The value of γ is the maximum surface area of quartz which can be placed within the growth zone without changing the kinetics of the growth process. It was shown above that the rate was independent of the surface area in the growth zone provided that surface area was less than one-fifth the surface area of the quartz in the dissolving zone. For calculations where γ was required it was taken to be one-fifth the estimated area of the small particle nutrient in the dissolving zone. Since in conventional hydrothermal experiments the ratio of surface area in the growth zone to surface area in the dissolving zone is much less than one-fifth, the dissolving step is not rate determining.

With the above data by the use of eq. 5 and the appropriate rate and supersaturation values k was calculated to be between 10^{-3} and 10^{-4} sec.$^{-1}$ for the basal plane at 80% fill and 400°. The frequency factor under these conditions from eq. 8 was found to be between 10^{11} and 10^{12} which compares sensibly with frequency factors of from 10^{12} to 10^{14} for most gaseous and many liquid unimolecular reactions. The calculation of frequency factors and velocity constants for other conditions and other faces awaits further solubility data.

The nature of the rate-determining step may profitably be considered further at this time. The surface area experiments assuredly eliminate dissolving as the rate-determining step under ordinary conditions. The dependence of rate on the temperature of the growth region and the apparent validity of eq. 5 seem to indicate that the step occurs at or near the interface: saturated solution-growing crystal and that the crystallization is probably first order and unimolecular but this is by no means an unequivocal conclusion. The fact that the Arrhenius relation and eq. 5 are obeyed is, of course, not sufficient proof that the mechanism is simple. In crystal growth from solution it is generally assumed that both volume diffusion of solute and surface migration of adsorbed molecules can contribute to the observed rate. The differences in rates for the various faces observed in this study suggest the importance of surface migration but do not exclude diffusion. The possibility that transport is rate determining under certain conditions is being investigated by systematic variation of the baffle which in this work was held constant at 10% open area.

Acknowledgments.—A. J. Caporaso performed much of the experimental work for which thanks are due. G. T. Kohman, J. W. Nielsen and A. A. Ballman are to be thanked for many stimulating discussions and suggestions.

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[CONTRIBUTION FROM THE CHANDLER LABORATORY OF COLUMBIA UNIVERSITY]

Photochemical Space Intermittency. A Proposal for Measuring Diffusion Coefficients of Reactive Free Radicals

BY RICHARD M. NOYES[1]

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If photochemically produced radicals are destroyed by a second-order process and if a cell is illuminated with a pattern of light and dark areas, the average concentration of radicals in space is dependent not only upon the total incident illumination but also upon the sizes of individual light areas. This space intermittent effect is similar to the familiar use of a rotating sector to produce light intermittent in time, and it permits measurement of the average distance a radical diffuses during its lifetime. If quantum yields and rate constants are known for a particular system, it would be possible to measure diffusion coefficients of highly reactive short lived radical intermediates. These diffusion coefficients cannot be determined by conventional methods, but precise values would contribute greatly to a detailed theory of molecular behavior in liquids.

Introduction

Let the equation

$$X + X \longrightarrow X_2 \qquad (1)$$

represent a reaction between two identical chemical species in solution. If the species are so reactive that the rate is determined by their diffusion together, and if the average age of the species is sufficiently great (about 10^{-8} second under most conditions), Smoluchowski[2] has shown that the rate constant for reaction 1 in liter/mole sec. is given by

$$k = \frac{4\pi\rho DN}{1000} \qquad (2)$$

where

ρ = encounter diameter of X in cm.
D = diffusion coefficient of X in cm.^{2}/sec.
N = Avogadro's number

If both k and D were measured independently for a particular diffusion controlled reaction, substitution into equation 2 should indicate a value of ρ identical with the van der Waals diameter of X. However, the derivation of equation 2 is based on an application of Fick's laws of diffusion to a system of molecular dimensions. Because this application involves certain assumptions of undetermined reliability, an exact test of equation 2 is desirable.

