Irreversible Phenomena
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Ignitions, Combustion and Detonation Waves

With 363 Figures and 23 Tables

Springer
Ideals are simple and able to be easily understood, but never exist in reality.

In this book a theory based on the second law of thermodynamics and its applications are described. In thermodynamics there is a concept of an ideal gas which satisfies a mathematical formula $PV = RT$. This formula can approximately be applied to the real gas, so far as the gas has not an especially high pressure and low temperature. In connection with the second law of thermodynamics there is also a concept of reversible and irreversible processes. The reversible process is a phenomenon proceeding at an infinitely low velocity, while the irreversible process is that proceeding with a finite velocity. Such a process with an infinitely slow velocity can really never take place, and all processes observed are always irreversible, therefore, the reversible process is an ideal process, while the irreversible process is a real process.

According to the first law of thermodynamics the energy increase $dU$ of the thermodynamic system is a sum of the heat $dQ$ added to the system and work $dW$ done in the system. Practically, however, the mathematical formula of the law is often expressed by the equation, or some similar equations derived from this formula, is applied to many phenomena. Such formulae are, however, theoretically only applicable to phenomena proceeding at an infinitely low velocity, that is, reversible processes or ideal processes. The question arrives whether or not such mathematical formulae which are only applicable to ideal processes can also approximately to real processes.

Since Jost wrote the book on combustion “Explosions-und Verbrennungsvorgänge in Gasen,” a lot of book on ignition, combustion, flames, and detonation waves have been published. In these books, the mathematical formulae which are applicable only to ideal processes are applied to all phenomena of ignition, combustion, and explosion, assuming that the mathematical formulae introduced for the reversible processes can approximately be applied to the irreversible phenomena, too.

Nevertheless there are still many phenomena, for example, fluctuating phenomena in ignition and detonation waves, or anomalous high temperature of...
free electrons and ions in the flame and behind detonation waves which cannot be explained by the theories introduced and applied in those books.

In an irreversible process at least once for a short time a nonequilibrium and heterogeneous state appears which causes some stochastic phenomena. In this book the author tries to explain that the reversible and irreversible processes are quite different from one another and that the mathematical formulae which are applicable to the reversible process cannot be applied to the irreversible process, not even approximately, in so far the process has a large entropy increase, i.e., a large irreversibility, and further tries to explain many phenomena in the combustion science applying the characteristics of the irreversible phenomena, since ignition, combustion, explosion, detonation, and other phenomena in the combustion are distinctly irreversible processes accompanied by a large entropy increase. By observing the phenomena in combustion as irreversible, we find quite a different world from that described according to classical concepts and theories.

In this book the theory and its applications are explained mainly according to the experimental results obtained by the author and his coworkers, because there are very little experiments carried out under the concept of an irreversible process. Therefore, only a few references are made of books on combustion science, since these books, using the classical concept, are written in a philosophy which is quite different from that used in this book.

The dimensions of the experimental apparatus illustrated in this book are shown as exactly as possible, because the irreversible phenomena proceed accompanied by some stochastic phenomena and the probabilities also depend on the quantity of materials used in the phenomena.

The theory is very simple and can easily be applied to the practical calculation and industrial purposes. The author is, however, only afraid, if he had preached Buddha, or carried owls to Athens.
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Introduction

According to the basic concepts of thermodynamics, a reversible process is that in which a phenomenon proceeds with an infinitely slow velocity. Practically such a process can never take place and we observe only irreversible processes in which some phenomena proceed with a certain finite velocity.

On the other hand, in order to analyze some physical or chemical phenomena quantitatively, it is convenient to apply some mathematical formula introduced from basic sciences. Such basic mathematical formulae are, however, in general introduced from the basic laws of sciences which can essentially be applied only to reversible processes, namely in equilibrium or quasiequilibrium states.

These mathematical formulae are very often applied also to irreversible phenomena under the assumption that the observed irreversible phenomena can approximately be treated as reversible ones. The formulae can be applied to phenomena proceeding very slowly, but never to distinctly irreversible phenomena, for example, rupture of material, electric discharge, or earthquake.

The combustion is an oxidation of materials being accompanied by light emission, heat release, and pressure or shock waves. The combustion phenomena have long time been investigated by many scientists and engineers not only from their academic interests but also with intentions of the practical and industrial applications and many books as well as reports of the phenomena have been published. In these books and reports the combustion phenomena have mainly been explained according to the theories based on the first law of thermodynamics expressed in mathematical formulae which can be applied only to reversible processes, though the combustion phenomena are distinctly irreversible.

In this book, comparing with the classical theories, ignition, explosion, combustion, and detonation waves are explained according to an irreversible theory based on the second law of thermodynamics. The explanations and results introduced from the irreversible theory are, therefore, quite different from those described in the classical books, but so clear and simple that they can easily be applied to the understanding, investigation, and numerical estimation.
of the combustion phenomena as well as detonation waves for practical and industrial purposes.

