Transient Entities in Chemical Reactions.

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THE study of the problem of chemical reactivity has progressed generally by a series of rather discontinuous steps in which new concepts have stimulated much experimental and theoretical work followed by periods of consolidation. In this Lecture there is described one such concept which has been developed especially vigorously since 1945 and has led to a fuller understanding of certain types of reaction in which atoms and radicals play an important part. In any reaction one of the essential pieces of information that must be obtained concerns the nature of the bodies that take part in those collisions leading to chemical transformation. This may seem to be a self-evident truth in simple reactions but in complex reactions the realisation of this fact has not always been appreciated. Not only is it necessary to establish the identity of the reacting species and the products of reaction, but precise information about their effective concentration must also be obtained. In reactions between molecules, whose mechanism is authenticated by methods now available, there is no difficulty in getting the necessary information. Similarly in reactions in solution between ions and molecules or other ions the information is also readily provided since the study of electrochemistry has produced a variety of methods whereby effective ionic concentration may be determined. The reactions mentioned above are, however, extremely simple because only two, and rarely three, bodies are concerned and the products do not in general affect the course of the reaction except by mass-action effects.

Unfortunately, investigations during the past two decades have demonstrated to an increasing extent that reactions are far more complex even although the reactants and products are relatively simple molecules. The underlying reason for this complexity is really economy of effort in carrying out a given transformation. In a reaction between molecules, a sufficiently violent collision serves to loosen certain bonds in a molecule so that at the moment of collision certain atoms or groups of atoms change partners and molecules of the product emerge from the collision, the chemical transformation having been effected. But there is another way in which even the same transformation may be brought about. It is now a well-established fact that an atom or a radical will attack a molecule much more readily than will another molecule. The product of such a reaction will be another atom or radical—maybe different, maybe identical. In due course another molecule is attacked and so the process goes on in which, according to the chain theory, many molecules may be transformed for each radical initially produced. The factor that limits the number of such occurrences is simply reactions which ultimately remove the radicals. The more highly competitive the latter, the smaller the number of molecules attacked.

Another important generalisation has also become evident during these developments. It is that when molecules are decomposed by heating or by exposure to radiation there is a tendency to undergo fission into radicals, because this is the simplest possible mode of decomposition since no complicated movements of atoms or groups of atoms are necessary. Thus, although rather more energy is needed to sever a bond than loosen it, once the radical is let loose many molecules may be induced to react, and thus the process is energetically economical. It is not surprising therefore that, owing to the operation of these principles, radical reactions are very common in non-ionic transformations.

A considerable effort has been made by using well-developed methods of chemical kinetics to prove the validity of the mechanisms, to get a general picture of the kind of reactions that molecules undergo, and in many cases to get fairly reliable evidence about the nature of the radicals involved. Until recently one vital piece of information has been lacking, namely, knowledge of the actual radical concentrations. If this knowledge is available it then becomes possible to account for the overall quantitative characteristics of the reaction in a completely satisfactory manner and to predict the course in any given circumstances. It is this particular aspect of the subject that will be dealt with in this Lecture. There are many lines of approach, some of which were developed just before the War; others have been extensively developed only during the past few years and progress is still rapid.

Direct Methods.

Normally, radical concentrations in the liquid phase do not exceed about 10^{-7} mole/litre, and in the gas phase about 10^{-3} mm.; hence direct measurement of radical concentration is impossible. With the very much less reactive radicals of the triphenylmethyl type much higher concentrations may be obtained, and the concentration can be determined either from measurement of the paramagnetism of the system or by observations on the rate of conversion of para-hydrogen bubbled through the solution. The unreactivity of such radicals, however, makes this method very restricted indeed.

Another direct spectroscopic method is useful and by certain modern developments has come into consideration as a very promising possibility, especially in the gas phase. Some twenty years ago it was observed that, when water vapour is heated to a sufficiently high temperature, the absorption spectrum of the hydroxyl radical can actually be observed, thus demonstrating the existence of the equilibrium $H_2O \rightleftharpoons H + OH$. With modern developments in intense sources of radiation the spectroscopic detection of radicals has become a possibility (Porter, *Proc. Roy. Soc.*, 1950, *A*, **200**, 284). In order to get sufficiently high concentrations of radicals, a brief flash of radiation may be conveniently produced by discharging a condenser through a suitable tube containing krypton or xenon. Flashes of energy content of the order of 1000 joules lasting for about 10^{-5} sec. are sufficient completely to decompose simple molecules like hydrogen sulphide. If the reaction tube is so arranged that an absorption spectrum of the gas during the period of discharge is obtained, it is in principle possible to detect those radicals having a well-defined absorption spectrum. The necessary intense and brief source of radiation is also provided by a flash tube. In this way simple diatomic radicals like HS and S_2 may be detected during the decomposition of H_2S. Furthermore, by mechanical methods exposures may be made after the source of decomposing radiation is cut off, so that some idea of the life-time and therefore reactivity may be obtained. Although the method is confined to the gas phase and to relatively simple radicals, it is applicable to a great variety of reactions in which knowledge even of this kind of radical is entirely lacking.

