

1 Introduction

1.1 Scope

This guidelines book provides practical aid for evaluating chemical reactivity and developing information that can be used to design and operate safer chemical processes. Understanding potential hazards from chemical reactions, such as runaways, fires, explosions from vapor or gas pressure build-up, and toxic releases, is essential for planning, operating, and maintaining safer chemical processes.

Loss of control of chemical reactions can lead to undesirable runaway reactions. The abnormal excursions in temperature and pressure caused by such runaway reactions have historically resulted in loss of containment and/or catastrophic vessel failure, business interruption, loss of life, environmental damage, damage to corporate reputation, and significant financial impacts and risks. To properly manage the hazards and risks related to chemical reactivity, they must be identified at the outset.

This book is intended for those involved in chemical research, process development, pilot plant scale-up, process design, and commercial plant operations. When considering alternative chemical process routes, it is important to understand the potential hazards from the main intended reactions and any unwanted side reactions. Chemical reactivity hazards should be considered when selecting and developing the final chemical process route(s).

Safe operating conditions and limits must be clearly defined when conceiving a pilot or commercial facility. These limits are typically established based on reliable chemical Process Safety Information (PSI) and may involve testing, measurements, result interpretation, and scale-up. Reliable chemical PSI is also necessary to develop adequate layers of protection to manage the reactions during credible upsets.

Since the publication of the original reactivity book in 1995, there have been significant advances in calorimetry, kinetic analysis, and computational methods, necessitating this second edition, which includes updated and significantly expanded content in these areas. Special emphasis is placed on combining fundamental theory, modern testing techniques, and best practices

in managing reactive materials. Specifically excluded from the guidelines are the following topics, which are covered and well-documented in other Center for Chemical Process Safety (CCPS) publications and non-CCPS material:

- Combustible dust
- Flammable vapor clouds
- Vapor phase fires and explosions
- Transportation issues

1.2 Overview

Chemical reactivity hazards are defined by Kohlbrand (1987):

"Hazardous chemical reactivity is any chemical reaction with the potential to exhibit rates of increase in temperature and/or pressure too high to be absorbed by the environment surrounding the system. Included are both reactive materials (those which enter into a chemical reaction with other stable or unstable materials) and unstable materials (those which in a pure state or as normally produced decompose or undergo vigorous changes)."

Exothermic reactions release thermal energy when reactants are converted into products. They can increase temperature, which in turn leads to higher reaction rates, and can trigger a thermal runaway if the energy is not controlled. Under heat-accumulating conditions, exothermic reactions tend to accelerate the release of energy, causing high temperatures and significant pressure changes that could result in catastrophic events. Conversely, endothermic reactions absorb thermal energy when the reactants are converted into products. Some endothermic reactions may also lead to substantial pressure generation, such as a failed-open heating utility fluid driving a decomposition reaction that generates light gas. Accidents with exothermic or endothermic reactions can result in loss of containment, equipment failure, explosions, blast impact, thermal radiation, severe burns, and toxic clouds. Ultimately, they may cause illness, injury, fatalities, and environmental and equipment damage.

Figure 1-1 shows the aftermath of an incident with a phenol-formaldehyde reaction that occurred at the Georgia-Pacific plant in Columbus, Ohio, on

September 10, 1997, illustrating the destructive impact of uncontrolled chemical reactions on an industrial scale.

This incident occurred in a 32 m³ (8,500-gallon) chemical reactor (EPA Report 550-F99-004, 1999). The resin produced was an adhesive for making plywood, particleboard, roof shingles, and kitchen countertops. The process reaction is highly exothermic and requires the chemicals (formaldehyde solution, phenol, sulfuric acid, and salicylic acid) to be added in a specific sequence.

The formaldehyde solution should have been slowly added last to control the heat generation rate, but the operator mistakenly added all the chemicals at once. Steam was applied to the full batch to heat the contents. The intense heat generated by the chemical reaction evaporated a substantial amount of the liquid, building pressure in the reactor. The very high pressure that developed likely caused the mechanical failure of the reactor, resulting in the propagation of a forceful blast wave and rapid ejection of shrapnel.