In combustible mixtures or materials some ignitions take place and then flames propagate from the ignition points, being accompanied by light emission, heat release, and shock waves. As the flame propagation is regarded as a succeeding ignition, the ignition phenomena are first to be studied for understanding the combustion phenomena. In this book, after the explanation of explosion according to the classical theories, a stochastic theory for irreversible phenomena, its application to nucleation and then shock tube as the experimental apparatus of ignition in gases are explained. Next the theoretical and experimental results of spontaneous and spark ignitions in gaseous mixtures are explained mainly according to the stochastic ignition theory. Then combustion waves, ionization in flames, detonation waves, interaction between shock and combustion waves are described as irreversible phenomena. Subsequently, some practical and industrial applications of the stochastic ignition theory and detonation waves are also proposed.
As the basic phenomenon of combustion the ignition in combustible mixtures has been investigated by many scientists. There are two types of ignition. One of them is the spontaneous ignition which is also called explosion and the other is the ignition by an external energy. The most basic ignition is the explosion in a homogeneous mixture and for it there have been two well-known theories, i.e., thermal explosion theory and chain-branching kinetics.

After a combustible mixture, a mixture of fuel and air or oxygen, for example, a propane–air mixture, is brought to a state in which an ignition can take place, none of remarkable changes, for example, pressure or temperature rise in the mixture, is observed for a certain short period, and then some phenomena like pressure or temperature rise, light emission, or heat release occur. In general, the ignition is defined by the instant in which pressure or temperature begins to rise, or the first light emission is observed. The period from the instant where the mixture is brought into the state in which an ignition can take place to the ignition instant is called induction period of ignition or ignition delay as shown in Fig. 2.1 with $t_{\text{ind}}$. Either in the thermal explosion theory or in the chain-branching kinetics, it is assumed that all phenomena during the induction period proceed steadily, since the pressure as well as the temperature is kept almost constant. What phenomena proceed during the induction period comes in question.

### 2.1 Thermal Explosion Theory

It has been believed that the physical state of a combustible mixture must be divided into two regions, namely, a region where a spontaneous ignition is always observed and the other having no spontaneous ignition. The border-line between both the regions is called explosion limit and one has discussed what mechanism defines such explosion limits.

In order to explain the mechanism of spontaneous ignition, i.e., explosion in a gaseous mixture, the thermal explosion theory was proposed by Van’t Hoff.
and Semenoff. A combustible mixture is filled in a vessel keeping the same temperature \( T_0 \) of the mixture at the initial state. During some chemical reactions proceed in the mixture, increasing the mixture temperature, some of the released heat is transformed through the vessel wall to the outside, keeping the wall temperature \( T_0 \) constant. It is also assumed that the mixture keeps a homogeneous state, namely the specific entropy is everywhere equal.

Let us assume

- \( V \), the vessel volume (expressed by mole number of the mixture)
- \( T_0 \), the initial mixture temperature (=the temperature of the vessel wall)
- \( P \), the mixture pressure
- \( n \), the concentration of reaction product
- \( t \), time,

then the reaction rate is expressed by the following equation, where \( E \) is called activation energy,

\[
\frac{dn}{dt} = f(P) \exp\left(-\frac{E}{RT}\right). \tag{2.1}
\]

In a reaction of second order,

\[
f(P) \approx \beta, \quad P^2, \tag{2.2}
\]

where \( \beta \) is a proportional constant. Further, if

- \( q \), reaction heat per unit mole mixture
- \( Q_1 \), whole reaction heat,

then

\[
\frac{dQ_1}{dt} = q \frac{dn}{dt} V = q V f(P) \exp\left(-\frac{E}{RT}\right). \tag{2.3}
\]

A part of the reaction heat heats the mixture, while the other heat is transformed to the outside through the vessel wall. If the heat \( Q_1 \) transferred outside is assumed to be proportional to the difference between the mixture temperature \( T \) and the wall temperature \( T_0 \).
\[
\frac{dQ_1}{dt} = C(T - T_0),
\]  
(2.4)

where \(C\) is the heat conductivity of the mixture depending on the form and size of the vessel, especially proportional to the surface area of the vessel, but in this case we assume it constant during the process. Near the wall the mixture temperature has a gradient, but we take here its mean value. Under these assumptions we discuss the conditions for the explosion. Plotting the released heat per unit time \(dQ/dt\) in combustible mixture having an initial pressure of \(P\) against the mixture temperature \(T\), we obtain a curve \(C.H.\) in the diagram of Fig. 2.2.

According to (2.4), the heat \(dQ_1/dt\) transferred outside is expressed as a straight line in the same diagram. If the line is expressed by line 1, the mixture temperature rises to the cross point \(T_c\) of the curve \(dQ_1/dt\) with the straight line 1, but then decreases and no ignition takes place, as the heat transferred outside is larger than the reaction heat. If the heat transferred outside is expressed by the line 2, the reaction heat is always larger than the transferred heat and an explosion takes place. As the limit of both the cases, the straight line of the transferred heat should be tangential to the curve of reaction heat, as shown by line 3. Then the contact point \(T_1\) of the curve with the straight line must be the explosion limit.

