DIFFUSION-CONTROLLED REACTIONS

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1. The Rôle of Diffusion in Chemical Reactions

With the exception of certain processes involving electromagnetic radiation, all chemical reactions require that at least two molecules (or related participating species) come into close proximity so that energy, electrical charge, or chemical groups may be exchanged between them. It is this very basic prerequisite that leads us straightaway to the subject of diffusion in chemical processes.

The importance of diffusion is well appreciated in systems which are initially heterogeneous on a macroscopic scale. Thus the interpretation of reactions in flames, at electrodes, or at interphase boundaries is based upon a consideration of both mass transport and chemical phenomena. However it is with liquid systems which appear homogeneous on a macroscopic scale that we shall be concerned in this Review.

As a simple example, let A and B represent two reactants, initially separated in a condensed phase. Then the overall process can be pictured as consecutive transport and chemical processes:

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A:B} \qquad\qquad \mathrm{A:B} \xrightarrow{k_c} \mathrm{C}$$

where A:B represents the two reactants in proximity, C is the product of chemical change, k_1 and k_{-1} are rate coefficients for the diffusive approach and separation of reactants, and k_c is the rate constant for chemical change in the proximate pair. Under conditions such that the overall concentration of A, B, and A:B are maintained constant, the reaction rate is given by

$$\frac{d[\mathrm{C}]}{dt} = k_c \left(\frac{k_1}{k_{-1} + k_c}\right) [\mathrm{A}]\,[\mathrm{B}] \qquad \ldots\ldots \quad (1)$$

An experimentally observed reaction rate constant would be defined as

$$k_{\mathrm{exp}} = \frac{d[\mathrm{C}]}{dt} [\mathrm{A}]^{-1} [\mathrm{B}]^{-1}$$

so that

$$k_{\mathrm{exp}} = \frac{k_c k_1}{k_c + k_{-1}} \qquad \ldots\ldots\ldots \quad (2)$$

It is thus immediately apparent that any experimentally determined rate constant is composed of terms descriptive of both the diffusive and the chemical processes. The exact form of the experimental constant is not always that expressed in equation (2), which covers only the simplest case involving stationary-state conditions.

It is also apparent that equation (2) can be written in two extreme forms, depending upon the relative rates of the diffusive and chemical processes. When the diffusive processes are much faster than the chemical step, $k_c \ll k_{-1}$, and a dynamic equilibrium concentration of paired reactants is set up in the system. Under this condition,

$$k_{\text{exp}} = \frac{k_1}{k_{-1}} \cdot k_c = k_c K_{AB} \qquad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where K_{AB} is the equilibrium constant for the formation of reactant pairs. Some consequences of adopting this two-stage approach to the interpretation of slow chemical reactions have been discussed in a recent monograph.[1]

The condition in which we are interested is the opposite case in which chemical change is very rapid, but diffusion is relatively slow. The chemical change can then take place only as fast as the reactants can diffuse together, and the overall process is designated a "diffusion-controlled reaction". In these circumstances $k_c \gg k_{-1}$, and equation (2) reduces to

$$k_{\text{exp}} = k_1 \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

The types of very fast reaction which exhibit this behaviour in liquids of normal viscosity encompass radical–radical reactions, ion-recombination reactions, the quenching of electronically or vibrationally excited species, and certain reactions involving macromolecular reactants of low diffusivity. As a rather general rule, bimolecular processes with a rate constant close to 10^{10} l.mole^{-1} sec.$^{-1}$, or (less reliably) with an activation energy less than 3·0 kcal. mole^{-1}, will usually be diffusion-controlled. In the case of two polymeric reactants, the rate constant may be as low as 10^{8} l.mole^{-1} sec.$^{-1}$. Of course, in solids, glasses, or in liquids of very high viscosity, mass-transport processes are very inefficient and chemical reactions which are normally considered rather slow can become diffusion-controlled.

So far, we have discussed only the quantitative effect of diffusion on the rate of a single chemical step. However, diffusive processes may govern which products are obtained from complex chemical reactions involving competitive reactions. Some particularly striking examples of this are to be found in photochemistry, where the diffusion-controlled quenching of excited states may compete with other relaxation processes. A competition between diffusive separation and reaction is also found when reactive entities (such as free radicals) are found in pairs.

2. Theoretical Calculations of Diffusion-controlled Reaction Rates

Diffusion-controlled processes represent the only broad class of chemical reaction for which it is now possible to calculate reaction rates from

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[1] A. M. North, "Collision Theory of Chemical Reactions in Liquids", Methuen, London, 1964.

fairly well authenticated first principles. The theoretical aspects of these calculations for liquid systems have recently been reviewed by Noyes.[2]

The theoretical treatments have involved two rather different lines of thought. The first applies Fick's laws of diffusion to the movement of reactant molecules across possible concentration gradients in the solution, whereas the second focuses attention on the potential reactivity of an isolated pair of molecules. Somewhere between these approaches lies a treatment based on a consideration of the reactant pair-probability distribution.

(a) **Simple Application of Fick's Laws.**—The problems associated with the diffusion together of reactant species are essentially the same as those dealt with in the coagulation of colloids. If one reactant, A, can remove several molecules of another, B, then the concentration of B in the immediate neighbourhood of A is reduced below the average value for the whole system. There is thus a gradient in the concentration of B about each A molecule, and there results a net flux of B molecules towards A. This net flux is equal to the rate of the reaction. Indeed, this concentration gradient can be postulated even for the case when each A molecule is capable of reacting with only one B molecule. Use of Fick's laws followed by solution of the relevant diffusion equations allows evaluation of the reaction flux, both when the concentration gradient is changing during the initial stages of the reaction, and when steady-state diffusion has been achieved.

By use of this treatment the observed rate constant when steady-state diffusion has been achieved is

$$k_{\text{obs}} = \frac{4\pi r_{\text{AB}} D_{\text{AB}}}{1 + (4\pi r_{\text{AB}} D_{\text{AB}})/k} \text{ molecules cm.}^{-3} \text{ sec.}^{-1} \quad . \; . \; . \; . \quad (5)$$

where r_{AB} is the radius of the "capture"-sphere formed by B molecules around an A molecule, D_{AB} is the relative diffusion coefficient of the approaching reactants and is the sum of the individual coefficients, $D_{\text{A}} + D_{\text{B}}$, and k is the rate constant which would be observed if the concentration of B molecules in the nearest-neighbour shell of an A molecule was the same as the average over the whole system.

The rate constant for the extreme case when reaction takes place at every encounter is often calculated by using the simple boundary condition that the concentration of B in the nearest-neighbour shell of each A molecule is zero:

$$k = 4\pi r_{\text{AB}} D_{\text{AB}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

This treatment, first carried out by Smoluchowski,[3] is in fact only applicable when $k \gg 4\,\pi\, r_{\text{AB}} D_{\text{AB}}$, which inequality may not always be attained. The choice of correct boundary conditions, and the assumptions inherent

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[2] R. M. Noyes, "Progress in Reaction Kinetics", ed. G. Porter, Pergamon Press London, 1961.

