Naminosuke Kubota

Propellants and Explosives

Thermochemical Aspects of Combustion

Second, Completely Revised and Extended Edition

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Naminosuke Kubota
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Propellants and Explosives
Thermochemical Aspects of Combustion

Second, Completely Revised and Extended Edition
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#### Barium Nitrate

#### Barium Chlorate

#### Strontium Nitrate

#### Sodium Nitrate

### Metallic Oxides

### Metallic Sulfides

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Preface to the First Edition

Propellants and explosives are composed of energetic materials that produce high temperature and pressure through combustion phenomena. The combustion phenomena include complex physicochemical changes from solid to liquid and to gas, which accompany the rapid, exothermic reactions. A number of books related to combustion have been published, such as an excellent theoretical book, Combustion Theory, 2nd Edition, by F. A. Williams, Benjamin/Cummings, New York (1985), and an instructive book for the graduate student, Combustion, by I. Glassman, Academic Press, New York (1977). However, no instructive books related to the combustion of solid energetic materials have been published. Therefore, this book is intended as an introductory text on the combustion of energetic materials for the reader engaged in rocketry or in explosives technology.

This book is divided into four parts. The first part (Chapters 1–3) provides brief reviews of the fundamental aspects relevant to the conversion from chemical energy to aerothermal energy. References listed in each chapter should prove useful to the reader for better understanding of the physical bases of the energy conversion process; energy formation, supersonic flow, shock wave, detonation, and deflagration. The second part (Chapter 4) deals with the energetics of chemical compounds used as propellants and explosives, such as heat of formation, heat of explosion, adiabatic flame temperature, and specific impulse.

The third part (Chapters 5–8) deals with the results of measurements on the burning rate behavior of various types of chemical compounds, propellants, and explosives. The combustion wave structures and the heat feedback processes from the gas phase to the condensed phase are also discussed to aid in the understanding of the relevant combustion mechanisms. The experimental and analytical data described in these chapters are mostly derived from results previously presented by the author. Descriptions of the detailed thermal decomposition mechanisms from solid phase to liquid phase or to gas phase are not included in this book. The fourth part (Chapter 9) describes the combustion phenomena encountered during rocket motor operation, covering such topics as the stability criterion of the rocket motor, temperature sensitivity, ignition transients, erosive burning, and combustion oscillations. The fundamental principle of variable-flow ducted rockets is also presented. The combustion characteristics and energetics of the gas-generating propellants used in ducted rockets are discussed.
Since numerous kinds of energetic materials are used as propellants and explosives, it is not possible to present an entire overview of the combustion processes of these materials. In this book, the combustion processes of typical energetic crystalline and polymeric materials and of various types of propellants are presented so as to provide an informative, generalized approach to understanding their combustion mechanisms.

Kamakura, Japan
March 2001

Naminosuke Kubota
Preface to the Second Edition

The combustion phenomena of propellants and explosives are described on the basis of pyrodynamics, which concerns thermochemical changes generating heat and reaction products. The high-temperature combustion products generated by propellants and explosives are converted into propulsive forces, destructive forces, and various types of mechanical forces. Similar to propellants and explosives, pyrolants are also energetic materials composed of oxidizer and fuel components. Pyrolants react to generate high-temperature condensed and/or gaseous products when they burn. Propellants are used for rockets and guns to generate propulsive forces through deflagration phenomena and explosives are used for warheads, bombs, and mines to generate destructive forces through detonation phenomena. On the other hand, pyrolants are used for pyrotechnic systems such as ducted rockets, gas-hybrid rockets, and igniters and flares. This Second Edition includes the thermochemical processes of pyrolants in order to extend their application potential to propellants and explosives.

The burning characteristics of propellants, explosives, and pyrolants are largely dependent on various physicochemical parameters, such as the energetics, the mixture ratio of fuel and oxidizer components, the particle size of crystalline oxidizers, and the decomposition process of fuel components. Though metal particles are high-energy fuel components and important ingredients of pyrolants, their oxidation and combustion processes with oxidizers are complex and difficult to understand.

Similar to the First Edition, the first half of the Second Edition is an introductory text on pyrodynamics describing fundamental aspects of the combustion of energetic materials. The second half highlights applications of energetic materials as propellants, explosives, and pyrolants. In particular, transient combustion, oscillatory burning, ignition transients, and erosive burning phenomena occurring in rocket motors are presented and discussed. Ducted rockets represent a new propulsion system in which combustion performance is significantly increased by the use of pyrolants.

