Chemical Reactivity Evaluation Tool Help Guide

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REACTIVITY MANAGEMENT
ROUNDTABLE

An AIChE Technology Alliance
CCPS
Center for Chemical Process Safety

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Table of Contents

Follow links ending with an ***** to a more detailed sectional table of contents.

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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 theses 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

Helpful Hint

Pitfall alert

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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.

Acknowledgments

The Center for Chemical Process Safety (CCPS) thanks all of the members of the Reactivity Subcommittee of CCPS' Technical Steering Committee for providing input, reviews, technical guidance and encouragement to the project team throughout the preparation of this book. CCPS also expresses appreciation to the members of the Technical Steering Committee for their advice and support.

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The RMR committee and CCPS gratefully acknowledge the contributions of the following organizations:

1. NOAA, its contractors and contributors for the use of the CAMEO database and its functional group based binary chemical interaction model.
2. The many corporations and organizations that donated the time and talents of the RMR committee members
3. CCPS and the RMR wish to specifically acknowledge the service of RMR Chairmen past and present.
    - 2003-2004 Georges Melhem, IoMosaic
    - 2004-2006 Don Connolley, BP
    - 2006-2007 Pete Lodal, Eastman Chemical Company
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    - 2008-2011 E. Mark Davis, Eli Lilly

The CCPS staff liaison for this project was Dan Sliva, who also coordinated meetings and facilitated subcommittee reviews and communications.

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The subcommittee consisted of the following active members, whose significant efforts and contributions are gratefully acknowledged:

Edward M. (Mark) Davis, Eli Lilly, Subcommittee Chair
Don Connolley, BP
Seshu Dharmavaram, DuPont
Jim Farr, U.S. National Oceanic and Atmospheric Administration
David Frurip, The Dow Chemical Company
Peter Howell, Mark Five
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Wayne Chastain, Eastman Chemical Company
Pete Lodal, Eastman Chemical Company
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Laura Turci, CCPS
Russell Davis, Honeywell

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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[1] 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

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[1] "Improving Reactive Hazard Management" (CSB 2002)

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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. http://www.microsoft.com/download/en/details.aspx?id=17851&WT.mc_id=MSCOM_EN_US_DLC_DETAILS_121LSUS007996. Follow the prompts as requested.

SQL 2005 Express edition is required. Please download and install from this location. http://www.microsoft.com/downloads/en/details.aspx?FamilyID=220549b5-0b07-4448-8848-dcc397514b41 . Download the file: "SQLEXPR.exe" and run.
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)**

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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[2]. 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[1] 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[3]. 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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[2] Johnson,L.E. and Farr, J.K., CRW 2.0: A Representative-Compound Approach to Functionality-Based Prediction of Reactive Chemical Hazards http://response.restoration.noaa.gov/book_shelf/1862_Paper_CRW2.pdf

[3] Chastain, J. Wayne, Doerr, William W., Berger, Scott, Lodal, Peter N.: Avoid Chemical Reactivity Incidents in Warehouses, CEP, (2008) Vol. 104, No. 2

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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.

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[4] Johnson, Robert. W.; Rudy, Steven W.; Unwin, Stephen D. (2003). Essential Practices for Managing Chemical Reactivity Hazards.. Center for Chemical Process Safety/AIChE.
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

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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.[5]

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.

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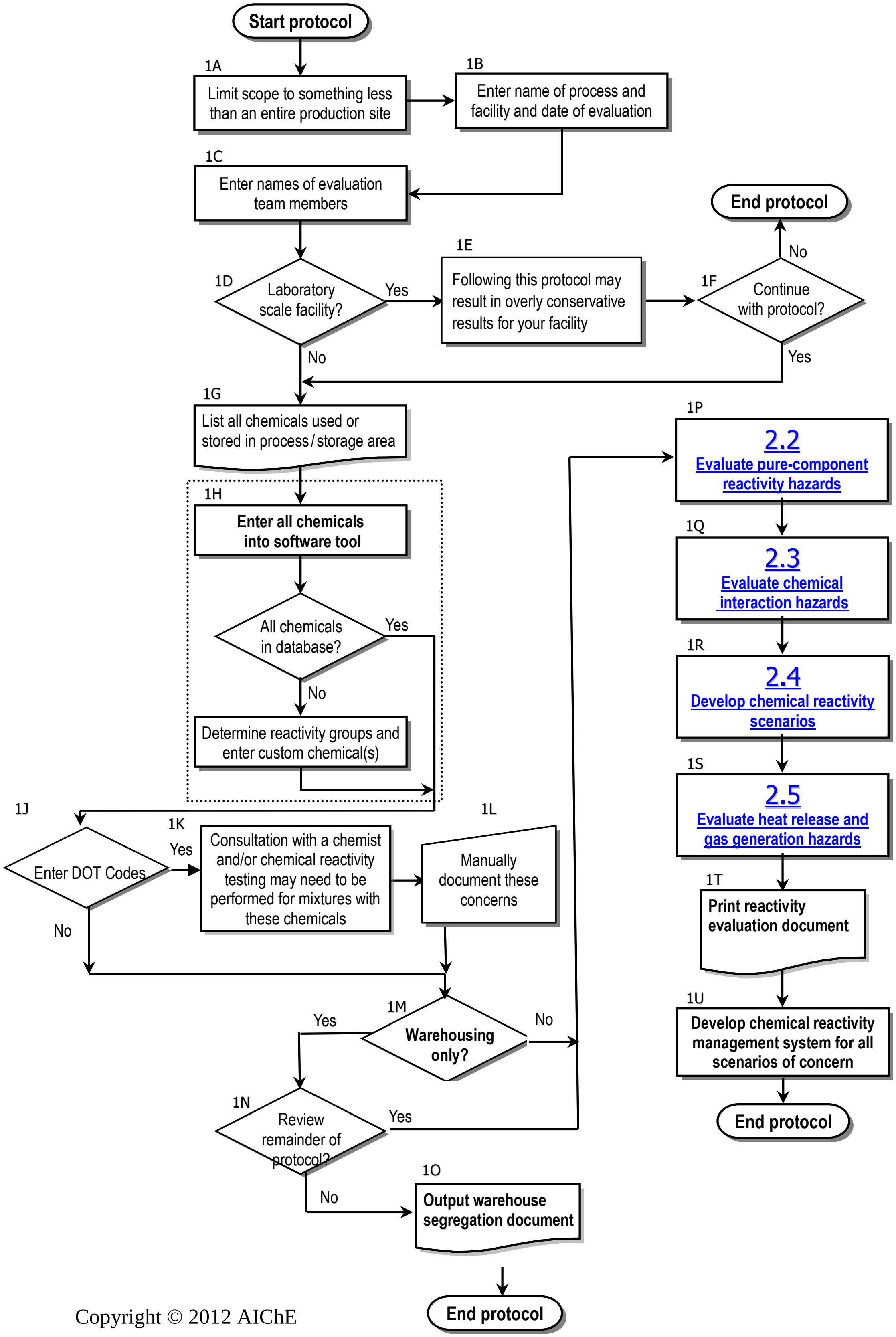
[5] For a database of material compatibility and chemical resistance see http://www.coleparmer.com/Chemical-Resistance, Last accessed Jan 09, 2012

