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The Steady-State Rate of a Chain Reaction for the Case of Chain Destruction at Walls of Varying Efficiencies[1]

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Bursian and Sorokin's[4] treatment of the rate of a chain reaction with destruction of the chain carriers at the wall considers only the case that every chain carrier striking the surface is destroyed. It is, however, well known that walls possess different efficiencies, as is shown, for example, by experiments with hydrogen atoms. The efficiencies may range from the order of 100% to <0.001%. Recently, Kassel and Storch[5] have treated the problem for a spherical vessel with varying efficiencies of the chain-breaking process. For the average concentration of chain carriers $\bar{n}$, transcendental equations are obtained. The reaction rate is equal to $Kc\bar{n}$, where c is the concentration of the gas with which the chain carrier undergoes reaction and K is the velocity coefficient.

In the present paper, the consequences of the theory for the experimental study of an unknown reaction are discussed. In particular, the influence of vessel diameter on the rate is described quantitatively by tabulation, since this can be done without knowledge of the reaction mechanism and since it serves adequately to explore regions of special kinetic interest. It is also shown that the exact transcendental equations can be replaced with good approximation by simple equations of the type customarily employed in kinetic work. This will serve to show the extent to which former treatments are valid.

It has often been assumed[6,7] that, in a quiescent mixture where chain carriers reach the wall by diffusion only, the concentration of chain carriers may be determined from the equation

$$\bar{n} = n_0 \Big/ \left(\frac{\text{const.}}{pd^2} - \alpha\right) \qquad (1)$$

in which n_0 is the rate of chain initiation per unit volume, $\alpha\bar{n}$ is the net rate of chain branching (α being the difference between the velocity coefficients of the rate of chain branching and the rate of chain destruction in the volume if such exists), p is the pressure, and d is a linear dimension of the reaction vessel. The term $(const./pd^2)\bar{n}$ would then be the rate of chain destruction at the wall, the constant being in some way dependent on the efficiency of chain destruction. The limitations of equation 1 do not seem always to have been fully appreciated. As will be seen later, the equation is approximately correct only for chain initiation in the gas phase, for relatively high efficiencies of chain destruction, and for vessel diameters and pressures that are not small compared with those necessary to induce explosion under the same conditions.

The two cases of chain initiation at the wall and in the gas phase will now be considered. For both cases chains are assumed to branch in the gas phase and to break principally at the wall.

Chain Initiation at the Wall

The concentration of chain carriers, n, at any distance, a, from the center of the spherical vessel of radius, r, is found by integrating the differential equation expressing that the change of concentration with time due to diffusion and net rate of branching is zero and introducing the boundary condition that the net rate of branching throughout the volume is equal to the rate of surface destruction of chains minus the rate of production of new chains at the surface. The rate of destruction of chains at the surface is ϵ times the rate at which the chain carriers strike it, ϵ being the efficiency of chain destruction with values ranging from 0 to 1.

The introduction of the boundary condition to determine the integration constant A in the expression $n = f(a)$ (equation 4 of Kassel and Storch[5]) requires the determination of the total number of chain carriers in the volume, that is, solution of $\int_0^r 4\pi a^2 n da$. Substituting for A

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[4] Bursian and Sorokin, *Z. physik. Chem.*, **B12**, 247 (1931).

[5] Kassel and Storch, THIS JOURNAL, **57**, 672 (1935).

[6] N. Semenoff, "Chemical Kinetics and Chain Reactions," Oxford University Press, 1935, pp. 49–51, 56–57.

[7] C. N. Hinshelwood and A. T. Williamson, "The Reaction Between Hydrogen and Oxygen," Oxford University Press, 1934, pp. 48–49.

equation 15[8] of Kassel and Storch, and solving for the average concentration of chain carriers, one obtains

$$\bar{n} = \frac{\gamma m_0}{\left[\frac{\epsilon r}{\lambda}\,\frac{1 - \sqrt{\alpha/D}\,\lambda\,\mathrm{ctn}\,\sqrt{\alpha/D}\,r}{1 - \sqrt{\alpha/D}\,r\,\mathrm{ctn}\,\sqrt{\alpha/D}\,r} - 1\right]\alpha} = \frac{\gamma m_0}{\left[\frac{\epsilon r}{\lambda}\,\frac{1-\lambda/r}{1 - \sqrt{\alpha/D}\,r\,\mathrm{ctn}\,\sqrt{\alpha/D}\,r} + \epsilon - 1\right]\alpha} \qquad (2)$$

m_0 is the rate of chain initiation per unit area and γ is the ratio of surface to volume and is equal to $3/r$. Therefore, γm_0 is the volume equivalent of the rate of chain initiation. D is the diffusion coefficient and λ is the mean free path.

