International Journal of Theoretical Physics, Vol. 26, No. 11, 1987

Stochastic Theory of Ignition Processes

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Received May 21, 1987

We consider a closed gaseous system immersed in a heat bath undergoing a thermal explosion. The effects of instantaneous fluctuations in the temperature on the heat removal mechanism and on the reaction rate are considered. The intensity of the fluctuations in situations far from equilibrium is determined by calculating the temperature self-correlation. This quantity scales with the inverse of an effective volume Ω obtained from generalized fluctuation-dissipation theory. This determines a virtual system corresponding to the localized ignition process, possibly leading to a global runaway. The induction period is identified with the Kramers mean passage time for diffusion across a kinetic barrier. The induction period is thus shown to be dependent on the fluctuation volume Ω. The diffusion process is hastened by the critical fluctuations. The explosive decomposition of ethyl azide was selected to test the theory and the results exhibit very good agreement with experimental data. Our treatment resolves the previous discrepancy between the predictions rooted in the classical Frank-Kamenetsky treatment and the premature ignition observed experimentally.

1. INTRODUCTION

The aim of this work is to provide a rigorous framework for demonstrating the stochastic contribution to ignition processes in gaseous closed systems. That is, we shall describe the phenomenon of ignition in a statistical sense. In an ensemble of realizations of the combustion experiment, some replicas of the system will present a delayed explosion and others an accelerated ignition. In order to appreciate the results presented in this work, we emphasize the physical difference between critical nonequilibrium fluctuations responsible for ignition and fluctuations near thermodynamic equilibrium. Critical fluctuations are assumed to be *localized in space* and the physical consequences of such an assumption will be examined. This issue is discussed in a general context in Graham (1975), Fernández (1985a),

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Baras *et al.* (1983), Fernández and Rabitz (1987), and Horsthemke and Brenig (1977). We shall show that the mean magnitude of the temperature fluctuations cannot be scaled with the inverse of the thermodynamic macroscopic volume *V*, as is the case near equilibrium. In previous work (Baras *et al.*, 1983), the critical fluctuations responsible for ignition were treated as if they were equilibrium fluctuations, scaling with V^{-1}. An estimate for the induction period under these equilibrium assumptions produces values off by several orders of magnitude (Baras *et al.*, 1983). Making use of the fact that fluctuations are localized in space, we shall implement a stochastic treatment of the problem that explains and circumvents the latter dramatic discrepancy. The new calculated induction periods in this paper exhibit very good agreement with the experimental results. The general theoretical background of the method will be presented in this section. The physical framework for the fluctuation-controlled ignition is determined by the following related features and assumptions:

1. An *ensemble of realizations of the combustion experiment* occurs under far-from-equilibrium conditions.
2. A *virtual volume* exists within which *localized critical fluctuations* are confined.
3. *The temperature is treated as a continuous stochastic variable* within the induction period. The volume-averaged temperature $\bar{T}$ admits to a probability distribution $P(\bar{T}, t)$ over the ensemble. The distribution P satisfies a Fokker–Planck equation whose drift term is determined by a potential $U = U(\bar{T})$. This model and the potential will be described in detail in the next section.
4. The induction period is associated with *a diffusion process* caused by the critical fluctuations that drive the system over a barrier in the potential *U*.

Based on these notions, two broad physical regimes will be considered for gas-phase ignition:

I. A low-pressure regime (0.01–0.05 atm), where an inhomogeneous temperature distribution affects the heat exchange process with the vessel walls. No convection or acoustic field effects are taken into account. In this case, the instantaneous fluctuations in $\bar{T}$ do not affect the reaction rate (Lermant and Yip, 1984; Frank-Kamenetsky, 1955; Bowden and Yoffe, 1958; Friedman, 1963; Tsugé and Sagara, 1976).

II. A moderately low-pressure regime (0.05–0.12 atm), where turbulence effects are given by the nonvanishing self-correlation of temperature (Tsugé and Sagara, 1976). The effect of instantaneous fluctuations in $\bar{T}$ is not negligible (Tsugé and Sagara, 1976) and both the heat exchange as well as the reaction rates are affected.