2 Program Flow

2.1 Primary Flow Chart



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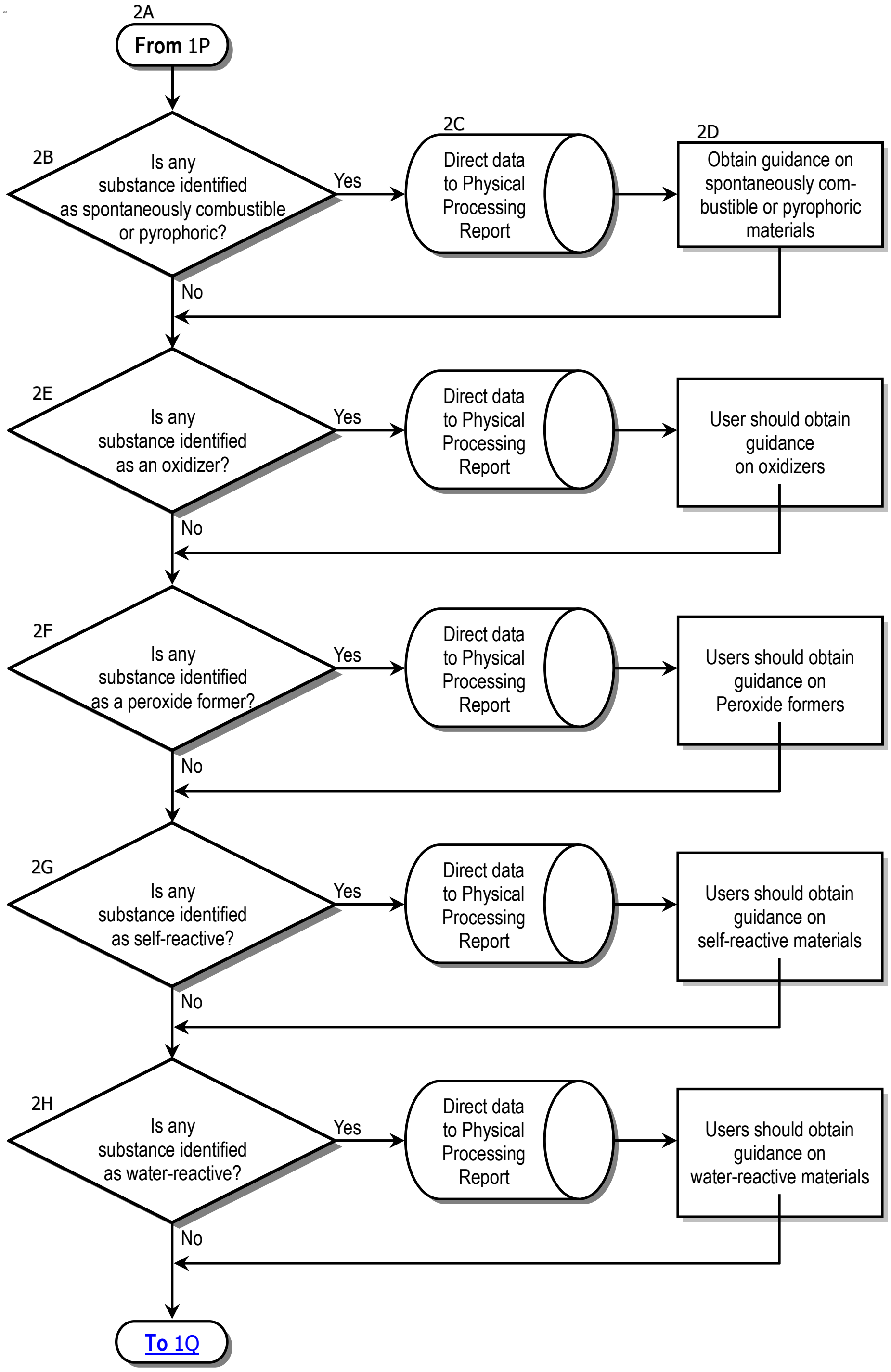
2.2 Evaluate Pure Componant Reactivity Hazards