$\bar{n}$ can have only positive values. The condition $\bar{n} = \infty$ marks the limit of the steady state where the reaction becomes explosive. Beyond this limit, that is, within the explosive region, equation 2 would give negative values for $\bar{n}$. It follows by inspection of equation 2 that for $\bar{n}$ to be positive $\sqrt{\alpha/D}\,r$ must not exceed π and as $\sqrt{\alpha/D}\,r$ approaches π, ϵ must approach 1.

Important deductions regarding the influence of experimental conditions on $\bar{n}$ may be made from the power series expansion of equation 2 for the limiting condition that $\sqrt{\alpha/D}\,r$ is close to zero. The term $1 - \sqrt{\alpha/D}\,r\,\mathrm{ctn}\,\sqrt{\alpha/D}\,r$ reduces to $\frac{1}{3}\frac{\alpha r^2}{D}$. If $D = \frac{\bar{v}\lambda}{4}$[9] ($\bar{v}$ being the average molecular velocity) and $\lambda/r \ll 1$, equation 2 becomes

$$\bar{n} = \frac{\gamma m_0}{\left(\frac{\epsilon r}{\lambda}\frac{3D}{\alpha r^2} + \epsilon - 1\right)\alpha} = \frac{\gamma m_0}{{}^3/_4\frac{\epsilon\bar{v}}{r} - (1 - \epsilon)\,\alpha} \qquad (3)$$

For small values of ϵ the positive term in the denominator becomes identical with the coefficient of the rate of chain destruction. In contradistinction to the corresponding term in equation 1, it is inversely proportional to the radius and independent of pressure if ϵ is independent of pressure. The functional dependence of ϵ is determined by the mechanism of the chain-destroying reaction in which will enter the natures of the surface and the chain carrier and possibly pressure, temperature and mixture composition. If ${}^3/_4\frac{\epsilon\bar{v}}{r}\left(=\frac{\epsilon\bar{v}}{4}\gamma\right) \gg (1 - \epsilon)\,\alpha$, $\bar{n}$ becomes independent of vessel size and dependent on pressure, temperature and mixture composition only to the extent that $m_0/\epsilon\bar{v}$ is dependent on these factors. Experimentally, this region is of particular interest, since it allows a direct kinetic investigation of the ratio of the chain-initiating reaction to the efficiency of chain destruction. This much-needed separation of variables finds its counterpart in the independent kinetic investigation of α from the determination of the explosion regions in a diagram of any two of the variables pressure, temperature, mixture composition, vessel size.

The condition ${}^3/_4\frac{\epsilon\bar{v}}{r} \gg (1 - \epsilon)\,\alpha$ can be approached by making r small or by decreasing α in a manner that does not simultaneously decrease ϵ to the same or to a greater degree. This would demand that the functional dependence of ϵ on any variable shall be a milder one than the dependence of α on that variable. As far as pressure and mixture composition are concerned this limitation would seem to be the usual case. α may be made small by reducing the pressure of the reactants involved in the branching reaction. Frequently, α can be made small by decreasing the temperature but here one often encounters very complex functional dependencies of both α and ϵ. This is illustrated by the reaction between oxygen and higher hydrocarbons.[10]

Whenever the rate of a chain reaction is found to be independent of diameter there exist only two alternatives. Either the above-discussed case applies or chains are both initiated and destroyed in the gas phase. In the latter case, however, the rate will remain independent of diameter for all diameters, whereas in case chains are initiated and destroyed at the wall, branching causes the rate eventually to increase with increasing diameter. No such well-defined criterion for distinguishing these two cases is obtained by varying the pressure, temperature or mixture composition.