Heat and mass transfer through the boundary layer flow over the burning surface of propellants dominates the burning process for effective rocket motor operation. Shock wave formation at the inlet flow of ducted rockets is an important process for achieving high propulsion performance. Thus, a brief overview of the fundamentals of aerodynamics and heat transfer is provided in Appendices B–D as a prerequisite for the study of pyrodynamics.

Tokyo, Japan

Naminosuke Kubota

September 2006
Preface to the Second Edition
Foundations of Pyrodynamics

Pyrodynamics describes the process of energy conversion from chemical energy to mechanical energy through combustion phenomena, including thermodynamic and fluid dynamic changes. Propellants and explosives are energetic condensed materials composed of oxidizer-fuel components that produce high-temperature molecules. Propellants are used to generate high-temperature and low-molecular combustion products that are converted into propulsive forces. Explosives are used to generate high-pressure combustion products accompanied by a shock wave that yield destructive forces. This chapter presents the fundamentals of thermodynamics and fluid dynamics needed to understand the pyrodynamics of propellants and explosives.

1.1 Heat and Pressure

1.1.1 First Law of Thermodynamics

The first law of thermodynamics relates the energy conversion produced by chemical reaction of an energetic material to the work acting on a propulsive or explosive system. The heat produced by chemical reaction ($q$) is converted into the internal energy of the reaction product ($e$) and the work done to the system ($w$) according to

$$dq = de + dw$$

(1.1)

The work is done by the expansion of the reaction product, as given by

$$dw = pdv \quad \text{or} \quad dw = pd\left(\frac{1}{\rho}\right)$$

(1.2)

where $p$ is the pressure, $v$ is the specific volume (volume per unit mass) of the reaction product, and $\rho$ is the density defined in $\nu = 1/\rho$. Enthalpy $h$ is defined by

$$dh = de + d\left(pv\right)$$

(1.3)
Substituting Eqs. (1.1) and (1.2) into Eq. (1.3), one gets

\[ dh = dq + vdp \]  

(1.4)

The equation of state for one mole of a perfect gas is represented by

\[ pv = R_gT \quad \text{or} \quad p = \rho R_gT \]  

where \( T \) is the absolute temperature and \( R_g \) is the gas constant. The gas constant is given by

\[ R_g = \frac{R}{M_g} \]  

(1.6)

where \( M_g \) is the molecular mass, and \( R \) is the universal gas constant, \( R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1} \). In the case of \( n \) moles of a perfect gas, the equation of state is represented by

\[ pv = nR_gT \quad \text{or} \quad p = n\rho R_gT \]  

(1.5a)

1.1.2 Specific Heat

Specific heat is defined according to

\[ c_v = \frac{de}{dT}_v \quad c_p = \frac{dh}{dT}_p \]  

(1.7)

where \( c_v \) is the specific heat at constant volume and \( c_p \) is the specific heat at constant pressure. Both specific heats represent conversion parameters between energy and temperature. Using Eqs. (1.3) and (1.5), one obtains the relationship

\[ c_p - c_v = R_g \]  

(1.8)

The specific heat ratio \( \gamma \) is defined by

\[ \gamma = \frac{c_p}{c_v} \]  

(1.9)

Using Eq. (1.9), one obtains the relationships

\[ c_v = \frac{R_g}{\gamma - 1} \quad c_p = \gamma R_g/(\gamma - 1) \]  

(1.10)

Specific heat is an important parameter for energy conversion from heat energy to mechanical energy through temperature, as defined in Eqs. (1.7) and (1.4). Hence, the specific heat of gases is discussed to understand the fundamental physics of the energy of molecules based on kinetic theory.\[1,2\] The energy of a single molecule, \( \varepsilon_m \), is given by the sum of the internal energies, which comprise translational energy,
\( \varepsilon_t \), rotational energy, \( \varepsilon_r \), vibrational energy, \( \varepsilon_v \), electronic energy, \( \varepsilon_e \), and their interaction energy, \( \varepsilon_i \):

\[
\varepsilon_m = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e + \varepsilon_i
\]

A molecule containing \( n \) atoms has \( 3n \) degrees of freedom of motion in space:

<table>
<thead>
<tr>
<th>Molecular Structure</th>
<th>Degrees of Freedom</th>
<th>Translational</th>
<th>Rotational</th>
<th>Vibrational</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monatomic</td>
<td>3</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diatomic</td>
<td>6</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Polyatomic Linear</td>
<td>( 3n )</td>
<td>3</td>
<td>2</td>
<td>( 3n-5 )</td>
</tr>
<tr>
<td>Polyatomic Nonlinear</td>
<td>( 3n )</td>
<td>3</td>
<td>3</td>
<td>( 3n-6 )</td>
</tr>
</tbody>
</table>

