Chemical Reactivity Evaluation Tool Help Guide

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READ ME FIRST

The authors do not expect the average user to read through the entire manual in order to become proficient in the use of the chemical reactivity evaluation Tool (RMT) however the novice would be well served to study the following sections prior to attempting to use the program or follow the step by stem instructions or worked examples:

- Entire Read Me First section
- Section 1 Introduction
- Section 2 Program Flow
- Section 4 Strategy
- Appendix D: Developing a Reactivity Management System.

The Table of Contents on the previous page has been set up to aid the user in quickly locating information on a particular topic. Main topics with an * next to the name denote that this section contains a more detailed table of contents to further aid the user in locating specific help within that section.

EVERYONE:
It is strongly suggested you use the QUICK START section to properly install the program and its independent supporting programs. More detailed step by step installation instructions are located in Section 3.1 should the user require them. The program has some “quarks” which are explained in the FAQ section. Reviewing these two sections will save the user much time and frustration.

It is critical that all users understand the objectives and limitations of the program and how these might relate to your specific site objectives and goals. This information is presented in the introduction section of this guide (pages 11 through 14).

The user, both experienced and inexperienced, will also benefit from reviewing the programs block flow diagram located in section 2. Sections 2.1 gives a one page overview of the entire program flow with links to four one page sub-routine block flow charts. Section 2.6 presents the entire program block flow with one to 2 sentence explanations of each block.

After that, even the user knowledgeable in process safety evaluations, will benefit from reading the STRATEGY section. Each strategy sub-section is a detailed how-to guide for the key program inputs.

Look for the following icons that call out helpful suggestions or common mistakes
PROCESS SAFETY NOVICES:

For those new to process safety evaluation, the *STEP BY STEP INSTRUCTIONS* in section 3 are laid out such that the user is taken through the program screen by screen with detailed information on the data required for each screen and how to obtain it.

Finally the *WORKED EXAMPLES* sections present detailed examples with screen by screen instructions from data entry through evaluation and report generation. The novice would be well advised to make full use of this section to practice process hazard evaluation.
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Legal Disclaimer and Limits of Liability

By downloading and using this software you agree to be bound by the following:

This software tool was developed to assist users by providing guidance for predicting chemical reactivity of chemical mixtures. The outputs and guidance supplied by this program and the associated Help Guide are not intended to fulfill the legal definition of a Process Safety Management System.

User entered chemicals and data are evaluated based entirely on the user inputs. Users must use their independent judgment in evaluating the program outputs and the information and references presented in either the guide book or program text.

All results, both positive and negative, should be confirmed by an expert for validity prior to incorporation into the user’s Process Safety Management System. For references on designing a Process Safety Management System see the help guide.

It is sincerely hoped that this tool will lead to an even more impressive safety record for the entire industry; however, the American Institute of Chemical Engineers, its consultants, CCPS Subcommittee members, their employers, and their employers’ officers and directors do not warrant or represent, expressed or by implication, including with respect to fitness, intended purpose, use or merchantability, the correctness or accuracy of the content of the information or calculation results presented by this software tool. As between (1) American Institute of Chemical Engineers, its consultants, Unwin Company, CCPS Subcommittee members, their employers, and their employers’ officers and directors and (2) the user of this software and accompanying documents (Help guide and other documents), the user accepts any legal liability or responsibility whatsoever for the consequence of its use or misuse.
Preface

Incidents involving uncontrolled chemical reactions continue to result in injuries, fatalities and economic loss and harm in industry. These incidents are often the result of not identifying or understanding the chemical reactivity hazards involved in storage, mixing or processing operations. The chemical reactivity evaluation tool (RMT) that this Help Guide accompanies can be used as a consistent approach to identifying and evaluating chemical reactivity hazards so that they may be effectively avoided or controlled.

The American Institute of Chemical Engineers (AIChE) has been closely involved with process safety and loss control issues in the chemical and allied industries for more than four decades. Through its strong ties with process designers, constructors, operators, safety professionals, and members of academia, AIChE has enhanced communications and fostered continuous improvement of the industry’s high safety standards. AIChE publications and symposia have become information resources for those devoted to process safety and environmental protection.

AIChE created the Center for Chemical Process Safety (CCPS) in 1985 after the chemical disasters in Mexico City, Mexico, and Bhopal, India. The CCPS was chartered to develop and disseminate technical information for use in the prevention of major chemical accidents. The center is supported by more than 140 chemical process industry (CPI) sponsors who provide the necessary funding and professional guidance to its technical committees. The major product of CCPS activities has been a series of guideline books to assist those implementing various elements of a process safety and risk management system. This Help Guide and software tool is part of that series.

The Reactivity Management Roundtable (RMR) was founded in 2003 by a small group of process safety professionals that meet independently of both AIChE and CCPS with the goal of reviewing the newly published Chemical Safety Board Reactive Hazard Investigation report that analyzed 167 serious chemical reactivity incidents over a twenty year period in order to recommend best practices that could reduce or eliminate reactivity incidents in the future. The group quickly swelled to over 100 members. Because most of the members were also AIChE members a strong association was forged between AIChE and the RMR which soon lead to the adoption of the RMR as an AIChE CCPS subcommittee. The first RMR meeting was held in Las Vegas, NV in October of 2003. The initial idea was to publish a traditional best practices guide book on the subject of chemical reactivity management. Later the idea evolved into a computer aided chemical reactivity incident prediction tool. The RMR officially requested CCPS project status and funding in 2009 in order to begin the task of producing a computer tool to predict chemical reactivity risks in the workplace. The Committee has been all volunteers. CCPS funding was only used for computer programming and technical writing services.

The work of the committee has always been directed toward part time process safety specialists who own or are employed by small to mid-size firms where chemicals are stored, handled or used. It was anticipated that these specialists would be employees actively engaged in primary functions other than process safety, and thus would not have the skills to assess that

1 “Improving Reactive Hazard Management” (CSB 2002)
reactivity hazard risk themselves nor the funds to employ a Process Safety Professional or Consultant to assess the risk for them. It is sincerely hoped that this product will help identify chemical reactivity risks within the workplace and direct the user, owners and managers of those at risk workplaces to resources to aid in quantifying and remediating that risk. This computer program is not designed to fulfill any legal requirement for a Chemical Reactivity Management system but it is hoped that it will form the basis for developing a strong Chemical Reactivity Management System.

As a word of warning users should be mindful of the security of the data entered into this program as it could be exploited by individuals or groups wishing to disrupt operations or otherwise cause harm to the company or community

The Help Guide is not meant to be read in its entirety but rather used as a reference when problems or further discussions are needed. The table of contents is designed to facilitate finding information as needed. By clicking on topic, you will be sent directly to the information you requested.
Quick Start

Refer to the section 3.1 for detailed step by step instructions.

Reactivity Management Tool Hardware Requirements:
1 gigahertz (GHz) or faster 32-bit (x86) or 64-bit (x64) processor
1 gigabyte (GB) RAM (32-bit) or 2 GB RAM (64-bit)
DirectX 9 graphics device with WDDM 1.0 or higher driver
50 MB Space required for Reactivity Management Tool installation.
400 MB of available hard-disk space
800 x 600 minimum screen resolution and 256 colors
Mouse or other compatible pointing device
PDF reader program

Installation
Download the latest version of the Reactivity Management tool from the AICHE web site onto your computer’s hard drive.
Run the installer and follow the on-screen prompts.
Before starting the Reactivity Management tool you must download and install two prerequisite programs as follows:

-.NET framework 4.0 is required. Please download and install from this location.

SQL 2005 Express edition is required. Please download and install from this location.
When installation is complete of the above programs, start Reactivity Management tool from your computer’s desktop or Programs menu (Programs / Reactivity Management Tool / Reactivity Management Tool).
Step through the program, answering the questions and entering all information on each screen as you come to it.

IMPORTANT
Copy files RMTHelpguide.pdf and Fast_Start.pdf to the RMT install directory (choose replace when warned that file already exists)
1 Introduction

This computer program and help guide book should be used as an aid in identifying possible chemical reactivity risks within your operations. Many times these risks are well hidden and their identification requires a thorough analysis of what might go wrong in your operations. Particular thought and care should be taken in understanding the Chemical Interaction Matrix where binary chemical reactivities are identified and the Scenario generation area where the user is asked to identify both intended operations and unintended-operations. This analysis is best done by a team including those familiar with manufacturing technology, chemistry, reactive chemical testing, and operations.

The binary chemical interaction section of the program is identical to the NOAA CAMEO CRW2. The CRW2 is based on functional group reactivities. Because a great number of chemical reactivities must be predicted by the program, many false positives can be generated - these must be identified and removed from the results to avoid wasting resources on unnecessary risk remediation. CRW2 seldom gives false negatives but user must always be aware that the possibility exists for missing a significant interaction based on heretofore unknown chemical reaction or on the unique characteristics of a molecule that might allow an unusual reactivity to occur between normally unreactive functional groups. This is one reason why a team approach is best. At least one of the 167 CSB incidents involved the inadvertent introduction, on large scale, of a contaminate not previously known to be a reaction catalyst – a lesson in the dynamic and evolving nature of chemical and scientific knowledge that cannot be captured in a static reactivity prediction tool and the need for reactive chemical testing.

The warehouse segregation section of the program is based on the work of Chastain, et al 2008. Some modifications have been made to their suggested segregations by the committee.

The Scenario identification section offers the “expert” user the opportunity to enter fault scenarios generated from a formal Process Hazard Analysis (PHA) but also contains an informal question and answer section where an experienced engineer or better yet a team as discussed above can generate many of the results that would come from a formal PHA. Extreme care should be taken in this section to closely examine all process unit operations one at a time while answering the computer generated questions. The CSB Hazard Investigation report concluded that only 25% of the reactive chemical incidents analyze occurred in reactors. Care must be taken to analyze process equipment where reaction is not intended. It is hoped that a team of hands-on experts on the process would answer each question for each unit operation reviewing flow sheets and piping and instrument diagrams and reactive chemical data and test results. Visiting the processing area to examine ideas for possible failure modes is strongly recommended. This will yield a much more satisfactory result than a lone expert at a keyboard reviewing the process from memory.

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1.1 Background

The AIChE defines a chemical reactivity hazard (also known as a reactive chemical hazard) as 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. Reactivity management is the application of management system principals to control chemical reactivity hazards. A strong reactivity management system is based on four simple principles: Inform, Implement, Communicate, Verify. The CCPS publication Essential Practices for Managing Chemical Reactivity Hazards (Johnson et al., 2003)\(^4\) contains a detailed discussion on reactivity management and how it can be implemented.

Chemical reactivity management is important because reactivity hazards have been involved in some of the most severe industry incidents in history including:

- The 1975 runaway reaction in Seveso, Italy that resulted in the contamination of several square miles of land with dioxin, a toxic chemical. This incident resulted in regulations requiring extensive safety analysis before constructing new chemical facilities in Europe.
- The 1984 methyl isocyanate release in Bhopal, India that resulted in over 2000 fatalities because of the exposure to this toxic chemical. This incident significantly damaged the financial condition and reputation of Union Carbide, the joint owner of the facility, leading to its eventual acquisition by the Dow Chemical Company.
- The 2001 massive ammonium nitrate explosion in Toulouse, France that resulted in 30 fatalities, 2500 injuries, damage to nearly a third of the city of Toulouse, and permanent closing of the facility involved in the incident.
- In 2009 a runaway reaction and explosion during the routine production of a gasoline additive at T2 Laboratories in Jacksonville FL killed 4 and hospitalized 13 others. The entire site was leveled and several nearby buildings severely damaged. The company never resumed operations. This incident highlighted the need for the inclusion of process safety and reactive chemicals in the undergraduate chemical engineering curriculum.

Numerous other recent incidents could also be cited. The U.S. Chemical Safety and Hazard Investigation Board report entitled “Improving Reactive Hazard Management” (CSB 2002)\(^1\) analyzed over 167 serious reactive chemical incidents that occurred over a twenty year period from January 1980 to June 2001. The primary objective of the chemical reactivity evaluation tool discussed in this Help Guide is to allow users, especially small to medium size companies, to identify most chemical reactivity hazards in their chemical processing and support operations so that serious reactive chemical incidents like those discussed can be prevented.


Online version available at: http://www.knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=898&VerticalID=0
1.2 Objectives

The purpose of this document is to serve as a “help guide” for the chemical reactivity evaluation tool by describing the tool and assisting users in its application. Together, the chemical reactivity evaluation tool and help guide have the following objectives:

• Allows users, especially small to medium size companies, to identify most chemical reactivity hazards associated with their chemical processing and support operations.
• Emphasize ease of use for non-experts.
• Direct users to CCPS documentation and other references of the best chemical engineering practices for the identification of reactivity hazards.
• Briefly summarize the targeted CCPS documentation in the directions for inputting data.
• Provide sufficient Help Screens and examples so that users gain an understanding of how to use the chemical reactivity evaluation tool.

1.3 Limitations

The chemical reactivity evaluation tool can only assist the user in identifying reactivity hazards. The software tool is designed to complement the user’s understanding of known reactivity hazards. There is no guarantee that all reactivity hazards will be identified. Also, the results obtained from using the software tool can be no better than the accuracy and completeness of the information entered into the program.

Warehouse segregations based are based on the DOT codes entered for each chemical. The recommended segregations must be checked against the Chemical Reactivity Binary interaction matrix as well as special hazards codes to make sure incompatible materials are properly segregated. Hidden hazards like storage of large quantities of water reactive materials in a warehouse that is fire protected by a water spray or water deluge system must also be thoughtfully considered.

Chemical reactivity is assessed by the program using a functional group approach. This can lead to errors. All predictions should be checked by either experiment or a competent chemist trained in chemical synthesis and chemical reactions.

The scenarios generated by the user are only assessed on thermal and pressure hazards. Serious risk can exist in many other forms such as toxicity or damage to the environment that are not addressed in this program. Generalized “rules of thumb” are utilized to screen out those scenarios that are unlikely to pose “serious” risks. It should be understood by the user that these “rules of thumb” may screen out as “unlikely to pose a serious risk” scenario consequences that the user or the user’s affiliated company may find unacceptable. The protocol in the computer program is targeted to identify only 80% of the 167 serious incidents listed by the CSB\(^1\). The CSB did not consider an incident “serious” unless there were fatalities or injuries and severe property damage, or a significant impact to the public outside the perimeter fence of the facility. You and or your company may have a much more conservative idea of what a “serious” incident looks like. One major international chemical company with a strong reactive chemical program often reports over 90 reactive chemical incidents per year because employees are encourage to report near misses and minor incidents so they may be investigated. Lessons learned from the
investigation of near misses and minor incidents can prevent major incidents. It should be noted that the CSB’s version of “serious incident” usually results in severe restrictions on the company’s freedom to operate within the local community often resulting in facility closure and more than occasionally the insolvency of the facility owner. (See section 1.1)

Once reactivity hazards have been identified, appropriate safeguards must be implemented to contain and control the chemical reactivity hazards. As previously discussed, management systems must also be developed and implemented to ensure procedures are in place to identify and control the hazards. See Appendix D

The software tool does not address oxidation reactions (burning) of ordinary flammable and combustible materials, including combustible dusts. However, it does identify and evaluate the hazards of oxidizers, organic peroxides, spontaneously combustible and pyrophoric materials. It does not assess the toxicity risks of a scenario or release nor does it consider environmental impact.

In addition, the software tool is not intended to be used to determine what materials of construction are appropriate to use to contain or convey reactive materials.  

1.4 Approach

The approach used in this Help Guide is to walk the user through the chemical reactivity evaluation protocol in Section 2 that describes how the program works, to provide a detailed discussion on how to use the software tool including installation and help screens, and to provide examples of the use of the chemical reactivity evaluation tool. The intent of this Help Guide is to assist the user in becoming proficient in the use of the chemical reactivity evaluation tool.

1.5 Intended Audience

The intended users of this Help Guide and the chemical reactivity evaluation tool are engineers, chemists, and management, particularly in small to moderately sized companies, who have responsibilities related to the safe handling of chemicals.

The tool can be used by experienced process safety professionals as well as less-experienced personnel who have a basic educational background in chemistry or chemical engineering.

---

2 Program Flow

2.1 Primary Flow Chart
2.2 Evaluate Pure Component Reactivity Hazards

2A From 1P

2B Is any substance identified as spontaneously combustible or pyrophoric?
   Yes → 2C Direct data to Physical Processing Report
   No → 2D Obtain guidance on spontaneously combustible or pyrophoric materials

2E Is any substance identified as an oxidizer?
   Yes → 2C Direct data to Physical Processing Report
   No → User should obtain guidance on oxidizers

2F Is any substance identified as a peroxide former?
   Yes → 2G Direct data to Physical Processing Report
   No → Users should obtain guidance on Peroxide formers

2G Is any substance identified as self-reactive?
   Yes → 2H Direct data to Physical Processing Report
   No → Users should obtain guidance on self-reactive materials

2H Is any substance identified as water-reactive?
   Yes → Direct data to Physical Processing Report
   No → Users should obtain guidance on water-reactive materials

To 1Q
2.3 Evaluate Chemical Interaction Hazards

3A From 1Q

3B

Compare reacting groups for pairs of entered chemicals to predict binary interactions

Direct interaction worksheet to processing report

To 1R
## 2.4 Develop Chemical Reactivity Scenarios

Users should develop list of reactions to be evaluated:
1. Self-reactivity (decomposition, polymerization, isomerization, etc.)
2. Intended reactions and identified side reactions
3. Additional scenarios (reaction hazards) identified by Hazard Evaluation

**Has a PHA been completed for this process?**
- **Yes**
  - Manually enter PHA scenarios with reactivity
  - Direct data to Report
- **No**
  - Go through RMT checklist Also?

**Are there any significant ternary interactions?**
- **Yes**
  - Consultation with a chemist and/or chemical reactivity testing may need to be performed for these mixtures
  - Manually document these concerns
- **No**

**Identify loss of utility scenarios**
- Manually enter scenario(s)
- Direct data to Report

**Identify process variation or upset scenarios**
- Manually enter scenario(s)
- Direct data to Report

**Identify energy input variation scenarios**
- Manually enter scenario(s)
- Direct data to Report

**Identify mechanical failure scenarios**
- Manually enter scenario(s)
- Direct data to Report

**Identify inadvertent mixing and wrong material of construction scenarios**
- Manually enter scenario(s)
- Direct data to Report

**Identify human error scenarios**
- Manually enter scenario(s)
- Direct data to Report

**Identify any other chemistry occurring**
- Manually enter scenario(s)
- Direct data to Report

---

**To 15**
2.5 Evaluate Heat Release and Pressure Generation Hazards

Based on the data entered and/or generally accepted rules of thumb, this scenario has a low probability of creating a serious pressure event—see help guide.

Based on the data entered and/or generally accepted rules of thumb, this scenario has a low probability of creating a serious thermal event—see help guide.

Safety of system cannot be determined based on thermodynamics; kinetic evaluation is required. Seek additional guidance for this reaction.
2.6 Overview of Workflow and Chemical Data Entry

The primary Flow page (section 2.1) of the RMR Flowchart, the top of which is shown below, shows the overall workflow for the chemical reactivity evaluation tool. The individual steps involved are explained in detail by the identifiers next to each flowchart block (1A, 1B, etc.). For detailed step by step program instructions illustrated with screen shots see section 3.2.

1A Limit the scope to something less than an entire production site

The reactivity hazard evaluation protocol will best be applied to one chemical process or unit at a time. Attempting to apply it to an entire production site will generally be too cumbersome. See section 3.2.3

For example, say a company named Charbroiled Chemicals owns a production facility that includes a warehouse and process units making ethylene, chlorine, and vinyl chloride. In this case, the protocol would best be applied four times, once for each of the three process units and once for the warehouse.

1B Enter name of process and facility and the date of evaluation

For the ethylene process unit in the 1A example, Ethylene Unit could be entered as the “Name of process being evaluated,” and Charbroiled Chemicals as the “Facility name.” The “Date of evaluation / update” can be entered as the evaluation starting date, the evaluation completion date or the date of the most recent update, but should be consistently applied.

1C Enter names of evaluation team members

The number of team members required to complete the chemical reactivity evaluation will depend on a number of factors. Sufficient team members should be present or available to accurately answer all questions. The evaluation needs to be completed by a team that collectively has knowledge of the process chemistry, chemical reactivity hazards, process equipment and controls, process technology and processing operations.
1D Laboratory-scale facility?

The RMR protocol is not designed for laboratory-scale reactions and processes. For this reason, a 30-gallon screen has been included in the flowchart. The user is asked to specify whether the process being evaluated has any vessels or containers with a volume greater than this amount. See “Laboratory Scale” in the glossary.

1E Caution statement

If the process is laboratory-scale, a caution is given that following the RMR flowchart with a lab-scale process may result in overly conservative results.

A link is given to the OSHA Lab Safety Standard, 29 CFR 1910.1450, with an explanation of its applicability. Note that in this OSHA standard, “Laboratory scale” is defined from a different perspective:

1F Continue with protocol, even if a lab-scale facility?

The evaluation team is given the opportunity to proceed through the remainder of the protocol for laboratory-scale facilities and take advantage of any portions that may be applicable and helpful in identifying and evaluating chemical reactivity hazards.

If it is decided not to proceed through the remainder of the protocol, then the question is asked whether the evaluation team has other processes to evaluate. If so, then the team is taken back to the beginning of the program for entry of another process name. If not, then a summary report of the evaluation up to this point can be printed before exiting the program.
1G  List all chemicals used or stored

If the process being evaluated is not laboratory-scale, or if the evaluation team wishes to proceed with a lab-scale process, then the first major step is to compile a list of all chemicals that are expected to be used or stored in the process area, plus those that may potentially be involved under abnormal or unusual situations. The list of chemicals can be compiled either off-line before proceeding with the evaluation, or can be generated at the same time as they are entered into the software in the next evaluation step. For help selecting the required chemicals See section 4.1

1H  Enter all chemicals into the software

All of the chemicals compiled in step 1G are now entered one at a time into the software tool. This list of chemicals forms a database that will be used throughout the remaining steps of the evaluation. The user should obtain the MSDS for the chemicals to be entered. If the chemicals are custom or there is not a MSDS available, the user should search the literature for DOT hazard data.

The evaluation tool contains the same database of over 5,000 chemicals that is used by the U.S. National Oceanic and Atmospheric Administration’s Chemical Reactivity Worksheet, or CRW2 (NOAA 2009). The user can search (see section 3.2.6.1) for a chemical by name or synonym, by Chemical Abstracts Service (CAS) number, or by UN/NA or DOT number.

Custom chemicals. If the correct chemical cannot be found by using the search features, such as for unusual or proprietary chemicals, then it will need to be entered as a “custom chemical” along with its associated reactive group(s) of the material in order for it to be included in the chemical reactivity evaluation. More information on determining reactivity groups and entering custom chemicals is given in Section 3.2.6.2 of this Help Guide.
Missing Chemical Data- This part of the program performs two functions it serves as a double check for custom chemicals and is an input form for the DOT labels for all NOAA chemicals. The DOT codes are required for the warehouse segregation function. The program will not allow the user to continue until all required data is entered. See section 4.2 For help in determining the proper DOT codes.

1M    Warehousing only?

Warehousing here means storing or transporting materials where the containers are never opened. The approach for warehousing is significantly different than that taken for physical or chemical processing. Warehousing poses fewer opportunities for an uncontrolled reaction to take place than for physical processing or intentional chemistry, so fewer measures are needed to contain and control the chemical reactivity hazards.

1N    Review Remainder of Protocol?

A user who is only warehousing prepackaged materials in unopened containers is not required by the protocol to go through the more rigorous evaluation of the physical and chemical processing portions, but is given the option of continuing with the more rigorous evaluation if desired.

1O    Warehouse report

If the process involves chemical warehousing only, then the chemical reactivity evaluation report generated at this step will include process identifying information, evaluation team members, a chemical listing and a warehouse segregation document (section 3.2.11.1), which is a matrix that provides recommendations for warehouse segregation of chemicals based on reactivity concerns.
1P Chemical reactivity evaluation protocol, Sheet 2

For each chemical entered the following pure-component chemical reactivity properties are automatically identified by the software tool using the NOAA Chemical Reactivity Worksheet database:

- Highly Flammable
- Explosive
- Polymerizable
- Strong Oxidizing Agent
- Strong Reducing Agent
- Water-Reactive
- Air-Reactive
- Pyrophoric
- Peroxidizable Compound
- Radioactive Material

1Q Chemical reactivity evaluation protocol, Sheet 3

After the evaluation of the pure-component hazards of the materials, the chemical interaction hazards need to be identified that could have a consequence of concern. Section 2.3 shows the detail of this process. 6

1R Chemical reactivity evaluation protocol, Sheet 4

It is necessary to identify not only normal reactions and possible self reactivity concerns, but also to determine credible upset conditions and the possible reactions that could result from these conditions.

This step in the protocol refers the user to Sheet 4 for developing a list of possible incident scenarios that could involve abnormal or uncontrolled chemical reactions, with stepwise details given in Section 4.4.

1S Chemical reactivity evaluation protocol, Sheet 5

The user is taken next to the steps on Sheet 5 of the flowchart, detailed in Sections 4.5 through 4.9. Each scenario is evaluated individually for heat release and pressure generation hazards.

---

6 For further information see NOAA: Johnson, L. E. and Farr, J.K., CRW 2.0: A Representative-Compound Approach to Functionality-Based Prediction of Reactive Chemical Hazards.
1T  **Full report**
The **Print Report** button prints the full chemical reactivity evaluation report, including the warehousing segregation document described earlier at step 1L. *(see section 3.2.11)*

1U  **Management system**
The information generated in the chemical reactivity evaluation protocol, including the hazards identified as requiring additional evaluation, have been given to the user in a report that can be used as the starting point for developing and implementing a Chemical Reactivity Management System to contain and control the identified chemical reactivity hazards and to provide preventive and mitigative safeguards for managing the risks associated with the identified scenarios of concern. *See Appendix D*
3 Program Usage

3.1 Installing and Starting the Program

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3.1.1 System Hardware Requirements
• 1 gigahertz (GHz) or faster 32-bit (x86) or 64-bit (x64) processor
• 1 gigabyte (GB) RAM (32-bit) or 2 GB RAM (64-bit)
• DirectX 9 graphics device with WDDM 1.0 or higher driver
• 50 MB Space required for Reactivity Management Tool installation.
• 400 MB of available hard-disk space
• 800 x 600 minimum screen resolution and 256 colors
• Mouse or other compatible pointing device

3.1.2 Software Requirements
Before staring the program you must download and install two prerequisite programs as follows:

• This software has only been tested on Microsoft Windows XP and Windows 7
• .NET framework 4.0 is required. Please download and install from this location.

• SQL 2005 Express edition is required. Please download and install from this location.

3.1.3 Downloading the Reactivity Management Tool and required prerequisite programs

1. Download the latest version of the Reactivity management Tool from the AICHE website onto your computer’s hard drive.
2. Download SQL Express 2005 and .NET Framework 4.x using links above
3.1.4 Windows XP install

- You must have administrator rights

- Double click on the installer icon.

- Choose Run
- Choose Next
- Select the default directory C:\Program Files\AIChE\Reactivity Management Tool\n- And "everyone"

- Press Next on this screen and the next screen
download SQL 2005 Express and .NET framework 4.0 from the links in 3.1.2
Run the installer dotNetFx40_Full_x86_x64.exe from the directory you specified during the download.

Check the Read and accept box and press install
Wait while the installer does a file security check and then installs the client. This can take a very long time.

Windows will ask you to reboot now. This is optional until after you have installed the SQL Express 2005.
Run the file SQLEXPR.EXE from the directory you selected during the download.

Check the accept box and press next

Press Install
Press next

The installer will do a configuration check

Press Next when the screen At right comes up.
Press Next
Your registration information will be requested. Press Next

Press next utilizing the default options
Press next utilizing the Default settings

Press Install utilizing the default options.
Press Next when the Install and configure is Complete.

Finally press complete at the final information screen.

Reboot your computer now.
Go to the windows update and get all current updates for your computer to complete this installation.

**IMPORTANT**
Copy files RMTHelpguide.pdf and Fast_Start.pdf to the RMT install directory C:\Program Files\AIChE\Reactivity Management Tool\ (choose replace when warned that file already exists)

3.1.5 Windows 7 Install (64 and 32Bit)
- You must have administrator rights
- Typically the download can be found in your personal Library in a folder called “Downloads”
- Double click to run the setup program
• Click Run

![Image of Open File - Security Warning dialog box]

The publisher could not be verified. Are you sure you want to run this software?

- Name: C:\Users\Mark\Downloads\RMTSetup.msi
- Publisher: Unknown Publisher
- Type: Windows Installer Package
- From: C:\Users\Mark\Downloads\RMTSetup.msi

- Run
- Cancel

- Always ask before opening this file

This file does not have a valid digital signature that verifies its publisher. You should only run software from publishers you trust.

How can I decide what software to run?

![Image of Reactivity Management Tool setup wizard]

Welcome to the Reactivity Management Tool Setup Wizard

The installer will guide you through the steps required to install Reactivity Management Tool on your computer.

WARNING: This computer program is protected by copyright law and international treaties. Unauthorized duplication or distribution of this program, or any portion of it, may result in severe civil or criminal penalties, and will be prosecuted to the maximum extent possible under the law.

- Cancel
- Back
- Next

• Click Next
Choose your directory and check “everyone”
Press Next
Press Next again to confirm the install
You may be asked by Windows security to allow the install. Press yes to allow Windows to do the install.
Close the install window

If you have not already downloaded SQL express 2005 do so now per the instructions and links in section 3.1.2

Run the file SQLEXPR.exe from your downloads folder
You may be asked by Windows security to allow the install. Press yes to allow Windows to do the install.
- Press run program

![Program Compatibility Assistant](image1)

- Accept the terms and conditions and press next
- Press install in the next window

![Microsoft SQL Server 2005 Setup](image2)

- Press next
- Press Next
- Press next
- Enter your registration information and press next
• Accept the default settings and press next

• Press next without entering a password

• Press Next
The following components will be installed:

- **SQL Server Database Services**
  (Database Services)

- Press install

- Press next when the install is finished
- Press finish on the final screen
Download the .NET framework file
Run dotNetFx40_Full_x86_x64.exe
Press yes at the windows security warning

Check the read and accept terms box and then the install button. After the install has completed, press Finish

Go to All Programs // Windows Update. Click on Check for updates.
• Click on the link below the arrow

![Windows Update](image)

• Make sure that one of your updates for SQL Server 2005 is service pack 3 or higher

<table>
<thead>
<tr>
<th>SQL Server 2005 (1)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Microsoft SQL Server 2005 Express Edition Service Pack 4 (KB2463332)</strong></td>
<td>55.8 MB</td>
</tr>
</tbody>
</table>

• Install all updates by checking the boxes in front of their names. Press OK
• You will be returned to the screen above.
• Press Install Updates. Your computer will want to reboot when the updates are installed.

**IMPORTANT**
• Copy files RMTHelpguide.pdf and Fast_Start.pdf to the RMT install directory
  C:\Program Files\AIChe\Reactivity Management Tool\ (choose replace when warned that file already exists)

### 3.1.6 Executable and Database File location and descriptions

The reactive management files are located in the following directory by default:

Windows 7:  C:/program files (x86)/aiche/reactivity management tool/

Window XP C:/program files/aiche/reactivity management tool/

There are two files in this directory which contain all the information for your process custom chemicals database. These files (**RMTDB_log.ldf** and **RMTDB.mdf**) can be imported or
exported to other users’ computers if you so desire. See section 3.1.7 for more information on how to export or import these files.

