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Introduction

1.1 Informal Description of Thermal Explosion

The notion of explosion is familiar to everyone. Explosions for high-rise building demolition, accidental domestic gas explosions, volcano eruptions and nuclear explosions are just few examples.

In everyday's perception, explosion power and its consequences are primary questions of interest. Most noticeable explosions are indeed accompanied by sound, thermal and/or shock waves, emission of electromagnetic impulses, radiation, etc., causing significant destruction.

Scientific perception is, however, different. In scientific investigation, the cause and mechanism of explosion and the analysis of conditions that lead to explosion take the center stage.

It is clear that, essentially, explosion is a quick release of a significant amount of energy. However, the mechanisms of such release may be vastly different. Moreover, phenomena that are intrinsically of explosive nature may not cause significant damage. As such, scientifically, in the notion of explosion, the intrinsic properties of the phenomenon and its mechanisms are of importance, rather than its appearance and consequences.

Thermal explosion is a good example. This term refers to explosion that is progressively driven by energy generation, which occurred at earlier stages of the explosion development. Energy, needed for explosion to progress, must be contained within the system, i.e. no external energy supply is required for such explosion to occur. Moreover, energy release is quickly self-accelerating. Self-acceleration means that the rate at which energy is being generated within the system is increasing as the total amount of energy that has been released increases. This is a very important necessary condition for thermal explosion.

Such self-acceleration may only occur in strongly non-linear physical or chemical systems. It should be noted, though, that before the rapid self-accelerating stage there may exist the so-called induction period of thermal explosion (in some cases, very long) during which energy accumulation in the system is very slow.

The present book is confined to the analysis of the very specific mechanism of energy generation in a thermal explosion, that is to the release of energy via exothermic chemical reactions. Heat generated in such reactions causes the reaction rate to grow rapidly, providing a positive feedback mechanism and causing reaction self-acceleration. The exact mechanism of such reaction rate self-acceleration (Arrhenius dependence of the reaction rate on the mixture temperature) will be clarified below.

It should be understood that, of course, in such a process, energy would also be lost from any real system. However, under certain circumstances, the rate of energy dissipation would become less

Thermal Explosion: Theory and Application, First Edition. Vasily B. Novozhilov.

than the rate of energy accumulation. Under such conditions, which are called critical conditions of thermal explosion, the progressive accumulation of energy would proceed.

Thermal explosion may be observed in laboratory conditions, in relatively small-scale vessels containing mixtures of reacting gases. Therefore, the damage caused by such explosions may in some cases be minimal.

This is not to say that the opposite cannot occur. Thermal explosions can be very severe. Some of these occasions have been well documented.

Such was the Texas City disaster that occurred on April 16, 1947 (Fire Prevention and Engineering Bureau of Texas and The National Board of Fire Underwriters 1947). It is believed to be the deadliest industrial accident in the United States history and one of the largest non-nuclear explosions in history with 581 deaths and more than 8,000 victims. The accident, which was a chain of different fires and explosions, started with a detonation of 2,300 tons of ammonium nitrate in the ship (S.S. GRANDCAMP) cargo due to thermal explosion.

Destructions were overwhelming. S.S. GRANDCAMP exploded violently, and there were reports of secondary explosions. An immense tidal wave flooded the vicinity of the explosion. The area was quickly filled with dense smoke from burning chemical facilities and oil refineries. Shock waves were easily felt 10 ml away. Shocks were able to shake buildings and shatter glass windows over wide areas.

Apart from fatalities and casualties, there was widespread property damage. The most extensive damage was sustained by Monsanto Chemical Company and Texas City Terminal Railway Company; however, many more businesses were affected.

Figure 1.1 is an artist's impression of the Texas City Disaster.

Another example is the thermal explosion of dinitolmide (or zoalene) which was used as a poultry feed additive, in a dryer at King's Lynn (Health and Safety Executive 1976) on 27 June, 1976. There was one death and extensive damage to the plant and adjacent buildings.

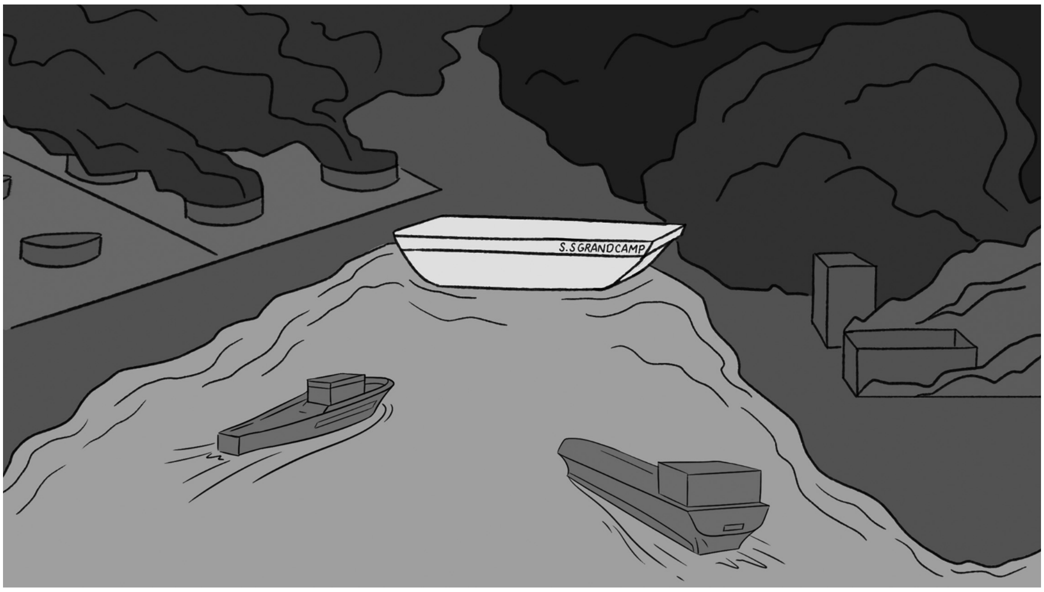

Figure 1.1 An artist's impression of the Texas City Disaster on April 16, 1947.