There are two time scales involved in these regimes: (1) a time scale associated with the local fluctuations in $\bar{T}$ and (2) a time scale associated with the fluctuations of the global spatial temperature profile about $\bar{T}$. Following Lermant and Yip (1984) and Tsugé and Sagara (1976) (see also Section 2), we shall assume that there exists a separation between these latter time scales so that the temperature profile adjusts itself faster than the first timescale, which is involved in the Fokker–Planck equation indicated in item 3 above. The regime I involves only the second time scale, while regime II involves both time scales.

The concept of localized fluctuations will be formalized by calculating the effective size Ω of a virtual hot spot where fluctuations are confined. The localized ignition will eventually lead to a global runaway. Critical fluctuations scale with Ω^{-1} and not with V^{-1}. The effective size of the hot spot will be obtained from generalized fluctuation-dissipation theory, making use of the property of conservation of energy: the total energy of the extended system comprising the closed gaseous system together with the heat bath is a constant. This effective size Ω is dependent on the thermodynamic volume V and the curvature of the maximum in the bistable potential U. The induction period is given by the Kramers mean passage time for the unsymmetric bistable potential. This potential is obtained from the competition between the heat source provided by the exothermic chemical reactions (Lermant and Yip, 1984; Frank-Kamenetsky, 1955; Bowden and Yoffe, 1958; Friedman, 1963; Tsugé and Sagara, 1976) and the heat removal process (Lermant and Yip, 1984; Frank-Kamenetsky, 1955; Bowden and Yoffe, 1958; Friedman, 1963). One minimum in this potential corresponds to the stationary nonexplosive temperature for the steady combustion, and the other minimum to the explosive temperature regime. The inflection point of interest lies between the minimum for the steady combustion and the maximum corresponding to the ignition temperature. The potential is parametrically dependent on the coefficient for heat exchange with the surroundings. In the situation under examination here, the heat exchange coefficient has reached its critical value. The shape of the potential at criticality is such that the inflection point coalesces with the steady combustion minimum to become a flat critical point. The discrepancy between the equilibrium thermodynamics approach as described above (Baras *et al.*, 1983) and the experiments can be explained as follows (see also Frank-Kamenetsky, 1955; Bowden and Yoffe, 1958; Friedman, 1963; Tsugé and Sagara, 1976; and van Kampen, 1981). Should the effective diffusion coefficient, which gives the temperature self-correlation, scale with the inverse of the macroscopic volume, the diffusion across the barrier of U induced by the equilibrium fluctuations would be a very slow process. However, since far-from-equilibrium critical fluctuations are localized, and therefore are enhanced with respect to their equilibrium counterparts, the diffusion process is accelerated substantially. This diffusion process will be modeled by means of a Fokker–Planck equation to be satisfied by the distribution $P(\bar{T}, t)$. Such an equation is only valid within the induction period, that is, before internal fluctuations lead to macroscopic consequences. After this period has elapsed, the probability density develops two peaks, one at each side of the flat maximum of the potential at criticality.

The scaling parameter Ω^{-1} can be regarded as a small parameter only in the thermodynamic limit for a rarefied gas in the regime I. In this situation, the notation $\Omega = \Omega_0$ will be adopted. In this case the only physical factor that accounts for the difference between Ω_0 and V is the inhomogeneous distribution of temperature in the vessel due to heat conduction with vessel walls. This distribution will be evaluated in this work for a heat conduction regime in a nonequilibrium gas. Despite the fact that the volume V and the size Ω of the virtual hot spots are different, they behave equivalently in the thermodynamic limit:

$$\lim_{V \to \infty} \Omega_0 = \infty \qquad \text{for regime I} \tag{1}$$

The behavior of the effective size parameter in the thermodynamic limit under regime II will be studied in Section 2. Numerical computations are presented in Section 4.