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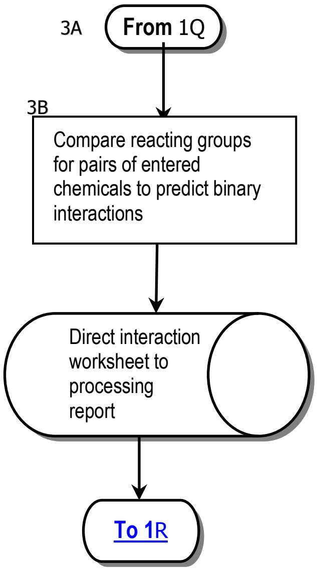
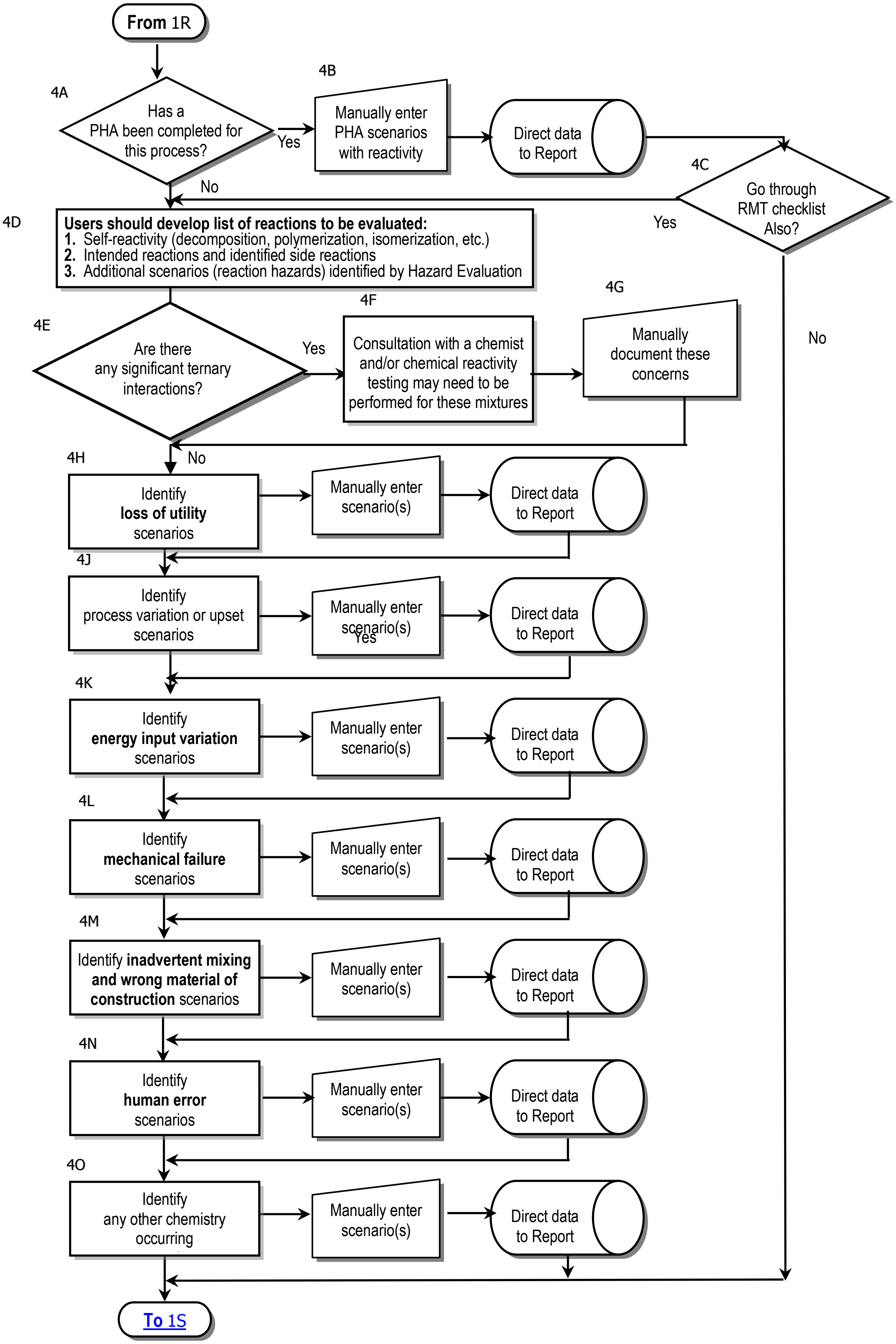
2.3 Evaluate Chemical Interaction Hazards



2.4 Develop Chemical Reactivity Scenarios



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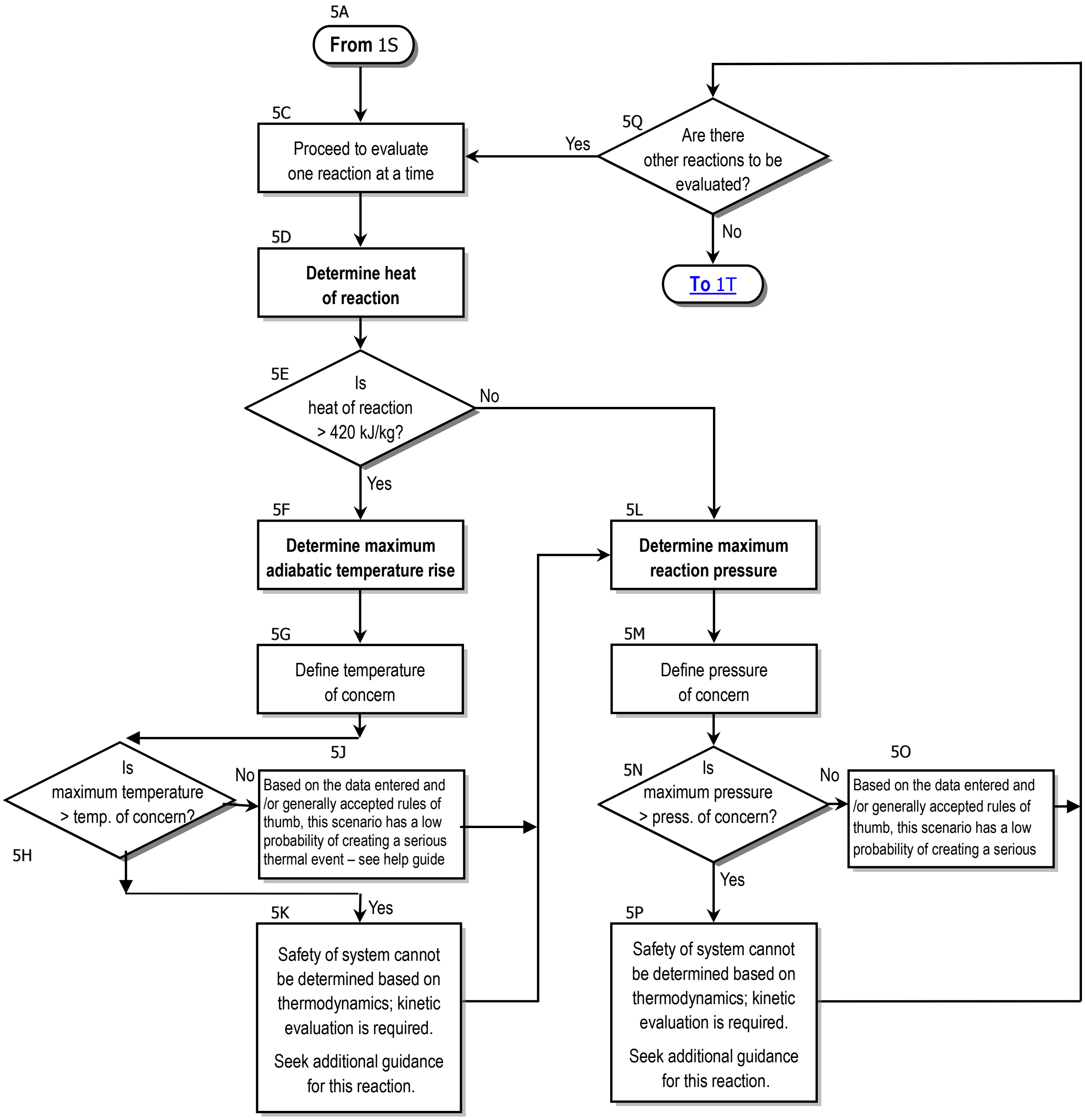
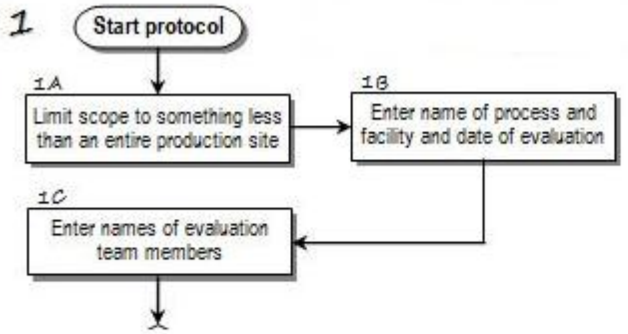
2.5 Evaluate Heat Release and Pressure Generation Hazards



