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Citation: [The Journal of Chemical Physics](#) **10**, 440 (1942); doi: 10.1063/1.1723745

View online: <http://dx.doi.org/10.1063/1.1723745>

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The potential energy, V , may or may not be expressible in simple form. If the various integrals (P , P' , P'') cannot be handled directly, graphical or other numerical methods should be feasible. Satisfactory results may be obtained using Simpson's rule with points spaced at surprisingly large intervals.

This approximate method may even prove worthwhile in cases where the solution of the infinite determinant, Eq. (19), would lead to

exact results but is too laborious. The two methods complement one another; that of this section is convenient and accurate for large moments of inertia and high temperatures while the exact quantum mechanical methods are necessary and not too difficult with small moments of inertia and moderate temperatures.

We have enjoyed discussions of certain phases of this work with Dr. Bryce L. Crawford.

JULY, 1942

JOURNAL OF CHEMICAL PHYSICS

VOLUME 10

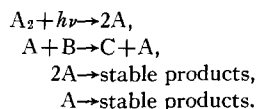
The Effect of Intermittent Light on a Chain Reaction with Bimolecular and Unimolecular Chain-Breaking Steps

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(Received April 6, 1942)

The effect of intermittent light, as produced by a rotating sector, has been considered for a chain reaction having the following mechanism:



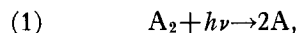
It has been shown how to calculate the reaction rate as a function of the sector speed for different values of a certain parameter which depends on the individual rate constants and the light intensity and gives, essentially, the relative importance of the bimolecular and unimolecular chain-breaking steps. The relationships have been exhibited graphically for the case in which one-fourth of the sector passes the light beam. These relationships may be reversed, making it possible to obtain the rate constants of the intermediate reactions from measurements with intermittent light.

WHEN a photochemical reaction proceeds by a chain mechanism it is frequently found that the rate is not directly proportional to I_{abs} , but depends on some more complicated function of I_{abs} , very commonly $I_{\text{abs}}^{1/2}$. Whenever this is the case we may find a valuable aid in the study of the reaction in intermittent light, produced by means of a rotating sector. Now let us suppose the $I_{\text{abs}}^{1/2}$ law holds. If the sector is run very slowly, this is equivalent to illuminating the system a fraction f of the total time, and the rate of reaction (per unit of the *total* time elapsed), will be proportional to $I_{\text{abs}}^{1/2}f$. On the other hand, using a very fast sector is equivalent to cutting

down the light intensity to the fraction f , and the rate will be proportional to $I_{\text{abs}}^{1/2}f^{1/2}$, which, since f is less than 1, is larger than the rate for slow sector speed. The sector speed at which the change takes place is an indication of the duration in time of the chain τ , or, what amounts to the same thing, the average lifetime of the chain-carrying radical or atom.

When using a rotating sector, it is convenient to have a sector with fixed sector fraction and to vary the speed of the sector. We are then interested in finding the rate of reaction in terms of the sector speed and the rate constants of the intermediate steps. The theoretical solution of

this problem has been completely worked out by Dickinson¹ for the following reaction scheme



In this scheme A is a free radical or atom which carries the chain. A reacts with B to give the final product, or products, symbolized by C, in a reaction (which may take place in two or more steps) in which A is regenerated. Reaction (3) is the chain-breaking step. Variations of this scheme are readily handled. For example, A₂ may be the same as B, and if different radicals are formed, only one of which takes part in the chain, this is also easily taken care of.

TABLE I. Notation.