At this point, we should comment on the conceptual difference between the "intrinsic" hot spot in our system, which arises from the spatial localization of the temperature fluctuations, and an "induced" hot spot, created by mechanical action on a solid explosive material (Bowden and Yoffe, 1958; Friedman, 1963). In the latter case, the effective size of the hot spot does not depend parametrically on the thermodynamic volume or on the temperature self-correlations, as is the case with our intrinsic hot spot. During the induction period, the amount of heat produced by the exothermic reaction in the induced hot spot is very small and the cooling process is little affected by the fact that the material is reactive or inert. The distribution of temperatures in the induced hot spot follows qualitatively the same law that we have derived for the temperature profile in our closed system, where the highest temperature occurs at the center in the case of a spherical vessel [cf. Section 3 of this work and Bowden and Yoffe (1958) and Friedman (1963)]. In the solid reactive material, an explosion will occur at the center of the hot spot only if the induction period is smaller than the time it takes the "cold front," or cooling wave, to reach the center. Making use of this property, one calculates a lower bound for the effective size of the induced hot spot. Instead, the effective size of our hot spots can be obtained directly by calculating the magnitude of the critical fluctuations that trigger the explosion.

2. A RECURSIVE RELATION LEADING TO A CONVERGENT SEQUENCE FOR THE SIZE PARAMETER Ω

We shall be concerned with fluctuations driving the system beyond the basin of attraction of a steady state into the basin of another steady state. In our case, each of these basins is a well in the potential U. The probability of fluctuations is not negligible if the system operates near the boundary of the basin of attraction of a minimum, as is the case with U at criticality (Horsthemke and Brenig, 1977; van Kampen, 1981). Rigorously, the proximity of the initial condition to the threshold of the basin of attraction leading to macroscopic consequences depends on the effective diffusion coefficient f^2, which gives the temperature autocorrelation in time. The proximity determines the magnitude of the barrier M that should be overcome to reach a new basin of attraction. The quantity M vanishes if the initial condition is at the threshold. Therefore, the relevant proximity is determined by an imposed range in the Kramers mean passage time, since this quantity is proportional to $\exp(M/f^2)$.

Ignition processes due to critical internal fluctuations leading to thermal explosions illustrate this situation (Lermant and Yip, 1984; Frank-Kamenetsky, 1955; Bowden and Yoffe, 1958; Friedman, 1963). We shall sketch the kinetic consequences of the hot spot formation, examine in detail the potential U, and derive, finally, the quantity Ω in order to calculate the induction periods in regimes I and II. We shall assume that a single exothermic reaction is the rate-determining step in the kinetics (Lermant and Yip, 1984; Frank-Kamenetsky, 1955; Bowden and Yoffe, 1958; Friedman, 1963). The detailed kinetics for the process are not required, since the present analysis is concerned with fluctuations in T (Tsugé and Sagara, 1976). Detailed chemistry can influence the significance of the temperature fluctuations and their inclusion could be considered for a more refined analysis. The net change in the reaction concentration (given by the number of molecules per unit volume) due to the microscopic occurrence of the exothermic elementary reaction will be denoted w. This quantity scales at equilibrium with the inverse volume:

$$w_{\mathrm{eq}} = \upsilon / V \tag{2}$$

where υ is the stoichiometric coefficient for the reactant. However, if the reaction is confined to a virtual volume Ω at the ignition temperature, the microscopic occurrence is amplified:

$$w = \upsilon / \Omega \tag{3}$$

We shall prove that the local character of the ignition fluctuations is reflected in the following relation, which holds in the thermodynamic limit:

$$\lim_{V\to\infty}(w_{\text{eq}}/w)=0 \tag{4}$$

This relation is valid even at low pressures, when Ω_0 is a good approximation for Ω [this is shown in the work leading to equation (35) below]

$$\lim_{V\to\infty} w_{\text{eq}}/w(\Omega_0)=\lim_{V\to\infty} V^{1/3}/V=0 \tag{5}$$

