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A review of one aspect of the thermal-explosion theory

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Abstract The historical development of the thermal-explosion theory is examined and reviewed, It is shown that the original formulation of the problem by Semenov accurately defines the phenomenon and explains the reason for the explosion. He showed that, when the heat generation within the solid exceeds the heat dissipation to the surroundings, explosion occurs. Frank-Kamenetskii's disapproval of Semenov's logic theorized that the difference between the temperatures at the center of the solid and its surface is the cause of the explosion. His famous and ingenious small-temperature model and the solution to the differential equation that resulted from that distorted the problem and delayed the progress to a full understanding of the problem. He concluded that explosion occurs when no solution to the problem exists. The exact solution to the problem by Shouman, Donaldson and Tsao reaffirmed the validity of the Semenov formulation. Further examination of the effect of reactant consumption on the problem produced full understanding of the physics of the problem.

Keywords Explosion · Thermal · Theory · Instantaneous ignition

Nomenclature

A_n frequency factor (s^{-1})
B $QC_0E/\rho c_v RT_s$
C concentration of reactant ($mol\,m^{-3}$)
C_0 initial concentration of reactant ($mol\,m^{-3}$)
c_v specific heat ($JK^{-1}\,kg^{-1}$)
E activation energy ($J\,mol^{-1}$)
h convection heat transfer coefficient ($JK^{-1}\,m^{-2}\,s^{-1}$)
n order of reaction
Q heat of reaction ($J\,mol^{-1}$)

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R	universal gas constant
V	volume (m^3)
T	temperature (K)
Z	C/C_0

Greek symbols

δ	Frank-Kamenetskii parameter
Φ	$(T - T_s)E/RT_s^2$
ρ	reactant density ($kg\,m^{-3}$)
θ	RT/E
τ	$QEtA_n C_0^n e^{-E/Rts}/\rho c_v RT_s^2$
Ψ	$QVA_n C_0^n E e^{-E/RT}/hSRT_a^2$

Subscripts

a	ambient condition
ad	adiabatic condition
i	condition at ignition or inflection
m	condition at maximum
o	initial condition
s	surface condition
∗	critical condition

1 Introduction

In this paper we shall review and examine the historical development of the thermal-explosion theory. Semenov's original formulation and treatment describes the problem accurately as caused by the imbalance between the heat generation within the solid and the heat dissipation to the surroundings. Frank-Kamenetskii's disapproval and criticism of Semenov's logic theorized that the most important factor is the difference in temperature between the center of the solid and its surface. This produced his ingenious small-temperature difference approximated differential equation and its exact solution. The fascination of the research community with his results delayed real progress towards a true understanding of the problem and discovering the real solution for it. This is amazing, since his solution produced no solution at all to the explosion state and simply stated that explosion occurs when no solution to the equation existed. This actually masked the nature of the explosion process as a jump phenomenon due to the existence of two solutions to the nonlinear problem, one at a low temperature and the second at a high temperature. The explosion phenomenon being a jump from the low-temperature solution to the high-temperature solution. An analogy to this problem is the problem of the jump from supersonic to subsonic flow and the production of a shock wave. The Semenov model was proved to be accurate and valid after Shouman and Donaldson exactly solved the original equation. Greater strides followed in understanding the problem and recognizing the influence of the reactant consumption on the problem.

2 Semenov's approach

Semenov [1, 2] originally formulated the thermal explosion problem in solids. He used a very simple model where he assumed that the solid, regardless of its shape, has a uniform temperature distribution and that the heat generated within the solid is dissipated to its surroundings by convection. He theorized that the explosion phenomenon occurs when the heat generation exceeds the heat dissipation. He examined the mathematical solution of this simple model. He examined both the heat generation and dissipation

as functions of the temperature difference between the solid and the surroundings. He noticed that the heat-dissipation line is tangent to the heat-generation line at one point, which he defined as the critical point. He also noticed that in the sub-critical region of the solution three different temperatures existed where the heat generation is equal to the heat dissipation, thus producing a possible equilibrium state. Both the low and high temperatures proved to be stable solutions, while the intermediate temperature proved to be unstable. He then correctly concluded that the explosion process occurs when the state of the system jumps from the low-temperature equilibrium state to the high-temperature equilibrium state (similar to the phenomenon of shock waves in modern gas dynamics). In the supercritical state, only one solution exists at high temperature, thus indicating that, if the solid reaches the critical temperature, it would run away to explosion. This then established the Semenov criterion that, if the solid temperature exceeds the surrounding temperature by a critical value, explosion will occur.