[3] M. V. Smoluchowski, *Z. phys. Chem.*, 1917, **92**, 129.

in the Fick's law treatment, have been extensively covered in a number of papers.[2,4–6] In particular, the facts that a liquid is not an isotropic continuum and that a degree of correlation may exist between the movements of the various reactants, cannot be encompassed by the use of Fick's equations.

(b) Diffusion and Pair-probability Distribution.—The alternative theoretical approach to the problem of rates of diffusion-controlled reaction has involved a study of the behaviour of molecular pairs, and an evaluation of the pair-probability distributions.

It is possible to discuss perturbations in the pair-probability distribution in terms of the same parameters used in the preceding section. In this fashion the effect of diffusive flux and chemical reaction on the reactant pair distribution function has been examined by Collins and Kimball[7] and by Waite.[6,8]

The treatment is quite general, and the simplified expression for a diffusion-controlled reaction rate constant is

$$k_{\text{obs}} = 4\pi r_{\text{AB}} D_{\text{AB}}[1 + r_{\text{AB}}/(\pi D_{\text{AB}} t)^{\frac{1}{2}}] \text{ molecules cm.}^{-3} \text{ sec.}^{-1} \quad . \quad . \quad . \quad (7)$$

This can be recognised as the time-dependent form of equation (6) for which $k \gg 4\,\pi r_{\text{AB}} D_{\text{AB}}$.

(c) The Behaviour of Molecular Pairs.—The discussion of the potential reactivity of an isolated molecular pair is attractive, because by this approach it might be possible to avoid the approximations involved in applying macroscopic continuum equations and concepts to molecular phenomena. This line of attack has been extensively investigated by Noyes.[9]

The problem is tackled by considering an imaginary system in which no real chemical reaction takes place during an encounter of an A molecule and a B molecule, but in which it is possible to distinguish molecules that have been in a situation where they would have reacted had the system been a real one. Using this idea we can express any reaction rate constant as a primary constant (characteristic of a truly random distribution of reactants or of zero time) modified by a function which accounts for the fact that long-lived reactants must have been formed a greater-than-average distance from other reactants. While the expression is quite general in character, it does involve certain parameters which cannot be related to experimentally observable quantities without the use of assumptions similar to those inherent in Fick's laws. However one self-consistent evaluation has been attempted.[9]

[4] H. K. Frisch and F. C. Collins, *J. Chem. Phys.*, 1952, **20**, 1797.

[5] F. C. Collins, *J. Colloid Sci.*, 1950, **5**, 499.

[6] T. R. Waite, *Phys. Rev.*, 1957, **107**, 463, 471.

[7] F. C. Collins and G. E. Kimball, *J. Colloid Sci.*, 1949, **4**, 425.

[8] T. R. Waite, *J. Chem. Phys.*, 1958, **28**, 103.

[9] R. M. Noyes, *J. Amer. Chem. Soc.*, 1955, **77**, 2042; 1956, **78**, 5486.

Despite the apparently greater rigour of the molecular pair approach, the fact that the use of Fick's laws requires only two quantities, r_{AB} and D_{AB} (both of which can be estimated easily for many systems), has meant that the latter equations have been most commonly applied to observed phenomena.

(d) Collisions on Pseudo-crystalline Lattices.—One of the first to appreciate the significance of the fact that collisions between reactants in liquids occur in isolated sequences was Rabinowitch.[10] Using a pseudo-crystalline model of the liquid state, he derived the first equation which included both chemical and diffusive processes. The derivation, based on calculations of jump diffusion between lattice sites, took no account of the non-random distribution of reactants in space, and has now been largely superseded by the treatments mentioned previously.

(e) Corrections for Long-range Interactions.—When two reactants are capable of exerting long-range interactions upon each other, the rates at which they diffuse together (or apart) will be affected.

The most widely used method[2,8,11] of allowing for these interactions is to replace the encounter radius r_{AB} in the equations derived previously by an "effective" value, r_{eff}. This parameter will be larger than r_{AB} for attractive forces, and less than r_{AB} for forces of repulsion.

The actual magnitude of r_{eff} can be found by integration of the long-range interaction from infinite separation up to r_{AB}, and is

$$r_{eff} = \left[\int_{r_{AB}}^{\infty} \exp\,(U/kt)\,(\mathrm{d}r/r^2)\right]^{-1} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

where U is the interaction energy and is a function only of the A–B separation. Electrostatic or any other relevant interactions can be inserted for U and the integration carried out without difficulty.

It is important to realise that r_{eff} has no physical significance. Indeed for intermolecular repulsions r_{eff} may be less than any realistic molecular dimension.

3. Free-radical Reactions

Almost all radical–radical termination reactions require so little activation energy that they are diffusion-controlled in liquids of normal viscosity.

(a) Atom Recombinations.—Quite extensive studies have been made of the factors affecting the diffusion-controlled recombination of iodine atoms. This particular reaction has been studied by flash photolysis, by

[10] E. Rabinowitch, *Trans. Faraday Soc.*, 1937, **33**, 1225.

[11] P. Debye, *Trans. Electrochem. Soc.*, 1942, **82**, 265.

measurement of the photostationary concentration of iodine atoms, by observation of radioiodine exchange reactions, and by the use of intermittent illumination to evaluate the lifetime of the iodine atom. All these methods yield values for the recombination rate constant in carbon tetrachloride at 25° close to 7×10^9 l.mole^{-1}sec.$^{-1}$. If a reasonable collision radius is assumed to be $4{\cdot}3 \times 10^{-8}$ cm. (twice the van der Waals radius of iodine) the diffusion coefficient of the iodine atoms can be calculated[3] by using the Smoluchowski equation, and is $5{\cdot}3 \times 10^{-5}$ cm.^{2} sec.$^{-1}$.

The actual diffusion coefficient of iodine atoms has been measured[12] using the photochemical space intermittency technique.[13] In such measurements a photochemical reaction is brought about by light which is intermittent in space. The reaction then shows different overall kinetic behaviour depending on whether the separation of the illuminated zones is greater or less than the mean diffusive displacement of a free radical during its lifetime. The experiment is simply a spatial analogue of the rotating sector technique which involves light intermittent in time. The latter case yields the radical lifetime, while the former yields the mean diffusive displacement. The value obtained for the diffusion coefficient, $8{\cdot}2 \times 10^{-5}$ cm.^{2} sec.$^{-1}$, is somewhat larger than that calculated using the equations of Section 2, although the difference is of the same order of magnitude as the experimental error.

The effect of solvent viscosity on this recombination rate constant has been studied[14] and the relationship, $k\,\eta\,/T =$ constant, did not hold when the viscosity was varied by alteration of the solvent. This is one example of the quite widely observed phenomenon that in long-chain or hydrogen-bonded solvents the macroscopic viscosity is no measure of the resistance to the translational motion of small solute molecules.

