Chemical Reactivity

Chemical Reactivity

Chemical reactivity hazard is “a situation with the potential for an uncontrolled chemical reaction that can result directly or indirectly in serious harm to people, property or the environment.”

- Reactive chemical hazards have resulted in many accidents
- Preventing reactive chemical accidents requires the following steps

1. **Background understanding**: Case histories provide an understanding of the consequences, frequency, and breadth of reactive chemical accidents.

   They analyzed 167 serious accidents in the U.S.

2. **Commitment**, awareness, and identification of reactive chemical hazards

Chemical Reactivity

3. **Characterization** of reactive chemical hazards, Calorimeter is used to acquire reaction data, and a fundamental model is used to estimate important parameters to characterize the reaction.

4. Control of reactive chemical hazards: This includes application of inherent, passive, active, and procedural design principles

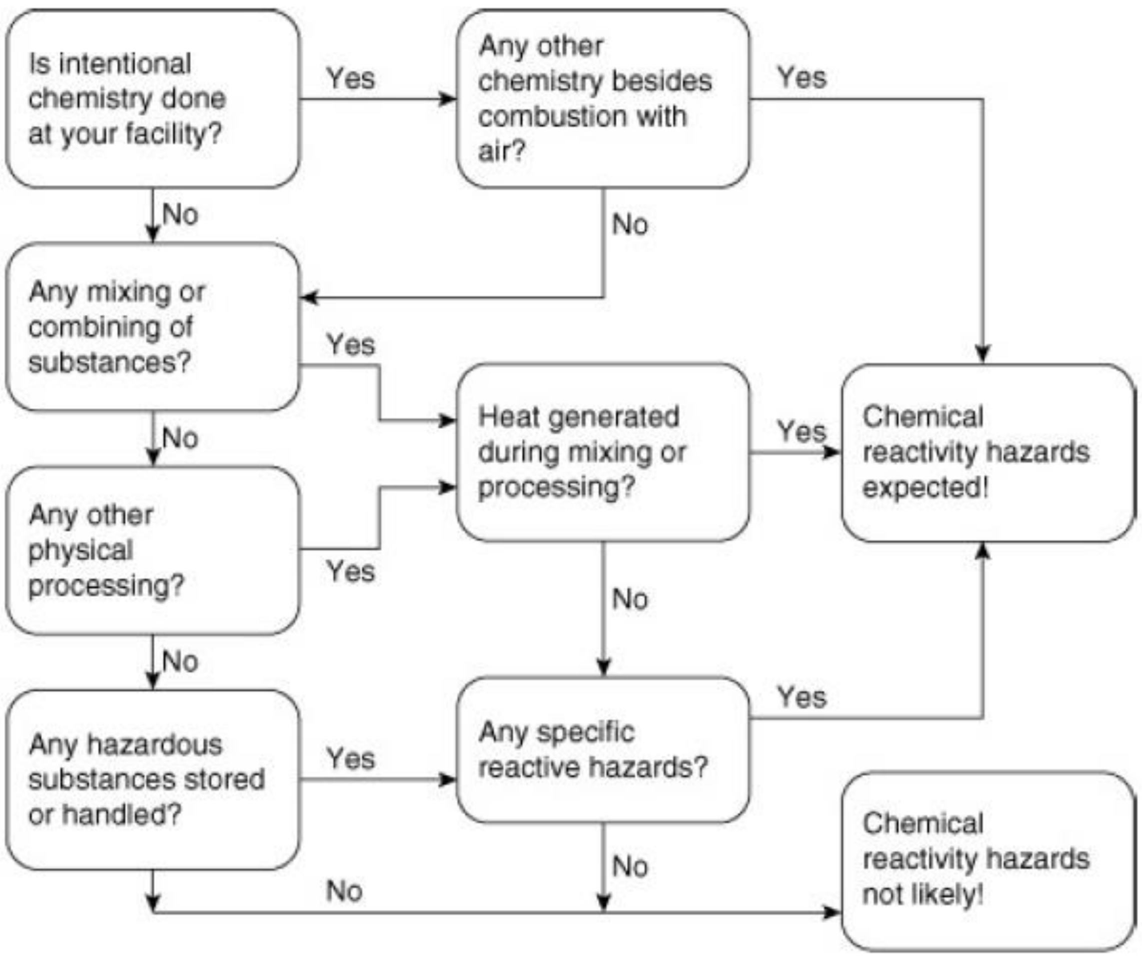
- The reaction may occur with a single chemical, called a **self reacting chemical** (monomer),
- or with another chemical, called **interaction** or **incompatibility**

Commitment, Awareness, and Identification

- Management, to properly identify and manage these hazards throughout the entire life cycle of a process
- Flow chart contains seven questions to help identify reactive chemical hazards

1. Is intentional chemistry performed at your facility?
2. *Is there any mixing or combining of different substances?*
3. *Does any other physical processing of substances occur in your facility?*
4. *Are there any hazardous substances stored or handled at your facility?*
5. *Is combustion with air the only chemistry intended at your facility?*
6. *Is any heat generated during the mixing, phase separation, or physical processing of substances?*
7. *Are there any specific reaction hazards that occur?*

Screening flowchart for reactive chemical hazards



Specific Reactive Chemical Hazard

Pyrophoric and spontaneously combustible: Substances that will readily react with the oxygen in the atmosphere, igniting and burning even without an ignition source. Ignition may be immediate or delayed.

Identification: MSDS or labeling identifies this as "spontaneously combustible."

NFPA Flammability rating of 4.

DOT/UN Hazard Class 4.2 (spontaneously combustible solids).

Examples: Aluminum alkyl, Grignard reagent, finely divided metals, iron sulfide, triethyl aluminum.