A, B, C, symbols for chemical substances
A, B, C, concentrations of A, B, C
\bar{A} , \bar{A}_l , \bar{A}_d , average value of A, average during illuminated period, average during dark period, respectively
A_s' , see Eq. (9)
b, see Eq. (15) (b_0 , see Eq. (4))
f, "sector fraction" (fraction of the sector permitting light to pass)
I_{abs} , light absorbed per unit volume per unit time
K, over-all rate constant of the reacting substance; is the average of $-(dB/dt)/B$, averaged over total time run has gone on, including any unilluminated periods
k_1 , probability that absorption of photon results in production of free radicals
k_2 , k_3 , etc., rate constants of similarly numbered reactions
t_l , time of illumination per flash
t_d , time of darkness between flashes
γ , see Eq. (8)
δ , see Eq. (11)
ρ , see Eq. (14) (ρ_0 , see Eq. (6))
ρ_∞ , value of ρ for very fast sector
τ , "chain-time" (average lifetime of chain carrying radicals)
Subscripts on A, K, τ , ρ :
s, refers to steady state conditions under continuous illumination (lack of subscript indicates quantity is a function of sector speed)
0, refers to reaction scheme consisting of reactions (1), (2), (3) [lack of subscript indicates quantity refers to scheme consisting of reactions (1), (2), (3), (4)]

¹ R. G. Dickinson, Stanford Photochemistry Conference, 1938. See W. A. Noyes, Jr., and P. A. Leighton, *The Photochemistry of Gases* (Reinhold Publishing Company, New York, 1941), pp. 202 ff.

Application of the steady state method gives in the case of *continuous* illumination, for the schemes consisting of reactions (1)–(3), the following expression for the concentration of A

$$A_{s,0} = (k_1 I_{\text{abs}} / k_3)^{1/2} \quad (1)$$

with the over-all rate constant of the reacting substance B (calculated as for a unimolecular reaction) given by

$$K_{s,0} = -(dB/dt)/B = k_2 A_{s,0} = k_2 (k_1 I_{\text{abs}} / k_3)^{1/2}. \quad (2)$$

The rate of destruction of A is $2k_3 A^2$, so that the chance of destruction of a particular A per unit time is $2k_3 A$, and the average lifetime (i.e., the chain-time) at the steady state with continuous irradiation is given by

$$\tau_0 = (2k_3 A_{s,0})^{-1} = \frac{1}{2} (k_1 k_3 I_{\text{abs}})^{-1/2}. \quad (3)$$

It is found that with given sector fraction the over-all rate constant in intermittent light K_0 is a function of only one parameter, which gives essentially the sector speed, namely,

$$b_0 = t_l / \tau_0 = 2t_l k_3 A_{s,0} = 2t_l (k_1 k_3 I_{\text{abs}})^{1/2}. \quad (4)$$

We can refer to Eq. (2) and write this in the form

$$b_0 = 2t_l K_{s,0} (k_3^{1/2} / k_2) k_3^{1/2}, \quad (5)$$

where $k_3^{1/2} / k_2$ can be considered known, having been experimentally determined from Eq. (2) (assuming k_1 is known or can be estimated). It is then convenient to plot the ratio

$$\rho_0 = 2K_0 / K_{s,0}, \quad (6)$$

against $\log (t_l K_{s,0} k_3^{1/2} / k_2)$. The shape of this curve should theoretically be definitely fixed. Since ρ_0 is, theoretically, a known function of b_0 , the curve can be used to find the value of b_0 for which $t_l K_{s,0} k_3^{1/2} / k_2$ has a given value. Equation (5) can then be used to find k_3 ; this possibility of the determination of the individual rate constants is the great advantage of the use of the rotating sector.

However, the results of experiments on acetaldehyde performed recently in our laboratory indicate that the square-root law for the intensity, as expressed by Eq. (2), does not hold precisely, and it appears necessary to consider at least one other chain-breaking step, namely

a unimolecular one.

(4) $A \rightarrow$ stable products.

The differential equations for this more complicated type of mechanism have been considered by Briers and Chapman² but their calculations are not cast into a form which is readily applicable to our experimental results. It, therefore, seemed that it would be worthwhile to consider this case, following the method outlined by Dickinson, and to present the results in a form which can be readily applied, not only to our own experimental work, but to those of any investigators who, in the future, carry out measurements along these lines.