Expressing these relations in mathematical formulae

\[
\left. \left( \frac{dQ_1}{dt} \right) \right|_{T=T_c} = \left. \left( \frac{\delta dQ_1}{\delta T} \right) \right|_{T=T_c},
\]  
(2.5)

\[
\left. \left( \frac{\delta dQ_1}{\delta T} \right) \right|_{T=T_c} = \left. \left( \frac{\delta dQ_2}{\delta T} \right) \right|_{T=T_c}.
\]  
(2.6)

**Fig. 2.2.** Heat release at the thermal explosion. (C.H.) Heat release by the reactions, (1, 2, and 3) heat loss by conduction
From (2.3)–(2.5) we obtain
\[
qVf \exp\left(-\frac{E}{RT}\right) = C(T_1 - T_0), \tag{2.7}
\]
then from (2.6)
\[
\frac{E}{RT^2_1} qVf \exp\left(-\frac{E}{RT}\right) = C. \tag{2.8}
\]
By division of (2.7) by (2.8)
\[
\frac{RT^2_1}{E} = T_1 - T_0,
\]
then
\[
T_1 = \frac{E}{2R} \pm \left(-T_0 \frac{E}{2R} + \frac{E^2}{4R^2}\right)^{1/2}.
\]
As the equation having plus sign means higher temperature and meaningless in this case, we take only that with minus sign, namely
\[
T_1 = \frac{E}{2R} - \left(-T_0 \frac{E}{2R} + \frac{E^2}{4R^2}\right)^{1/2} = \frac{E}{2R} - \frac{E}{2R}\left(1 - T_0 \frac{4R}{E}\right)^{1/2}
\]
\[
= T_0 + \frac{T_0^2 R}{E}.
\]
Substituting this relation into (2.7)
\[
qVf \exp\left[-\frac{E}{RT_0 (1 + RT_0/E)}\right] = C \frac{RT^2_0}{E}.
\]
As \(RT_0/E\) is much smaller than 1, we approximately obtain the following relation:
\[
1\left(1 + \frac{RT_0}{E}\right) \approx 1 - \frac{RT_0}{E}.
\]
Therefore
\[
qVf \exp\left[-\frac{E}{RT_0} \left(1 - \frac{RT_0}{E}\right)\right] = eqVf \exp\left(-\frac{E}{RT_0}\right), \tag{2.9}
\]
\[
eq qVf \exp\left(-\frac{E}{RT_0}\right) = \frac{CRT^2_0}{E}.
\]
Using the pressure $P_{cr}$ at the explosion limit, we obtain the following relation:

$$\ln eqV\beta_r + 2 \ln P - \frac{E}{RT_0} = \ln \frac{CR}{E} + 2 \ln T_0. \quad (2.10)$$

From this equation we can obtain the relation among the pressure $P_{cr}$ and temperature $T_0$ at the explosion limit and the activation energy $E$. In other reactions like single molecule or three molecule reaction the formula should be somewhat reformed, but in general we observe mostly the second-order reaction. If we plot the values of $\ln (P_{cr}/T_0)$ against $1/T_0$, we obtain a straight line, from whose gradient the activation energy $E$ is calculated.

According to the thermal explosion theory the explosion limit is thus expressed in a pressure–temperature diagram with a monotone curve as shown in Fig. 2.3. In order to suppress the explosion, some gases having large specific heat and higher heat conductivity should be mixed into the combustible mixture.

In most combustible mixtures such an explosion limit shown in Fig. 2.3 is observed, but in someones like hydrogen–oxygen mixture we observe a curve having an inverse $S$-form as shown in Fig. 2.4. As such explosion limit having an inverse $S$-form curve could not be explained by the thermal explosion theory. Semenoff, Hinshelwood, and others proposed the chain-branching kinetics.

The activation energy is now to be explained. In a substance, although in an equilibrium state having a certain finite physical state, a certain definite temperature and pressure, the particles composing the substance have different motion and never keep their velocity and direction constant, namely have never constant energy. In a substance having a constant equilibrium temperature $T$, for example, it has an energy distribution, that is, so-called Boltzmann’s distribution as shown in Fig. 2.5. The particles having energies higher than a certain energy $E_0$ can participate in the reaction like a combustion, whereas the other particles play no role for the reaction. The reaction
rate is thus proportional having an energy higher than $E_0$ as shown in Fig. 2.5, while the probability that a particle has an energy higher than $E_0$ is proportional to $\exp(-E_0/RT)$, i.e.,

$$\frac{dn}{dt} = A \exp\left(-\frac{E_0}{RT}\right),$$  \hfill (2.12)$$

which is called Arrhenius' equation.

### 2.2 Chain-Branching Kinetics

As mentioned above, we observe an explosion limit having an inverse $S$-form curve with a so-called explosion peninsula in a hydrogen–oxygen mixture. In order to explain the limit, the chain-branching kinetics has been developed. Namely, the chemical kinetics has been applied to explain the phenomenon, assuming the explosion as a chemical reaction composed of several simple elementary single-, two-, or three-molecule reactions.
The chemical kinetics is based on the law of mass action, in which the reaction rate is proportional to the mass of each element. This theory, however, can be applied only to reversible processes. A single molecule reaction (first-order reaction) is expressed by

(I) \( A \rightarrow x + y \ldots \ldots \)

and a two molecule reaction (second-order reaction) by

(II) \( A + B \rightarrow x + y \ldots \ldots \)

The decrease rate of one element in the left-side or increase of one element in the right-side means the reaction rate. Expressing the concentration of each element by square bracket and rate coefficient of reaction by \( k_n \), the rate of the single molecule (first order) reaction is expressed by the following equation:

\[
-\frac{d[A]}{dt} = k_1 [A].
\]