Indirect Methods.

All the other methods which have been devised are really indirect although they are completely valid. In any reaction occurring steadily the rate of radical production (I) must always be equal to the rate of radical removal. If only one kind of radical is involved in the rate-determining step of the reaction and such a radical disappears by interacting with another of its kind, then $I = kP^2$ and $P = (I/k)^{\frac{1}{2}}$. There is a further simple relation, namely, $P = I\tau$. Hence if we can measure the rate of production of radicals and their life-time (τ), all the necessary information is at once available to obtain a complete analysis of reaction mechanism.*

Determination of the Rate of Production of Radicals.—The accurate determination of I is not an easy matter but methods have been evolved over a long period. One method consists in the measurement of the length of an induction period when a specified amount of inhibitor is added. It is then assumed that all the radicals initially produced interact chemically with the inhibitor, which is likewise destroyed. The rate of consumption of inhibitor is then computed from its initial concentration and the duration of the induction period. Two important conditions need to be fulfilled—the inhibitor should not affect radical production, and the product of reaction should be inert in so far as the reaction itself is concerned. Alternatively, a retarder is added in such a concentration that the reaction chains are wholly stopped by chemical interaction with one of the radicals propagating the chain. The rate of consumption of the retarder, which may be measured by various methods, then gives the rate of production of radicals. In polymerisation there is, fortunately, a very direct method provided conditions are chosen suitably. In vinyl polymerisation each radical that induces polymerisation produces one polymer molecule. The number of polymer molecules may be conveniently counted by osmotic-pressure determinations and hence the rate of radical production may be computed.

The Determination of Radical Life-times.—The determination of the life-time of radicals is a much more complex matter for, in general, these are usually short, anything from 10^{-3} to 10^2 seconds. Many methods are now available for this determination, and the main theme of this Lecture is to describe some of the methods that have been devised to solve this question. The problem can be approached in this way : Suppose we consider one of the simplest radical reactions, namely, addition polymerisation in which the repeating reaction is the addition of a

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* When two or more radicals are involved in the rate-determining steps the problem can also be oslved though the analysis becomes much more complicated.

monomer molecule to a polymer radical to make a bigger polymer radical. In this way, starting with a small radical, as many as 10 000 molecules of monomer may be added on to such a radical. Further, suppose that small radicals are suddenly produced in the monomer medium, *e.g.*, by radiation with ultra-violet light, then if we plot radical concentration as a function of time (Fig. 1), the curve will rise at first linearly but will soon fall off since radicals will tend to combine with each other until a steady state is reached in which radical production and removal are equal. Now the rate of reaction is proportional to the radical concentration, so another curve (Fig. 2) may be drawn showing the amount of reaction as a function of time. It will be seen that a finite time is required for the reaction to go steadily. In this so-called non-stationary state the radical concentration is increasing to a steady value. Similarly, if the light is cut off the reaction will continue in the dark at a decreasing speed. On the assumption that there exists means whereby these curves may be delineated, the problem is how to calculate precisely the life-time of the radicals when the reaction is going steadily. During the non-stationary period the net rate of production of radicals is given by

FIG. 1. *Radical concentration–time curves in a photochemical reaction.*

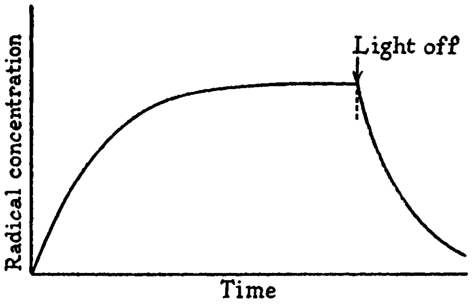
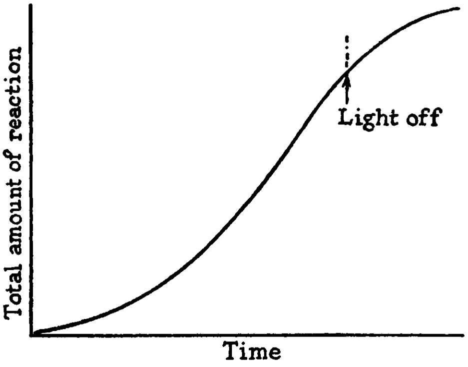