(a) Equation 2 assumes X species can be treated as spherically symmetrical in their interactions with each other. This assumption is almost certainly valid for iodine atoms in solution but is not strictly valid for polyatomic species.

(b) The derivation assumes that individual diffusive displacements are small compared to ρ. If the magnitudes of these displacements are significant, equation 2 becomes[3]

$$k = \frac{12\pi\rho^2 DN}{1000(3\rho + \sigma)} \qquad (3)$$

where σ is the root-mean-square distance for diffu-

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(2) M. v. Smoluchowski, *Z. physik. Chem.*, **92**, 129 (1917).

(3) R. M. Noyes, THIS JOURNAL, **78**, 5486 (1956).

sive displacements. If diffusive displacements are comparable to molecular diameters, substitution of measured values of k and D into equation 2 would give a value of ρ *smaller* than the actual encounter diameter. The effect is not large, and for $\sigma = \rho$, the apparent ρ would be 75% of the value for infinitesimal σ.

(c) The derivation assumes that the solution can be treated as a continuum even at molecular dimensions. However, the existence of an X species at a certain point in space certainly predisposes the distribution of solvent molecules in the immediate vicinity. This distribution will be such as to make more probable the encounter of two X species once they have attained a certain minimum separation in which they are not yet in physical contact, and the effect will tend to make the ρ calculated from equation 2 *larger* than the van der Waals diameter of X. The effect was discussed by Rabinowitch,[4] but there has been no experimental verification.

(d) The derivation uses equations for diffusion under a concentration gradient into a stationary sink. The relative displacements of two molecules can indeed be treated mathematically by regarding one as fixed and letting the other move with twice the frequency. Apparently it has not been recognized previously that this mathematical device is not strictly valid for the present situation. Nonvalidity of the assumption will also tend to make ρ from equation 2 *larger* than the van der Waals diameter of X. We hope to develop a quantitative treatment of this effect in the near future.

Because of the uncertainties introduced by these assumptions, it seems desirable to obtain a rigorous test of equation 2. The recombination of iodine atoms in inert solvents seems to be a reaction well suited for such a test. They almost certainly recombine at every encounter without concern for orientation effects, and the van der Waals diameters of atomic species are generally well known. As a result of several measurements by different methods and in different laboratories, the rate constant k for reaction in carbon tetrachloride at 25° is known[5] with a probable uncertainty of less than 10%.

An independent measurement of the diffusion coefficient of *atoms* is not possible by any conventional method involving a macroscopic concentration gradient, but it has occurred to us that this quantity could be calculated from measurements with light that is intermittent in space.

The rotating sector technique to produce light that is intermittent in time has been used frequently[6] and has permitted measurement of rate constants for individual steps in several chain reactions.

Very little attention has been paid to the related problem of space intermittency. Burnett, Valentine and Melville[7] worked out the theory of effects from one-dimensional inhomogeneities in light intensity as a beam traverses an absorbing medium, and Jones and Melville[8] showed that the rate of a photochemical gas-phase polymerization could be influenced by the distance separating two parallel beams of light. Although their experiments demonstrate the effect of interest here, their system does not lend itself easily to a rigorous theoretical treatment.

The only other publication of which we are aware is a brief paragraph in which Dickinson[9] presented the basic ideas we develop here. Although he is said to have thought through more of the implications, we cannot find any evidence that they were ever written up.

The principle can be illustrated by a system illuminated with a pattern of light and dark areas so that 1% of the total volume is illuminated. If the light is absorbed by species like halogen molecules that can be dissociated to produce a photostationary concentration of radical fragments and if the individual light areas are so large that most fragments recombine in the same region in which they were formed, the average concentration of fragments in the whole system will be 1% of the concentration that would be obtained if it were illuminated homogeneously with light of the same intensity. However, if the individual light regions are so small that almost all fragments escape from the region in which they were formed, the situation will approach that of homogeneous illumination with light of 1% the intensity in an individual beam; the average concentration of radicals in the system will then be 10% of the value for homogeneous illumination at full intensity. The sizes of the regions for intermediate average fragment concentrations will involve dimensions of the order of the distance a fragment diffuses during its lifetime. This situation resembles the more familiar rotating sector situation for time intermittency where intermediate concentrations of fragments are observed for light flashes of the same order of magnitude as the lifetimes of individual fragments.

