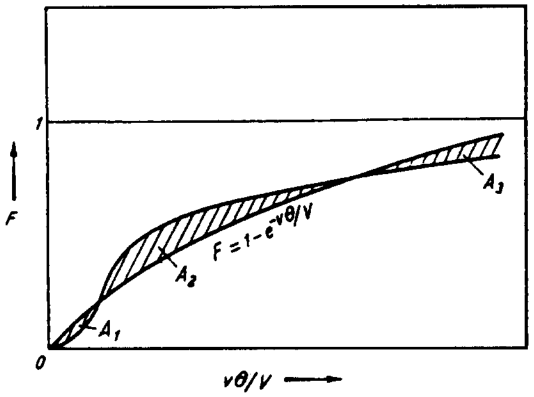

Fig. 6.

since longitudinal mixing must take place. Many cases, however, are probably amenable to the mathematical treatment which follows.

Consider a packed tubular vessel of length L, through which fluid flows with a mean axial velocity u. At time $\theta = 0$ the colour of the fluid changes from white to red. Now if the flow were of piston-type, the plane boundary between red and white would move down the tube with velocity u. We shall denote this imaginary plane by $x = 0$ and use it as the origin of a frame of reference moving down the tube with uniform velocity u, so that at time θ the plane $x = 0$ is distant $u\theta$ from the entry, and the x-coordinates of the ends of the tube are $(-u\theta)$ and $(L - u\theta)$, respectively (see Fig. 7).

The longitudinal velocity of any element of fluid relative to the plane $x = 0$ will fluctuate irregularly. At times the element will be close to a solid surface, and viscous forces will slow it down, while at other times it will be near the centre of a channel and moving at a velocity greater than the mean; part of the time may be spent in regions of turbulence where the element will undergo rapid and irregular fluctuations in velocity. If the packing is quite randomly arranged, without any channelling, each element of fluid will travel at the same average velocity, and will experience fluctuations of the same average magnitude and frequency. It is clear that the ordinary "random walk" theory [10] can be applied to such behaviour; the result will be redistribution of red and white material according to the laws of diffusion. That is, if c is the mean concentration (volume fraction) of red material at a plane x at time θ,

$$\frac{\partial c}{\partial \theta} = D\frac{\partial^2 c}{\partial x^2}. \tag{15}$$

D is a "diffusivity" which must be determined empirically; it will presumably depend on the viscosity, density and velocity of the liquid, and on the size and shape of the packing. The following boundary conditions will represent the facts with sufficient precision under many circumstances:

$$\begin{aligned} c &= 0, \quad x > 0, \quad \theta = 0 \\ c &= 1, \quad x < 0, \quad \theta = 0 \\ c &= 0, \quad x = \infty, \quad \theta > 0 \\ c &= 1, \quad x = -\infty, \quad \theta > 0. \end{aligned} \tag{16}$$

(The above conditions hold if the concentration of white material at the entry falls virtually to zero at a time very much less than L/u. It can be shown that this will occur if $4D/Lu \ll 1$—that is, provided mixing is not too effective or the tube too short.) Under these conditions the solution to eq. (15) is

$$c = \tfrac{1}{2}\left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{D\theta}}\right)\right] \tag{17}$$

[where $\operatorname{erf}(x/2\sqrt{D\theta}) = (2/\sqrt{\pi})\int^{x/2\sqrt{D\theta}} e^{-y^2}\,dy$; numerical values may be found in tables and are shown in Fig. 8]. Hence

$$2F(\theta) = 1 - \operatorname{erf}\left(\frac{L - u\theta}{2\sqrt{D\theta}}\right) \tag{18}$$

and since $v/V = u/L$ (V being the void volume of the vessel)

$$2F(\theta) = 1 - \operatorname{erf}\left(\frac{1 - v\theta/V}{2\sqrt{(v\theta/V)(D/Lu)}}\right). \tag{19}$$

The F-diagram will thus be determined entirely by the value of D/Lu. It will have the general shape shown in Figs 1(b) and 9.

If we let

$$\operatorname{erf}(z) = 1 - 2F \tag{20}$$

eq. (19) becomes, on rearrangement,

$$\frac{1 - v\theta/V}{z\sqrt{v\theta/V}} = 2\sqrt{\frac{D}{Lu}}. \tag{21}$$

(Values of z corresponding to given values of F can be found with the help of Fig. 8.)