The introduction of reaction (4) results in a new equation for the steady state value of A , which is obtained by setting

$$dA/dt = 2k_1I_{\text{abs}} - 2k_3A^2 - k_4A = 0.$$

Solution of this equation gives

$$A_s = -\frac{k_4}{4k_3} + \left[\left(\frac{k_4}{4k_3} \right)^2 + \frac{k_1}{k_3} I_{\text{abs}} \right]^{1/2}, \quad (7)$$

which reduces to Eq. (1) if $k_4 = 0$. It is now found convenient to set

$$\gamma = k_4/4k_3 \quad (8)$$

and

$$A'_s = (\gamma^2 + A_{s,0}^2)^{1/2}, \quad (9)$$

which gives

$$A_s = A'_s - \gamma. \quad (10)$$

Further setting

$$\delta = \gamma/A'_s = (1 + A_{s,0}^2/\gamma^2)^{-1/2} \quad (11)$$

we have

$$A_s = \gamma(\delta^{-1} - 1) \quad (12a)$$

with the over-all rate constant given by

$$K_s = k_2A_s = k_2\gamma(\delta^{-1} - 1). \quad (12b)$$

Of interest, also, is the equation

$$K_s/K_{s,0} = (1 - \delta)^{1/2}/(1 + \delta)^{1/2} \quad (13)$$

derived from Eqs. (11), (12b), and (2).

The quantity δ is the parameter which determines the relative importance of the unimolecular and bimolecular chain-breaking steps. If γ is not too large compared to $A_{s,0}$, then, from Eq. (9),

² F. Briers and D. L. Chapman, J. Chem. Soc., p. 1802 (1928).

$A'_s = A_{s,0}$ (correct to terms containing γ , but not terms containing γ^2), whence we get from Eqs. (11) and (8), $2\delta \cong k_4/2k_3A_{s,0}$; that is, in words, 2δ is equal to the ratio of the rate of chain breaking by reaction (4) to the rate of chain breaking by reaction (3) if reaction (4) did not occur. At the same time, however, the rate of chain breaking by reaction (3) decreases, since $A_s \cong A_{s,0} - \gamma$. The decrease in the rate of chain breaking by reaction (3) is obviously in the ratio $\gamma/A_{s,0} \cong \delta$ to the original rate of chain breaking, and hence $2\delta - \delta = \delta$ gives the net relative increase in the rate of chain breaking, and the chain time will be decreased in the ratio $1/(1 + \delta)$, that is $\tau \cong \tau_0(1 + \delta)^{-1}$.

If we fix f , the sector factor, then it may be shown that for each possible value of δ from 0 to 1 (δ goes from 0 to 1 as γ goes from 0 to ∞) there is a relation, analogous to that between ρ_0 and b_0 , giving the ratio in this case,

$$\rho = 2K/K_s, \quad (14)$$

as a function of a parameter which depends on the sector speed. In this case the parameter used is

$$b = 2t_l k_3 A'_s = 2t_l k_3 (A_s + \gamma). \quad (15)$$

It is clear from the remarks following Eq. (13) that b continues to be equal to t_l/τ_0 if γ is small.

The shape of the curves in this case is obtained in a way which is quite analogous to the method used by Dickinson in dealing with the simpler mechanism. We note that during the light period

$$dA/dt = 2k_1I_{\text{abs}} - 2k_3A^2 - k_4A, \quad (16)$$

while during the dark period

$$dA/dt = -2k_3A^2 - k_4A. \quad (17)$$

Integration of these equations gives, after some rearrangement, for the light period