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.

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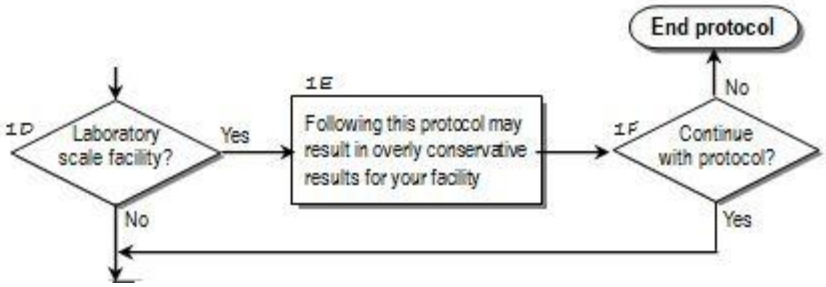


1D **Laboratory-scale facility?**

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**

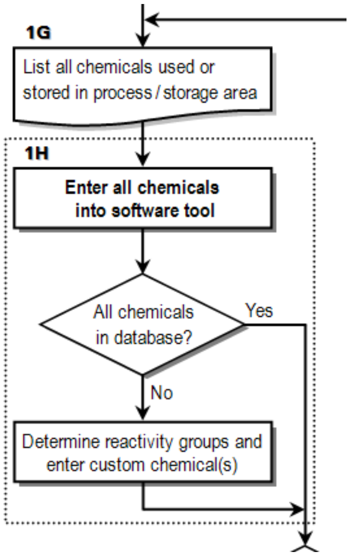
If the process is laboratory-scale, a caution is given that following the RMR flowchart with a lab-scale process may result in overly conservative results.

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*.

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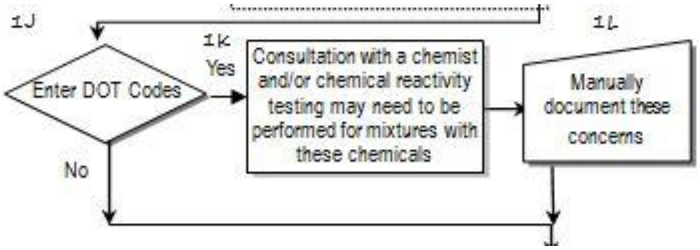
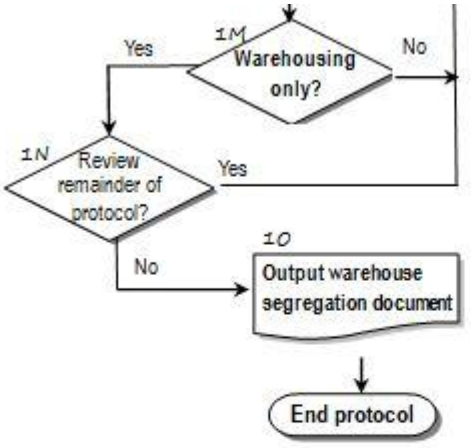


Missing Chemical Data- This part of the program performs two functions it serves as a double check for custom chemicals and is an input form for the DOT labels for all NOAA chemicals. The DOT codes are required for the warehouse segregation function. The program will not allow the user to continue until 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.