It has usually been found difficult to determine with accuracy the dependence of the reaction rate on diameter. There may be various reasons for this, the most obvious being the difficulty of controlling, experimentally, properties of the surface on which m_0 and ϵ depend. Often, it has only been possible to state that a reaction rate is either independent of or roughly dependent on some power of the diameter. In the light of the

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(8) More exactly, the term $\frac{\epsilon\bar{v}r}{4}\sin\sqrt{\alpha/D}\,r$ in their equation 15 should be replaced by $\frac{\epsilon\bar{v}r}{4}\sin\sqrt{\alpha/D}\,(r - \lambda)$.

(9) The difference between this value of D and the usual value $\bar{v}\lambda/3$ arises from the assumption that all free paths are equal as has been done in Kassel and Storch's[5] treatment.

(10) Von Elbe and Lewis, THIS JOURNAL, 59, 976 (1937).

TABLE I

$\frac{1}{\pi}\sqrt{\alpha/D}\,r_0$	0		0.318		0.605		0.701		0.800		0.933		1	
$\frac{\epsilon r_0}{\lambda}\frac{1}{1-\epsilon}$	0		.358		1.65		2.60		4.46		14.80		∞	
ϵ_7/ϵ_i	$6/\pi^2$		.630		0.700		0.739		0.798		0.913		1	
r/r_0	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_a}{\bar{n}_b}$	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_a}{\bar{n}_b}$	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_a}{\bar{n}_b}$	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_a}{\bar{n}_b}$	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_a}{\bar{n}_b}$	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_a}{\bar{n}_b}$	$\frac{\alpha\bar{n}}{\gamma m_0}\frac{r_0}{r}$	$\frac{\bar{n}_a}{\bar{n}_b}$
0	1	1	0.93	0.96	0.73	0.87	0.62	0.82	0.47	0.76	0.19	0.67	$3.3\ \lambda/r_0$	0.61
0.1	1.11	1	1.04	.96	.79	.87	.66	.82	.49	.76	.19	.67	$3.3\ \lambda/r_0$	.61
.2	1.25	1	1.15	.96	.86	.87	.72	.82	.53	.76	.20	.67	$3.4\ \lambda/r_0$	.62
.3	1.43	1	1.31	.96	.96	.87	.78	.82	.58	.76	.22	.67	$3.5\ \lambda/r_0$	.63
.4	1.67	1	1.55	.96	1.09	.87	.89	.82	.64	.76	.24	.68	$3.7\ \lambda/r_0$	.65
.6	2.50	1	2.23	.95	1.54	.86	1.23	.83	.85	.77	.29	.71	$4.5\ \lambda/r_0$	.70
.8	5.0	1	4.43	.94	2.91	.85	2.25	.84	1.50	.80	.48	.79	$7.0\ \lambda/r_0$	.80
1.0	∞	1	∞	.94	∞	.85	∞	.84	∞	.85	∞	.92	∞	1

above results and others to be presented later, even such comparatively rough experimental data may provide considerable knowledge concerning the reaction mechanism.

The dependence of the reaction rate on diameter will now be investigated quantitatively. For given values of ϵ, λ, D and α there exists a vessel radius r_0 at which the rate becomes explosive, that is, $n = \infty$. For radii $r < r_0$ the slow steady-state rate will be established, that is, $\bar{n}$ is finite and positive.

From equation 2 and $\lambda/r \ll 1$

$$\frac{\epsilon r}{\lambda} = (1 - \sqrt{\alpha/D}\,r_0\,\mathrm{ctn}\,\sqrt{\alpha/D}\,r_0)\frac{r}{r_0}(1 - \epsilon) \qquad (4)$$

ϵ is small compared with 1 unless $\sqrt{\alpha/D}\,r_0$ is very close to π. If, for example, λ/r is of the order 10^{-3} corresponding to low pressures (a few mm. mercury) and ordinary vessel dimensions, ϵ is greater than the order of 0.1 only when $\sqrt{\alpha/D}\,r_0$ exceeds 0.99 π. For higher pressures, $\sqrt{\alpha/D}\,r_0$ must approach even closer to π before ϵ reaches this value.