A statistical theorem on the equipartition of energy shows that an energy amounting to \( kT/2 \) is given to each degree of freedom of translational and rotational modes, and that an energy of \( kT \) is given to each degree of freedom of vibrational modes. The Boltzmann constant \( k \) is \( 1.38065 \times 10^{-23} \) J K\(^{-1} \). The universal gas constant \( R \) defined in Eq. (1.6) is given by

\[
R = \frac{k}{\zeta}, \quad \zeta = 6.02214 \times 10^{23} \text{ mol}^{-1}.
\]

When the temperature of a molecule is increased, rotational and vibrational modes are excited and the internal energy is increased. The excitation of each degree of freedom as a function of temperature can be calculated by way of statistical mechanics. Though the translational and rotational modes of a molecule are fully excited at low temperatures, the vibrational modes only become excited above room temperature. The excitation of electrons and interaction modes usually only occurs at well above combustion temperatures. Nevertheless, dissociation and ionization of molecules can occur when the combustion temperature is very high.

When the translational, rotational, and vibrational modes of monatomic, diatomic, and polyatomic molecules are fully excited, the energies of the molecules are given by

\[
\varepsilon_m = \varepsilon_t + \varepsilon_r + \varepsilon_v
\]

\[
\varepsilon_m = 3 \times kT/2 = 3 \frac{kT}{2} \text{ for monatomic molecules}
\]

\[
\varepsilon_m = 3 \times kT/2 + 2 \times kT/2 + 1 \times kT = 7 \frac{kT}{2} \text{ for diatomic molecules}
\]

\[
\varepsilon_m = 3 \times kT/2 + 2 \times kT/2 + (3n - 5) \times kT = (6n - 5) \frac{kT}{2} \text{ for linear molecules}
\]

\[
\varepsilon_m = 3 \times kT/2 + 3 \times kT/2 + (3n - 6) \times kT = 3(n - 1) kT \text{ for nonlinear molecules}
\]

Since the specific heat at constant volume is given by the temperature derivative of the internal energy as defined in Eq. (1.7), the specific heat of a molecule, \( c_{v,m} \), is represented by

\[
c_{v,m} = \frac{d\varepsilon_m}{dT} = \frac{d\varepsilon_t}{dT} + \frac{d\varepsilon_r}{dT} + \frac{d\varepsilon_v}{dT} + \frac{d\varepsilon_e}{dT} + \frac{d\varepsilon_i}{dT} \quad \text{J molecule}^{-1} \text{ K}^{-1}
\]
Thus, one obtains the specific heats of gases composed of monatomic, diatomic, and polyatomic molecules as follows:

\[ c_v = \frac{3R}{2} = 12.47 \text{ J mol}^{-1} \text{ K}^{-1} \text{ for monatomic molecules} \]

\[ c_v = \frac{7R}{2} = 29.10 \text{ J mol}^{-1} \text{ K}^{-1} \text{ for diatomic molecules} \]

\[ c_v = \frac{(6n - 5)R}{2} \text{ J mol}^{-1} \text{ K}^{-1} \text{ for linear molecules} \]

\[ c_v = 3(n - 1)R \text{ J mol}^{-1} \text{ K}^{-1} \text{ for nonlinear molecules} \]

The specific heat ratio defined by Eq. (1.9) is 5/3 for monatomic molecules; 9/7 for diatomic molecules. Since the excitations of rotational and vibrational modes only occur at certain temperatures, the specific heats determined by kinetic theory are different from those determined experimentally. Nevertheless, the theoretical results are valuable for understanding the behavior of molecules and the process of energy conversion in the thermochemistry of combustion. Fig. 1.1 shows the specific heats of real gases encountered in combustion as a function of temperature. The specific heats of monatomic gases remain constant with increasing temperature, as determined by kinetic theory. However, the specific heats of diatomic and polyatomic gases are increased with increasing temperature as the rotational and vibrational modes are excited.

1.1.3

Entropy Change

Entropy \( s \) is defined according to

\[ ds = dq/T \quad (1.11) \]
Substituting Eqs. (1.4), (1.5), and (1.7) into Eq. (1.11), one gets

\[ ds = c_p \frac{dT}{T} - \frac{R_g dp}{p} \]  

(1.12)

In the case of isentropic change, \( ds = 0 \), Eq. (1.12) is integrated as

\[ \frac{p}{p_1} = \left( \frac{T}{T_1} \right)^{\frac{\gamma}{\gamma - 1}} \]  

(1.13)

where the subscript 1 indicates the initial state 1. Using Eqs. (1.10), (1.5), and (1.13), one gets

\[ \frac{p}{p_1} = \left( \frac{T}{T_1} \right)^{\frac{\gamma}{\gamma - 1}} \quad \text{and} \quad p \left( \frac{1}{\rho} \right)^\gamma = p_1 \left( \frac{1}{\rho_1} \right)^\gamma \]  

(1.14)

When a system involves dissipative effects such as friction caused by molecular collisions or turbulence caused by a non-uniform molecular distribution, even under adiabatic conditions, \( ds \) becomes a positive value, and then Eqs. (1.13) and (1.14) are no longer valid. However, when these physical effects are very small and heat loss from the system or heat gain by the system are also small, the system is considered to undergo an isentropic change.