We define recursively the hierarchy

$$V\geq\Omega_0\geq\Omega_1\geq\Omega_2\geq\cdots\geq\Omega \tag{6}$$

This sequence is a computational artifact arising in a recursive relation for a self-consistent derivation of Ω. The recursive relation will be derived below. The only meaningful elements in the sequence are V, Ω_0, and Ω. The effective size Ω_0 corresponds to the regime I as given in the introduction and the Ω_j can be regarded as approximations to Ω. The convergence of the sequence is faster at low pressures (as we approach regime I), as shown in our example of the ethyl azide in Section 4. The monotonically decreasing sequence is bounded from below; hence, its limit exists and is given by

$$\lim_{j\to\infty}\Omega_j=\Omega \tag{7}$$

The drift term in the transient bimodality regime is determined by a bistable potential $U=U(\bar{T})$ (van Kampen, 1981; Fernández, 1985b). A bar on top of any quantity denotes its volume average. This potential is parametrically dependent on Ω and on y, a quantity that gives the degree of inhomogeneity in the temperature distribution:

$$\begin{gathered} y=(\overline{x^2})^{1/2}; \qquad T=\bar{T}+x; \qquad \bar{x}=0; \qquad |x/\bar{T}|\ll 1, \\ |x/(T_i-T_0)|\ll 1 \end{gathered} \tag{8}$$

The variable x corresponds to the rapidly evolving temperature profile. Thus, x is a space-dependent variable. T_i is the ignition temperature and T_0 is the temperature of the heat bath.

These local fluctuations in the temperature profile are assumed to occur on a faster time scale than the time-dependent global fluctuations of the average temperature $\bar{T}$. This is a basic tenet in previous approaches (Tsugé and Sagara, 1978), in which the inhomogeneous distribution of temperature is averaged to yield $\bar{T}$ and only the fluctuations of $\bar{T}$ are considered. It is precisely this tenet that justifies the separation of the time and space dependences of temperature fluctuations.

We shall make explicit use of this fact in the present work: Since x adjusts itself on a faster time scale, the average quantity y enters as a parameter in the evolution equation (Horsthemke and Brenig, 1977) for $\bar{T}$. In our stochastic formulation, the self-correlation in time for the fluctuations of $\bar{T}$ will also be shown to be dependent parametrically on y. The dependence of U on Ω is due to the instantaneous fluctuations, which affect the reaction rate (Tsugé and Sagara, 1978). It is precisely this fact that will allow us to derive a recursive formula of the form

$$\Omega_{j+1} = F(\Omega_j), \qquad j = 0, 1, \ldots \tag{9}$$

The potential will be given by the indefinite integral over $\bar{T}$ of the difference between the heat production rate, determined by the exothermic reaction, and the heat removal rate in a thermal conduction regime [cf. equation (14) below]. The graphs for the two rates as functions of $\bar{T}$ intersect in three points, which correspond, respectively, to the three critical points in the bistable potential U (Baras *et al.*, 1983).

In order to define U explicitly, a few concepts need to be introduced. The function $f^2 = f^2(\Omega)$ will denote the intensity of the time-dependent fluctuations as determined by the following ensemble averages:

$$\langle \Delta \bar{T}(t) \rangle = 0; \langle \Delta \bar{T}(t) \Delta \bar{T}(t') \rangle = f^2(\Omega)\delta(t - t') \tag{10}$$

These fluctuations occur on a slower time scale than that for the adjustment of the profile x. In the case of a large activation energy ($E/RT \gg 1$), typically the case for thermal explosions, the Arrhenius rate should be replaced by a turbulent reaction rate (Tsugé and Sagara, 1978):

$$\text{Arrhenius rate} = A \exp(-E/R\bar{T}) \tag{11}$$

$$\text{turbulent rate} = \tfrac{1}{2}A \exp[-E/R(\bar{T} + 4f)] \tag{12}$$

We shall obtain explicitly the covariance f^2 in the heat conduction regime for a nonequilibrium gas in contact with a heat bath. This quantity is taken as an adjustable parameter in Tsugé and Sagara (1978).