3.1.7 Exporting / Importing the RMT Process Analysis

This version of the reactivity management tool was designed to be used by one user and not as a shared network tool. However, it is possible to share your process analysis program with other users and/ or add to a user’s process analysis program by importing or exporting two specific files – RMTDB.mdf and RMTDB_LOG.ldf.

The process for exporting a user’s process analysis program is as follows:

1. Close the Reactivity management tool
2. The importing user should locate the two files (RMTDB.mdf and RMTDB_LOG.ldf) on your hard drive and change the file extensions to your initials; example – RMTDB.mdf becomes RMTDB.mdf.des and RMTDB_LOG.ldf becomes RMTDB_LOG.ldf.des.

3. The exporting user copies and sends these two files from their reactivity management tool directory to the importing user. The importing user places the exported files in their reactivity management tool directory

4. In the example above the importing user now has the following files in their directory.
   - User’s old files containing all their previous processes and chemicals
     - RMTDB.mdf.des
     - RMTDB_LOG.ldf.des
   - Imported files containing the processes and chemicals of the exporting user
     - RMTDB.mdf
     - RMTDB_LOG.ldf

5. If you want to again use your original process and chemical files, simply rename your current working files and then remove your initials from your original files to make them the active database files once more – steps 1 through 4.

There is no known way to merge imported files into a user’s current file.
3.2 Step by Step Program Instructions

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3.2.0 Starting the program

- Install the program and the prerequisite software
- Open the Reactivity management Tool using the shortcut located in your start menu
  All Programs // Reactivity management Tool // Reactivity management Tool
- Upon starting the program A process window will open after acknowledging the opening splash screen.

3.2.1 File Menu

Help will open this help guide from the program.
Located in the upper left corner of the screen this grouping of dropdown menus allows the user to access the following functions:

- **Process**: Open a new process window (multiple process windows may be open at one time)
- **Reports**
  - **Reactivity Matrix**: Opens a window to view a binary interaction matrix for the current process and all previously entered processes
  - **Warehousing Segregation Report**: Opens a window to view a warehousing segregation matrix for the current process and all previously entered processes
  - **Chemical reactivity evaluation Report**: Opens a window to view the scenario evaluation results for the current process and all previously entered processes
- **Disclaimer**: Opens the opening splash screen containing the program legal disclaimers
- **Exit**: ends the program
3.2.2 Navigation Within The Process Window

Definitions:

The Process Window can be navigated using the tabs however certain tabs are grayed out (navigation forbidden) until the appropriate data entries have been made in all previous Tabs.
3.2.3 Process Tab

The Program will open on the “Process” tab

- **Create Process**: Starts a new process evaluation in the RMT. Enter your process in the Process name field
  - Enter an *area or facility name* in the Facility name. See section 4.1 for help in selecting the proper scope of your evaluation.
  - Save your entries with the “save” button before pressing “Next”
  - Process name can not contain any special characters or be longer than 31 characters. The program will allow this but exports to excel will be disabled.

- **Load Process**: Allows the user to work on a previously entered process
  - Select the process name by pressing on the arrows to the right of the process name entry box and highlighting the desired process.
  - The “load” button to the right of the box becomes active
  - Press the “Load” button

- **Save**: You must save your work before proceeding to the next screen.
- **Clear**: Removes the data from all fields. WARNING there is no undo.
- **Unload Process**: Allows user to unload the process from the open process window so that another process can be loaded.
- **Close**: closes the process window. Use the file menu to open a new one

3.2.4 Team Members Tab

- Select the “Add” button to enter information on at least one evaluation team member.
- Use the “Save” button after entering the information on each team member
- Continue adding team members until your evaluation team list is complete
- Use the save “Next” button to move to next screen
- Team members can be edited by double clicking on the members name or they can be deleted by checking the box in front of their name and pressing the delete button.

3.2.5 Laboratory Scale facility Tab

- You will be asked if your operation is defined as a “Laboratory Operation”. Choosing yes terminates the program. The default answer is No with next taking you on in the program. Press the “help” button for a definition of Laboratory operations.

3.2.6 Process Chemicals tab

3.2.6.1 Searching for chemicals

- Press the “Search Chemical Databases” button to begin by searching the built in NOAA CAMEO database for your chemicals. Note: if you have entered custom chemicals in your RMT custom database these are searched at the same time. Results will be tagged
with the database location. SQL is your custom database and NOAA is the NOAA CAMEO database.

- Enter the name of your first chemical in the pop-up search box and press search button.
- Utilize several different options to either widen or narrow your search results. Be persistent the NOAA CAMEO database has many synonyms for each chemical but sometimes a slight name difference between your entry and the synonyms will prevent a search hit. CAS number is very helpful. Be sure to enter the dashes in their proper place. Toggling between “contains” or “starts with” will expand, shrink your number of hits and sometimes even get a few different hits. Completing 2 fields produces an “and” search. Note the official name will appear in the search hits window name field. If you search “THF” your hits will read “tetrahydrofuran”
- Search through your hits for your desired chemical. Check the box in front of the name. (you may make multiple selections.) them press the “Add to process” button

- To search your next chemical simply type over the last chemical name and hit “search”
- When you have finished searching use the close button to return to the Process Chemicals Tab
3.2.6.2 Custom Chemicals entry and editing pop-up form

- Press the “administer Custom Chemicals” button to open the Custom Chemicals database. This data is stored where you have installed the program and never shared over a network or the internet. See special instructions for database sharing in the help guide.
- All functions of the custom chemical database are accessed from this pop-up.
  - “Export to Excel” data dumps your custom database to Excel 2007 or later. This is helpful for data checking.
  - “Add custom chemicals” opens another pop-up where you can input data for your own chemicals or those not found in the NOAA database.
  - “Add to Process” adds the chemicals that have a check in the box in front of their name.
  - “Delete selected Chemicals” deletes the chemicals that have a check in the box in front of their name.
  - Editing an entry: Double clicking on the name of a chemical allows you to edit that chemical.
- Press the “add custom chemicals” button or double click on the custom chemical you want to edit to access this pop-up form.

Do not get confused by the primary and secondary DOT labels. You MUST enter a primary DOT code in the collapsed box pointed out by the RED arrow. The much more obvious scroll bar box with the ORANGE arrow pointing to it is only for a secondary code if there is one.
You must enter at least the following data by selecting from the dropdown lists. For multiple selections hold down the Ctrl key and left click to toggle selection deselection.

- **Chemical name** – Type in “Line Kleen”
- **PRIMARY DOT code** – select “Corrosive – acid”
- At least one reactivity group –
- At least one Special Hazards group

To deselect a secondary DOT code, hold down the Ctrl key and left click in the code you want to remove. The code will change from highlighted to outlined. Click anywhere outside the selection box to make the deselection permanent.

**Entering Reactivity groups.**

- All applicable MUST be selected. Hold down the “Ctrl” key and select with the left mouse button or space bar. This information is only available by viewing the chemical structure. Often the structure can be found by searching the chemical name or CAS number on the Web. **Failure to select all applicable groups or selection of improper groups will give false reactivity predictions that might cause the program to miss a serious chemical reactivity issue. Selection of the proper groups may require the expertise of a trained chemist knowledgeable in both chemical reactivity and chemical nomenclature.**

- Note there are groups that start with the number 101 and higher that are not utilized by the program. You MUST however enter “100 Water” if the material contains more than trace amounts of water. An example would be the hydrate of a metal salt.

**Entering “Reactivity hazard Group”**

- All applicable must be selected or “none”
- This information will be found in the NFPA diamond or disbursed throughout the MSDS.

### 3.2.6.3 Editing Custom Chemicals

- Press the **Administer custom chemicals button** to access the pop-up
- Double click on the chemical name
- The edit form for that chemical will pop-up.
- Enter or change the desired fields
- Press save and then close

### 3.2.6.4 Adding custom chemicals to the process

- There are 2 ways to add custom chemicals into your process.
  1. You can perform a search of the databases exactly as described in the section 3.2.6.1.
  2. From the Administer Custom Chemicals pop-up (see screen shot next page)
Check the box in front of the name of the chemical(s) you wish to add
- Press the “Add to Process” button
- Press the “Close” button to close the pop-up and return you to the Process Chemicals tab

3.2.6.5 Viewing and Navigation

- Use the scroll bar to view all the chemicals entered for the process.
- Use “Export to Excel” to data check all entries.
• The form tells you where the chemical information resides under **DB identification**
• When satisfied with all entries, press “next”

### 3.2.7 Missing Data Warning box

This box performs two functions; it serves as a double check for custom chemicals and is an input form for the DOT labels for all NOAA chemicals. The DOT codes are required for the warehouse segregation function. The program will not allow the user to continue until all required data is entered.

If the next button does not work recheck that at least a primary DOT code and at least one reactivity group has been entered for each chemical. Use the scroll bar on the bottom to scroll right to see the reactivity group column. See section 4.2 for how to determine the proper DOT codes.

To deselect a secondary DOT code choice made in error, hold down the Ctrl key and left click in the code you want to remove. The code will change from highlighted to outlined. Click anywhere outside the selection box to make the deselection permanent.

### 3.2.8 Warehousing vs. Chemical processing

• The program seeks to determine if the Facility being evaluated is solely a Warehouse or if other operations are performed there. Press the Help button or see the help guide for definitions.
3.2.9 Reactivity and Failure Scenarios

- The user should be very familiar with HAZOps scenario building or consult the Help Guide and incorporated references for detailed information on how to build credible scenarios for evaluation. It is critical to the satisfactory performance of the program that the user identifies all credible scenarios applicable to the processing area. Failure to identify even one high hazard scenario could jeopardize the safety of your facility.

- The program first asks if you have already performed a formal Process Hazard Analysis on the facility by one of the established and accepted methods.

- You should expect to build at least 25-50 credible scenarios for a narrow scope process evaluation as explained in section 4.4 of the help guide.

- You can also view worked examples.

3.2.9.1 Scenario build screens: Navigation and data entry

All the scenario building screens are laid out the same. There is a thought provoking question. A selection of yes is followed by an entry screen similar in this format.

The information area provides a brief summary of the type of scenario to be created for this section.
Click the “add” button to activate the screen for data entry
Utilize the explanations in the help button and references in the help guide to fully explore each topic.
When naming scenarios use a common convention throughout. The author suggests three letters designating the tab where the scenario was entered followed by a dash and consecutive numbers. Ex PHA-001 for the first scenario built under the PHA Scenarios tab.
An example of a scenario build is captured below.

Mandatory fields are:
- Scenario name
- Full description: fully detail the failure
- Comments: Utilize this area to enter consequences or protections
It is optional to enter the heat of reaction on this screen

Press the save button before attempting to go on using the next button
Select either continue adding scenarios to this tab or move to the next type of scenario.
Repeat this process until all scenarios are built.

There is no obvious place to enter your intended chemical reactions and chemical reactivities described in the chemical interaction matrix. Enter these under the “Other” tab. They can be
A list of all previously entered scenarios can be seen by pressing the “list all scenarios” button. From this pop-up you can view, edit and delete any scenario.

- Double click on the scenario name to edit.
3.2.9.3 Identifying significant chemical interactions

Significant binary chemical interactions and pure component hazards should be entered into the program as scenarios. The “others” section is the recommended place for this.

Open a reactivity matrix for your process (see the reports section for step by step instructions) and study each interaction for serious consequences. Utilize the information provided, reference material, chemical knowledge and process area knowledge to come up with credible mixing scenarios to be entered.

Add a new scenario for each serious interaction in the “Any Other Scenario” tab

For a listing of the pure component hazards of your process chemicals, see Reports – Chemical reactivity evaluation report. Load your process and select the Pure components hazards tab.
Consider the comments box for entering other relevant information about the reaction such as “Reaction produces 1 mole of hydrogen bromide gas - Toxic”. This will help us during the evaluation of the pressure for this scenario.

3.2.10 Evaluation of Scenarios

3.2.10.1 Scenarios Tab

Upon saving your last scenario press the next button. This will pop-up a box asking if you want to create any more scenarios. Answer NO to move to the scenario evaluation phase. Alternately use the tabs to navigate to scenario evaluation.
To evaluate a scenario, double click on the name. The grayed out text becomes editable.
  
  - Note the status of each scenario is displayed.
  - Look over the text. Edit if necessary.

If you have not already done so a heat of reaction must be entered now.

- Press the “Evaluate scenario” button
- The scenario evaluation tab opens and requests information about the adiabatic heat rise and starting temperature

3.2.10.2 List All Scenarios Pop-up - Editing / Deleting a scenario
You can edit all scenario fields except the name using the Scenario tab
To delete or edit a scenario, go back to any Scenario entry tab. Press the “list all Scenarios” button.

The following pop-up box appears.

Check the box in front of the scenarios you wish to delete and press “delete selected”
Note that you can edit a scenario from this pop-up form. Double click on the scenario and the scenario will be editable in the top half.

Because of the database structure of the program, there is no way to edit the scenario name once entered – choose wisely.
3.2.10.3 Determine Maximum Adiabatic Temperature Tab

There are two methods of data entry here.

Method A

- You can enter the adiabatic heat rise directly

Method B

- The program will calculate it for you from the heat of reaction and heat capacity of the mixture
For organic reactions a heat capacity of 2\,j/g°C is typical. For aqueous solutions 3-4 \,j/g°C is typical.

- Press Save and Next to continue the evaluation. Note that when using this method, the heat rise is entered into the proper field for you as soon as the save is pressed.

3.2.10.4 Define Temperature of Concern Tab
- Press the Next button.

- The program now asks us for the temperature of concern.
- Consult guide book section 4.7 and the references contained therein for help setting a temperature of concern.
- Press **save** then **next** to display the evaluation of the thermal scenario.
The program will now display one of two messages:

The safety of this scenario cannot be determined based on thermodynamics, a kinetic evaluation or other evaluation methodology is required. Seek additional guidance for this reaction.

In this case this reaction must be studied further to determine if it can be operated safely. It is highly recommended that the user consult an experienced process safety professional for guidance as this scenario has a high likelihood of creating a chemical reactivity incident capable of causing injury, death and severe property damage.

Or

Based on the data you entered and/or generally accepted rules of thumb this scenario has a low probability of creating a serious thermal event. See help guide.

In this case the user should check all data entries and also fully understand the limitations of this program before judging the scenario “safe”.

3.2.10.5 Determine Maximum Pressure Tab
- Press the next button to continue with the evaluation
The program will now evaluate the Pressure hazard.

- The program asks us for a **maximum reaction pressure**. Thought should be put into how this is calculated. You may at this point want to go back and split this scenario into two or more scenarios depending on how you calculate the maximum pressure.
  - This could be calculated for a vessel vented through a 3” vent
  - Another way would be to assume the vent was closed
  - All at once addition of reagent that should be added over time
  - And so on

Choose your pressure units from the drop-down menu.

- Press save then Next
3.2.10.6 Determine Pressure of Concern Tab

- The program now asks for the pressure of concern.
- Consult guide book section 4.7 Determining Temperature of concern and the references contained therein for help setting a pressure of concern.
- Note that the pressure of concern must be entered in the units selected on the pervious screen.
- Press save then next to display the evaluation of the pressure scenario.
- The program will now display one of two messages:

The safety of this scenario cannot be determined based on thermodynamics, a kinetic evaluation or other evaluation methodology is required. Seek additional guidance for this reaction.

- In this case this reaction must be studied further to determine if it can be operated safely. It is highly recommended that the user consult an experienced process safety professional for guidance as this scenario has a high likelihood of creating a chemical reactivity incident capable of causing injury, death and severe property damage.
- Or

The information entered for the pressure analysis of this scenario indicates that the scenario has a low probability of causing a major chemical reactivity incident. See help guide.
In this case the user should check all data entries and also fully understand the limitations of this program before judging the scenario “safe”.

3.2.10.7 Conclusion Tab – setting scenario status

- Press the “Next” button. The program will ask you if you would like to change the status of this scenario. Your choices are:
  1. Unevaluated
  2. Needs updating
  3. Complete

Press save and next

The box below may appear below the status in the above screen shot.
The first choice takes you back to the Scenarios pane so that you can choose another scenario to evaluate.

Choosing Print will open up the evaluation report pop-up. This is the same pop-up that can be accessed through the file menu as described in the reports section of these step by step instructions.

Repeat the instructions under 3.2.10 Evaluation of Scenarios until all scenarios are complete.

### 3.2.11 Reports

Reports are accessed from the FILE menu and also through shortcut buttons at various points in the program. The only way to get a complete set of reports is to access them through the FILE menu. Rarely users have reported incorrect display of data when generating reports from an open process. It is recommended that the user close the program completely and then access the reports menu after restarting the program without loading the process in the process window.

#### 3.2.11.1 Warehousing Segregation Report

Select: File – Reports-Warehousing Segregation report
Selecting this report opens up the pop-up window shown below

- Select your process from the drop-down list and press Load

- Depending on the number of chemicals in your process the grid may only be partially visible.
- To print or otherwise manipulate this grid use the export to Excel button.
This segregation matrix MUST be studied and given a “reality check. Valuable information, that known to this program, is not taken into account in calculating the segregation distances. This information can be found in both the Reactivity matrix Report and the Pure Component hazards tab of the Chemical reactivity evaluation report.

3.2.11.2 Reactivity matrix
The reactivity matrix report is accessed through the file menu

Select: File – Reports-Reactivity matrix

A blank form is opened.

- Select your process from the drop-down list and press Load
- Select your process and press the load button
- You will see the binary interaction matrix for your process
Double click a cell with an entry to view the identified interaction.

In the following screen shot we have double clicked on the interaction of Bromine with Acetophenone. As you can see any possibility that these two chemicals could be mixed in an uncontrolled fashion should be seriously considered as a credible scenario with serious consequences. Use the scroll bar to scroll through all of the supplemental information and references provided.

Use the scroll bar to review entries to the right and bottom.

Use the Export to Excel button to export a printable reactivity matrix into Excel.

Use the print button to print only the text displayed in the lower portion of the window.

Use the Print All button to print the text display for all interactions at one time.
3.2.11.3 Chemical reactivity evaluation report

This report displays all of the scenarios along with their evaluation data.

File – Reports – Reactivity Evaluation report

Displays a blank form.

Select your process from the drop-down menu and press **Load**
Note the Tabs. Each tab must be printed or exported separately for a complete report.

The print function for many of the tabs is cumbersome with many unwanted fields displayed and printed. The authors recommend the Export to Excel function for these tabs where the data can be edited such that only the desired information is printed.

The Print button for the Binary matrix tab acts like the PrintAll button on the Reactivity matrix when the report is accessed directly from the file menu (File – Reports-Reactivity matrix) Ti prints only the text for each of the interactions. A print in matrix format must be accessed through: File – Reports - Reactivity matrix // Load process //export to Excel

Valuable pure component reactive hazard or special hazards information for process chemicals is only displayed under the Pure component reactivity hazard tab of this report. This information is also reported under the column “Special Hazards” in the process chemicals report. This information may lead to building new scenarios.
3.2.11.3.1 Team Members Tab
From this tab you can view, print or export to Excel the information entered about the Process Hazard Review team.

3.2.11.3.2 Process Chemicals Tab
From this tab you can view, print or export to Excel all information collected by the program relating to the chemicals in the process. Use the scroll bar along the right side and across the bottom to view all the information.

3.2.11.3.3 Binary Matrix Tab
The information and functionality of this tab is identical to that of the Reactivity Matrix described in section 3.2.11.2 Reactivity matrix.

3.2.11.3.4 Evaluate Pure-component Reactivity Hazards Tab
From this tab you can view, print or export to Excel all information collected by the program relating to the Special Hazards associated with the chemicals in the process.

Cross-check the column “Special Hazards” on the process chemicals tab to make sure the program properly updated this tab for your custom chemicals. See FAQ 11) Updated custom chemical data does not appear in process window.

3.2.11.3.5 Scenarios Tab
From this tab you can view, print or export to Excel all information entered into the scenarios section plus the program’s evaluation of each scenario.

Only checked scenarios are printed or exported. The print function will crop text. It is advised that each scenario be exported to excel so that the size of the box can be adjusted to show all information.

4 Strategy

4.1 Selection of Process Chemicals

4.1.1 limiting the scope of the evaluation
The reactivity hazard evaluation protocol will best be applied to one chemical process or unit at a time. Attempting to apply it to an entire production site will generally be too cumbersome. For example, say a company named Charbroiled Chemicals owns a production facility that includes a warehouse and process units making ethylene, chlorine, and vinyl chloride. In this
case, the protocol would best be applied four times, once for each of the three process units and once for the warehouse.

4.1.2 Developing an inclusive chemicals list
The chemicals list for a process must first contain all of the raw materials, intermediates and products of the process (including waste and by-products). In addition you should include any chemicals which are readily available within the immediate area of the processing. This might include any, all or more than the following.

- **Water**
- **Processing solvents, chemicals or gasses hard piped to the reactor or available at a shared solvent or weighing station.**
- **Process chemicals from a near-by process that could be confused or miss directed into the processing area.**
- **Utility services**
  - Air
  - Heat transfer fluids, steam
  - Inertion gasses
  - Hydraulic fluids
  - Lubricants
  - Wet seal fluids
  - Vacuum pump oil or steam / water/ rust from a steam jet vacuum system
- **Cleaning reagents and solvents**
- **Materials flowing through a common drain, waste or chemical sewer system.**
- **Gasses or vapors that could be present in a shared or common vent header or vacuum header.**
- **Scrubber solutions, or emergency quenching agents**
- **Fire protection chemicals including water**
- **Equipment materials of construction for process wetted areas and those that are exposed to potential off gassing of reactive gasses like hydrazoic acid or perchloric acid**
- **Waste streams**
4.2 How to Determine DOT Information from an MSDS

You can download a complete list of DOT codes on the US Department of Transportation web site. Or use the section 14 information from an MSDS. The following are excerpts from the MSDS for tert-Butyl hydroperoxide which was found on the internet using the following search string: “MSDS tert-Butyl hydroperoxide solution”

14. TRANSPORT INFORMATION

_**DOT (US)**_

**UN number:** 3109  **Class:** 5.2 (8)  **Packing group:** II

**Proper shipping name:** Organic peroxide type F, liquid (tert-Butyl hydroperoxide)

**Reportable Quantity (RQ):**

**Marine pollutant:** No

**Poison Inhalation Hazard:** No

9. PHYSICAL AND CHEMICAL PROPERTIES

**Appearance**

*Form clear, liquid*

*Colour colourless, light yellow*

**Safety data**

**pH 4.3**

**Melting point/freezing point**

_Melting point/range:_ -3 °C (27 °F) at 1,013 hPa (760 mmHg)

Utilizing the highlighted data: The primary code is 5.2 with a secondary of 8 (corrosive). To determine if it is a corrosive acid or base go to the Chemical properties and look for the pH. If the pH is less than 7 it is an acid. If >7 it is a base.

The correct DOT entry would be

**Primary:** 5.2 Organic Peroxide

**Secondary:** 8.0 Corrosive acidic

---

4.3 Guidance on Selected Pure Componant Hazards

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4.3.0 General Guidance

Sections 4.3 is edited from the AIChE/CCPS Guide Book Essential Practices for Managing Chemical Reactivity Hazards. Specific guidance on handling most categories of pure reactivity hazards can be found in the AIChE/CCPS guide book series available through Knovel. These should be considered the definitive source for this information as this series is regularly updated with information beyond the scope of any brief discussion of the topic presented within this help guide. Recognized and Generally Accepted Good Engineering Practices change with the experience of time and should be sought from the most recent sources.

4.3.1 Hazard Guide for Spontaneously Combustible Materials

4.3.1.1 How to identify Spontaneously combustible materials:

This hazard guide provides resources that should be utilized in the development of a Reactive Chemical Management System for spontaneously combustible materials. Spontaneously combustible materials are those that will react with oxygen and generate sufficient heat from that reaction to auto-ignite. There are a wide range of materials, including solids, liquids and gases that are spontaneously combustible.

---

4.3.1.2 Definitions and Common Spontaneously Combustible Materials

Spontaneously heating materials - materials that ignite because of a slow buildup of heat from an oxidation reaction;

Hypergolic materials - materials that immediately ignite upon exposure to an oxidizing agent (not necessarily oxygen);

Pyrophoric materials - a special case of hypergolic materials - materials that ignite on short exposure to air under ordinary ambient conditions. Some materials that are considered pyrophoric require a minimum relative humidity in the atmosphere for spontaneous ignition to occur. It should be noted that many pyrophoric materials also ignite upon exposure to water.

The potential of spontaneously combustible materials to exhibit this behavior is often well documented due to the extreme care required for their safe handling. However, in some cases, knowing the chemical composition of a material is not enough to determine whether it is spontaneously combustible. For example, some metals are pyrophoric when in finely divided or powdered form, but are not pyrophoric when in massive solid form.

Pyrophoric and other spontaneously combustible substances will generally be identified as such on their product literature, MSDSs or International Chemical Safety Cards. These substances should be identified as DOT/UN Hazard Class 4.2 materials for shipping purposes and labeled as SPONTANEOUSLY COMBUSTIBLE. For pyrophoric substances, if the NFPA diamond (NFPA 704) is used for container or vessel labeling, the red (top) quadrant would have a rating of 4, indicating the highest severity of flammability hazard.

The characteristics of pyrophoric chemicals and some common examples, are shown in the Table below. Other spontaneously combustible substances are tabulated by their proper shipping names and UN/NA numbers in the U.S. Department of Transportation regulation 49 CFR 172.101. For an extensive listing of pyrophoric materials, refer to reference 9 – Bretherick’s Hazardous Chemicals Handbook.
Examples of Pyrophoric Materials

<table>
<thead>
<tr>
<th>Category</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finely divided metals (without an oxide film)</td>
<td>Aluminum, calcium, cobalt, iron, magnesium, manganese, palladium, platinum, titanium, tin, zinc and zirconium</td>
</tr>
<tr>
<td>Many hydrogenated catalysts containing adsorbed hydrogen (before or after use)</td>
<td>Raney nickel catalyst with adsorbed hydrogen</td>
</tr>
<tr>
<td>Alkali metals</td>
<td>Sodium, potassium</td>
</tr>
<tr>
<td>Metal hydrides</td>
<td>Germane, lithium aluminum hydride, silane, and sodium hydride</td>
</tr>
<tr>
<td>Partially or fully alkylated metal hydrides</td>
<td>triethylbismuth, trimethylaluminum, triethylaluminum, butyl lithium, diethylaluminum hydride</td>
</tr>
<tr>
<td>Aryl metals</td>
<td>Phenyl sodium</td>
</tr>
<tr>
<td>Alkyl metal derivatives</td>
<td>Diethoxyaluminum, dimethylbismuth chloride, diethylaluminum chloride</td>
</tr>
<tr>
<td>Analogous derivatives of non-metals</td>
<td>Diborane, dimethylphosphine, phosphine, triethylarsine</td>
</tr>
<tr>
<td>Carbonmetals</td>
<td>Pentacarbonyliron, octocarbonylcobalt</td>
</tr>
<tr>
<td>Grignard reagents (RMgX)</td>
<td>Ethylmagnesium chloride, methylmagnesium bromide</td>
</tr>
<tr>
<td>Others</td>
<td>Phosphorus (white or yellow), titanium dichloride</td>
</tr>
</tbody>
</table>

4.3.1.3 General Guidance on Handling Spontaneously Combustible Materials

Spontaneously heating materials – These are materials that slowly react with oxygen. Many scenarios involving spontaneous heating materials involve a combination of materials exposed to air, in an insulating situation that prevents heat from a slow oxidation reaction to dissipate and thus results in a self-heating situation. Common examples are mixtures of paper, sawdust, or cloth containing hydrocarbons. In this example, the hydrocarbon is on or in the combustible material, which creates a large surface area. Because of the large surface area, the hydrocarbon oxidizes relatively rapidly. If the paper, sawdust or cloth is in a large pile or in a container, the rate of heat loss will be slow. The heat generated can increase the temperature of the mixture until it self-ignites.

Common methods for controlling these hazards are:

- Prevent hydrocarbons from coming in contact with combustible materials such as paper, sawdust and cloth;
- Do not allow hydrocarbon contaminated combustible materials such as paper, sawdust or cloth to accumulate in piles; spread it out so that the heat generated is dissipated;

---

Another example of spontaneously heating materials are peroxide formers. These are hydrocarbons that react with oxygen to form a peroxide. In this case, the oxygen can come from the air, water, or rust. The heat of reaction increases the temperature of the mixture until the hydrocarbon either ignites or starts to react with the peroxide. Another example is activated carbon in an air filter exposed to a high concentration of organic vapors.

Common methods for controlling these hazards are:

- Use a peroxide forming inhibitor to the hydrocarbon;
- Keep the hydrocarbon cool;
- Develop methods to ensure that oxygen (air) does not get into the system containing the hydrocarbon, such as using a nitrogen pad on tanks;
- Use corrosion resistant materials of construction;

Hypergolic materials – These materials react instantly with oxidizers. These materials are extremely dangerous. They are commonly used as a rocket fuel where they are mixed with a liquid oxidizing agent.

Common methods for controlling these hazards are:

- Develop methods to ensure that oxygen (air) does not get into the system containing the hydrocarbon, such as maintaining a nitrogen pad on tanks;
- Use corrosion resistant materials of construction;
- Develop methods to ensure that the material does not come in contact with any oxidizing agent

Pyrophoric materials – These materials react spontaneously with air. For pyrophoric liquid and gases, loss of containment and exposure of the material to air, or the introduction of air into the process are the most common hazards. Many pyrophoric materials also react with water.

An example of a scenario that has resulted in many fires and explosions in refineries relates to iron sulfide. An impure, pyrophoric sulfide is formed when streams containing hydrogen sulfide or other volatile sulfur compounds are processed in ferrous equipment. Oxidation of moist iron sulfide is highly exothermic. Opening of sulfide-containing equipment without adequate water purging can result in rapid self-heating and ignition of the iron sulfide, which can then ignite other residual flammable gases or liquids in the equipment.

Common methods for controlling these hazards are:

- Develop methods to ensure that oxygen (air) does not get into the system containing the hydrocarbon, such as maintaining a nitrogen pad on tanks;
- Use corrosion resistant materials of construction;
- Transfer materials by means of nitrogen pressurization. Do not use pumps;
- Nitrogen purge all opened equipment until a dew point of at least -40 °F (-40 °C) is obtained, prior to introducing any pyrophoric materials;
- Install an air-to-open actuated block valve on every pipeline or hose to and from the tank or container containing the pyrophoric material. Locate the block valve as close
to the container as possible. Place a solenoid valve in the air supply line to these valves that can be actuated from several locations in the area and the control room;

- Use plastic tubing for the air supply line. Run and securely attach the plastic tubing to the pipeline containing the air-to-open valve for a distance of at least 10’ from the container. For hoses, run the plastic tubing for the entire length of the hose. In the event of fire, the tubing will melt and the block valve will close. Configure the controls for the solenoid valves so that the deactivation of any one, deactivates all of the others;

- Dilute the material with a compatible hydrocarbon (mineral oil is frequently used for this) until the mixture is no longer pyrophoric. Even if this is done, all of the other recommendations should still be followed;

- For non-water reactive materials, such as phosphorus and ferrous sulfide, the material may be stored and handled under a water blanket;

Many metals that are usually thought of as highly corrosion resistant, such as titanium, tantalum and zirconium, will react with oxygen (air) if they are in the form of dusts or shavings or thin sheets or tubes, especially at higher temperatures. Aluminum and magnesium can also ignite under these conditions. Common hazards are machining or grinding on these metals because the dusts or shavings can ignite, and in turn ignite other dusts, shaving, thin sheets or tubes in the area. It is not uncommon for towers packed with these materials, or heat exchangers tubed with these materials to catch on fire during maintenance activities.

Some pyrophoric metals, like aluminum, magnesium, titanium, zirconium and zinc, that don’t have sufficient surface area to spontaneously ignite; if hot, react with water to generate hydrogen gas. This creates the potential for a hydrogen explosion.