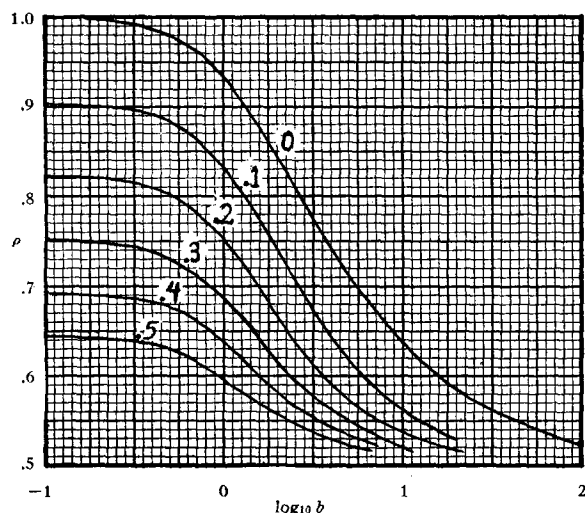
$$A = -\gamma + A'_s \tanh(2k_3tA'_s + C_l) \quad (18)$$

and for the dark period

$$A = 2\gamma(\exp(k_4t + C_d) - 1)^{-1}, \quad (19)$$

where C_l and C_d are integration constants.³ We

³ Equation (18) is obtained from Eq. (16) by use of B. O. Peirce, *A Short Table of Integrals* (Ginn and Company), formulas No. 67 and 654, afterwards solving for A . Similarly, Eq. (19) follows from Eq. (17) using Peirce, No. 34.

FIG. 1. The numbers on the curves indicate values of δ .

do not, of course, have a steady state, but the system will quickly reach a quasi-steady state in which the sequence of events through a light and a dark period is repeated in each cycle. In this situation the constants C_l and C_d can be eliminated by use of the fact that A at the end of a light (dark) period is equal to A at the beginning of a dark (light) period. One can then by integration through the light and dark periods, respectively, evaluate the average values, \bar{A}_l and \bar{A}_d . Now the apparent over-all rate of reaction will be proportional to

$$\bar{A} = (t_l \bar{A}_l + t_d \bar{A}_d)(t_l + t_d)^{-1}. \quad (20)$$

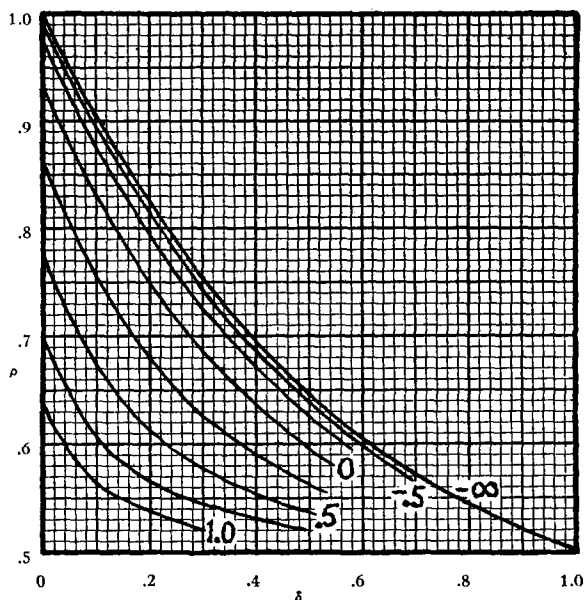
By evaluating \bar{A} the value of ρ is readily found as a function of b for any value of f . The mathematical details are given in the Appendix.

Experimentally it has proved very convenient to let $f = \frac{1}{4}$, and in Fig. 1, we show ρ as a function of b for various values of δ with $f = \frac{1}{4}$. Curves for intermediate values of δ may be found by interpolation, and to facilitate this we give in Fig. 2 curves for ρ as a function of δ with various fixed values of b .

The limiting value of ρ when K corresponds to a very fast sector speed depends, with fixed f , only on δ . This limiting value may be found by using the proportionality of K to \bar{A} and writing

$$\rho = 2\bar{A}/A_s. \quad (21)$$

A_s may be evaluated by using Eq. (7) and \bar{A} , for a very rapidly rotating sector, may be obtained by replacing I_{abs} in Eq. (7) by fI_{abs} .

FIG. 2. The numbers on the curves indicate values of $\log_{10} b$.

