GUIDELINES FOR

Safe Storage and Handling of Reactive Materials

CENTER FOR CHEMICAL PROCESS SAFETY
of the
AMERICAN INSTITUTE OF CHEMICAL ENGINEERS
345 East 47th Street, New York, New York 10017
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Safe Storage and Handling of Reactive Materials
Publications Available from the
CENTER FOR CHEMICAL PROCESS SAFETY
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Guidelines for Safe Storage and Handling of Reactive Materials
Guidelines for Technical Planning for On-Site Emergencies
Guidelines for Process Safety Documentation
Guidelines for Safe Process Operations and Maintenance
Guidelines for Process Safety Fundamentals in General Plant Operations
Guidelines for Chemical Reactivity Evaluation and Application to Process Design
Tools for Making Acute Risk Decisions with Chemical Process Safety Applications
Guidelines for Preventing Human Error in Process Safety
Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires, and BLEVEs
Guidelines for Implementing Process Safety Management Systems
Guidelines for Safe Automation of Chemical Processes
Guidelines for Engineering Design for Process Safety
Guidelines for Auditing Process Safety Management Systems
Guidelines for Investigating Chemical Process Incidents
Guidelines for Hazard Evaluation Procedures, Second Edition with Worked Examples
Guidelines for Technical Management of Chemical Process Safety
Guidelines for Chemical Process Quantitative Risk Analysis
Guidelines for Process Equipment Reliability Data, with Data Tables
Guidelines for Vapor Release Mitigation
Guidelines for Safe Storage and Handling of High Toxic Hazard Materials
Guidelines for Use of Vapor Cloud Dispersion Models
Understanding Atmospheric Dispersion of Accidental Releases
Expert Systems in Process Safety
Concentration Fluctuations and Averaging Time in Vapor Clouds
Safety, Health, and Loss Prevention in Chemical Processes: Problems for Undergraduate Engineering Curricula
Workbook of Test Cases for Vapor Cloud Source Dispersion Models
CCPS/AIChe Directory of Chemical Process Safety Services
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345 East 47th Street, New York, New York 10017
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Preface

The Center for Chemical Process Safety (CCPS) was established in 1985 by the American Institute of Chemical Engineers (AIChE) for the express purpose of assisting industry in avoiding or mitigating catastrophic chemical accidents. To achieve this goal, CCPS has focused its work on four areas:

- Establishing and publishing the latest scientific, engineering, and management practices for prevention and mitigation of incidents involving toxic, flammable, and/or reactive material.
- Encouraging the use of such information by dissemination through publications, seminars, symposia, and continuing education programs for engineers.
- Advancing the state of the art in engineering practices and technical management through research in prevention and mitigation of catastrophic events.
- Developing and encouraging the use of undergraduate engineering curricula that will improve the safety, knowledge, and consciousness of engineers.

In 1988, Guidelines for Safe Storage and Handling of High Toxic Hazard Materials was published. A more recent work, Guidelines for Chemical Reactivity Evaluation and Applications to Process Design, gives details of current methods for evaluating chemical reactivity and the use of evaluation results in the engineering design of reactive chemical processes. This document, Guidelines for Safe Storage and Handling of Reactive Materials, builds on the preceding CCPS guidelines, but nevertheless is intended as a stand-alone resource for persons responsible for reactive chemical handling. Many books and articles have been written on chemical reactivity, and the intent of this book is not to give an exhaustive discussion of reactivity. Rather, the purpose of this book is to summarize current process industry practices for designing and operating facilities to safely store and handle reactive materials.
The current book is the result of a project begun in 1992 in which a committee of process safety professionals representing CCPS sponsor companies worked with Battelle’s Process Safety and Risk Management group to develop this document. The project included an extensive survey of CCPS sponsor companies and their current practices related to the safe storage and handling of reactive materials. The survey results are included as part of this text.

The safe storage and handling of reactive materials requires a sound and responsible management philosophy, together with a combination of superior siting, design, fabrication, erection, inspection, monitoring, maintenance, operation, and management of such facilities. These elements are necessary parts of a reliable system to prevent equipment or human failures that might lead to a reactive chemical incident such as a vessel rupture explosion. These Guidelines deal with each of the above elements, with emphasis on design considerations.

