0.034 mg./ml. per degree over the range from 15 to 50°, and a solubility of 1.35 mg./ml. at 20°. A tenfold reduction in the solubility can be obtained by the addition of an equal volume of ethanol to the water solution. Moreover the concentration of the thiosulfate in the supernatant can be decreased further by the presence of excess $(\mathrm{Nien_3})^{++}$. The fact that less than 0.1 mg./ml. of the thiosulfate ion remains in solution makes $\mathrm{Ni\ en_3(NO_3)_2}$ a very suitable reagent for quantitative precipitation of thiosulfate.[7] However, in the presence of sulfate, some $\mathrm{Ni\ en_3SO_4}$ is coprecipitated by alcohol from water solution, even though it is considerably more soluble than the thiosulfate. This precludes determination of the $\mathrm{Ni\ en_3S_2O_3}$ spectrophotometrically because of the absorption of the sulfate salt in ultraviolet,[9] but it does not interfere with the determination of the thiosulfate iodometrically.[10]

No attempt has been made in this study to ascertain the solubility of thiosulfate salts containing less than three molecules of ethylenediamine. The presence of additional ethylenediamine in small amounts was found to have no effect on the solubility in water at 20°. This seems to indicate that lower complexes were not being formed to influence the solubility data. Alcohol precipitation did not affect the composition of the triethylenediaminenickel thiosulfate, since no change in the O.D. or iodine equivalent was observed.

HOUSTON, TEXAS RECEIVED DECEMBER 20, 1950

[9] J. H. Gast and F. L. Aldrich, unpublished data.

[10] K. Arai, F. L. Aldrich and J. H. Gast, *Federation Proc.*, **9**, 146 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Wall Effects in Photochemically Induced Chain Reactions

BY RICHARD M. NOYES

A mathematical solution has been developed for the situation in which photochemically produced atoms or radicals may combine homogeneously at a rate which is second order in the reactants, and simultaneously may combine heterogeneously on the wall by a first order mechanism. The treatment suggests that the walls may serve to remove those atoms or radicals located in a shell of thickness $0.9(D^2/Qk)^{1/4}$ where D is the diffusion coefficient, Q is the rate of production of chains and k is the rate constant for homogeneous termination. If the volume of this shell is significant compared to the total volume of the system, the walls may be responsible for terminating an important fraction of the chains which are formed. It appears that even in vessels having diameters of several centimeters a very large fraction of photochemically produced chains may terminate on the wall unless the absorption of radiation is much greater than 10^{12} quanta/ml. sec. and/or the pressure is considerably in excess of atmospheric. The treatment also shows the applicability of kinetic data to determine the probability that an atom or radical striking the wall of the vessel will undergo recombination.

A great many gas-phase photochemical reactions involve chain mechanisms in which the active intermediates are atoms or radicals produced by the primary photochemical process. The chains may be terminated either homogeneously in the gas phase or heterogeneously on the walls of the vessel. The homogeneous termination reaction is usually second order in the active intermediate. The heterogeneous termination reaction is usually first order in the active intermediate except at elevated temperatures.[1] As a result of the heterogeneous termination a gradient will be established in the concentration of active intermediate.

The exact mathematical treatment of this situation is complex, and experimenters have frequently claimed that wall effects could be ignored but have failed to provide adequate justification. Rashevsky[2] has integrated the diffusion equation for a number of biological systems; however, he does not consider the combined generation and destruction of substances according to the kinetics discussed above. Hill[3] has made detailed calculations of a special case in the photochemical decomposition of acetone; but, because of mathematical difficulties, he only allowed first order kinetics for the homogeneous termination process in the region near the walls.

While we were considering the interpretation of data on some gas-phase chlorination reactions,[4] we developed some expressions which are of general applicability to photochemical reactions of this type. This treatment should directly apply to some systems, and at the very least it will provide criteria to determine whether more complicated calculations are necessary.