The two above-mentioned examples represent a traditional risk of thermal explosion associated with processing, storage or transportation of large amounts of particular chemicals. Recently, less obvious areas of thermal explosion hazards emerged, for example, solid biomass fuels (Koseki, H. 2011) and lithium-ion batteries (British Broadcasting Corporation 2013) industries.

1.2 Historical Remarks and Terminology

The discovery of the theory of thermal explosion was a logical consequence of all the preceding studies on combustion.

A scientific study of combustion began in the eighteenth century, along with the rapid development of chemistry. It was at that time when Lomonosov and Lavoisier rejected false beliefs of their contemporaries that substances capable of combustion must contain a specific element, the so-called phlogiston. In 1773, Lavoisier finally arrived at the correct conclusion that combustion is a process of a chemical combination (reaction) of substances with the oxygen in the air. The developments of the latter half of the eighteenth century (such as the discoveries of nitrogen, hydrogen, carbon monoxide and dioxide) supported Lavoisier's theory.

In the early nineteenth century, Davy conducted some experimental research on combustion, in particular, he measured flame temperatures, studied the effects of dilution and discovered catalytic combustion. He also succeeded in practical inventions related to combustion and is known for Davy's safety lamp, which had flame surrounded by a metallic mesh screen, considerably reducing the risk of its use in mining.

A significant progress in understanding the laws of chemical kinetics was made in the second half of the nineteenth century. Guldberg and Waage discovered the law of mass action, which establishes the direct proportionality of the reaction rate to the product of the concentrations of the reactants. Further, van't Hoff in 1884 and, based on his work, Arrhenius in 1889 quantified the dependence of the reaction rate on mixture temperature. Moreover, Arrhenius uncovered the kinetic essence of Van't Hoff's law, relating a number of active molecules, capable of chemical reaction, to considerations of kinetic theory of gases. The final result of this work, the so-called Arrhenius equation for the reaction rate constant, is a cornerstone of the modern combustion theory and is immensely important for understanding and predicting thermal explosion. The laws of chemical kinetics are reviewed in Section 1.3 below.

A correct understanding of the chemical nature of combustion at this early stage of modern science laid the foundation for the development of power engineering and thermodynamics, as the process of combustion was the major supplier of high-temperature gases and energy. At the end of nineteenth century, intensive investigations were conducted on chemical-thermodynamic equilibria in the system $H_2 – H_2O – CO – CO_2 – C – O_2$, which determines, in the first approximation, the combustion temperature of hydrocarbons.

The application of combustion process continued alongside its scientific investigation. Knowledge gained in laboratories warranted a great contribution of combustion to Industrial Revolution, steadily expanding its application from primitive use in fireplaces and outdoor gas lamps to sophisticated power generation in steam and internal combustion engines (Figure 1.2).

At the early stages of the combustion theory development, the names of Michelson, Berthelot, Vieille, Jouguet, Taffanel, Daniell and Chapman are worth mentioning.

In 1928, Russian scientist Nikolay Nikolaevich Semenov published a paper (Semenov 1928a), which laid the foundation of thermal explosion and, in fact, the whole modern combustion theory.