These Guidelines are technical in nature. They are intended for use by engineers and other persons familiar with the manufacture and use of chemicals. They include discussion of some of the current industry practices for controlling reactivity hazards, both for existing facilities and for plants presently being designed. They are not a “standard,” and make no attempt to cover all the legal requirements that may relate to the construction and operation of facilities for the storage and handling of reactive chemicals. Meeting such legal requirements is a minimum basis for design and operation of all facilities. These Guidelines highlight and supplement those basic requirements that are particularly important to the safe storage and handling of reactive chemicals. Thus, they should be applied with engineering judgment as well as a knowledge of the hazards and properties of each particular reactive chemical.

Existing facilities may have been designed and constructed to earlier versions of codes and standards, and thus may not fully reflect current practices. When major modifications or additions are made to older facilities, the new portions should meet current design practices for new facilities. However, it is the responsibility of management to decide whether additional safety-related design changes in older facilities are necessary and warranted. Nevertheless, the management of existing facilities for the storage and handling of reactive chemicals should apply current standards and safety practices to their operating, maintenance, management, and emergency procedures and should also reassess safety monitoring and control systems to see whether enhancement of such systems is needed to meet current levels of good practice.
Acknowledgments

The American Institute of Chemical Engineers wishes to thank the Center for Chemical Process Safety (CCPS) and those involved in its operation, including its many sponsors whose funding made this project possible. Thanks are due to the members of its Technical Steering Committee who conceived the idea and supported this project, and to the members of the Subcommittee on Reactive Materials Storage for their dedicated efforts, technical contributions, and enthusiasm.

The members of the Subcommittee on Reactive Materials Storage are:

Robert W. Nelson, Industrial Risk Insurers (Chairman)
Laurence G. Britton, Union Carbide Corporation
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John V. Birtwistle (Monsanto Chemical Company), Stanley J. Schechter (Rohm and Haas Company), and Stanley M. Englund (The Dow Chemical Company) also served on the subcommittee during its early work. The members of this subcommittee especially wish to thank their employers for providing the time to participate in this project.

The Battelle project manager and principal author of this book was Robert W. Johnson, with significant contributions by Steven W. Rudy and Amy J. Sato of Battelle’s Process Safety and Risk Management group. Grateful acknowledgement is given to Caroline J. Cadwell for compiling the survey results of Appendix B and to Vicki G. Paddock for her careful editing.
We gratefully acknowledge the comments and suggestions submitted by the following companies and peer reviewers:

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Reviews and comments from Harold G. Fisher and Jonathan Kurland of Union Carbide Corporation are gratefully recognized. We also express our appreciation to Thomas W. Carmody, former director of CCPS; Bob G. Perry, AIChE Managing Director, Technical Activities; and Jack Weaver, Director of CCPS, for their support and guidance.
Acronyms used only in a particular section of this book are defined where they are used in the book. Acronyms that are used more prevalently are listed and defined here.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AICHE</td>
<td>American Institute of Chemical Engineers</td>
</tr>
<tr>
<td>AIT</td>
<td>Autoignition temperature</td>
</tr>
<tr>
<td>ARC</td>
<td>Accelerating Rate Calorimeter (Columbia Scientific Instrument Company)</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CCPS</td>
<td>Center for Chemical Process Safety</td>
</tr>
<tr>
<td>CHETAH</td>
<td>Chemical Thermodynamic and Energy Release Program</td>
</tr>
<tr>
<td>DIERS</td>
<td>Design Institute for Emergency Relief Systems</td>
</tr>
<tr>
<td>DOT</td>
<td>U.S. Department of Transportation</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimeter; differential scanning calorimetry</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential thermal analysis</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron scanning chemical analysis</td>
</tr>
<tr>
<td>HAZOP</td>
<td>Hazard and Operability [Study]</td>
</tr>
<tr>
<td>LFL</td>
<td>Lower flammable limit</td>
</tr>
<tr>
<td>LOC</td>
<td>Limiting oxidant concentration</td>
</tr>
<tr>
<td>MSDS</td>
<td>Material safety data sheet</td>
</tr>
<tr>
<td>NFPA</td>
<td>National Fire Protection Association</td>
</tr>
<tr>
<td>P&amp;ID</td>
<td>Piping and instrumentation diagram</td>
</tr>
<tr>
<td>PSM</td>
<td>Process safety management</td>
</tr>
<tr>
<td>SADT</td>
<td>Self-accelerating decomposition temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>UFL</td>
<td>Upper flammable limit</td>
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</tbody>
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Introduction