FIG. 2. *Total amount of reaction–time curves for photochemical reactions.*



$$dP/dt = I - k_t P^2$$

(This will of course become zero when the steady state is reached.) The total amount of reaction that will have occurred up to time t is proportional to

$$\int dP = \text{const.} \int_0^t (I - k_t P^2) dt$$

where the constant is calculable from the nature of the reaction. On integration of this equation it may be shown that the fractional amount of reaction $\Delta M/M$ is given by

$$\frac{\Delta M}{M} = \frac{k_p}{k_t^{\frac{1}{2}}} I^{\frac{1}{2}} t - \frac{k_p}{k_t} \ln 2$$

where k_p is the reaction coefficient for the interaction of a polymer radical with a monomer molecule. There is thus at high enough values of t a linear relationship between $\Delta M/M$ and t with a slope of $k_p/k_t^{\frac{1}{2}}I^{\frac{1}{2}}$ and an intercept on the time axis of $(k_p/k_t) \ln 2$. The ratio of slope to intercept is $k_t^{\frac{1}{2}}I^{\frac{1}{2}}/\ln 2$, and since I is known k_t may be calculated and so the value of the life-time may be determined. Similarly, the value of k_p may be calculated and therefore all the detailed information about quantitative radical reactivity at once obtained, for the effect of temperature on k_p and k_t may be easily determined.

No chemical method for this delineation is applicable because of the time limitation, and therefore physical methods alone must be employed. In almost any chemical reaction there is a change in the physical properties of the system. The problem here is to develop physical methods of the requisite sensitivity and such that records may easily be obtained. The following methods have proved suitable for this purpose: dilatometry, dielectric-constant change, refractive-index change, temperature and viscosity changes. Each method has its particular virtues and defects but together they cover at present every reasonable requirement. It is convenient to consider the basis of operation of the methods and the development of suitable instruments for these experiments.

Super-dilatometer.—In an addition polymerisation reaction there may be a contraction of as much as 20%. In a thermostat regulated to 0·01° it is a straightforward matter to detect by this means the formation of 1 part of polymer in 10^3 parts. Further increase in accuracy is limited by the constancy of temperature of the thermostat. In this particular case, however, constancy for a long period is not really necessary (Burnett, *Trans. Faraday Soc.*, 1950, **46**, 772). If one therefore uses a very sensitive dilatometer as a thermometer the surprising result is that in a period of 1 minute the bath temperature may not drift more than 10^{-5}°. Hence a sensitivity of 1 part in 10^7 of volume change may be detected in this interval of time, and the method becomes applicable to study the problem. Unfortunately, polymerisations and oxidations are exothermic reactions and hence the temperature of the reaction system may rise, giving a volume increase as opposed to decrease that occurs in polymerisation. The heat must be conducted away more rapidly than would normally occur through the glass walls of a dilatometer. This can conveniently be done by introducing liquid mercury into the dilatometer. Fig. 3 shows the result when the amount of reaction is plotted against time for the photopolymerisation of styrene. It will be seen that the true induction period of the reaction is well displayed, and the extrapolation of the straight line when the steady state of the reaction is established gives an accurately measurable intercept on the time axis.

Fig. 3. *Course of reaction for photopolymerisation of styrene.*

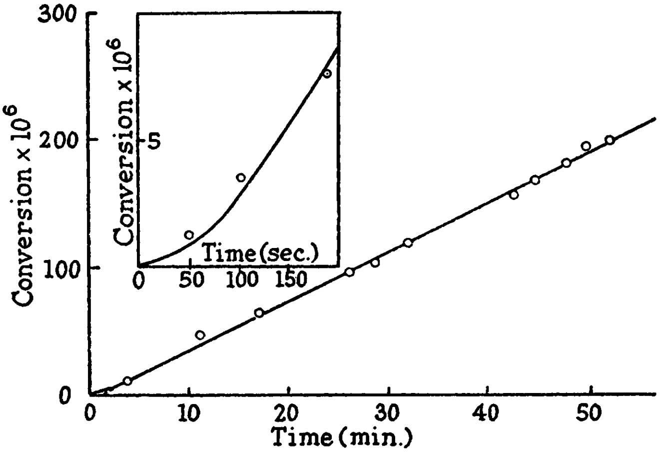


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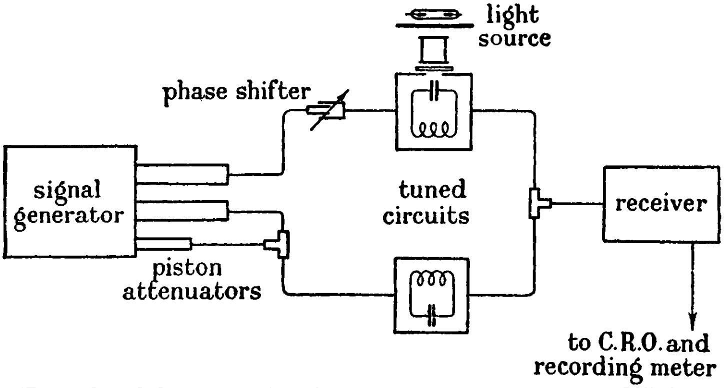
Fig. 4. *Block diagram of the capacity bridge.*