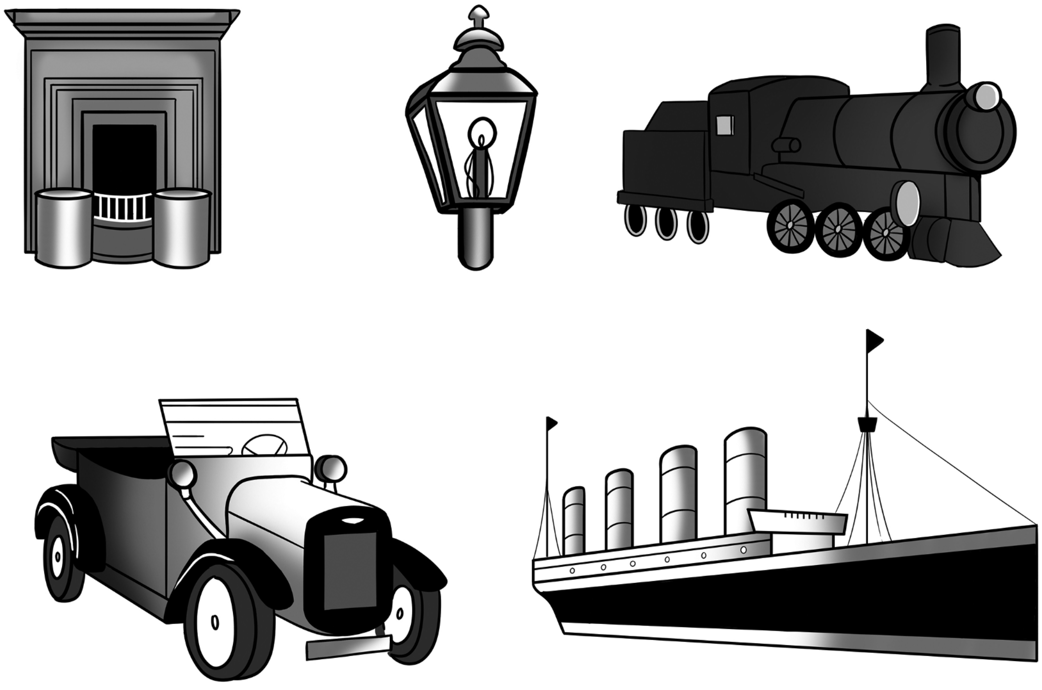

Figure 1.2 Some applications of combustion.

Semenov's paper considered only the absolutely essential elements of thermal explosion, the features without which autoignition simply cannot exist. He took into account the Arrhenius law of heat generation, using the simplest zeroth-order reaction model, and Newton's law of heat dissipation driven by the difference between the mixture temperature (assumed uniform) and the background one.

Yet, this simplest formulation crystallized a powerful insight into the very nature of autoignition as progressive thermal self-acceleration in the absence of comparable heat dissipation. The same process is at the base of all combustion phenomena; for example, it is occurring on a continuous self-supporting basis in a travelling combustion wave. The explosive self-acceleration of a chemical reaction is at the centre of the modern definition of combustion: 'Combustion is a chemical reaction proceeding under conditions of progressive self-acceleration ...' (Frank-Kamenetskii 2016). In other words, reaction is classified as combustion based on the characteristic features of the chemical process, rather than on the nature of substances involved. From this point of view, one can speak, for example, about the flame of ozone decomposition $2O_3 \rightarrow 3O_2$, although oxygen is released in this reaction rather than being consumed. One can equally speak about combustion processes in the complete absence of oxygen, such as combustion of hydrogen in chlorine.

Semenov considered the theory of thermal explosion as one of the his three major scientific achievements, along with the theory of thermal dielectric breakdown and the theory of chain reactions (Semenov 2004).

The latter theory also contributed greatly to the progress of combustion science. About the same time when Semenov's first paper on thermal explosion appeared, it had become apparent that not all explosive behaviours in chemical processes could be explained by thermal self-acceleration. An alternative self-acceleration mechanism, chain-branching reaction, was predicted by Christiansen and Kramers in 1923, who, however, did not elaborate on the idea further. Semenov demonstrated that such a mechanism indeed explains observed facts (a peculiar combustion behaviour of phosphorus vapour/oxygen mixtures studied by Chariton and Valta in 1926). It is this discovery that eventually resulted in Semenov and Sir Cyril Hinshelwood, who conducted similar studies at Oxford, being awarded the Nobel Prize in Chemistry in 1956 'for their researchers into the mechanism of chemical reactions' (Ölander 1956). Notably, Semenov and Hinshelwood's award was closely related to the very first Nobel Prize in Chemistry given in 1901 to Van't Hoff for '…"the discovery of the laws of chemical dynamics", i.e. the velocity of chemical reactions' (Ölander 1956).

Both thermal explosion and chain reaction studies have been significantly advanced by Semenov and his research school (Berlin and Golubkov 2021; Azatyan 2021) at the Institute of Chemical Physics, the Russian Academy of Sciences, founded by Semenov in 1931. This institute is presently known as the N.N. Semenov Federal Research Centre for Chemical Physics, the Russian Academy of Sciences (Figures 1.3 and 1.4).

Further significant progress in the thermal explosion theory before the Second World War was made by Frank-Kamenetskii (invited by Semenov to work at the Institute of Chemical Physics) who proposed his own formulation of the problem, dropping the assumption of mixture temperature uniformity.

Up to this day, Semenov and Frank-Kamenetskii approaches remain a solid foundation for theoretical and experimental studies on thermal explosion.

Semenov became a full member of the Academy of Science of the Soviet Union in 1932, and he was also elected as a member of several foreign academies.

The final remark must be made on terminology. The terms 'thermal explosion', 'thermal runaway' and 'autoignition' have become synonyms and are used as such throughout the book. In the literature (especially in relation to liquid and solid fuels), the term 'spontaneous ignition' is also being used in the same sense. The latter term emphasizes the absence of any external energy source as a trigger for thermal explosion (as opposed to 'piloted ignition', using various pilots, e.g. spark).