What is a reactive material? It is a substance that can liberate sufficient energy for the occurrence of a hazardous event by readily polymerizing, decomposing, rearranging, oxidizing in air without an ignition source, and/or reacting with water. Some commercially produced reactive materials are listed in Table 1.

Thus, reactive materials are not a homogeneous group; this definition can include such diverse substances as monomers, explosives, organic peroxides, pyrophorics, and water-reactive materials. Likewise, initiation of a hazardous reaction can be spontaneous, by heat input, by mechanical shock or friction, or by catalytic activity. Nevertheless, there is much in common among the various reactive materials with respect to their safe storage and handling.

This book addresses the on-site storage and handling of reactive materials. Off-site transportation, laboratory handling, and general warehousing requirements are not covered. Operations other than storage and handling, such as chemical processing, mixing, and blending are likewise not addressed. The scope of this book does not include commercial explosives or materials that are only flammable or combustible.

This book contains guidelines. These guidelines are intended to provide engineers, managers, and operations personnel with a technical overview of current good industry practice. They can, if prudently employed, significantly reduce the likelihood and severity of accidents associated with storing and handling reactive materials.

To store and handle reactive materials safely, the following questions must be addressed:

What kind of reactivity hazards are posed?

What is the magnitude of the reactivity hazards?

How can we design and operate our facility to store and handle safely the reactive materials?
### TABLE 1
High-Volume Commercial Reactive Materials
(see Note below for explanation)

<table>
<thead>
<tr>
<th>Nr</th>
<th>Material</th>
<th>1993 Volume</th>
<th>Self-Reactive</th>
<th>Reactive with Other Materials</th>
<th>Oxidizer</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Ammonium nitrate</td>
<td>16,790</td>
<td>shock-sensitive</td>
<td></td>
<td>yes</td>
</tr>
<tr>
<td>3</td>
<td>Ethylene oxide</td>
<td>5,684</td>
<td>polymerizing, decomposing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Hydrogen peroxide, 100% (1991 data)</td>
<td>500</td>
<td>decomposing</td>
<td></td>
<td>yes</td>
</tr>
<tr>
<td>2</td>
<td>Sulfuric acid</td>
<td>80,306</td>
<td></td>
<td>water-reactive</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ethylene</td>
<td>41,244</td>
<td>polymerizing, decomposing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Vinyl chloride</td>
<td>13,746</td>
<td>polymerizing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Styrene</td>
<td>10,063</td>
<td>polymerizing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Propylene oxide</td>
<td>3,300</td>
<td>polymerizing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1,3-Butadiene</td>
<td>3,092</td>
<td>polymerizing</td>
<td>peroxide-forming</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Vinyl acetate</td>
<td>2,827</td>
<td>polymerizing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Acrylonitrile</td>
<td>2,508</td>
<td>polymerizing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Methyl methacrylate</td>
<td>1,088</td>
<td>polymerizing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Phosphorus</td>
<td>534</td>
<td></td>
<td>pyrophoric</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Lithium</td>
<td>6</td>
<td></td>
<td>water-reactive</td>
<td></td>
</tr>
</tbody>
</table>

*Note:* U.S. production volumes in millions of pounds (Chemical & Engineering News, July 4, 1994). Only the highest-volume materials with Nr of 2 or higher in the categories of inorganic chemicals, organic chemicals, and minerals are listed. The Nr numbers are the NFPA reactivity ratings for each material from NFPA 49 (Hazardous Chemical Data, NFPA, Quincy, Mass., 1994) or NFPA 325M (Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids, NFPA, Quincy, Mass., 1994). Only pyrophoric, peroxide-forming, and water-reactive characteristics are considered under "Reactive with Other Materials."