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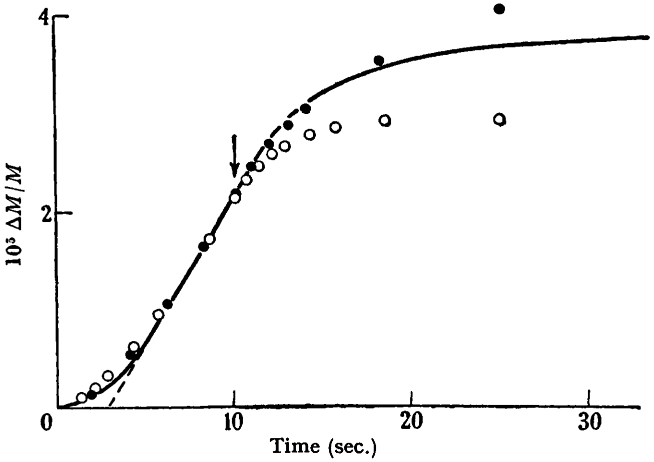
Dielectric-constant Method.—It is safe to say that in almost any reaction there will be a change of dielectric constant. Again, if we consider polymerisation the general rule is that the polymer has a higher dielectric constant than the monomer. In order to get the maximum possible sensitivity for an instrument, it is convenient to operate at a frequency of the order of 100 Mc./s. To achieve the necessary sensitivity a very special design of bridge circuit is required. The principles of operation can most readily be seen from a block diagram (Fig. 4) of the electrical circuit of the instrument (Majury and Melville, *Proc. Roy. Soc.*, 1951, *A*, **205**, 309). The signal generator is constructed in such a way that two separate outputs are derived from it, the two output voltages being 180° out of phase. The two output voltages are made nearly equal by means of a device known as a piston attenuator in which a small receiving aerial may be moved up and down a brass tube. A third auxiliary attenuator is fitted so as to provide a fine adjustment for the equalisation of output voltage. By this means the voltages are made equal to within 1 part in 10^8 parts. These two signals are transmitted by means of co-axial lines to each of two oscillating circuits which are precisely identical mechanically and electrically. In order to ensure that the voltages be 180° out of phase, a slight alteration is made in the length of one-axial cable. Since the wave-length used is about 6×10^2 cm., an alteration of 10^{-3} cm. in length gives a very precise means of adjustment. Any signal received from the oscillating circuit is reunited and fed to a suitable amplifier, rectified, and displayed on a voltmeter, cathode-ray oscillograph, or pen recorder. The capacity of the circuit consists of a flat silica cell which is filled completely with the monomer to be investigated. A hole is cut in the side of the box to admit radiation to the cell. Fortunately, although light gets in, electromagnetic radiation does not get out. If now the whole circuit is energised and the cell in one arm of the bridge illuminated, polymerisation is induced and the dielectric constant will change. The result is that the frequency of oscillation is slightly altered and a signal is produced at the T-junction of the bridge. This signal is displayed on the cathode-ray tube. On switching on the radiation, a time base circuit is also brought into action and hence the change of dielectric constant as a function of time is displayed on the screen and photographed in the ordinary way. By this method it proves possible to detect 1 part in 10^8 of change in dielectric constant in 10^{-3} second. When the experiment is done the most surprising result is that the dielectric constant *decreases* instead of increasing. Four factors can, however, contribute to the change in dielectric constant. First, infra-red and ultra-violet radiation absorbed by the system can raise the temperature and so decrease the dielectric constant: these can be eliminated by suitable filters. Radical production may be inefficient, which means that radiation is degraded to thermal energy: efficient photosensitisers combined with a long chain length can minimise this effect. Then, since polymerisation is exothermic and since, moreover, such measurements can be made in very short intervals of time, the heat so generated stays in the reaction system, causing the liquid to expand and so to lower the dielectric constant: the reaction is therefore carried out adiabatically. When the calculations are made it turns out that the dielectric constant decreases owing to the adiabatic character of the reaction being greater than the increase due to polymerisation. The net result is therefore a decrease when liquid completely fills the reaction cell.

FIG. 5. *Polymerisation of methyl acrylate, showing natural induction period and photochemical after-effect. The full circles correspond to second-order decay of radicals; the open circles to first-order decay.*



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In flat cells of a thickness of 5 mm., half the heat in the cell escapes in about 60 seconds under normal conditions. In effect therefore the instrument is a recording thermometer. It may be shown that the temperature sensitivity is $10^{-5°}$ and that it is an easy matter to measure an amount of heat as small as 10^{-3} calorie generated in any time up to 60 seconds. Even a direct measure of the quantum yield of the reaction can also be made. By using the appropriate photosensitiser of the polymerisation in an inert liquid like benzene, the instrument can be used as a radiometer to measure the total energy absorbed by the system. The quantum yield is directly calculable, since the wave-length of the activating radiation is known.