Formulation of Problem.—If a solution is illuminated with a pattern of sharply defined light and dark areas until a steady state distribution of radical fragments is attained, the local distribution is governed by Fick's second law of diffusion that

$$D\nabla^2 c + 2\phi q - 2kc^2 = \frac{\partial c}{\partial t} = 0 \text{ (in light)} \qquad (4)$$

$$D\nabla^2 c - 2kc^2 = \frac{\partial c}{\partial t} = 0 \text{ (in dark)} \qquad (5)$$

where

c = local concn. of radical fragments
D = diffusion coefficient for fragments
q = rate of local light absorption in illuminated area
ϕ = quantum yield for producing a pair of fragments that escape their original partners

The formulation assumes that the concentration of fragments is so low that D is constant throughout the system. It also assumes that even in the illuminated regions the fragments live long enough that

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[4] E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1225 (1937).

[5] H. Rosman and R. M. Noyes, THIS JOURNAL, **80**, 2410 (1958).

[6] For a review of the principles, see G. M. Burnett and H. W. Melville in S. L. Friess and A. Weissberger, "Technique of Organic Chemistry," Vol. VIII, Investigation of Rates and Mechanisms of Reactions," Interscience Publishers, New York, N. Y., 1953, pp. 133-168.

[7] G. M. Burnett, L. Valentine and H. W. Melville, *Trans. Faraday Soc.*, **45**, 960 (1949).

[8] T. T. Jones and H. W. Melville, *Proc. Roy. Soc.* (*London*), **A175**, 392 (1940).

[9] R. G. Dickinson in W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 203.

the rate constant k describes their limiting reactivity[10]; otherwise k would not be constant throughout the system.

Equations 4 and 5 are non-linear and cannot be solved in terms of known functions. In fact, the non-linearity is associated with the effect of interest, for a first-order destruction of fragments would give an average fragment concentration dependent only on the total illumination and independent of the sizes of individual light and dark areas. We have worked out numerical solutions for a range of situations encountered for two light patterns falling perpendicularly upon the flat window of a cell. In all of the following calculations, the cell is assumed to be thin enough that the beam is not greatly attenuated in traversing the cell so that the local rate of light absorption along a beam will never vary more than a few per cent. from the value half way through the cell.

The *zebra* pattern is the simplest of the two studied. It consists of alternate parallel light and dark strips covering the face of the whole cell. If the cell itself is sufficiently large, the mathematical solution involves only one dimension and equations 4 and 5 become

$$D\frac{d^2c}{dx^2} + 2\phi q - 2kc^2 = 0 \text{ (in light)} \qquad (6)$$

$$D\frac{d^2c}{dx^2} - 2kc^2 = 0 \text{ (in dark)} \qquad (7)$$

where x is a coördinate perpendicular to the strips. It is convenient to rewrite these equations in dimensionless variables similar to our previous treatment of a rather similar problem.[11]

$$\frac{d^2\gamma}{d\nu^2} = \gamma^2 - 1 \text{ (in light)} \qquad (8)$$

$$\frac{d^2\gamma}{d\nu^2} = \gamma^2 \text{ (in dark)} \qquad (9)$$

where

$$\gamma = \left(\frac{k}{\phi q}\right)^{1/2} c \qquad (10)$$

$$\nu = \left(\frac{4\phi qk}{D^2}\right)^{1/4} x \qquad (11)$$

In these equations, γ is a normalized concentration that would attain a value of unity for homogeneous illumination of the entire cell with light of the same intensity as that in the individual strips. Similarly, a value of unity for ν corresponds to a distance x equal to $1/\sqrt{2}$ times the root-mean-square distance that a fragment diffuses during an average lifetime in a solution under homogeneous illumination.