The mean heat removal term is given by $\gamma_0(\bar{T} - T_0)$, where γ_0 is the heat exchange coefficient. A more realistic analysis with an inhomogeneous temperature distribution requires

$$\gamma = \gamma_0 + \beta(y) \tag{13}$$

where γ is the actual heat exchange coefficient and γ_0 the apparent one, which occurs in the limit $y = 0$. The derivation of the size-dependent parameter $\beta(y)$ is given in Section 3. A spherical vessel will be considered not only for mathematical simplicity, but also since this situation corresponds to the experimental conditions of relevance (Rice, 1940; Rice *et al.*, 1935; Boddington *et al.*, 1983).

The potential is given by

$$\begin{aligned} U &= U(\bar{T}, y, \Omega) \\ &= \int d\bar{T}\,([\gamma_0+\beta(y)](\bar{T}-T_0)-\tfrac{1}{2}T_0\exp\{-E/R[\bar{T}+4f(\Omega)]\}) \end{aligned} \tag{14}$$

where

$$\gamma = S\theta\mu/2Vr_0 \tag{15}$$

and the following notation has been adopted: S is the surface area; V is the volume; R is the universal gas constant; r_0 is the radius of the vessel; $\theta=\lambda/\sigma$; $c\rho\lambda$ is the heat conduction constant; c is the specific heat; ρ is the density; $\sigma=QA(\rho cT_0)^{-1}$; Q is the exothermic heat of reaction; μ is the Nusselt number; and A is a preexponential factor in the reaction rate. The parameter σ allows us to introduce a dimensionless time τ, defined as $\tau=\sigma t$, associated with the chemical rate process.

The ignition temperature T_i corresponds to a flat maximum at the critical regime considered, since the inflection point between T_a, the temperature for steady combustion, and T_i coalesces with T_a, thus determining that the curvature of U at T_i should be regarded as a small parameter of the system. Thus, at the ignition temperature, we have

$$u=\frac{\partial^2}{\partial\bar{T}^2}U(T_i)\lesssim 0; \qquad \frac{\partial}{\partial\bar{T}}U(T_i)=0 \tag{16}$$

The ignition temperature is related to the temperature for steady combustion by the following approximate formula (Frank-Kamenetsky, 1955; Bowden and Yoffe, 1958; Friedman, 1963);

$$T_i = T_a + 1.60RT_0^2/E \tag{17}$$

Within the time scale given by the induction period, the potential can be approximated by the parabola given by (van Kampen, 1981)

$$U = U(T_i) + u/2(\bar{T}-T_i)^2 \tag{18}$$

This approximation is adequate only within the time scale for validity of the Fokker-Planck equation, that is, during the induction period. After this period, the probability density develops two peaks and does not satisfy the Fokker-Planck equation.

The next stage is to determine the effective size of the hot spot. The Fokker-Planck equation for $P(\bar{T}, t)$ is subject to the detailed balance principle under generalized fluctuation-dissipation conditions (van Kampen, 1981). In the context of interest to us, the total energy of the closed gaseous system together with the heat bath is a constant. Thus, the equation for the distribution of temperature deviations is

$$\frac{\partial P}{\partial \tau}(z,\tau)=\frac{1}{2}\frac{\partial}{\partial z}P^{s}(z)f^{2}\frac{\partial}{\partial z}\left(\frac{P(z,\tau)}{P^{s}(z)}\right) \tag{19}$$

where $z=\bar{T}-T_i$, $P(z,\tau)$ is the probability distribution, $P^s(z)$ is the stationary distribution $= N^{-1}\exp[-U(z+T_i)/f^2]$, and N^{-1} is the normalization constant.