Common methods for controlling these hazards are:

- Do not try to cut these materials with an oxy-acetylene torch; use a saw with a sharp blade. Use lots of water or cutting fluid to keep the metal and shaving cool;

- Use copious quantities of cutting oil or fluid when machining the metal; do not let the shaving get hot;

- Keep the shavings or dust wet or under water;

Common causes of uncontrolled reactions associated with spontaneously combustible materials include abnormal events such as the following:

- Inadequate cleanout of equipment containing spontaneously combustible substances, prior to opening to the air for maintenance;

- Inadequate purging of air prior to introducing spontaneously combustible material into piping, tubing or container

- Equipment or container purged with air instead of an inert gas;

- Air drawn into the system when it is under vacuum;

- Containment over pressurized and vented to atmosphere through a rupture disk or pressure relief valve
• Containment over pressurized and ruptured;
• Piping/vessel/container punctured;
• Piping/vessel/container corroded;
• Leakage at seal or connection;
• Mechanical failure of piping, hose or tubing;
• Evaporation of diluent solvent or insufficient solvent added;
• Cutting/grinding/milling without sufficient coolant;
• Mechanical attrition; e.g., of metal packing.

An example of a scenario that has resulted in many fires and explosions in refineries relates to iron sulfide. An impure, pyrophoric sulfide is formed when streams containing hydrogen sulfide or other volatile sulfur compounds are processed in ferrous equipment. Oxidation of moist iron sulfide is highly exothermic. Opening of sulfide-containing equipment without adequate purging can result in rapid self-heating and ignition of the iron sulfide, which can then ignite other residual flammable gases or liquids in the equipment.

4.3.2 Hazard Guide for Self Reactive Materials

4.3.2.1 How to identify Self Reactive materials:
This hazard guide provides resources that should be utilized in the development of a Reactive Chemical Management System for self reacting materials. These substances can react with themselves, often with accelerating or explosive rapidity. These substances have various chemical structures that make them susceptible to at least one of four forms of self-reaction: polymerizing, decomposing or rearranging or shock sensitive.

Materials carry an instability classification rating (according to the definitions in NFPA 704 - Standard System for the Identification of the Hazards of Materials for Emergency Response) when the material poses an instability hazard. **Having a nonzero NFPA instability rating is a straightforward means of identifying self-reactive materials.** NFPA 49 and NFPA 325 give instability ratings for many different industrial chemicals.

4.3.2.2 Definitions and Common Self reactive Materials
Polymerizing – Polymerizing materials are individual molecules that can combine together to form dimers, trimers or very large, chain-like or cross linked molecules called polymers. Polymerization reactions are exothermic and often generate a gas. This increases the probability that the vessel will be over pressurized if adequate controls are
Examples of common self-polymerizing materials\(^\text{10}\)

<table>
<thead>
<tr>
<th>Acrolein</th>
<th>Ethyl cyanohydrin</th>
<th>Propylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylamide</td>
<td>Ethylene Oxide</td>
<td>Propylene Oxide</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>Ethylenimine</td>
<td>Styrene</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>2-Ethylhexyacrylate</td>
<td>Tetrafluoroethylene</td>
</tr>
<tr>
<td>1,2-Butene oxide</td>
<td>Hydrogen cyanide</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>Butyl acrylate</td>
<td>Isoprene</td>
<td>Toluene diisocyanate</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>Methacrylic acid</td>
<td>Trimethoxy silane</td>
</tr>
<tr>
<td>Butyraldehyde</td>
<td>Methyl acrylate</td>
<td>Vinyl acetate</td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>Methyl isocyanate</td>
<td>Vinyl Acetylene</td>
</tr>
<tr>
<td>Dichloroethylene</td>
<td>Methyl methacrylate</td>
<td>Vinyl chloride</td>
</tr>
<tr>
<td>Diketene</td>
<td>Methyl vinyl ketone</td>
<td>Vinyl ether</td>
</tr>
<tr>
<td>Divinylbenzene</td>
<td>Methylchloromethyl ether</td>
<td>Vinyl toluene</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>Propargyl alcohol</td>
<td>Vinylidene chloride</td>
</tr>
<tr>
<td>Ethylene</td>
<td>Propionaldehyde</td>
<td></td>
</tr>
</tbody>
</table>

\(^{10}\) Includes material extracted from NFPA 49, 1994 edition, amended 2001
Decomposing – Decomposing materials are larger molecules that have the potential for breaking apart into smaller, more stable molecules.

Examples of Decomposing materials that generate heat and toxic or reactive gas:\textsuperscript{11}

<table>
<thead>
<tr>
<th>Material</th>
<th>Decomposition products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum phosphide</td>
<td>Phosphine</td>
</tr>
<tr>
<td>Benzenesulfonyl Chloride</td>
<td>Hydrogen chloride, Chlorine, Sulfur oxides</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>Ammonia, Hydrogen chloride, NOx</td>
</tr>
<tr>
<td>Calcium hypochlorite</td>
<td>Chlorine, oxygen</td>
</tr>
<tr>
<td>Calcium hydrosulfite</td>
<td>Sulfur dioxide, Hydrogen sulfide, Sulfur dust</td>
</tr>
<tr>
<td>Dichloroisocyanuric acid (Diclor)</td>
<td>Nitrogen trichloride, Chlorine, Nitrous oxides, Carbon monoxide</td>
</tr>
<tr>
<td>Disulfur dichloride</td>
<td>Hydrogen sulfide, Hydrogen chloride, Sulfur oxides</td>
</tr>
<tr>
<td>Formic acid</td>
<td>Hydrogen, Formaldehyde, Carbon monoxide</td>
</tr>
<tr>
<td>Sodium hydrosulfite</td>
<td>Sulfur dioxide, hydrogen sulfide, sulfur dust</td>
</tr>
<tr>
<td>Sodium hexafluorosilicate</td>
<td>Fluorine</td>
</tr>
<tr>
<td>Terephthaloyl Chloride</td>
<td>Phosgene, Hydrogen Chloride, Carbon monoxide</td>
</tr>
<tr>
<td>Trichloroisocyanuric acid (Triclor)</td>
<td>Nitrogen trichloride, Chlorine, Nitrous oxides, Carbon monoxide</td>
</tr>
</tbody>
</table>

Rearranging – Rearranging materials are those where the atoms in a molecule reposition themselves to form a different molecular structure, such as a different isomer.

\textsuperscript{11} Includes material extracted from NFPA 49, 1994 edition, amended 2001
**Shock Sensitivity** – Shock sensitive materials are those where decomposition can be initiated by mechanical energy input from an impact or shock wave.

Some common examples of shock sensitive materials

<table>
<thead>
<tr>
<th><strong>Acetylenic Compounds</strong>, especially polyacetylenes, haolacetylenes and heavy metal salts of Acetylenes (copper, silver, and mercury salts are especially sensitive);</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acyl Nitrates</strong></td>
</tr>
<tr>
<td><strong>Alkyl Nitrates</strong>, particularly polyol nitrates such as nitrocellulose and nitro glycerin</td>
</tr>
<tr>
<td><strong>Alkyl and Acyl Nitrites</strong></td>
</tr>
<tr>
<td><strong>Alkyl Perchlorates</strong></td>
</tr>
<tr>
<td><strong>Amminemetal Oxosalts</strong>: metal compounds with coordinated ammonia, hydrazine, or similar nitrogenous donors and ionic perchlorate, nitrite, permanganate, or other oxidizing group</td>
</tr>
<tr>
<td><strong>Azides</strong>, including metal, nonmetal, and organic azides</td>
</tr>
<tr>
<td><strong>Chlorite salts of metals</strong>, such as silver chlorite (AgClO₂) and Mercury chlorite (Hg(ClO₂)₂)</td>
</tr>
<tr>
<td><strong>Diazocompounds</strong> such as diazomethane (CH₂N₂)</td>
</tr>
<tr>
<td>** Diazonium salts**, such as benzenediazonium chloride (Ar-N≡N⁺Cl⁻), when dry</td>
</tr>
<tr>
<td><strong>Nitrides</strong>, such as silver nitride (Ag₃N);</td>
</tr>
<tr>
<td><strong>Hydrogen peroxide</strong> (H₂O₂) becomes increasingly treacherous as the concentration rises, forming explosive mixtures with organic materials and decomposing violently in the presence of trace transition metals, such as manganese (Mg), iron (Fe), chromium (Cr), tungsten (W), silver (Ag) and molybdenum (Mo);</td>
</tr>
<tr>
<td><strong>N-Halogen compounds</strong> such as difluoroamino compounds and halogen azides;</td>
</tr>
<tr>
<td><strong>N-Nitro compounds</strong> such as N-nitro methylamine, nitro urea, nitroguanidine, nitric amide;</td>
</tr>
<tr>
<td><strong>Oxo salts of nitrogenous bases</strong>: perchlorates, dichromates, nitrates, iodates, chlorites, chlorates, and permanganates of ammonia, amines, guanidide, etc.;</td>
</tr>
<tr>
<td><strong>Perchlorate salts</strong>: most metal, nonmetal and amine perchlorates can be detonated and may undergo violent reaction in contact with combustible materials;</td>
</tr>
<tr>
<td>** Peroxides** and <strong>hydroperoxides</strong>, organic;</td>
</tr>
<tr>
<td>** Peroxides (solid)** that crystallize from or are left from evaporation of peroxidizable solvents;</td>
</tr>
<tr>
<td>** Peroxides**, transition metals salts</td>
</tr>
<tr>
<td><strong>Picrates</strong>, especially salts of transition and heavy metals, such as nickel (Ni), lead (Pb), mercury (Hg), carbon (C), and zinc (Zn): picric acid is explosive but is less sensitive to shock or friction than its metal salts and is relatively safe as a water-wet paste;</td>
</tr>
<tr>
<td>** Polynitroalkyl compounds** such as tetryanitromethane and dinitroacetonitrile;</td>
</tr>
<tr>
<td>** Polynitroaromatic compounds**, especially polynitro hydrocarbons, phenols, and amines.</td>
</tr>
</tbody>
</table>
4.3.2.3 General Guidance on Handling Self-reactive Material

There are five general categories of what can go wrong with self-reactive materials:

- The occurrence of an abnormal energy input that is sufficient to initiate an uncontrolled self-reaction
- The presence of a catalytic substance that lowers the energy needed to initiate an uncontrolled self-reaction
- A reduction in the rate at which energy is dissipated to its surroundings, allowing initiation of an uncontrolled self-reaction
- The absence of sufficient activated inhibitor or stabilizer that is needed to prevent initiation of an uncontrolled self-reaction
- Concentration of self-reactive material, resulting in an uncontrolled increase in reaction rate. (Abnormal reactions with other, incompatible materials that may also serve to initiate self-reactions that are more energetic are also possible. These can be addressed by the scenario approach that goes with Question 12.) Initiation of uncontrolled self-reactions at a given facility can occur in storage or during handling, mixing, physical processing or chemical reactions.

A few of the many possible causes of uncontrolled reactions associated with self-reactive materials include the following:

- External fire
- Building or process temperature control fails high
- Loss of building or process cooling

**Polymerizing Materials** – Polymerizing materials self-react to form polymers. This also generates heat and often gas(s). This type of reaction has caused numerous runaway reaction incidents resulting in deaths, serious injuries and extensive property loss. Polymers may restrict flow through the vent line to the pressure relief device, or plug it off completely. The viscosity of the material will increase making it more difficult to remove heat by circulating the material through a cooler or the cooling coils within the vessel. The high viscosity can also create stagnant zones making it impossible to obtain an accurate measurement of the temperature in the vessel.

Common methods for controlling these hazards are:

- Use an inhibitor when possible. Monitor the inhibitor concentration periodically to ensure that there is a sufficient amount present. If oxygen is needed to activate the inhibitor, monitor the oxygen concentration to ensure that there is a sufficient amount present;
- Keep the material cool. This will reduce the rate of polymer formation;
- Provide means to ensure that the temperature in the vessel is always at least 50 °C below the onset temperature;
- Provide a redundant rupture disk mounted directly to the top of the vessel in addition to the code required rupture disk – pressure relief valve combination;
Provide a nitrogen purge below the rupture disk and into the vent line to the pressure relief device;

Use redundant temperature and pressure monitors, alarms and interlocks to take the process to a safe condition if the process is deviating from the safe operating envelope;

Use an inert material of construction. Corrosion products like rust often act to lower the onset temperature and or catalyze the polymerization reaction;

Decomposing materials – Decomposing materials are those that breakdown into their primary components, such as C, CO₂, CL₂, H₂, HCl, and SO₂. This decomposition is usually initiated by heat input (temperature) or physical energy input. Some materials like calcium hypochlorite, sodium hydrosulfite and trichloroisocyanurate decompose slowly at ambient temperature. If containers of these materials contain too much material, or the containers are packed closely together, the heat of decomposition will not be adequately dissipated. This will cause the temperature of the material to increase, which increases the decomposition rate. If action is not taken quickly, the material will catch on fire. A runaway reaction can sometimes obtain a temperature where the materials present breakdown into gases, which causes the pressure in the vessel to rise even quicker. Frictional heat from shaft seals and packing can sometimes generate sufficient heat to initiate a decomposition reaction. The heat of compression within a compressor may generate sufficient heat to initiate a decomposition reaction.

Common methods for controlling these hazards are:

- Determine and understand the thermochemical characteristics of the materials in the process;
- Determine the maximum amount of material that can be piled, stored or shipped in a given piece of process equipment or container and use a size of container that provides a significant safety margin;
- Store materials with a spacing that is adequate to allow dissipation of the heat of decomposition;
- Provide a means to ensure that materials are at least 50 °C below their self accelerating decomposition temperature;
- Provide area monitors and alarms in enclosed areas for decomposition products;
- Provide redundant temperature and pressure monitors, alarms and interlocks that will take the process to a safe condition if the process deviates from the safe operating envelope;
- Provide a means to ensure that gases are not compressed to a pressure that approaches that with will cause decomposition of the gas;
- Provide redundant temperature monitors, alarms and interlocks that will take the process to a safe condition if the temperature of the compressor heads or cooling water exceeds a predetermined safe level;
- Provide dry air or inert gas purges to shaft seals or packings on all solids handling equipment;
A few of the many possible causes of uncontrolled reactions associated with self-reactive materials include the following:

- External fire
- Building or process temperature control fails high
- Loss of building or process cooling
- Excess heating or drying
- Contact with hot surface/equipment
- Overheated seal or bearing
- Cavitation or dead-head pumping of liquid
- Adiabatic compression of self-reactive gas or vapor
- Hot work in area or on equipment containing self-reactive material
- Electric sparking or arcing
- Dropping of or impact with container
- Foreign object caught between agitator and tank wall
- Catalytic substance remains in container or equipment due to reuse, corrosion or inadequate clean-out
- Catalytic substance inadvertently added to process
- Improper material of construction or incorrect seal material, etc. in contact with substance
- Packaging material in too large of a container
- Overstacking of containers or insufficient spacing between containers
- Loss of heat transfer due to fouling, added insulation, inadequate air movement, etc.
- Concentration of diluted formulation by evaporation or distillation
- Leak or spill of substance, especially where heat transfer is minimal (e.g., insulation)
- Accumulation of dust/powder in dust collection or vent system
- No or insufficient stabilizer/inhibitor added
- Wrong substance added as stabilizer or inhibitor
- Inhibitor consumed or reacted
- Air totally displaced in vapor space of container, not allowing inhibitor to be activated
- Overheating or contamination of material disables stabilizer/inhibitor
- Material stored for longer than its recommended shelf life; inhibitor or stabilizer consumed over time
- Segregation of inhibitor or stabilizer, resulting from freezing or precipitation
- Operation at too high pressure (e.g., acetylene, ethylene, ethylene oxide)
- Tool or other equipment dropped on shock-sensitive material
- Other abnormal energy input such as by electrical discharge or friction.
4.3.1 Hazard Guide for Oxidizers and Peroxide Formers

4.3.1.1 How to identify oxidizers:
This hazard guide provides resources that should be utilized in the development of a Reactive Chemical Management System for oxidizers. These substances readily yield oxygen or other oxidizing gas, or readily react to promote or initiate combustion of combustible materials. Organic peroxides are one special class of oxidizers that may also be flammable or combustible and are often self-reactive (thermally decomposing).

Oxidizing materials are identified with an Oxidizer (OX) classification rating as a special hazard in the white (bottom) quadrant of the NFPA diamond, according to the definitions in NFPA 704 - Standard System for the Identification of the Hazards of Materials for Emergency Response. Being identified with a NFPA designation of OX is a straightforward means of identifying oxidizers. NFPA 49 and NFPA 325 give ratings for many different industrial chemicals.

In addition, oxidizers will nearly always be identified as such on their MSDSs or International Chemical Safety Cards. They may be identified as DOT/UN Hazard Class 5.1 or 5.2 materials for shipping purposes and labeled as oxidizers or organic peroxides, respectively. However, some oxidizers are classified otherwise. Chlorine, for example, is DOT/UN Class 2.3 (gases toxic by inhalation) and labeled as POISON GAS for shipping purposes; it may also be labeled as a corrosive material. Liquid oxygen is Class 2.2 (nonflammable non-toxic compressed gases) but should be labeled as NONFLAMMABLE GAS and OXIDIZER.

4.3.3.2 Definitions and Common Oxidizers

Organic peroxide – An organic compound that contains the bivalent –O–O– structure and which may be considered to be a structural derivative of hydrogen peroxide where one or both of the hydrogen atoms has been replaced by an organic radical.

Oxidation – Depending on the context, oxidation can either refer to (a) a reaction in which oxygen combines chemically with another substance, or (b) any reaction in which electrons are transferred. For the latter definition, oxidation and reduction always occur simultaneously (redox reactions), and the substance that gains electrons is termed the oxidizing agent. Electrons might also be displaced within a molecule without being completely transferred away from it.

Oxidizer – Any material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion of combustible materials. More generally, an oxidizer is any oxidizing agent.

Peroxide – A chemical compound that contains the peroxy (–O–O–) group, which may be considered a derivative of hydrogen peroxide (HOOH).
Typical Oxidizers (Johnson et al., 2003)

<table>
<thead>
<tr>
<th>Typical Oxidizer</th>
<th>Lead Dioxide</th>
<th>Silver Peroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium dichromate</td>
<td>Lead perchlorate</td>
<td>Sodium bromate</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>Lithium chlorate</td>
<td>Sodium carbonate peroxide</td>
</tr>
<tr>
<td>Ammonium perchlorate</td>
<td>Lithium hypochlorite</td>
<td>Sodium chlorate</td>
</tr>
<tr>
<td>Ammonium persulfate</td>
<td>Lithium perchlorate</td>
<td>Sodium chlorite</td>
</tr>
<tr>
<td>Amyl nitrate</td>
<td>Lithium hydroxide</td>
<td>Sodium dichloro-s-triazinetrione dihydrate</td>
</tr>
<tr>
<td>Barium bromate</td>
<td>Magnesium bromate</td>
<td>Sodium dichloro-s-triazinetrione</td>
</tr>
<tr>
<td>Barium chlorate</td>
<td>Magnesium chloride</td>
<td>Sodium dichromate</td>
</tr>
<tr>
<td>Barium hypochlorite</td>
<td>Magnesium perchlorate</td>
<td>Sodium perborate (anhydrous)</td>
</tr>
<tr>
<td>Barium perchlorate</td>
<td>Manganese dioxide</td>
<td>Sodium perborate tetrahydrate</td>
</tr>
<tr>
<td>Barium permanganate</td>
<td>Mercurochlorate</td>
<td>Sodium percarbonate</td>
</tr>
<tr>
<td>Barium peroxide</td>
<td>Monochloro-s-triazinetrione acid</td>
<td>Sodium perchlorate</td>
</tr>
<tr>
<td>Bromine pentafluoride</td>
<td>Mono-(trichloro)-tetra-(monopotassium dichloro)-penta-s-triazinetrione</td>
<td>Sodium perchlorate monohydrate</td>
</tr>
<tr>
<td>Bromine trifluoride</td>
<td>Nitric acid and fuming nitric acid</td>
<td>Sodium permanganate</td>
</tr>
<tr>
<td>1-Bromo-3-chloro-5,5-dimethylhydantoin (BCDMH)</td>
<td>Nitrogen oxides (NO₂)</td>
<td>Sodium persulfate</td>
</tr>
<tr>
<td>Calcium chlorate</td>
<td>Oxygen</td>
<td>Strontium chlorate</td>
</tr>
<tr>
<td>Calcium hypochlorite</td>
<td>Peracetic acid</td>
<td>Strontium perchlorate</td>
</tr>
<tr>
<td>Calcium perchlorate</td>
<td>Perchloric acid solutions</td>
<td>Strontium peroxide</td>
</tr>
<tr>
<td>Calcium permanganate</td>
<td>Potassium bromate</td>
<td>Tetranitromethane</td>
</tr>
<tr>
<td>Calcium peroxide</td>
<td>Potassium dichromate</td>
<td>Thallium chloride</td>
</tr>
<tr>
<td>Chloric acid (10 percent maximum concentration)</td>
<td>Potassium chlorate</td>
<td>Trichloro-s-triazinetrione (trichloroisocyanurate) (acid all forms)</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Potassium dichloro-s-triazinetrione (potassium dichloroisocyanurate)</td>
<td>Urea hydrogen peroxide</td>
</tr>
<tr>
<td>Chlorine trifluoride</td>
<td>Potassium percarbonate</td>
<td>Zinc bromate</td>
</tr>
<tr>
<td>Chlorosulfonic acid</td>
<td>Potassium perchlorate</td>
<td>Zinc chloride</td>
</tr>
<tr>
<td>Chromium trioxide (chromic acid)</td>
<td>Potassium permanganate</td>
<td>Zinc permanganate</td>
</tr>
<tr>
<td>Copper chloride</td>
<td>Potassium peroxyde</td>
<td>Zinc persulfate</td>
</tr>
<tr>
<td>Guanidine nitrate</td>
<td>Potassium persulfate</td>
<td>Zinc peroxide</td>
</tr>
<tr>
<td>Halane (1,3-dichloro-5,5-dimethylhydantoin)</td>
<td>Potassium superoxide</td>
<td></td>
</tr>
<tr>
<td>Hydrogen peroxide solutions</td>
<td>n-Propyl nitrate</td>
<td></td>
</tr>
</tbody>
</table>

4.3.3.3 General Guidance on Handling Oxidizing Materials and Peroxide Forming Materials

Inadvertent contact of oxidizers with reducing agents, including combustible materials, is the most important issue regarding what can go wrong when handling oxidizing substances (Johnson et al., 2003). This contact will increase the burning rate of the combustible materials; it may also cause a fire to ignite without any additional ignition source. Some oxidizers can also undergo self-sustained decomposition, vigorously or explosively, when contaminated or exposed to heat.

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12 The table was derived from NFPA 49 and Appendix B of NFPA 430 which list some typical oxidizers. It is by no means a complete list. Organic peroxides are not included individually in this list. NFPA 432 can be consulted for typical organic peroxide formulations. Volume 2 of Bretherick’s Handbook (Urben 1999, 287-291) lists many structures and individual chemical compounds having oxidizing properties.
or shock. Possible causes of uncontrolled reactions associated with oxidizers include abnormal events such as:

- Leak or spill of oxidizer from its containment
- Contamination of oxidizer with material that will promote or initiate its decomposition
- Water-soluble oxidizer dissolved in water, which contaminates packing material, pallets, or drainage system
- Contact of oxidizer with heated surface
- Overheating of room or process containing oxidizer
- Involvement of both oxidizer and combustibles in building fire
- Improper disposal of off-specification or spilled oxidizer
- Re-use of containers without sufficient cleaning
- Inadvertent mixing of oxidizer with reducing agent/combustible material in process equipment
- Common dust collection system used for solid oxidizer and reducing agent/combustible material.

NFPA 430, Code for the Storage of Liquid and Solid Oxidizers, gives recognized and generally accepted good engineering practices for controlling liquid and solid oxidizer hazards. For gaseous oxidizers, codes, standards, and recommended practices will be specific to the actual oxidizer in use. For example, Chlorine Institute publications (www.chlorineinstitute.org) should be consulted when chlorine is the oxidizer of concern. The Compressed Gas Association (www.cganet.com) is another source to be consulted for other gaseous oxidizers such as oxygen.

**Organic peroxides (CCPS, 1995)** – The organic peroxides are a class of chemicals that have a peroxide (O-O) bond with organic substituents. Organic peroxides are commercially important because they are relatively unstable. They are readily decomposed by heat or chemical agents, yielding free radicals that function as polymerization initiators and curing agents. The same instability that makes organic peroxides useful requires that special precautions be taken in their storage and handling. If not handled properly, organic peroxides can be extremely hazardous. However, the degree of hazard differs from product to product. Some peroxides, such as methyl ethyl ketone (MEK) peroxide, are so reactive they are not commercially available in concentrations over 60%. Explosive decomposition of dibenzoyl peroxide can be initiated by friction if allowed to dry and be carelessly handled. However, many other organic peroxide formulations are no more hazardous than ordinary combustibles.

The primary hazards involved in the safe storage and handling of organic peroxides are thermal sensitivity and, in many cases, flammability or combustibility. In addition, the stability of organic peroxides can be significantly affected by various contaminants.
All organic peroxides should be considered flammable or combustible unless and until the specific flammability characteristics are known. Most will burn vigorously once ignited, and some are susceptible to detonation if not diluted (such as dry benzoyl peroxide) or if confined when decomposition occurs.

Organic peroxides also all exhibit sensitivity to heat, which increases with the reactivity of the peroxide. Organic peroxides are constantly undergoing decomposition, at a rate that is dependent on the temperature of the material. When thermal energy available from the heat of decomposition exceeds the rate of heat dissipation to the surroundings, the increasing temperature accelerates the decomposition of the remaining peroxide. This may proceed out of control in a characteristic “runaway reaction” decomposition. The danger of runaways is increased for some peroxides, such as cumene hydroperoxide, because the decomposition is autocatalytic; i.e., the decomposition products catalyze further decomposition and cause the reaction to self-accelerate.

Accelerated decomposition of organic peroxides can also be caused by chemical contamination. Certain chemicals initiate rapid decomposition at ambient temperatures. These hazards demonstrate the importance of safety in the storage and handling of organic peroxides.

NFPA 432, Code for the Storage of Organic Peroxide Formulations, provides recognized and generally accepted good engineering practices for specific details of organic peroxide storage arrangements. This standard also gives a classification of organic peroxide formulations relative to their decomposition and flammability hazards.

4.3.4 Hazard Guide for Water Reactive Materials

4.3.4.1 How to identify water reactive materials:
This hazard guide provides resources that should be utilized in the development of a Reactive Chemical Management System for water reactives. These substances readily react with water humid air which often promotes or initiates combustion of combustible materials or flammable off gasses.

Water reactive materials are identified with a $\Psi$ classification rating as a special hazard in the white (bottom) quadrant of the NFPA diamond, according to the definitions in NFPA 704 - Standard System for the Identification of the Hazards of Materials for Emergency Response. NFPA 49 and NFPA 325 give ratings for many different industrial chemicals.

In addition, water reactives will nearly always be identified as such on their MSDSs or International Chemical Safety Cards. They may be identified as DOT/UN Hazard Class 4.2 or sometimes 4.3 materials for shipping purposes and are labeled as Dangerous when wet or
Spontaneously Combustible solid, respectively. Not all DOT 4.3 combustible solids are water reactive but many water reactives are also 4.3 combustible solids.

4.3.4.2 Definitions and Common Water Reactives
A large number of compounds react exothermally and violently with water, particularly with restricted amounts of the water. Many of these compounds fall within the groups: acid anhydrides, acyl halides, alkali metals, alkylaluminium derivatives, alkynon-metal halides, complex hydrides, metal halides, metal hydrides, metal oxides, non-metal halides (and their oxides), non-metal oxides. These compounds are sometimes identified with the symbol W below the NFPA ratings. Please be aware that the absence of W in the ratings area does not necessarily mean the compound is not water reactive. For the final word one must check the chemical compatibility section of the MSDS.