And that of two molecule (second order) reaction by

\[
-\frac{d[A]}{dt} = k_2 [A][B].
\]

Assuming the initial concentration of each element to be \([A_0]\) and \([B_0]\), we obtain the following equation for the first-order reaction,

\[
\frac{-d[A]}{[A]} = k_1 dt.
\]

As \([A] = [A_0]\) at \( t = 0 \),

\[
[A] = [A_0] \exp (-k_1 t).
\]

For the second-order reaction

\[
-\frac{d[A]}{dt} = k_2 \left\{ [A_0] - [A] \right\} \left\{ [B_0] - [B] \right\}.
\]

As \([A_0] = [B_0]\)

\[
-\frac{d[A]}{dt} = k_2 \left\{ [A_0] - [A] \right\}^2,
\]

\[
\frac{[A]}{\left\{ [A_0] - [A] \right\}[A_0]} = k_2 t.
\]

We can approximately take the average concentration \([\bar{A}]\) or \([\bar{B}]\) of each element during the reaction:

\[
-\frac{d[\bar{A}]}{dt} \propto k_2 [\bar{A}][\bar{B}].
\]
If only the first stage of reaction comes in question, we can here approximately take the initial concentration of the elements except that calculated as the reaction rate.

Assuming that the reaction of hydrogen with oxygen $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ is composed of several elementary reactions supported by some activated atoms or radicals, we can assume the following reaction system as an example, whose scheme is shown in Fig. 2.6.

1. **Chain-branching reaction:**
   
   - [1] $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} + 12 \text{ kcal}$ \hspace{1cm} (k_1)
   - [2] $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} − 14 \text{ kcal}$ \hspace{1cm} (k_2)
   - [3] $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} + 0.5 \text{ kcal}$ \hspace{1cm} (k_3)

2. **Chain-breaking reaction:**
   
   - [4] $\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$ \hspace{1cm} (k_4)

where $\text{M}$ is the third element, for example, a metal molecule.

In reactions [2] and [3], not only activated atoms $\text{H}$ and $\text{O}$ appear in the right-hand side, but also $\text{OH}$ is formed together with $\text{O}$ or $\text{H}$. When the activated radical $\text{OH}$ is formed more than that decreased in the reaction [4], the reaction accelerated to the explosion by increasing the concentration $\text{OH}$. When the activated atoms and radicals are formed in the mixture more than a certain definite concentration, an explosion takes place, after which the chain-branching reactions do not play any role for the reaction, we should only consider the balance of the increase of the activated atoms and radicals in the reactions [2] and [3] with those decreased in the reaction [4], so long as the explosion limit comes in question.
Assuming steady reactions, the reaction rates can be calculated as follows:

[I] \[ \frac{d[H]}{dt} = k_1[OH][H_2] - k_2[H][O_2] + k_3[O][H_2] - k_4[H][OH][M] \]

[II] \[ \frac{d[O]}{dt} = k_2[H][O_2] - k_3[O][H_2] \]

[III] \[ \frac{d[OH]}{dt} = -k_1[OH][H_2] + k_2[H][O_2] + k_3[O][H_2] - k_4[H][OH][M] \]

Applying the conditions of steady reactions \[ \frac{d[H]}{dt} = 0, \frac{d[O]}{dt} = 0, \frac{d[OH]}{dt} = 0, \]

\[ [O] = \frac{k_2[H][O_2]}{k_3[H_2]} \] from [II]

\[ 2k_1[OH][H_2] - 2k_2[H][O_2] = 0 \] from [I] and [III], then

\[ [OH] = \frac{k_2[H][O_2]}{k_3[H_2]} \]

Substituting the relations above into [I], we obtain the following relations:

\[ [H] = \frac{k_1[H_2]}{k_4[M]} \]

\[ [O] = \frac{k_1k_2[H_2][O_2]}{k_3k_4[H_2][M]} = \frac{k_1k_2[O_2]}{k_3k_4[M]} \]

\[ [OH] = \frac{k_1[OH][H_2]}{k_4[M]} \cdot \]

From [1], [4], and the equations described above the formation of \( H_2O \) is

\[ \frac{d[H_2O]}{dt} = k_4[H][OH][M] = \frac{2k_1k_2[H_2][O_2]}{k_4[M]} \]

Thus, we obtain the rate of overall reaction, but still know nothing of the explosion limit.

Considering the repeating of chain-branching reactions [1], [2], and [3], a reaction scheme as shown in Fig. 2.6 can be proposed. Putting \( H_2 \) A or C, \( H_2O \) B and activated radicals or atoms \( OH, O, H, R \), the reaction can be expressed by the following schemes:

\[ R + A \xrightarrow{k_1} B + R \] (2.20)

\[ R + C \xrightarrow{k_1} 2R + D \] (2.21)

\[ R + E \xrightarrow{k_1} E' \] (2.22)

Besides, considering an active dissociation or first-order reaction

\[ U \xrightarrow{k_1} nR. \] (2.23)
In a steady reaction
\[
\frac{d[R]}{dt} = k_0[U] + k_2[R][C] - k_3[R][E] = 0.
\]
Thus
\[
[R] = \frac{k_0[U]}{k_3[E] - k_2[C]}
\]  \hspace{1cm} (2.24)

The reaction rate of \( B \) is obtained from (2.20)
\[
\frac{d[B]}{dt} = k_1[R][A] = \frac{k_1k_0[A][U]}{k_3[E] - k_2[C]}.
\]  \hspace{1cm} (2.25)

So long as the denominator is positive, the reaction proceeds with a certain finite rate, but if it is zero, that is,
\[
k_3[E] - k_2[C] = 0
\]
the reaction proceeds with an infinitely large rate, namely it means the explosion limit.