The first question is addressed in Chapters 1 and 2, which describe the several kinds of reactive chemical hazards and how they have been classified. The third question is addressed in Chapters 3 and 4, which summarize methods to conduct reactivity testing and calculate the severity of consequences of a reactive chemical incident. The last question is addressed in Chapters 5 through 7, which give both general and chemical-specific design considerations and operating practices.
This chapter gives a systematic overview of chemical reactivity hazards. It will enable the user to answer the questions

What kind of reactivity hazards are posed?

The chemical process industry by nature involves chemical reactions, the production of reactive chemicals and intermediates, and the handling of reactive materials. Most chemicals handled in the industry are not unstable or reactive under normal storage conditions without a strong initiator; however, the reaction of some materials is easily initiated with only a slight deviation from normal conditions, releasing sufficient energy to cause a hazardous event. Reactive chemicals and uncontrolled chemical reactions are often described using various descriptive adjectives such as unstable, shock-sensitive, vigorous, violent, runaway, and explosive.

Accident and Postaccident Concerns
Potential reactive chemical accidents include fires, explosions, and the generation and release of toxic materials. Reactive chemical incidents have resulted in the loss of hundreds of lives and many millions of dollars in property. Perhaps the most notable reactive chemical incidents are those that are now known merely by the location of their occurrence; namely, the Bhopal methyl isocyanate release and the Seveso dioxin release (documented in Marshall, 1987 and elsewhere).

Reactivity hazards may continue to exist after an incident has occurred and mitigation efforts are underway. Water-reactive materials such as aluminum alkyls, for example, can pose particularly difficult fire-fighting problems. Reactive metals such as sodium and metal hydrides also preclude the use of carbon dioxide or halogenated extinguishing agents. Many reactive materials are thermally unstable and can decompose rapidly if involved in a fire situation. Some reactive chemicals can cause spontaneous combustion in absorbents used for spill control. These examples illustrate the necessity for thorough analysis and careful
design of systems to identify, contain, and control reactive chemicals and respond to reactive chemical incidents.

1.1. Framework for Understanding Reactivity Hazards

In order to identify reactive chemical hazards in a storage or handling facility systematically, a structured understanding of reactivity hazards is important. To this end, an overall framework for identifying reactive chemical hazards is presented in Section 1.2.1, along with brief descriptions of the types of hazards encountered within the given framework. In Section 1.2.2, some fundamentals of chemical reactivity are reviewed in the context of how both thermodynamic and kinetic factors affect reactive chemical systems. The common concept of “runaway reactions,” which cuts across many types of reactivity hazards, is discussed in Section 1.2.3. Initiators of reactive chemical incidents are examined in Section 1.2.4.

1.1.1. Grouping of Reactivity Hazards into General Categories

Reactive materials can be grouped into several general categories, as shown in Table 1.1 and described below. While there is some overlap between the categories and subcategories presented here, they nevertheless can serve as a useful framework for understanding the range of reactivity hazards presented by industrially important chemicals.

Table 1.1 divides reactive chemicals into two major groups: namely, those that "self-react" and those that react with other materials. Each of the common types of reactive materials, such as pyrophoric and shock-sensitive materials, are discussed below within this framework. Those items discussed in detail in this book are shaded in Table 1.1.

**Self-Reactive Materials**

Reactive materials that are capable of self-reaction will react in one or more of three ways: they will polymerize, or form more complex molecules by polymerization-type mechanisms; decompose, or break down into simpler molecules such as water and nitrogen; and/or rearrange to form variants on the same basic chemical structures or formulas.

Polymerizing compounds are often monomers that self-react, often in the presence of a catalyst, to form polymers or other similar larger, more complex molecular structures by chaining, crosslinking, or similar reactions. Polymerization reactions are generally self-sustaining once initiated, and often highly exothermic. In addition to the heat of reaction, off-gases from the reaction can also pose a significant overpressurization hazard.