Some Chemical Categories Susceptible to Water Reactivity

<table>
<thead>
<tr>
<th>Category</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali and alkaline-earth metals</td>
<td>Calcium, potassium, sodium, lithium</td>
</tr>
<tr>
<td>Anhydrous metal halides</td>
<td>Aluminum tribromide, germanium tetrachloride, titanium tetrachloride</td>
</tr>
<tr>
<td>Anhydrous metal oxides</td>
<td>Calcium oxide</td>
</tr>
<tr>
<td>Chlorosilanes</td>
<td>Methylidichlorosilane, trichlorosilane, trimethylchlorosilane</td>
</tr>
<tr>
<td>Epoxides (e.g., with acid present)</td>
<td>Butylene oxide, ethylene oxide, diepoxy butane, epibromohydrin</td>
</tr>
<tr>
<td>Finely divided metals (no oxide film)</td>
<td>Aluminum, cobalt, iron, magnesium, titanium, tin, zinc, zirconium</td>
</tr>
<tr>
<td>Grignard reagents; organometalics</td>
<td>Ethylmagnesium chloride, methylmagnesium bromide</td>
</tr>
<tr>
<td>Inorganic acid halides</td>
<td>Phosphoryl chloride, sulfuryl chloride, chlorosulfonic acid</td>
</tr>
<tr>
<td>Inorganic cyanides</td>
<td>Barium cyanide, calcium cyanide, cyanogen chloride, silver cyanide</td>
</tr>
<tr>
<td>Isocyanates</td>
<td>n-Butyl isocyanate, methyl isocyanate, toluene diisocyanate</td>
</tr>
<tr>
<td>Metal alkyls</td>
<td>Triethylaluminum, Butyl lithium</td>
</tr>
<tr>
<td>Metal amides</td>
<td>Lead amide, potassium amide, silver amide, sodium amide</td>
</tr>
<tr>
<td>Metal hydrides</td>
<td>Calcium hydride, lithium aluminum hydride, sodium borohydride</td>
</tr>
<tr>
<td>Non-metal hydrides</td>
<td>Boron trifluoride, phosphorus trichloride, silicon tetrachloride</td>
</tr>
<tr>
<td>Nonmetal oxides</td>
<td>Phosphorus pentoxide, sulfur trioxide</td>
</tr>
<tr>
<td>Organic acid halides and anhydrides</td>
<td>Acetic anhydride, acetyl chloride</td>
</tr>
<tr>
<td>Nitrides, phosphides and carbides</td>
<td>Aluminum phosphide, calcium carbide, gallium phosphide</td>
</tr>
</tbody>
</table>

13 Bretherick’s Reactive Chemical Hazards
### Some Materials That React with Water

<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction Product</th>
<th>Reaction Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Anhydride</td>
<td>Diethylaluminum hydride</td>
<td>Phosphorus oxychloride</td>
</tr>
<tr>
<td>Acetyl chloride</td>
<td>Diethylzinc</td>
<td>Phosphorus pentachloride</td>
</tr>
<tr>
<td>Alkyl aluminums</td>
<td>Diketene</td>
<td>Phosphorus pentasulfide</td>
</tr>
<tr>
<td>Allyl trichlorosilane</td>
<td>Diisobutylaluminum hydride</td>
<td>Phosphorus tribromide</td>
</tr>
<tr>
<td>Dipropylaluminum hydride</td>
<td>Dimethyldichlorosilane</td>
<td>Phosphorus trichloride</td>
</tr>
<tr>
<td>Aluminum chloride (anhydrous)</td>
<td>Diphenyldichlorosilane</td>
<td>Potassium, metal</td>
</tr>
<tr>
<td>Aluminum phosphide</td>
<td>1,2-Ethanediol Diformate</td>
<td>Potassium-sodium alloys</td>
</tr>
<tr>
<td>Amyl trichlorosilane</td>
<td>Ethyl Chloroformate</td>
<td>Propionic anhydride</td>
</tr>
<tr>
<td>Benzoyl chloride</td>
<td>Ethylidichlorosilane</td>
<td>Propionyl chloride</td>
</tr>
<tr>
<td>Boron tribromide</td>
<td>Ethyl oxalate</td>
<td>Propyrltrichlorosilane</td>
</tr>
<tr>
<td>Boron trifluoride</td>
<td>Ethyl silicate</td>
<td>Silicon tetrachloride</td>
</tr>
<tr>
<td>Boron trifluoride etherate</td>
<td>Ethyl trichlorosilane</td>
<td>Silicon tetrafluoride</td>
</tr>
<tr>
<td>Bromine pentafluoride</td>
<td>Ethylaluminum dichloride</td>
<td>Sodium, metal</td>
</tr>
<tr>
<td>Bromine trifluoride</td>
<td>Ethylaluminum sesquichloride</td>
<td>Sodium dichloro-s-triazinetron dihydrate</td>
</tr>
<tr>
<td>Butylacrylate</td>
<td>Fluorine</td>
<td>Sodium hydride</td>
</tr>
<tr>
<td>n-Butyl isocyanate</td>
<td>Gallium arsenide</td>
<td>Sodium hydrosulfite</td>
</tr>
<tr>
<td>Butyl lithium</td>
<td>Gallium phosphide</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>Butyric anhydride</td>
<td>Germane</td>
<td>Sulfur chloride</td>
</tr>
<tr>
<td>Calcium, metal</td>
<td>Isobutyric anhydride</td>
<td>Sulfur dichloride</td>
</tr>
<tr>
<td>Calcium carbide</td>
<td>Isophorone diisocyanate</td>
<td>Sulfuryl chloride</td>
</tr>
<tr>
<td>Calcium chloride</td>
<td>Lithium, metal</td>
<td>Tetraethyl lead</td>
</tr>
<tr>
<td>Capryl chloride</td>
<td>Lithium aluminum hydride</td>
<td>Tetramethyl lead</td>
</tr>
<tr>
<td>Chlorine trifluoride</td>
<td>Lithium hydride</td>
<td>Titanium tetrachloride</td>
</tr>
<tr>
<td>2-Chloropropionyl chloride</td>
<td>Thionyl chloride</td>
<td>Tributyl phosphate</td>
</tr>
<tr>
<td>Chlorosilanes</td>
<td>Methylaluminum sesquibromide</td>
<td>Trichlorosilane</td>
</tr>
<tr>
<td>Chlorosulfonic acid</td>
<td>Toluene-2,4-disocyanate</td>
<td>Triethylaluminum</td>
</tr>
<tr>
<td>Chromium oxychloride</td>
<td>Methylaluminum sesquichloride</td>
<td>Triethylborane</td>
</tr>
<tr>
<td>Cyanamide</td>
<td>Methyl borate</td>
<td>Trihexyl phosphate</td>
</tr>
<tr>
<td>Decaborane</td>
<td>Methylidichlorosilane</td>
<td>Trisobutylaluminum</td>
</tr>
<tr>
<td>Diborane</td>
<td>Methyl isocyanate</td>
<td>Trimethylaluminum</td>
</tr>
<tr>
<td>Dichloroacetyl chloride</td>
<td>Methyleneediisocyanate</td>
<td>Trimethylchlorosilane</td>
</tr>
<tr>
<td>Dichlorosilane</td>
<td>Methyl lactate</td>
<td>Tripropylaluminum</td>
</tr>
<tr>
<td>Diethylaluminum chloride</td>
<td>Methylpentadecane</td>
<td>Vanadium tetrachloride</td>
</tr>
<tr>
<td>Diethylamine)ethy Acrylate</td>
<td>Methyltrichlorosilane</td>
<td>Vinyl trichlorosilane</td>
</tr>
<tr>
<td>Diethyl carbamyl chloride</td>
<td>Monochloro-s-triazinetron acid</td>
<td>Zirconium tetrachloride</td>
</tr>
<tr>
<td>Diethyl telluride</td>
<td>Mono-(trichloro) (monopotassiumdichloro)- penta-s-triazinetron</td>
<td></td>
</tr>
</tbody>
</table>

#### 4.3.4.3 General Guidance on Handling Water Reactive Materials

With water being ubiquitous in most manufacturing settings, care must be taken to exclude these compounds from all potential sources of water. Sources of water include floor washing, fire sprinklers, humid air and many others. Water reactives are best handled in sealed, inerted systems if at all possible. Often with water reactive solids this is not possible and inadvertent commingling with water must be considered a highly credible mixing scenario for purposes of this tool or the Process Hazard Review.
In addition to heat generation one must pay attention to the possibility of flammable, toxic or corrosive gas emission in the presence of water or moist air. Many compounds with low water solubility react only slowly at first, erupting unexpectedly and violently upon mixing by either mechanical means or by gas evolution or boiling. Examples of this are chunk sodium metal, oxalyl chloride, Phosphorous Oxchloride. Many liquid acid chlorides can phase separate from water to create this phenomenon. One must be careful of this phasing during “controlled” water quenches of these compounds. Often reactor sensors will give little clue (until it is too late) that dangerous amounts of water are building up in the presence of the water reactive being quenched. One must also be aware that aqueous waste from a water reactive quench may still contain phase separated water reactives which will continue to react, causing a burst drum. Analytical testing should assure complete quench prior to drumming or otherwise disposing of the waste. Relying on a loose drum bung for venting of an incomplete quench is a recipe for disaster. Sealing of water reactive compounds in non-inerted or poorly inerted drums can cause drum bulging or rupture from slow reactivity (and subsequent gas production) with the moist air within.

What Can Go Wrong?

Inadvertent contact of a water-reactive material with water is obviously the most important issue regarding what can go wrong. Due to the prevalence of water in living tissues, water-reactive materials are often toxic or corrosive as well, so loss of containment is often an additional concern. The following are some of the possible causes of uncontrolled reactions associated with water-reactive materials:

- Inadequate drying or purging of equipment before adding material
- Humidity in incoming air or gas
- Leakage of water from cooling coil into process
- Water line connected and valved in
- Aqueous instead of anhydrous raw material added
- Anhydrous instead of aqueous raw material received or selected
- Rainwater, sprinkler water, etc. onto cardboard container
- Cleanouts for maintenance
- Steam-out of equipment before use
- Piping/vessel/container punctured
- Piping/vessel/container corroded
- Spill into dike or trench containing water
- Mechanical failure of piping or tubing
- Uncontrolled mixing of reactive phases.
4.4 Developing Credible Scenarios
A process hazard analysis (PHA) is a structured approach to search a chemical process for hazards. It answers the question “What can go wrong?” For the purpose of the Reactivity Management Tool we are searching for reactivity hazards in the process. The CCPS Risk Based Process Safety Management (RBPS) system and the OSHA Process Safety Management Standard (PSM) require that a process hazard analysis be done on chemical processes. RBPS requires a PHA on all chemical process while OSHA PSM requires a PHA on processes with listed chemicals at or above the threshold quantities.

Some companies have a structured a review process that specifically focuses on identifying reactivity hazard scenarios and evaluating the need for safe guards. Other approaches include the use of traditional hazard evaluation techniques including:

- Hazop
- FMEA
- What if
- Check list
- What if/Check List

“What if” analysis is a brainstorming method that asks the question “what if” for the process being evaluated. For example, the question could be asked “what if catalyst is not charged at the right time?” The consequence may be layering of unreacted material with the chance of a sudden exothermic reaction when catalyst is added. The scenario would be “adding catalyst at the wrong time resulting in a sudden exothermic reaction of A and B”. This approach requires an experienced team with the expertise to ask all the relevant “what if” questions so all the reactivity scenarios are identified.


If you have done a PHA on the process of concern, you can enter the scenarios identified in the PHA into the Reactivity Management tool program.

If you have not done a PHA, the program will step through a check list of questions you can use to identify reactivity scenarios (What can go wrong).

Examples include:

- Loss of utility scenarios
  For example a loss of electrical power could shut down a critical reactor cooling water pump with a loss of cooling resulting in overpressure of the reactor and loss of containment.

- Process variation or upset scenarios
  For example, if a process is normally run at a temperature close to the onset temperature of a runaway reaction, a process upset may result in the temperature of

---

the process exceeding the onset temperature resulting in a runaway reaction and loss of containment.

- Energy input or variation scenarios
  For example, if 150 psig steam is used to heat up a reactor, and a regulator failure results in 400 psig steam inadvertently flowing to the reactor, the higher temperature of the steam may result in an unanticipated rate of reaction or a runaway reaction.

- Mechanical failure scenarios
  For example, if agitation is lost while reactants are being added into a reactor, the lack of mixing may result in a layering of reactants that could suddenly mix with a heat generation rate exceeding the heat transfer capacity of the reactor resulting in over pressure and lack of containment.

- Inadvertent mixing and wrong material of construction scenarios
  For example, if caustic is inadvertently added to a sulfuric acid storage tank, the unanticipated heat of reaction may result in overpressuring the tank and a loss of containment.

- Human error scenarios
  For example, the scenario above could be caused by the operator inadvertently connecting the caustic unloading hose to the inlet piping of the sulfuric acid storage tank.

- Any other scenarios
  - The intended chemistry should be evaluated as a scenario. Also any strong interactions identified by the binary interaction matrix should also be evaluated.
  - Careful analysis by a team of process experts may identify other reactive scenarios of concern.

You may want to step through the check list questions to identify additional reactivity scenarios you may have missed during the PHA.

4.5 Determining Heat of Reaction

4.5.1 Calculating heat of reaction
A quick estimation of the heat of reaction can be determined using Benson groups. A convenient way to do these calculations is with a program such as CHETAH®.15

Entering the reaction Acetophenone + Bromine → Bromoacetophenone + HBr into CHETAH® results in a ΔH_rxn value of -3.96Kcal/mole. This converts to -16.6 kJ/mole

15 See www.astm.org
The molecular weight of acetophenone = 120.2g/mole
The molecular weight of bromine is 159.8g/mole

Thus the total weight of a 1 mole reaction would be 120.2 + 159.8 = 280g = 0.28kg

Set up the ratio:

Thus we have estimated the reaction energy of this interaction to be -59.3 kJ/kg
This must be entered into the program as a positive number because it results in an exotherm.

4.5.2 Crude experimental methods for estimating heat of reaction

Presented here is a quick but crude method to assess heats of reaction experimentally. One or both materials must be a liquid. This method is unlikely to properly assess reactivity between two dry solids.

Safety Note: in a case such as this one where an explosion is predicted a pre-test on milligram scale is recommended. Take a minute amount of the first material, place on a non-porous surface inside a fume hood and behind a blast shield. Carefully add a minute amount of the second reagent using a long handled spatula or pipette and observe several minutes for reaction.

Small amounts of the reactants can be quickly mixed on a well insulated flask or dewer. This method will ALWAYS give lower than actual exotherm results. Small volume reactions have very high heat transfer to the environment and also a large sample mass to container mass ratio. To get an accurate heat value requires absolute adiabaticity and a phi = 1- neither condition is met by this method. The phi-factor is the ratio of the thermal mass of the sample and sample holder to the thermal mass of the sample alone.

Possible procedure:

- The reactants must be at room temperature.
- Put the stir bar into the flask and begin stirring.
- Add approximately 5ml or 5g the liquid reagent at room temperature.
- Insert thermocouple or thermometer into liquid
- Begin stirring and allow thermocouple to settle
- Install secondary blast protection
- Carefully add 5ml or 5g of the second material
Observe and record temperature for at least 5 min or until it stops rising and starts to fall.

Subtract the Highest temperature recorded from the start temperature this will be your crude adiabatic heat rise. Remember this value is less than your actual value and there is no good way of estimating how much less. The longer it took for the maximum temperature to be reached or the higher the temperature reached the worse the accuracy of your results will be.

You must guess the heat capacity of the solution. Usually ~2 kJ/°C*kg for organics and ~4 kJ/°C*kg for aqueous solutions.

**Example calculation:**
Upon mixing, the reaction temperature proceeded from 22°C to 62.5°C and then started to drop as recorded in the data set below

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>22</td>
</tr>
<tr>
<td>30</td>
<td>23</td>
</tr>
<tr>
<td>60</td>
<td>25</td>
</tr>
<tr>
<td>90</td>
<td>28</td>
</tr>
<tr>
<td>120</td>
<td>35</td>
</tr>
<tr>
<td>150</td>
<td>50</td>
</tr>
<tr>
<td>180</td>
<td>60</td>
</tr>
<tr>
<td>187</td>
<td>62.5</td>
</tr>
<tr>
<td>200</td>
<td>60</td>
</tr>
</tbody>
</table>

\[ \Delta T_{ad} = 62.5°C - 22°C = 40.5°C \]

Assume an organic reaction so heat capacity estimate will be 2 kJ/°C*kg

\[ 40.5°C \times 2 \text{ kJ/°C*kg} = 81 \text{ kJ/kg} \]

This result may be entered directly into the scenario heat of reaction box without changing the sign as it already denotes an exotherm. In the case of large heat rises such this it would be a good idea to add a margin of safety to this value – perhaps multiplying it by two or three to compensate for the non-adiabaticity of the test.

**Common miss-uses of this method**
- Running above ambient temperature
- Using a heating or cooling bath instead of dry insulation or a dewer.
- Experiment reaches maximum temperature more than 5 minutes after mixing

**4.5.3 Reaction calorimetry for heat of reaction determination**
By far the best way to definitively determine the heat of reaction is using a reaction calorimeter. Calorimeters vary widely in price and in actual fact any jacketed reactor that measures Tr and Tj can be used as a calorimeter once properly calibrated. The heat of reaction data required to assess safety does not need to be accurate to the third decimal place. In fact plus or minus 10 or even 20% is quite acceptable. One wonders whether one should actually be scaling up a reaction
that is declared safe because the uncertainty of the measurement has been reduced to a few percent from 10 or 20%. Calibration methods for jacketed flasks can be as simple as performing an acid base reaction of known energy.

It is highly recommended that users pursue testing in a real calorimeter when heats of reactions become large or when the evaluation of the process scenario cannot determine the safety of the scenario. There are many consulting and testing laboratories throughout the world eager and able to help for the proper fee. This is money well spent considering the consequences a severe reactivity incident.

4.6 Calculation of Adiabatic Temperature Rise and MTSR

The program provides the user two methods of entering the adiabatic temperature rise. You can enter the value directly or have the program calculate it for you from the Heat of reaction you have entered previously and a heat capacity.

The starting temperature is needed for each reaction in question. Since a chemical interaction or decomposition may be occur under a variety of starting conditions in different equipment, the same reactivity may need to be evaluated multiple times using different parameters for each. The heat capacity of the reaction mixture is also needed. For organic systems, in the absence of any other data, a value of 2 J/g°C can be used most aqueous systems have a heat capacity of 3 to 4J/°C.

Once the program has the adiabatic temperature rise it adds this value to the Starting temperature to obtain an MTSR for the scenario. It is important that you compare this MTSR to any decomposition onset that is not included in the heat of reaction value inputted earlier. If the MTSR exceeds the decomposition onset minus an appropriate safety margin then the decomposition energy must be added to the heat of reaction and the MTSR recalculated using the larger heat of reaction value.

A temperature of concern needs to be established. These values are determined by the user but may include values such as the maximum allowable temperature of the equipment, the onset temperature of a runaway reaction, or some other value.

4.7 Determining Temperature of Concern

A temperature of concern needs to be established. The temperature of concern is the temperature that results in an unsafe condition or incident. These values are determined by the user and are specific to the process being evaluated. The temperature of concern should be selected as the lowest temperature that results in an unacceptable safety risk. This requires an understanding of the process and the processing equipment.

Examples include:
- The maximum allowable temperature of the equipment
- The onset temperature of a decomposition leading to gas evolution or thermal runaway
- The temperature that produces an over pressure in a sealed vessel - remembering that normally vented vessels can and do get sealed by mistake or failure
The temperature that increases the reaction heat output beyond the heat removal capacity of the vessel (runaway reaction)
- The temperature that increases the gas generation rate beyond the vessel's ability to vent
- The temperature at which gas evolution causes unacceptable swelling or foaming
- The flash point of the reaction mixture when inerting is not present (more conservatively the fire point)

Examples of conditions not usually chosen
- The temperature at which unacceptable product or yield occurs (not safety related)
- The boiling point of the reaction mixture unless the vapors present a safety concern

There are some cases such as some uncontained spill scenarios involving non-combustibles producing non-combustible products\(^\text{16}\) where there may not be a temperature of concern. In this case just input a large number as heat is not a safety risk factor.

### 4.8 Determining Maximum Reaction Pressure

The maximum reaction pressure needs to be determined for the reaction in question. This pressure is not only a function of the gas generated by the reaction but also the vapor pressure of the components in the reaction mixture. For this reason, not only is the amount of gas generated needed, but the starting pressure and temperature, the heat of reaction, the heat capacity, the vapor space available, and the vapor pressure of the mixture.

The data needed to conduct this calculation includes stoichiometry of the reaction which includes the quantity of gas generation, the starting temperature, the starting pressure, and the heat of reaction. Details about the specific equipment being used are also needed such as the amount of material present and the available vapor space.

For a known reaction that generates gas, such as a synthesis reaction, determination of the stoichiometry is straightforward. However, in the case of a decomposition reaction, literature, testing, or calculation will likely be needed to determine the products of the reaction. In this case, calculation of the products of the reaction can grossly over predict the amount of gas generation if the calculation depends on the maximization of enthalpy. Minimization of Gibb's free energy is the preferred calculation method.

#### 4.8.1 Calculating P\text{max} for Napp Scenario from 5.2 Worked Examples

We know from the CSB report that the adiabatic heat rise of the ACR 9031 is 486\(^\circ\)C. Thus even a little water would initiate a self-sustaining decomposition throughout the batch.

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\(^{16}\) An example is a spill on the processing floor of 37% hydrochloric acid and sodium chloride the result of a pallet falling off a forklift causing the drums to burst open. The product will be hydrogen chloride gas and salt water. This may have serious consequences because of toxic gas or corrosion but the temperature of the resulting mixture will - in most cases - be inconsequential to the hazardous conditions created because none of the products have a flashpoint or autoignition temperature.
Thus the blender charge would be:

*5400 lb = 2115.5 kg Na2S2O3 molecular weight 158g/mole

\[
\frac{2,115,500g}{158g/mole} = 13,389 \text{ moles Na2S2O3}
\]

Each mole of decomposing Na2S2O3 gives off 1 mole of SO2 thus 13,389 moles of SO2 are released on complete decomposition.

*900 lb = 335.9 kg K2CO3 molecular weight 138 g/mole

\[
\frac{335,900g}{138g/mole} = 2434 \text{ moles}
\]

Each mole of decomposing K2CO3 gives off 1 mole of CO2 thus 2434 moles of CO2 are released on complete decomposition.

\[
P = \frac{nRT}{V}
\]

- \( R = 0.083 \text{ bar*L/mole*K} \)
- \( T = 779K : 7293K \text{ (20°C starting temp) + 486 (adiabatic heat rise)} \)
- \( V \text{ Assumed from drawing in CSB report that head volume is roughly equal to the fill volume of } 6 \text{ m}^3 = 6 \text{ m}^3 = 6,000L \)
- \( n = 9,948 = 8354 \text{ moles Na2S2O3} + 1594 \text{ moles CO2} \)

\[
P = 0.083*15823*779/6000=175 \text{ bar or } 2572.5 \text{ psig.}
\]

In the above calculation, if the relief valve on the reactor is set at 100 psig. (Pressure of concern) there will be a release and loss of containment.

**4.9 Determining Pressure of Concern**

A pressure of concern needs to be established. The pressure of concern is the pressure that results in an unsafe condition or incident, this value is determined by the user and may include values such as the maximum allowable working pressure of the equipment, the set pressure of a relief device on the equipment, or some other value. The pressure of concern can result in a loss of containment, equipment failure and injury to personnel from thermal effects, explosion, shrapnel or toxic release.
4.10 Determining the Validity of Information from Matrix Reports

The matrix reports generated are extremely conservative. If any compound with a certain functional group is known to react with another - ALL chemical pairs with the same reactivity group pairings are flagged as having that reactivity. The reactivity matrix should be used as the starting point for where to look for reactivity problems - NEVER as the definitive answer to what reactivities will occur.

The outputted reports must be checked for accuracy prior to taking action or determining that no action is required. The reactivity matrix is based on functional group reactivities and makes sweeping generalizations to accomplish these reactivity predictions. This will result in the possibility of a small number of false negatives where no reactivity is predicted by the tool but reactivity does actually exist. By far the majority of the inaccuracies will be over prediction of reactivity. This is a conservative approach that can cost a lot of time and money on remediation of problems that do not exist. It is recommended that all predictions of violent reactivity be investigated safely on a very small scale to confirm the CRW2 predictions.

The warehousing segregation matrix is even more likely to produce conservative separations because it’s algorithm relies on only a handful DOT labels which are essentially high level reactivity categories. Chemicals marked in the program with a label of “unknown”, “Radioactive” or “explosive” result in very large separation predictions. Utilizing the reactivity matrix produced above may allow the more savvy user to significantly reduce predicted segregations. It is strongly suggested that the reactivity matrix be checked by testing before attempting any reduction of segregation distances. The segregation matrix makes no attempt to segregate water reactive compounds from sources of water such as warehouse fire protection or drains. The user should always be mindful of the potential consequences or fate of any potential spill when selecting a storage facility.
5 Worked Examples

5.0 Common Preliminary Steps

5.0.1 Starting the program
The program is located in the all programs menu under “Reactivity Management Tool”.
The program will open to a CCPS splash screen followed by an information screen. This screen
has the option to check a box “do not show again”. You can view this information screen again
by going to “File”, “disclaimer”

5.0.2 Process Tab
• Open a new process in the RMT. By pressing the “create process” button on the
  Process tab.
• Enter “Process 1” in the Process name field
• Enter “Building 1” in the Facility name. See section 4.1 for help in selecting the proper scope of your evaluation.
• Save your entries with the “save” button before pressing “Next”

5.0.3 Team Members Tab
• Select the “Add” button to enter information on at least on evaluation team member. Use the save button before moving to next screen
• Team members can be edited by double clicking on the members name or they can be deleted by checking the box in front of their name and pressing the delete button.

5.0.4 Laboratory Scale facility Tab
• You are now asked if your operation is defined as a “Laboratory Operation”. Choosing yes terminates the program. The default answer is No with next taking you on in the program. Press the “help” button for a definition of Laboratory operations.

5.0.5 Process Chemicals tab – searching for chemicals
• Press the “Search Chemical Databases” button to begin by searching the NOAA CAMEO database for your chemicals. Note: if you have entered custom chemicals in your RMT custom database these are searched at the same time.
• Enter the name of your first chemical in the pop-up search box and press search button.
• Utilize several different options to either widen or narrow your search results. Be persistent the NOAA CAMEO database has many synonyms for each chemical but sometimes a slight name difference between your entry and the synonyms will prevent a search hit. CAS number is very helpful. Be sure to enter the dashes in their proper place. Toggling the “contains” or “starts with” you can expand, shrink or sometimes even get a few different hits. Completing 2 fields produced an “and” search. Note the official name will appear in the search hits window name field. If you search “THF” your hits will read “tetrahydrofuran”
• Search through your hits for your desired chemical. Check the box in front of the name. (you may make multiple selections.) them press the Add to process” button

• To search your next chemical simply type over the last chemical name and hit “search”
• When you have finished searching use the close button to return to the Process Chemicals Tab

5.0.6 Process chemicals Tab – RMT custom Database pop-up form
• Press the “administer Custom Chemicals” button to open the Custom Chemicals database. This data is stored where you have installed the program and never shared over a network or the internet. See special instructions for database sharing in the help guide.
• All functions of the custom chemical database are accessed from this pop-up.
  o “Export to Excel” data dumps your database to Excel 2007 or later. This is helpful for data checking.
  o “Add custom chemicals” opens another pop-up where you can input data for your own chemicals or those not found in the NOAA database.
  o “Add to Process” adds the chemicals that have a check in the box in front of their name.
○ “Delete selected Chemicals” deletes the chemicals that have a check in the box in front of their name.
○ Double clicking on the name of a chemical allows you to edit that chemical.

5.0.7 Custom Chemicals entry and editing pop-up form

- Press the “add custom chemicals” button or double click on the custom chemical you want to edit to access this pop-up form

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Do not get confused by the primary and secondary DOT labels. You MUST enter a primary DOT code in the collapsed box pointed out by the RED arrow. The much more obvious scroll bar box with the ORANGE arrow pointing to it is only for a secondary code if there is one.

- You must enter at least the following data to add a custom chemical to the database
  - Chemical name – Type in “Line Kleen”
  - PRIMARY DOT code – select “Corrosive – acid”
  - At least one reactivity group –
  - At least one Special Hazards group

- Entering Reactivity groups.
  - All applicable MUST be selected. Hold down the “Ctrl” key and select with the left mouse button or space bar. This information is only available by viewing the chemical structure. Often the structure can be found by searching the chemical
name or CAS number on the Web. **Failure to select all applicable groups or selection of improper groups will give false reactivity predictions that might cause the program to miss a serious chemical reactivity issue. Selection of the proper groups may require the expertise of a trained chemist knowledgeable in both chemical reactivity and chemical nomenclature.**

- Note there are groups that start with the number 101 and higher that are not utilized by the program. You MUST however enter “100 Water” if the material contains more than trace amounts of water. An example would be the hydrate of a metal salt.

- Entering “Special hazards Group”
  - All applicable must be selected or “none”
    - For Line Kleen enter “none”
  - This information will be found in the NFPA diamond or disbursed throughout the MSDS.

5.0.7.1 Entering chemicals not found in the NOAA database

Entering the custom chemical Line Kleen™

- Type “Line Kleen” into the chemical name box
- **PRIMARY DOT code** – select “Corrosive – acid”
- Make no selection under secondary DOT because there is not one listed in the MSDS
- Reactivity groups: select the following by holding down the “Ctrl” key. Using the scroll bar and the left mouse button select the following. They will gray out when selected.
  - “1 Acids – inorganic non-oxidizing” because MSDS lists Phosphoric acid
  - “38 Salts acidic inorganic” because it is assumed that the solution is pH is buffered
  - “100 water” because water is an ingredient
- Special Hazards group
  - Select “none”

5.0.7.2 Editing Chemicals in the Administer custom chemicals pop-up form

- Double click on “water”
- The edit form for water will pop-up.
- Select a primary DOT label of “non-hazardous”
- Press save and then close
5.0.7.3 Adding custom chemicals to the process

- Select Water, Syltherm, Line Kleen and compound 987654321 by checking the boxes in front of the names in the Administer custom chemicals pop-up form.
- Press the “Add to Process” button then close the pop-up. This will return you to the Process Chemicals tab
Use the scroll bar to view all the chemicals entered for the process.
Use “Export to Excel” to data check all entries.
Note the form tells you where the chemical information resides under DB identification
When satisfies with all entries, press “next”

5.0.8 Missing Data Warning box
This box performs two functions. It serves as a double check for custom chemicals data and is an input form for DOT labels. The DOT codes are required for the warehouse segregation function of this tool. The program will not allow the user to continue until all required data has been entered.
If the next button does not work recheck that at least a primary DOT code and at least one reactivity group has been entered for each chemical. Use the scroll bar on the bottom to scroll right to see the reactivity group column.

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5.0.9 Warehousing vs. Chemical Processing

The program seeks to determine if the Facility being evaluated is solely a Warehouse or if other operations are performed there. Press the Help button or see the help guide for definitions.

- Press the Next button to move on to the next section of the evaluation.

Note to assure a complete report: you must check the box for chemical processing and then the Next button. You need not go any further in the protocol if you are doing only warehousing. Simply close the process window and open the reports window. See Appendix G: Known Programming Bugs and Appendix B: FAQ.
This completes the preliminary data entry section common to all worked examples:
Jump to Napp Technologies
Jump to XYZ Pharmaceutical Intentional Chemistry Example

5.1 Warehousing Example
Jump to Common Preliminary Step section 5.0
Start with section 5.0 before completing these steps

This example illustrates the use of the reactivity management tool to determine how a mixture of several chemicals should be segregated in a safe manner for storage in a warehouse.

Please see sections 3.2 and 5.0 for the detailed procedure for starting the reactivity management tool and initializing a new process analysis program.

Information you will need
- The preparation for using the reactivity management tool requires you to obtain the MSDS documents for the chemicals under evaluation.
  - The information from the MSDS documents should include the primary and secondary DOT labels.
- Chemicals which are proprietary or are not in the database will require you to use other sources in the literature.
  - The information that you need will include the primary and secondary DOT labels as well as the reactivity groups, and reactivity hazards for these new or proprietary chemicals. See section 3.2
- The information provided by the reactive management tool will be a warehouse segregation grid which provides information of how you will be able to store these collective chemicals in a warehouse.
  See section 4.2 for finding and reading an MSDS.

In addition, the reactivity matrix and a Chemical reactivity evaluation report for the chemicals under evaluation will also be provided. These two documents provide additional information as to the chemical hazards of the chemicals under consideration. You will need to review these reports to make sure the warehouse segregation is consistent with the binary interaction matrix.
The list of chemicals for this warehouse example is as follows:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Primary DOT</th>
<th>Secondary DOT(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric Acid, 93%</td>
<td>8</td>
<td>Corrosive acidic</td>
</tr>
<tr>
<td>Sodium Hydroxide, 50% solution</td>
<td>8</td>
<td>Corrosive basic</td>
</tr>
<tr>
<td>tert-Butyl Hydroperoxide, 70%</td>
<td>5.2</td>
<td>Organic Peroxide</td>
</tr>
<tr>
<td>Sodium Hydrosulfide, 18-22%</td>
<td>8</td>
<td>Corrosive basic</td>
</tr>
<tr>
<td>6.1 poison</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropyl Chloroformate</td>
<td>3.1</td>
<td>Flammable Liquid</td>
</tr>
<tr>
<td>Dimethyl Sulfate</td>
<td>6.1</td>
<td>poison</td>
</tr>
<tr>
<td>Phosphorus Trichloride, 90 - 100%</td>
<td>6.1</td>
<td>poison</td>
</tr>
<tr>
<td>Ethylene Oxide</td>
<td>2.3</td>
<td>Toxic gas</td>
</tr>
<tr>
<td>Hydrochloric Acid, 33 - 40%</td>
<td>8</td>
<td>Corrosive acidic</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>Non-hazardous</td>
</tr>
<tr>
<td>Aluminum, powder</td>
<td>4.3</td>
<td>Dangerous when wet</td>
</tr>
<tr>
<td>Triethyl Aluminum</td>
<td>4.2</td>
<td>spontaneously combustible</td>
</tr>
<tr>
<td>Ethanol, denatured, 200 proof</td>
<td>3.1</td>
<td>Flammable Liquid</td>
</tr>
<tr>
<td>Chlorine</td>
<td>2.3</td>
<td>Toxic gas</td>
</tr>
<tr>
<td>Sodium Hypochlorite, 5-15% solution</td>
<td>8</td>
<td>Corrosive basic</td>
</tr>
<tr>
<td>Aqueous Ammonia, 10% solution</td>
<td>8</td>
<td>Corrosive basic</td>
</tr>
</tbody>
</table>

For detailed step by step instructions on how to enter this data, see section 3.2.1 through 3.2.8.