Fig. 5 shows how the amount of polymerisation varies with time. It will be seen that there is a period of induction followed by steady reaction, and a decay when the light is switched off. This permits the intercept to be accurately determined and therefore the average life-time of the reaction chain. It is of interest to consider the decay curve. This might follow a first-order law, *i.e.*, the radical interacts with a molecule, or a second-order law, *i.e.*, radical–radical interaction. These two relationships are drawn in Fig. 5, and it will be seen that the results conform much more closely to the second-order law, giving a direct indication as to how the radicals disappear. This method may also be used in quite a different way. Instead of continuously illuminating the system during the non-stationary phase, we may make use of high-intensity flash tubes giving a pulse of radiation lasting a time much shorter than that of the reaction chain. A krypton discharge tube with a flash time of 10—100 microseconds is convenient for this purpose. The result of using such a technique is that many small radicals are produced simultaneously in the vessel. These then start to grow as polymer radicals, their concentration gradually decreasing as they interact with each other. In this case, as Fig. 6 shows, there is no induction period because the steady concentration is in a way established right at the start of the reaction. The initial slope of the trace is thus a direct measure of the rate of molecular growth (although, of course, many molecules are growing at the same time). One might with reason say that molecules can be seen growing. A theoretical bimolecular curve is shown alongside the experimental points, and it will be seen that the decay accurately follows the bimolecular law. The constants of this bimolecular decay curve enable the average life-time of the radicals to be computed.

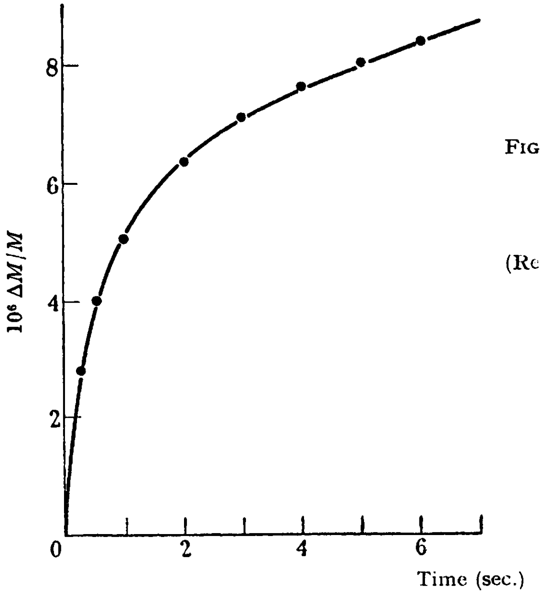

FIG. 6. *Polymerisation of vinyl acetate with flash technique showing absence of induction period. Full circles correspond to bimolecular decay of radical concentration.*

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Recording Interferometer.—Another physical method which in principle is suitable for study of the non-stationary state is the change of refractive index. To get the necessary sensitivity an interferometer technique is essential to detect a change of 1 part in 10^7 parts. The Jamin type of interferometer is the most suitable for it can conveniently be modified as a recording instrument to work in short time intervals (Grassie and Melville, *Proc. Roy Soc.*, 1951, *A*, **207**, 285). The principles of operation are shown by Fig. 7. An intense source of radiation illuminates the slit, and the beam is split by a glass block. The two beams pass through two tubes which form the reaction system. The beams are reunited by another glass block, giving rise to an interference pattern. Both tubes are filled with monomer, and reaction is induced in one by radiation, the other serving as a compensator. As a result, the fringe pattern moves past a reference point and the rate of movement may be observed visually or, if it is fast, by means of a cinema camera. Fig. 8 shows the movement of the fringes as a function of time, the movement indicating a *decrease* in refractive index. It is, however, a general rule that the refractive index of a polymer is greater than that of the monomer from which it is derived. The explanation of this apparent anomaly is similar to that in the dielectric-constant method, namely, that the reaction is mainly adiabatic. The resultant small temperature increase causes a decrease in refractive index which more than compensates for the increase due to polymerisation. It will be seen that there is again a finite induction period before a steady rate of reaction is attained. Consequently, the average life-time of the reaction chain may be obtained by means of the theory mentioned above. The method is not so sensitive as the dielectric-constant change, but it has the merit that the reaction system need not be an organic liquid with a relatively low dielectric loss.