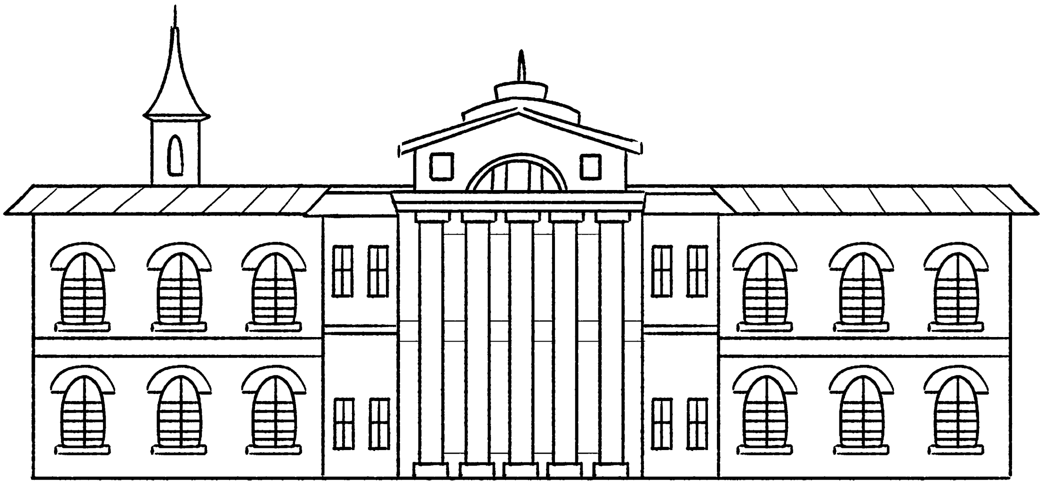

Figure 1.3 Artist's impression of the main building of the N.N. Semenov Federal Research Centre for Chemical Physics, the Russian Academy of Sciences in Moscow.

Figure 1.4 N.N. Semenov monument in front of the main building of the N.N. Semenov Federal Research Centre for Chemical Physics, the Russian Academy of Sciences in Moscow. *Source:* Photo by the author.

1.3 Fundamentals of Chemical Kinetics

The present section presents a brief overview of chemical kinetics, limited to the facts used directly in subsequent chapters.

A general one-step irreversible chemical reaction of arbitrary complexity may be represented by the following formal equation:

$$\sum_{i=1}^{N} \upsilon_i M_i \to \sum_{i=1}^{N} \mu_i M_i \tag{1.1}$$

Here M_i are molecular or radical species, υ_i are reactants stoichiometric coefficients, and μ_i are products stoichiometric coefficients. The stoichiometric coefficient υ_i or μ_i may be zero if the species M_i is missing in the list of reactants or products, respectively.

The sum of reactants stoichiometric coefficients

$$\sum_{i=1}^{N} \upsilon_i = m \tag{1.2}$$

is called the order of chemical reaction.

Formally, notation (1.1) may be applied to both elementary reactions, expressing the results of direct collision between a number of molecules and radicals, and global reactions, describing the overall chemical transformation of molecular species and consisting of a number of elementary steps (Kuo 1986).

In the former case, kinetic parameters discussed later may be, theoretically, derived from first principles (Gardiner 1972; Benson 1960). In the latter case kinetic parameters, obtained by fitting experimental data, have the meaning of their effective values.

Depending on how many molecular species appears on the LHS of Eq. (1.1), chemical reactions are classified into monomolecular, bimolecular, trimolecular, and so on.

The rate of reaction transformation (1.1) is given by the law of mass action, discovered experimentally by Guldberg and Waage in 1864 (Kuo 1986; Penner 1955)

$$\dot{\tilde{w}} = \tilde{k}\left(\tilde{T}\right)\prod_{i=1}^{N}\left(\tilde{C}_i\right)^{\upsilon_i} \tag{1.3}$$

where $\tilde{C}_i$ is the molar concentrations of reactants M_i, and $\tilde{k}$ is the temperature-dependent proportionality factor called the specific reaction rate constant.

Net rate of change of the species M_i is given, according to Eqs. (1.1) and (1.3), by

$$\frac{d\tilde{C}_i}{d\tilde{t}} = (\mu_i - \upsilon_i)\dot{\tilde{w}} \tag{1.4}$$

Since the concentration of the reactants is proportional to the mixture pressure (given that they obey stoichiometric restriction (1.1)), the law (1.3) implies that the reaction rate is proportional to pressure raised to the power equal to reaction order m. Order of the reaction has, therefore, a distinctive meaning of exponent in power dependence of the reaction rate on pressure.

Specific reaction rate constant, as its name suggests, is independent of concentrations and depends on the mixture temperature $\tilde{T}$ only. The collision frequency analysis of molecules (Kuo 1986) shows that it has the following structure:

$$\tilde{k}\left(\tilde{T}\right) = \tilde{A}\left(\tilde{T}\right)\exp\left(-\frac{\tilde{E}}{\tilde{R}\tilde{T}}\right) \tag{1.5}$$

where $\tilde{A}\left(\tilde{T}\right)$ is called the pre-exponential factor, $\tilde{E}$ is the activation energy of chemical reaction, and $\tilde{R}$ is the universal gas constant. Equation (1.5) is called the Arrhenius (essentially, Arrhenius in (1.5) made use of Boltzmann factor) law of temperature dependence, or the Arrhenius function.

Activation energy is a critical kinetic energy level of colliding particles required to break molecular bonds. Its value is typically of the order of bond energy and is specific for a particular reaction. As such, it is an analogy of a potential barrier between two potential wells (upper part of Figure 1.5). For an exothermic reaction, the supply of activation energy to reacting molecules results in the liberation of an amount of energy, exceeding the heat of reaction by an amount exactly equal to activation energy (bottom part of Figure 1.5). The exponential factor in (1.5), arising from Maxwell–Boltzmann distribution, describes the fraction of colliding molecules having energies greater than the activation energy.