NOMENCLATURE

c = local concentration of atoms or radicals per ml.
k = rate constant for second-order homogeneous termination of chains in $(\text{atom/ml.})^{-1}$ sec.^{-1} (This is twice the customary rate constant based on number of collisions)
r = distance from center of reaction vessel in cm.
$t = cr$
$v = (8RT/\pi M)^{1/2}$ = average velocity of atom or radical in cm./sec.
D = diffusion coefficient of atom or radical in cm.^{2}/sec.
Q = rate of production of chains in atom/ml. sec. (This may be as great as twice the rate of absorption of radiation in quanta/ml. sec.)
α = recombination coefficient or probability that an atom or radical striking the wall will undergo recombination
β = fraction of chains terminating on the wall
$\gamma = \tau/\rho = (k/Q)^{1/2}c$ = ratio of local concentration to concentration which would prevail in absence of wall reaction
$\mu = v/4(D^2Qk)^{1/4}$
$\rho = (Qk/D^2)^{1/4}r$
$\sigma = \rho - \tau$
$\tau = (k^3/D^2Q)^{1/4}t$

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[1] K. E. Shuler and K. J. Laidler, *J. Chem. Phys.*, **17**, 1212 (1949).

[2] N. Rashevsky, "Mathematical Biophysics," Revised edition, University of Chicago Press, Chicago, Ill., 1948.

[3] T. L. Hill, *J. Chem. Phys.*, **17**, 1125 (1949).

[4] L. Fowler and J. J. Beaver, THIS JOURNAL, **73** in press; R. M. Noyes and L. Fowler, *ibid.*, **73**, 3043 (1951).

A subscript 0 refers to a value at the center of the reaction vessel. A subscript w refers to a value at or immediately adjacent to the wall of the reaction vessel.

Mathematical Development

Let us postulate a spherical flask throughout which radiation is being absorbed uniformly.[5] Let the rate of homogeneous production of atoms or radicals be Q atoms/ml. sec. If the absorption of each quantum produces two atoms in the primary process, as in the photo-dissociation of a halogen, then Q will be twice the rate of absorption of radiation in quanta/ml. sec. Finally, let the rate of disappearance of atoms by homogeneous recombination be kc^2, where c is the concentration of atoms per ml. and k is the rate constant for the disappearance of atoms. Since two atoms are removed in each effective collision, k is twice the rate constant which is usually calculated for such a process.

In most photochemical systems the concentrations of active intermediates are so small that they may be considered to be in a stationary state. Then by the use of Fick's second law we obtain

$$D\nabla^2 c + Q - kc^2 = 0 \qquad (1)$$

In this expression D is the diffusion coefficient of atoms in cm.^{2}/sec. Strictly speaking, D is a function of concentration and hence of position in the reaction vessel; however, the concentration of atoms is so small that changes do not affect diffusion properties of the medium, and secondary chemical reactions are usually so slow compared to diffusion that there are no significant gradients in any other concentrations. Therefore, we shall lose little in generality if we assume D to be constant throughout the system.

Since the system is spherically symmetrical, we can rewrite Equation (1) as

$$\frac{d^2c}{dr^2} + \frac{2dc}{rdr} + \frac{Q - kc^2}{D} = 0 \qquad (2)$$

where r is the distance of a point from the center of the reaction vessel. In order to solve this equation we have found it simplest to make the substitution $t = cr$. Equation (2) then becomes

$$\frac{d^2t}{dr^2} + \frac{Q}{D}r - \frac{kt^2}{Dr} = 0 \qquad (3)$$

For the sake of generality in the solution, it is convenient to define the dimensionless variables τ, ρ and γ by means of the equations presented in the Nomenclature section. It is apparent that at different positions in any specific reaction vessel values of τ, ρ and γ vary directly as t, r and c, respectively. In terms of the new variables Equation (3) may be rewritten as