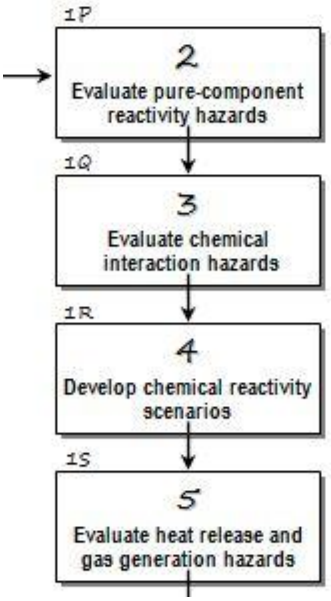
1N **Review Remainder of Protocol?**

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**

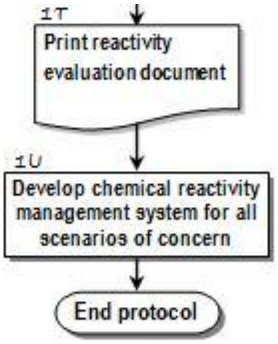
It is necessary to identify not only normal reactions and possible self reactivity concerns, but also to determine credible upset conditions and the possible reactions that could result from these conditions.
This step in the protocol refers the user to Sheet 4 for developing a list of possible incident 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

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3 Program Usage

3.1 Installing and Starting the Program

Link To Full TOC

Table of Contents

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. http://www.microsoft.com/download/en/details.aspx?id=17851&WT.mc_id=MSCOM_EN_US_DLC_DETAILS_121LSUS007996.

- SQL 2005 Express edition is required. Please download and install from this location. http://www.microsoft.com/downloads/en/details.aspx?FamilyID=220549b5-0b07-4448-8848-dcc397514b41 .

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

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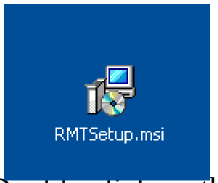
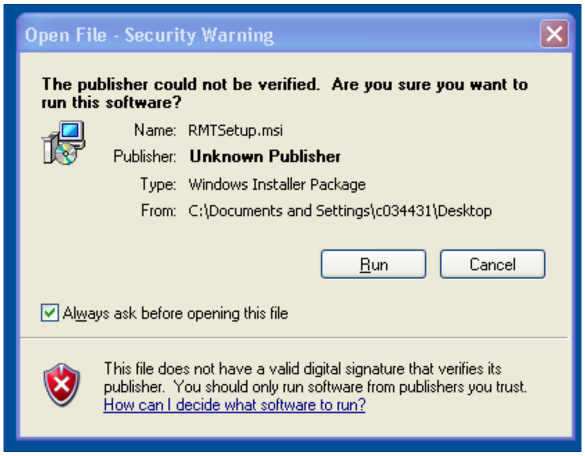
3.1.4 Windows XP install

- You must have administrator rights



- Double click on the installer icon.



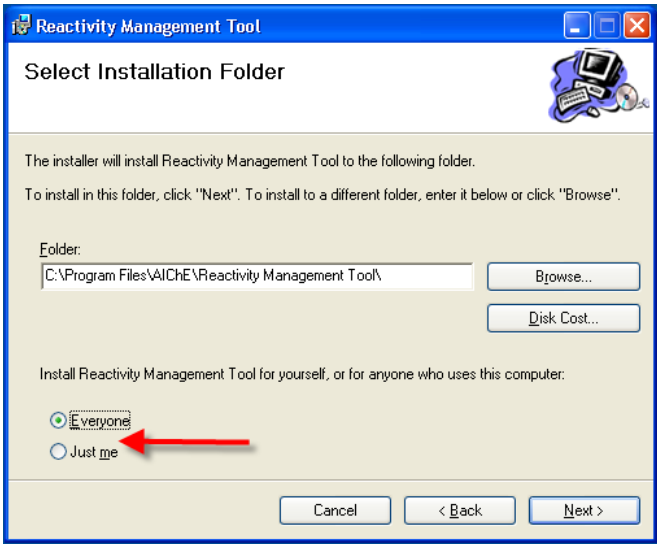
The publisher could not be verified. Are you sure you want to run this software?

Name: RMTSetup.msi
Publisher: **Unknown Publisher**
Type: Windows Installer Package
From: C:\Documents and Settings\c034431\Desktop

☑ 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?

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



Select Installation Folder

The installer will install Reactivity Management Tool to the following folder.

To install in this folder, click "Next". To install to a different folder, enter it below or click "Browse".

Folder: C:\Program Files\AIChE\Reactivity Management Tool\

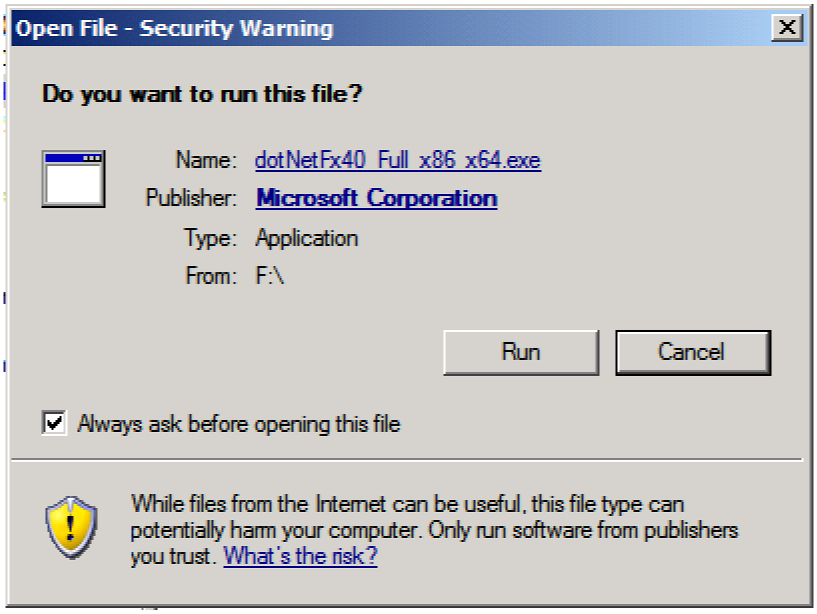
Install Reactivity Management Tool for yourself, or for anyone who uses this computer:

● Everyone
○ Just me

- 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.