For a given flow-rate and depth of packing, the left-hand side of eq. (21) should be constant if the diffusion equation (15) is obeyed. However, eq. (21) is not very suitable for testing the diffusion hypothesis or for determining the value of D since the expression on the left-hand side is very sensitive to small errors in F over the range of greatest importance. The value of D is probably more easily determined from the slope

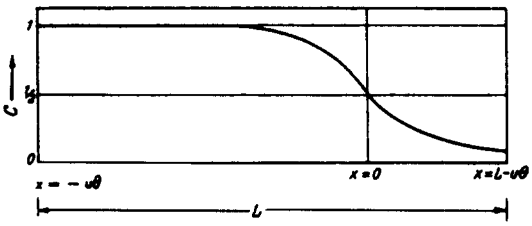

Fig. 7.

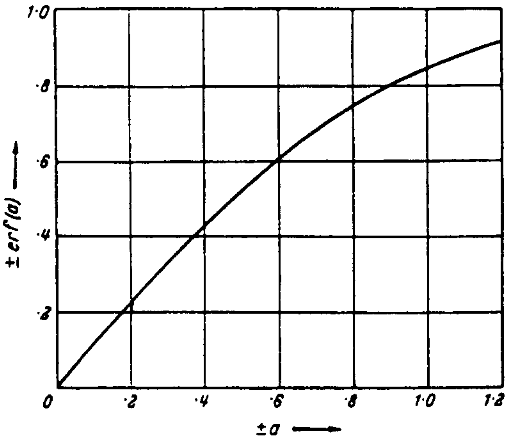

Fig. 8. $\operatorname{Erf}(a) = \frac{2}{\sqrt{\pi}}\int_0^a e^{-y^2}\,dy.$

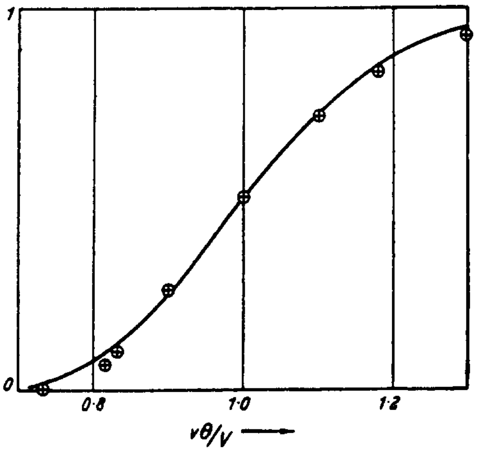

Fig. 9. F-diagram calculated for flow through packed column compared with experimental points.

of the F-diagram at $v\theta/V = 1$, we find

$$\left[\frac{\mathrm{d}F}{\mathrm{d}(v\theta/V)}\right]_{v\theta/V=1} = \tfrac{1}{2}\sqrt{\frac{Lu}{\pi D}}. \tag{22}$$

D/Lu can be calculated from this expression, the F-diagram calculated from eq. (19), and the results compared with the experimental curve. D should, of course, be independent of L for a given u.

The hold-back in the system is equal to $\sqrt{DV/\pi v}$ or $\sqrt{DL/\pi u}$.

Figure 9 shows the F-diagram obtained when water flowed through a bed of $\frac{3}{8}$ in. Raschig rings (tube diameter 4.8 cm; $L = 140$ cm; fractional free volume 0.62; volumetric flow-rate 4.5 cm^3/s). The curve calculated from eq. (19) with $D/Lu = 0.013$ is compared with the experimental points and shown to agree well.

The liquid running over the packing in an absorption tower is presumably subject to the same kind of mixing, although channelling may prevent eq. (15) from being very closely obeyed. The quantity V in this case is equal to the total liquid hold-up.

The effect of longitudinal mixing on the performance of tubular reactors is discussed later.