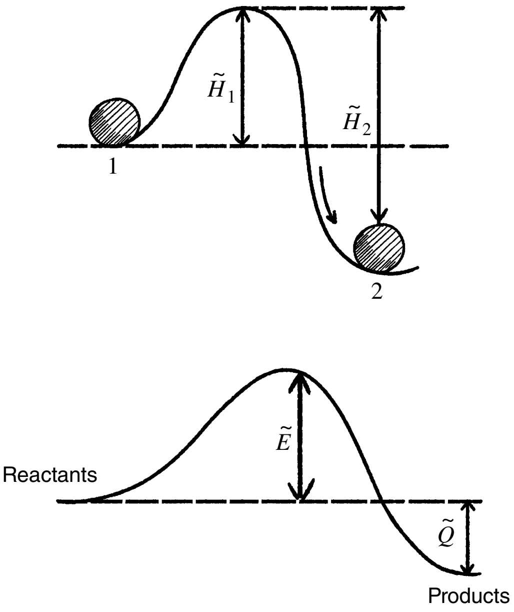

Figure 1.5 Role of the activation energy in an exothermic reaction.

Pre-exponential factor is a weak function of temperature

$$\tilde{A}(\tilde{T}) = \tilde{A}_0 \tilde{T}^{\alpha} \qquad (1.6)$$

with the exponent α is typically between 0 and 1 (Kuo 1986). As Arrhenius function, in contrast, is extremely strongly temperature-dependent (see Problem 1), weak temperature dependence in (1.5) is typically neglected in combustion problems, in comparison with the temperature dependence of the Boltzmann factor.

Due to specific form of the Arrhenius function (1.5), temperature scale playing a very important role in thermal explosion problems (and in combustion problems in general), is the so-called characteristic temperature interval $\frac{\tilde{R}\tilde{T}_0^2}{\tilde{E}}$, where $\tilde{T}_0$ is the initial temperature of the reactant (potentially undergoing thermal explosion) mixture.

It is equal to the product of the initial temperature and the so-called Arrhenius number, $Ar = \frac{\tilde{R}\tilde{T}_0}{\tilde{E}}$. The latter property may be considered as the inverse of non-dimensional activation energy. While this number is an essential fundamental factor in combustion kinetics, it is important to realize that in most combustion problems the Arrhenius number is a small parameter.

For typical values of activation energies (Borman and Ragland 1998) and initial temperatures close to room levels, the typical range of Arrhenius numbers is $Ar = 1.2 \cdot 10^{-2} - 2.0 \cdot 10^{-2}$.

For small values of Arrhenius number, it follows immediately from (1.4) that temperature increase, above the initial level, by one characteristic temperature interval results in the reaction constant (and correspondingly, at the same values of reactants concentrations, reaction rate) increase by approximately the factor of e (Problem 2). As will be shown in the next section, this circumstance plays a pivotal role in defining the necessary conditions for thermal explosion.

Correspondingly, non-dimensional temperature in thermal explosion studies is often introduced using the characteristic temperature interval as the natural scale. Specifically, non-dimensional temperature corresponding to the real physical temperature $\tilde{T}$ at given location and time may be defined as $\theta = \frac{\tilde{T} - \tilde{T}_0}{\left(\tilde{R}\tilde{T}_0^2/\tilde{E}\right)}$.

With the introduction of a non-dimensional temperature, exponential factor in the Arrhenius function may be transformed to the following equivalent form:

$$\begin{aligned}
\exp\left(-\frac{\tilde{E}}{\tilde{R}\tilde{T}}\right) &= \exp\left(-\frac{\tilde{E}}{\tilde{R}\tilde{T}_0}\right)\exp\left(\frac{\tilde{E}}{\tilde{R}}\left(\frac{1}{\tilde{T}_0} - \frac{1}{\tilde{T}}\right)\right) \\
&= \exp\left(-\frac{\tilde{E}}{\tilde{R}\tilde{T}_0}\right)\exp\left(\frac{\tilde{E}}{\tilde{R}\tilde{T}_0}\left(\frac{\tilde{T}-\tilde{T}_0}{\tilde{T}}\right)\right) \\
&= \exp\left(-\frac{\tilde{E}}{\tilde{R}\tilde{T}_0}\right)\exp\left(\frac{\tilde{E}(\tilde{T}-\tilde{T}_0)}{\tilde{R}\tilde{T}_0^2}\,\frac{\tilde{T}_0}{\left(\tilde{T}_0 + \frac{\tilde{R}\tilde{T}_0^2}{\tilde{E}}\theta\right)}\right) \qquad (1.7) \\
&= \exp\left(-\frac{\tilde{E}}{\tilde{R}\tilde{T}_0}\right)\exp\left(\frac{\theta}{(1 + Ar\theta)}\right)
\end{aligned}$$

and consequently, the rate of reaction to the form

$$\tilde{w} = \tilde{k}_0(\theta)\exp\left(\frac{\theta}{(1+Ar\theta)}\right)\prod_{i=1}^{N}\left(\tilde{C}_i\right)^{\upsilon_i} \tag{1.8}$$

with $\tilde{k}_0(\theta)$ being the value of the Arrhenius function at an initial temperature

$$\tilde{k}_0\left(\tilde{T}\right) = \tilde{A}(\theta)\exp\left(-\frac{\tilde{E}}{\tilde{R}\tilde{T}_0}\right) = \exp\left(-\frac{1}{Ar}\right)\tilde{A}(\theta) \tag{1.9}$$

The abbreviated notation $\tilde{k}_0 \overset{def}{=} \tilde{k}_0\big|_{\theta=0}$ will also be used.