Open File - Security Warning

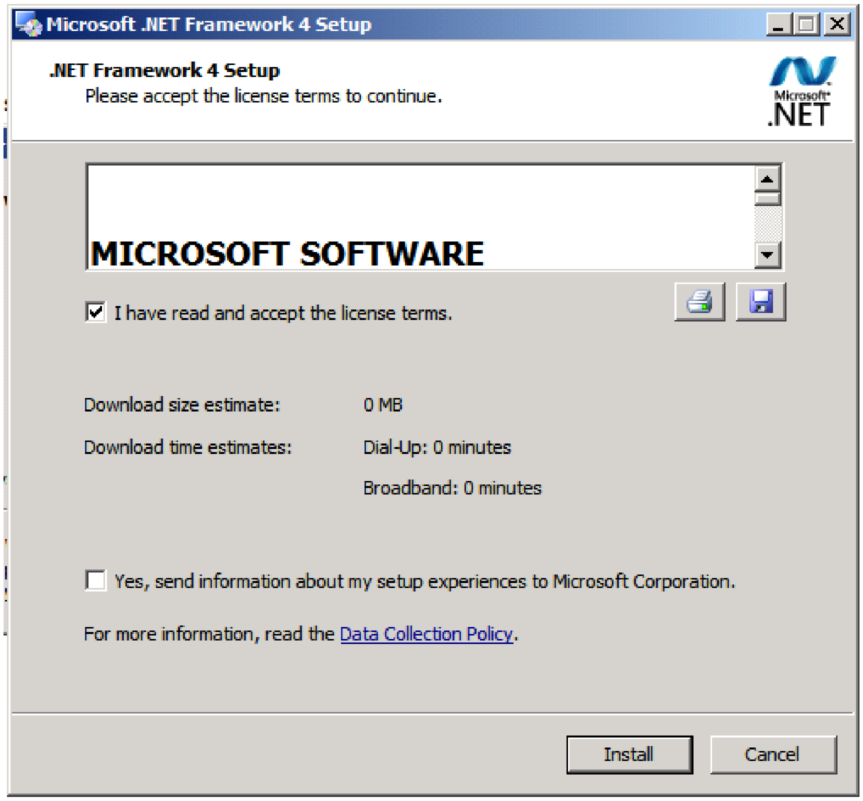
Do you want to run this file?

Name: dotNetFx40_Full_x86_x64.exe
Publisher: **Microsoft Corporation**
Type: Application
From: F:\

☑ Always ask before opening this file

While files from the Internet can be useful, this file type can potentially harm your computer. Only run software from publishers you trust. What's the risk?

Check the Read and accept box and press install



Microsoft .NET Framework 4 Setup

.NET Framework 4 Setup
Please accept the license terms to continue.

MICROSOFT SOFTWARE

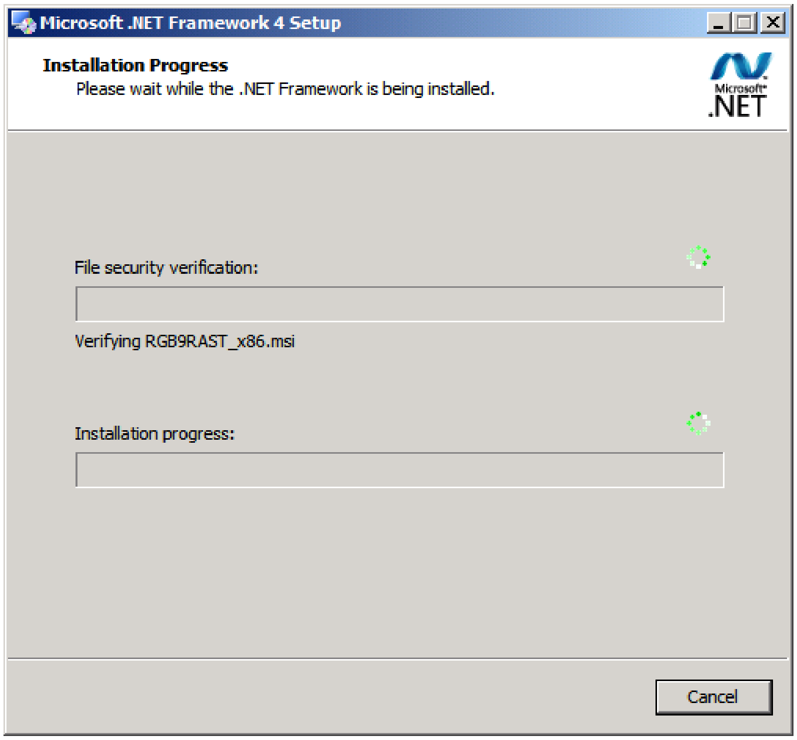
☑ I have read and accept the license terms.

Download size estimate: 0 MB
Download time estimates: Dial-Up: 0 minutes
Broadband: 0 minutes

☐ Yes, send information about my setup experiences to Microsoft Corporation.

For more information, read the Data Collection Policy.

Copyright © 2012 AIChE



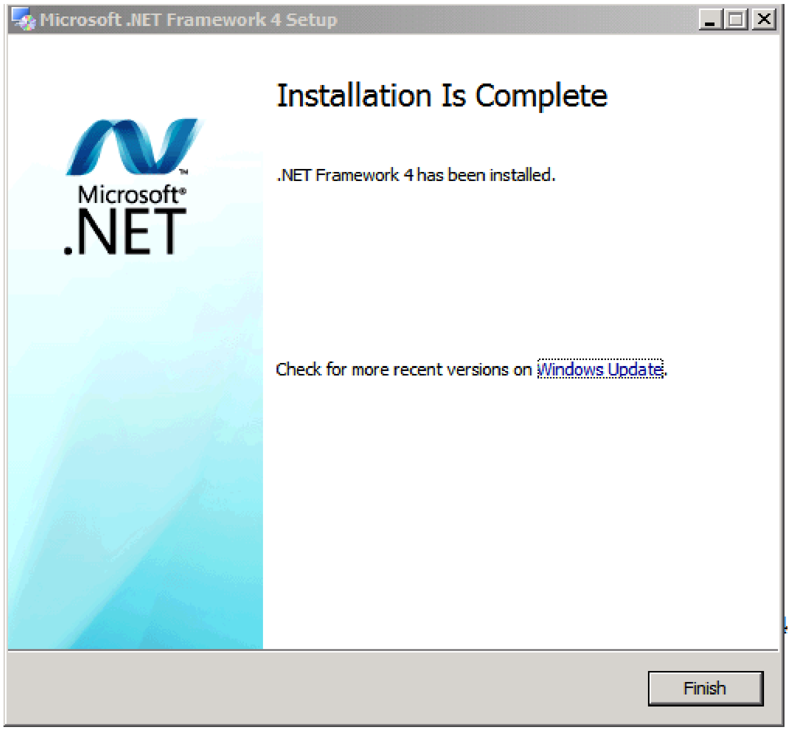
Installation Progress
Please wait while the .NET Framework is being installed.