Decomposing materials have chemical structures that are relatively unstable and break down easily. Decomposing materials include shock-sensitive and thermally decomposing compounds. The decomposition of a shock-sensitive
TABLE 1.1
Reactivity Hazard Types

<table>
<thead>
<tr>
<th></th>
<th>REACTIVE MATERIALS</th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Self-Active (Unstable)</td>
<td>Reactive with Other Materials</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polymerizing</td>
<td>Decomposing</td>
<td>Rearranging</td>
<td>Oxygen-reactive</td>
<td>Water-reactive</td>
</tr>
<tr>
<td></td>
<td>Shock-sensitive</td>
<td>Isomerizing</td>
<td>Disproportionating</td>
<td>Pyrophoric</td>
<td>Class A</td>
</tr>
<tr>
<td></td>
<td>Thermally</td>
<td></td>
<td></td>
<td>Flammable</td>
<td>Class B</td>
</tr>
<tr>
<td></td>
<td>decomposing</td>
<td></td>
<td></td>
<td>Combustible</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Peroxide former</td>
<td></td>
</tr>
<tr>
<td>Section 1.2</td>
<td>Section 1.3</td>
<td>Section 1.4</td>
<td>Section 1.5</td>
<td>Section 1.6</td>
<td>Sections 1.7, 1.8</td>
</tr>
</tbody>
</table>

NOTES: Only the shaded categories are treated in detail in these guidelines. Section numbers indicate text sections where categories are discussed. Many reactive materials such as 1,3-butadiene fall into two or more categories. Subcategories within the categories of Decomposing, Rearranging, Oxygen-reactive, and Water-reactive are listed in approximate order of decreasing reactivity.

Material can be initiated by a sudden input of mechanical energy. This "shock" can be generated by a number of different mechanisms, such as by the impact of a dropped weight or by hydraulic shock. The decomposition reaction for shock-sensitive materials generally has a relatively small activation energy (discussed in Section 1.2.2), such that the mechanical energy input is sufficient to initiate the reaction, and the reaction is exothermic enough to be readily self-sustaining once initiated.

Thermally decomposing materials require a minimum thermal input before a significant decomposition reaction occurs; however, once initiated, the material may decompose at an accelerating rate until it proceeds at an uncontrollably high rate of reaction ("runaway" decomposition reaction).

Peroxides are a subset of decomposing materials that deserve special mention because of their industrial importance. Peroxides are chemical compounds that contain the peroxy (–O–O–) group. Peroxides can be considered as derivatives of hydrogen peroxide (HOOH), with organic and/or inorganic substituents replacing one or both hydrogens. Some peroxide formulations are shock-sensitive, but most are thermally decomposing. Many organic peroxides have particular stability problems that make them among the most hazardous of industrial chemicals.
Rearranging materials may undergo reactions in which their chemical bonds or chemical structure is simply rearranged. Isomerizing and disproportionating chemicals are part of this group.

**Reactive with Other Materials**

Substances may be stable by themselves, but will readily react with one or more common materials such as atmospheric oxygen, water, or metals. While quantitative chemical reactions such as oxidation-reduction and acid-base reactions, as well as biological reactivity (toxicity), are also in this category, they will not be treated in detail in this book. Likewise, materials that are only flammable or combustible are not given detailed treatment. They are not generally considered "reactive" chemicals, and the storage and handling of flammable and combustible materials are covered extensively in publications by such organizations as the National Fire Protection Association and the American Petroleum Institute.

Oxygen-reactive materials may be further broken down into pyrophoric, low-temperature autoignition, flammable, combustible, and peroxide-forming substances.

Pyrophoric materials are highly reactive with atmospheric oxygen and/or humidity. The energy released by the oxidation and/or hydrolysis reaction is great enough to cause ignition of the material after only a brief delay.

Materials exhibiting low-temperature autoignition require an above-ambient temperature but well below the normal autoignition temperature (AIT) range for self-sustained combustion in air to be initiated. A notable example is carbon disulfide, which has an AIT around 212°F (100°C).