FLOW IN PIPES

Hold-back will always arise when a true fluid flows through a pipe. In the first place, there is a variation in velocity from the axis to the wall of the pipe, so that the central "core" of fluid moves with a velocity greater than the mean, while the fluid near the wall lags behind. This effect will be most marked when flow is laminar; in turbulent flow the velocity is more uniform across the pipe, and the hold-back is less, although eddy-diffusion contributes to the longitudinal mixing. In some circumstances molecular diffusion may also contribute appreciably to the hold-back. It will be convenient to discuss laminar and turbulent flow separately.

When viscous liquids such as heavy petroleum oil or rayon dope are pumped through pipes, the flow may be laminar. If the flow is changed, say, from one type of petroleum to another, or from normal to pigmented dope, the mean composition of the liquid leaving the pipe will change only gradually from one pure component to the other, and a large volume of mixed liquid will be discharged. If certain simplifying assumptions are made, the form of the F-diagram is easily calculated. (Similar calculations have been made by Bosworth [2] and by Fowler and Brown [7].)

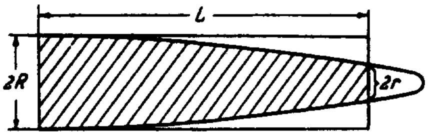

Fig. 10.

In the first place, entrance-effects will be ignored (as in the derivation of Poiseuille's formula), and the liquid will be assumed to be everywhere in unaccelerated laminar flow with a parabolic velocity-distribution; provided the ratio of the length to the diameter of the pipe is sufficiently large ($\gg 0.06Re$) entrance effects will in fact be unimportant. Secondly, it will be assumed that the two liquids have the same density and viscosity, and behave as Newtonian fluids. Thirdly, molecular diffusion will be ignored.

If $\bar{u}$ is the mean velocity and u the velocity at a distance r from the axis of a pipe of radius R, we have the well-known relationship

$$u = 2\bar{u}\left(1 - \frac{r^2}{R^2}\right). \tag{23}$$

The follow-up liquid will thus first appear at the exit of a pipe of length L after a time $L/2\bar{u}$; after a greater time, θ, the situation will be as shown in Fig. 10, with a core of follow-up liquid of diameter $2R\sqrt{1 - L/2\bar{u}\theta}$ at the exit. Allowing for the variation of velocity from the centre to the edge of the core, the fraction of follow-up liquid in the stream leaving the pipe is seen to be

$$F(\theta) = \frac{1}{\pi R^2 \bar{u}} \int_0^{R\sqrt{1 - L/2\bar{u}\theta}} 2\bar{u}\left(1 - \frac{r^2}{R^2}\right) 2\pi r \,\mathrm{d}r \tag{24}$$

$$\begin{aligned} &= 1 - L^2/4\bar{u}^2\theta^2, \quad \bar{u}\theta/L > \tfrac{1}{2} \\ &= 1 - V^2/4v^2\theta^2, \quad v\theta/V > \tfrac{1}{2}. \end{aligned} \tag{25}$$

The resulting F-diagram is shown in Fig. 11. Its shape is independent of the length and diameter of the pipe, and of the viscosity and velocity of the fluid (provided of course that flow is laminar). The hold-back is $\frac{1}{4}$. Bosworth [2] has calculated the effect of molecular diffusion on systems of this kind [his F_τ is equivalent to the present author's $E(\theta)$]. He shows that it can be ignored providing the following conditions are fulfilled:

$$R > 13\sqrt{D_m L/\bar{u}}$$

$$L > 6.5 \times 10^4\, D_m/\bar{u}$$

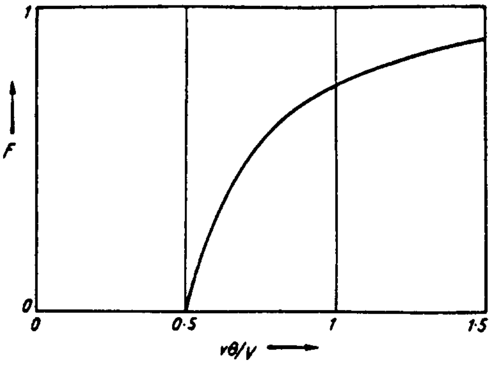

Fig. 11. F-diagram for viscous flow in pipe.

(where D_m is the molecular diffusivity), and points out that in the case of gases turbulence usually occurs while R is too small for the first condition to be satisfied. With liquids, however, which have much higher Schmidt numbers ($\mu/\rho D_m$), there may be a considerable range of pipe-diameters for which flow is laminar and the first condition is also satisfied.