This is an export to Excel of the above list of chemicals used for this warehouse example,

<table>
<thead>
<tr>
<th>DBIdentification</th>
<th>Chemical_Name</th>
<th>CAS Number</th>
<th>DOT Labels</th>
<th>Chemical_Formula</th>
<th>Reactivity Ids</th>
<th>Chemical_Name</th>
<th>CAS Number</th>
<th>DOT Labels</th>
<th>Chemical_Formula</th>
<th>Reactivity Ids</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOAA</td>
<td>SULFURIC ACID</td>
<td>7664-93-9</td>
<td>8.0</td>
<td>Corrosive Acidic</td>
<td>H2SO4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOAA</td>
<td>CAUSTIC SODA, SOLUTION</td>
<td>1310-73-2</td>
<td>8.0</td>
<td>Corrosive Basic</td>
<td>NaOH (aq)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOAA</td>
<td>TERT-BUTYL HYDROPEROXIDE, NOT MORE THAN 80% IN DI-TERT-BUTYL PEROXIDE AND/OR SOLVENT</td>
<td>75-91-2</td>
<td>5.2</td>
<td>Organic Peroxide</td>
<td>C4H10O2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOAA</td>
<td>ISOXYL CHLOROFORMATE</td>
<td>108-23-6</td>
<td>0.X</td>
<td>Flammable liquid</td>
<td>C4H7CO2</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOAA</td>
<td>DIMETHYL SULFATE</td>
<td>77-78-1</td>
<td>6.1</td>
<td>Poison</td>
<td>C2H5SO3</td>
<td>10</td>
<td></td>
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<tr>
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<td>PHOSPHORUS TRICHLORIDE</td>
<td>21256-83</td>
<td>6.1</td>
<td>Poison</td>
<td>C3P2Cl2</td>
<td>30</td>
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<tr>
<td>NOAA</td>
<td>ETHYLENE OXIDE</td>
<td>75-21-8</td>
<td>2.3</td>
<td>Toxic gas</td>
<td>C2H4O</td>
<td>34</td>
<td></td>
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<td></td>
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<tr>
<td>NOAA</td>
<td>HYDROCHLORIC ACID, SOLUTION</td>
<td>7647-01-0</td>
<td>8.0</td>
<td>Corrosive Acidic</td>
<td>HCl (aqueous)</td>
<td>1, 100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOAA</td>
<td>ALUMINUM POWDER, UNCOATED</td>
<td>7429-90-5</td>
<td>4.3</td>
<td>Dangerous when wet</td>
<td>Al</td>
<td>22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOAA</td>
<td>ALUMINUM ALKYL</td>
<td>64-17-5</td>
<td>3.X</td>
<td>Flammable liquid</td>
<td>C2H6O</td>
<td>4</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>NOAA</td>
<td>CHLORINE</td>
<td>7782-50-5</td>
<td>2.3</td>
<td>Toxic gas</td>
<td>Cl2</td>
<td>44, 59</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>NOAA</td>
<td>SODIUM HYPOCHLORITE SOLUTION</td>
<td>3081-52-9</td>
<td>8.0</td>
<td>Corrosive Basic</td>
<td>ClO.Na (aqueous)</td>
<td>44, 100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOAA</td>
<td>AMMONIA, SOLUTION, WITH MORE THAN 10% BUT NOT MORE THAN 35% AMMONIA</td>
<td>7664-41-7</td>
<td>8.0</td>
<td>Corrosive Basic</td>
<td>H3N</td>
<td>10, 100</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>NOAA</td>
<td>SODIUM HYDROSULFIDE, SOLUTION</td>
<td>16721-60-5</td>
<td>8.0</td>
<td>Corrosive Basic</td>
<td>H2SNa</td>
<td>33, 100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SQL</td>
<td>WATER</td>
<td>7752-18-5</td>
<td>Non-hazardous material</td>
<td></td>
<td>H2O</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The user can now proceed to the warehouse evaluation part of the program.

The screen shown right is the warehouse vs. chemical processing screen of the reactivity management tool:

Since this example evaluates the storage of chemicals in a warehouse, the first selection should be selected as shown. Press “next” to continue or if you do want to continue with physical and chemical processing evaluation, check the third box.

The user can also return to the warehouse part of the program after completion of the physical and chemical processing evaluation. Through the report menu

The screenshot below displays the resulting warehouse segregation report after "next” is pressed on the above screen:

This report grid displays the separation distances for pairs of chemicals. For example: Ethylene oxide and isopropyl Chloroformate have a code of “2” which designates to store these materials in “separate storage areas divided by a 30 minute firewall”.
The displayed color-coded report can also be printed by pressing the "export grid to Excel" as shown below:

Note that intersections above the red stepped line are self intersections or duplicates of the information below the line. (this line does not appear on your output.) This output was also modified by turning the top row text sideways. To do this, Select the top row and right click. Select format cells. Select text for the type of input under the Number tab. Move to the Alignment tab. Move the red dot to vertical per the red arrow and check the circled box and set the other circled box to context. Then click OK.

All other reports for this warehouse example can also be viewed going to the reports section of the reactivity management tool.

For detailed step by step instructions on how to enter use the reports section of the reactivity management tool go to section 3.2.11 of the help guide.

The 2 circled intersections are segregations from self. Examine these carefully for error or manufacturers storage requirements.
Remember that in order to store items together on the same isle they ALL must have a zero separation from each other. The numbers on the grid only determine compatibility for storage of the pair on who’s intersection they lay.

Example:

Hydrochloric acid has a 0 separation from Ethanol
Ethanol has a zero separation form Sodium Hypochlorite.

One might be tempted to stop there and store them together on the same isle however: Sodium Hypochlorite must be separated from hydrochloric acid by an isle way (1) and thus you can place a drum of ethanol in the same isle as either one but hydrochloric acid and Sodium Hypochlorite must be placed in different isles.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>DIMETHYL SULFATE</th>
<th>ETHANOL</th>
<th>ETHYLENE OXIDE</th>
<th>CAUSTIC SODA, SOLUTION</th>
<th>CHLORINE</th>
<th>HYDROCHLORIC ACID, SOLUTION</th>
<th>ISOPROPYL CHLOROFORMATE</th>
<th>PHOSPHORUS TRICHLORIDE</th>
<th>SODIUM HYDROSULFITE, SOLUTION</th>
<th>SODIUM HYPOCHLORITE SOLUTION</th>
<th>SULFURIC ACID</th>
<th>TERT-BUTYL HYDROPEROXIDE</th>
<th>ALUMINUM ALKYS</th>
<th>ALUMINUM POWDER, UNCOATED</th>
<th>AMMONIA, SOLUTION</th>
<th>WATER</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIMETHYL SULFATE</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
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<td>1</td>
<td>1</td>
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<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>CAUSTIC SODA, SOLUTION</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
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<td>1</td>
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<td></td>
</tr>
<tr>
<td>CHLORINE</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>HYDROCHLORIC ACID, SOLUTION</td>
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<td>0</td>
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<td>1</td>
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<td></td>
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</tr>
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<td>0</td>
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<td>2</td>
<td>1</td>
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<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SODIUM HYDROSULFITE, SOLUTION</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SODIUM HYPOCHLORITE SOLUTION</td>
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<td>1</td>
<td>1</td>
<td>1</td>
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<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SULFURIC ACID</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>1</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>TERT-BUTYL HYDROPEROXIDE</td>
<td>0</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>1</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALUMINUM ALKYS</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALUMINUM POWDER, UNCOATED</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>AMMONIA, SOLUTION</td>
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<td>1</td>
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<td>1</td>
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<td>WATER</td>
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<td>0</td>
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<td>0</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Aluminum powder and triethyl aluminum are “Dangerous when wet” and therefore must be segregated from water. (Don’t forget fire protection water and floor drain traps)

You should now check the reactivity matrix to confirm that no other reactivity exists between any of the compounds with no separation (i.e. a zero). Compounds with reactivity reported must be stored separate from each other. This is an extremely important double check of the system that should not be skipped.

Check all combinations of no separation (0) above in the Reactivity Matrix. See section 3.2.11.2 for details.
Look for any code A, B1, B3, B4, D1, G these indicate a serious reactivity issue that require segregation. In addition any other code starting with B, C or D not listed above may pose a serious risk to your warehouse under certain conditions.

The red circled segregations were flagged by the reactivity matrix as too small.

![Reactivity Matrix]

It is recommended that these be given a 2 segregation. Thus the new edited matrix would look like this:

![Edited Reactivity Matrix]
5.2 Napp Technologies - Physical Processing

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5.2.1 Background

“On April 21, 1995, at approximately 7:45 a.m., a violent explosion and fire occurred at the
Napp Technologies, Inc. specialty chemical plant in Lodi, New Jersey. Five employees of Napp
ultimately died. A majority of the facility was destroyed as a result of the fire, and other
businesses near the facility were destroyed or significantly damaged. Approximately 300
residents in the area were evacuated from their homes and a school. Additionally, firefighting
efforts generated chemically contaminated water that ran off into the streets and nearby Saddle
River.

At the time of the explosion and fire, Napp was conducting a blending operation…to produce a
formulation called ACR 9031 GPA\textsuperscript{17}, a gold precipitating agent.”\textsuperscript{18}

The following example is based on the information provided in the referenced report and other
publically available data. Assumptions are footnoted.

\textsuperscript{17} TM Technic Inc, Cranston RI
\textsuperscript{18} Based on EPA/OSHA Joint Chemical Accident Investigation Report, Napp Technologies, inc. Lodi, NJ EPA
550-R-97-002, October 1997
5.2.2 Scope and Process

Process Materials:
- Sodium hydrosulfite
- Aluminum powder
- Potassium carbonate
- Benzaldehyde

Other Materials Present in the processing area
- Water
- Isopropyl Alcohol

Intended Procedure:
- To a clean and dry 6 m³ tumble dryer / mixer PK-125 add:
  - 1,800 lb Aluminum powder
  - 900 lb Potassium Carbonate
  - 5,400 lb Sodium hydrosulfite
- Blend for 1 hour – Rotating 10 min with intensifier bar off and 5 min with intensifier on
- Spray in 8 L of benzaldehyde
- Blend
- Dispense into 18 to 22 - 55 gal plastic lined drums

5.2.3 Facility and Team entry
See Section 5.0 for detailed instructions.

5.2.4 Entering the Process Chemicals
See Section 5.0 for detailed instructions.

5.2.4.1 Searching the database
See Section 5.0 for detailed instructions

The following chemicals can be found in the pre-loaded NOAA database
- Sodium hydrosulfite (Sodium hydrogen sulfite)
- Aluminum powder uncoated
- Benzaldehyde

5.2.4.2 Entering chemicals not found in the database
The following chemicals must be entered into the user’s database using information from the table in section 5.2.4.3
- Potassium Carbonate
- ACR 9031 GPA
5.2.4.3 Entering Missing Chemical Information
See Section 5.0 for detailed instructions

<table>
<thead>
<tr>
<th>Name</th>
<th>Primary DOT code</th>
<th>Secondary DOT</th>
<th>Reactivity groups</th>
<th>Reactivity hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hydrogen sulfite</td>
<td>4.2 Spontaneously</td>
<td>none</td>
<td>Already in database</td>
<td>Already in database</td>
</tr>
<tr>
<td></td>
<td>combustible</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum powder uncoated</td>
<td>4.3 Dangerous when wet</td>
<td>None</td>
<td>Already in database</td>
<td>Already in database</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>3.X Flammable liquid</td>
<td>None</td>
<td>Already in database</td>
<td>Already in database</td>
</tr>
<tr>
<td>Potassium Carbonate</td>
<td>Non-hazardous</td>
<td>None</td>
<td>39</td>
<td>none</td>
</tr>
<tr>
<td>ACR 9031 GPA</td>
<td>4.3 Dangerous when wet</td>
<td>4.2 Spontaneously combustible</td>
<td>5,22,39,45</td>
<td>Highly Flammable Strong reducing agent, Water-Reactive Pyrophoric</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>3.X Flammable liquid</td>
<td>none</td>
<td>Already in database</td>
<td>Already in database</td>
</tr>
</tbody>
</table>

When unsure of the properties of a particular compound such as potassium carbonate. In this case I was unsure if Potassium carbonate should have the reactivity group of 10-bases, 39-inorganic bases or both. Look up “carbonate” then choose an analogous compound. In this case I chose Lithium carbonate. I added Lithium carbonate to my process then returning to the “Process Chemicals” tab I used the export to grid function to see what reactive groups were listed in the NOAA database for lithium carbonate. Finally I delete Lithium carbonate from the process and add the custom chemical Potassium Carbonate with the reactivity group of 39.

For ACR 9031 GPA and other mixtures simply add all reactivity groups for the individual components. See previous Helpful Hint for how to do this.

5.2.5 Displaying the pure compound hazards
See Section 5.0 for detailed instructions

The following is a display of the pure component hazards for this process.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Special Hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALUMINUM POWDER, UNCOATED, ISOPROANOL, ACR 9031 GPA</td>
<td>Highly Flammable</td>
</tr>
<tr>
<td>ALUMINUM POWDER, UNCOATED, SODIUM HYDROSULFITE, ACR 9031 GPA</td>
<td>Water-Reactive</td>
</tr>
<tr>
<td>SODIUM HYDROSULFITE</td>
<td>Air-Reactive</td>
</tr>
<tr>
<td>ALUMINUM POWDER, UNCOATED, ACR 9031 GPA</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>ISOPROANOL</td>
<td>Peroxidizable Compound</td>
</tr>
</tbody>
</table>
5.2.6 Displaying the binary chemical interactions

See Section 5.0 for detailed instructions.

Use the decoder in the help guide Appendix A. You can paste the decoder sheet into your matrix sheet for convenience. Or click on each filled square to read the interactions in the lower box.

5.2.7 Developing and Entering Scenarios

A quick read of the referenced report identifies the following short list of example failure scenarios. There are many more scenarios evident from reading the text. In developing a list for an actual process you would be expected to develop a list at least several pages long. Many of the listed scenarios could be simply assessed without a formal evaluation because their consequences are obvious. For instance, a static ignition of benzaldehyde need not be evaluated through this program because the obvious result is a fire however the consequences of the fire must be thought through, Fire suppression activated, initiation of the combustion of a large amount of aluminum powder, etc.. One does not need a computer program to determine that inerting is very important to the safety of this operation.

- Bearing failure
  - Coolant leak into blender
  - Overheat could lead to decomposition
- Jacket temperature control lost
  - Overheat could lead to decomposition
- Miss-charge / over charge
  - Wrong ratio of materials
  - Over fill of blender
  - Under fill of blender
- Loss of inertion gas
  - Introduction of humidity
  - Static ignition of benzaldehyde
- Inadvertent mixing
5.2.7.1 Loss of Utilities

Inertion gas flow interrupted causing blender inertion to be lost.

- Navigate to the Loss of Utilities Tab
- Enter the information below
- Press the “Save” button then the “Next Button
- Press the “next” button again to navigate to the “Process variation and Upset screen”
5.2.7.2 Process variation or upset example
Over fill of blender causes stress on intensifier bar seals causing leakage of coolant into blender.

- Enter the information below

- Press the “Save” button then the “Next Button
- Press the “next” button again to navigate to the “Energy Input Variation”

5.2.7.3 Energy Input variation example
Jacket steam valve leak causes jacket to exceed setpoint. Worst case jacket reaches boiling at 120°C.
Enter the information shown below

- Press the “Save” button then the “Next Button
- Press the “next” button again to navigate to the Mechanical failure

5.2.7.4 Mechanical failure example
Bearing failure leads to overheating of material contacting the near-by surfaces with resulting self sustaining decomposition spreading to entire batch.

Enter the information shown below
Press the “Save” button then the “Next Button”
Press the “next” button again to navigate to the Mechanical failure

5.2.7.5 Inadvertent mixing

Fire suppression system activated by event not connected with process during charging.
(note that same event during packaging has different consequences and must be entered separately.)

Enter the information shown below

![Image of RMT Help Guide interface]

We have completed entering scenarios in this example.
5.2.8 Evaluating the Scenarios

We will now begin evaluating each scenario one by one for thermal and pressure risk

- Navigate to the “scenario” tab if you are not already there. Here you can view all the scenario information and also quickly see the status of each one.

- Double click on a scenario
- The information entered thus far appears in editable format
- Make any changes necessary. You must enter a heat of reaction in kJ/kg of reaction mixture at this time.
- Since this is a fire scenario enter any large number or calculate the heat of combustion.
- Press Update and Evaluate scenario.

Again because this is a fire scenario enter a very large number into the Adiabatic Temperature Rise box.
- Enter the initial reaction temperature
- Press ‘save’ then “Next”
- Enter the max working temperature of the vessel because we are concerned with combustion not decomposition in this scenario.
• Press ‘save’ then “Next”
• The program displays a message that this scenario could cause a serious incident.
• Press “next” to evaluate the pressure portion of the scenario
• Enter the Maximum pressure. For this example we are assuming a sealed vessel so the rule of thumb is 10 times the starting pressure under ambient oxygen concentration. **IMPORTANT:** In all likelihood this fire would cause a runaway decomposition of the remaining ingredients creating large amounts of gas. We have ignored this possibility for the sake simplicity in this example.
• Enter 10 and select Bar

- Press ‘save” then “Next”
Enter a pressure of concern. In this case you could either enter the rupture disk setting, the MAWP of the tank or tank the failure pressure (2.5 times MAWP for an ASME rating)

- We will imagine the vessel was rated at 100psi. 2.5 times 100psi = 250psi
- Note we cannot enter PSI because we selected Bar on the previous page. 250psi=17.2bar

- Press “save” then “Next”

- The program displays a message that this scenario should be contained by the vessel and not pose a danger to plant or equipment. A word of caution before you except this conclusion blindly. This pre-supposes that no decomposition of the material inside the vessel occurred. Recall that binary interaction matrix suggested that thermal decomposition of several of the components causes gas formation. Thus we need to re-think this scenario. Consulting an expert would be a prudent choice as you consider the consequences and preventive measures associated with this scenario.
- Press “Next”
- Choose “completed”
- Press ‘save’ select evaluate another scenario and then press “Next”
- Double click on the UTL-01 scenario and edit the comments section to reflect our uncertainty about the conclusions, press update to save comments.
Continue to evaluate the scenarios one at a time using the following data

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Heat kJ/kg</th>
<th>Adiabatic temp rise</th>
<th>Heat capacity</th>
<th>Temp of concern</th>
<th>Starting temp</th>
<th>Max pressure</th>
<th>Pressure of concern</th>
</tr>
</thead>
<tbody>
<tr>
<td>UTL-01</td>
<td>5000</td>
<td>2</td>
<td>200</td>
<td>20</td>
<td>10bar</td>
<td>17.2bar</td>
<td></td>
</tr>
<tr>
<td>VAR-01</td>
<td>972</td>
<td>486</td>
<td>200</td>
<td>20</td>
<td>175bar *</td>
<td>17.2bar</td>
<td></td>
</tr>
<tr>
<td>ERG-01</td>
<td>972</td>
<td>486</td>
<td>200</td>
<td>20</td>
<td>175bar</td>
<td>17.2bar</td>
<td></td>
</tr>
<tr>
<td>MEC-01</td>
<td>972</td>
<td>486</td>
<td>200</td>
<td>20</td>
<td>175bar</td>
<td>17.2bar</td>
<td></td>
</tr>
<tr>
<td>MIX-01</td>
<td>5000</td>
<td>2</td>
<td>200</td>
<td>20</td>
<td>unknown 19</td>
<td>17.2bar</td>
<td></td>
</tr>
</tbody>
</table>

*Calculating P_max for scenario VAR-01, ERG-01 and MEC-01*

We know from the CSB report that the adiabatic heat rise of the ACR 9031 is 486°C. Thus even a little water would initiate a self sustaining decomposition throughout the batch.

Thus the charge would be:
- 5400 lb = 2,115.5 kg Na\(_2\)S\(_2\)O\(_3\) molecular weight 158g/mole

\[\frac{2,115,500g}{158 g/mole} = 13,389 \text{ moles Na}_2\text{S}_2\text{O}_3\]

Each mole of decomposing Na\(_2\)S\(_2\)O\(_3\) gives off 1 mole of SO\(_2\) thus 13,389 moles of SO\(_2\) are released on complete decomposition.

- 900 lb = 335.9 kg K\(_2\)CO\(_3\) molecular weight 138 g/mole

\[\frac{335,900g}{138 g/mole} = 2,434 \text{ moles}\]

Each mole of decomposing K\(_2\)CO\(_3\) gives off 1 mole of CO\(_2\) thus 2434 moles of CO\(_2\) are released on complete decomposition.

- \(R=0.083 \text{ bar*L/mole*K}\)
- \(T=779K:7293K\) (20°C starting temp) + 486 (adiabatic heat rise)
- \(V^{20}=6 \text{ m}^3=6,000L\)
- \(n=15823=13389 \text{ moles SO}_2 + 2434 \text{ moles CO}_2\)

---

19 Requires a venting calculation based on an open manway. But does it really matter since you have flames shooting out of the manway?
20 Assumed from drawling in CSB report that head volume is roughly equal to the fill volume of 6 m\(^3\)
5.2.9 Reporting and Proof Reading

The user should print out all applicable reports. See section 3.2.11 for report generation. Reports should be examined carefully for incorrect or misleading information. This program must by necessity simplify chemical reactivity evaluation, binary chemical reactivities and warehousing segregation into general rules of thumb and generalized assumptions of chemical behavior. This can lead to either under estimation and overestimation of the potential for an incident.

These Reports are intended to be a starting point toward an in depth discussion of the results in the context of an overall process safety management system and not the fulfillment of one’s legal or moral obligation to handle and use chemicals safely.

Selected screen shots of reports:

Chemicals report exported to Excel:

<table>
<thead>
<tr>
<th>DB identification</th>
<th>Chemical Name</th>
<th>CAS Number</th>
<th>DOT Labels</th>
<th>Chemical Formula</th>
<th>Chemical_id</th>
<th>Reactivity Ids</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOAA</td>
<td>ALUMINUM POWDER, UNCOATED</td>
<td>7429-90-5</td>
<td>4.2 Spontaneously Combustible</td>
<td>Al</td>
<td>14008</td>
<td>22</td>
</tr>
<tr>
<td>NOAA</td>
<td>SODIUM HYDROSULFITE</td>
<td>7775-14-6</td>
<td>4.3 Dangerous when wet</td>
<td>Na2S2O4</td>
<td>4500</td>
<td>45</td>
</tr>
<tr>
<td>NOAA</td>
<td>BENZALDEHYDE</td>
<td>100-52-7</td>
<td>9.0 Other Hazard</td>
<td>C7H6O</td>
<td>216</td>
<td>5</td>
</tr>
<tr>
<td>NOAA</td>
<td>ISOPROPNOL</td>
<td>67-63-0</td>
<td>3.X Flammable liquid</td>
<td>C3H8O</td>
<td>946</td>
<td>4</td>
</tr>
<tr>
<td>SQL</td>
<td>WATER</td>
<td>7732-18-5</td>
<td>Non-hazardous material</td>
<td>H2O</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>SQL</td>
<td>Potassium carbonate</td>
<td>584-09-7</td>
<td>Non-hazardous material</td>
<td>K2CO3</td>
<td>2</td>
<td>39</td>
</tr>
<tr>
<td>SQL</td>
<td>ACR 9031</td>
<td></td>
<td>4.3 Dangerous when wet</td>
<td></td>
<td>35</td>
<td>22, 39, 45</td>
</tr>
</tbody>
</table>

Pure component hazards

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Reactive Group Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALUMINUM POWDER, UNCOATED,ISOPROPNOL</td>
<td>Highly Flammable</td>
</tr>
<tr>
<td>ALUMINUM POWDER, UNCOATED,SODIUM HYDROSULFITE</td>
<td>Water-Reactive</td>
</tr>
<tr>
<td>SODIUM HYDROSULFITE</td>
<td>Air-Reactive</td>
</tr>
<tr>
<td>ALUMINUM POWDER, UNCOATED</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>ISOPROPNOL</td>
<td>Peroxidizable Compound</td>
</tr>
</tbody>
</table>
Binary interaction matrix reformatted in Excel for readability

<table>
<thead>
<tr>
<th>Matrix</th>
<th>ALUMINUM POWDER, UNCOATED</th>
<th>BENZALDEHYDE</th>
<th>ISOPROPANOL</th>
<th>SODIUM HYDROSULFITE</th>
<th>WATER</th>
<th>Potassium carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>BENZALDEHYDE</td>
<td></td>
<td>B5, D1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISOPROPANOL</td>
<td>B5, C</td>
<td>C, G</td>
<td></td>
<td>A6, B1, B5, C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SODIUM HYDROSULFITE</td>
<td>A2, C, G</td>
<td>B5, C</td>
<td>A6, B1, B5, C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WATER</td>
<td>B6</td>
<td></td>
<td></td>
<td>B6, D3, D6, D7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium carbonate</td>
<td>A3, A6, B1, B5, C</td>
<td>A6, C, D4</td>
<td>C, D3</td>
<td>B5, D7, E</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACR 9031</td>
<td>B5, D1, A3, A6, B1, C, A2, G</td>
<td>B5, D1, A6, C, D4</td>
<td>C, G, B5, A6, B1</td>
<td>B5, C, A2, G, D3, F</td>
<td>B6, B5, D7, E, D3, D6</td>
<td>A6, C, D4, A3, B1, B5, D3</td>
</tr>
</tbody>
</table>

A1: Explosive when dry.
A2: Risk of explosion by shock, friction, fire or other sources of ignition.
A3: Forms very unstable explosive metallic compounds.
A4: External heating may cause an explosion.
A5: May form explosive peroxides.
A6: Reaction proceeds with explosive violence and/or forms explosive products.
A8: Explosive when mixed with combustible material.
A9: Heat generated from chemical reaction may initiate explosion.
A10: Increased sensitivity to detonation.
B1: May become highly flammable or may initiate a fire, especially if other combustible materials are present.
B3: Spontaneously flammable in air.
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.
B6: Combination liberates gaseous products, including both flammable and toxic gases. May cause pressurization.
C: Exothermic reaction. May generate heat and/or cause pressurization.
D1: Exothermic, potentially violent polymerization. May cause pressurization.
D3: Combination liberates gaseous products, at least one of which is toxic. May cause pressurization.
D4: Combination liberates nonflammable, nontoxic gas. May cause pressurization.
D5: Combination liberates combustion-enhancing gas (e.g., oxygen). May cause pressurization.
D6: Exothermic, generation of toxic and corrosive fumes.
D7: Generation of corrosive liquid.
E: Generates water soluble toxic products.
F: May be hazardous but unknown.
G: Reaction may be intense or violent.
H: Possible exposure to radiation.
I: Members of this group are highly reactive. They may be incompatible with members of the same group.
### Scenario analysis

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Description</th>
<th>Model</th>
<th>Variables</th>
<th>Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 1</td>
<td>Description</td>
<td>Model</td>
<td>Variables</td>
<td>Constants</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>Description</td>
<td>Model</td>
<td>Variables</td>
<td>Constants</td>
</tr>
<tr>
<td>Scenario 3</td>
<td>Description</td>
<td>Model</td>
<td>Variables</td>
<td>Constants</td>
</tr>
</tbody>
</table>
5.2.10 Developing a Reactivity Management System

The user should now incorporate the output information into their site chemical reactivity management system. For references on developing and implementing a chemical reactivity management system in accordance with the expectation of local, state and Federal authorities please see Appendix D of this guide.

5.2.11 Example Summary

It is clear that the outputs of this program would have prevented this devastating event had they been utilized properly. Given Napp’s attention to details like covering floor drains to avoid the GPA from contacting water in the sewer, it is clear that some thought was put into fault scenarios. The fact that they missed the potential of a leaky seal, an un-cleaned header pipe, energy input from the intensifier bar, miss charging, charging to a wet blender and many more shows the importance of exploring the consequences all possible failures. A good rule of thumb when assessing failures is: If it absolutely could not happen it will.
5.3 XYZ Pharmaceuticals – Intentional Chemistry

Jump to Common Preliminary Step section 5.0
Start with section 5.0 before completing these steps

The following example has no basis in reality. XYZ Pharmaceutical company uses a two step process to manufacture a bulk pharmaceutical ingredient Lopoduradyn.

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5.3.1 Process Tab
- Open a new process in the RMT. By pressing the “create process” button on the Process tab.

- Enter “Process 1” in the Process name field
- Enter “Building 1” in the Facility name. See section 4.1 for help in selecting the proper scope of your evaluation.
- Save your entries with the “save” button before pressing “Next”

5.3.2 Laboratory Scale facility Tab
- You are now asked if your operation is defined as a “Laboratory Operation”. Choosing yes terminates the program. The default answer is No with next taking you on in the program. Press the “help” button for a definition of Laboratory operations.

5.3.3 Process Chemicals tab – searching for chemicals
- Press the “Search Chemical Databases” button to begin by searching the NOAA CAMEO database for your chemicals. Note: if you have entered custom chemicals in your RMT custom database these are searched at the same time.
- Enter the name of your first chemical in the pop-up search box and press search button.
- Search through your hits for your desired chemical. Check the box in front of the name. (you may make multiple selections.) then press the Add to process” button
5.3.4 Entering chemicals not found in the NOAA database:

Entering the custom chemical Line Kleen™

- Type “Line Kleen” into the chemical name box
- **PRIMARY** DOT code – select “Corrosive – acid”
- Make no selection under secondary DOT because there is not one listed in the MSDS
- Reactivity groups: select the following by holding down the “Ctrl” key. Using the scroll bar and the left mouse button select the following. They will gray out when selected.
  - “1 Acids –inorganic non-oxidizing” because MSDS lists Phosphoric acid
  - “38 Salts acidic inorganic” because it is assumed that the solution is pH is buffered
  - “100 water” because water is an ingredient
- Special Hazards groups
  - Select “none”

Enter the other two chemicals not found in the NOAA database bases on their MSDS.

<table>
<thead>
<tr>
<th>Name</th>
<th>Primary DOT</th>
<th>Secondary DOT</th>
<th>Reactive Groups</th>
<th>React hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 987654321</td>
<td>3</td>
<td>none</td>
<td>6, 38</td>
<td>none</td>
</tr>
<tr>
<td>Syltherm XLT</td>
<td>8A</td>
<td>none</td>
<td>28</td>
<td>none</td>
</tr>
</tbody>
</table>
5.3.5 Missing Data Warning box

Input the DOT labels for all NOAA chemicals. The DOT codes are required for the warehouse segregation function. The program will not allow the user to continue until all required data is entered.

Pitfall alert

If the next button does not work recheck that at least a primary DOT code and at least one reactivity group has been entered for each chemical. Use the scroll bar on the bottom to scroll right to see the reactivity group column.

5.3.6 Warehousing vs. Chemical processing

- The program seeks to determine if the Facility being evaluated is solely a Warehouse or if other operations are performed there. Press the Help button or see the help guide for definitions.
For this example we are reacting chemicals in a chemical reactor and therefore we shall select the answer: **Physical or Chemical processing may occur in this area.**

- Press the Next button to move on to the next section of the evaluation.

### 5.3.7 Building Credible Reactivity and Fault Scenarios

- The user should be very familiar with HAZOps scenario building or consult the Help Guide and incorporated references for detailed information on how to build credible scenarios for evaluation. It is critical to the satisfactory performance of the program that the user identifies all credible scenarios applicable to the processing area. Failure to identify even one high hazard scenario could jeopardize the safety of your facility.
- The program first asks if you have already performed a **formal** Process Hazard Analysis on the facility by one of the established and accepted methods.
- For the purposes of this example we will answer NO.

#### 5.3.7.1 Scenario Building example: Ternary Mixtures

- This is the first of a series of fault scenarios presented to the user to spark ideas for credible scenarios.
- For the purposes of this exercise we will skip most of them. In a real facility one would expect to build 25-50 credible scenarios for a narrow scope evaluation such as this one.
- Utilize the explanations in the help button and references in the help guide to fully explore each topic.
- When naming scenarios use a common convention throughout. The authors suggest three letters designating the tab where the scenario was entered followed by a dash and
consecutive numbers. Ex TER-001 for the first scenario built under the Ternary mixtures tab.