The event caused the instant fatality of an operator, according to investigators from the Occupational Safety and Health Administration (OSHA), the Columbus Fire Department's Arson Division, the Ohio Environmental Protection Agency, and Georgia-Pacific. Four other workers were injured.



Figure 1-1. Incident at the Georgia Pacific Plant. Image Credit to the Ohio EPA

It is necessary to organize and classify chemical reactions. In the most basic sense, reactions among materials proceed in two ways:

1. Stable materials under normal conditions can become hazardous when combined. Typically, this situation applies to the intended reaction(s) for forming the desired products, such as in the catalyzed, exothermic copolymerization of phenol and formaldehyde. Normally, the process is designed with adequate controls to operate these reactions safely. However, a process upset, such as a loss of cooling or failure of a vent valve, could lead to loss of control of the reaction and elevated pressure.

Unintentional mixtures are also within this category. For example, nitric acid and organic materials such as acetic acid are stable at ambient temperature but can react vigorously if mixed and not kept cold. In high concentrations, the material may detonate.

2. Stable materials at the intended conditions can become unstable under upset conditions. This material class applies to individual components or mixtures, such as a reactive monomer that is stable at 25°C (77°F) but undergoes a vigorous polymerization reaction if subjected to unintended increased temperature (e.g., due to the failure of temperature controls) or loss of the stabilizer or inhibitor. Another example is a hydrogen peroxide solution that is stable when stored under proper conditions but vigorously decomposes when contaminated by iron.

Within these categories, reactions can be classified as either synthetic or secondary chemistry. Synthesis chemistry is the intentional chemical route chosen to form the desired product(s). Often, this chemistry is studied in depth during process development and is reasonably well characterized, with the quantified requirements for heat removal or venting under intended conditions designed into the equipment. However, secondary chemistry occurs unintentionally or without knowledge. It is often realized after a process upset, such as contamination, incorrect raw material charges, equipment malfunction, inadequate equipment or material selection, inadequate temperature or pressure control, software failure, or other human errors. The nature of secondary chemistry is often poorly understood.

Both synthesis and secondary reactions can be hazardous and must be understood. An example of an unintentional (secondary) reaction is a contaminant-catalyzed runaway reaction. Hazards can also result from intentional (synthesis) reactions when control is lost. An intentional reaction example with loss of control is insufficient cooling capacity when scaling up an exothermic process due to disregarding the relatively smaller heat-transfer surface area per unit volume on a large scale compared to a laboratory experiment.

Unfortunately, the chemical industry has experienced many incidents that were ultimately caused by the loss of control of chemical reactions, and these events continue to occur today.

Some recent examples include:

- Explosion and fire due to a leak of 70% hydrogen peroxide into the wrong tank, where contaminants caused it to decompose and run away at a Sinochem petrochemical plant in eastern China's Shandong province in January 2023 (Shu, 2023).
- An LG Polymers styrene tank lost the inhibitor and experienced a runaway reaction in Visakhapatnam, India, in June 2020 (Nichenametla, 2020).
- A worker was seriously injured after exposure to chlorine gas following a chemical reaction between sodium hypochlorite and sulfuric acid at a water-treatment plant in Queensland, Australia, in March 2022 (Queensland Government Website, 2022).
- Seven workers were fatally injured, and 31 were injured at Currenta, located in the Chempark industrial area of Leverkusen, Germany, where a chemical reaction inside a waste storage tank containing chlorinated solvents initiated a fire that sent a plume of black smoke into the air in July 2021 (EuroNews website, 2021).
- Ammonium nitrate explosions with multiple fatalities, including facilities in West, Texas, in 2013 and in the Port of Beirut in 2020 (CSB, 2013, and El Sayed, 2020).

Preventing these types of incidents requires the safe design of reactive chemical processes. Some incidents have been severe, resulting in the

complete closure of facilities and/or leading to manufacturers losing the right to operate. With the full support of a manufacturer's organization (from development through design, manufacturing, maintenance, and management) in implementing the best-practice methods outlined in this book, companies can understand the nature of their reactive processes, design safe and robust plants, and operate safely under both desired and credible upset conditions.