Bosworth [3] has also derived expressions for $E(\theta)$ (F_τ in his nomenclature) for turbulent flow in pipes, starting from simplified expressions for the values of the axial velocity and eddy-diffusivity at various distances from the pipe wall. The following expression for $F(\theta)$ can be derived from Bosworth's formula:

$$F(\theta) = 1 - 2\alpha^n[1 - \beta n - \tfrac{1}{2}\beta - \alpha^n(\tfrac{1}{2} - \tfrac{5}{2}\beta n - \tfrac{5}{4}\beta) - \beta(2n+1)(\alpha^{2n} - \tfrac{1}{4}\alpha^{3n})] \tag{26}$$

where

$$\frac{1}{\alpha} = 2\frac{v\theta}{V}\left[(1 - \beta n - \beta/2)\frac{n}{n-1} + \left(-\frac{1}{2} + \frac{5}{2}\beta n + \frac{5\beta}{4}\right) \times \left(\frac{2n}{2n-1}\right) - \beta(2n+1)\left(\frac{3n}{3n-1} + \frac{4n}{4n-1}\right)\right]$$

$$\beta = (n-1)^2 R/0.32\, nL$$

$$n = 7,\ 2000 \leqslant Re \leqslant 100{,}000$$

$$n = 8,\ Re > 100{,}000$$

R being the radius and L the length of the pipe.

Comparison can be made with the experimental results of Fowler and Brown [7]. Figure 12 shows an experimental F-diagram compared with that calculated from Bosworth's formula. In Fig. 13 a comparison is made between calculated and observed values of $(v/V)(\theta_{0.8} - \theta_{0.2})$ for various Reynolds numbers in a given pipe (i.e. F has the value 0.8 at $\theta_{0.8}$, and the value 0.2 at $\theta_{0.2}$). It will be seen that Bosworth's formula predicts (at least under the condition chosen for the comparison) a much greater degree of longitudinal mixing than is actually observed, and also that it fails to predict the marked effect of velocity of flow on the F-diagram for a given pipe.

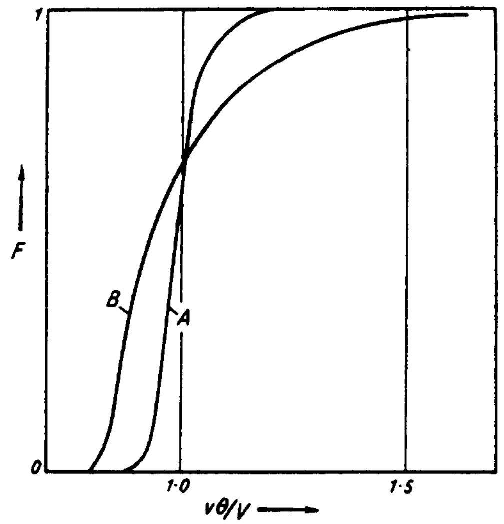

Fig. 12. Experimental (A) and calculated (B) F-diagrams. Water in circular tube, $Re = 6940$, $R/L = 6.3 \times 10^{-4}$.

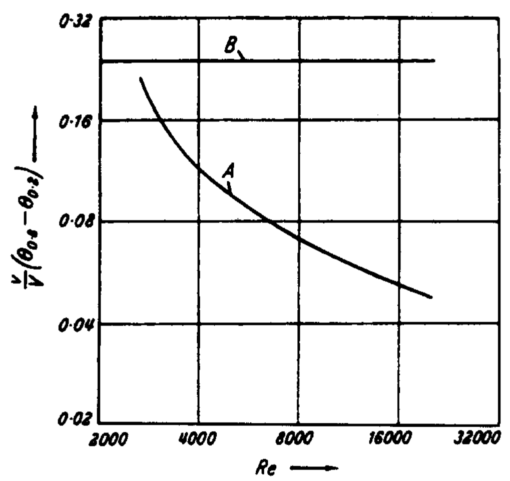

Fig. 13. Experimental (A) and calculated (B) values of $(v/V)(\theta_{0.8} - \theta_{0.2})$. $R/L = 6.3 \times 10^{-4}$.