Combining equations 2 and 4, the exact equation becomes

$$\frac{\alpha\bar{n}}{\gamma m_0} = \frac{1}{(1-\epsilon)\left(\frac{1 - \sqrt{\alpha/D}\,r_0\,\mathrm{ctn}\,\sqrt{\alpha/D}\,r_0}{1 - \sqrt{\alpha/D}\,r\,\mathrm{ctn}\,\sqrt{\alpha/D}\,r}\frac{r}{r_0} - 1\right)} \qquad (5)$$

If $\bar{n}$ is independent of diameter the function $\alpha\bar{n}r_0/\gamma m_0 r$ must be constant. Values of this function calculated from equation 5 for $\sqrt{\alpha/D}\,r_0$ from 0 to π and r/r_0 from 0 to 1 are given in Table I. The corresponding values of $\frac{\epsilon r_0}{\lambda}\frac{1}{1-\epsilon}$ are given in the second horizontal line. It is seen that the range of diameters within which the reaction rate is reasonably independent of diameter widens for increasing values of $\frac{\epsilon r_0}{\lambda}\frac{1}{1-\epsilon}$. Thus, for $\epsilon r_0/\lambda = 0$, about a 10% increase in the value of the function occurs between $r/r_0 = 0$ and 0.1, whereas for $\epsilon r_0/\lambda = r_0/\lambda$ the same increase occurs between $r/r_0 = 0$ and 0.4. It is plain that for otherwise identical conditions the replacement of a vessel with a wall of high chain-breaking efficiency by one with low chain-breaking efficiency should markedly increase the dependence of the reaction rate on vessel diameter.

The following considerations give some idea of the magnitude of ϵ for a given value of $\frac{\epsilon r_0}{\lambda}\frac{1}{1-\epsilon}$.

In the usual experiments the pressure may be between a few millimeters and 1 atmosphere, for which λ is of the order 10^{-2} to 10^{-4} cm., respectively. Values of the explosion radius r_0 depend on a number of conditions. In actual experiments it will probably not be less than the order of 10 cm. Thus, when $\frac{\epsilon r_0}{\lambda}\frac{1}{1-\epsilon} =$ 14.80, ϵ would not be larger than 0.01 to 0.0001, depending on the above pressure range. This example illustrates that the effect of ϵ on the dependence of the rate on diameter becomes noticeable only in vessels with walls having extremely small chain-breaking efficiencies.

The influence of ϵ on the reaction rate itself is very pronounced over the whole range of values from 0 to 1, the rates decreasing with increasing ϵ.

Previously, non-transcendental equations were obtained for $\bar{n}$ on the basis of Bursian and Sorokin's treatment, which strictly apply only to the case of large efficiency of chain destruction (ϵ close to 1) and to the neighborhood of the explosion limit.[6] It will now be shown that for this condition, namely, $\sqrt{\alpha/D}\,r$ close to π, equation 2 can be reduced to a non-transcendental equation that describes with good approximation all the essential features of the theory. The term $1 - \sqrt{\alpha/D}\, r \operatorname{ctn} \sqrt{\alpha/D}\, r$ now reduces, in the limit, to $1 \Big/ \left(\frac{\pi}{r}\sqrt{\alpha/D} - 1\right)$ or the general form $2^x/(y^{2^x} - 1)$ where $x = 0, 1, 2, 3 \ldots$ and $y = (\pi/r)\sqrt{\alpha/D}$. The desired reduction is obtained for $x = 1$. If $\lambda/r \ll 1$ equation 2 becomes

$$\bar{n} = \frac{\gamma m_0}{\left[\frac{\epsilon r}{2\lambda}\left(\frac{\pi^2 D}{\alpha r^2} - 1\right) + \epsilon - 1\right]\alpha} \qquad (6)$$

To compare equation 6 with equation 2 for the influence of diameter, $\epsilon r/\lambda$ must be expressed as a function of r_0. This expression is obtained readily from equation 4, since $\sqrt{\alpha/D}\, r_0$ is also close to π. Thus

$$\frac{\epsilon r}{\lambda} = \frac{2}{\frac{\pi^2 D}{\alpha r_0^2} - 1}\frac{r}{r_0}(1 - \epsilon) \qquad (7)$$