Flammable and combustible materials will burn in air at normal or elevated temperatures but require an ignition source to start the oxidation reaction. "Combustible" is the more general of the two terms, and can refer to any solid, liquid, or gaseous substance that will burn in air. When applied to liquids, it generally refers to those liquids having a closed-cup flash point of 100°F (37.8°C) or greater. Flammable liquids are those having a closed-cup flash point below 100°F (i.e., that can be easily ignited at normal ambient temperatures). NFPA 321 (1991) gives more specific information on the classification of combustible and flammable liquids.

A peroxide former is a material that slowly reacts with air without an ignition source ("autoxidation") to form a peroxidic compound. Peroxide formers pose longer-term hazards; nevertheless, these hazards are significant in that the reaction products can include highly unstable organic peroxides. A few inorganic compounds, such as potassium and the higher alkali metals and sodium amide, can autoxidize and form peroxides or similarly hazardous reaction products.

Water-reactive materials are another category of reactive materials that will react with water, more or less violently. In addition to the problems surrounding the exclusion of all water in storage and handling operations, water-reactive materials also pose obvious fire-fighting difficulties.
1.1. Framework for Understanding Reactivity Hazards

1.1.2. Key Parameters That Drive Reactions

The reactions associated with the types of reactive materials outlined above have several governing principles in common. Thermodynamic, kinetic, and physical parameters are important in determining the potential for, and nature of, uncontrolled reactions. Table 1.2 summarizes these parameters.

Smith (1982) provides a good summary of both the objective and the difficulties of obtaining the proper thermodynamic and kinetic data:

The primary objective of thermokinetic studies is to determine a temperature ceiling below which one can safely work. In principle, it is not possible to state such a temperature because the reaction-rate curve does not simply decrease to zero as temperature decreases. In fact, there is no [fundamental] physical quantity such as the decomposition or onset temperature, except for decompositions that start at melting points.

The heat generation rates of specific samples depend on temperature, degree of conversion, and often, previous thermal history. The onset of a particular heat release rate will be detected at widely different temperatures, depending on the sensitivity of the instrument used.

To be able to obtain and interpret the necessary thermokinetic data properly, a basic understanding of reactivity parameters is necessary. Stepwise assessment of reactivity hazards by theoretical calculations and physical testing is detailed in Chapters 3 and 4.

### TABLE 1.2
Parameters of Exothermic and Runaway Reactions

<table>
<thead>
<tr>
<th>THERMODYNAMIC PARAMETERS</th>
<th>KINETIC PARAMETERS</th>
<th>PHYSICAL PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction energy</td>
<td>Reaction rate</td>
<td>Heat capacity</td>
</tr>
<tr>
<td>Adiabatic temperature increase</td>
<td>Rate of heat production</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>Specific quantity of gas generated</td>
<td>Rate of pressure increase in a closed vessel</td>
<td>Surface-to-volume ratio</td>
</tr>
<tr>
<td>Maximum pressure in a closed vessel</td>
<td>Adiabatic time to maximum rate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Apparent activation energy</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Initial temperature of detectable exothermic reaction</td>
<td></td>
</tr>
</tbody>
</table>

*After Smith, 1982.*
One of the key measures of the magnitude of a reactive chemical hazard is the overall energy that could be released in the event that a reaction does take place. This potential energy release is known by various terms, depending on the type of reactive system. For self-reactive chemicals, it is the heat of polymerization, heat of decomposition, or heat of rearrangement. For systems with more than one reactant, the potential energy release is the heat of reaction. (For combustion reactions, the heat of reaction is further specified as the heat of combustion.)

The potential energy release is calculated as the difference between the total heat of formation of the product(s) and the total heat of formation of the reactant(s). Heats of formation for many individual chemicals can be obtained from standard chemical engineering and thermodynamics references (e.g., Perry and Green, 1984, 3-147ff). Most reactive chemical systems of concern for safe storage and handling considerations have a greater total chemical energy “content” in the initial reactant(s) than in the products; consequently, energy is released when the reaction occurs, the reaction is termed exothermic, and the reaction energy such as the heat of decomposition or the heat of combustion has a negative value. (The international convention of positive values for energy absorption and negative values for energy release is used here.)