REACTORS

The performance of a steady-flow reactor can be calculated from the F-diagram provided the reaction is first-order, or pseudo-first-order, with a velocity-constant which does not vary from place to place in the reactor. For instance, if an effluent containing a radioactive element is allowed to flow through a reservoir, the concentration of the element at the exit can be calculated if its radioactive decay-constant k and the F-diagram of the system are known.

Consider those elements of fluid which have ages between θ and $(\theta + d\theta)$ at the exit. A fraction $(1 - e^{-k\theta})$ of the reactant originally contained in these elements will have reacted during its passage through the vessel. Hence the total fraction $(1 - f)$ of reactant which reacts during its passage through the vessel is

$$1 - f = \int_0^\infty (1 - e^{-k\theta}) E(\theta)\,\mathrm{d}\theta. \tag{27}$$

From eq. (3)

$$E(\theta)\,\mathrm{d}\theta = \mathrm{d}F(\theta). \tag{28}$$

Hence,

$$\begin{aligned} 1 - f &= \int_{\theta=0}^\infty (1 - e^{-k\theta})\,\mathrm{d}F(\theta) \\ &= 1 - \int_{\theta=0}^\infty e^{-k\theta}\,\mathrm{d}F(\theta). \end{aligned} \tag{29}$$

f can be evaluated by graphical integration if the F-diagram is available.

In the special case, previously discussed, of a tubular packed vessel, the expression for F given in eq. (19) is unsuitable for use in eq. (29) because of the approximations which have been made. Instead we set up the differential equation for a tubular reactor with longitudinal diffusion as well as flow (changes in volume are assumed not to occur, so that the mean longitudinal velocity, u, is the same at all cross-sections). The equation is easily shown, by making a balance on a section of differential length $\mathrm{d}y$, to be

$$\frac{\mathrm{d}^2 c}{\mathrm{d}y^2} - \frac{u}{D}\frac{\mathrm{d}c}{\mathrm{d}y} - \frac{kc}{D} = 0 \tag{30}$$

where c is the concentration of reactant at cross-section y. The concentration of reactant in the entering stream is c^*; owing to diffusion the concentration just within the entrance of the reactor, at $y = 0$, is less than c^*. The following boundary condition expresses the fact that the rate at which reactant is fed to the reactor is equal to the rate at which it crosses plane $y = 0$ by combined flow and diffusion.

$$uc^* = uc - D\,\mathrm{d}c/\mathrm{d}y, \quad y = 0. \tag{31}$$

At the outlet ($y = L$)

$$ufc^* = uc - D\,\mathrm{d}c/\mathrm{d}y, \quad y = L$$

fc^* being the concentration of the exit stream. Now if $\mathrm{d}c/\mathrm{d}y$ were negative, the concentration in the exit stream would be greater than that at the end of the packing. If $\mathrm{d}c/\mathrm{d}y$ were positive the concentration would pass through a minimum somewhere in the reactor and then rise towards the downstream end. Intuition suggests that neither of these situations can arise, so that the boundary condition must be

$$\frac{\mathrm{d}c}{\mathrm{d}y} = 0, \quad y = L. \tag{32}$$

The solution to eq. (30) with these two boundary conditions is

$$\frac{c}{c^*} = \exp\left(\frac{uy}{2D}\right) \times \left[\frac{2(1 + a)\exp(ua/2D)(L - y) - 2(1 - a)\exp(ua/2D)(y - L)}{(1 + a)^2 \exp(uaL/2D) - (1 - a)^2 \exp(-uaL/2D)}\right] \tag{33}$$

where

$$a = \sqrt{1 + 4kD/u^2}.$$

The value of $(1 - c/c^*)$ at the exit ($y = L$) is equal to $(1 - f)$, the fraction reacted. Hence

$$1 - f = 1 - \frac{4a}{(1 + a)^2 \exp(-uL/2D)(1 - a) - (1 - a)^2 \exp(-uL/2D)(1 + a)}. \tag{34}$$

As $D \to 0$ this expression tends to

$$1 - f = 1 - \exp\frac{-kL}{u} \tag{35}$$

which is the well-known solution for "piston-flow". As $D \to \infty$, we find

$$1 - f = \frac{kL}{u + kL} \tag{36}$$

which is the solution for complete mixing. For very small values of D

$$1 - f \approx 1 - (1 + k^2 DL/u^3)\exp\frac{-kL}{u}. \tag{37}$$

From this it can be seen that the effect of diffusion is to decrease the fractional conversion compared to that for piston-flow, but that the effect will be negligible provided $k^2 DL/u^3 \ll 1$, or $[\ln f]^2 D/Lu \ll 1$. Thus for specified operating conditions it is possible to decide, if an approximate value of D is available, whether neglect of longitudinal diffusion will lead to serious error in calculating the output of the reactor.