Combining equations 6 and 7

$$\frac{\alpha \bar{n}}{\gamma m_0} = \frac{1}{(1 - \epsilon)\left(\frac{\frac{\pi^2 D}{\alpha r^2} - 1}{\frac{\pi^2 D}{\alpha r_0^2} - 1}\frac{r}{r_0} - 1\right)} \qquad (8)$$

A direct comparison of equations 8 and 5 is furnished by the tabulation of the ratio $\bar{n}_8/\bar{n}_5$ for the entire range of $\sqrt{\alpha/D}\, r_0$ and r/r_0. This is given in Table I. It is seen that equation 8 follows the trend of equation 5 over practically the entire range. Even in the columns toward the right of Table I it represents the region in which the rate is independent of vessel size over much the same range of r/r_0 as equation 5. The gradual improvement of the numerical agreement toward the left of Table I is accompanied by an increasing but always unimportant discrepancy in $\frac{\epsilon r}{\lambda}\frac{1}{1 - \epsilon}$ introduced through equation 7. Thus by the approximate treatment reaction vessels possess apparent chain-breaking efficiencies that are smaller than the actual ones. Ratios of such apparent to actual efficiencies calculated from equations 7 and 4 are listed in the third horizontal line in Table I.

The comparison of equations 2 and 6 will now be made in a perfectly general way, to include variations not only in diameter but in any physical condition such as pressure, temperature and mixture composition. According to equation 2, the condition for explosion may be written

$$1 - (\sqrt{\alpha/D}\, r)_0 \operatorname{ctn} (\sqrt{\alpha/D}\, r)_0 = \left(\frac{\epsilon r}{\lambda}\frac{1}{1 - \epsilon}\right)_0 \qquad (9)$$

and according to equation 6

$$\frac{2}{\left(\frac{\pi^2 D}{\alpha r^2}\right)_0 - 1} = \left(\frac{\epsilon r}{\lambda}\frac{1}{1 - \epsilon}\right)_0 \qquad (10)$$

If $(\sqrt{\alpha/D}\, r)_0$ is close to 0, the left hand sides of equations 9 and 10 become $\frac{1}{3}\left(\frac{\alpha r^2}{D}\right)_0$ and $\frac{2}{\pi^2}\left(\frac{\alpha r^2}{D}\right)_0$, respectively. Since $\sqrt{\alpha/D}\, r$ is ordinarily also close to 0, both equations 2 and 6 after substituting equations 9 and 10, respectively, become identical, namely

$$\frac{\alpha \bar{n}}{\gamma m_0} = \frac{1}{1 - \epsilon\left(\frac{(\alpha r^2/D)_0}{\alpha r^2/D} - 1\right)} \qquad (11)$$

It is now clear why $\bar{n}_8/\bar{n}_5$ should have been found equal to 1 for $\frac{\epsilon r}{\lambda}\frac{1}{1 - \epsilon}$ equal to 0 (Table I).

Let us now consider $\sqrt{\alpha/D}\, r \ll (\sqrt{\alpha/D}\, r)_0$ for any value of the latter between 0 and π. The more complete expansion of $1 - \sqrt{\alpha/D}\, r \operatorname{ctn} \sqrt{\alpha/D}\, r$ is given by $\frac{1}{3}\frac{\alpha r^2}{D} + \frac{1}{45}\frac{\alpha^2 r^4}{D^2} + \ldots$, whence $\frac{1}{1 - \sqrt{\alpha/D}\, r \operatorname{ctn} \sqrt{\alpha/D}\, r} = \frac{3D}{\alpha r^2}\frac{1}{1 + \frac{1}{15}\frac{\alpha r^2}{D} + \ldots}$. The corresponding term in equation 6, $\frac{1}{2}\left(\frac{\pi^2 D}{\alpha r^2} - 1\right) = \frac{\pi^2 D}{2\alpha r^2}\left(1 - \frac{1}{\pi^2}\frac{\alpha r^2}{D}\right)$ becomes, for small values of $\sqrt{\alpha/D}\, r$, equal to $\frac{\pi^2}{2}\frac{D}{\alpha r^2}\frac{1}{1 + \frac{1}{\pi^2}\frac{\alpha r^2}{D}}$. As $\sqrt{\alpha/D}\, r$ becomes small the two denominators, namely, $1 + \frac{1}{15}\frac{\alpha r^2}{D}$ and $1 + \frac{1}{\pi^2}\frac{\alpha r^2}{D}$ approach 1 almost simultaneously. Thus, both equations 2 and 6 approach an identical form almost simultaneously (apart from an unimportant numerical factor). This explains why the range over which the rate may be considered independent of diameter should have been found almost equally well described by equation 8 (Table I).