The liberated thermal energy can cause pressure generation by vaporization and/or gas generation, ignition of nearby materials, acceleration of chemical reactions, burns to nearby personnel, etc., and thus is the major concern in safely storing and handling reactive chemicals. This reaction energy parameter can be used, for example, to calculate the adiabatic temperature rise for a reaction, which can be combined with the specific volume of the gas generated by the reaction to calculate a maximum internal pressure that can be developed inside a storage tank or other containment.

A highly exothermic reaction usually indicates a very energetic and reactive material or combination of materials. For example, as a rule of thumb, an individual compound is apt to be “explosive” if its heat of decomposition is greater than about 100 cal/g (420 kJ/kg). However, the spontaneity or irreversibility of a reaction is determined by both the reaction energy (enthalpy) and the tendency of a system to go from an ordered state to a more disordered state (increased entropy). A measure that combines enthalpy and entropy is the Gibbs free energy, calculated as follows for a compound:

$$\Delta G_f = \Delta H_f - T \Delta S_f$$

where $\Delta G_f$ is the Gibbs free energy of formation of the compound in J/mol, $\Delta H_f$ is the heat of formation of the compound in J/mol, $T$ is the absolute temperature in Kelvin, and $\Delta S_f$ is the entropy of formation of the compound in J/mol·K. The more negative the Gibbs free energy of reaction, the greater the tendency of the material(s) to react spontaneously and irreversibly at the conditions of interest (such as standard state). Stull (1977, 10–13) gives a basic discussion of entropy
and Gibbs free energy. The heat of reaction is likely used more than the Gibbs free energy in thermodynamic evaluations because it is a measure of the total energy available if the reaction occurs.

One other commonly used thermodynamic term used in identifying reactive materials needs to be noted. Self-reactive materials that have a significantly positive heat of formation are often called endothermic compounds, since these substances require energy input for their formation from constituent elements. For example, acetylene gas has a heat of formation \( \Delta H_f \) of +54.2 kcal/g-mol. This 54.2 kcal/g-mol would be released to the environment as thermal energy upon decomposition of acetylene to its elements. Consequently, endothermic compounds tend to be relatively unstable, unless the entropy change for the decomposition reaction is significantly positive. This terminology can lead to confusion, since the decomposition of an endothermic compound is an exothermic or heat-releasing reaction.

**Kinetic Parameters**

The basic kinetic variable that must be considered in reactive chemical systems is the reaction rate. The reaction energy (e.g., heat of decomposition) and the reaction rate together determine the rate of heat release that must be dealt with in the control of reactive chemical systems. The reaction rate, in turn, is a function of both temperature and reactant concentrations:

\[
\text{Rate} = k_T \cdot \text{[concentration-dependent term]}
\]

where \( k_T \) is the temperature-dependent "rate constant." In most chemical reactions, the temperature dependence of the reaction rate is of the form shown in Figure 1.1. This particular temperature dependence is commonly characterized using the empirical Arrhenius relationship:

\[
k_T = A e^{-E_a/RT}
\]

where \( A \) is the Arrhenius frequency factor (usually assumed to be independent of temperature), \( E_a \) is the activation energy of the reaction, \( R \) is the gas constant, and \( T \) is the temperature. More detailed treatment of reaction rate parameters can be found in texts such as Levenspiel (1972) and Carberry (1976).

The activation energy can be considered as the energy input or "barrier" required by a reactive system to initiate a particular chemical reaction, as illustrated in the energy diagram of Figure 1.2. This figure also shows the interrelationship between the kinetic parameter of activation energy and the thermodynamic factor of reaction energy (heat of reaction). The most hazardous reactive systems have low activation energies (and therefore easily initiated) and highly negative heats of reaction (and therefore capable of releasing large amounts of energy). Reactive chemical types are qualitatively tabulated as to their expected activation energy and reaction energy in Table 1.3 for self-reactive chemicals and Table 1.4 for systems involving more than one reactant.
1. Chemical Reactivity Hazards

**FIGURE 1.1. Basic Temperature Dependence of Reaction Rate**

**FIGURE 1.2. Activation Energy and Heat of Reaction.**