1.2 Thermodynamics in a Flow Field

1.2.1 One-Dimensional Steady-State Flow

1.2.1.1 Sonic Velocity and Mach Number
The sonic velocity propagating in a perfect gas, \( a \), is given by

\[ a = \left( \frac{\partial p}{\partial \rho} \right)_s^{1/2} \]  

(1.15)

Using the equation of state, Eq. (1.8), and the expression for adiabatic change, Eq. (1.14), one gets

\[ a = \left( \gamma R_g T \right)^{1/2} \]  

(1.16)

Mach number \( M \) is defined according to

\[ M = \frac{u}{a} \]  

(1.17)

where \( u \) is the local flow velocity in a flow field. Mach number is an important parameter in characterizing a flow field.
1.2.1.2 Conservation Equations in a Flow Field

Let us consider a simplified flow, that is, a one-dimensional steady-state flow without viscous stress or a gravitational force. The conservation equations of continuity, momentum, and energy are represented by:

rate of mass in − rate of mass out = 0

\[ \frac{d}{dt}(\rho u) = 0 \]  
(1.18)

rate of momentum gain by convection + pressure difference acting on flow = 0

\[ \rho u \frac{du}{dt} + dp = 0 \]  
(1.19)

rate of energy input by conduction + rate of energy input by convection = 0

\[ \frac{d}{dt}(h + \frac{u^2}{2}) = 0 \]  
(1.20)

Combining Eqs. (1.20) and Eq. (1.4), one obtains the relationship for the enthalpy change due to a change of flow velocity as

\[ dh = dq - u \frac{du}{dt} \]  
(1.21)

1.2.1.3 Stagnation Point

If one can assume that the process in the flow field is adiabatic and that dissipative effects are negligibly small, the flow in the system is isentropic \((\frac{ds}{dt} = 0)\), and then Eq. (1.21) becomes

\[ dh = -u \frac{du}{dt} \]  
(1.22)

Integration of Eq. (1.22) gives

\[ h_0 = h + \frac{u^2}{2} \]  
(1.23)

where \( h_0 \) is the stagnation enthalpy at \( u = 0 \) of a stagnation flow point. Substituting Eq. (1.7) into Eq. (1.23), one gets

\[ c_p T_0 = c_p T + \frac{u^2}{2} \]  
(1.24)

where \( T_0 \) is the stagnation temperature at \( u = 0 \).

The changes in temperature, pressure, and density in a flow field are expressed as a function of Mach number as follows:

\[ \frac{T_0}{T} = 1 + \frac{\gamma - 1}{2} M^2 \]  
(1.25)

\[ \frac{p_0}{p} = \left(1 + \frac{\gamma - 1}{2} M^2\right)^{\frac{\gamma}{\gamma - 1}} \]  
(1.26)

\[ \frac{\rho_0}{\rho} = \left(1 + \frac{\gamma - 1}{2} M^2\right)^{\frac{1}{\gamma - 1}} \]  
(1.27)
1.2.2

Formation of Shock Waves

One assumes that a discontinuous flow occurs between regions 1 and 2, as shown in Fig. 1.2. The flow is also assumed to be one-dimensional and in a steady state, and not subject to a viscous force, an external force, or a chemical reaction.

The mass continuity equation is given by

\[ \rho_1 u_1 = \rho_2 u_2 = m \]  

(1.28)

The momentum equation is represented by

\[ p_1 + \rho_1 u_1^2 = p_2 + \rho_2 u_2^2 \]  

(1.29)

The energy equation is represented by the use of Eq. (1.20) as

\[ c_p T_1 + \frac{u_1^2}{2} = c_p T_2 + \frac{u_2^2}{2} \]  

(1.30)

where \( m \) is the mass flux in a duct of constant area, and the subscripts 1 and 2 indicate the upstream and the downstream of the discontinuity, respectively. Substituting Eq. (1.29) into Eq. (1.30), one gets

\[ p_1 + \rho_1 u_1^2 = p_2 + \rho_2 u_2^2 \]  