$$\frac{d^2\tau}{d\rho^2} = \frac{\tau^2}{\rho} - \rho \qquad (4)$$

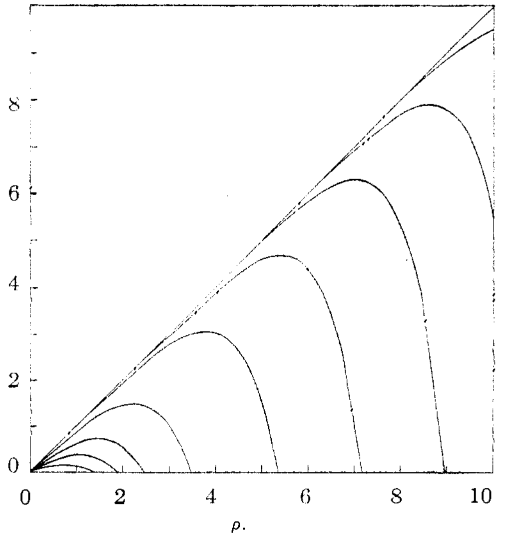

Fig. 1.—Dependence of τ and ρ. Curves correspond to values of $1 - \gamma_0$ of 0.7, 0.5, 0.3, 0.1, 0.01, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6} and 10^{-7}.

For the situation of interest this equation is satisfied by a family of curves the members of which can be identified by a single parameter. We have chosen to use the parameter γ_0, the value of γ when $\rho = 0$. It is apparent that γ_0 is the ratio of the concentration of atoms at the center of the flask to the concentration which would exist everywhere if there were no recombination on the walls. Solutions of Equation (4) for various values of γ_0 are shown in Fig. 1; the details of the solution are described in a Mathematical Appendix.

The physical significance of the solutions is more apparent if γ is plotted against ρ. Curves of this sort are shown in Fig. 2. To a good first approximation for $\gamma > 0.9$ or for $\rho < 2$ these curves can be described analytically by the expression[6]

$$\gamma = 1 - \frac{1 - \gamma_0}{(1 + \gamma_0)^{1/2}\rho}\sinh(1 + \gamma_0)^{1/2}\rho \qquad (5)$$

For situations other than small ρ or large γ, different approximations are more satisfactory.

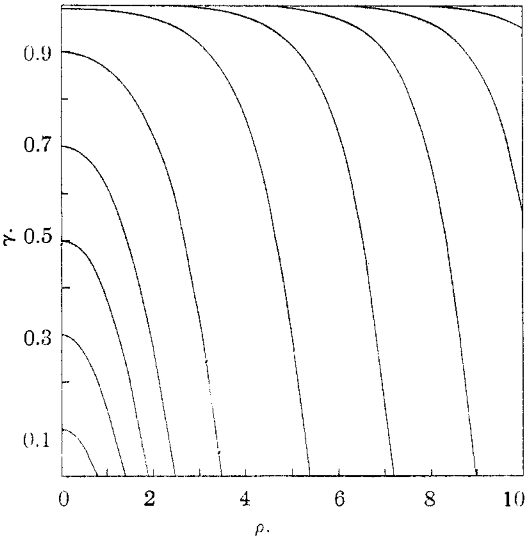

Fig. 2.—Dependence of concentration (γ) on radius (ρ). Curves correspond to values of $1 - \gamma_0$ of 0.9, 0.7, 0.5, 0.3, 0.1, 0.01, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6}.

Discussion

Maximum Influence of Wall.—Let ρ_w be the value of ρ at the wall of the reaction vessel. If the wall is so efficient at removing atoms that the concentration in its immediate neighborhood is negligibly small, the system may be represented by the curve of the type shown in Fig. 2 for which γ vanishes at ρ_w. If ρ_w is large, the curve is very steep, and no matter how efficient the walls are they may reduce the concentration of atoms in only a very localized portion of the vessel. For $\rho_w > 5$ the curves are nearly exponential and may be approximated by an expression of the form

$$\gamma = 1 - e^{-1.15(\rho_w - \rho)} \qquad (6)$$

Then γ will be $1 - 1/e$ when $\rho_w - \rho = 0.9$, and we may approximate the situation in a photochemical system by saying that the concentration

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(5) Of course photochemical reaction vessels are usually not spherical, and the absorption of radiation in a system of finite thickness is never absolutely uniform. In later sections we shall consider modifications for real systems.