The *leopard* pattern consists of a two-dimensional grid of circular light areas with the remainder of the cell dark. The maximum symmetry possible is that of the typical honeycomb arrangement in which each illuminated area has six identical nearest neighbors, and the calculations have been carried out for this symmetry. If the origin is taken at the center of an illuminated area and if polar coordinates are used, equations 4 and 5 become

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dc}{dr}\right) + \frac{1}{r^2}\frac{d^2c}{d\theta^2} = \frac{2kc^2 - 2\phi q}{D} \text{ (in light)} \qquad (12)$$

$$= 2kc^2/D \text{ (in dark)} \qquad (13)$$

These equations also rearrange in terms of dimensionless variables and become

$$\frac{1}{\rho}\frac{d}{d\rho}\left(\rho\frac{d\gamma}{d\rho}\right) + \frac{1}{\rho^2}\frac{d^2\gamma}{d\theta^2} = \gamma^2 - 1 \text{ (in light)} \qquad (14)$$

$$= \gamma^2 \text{ (in dark)} \qquad (15)$$

where γ is given by equation 10 and where

$$\rho = \left(\frac{4\phi qk}{D^2}\right)^{1/4} r \qquad (16)$$

By the experimental methods discussed below, it is possible to determine the value of ν corresponding to a known x or the value of ρ corresponding to a known r. Then if q is measured also and if ϕ and k are known independently for the system of interest, the data permit evaluation of D.

Numerical Solutions.—Experimental measurements can give $\bar{\gamma}$, the ratio of the average concentration of fragments in the cell to the concentration that would be observed if the whole cell were illuminated homogeneously with the same intensity. For a sufficiently coarse pattern, $\bar{\gamma}$ will be the fraction of the cell face that is actually illuminated; for a finer pattern, with the same total incident light energy, $\bar{\gamma}$ will be greater. The effect is illustrated in Fig. 1 showing detailed calculations for three zebra patterns having the same ratio of light to dark areas but different widths of individual strips.

For purposes of comparison with experiment, the most useful quantity to report is probably not $\bar{\gamma}$ but $\bar{\gamma}/\bar{\gamma}_\infty$ where $\bar{\gamma}_\infty$ is the limiting $\bar{\gamma}$ for a very coarse pattern having the same fraction of the cell illuminated.

A number of zebra and leopard patterns were chosen to represent situations of greatest potential interest, and numerical solutions were obtained with an IBM-650 digital computer generously made available through the Watson Scientific Computing Laboratory of the International Business Machines Corporation. The details of the computational procedures are described elsewhere.[12]

Table I summarizes the calculations for the zebra patterns. Here ν_L is half the width of a light strip and ν_D is half the width of a dark strip. Of course the ratio of dark to light areas is uniquely determined by ν_D/ν_L, and the computations for five values of this ratio cover a wide range of values of ν_L. The quantity reported is $\bar{\gamma}/\bar{\gamma}_\infty$ because this ratio best shows both the effect of changing strip width at constant total light incidence and also the effect of changing total light incidence at constant width of individual light stripes. Probably none of the values in Table I is uncertain by more than one unit in the last figure, and for many examples we can provide more significant figures on request. The last line in the table reports $\bar{\gamma}_\infty$ for each value of ν_D/ν_L in case it is desired to compare average fragment concentrations with those observed for homogeneous illumination.

Table II summarizes the calculations for the leopard patterns. Here ρ_L is the radius of a light spot, and f is the ratio of the separation of the centers of adjacent spots to the diameter of a single spot. The ratio of light to dark areas is uniquely

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(10) R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954).

(11) R. M. Noyes, THIS JOURNAL, **73**, 3039 (1951).