3 Frank-Kamenetskii's approach

Frank-Kamenetskii [3–6] criticized Semenov's model of assuming uniform temperature distribution within the solid and theorized that the temperature difference between the center of the solid and its surface is the most important parameter for causing explosion. He considered the differential equation governing the temperature distribution within a solid and transformed it to a solvable form by using his ingenious small-temperature-difference approximation. The analytical solution to the equation produced an analytic function defining the relationship between δ and Φ which demonstrated a maximum which was designated as the critical $\delta(\delta_c)$. The function indicated that in the region below δ_c, which was defined as the sub critical region, two solutions existed for the problem, one at low temperature and the other at high temperature. The region above δ_c, which was defined as the supercritical region, has no solution. Hence the explosion domain was defined as the region where no solution to the problem exists. This result distorted the physical picture of the problem and set back the progress towards gaining a better understanding of it.

4 Shouman, Donaldson and Tsao's contribution

Shouman et al. (7) solved the governing equation for the slab exactly. Their findings confirmed Semenov's interpretation of thermal explosion as a jump phenomenon from a low-temperature stable solution to a high-temperature stable solution. The solution indicated three zones, subcritical, critical and supercritical. In both the subcritical and supercritical zones, only one solution exists for the problem. In the critical zone, three solutions exist, two stable solutions and a third that is unstable. The unstable solution is at an intermediate temperature between the low- and high-temperature stable solutions. When explosion occurs, the state of the solid jumps from the low-temperature stable solution point to the high-temperature stable solution point. This phenomenon occurs when the heat generated within the solid exceeds the heat dissipated to the surroundings.

5 Consideration of reactant consumption

Rice et al. (8) considered the effect of reactant consumption on the criticality of thermal explosion. They defined criticality as the attainment of an inflection in the temperature-time trajectories before the maximum temperature is reached. This definition was further used by Todes and Melentev (9,10) as well as Ashmove et al. (11). Thomas (12) approximated the problem by an Airy equation and defined criticality by designating certain boundary conditions. Kordeylewski and Wach (13) used the same criterion defined by Thomas. Squire (14) was the first to transfer the problem to the dimensionless temperature (τ)-concentration (Z)-plane. This produced a first-order nonlinear differential equation with initial boundary

condition. He defined the induction time as the time for a supercritical system to reach $\Phi = 2.0$ for a first-order reaction. He used τ as the independent variable and numerically integrated the equation up to $\Phi = 2.0$, hence obtaining what he defined as the induction time. He states that the values he obtained for the critical conditions were not as accurate as those obtained by Thomas. Adler and Enig (15) challenged the classical definition of the critical state and defined the critical parameters as those necessary to produce a solution to the equation in the (Φ, Z)-plane that possesses a point of tangency with the locus of inflection points in the (Φ, Z)-plane. They hence recommended the definition of the critical solution as that which possesses a single inflection point in the (Φ, Z)-plane instead of the (Φ, τ)-plane before reaching the maximum Φ. They predicted for the first-order reaction a universal critical temperature difference $\Phi^* = 2.0$ and hence established the boundary line between subcritical and supercritical states. They also extended their analysis to higher-order reactions and used Φ as the independent variable in their analysis. They showed that $\Phi^* = 1 + \sqrt{n}$ for all degrees of reaction. Gray and Sherrington (16) condemned Adler and Enig's work by wrongly concluding that their results do not lead to the classical Semenov answer of $\Phi^* = 1.0$ for $B = \infty$ although substituting for $n = 0$ gives the desired result. Instead they concluded that there was something wrong with the use of the (Φ, Z)-plane. However, they later suggested (17) the use of Liapounov functions in the (Φ, Z)-plane to analyze the problem. They in essence suggested replacing Adler and Enig's exact functions by approximate functions to be chosen by trial and error. Boddington et al. (18) defined an empirical relationship for the concentration as a function of time and used as a criterion for criticality the existence of an inflection in the (Φ, τ)-plane, Boddington et al. (19) defined criticality as the point of maximum sensitivity of Φ_m (maximum excess temperature) to Ψ (Semenov number). They hence defined criticality as the point where $\mathrm{d}^2 \Phi_m / \mathrm{d} \Psi^2 = 0$. Shouman and El-Saved (20) reviewed the work on criticality and showed that there is no contradiction between Adler and Enig's results and the classical Semenov problem. They intuitively, without proof, defined criticality in the (Φ, τ)-plane as the point where $\mathrm{d}^2 \Phi / \mathrm{d} Z^2 = 0$ and $\mathrm{d}^3 \Phi / \mathrm{d} Z^3 = 0$, which produced the same result as Adler and Enig. Shouman (21) suggested an approximate method for accounting for reactant consumption in the Semenov problem. Shouman and El-Sayed (22) examined the mathematical foundation of criticality for the thermal explosion problem. They proved that criticality in the (Φ, τ)-plane is defined by the point where $\mathrm{d}^2 \Phi / \mathrm{d} \tau^2 = 0$ and $\mathrm{d}^3 \Phi / \mathrm{d} \tau^3 = 0$. This agrees with the definition of the critical trajectory as the one that is tangent to the locus of inflection points in the (Φ, τ)-plane. Similarly they defined criticality in the (Φ, Z)-plane as the point where $\mathrm{d}^2 \Phi / \mathrm{d} Z^2 = 0$ and $\mathrm{d}^3 \Phi / \mathrm{d} Z^3 = 0$. This trajectory is tangent to the locus of the inflection points in the (Φ, Z)-plane. Criticality in the (Φ^*, Ψ^*)-plane was defined as the point where $\mathrm{d} \Phi^* / \mathrm{d} \Psi^* = 0$. It was shown that criticality in the (Φ, Z)-plane is identical to that in the (Φ^*, Ψ^*)-plane while different from that in the (Φ, τ)-plane. It was proved that the critical state in the (Φ, τ)-plane is a subcritical state in the (Φ, Z)-plane and the critical state in the (Φ, Z)-plane is a supercritical state in the (Φ, τ)-plane. Proof was provided that criticality in (Φ, τ)-plane and (Φ, Z) plan becomes identical only when $n = 0$ or $B = \infty$. It was also shown that, as B approaches infinity, the dependence of Φ on τ becomes independent of n and approaches that for $n = 0$ and the opposite is not true. The criticality limits for zero-order reaction with finite B were established, showing the effect of initial cooling and heating. The effect of the degree of reaction on the induction time was demonstrated and the conditions for ignition of subcritical systems were defined.

