A Method of Measuring the Velocity of Very Rapid Chemical Reactions.

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CONTENTS.

§1.—*General Principles and the Two Essential Conditions.*

In devising methods for determining the velocity of any chemical reaction there are two experimental problems which invariably arise: (1) To arrange that the chemical system under investigation be made initially unstable in a period of time that is negligibly short in comparison with that taken by the chemical reaction. (2) To record from time to time the stages reached by the system (during its passage from the initial unstable state to the final stable condition wherein the several reacting substances are in chemical equilibrium) by means of methods which take a negligibly short time in comparison with that taken by the chemical reaction.

A perusal of the literature shows that previous investigators have, in the main, restricted themselves to the study of slow reactions, such as may require many minutes or even hours to reach completion. In such cases, both requirements which we have mentioned can be easily met. For the production of the initially unstable condition can be achieved without difficulty by merely mixing the several reacting substances together in proportions far removed from those which prevail when equilibrium has been attained. The time required by the mixing operation can be reduced to a few seconds, and can therefore be neglected when dealing with a process which may last many minutes or even hours. The slow reactions possess a further attraction, in that the procedure for estimating the concentrations of the several reactants at different stages during the progress of the reaction need not be a hurried

one. This permits the use of a wide variety of methods, *e.g.*, polarimetry as in the study of the inversion of sucrose, ordinary titration as in the saponification of esters, and separation of one of the constituents as a gas phase as in the decomposition of diazo-acetic ester by water, *i.e.*, $N_2.CHCOOC_2H_5+H_2O \longrightarrow OHCH_2.COOC_2H_5+N_2$ (gas phase).

The dynamical study of slow reactions has thrown so much light upon the general mechanism of chemical reactions that the value of a method for measuring the velocity of rapid reactions can hardly be questioned. But in the case of reactions so rapid that equilibrium is reached within a second or less, such methods as those just mentioned break down completely, and it is necessary to search for new modes of attack.

In a previous paper (1) we have described measurements of the rate at which carbon monoxide displaces oxygen from combination with the blood pigment, hæmoglobin. In several of the experiments reported by us, the chemical process was a very rapid one reaching completion within a space of two seconds. The " initial unstable " condition was obtained by use of the fact that the reaction in question is photochemically reversible. Therefore when the system was illuminated by a powerful beam of light, the concentrations of the reactants adjusted themselves to the new values. A subsequent interruption of the beam of light, which could be performed instantaneously, caused the concentration of the reactants to return to their previous " dark " values. We had thus obtained in the case of this very rapid reaction a solution to the first of the two problems, which, as mentioned in the introduction, invariably arises in connection with the velocity measurements of chemical reactions.

Two separate methods were used for ascertaining the time taken by the system to reach various stages during its return to equilibrium. It is of importance to refer to one only of these two methods here. The solution of hæmoglobin under investigation passed through a vertical tube, in which it was exposed to a strong beam of light (which displaced the system from its dark equilibrium) and then flowed down a horizontal tube which was kept in darkness. Directly the solution had left the light tube, the system of reactants began to return to their position of dark equilibrium, and various cross-sections of the dark tube were examined by the reversion spectroscope (2), the readings of which gave the ratio of the respective concentrations of the two hæmoglobin compounds in this system. From this ratio the value of the concentrations of all the constituents at the cross-section under examination could be calculated. By this arrangement the solution was examined

at a certain instant of time after the return to the dark equilibrium had begun, and yet observation by the spectroscope could be continued for as long a time as might be required. It is clear, therefore, that we had also obtained a solution to the second of the two problems which, as mentioned in the introduction, invariably arises in connection with the velocity measurements of chemical reactions. It was also clear that this method of analysis is applicable to a large number of cases so that the second problem may be considered to be solved for other reactions beside the one we had investigated. Thus provided, we could always arrange that the solution, which contained the reacting system to be investigated, should enter the observation tube in an unstable condition (*i.e.*, with the concentrations of the reacting constituents far removed from values which would give chemical equilibrium) then we had only to devise some optical or other physical method of ascertaining the chemical composition of the moving fluid at different cross-sections of the observation tube.

Unfortunately, the solution which we had obtained to the first problem is only applicable to a few cases, because the photo-chemical device for producing an initially unstable condition is not capable of general application. Very few chemical reactions are photo-chemically reversible, and even in such cases it is also desirable to find some alternative method, for, as Dr. Rideal has pointed out to us, it is not legitimate to assume without proof, that the effects of the light upon the system disappear at the instant at which the light beam is interrupted. Instead, we have sought to devise a mechanical process of mixing together two solutions which must be so rapid, and yet so efficient in action, that complete mixture would be obtained before any appreciable degree of chemical action could have taken place. Granted this ideal had been attained, it would be simple to arrive at an initial unstable system by suitable adjustment of the composition and temperature of the two solutions before mixture.