- For the purposes of this exercise we will now skip ahead to the tab called “Loss of Utility Scenario” by clicking on that tab

- Click the “add” button
- Enter the data as shown below

Because this is a fire scenario and not a chemical reactivity scenario we simply entered “0” in the heat of reaction box. This is an option field at this time so don’t worry if you are missing the data. A note could also be made that we are not interested in evaluating the heat of reaction of a fire scenario so zero was entered as a place holder.
- Press the save button before attempting to go on using the next button.

For the purposes of this example we will now move on to the intended chemistry.

Select the “Any Other Scenario” tab. To view this tab you must use the arrows in the upper right corner of the process window.

Use this tab to enter your intended chemistry reactions, any strong chemical reactivity issues identified by the Reactivity Matrix and any scenario that does not fit into the other categories.

We will first enter the intended chemistry reactions.
Select the add button. Enter the text as shown:

Note that the -16.6kJ/kg reaction energy (exothermic) is entered as positive number.
Press the save button and enter the next Reaction as shown. With a heat of reaction = 464kJ/kg

5.3.7.2 Identifying significant Binary interactions
We will now search for any binary chemical interactions identified by the program

Under the “File” menu select reports; Reactivity Matrix

This opens a blank report window.
Select your process and press the load button. You will see the binary interaction matrix for your process. Double click on each cell with an entry to view the identified interaction.

In the following screen shot we have double clicked on the interaction of Bromine with Acetophenone. As you can see any possibility that these two chemicals could be mixed in an uncontrolled fashion should be seriously considered as a credible scenario with serious consequences. Use the scroll bar to scroll through all of the supplemental information and references provided.
Now:
Click through the rest of the matrix to identify any other mixtures that could release large amounts of heat or gas. Use the scroll bar to review entries to the right and bottom.

For the purpose of brevity, in this example we will only be entering the interaction between acetophenone and bromine even though there are several other violent interactions identified by the matrix.

Entering the reaction Acetophenone + Bromine \( \rightarrow \) Bromoacetophenone + HBr into CHETAH® results in a \( \Delta H_{\text{rxn}} \) value of -3.96Kcal/mole. This converts to -16.6 kJ/mole
The molecular weight of acetophenone = 120.2g/mole
The molecular weight of bromine is 159.8g/mole

Thus the total weight of a 1 mole reaction would be 120.2+159.8 = 280g = 0.28kg

Set up the ratio:

Thus we have estimated the reaction energy of this interaction to be 59.3 kJ/kg

Add a new scenario in the “Any Other Scenario” tab

Into the comments box we now enter the following “Reaction produces 1 mole of hydrogen bromide gas - Toxic”. This will help us during the evaluation of the pressure for this scenario.
5.3.8 Evaluation of Scenarios

Upon saving your last scenario press the next button. The program will pop-up a box asking if you want to create any more scenarios. Answer NO to move to the scenario evaluation phase. Alternately use the tabs to navigate to scenario evaluation.
5.3.8.1 Evaluation of Utl-01

To evaluate the first scenario, double click on the name. The grayed out text becomes editable.

Press the “Evaluate scenario” button
Notice that the text becomes un-editable again. Also in this case no further heat of reaction information was required to evaluate the thermal hazard of the scenario. As you recall this was a fire scenario so we entered zero for the heat of reaction because we were not interested in evaluating this aspect of the scenario.

The program is requesting that we enter a Maximum pressure. In this case we used the rule of thumb of 8-10X starting pressure for an explosion / fire starting at ambient pressure and ~20% oxygen content. We entered 10 in the pressure and selected Bar as the units.

Press “Save” then “Next” to continue the evaluation

We are now asked to enter a pressure of concern. In this case we used the ASME failure pressure of 2.5X the MAWP of the vessel.

Note that the pressure of concern must be entered in the units selected on the pervious screen.

Press “Save” then “Next” to complete the evaluation

A conclusion is displayed for the pressure calculation indicating this scenario is unlikely to cause a serious chemical reactivity incident.
Press the “Next” button. The program will ask you if you would like to change the status of this scenario. Your choices are:

4. Unevaluated
5. Needs updating
6. Complete

In this case we are done with this scenario and will select “completed” from the drop-down menu and press the save button.

We are then asked if we want to go back to the scenario evaluation area or open a report form. Choose evaluate another scenario.
5.3.8.2 Evaluation of Reaction step 1 (Oth-001)

Select Util-001 by double clicking. Look over the text. Edit if necessary. Press “update” then Evaluate

Once again the program did not require any more information to evaluate the thermal hazard of the scenario and went right into the pressure evaluation.

In this case the reaction cannot reach reflux and thus build pressure in a sealed vessel and we will say that it does not evolve any gas. Therefore the maximum pressure is ~0psi

Enter 0 and select psi from the dropdown menu for units.

Press the Save and Next buttons to continue the evaluation

We entered 250 PSI as the pressure of concern (2.5X MAWP of the vessel)

Press “Save” then “Next” to complete the evaluation

A conclusion is displayed for the pressure calculation indicating this scenario is unlikely to cause a serious chemical reactivity incident.

In this case we are done with this scenario and will select “completed” from the drop-down menu and press the save button.
Go back to the scenario evaluation area by choosing evaluate another scenario.

5.3.8.3 Evaluation of Reaction step 2 (Oth-002)
Select Util-002 by double clicking. Look over the text. Edit if necessary. Press “update” then Evaluate

This time the program asks for more information for assessing the thermal hazard of the process.
There are two methods of data entry here.

Method A

You can enter the adiabatic heat rise directly.

Method B

The program will calculate it for you from the heat of reaction and heat capacity of the mixture.
In this case we have a reaction mixture with a heat capacity of 2\text{j/g}^\circ\text{C} which is typical for an organic reaction mixture. Our reaction starts at 0\circ\text{C}.

Press Save and Next to continue the evaluation. 

Note that the heat rise is entered into the proper field for you as soon as the save is pressed.

The program now asks us for the temperature of concern. In this case we will examine the temperature required to exceed the MAWP * 2.5 or 250psi. 

Vapor pressure curves are available on the internet and also can be calculated by computer programs such as Aspen. Let us say that we estimated the vapor pressure of our lowest boiler to be 250PSI at 219\circ\text{C}. We will enter 219 as the temperature of concern. Other temperatures of concern may apply to your reaction please consult guide book section 4.7 and the references contained therein.

Press save then next to display the evaluation of the thermal scenario.

The safety of this scenario cannot be determined based on thermodynamics, a kinetic evaluation or other evaluation methodology is required. Seek additional guidance for this reaction.

In this case this reaction must be studied further to determine if it can be operated safely. It is highly recommended that the user consult an experienced process safety professional for guidance as this scenario has a high likelihood of creating a chemical reactivity incident capable of causing injury, death and severe property damage.
The program will now evaluate the Pressure hazard

From our vapor pressure curve we determined that the vapor pressure of the reaction was approximately 250psi. at the MTSR. The MTSR has been calculated behind the scenes by the program and will report it in the scenario report. You can easily calculate it however by taking the adiabatic heat rise from the thermal evaluation and adding it to the starting temperature. This assumes that you do not have any exothermic decompositions too. We will assume that we do not. If you did you must also add the adiabatic heat rise of the decomposition to the sum of your starting temperature and your reaction heat rise.

Thus our starting temp was 0°C and our heat rise calculated to 232°C. (if you forgot these numbers hit the previous button a few times to go back to that screen.)

\[ 0 + 232 = 232°C \text{ MTSR} \]

Looking on our hypothetical vapor pressure curve we see that the vapor pressure at 235°C is about 450psi. Enter 450 and select psi as the units.

Press save and next
Recall our MAWP times 2.5 was 250psi so this becomes our temperature of concern

Press save and Next

The safety of this scenario cannot be determined based on thermodynamics, a kinetic evaluation or other evaluation methodology is required. Seek additional guidance for this reaction.

The pressure evaluation like the thermal evaluation indicates that this reaction must be studied further to determine if it can be operated safely. It is highly recommended that the user consult an experienced process safety professional for guidance as this scenario has a high likelihood of creating a chemical reactivity incident capable of causing injury, death and severe property damage.

Press next and navigate to evaluate our fourth and final example scenario.
5.3.8.3 Evaluation of Oth-003
For this scenario we are not asked for any further thermal inputs. The team has determined that this mixing could only occur as an unconfined spill therefore we will enter 0 for the maximum pressure and 0 for the pressure of concern, noting in the comments section that we have determined that these 2 chemicals could only reasonably interact outside of a vessel in a spill scenario.
To enter the comment navigate back to the list scenarios screen

Note that the comment added below the original text. The original text is no longer visible but it is captured on the report however. The hazards of releasing 1 mole equivalent of hydrogen bromide into the work area should be examined. The comments section might be a suitable place to maintain a summary of your findings on this matter.

Press Update to complete to record your change.

You have now completed the evaluation of your process.

5.3.9 Reports

Refer to the section on viewing and printing reports.

5.3.9.1 Warehouse

Because storage of these chemicals is the responsibility of the warehousing staff we did not produce a warehouse segregation report. The program did however produce one anyway should you want to view or print it.
5.3.9.2 Reactivity Matrix

This matrix was reformatted to reorient the text direction of the columns and colored to identify unused squares (grayed out) and no interaction pairs (green).

<table>
<thead>
<tr>
<th>Compound 987654321</th>
<th>Siltherm XLT</th>
<th>Line Kleen</th>
<th>WATER</th>
<th>TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID</th>
<th>TETRAHYDROFURAN</th>
<th>SODIUM AZIDE</th>
<th>PHENACYL BROMIDE</th>
<th>DICHLOROMETHANE</th>
<th>BROMINE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACETOPHENONE</td>
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<td>DICHLOROMETHANE</td>
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<td>PHENACYL BROMIDE</td>
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<td>SODIUM AZIDE</td>
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<td>TETRAHYDROFURAN</td>
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<td></td>
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<tr>
<td>TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID</td>
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<tr>
<td>TRIPHENYL PHOSPHINE</td>
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</tbody>
</table>
5.3.9.3 Chemical reactivity evaluation Report

5.3.9.3.1 Team tab

<table>
<thead>
<tr>
<th>Member Name</th>
<th>Department Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mark</td>
<td>TTO</td>
</tr>
<tr>
<td>John</td>
<td>Processing</td>
</tr>
</tbody>
</table>
### 5.3.9.3.2 Chemicals tab

<table>
<thead>
<tr>
<th>Chemical Identity</th>
<th>Chemical Name</th>
<th>CAS Number</th>
<th>DOT Labels</th>
<th>Chemical Formula</th>
<th>Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>N0AA</td>
<td>ACETOPHENONE</td>
<td>10-46-2</td>
<td>C, X Flammable</td>
<td>C8H8O</td>
<td>19</td>
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<tr>
<td>N0AA</td>
<td>BROMINE</td>
<td>7725-95-6</td>
<td>1.1 Corrosive</td>
<td>Br</td>
<td>44.59</td>
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<tr>
<td>N0AA</td>
<td>DICHLOROMETHANE</td>
<td>75-09-2</td>
<td>1.1 Poison</td>
<td>CH2Cl2</td>
<td>17</td>
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<td>76-11-1</td>
<td>1.1 Poison</td>
<td>C6H5Br</td>
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<td>SODIUMAZIDE</td>
<td>25628-22-8</td>
<td>1.1 Poison</td>
<td>Na</td>
<td>8</td>
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<tr>
<td>N0AA</td>
<td>TETRAMETHYL FURAN</td>
<td>109-89-8</td>
<td>C, X Flammable</td>
<td>C6H10</td>
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<tr>
<td>N0AA</td>
<td>TRIPHENYL PHOSPHINE</td>
<td>80-02-4</td>
<td>1.1 Poison</td>
<td>C10H15P</td>
<td>25</td>
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<tr>
<td>N0AA</td>
<td>TRIOXANE, SULFURIC ACID LIQUID WITH MORE THAN 5% FREE SULFURIC ACID</td>
<td>76-05-1</td>
<td>1.1 Corrosive Acid</td>
<td>H2SO4</td>
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<td>Linseed</td>
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<td>Compound 987155421</td>
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<td></td>
<td>28</td>
</tr>
</tbody>
</table>
5.3.9.3.3 Binary Matrix tab

Citations:

Possible Gases: Halocarbons

Citations:

Possible Gases:
Chemical Reactivity Report for: Phenacyl bromide mixed with Acetophenone

Evaluation Date: 01/06/2011

Citations:

**Phenacyl bromide:***

- Chlorofluorocarbons, their effects on the environment and human health (A. L. J. 1980). Chlorofluorocarbons are effective as solvents and cleaning agents, but they deplete the earth's ozone layer.
- Phenyldihydroxyacetone (PDA) and phenol:***

4) Phenacyl bromide mixed with Acetophenone

Possible Gases:

- **Acetophenone:**

  - May be toxic to humans.
  - May cause nausea and vomiting.
  - May cause respiratory irritation.
  - May cause dermatitis.

  **Possible Gases:**

  - May be toxic to humans.
  - May cause nausea and vomiting.
  - May cause respiratory irritation.
  - May cause dermatitis.

Citations:

- Chlorofluorocarbons, their effects on the environment and human health (A. L. J. 1980). Chlorofluorocarbons are effective as solvents and cleaning agents, but they deplete the earth's ozone layer.
- Phenyldihydroxyacetone (PDA) and phenol:***
4) PHENACYL BROMIDE mixed with
3) DIOXORONOMETHANE

Possible Gases: N2, CO2

Citations:

5) SODIUM AZIDE mixed with
1) ACETOPHENONE
- Exothermic reaction. May generate heat and/or cause pressurization.
- Combination liberates combustible gas/liquid. May cause pressurization.

Possible Gases: N2, CO2

Citations:

5) SODIUM AZIDE mixed with
2) BROMINE
- Reaction proceeds with explosive violence and/or forms explosive products.
- Heat generated from chemical reaction may initiate explosion.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Combination liberates explosive products, at least one of which is toxic. May cause pressurization.
- Reaction may be in excess or violent.

Possible Gases: N2, NO, HX

Citations:

NaNO3 reacts explosively with chloromethyl chloride (Keller, 1967, Volume 3, Supplemental 2, 2, pp. 29-30).

Zn reacts violently with bromine dichloride (Lewis, R. J., J. Org. Chem., 7 (1941), 515) and with dichloroethylene (Towle, R. J., J. Org. Chem., 7 (1941), 515). The reaction of NaNO3 with chlorine is explosive (Lambert, 1967, Supplemental 2, 2, (19)): 6 NaNO3 + 2 Cl2 = 6 NaCl + 3 NO2 + NO + N2O5. The reaction of NaNO3 with bromine vapor is explosive (Keller, 1942, Volume 8, pp. 29-30).

5) SODIUM AZIDE mixed with
3) DIOXORONOMETHANE
- Reaction proceeds with explosive violence and/or forms explosive products.
- Combination liberates gaseous products, including both flammable and toxic gas. May cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.

Possible Gases: HNO3

Citations:


5) SODIUM AZIDE mixed with
4) HYPONITRITE BROMIDE
- Reaction proceeds with explosive violence and/or forms explosive products.
- Combination liberates gaseous products, including both flammable and toxic gas. May cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Combination liberates nonflammable, nontoxic gas. May cause pressurization.

Possible Gases: HNO3, N2O, CO2

Citations:
6) **TETRAHYDROFURAN** mixed with
   1) **ACETOPHENONE**

   **Possible Gases:**

   

   **Citation:**

   

   6) **TETRAHYDROFURAN** mixed with
   2) **EROSITOL**

   - Risk of explosion by shock, friction, fire or other sources of ignition.
   - Reaction proceeds with a positive reaction and forms explosive products.
   - Explosive or when mixed with combustible material.
   - Spontaneous combustion or reaction due to reaction heat.
   - Isothermal reaction. May generate heat and cause pressurization.
   - Combination releases gas at a rate, at least one of which is toxic. May cause pressurization.

   **Possible Gases:** XX

   **Citation:**

   

   6) **TETRAHYDROFURAN** mixed with
   3) **LICHLOROMETHANE**

   - Combination releases gaseous products, at least one of which is toxic. May cause pressurization.
Possible Gases: HK

Citations:

6) TETRAHYDROFURAN mixed with
   4) PHENACETYLBROMIDE
   - Combination liberates gaseous products, at least one of which is toxic. May cause pressurization.

Possible Gases: HK

Citations:

6) TETRAHYDROFURAN mixed with
   5) SODIUM AZIDE
   - Reaction proceeds with explosive violence and/or forms explosive products.
   - Exothermic reaction. May generate heat and/or cause pressurization.

Possible Gases:

Citations:


7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID mixed with
   1) ACETOPHENONE
   - Reaction proceeds with explosive violence and/or forms explosive products.
   - Spontaneous ignition of reagents or products due to reaction heat.
   - Exothermic reaction. May generate heat and/or cause pressurization.
   - Combination liberates gaseous products, at least one of which is toxic. May cause pressurization.

Possible Gases: NOx(100%02)C02

Citations:


7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID mixed with
   2) TETRONINE
   - Reaction proceeds with explosive violence and/or forms explosive products.
   - Exothermic reaction with combustible materials.
   - Heat generated from chemical reaction may initiate explosion.
   - Exothermic reaction. May generate heat and/or cause pressurization.
   - Combination liberates gaseous products, at least one of which is toxic. May cause pressurization.

Possible Gases: F04(20%02)H2O2/H2O4(100%02)C02

Citations:

7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID mixed with 3) DICHLOROMETHANE
- Risk of explosion by shock, friction, fire or other sources of ignition.
- May become highly flammable or may initiate a fire, especially if other combustible materials are present.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Combination liberates gaseous products. At least one of which is toxic. May cause pressurization.

Possible Gases: HCl CO CO

CITED:

Possible Gases: H2SO4 N2
7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID mixed with
6) TETRAHYDROPURPURAN
- Reaction proceeds with explosive violence and/or forms explosive products.
- Spontaneous ignition of a mixture or products due to reaction heat.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Generates water soluble toxic products.

Possible Gases:

Citation:
Dicyclopentadiene may react with certain peroxides to form explosive products. In addition, it may react with certain catalysts to form products which are themselves explosive. (Hoffman, 1988, J. Am. Chem. Soc., 110, 1225.)

8) TRIETHYLMONOSYLMINPHOSPHINE mixed with
1) ACETOPHENOINE
- Combustion liberates gaseous products, at least one of which is flammable. May cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.

Possible Gases: H2

Citation:

9) TETRAPHENYLPHOSPHINE mixed with
2) BROMINE
- Heat generated from chemical reaction may initiate explosion.
- Spontaneous ignition of a mixture or products due to reaction heat.
- Combustion liberates gaseous products, at least one of which is flammable. May cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.

Possible Gases: HCl, HBr, HI

Citation:
IClO4 forms explosive mixtures with THF (Mazzis, T. H. et al., 1979, Recl. Soc. Chim., 75, 5036.)


10) TETRAPHENYLPHOSPHINE mixed with
3) LITHIUM METHANE
- Heat generated from chemical reaction may initiate explosion.
- Spontaneous ignition of a mixture or products due to reaction heat.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Combustion liberates gaseous products, at least one of which is toxic. May cause pressurization.

Possible Gases: H2

Citation:
6) TRIETHYLPHOSPHINE mixed with
4) PHENACYLCHLORIDE
- Heat generated from chemical reaction may initiate explosion.
- Spontaneous ignition of reaction or products due to reaction heat.
- Combustion produces gaseous products, at least one of which is flammable. May cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Combustion liberates gaseous products, at least one of which is toxic. May cause pressurization.
Possible Gases: HCHO

Citations:

7) TRIETHYLPHOSPHINE mixed with
S) SODIUM AZIDE
- Reaction proceeds with explosive violence and/or forms explosive products.
- Combustion produces gaseous products, including both flammable and toxic gases. May cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.
Possible Gases: NaN3

Citations:

8) TRIETHYLPHOSPHINE mixed with
Q) TETRASODIUM YORURAN
- Heat of explosion and/ or reaction, from other sources of ignition.
- Reaction proceeds with explosive violence and/or forms explosive products.
- Spontaneous ignition of reaction or products due to reaction heat.
- Combustion liberates gaseous products, at least one of which is flammable. May cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.
Possible Gases: H2

Citations:
WANH can react exothermically with peroxided Teflon fluorinate, evolving hydrogen which may be ignited by heat of reaction (Metcal, R. E. 1974. Chemical and Engineering News 32:4258.).

9) TRIETHYLPHOSPHINE mixed with
T) HYDROCARBONS
- Heat generated from chemical reaction may initiate explosion.
- Spontaneous ignition of reaction or products due to reaction heat.
- Combustion produces gaseous products, at least one of which is flammable. May cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.
Possible Gases: H2, Hydrocarbons

Citations:
WANH can react exothermically with peroxided Teflon fluorinate, evolving hydrogen which may be ignited by heat of reaction (Metcal, R. E. 1974. Chemical and Engineering News 32:4258.).
0) TRIPHENYLPROPIONENE mixed with
1) TOLUENE SULFURIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID
- Reaction proceeds with explosive violence and/or forms explosive products.
- Heat generated from chemical reaction may initiate explosion.
- Spontaneous ignition of reactions or products due to reaction heat.
- Combustion liberates gaseous products, at least one of which is flammable. May cause pressurization.
- Endothermic reaction. May generate heat and/or cause pressurization.

Possible Gases: H2

Citations:

9) WATER mixed with
1) ACETOPHENONE

Possible Gases:

Citations:

9) WATER mixed with
2) BROMINE
- Endothermic reaction. May generate heat and/or cause pressurization.
- Combustion liberates gaseous products, at least one of which is toxic. May cause pressurization.
- Combination liberates combustion-enhancing gas (e.g., oxygen). May cause pressurization.
- Endothermic, generation of toxic and corrosive fumes.
- Generation of corrosive liquid.
- Reaction may be intense or violent.

Possible Gases: X2O3Cl2O2 CorrosiveFumesH2O2[O2]O2[ClO2O2]

Citations:

9) WATER mixed with
3) TRICHLOROMETHANE
- Combustion liberates gaseous products, at least one of which is toxic. May cause pressurization.
- Generation of corrosive liquid.

Possible Gases: HX

Citations:

9) WATER mixed with
4) PHENACYL BROMIDE
- Combustion liberates gaseous products, at least one of which is toxic. May cause pressurization.
- Generation of corrosive liquid.

Possible Gases: HX

Citations:

9) WATER mixed with
5) SODIUM AZIDE
- Combustion liberates nonflammable, noxious gas. May cause pressurization.

Possible Gases: N2

Citations:
Chemical Reactivity Report for Process 1

Evaluation Date: 01/01/2011

8/23/2011 10:42:34 AM

Citations:

1) WATER mixed with
   a) TETRAHYDROFURAN
      - Combination liberates gaseous products, at least one of which is toxic. May cause pressurization.
      - Generation of corrosive liquid.
      - Generation of water-soluble toxic products.
      Possible Gases: HCN, Aldehydes

Citations:

3) WATER mixed with
   a) TOLUENE, LIQUID, WITH MORE THAN 5% FREE SULPHURIC ACID
      - Exothermic, generation of toxic and corrosive fumes.
      - Generation of corrosive liquid.
      Possible Gases: Acid Fumes

Citations:

3) WATER mixed with
   a) TRI-PHENYL PHOSPHINE
      - Spontaneous ignition of reagents or products due to reaction heat.
      - Combination liberates gaseous products, at least one of which is flammable. May cause pressurization.
      - Combination liberates gaseous products, at least one of which is toxic. May cause pressurization.
      - Exothermic, generation of toxic and corrosive fumes.
      - Generation of corrosive liquid.
      - Reaction may be intense or violent.
      Possible Gases: H2, Hydrocarbons, N2, O2, HX, Corrosive Fumes

Citations:

10) Line 11 mixed with
    a) ACETOPHENONE
       - Exothermic reaction. May generate heat and/or cause pressurization.

Citations:

10) Line 11 mixed with
    a) BROMINE
       - Reaction proceeds with explosive violence and/or forms explosive products.
       - Heat generated from chemical reaction may initiate explosion.
       - Spontaneous ignition of reagents or products due to reaction heat.
       - Combination liberates gaseous products, including both flammable and toxic gases. May cause pressurization.
       - Exothermic reaction. May generate heat and/or cause pressurization.
       - Combination liberates gaseous products, at least one of which is toxic. May cause pressurization.
       - Combination liberates combustion-enhancing gas (e.g., oxygen). May cause pressurization.
       - Exothermic, generation of toxic and corrosive fumes.
       - Generation of corrosive liquid.
       - Reaction may be intense or violent.

Possible Gases: X2O2, HX, HCl, Chlorinated Amines, Chlorinated Amines, H2, N2, O2, Corrosive Fumes, HX, O2, D2X, D21X, 021S, 0x

Citations:
Chemical Reactivity Reports for Process 1

Evaluation Date: 01/06/2011


10. Use Keene mixed with

1) Dichloroethane
   - May become highly flammable or may initiate fire, especially if other combustible materials are present.
   - Exothermic reaction. May generate heat and cause pressurization.
   - Combustion by-products gaseous products, at least one of which is toxic. May cause pressurization.
   - Generation of corrosive liquid.
   - Reaction may be intense or violent.

Possible Gases: HCl/Cl2

Citations:
HCl can react violently with F2Cl=CH2 (vinylidene fluoride), even at -40°C, causing rapid decomposition and pressurization, including evolution of highly toxic F2 gas. The reaction is catalyzed by AIC3, which is commonly found in HCl solution (Jennings, J. H. 1981. Chemical Engineering News 39(1):50). Dichloromethane may react exothermically with AIC3 (Braker, G. M. et al., 1986. Accounts of Chemical Research 19(3):75-84).

10. Use Keene mixed with

4) Phenacel bromide
   - May become highly flammable or may initiate fire, especially if other combustible materials are present.
   - Exothermic reaction. May generate heat and cause pressurization.
   - Combustion by-products gaseous products, at least one of which is toxic. May cause pressurization.
   - Generation of corrosive liquid.
   - Reaction may be intense or violent.

Possible Gases: HCl/Cl2

Citations:
HCl can react violently with F2Cl=CH2 (vinylidene fluoride), even at -40°C, causing rapid decomposition and pressurization, including evolution of highly toxic F2 gas. The reaction is catalyzed by AIC3, which is commonly found in HCl solution (Jennings, J. H. 1981. Chemical Engineering News 39(1):50). Dichloromethane may react exothermically with AIC3 (Braker, G. M. et al., 1986. Accounts of Chemical Research 19(3):75-84).

10. Use Keene mixed with

5) Sulfur (thioformic acid)
   - Increased sensitivity to detonation.
   - Forms very unstable explosive metallic compounds.
   - Reaction proceeds with explosive violence and/or forms explosive products.
Chemical Reactivity Report for: Process 1

Evaluation Date: 01/10/2011

- Combination liberates gaseous products, including both flammable and toxic gases. May cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Combination liberates nonflammable, non-toxic gas. May cause pressurization.

Possible Gases: HN₃, NO, NH₃, NH₄NO₃, N₂O

Citations:

- TETRAHYDROFURAN
- Reaction proceeds with explosive violence and/or forms explosive products.
- Combination liberates gaseous products, at least one of which is flammable. May cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Combination liberates gaseous products, at least one of which is toxic. May cause pressurization.
- Generation of corrosive liquid.
- Generates water soluble toxic products.

Possible Gases: Hydrocarbons, Alcohols, HX, Adehyde

Citations:

10) Line Klein mixed with

1) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID
- Heat generated from exothermic reaction may initiate explosion.
- May become highly flammable or may initiate an especially fast or corrosive reaction.
- Combustible decomposition products may cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Exothermic, generation of toxic and corrosive fumes.
- Generation of corrosive liquid.

Possible Gases: H₂S, CO₂, H₂, Ar, Air Fumes

Citations:

10) Line Klein mixed with

- Hydrophobic peroxides, chlorine dioxide gas, nascent highly flammable.
Chemical Reactivity Reports for: Process 1
Evaluation Date: 01/04/2011

10 | Line A is mixed with
8 | TRIPHENYLPHOSPHINE
- Reaction proceeds with explosive violence and/or forms explosive products.
- May become highly flammable or may initiate a fire, especially if other combustible materials are present.
- Spontaneous ignition of reactants or products due to reaction heat.
- Combustion liberates gaseous products, at least one of which is flammable. May cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Combustion liberates gaseous products, at least one of which is toxic. May cause pressurization.
- Exothermic, generation of toxic and corrosive fumes.
- Generation of corrosive liquid.
- Reaction may be intense or violent.

Possible Gases: H2, PH3, Corrosive Fumes

Citations:

10 | Line B is mixed with
9 | WATER
- Reaction proceeds with explosive violence and/or forms explosive products.
- Combustion liberates gaseous products, at least one of which is flammable. May cause pressurization.
- Combustion liberates gaseous products, at least one of which is toxic. May cause pressurization.
- Exothermic, generation of toxic and corrosive fumes.
- Generation of corrosive liquid.
- Generation of water soluble toxic products.

Possible Gases: H2O, PH3, Corrosive Fumes

Citations:

11 | Silphur X is mixed with
1 | ACETOPHENONE

Possible Gases:

Citations:


11 | Silphur X is mixed with
2 | BROMINE
- Reaction proceeds with explosive violence and/or forms explosive products.
- May become highly flammable or may initiate a fire, especially if other combustible materials are present.
- Spontaneous ignition of reactants or products due to reaction heat.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Exothermic, potentially violent polymerization. May cause pressurization.
- Combustion liberates gaseous products, at least one of which is toxic. May cause pressurization.

Possible Gases: H2O, Halocarbons

Citations:


(Reaction of acetone and hydrogen peroxide may be explosive. pancre agility of activated light including sunlight is present [von Schrader, 1916, pp. 142, 312; MCA 3D-7, 1957].) Reaction of ethylene oxide and chlorine can be explosive if activated light (including sunlight), mercury oxide, or silver oxide is present [National Fire Protection Association, 1975. NFPA 901, pp. 103].

Chemical Reactivity Reports for: Process I

11) Silicium X: Trimmed with
3) DICHLOROMETHANE

Possible Gases:

Citations:

11) Silicium X: Trimmed with
4) PHENACYLCHLORIDE

Possible Gases:

Citations:

11) Silicium X: Trimmed with
5) SODIUM AZIDE
- Exothermic reaction. May generate heat and/or cause pressurization.

Possible Gases:

Citations:

11) Silicium X: Trimmed with
6) TETRAHYDROFURAN

Possible Gases:

Citations:

11) Silicium X: Trimmed with
7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID
- Reaction proceeds with explosive violence and/or forms explosive products.
- Spontaneously flammable in air.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Combustion liberates gaseous products, at least one of which is toxic. May cause pressurization.

Possible Gases: CO2, H20

Citations:

11) Silicium X: Trimmed with
8) TRIPHENYLPHOSPHINE
- Reaction proceeds with explosive violence and/or forms explosive products.
- Combustion liberates gaseous products, at least one of which is flammable. May cause pressurization.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Exothermic, potentially violent polymerization. May cause pressurization.

Possible Gases: H2

Citations:
Alkenes react explosively with aluminum isopropoxide. If oxygen is present, explosions may occur immediately after an induction period (Carter, 1935, pp. 28). Vinylacetylene and sodium hydride react violently at low temperature if moisture is present, or at slightly elevated temperatures in dry (Meller, 1946-7, 2:493). Vinylacetylene polymerizes at low pressure if aluminum alkyls are present to catalyse the reaction (Bundaram, K. M.; M. M. Shrestha, and E. F. Olcese, 2001, Ethylene in Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc.).
Chemical Reactivity Report for: Process 1

1) Sulfur: XLT mixed with
WATER

Possible Gases:

Citations:

1) Sulfur: XLT mixed with

1) Use Neu
- Sulfuric reaction. May generate heat and cause pressurization.