The smallest radical or atom is hydrogen, and very high diffusivities (and hence recombination rate constants) would be expected for reactions of hydrogen atoms in liquids. Experimental observations[15] of the rate of addition of hydrogen atoms to propene in liquid butane at 77°K allows estimation[16] of the hydrogen atom recombination rate constant, and the diffusion coefficient of H atoms. The results:

$$k \geqslant 3{\cdot}8 \times 10^{10}\ \text{l.mole}^{-1}\ \text{sec.}^{-1};\ D \geqslant 1 \times 10^{-3}\ \text{cm.}^2\ \text{sec.}^{-1}$$

do indicate a quite anomalously high diffusivity.

(b) Low Molecular-weight Free-radical Reactions.—Recombination rate constants have not yet been measured directly for simple alkyl radicals (methyl, ethyl) in solution. However Lyon[17] has used a comparison of disproportionation-to-combination ratios in gas and liquid phases to

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[12] G. A. Salmon and R. M. Noyes, *J. Amer. Chem. Soc.*, 1962, **84**, 672.
[13] R. M. Noyes, *J. Amer. Chem. Soc.*, 1959, **81**, 566.
[14] H. Rosman and R. M. Noyes, *J. Amer. Chem. Soc.*, 1958, **80**, 2410.
[15] R. Klein, M. D. Scheer, and J. G. Waller, *J. Phys. Chem.*, 1960, **64**, 1247.
[16] M. Szwarc, *J. Phys. Chem.*, 1964, **68**, 385.
[17] R. K. Lyon, *J. Amer. Chem. Soc.*, 1964, **86**, 1907.

calculate values for the recombination constants. The calculation is based upon an idealised model of the "cage" effect in liquids and dense gases, and requires estimated values for the radical diffusivities. The values obtained ($1{\cdot}8 \times 10^{10}$ l.mole^{-1} sec.$^{-1}$ for methyl and $0{\cdot}47 \times 10^{10}$ l.mole^{-1} sec.$^{-1}$ for ethyl radical recombination, both in 2,2,4-trimethylpentane at 25°C) appear reasonable. One cannot use these values as a test of diffusion-controlled reaction rate equations, of course, since just such an equation was used in their derivation.

An interesting case is the rate constant for the recombination of trichloromethyl radicals which has been found[18] to be 5×10^{7} l.mole^{-1} sec.$^{-1}$ in cyclohexane at 30°C. This is smaller than the value predicted by the Smoluchowski equation. It is possible that the radical recombination requires appreciable activation energy and is not completely diffusion-controlled, or that some polarisation placing a negative charge on the periphery of the radicals causes long-range electrostatic interactions which lower the effective collision radius. In view of the current debate[19] as to whether or not the recombination of trifluoromethyl radicals requires activation energy, further studies on trichloromethyl radicals seem desirable.

Absolute rate constants for the reactions of hydroxyl radicals with a variety of substrates have recently been measured by use of pulse radiolysis techniques.[20] The rate constants for reaction with thiocyanate and selenite anions, and with ethanol, lie in the 10^{9}—10^{10} l. mole^{-1} sec.$^{-1}$ range which might be expected for diffusion-controlled reactions. However no study aimed specifically at elucidating the rôle of diffusion in these reactions has yet been carried out.

(c) Macroradical Reactions.—The termination reaction of free-radical polymerisation is a process which seems ideally suited for studies of diffusion-controlled phenomena. In this case the reactants have very high chemical reactivity, and very low diffusivities, both essential conditions for a rate-determining transport process. However, studies of this type of reaction are complicated in a fascinating way because the reactive positions on the molecule occupy a very small fraction of the total molecular volume. Furthermore for flexible polymers the geometrical location of the positions may not be fixed with respect to the rest of the molecule.

Interest in the effects of diffusion in polymeric free-radical systems has been maintained since first Norrish and Smith[21] and later Tromsdorff, Kohle, and Lagally[22] suggested that the auto-acceleration or "gel-effect" observed in the later stages of many free-radical polymerisations was due to

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[18] H. W. Melville, J. C. Robb, and R. C. Tutton, *Discuss. Faraday Soc.*, 1953, **14**, 150.

[19] R. D. Giles and E. Whittle, *Trans. Faraday Soc.*, 1965, **61**, 1425.

[20] G. E. Adams, J. W. Boag, and B. D. Mitchell, *Trans. Faraday Soc.*, 1965, **61**, 1417.

[21] R. G. W. Norrish and R. R. Smith, *Nature*, 1942, **150**, 566.

[22] E. Tromsdorff, H. Kohle, and P. Lagally, *Makromol. Chem.*, 1947, **1**, 169.

diffusion-control of the termination process. The original suggestion was that termination is initially chemically controlled, but that as monomer is converted into polymer the viscosity of the system rises, the reactant diffusivities fall, and at a critical viscosity the termination reaction becomes diffusion-controlled and so markedly reduced. This theory was strengthened by calculations[23,24] of the critical conversion which seemed to agree well with experimental observations.

However, the general feeling today is that the majority of these reactions are diffusion-controlled even during the initial stages of the polymerisation. Demonstration of this point requires a rather careful study of the way in which the radical termination reaction depends on the viscosity of the system.

The effect of solvent viscosity has been studied for a number of methacrylate homopolymerisations and copolymerisations,[25–29] and also for the polymerisation of acrylamide,[30] and in each case the reaction was diffusion-controlled at low conversions.

Unfortunately it is not an adequate test for diffusion-control of the termination reaction to measure this reaction rate constant when the viscosity of the system is due to the presence of dissolved polymer.[31,32] There are two reasons for this. In the first place, the macroscopic viscosity of solutions of long-chain molecules contains contributions from chain-tangling effects, and may grossly overestimate the resistance to molecular diffusion. In the second place, the dimensions of the polymer chain may alter with increasing polymer concentration,[33] and in fact the polymer diffusion coefficient may increase with increasing polymer concentration. Such an increase has been shown to take place in the initial stages of the polymerisation of methyl methacrylate,[26] so that the overall rate of polymerisation falls, not rises, over the first few per cent. conversion.

Three methods have been used in an attempt to evaluate kinetic equations for the diffusion-controlled reactions of macroradicals.

In one approach[25–27,34,35] the overall process is visualised as three consecutive reversible processes: translational diffusion of the centres of gravity of the macroreactants, followed by a segmental rearrangement diffusion bringing the reactive ends into proximity, followed by chemical reaction. It appears that the segmental rearrangement motion is the process

[23] M. F. Vaughan, *Trans. Faraday Soc.*, 1952, **48**, 376.
[24] G. V. Schulz, *Z. phys. Chem. (Frankfurt)*, 1956, **8**, 290.
[25] S. W. Benson and A. M. North, *J. Amer. Chem. Soc.*, 1959, **81**, 1339.
[26] A. M. North and G. A. Reed, *Trans. Faraday Soc.*, 1961, **57**, 859.
[27] A. M. North and G. A. Reed, *J. Polymer Sci.*, 1963, **A1**, 1311.
[28] J. N. Atherton and A. M. North, *Trans. Faraday Soc.*, 1962, **58**, 2049.
[29] A. M. North and D. Postlethwaite, *Polymer*, 1964, **5**, 237.
[30] G. K. Oster, G. Oster, and G. Prati, *J. Amer. Chem. Soc.*, 1957, **79**, 595.
[31] C. R. Patrick, *Makromol. Chem.*, 1961, **43**, 248.
[32] A. M. North, *Makromol. Chem.*, 1961, **49**, 241.
[33] T. B. Grimley, *Trans. Faraday Soc.*, 1961, **57**, 1974.
[34] S. W. Benson and A. M. North, *J. Amer. Chem. Soc.*, 1962, **84**, 935.
[35] R. D. Burkhart, 146th meeting Amer. Chem. Soc., Denver, 1964.

which determines the overall rate of reaction (at least in the case of polymerisations and copolymerisations of methyl methacrylate).[25–29]

A second approach to the kinetic problem is to consider only the translational motion of the active end, but to ascribe to it the low diffusion coefficient of the whole polymer molecule.[25,36] This method seriously underestimates the mobility of the ends of the radical chain at small reactant–reactant separations.