The basic conditions of an apparatus for measuring the velocity of rapid chemical reactions in the liquid phase are therefore :—

(1) In order that problem (1) above should be disposed of, it is necessary that the thorough mixture of the two solutions should be completed in a time short in comparison with that taken by the chemical reaction.

(2) In order that problem (2) above should be disposed of, it is necessary that all parts of the fluid should travel with uniform velocity down the observation tube. There should also, as mentioned above, be a suitable method of measurement, and the concentrations should be those which are found to give the optimum accuracy.

Now the two parts of condition 1 are mutually antagonistic, since for mixing to be perfect it must also be very prolonged. But in spite of this difficulty, an apparatus has been constructed which fulfils both these conditions with a closeness sufficient for all practical purposes to which it has so far been applied, and at the same time it complies with the requirements of condition (2).

§ 2. *A Description of the Apparatus.*

(*a*) *The principle of the method.*—The principle of the method consists in causing the fluids to be mixed to come together at a high velocity within a restricted space. The high velocity of flow was obtained by forcing the fluids through jets under considerable pressure. The streams of fluid having met one another mixed very rapidly and completely, thus fulfilling condition 1 above. They then passed down the observation tube, the diameter of this tube and the rate of flow being suitable for the fulfilment of condition 2 above.

Several types of mixing chamber were tested, *see* fig. 1. (α) Y-shaped, the two jets connecting with the upper limbs the observation tube with the lower (β) like the glass worker's blow pipe jets, (γ) a circular chamber with the jets entering at the side and pointing at one another, (δ) a circular chamber with the jets entering tangentially so that vortex motion should be produced. (ϵ) similar to (γ) or (δ), but with a very high speed electrically driven stirrer

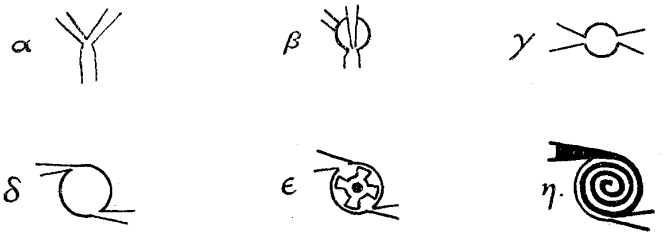

FIG. 1.

inside the mixing chamber. Of these, all except (ϵ) were tested, the first two being found inferior to (γ) and (δ). These latter were given extended tests by methods which will be described in detail in the next section of this paper. It was found that while there was little difference to be found at high pressures, and therefore high rates of flow, at low pressures, and therefore low rates, the tangential type (δ) gave the more perfect mixing as shown in the table below :—

	Type γ Per cent.	Type δ Per cent.
Jet velocity 100 cms. per second	6·0*	1·0*
„ „ 400 „ „	2·0*	1·0*

This superiority of method (δ) is probably due to the vortex motion which is set up. This causes the angular velocity of the fluid near the centre of the chamber (where it passes out into the observation tube) to be greater than it is near the periphery. This difference in angular velocity causes shear to occur between the spiral rings produced by the two liquids, thus producing mixing at their interfaces. (*See* fig. 1, γ.)

The reason for the difference in the efficiency of γ and δ being less at high speeds than at low is probably due to the violence of the eddies set up in type γ at high speeds, which would not occur to the same extent at low ones.

(*b*) *The dimensions of the apparatus.*—The dimensions of two successful types of apparatus are shown in the table below :—

Apparatus number	I	II
Jets, number of	6	4
Jets, diameter in mm.	2·6	2·5
Mixing chamber, diameter in mm.	7·9	12·4
Mixing chamber, depth in mm.	2·6	3·1
Mixing chamber, diameter of outlet in mm.	4·2	6·0
Observation tube, diameter in mm.	6·28	12·8
Observation tube, length in mm.	300	300
Volume of liquid in c.c. passed through apparatus at 600 mm. of Hg pressure	7500	7000
Linear velocity of flow in mm. per second down observation tube at 600 mm. Hg pressure	4000	900
Minimum linear velocity for turbulent flow in mm. per sec.	400	170

The plan of apparatus number (II) is shown in fig. 2 below.

The apparatus enables two fluids to be mixed and observations to be made on the mixed fluid after it has travelled distances ranging from a mean length of 1 cm. to a mean length of 30 cms. from the mixing chamber. Thus supposing the rate of flow down the observation tube to be 100 cms. per second, then the first observation can be made in one-hundredth of a second after the reaction

* These values show the approximate amount of fluid which remains unmixed after passing through the mixing chamber. The method of obtaining these values will be described later.

has commenced, and the reaction can be observed for a total time of one-third of a second. Given a suitable physical method of measuring the concentrations of the constituents at any cross-section of the tube, one can ascertain the stage reached by the reaction after any interval of time between one-hundredth and one-third of a second.