The foregoing treatment of reactors will seldom be applicable to practical problems except as a rough guide. In the first place, the heat of reaction often gives rise to temperature-gradients, and hence point-to-point variations in the value of the reaction-velocity constant, so that the chance of a molecule reacting depends on its path through the reactor, as well as its residence-time. Secondly, if the reaction is of order other than first, the chance of a given molecule reacting depends on the molecules which it encounters in its passage through the reactor; the nature of these encounters is largely determined by diffusional processes caused by point-to-point variations in composition in the fluid, which cannot be deduced from the F-diagram. Second-order reactions between imperfectly mixed fluids have been considered by the author [5]. Denbigh [6] has considered second-order reactions taking place in a fluid in laminar flow in a pipe, under conditions such that molecular diffusion may be ignored.

BLENDERS

A continuous-flow blender is a mixing vessel into which flows a stream of material of continuously varying composition. In the vessel, elements of material which have entered at different times are mixed, so that the outflowing stream shows less variation in composition than the input. The case of a perfectly mixed blender has been considered in detail elsewhere [4], with special reference to the flow of town gas through a gas-holder, and consequent smoothing-out of fluctuations in the calorific value. Beaudry [1] has considered the special case of a perfectly mixed blender with a feed consisting of batches of material of finite volume. A blender which displays segregation will be less effective in reducing fluctuations than one in which perfect mixing occurs.

Suppose the concentration of some component in the entering stream has a concentration c_i which fluctuates with time. Its value at any time is $(\bar{c} + \delta_i)$, where $\bar{c}$ is the mean value of c_i which is assumed to show no trend. A convenient measure of magnitude of the fluctuations in c_i is its standard deviation σ_i:

$$\sigma_i^2 = \overline{\delta_i^2}. \tag{38}$$

σ_i is assumed to show no trend. The concentration $c_0 = (\bar{c} + \delta_c)$ of the outgoing stream has a standard deviation σ_0. The problem is to find the ratio σ_0/σ_i. The rates of inflow and outflow are assumed constant and equal to v. The concentration $c_0(t)$ in the outflow at time t is then given by

$$c_0(t) = \int_{\theta=0}^{\infty} c_i\{t-\theta\}\, E(\theta)\,\mathrm{d}\theta \tag{39}$$

where $c_i\{t-\theta\}$ is the concentration in the inflow at time $(t-\theta)$. Hence

$$\delta_0(t) = \int_{\theta=0}^{\infty} \delta_i\{t-\theta\}\, E(\theta)\,\mathrm{d}\theta \tag{40}$$

and

$$[\delta_0(t)]^2 = \left[\int_{\theta=0}^{\infty} \delta_i\{t-\theta\}\, E(\theta)\,\mathrm{d}\theta\right]^2. \tag{41}$$

However, it is generally true that

$$\left[\int_0^{\infty} f(y)\,\mathrm{d}y\right]^2 = 2\int_{y=0}^{\infty}\int_{r=0}^{\infty} f(y)f(y+r)\,\mathrm{d}y\,\mathrm{d}r \tag{42}$$

where $f(y)$ is any function of y. Applying this to eq. (42),

$$[\delta_0(t)]^2 = 2\int_{y=0}^{\infty}\int_{r=0}^{\infty} \delta_i\{t-\theta\} \times \delta_i(t-\theta-r)E(\theta)E(\theta+r)\,\mathrm{d}\theta\,\mathrm{d}r. \tag{43}$$

Averaging this with respect to t,

$$\sigma_i^2 = \overline{\delta_0^2} = 2\iint \overline{\delta_i\{t-\theta\}\,\delta_i(t-\theta-r)} \times E(\theta)E(\theta+r)\,\mathrm{d}\theta\,\mathrm{d}r. \tag{44}$$