(12) R. M. Noyes, "Proceedings of Symposium on Digital Computing in the Chemical and Petrochemical Industries," International Business Machines Publication, 1958. A limited number of reprints are available from the author.

TABLE I

NUMERICAL SOLUTIONS FOR ZEBRA PATTERNS

Quantity	ν_L	$\nu_D/\nu_L = 1$	$\nu_D/\nu_L = 3$	$\nu_D/\nu_L = 8$	$\nu_D/\nu_L = 24$	$\nu_D/\nu_L = 99$
$\bar{\gamma}/\bar{\gamma}_\infty$	Infinitesimal	1.4142	2.0000	3.0000	5.0000	10.0000
	0.01	1.4142	2.0000	3.0000	5.0000	9.9989
	.02	1.4142	2.0000	3.0000	4.9999	9.9847
	.05	1.4142	2.0000	2.9999	4.9952	9.6782
	.1	1.4142	1.9999	2.9979	4.9438	8.5246
	.2	1.4141	1.9984	2.9748	4.6240	6.5313
	.5	1.4120	1.9645	2.7115	3.4830	3.9867
	1	1.3948	1.8227	2.2261	2.5166	2.6643
	2	1.3352	1.5752	1.7342	1.8240	1.8638
	5	1.2155	1.2910	1.3262	1.3426	1.3493
	10	1.1339	1.1592	1.1692	1.1735	1.1752
	20	1.0760	1.0835	1.0862	1.0873	1.0878
	50	1.0331	1.0344	1.0349	1.0351	1.0351
	100	1.0171	1.0174	1.0175	1.0176	1.0176
$\bar{\gamma}_\infty$		0.5000	0.2500	0.1111	0.0400	0.0100

determined by f regardless of the sizes of individual spots. Because the computational method[12] was an approximation procedure based on solutions for cylindrical symmetry, some of the values of $\bar{\gamma}/\bar{\gamma}_\infty$ for intermediate ρ_L may be uncertain by as much as 0.002. There seems little prospect that the precision of any experimental test will justify concern about this uncertainty.

TABLE II

NUMERICAL SOLUTIONS FOR LEOPARD PATTERNS

Quantity	ρ_L	$f = 2$	$f = 3$	$f = 5$
$\bar{\gamma}/\bar{\gamma}_\infty$	Infinitesimal	2.1002	3.1502	5.2504
	0.1	2.1002	3.1502	5.2502
	.2	2.1001	3.1498	5.2472
	.5	2.0972	3.1337	5.1566
	1	2.0673	2.9975	4.6002
	1.5	2.0037	2.7684	3.9222
	2	1.9227	2.5366	3.3800
	3	1.7771	2.1850	2.6785
	5	1.5725	1.7866	2.0137
	10	1.3374	1.4119	1.4812
	20	1.1813	1.2037	1.2228
	50	1.0738	1.0779	1.0812
	100	1.0366	1.0376	1.0385
$\bar{\gamma}_\infty$		0.226725	0.100767	0.036276

The data indicate that $\bar{\gamma}$ differs significantly from $\bar{\gamma}_\infty$ even when the smallest dimensions of individual light areas are many times the average distance a fragment diffuses during its lifetime under homogeneous illumination. This effect is similar to that observed with time intermittency[6] where the time average concentration differs from the slow sector limit even when individual flashes are many times the average lifetimes of fragments under homogeneous illumination. The effects arise because in regions that are dark or during times without illumination the few fragments present live so long that they contribute disproportionately to the averages.

Analytical Approximations.—Tables I and II contain numerical solutions that could be used to prepare plots of $\bar{\gamma}$ against log ν_L or log ρ_L at constant total illumination. These curves could then be fitted to experimental plots similar to the usual methods[6] for estimating average lifetimes from rotating sector data. However, for at least the simplest case rotating sector curves can be described analytically in terms of known functions, and this analytical formulation is sometimes useful for making calculations and estimating the accuracy of experimental data.[5] We have therefore examined the numbers in Tables I and II in search of approximate analytical expressions that can be used for interpolation or extrapolation calculations. The choice of these functions is ultimately empirical, but it has been dictated by known solutions of the equations for special cases.