Possible Gases:

Citations:

12) Compound 30765421 mixed with

1) ACETOPHENONE

Possible Gases:

Citations:

12) Compound 30765421 mixed with

2) ERUVINE
- Reaction proceeds with explosive violence and forms explosive products
- Spontaneous ignition of reactants or produce a deadly reaction heat
- Combination liberates gaseous products, including both flammable and toxic gases. May cause pressurization
- Sulfuric reaction. May generate heat and cause pressurization.
- Combination liberates gaseous products, at least one of which is toxic. May cause pressurization.

Possible Gases: COCl2(CCl)2HC1(HC1)2Cl(NH)2Cl(NH)2Cl(NH)2Cl(NH)2Cl(NH)2

Citations:


12. Compound 387654321 mixed with
3) Dichloroethene
- Exothermic reaction. May generate heat and cause pressurization.
- Reaction may be intense or violent.

Possible Gases:

Citations:

12. Compound 387654321 mixed with
4) Phenacyl bromide
- Exothermic reaction. May generate heat and cause pressurization.
- Reaction may be intense or violent.

Possible Gases:

Citations:

12. Compound 387654321 mixed with
5) 3,001 Li/AZEIDE
- Increased sensitivity to detonation.
- Forms very unstable explosive metallic compounds.
- Reaction proceeds with explosive violence and forms explosive products.
- Exothermic reaction. May generate heat and cause pressurization.
- Combination induces nonflammable, non-toxic gas. May cause pressurization.

Possible Gases: N2

Citations:

12. Compound 387654321 mixed with
6) TETRAHYDROFURAN

Possible Gases:

Citations:
Chemical Reactivity Report for: Process 1

Evaluation Date: 01/26/2011

1) Compound 98755032 mixed with 7) Toluene Sulfonic Acid, Liquid, with more than 5% free sulfuric acid.
   - May become highly flammable or may initiate fire, especially if other combustible materials are present.
   - Combustion liberates gaseous products, including both flammable and toxic gases. May cause pressurization.
   - Exothermic reaction. May generate heat and/or cause pressurization.

Possible Gases: NOx/CO2

Citations:


12) Compound 98755032 mixed with 6) Trimethylphosphine
   - Heat generated from chemical reaction may initiate explosion.
   - May become highly flammable or may initiate fire, especially if other combustible materials are present.
   - Combustion liberates gaseous products, at least one of which is flammable. May cause pressurization.
   - Combustion liberates gaseous products, including both flammable and toxic gases. May cause pressurization.
   - Exothermic reaction. May generate heat and/or cause pressurization.

Possible Gases: H2S/HCN/H3PO4

Citations:


12) Compound 98755032 mixed with 9) WATER
   - Combustion liberates gaseous products, at least one of which is flammable. May cause pressurization.
   - Combustion liberates gaseous products, at least one of which is toxic. May cause pressurization.
   - Exothermic, generation of toxic and corrosive fumes.
   - Generation of corrosive liquid.
   - Generates water-soluble toxic products.

Possible Gases: H2/CH4/Corrosive Fumes

Citations:

12) Compound 98755032 mixed with 10) air
   - Combustion liberates gaseous products, at least one of which is flammable. May cause pressurization.
   - Combustion liberates gaseous products, including both flammable and toxic gases. May cause pressurization.
   - Exothermic reaction. May generate heat and/or cause pressurization.
   - Combustion liberates gaseous products, at least one of which is toxic. May cause pressurization.
   - Exothermic, generation of toxic and corrosive fumes.
   - Generation of corrosive liquid.
   - Generates water-soluble toxic products.
Chemical Reactivity Report for: Process 1
Evaluation Date: 01/06/2011

- Reaction may be intense or violent.

Possible Bases: CO2, HCl, Corrosive Fumes

Citations:

12) Compound 91705-42-1 mixed with
11) ... XLF

Possible Bases:
Citations:
### 5.3.9.3.4 Pure Component Hazards Tab

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Reactive Group Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>TETRAHYDROFURAN, TRIPHENYLPHOSPHINE</td>
<td>Highly Flammable</td>
</tr>
<tr>
<td>SODIUM AZIDE</td>
<td>Explosive</td>
</tr>
<tr>
<td>BROMINE TOLUENE SULFONIC ACID, LIQUID WITH MORE THAN 5% FREE SULFURIC ACID</td>
<td>Strong Oxidizing Agent</td>
</tr>
<tr>
<td>BROMINE</td>
<td>Air-Resistant</td>
</tr>
<tr>
<td>TETRAHYDROFURAN</td>
<td>Peroxidizable Compound</td>
</tr>
</tbody>
</table>
5.3.9.3.5 Scenario Evaluation Tab

It is recommended that this tab be exported to excel so that it can be formatted to show all results and conclusions.

<table>
<thead>
<tr>
<th>Scenario Name</th>
<th>Scenario Type</th>
<th>Date</th>
<th>Heat Of Reaction</th>
<th>Full Description</th>
<th>Comments</th>
<th>Initial Temp</th>
<th>Max Temp</th>
<th>Temperature</th>
<th>Pressure</th>
<th>MT5R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uit-01</td>
<td>Loss of utility scenario</td>
<td>Compl.</td>
<td>0.00</td>
<td>Pneumatic valve on section-gate T-1 fails closed or manual bar</td>
<td>Consequences: T-1 not energized and remain off</td>
<td>0.00</td>
<td>10</td>
<td>0</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Oih-001</td>
<td>Any other scenario</td>
<td>Compl.</td>
<td>18.60</td>
<td>Process reaction step 1, run under normal operating cond.</td>
<td>Operating conditions outside normal operating</td>
<td>0.00</td>
<td>1</td>
<td>0</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Oih-002</td>
<td>Any other scenario</td>
<td>Compl.</td>
<td>46.00</td>
<td>Process reaction 2, run under normal operating cond.</td>
<td>Operating conditions outside normal operating</td>
<td>282.00</td>
<td>450</td>
<td>187</td>
<td>230</td>
<td>230.00</td>
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<tr>
<td>Oih-003</td>
<td>Any other scenario</td>
<td>Compl.</td>
<td>59.30</td>
<td>Physical reaction: exothermic, non-equilibrium, and scavenging.</td>
<td>Reaction produces 1 mole of hydrogen</td>
<td>0.00</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
APPENDICLES

Appendix A: Program Code Keys

A.1 DOT Segregations

The grid below was used for the coding of the warehousing segregations. The program compares the makes all possible pairings of DOT codes from two compounds and selects the pair that gives the largest segregation.

<table>
<thead>
<tr>
<th>DOT/AIN Category</th>
<th>1.0</th>
<th>2.1</th>
<th>2.2</th>
<th>2.3</th>
<th>3</th>
<th>4.1</th>
<th>4.2</th>
<th>4.3</th>
<th>51</th>
<th>52</th>
<th>6.0</th>
<th>6.1</th>
<th>6.2</th>
<th>7.0</th>
<th>8.0-base</th>
<th>8.8-base</th>
<th>9.0</th>
<th>9.8</th>
<th>Non-Haz</th>
<th>Unknown</th>
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<tbody>
<tr>
<td>1.1 Explosives</td>
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<td>2.1 Flammable gas</td>
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<td>2.2 Non-flammable gas</td>
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<td>2.3 Toxins</td>
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<td>3.0 Flammable liquids</td>
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<td>4.1 Reactivity Matrix Interaction Codes</td>
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<td>4.2 Spontaneously Combustible</td>
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<td>5.1 Dangerous when wet</td>
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<td>5.2 Organic Peroxide</td>
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<td>6.0 Toxins/Substances</td>
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<td>6.2 Infectious Substances</td>
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<td>7.0 Radioactive Materials</td>
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<td>8.0 acid &amp; Corrosives - acids</td>
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<td>8.0 base &amp; Corrosives - bases</td>
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<td>9.0 Other Hazards</td>
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<td>9.8 Non-Haz &amp; Unknown</td>
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</table>

Copyright © 2012 AIChE
### A.2 Reactivity Matrix Interaction Codes

<table>
<thead>
<tr>
<th>Matrix code</th>
<th>Explanation long</th>
<th>Explanation short</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Explosive when dry.</td>
<td>Explosive</td>
</tr>
<tr>
<td>A2</td>
<td>Risk of explosion by shock, friction, fire or other sources of ignition.</td>
<td>Explosive</td>
</tr>
<tr>
<td>A3</td>
<td>Forms very unstable explosive metallic compounds.</td>
<td>Explosive</td>
</tr>
<tr>
<td>A4</td>
<td>External heating may cause an explosion.</td>
<td>Explosive</td>
</tr>
<tr>
<td>A5</td>
<td>May form explosive peroxides.</td>
<td>Explosive</td>
</tr>
<tr>
<td>A6</td>
<td>Reaction proceeds with explosive violence and/or forms explosive products.</td>
<td>Explosive</td>
</tr>
<tr>
<td>A8</td>
<td>Explosive when mixed with combustible material.</td>
<td>Explosive</td>
</tr>
<tr>
<td>A9</td>
<td>Heat generated from chemical reaction may initiate explosion.</td>
<td>Explosive</td>
</tr>
<tr>
<td>A10</td>
<td>Increased sensitivity to detonation.</td>
<td>Explosive</td>
</tr>
<tr>
<td>B1</td>
<td>May become highly flammable or may initiate a fire, especially if other combustible materials are present.</td>
<td>Flammable</td>
</tr>
<tr>
<td>B3</td>
<td>Spontaneously flammable in air.</td>
<td>Flammable</td>
</tr>
<tr>
<td>B4</td>
<td>Spontaneous ignition of reactants or products due to reaction heat.</td>
<td>Flammable</td>
</tr>
<tr>
<td>B5</td>
<td>Combination liberates gaseous products, at least one of which is flammable. May cause pressurization.</td>
<td>Flammable gas</td>
</tr>
<tr>
<td>B6</td>
<td>Combination liberates gaseous products, including both flammable and toxic gases. May cause pressurization.</td>
<td>Flammable gas</td>
</tr>
<tr>
<td>C</td>
<td>Exothermic reaction. May generate heat and/or cause pressurization.</td>
<td>Heat generation</td>
</tr>
<tr>
<td>D1</td>
<td>Exothermic, potentially violent polymerization. May cause pressurization.</td>
<td>Heat generation</td>
</tr>
<tr>
<td>D3</td>
<td>Combination liberates gaseous products, at least one of which is toxic. May cause pressurization.</td>
<td>Toxic gas</td>
</tr>
<tr>
<td>D4</td>
<td>Combination liberates nonflammable, nontoxic gas. May cause pressurization.</td>
<td>Nonflammable, nontoxic gas</td>
</tr>
<tr>
<td>D5</td>
<td>Combination liberates combustion-enhancing gas (e.g., oxygen). May cause pressurization.</td>
<td>Combustion-enhancing gas</td>
</tr>
<tr>
<td>D6</td>
<td>Exothermic, generation of toxic and corrosive fumes.</td>
<td>Heat generation</td>
</tr>
<tr>
<td>D7</td>
<td>Generation of corrosive liquid.</td>
<td>Corrosive</td>
</tr>
<tr>
<td>E</td>
<td>Generates water soluble toxic products.</td>
<td>Toxic</td>
</tr>
<tr>
<td>F</td>
<td>May be hazardous but unknown.</td>
<td>Unknown</td>
</tr>
<tr>
<td>G</td>
<td>Reaction may be intense or violent.</td>
<td>Intense reaction</td>
</tr>
<tr>
<td>H</td>
<td>Possible exposure to radiation.</td>
<td>Radiation</td>
</tr>
<tr>
<td>I</td>
<td>Members of this group are highly reactive. They may be incompatible with members of the same group.</td>
<td></td>
</tr>
</tbody>
</table>

---

21 NOAA: Johnson, L.E. and Farr, J.K., CRW 2.0: A Representative-Compound Approach to Functionality-Based Prediction of Reactive Chemical Hazards
A.3 Reactive Groups

<table>
<thead>
<tr>
<th>Reactive group #</th>
<th>Reactive Group description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acids, Inorganic Non-oxidizing</td>
</tr>
<tr>
<td>2</td>
<td>Acids, Inorganic Oxidizing</td>
</tr>
<tr>
<td>3</td>
<td>Carboxylic Acids</td>
</tr>
<tr>
<td>4</td>
<td>Alcohols and Polyols</td>
</tr>
<tr>
<td>5</td>
<td>Aldehydes</td>
</tr>
<tr>
<td>6</td>
<td>Amides and Imides, Organic</td>
</tr>
<tr>
<td>7</td>
<td>Amines</td>
</tr>
<tr>
<td>8</td>
<td>Azo, Diazo, and Azido Compounds and Organic Hydrazines, Organic</td>
</tr>
<tr>
<td>9</td>
<td>Carbamates and Esters</td>
</tr>
<tr>
<td>10</td>
<td>Bases</td>
</tr>
<tr>
<td>11</td>
<td>Cyanides, Inorganic</td>
</tr>
<tr>
<td>12</td>
<td>Thiocarbamate Esters and Salt/Dithiocarbamate Esters and Salts</td>
</tr>
<tr>
<td>13</td>
<td>Esters</td>
</tr>
<tr>
<td>14</td>
<td>Ethers</td>
</tr>
<tr>
<td>16</td>
<td>Hydrocarbons, Aromatics</td>
</tr>
<tr>
<td>17</td>
<td>Halogenated Organic Compounds</td>
</tr>
<tr>
<td>18</td>
<td>Isocyanates and Isothiocyanates, Organic</td>
</tr>
<tr>
<td>19</td>
<td>Ketones</td>
</tr>
<tr>
<td>20</td>
<td>Sulﬁdes, Organic</td>
</tr>
<tr>
<td>21</td>
<td>Metals, Alkali, Very Active</td>
</tr>
<tr>
<td>22</td>
<td>Metals, Elemental &amp; Powder, Active</td>
</tr>
<tr>
<td>23</td>
<td>Metals, Less Reactive</td>
</tr>
<tr>
<td>26</td>
<td>Nitriles</td>
</tr>
<tr>
<td>27</td>
<td>Nitrites, Nitrates, and Nitro Compounds, Organic</td>
</tr>
<tr>
<td>28</td>
<td>Hydrocarbons, Aliphatic Unsaturated</td>
</tr>
<tr>
<td>29</td>
<td>Hydrocarbons, Aliphatic Saturated</td>
</tr>
<tr>
<td>30</td>
<td>Peroxides, Organic</td>
</tr>
<tr>
<td>31</td>
<td>Phenols, Cresols</td>
</tr>
<tr>
<td>32</td>
<td>Phosphates and Thiophosphates, Organic</td>
</tr>
<tr>
<td>33</td>
<td>Sulﬁdes, Inorganic</td>
</tr>
<tr>
<td>34</td>
<td>Epoxides</td>
</tr>
<tr>
<td>35</td>
<td>Metal Hydrides, Alkyls and Aryls</td>
</tr>
<tr>
<td>37</td>
<td>Anhydrides</td>
</tr>
<tr>
<td>38</td>
<td>Salts, Acidic Inorganic/Organic</td>
</tr>
<tr>
<td>39</td>
<td>Salts, Basic Inorganic/Organic</td>
</tr>
<tr>
<td>40</td>
<td>Acid Halides</td>
</tr>
<tr>
<td>42</td>
<td>Organometallics</td>
</tr>
<tr>
<td>44</td>
<td>Inorganic Oxidizing Agents</td>
</tr>
<tr>
<td>45</td>
<td>Inorganic Reducing Agents</td>
</tr>
<tr>
<td>46</td>
<td>Inorganic Compounds/Neither Reducing nor Oxidizing</td>
</tr>
<tr>
<td>47</td>
<td>CFCs and HCFCs (chlorofluorocarbons and chlorofluorohydrocarbons)</td>
</tr>
<tr>
<td>51</td>
<td>Nitrides, Phosphides, Carbides, and Silicides, Inorganic</td>
</tr>
<tr>
<td>55</td>
<td>Chlorosilanes</td>
</tr>
<tr>
<td>59</td>
<td>Halogenating Agents, Strong</td>
</tr>
<tr>
<td>98</td>
<td>Not Chemically Reactive</td>
</tr>
<tr>
<td>99</td>
<td>Insufﬁcient Information for Classiﬁcation</td>
</tr>
<tr>
<td>100</td>
<td>[contains] Water</td>
</tr>
</tbody>
</table>

Continued on next page
Note the following codes > 100 are not used for determining binary interactions but can be useful to keep track of component hazards

<table>
<thead>
<tr>
<th>Reactive group #</th>
<th>Reactive Group description</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>Highly Flammable</td>
</tr>
<tr>
<td>102</td>
<td>Explosive</td>
</tr>
<tr>
<td>103</td>
<td>Polymerizable</td>
</tr>
<tr>
<td>104</td>
<td>Strong Oxidizing Agent</td>
</tr>
<tr>
<td>105</td>
<td>Strong Reducing Agent</td>
</tr>
<tr>
<td>107</td>
<td>Water-Reactive</td>
</tr>
<tr>
<td>108</td>
<td>Air-Reactive</td>
</tr>
<tr>
<td>109</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>111</td>
<td>Peroxidizable Compound</td>
</tr>
<tr>
<td>400</td>
<td>Radioactive Material</td>
</tr>
</tbody>
</table>

A.4 Special Hazards choices

<table>
<thead>
<tr>
<th>Select One or More</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Highly Flammable</td>
<td></td>
</tr>
<tr>
<td>Explosive</td>
<td></td>
</tr>
<tr>
<td>Polymerizable</td>
<td></td>
</tr>
<tr>
<td>Strong Oxidizing Agent</td>
<td></td>
</tr>
<tr>
<td>Strong Reducing Agent</td>
<td></td>
</tr>
<tr>
<td>Water-Reactive</td>
<td></td>
</tr>
<tr>
<td>Air-Reactive</td>
<td></td>
</tr>
<tr>
<td>Pyrophoric</td>
<td></td>
</tr>
<tr>
<td>Peroxidizable Compound</td>
<td></td>
</tr>
<tr>
<td>Radioactive Material</td>
<td></td>
</tr>
</tbody>
</table>
A.5 DOT Codes

<table>
<thead>
<tr>
<th>Select 1 primary, 0 to 3 secondary</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.x Explosive</td>
</tr>
<tr>
<td>2.1 Flammable Gas</td>
</tr>
<tr>
<td>2.2 Non-Flammable Gas (also Oxygen)</td>
</tr>
<tr>
<td>2.3 Toxic Gas or Inhalation Hazard</td>
</tr>
<tr>
<td>3 Flammable Liquid or combustible liquid</td>
</tr>
<tr>
<td>4.1 Flammable Solid</td>
</tr>
<tr>
<td>4.2 Spontaneously Combustible solid</td>
</tr>
<tr>
<td>4.3 Dangerous when wet</td>
</tr>
<tr>
<td>5.1 Oxidizer</td>
</tr>
<tr>
<td>5.2 Organic peroxide</td>
</tr>
<tr>
<td>6.0 Infectious substance</td>
</tr>
<tr>
<td>6.1 Inhalation Hazard, Poison, Toxic</td>
</tr>
<tr>
<td>7 Radioactive</td>
</tr>
<tr>
<td>8 Corrosive – acidic</td>
</tr>
<tr>
<td>8 Corrosive - basic</td>
</tr>
<tr>
<td>9 Miscellaneous Hazard</td>
</tr>
<tr>
<td>Non-hazardous</td>
</tr>
<tr>
<td>Unknown</td>
</tr>
</tbody>
</table>

Note: that the code “unknown” will result in very large segregation predictions
Appendix B: FAQ

1. Deselect a secondary DOT code
   Hold down the Ctrl key and left click in the code you want to remove. The code will change from highlighted to outlined. Click anywhere outside the selection box to make the deselection permanent.

2. Chemical adds twice
   This is an intermittent problem for a small number of chemicals such as isopropanol and toluene. Certain chemicals will add to your process twice but when you try to delete the duplicate both entries delete. To remove the duplicate entry simply close the process containing the double entry and re-open it. Upon reopening the process, only one entry per chemical will appear.

3. Next button not available or program will not advance
   Check for messages in the lower left corner of the active process window. Often a mandatory field was neglected. Also see FAQ 7) Program Freezes or FAQ 0
8) Error message “Unable to add due to some technical problem…”

4.) Navigation tabs grayed out
Certain portions of the program depend upon data entered on earlier screens. The program prevents the user from advancing until the data is required has been entered. Once you have advanced to a given point in the program you will be able to go back and enter new data or update previously entered data.

5.) Importing chemicals and processes from other users
See section 3.1.7 Exporting / Importing the RMT Process Analysis

6) My reactivity matrix predicts severe reactivity where I know it does not exist
This is a common problem. The matrix should be used as a starting point or research guide for where one should look for possible reactivity issues. Chemical pairs where no reactivity is predicted can generally be taken as correct however the generalizations made by necessity in the CRW2 create many false positives that must be screened out by the user. See section 4.10 Determining the Validity of Information from Matrix Reports for more detailed discussion of this topic. Section 1 Introduction presents an overview of the NOAA CRW2 reactivity prediction strategy along with literature references.

7) Program Freezes
Check the lower portion of the process window for messages in red.
8) Error message “Unable to add due to some technical problem...”
This is a database error. Make sure you have the files RMTDB.mdf and RMTDB_log.ldf in your program directory (see section 3.1.6 Executable and Database File location and descriptions for location). Next check that you have SQL express 2005 installed. (see section 3.1.3 Downloading the Reactivity Management Tool and required prerequisite programs). Next go to start programs menu select Microsoft server 2005 → Configuration Tools → SQL Server Configuration manager.

From the left menu select “SQL Server 2005 services” and right click on “SQL Server (SQLEXPRESS)” and select properties.
In the popup box above select “Local System” and then the “apply” button. A warning message will pop up stating that the change will cause the service to be restarted. Press yes. Exit the popup using the OK button and close the configuration window. Shut down reactivity management tool and reopen. (you may want to reboot before reopening the RMT. If you do use the above procedure to make sure your selection survived the reboot. Some users have reported that they must repeat the above several times before the new settings survive a re-start.

9) Reactivity groups for custom chemicals shown in the Process Chemicals window are missing or different than those entered.
See paragraph 2 of Appendix G: Known Programming Bugs

10) The Special Hazards entered for a custom chemical do not show up in the “Evaluate Pure-componant reactivity hazards” tab of the report.
This is a problem in the code of the program that causes this particular tab to remain incomplete until after a specific point has been passed in the protocol. All NOAA database chemicals will display correctly but custom chemicals will not appear on this list until you have answered the warehousing question (see 5.0.9 Warehousing vs. Chemical Processing) that you are doing physical or chemical processing in the area and press next. Reopening the report at this point will give you a fully completed report. Note all other tabs contain complete information without this extra step.

11) Updated custom chemical data does not appear in process window.
If you update a custom chemical after it has been added to a process the information will not update in the process window until either you close the window and reopen the process or you delete the chemical then re-add it. Also see question 10.
### Appendix C: Abbreviations and Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIChE</td>
<td>American Institute of Chemical Engineers</td>
</tr>
<tr>
<td>ARC</td>
<td>Accelerating Rate Calorimeter; accelerating rate calorimetry (THT ltd.)</td>
</tr>
<tr>
<td>ARSST™</td>
<td>Advanced Reactive Systems Screening Tool (Fauske &amp; Associates, LLC)</td>
</tr>
<tr>
<td>ASME</td>
<td>American Society of Mechanical Engineers</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CAMEO</td>
<td>Computer – Aided Management of Emergency Operations (NOAA)</td>
</tr>
<tr>
<td>CAS</td>
<td>Chemical Abstracts Service</td>
</tr>
<tr>
<td>CCPS</td>
<td>Center for Chemical Process Safety</td>
</tr>
<tr>
<td>CFR</td>
<td>Code of Federal Regulations (U.S.)</td>
</tr>
<tr>
<td>CRW</td>
<td>[NOAA] Chemical Reactivity Worksheet</td>
</tr>
<tr>
<td>CHETAH®</td>
<td>ASTM computer program for Chemical Thermodynamic and Energy Release Evaluation</td>
</tr>
<tr>
<td>CSB</td>
<td>U.S. Chemical Safety and Hazard Investigation Board</td>
</tr>
<tr>
<td>DIERS</td>
<td>Design Institute for Emergency Relief Systems</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimeter; Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DOT</td>
<td>U.S. Department of Transportation</td>
</tr>
<tr>
<td>DPT</td>
<td>Decomposition Pressure Test</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>EPA</td>
<td>U.S. Environmental Protection Agency</td>
</tr>
<tr>
<td>HAZOP</td>
<td>Hazard and Operability [Study]</td>
</tr>
<tr>
<td>IPL</td>
<td>Independent Protection Layer</td>
</tr>
<tr>
<td>LOPA</td>
<td>Layer of Protection Analysis</td>
</tr>
<tr>
<td>MAWP</td>
<td>Maximum Allowable Working Pressure</td>
</tr>
<tr>
<td>MAWT</td>
<td>Maximum Allowable Working Temperature</td>
</tr>
<tr>
<td>MSDS</td>
<td>Material Safety Data Sheet</td>
</tr>
<tr>
<td>MTSR</td>
<td>Maximum Temperature of a Stirred Reactor</td>
</tr>
<tr>
<td>NFPA</td>
<td>National Fire Protection Association (U.S.)</td>
</tr>
<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration (U.S.)</td>
</tr>
<tr>
<td>OSHA</td>
<td>U.S. Occupational Safety and Health Administration</td>
</tr>
<tr>
<td>PHA</td>
<td>Process Hazard Analysis</td>
</tr>
<tr>
<td>PSM</td>
<td>Process Safety Management</td>
</tr>
<tr>
<td>RBPS</td>
<td>Risk Based Process Safety</td>
</tr>
<tr>
<td>RMP</td>
<td>Risk Management Plan/Program</td>
</tr>
<tr>
<td>RSST</td>
<td>Reactive Systems Screening Tool</td>
</tr>
<tr>
<td>RMR</td>
<td>Reactivity Management Roundtable</td>
</tr>
<tr>
<td>RMT</td>
<td>Chemical reactivity evaluation Tool or Reactivity Management Tool</td>
</tr>
<tr>
<td>SADT</td>
<td>Self-Accelerating Decomposition Temperature</td>
</tr>
<tr>
<td>UN</td>
<td>United Nations</td>
</tr>
<tr>
<td>VSP2™</td>
<td>Vent Sizing Package, Version 2 (Fauske &amp; Associates, LLC)</td>
</tr>
</tbody>
</table>
Appendix D: Developing a Reactivity Management System

The following has been abstracted from the CCPS guide series book *Essential Practices for Managing Chemical Reactivity Hazards (2003)*\(^{22}\). It is sincerely hoped that enough of the book’s concepts are summarized here to prompt the reader obtain the book and make use of it to develop and maintain an effective reactivity hazards management program.

There are ten essential practices for managing chemical reactivity hazards. Management elements common to all safety management systems, such as emergency response, have not been included in this chapter. These practices come together in a logical framework for developing and maintaining chemical reactivity hazard management throughout the life cycle of a facility.

1. **Put into Place a System to Manage Chemical Reactivity Hazards**
   Managing chemical reactivity hazards starts with a management system. To prevent incidents, a facility must not only be well designed, but also properly operated and maintained. A commitment to safety from all levels of management is essential, to ensure that all safety aspects receive adequate priority. In practice, conflicts of interest may arise between safety and other goals such as production demands and budgets. In these cases, the management attitude will be decisive. In reality such a conflict may only be an apparent one, because safety, efficiency and product quality all depend on a reliable production facility with a low frequency of technical troubles and safety problems. Developing a management system is not a one-time project. It must be able to manage even subtle material, equipment or personnel changes that may have a significant effect on the safety of the operation. These may include a minor change in raw material purity, a modification to the shape of a vessel where heat transfer is important, or a change in how an operation is supervised.

   Table 1 lists essential ingredients of a management system for successfully managing chemical reactivity hazards. An honest comparison of a company’s current practice with the items in this list can be used to point out the gaps that need to be filled. If you are just getting started with chemical reactivity hazard management, this shows what is needed to develop a successful management system. It is fully recognized that having a management system in place that matches all of the items in Table 1 can be a major undertaking, and may require some significant changes in “corporate culture” that may not happen overnight. Nevertheless, these items are fundamental, and attempts to continue with the remaining essential elements in this chapter will not likely succeed over time if management commitment and involvement are not obvious or adequate resources are not made available.

2. **Collect Reactivity Hazard Information**
3. **Identify Chemical Reactivity Hazards**

4. **Test for Chemical Reactivity**  
5. **Assess Chemical Reactivity Risks**  
6. **Identify Process Controls and Risk Management Options**  
7. **Document Chemical Reactivity Risks and Management Decisions**  
8. **Communicate and Train on Chemical Reactivity Hazards**  
9. **Investigate Chemical Reactivity Incidents**  
10. **Review, Audit, Manage Change, and Improve Hazard Management Practices and program**

**Gap Analysis: Chemical Reactivity Hazard Management System**

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>_____ Top management commitment has been expressed in written form and personally communicated to site management and employees.</td>
</tr>
<tr>
<td>_____ Business decisions and allocation of resources are consistent with this expressed top management commitment.</td>
</tr>
<tr>
<td>_____ Ownership of the facility or process involving chemical reactivity hazards is clearly established.</td>
</tr>
<tr>
<td>_____ Line management is committed to managing chemical reactivity hazards, from the chief executive officer to first-level supervisors.</td>
</tr>
<tr>
<td>_____ An appropriate system to manage chemical reactivity hazards has been developed and formally documented.</td>
</tr>
<tr>
<td>_____ This system includes clear, written statements of what needs to be done and documented, when, how, how often, and by whom.</td>
</tr>
<tr>
<td>_____ Means and resources have been permanently allocated, and training to the appropriate level is conducted and verified, to equip every person throughout the organization with the knowledge and skills needed to carry out his/her responsibilities.</td>
</tr>
<tr>
<td>_____ It is understood by every person that following all established procedures for managing chemical reactivity hazards is a condition of employment.</td>
</tr>
<tr>
<td>_____ Technical resources are readily available to identify chemical reactivity hazards, acquire needed data, assess risks, and develop safeguards.</td>
</tr>
<tr>
<td>_____ The design basis of the facility and its safety systems, including operating and maintenance procedures, are established and documented.</td>
</tr>
<tr>
<td>_____ All process, equipment and personnel changes are managed such that the safety of the facility is not compromised by any change.</td>
</tr>
<tr>
<td>_____ Line management participates in regularly scheduled audits to ensure the procedures and practices for managing chemical reactivity hazards are being consistently followed.</td>
</tr>
<tr>
<td>_____ Line management participates in the investigation of all chemical reactivity incidents and near misses, and makes resources available to implement corrective actions.</td>
</tr>
<tr>
<td>_____ An attitude and practice of continuous improvement is cultivated within the organization, including looking outside to keep abreast of new or updated information.</td>
</tr>
</tbody>
</table>

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Appendix E: Glossary
Presented here is a glossary of terms related to the topics of this Help Guide. Some glossary entries are not used elsewhere in this document; they have been included in case the user comes across an unfamiliar term in the course of evaluating chemical reactivity hazards.