A very important class of chemical reactions is represented by chain reactions. Chain reactions consist of a number of elementary steps (1.1) involving radical species.

In a simplest form (non-branching chain reaction) radicals are produced (chain-initiation) and react with molecular species in such a way that after radical/molecular collision the number of radicals is preserved (chain-propagation). There are also chain-terminating elementary steps where stable molecules are formed upon radicals collision. It should be noted that chain length, which is a number of molecules of the final product per one originally produced radical, may reach hundreds of thousands and even millions.

The number of radicals may also increase as a result of the elementary reaction step in the chain, in which case branching of the chain occurs, and the reaction is classified as chain-branching. This effect is demonstrated in the mechanism presented in Figure 1.6. Here, chain-branching occurs upon the radical/molecule collisions (r_1, M_2) and (r_4, M_1).

Semenov and his school demonstrated that significant number of chemical reactions propagate by the chain-branching mechanism.

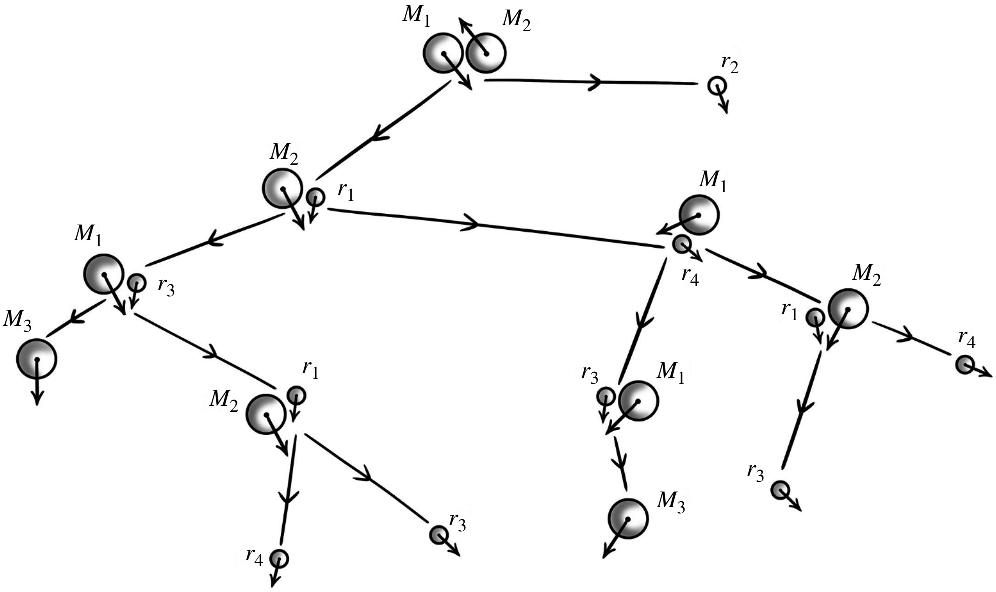

Figure 1.6 An example of the chain-branching reaction with a global kinetic scheme $M_1 + M_2 \longrightarrow M_3$. M_i – molecular species; r_i – radical species.

Chain-branching leads to the progressive accumulation of intermediate products (i.e. free radicals) in the mixture, leading potentially to the explosive reaction behaviour. An explosion of this type is called chain explosion, in contrast to thermal explosion. The chain-branching mechanism is responsible for the explosion of hydrogen–oxygen mixtures. All three observable explosion limits are explained based on chain-branching and chain-terminating kinetics (Kuo 1986; Turns 2000).

Before the chain reaction mechanism became known, some chemical phenomena could not be explained. It is exactly the phenomenon of this type (existence of a lower autoignition limit in the reaction between phosphorus and oxygen, discovered by a group of physicists in Leningrad, USSR in 1925) that led to the experimentally-verified discovery of chain-branching reactions. A comprehensive theory of such reactions had been subsequently developed by Semenov in 1920s–1930s.

1.4 Definition of Thermal Explosion

As is the case with any phenomenon, thermal explosion, for its proper study, must be conceptually separated from other phenomena, including similar ones, by some kind of clear and unambiguous definition.

Thermal explosion is distinguished by the fact that the primary effect controlling its development is the reaction rate's dependence on temperature, rather than concentrations. In contrast, in chain explosion, or explosions of mixed chain-thermal type (Barzykin 2004), dependence on radical concentrations is equally important, as these concentrations are affected by chain-branching.

The best definition of thermal explosion was given by the founder of its theory. In his Nobel Lecture Semenov stated:

> 'According to Arrhenius' law, the heat generated by the reaction itself increases the velocity of reaction. The existence of such retroaction is to the greatest possible extent characteristic of most phenomena of the combustion process.
>
> As a result of the reciprocal effect of the reaction on the generation of heat in the mixture on the one hand and the increase in reaction velocity due to this greater heat, as already mentioned, on the other, a self-accelerating surge of heat is set up which we term auto-ignition'. (Semenov 1956).

More than that, Semenov went on explaining that thermal explosion requires specific circumstances for its occurrence.