File security verification:

Verifying RGB9RAST_x86.msi

Installation progress:

Wait while the installer does a file security check and then installs the client. This can take a very long time.



Installation Is Complete

.NET Framework 4 has been installed.

Check for more recent versions on Windows Update.

Windows will ask you to reboot now. This is optional until after you have installed the SQL Express 2005.

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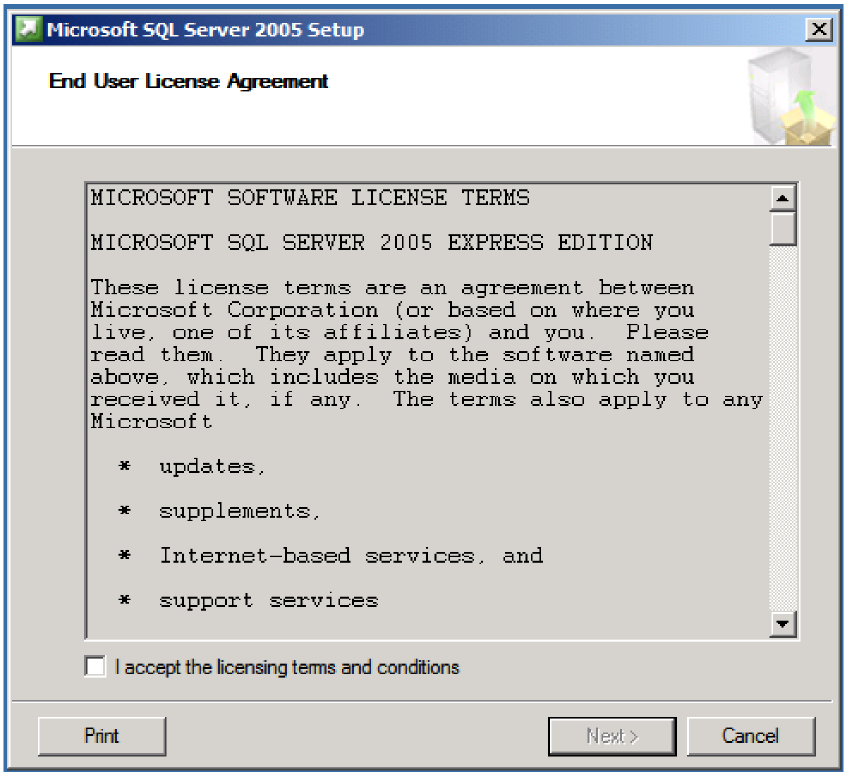
Run the file SQLEXPR.EXE from the directory you selected during the download.



End User License Agreement

MICROSOFT SOFTWARE LICENSE TERMS

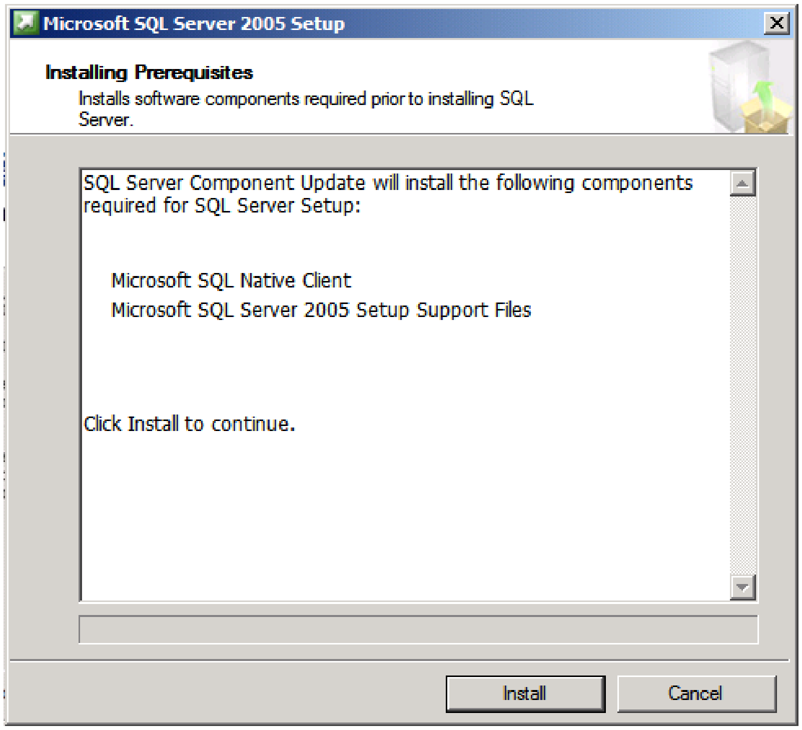
MICROSOFT SQL SERVER 2005 EXPRESS EDITION

These license terms are an agreement between Microsoft Corporation (or based on where you live, one of its affiliates) and you. Please read them. They apply to the software named above, which includes the media on which you received it, if any. The terms also apply to any Microsoft

- updates,
- supplements,
- Internet-based services, and
- support services

☐ I accept the licensing terms and conditions

Check the accept box and press next



Installing Prerequisites

Installs software components required prior to installing SQL Server.

SQL Server Component Update will install the following components required for SQL Server Setup:

Microsoft SQL Native Client
Microsoft SQL Server 2005 Setup Support Files

Click Install to continue.