A third approach is to consider the overall pre-chemical diffusive processes as translational diffusion of the macroradicals modified by the probability that both reactant chain ends are in positions "accessible" to segments of other polymeric molecules.[37]

Of these three ideas, only the first can be easily fitted to observations of the way in which the reaction rate depends on the polymer chain "stiffness". This stiffness can be varied by the use of different side groups,[27] by the introduction of cyclic co-monomers,[29] or by reducing the temperature.[38,39] On the other hand the second approach also seems to predict a reasonable value for the reaction rate constant.

Revised kinetic equations have been published for diffusion-controlled copolymerisations,[28,29,40] in which the termination rate depends on the composition of the whole chain, not just the chain end.

4. Ion-combination Reactions

The recent development of techniques for the study of very fast reactions has resulted in the evaluation of rate constants for diffusion-controlled ion-combination reactions.[41,42] The most comprehensive studies have dealt with acid–base recombination processes, and the rate constants for sixty-four such reactions have been listed in a recent review by Eigen.[43]

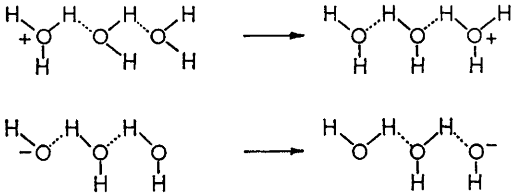
(a) Acid–Base Recombinations.—The most common, and indeed the most interesting, acid–base reaction is the combination of the solvated proton with the defect proton (solvated OH^- ion). This reaction has[44] one of the largest rate constants known for liquid-phase reactions, $1{\cdot}4 \times 10^{11}$ l.mole^{-1} sec.$^{-1}$ at 25°c. Perhaps even more surprising at first sight is the fact that the rate constant is even larger in ice ($8{\cdot}6 \times 10^{12}$ l.mole^{-1} sec.$^{-1}$ at $-10°$).[45]

The reason for these values, as for the high apparent ionic mobilities measured by conductivity experiments, lies in the tetrahedral hydrogen-

[36] P. E. M. Allen and C. R. Patrick, *Makromol. Chem.*, 1964, **72**, 106.
[37] A. M. North, *Makromol. Chem.*, 1965, **83**, 15.
[38] J. Hughes and A. M. North, *Trans. Faraday Soc.*, 1964, **60**, 960.
[39] J. Hughes and A. M. North, *Proc. Chem. Soc.*, 1964, 404.
[40] A. M. North, *Polymer*, 1963, **4**, 134.
[41] M. Eigen and J. S. Johnson, *Ann. Rev. Phys. Chem.*, 1960, **11**, 307.
[42] M. Eigen, *Z. Elektrochem.*, 1963, **67**, 753.
[43] M. Eigen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 1.
[44] M. Eigen and L. de Mäyer, *Z. Elektrochem.*, 1955, **59**, 986.
[45] M. Eigen and L. de Mäyer, *Proc. Roy. Soc.*, 1958, *A*, **247**, 505.

bonded structure of ice and water. Proton and hydroxyl ion migration does not occur by transport of specific identifiable ions, but involves a rapid rearrangement of bonds (see Scheme 1).

SCHEME 1



The more perfect structure of the ice lattice facilitates this type of transfer. These structural phenomena influence the effective collision diameter as well as the reactant mobilities. Indeed if the measured ionic mobilities are substituted in the diffusion-controlled rate equation, agreement with experiment is obtained only on the assumption that the collision sphere in water extends over three or four hydrogen bridges.

Comparably large rate constants (*ca.* 10^{11} l.mole^{-1} sec.$^{-1}$) are exhibited by certain other reactions involving recombination of the hydrated proton with a conjugate base. Into this context fall the familiar reactions

$H^+ + HSO_4^-$ ($k = 1 \times 10^{11}$ l.mole^{-1} sec.$^{-1}$ at 20°)[46]
$H^+ + F^-$ ($k = 1 \times 10^{11}$ l.mole^{-1} sec.$^{-1}$ at 25°)[47]
$H^+ + CH_3{\cdot}CO_2^-$ (k = 4 to 9 $\times 10^{10}$ l.mole^{-1} sec.$^{-1}$ at 25°)[48]
$H^+ + NH_3$ ($k = 4{\cdot}3 \times 10^{10}$ l.mole^{-1} sec.$^{-1}$ at 20°)[49]

Rather interestingly, the hydrogen bond-forming dimerisation of carboxylic acids in non-polar solvents also occurs with a large rate constant. Thus the association of benzoic acid in several solvents has been studied by use of ultrasonic irradiation,[50] and the dimerisation rate constant in carbon tetrachloride at 20° is $6{\cdot}8 \times 10^{10}$ l.mole^{-1} sec.$^{-1}$. Also, the formation of the hydrogen bond in the dimerisation of hexanolactam occurs with a rate constant for formation of the first hydrogen bond of 1×10^{10} l.mole^{-1} sec.$^{-1}$.[51]

The rates of reactions of the defect proton with its conjugate acids are, in general, slower than comparable proton–base reactions. Thus the recombination of NH_4^+ and OH^- has a rate constant $3{\cdot}4 \times 10^{10}$ l.mole^{-1} sec.$^{-1}$ at 25°.[52]

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[46] M. Eigen, G. Kurze, and K. Tamm, *Z. Elektrochem.*, 1953, **57**, 103.
[47] M. Eigen and K. Kustin, *J. Amer. Chem. Soc.*, 1960, **82**, 5952.
[48] J. Gimer and W. Vielstik, *Z. Elektrochem.*, 1960, **64**, 128.
[49] M. Eigen and J. Schoen, *Z. Elektrochem.*, 1955, **59**, 483.
[50] W. Maier, *J. Chim. phys.*, 1964, **61**, 239.
[51] K. Bergmann, M. Eigen, and L. de Mäyer, *Z. Elektrochem.*, 1963, **67**, 819.
[52] E. Grunwald, P. J. Jarabatsos, R. A. Kronhaut, and E. L. Purlee, *J. Chem. Phys.*, 1960, **33**, 556.

The influence of electrostatic interactions in protonations is not as large as might be inferred from the theoretical equations. The reason is that the H^+ adds on to an electron lone pair on the base, and repulsion effects due to excess of charges of similar sign are associated with more distant parts of the molecule.