FIG. 7. *Interferometric method of following polymerisation in the non-stationary-state.*

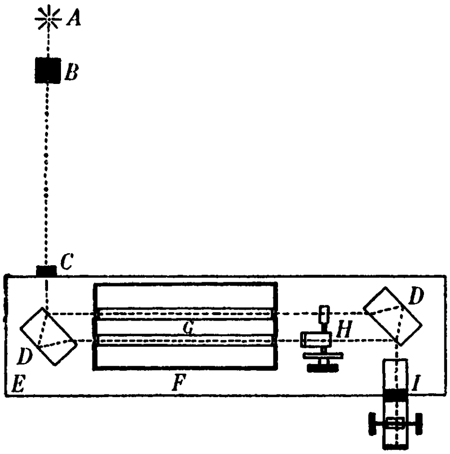

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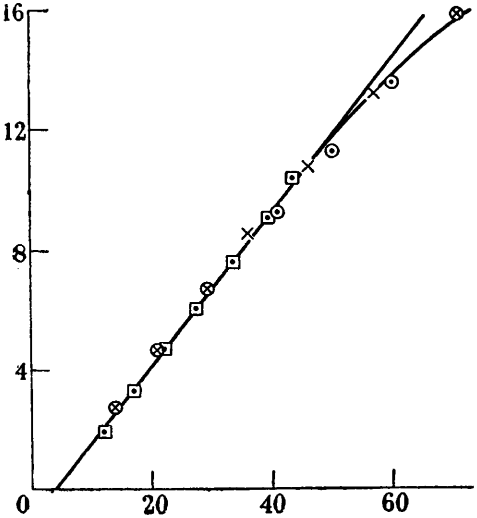
FIG. 8. *Polymerisation of methyl acrylate.*



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Recording-thermometer Method.—The results with the dielectric-constant and interferometer methods suggest that the most direct way of following the non-stationary state of reactions is to use some direct recording thermometer which must be sufficiently sensitive, and to arrange conditions so that the reaction is adiabatic. This has become possible by recent developments of direct-current electronic amplifiers. The experimental arrangement simply consists in suspending a tungsten wire down the axis of a dilatometer tube, the wire forming part of a balanced bridge (Ross, unpublished experiments). The out-of-balance current produced when polymerisation is induced photochemically is amplified and recorded on a suitable scale. Provided the experiment is not continued for longer than 1 minute, conditions in the centre of the tube are substantially adiabatic, and hence, if the heat of polymerisation and the specific heat of the monomer are known, the temperature increase gives a direct measure of the amount of reaction that has occurred. Fig. 9 shows the increase in temperature during the polymerisation of methyl acrylate, the curve being of a similar shape to that with the other non-stationary state method.

Viscometry.—The non-stationary state in a polymerisation reaction may be studied in another, less direct fashion. The viscosity of a monomer undergoing polymerisation is very markedly increased by the addition of relatively small amounts of polymer, and the higher the molecular weight the more marked is the increase. When polymerisation is proceeding steadily the viscosity of the system increases according to a complex relationship which depends, not only on the rate of production of polymer molecules, but also on their molecular weight and concentration. If the reaction is initiated photochemically and the light is cut off, the viscosity goes on increasing in the dark, but at a diminishing rate (Bamford and Dewar, *Proc. Roy. Soc.*, 1947, *A*, **192**, 309). This is due to the diminution in radical concentration as they interact with each other. Although viscometric measurements can only be made relatively slowly, if the reaction rate is small enough radical life-times can be made very large—many minutes—so that there is no difficulty in observing viscosity as a function of time. Although the analysis of the results is not easy, this kind of photochemical after-effect may be used to calculate velocity coefficients.

Sector Method.—The first method developed to measure the absolute reactivity of radicals was that of the so-called rotating sector (Burnett and Melville, *Proc. Roy. Soc.*, 1947, *A*, **189**, 456). Here, intermittent radiation is used, and the rate of reaction is a function of the time between the flashes of radiation. The effect of intermittency was discovered in 1926, but it was not until 1940 that it was shown how, by combining this effect with other kinetic data, absolute reactivity of radicals could be obtained, and the first measurements of any accuracy were not made until 1945. This method is much less direct than that of the non-stationary state, but it is easy to use and needs no elaborate equipment. The only essential is that the radicals disappear mainly by interaction with each other. The principle of the method is simply the temporal interference between radical production during the flashes of radiation. When a finite number of radicals is produced during a brief flash, then in the following period of darkness the concentration will fall off at a rate depending on the reactivity of the radicals and on their concentration. If a second flash is produced before the first lot of radicals has disappeared, then the second crop of radicals will interfere with the first lot and alter the decay period. It has already been seen that considerable effort must be made to follow such phenomena in the non-stationary state methods. The sector method possesses the great advantage of integrating the effect over many cycles of light and dark; therefore relatively simple methods of following the reaction may be used. It is, of course, restricted to reactions in which radicals disappear two at a time, and this fact makes it essential to have other methods available, for there are in fact quite a large number of reactions in which radical disappearance is a first-order reaction. The reason for this behaviour is the transformation, by collision with a molecule, of a reactive radical into a highly stabilised radical.