It has now been demonstrated that the approximate treatment (equation 6) is satisfactory for small chain-breaking efficiencies from slow reaction to explosion and for any chain-breaking efficiency in the region where the reaction rate is reasonably independent of diameter. The equation applies strictly to the range for which it was derived, namely, large chain-breaking efficiencies and reaction rates close to explosion. There remains the intermediate range in which discrepancies between approximate and exact treatments would be greatest. This range cannot be investigated in a general way because the functional dependencies of ϵ, α, D and λ vary for different reactions. Only for changes in vessel size is a comparison possible. Judging from the rather satisfactory agreement (Table I) it may be expected that for most kinetic purposes with emphasis placed on trend rather on exact numerical agreement, the approximate treatment will be found satisfactory.

Chain Initiation in the Gas Phase

In this case the concentration of chain carriers at any distance from the center of the spherical vessel is found by integrating the differential equation expressing the fact that the change of concentration with time due to diffusion, net rate of branching and initiation is zero and introducing the boundary condition that the net rate of branching plus the rate of chain initiation throughout the volume is ϵ times the rate at which chain carriers strike the surface. Using the same treatment as before, except that now $n = f(a)$ and the integration constant A are given by equations 13 and 14,[11] respectively, of Kassel and Storch,[5] one obtains

$$\bar{n} = \frac{n_0}{\alpha} \frac{\frac{3D}{\alpha r^2}(1 - \lambda/r)}{\frac{1 - \lambda/r}{1 - \sqrt{\alpha/D}\, r \operatorname{ctn} \sqrt{\alpha/D}\, r} - \frac{\lambda}{\epsilon r}(1 - \epsilon)} - 1 \quad (12)$$

where n_0 is the rate of chain initiation per unit volume.

As before, in order that $\bar{n}$ be positive $\sqrt{\alpha/D}\, r$ must not exceed π and as $\sqrt{\alpha/D}\, r$ approaches π, ϵ approaches 1.

For $\sqrt{\alpha/D}\, r$ close to 0, the series expansion

$$\frac{{}^1/_3 \frac{\alpha r^2}{D}}{1 - \sqrt{\alpha/D}\, r \operatorname{ctn} \sqrt{\alpha/D}\, r} = \frac{1}{1 + \frac{1}{15}\frac{\alpha r^2}{D} + \ldots}$$

becomes equal to $1 - \frac{1}{15}\frac{\alpha r^2}{D}$ and equation 12 reduces to, for $\lambda/r \ll 1$

$$\bar{n} = \frac{n_0}{\frac{15D}{r^2}\frac{1}{1 + \frac{5\lambda}{\epsilon r}(1 - \epsilon)} - \alpha} \quad (13)$$

It is seen that if $\frac{5\lambda}{\epsilon r}(1 - \epsilon) \ll 1$ the rate of chain destruction is inversely proportional both to the pressure and to the square of the diameter. If, in addition, $15D/r^2 \gg \alpha$, the reaction rate is proportional to the square of the diameter. If $\frac{5\lambda}{\epsilon r}(1 - \epsilon) \gg 1$, equation 13 becomes

$$\bar{n} = \frac{n_0}{{}^3/_4 \frac{\epsilon \bar{v}}{r} - \alpha} \quad (14)$$

and the rate of chain destruction is now inversely as the diameter. In this case, if $3/4\ \epsilon\bar{v}/r \gg \alpha$ the reaction rate is proportional to the first power of the diameter.