Now the quantity

$$R(r) = \frac{\overline{\delta_i\{t'\}\,\delta_i(t'-r)}}{\sigma_i^2} \tag{45}$$

(the numerator being averaged with respect to t') is known as the autocorrelation coefficient or serial correlation coefficient of c_i for a time-interval r. Substituting eq. (45) in eq. (44) we have

$$\sigma_0^2/\sigma_i^2 = 2\int_{\theta=0}^{\infty}\int_{r=0}^{\infty} R(r)E(\theta)E(\theta+r)\,\mathrm{d}\theta\,\mathrm{d}r. \tag{46}$$

$R(r)$ may be found as a function of r from a representative record of c_i vs t in various ways which have been discussed elsewhere [4]. [The relationship between $R(r)$ and r indicates whether the fluctuations in c_i are on the whole rapid or slow, and whether they display any regular periodicity.] Assuming that $R(r)$ is known for a sufficient range of values of r, in order to evaluate the integral into eq. (46) it is necessary to know $E(\theta)$ as a function of θ. The necessary information is contained in the F-diagram of the system, and the following is perhaps the simplest way of doing the calculation. First fit some simple function of θ (such as a power-series) to the F-diagram up to a value θ_1, at which $F(\theta_1)$ is very close to 1. Differentiate this function with respect to θ. From eq. (3) we see that

$$\frac{\mathrm{d}F(\theta)}{\mathrm{d}\theta} = E(\theta) \tag{47}$$

so that $E(\theta)$ is now a known function of θ. For a given value of θ, $E(\theta + r)$ is the value obtained by replacing θ by $(\theta + r)$. It will now be possible to evaluate the integral

$$I(r) = \int_{\theta=0}^{\theta_1} E(\theta)E(\theta+r)\,\mathrm{d}\theta \approx \int_0^{\infty} E(\theta)E(\theta+r)\,\mathrm{d}\theta \tag{48}$$

algebraically for a number of values of r. The integral

$$\sigma_0^2/\sigma_i^2 = 2\int_{r=0}^{\infty} R(r)I(r)\,\mathrm{d}r \tag{49}$$

can now be evaluated graphically. (In practice, of course, the upper limit will be taken at some value of r for which the integrand has become vanishingly small.)

THE USE OF MODELS FOR PREDICTING F-DIAGRAMS

Under certain circumstances the F-diagram of a large system can be predicted with confidence from that for a model. The conditions to be fulfilled are: (a) The model must be geometrically similar to the system. (b) The Reynolds number must be the same in the model and the system. (c) Gravity-waves, density-differences, surface tension, and other influences apart from inertia and viscosity, must be unimportant in determining the behaviour of the fluid in both model and system.

In the simple case of a fluid flowing through a tank or a fixed bed of solids, the same fluid being used in the model as in the system, equality of the Reynolds numbers requires that

$$\frac{v_1}{v_2} = \frac{L_1}{L_2} \tag{50}$$

where v_1, v_2 are the volumetric flow-rates and L_1, L_2 the linear dimensions of the model and system, respectively. That is, in a 1/10 scale model the volumetric flow-rate must be 1/10 that in the full-scale system. If the system incorporates a rotating stirrer, the angular velocities, ω, of the stirrers in model and system are related by

$$\frac{\omega_1}{\omega_2} = \left(\frac{L_2}{L_1}\right)^2. \tag{51}$$

In the 1/10 scale model the stirrer must rotate 100 times as fast as in the system.

If these conditions are fulfilled the flow-patterns of the fluid will be geometrically similar in model and system, hence both will have the same F-diagram.

The simple type of model experiment described here cannot be applied to systems in which the fluid is of non-uniform density or viscosity owing to variations in temperature or composition from point to point, or to fluidised beds.