The necessary and sufficient condition to be satisfied by equations (18) and (19) in order to have detailed balance under generalized fluctuation-dissipation conditions is (van Kampen, 1981)

$$uz=\tfrac{1}{2}[P^{s}(z)]^{-1}\frac{\partial}{\partial z}[P^{s}(z)f^{2}] \tag{20}$$

This relation can be interpreted as a flux or current-matching condition. An expression for the covariance can be obtained by expanding P^s around T_i in powers of z and making use of the definition given by equation (14). Retaining only the lowest order term in z and substituting into equation (20), we get

$$f^{2}=f_{1}^{2}(\Omega)V^{-1}=V^{-1}\{T_{0}^{2}\exp[-E/R(T_{i}+4f)]+[\gamma_{0}+\beta(y)](T_{i}^{2}+T_{0}^{2})\} \tag{21}$$

The inverse size parameter Ω^{-1} is defined as the scaling factor for the time-dependent fluctuations that appear when we make use of classical Semenov theory in the equilibrium problem at the hot spot. Within this virtual system, $y=0$ and the rate of reaction is nonturbulent:

$$f^{2}=f_{0}^{2}\Omega^{-1}=\Omega^{-1}[T_{0}^{2}\exp(-E/RT_{i})+\gamma_{0}(T_{i}^{2}+T_{0}^{2})] \tag{22}$$

Thus, from equations (21) and (22), we obtain

$$\Omega/V=f_{0}^{2}/f_{1}^{2}(\Omega) \tag{23}$$

Equation (23) is a transcendental relation, which will be solved in an iteratifve self-consistent way. This recursive method requires a sequence (or hierarchy) of Ω_j defined in an inductive way:

$$\begin{aligned}\Omega_{0}/V&=f_{0}^{2}\{T_{0}^{2}\exp(-E/RT_{i})+[\gamma_{0}+\beta(y)](T_{i}^{2}+T_{0}^{2})\}^{-1}\\ \Omega_{j+1}/V&=f_{0}^{2}/f_{1}^{2}(\Omega_{j})\end{aligned} \tag{24}$$

As can be easily verified, the sequence is monotonically decreasing and bounded from below; therefore, relation (7) holds. The sequence of Ω_j should be regarded as a result of the computation of Ω. At very low pressures, approaching regime I, Ω_0 coincides with Ω. Within regime II, Ω_3 is already a good approximation for Ω, as shown in Section 4.

3. SCALING OF FLUCTUATIONS FOR AN INHOMOGENEOUS DISTRIBUTION OF TEMPERATURES

The purpose of this section is to analyze how Ω_0 behaves near the thermodynamic limit. This requires the calculation of $\beta = \beta(y)$, which determines the size effects on the heat exchange coefficient when the system operates in a heat conduction regime. It is easily demonstrated that

$$\lim_{y \to 0} \beta = 0 \tag{25}$$

Therefore, in the limit of a homogeneous distribution, we have

$$\lim_{y \to 0} \Omega_0 = V \tag{26}$$

In order to proceed with the evaluation of β, we first consider the thermal diffusion equation for the temperature evolution including the reactive heat source:

$$(d/d\tau)(\bar{T}+x) - \theta \operatorname{div} \operatorname{grad}(\bar{T}+x) = T_0 \exp[-E/R(\bar{T}+x)] \tag{27}$$

By taking the volume average in this equation and making use of equation (12) and the facts that $\bar{x}=0$ and grad $\bar{T}=0$, we get

$$(d/d\tau)\bar{T} - \theta\, \overline{\operatorname{div} \operatorname{grad} x} = T_0 \exp\{-E/R[\bar{T}+4f(\Omega)]\} \tag{28}$$

The heat exchange at the walls is governed in the thermal conduction regime by the following relation (Frank-Kamenetsky, 1955; Bowden and Yoffe, 1958; Friedman, 1963):

$$-\mathbf{n} \cdot (\operatorname{grad} x)_b = \frac{\mu_0}{2r_0}(\bar{T}_b - T_0) \tag{29}$$

The index b indicates that the quantities are evaluated at the boundary.