See Table F-1 in Appendix F.

Peroxide-forming: Reacts with oxygen in the atmosphere to form unstable peroxides.

Identification: Not easily identified as a peroxide former from MSDS or other resources.

Examples: 1,3-butadiene, 1,1-dichloro-ethylene, isopropyl and other ethers, alkali metals.

See Table F-2.

Water-reactive chemicals: Chemically reacts with water, particularly at normal ambient conditions.

Identification: Usually identified as water-reactive on MSDS.

May be identified as DOT/UN Hazard Class 4.3 (dangerous when wet).

May be labeled as "dangerous when wet."

NFPA Special Rating with symbol.

Examples: Sodium, titanium tetrachloride, boron trifluoride, acetic anhydride.

See Tables F-3 and F-4.

Oxidizers: Readily yields oxygen or other oxidizing gas, or readily reacts to promote or initiate combustion of combustible materials.

Chemical Compatibility Matrix and Hazards

No.	Chemical name		
1	Hydrochloric acid solution	1	
2	Acetic anhydride	C, D7, E, G	2
3	Methanol	C	B5, C
4	Caustic soda, beads	B4, C, D3, D5, D6, D7, G	A6, C, D4

A6 Reaction proceeds with explosive violence and/or forms explosive products.
B1 May become highly flammable or may initiate a fire, especially if other combustible materials are present.
B4 Spontaneous ignition of reactants or products due to reaction heat.
B5 Combination liberates gaseous products, at least one of which is flammable. May cause pressurization.
C Exothermic reaction. May generate heat and/or cause pressurization.

Individual Chemical Hazards and Functional Groups

Chemical	Reactive hazard	Functional group
Acetic anhydride	Water-reactive	Anhydride
Caustic soda, beads	Water-reactive	Base
Hydrochloric acid solution	Mildly air-reactive	Acid, inorganic, non-oxidizing
Methanol	Highly flammable	Alcohol

Characterization of Reactive Chemical Hazards Using Calorimeters

- It is essential that the behavior of these reactions be well characterized prior to using these chemicals in large commercial reactors.
- Calorimeter analysis is important to understand both the desired reactions and also undesired reactions.
- Design control systems to remove heat from the reaction to prevent a runaway;
- Design safety systems, such as a reactor relief, to protect the reactor from the effects of high pressure

Important Questions for the Characterization of Reactive Chemicals

1. At what temperature does the reaction rate become large enough for adequate energy to be produced for heating of the reaction mixture to be detected?
2. What is the maximum temperature increase due to adiabatic self-heating of the reactants?
3. What is the maximum self-heat rate? At what time and temperature does this occur?
4. What is the maximum pressure during the reaction? Is this pressure due to the vapor pressure of the liquid, or due to the generation of gaseous reaction products?
5. What is the maximum pressure rate? At what time and temperature does this occur?

Introduction to Reactive Hazards Calorimetry

- Calorimetry is an experimental method that allows one to calculate the heat change in a chemical process. calorimeter is just a reaction vessel.

- Calorimetry is a method of measuring the heat transfer within a chemical reaction or other physical processes, such as a change between different states of matter. The term "calorimetry" comes from the Latin calor ("heat") and Greek metron ("measure"), so it means **"measuring heat."**. **The**
- **different calorimeters types are given below:**
- Adiabatic Calorimeters
- Reaction Calorimeters
- Bomb Calorimeters (Constant Volume Calorimeters)
- Constant Pressure Calorimeters
- Differential Scanning Calorimeters

Introduction to Reactive Hazards Calorimetry

The calorimeter technology presented here was developed mostly in the 1970s.

summarizes the commonly used calorimeters that are available for reactive chemicals testing.

Calorimeter	Supplier	Type	Typical test vessel volume ml	Nominal phi-factor ϕ	Adiabatic reaction tracking limits k/min	Operation time	Comments
DSC Differential Scanning Calorimeter	Various	Open	<1	Not applicable	Not applicable	1 hour	Used mostly for initial screening. Closed sample cells can be used.
ARRST Advanced Reactive System Screening Tool	Fauske and Associates *www.fauske.com*	Open	10	1.05	0.1–200	Hours	Used mostly for initial screening due to short operation time.

Controlling Reactive Hazards

- Partial list of methods—many more methods are available. The methods are classified as inherent, passive, active or procedural.

Inherent

- Use a reaction pathway that uses less hazardous chemicals.
- Use a reaction pathway that is less energetic, slower, or easier to control.
- Use smaller inventories of reactive chemicals both in the process and in storage. Reduce pipe length and size to reduce inventory.

Passive

- Ensure that incompatible chemicals are always separated.
- Provide adequate separation distances between storage vessels, reactors and other process equipment using reactive chemicals.
- Provide passive engineering controls, such as dikes and containment, to control reactive chemical spills.

Active

- Screen all chemicals for reactive chemical hazards.
- Provide or have access to experimental calorimeter characterization of reactive chemicals.
- Provide properly designed control systems to control reactive chemicals in the process.
- Provide properly designed heat transfer equipment to remove energy released by reactive chemistry.
- Identify and characterize all possible reactions, including reactions or decompositions at higher temperatures, reactions induced by fire exposure, and reactions due to contamination.
- Use quench, stop, or dump systems to quickly stop out-of-control reactive chemistry.

Procedural

- Provide reactive chemical reviews of existing processes and new processes.
- Document chemical reactivity risks and management decisions.
- Communicate and train on chemical reactivity hazards.
- Manage process changes that may involve reactive chemicals.
- Review and audit your reactive chemicals program to ensure that it is operating properly.
- Investigate chemical reactivity incidents.

Thanks