According to the proposal of Semenoff,8 if
- \( n_0 \): number of initiating reaction
- \( \alpha \): probability of chain breaking
- \( \beta \): probability of chain branching
The reaction rate \( w \) is expressed by the following equation:
\[
w = \frac{n_0}{\beta - \alpha}.
\]  \hspace{1cm} (2.26)

The condition \( \beta = \alpha \) defines the explosion limit. The explosion limit of the hydrogen–oxygen mixture has an inverse S-form in a pressure \( P \) vs. temperature \( T \) diagram, as shown in Fig. 2.7 having a so-called explosion peninsula in the low-pressure region. Dividing the curve of the explosion limit into three parts by two turning points, one calls them first, second, and third limit corresponding to that in the lowest pressure region, that in the middle pressure region, and that in highest pressure region, respectively.

Semenoff explains as follows:

1. At the first limit the activated particles (chain carriers) are destructed on the vessel wall
2. At the second limit they are destructed in the gas phase
3. The third limit is that of thermal explosion

At the first limit the metal of the vessel wall destroys the chain carriers and breaks the chain-branching reaction. In order to prove the theory, he points out

1. The explosion limit is enlarged to the region having lower pressure and temperature with enlargement of the mixture vessel, as the mixture quantity
increases against the surface area of the vessel and the collision probability of the chain carriers with the surface decreases.

2. The explosion limit is also enlarged, if the vessel surface is coated with KCl to avoid the direct contact of the mixture with the wall.

3. The knocking phenomenon in spark ignition engines believed to be a kind of spontaneous ignition is suppressed by adding tetra-ethyl-lead to the fuel, as the metal lead hinders the spontaneous ignition in the engine combustion chamber.

The chain-branching kinetics in the combustion phenomena is still now generally supported by the explanation, experimental and empirical results described above. This chain-branching kinetics, however, can theoretically be applied only to reversible processes, while the explosion is an irreversible phenomenon. It is, therefore, doubtful to apply the theory to such irreversible phenomena as explosion and combustion, even if approximately. The thermal explosion theory is also introduced under the assumption of equilibrium state and cannot be applied to irreversible phenomena. We can here show an experimental result contradicting the chain-branching kinetics.

Let small balls of platinum having different diameters from 1.0 mm to 6.0 mm heated to different temperatures between 800°C and 1,400°C fall in a mixture of 3.0% benzene in air or that of 20% hydrogen in air, observing the ignition. From the experimental results the relation between the ignition temperature and the
diameter of the ball in both the mixtures are illustrated in Fig. 2.8. The result suggests that the ignition temperature decreases with enlargement of the ball that means that the mixture ignites more easily, when the mixture contacted with metal surface increases. This result contradicts the explanation by the chain-branching kinetics.

2.3 Induction Period of Ignition and Ignition Mechanism

The period from the instant when a combustible substance or mixture is put in a state where it can ignite to that of ignition is called induction period of ignition or ignition delay. When a combustible mixture is compressed adiabatically or by shock waves, it keeps the compressed state for a while, then its pressure or temperature rises first slowly, but then rapidly and it emits light. The instant when the mixture begins to change its state or to emit light, or that when the concentration of some activated radicals like OH increases and reaches a certain definite value, can be defined to be the ignition instant. We can, thus, measure the induction period by observing the light emission, pressure, temperature, or concentration of the activated radicals.

As such induction period of ignition is able to be measured easily; experiments for measuring the ignition induction period are often carried out. In Fig. 2.9 a schematic diagram of the reaction between the logarithm of the induction period ln $t_i$ and the reciprocal mixture temperature $1/T$ after the compression is illustrated. As the induction period $t_i$ is reciprocally proportional to the reaction rate, we obtain the following relation according to (2.12):
where $C$ is a proportional constant and $E_e$ the effective activation energy. According to the relation:

$$\tan \theta = \frac{E_e}{R},$$  \hspace{1cm} (2.28)

where $\theta$ is the inclination of $\ln t_i$ to the axis of $1/T$, we can obtain the activation energy $E_e$.

2.3 Induction Period of Ignition and Ignition Mechanism

![Fig. 2.9. Schematic relation between logarithm of ignition induction period \( \ln t_i \) and reciprocal mixture temperature \( 1/T \)](image)

In order to investigate and analyze the ignition mechanism according to the classical theories, a combustible mixture is ignited by compressing and heating through some methods and

1. The ignition induction period is measured to estimate the activation energy
2. While the intermediates are measured during the induction period
3. Considering some elementary reactions having the intermediates observed during the induction period and the same activation energy as that estimated from the above observed ignition induction period, the ignition mechanism is estimated.

It is, however, quite difficult to find all elementary reactions, as all of intermediates cannot be detected.