An interesting class of diffusion-controlled reactions have recently been discovered with the advent of pulse radiolysis techniques.[53,54] These are the combination reactions of the solvated electron.

The hydrogen bridging in water does not form so beneficial a structure for these reactions, with the result that the reaction rate constants are slightly lower than those for the OH^- ion. Thus[42]

$$e^-_{aq} + H_3O^+ \rightarrow H\cdot + H_2O;\ k = 2{\cdot}4 \times 10^{10}\ \text{l.mole}^{-1}\ \text{sec.}^{-1}$$
$$e^-_{aq} + H_2PO_4^- \rightarrow H\cdot + HPO_4^{--};\ k \sim 10^7\ \text{l.mole}^{-1}\ \text{sec.}^{-1}$$

(b) Inorganic Exchange Reactions.—Many of the exchange reactions which take place in metal complexes or hydrates are extremely rapid, and have only recently been subjected to quantitative rate studies. While many of these rearrangements are unimolecular processes, a certain number of diffusion-controlled bimolecular reactions have been observed.

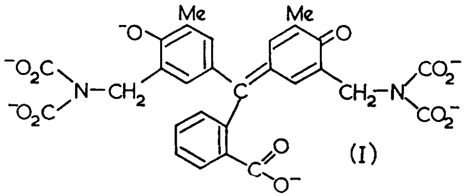
Nuclear magnetic resonance techniques have been used to evaluate rate constants for the formation of cadmium complexes:[54]

$$Cd^{++} + Br^- \rightarrow CdBr^+;\ k = 1{\cdot}4 \times 10^9\ \text{l.mole}^{-1}\ \text{sec.}^{-1}$$
$$CdBr^+ + Br^- \rightarrow CdBr_2;\ k = 1 \times 10^8\ \text{l.mole}^{-1}\ \text{sec.}^{-1}$$
$$CdBr_2 + Br^- \rightarrow CdBr_3^-;\ k = 2{\cdot}8 \times 10^7\ \text{l.mole}^{-1}\ \text{sec.}^{-1}$$

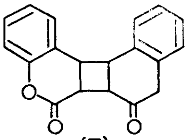
The effect of alteration in electrostatic interaction is clearly discernible in these three reaction rate constants. Lower ones have been recorded[55] for the recombination

$$Mg^{++} + X;\ k = 1{\cdot}6 \times 10^6\ \text{l.mole}^{-1}\ \text{sec.}^{-1}$$
$$Ca^{++} + X;\ k = 7 \times 10^8\ \text{l.mole}^{-1}\ \text{sec.}^{-1}$$

where X is a bis(dicarboxy trimethylamino)-derivative of fluorescein (I).



(I)



(II)

In this case the very large electrostatic attractions are overweighed by low ionic mobilities, and there is some doubt as to whether the reactions are

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[53] F. S. Dainton and D. B. Peterson, *Nature*, 1960, **186**, 878.

[54] F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc.*, 1962, *A*, **267**, 443.

[55] G. Czerlinski, H. Diebler, and M. Eigen, *Z. phys. Chem.* (*Frankfurt*), 1959, **19**, 246.

in fact diffusion-controlled. The bimolecular charge transfer of naphthacene anion is similar.[56]

5. The Quenching of Electronic Excited States

When a molecule has been energised into an electronically excited state in a condensed phase, there always exists the possibility of a radiative transition to the ground state. Non-radiative mechanisms of energy transfer must then be sufficiently rapid to take place during the lifetime of the excited states. As a general rule only "spin-forbidden" transitions (such as the radiative transition from a triplet excited state to a singlet ground state) provide excited states sufficiently long-lived for even the most rapid bimolecular processes to occur.

(a) Competitive Quenching Processes.—The importance of diffusive processes in determining the products (and quantum yield) of a photochemical reaction arises because of the competition between bimolecular quenching and unimolecular relaxation processes.

A simple example of the course of a chemical reaction depending on two competitive quenching processes is found in the photosensitised reductions of benzophenone by alcohols.[57–59] In this reaction the triplet state of benzophenone can either emit radiation, abstract a hydrogen atom from an alcohol to form the so-called ketyl radical,[60] or transfer energy to a quenching molecule.[61–62] If this transfer is exothermic, the reaction is extremely fast and is, in fact, diffusion-controlled. The quencher thus blocks the formation of ketyl radicals, and consequently the subsequent formation of diphenylmethanol. The photochemical reduction of anthraquinone can be quenched in the same way.[63] As would be expected for diffusion-controlled processes, the quenching efficiencies of compounds as different as penta-1,3-diene, methyl 2-naphthyl ketone, and azulene are the same.

Similar quenching of chemical change has been observed in *cis–trans* photo-isomerisations of azo-compounds and of stilbenes.[64,65]

Competitive processes of a rather different type have been observed in the photodimerisation of coumarin.[66] In this case the ground-state molecule quenches the excited state to form the dimer (II). When photo-

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[56] H. Linschitz and J. Eloranta, *Z. Elektrochem.*, 1960, **64**, 169.

[57] G. S. Hammond and R. P. Foss, *J. Phys. Chem.*, 1964, **68**, 3739.

[58] R. P. Foss, D. O. Cowan, and G. S. Hammond, *J. Phys. Chem.*, 1964, **68**, 3747.

[59] J. N. Pitts, H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, 1962, **66**, 2456.

[60] G. Porter and F. Wilkinson, *Proc. Roy. Soc.*, 1961, *A*, **264**, 1.

[61] G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, 1962, **66**, 1148.

[62] H. L. J. Backstrom and K. Sandros, *Acta Chem. Scand.*, 1958, **12**, 823; 1960, **14**, 48.

[63] F. Wilkinson, *J. Phys. Chem.*, 1962, **66**, 2569.

[64] S. Malkin and E. Fischer, *J. Phys. Chem.*, 1962, **66**, 2482.

[65] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, **86**, 3197.

[66] G. S. Hammond, C. A. Stout, and A. A. Lamola, *J. Amer. Chem. Soc.*, 1964, **86**, 3103.

sensitiser is absent, the reaction involves the excited singlet state. The dimerisation in alcohol leads to the *cis* adduct, but in very low yield since the quenching is much less rapid than the unimolecular relaxation. On the other hand photosensitisation by a molecule with a stable triplet state leads to the formation of triplet excited coumarin. The dimerisation now leads to *trans* dimer, which is obtained in good yields because of the slow competing unimolecular relaxation of the triplet state.

(b) The Rates of Bimolecular Quenching Reactions.—Experimental observations of quenching rates afford a critical examination of the validity of the diffusion-controlled rate equations.