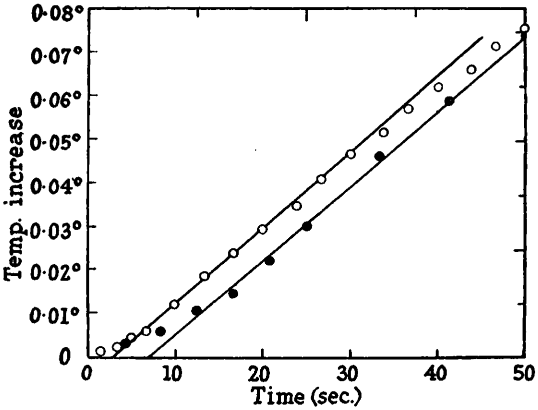

FIG. 9. *Rise of temperature during the adiabatic polymerisation of methyl acrylate.*

Spatial Interference.—The principle of temporal interference may be extended to provide another method of spatial interference which is applicable in both the gas and the liquid phase. In the gas phase this is done in the following manner (Jones and Melville, *Proc. Roy. Soc.*, 1940, *A*, **175**, 392). If a narrow pencil of radiation is projected into a reaction vessel, reaction will occur not only in the illuminated zone but will spread out into the surrounding unilluminated zones to an extent that will depend on the life-time of the radicals. Further, if it were possible to explore radical concentrations spatially, the life-time could readily be calculated from the diffusion coefficient of the radicals, but this is experimentally a very difficult problem to solve. The principle of interference, however, can be utilised to obtain the necessary information. A second similar beam is projected into the vessel parallel to the first. If these beams are far enough apart the radicals in the two reactive zones will not interfere. When the beams are brought closer together so that the zones overlap, interference will occur and there will be an overall drop in the velocity of the reaction. Thus the rate of reaction is a function of the distance between the two beams of radiation. By appropriate analysis, the life-time of the radicals may be calculated. Even in the liquid phase this principle may be used to get some idea of the distribution of radical concentrations, since convection currents so disturb the distribution of radicals that it is impossible to make the calculations even though radical reactivity is known (Burnett, Valentine, and Melville, *Trans. Faraday Soc.*, 1949, **45**, 960). In this case it is convenient to employ two similar sources of initiating radiation on either side of a reaction vessel. If the radicals are confined to a zone close to the wall of the vessel there will be no interference; on the other hand, if the radicals are uniformly distributed throughout the vessel there will be complete interference. Once more, the rate of reaction will be dependent on the distribution of radical concentration, and the extent of the distribution of radical concentration and the extent of the distribution may be explored by this interference method.

Spatial Competition.—The above-developed methods are particularly applicable to chain reactions—oxidations, polymerisations, etc.—but there are many reactions of different types where these methods would be inapplicable. In the gas phase a simple example is the addition of a hydrogen atom (the simplest radical) to an olefin, for example, ethylene. Here another principle may be invoked. If matters can be so arranged that there are two competing reactions for a given radical, the extent of the competition is known and the absolute velocity of *one* of the reactions is known or is calculable, and the absolute velocity of the other may of course be calculated. This can be done in the following fashion (Robb and Melville, *Proc. Roy. Soc.*, 1949, *A*, **196**, 445). A convenient competitive reaction is the interaction of atomic hydrogen with solid molybdenum oxide. If in a reaction vessel atomic hydrogen is generated photochemically (*e.g.*, by photosensitisation with mercury vapour) and at the bottom of the vessel there is a layer of molybdenum oxide, then the geometry of the system can be so arranged that all the hydrogen atoms produced reach and are absorbed by the oxide. If now ethylene is introduced at such a pressure that an appreciable fraction of the atoms is captured by the ethylene, then fewer atoms will be taken up by the oxide. The uptake of atoms by ethylene can be measured by micro-analytical methods. A more convenient method makes use of the fact that molybdenum oxide goes blue on absorbing hydrogen atoms. The blue colour can be measured photometrically and this provides a far more sensitive means of following the reaction. The surprising fact is that the ethyl radicals are also absorbed quantitatively and give rise to a blue colour. Fortunately, the rate of development of blue colour with ethyl radicals is less than that due to atomic hydrogen so the introduction of ethylene results in a decrease of this rate. Owing to