If the linear rate of flow is faster or slower than this, the time between the first possible and last possible reading will be correspondingly altered. Thus the apparatus can be suited to reactions of different velocity by altering the rate of flow.

(*c*) *The method of applying pressure to the fluids.*—The methods available

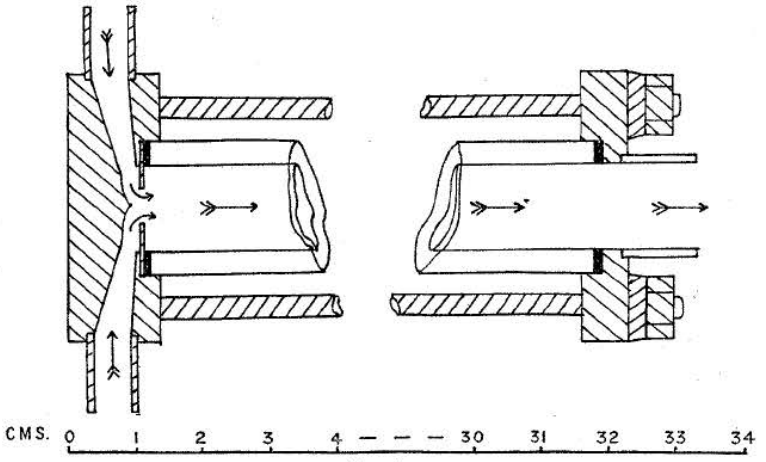

FIG. 2.

would appear to be three in number, (1) hydrostatic head, (2) by a compressed gas, (3) mechanically, *e.g.*, by rotary pumps.

(1) The hydrostatic head is limited in its use to liquids such as aqueous solutions. We have found it very convenient for pressures between 2 cms. and about 2 metres head of fluid. The two fluids under investigation are put into two receptacles and are allowed to flow viâ suitable connections to the apparatus. Since it is the difference in level of the fluids on the entrance and exit side which produces the pressure head, Marriotte's bottles and a constant level overflow should be used wherever possible.

(2) The compressed gas method is applicable to both liquids and gases. In the case of liquids which have been placed in receptacles (*e.g.*, Marriotte's bottles as described), it is only necessary to connect tubes passing through

bungs closing the necks of the bottles to a cylinder of compressed nitrogen or air fitted with an automatic regulator (such as Beards or the universal) and a mercury pressure gauge. We have found this method very satisfactory. When really high pressures are required this also appears to be the simplest method of obtaining them. The containers connecting tubing, etc., should in this case be of suitable design to stand the required pressure with safety.

(3) The mechanical method has advantages where pressures are required which are higher than those which Marriotte's or other bottles will stand since it avoids the cost of supplying special containers. We have used two of the gear wheel type rotary pumps driven by an electric motor with satisfactory results.

(*d*) *The methods of measurement available.*—We have already pointed out in the introduction that in order to measure the velocity of any given chemical reaction the two sets of measurements that are required are (1) the time during which the reaction has been allowed to proceed, (2) the quantitative analysis of the constituents taking part in the reaction at the end of that time. In the apparatus described above the reaction commences immediately the two reagents, entering the mixing chamber by their respective jets, have been brought into intimate contact. The reaction proceeds during the time that the reagents flow down the observation tube. The quantitative analysis at different cross-sections of the observation tube must, therefore, be obtained by methods that are applicable to a moving fluid. Such for example are optical methods involving measurements of (*a*) opacity, (*b*) colour, (*c*) absorption in definite spectral regions, (*d*) mean wave-length or boundary wave-length of absorption bands, (*e*) rotation of plane of polarisation, (*f*) refractive index. But other methods may sometimes be available, such as measurements of temperature, *e.g.*, by thermocouples, or specific inductive capacity or electrical conductivity. The other set of measurements, namely the lengths of time during which the reaction has proceeded, are equal to the intervals which elapse between the instant at which mixture occurs, and the instant at which the fluid reaches the respective cross-sections where determinations had been made. These intervals are readily ascertained from a knowledge of (1) the distance between the cross-sections just mentioned and the mixing-chamber, and of (2) the linear rate of flow. The latter is obviously the quotient of the volume of fluid passing through the apparatus in unit time divided by the area of the cross-section of the observation tube.