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerating rate calorimetry (ARC)</td>
<td>A technique in which a substance is heated in stages until very slow decomposition or other reaction is detected. The substance is then held under adiabatic conditions and the course of the decomposition or other reaction is monitored. (Also the name of a commercial test apparatus.)</td>
</tr>
<tr>
<td>Activation energy</td>
<td>The constant $E$ in the exponential part of the Arrhenius equation, associated with the minimum energy difference between the reactants and an activated complex (transition state), which has a structure intermediate to those of the reactants and the products, or with the minimum collision energy between molecules that is required to enable a reaction to occur. It is a constant that defines the effect of temperature on reaction rate.</td>
</tr>
<tr>
<td>Adiabatic</td>
<td>No heat transfer occurs to or from the environment surrounding the sample, including the sample container.</td>
</tr>
<tr>
<td>Adiabatic temperature rise</td>
<td>An estimation of the temperature which a specimen would attain if all of the enthalpy (heat) of decomposition and or reaction were to be absorbed by the sample itself. High values represent high hazard potential.</td>
</tr>
<tr>
<td>Air-reactive</td>
<td>A chemical that reacts with some component of ambient air (usually water or oxygen) to form heat and or gas. Also see Pyrophoric</td>
</tr>
<tr>
<td>Arrhenius equation</td>
<td>$k = Z e^{-E/RT}$ where $k$ is the specific reaction rate constant in reciprocal minutes for first order, $Z$ is the pre-exponential factor in reciprocal minutes, $E$ is the Arrhenius activation energy in J/mol, $R$ is the gas constant, 8.32 J/mol K, and $T$ is the temperature in kelvin.</td>
</tr>
<tr>
<td>Autocatalysis</td>
<td>The increase of the rate of reaction due to the catalyzing effect of the reaction products.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>------------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Auto decomposition</td>
<td>The sustained decomposition of a substance without introduction of any other apparent ignition source besides thermal energy and without air or other oxidants present. Auto decomposition is the result of a thermal self-decomposition reaction for given initial conditions (temperature, pressure, volume) at which the rate of heat evolution exceeds the rate of heat loss from the reacting system, thus resulting in an increasing reaction temperature and reaction rate.</td>
</tr>
<tr>
<td>Auto decomposition temperature</td>
<td>The minimum temperature for a specified test method, test apparatus (including material of construction and test volume), and initial pressure required to initiate self-sustained decomposition of a solid, liquid, or gaseous substance without any other apparent source of ignition and without air or other oxidants present.</td>
</tr>
<tr>
<td>Autoxidation</td>
<td>Also autooxidation or auto-oxidation. A slow, easily initiated, self-catalyzed reaction, generally by a free-radical mechanism, between a substance and atmospheric oxygen. Initiators of autoxidation include heat, light, catalysts such as metals, and free-radical generators. Davies (1961) defines autoxidation as interaction of a substance with molecular oxygen below 120°C without flame. Possible consequences of autoxidation include pressure buildup by gas evolution, autoignition by heat generation with inadequate heat dissipation, and the formation of peroxides.</td>
</tr>
<tr>
<td>Catalyst</td>
<td>A chemical substance that accelerates the rate of a chemical reaction by lowering the energy of activation required for the chemical reaction to occur.</td>
</tr>
<tr>
<td>Chemical</td>
<td>Any element, chemical compound, or mixture of elements and/or compounds.</td>
</tr>
<tr>
<td>chemical reactivity</td>
<td>The tendency of substances to undergo chemical change.</td>
</tr>
<tr>
<td>Chemical reactivity hazard</td>
<td>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. The uncontrolled chemical reaction might be accompanied by a temperature increase, pressure increase, gas evolution, or other form of energy release.</td>
</tr>
<tr>
<td>Compatibility</td>
<td>The ability of materials to exist in contact without specified (usually hazardous) consequences under a defined scenario.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>Cool-flame ignition</strong></td>
<td>A relatively slow, self-sustaining, barely luminous gas-phase reaction of the sample or its decomposition products with an oxidant. Cool flames are visible only in a darkened area.</td>
</tr>
<tr>
<td><strong>Critical half thickness</strong></td>
<td>An estimation of the half thickness of a sample in an <em>unstirred container</em>, in which the heat losses to the environment are less than the retained heat. This buildup of internal temperature leads to a thermal-runaway reaction.</td>
</tr>
<tr>
<td><strong>Decomposition</strong></td>
<td>To undergo chemical breakdown, separating into constituent parts or elements or into simpler compounds.</td>
</tr>
<tr>
<td><strong>Decomposition energy</strong></td>
<td>The maximum amount of energy which can be released upon decomposition. The product of decomposition energy and total mass is an important parameter for determining the effects of a sudden energy release—for example, in an explosion. The decomposition energy can occasionally be obtained from the literature or calculated theoretically.</td>
</tr>
<tr>
<td><strong>Decomposition temperature</strong></td>
<td>See <em>auto decomposition temperature</em>.</td>
</tr>
<tr>
<td><strong>Deflagration</strong></td>
<td>A release of energy caused by the propagation of a chemical reaction in which the reaction front advances into the unreacted substance at less than sonic velocity in the unreacted material. Where a blast wave is produced with the potential to cause damage, the term <em>explosive deflagration</em> may be used.</td>
</tr>
<tr>
<td><strong>Detonation</strong></td>
<td>A release of energy caused by the propagation of a chemical reaction in which the reaction front advances into the unreacted substance at greater than sonic velocity in the unreacted material.</td>
</tr>
<tr>
<td><strong>Differential thermal analysis (DTA)</strong></td>
<td>A technique in which the temperature difference between a substance and reference material is measured as a function of temperature while the substance and the reference material are subjected to a controlled temperature program.</td>
</tr>
<tr>
<td><strong>Differential scanning calorimetry (DSC)</strong></td>
<td>A technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature, while the substance and the reference material are subjected to a controlled temperature program.</td>
</tr>
<tr>
<td><strong>Disproportionation</strong></td>
<td>A chemical reaction in which a single compound serves as both oxidizing and reducing agent and is thereby converted into a more oxidized and a more reduced derivative; e.g., a hypochlorite upon appropriate heating yields a chlorate and a chloride.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
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</tr>
<tr>
<td><strong>Endothermic</strong></td>
<td>A physical or chemical change that requires or is accompanied by the absorption of heat.</td>
</tr>
<tr>
<td><strong>Exothermic</strong></td>
<td>A process or chemical reaction that is accompanied by release of heat.</td>
</tr>
<tr>
<td><strong>Explosion</strong></td>
<td>A release of energy sufficient to cause a pressure wave; a rapid or sudden release of energy that causes a pressure discontinuity or blast wave.</td>
</tr>
<tr>
<td><strong>Explosive</strong></td>
<td>A chemical that causes a sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden shock, pressure, or high temperature.</td>
</tr>
<tr>
<td><strong>Extrinsic factor</strong></td>
<td>As used in this publication, a factor that is not an intrinsic property of a material being handled (see intrinsic property).</td>
</tr>
<tr>
<td><strong>Flammable gas</strong></td>
<td>(NFPA 55)-A gas that is flammable in a mixture of 13 percent or less (by volume) with air, or the flammable range with air is wider than 12 percent regardless of the lower limit, at atmospheric temperature and pressure.</td>
</tr>
<tr>
<td><strong>Flammable liquid</strong></td>
<td>Any liquid that has a closed-cup flash point below 100°F (37.8°C), as determined by the test procedures described in NFPA 30 and a Reid vapor pressure not exceeding 40 psia (2068.6 mm Hg) at 100°F (37.8°C), as determined by ASTM D 323, Standard Method of Test for Vapor Pressure of Petroleum Products (Reid Method). Flammable liquids are classified as Class I as follows:</td>
</tr>
<tr>
<td></td>
<td>(a) Class IA liquids shall include those liquids that have flash points below 73°F (22.8°C) and boiling points below 100°F (37.8°C).</td>
</tr>
<tr>
<td></td>
<td>(b) Class IB liquids shall include those liquids that have flash points below 73°F (22.8°C) and boiling points at or above 100°F (37.8°C).</td>
</tr>
<tr>
<td></td>
<td>(c) Class IC liquids shall include those liquids that have flash points at or above 73°F (22.8°C), but below 100°F (37.8°C). (NFPA 30)</td>
</tr>
<tr>
<td><strong>Hazard</strong></td>
<td>A chemical or physical condition that has the potential for causing damage to people, property, or the environment.</td>
</tr>
<tr>
<td><strong>Hazardous chemical</strong></td>
<td>Any chemical that is a physical hazard or a health hazard.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
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</tr>
<tr>
<td>Hazardous material</td>
<td>In a broad sense, any substance or mixture of substances having properties capable of producing adverse effects on health, safety, or the environment. These dangers may arise from but are not limited to flammability, explosibility, toxicity, reactivity, instability, or corrosivity.</td>
</tr>
<tr>
<td>Health hazard</td>
<td>A chemical for which there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed employees.</td>
</tr>
<tr>
<td>Heat of reaction</td>
<td>The total quantity of thermal energy liberated or absorbed during a chemical reaction. (see section 4.5)</td>
</tr>
<tr>
<td>Highly flammable liquid</td>
<td>See Flammable Liquid Class 1A</td>
</tr>
<tr>
<td>Hot-flame ignition</td>
<td>A rapid, self-sustaining, sometimes audible gas-phase reaction of the sample or its decomposition products with an oxidant. A readily visible yellow or blue flame usually accompanies the reaction.</td>
</tr>
<tr>
<td>Hydration</td>
<td>The incorporation of molecular water into a complex molecule with the molecules or units of another species. The complex may be held together by relatively weak forces or may exist as a definite compound.</td>
</tr>
<tr>
<td>Hypergolic</td>
<td>Hypergolic behavior is characterized by immediate, spontaneous ignition of an oxidation reaction upon mixing of two or more substances.</td>
</tr>
<tr>
<td>Incompatible</td>
<td>The term can refer to any undesired results occurring when substances are combined. In the context of this publication, it refers to incompatible substances giving an undesired chemical reaction when combined, posing a chemical reactivity hazard under a defined scenario.</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>A chemical substance used to prevent or stop a chemical reaction, such as polymerization, from occurring.</td>
</tr>
<tr>
<td>Instability</td>
<td>The degree of intrinsic susceptibility of a material to release energy through self-reaction (polymerizing, decomposing, or rearranging).</td>
</tr>
<tr>
<td>Intentional chemistry</td>
<td>The mixing or blending of chemicals designed to produce a chemical reaction.</td>
</tr>
<tr>
<td>Intrinsic property</td>
<td>In relation to materials, a property of the material itself, regardless of use or environmental conditions.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
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</tr>
<tr>
<td>Isomerization</td>
<td>The conversion of a chemical with a given molecular formula to another compound with the same molecular formula but a different molecular structure, such as from a straight-chain to a branched-chain hydrocarbon or an alicyclic to an aromatic hydrocarbon. Examples include the isomerization of ethylene oxide to acetaldehyde (both C₂H₄O) and butane to isobutane (both C₄H₁₀).</td>
</tr>
<tr>
<td>Isoperibolic system</td>
<td>A system in which the controlling external temperature is kept constant.</td>
</tr>
<tr>
<td>Isothermal</td>
<td>A system condition in which the temperature remains constant.</td>
</tr>
<tr>
<td>Laboratory scale</td>
<td>Work with substances in which the containers used for reactions, transfers, and other handling operations are designed to be easily and safety manipulated by one person without mechanical aid. “Laboratory scale” excludes those workplaces whose function is to produce commercial or semi-commercial quantities of materials. Operations in a laboratory are highly variable on a daily basis. Non-laboratory operations often follow a “recipe” or formula with the goal of producing a specified quantity of material usually for sale or further processing. Operations that fit the “easily manipulated by one person” definition above should not be considered as laboratory operations if the goal is to produce multiple near identical batches over a period of weeks, months or years.</td>
</tr>
<tr>
<td>Minimum ignition energy</td>
<td>Electrical energy discharged from a capacitor, which is just sufficient to effect ignition of the most ignitable mixture of a given fuel-mixture under specific test conditions.</td>
</tr>
<tr>
<td>Monomer</td>
<td>A simple molecule that is capable of combining with a number of other molecules to form a polymer.</td>
</tr>
<tr>
<td>MTSR</td>
<td>Maximum Temperature Synthetic Reaction, The sum of the starting reaction temperature all adiabatic heat rises associated with a particular set of reaction conditions or failure modes. (see section 4.6)</td>
</tr>
<tr>
<td>Near miss</td>
<td>An unplanned sequence of events that could have caused harm or loss if conditions were different or were allowed to progress, but actually did not.</td>
</tr>
<tr>
<td>Onset temperature</td>
<td>The temperature at which a deflection from the established baseline is first observed.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
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</tr>
<tr>
<td><strong>Organic peroxide</strong></td>
<td>An organic compound that contains the bivalent –O–O– structure and which may be considered to be a structural derivative of hydrogen peroxide where one or both of the hydrogen atoms has been replaced by an organic radical.</td>
</tr>
<tr>
<td><strong>Oxidation</strong></td>
<td>Depending on the context, oxidation can either refer to (a) a reaction in which oxygen combines chemically with another substance, or (b) any reaction in which electrons are transferred. For the latter definition, <em>oxidation</em> and <em>reduction</em> always occur simultaneously (redox reactions), and the substance that gains electrons is termed the <em>oxidizing agent</em>. Electrons might also be displaced within a molecule without being completely transferred away from it.</td>
</tr>
<tr>
<td><strong>Oxidizer</strong></td>
<td>Any material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion of combustible materials. More generally, an oxidizer is any oxidizing agent.</td>
</tr>
<tr>
<td><strong>Oxidizing agent</strong></td>
<td>See definition for <em>oxidation</em>.</td>
</tr>
<tr>
<td><strong>Partial oxidation</strong></td>
<td>The combination of oxygen with a material in an oxygen-deficient atmosphere that generally results in carbon monoxide being one of the combustion products.</td>
</tr>
<tr>
<td><strong>Peroxide</strong></td>
<td>A chemical compound that contains the peroxy (–O–O–) group, which may be considered a derivative of hydrogen peroxide (HOOOH).</td>
</tr>
<tr>
<td><strong>Peroxide former</strong></td>
<td>A material that reacts with oxygen or hydrogen peroxide to produce a peroxide of the reactant.</td>
</tr>
<tr>
<td><strong>Peroxidizable compound</strong></td>
<td>A material that reacts with oxygen or hydrogen peroxide to produce a peroxide of the reactant.</td>
</tr>
<tr>
<td><strong>Physical hazard</strong></td>
<td>A chemical for which there is scientifically valid evidence that it is a combustible liquid, a compressed gas, explosive, flammable, an organic peroxide, an oxidizer, pyrophoric, unstable (reactive), or water-reactive.</td>
</tr>
<tr>
<td><strong>Physical processing</strong></td>
<td>The transfer, blending, mixing, grinding, sampling or other handling of open packages of chemicals where no chemical reaction is expected to occur.</td>
</tr>
<tr>
<td><strong>Polymer</strong></td>
<td>Substance made of giant molecules formed by the union of simple molecules (monomers); for example, polymerization of ethylene forms a polyethylene chain, or condensation of phenol and formaldehyde (with production of water) forms phenol-formaldehyde resins.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
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</tr>
<tr>
<td>Polymerizable</td>
<td>A chemical reaction generally associated with the production of plastic substances. The individual molecules of the chemical (liquid or gas) react with each other to produce what can be described as a long chain.</td>
</tr>
<tr>
<td>Polymerization</td>
<td>A chemical reaction generally associated with the production of plastic substances. The individual molecules of the chemical (liquid or gas) react with each other to produce what can be described as a long chain.</td>
</tr>
<tr>
<td>Pressure of concern</td>
<td>The pressure above which unacceptable consequences occur (see section 4.9).</td>
</tr>
<tr>
<td>Pyrophoric</td>
<td>A chemical that will ignite spontaneously in air at a temperature of 130°F (54.4°C) or below.</td>
</tr>
<tr>
<td>Note that definitions of pyrophoric from other sources may specify a time frame, usually seconds or minutes, within which ignition must be observed.</td>
<td></td>
</tr>
<tr>
<td>Quenching</td>
<td>Abruptly stopping a reaction by severe cooling or by catalyst inactivation in a very short time period; used to stop continuing reactions in a process thus preventing further decomposition or runaway.</td>
</tr>
<tr>
<td>Radioactive material</td>
<td>Substance or material which contains an elemental component that decomposes to a different element by ejection of mass or energy from the nucleus of the decomposing atom.</td>
</tr>
<tr>
<td>Reaction</td>
<td>Any transformation of material accompanied by a change of enthalpy which may be endothermic or exothermic.</td>
</tr>
<tr>
<td>Reaction induction time (RIT value)</td>
<td>The time a chemical compound or mixture may be held under isothermal conditions until it exhibits a specific exothermic reaction.</td>
</tr>
<tr>
<td>Reactive chemical</td>
<td>A substance that can pose a chemical reactivity hazard by readily oxidizing in air without an ignition source (spontaneously combustible or peroxide forming), initiating or promoting combustion in other materials (oxidizer), reacting with water, or self-reacting (polymerizing, decomposing, or rearranging). Initiation of the reaction can be spontaneous, by energy input such as thermal or mechanical energy, or by catalytic action increasing the reaction rate.</td>
</tr>
<tr>
<td>Reactive group</td>
<td>A chemical substructure that evokes a specific reactivity upon the molecule that contains it. Chemicals are grouped by these substructures to help predict their reactivity with other chemicals.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>------------------------------------------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Reactivity Management System</td>
<td>A complete and comprehensive system for dealing with chemical reactivity hazards both legally and responsibly (See Appendix D)</td>
</tr>
<tr>
<td>Reactivity, chemical</td>
<td>See chemical reactivity.</td>
</tr>
<tr>
<td>Rearrangement</td>
<td>Disproportionation, isomerization, or tautomerization.</td>
</tr>
<tr>
<td>Runaway reaction</td>
<td>A reaction that is out of control because the rate of heat generation by an exothermic chemical reaction exceeds the rate of cooling available.</td>
</tr>
<tr>
<td>Scenario</td>
<td>In the context of identifying incompatibilities: A detailed physical description of the process whereby a potential inadvertent combination of materials may occur.</td>
</tr>
<tr>
<td>Self-accelerating decomposition temperature (SADT)</td>
<td>Certain compounds, such as organic peroxides, when held at moderate ambient temperatures for an extended period of time, may undergo an exothermic reaction that accelerates with increase in temperature. If the heat liberated by this reaction is not lost to the environment, the bulk material increases in temperature, which leads to an increase in the rate of decomposition. Unchecked, the temperature grows exponentially to a point at which the decomposition cannot be stopped or slowed. The minimum temperature at which this exponential growth occurs in a material packed in its largest standard shipping container is defined as the self-accelerating decomposition temperature. Self-accelerating decomposition temperature is a measure of the ease in which decomposition occurs under normal storage conditions. It is not an indicator of the violence of any decomposition reaction under conditions of fire exposure or contact with incompatible materials.</td>
</tr>
<tr>
<td>Self-reactive</td>
<td>Capable of polymerization, decomposition, or rearrangement. Initiation of the reaction can be spontaneous, by energy input such as thermal or mechanical energy, or by catalytic action increasing the reaction rate.</td>
</tr>
<tr>
<td>Shock sensitive</td>
<td>A relatively unstable material, the energetic decomposition of which can be initiated by merely the input of mechanical energy at normal ambient conditions. Materials are considered as shock sensitive if they are more easily initiated than dinitrobenzene in a standard drop-weight test.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
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<td>-------------------------------</td>
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</tr>
<tr>
<td>Spontaneously combustible</td>
<td>Capable of igniting and burning in air without the presence of an ignition source. Pyrophoric materials are spontaneously combustible, although some pyrophorics require the presence of a minimum amount of moisture (humidity) to spontaneously ignite. Other spontaneously combustible substances and mixtures may require more time or an insulating environment to self-heat to the point of ignition.</td>
</tr>
<tr>
<td>Stable materials</td>
<td>Those materials that normally have the capacity to resist changes in their chemical composition, despite exposure to air, water, and heat as encountered in fire emergencies.</td>
</tr>
<tr>
<td>Strong oxidizing agent</td>
<td>A chemical or substance which brings about an oxidation reaction. The agent may (1) provide the oxygen to the substance being oxidized (in which case the agent has to be oxygen, or contain oxygen), or (2) it may receive electrons being transferred from the substance undergoing oxidation. DOT defines an oxidizer or oxidizing material as a substance which yields oxygen readily to stimulate combustion oxidation) or organic matter. Important: If a substance is listed as an oxidizer on the MSDS, precautions must be taken in the handling and storage of the substance. Keep away from flammables, combustibles and reducing agents.</td>
</tr>
<tr>
<td>Strong reducing agent</td>
<td>In a reduction reaction (which always occurs simultaneously with an oxidation reaction) the reducing agent is the chemical or substance which (1) combines with oxygen, (2) loses electrons in the reaction. See also, &quot;Oxidizing Agent&quot; Important: If a material is listed as a reducing agent on the MSDS, precautions must be taken in the handling and storage of the substance. Keep separate from oxidizing agents</td>
</tr>
<tr>
<td>Tautomerizing</td>
<td>Converting from one isomer into another in organic compounds that differ from one another in the position of a hydrogen atom and a double bond.</td>
</tr>
<tr>
<td>Temperature of concern</td>
<td>The temperature above which unacceptable consequences occur (see section 4.7)</td>
</tr>
<tr>
<td>Temperature of no return</td>
<td>The temperature at which the rate of heat generation of a reaction or decomposition is equal to the maximum rate of cooling available. Above this temperature the reaction mixture will increase in temperature uncontrollably.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>------------------------------</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Thermally unstable</td>
<td>A material that will undergo an exothermic, self-sustaining, or accelerating self-reaction (decomposition, polymerization, or rearrangement) when heated to a specific temperature for given conditions of pressure, volume, composition, and containment. Thus, the self-reaction can be initiated by thermal energy alone.</td>
</tr>
<tr>
<td>Time to thermal runaway (TMR)</td>
<td>An estimation of the time required for an exothermic reaction, in an adiabatic container, (that is, no heat gain or loss to the environment), to reach the point of thermal runaway.</td>
</tr>
<tr>
<td>Toll manufacturer</td>
<td>Contract manufacturer (external manufacturer).</td>
</tr>
<tr>
<td>Unstable material</td>
<td>A material that, in the pure state or as commercially produced, will vigorously polymerize, decompose, or condense, become self-reactive, or otherwise undergo a violent chemical change under conditions of shock, pressure, or temperature.</td>
</tr>
<tr>
<td>Warehousing</td>
<td>The handling of sealed packages of chemicals for the sole purposes of storage and distribution.</td>
</tr>
<tr>
<td>Water reactive</td>
<td>A material that will react upon contact with water under normal ambient conditions. Includes materials that react violently with water and other materials that react slower but can generate heat or gases that can result in elevated pressure if contained.</td>
</tr>
</tbody>
</table>
# Appendix F: Bibliography: Suggested References for Further Reading

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- **F.2 Topical Guidebooks and Publications** ................................................................. 209
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  - F.3.2 Safe Storage and Handling of Self Reacting Materials ........................................ 212
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## F.1 Foundational Process Safety Textbooks and Publications

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<tr>
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<th>Notes</th>
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</thead>
</table>

## F.2 Topical Guidebooks and Publications

<table>
<thead>
<tr>
<th>Source</th>
<th>Title</th>
<th>Edition</th>
<th>Publisher</th>
<th>ISBN</th>
<th>Notes</th>
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<tr>
<td>Reference</td>
<td>Title</td>
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</tr>
<tr>
<td>David Leggett</td>
<td>Chemical reaction hazard identification and evaluation: Taking the first steps</td>
<td></td>
<td></td>
<td>Process Safety Progress, March 2004, Volume 23, No. 1, AIChE</td>
<td></td>
</tr>
<tr>
<td>NOAA: Johnson, L.E. and Farr, J.K.</td>
<td>CRW 2.0: A Representative-Compound Approach to Functionality-Based Prediction of Reactive Chemical Hazards</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perry, Judy</td>
<td>Strategy for Managing Reactivity Hazards, An ioMosaic Corporation Whitepaper; available free of charge (registration required)</td>
<td></td>
<td></td>
<td><a href="http://www.iomosaic.com">http://www.iomosaic.com</a></td>
<td></td>
</tr>
</tbody>
</table>
## F.3 Pertinent References on Common Pure Component Hazards

### F.3.1 Safe Storage and Handling of Spontaneously Combustible Materials

- **Guidelines For The Safe Handling of Powders and Bulk Solids**, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (2005); [www.aiche.org/ccps](http://www.aiche.org/ccps)
- **Organoaluminum Compounds**, J. Mole and EA Jeffery (1972); Elsevier Publishing Company, Amsterdam, The Netherlands
- **NFPA 400 Hazardous Chemicals Code**, National Fire Protection Association, Quincy MA; [www.nfpa.org](http://www.nfpa.org)
- **NFPA 484 Standard for Combustible Metals**, National Fire Protection Association, Quincy MA; [www.nfpa.org](http://www.nfpa.org)
## Primer on Spontaneous Heating and Pyrophoricity

## Handling Procedures for Organometalics
Albemarle Corporation, Baton Rouge, LA; [www.albemarle.com](http://www.albemarle.com)

## Creating the Right Chemistry - Metal Alkyls from Akzo Nobel
Akzo Nobel Polymer Chemicals, Chicago, IL (2003); [www.akzonobel-polymerchemicals.com](http://www.akzonobel-polymerchemicals.com)

## Personal Protective Equipment for Handling Metal Alkyls
Akzo Nobel Polymer Chemicals, Chicago, IL (2003); [www.akzonobel-polymerchemicals.com](http://www.akzonobel-polymerchemicals.com)

## Metal Alkyls and Their Burning Properties
Akzo Nobel Polymer Chemicals, Chicago, IL (2003); [www.akzonobel-polymerchemicals.com](http://www.akzonobel-polymerchemicals.com)

## Pyrophoricity of Metal Alkyls
Akzo Nobel Polymer Chemicals, Chicago, IL (2003); [www.akzonobel-polymerchemicals.com](http://www.akzonobel-polymerchemicals.com)

## Unloading Procedure for Metal Alkyls in C-Type Portable Tanks
Akzo Nobel Polymer Chemicals, Chicago, IL (2003); [www.akzonobel-polymerchemicals.com](http://www.akzonobel-polymerchemicals.com)

## Control of Metal Alkyl Fires
Akzo Nobel Polymer Chemicals, Chicago, IL (2003); [www.akzonobel-polymerchemicals.com](http://www.akzonobel-polymerchemicals.com)

## Metal Alkyls and Their Solutions
Akzo Nobel Polymer Chemicals, Chicago, IL (2003); [www.akzonobel-polymerchemicals.com](http://www.akzonobel-polymerchemicals.com)

## Unloading Procedures for Metal Alkyls in ISO Portable Tanks
Akzo Nobel Polymer Chemicals, Chicago, IL (2003); [www.akzonobel-polymerchemicals.com](http://www.akzonobel-polymerchemicals.com)

## Disposal of Metal Alkyl Residues
Akzo Nobel Polymer Chemicals, Chicago, IL (2003); [www.akzonobel-polymerchemicals.com](http://www.akzonobel-polymerchemicals.com)

### F.3.2 Safe Storage and Handling of Self Reacting Materials

<table>
<thead>
<tr>
<th><strong>Reference</strong></th>
<th><strong>Details</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>NFPA 432 Code for the Storage of Organic Peroxide Formulations, National Fire Protection Association, Quincy MA; <a href="http://www.nfpa.org">www.nfpa.org</a></td>
<td></td>
</tr>
<tr>
<td><em>Popcorn Polymer Resource Book, 1,3-Butadiene</em>; International Institute of Synthetic Rubber Producers, Inc. (1995); <a href="http://www.iisrp.com">www.iisrp.com</a></td>
<td></td>
</tr>
</tbody>
</table>

F.3.3 Safe Storage and Handling of Oxidizers and Peroxide Formers

<table>
<thead>
<tr>
<th><strong>Reference</strong></th>
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<tbody>
<tr>
<td>Reference</td>
<td>Description</td>
</tr>
<tr>
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</tr>
<tr>
<td>NFPA 68</td>
<td>Standard on Explosion Protection by Deflagration Venting</td>
</tr>
<tr>
<td>NFPA 69</td>
<td>Standard on Explosion Prevention Systems</td>
</tr>
<tr>
<td>NFPA 430</td>
<td>Code for the Storage of Liquid and Solid Oxidizers</td>
</tr>
<tr>
<td>Popcorn Polymer Resource Book, 1,3-Butadiene</td>
<td>International Institute of Synthetic Rubber Producers, Inc.</td>
</tr>
</tbody>
</table>

### F.3.4 Safe Storage and Handling of Water reactives

<table>
<thead>
<tr>
<th>Reference</th>
<th>Description</th>
<th>Publisher/Website</th>
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</table>
Appendix G: Known Programming Bugs

Many of the bugs found thus far involve improper display of information. Thus far most of these are easily resolved by closing the program and then reopening the program and reloading the process. It is therefore recommended that the user close the program and then open and reload the process prior to printing reports or viewing results. No saved data is lost during this process.

The Reactivity groups of custom chemicals added to the process will sometimes display incorrectly in the “Process Chemicals” window. This issue corrects itself when the user advances to the next screen which is “Missing Chemical Data”. Once the requested missing data is entered, use the previous button to view the Process Chemicals screen which will now display correctly.

The flow of the program can cause incomplete reports unless you have passed certain key steps in the evaluation protocol. The Chemical reactivity evaluation Report – Evaluate Pure-component hazards tab will not contain complete information until certain tabs in the process protocol have been visited. You must proceed past the Warehousing question by either answering “physical or chemical processing may occur in this area” or answering that only storage is occurring but checking the check box stating that you wish to continue with the rest of the protocol anyway and then the Next button. Once this point in a particular process has been passed, the updates will occur by clicking on any tab beyond this point. See the screen shot in the Worked examples section 5.0.9. Should any custom chemical information be changed or a new custom chemical added to the process, the information will not update until you visit any tab later in the protocol than the “identify PHA Process” tab under the Main tab of “chemical Reactivity Hazards”

Exporting to Reports to Excel:

Process name can not contain any special characters or be longer than 31 characters. The program Process window will allow this without caution or error message but exports to excel will be disabled. Because process names cannot be changed, you must start over with a conforming process name.
Afterword: Future Direction

As currently implemented, the chemical reactivity evaluation tool gives the basic framework for identifying and evaluating chemical reactivity hazards.

Future revisions of the NOAA CAMEO database will contain DOT labels for many entries. Indeed the current database contains some DOT label entries in a un-data checked beta form. Because the data checked version of CAMEO was not available during the programming, the decision was made to require the user to input all DOT codes. Future releases will likely extract this data from the updated CAMEO database.

This tool currently utilizes manually inputted data available from MSDS and literature data to help develop reactivity scenarios. However, for new chemicals, information such as heats of reaction, heat capacities are not readily available. Empirical methods to determine this information are available but require comprehensive and time consuming analytical work.

Future enhancements for this software tool should focus on the use of computational programs such as CHETAH® for predicting thermochemical properties and certain "reactive chemicals" hazards associated with a pure chemical, a mixture of chemicals, or a chemical reaction.

The integration of CHETAH® and other computational approaches in the reactivity tool can accomplish the prediction of thermochemical properties using the molecular structure(s) of new chemical materials at an early stage of process development helping to avoid or control reactivity hazards.

These computational results can provide early reactivity guidance and should be used to complement experimental work to help identify the need for further reactivity testing in the areas of impact sensitivity and/or flammability.

Further enhancement of the process for importing and exporting the process and custom chemical databases should be considered. The ability to import a process or custom chemical into ones existing databases rather than the current method of replacing ones files would enable easy sharing of data between multiple users.

It has also been suggested that the warehouse separation distances be editable by the user. This could be accomplished by reading them from a user editable table rather than hard coding them into the program.
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