> 'The dissipation of heat on the walls of the vessel renders the development of a heat surge possible only under certain conditions, which are therefore all-important to the temperature of this autoignition. This temperature, which is a relative value (and by no means a constant of the substance, as was previously assumed by some authorities), is a function of the kinetic and thermal parameters, namely of the order of reaction, the activation energy, the density and composition of the combustible mixture, the heat of reaction, and the dissipation of heat on the vessel walls' (Semenov 1956).

In the space of parameters describing the state (condition) of the system, there are regions corresponding to both non-explosive and explosive reaction regimes, divided by a boundary. Conditions at the boundary are conventionally called critical conditions of thermal explosion.

Semenov's definition makes it possible to formulate necessary conditions for thermal explosion in a quantitative, mathematical form.

The rapid self-acceleration of a chemical reaction requires a noticeable change in the reaction rate upon small temperature changes. As has been discussed in Section 1.3, this occurs for small values of Arrhenius number (reaction rate increases approximately by a factor of e over one characteristic temperature interval). Therefore, the first necessary condition is written in the following form:

$$Ar = \frac{\tilde{R}\tilde{T}_0}{\tilde{E}} \ll 1 \tag{1.10}$$

In addition, of course, the temperature increase by one characteristic interval should not consume too large amounts of reactants, leading to the degeneration of the explosion.

If η is a fraction of substance that has reacted, the temperature increase of the mixture is represented through the following equation:

$$\tilde{T} - \tilde{T}_0 = \frac{\tilde{Q}\eta}{\tilde{c}_p} \tag{1.11}$$

The requirement of $\eta \ll 1$ at $\tilde{T} = \tilde{T}_0 + \dfrac{\tilde{R}\tilde{T}_0^2}{\tilde{E}}$ brings up the second necessary inequality

$$\frac{\tilde{R}\tilde{T}_0^2}{\tilde{E}}\frac{\tilde{c}_p}{\tilde{Q}} \ll 1 \tag{1.12}$$

Inequalities (1.10) and (1.12) form necessary conditions for thermal explosion (Novozhilov 1980).

Once they are fulfilled, the consumption of a small amount of reactants raises the mixture temperature by such a degree that the reaction self-acceleration becomes noticeable. This progressive self-acceleration leads to thermal explosion.

The self-acceleration of a chemical reaction means that the reactive system cannot be in the state of thermal equilibrium (until reactants have been fully consumed). It follows from here that the definition of thermal explosion opens two ways of developing the thermal explosion theory: steady-state and nonsteady. Under the first approach, thermal explosion is equivalent to the impossibility of thermal equilibrium in the system. Under the second, the temperature evolution of the system may be followed until a certain point that, in some sense, corresponds to the total mixture involvement in combustion.

While the mathematical interpretation of the steady-state approach is conceptually straightforward (it amounts to investigating equilibrium points of the system), the nonsteady approach requires some criterion against which system temperature evolution may be judged, qualitatively or quantitatively. It is also clear that such criterion must be related to the inherent properties of the system.

There are a number of possibilities that should be discussed in this regard. The unboundedness (infinite growth) of the system temperature could serve as a qualitative criterion. Unfortunately, it is not suitable for the general (and practically relevant) case $Ar > 0$ for the following reason. The reaction rate function (1.8) and (1.9) has (neglecting pre-exponential temperature dependence and, in line with the necessary condition for explosion, concentration variation) a finite limit at $\theta \to \infty$ ($\tilde{T} \to \infty$). On the other hand, rate of conduction heat dissipation from the system is proportional, in the first approximation, to the difference between the average temperature of the system (Semenov model, in fact, assumes temperature uniformity throughout the mixture) and the temperature of surroundings. This means that the combined contribution of the rate of reaction and the rate of heat dissipation to overall energy balance causes the system temperature to be, strictly speaking, bounded at all temperatures and infinite growth of solution cannot be used as a precise mathematical criterion for explosion for any positive Arrhenius numbers.

Intrinsic properties driving the reactive system's behaviour essentially amounts to the properties of the reaction rate (which is controlled by the Boltzmann factor, neglecting pre-exponential temperature dependence and reactants consumption) and energy dissipation functions. The latter, as mentioned, is a linear function of temperature.

A natural characteristic point of the Boltzmann factor function is its inflection point. (For any criteria which involves the derivatives of the order higher than one linear energy dissipation function may be taken out of consideration.) However, an attempt to relate reaction progression to this point with thermal explosion is equally unsatisfactory.

An inflection point of the Boltzmann factor (which is also an inflection point of the function describing net energy accumulation) is found trivially:

$$\theta_{\inf l} = \frac{1}{Ar}\left[\frac{1}{2Ar} - 1\right] \tag{1.13}$$

It is not difficult to see that physical temperatures corresponding to this point, for Arrhenius numbers in the range $Ar = 1.2 \cdot 10^{-2} - 2.0 \cdot 10^{-2}$, are unrealistically high for combustion reactions, of the order of $\tilde{T}_{\inf l} \approx 5 \cdot 10^{3} - 2.0 \cdot 10^{4^\circ}$ K.

The alternative proposed in the present book is to use the point of maximum of the second derivative of the Boltzmann factor as a characteristic point describing the onset of thermal explosion. This point corresponds (in temperature space) to the maximum acceleration of the chemical reaction, which is consistent with the criterion proposed by some other researchers (Barzykin 2004).