The safe design of chemical processes starts with the quantitative understanding of how heat can be released and pressure generated, given the chemicals involved. When these characteristics are well-defined, the facility can be designed to remove the heat produced, contain the pressure and temperature, and appropriately cool and/or vent material during normal and upset reaction conditions. The visualization of the potential thermochemistry (energy and/or pressure), the rates of energy and/or gas production leading to pressure generation, and the facility design are illustrated in Figure 1-2.

The three main factors that interact with each other and determine the design of safe chemical processes are:

- The potential thermochemistry of the chemicals involved.
- The reaction rates of primary and secondary reactions.
- The process design/configuration and its capability to manage released energy, fluids, and solids.

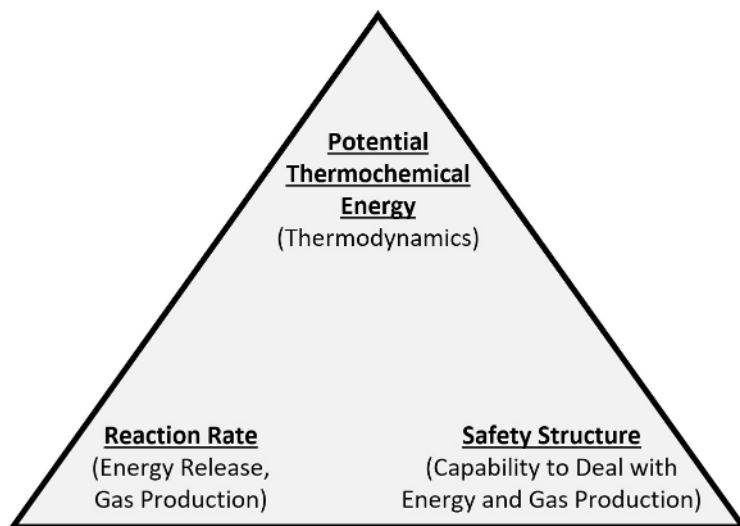


Figure 1-2. Key Parameters That Determine the Design of Safe Chemical Plants

- **Potential Thermochemical Energy (Thermodynamics).** Designing a safe process begins with understanding the inherent changes in heat and pressure energy associated with chemical reactions, such as exothermic heat release or endothermic heat absorption, and the maximum pressure that can be generated in a closed system. It is important to realize that endothermic reactions can create high-energy, high-risk unstable materials. This information is obtained from reliable literature, thermodynamic calculations, and laboratory experimentation. The potential pressure that may develop in the process is also an important design consideration.
- **Reaction Rate (Energy Release and Gas Production).** Once the thermodynamically possible heat and pressure are understood, the generation rate is characterized for normal process operations and credible upset conditions, typically with a combination of reaction rate expressions and thermodynamic models. The reaction rate depends on the mixture's temperature, pressure, and concentration. Reaction rates during normal and abnormal operations, including the worst-credible case, must be determined to design safe processes that manage toxic by-products and overpressure. The determination of the reaction rates almost always requires measurements.
- **Safety Structure.** Plant design includes the process manufacturing equipment and support processes, including utilities and other manufacturing infrastructure. It comprises all procedures and safeguards (passive, active, and administrative) installed and implemented to prevent or mitigate unplanned events as defined in Section 2.6 below. The energy released by the chemical reaction must be adequately controlled to prevent undesired temperature excursions. Any gas or vapor generation must be managed to avoid excessive pressure buildup in the equipment. The effects and requirements of scale-up (the relationship between bench scale, selection of construction materials, and plant equipment) must be considered using the thermodynamic and kinetic information from 1 and 2 above.

These three key parameters are highly interrelated. A significant amount of energy can be removed during normal operation if the energy release rate

is relatively low and is controlled by sufficient cooling. However, careful evaluation of transport properties, thermochemistry, and reaction rates is necessary to ensure adequate cooling capacity. A sound approach to safer process design and operation is based on science, technology, and data. The evaluation should consider principles of experimentation, thermodynamics, chemical kinetics, and reaction engineering.