(6) If the homogeneous chain termination is first order in atoms so that the rate is $k'c$, an exact solution of the diffusion equation is $\gamma' = 1 - (1 - \gamma'_0)\sinh\rho'$ where $\gamma' = (k'/Q)c$ and $\rho' = (k'/D)^{1/2}r$.

of atoms is $(Q/k)^{1/2}$ in most parts of the system but is zero in a shell which goes in from the wall a distance of $0.9(D^2/Qk)^{1/4}$ cm. This distance is about two-thirds of the root mean square distance an atom diffuses during its mean lifetime, the quantity which Hill[3] proposes as the criterion for the distance through which the walls exert an influence. Either criterion would seem to be a satisfactory way to calculate whether the walls can exert any significant influence on a reaction.

Although the curves in Fig. 2 were calculated for a spherical flask, the conclusions of the preceding paragraph are applicable to any vessel provided $0.9(D^2/Qk)^{1/4}$ is small compared to the linear dimensions. Similarly, the value of Q can be allowed to vary in different parts of the flask to take account of changes throughout the system. However, the approximations are sufficiently large that such corrections cannot be justified unless the greater part of the incident radiation is absorbed in the reaction vessel.

It is instructive to consider the magnitudes of the quantities which may be involved. In many photochemical experiments Q is of the order of 10^{12} or more atom/ml. sec. If homogeneous recombination takes place at every collision between atoms, k will be of the order of 10^{-10} (atom/ml.)$^{-1}$ sec.$^{-1}$. At pressures of one atmosphere D is about 0.2 cm.^{2}/sec. Then we find that $0.9(D^2/Qk)^{1/4}$ is of the order of a few tenths of a centimeter, and the walls may influence a significant but calculable fraction of the volume of the system. On the other hand, homogeneous recombination of atoms and perhaps of many radicals takes place much less frequently than on every collision. It therefore appears that wall effects in gas-phase reactions can be eliminated with certainty only with very high light intensities and/or the use of total gas pressures considerably in excess of atmospheric. These criteria are seldom obeyed.

The situation in liquid phase is very different. Here Q may still be of the order of 10^{12} atoms/ml. sec. Values of k reported are 3.6×10^{-11} (atom/ml.)$^{-1}$ sec.$^{-1}$ for the recombination of iodine atoms in hexane[7] and 1.0×10^{-13} (atom/ml.)$^{-1}$ sec.$^{-1}$ for chain termination in the polymerization of vinyl acetate.[8] The principal difference from gas-phase reactions is that D is of the order of 10^{-5} cm.^{2}/sec. for small atoms and radicals and may be even less for the long-chain radicals in vinyl type polymerizations. Therefore $0.9(D^2/Qk)^{1/4}$ will be of the order of 0.01 cm., and the kinetic data will rarely if ever be precise enough to justify consideration of any correction.

Effect of Recombination Coefficient on Wall Concentration.—The discussion of the preceding section was based on the assumption that the concentration of atoms adjacent to the wall is very low. Such a situation will exist only if a sufficient fraction of the atoms which strike the wall undergo recombination. However, there is evidence[1,4,9] that wall reactions may have collision efficiencies very much less than unity. Let us define α as the recombination coefficient or probability that an atom which strikes the wall will not re-enter the gas phase *as an atom.* If the heterogeneous kinetics are first order in atoms, α will be independent of c_w, the concentration in the gas next to the wall; however, the argument is not affected even if α is allowed to be a function of c_w. It may also be that some atoms are adsorbed on the wall but subsequently re-evaporate as atoms. Of course in the steady state we cannot distinguish between this effect and simple elastic collisions.