The normalized outward unit vector at the boundary is $\mathbf{n}$, and μ_0 is the Nusselt number theoretically estimated by Frank-Kamenetsky (1955). His estimation is $\mu_0 = 3.39$.

We can now make use of Gauss' divergence theorem and combine equations (28) and (29) to obtain

$$(d/d\tau)\bar{T} + \gamma(\bar{T} - T_0) + \mu_0\lambda(2V\sigma r_0)^{-1} \int_S x\, ds$$
$$= T_0 \exp[-E/R(\bar{T}+4f)] \tag{30}$$

In order to obtain an equation for x, we subtract equation (30) from (27). This gives, disregarding terms of order x^2, a stationary equation for x in which the transport effects are decoupled from the kinetics:

$$\theta \operatorname{div} \operatorname{grad} x + \lambda\mu_0(\sigma 2 V r_0)^{-1}\left\{\int_S x\, ds + S(\bar{T} - T_0)\right\} = 0 \tag{31}$$

Given that the magnitude of x is small compared to the difference $\bar{T} - \bar{T}_0$ near the ignition point (see Tsugé and Sagara, 1978), we can disregard the integral when compared with the term $S(\bar{T} - T_0)$ in (31). Then, to order x, we get by direct integration of (31) for the case of a spherical vessel

$$x = \frac{\gamma_0}{2\theta}(\bar{T} - T_0)(\tfrac{3}{5}r_0^2 - r^2) \tag{32}$$

$$\beta = \frac{\gamma_0^2}{5\theta} r_0^2 \tag{33}$$

$$y = (x^2)^{1/2} = \left(\frac{3}{175}\right)^{1/2} \frac{\gamma_0 r_0^2 (T_i - T_0)}{\theta} \tag{34}$$

Relation (32) can be verified directly by differentiating twice with respect to r: we can see that (31) is satisfied if we disregard the term proportional to the surface integral of x. This is a valid approximation according to equation (8). The integration constant $(3/5)r_0^2$ is determined from the condition $\bar{x} = 0$ already specified in (8).

The behavior of Ω_0 at the thermodynamic limit can be obtained from equations (22), (24), and (33): V is of order r_0^3, and Ω_0/V is of order r_0^2 for large r_0 corresponding to the thermodynamic limit. Therefore, we get

$$\Omega_0 \sim O(V^{1/3}) \tag{35}$$

4. THE INFLUENCE OF TURBULENT INSTANTANEOUS FLUCTUATIONS ON THE INDUCTION PERIOD

In this section the theory presented will be tested against experimental evidence. The induction time $t_{\mathrm{in}}(\Omega)$ is obtained by determining the mean passage time for the parabolic approximation from equations (16)–(18):

$$t_{\mathrm{in}}(\Omega) = \frac{\int_{-\infty}^{0} P^{s}(z)\, dz}{f^2(\Omega)\sigma} N \exp \frac{U(T_i)}{f^2(\Omega)} \left[\frac{2\pi f^2(\Omega)}{|u|}\right]^{1/2} [1 + O(f^2)] \tag{36}$$

It should be noticed that the induction period, or, equivalently, the Kramers mean passage time for the diffusion across the barrier is not a stochastic variable. This is so since it is a function of the ensemble-averaged quantity f and not of the stochastic variable $\Delta\bar{T}(t)$.

Numerical computations for the case of the thermal explosions of ethyl azide (Rice, 1940; Rice *et al.*, 1935; Boddington *et al.*, 1983) reveal that in the case of a rarefied gas (0.01–0.05 atm) the convergence of the numerical sequence $t_{\mathrm{in}}(\Omega_j)$ is extremely fast and $t_{\mathrm{in}}(\Omega_0)$ is already a very good approximation to the actual ignition time given by

$$\lim_{j \to \infty} t_{\mathrm{in}}(\Omega_j) = t_{\mathrm{in}} \tag{37}$$

The experimental data are as follows (Rice, 1940; Rice *et al.*, 1935);

$$r_0 = 3.63 \text{ cm}, \qquad Q = 55 \text{ kcal/mole}, \qquad E = 39 \text{ Kcal/mole}$$

$$c\rho\lambda = 10^{-4} \text{ cal K}^{-1} \text{ cm}^{-1} \text{ sec}^{-1}.$$

Two cases will be considered:

(a) $P = 16$ mm, $A = 0.028 \exp(E/RT_0) \text{ sec}^{-1}$, $T_0 = 553$ K, $n = 0.46 \times 10^{-6}$ mole/cm^3

(b) $P = 92$ mm, $A = 0.0085 \exp(E/RT_0) \text{ sec}^{-1}$, $T_0 = 533$ K, $n = 2.76 \times 10^{-6}$ mole/cm^3

Making use of the working equations (21)-(24), we find for case (a)

$$f(\Omega_0)/T_i = 0.00201, \qquad f(\Omega)/T_i = f(\Omega_1)/T_i = 0.00205 \tag{38}$$

The enhancement of fluctuations with respect to the equilibrium situation can thus be attributed exclusively to the β contribution, that is, to the inhomogeneous temperature distribution, and we find

$$t_{\text{in}}(\Omega_0) = t_{\text{in}} = 1.66 \text{ sec}$$

This value is in satisfactory agreement with the experimental value estimated as 2 sec. In case (b), the situation is radically different, as the following results show:

$$f(\Omega_0)/T_i = 0.0044; \qquad f(\Omega_1)/T_i = 0.027; \qquad f(\Omega_2)/T_i = 0.030$$

$$f(\Omega_3)/T_i \approx f(\Omega_4)/T_i \approx f(\Omega)/T_i = 0.031$$

$$\Omega_0/V = 0.81; \qquad \Omega_1/V = 0.29; \qquad \Omega_2/V = 0.014; \qquad \Omega_3/V = 0.012$$

$$\Omega_3/V \approx \Omega_4/V \approx \Omega/V \approx 0.012$$

$$t_{\text{in}}(\Omega_0) = 16.6 \text{ sec}; \qquad t_{\text{in}}(\Omega_1) = 7.13 \text{ sec}; \qquad t_{\text{in}}(\Omega_2) = 5.55 \text{ sec}$$

$$t_{\text{in}}(\Omega_3) = 5.22 \text{ sec}; \qquad t_{\text{in}}(\Omega_3) \approx t_{\text{in}}(\Omega_4) \approx t_{\text{in}}(\Omega) = 5.22 \text{ sec}$$

This last result exhibits again satisfactory agreement with the experimental measurements, which give an ignition time of 5 sec.

We can conclude that the turbulent effects due to temperature autocorrelations are very crucial even at moderately low pressures.

Finally, a computation has been carried out at pressures beyond the experimental range II for the sake of studying the rate of convergence of the sequence of size parameters and to compare with previous cases. The conditions chosen are

$$A = 7 \times 10^{-2} \exp(E/RT_0) \text{ sec}^{-1}, \qquad T_0 = 533 \text{ K}$$

with the other parameters being the same. Since the turbulent effects become crucial in the evaluation of the reaction rate, even more so than in regime II, the results show, as expected, a slower rate of convergence:

$$\Omega_0/V = 0.86, \qquad \Omega_1/V = 0.20, \qquad \Omega_8/V = 9\times 10^{-3}$$
$$\Omega_9/V \approx \Omega_{10}/V = 6.6\times 10^{-4} \approx \Omega/V$$

The turbulent effects are so considerable that ten iterations are required and the ignition period has departed considerably from the starting term:

$$t_{\text{in}}(\Omega_0) = 19\text{ sec}, \qquad t_{\text{in}}(\Omega_9) \approx t_{\text{in}}(\Omega_{10}) \approx t_{\text{in}}(\Omega) = 0.87\text{ sec}$$

ACKNOWLEDGMENTS

We thank Prof. Forman Williams and Dr. Richard Yetter for helpful discussions. We acknowledge support from the department of Energy for this research.

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