For example, at the first stage of research on the ignition of methane $\text{CH}_4$, only six elementary reactions were proposed, but as no correct mechanism was found, so many elementary reactions have been proposed as listed in Table 2.1. Using some computers such complicated reactions can be calculated, nevertheless the results do still not agree with the results experimentally observed.

The classical theories can essentially be applied only to the reversible phenomena. For the irreversible phenomena like ignition, explosion, and combustion, other theories must be proposed.
Table 2.1. Methane–oxygen reaction scheme \(^{14}\)

\[
\frac{1}{k} = A T \exp(-E/T) \quad \text{(m mol s)}
\]

<table>
<thead>
<tr>
<th>no.</th>
<th>reaction</th>
<th>(A)</th>
<th>(N)</th>
<th>(E) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{CH}_4 + \text{M} \rightarrow \text{CH}_3 + \text{H} + \text{M})</td>
<td>1.41</td>
<td>0.0</td>
<td>44,500.0</td>
</tr>
<tr>
<td>2</td>
<td>(\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O})</td>
<td>3.47</td>
<td>3.08</td>
<td>9100.0</td>
</tr>
<tr>
<td>3</td>
<td>(\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2)</td>
<td>2.20</td>
<td>3.0</td>
<td>4,400.0</td>
</tr>
<tr>
<td>4</td>
<td>(\text{CH}_4 + \text{O} \rightarrow \text{CH}_3 + \text{OH})</td>
<td>1.20</td>
<td>2.1</td>
<td>3,810.0</td>
</tr>
<tr>
<td>5</td>
<td>(\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_3\text{O} + \text{OH})</td>
<td>3.24</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>(\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O})</td>
<td>2.51</td>
<td>0.0</td>
<td>14,600.0</td>
</tr>
<tr>
<td>7</td>
<td>(\text{CH}_3 + \text{OH} \rightarrow \text{HCHO} + \text{H}_2)</td>
<td>3.98</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>(\text{CH}_3 + \text{O} \rightarrow \text{HCHO} + \text{H})</td>
<td>7.00</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>(\text{CH}_3\text{O} + \text{O} \rightarrow \text{HCHO} + \text{HO}_2)</td>
<td>1.00</td>
<td>0.0</td>
<td>3,020.0</td>
</tr>
<tr>
<td>10</td>
<td>(\text{CH}_3\text{O} + \text{M} \rightarrow \text{HCHO} + \text{H} + \text{M})</td>
<td>5.0</td>
<td>0.0</td>
<td>10,600.0</td>
</tr>
<tr>
<td>11</td>
<td>(\text{HCHO} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O})</td>
<td>7.59</td>
<td>0.0</td>
<td>85.5</td>
</tr>
<tr>
<td>12</td>
<td>(\text{HCHO} + \text{H} \rightarrow \text{CHO} + \text{H}_2)</td>
<td>3.31</td>
<td>0.0</td>
<td>5,280.0</td>
</tr>
<tr>
<td>13</td>
<td>(\text{HCHO} + \text{O} \rightarrow \text{CHO} + \text{OH})</td>
<td>1.20</td>
<td>2.1</td>
<td>3,810.0</td>
</tr>
<tr>
<td>14</td>
<td>(\text{HCHO} + \text{M} \rightarrow \text{CHO} + \text{H} + \text{M})</td>
<td>3.31</td>
<td>0.0</td>
<td>40,800.0</td>
</tr>
<tr>
<td>15</td>
<td>(\text{CHO} + \text{OH} \rightarrow \text{CO} + \text{H}_2)</td>
<td>2.00</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>16</td>
<td>(\text{CHO} + \text{O} \rightarrow \text{CO} + \text{OH})</td>
<td>1.00</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>17</td>
<td>(\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2)</td>
<td>3.98</td>
<td>0.0</td>
<td>3,520.0</td>
</tr>
<tr>
<td>18</td>
<td>(\text{CHO} + \text{M} \rightarrow \text{CO} + \text{H} + \text{M})</td>
<td>1.42</td>
<td>0.0</td>
<td>8,460.0</td>
</tr>
<tr>
<td>19</td>
<td>(\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H})</td>
<td>4.40</td>
<td>1.5</td>
<td>-373.0</td>
</tr>
<tr>
<td>20</td>
<td>(\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M})</td>
<td>5.89</td>
<td>0.0</td>
<td>2,060.0</td>
</tr>
<tr>
<td>21</td>
<td>(\text{CO} + \text{HO}_2 \rightarrow \text{CO}_2 + \text{OH})</td>
<td>1.51</td>
<td>0.0</td>
<td>11,900.0</td>
</tr>
<tr>
<td>22</td>
<td>(\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O})</td>
<td>3.16</td>
<td>0.0</td>
<td>18,900.0</td>
</tr>
<tr>
<td>23</td>
<td>(\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O})</td>
<td>2.20</td>
<td>0.0</td>
<td>8,450.0</td>
</tr>
<tr>
<td>24</td>
<td>(\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H})</td>
<td>1.80</td>
<td>1.0</td>
<td>4,480.0</td>
</tr>
<tr>
<td>25</td>
<td>(\text{OH} + \text{OH} \rightarrow \text{O} + \text{H}_2\text{O})</td>
<td>6.30</td>
<td>0.0</td>
<td>550.0</td>
</tr>
<tr>
<td>26</td>
<td>(\text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O})</td>
<td>2.20</td>
<td>0.0</td>
<td>2,590.0</td>
</tr>
<tr>
<td>27</td>
<td>(\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M})</td>
<td>2.60</td>
<td>-1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>28</td>
<td>(\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M})</td>
<td>1.90</td>
<td>0.0</td>
<td>-900.0</td>
</tr>
<tr>
<td>29</td>
<td>(\text{H} + \text{O} + \text{M} \rightarrow \text{OH} + \text{M})</td>
<td>3.60</td>
<td>-1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>30</td>
<td>(\text{OH} + \text{H} + \text{M} \rightarrow \text{HO}_2 + \text{M})</td>
<td>4.06</td>
<td>-0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>31</td>
<td>(\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_3 + \text{M})</td>
<td>5.00</td>
<td>0.0</td>
<td>-500.0</td>
</tr>
<tr>
<td>32</td>
<td>(\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2)</td>
<td>2.50</td>
<td>0.0</td>
<td>350.0</td>
</tr>
<tr>
<td>33</td>
<td>(\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2)</td>
<td>2.50</td>
<td>0.0</td>
<td>950.0</td>
</tr>
<tr>
<td>34</td>
<td>(\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2)</td>
<td>9.00</td>
<td>0.5</td>
<td>-2,000.0</td>
</tr>
<tr>
<td>35</td>
<td>(\text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{O}_2)</td>
<td>5.00</td>
<td>0.0</td>
<td>500.0</td>
</tr>
<tr>
<td>36</td>
<td>(\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2)</td>
<td>6.30</td>
<td>0.0</td>
<td>350.0</td>
</tr>
</tbody>
</table>
According to the second law of thermodynamics, an irreversible process must at least once pass a state of minimum entropy and this means the existence of a heterogeneous and nonequilibrium state which governs the process and causes some fluctuating phenomena. As the fluctuations are governed by a certain probability, a stochastic theory should be applied to investigate and analyze distinctly irreversible phenomena, for which the classical theories developed for a reversible process cannot be used. Applying the stochastic theory developed for irreversible phenomena to experimental results obtained in the spontaneous ignition in combustible mixtures behind shock waves, not only many empirically observed phenomena are well and simply explained, but also some unknown phenomena which have not been found by the classical theories are unveiled.