By combining Fick's first law with the standard formula for rate of collisions with a surface, we can write

$$-(\mathrm{d}c/\mathrm{d}r)_w = c_w v \alpha / 4D \qquad (7)$$

where v is the average velocity of an atom in cm./sec. Then by appropriate substitution we obtain

$$-\left(\frac{\mathrm{d}\gamma}{\mathrm{d}\rho}\right)_w = \frac{\gamma_w v \alpha}{4(D^2Qk)^{1/4}} = \mu\gamma_w\alpha \qquad (8)$$

If μ and ρ_w are known, Equation (8) may be used to obtain a relationship between γ_w and α and thus to calculate the effect which a given recombination coefficient will have on the concentration of atoms adjacent to the wall. The relationship is not simple for small values of ρ_w, but for $\rho_w > 5$ we may use the approximation of Equation (6) and obtain

$$\mathrm{d}\gamma/\mathrm{d}\rho = -1.15(1 - \gamma) \qquad (9)$$

and

$$\gamma_w = 1.15/(\mu\alpha + 1.15) \qquad (10)$$

In the general case in which α is a function of γ_w, little has been gained by the derivation of Equation (10). However, many heterogeneous recombinations appear to exhibit first order kinetics so that α is independent of γ_w. We have illustrated these systems in Fig. 3, where γ_w from Equation (10) is plotted against log $\mu\alpha$. We see that if $\mu\alpha > 115$, the concentration of atoms near the wall has fallen to less than 1% of that in the main body of the vessel; while if $\mu\alpha < 0.0115$, the concentration of atoms at the wall is not significantly less than that in the body of the vessel. For a gas at one atmosphere pressure absorbing 10^{12} quanta/ml. sec. and in which the atoms recombine on every collision, we can say that μ is about 10^4 and that the concentration of atoms at the walls is very low unless $\alpha < 10^{-2}$. These results are in agreement with the observations of Hill[3] on a specific system. For liquids we can say that μ is roughly one hundred times the value which

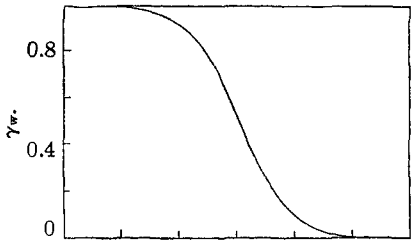

Fig. 3.—Dependence of concentration near wall (γ_w) on recombination coefficient (α).

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[7] J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 658 (1950).

[8] H. Kwart, H. S. Broadbent and P. D. Bartlett, THIS JOURNAL, **72**, 1060 (1950).

[9] M. Bodenstein and E. Winter, *Sitzber. preuss. Akad. Wiss., Physik.-Math. Klasse*, 2 (1936).

would be obtained for a gas at one atmosphere with the same values of Q and k.

Calculation of Recombination Coefficient from Kinetic Data.—The equations developed in the preceding section do not lend themselves easily to experimental test, for neither the recombination coefficient nor the concentration of atoms at the wall can usually be measured directly. However, if the kinetic orders of the homogeneous and heterogeneous recombinations are different and are known, then it is possible to determine the fraction of chains terminated by each mechanism. In this paper we are considering the situation in which the termination of chains on the wall is first order in the concentration of atoms adjacent to the wall. Then the total rate of production of chains is $4\pi r_w^3 Q/3$, and the total rate of termination on the wall is $4\pi r_w^2(c_w v\alpha/4)$, where α is independent of c_w. Let β be the fraction of chains terminating on the wall. Then

$$\beta = \frac{3c_w v\alpha}{4r_w Q} = \frac{3\gamma_w v\alpha}{4(D^2Qk)^{1/4}\rho_w} = -\frac{3}{\rho_w}\left(\frac{d\gamma}{d\rho}\right)_w = \frac{3\mu\gamma_w\alpha}{\rho_w} \quad (11)$$

If β is determined from a careful analysis of kinetic data, then $(d\gamma/d\rho)_w$ can be calculated. If $\rho_w > 5$, we can use Equation (9) to calculate γ_w and hence α. Otherwise the family of curves illustrated in Figure 2 can be used to find the value of γ corresponding to the observed values of ρ_w and $(d\gamma/d\rho)_w$.