It immediately becomes apparent that for the case of chain initiation in the volume, the region in which the reaction rate is proportional to the first or second power of the diameter acquires similar importance for the study of reaction kinetics as the region of independence of diameter in the case of wall initiation. In the region of strict diameter-squared proportionality, $\bar{n}$ is proportional to n_0/D, whereas in the region of diameter to the first-power proportionality it is proportional to $n_0/\epsilon\bar{v}$. The separate investigation of α can be made by a study of the explosion regions as mentioned before.

Equation 12 will now be investigated for the dependence of reaction rate on diameter. $\epsilon r/\lambda$ is again given by equation 4. Combining equations 4 and 12, one obtains

$$\frac{\alpha\bar{n}}{n_0} = \frac{1}{{}^1/_3 \frac{\alpha r^2}{D}\left(\frac{1}{1 - \sqrt{\alpha/D}\, r \operatorname{ctn} \sqrt{\alpha/D}\, r} - \frac{r_0/r}{1 - \sqrt{\alpha/D}\, r_0 \operatorname{ctn} \sqrt{\alpha/D}\, r_0}\right)} - 1 \quad (15)$$

Table II contains values of the functions $\frac{\alpha\bar{n}}{n_0}\frac{r_0}{r}$ and $\frac{\alpha\bar{n}}{n_0}\frac{r^2_0}{r^2}$ calculated from equation 15 for $\sqrt{\alpha/D}\, r_0$ from 0 to π and r/r_0 from 0 to 1. Wherever these functions can be considered constant with respect to r/r_0, the rate is proportional to the first or second power, respectively, of the diameter. It is seen that the range of diameters within which the reaction rate is reasonably proportional to the first power of the diameter decreases as $\frac{\epsilon r_0}{\lambda}\frac{1}{1 - \epsilon}$ increases and that even in the most favorable case ($\epsilon r_0/\lambda = 0$) it does not begin until small fractions of the explosion diameter. For $\epsilon r_0/\lambda = r_0/\lambda$ there is no range over which the diameter to the first-power proportionality holds. In the latter case there is a large range of diameters over which the reaction rate is proportional to the square of the diameter. This range is considerably decreased and is shifted toward larger ratios of r/r_0 as $\frac{\epsilon r_0}{\lambda}\frac{1}{1 - \epsilon}$ decreases. It is seen that most of this narrowing and shifting of the range occurs for large values of $\frac{\epsilon r_0}{\lambda}\frac{1}{1 - \epsilon}$. There is very little additional change below 14.80.

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[11] Strictly, a factor of $1 - \lambda/r_0$ should be inserted in the numerator of equation 14 of Kassel and Storch.