§ 3. *Tests of Obedience to Condition I.*

(*a*) *The efficiency of mixing of the fluid leaving the mixing chamber.*—Information on this point was obtained by the following method. Two solutions were prepared :—Solution 1 consisted of N/100 NaOH, to which 0·1 per cent. phenolphthalein was added, and was therefore deeply coloured, whilst Solution 2 consisted of colourless N/100 HCl. These were placed in bottles 1 and 2 respectively, and the bottles connected with the apparatus, a pressure of 400 mm. Hg being applied to the liquids in the usual manner. With both taps full on, a crimson tinted fluid was seen to pass down the observation tube of the apparatus, but on collecting some of the fluid and allowing it to stand the colour was slowly discharged. By keeping the tap from bottle 2 full open, and slowly turning off the alkaline fluid from bottle 1, the pink tint gradually disappeared from the solution until there was only a trace left at the outlet of the mixing chamber. A quantity of the colourless fluid leaving the apparatus was now collected and its P_H,* after thorough mixture, was found by suitable indicators to be 5·6.

The factors which may be responsible for the above phenomenon would appear to be three in number, namely :—

(i) The time taken for chance irregularities in the fluid to disappear by diffusion, convection and stirring.

(ii) The time taken for acid to neutralise base.

(iii) The time taken for the phenolphthalein to tautomerise to the colourless modification which the substance assumes at $P_H < 8$.

We shall postpone the detailed explanation and discussion of the relative importance of these three factors till later in the present section. Our object at the moment is to ascertain the efficiency of the mixing and we shall start with the unfavourable assumption that factors (ii) and (iii) can be neglected, and that factor (i), *i.e.*, imperfect mixing, is entirely responsible for the fact that the final P_H of the thoroughly mixed fluid must be made equal to 5·6 in order that no trace of pink should be visible beyond the outlet of the mixing chamber.

For purposes of calculation it is necessary to make some assumption as to the amount of the coloured variety of phenolphthalein which is seen issuing with the fluid from the orifice of the mixing chamber. The probability is that the amount is small, since the eye will detect quite small amounts of residual colour, because the solution in the rest of the observation tube is

* P_H of x denotes hydrogen ion concentration of 10^{-x} gramme ions per litre.

colourless. The amount is probably well under 1 per cent. Since, however, it is the maximum possible imperfection in mixing that is to be calculated, it is better to assume that the amount is larger than it actually is. The value that we have taken for this purpose therefore is 1 per cent.

Now phenolphthalein commences to turn colour as the P_H is raised beyond about 8, and continues to increase in colour until its full tint is attained at about P_H 9·6. Of the fluid which issues from the mixing chamber, a part will lie on the acid side of P_H 8 and the phenolphthalein associated with it will remain uncoloured, a part also will lie on the alkaline side of P_H 9·6 and the phenolphthalein associated with it will be completely coloured, while the part between P_H 8 and 9·6 will have with it partially coloured phenolphthalein. Now the coloured molecules which we have assumed above to be present to the extent of 1 per cent. are composed of both the two latter. We prefer, however, to make a further unfavourable assumption that they are due entirely to parts of the liquid which exceed P_H 9·6.

With these assumptions we can now proceed to form an estimate of the maximum extent to which the fluid is imperfectly mixed.

It is necessary first to ascertain the hydrogen ion concentration of the fluid obtained by mixing varying proportions of N/100 HCl and N/100 NaOH. This can be obtained by a quite simple calculation, and the results for temperature = 15° C. are given in the following table :—

Table I.

P_H.	Percentage. N/100 HCl	Percentage. N/100 NaOH
4	50·50	49·50
4·4	50·20	49·80
4·8	50·08	49·92
5·2	50·03	49·97
5·6	50·012	49·988
9·2	49·988	50·012
9·6	49·97	50·03

The use of the table may be readily explained as follows :—When 50·012 parts of N/100 HCl are mixed with 49·988 parts of N/100 NaOH, reference to the table shows that a fluid of P_H 5·6 is formed. Thus, in the experiment in which the final mixed fluid was at P_H 5·6, the rate of delivery of bottle 2 must have been 50·012/49·988 times greater than the delivery of bottle 1. According to our assumption, 1 per cent. of the fluid in this experiment had a $P_H = 9·6$. Now a P_H of 9·6 corresponds, as will be seen from the table, to

a mixture of 49·97 parts of N/100 HCl with 50·03 parts of N/100 NaOH, and if we define portions of the fluid of P_H 5·6 as constituting a mixture of 100 per cent. efficiency, then the degree of mixture of portions of fluid of P_H 9·6 must be equal to $100 \times \frac{49 \cdot 97}{50 \cdot 03} \div \frac{50 \cdot 013}{49 \cdot 988}$ per cent. = 99·8 per cent. efficiency. Thus 1 per cent. of the fluid just after leaving the mixing chamber will be mixed to the extent of 99·8 per cent. and under, the alkali predominating over the acid, and by symmetry a second 1 per cent. of the fluid will be mixed to the extent of 99·8 per cent. and under, the acid in this portion predominating over the base.