A modification to these equations which has been very widely used is usually ascribed to Debye.[67] Because of the difficulty of measuring the diffusion coefficients of the very short-lived species involved, and of estimating the encounter radius, apparent simplification can be achieved by writing a Stokes–Einstein relationship for the combined diffusion coefficients, and then setting the encounter radius equal to the hydrodynamic diameter.

$$\text{If } D_A + D_B = \frac{2\boldsymbol{k}T}{3\,\pi\,\eta\,d_A} \text{ and } d_A = r_{AB} \quad \dots\dots\dots\dots \quad (13)$$

where η is the solution viscosity, $\boldsymbol{k}$ is Boltzmann's constant, d_A is a mean hydrodynamic diameter of the diffusing reactants, then

$$k = \frac{8\,\boldsymbol{R}T}{3 \times 10^3\eta} \text{ l.mole}^{-1}\text{ sec.}^{-1} \quad \dots\dots\dots \quad (14)$$

Although the approximations in this procedure are difficult to justify in the general case, the extreme simplicity of the relationship has led to its use.

The validity of this equation has been examined in a number of cases. The quenching of the phosphorescence of anthracene by oxygen has been measured in a variety of solvents.[68] The observed quenching constant was compared with values calculated on the basis of the Stokes–Einstein–Debye relationship (14), and also with values calculated using the Smoluchowski equation (5) with experimentally determined values for the diffusion coefficient of oxygen. Agreement was not good if the Stokes–Einstein substitution was used. This might be expected because the reactants are very different in size, and also because with the hydrogen-bonded solvents the macroscopic viscosity is not always a good measure of the resistance to molecular motion.

A more successful comparison between calculated and observed rate constants has been observed by Osborne and Porter for the quenching of triplet naphthalene by 1-iodonaphthalene.[69] In this case the reactants are

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[67] P. Debye, *Trans. Electrochem. Soc.*, 1942, **82**, 265.
[68] W. Ware, *J. Phys. Chem.*, 1957, **66**, 455.
[69] A. D. Osborne and G. Porter, 6th Symp. Free Radicals, Cambridge, 1963.

similar in size. The agreement can be further improved if the Stokes–Einstein diffusion coefficient, $kT/6\pi\eta r$ is replaced by the value $kT/4\pi\eta r$ which is more relevant for small molecules.[70] Once again, however, the failure of the Stokes–Einstein relationship in long-chain liquids was apparent. Furthermore, measurements of the diffusion coefficients in isopropyl alcohol[71] showed that the Stokes–Einstein equation *underestimated* the diffusion coefficient by a factor of at least two.

Dubois and Van Hennert[72] have concluded that for reactants of similar size, equation (14) often gives a reasonable estimate of the quenching rate constant, although in general the estimate is low.

The large number of diffusion-controlled quenching rate constants reported illustrate two points.[60,73–78] One is that reactants of quite different chemical composition exhibit similar rate constants, a feature of all diffusion-controlled processes, and the other is that planar molecules appear to diffuse faster than might be expected from their radius of gyration.[71]

(c) Further Rate Equations for Quenching Processes.—An outstanding feature of quenching processes is that any reference reactant molecule is only available for bimolecular quenching for a finite time before unimolecular relaxation occurs. The conventional equations for diffusion-controlled reactions should then be modified to take this into account.

The fact that the lifetime of the excited state decreases with increasing quencher concentration implies that the rate constant for the process should increase from the "long-time value" to the "short-time value" as the quencher concentration is raised. Such an effect was predicted theoretically by Noyes,[79] and had in fact been observed earlier in the quenching of anthracene by carbon tetrabromide[80] and of uranin by aniline.[81]

The diffusion equations relevant to quenching processes have been examined further by Yguerabide, Dillon, and Burton.[82] These authors calculate the effects of diffusion subsequent to an initial condition, and also during steady-state conditions, and suggest that the steady-state constant be written as

$$k = \frac{4\,\pi\, r_{\mathrm{AB}} D_{\mathrm{AB}} N}{10^3} \left\{ 1 + \frac{r_{\mathrm{AB}}}{(2 D_{\mathrm{AB}} \tau_0)^{\frac{1}{2}}} \right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

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[70] E. McGlaughlin, *Trans. Faraday Soc.*, 1959, **55**, 28.

[71] A. D. Osborne, H. J. V. Tyrrell, and M. Zaman, *Trans. Faraday Soc.*, 1964, **60**, 395.

[72] J. T. Dubois and R. L. Van Hennert, *J. Chem. Phys.*, 1964, **40**, 923.

[73] G. Porter and M. R. Wright, *Discuss. Faraday Soc.*, 1959, **27**, 18.

[74] W. Ware, *J. Chem. Phys.*, 1962, **37**, 923.

[75] G. Jackson, R. Livingston, and A. C. Pugh, *Trans. Faraday Soc.*, 1960, **56**, 1635.

[76] H. L. J. Backstrom and K. Sandros, *Acta. Chem. Scand.*, 1958, **12**, 823.

[77] A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, 1956, **52**, 1042.

[78] G. R. Haugen and W. H. Melhuish, *Trans. Faraday Soc.*, 1964, **60**, 386.

[79] R. M. Noyes, *J. Amer. Chem. Soc.*, 1957, **79**, 551.

[80] E. J. Bowen and W. S. Metcalf, *Proc. Roy. Soc.*, 1951, *A*, **206**, 437.

[81] B. Williamson and V. K. La Mer, *J. Amer. Chem. Soc.*, 1948, **70**, 717.

[82] J. Yguerabide, M. A. Dillon, and M. Burton, *J. Chem. Phys.*, 1964, **40**, 3040.

where τ_0 is the lifetime of the excited state in the absence of quencher and N is Avogadro's number.

Such an equation has been applied successfully to the quenching of triplet *p*-terphenyl by carbon tetrachloride, for which the observed rate constant is $3{\cdot}6 \times 10^{10}$ l.mole^{-1} sec.$^{-1}$.[83]

6. Diffusive Separation of Reactive Moities

A wide class of competitive processes exists in which species (capable of reacting with each other) are formed in high local concentrations and must diffuse apart in order to react with some substrate. Because the diffusive processes in liquids tend to keep neighbouring molecules in proximity for periods which may be long compared with reaction times, the probability of mutual interaction of the original reactant partners may be quite large. Such effects are particularly important when two species, usually free radicals, are formed from a single reactant molecule (when the phenomenon is usually referred to as a "cage" effect) and when a high concentration of reactive ions or radicals are formed along the track of a quantum of high-energy radiation or of resulting ejected particles ("track" or "spur" effects).

(a) "Cage" Effects.—The concept of a solvent "cage" restricting the separation of two reactants was first introduced by Franck and Rabinowitch.[84] The picture of the "cage" need not involve only the surrounding nearest-neighbour solvent molecules, since even reactants which have diffused a finite distance apart in a solvent continuum are likely to reunite.[85]

The competing processes can be simplified to five major reactions (Scheme 2). In this scheme parentheses represent the caged species, I is the molecule capable of dissociation into radicals R·, S is the substrate, and P_1, P_2 are the products from radical–radical and radical–substrate reactions respectively. P_1 may, or may not, be the same as I.