In different fields of physics, chemistry, and engineering some basic theories which are introduced from the first law of thermodynamics and which are essentially valid only for reversible processes are often applied to investigate irreversible phenomena. As the reversible process is an ideal one and practically never takes place, we observe only irreversible processes. It is, therefore, very important to confirm, if the theories can be applied to irreversible processes, even approximately, or not.

This section first presents the differences between both the reversible and irreversible processes according to the second law of thermodynamics and clarifies that the theories are valid only for reversible processes, for example, chemical kinetics, nucleation theory, etc., cannot be applied to distinctly irreversible processes, even approximately, and then explains a stochastic theory developed for the irreversible process, reporting the results experimentally obtained by application of the stochastic theory to spontaneous ignition in combustible mixtures behind shock waves in a shock tube.
3.1 Irreversible Process

The definition of a reversible process in thermodynamics is the process proceeding with an infinitely slow velocity, while that of the irreversible process is the process with a finite velocity.\(^1\) Practically there is no reversible process and we observe only irreversible ones.\(^15, 16\)

The first law of thermodynamics applied everywhere in phenomena influenced by heat or temperature is an expression of energy conservation and often expressed as a practical formula with the following equation:

\[
dU = dQ - PdV
\]

or with those modified from this equation, where \(U\) is energy, \(Q\) the heat, \(P\) the pressure, and \(V\) the volume of the system concerned. They are used everywhere in the fields of physics, chemistry, and engineering. These formulae are, however, theoretically valid only for the process proceeding with an infinitely slow velocity, that is, only for the reversible process. The question is now whether the mathematical formulae introduced from the first law can also be applied to the irreversible process or not.

According to the second law of thermodynamics the entropy \(S\) in a closed system never decreases and therefore an equilibrium state has a maximum entropy.\(^17, 18\) An entropy increase is observed in an irreversible process from one equilibrium state to another. As both the initial and final states have a maximum entropy, the process must pass through a minimum entropy state at least once, as shown in Fig. 3.1. What is the meaning of the minimum entropy state or the entropy decrease \(\Delta S_{m f}\) from the initial state \(S_i\) to the minimum entropy state \(S_m\) in the irreversible process?

We can assume an adiabatic process changing from the initial state to the minimum entropy state, in which the macroscopic values of thermodynamic coordinates are kept constant, since no macroscopic change is observed during the process. Considering first a state in a perfect gas as an example, it has an entropy described as follows:\(^19\)

\[
S_i = N \left( c_v \ln T_0 + k \ln \frac{V_0}{N} + \sigma \right),
\]

where \(N\) is the number of particles, \(c_v\) the specific heat of the gas per particle at constant volume, \(T_0\) the temperature of the gas, \(k\) the Boltzmann constant, \(V_0\) the gas volume, and \(\sigma\) is a constant.