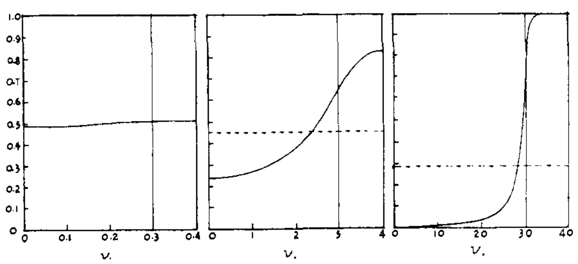

Fig. 1.—Fragment concentrations for three different zebra patterns with $\nu_D/\nu_L = 3$. Left figure: $\nu_L = 0.1$, $\bar{\gamma}$ (not indicated) = 0.4999. Middle figure: $\nu_L = 1$, $\bar{\gamma}$ (dashed line) = 0.4557. Right figure: $\nu_L = 10$, $\bar{\gamma}$ (dashed line) = 0.2898.

Zebra Approximations.—For the zebra pattern with a given ratio of ν_D/ν_L, the limiting $\bar{\gamma}$ at large ν_L is given by

$$\bar{\gamma}_\infty = \frac{\nu_L}{\nu_D + \nu_L} \tag{17}$$

and the limiting $\bar{\gamma}$ at small ν_L is given by

$$\bar{\gamma}_0 = \sqrt{\frac{\nu_L}{\nu_D + \nu_L}} \tag{18}$$

Of course

$$\bar{\gamma}_0/\bar{\gamma}_\infty = \sqrt{\frac{\nu_D + \nu_L}{\nu_L}} \tag{19}$$

and this is the limiting value given in Table I for infinitesimal ν_L.

For moderately large ν_L, the data in Table I can be fitted fairly well by the equation

$$\bar{\gamma}/\bar{\gamma}_\infty = 1 + \frac{2/\nu_L}{1 + 2.6716/\nu_D} - 0.24264/\nu_L \tag{20}$$

This expression is exact to much better than 0.001 for all $\nu_L \geq 10$, and even at $\nu_L = 2$ it is good to better than 0.005 except for $\nu_D/\nu_L = 1$. It begins to fail rather badly for smaller ν_L.

We failed in a half-hearted attempt to find a good empirical expression to fit the data of Table I at small ν_L. As is indicated by the discussion below, this region will be difficult to study experimentally, and the utility of the method probably will depend chiefly on measurements made at values of ν_L where equation 20 is applicable.

Leopard Approximations.—For the leopard pattern with a given value of f, the limiting $\bar{\gamma}$ at large ρ_L is given by

$$\bar{\gamma}_\infty = \frac{\pi}{2\sqrt{3}f^2} = \frac{0.90689967}{f^2} \tag{21}$$

and the limiting $\bar{\gamma}$ at small ρ_L is given by

$$\bar{\gamma}_0 = \sqrt{\bar{\gamma}_\infty} = 0.95231280/f \tag{22}$$

Then

$$\bar{\gamma}_0/\bar{\gamma}_\infty = 1.05007514 \tag{23}$$

This is the value given in Table II for negligible ρ_L

For large ρ_L, the data in Table II can be approximated by the purely empirical expression

$$\bar{\gamma}/\bar{\gamma}_\infty = 1 + \frac{3.650}{\rho_L} + \frac{29.03}{\rho_L^2} - \frac{105.5}{\rho_L^3} + \cdot \frac{0.5957/\rho_L}{1 + 0.05625\rho_L^2}\left(f - \frac{4.96\rho_L}{f}\right) \quad (24)$$

This expression is valid to 0.02 for $\rho_L = 10$ and to 0.04 for $\rho_L = 5$; it is not even an approximate solution for small values of ρ_L and has not been tested for applicability to f values outside of the extremes of 2 and 5 calculated in this work.