SCHEME 2

$$\begin{array}{llll}
(1) & \mathrm{I} & \rightarrow (2\mathrm{R}\cdot) & k_\mathrm{I} \\
(2) & (2\mathrm{R}\cdot) & \rightarrow \mathrm{P}_1 & k'_\mathrm{r} \\
(3) & (2\mathrm{R}\cdot) + \mathrm{S} & \rightarrow \mathrm{R}\cdot + \mathrm{P}_2 & k'_\mathrm{s} \\
(4) & (2\mathrm{R}\cdot) & \rightarrow 2\mathrm{R}\cdot & k_\mathrm{D} \\
(5) & \mathrm{R}\cdot + \mathrm{S} & \rightarrow \mathrm{P}_2 & k_\mathrm{s}
\end{array}$$

The simplest kinetic analysis of these reactions assumes that a stationary-state concentration of all species is attained and that the rate constants are time-independent. Then

$$\frac{\mathrm{dP}_2}{\mathrm{d}t} = \frac{2k_\mathrm{I}\,[\mathrm{I}]\,(k_\mathrm{D} + k'_\mathrm{s}\,[\mathrm{S}])}{k'_\mathrm{r} + k_\mathrm{D} + k'_\mathrm{s}[\mathrm{S}]} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

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[83] C. R. Mullin, M. A. Dillon, and M. Burton, *J. Chem. Phys.*, 1964, **40**, 3053.

[84] J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, 1934, **30**, 120.

[85] R. M. Noyes, *J. Chem. Phys.*, 1950, **18**, 999.

If radicals escape from the "cage" mainly by the diffusive process rather than by reaction with substrate, $k_D \gg k'_S[s]$ and the rate of formation of P_2 is independent of the substrate concentration; the efficiency of this reaction (the fraction of radicals produced that react with substrate) will be less than unity only if P_1 yields radicals more slowly than I.

On the other hand, if reaction (3) is faster than the diffusive process, the rate of reaction does depend on the substrate concentration and on the competition between reactions (2) and (3). The efficiency will again be less than unity when P_2 is different from I, but in this case the efficiency will depend on the concentration of S. The former situation exists in the initiation of free-radical polymerisation (when the substrate S is monomer) although the classic paper[86] on cage effects in polymerisation dealt with the latter case.

A more rigorous treatment of these reactions, based on the molecular-pair-reactivity approach, has been formulated by Noyes.[87] In this case attention is paid to the dependence of the diffusion-controlled rate constants on the lifetime of the reactants, and general expressions are presented for the efficiency of the radical–substrate reaction. These expressions involve certain parameters not discussed in section 2, and a considerable amount of algebraic manipulation may be involved in their use.

A rather simpler approach to photo- and thermal dissociation has also been presented by Noyes.[88] In this theory the solvent is treated as a continuum, and the probability that two atoms (or radicals) diffuse together after dissociation is calculated from the excess of kinetic energy of the separating species and the viscous drag exerted by the solvent. The equations have been found to predict quantum yields for halogen dissociation in solution when fission is caused by the absorption of light of energy more than 30 kcal. mole^{-1} in excess of that required for dissociation. When the calculated separation of the fragments is of the order of a molecular diameter,[89] or when solvents of high macroscopic viscosity are employed,[90] there is only a poor correlation between theory and experiment. There is no clear evidence, however, of a sharp critical distance (corresponding to a "cage radius") at which quantum yields alter from less than to more than calculated values.

Some interesting phenomena pertaining to "cage effects" have been studied by Szwarc and his co-workers. They have shown,[91] for example, that the probability of recombination of methyl radicals is larger when they are formed from azomethane (and separated only by a small N_2 molecule) than when they are formed from acetyl peroxide. However the use of light with excess of energy did not lower the probability of "cage" re-

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[86] M. S. Matheson, *J. Chem. Phys.*, 1945, **13**, 584.
[87] R. M. Noyes, *J. Phys. Chem.*, 1961, **65**, 763.
[88] R. M. Noyes, *Z. Elektrochem.*, 1960, **64**, 153.
[89] L. F. Meadows and R. M. Noyes, *J. Amer. Chem. Soc.*, 1960, **82**, 1872.
[90] D. Booth and R. M. Noyes, *J. Amer. Chem. Soc.*, 1960, **82**, 935.
[91] L. Herk, M. Feld, and M. Szwarc, *J. Amer. Chem. Soc.*, 1961, **83**, 2998.

combination in the case of the photolysis of azomethane. The difference between this and the dissociation of halogen molecules[89] may be due to the localisation of kinetic energy on the nitrogen, or to the relatively low mass of the methyl radicals compared with that of the solvent molecules. Attempts to modify the combination–disproportionation ratio in the termination reactions of ethyl radicals by using the "cage" to hinder radical rotation and reorientation have proved successful,[92] although reasons for a temperature–dependence of this ratio remain obscure.

It has also been shown[91] that methyl radicals stand a greater chance of "escaping" from the "cage" than the larger ethyl radicals.

Hammond and his co-workers[93–95] have published several studies of cage effects in the decomposition of azo-compounds. Perhaps one of the most ingenious experiments was an attempt to reduce the amount of cage recombination by forming the radicals with parallel spins.[96] This was achieved by inducing the decomposition of the azo-compound with an excited triplet-state photosensitiser. The triplet-state sensitiser formed triplet azo-compound, which then dissociates. The efficiency of cage-recombination was then a measure of the competitive processes, spin inversion or diffusive escape from the "cage". It was found that spin inversion was the more rapid in the case of azo-1-cyanocyclohexane, but not in the case of *N*-(1-cyanocyclohexyl)pentamethyleneketeneimine.

"Cage" effects are important in the decomposition of acyl and related peroxides, since the radicals initially formed can decompose further to lose CO_2. If the secondary fission is rapid compared with diffusion, any ester formed in the system must be formed in a "cage" reaction. Observations of ester formation in this type of reaction have been made on a wide variety of systems, key references to which can be found in the papers of Bevington,[97–99] Szwarc,[91,92] De Tar,[100–102] and their co-workers.

Although these phenomena are commonly considered to be characteristic of the liquid phase, they are also exhibited in compressed gases.[17]

(b) "Spur" Effects.—When a quantum (or particle) of high-energy radiation enters a condensed phase, the energy is ultimately localised in a track (possibly branched) 20—30 Å in diameter.[103] The formation and reaction of high local concentrations of excited species or radicals in this region, and their diffusion to substrate molecules in other regions of the

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[92] P. S. Dixon, A. P. Stefani, and M. Szwarc, *J. Amer. Chem. Soc.*, 1963, **85**, 2551, 3344.
[93] G. S. Hammond and R. C. Newman, *J. Amer. Chem. Soc.*, 1963, **85**, 1501.
[94] H. P. Waits and G. S. Hammond, *J. Amer. Chem. Soc.*, 1964, **86**, 1911.
[95] G. S. Hammond and J. R. Fox, *J. Amer. Chem. Soc.*, 1964, **86**, 1918.
[96] G. S. Hammond and J. R. Fox, *J. Amer. Chem. Soc.*, 1964, **86**, 4031.
[97] J. C. Bevington and T. D. Lewis, *Trans. Faraday Soc.*, 1958, **54**, 1340.
[98] J. K. Allen and J. C. Bevington, *Polymer*, 1961, **2**, 265.
[99] J. C. Bevington, J. Toole, and L. Trossarelli, *Trans. Faraday Soc.*, 1958, **54**, 863.
[100] D. F. De Tar and D. V. Wells, *J. Amer. Chem. Soc.*, 1960, **82**, 5839.
[101] D. F. De Tar and R. C. Lamb, *J. Amer. Chem. Soc.*, 1959, **81**, 122.
[102] D. F. De Tar and C. Weiss, *J. Amer. Chem. Soc.*, 1957, **79**, 3041.
[103] J. L. Magee, *Ann. Rev. Nucl. Sci.*, 1953, **3**, 171.

system, constitutes a series of competitive processes similar to those encountered in "cage" phenomena. In this case, however, both the geometry of the system and the reactant concentration in the "formation-zone" are much more complicated functions of the reaction conditions.