NOTATION

A	area under curve
c	concentration
c^*	concentration of stream entering reactor
$C(\theta)$	concentration at exit of vessel at time θ
D	apparent diffusivity
D_m	molecular diffusivity
erf(z)	$\left(\frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}\,\mathrm{d}y\right)$
$E(\theta)$	distribution-function for residence-times θ
f	fraction of reactant unreacted
$F(\theta)$	fraction of material in outflow which has been in system for a time less than θ
H	hold-back [eq. (14)]
$I(\theta)$	distribution-function for "ages", θ, of material in system
k	first-order reaction-velocity constant
L	length of tube or reactor
n	parameter in eq. (26)
Q	quantity of tracer material injected
r	radial distance from tube-axis; or time-interval
R	radius of pipe
$R(r)$	serial correlation-coefficient of c_i for time-interval r
Re	Reynolds number
S	segregation (Figs 4, 5, and 6)
t	time
u	velocity of flow
$\bar{u}$	mean velocity of flow in open pipe
v	volumetric flow-rate
V	volume of vessel
x	distance referred to coordinates moving with velocity u
y	distance referred to stationary coordinates
z	defined by eq. (20)

Greek letters

α	parameter in eq. (26)
β	parameter in eq. (26)
δ_i, δ_0	instantaneous deviations of c_i, c_0 from $\bar{c}$
θ	time interval, residence-time or "age"
σ_i, σ_0	standard deviations of c_i, c_0 from $\bar{c}$
ω	angular velocity

REFERENCES

[1] Beaudry, J. P., 1948, *Chem. Engng* **55**, 112.
[2] Bosworth, R. C. L., 1948, *Phil. Mag.* **39**, 847.
[3] Bosworth, R. C. L., 1949, *Phil. Mag.* **40**, 314.
[4] Danckwerts, P. V. and Sellers, E. S., 1951, *Ind. Chemist* **27**, 395; 1952, *Coke and Gas* **14**, 247.
[5] Danckwerts, P. V., 1952, *Appl. Sci. Res. A* **3**, 279.
[6] Denbigh, K. G., 1951, *J. Appl. Chem.* **1**, 227.
[7] Fowler, F. C. and Brown, G. G., 1943, *Trans. Amer. Inst. Chem. Engng* **39**, 491.
[8] Gilliland, E. R. and Mason, E. A., 1949, *Ind. Engng Chem.* **41**, 1191.
[9] Gilliland, E. R. and Mason, E. A., 1952, *Ind. Engng Chem.* **44**, 218.
[10] Kennard, E. H., 1938, *Kinetic Theory of Gases*, p. 268, McGraw-Hill, New York.
[11] Hull, D. E. and Kent, J. W., 1952, *Ind. Engng Chem.* **44**, 2745.
[12] Hull, D. E., Kent, J. W. and Lee, R. D., 1949, *World Oil* **129**, 188.
[13] Smith, S. S. and Schulze, R. K., 1948, *Petroleum Engng.* **19**, 94; 1948, **20**, 330.
[14] Lapidus, L. and Amundson, N. R., 1952, *J. phys. Chem.* **56**, 984.
[15] Bernard, R. A. and Wilhelm, R. H., 1950, *Chem. Engng. Prog.* **46**, 233.
[16] Arthur, J. R., Linett, J. W., Raynor, E. J. and Sington, E. P. C., 1950, *Trans. Faraday Soc.* **46**, 270.
[17] Morales, M., Spinn, C. W. and Smith, J. M., 1951, *Ind. Engng. Chem.* **43**, 225.

NOTE ADDED IN PROOF

Flow in pipelines—Hull and Kent [11] have recently published an account of experiments on petroleum flowing in a 182-mile long 10-inch diameter pipe line. A radioactive tracer was used to obtain (in effect) C-diagrams for various lengths of pipe. With a Reynolds number of 20,000–30,000 the diagrams obtained were close to those which would be expected if the "diffusion" equation (15) were followed, D having a value of 1.3 ft^2/s. Further experimental work on mixing in pipe-lines is referred to by the authors [12, 13].

Flow in packed beds—Lapidus and Amundson [14] have analysed the consequences of longitudinal mixing in adsorption columns. Bernhard and Wilhelm [15] have measured the apparent *radial* diffusivity in fluids flowing through beds of solids. It seems likely that the longitudinal diffusivity D [eq. (15)] will have a different value. Arthur *et al.* [16] and Morales *et al.* [17] have shown that the fluid velocity differs markedly from the mean in the neighbourhood of the wall of the column.