The remaining 98 per cent. of the fluid will be mixed to an extent which exceeds 99·8 per cent. of perfect efficiency. To calculate the average efficiency of mixing for the whole fluid would necessitate a knowledge of the manner in which the 98 per cent. of the fluid is distributed between the efficiencies of 100 per cent. (upper limit) and 99·8 per cent. (lower limit), and the remaining 2 per cent. of the fluid between the efficiencies of 99·8 and 0 per cent. With an assumption which, like the previous ones in this treatment, is almost certainly less favourable than the actual circumstances warrant, the average efficiency of mixture was found to be 99 per cent. Thus there is $\frac{1}{2}$ per cent. unmixed alkali and $\frac{1}{2}$ per cent. unmixed acid.

This value just given is for the fast rate of flow, *i.e.* of 400 cms. per second. With a slow rate of flow, *i.e.* of 100 cms. per second, a slightly less beneficial result was obtained, experiment showed that the final P_H of the mixture of acid and alkali in which only the minimum trace of pink was discernable was 4 (instead of 5·6) for the fast rate, and if this be made the basis of the calculations, the result finally obtained is that the efficiency of mixture is 98 per cent. (*i.e.* 1 per cent. unmixed acid and 1 per cent. unmixed base).

In both cases this approach to perfection would be amply close enough in all cases where the method of measuring the composition of the fluid, as it passes down the observation tube, is only accurate to 2 per cent. or over. Such was the case in the investigation in which we were engaged. Where a more exact method of analysis was available, we should attempt to define between closer limits the composition of the fluid leaving the mixing chamber. The true value for the average efficiency of mixture lies somewhere between 100 per cent. and the figure given above, *i.e.* 99 per cent., the latter being a minimum value on account of the fact that none of the assumptions made use of in obtaining it could possibly have produced too high a value, whereas one at least of the assumptions tended definitely to produce too low a result. For

the purposes of the treatment just given, it was justifiable and indeed desirable to neglect any possible delay which might be caused either by the neutralisation of acid with base or by tautomerisation of the phenolphthalein. We feel, however, that a short discussion of these processes is now desirable. Physical chemists generally assume that ionic reactions, such as the neutralisation of acids by bases, are extremely rapid, and in a later paper we shall advance experimental evidence in favour of this view. The change of colour of indicators is, however, in many cases so slow that it can be measured by the usual methods. for example, in the case of certain indicators Hantzsch found that intervals of half an hour and upwards were required.

In the present instance, information as to the speed of these processes could be readily gained by varying the strength of the acid and alkali employed. Thus in one experiment the one-hundredth normal solutions were replaced by one-tenth normal solutions. If, in the previous test, mixing were really perfect, and the necessity of lowering the P_H of the mixed fluid to 5·6 in order to reduce the pink tint to the merest trace, arose from the slowness of neutralisation and tautomerisation, then it should follow that, in order to secure the same result with N/10 solutions instead of N/100 solutions, the P_H of the final fluid would again have to be 5·6. If, on the other hand, the neutralisation and tautomerisation changes were "infinitely" fast and the mixing imperfect, to the extent indicated by the previous calculations, then it can be shown that with N/10 solutions instead of N/100 solutions the P_H for the minimum trace of pink should be 4·6. If, finally, both mixture and neutralisation and tautomerisation are not quite completed in the mixing chamber, then the P_H required for the minimum trace of pink would lie between 4·6 and 5·6. The actual experiment with the fast rate of flow showed that the P_H required was about 5·6, from which we infer that it is tautomerisation rather than mixture which is not quite perfected in the mixing chamber in the course of these experiments. With the slow rate of flow, on the other hand, similar considerations show that it is mixture rather than tautomerisation which is not quite perfected.

When the taps from both bottles were turned full on, it was found, as mentioned above, that the pink tint of the mixed fluid persisted for some time. The P_H of the final fluid was, however, in this case about 7·4, *i.e.* quite near to the point P_H 8 at which coloured phenolphthalein begins to be formed in appreciable quantities if allowed an infinite time. We believe that the speed of tautomerisation of phenolphthalein is slow when the P_H is nearly equal to 8 but increases very rapidly as the P_H of the solution is reduced below 8, and that when P_H of 5·6 or lower is reached the reaction can proceed extremely

fast. This view can, without much difficulty, be brought into line with Hantzsch's theory of indicators.

(*b*) *The time taken for the mixing of the fluid.*—It is now necessary to ascertain whether the length of time occupied by the mixing process may interfere with the validity of the reaction velocity measurements. In the arguments which follow, it is assumed that the fluid travels with uniform rate of flow down the observation tube. The evidence for this assumption will be found in the next section.