Experimental Feasibility

If this paper is to represent anything except a mathematical exercise, we must indicate the possibility of measuring the effect discussed. We have already shown[13] that the rate of isotopic exchange between iodine and *trans*-diiodoethylene is proportional to the concentration of iodine atoms in a solution. If a cell were illuminated with successively finer patterns of light areas but with the same total amount of illumination, the rates of exchange could be used to give direct measures of $\bar{\gamma}/\bar{\gamma}_\infty$. The interpretation would, of course, require that the total illumination was indeed the same for the different patterns, and this point could be checked with a reaction like ferrioxalate decomposition[14] for which the quantum yield is independent of intensity.

An experimental test would require measurable effects with patterns that were not too fine to produce easily. For iodine in carbon tetrachloride at 25° and with light of 4358 Å. it seems well established[5] that $\phi = 0.14$ and $k = 7 \times 10^9$ liter/mole sec. Probably D is approximately 2×10^{-5} cm.^{2}/sec. and we have done considerable experimental work with q about 5×10^{-9} einstein/liter sec. For these conditions, $(D^2/4\phi qk)^{1/4} = 2 \times 10^{-3}$ cm. and this is the distance corresponding to unit values of ν and ρ. Although this distance seems rather small, the experimental effects are appreciable at values of ν_L and ρ_L corresponding to several units. Thus the data in Tables I and II indicate that the average atom concentration could be 50% greater than for a very coarse pattern if zebra light strips were about 0.016 cm. wide or if leopard spots were about 0.04 cm. in diameter.

The computations apply to a discontinuous transition between light and dark areas. Any fuzziness of the boundary will work unidirectionally to increase the average atom concentration, but we have not made even semi-quantitative estimates of magnitude. The distances computed above are great enough to avoid significant diffraction effects with visible light, but scattering along a light path can fuzz an initially sharp pattern. The cell must be thick enough that wall effects are not important but thin enough that the pattern will remain sharp. We believe that a thickness of several millimeters would provide a satisfactory compromise.

The measurements would be vitiated by any convection currents that carried iodine atoms from illuminated into dark areas. Good thermostating of any experiments would be imperative, and the energy absorbed from the light beam could not be enough to cause thermal density gradients. The intensity suggested corresponds to dissipation of light energy at the rate of about 3×10^{-7} cal./ml. sec. Even if there were no flow of energy between light and dark areas, it should be possible to perform an experiment before illuminated areas were heated as much as 0.001° and thermal energy is actually transported much more easily than the iodine atoms being studied. A good test for the importance of convection would be the ability of illumination with a coarse pattern to approach the limiting value of $\bar{\gamma}$ predicted from studies with homogeneous illumination. Another test would be whether the same results were obtained for a zebra pattern whether the strips were horizontal or vertical.

Except for this application to a convection test, the zebra pattern does not appear to be as useful as the leopard. Fragments will escape from a leopard spot of a given diameter more easily than from a zebra strip of the same width, and those that do escape from the spot will be less apt to recombine while still near the illuminated area. As Tables I and II show, effects produced by a fairly coarse leopard pattern are over twice as great as those produced by a zebra pattern involving illuminated areas of the same widths.

In summary, an experimental application appears to be somewhat difficult but probably feasible, and a successful application would provide valuable information for the detailed understanding of very fast molecular processes in liquid phase. We propose soon to initiate experiments at the University of Oregon.

Acknowledgments.—It is a pleasure to acknowledge the assistance of Mr. Jean-Paul Auffray who introduced me to the lore of programming and operating a digital computer.

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[14] C. A. Parker, *Proc. Roy. Soc.* (*London*), **220A**, 104 (1953); **235A**, 518 (1956).