(1.31)

Using Eq. (1.25), the temperature ratio in regions 2 and 1 is represented by the Mach number in 2 and 1 according to

\[ \frac{T_2}{T_1} = \frac{1 + \frac{\gamma - 1}{2} M_1^2}{1 + \frac{\gamma - 1}{2} M_2^2} \]  

(1.32)

Using Eqs. (1.5), (1.17), and (1.28), one gets

\[ \frac{T_2}{T_1} = \left( \frac{M_2}{M_1} \right)^2 \left( \frac{p_2}{p_1} \right)^{\frac{\gamma - 1}{2}} \]  

(1.33)

Combining Eqs. (1.31) and (1.32), the pressure ratio is obtained as a function of \( M_1 \) and \( M_2 \):

\[ \frac{p_2}{p_1} = \frac{M_1}{M_2} \sqrt{1 + \frac{\gamma - 1}{2} M_1^2} \]  

(1.34)

\[ \begin{array}{c}
\text{Upstream} \\
\text{Downstream}
\end{array} \]

\[ \begin{array}{c}
\begin{array}{c}
\rho_1 \\
T_1 \\
M_1 \\
u_1
\end{array} \\
\begin{array}{c}
p_1 \\
T_2 \\
M_2 \\
u_2
\end{array}
\end{array} \]

\[ \begin{array}{c}
1 \\
2
\end{array} \]

Fig. 1.2 Shock wave propagation.
Combining Eqs. (1.33) and (1.34), the Mach number relationship in the upstream 1 and downstream 2 is obtained as

\[
\frac{M_1\sqrt{1 + \frac{\gamma - 1}{2} M_1^2}}{1 + \gamma M_1^2} = \frac{M_2\sqrt{1 + \frac{\gamma - 1}{2} M_2^2}}{1 + \gamma M_2^2}
\]

(1.35)

One obtains two solutions from Eq. (1.35):

\[M_2 = M_1\] (1.36)

\[M_2 = \left[\frac{2 + M_1^2}{\frac{\gamma - 1}{2} M_1^2 - 1}\right]^{\frac{1}{2}}\] (1.37)

The solution expressed by Eq. (1.36) indicates that there is no discontinuous flow between the upstream 1 and the downstream 2. However, the solution given by Eq. (1.37) indicates the existence of a discontinuity of pressure, density, and temperature between 1 and 2. This discontinuity is called a “normal shock wave”, which is set-up in a flow field perpendicular to the flow direction. Discussions on the structures of normal shock waves and supersonic flow fields can be found in the relevant monographs.[4,5]

Substituting Eq. (1.37) into Eq. (1.34), one obtains the pressure ratio as

\[
\frac{p_2}{p_1} = \frac{2\gamma}{\gamma + 1} M_2^2 - \frac{\gamma - 1}{\gamma + 1}
\]

(1.38)

Substituting Eq. (1.37) into Eq. (1.33), one also obtains the temperature ratio as

\[
\frac{T_2}{T_1} = \left[\frac{2(\gamma - 1)}{\gamma + 1} M_2^2 \left(1 + \frac{\gamma - 1}{2} M_1^2\right) \left(\frac{2\gamma}{\gamma - 1} M_1^2 - 1\right)\right]^{1/2}
\]

(1.39)

The density ratio is obtained by the use of Eqs. (1.38), (1.39), and (1.8) as

\[
\frac{\rho_2}{\rho_1} = \frac{p_2}{p_1} \frac{T_2}{T_1}
\]

(1.40)

Using Eq. (1.24) for the upstream and the downstream and Eq. (1.38), one obtains the ratio of stagnation pressure as

\[
\frac{p_{02}}{p_{01}} = \left(\frac{\gamma + 1}{2} M_2^2\right)^{\gamma/\gamma - 1} \left(1 + \frac{\gamma - 1}{2} M_1^2\right)^{\gamma/\gamma - 1} \left(\frac{2\gamma}{\gamma + 1} M_1^2 - \frac{\gamma - 1}{\gamma + 1}\right)^{1/\gamma - 1}
\]

(1.41)

The ratios of temperature, pressure, and density in the downstream and upstream are expressed by the following relationships:

\[
\frac{T_2}{T_1} = \frac{p_2}{p_1} \left(1 + \frac{1}{\xi} \frac{p_2}{p_1}\right) \left(1 + \frac{p_2}{p_1}\right)
\]

(1.42)

\[
\frac{p_2}{p_1} = \left(\xi \frac{p_2}{p_1} - 1\right) \left(\xi \frac{p_2}{p_1}\right)
\]

(1.43)