If the fluid as it reached any one cross-section could be divided up into a very large number of parts, and if each part could be separately (and instantaneously) analysed, then a uniform value would only be obtained if the chemical reaction had started at the same instant in all such parts. There are, however, two factors which must certainly prevent this stipulation being realised. These are :—

(i) Some parts of the fluid which enter the mixing-chamber probably become completely mixed (and therefore commence to react) at once, whereas other parts may not become completely mixed until they have almost reached the orifice of the mixing-chamber.

(ii) The fluid which enters the side of the jets further from the observation tube has a longer distance to travel (and therefore a longer time in which to react) than has the fluid which enters at the near side of the jets.

The readings obtained by the measuring instrument at different cross-sections will, therefore, be only average values, and we must now inquire how closely the curve obtained by plotting against time the concentration of the components (as calculated from these average values at different cross-sections of the physical property which is made the basis of measurement) will agree with the true reaction velocity curve.

The extent of heterogeneity possessed by the fluid at any given cross-section is clearly limited by the time interval which separates the earliest and the latest instants, at which the fluid reaching this cross-section could have commenced to react. This time interval cannot exceed that taken by the fluid to travel from the back wall of the mixing-chamber to the orifice, or to travel through a length of the observation tube given by

$$L_0 = \frac{\pi R_m^2 L_m^2}{\pi R_0^2}$$

where R_m is the radius, L_m the length of the mixing chamber and R_0 the

radius of the observation tube. L_0, which may be referred to as "the equivalent length of the mixing chamber," should therefore be made as small as possible. With the small apparatus described above, the value of L_0 was found to be 4·1 mm., and for the wide apparatus 2·9 mm.

Consideration will show that the effect of heterogeneity can be safely neglected if the two extremes values, at every cross-section, of the concentration of the component under investigation differ from one another by an amount less than twice the experimental error of the method of observation. This will be the case, if throughout the whole course of the reaction

$$\frac{L_0}{v} \times \frac{dc}{dt} < \frac{2A}{100},$$

where c is the concentration of the component measured, t is time in seconds, v the linear velocity of the fluid down the observation tube in mms. per second, and A the percentage accuracy of the method of measurement. In order to apply this test, the relation between c and t should be determined experimentally for the reaction under investigation, and by reference to the curve so obtained it can readily be determined whether or not this condition is satisfied. In reactions so swift that the condition cannot be satisfied even when the fastest rates of linear flow are made use of, it is necessary to proceed to more elaborate tests.

These have been based both on experiment and on calculation. The method of experiment consists simply in making determinations of the reaction velocity with different rates of linear flow down the observation tube. With fast rates of flow, the heterogeneity of the fluid reaching different cross-sections must obviously be less than with slower rates of flow. If, however, the results obtained in the two cases agree with one another within the limits of experimental error, then it appears fair to conclude that they must also agree with the results which would be obtained if heterogeneity were entirely absent. As an example, the values shown in fig. 3 may be given.

Both circles and dots were values obtained for the same monomolecular reaction, which will be seen from the figure to be half completed in one-hundredth of a second. But whereas the circles were obtained with a rate of flow of 300 cms. per second and a heterogeneity factor corresponding approximately to that given by the above formula, the dots were obtained with a slower rate of flow of about 100 cms. per second, and a correspondingly higher heterogeneity factor, namely one about three times greater than that given by the above formula. But since the circles and dots plotted in the figure fall with approximately equal accuracy along the same straight line, the velocity measurements

are clearly not affected by the large difference in heterogeneity, or the fact that in the one case it greatly exceeds the value given by the above formula. The conclusion is that in the case of monomolecular reactions the value given by the formula can be safely exceeded by three times. For example at a rate of flow of 300 cms. per second, for which the formula gives one-hundredth of a second, as the time to be occupied by half the reaction a value that could be safely used is one-third of this, namely, one-three-hundredth part of a second. With faster rates of flow correspondingly faster reactions could be studied, and we have recently constructed an apparatus in which a rate of flow of 1000 cms. per second is readily obtainable.

The method of calculation is too complicated to describe in detail, but when applied to monomolecular reactions it agreed with experiment in showing

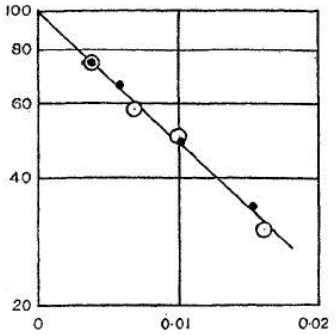

Fig. 3.—Abscissæ. Time in seconds. Ordinates. Logarithm of concentration of component measured. Numerals denote the corresponding values of

$$\frac{\text{actual concentration}}{\text{initial concentration}} \times 100.$$

that heterogeneity was entirely without importance even when the time for half-completion was as short as 1/1000 second, and the value of $L_0\, dc/dt$ ten times greater than $2x/100$. These tests are generally applicable to all classes of rapid reactions. Up to the present, however, we have only had actual occasion to apply them to monomolecular reactions.