An alternative method for obtaining α is to use an integration to obtain the fraction of chains terminating homogeneously. Thus

$$1 - \beta = \frac{\int_0^{r_w} 4\pi kc^2r^2dr}{\int_0^{r_w} 4\pi Qr^2dr} = \frac{\int_0^{\rho_w} \tau^2 d\rho}{\int_0^{\rho_w} \rho^2 d\rho} = \frac{\int_0^{\rho_w} \tau^2 d\rho}{\rho w^3/_3} \quad (12)$$

A series of plots of τ^2 against ρ are presented in Fig. 4. The uppermost curve in the series is the parabolic plot of ρ^2 against ρ. If β and ρ_w are known, one can use Fig. 4 to select that curve having the proper area beneath it. One can then calculate γ_w from the value of the curve at $\rho = \rho_w$ and can then evaluate α from Equation (11). This method is not as satisfactory in practice, but the curves in Fig. 4 provide some insight into the extent to which the walls of the reaction vessel may cut down the amount of homogeneous chain termination.

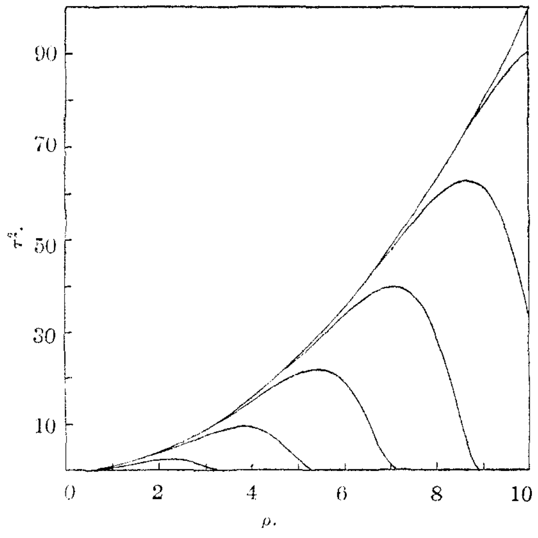

Fig. 4.—Dependence of τ^2 on ρ. Curves correspond to values of $1 - \gamma_0$ of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6} and 0.

Effect of Convection.—All of the equations in this paper have been developed on the assumption that there are no significant temperature gradients in the reaction vessel. This assumption is frequently justified, but strong illumination or exothermic secondary reactions may cause convection currents to develop. These currents will have little effect on the argument if γ_w is almost unity. However, if γ_w is small, convection currents will increase the distance through which the walls exert an effect and will also increase γ_w and β. It would appear to be preferable to design experiments to avoid serious thermal gradients rather than to try to treat them mathematically.

Acknowledgment.—The author is indebted to Drs. Jacob J. Beaver and Lewis Fowler for many helpful discussions during the formulation of this problem and to Dr. George E. Kimball for some suggestions on the solution of the differential equations. He is also indebted to Dr. J. M. Miller for an examination of the first draft of the manuscript and to Winninette Arnold Noyes for assistance with the calculations and figures.

Mathematical Appendix

It is desired to solve the equation

$$\frac{d^2\tau}{d\rho^2} = \frac{\tau^2}{\rho} - \rho \quad \text{(A-1)}$$

Let a subscript zero designate the situation $\rho = 0$. The boundary conditions imposed by the physical situation are

$$\tau_0 = 0 \quad \text{(A-2)}$$

$$(d^2\tau/d\rho^2)_0 = 0 \quad \text{(A-3)}$$

Then the equation is satisfied by a family of curves identified by the parameter γ_0 defined by the relationship

$$\gamma_0 = (d\tau/d\rho)_0 \quad \text{(A-4)}$$

These solutions will have physical significance only as long as $0 \leqslant \tau \leqslant \rho$.