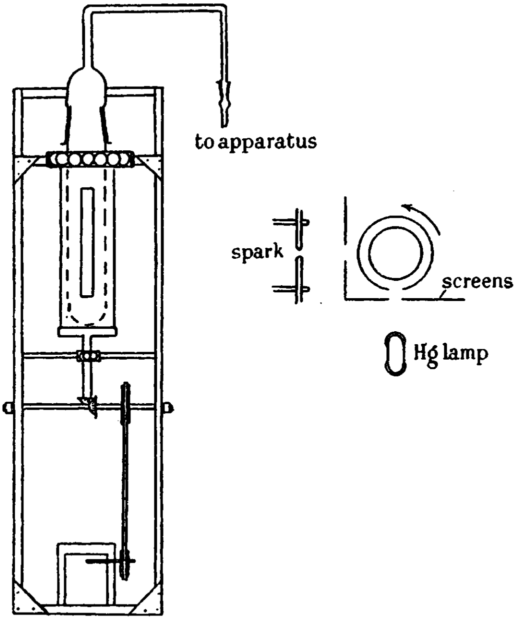

FIG. 10. *Arrangement to measure life-time of* NH_2 *radicals. The spark decomposes the ammonia, and the mercury lamp decomposes the hydrogen.*

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the simplicity of the geometry of the system and to the fact that boundary conditions are precisely known, accurate diffusion calculations can be carried out and the velocity coefficient can be evaluated. This technique enables many fast reactions to be measured with collision efficiencies up to 1×10^{-3}. It is of general applicability with atomic hydrogen because many alkyl radicals have blueing coefficients significantly different from those of atomic hydrogen. Occasionally, alkyl radicals have the same blueing coefficient as that of atomic hydrogen, but fortunately tungsten oxide is also useful in this connection and the blueing coefficients are then significantly different.

Finally, there is another type of interference method in which one radical is made to catch the other (Birsi and Melville, *Proc. Roy. Soc.*, 1940, *A*, **175**, 187). If ammonia is decomposed photochemically, NH_2 and hydrogen atoms are the primary products. In presence of excess of atomic hydrogen produced independently by mercury photosensitisation, recombination to ammonia occurs and thus hydrogen atoms are inhibitors of the decomposition. If, however, the source of hydrogen atoms is not switched on until an appreciable time after the NH_3 has been illuminated, then there is no inhibition because there are no NH_2 radicals to react with atomic hydrogen. On the other hand, if the hydrogen atoms are generated quickly enough after illumination of the ammonia then they will catch the NH_2 radicals. This is done by the arrangement shown in Fig. 10, in which one source of radiation decomposes the ammonia and the other produces atomic hydrogen. A rotating shutter permits the interval between the two processes to be regulated so that the life-time of the NH_2 radical can be determined.

This Lecture has been mainly concerned with the development of new methods for the study of quantitative free-radical chemistry. There is no time or space to discuss the results which are mounting rapidly as a result of these advances in chemical kinetics. But perhaps it is worth while to indicate generally the kinds of new knowledge that have become available in the course of the last few years. Radical concentrations are now known for the oxidation of hydrocarbons and aldehydes, the decomposition of acetaldehyde and of dimethylmercury, the polymerisation of a great many vinyl derivatives, the degradation of polymers, *e.g.*, poly(methyl methacrylate), and the interaction of bromotrichloromethane with olefins, such as *cyclo*hexene. This information at once makes it possible to calculate the velocity coefficients for the interaction of radicals with molecules, for example, in oxidations the rates at which peroxide radicals of the RO_2 interact with hydrocarbons and with retarders added to the system. Similarly, in polymerisation the rate of monomer addition to polymer radicals is known. Experiments of this kind have also demonstrated that a polymer radical grows at a speed almost independent of its size. In the more complicated case of copolymerisation of two monomers there are a minimum of ten elementary radical reactions. The velocity of each one may be calculated with a considerable degree of precision and the reaction mechanism may be said to be completely elucidated. By studying the copolymerisation system in which one of the reactants is fixed, it is possible to specify velocity coefficients of a given polymer radical with a great variety of other monomers, so shedding much light on the factors that govern radical reactivity.

The interaction of radicals provides many interesting problems. Although such reactions proceed without energy of activation, they are relatively inefficient since, except for the methyl radical, none so far discovered proceeds at a rate equal to the collision rate. Further, interactions are highly specific and may range over many orders of magnitude. This clearly demonstrates that chemical structure has in these cases a very great effect on the entropy terms in velocity coefficients. One even more surprising result is that dissimilar radicals interact much more quickly than would be expected from the separate reactivity of the radicals. Again, environment affects reactivity. If in polymerisation the viscosity of the system increases by the accumulation of polymer, radical–molecule interactions are unaffected but radical–radical interaction may be slowed up. This is due to immobilisation of the polymer radicals, whereas monomer can diffuse relatively easily to the polymer radical. This and many other surprising observations are the natural result of this new development. By such means there is the reasonable prospect in the near future that the mechanism of many chemical reactions involving radicals will be completely elucidated and set out in a satisfying quantitative fashion.