A further cause of "heterogeneity" which does not strictly come under condition 1, but which may be conveniently mentioned in this section, arises from the fact that most methods of measurement necessitate the examination of a certain finite width of fluid in the observation tube. Thus, in the case of the spectroscope the width of fluid examined depends on the width of the beam of light which enters the slit of the instrument, and which therefore

contributes to the formation of the parts of the spectrum being used for the measurements. This type of heterogeneity can usually be kept small in comparison with the equivalent length of the mixing chamber by careful attention to detail.

§ 4. *Tests of Obedience to Condition* 2.

(*a*) *The type of flow taking place in the observation tube.*—It is well known that in the stream-line flow which takes place within a smooth cylindrical tube, when the velocity is below that given by Osborne Reynold's formula, the central core of fluid moves with much greater velocity than do the more peripheral parts of the fluid. On the other hand, in the turbulent flow which occurs above the critical velocity there is no such tendency on the part of different parts of the liquid to move with different velocities. The flow of the liquid passing down the observation tube of the apparatus described in this paper is quite different in its appearance to that seen either in streamline flow or in turbulent flow. If, for example, one fluid forced into the mixing chamber was colourless paraffin oil and the other water stained with some water soluble dye, the motion performed in the observation tube was seen to be that of a coarse spiral, the particles of the liquid moving in a direction making an angle of roughly 45 degrees with the long axis of the tube. It is clear that this spinning motion must impose considerable centrifugal force on the fluid, and an important question, therefore, arises as to whether this force is sufficient to draw liquid from the centre core towards the edges. If this were to happen it would tend to increase the velocity of the periphery and decrease that of the central core. In fact in an extreme case the central core might not move at all or might indeed tend to flow in the opposite direction to that taken by the peripheral portion. Additional emphasis was given to this view by the behaviour of small air bubbles which might happen to be in the observation tube. For on admitting the fluids under full pressure into the mixing chamber and then along the observation tube it was seen that the bubbles first left the upper part of the tube and lined up near the central core. They then travelled along in two directions, those nearer the mixing chamber than about 15 cms. moving towards the mixing chamber to take up a fixed position near its outlet, those further away than 15 cms. moving towards the exit tube of the apparatus. If, on the other hand, the fluids were admitted to the apparatus under reduced pressure, all the bubbles tended to be swept out at the exit tube. The important question to be decided was the cause of this movement of the bubbles towards the mixing chamber when the high fluid pressures (and, there-

fore, big centrifugal forces) were obtaining. Was it due to movements of the bubbles only (owing to the difference between their specific gravity and the fluid in which they lay), or was it due to movement of the core of fluid which carried the bubbles along with it ?

Three independent tests were applied in order to answer this question : (1) To cause alternately colourless and coloured fluid to pass down the observation tube, (2) to compare spectroscopic readings taken through the centre of the tube which would therefore include the core with those taken through the periphery of the tube which would not include the core, (3) to compare the spectroscopic readings obtained on one and the same reaction at slow speeds and at fast.

(1) The fluid in bottle 1 was N/100 NaOH containing 0·1 per cent. phenolphthalein, whilst the fluid in bottle 2 was N/100 HCl. With both taps full on a coloured fluid passed down the observation tube, whereas with the tap of bottle 1 turned off slightly the excess of acid caused tautomerisation of the phenolphthalein and thus a colourless mixture resulted. The difference in rate of flow due to the turning off of this tap was trifling, but by doing so the fluid passing down the observation tube could be changed almost instantaneously from coloured to colourless and *vice versa*. By rapidly altering the tap it was possible to cause blocks of colourless and coloured fluid to pass in succession down the observation tube, and any difference in direction or velocity of central and peripheral parts of the fluid would be at once shown. No such effect could be observed however.

(2) The second test was based on the following considerations. In any quickly changing reaction the fluid at any instant will be chemically different from that at a subsequent instant, therefore if there is any return flow near the core of the fluid it will show itself by the readings taken by light that has passed through the core, corresponding to a later stage than those obtained by light that has passed through the periphery. No trace of such an effect has, however, been obtained in any of our experiments.

(3) Lastly, measurements taken at slow rates of flow (at which bubbles do not tend to travel towards the mixing chamber) should differ from those taken at fast rates, if in the latter there is a difference in motion of the core to that of the periphery. No such difference was, however, to be found.

Our conclusion is that all parts of the fluid travel with the same velocity down the observation tube.