Best-practice techniques use proven rules for scale-up across bench, pilot, and commercial operations to account for factors such as thermal inertia, area-to-volume ratio, and mixing. Serious industrial incidents involving reactive systems have occurred when scale-up was not properly incorporated, as discussed throughout Section 7 for new toll production, the first commercial batch, and scale-up.

The relative magnitudes of potential thermochemistry and pressure generation collectively influence the design concept. For example, a large amount of energy can be removed during normal operation if the energy generation rate is relatively low. Temperature control for such materials is often readily achieved with typical cooling systems, such as cooling towers. Careful evaluation of the thermochemistry and reaction rates is necessary to ensure sufficient cooling capacity is available. However, under upset conditions, the heat generation rate may become overwhelming, and removing that heat might exceed the capacity of typical cooling towers. As such, an alternative means of controlling the process during such an upset would be required. Thorough process design methodologies and best-practice hazard assessments typically account for this situation and safely accommodate the reactive material's behavior under normal and upset conditions.

1.3 Effective Reactive Chemical Management

Effectively managing reactive chemistry requires personnel across multiple functions within an organization to actively participate in the overall management program and to have varying levels of understanding of the facility's materials and systems. In general, these functions fall into three broad categories: 1) quantitative characterization of the nature of the reactive chemistry – typically performed by technical subject matter experts; 2) design of the facility by qualified engineers; and 3) safe operation of the facility –

typically involving a wide range of personnel, including management, process engineering, operations, maintenance, and contractors. Additional details and specifics will be discussed in Chapters 2-7.

1.3.1 Characterization of the Reactive Chemistry

The reactive nature of chemicals is often characterized by Research and Development (R&D) or an R&D-like environment using in-house qualified personnel, partnering with a qualified third party, or sometimes collaborating with industry consortia or academia.

Typically, the subject matter experts in this work are highly skilled engineers and scientists with expertise in fundamental subjects such as thermodynamics, reaction kinetics, heat transfer, and fluid flow, and they often have excellent laboratory techniques. Drawing on experience and theoretical knowledge, reliable literature is reviewed, rigorous experiments are performed, and a detailed engineering analysis of the results is performed to systematically establish a quantitative characterization of the materials' behavior under normal and upset conditions. The results are then organized and made available for development, hazard reviews, process design, and plant operations.

1.3.2 Design of the Facility

Once a safe and viable process has been conceived, successfully developed, and selected to move forward, the information described above becomes part of the overall basic data package used during the facility's design. The design decisions for facility systems, such as utilities, heat transfer, pressure rating, venting, storage, and siting, rely on various thermodynamic and kinetic reaction information. This knowledge is combined with other typical developmental data (e.g., synthesis, purification, capacity, materials of construction, health, environmental, and regulatory) to ensure the final facility operates safely and robustly.

1.3.3 Safe Operation of the Facility

Once the facility is constructed, various functions support its operation throughout its lifecycle, ensuring safe and efficient performance. A well-defined organizational structure, robust, comprehensive policies, and established procedures for introducing or modifying chemistries or processes

are required for safe operations. These management systems include a thorough understanding of the nature of the chemicals and the systems designed and installed to control them. Further, as part of Management of Change, management systems must involve reactive subject matter experts, where relevant, and seek new or expanded data and analysis to evaluate and implement facility or process additions or modifications.

Many other on-site functions must also have varying levels of understanding of reactive chemicals in the facility. Process engineering typically serves as the technology owner, tracks process performance, and drives continuous improvement. Operations must adhere to established safe operating limits, ensure the facility operates effectively and safely, respond to process upsets, and maintain operating discipline and asset integrity. Both functions usually participate in regular hazard assessments as part of Process Safety Management. During these assessments, chemical reactivity information is routinely reviewed in the context of normal operations and potential upset conditions.

1.4 Summary

Chapter 1 introduced basic concepts of chemical reactivity hazards. Chapter 2 applies these concepts within the framework of Essential Practices, providing the basis for understanding chemical reactivity hazards when developing new products and processes or introducing established raw materials, intermediates, and products into new equipment (Johnson et al., 2003).