Expressing the k 's in terms of γ and $A_{s,0}$ we get for ρ in this case

$$\rho_\infty = \frac{2(\gamma^2 + fA_{s,0}^2)^{\frac{1}{2}} - 2\gamma}{(\gamma^2 + A_{s,0}^2)^{\frac{1}{2}} - \gamma} = \frac{2(f\delta^{-2} + 1 - f)^{\frac{1}{2}} - 2}{\delta^{-1} - 1}. \quad (22)$$

Equation (22) may be used to determine δ for any given conditions of illumination (δ , of course, depends on I_{abs}) by performing a continuous run and a run with a rapidly rotating sector under as nearly as possible identical experimental conditions. In doing this, one will naturally determine K_s , and then, knowing δ from Eq. (22) (or Fig. 2), $k_2\gamma$ may be determined from Eq. (12b). $k_2\gamma$, it should be noted, is a quantity depending only upon the reaction constants and the temperature. The quantity $k_3^{\frac{1}{2}}/k_2$ can clearly be obtained from Eq. (7) once $K_s = k_2A_s$ has been measured, if $k_2\gamma$ is known, if I_{abs} has been determined, and if k_1 is known or can be estimated. Having $k_2\gamma$ and $k_3^{\frac{1}{2}}/k_2$, the value of k_3 itself may be obtained by experiments at various sector speeds, much as in the case of the simpler reaction mechanism. After k_3 is thus determined, k_2 and k_4 may, of course, also be found.

It is again convenient to express b in terms of the observed steady state reaction rate K_s . From Eq. (15), remembering $K_s = k_2A_s$, we have

$$b = 2t_l(K_s + \gamma k_2)(k_3^{\frac{1}{2}}/k_2)k_3^{\frac{1}{2}}. \quad (23)$$

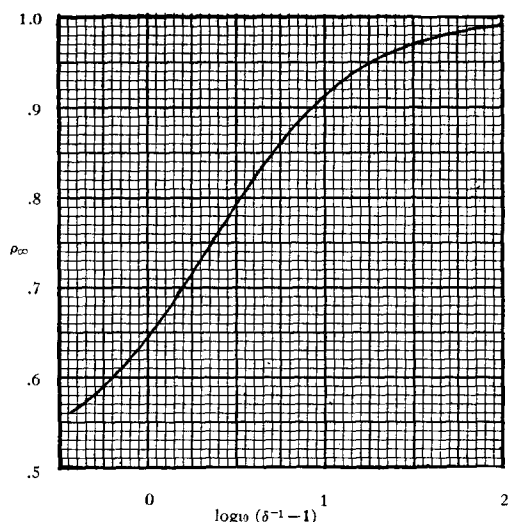


FIG. 3.

The procedure now is to plot ρ against $\log [t_l(K_s + \gamma k_2)(k_3^{1/2}/k_2)]$. Knowing ρ as a function of b , we find the value of b which corresponds to some particular value of $t_l(K_s + \gamma k_2)(k_3^{1/2}/k_2)$. Then we immediately find k_3 from Eq. (23). This, of course, assumes that δ is fixed and known. But δ does depend upon the light intensity, and it is sometimes difficult to keep the light intensity constant when experiments are performed over some interval of time. However, once $k_2\gamma$ is known δ can be readily found directly from the measured value of K_s by Eq. (12b). If the values of δ in a series of runs vary only slightly they may readily be reduced to a single value of δ by means of a set of curves such as is shown in Fig. 2.

It may be noted in closing that it may be worth while in studying a reaction to check the validity of the mechanism consisting of reactions (1)–(4) by making measurements with a very fast sector over a range of light intensities, thus varying δ . According to Eq. (22) ρ_∞ for fixed f depends only on δ . Therefore, we see from Eq. (12b) that the curve obtained by plotting $\log K_s$ against ρ_∞ should have a definite shape which can readily be calculated. It is given, for $f = \frac{1}{4}$, in Fig. 3.