We have not been able to obtain an exact analytical expression for τ but have obtained satisfactory numerical solutions by introducing the new variable σ defined by the relationship

$$\sigma = \rho - \tau \quad \text{(A-5)}$$

Equation (A-1) may then be rewritten

$$\frac{d^2\sigma}{d\rho^2} = 2\sigma - \frac{\sigma^2}{\rho} \quad \text{(A-6)}$$

We then define a function $\sigma_{max.}$ which is always greater than σ in the region of experimental interest and which is given by the relationship

$$\sigma_{max.} = \frac{1 - \gamma_0}{(1 + \gamma_0)^{1/2}} \sinh (1 + \gamma_0)^{1/2}\rho \quad \text{(A-7)}$$

Since $\gamma_0 = 1 - (d\sigma/d\rho)_0$, we may write

$$\frac{d^2\sigma_{max.}}{d\rho^2} - \frac{d^2\sigma}{d\rho^2} = \sigma_{max.}(1 + \gamma_0) - \sigma\left(2 - \frac{\sigma}{\rho}\right) \quad \text{(A-8)}$$

and

$$\sigma_{max.} - \sigma = \int_0^\rho \int_0^\rho \left(\frac{\sigma_{max.}}{\rho} + \gamma_0 - 1\right)\sigma_{max.} d\rho d\rho + \int_0^\rho \int_0^\sigma \left(2 - \frac{\sigma_{max.} + \sigma}{\rho}\right)(\sigma_{max.} - \sigma)\, d\rho d\rho \quad \text{(A-9)}$$

By similar reasoning

$$\frac{d\sigma_{max.}}{d\rho} = (1 - \gamma_0) \cosh (1 + \gamma_0)^{1/2}\rho \quad \text{(A-10)}$$

and

$$\frac{d\sigma_{\text{max.}}}{d\rho} - \frac{d\sigma}{d\rho} = \int_0^\rho \left(\frac{\sigma_{\text{max.}}}{\rho} + \gamma_0 - 1\right)\sigma_{\text{max.}}d\rho + \int_0^\rho \left(2 - \frac{\sigma_{\text{max.}} + \sigma}{\rho}\right)(\sigma_{\text{max.}} - \sigma)d\rho \quad \text{(A-11)}$$

The use of series expansions for the hyperbolic functions gives

$$\int_0^\rho \int_0^\rho \left(\frac{\sigma_{\text{max.}}}{\rho} + \gamma_0 - 1\right)\sigma_{\text{max.}}\, d\rho d\rho =$$

$$\frac{(1-\gamma_0)^2}{(1+\gamma_0)^{3/2}} \sum_{n=1}^{\infty} \frac{[(1+\gamma_0)^{1/2}\rho]^{2n+3}}{(2n+3)(2n+2)} \sum_{i=0}^{n-1} \frac{1}{(2i+1)!(2n-2i+1)!} \quad \text{(A-12)}$$

and

$$\int_0^\rho \left(\frac{\sigma_{\text{max.}}}{\rho} + \gamma_0 - 1\right)\sigma_{\text{max.}}d\rho =$$

$$\frac{(1-\gamma_0)^2}{1+\gamma_0} \sum_{n=1}^{\infty} \frac{[(1+\gamma_0)^{1/2}\rho]^{2n+2}}{2n+2} \sum_{i=0}^{n-1} \frac{1}{(2i+1)!(2n-2i+1)!} \quad \text{(A-13)}$$

In order to evaluate σ one first evaluates $\sigma_{\text{max.}}$ from Equation (A-7) and then applies the correction due to the first double integral in Equation (A-9). This integral can be evaluated by Equation (A-12) for $\rho < 5$, but for larger ρ it is more convenient to use a double graphical integration. The approximate value of σ obtained in this way can then be used to obtain the correction due to the second double integral in Equation (A-9). In principle the recorrected σ could then be used to obtain a more precise value by recalculating the second integral, but such a procedure is unnecessary. The calculated values of σ and γ are available from the American Documentation Institute.[10]