Now we divide the system into two parts having the same number of particle \(N/2\) and let each part have different temperatures \(T_1\), \(T_2\), different volumes \(V_1\), and \(V_2\), respectively, in adiabatic states, as shown schematically in Fig. 3.2. Then we have the following relations

\[
\frac{T_1 + T_2}{2} = T_0, T_1 = T_0 + \Delta T, T_2 = T_0 - \Delta T, V_1 + V_2 = V_0,
\]
The system after the division has entropy as follows:

\[ S_{e} = \frac{N}{2} \left[ c_{i} \ln (T_{0} + \Delta T) + k \ln \frac{V_{0} + \Delta V}{N} + \sigma \right] + \frac{N}{2} \left[ c_{i} \ln (T_{0} - \Delta T) + k \ln \frac{V_{0} - \Delta V}{N} + \sigma \right]. \]
The difference of the entropy between both the states before and after the division is:

\[
\Delta S = S_2 - S_1 = \frac{N}{2} \left[ c_v \ln \left( 1 - \left( \frac{\Delta T}{T_0} \right)^2 \right) + k \ln \left( 1 - \left( \frac{\Delta V}{V_0} \right)^2 \right) \right].
\] (3.4)

As \( 0 < \frac{\Delta T}{T_0} < 1 \)

and \( 0 < \frac{\Delta V}{V_0} < 1, \)

then \( 0 < \left[ 1 - \left( \frac{\Delta T}{T_0} \right)^2 \right] < 1 \) and \( 0 < \left[ 1 - \left( \frac{\Delta V}{V_0} \right)^2 \right] < 1, \)

consequently, \( \Delta S < 0. \) The entropy decreases with this division.

If we repeat this process in each part and consequently divide the system into many parts having the same number of particles, but different temperatures and volumes, keeping the mean temperature and the whole volume constant, we obtain a much lower entropy state. In the case of condensed states, we need only to consider the temperature.

Thus, in order to decrease the entropy, it is necessary to have a state having different temperatures everywhere in the system like a mosaic. In the irreversible process such a heterogeneous and nonequilibrium state must appear for a short period somehow at the minimum entropy state even though the macroscopic thermodynamic coordinates are kept constant.

The definition of homogeneous state in thermodynamics is the state in which the entropy \( S(qU, qV, qN_j) = q S(U, V, N_j), \) where \( q \) is an arbitrary number, \( U \) energy, \( V \) volume, and \( N_j \) is the particle number. This means that the specific entropy is everywhere the same in the homogeneous system. The quantity of each part composing the mosaic and having the same temperature must, therefore, be so large that the entropy, eventually the temperature can exist in it, that is, each part must be consisted of more than several thousand particles. The heterogeneous state appearing at the entropy minimum state even if in a short time, causes some fluctuating phenomena not only in time but also in space, as the phenomena are initiated in the parts having higher temperature and develop to an observable scale. We can thus conclude that in an irreversible process the following two states appear:

1. A heterogeneous state which causes some fluctuations in time and space.
2. A nonequilibrium state.

The irreversible process is quite different from the reversible process. The mathematical formulae which are introduced from the first law of thermodynamics and valid only for the reversible processes, therefore, cannot be applied to irreversible processes. Only for very slow processes the theories may approximately be available, but never for distinctly irreversible phenomena.
Remark 1. The first law of thermodynamics for the irreversible process
The mathematical formulae of first law of thermodynamics generally are introduced under an assumption of reversible process. The first law should naturally be available not only for the reversible process, but also for the irreversible one. The first law is, however, applied to the irreversible process considering an entropy increase from a maximum value at an equilibrium state step by step, keeping an equilibrium state, at each step, but considering never the entropy decrease by an irreversible process. The entropy increase directly from a maximum value, keeping an equilibrium, however, is physically impossible.21, 22

Remark 2. Fluctuating phenomena at an equilibrium state
As a thermodynamic system is composed of many particles having different energies under a Maxwellian distribution, a phenomenon observed at an equilibrium state has always some fluctuation, but the range of the fluctuation is very small. For example, the broadening of the distribution of the ignition probability density calculated according to the molecular dynamics is roughly estimated to have an order less than 1/10 of those experimentally observed, which are later shown in this book. Besides, there is no experimental result supporting the stochastic theory introduced from the molecular dynamics.23–25

3.2 Fluctuation in Irreversible Processes

As an irreversible process must pass a minimum entropy state, the fluctuations observed in the irreversible process take place not at random, but are governed by the probability passing the minimum entropy state. In many irreversible phenomena we really observe some fluctuations. In Fig. 3.3, a histogram of delay of electrical discharge is observed by Zuber26, 27 and Hirata28 and in Fig. 3.4 that of rupture of glass pieces is observed by Hirata and Terao.29 Both histograms show a large fluctuation. Such fluctuations are governed by the probability passing the minimum entropy state.

As the entropy $S$ is expressed as a product of the Boltzmann constant $k$ and the logarithm of the probability $W$ of the state, namely30, 31

$$S_i = k \ln W_i, \quad S_m = k \ln W_m \quad \text{and} \quad S_f = k \ln W_f,$$

(3.5)

where the subscript $i$ means the initial state, $m$ the minimum entropy state, and $f$ is the final state. Therefore

$$-\Delta S = S_m - S_i = k \ln W_m - k \ln W_i = k \ln \left( \frac{W_m}{W_i} \right).$$

(3.6)

Then

$$\frac{W_m}{W_i} = \exp \left( \frac{-\Delta S}{k} \right).$$

(3.7)