The point where the second derivative of the Boltzmann factor reaches its maximum is found by calculating its third derivative. It turns out that it corresponds to the least root of the equation:

$$\begin{gathered} 6\hat{\theta}^2 - 6\hat{\theta} + 1 = 0 \\ \hat{\theta} = Ar(1 + Ar\theta) \end{gathered} \tag{1.14}$$

which is equal to

$$\hat{\theta}_1 = \frac{1}{2} - \frac{\sqrt{3}}{6}$$

At this point, $\theta_{F^{(2)}_{\max}} \overset{def}{=} \frac{1}{Ar}\left(\frac{\hat{\theta}_1}{Ar} - 1\right)$, third derivative is equal to zero, and changes its sign from positive to negative.

Physical temperatures, in the relevant range of Arrhenius numbers, corresponding to the point $\theta_{F^{(2)}_{\max}}$ are presented in Table 1.1. Their range, $\tilde{T}_{F^{(2)}_{\max}} \approx 3150 - 5250^\circ$ K correlates much better with the upper limit of combustion temperatures ($\tilde{T} \approx 300 - 4000^\circ$ K; Zeldovich *et al.* 1980).

The point of maximum of the second derivative of the Boltzmann factor will be used as the criterion for the onset of autoignition in the non-steady theory of thermal explosion, throughout the book.

Table 1.1 Point of maximum of the second derivative of the Boltzmann factor for different values of Arrhenius number.

Arrhenius number, *Ar*	**Point of maximum value of second derivative of the Boltzmann factor, non-dimensional temperature $\theta_{F^{(2)}_{\max}}$**	**Point of maximum value of second derivative of the Boltzmann factor, absolute temperature, °K**
0.012	1,375	5,250
0.015	867	4,200
0.020	475	3,150

1.5 Similarities and Differences with Other Phenomena

Thermal autoignition is by no means the only phenomenon exhibiting intrinsic self-acceleration.

In fact, Semenov developed the theory of thermal explosion using analogy with his earlier work on thermal dielectric breakdown (Inge *et al.* 1925). Similar ideas on the latter phenomenon were developed by Fock (1928).

Processes, analogous to thermal explosion, have been noticed in other phenomena associated with the release of energy. Such phenomena include, for example, thermonuclear fusion (Nastoyashii 1972; Nastoyashii and Shevchenko 1972), electrical and optical discharges (Selezneva 1972; Rizer 1973; Makhviladze and Myshenkov 1977), thermal extinguishment of luminescence (Ramsden and Savic 1964; Makshantsev and Finkelburg 1974), formation of solid solutions (Bloshenko *et al.* 1970), baking of metallic powders (Lidorenko and Sidyakin 1972), inductive heating of some bodies, decay of supercooled liquids, and others (Merzhanov and Rumanov 1987).

Best understood is an analogy between thermal explosion and self-heating occurring in flows, or under deformation, of some viscous polymers (Schapery 1964; Gruntfest *et al.* 1964; Korobov and Ratner 1965; Bostanjiyan *et al.* 1965; Barenblatt *et al.* 1965, 1966).

Self-heating emerges in a flow of a melted polymer due to the strong dependence of viscosity (in some approximation, Frenkel 1946) on temperature

$$\tilde{\mu} = \tilde{\mu}_0 \exp\left(\frac{\tilde{B}}{\tilde{R}\tilde{T}}\right) \tag{1.15}$$

Bostanjiyan *et al.* (1965) considered a steady-state flow of the melted polymer in a round infinitely long pipe. They reduced, with a certain change of variables, the problem description to exactly the same equation that appears in the Frank-Kamenetskii formulation of the thermal explosion theory, that is, Eq. (2.27) with $m = 1$. Therefore, the critical value of Frank-Kamenetskii parameter (which for this problem has, of course, different definition) equals to two. For supercritical conditions, the progressive dissipation of kinetic energy leads to self-acceleratory fluid heating. Bostanjiyan *et al.* (1965) termed this phenomenon hydrodynamic thermal explosion.

The same effect is predicted for certain regimes of the Couette flow. The existence of hydrodynamic thermal explosion has been confirmed experimentally by using a rotational viscometer (Merzhanov and Stolin 1971).

Mathematical aspects of hydrodynamic thermal explosion and some related problems have been considered by Khudyaev (2003).

There also exist phenomena of explosive nature, which, despite apparent similarity with thermal explosion, proceed by different mechanisms.

The first example, which should be pointed out, is nuclear fission. In contrast to the above-mentioned thermonuclear fusion, which relies on the high thermal energy input (in order to sustain high-temperature plasma), nuclear fission is driven by progressively increasing production rate of neutrons. In order for fission to proceed, the number of neutrons must increase as a result of a single act of neutron capture by nucleus. Moreover, the average number of secondary neutrons, that is, neutrons produced per one neutron capture act, must be significantly more than one. This process is therefore an analogy of the chain-branching mechanism in chemical reactions.

The second example that may be given lies outside both chemistry and physics. This is an explosively rapid, in the form of epidemic or pandemic, virus spread. There have been an attempts to describe these phenomena using both chain and thermal explosion methods (Philippov 2024). However, it seems that the predominant mode of spread is a chain-like mechanism. The progressive accumulation of virus carriers, driven by interaction between individuals, again makes it an analogy of the chain-branching chemistry mechanism. The COVID-19 pandemic is a recent example of such catastrophic spread.