(*b*) *The effect of specific gravity.*—The previous experiments show the conditions existing in the observation tube when two fluids of nearly the same

specific gravity are used, but it was possible, however, that different conditions would be met with if the specific gravities of the fluids were very different. It was important to rule out the possibility of such a difference, because in certain of our experiments the salt content of one fluid was very different to that of the other. The matter was tested by placing in bottle 1 a colourless fluid of specific gravity 1·033, and in bottle 2 an aqueous solution of a pigment (specific gravity 1·001) showing marked absorption bands, the strength of which could be accurately ascertained by optical means. The readings obtained on the fast moving fluid both central and peripheral were compared with similar readings made on a stationary intimate mixture of equal parts of 1 and 2. The converse experiment was also tried in which the pigment was added to the solution of greater specific gravity. In neither experiment was any "settling out" of the denser fluid towards the peripheral parts of the observation tube to be detected.

(*c*) *The effect of difference in surface tension.*—As a further test of the mixing powers of the apparatus two fluids were used which show a high interfacial tension. Water was used in bottle 1 and paraffin oil in bottle 2. It was considered evident that if an emulsion of one fluid in the other is obtained at slow rates of flow, this also must be the case at fast, since other experiments show the greater efficiency of mixing obtained with the latter. A slow rate of flow of about 100 cms. per second alone was tried, and it was found that a very fine emulsion of the one fluid in the other was obtained, the water phase being, of course, the continuous one. This experiment shows that a considerable interfacial tension does not prevent a mixture being formed.

(*d*) *The relationship between pressure and rate of flow.*—A knowledge of this relationship is important for two reasons : (*a*) the rate being found at a certain pressure, the rate at other pressures can be obtained without any further measurements, (*b*) from the point of view of design.

Tests performed on the 6-jet apparatus by varying the pressure head on the fluids entering the apparatus and measuring the volume of fluid passed through it per minute, showed that the rate of flow is almost exactly proportional to the square root of the pressure. This is readily seen from fig. 4, which shows rate of flow plotted against the square root of the pressure. An important practical conclusion results from this, namely, that small variations in pressure during an experiment will cause negligible variations in the rate of flow.

(*e*) *The applicability of the apparatus.*—We have already used the apparatus described in this paper for the study of reactions varying in rapidity (*i.e.* time taken for half of the total chemical change to occur) from two seconds

to one-three-hundredth of a second. With longer observation tubes, it would be possible to cope with much slower reactions. On the other hand, there appears to be no reason why, with careful attention to design, the method could not be extended to the measurement of reaction taking one-thousandth of a second or even less. A possible modification, which might be of value in the study of reactions of the highest rapidity, would be to cause the reaction to take place within minute droplets suspended as a spray in a rapidly moving gas phase. The resistance to flow offered by a gas is so very much less than that

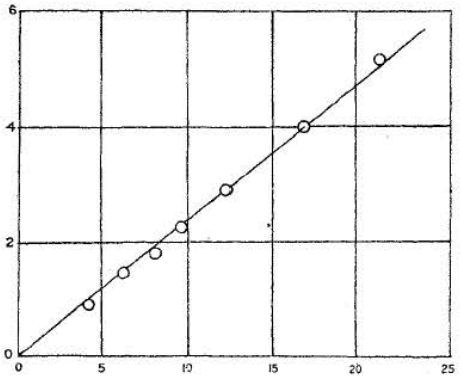

FIG. 4.

offered by a liquid, and therefore much higher linear velocities would be obtainable, and consequently more rapid reactions could be studied. The apparatus might with suitable modifications be also applied to the measurement of rapid reactions between gases.

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Summary.

In order to determine the velocity of any chemical reaction it is necessary (1) to make the chemical system unstable, (2) to record from time to time the stages reached by the system in its progress towards equilibrium. Both these processes have to be performed so rapidly that the time taken is negligible compared with that taken by the chemical reaction.

The apparatus used by the authors satisfies the above conditions.

By its means two fluids which contain the necessary chemical reagents are caused to mix together at a high velocity within a restricted space. The

mixture then flows with uniform velocity down a glass tube in such a way that estimations of the composition of the fluid can be made at any required cross-section, that is at any required instant of time after mixing.

Of various methods available for forcing the fluids through the apparatus a convenient one is to admit compressed air or gas into the containers which are partially filled by the fluids. Several types of mixing chambers were tested and the greatest efficiency found with one fitted with a number of tangential jets through which the fluids were forced.

The thoroughness of the mixing was tested by using as fluids one-tenth normal soda solution containing phenolphthalein and one-tenth normal acid. The rates of admission were varied until the pink tint of the dye just disappeared. With a knowledge of these rates and with certain assumptions which are fully discussed in this paper, a minimum value for the thoroughness of the mixing can be calculated; with rates of flow down the observation tube of 400 cms. per second not more than 1 per cent. of the fluid remains unmixed. This apparatus has enabled us to measure the velocity of certain chemical reactions. We find that under suitable conditions, the velocities of monomolecular reactions of which the half reaction takes as short a time as one-three-hundredth part of a second can be accurately measured.

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