(10) For numerical data order Document 3177 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.50 for photocopies (6 × 8 inches) readable without optical aid.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Mechanisms of Chain Termination in Chlorine Atom Reactions[1]

BY RICHARD M. NOYES AND LEWIS FOWLER

Photochemical gas reactions involving chlorine atoms exhibit simultaneous chain-termination steps which are first and second order in the concentration of atoms. The rate of first order termination has frequently been assumed to involve an impurity present in the gas phase. We have shown that the data can also be explained by assuming a wall reaction with a recombination coefficient of about 5 × 10^{-5}. Experiments at much higher total pressures than have been employed in the past will be necessary to distinguish unequivocally between this interpretation and the homogeneous mechanism involving reaction of chlorine atoms with an impurity present in small equilibrium concentration.

Several gas-phase chlorination reactions appear to proceed by a chain mechanism involving chlorine atoms. In those situations in which the concentration of chlorine atoms is comparatively large, the chain-terminating step is second order in these atoms and is usually postulated to be

$$\text{Cl} + \text{Cl} + \text{M} \longrightarrow \text{Cl}_2 + \text{M} \quad (1)$$

In this expression M is taken to be a molecule which is close enough to the two atoms at the moment of collision to stabilize the incipient molecule of chlorine by removing excess energy.

However, when the concentration of chlorine atoms is decreased, a first order termination process becomes more important. There appear to have been two attempts to explain this observation. Some workers[2a,b] have assumed that the chain is terminated when a chlorine atom reacts with an impurity present in gas phase at an equilibrium concentration. This possibility is very difficult to rule out, for 10^{-8} mm. of active impurity would be sufficient to account for rates of chain termination which are frequently observed. However, it is customary to resort to such an explanation only when it is impossible to explain the data by more conventional methods.

A second mechanism involves the reaction of chlorine atoms with the wall. Since the rate constant for the chain-termination process appears to be independent of the total pressure of gas, a wall reaction is admissible only if there are no significant gradients in the concentration of chlorine atoms. Bodenstein and Winter[3] considered the problem and concluded that they could account for their observations if a chlorine atom striking a glass surface has a probability of 1.6 × 10^{-4} of being captured. They assert, but do not prove, that this probability is so small that no serious concentration gradients would be built up. We have recently carried out[4] a detailed mathematical analysis of this situation. In the present paper we shall attempt to prove that experimental results obtained in these laboratories[5] and data reported in the literature can be interpreted in terms of wall effects without the necessity for postulating the existence of homogeneous impurities.

Data from Phosgene Synthesis.—Fowler and Beaver[5] studied the photochemical reaction between chlorine and carbon monoxide over a range of conditions and concluded that all of their observations could be fitted by an expression of the form

$$d(\text{COCl}_2)/dt = k'(\text{Cl}_2)\{-1 + [1 + k''(\text{CO})(\text{Cl}_2)]^{1/2}\}$$

The mechanism of the reaction is generally conceded to be a chain involving chlorine atoms in the following way

$$\text{Cl} + \text{CO} \rightleftarrows \text{COCl} \quad (2)$$

$$\text{COCl} + \text{Cl}_2 \longrightarrow \text{COCl}_2 + \text{Cl} \quad (3)$$

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(1) For details of some of the calculations order Document 3176 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.05 for photocopies (6 × 8 inches) readable without optical aid.

(2) (a) M. Bodenstein and W. Unger, *Z. physik. Chem.*, **11B**, 253 (1930); (b) W. J. Kramers and L. A. Moignard, *Trans. Faraday Soc.*, **45**, 903 (1949).

(3) M. Bodenstein and E. Winter, *Sitzber. preuss. Akad. Wiss., Physik.-Math. Klasse*, 2 (1936).

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

(5) L. Fowler and J. J. Beaver, *ibid.*, **73**, in press.