Shouman and E1-Sayed (23) applied their definition of the criticality condition to the Arrhenius model. The dependence of the critical temperature θ^* on the ambient temperature θ_a and the order of reaction n was demonstrated. It was found that all solutions for θ^* as a function of θ_a for any value of n passed through the point of $\theta_a = 0.25$ and $\theta^* = 0.5$ (the transition point for $n = 0$). It was shown that a transition temperature exists for all degrees of reaction, except for $0 < n < 1.0$. For a first-order reaction, θ^* monotonically increases with the ambient temperature and reaches ∞ at $\theta_a = 0.5$. For $0 < n < 1.0$ no solution exists for $\theta^* = 0.5/(1 - n)$, no transition temperature and extinction branch exist. The solution for θ^* as a function of θ_a passes through an inflection point at $\theta_a = 0.25$, $\theta^* = 0.5$. It was shown that a significant difference exists between the results obtained from the Arrhenius model and those obtained from the Frank-Kamenetskii approximated model. The critical state in the (θ, τ)-plane was found to be sub-critical in both the (θ, Z)

and (θ^*, Ψ) –planes, which produced identical results. Proof was provided that criticality in the (θ, τ)-plane coincides with that in the (θ, Z) and (θ, Ψ)-planes only when $n = 0$ or $B = \infty$. The criticality limits for zero-order reaction with various ambient temperatures and initial conditions was discussed.

Shouman and El-Sayed (24) utilized the marching Taylor-expansion method to examine the critical conditions for the thermal- explosion problem governed by the Arrhenius reaction-kinetic equation. They showed the contrast between the behavior of systems with high θ_{ad} and high θ_a, low θ_{ad} and low θ_a, as well as high Old θ_{ad} and low θ_a. The criticality boundaries with different degrees of reaction as a function of ambient temperature were established. They compared their results with those existing in the literature.

6 Conclusion

In this paper we traced the progress made in the thermal-explosion theory since it was first considered by Semenov. Semenov originally theorized that thermal explosion occurs when the heat generation within the solid exceeds the heat dissipation from its surface. Semenov's model was criticized for assuming uniform temperature to exist through the solid. Frank-Kamenetskii suggested that the most important parameter for explosion to occur is the temperature difference between the center of the solid and its surface. He used his ingenious small temperature approximation to produce an exact solution to the approximated differential equation. Unfortunately this solution contradicted the physical reality of the thermal-explosion problem. When finally the equation describing the problem was solved exactly, it was proved that Semenov's original theory was the correct one. It was not possible to understand correctly the nature of a thermal explosion until the effect of reactant consumption was taken in consideration. It is hoped that this paper gives an honest and accurate evaluation about the strides made towards understanding the thermal-explosion problem and how bias and prejudice can delay progress, even in scientific endeavors.

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