TABLE II

$\frac{1}{\pi}\sqrt{\alpha/D}\,r_0$	0			0.605			0.933			0.987			0.999			1.000		
$\frac{\epsilon r_0}{\lambda}\frac{1}{1-\epsilon}$	0			1.65			14.80			75.43			1000			∞		
r/r_0	$\frac{\alpha\bar n}{n_0}\frac{r_0}{r}$	$\frac{\alpha\bar n}{n_0}\frac{r_0^2}{r^2}$	$\frac{\bar n_{16}}{n_{12}}$	$\frac{\alpha\bar n}{n_0}\frac{r_0}{r}$	$\frac{\alpha\bar n}{n_0}\frac{r_0^2}{r^2}$	$\frac{\bar n_{16}}{n_{12}}$	$\frac{\alpha\bar n}{n_0}\frac{r_0}{r}$	$\frac{\alpha\bar n}{n_0}\frac{r_0^2}{r^2}$	$\frac{\bar n_{16}}{n_{12}}$	$\frac{\alpha\bar n}{n_0}\frac{r_0}{r}$	$\frac{\alpha\bar n}{n_0}\frac{r_0^2}{r^2}$	$\frac{\bar n_{16}}{n_{12}}$	$\frac{\alpha\bar n}{n_0}\frac{r_0}{r}$	$\frac{\alpha\bar n}{n_0}\frac{r_0^2}{r^2}$	$\frac{\bar n_{16}}{n_{12}}$	$\frac{\alpha\bar n}{n_0}\frac{r_0}{r}$	$\frac{\alpha\bar n}{n_0}\frac{r_0^2}{r^2}$	$\frac{\bar n_{16}}{n_{12}}$
0	1	∞	0.61	0.73	∞	0.53	0.19	∞	0.41	0.04	∞	0.37	0.003	∞	0.37	0	0.66	0.37/.92
0.02	1.02	51	.61	.74	37	.53	.20	10	.42	.06	2.8	.49	.02	.82	.81	.01	.66	.92
.04	1.04	26	.61	.76	19	.53	.22	6	.45	.07	1.7	.57	.03	.74	.86	.03	.66	.92
.07	1.07	15	.61	.79	11	.53	.24	3.4	.49	.09	1.25	.65	.05	.71	.90	.05	.66	.92
.1	1.11	11	.61	.82	8.2	.53	.26	2.6	.52	.11	1.07	.71	.07	.69	.91	.07	.66	.93
.2	1.25	6.3	.61	.92	4.6	.54	.33	1.6	.60	.18	.89	.79	.14	.70	.91	.14	.68	.93
.3	1.43	4.8	.61	1.05	3.5	.55	.41	1.4	.66	.26	.86	.83	.22	.72	.92	.22	.72	.93
.4	1.67	4.2	.61	1.23	3.1	.56	.53	1.3	.68	.36	.89	.85	.32	.79	.92	.31	.78	.93
.6	2.50	4.2	.61	1.87	3.1	.57	.87	1.5	.75	.66	1.10	.89	.61	1.0	.94	.60	1.0	.95
.8	5.0	6.3	.61	3.7	4.7	.59	1.87	2.3	.79	1.5	1.9	.92	1.4	1.8	.96	1.4	1.7	.97
1.0	∞	∞	.61	∞	∞	.60	∞	∞	.84	∞	∞	.96	∞	∞	1.0	∞	∞	1.0

The influence of ϵ on the reaction rate itself varies with $\frac{\epsilon r_0}{\lambda}\frac{1}{1-\epsilon}$ and r/r_0. It is largest for small values of these functions and becomes rather negligible for large values.

Again, the essential features of the theory can be expressed with good approximation by a non-transcendental equation derived from equation 12 for the condition that $\sqrt{\alpha/D}\,r$ is close to π. Using the series expansion given earlier in connection with equation 6, equation 12 for $\lambda/r \ll 1$ reduces to

$$\bar n = \frac{(6/\pi^2)\,n_0}{\left[\frac{\pi^2 D}{\alpha r^2} - 1 - \frac{2\lambda}{\epsilon r}(1-\epsilon)\right]\alpha} - 1$$

Since $\frac{\pi^2 D}{\alpha r^2} - 1$ and $\frac{2\lambda}{\epsilon r}(1-\epsilon)$ become vanishingly small for $\sqrt{\alpha/D}\,r$ close to π, the reduction may be carried further to

$$\bar n = \frac{(6/\pi^2)\,n_0}{\frac{\pi^2 D}{r^2}\,\frac{1}{1+\frac{2\lambda}{\epsilon r}(1-\epsilon)} - \alpha} \qquad (16)$$

It can again be demonstrated that equation 16 is for most kinetic purposes a satisfactory substitute for equation 12, as was shown earlier for equation 6. This will be perhaps sufficiently evident from the similarity of equations 13 and 16, which were derived for opposite extremes. It is demonstrated in Table II specifically for the case of diameter dependence by the columns (n_{16}/n_{12}).

Summary

The steady-state treatment of chain reactions in which chains are broken at walls of varying efficiencies is discussed. Two cases are considered, namely, chain initiation at the wall and in the gas phase. It is shown that under conditions of negligible branching there exist characteristic relations between rate and vessel diameter. This may be used for a kinetic study of the unbranched reaction, whereas the branching reaction may be studied from explosion limits. The influence of vessel diameter on the rate has been described quantitatively for varying chain-breaking efficiencies. It is also shown that the exact transcendental equations may be replaced with good approximation by simple non-transcendental equations.

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