APPENDIX—EVALUATION OF ρ AS A FUNCTION OF b

In using Eqs. (18) and (19) to evaluate A_l and A_d , we shall assume that $t=0$ at the beginning of a light

period, and that C_l and C_d are evaluated accordingly. Then we have

$$\bar{A}_l = t_l^{-1} \int_0^{t_l} A dt \quad (24)$$

and

$$\bar{A}_d = t_d^{-1} \int_{-t_d}^0 A dt. \quad (25)$$

Inserting Eq. (18) in Eq. (24) and using Peirce No. 448 we get

$$\bar{A}_l = -\gamma + \frac{1}{2k_2 t_l} \ln \frac{\cosh (2k_2 t_l A'_s + C_l)}{\cosh C_l}. \quad (26)$$

Expanding the cosh term in the numerator as the hyperbolic cosine of the sum of two arguments (Peirce No. 661) we get (using also Peirce No. 654 and noting Eq. (15))

$$\bar{A}_l = -\gamma + (2k_2 t_l)^{-1} \ln [\cosh b(1 + \tanh b \tanh C_l)]. \quad (27)$$

Now let us set $y = A/A'_s$ at $t=0$ and $x = A/A'_s$ at $t=t_l$ or $t=-t_d$ (A is the same at t_l and $-t_d$ in the quasi-stationary state). By setting $t=0$ in Eq. (18) we see, using Eq. (11), that $\tanh C_l = y + \delta$, while from Eqs. (11) and (15) we see that $2k_2 t_l = b\delta/\gamma$. Equation (27) becomes

$$\bar{A}_l = -\gamma + (\gamma/b\delta) \ln \{\cosh b[1 + (y + \delta) \tanh b]\}. \quad (28)$$

Evaluating \bar{A}_d from Eqs. (25) and (19), using Peirce No. 410, we get

$$\begin{aligned} \bar{A}_d &= -2\gamma + (2\gamma/k_2 t_d) \ln (x/y) \\ &= -2\gamma + (\gamma/b\delta)(t_l/t_d) \ln (x/y) \\ &= -2\gamma + (\gamma/b\delta)f(1-f)^{-1} \ln (x/y). \end{aligned} \quad (29)$$

\bar{A}_l and \bar{A}_d can be evaluated from Eqs. (28) and (29) if x and y can be found. The integration of Eqs. (16) and (17), which ultimately gives Eqs. (18) and (19), results, in the intermediate steps, in the following relations, which have been transformed with the aid of Eqs. (8), (11), and (15).

$$\tanh^{-1}(AA'_s^{-1} + \delta) = bt/t_l + C_l, \quad (30)$$

$$\ln [(A + 2\gamma)/A] = k_2 t + C_d. \quad (31)$$

Evaluating Eq. (30) at $t=t_l$ and at $t=0$ and subtracting the latter from the former

$$\tanh^{-1}(x + \delta) = b + \tanh^{-1}(y + \delta). \quad (32)$$

Taking the hyperbolic tangent of both sides of Eq. (32),

$$x + \delta = \frac{\tanh b + y + \delta}{1 + (y + \delta) \tanh b}. \quad (33)$$

Similarly, evaluating Eq. (31) at $t=0$ and $t=-t_d$, and subtracting the latter from the former, noticing at the same time that $k_2 t_d = 2b\delta t_l/t_l = 2b\delta(f^{-1} - 1)$

$$\ln \frac{(y + 2\delta)x}{y(x + 2\delta)} = 2b\delta(f^{-1} - 1), \quad (34)$$

or

$$\frac{(y + 2\delta)x}{y(x + 2\delta)} = \exp [2b\delta(f^{-1} - 1)]. \quad (35)$$

Simultaneous solution of Eqs. (33) and (35) gives x and y . These may now be used to evaluate \bar{A}_l and \bar{A}_d , and hence \bar{A} , which, together with Eq. (12a) gives ρ (Eq. (21)). It will be noticed that the factor γ appears both in \bar{A} and A_s . It will cancel out when the expression for ρ is formed, and so, for given f , the ratio ρ depends solely on δ and b .