Despite the complexity of the problem, it is still possible to set up Fickian diffusion equations for specific boundary (or geometrical) conditions. Indeed the problem has much in common with the photochemical space intermittency effect mentioned previously.[13]

A simple, but general, model of these geometrical effects was first considered by Magee.[104] This featured expanding tracks of cylindrical symmetry and definite volume, with a discontinuity in the reactant concentration at the track boundary. With these conditions it is possible to obtain closed-form solutions of the diffusion–recombination differential equations.

The mathematical aspect of these calculations has become increasingly complex as successive authors[105] have sought to add further geometrical rigour or generality to the original Magee model. Thus, solutions have also been obtained for the case when the original cylindrical "track" contains randomly placed spherically symmetrical side "spurs".[106,107] Furthermore, just as in the case of diffusion-controlled reactions discussed in section 2, mathematical recognition must be made of the fact that a large degree of correlation may exist between the movements of the different reactants.[108,82]

The general physical significance of these calculations is the same as in the photochemical space intermittency experiment. It is that under what are called low-background conditions, the spurs are widely spaced (compared with the mean diffusive displacement of the reactants) and contain reactant concentrations much higher than the average for the whole system. Then the yield is the sum of the chemical changes in the individual spurs and is proportional to the dose. On the other hand, under so-called high-background conditions, the spurs are close together (compared with the mean diffusive displacement of the reactant) and contain reactant concentrations close to the bulk average. The kinetics are then similar to those of photochemistry, and in the case of radical reactions with bimolecular termination the yield will depend on the square-root of the intensity.

The theoretical equations have been applied[108] to the irradiation of water with electrons,[109] and the reasonable value 5×10^{10} l.mole^{-1} sec.$^{-1}$ obtained for the radical recombination rate constant.

7. Reactions, Normally Chemically Controlled, in Viscous Media

Any liquid-phase bimolecular chemical reaction, unless it is ridiculously slow at the temperature under consideration, can become diffusion-

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[104] J. L. Magee, *J. Amer. Chem. Soc.*, 1951, **73**, 3270.
[105] A. Kuppermann and G. G. Belford, *J. Chem. Phys.*, 1962, **36**, 1412, 1427.
[106] A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, 1953, **21**, 1080.
[107] A. H. Samuel, *J. Phys. Chem.*, 1962, **66**, 242.
[108] L. Monchick, J. L. Magee, and A. H. Samuel, *J. Chem. Phys.*, 1957, **26**, 935.
[109] J. Rotblat and H. C. Sutton, *Proc. Roy. Soc.*, 1960, *A*, **255**, 490.

controlled if the viscosity of the system can be made sufficiently large. This is frequently achieved in one of three ways; by the application of very high pressures, or by carrying out the reaction in a gel or in a glass.

(a) Reactions at High Pressures.—When pressure is applied to a liquid-phase reaction, both the transport and the chemical steps may be quite markedly altered. Since these consecutive processes may be altered to different extents, indeed even in different directions, it does not necessarily follow that the step which is rate-determining at atmospheric pressure is still so under the high-pressure conditions.

Organic liquids show a roughly exponential rise in viscosity with increasing pressure, so that the rate of relative diffusion of two reactants decreases in the same fashion. If the rate of the chemical step increases with pressure (a negative activation volume) or decreases more slowly than diffusion, the diffusive process can become rate-determining, even for reactions with a high chemical activation energy. This phenomenon has been convincingly demonstrated by Hamann for the bimolecular etherification of ethyl bromide in branched-chain alcohols.[110] In this case the diffusion step becomes rate-determining at a solvent viscosity which agrees quite well with that calculated using Smoluchowski's equation.

The effect of pressure on polymerisations has been reviewed by Weale.[111] Individual rate constants are available only for styrene,[112] and the propagation rate increased (but did not become diffusion-controlled) up to 3000 kg.wt. cm.$^{-2}$. It seems, too, that transfer reactions are not diffusion-controlled up to pressures of 4000 atm.[113] Both of these processes would be expected to become diffusion-controlled at higher pressures (and viscosities).

(b) Reactions in Gels and Glasses.—Studies of reactions in gels have been confined mainly to those reactions which occur in the later (high conversion) stages of polymerisation. For a reaction such as the propagation of free-radical polymerisation to become diffusion-controlled, the smaller reactant (monomer in this case) would have to have a diffusion coefficient less than 10^{-10} cm.^{2} sec.$^{-1}$. The diffusivities of small molecules are often not as low as this, even in apparently solid polymer.

However in certain polymerisations carried to high conversions it is possible to assert with confidence that the propagation has become diffusion-controlled at some stage, since the polymerisation stops well short of 100% conversion. It has been found[114,115] that a correlation exists between the limiting conversion and temperature, and that 100% conver-

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[110] S. D. Hamann, *Trans. Faraday Soc.*, 1958, **54**, 507.
[111] K. E. Weale, *Quart. Rev.*, 1962, **16**, 267.
[112] A. E. Nicholson and R. G. W. Norrish, *Discuss Faraday Soc.*, 1956, **22**, 97, 104.
[113] A. C. Toohey and K. E. Weale, *Trans. Faraday Soc.*, 1962, **58**, 2446.
[114] G. V. Schulz, *Z. phys. Chem.* (*Frankfurt*), 1956, **8**, 290.
[115] G. M. Burnett and G. L. Duncan, *Makromol. Chem.*, 1962, **51**, 177.

sion can be achieved above the glass transition temperature of the polymer. Such evidence strongly favours the view that monomer molecules become completely immobilised in the glassy polymer, but not in the more flexible gel.

Determinations of the rate constant of propagation at high conversions[116,117] do in fact show a progressive decrease as complete conversion is approached.

It is interesting that polymerisation has been observed in supercooled glassy monomer, but not in crystalline monomer at the same temperature.[118] That some form of disorder or mobility is necessary for reaction in these very rigid systems is also shown by the fact that many reactions take place only during phase transitions in crystalline or glassy materials.[119]

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[116] P. Hayden and H. W. Melville, *J. Polymer Sci.*, 1960, **43**, 201.

[117] W. I. Bengough and H. W. Melville, *Proc. Roy. Soc.*, 1955, *A*, **230**, 429.

[118] Y. Amagi and A. Chapiro, *J. Chim. phys.*, 1962, 537.

[119] R. Bensasson, A. Dworkin, and R. Marx, *J. Polymer Sci., Part C, Symposia*, 1963, **4**, 881.