Press Install

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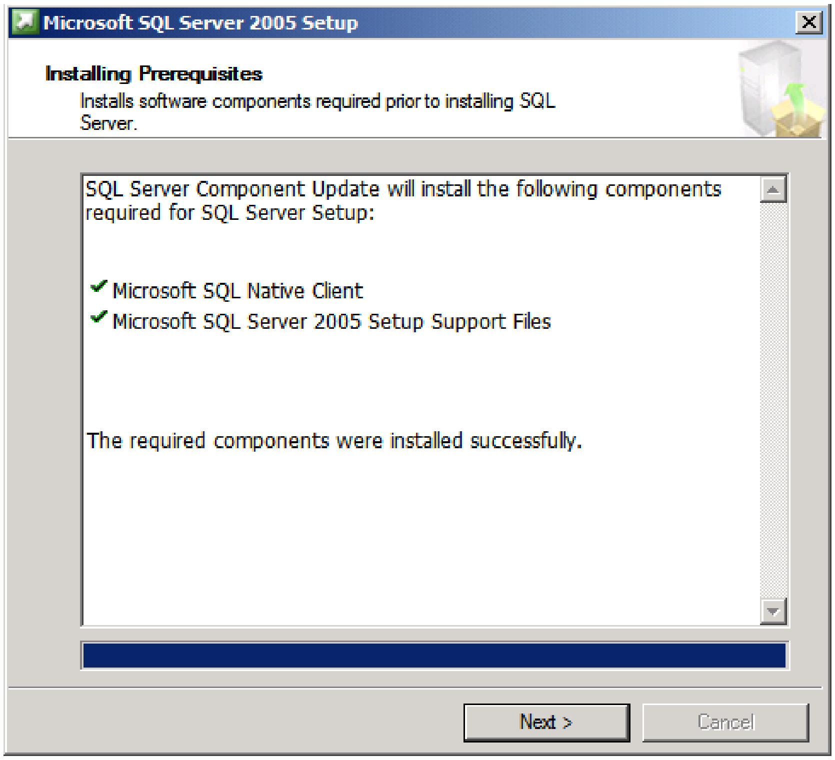


Microsoft SQL Server 2005 Setup

Installing Prerequisites

Installs software components required prior to installing SQL Server.

SQL Server Component Update will install the following components required for SQL Server Setup:

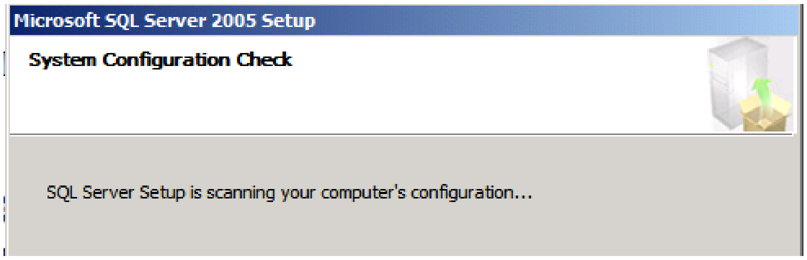
✓ Microsoft SQL Native Client

✓ Microsoft SQL Server 2005 Setup Support Files

The required components were installed successfully.

Press next

The installer will do a configuration check



Microsoft SQL Server 2005 Setup

System Configuration Check

SQL Server Setup is scanning your computer's configuration...

Press Next when the screen
At right comes up.

Microsoft SQL Server 2005 Setup

Welcome to the Microsoft SQL Server Installation Wizard

Setup will help you install, modify or remove Microsoft SQL Server. To continue, click Next.

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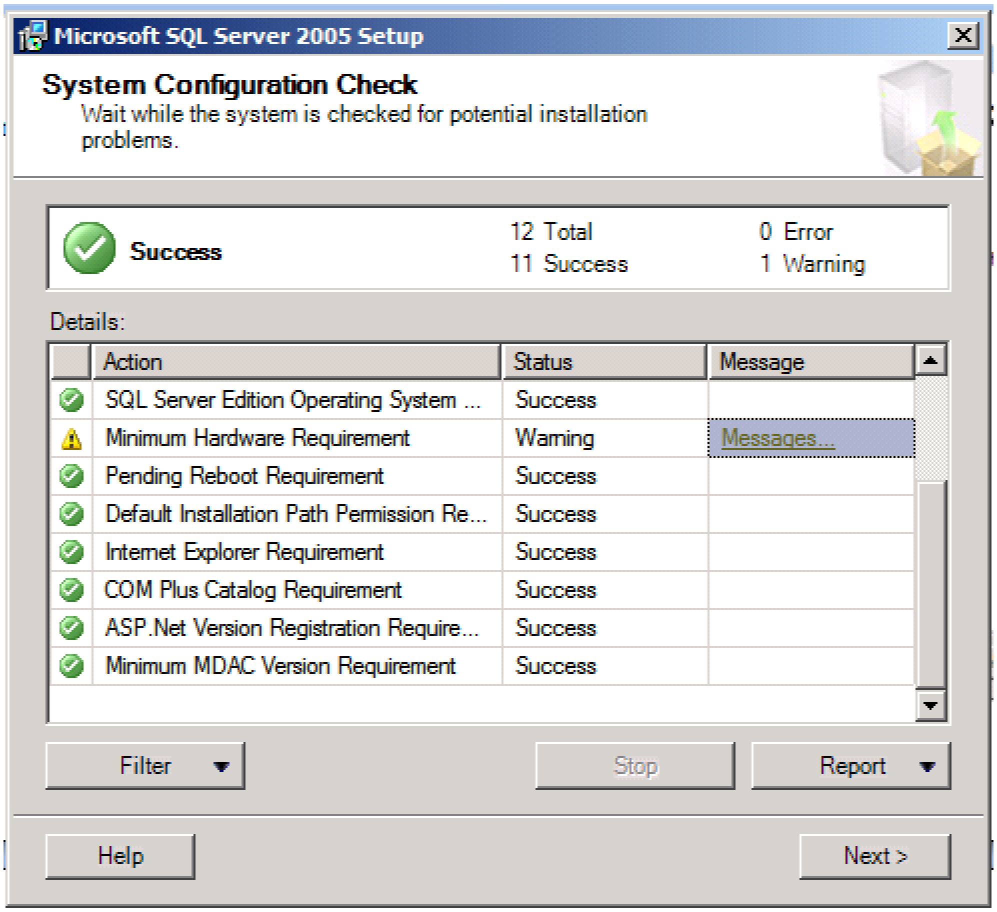


System Configuration Check

Wait while the system is checked for potential installation problems.

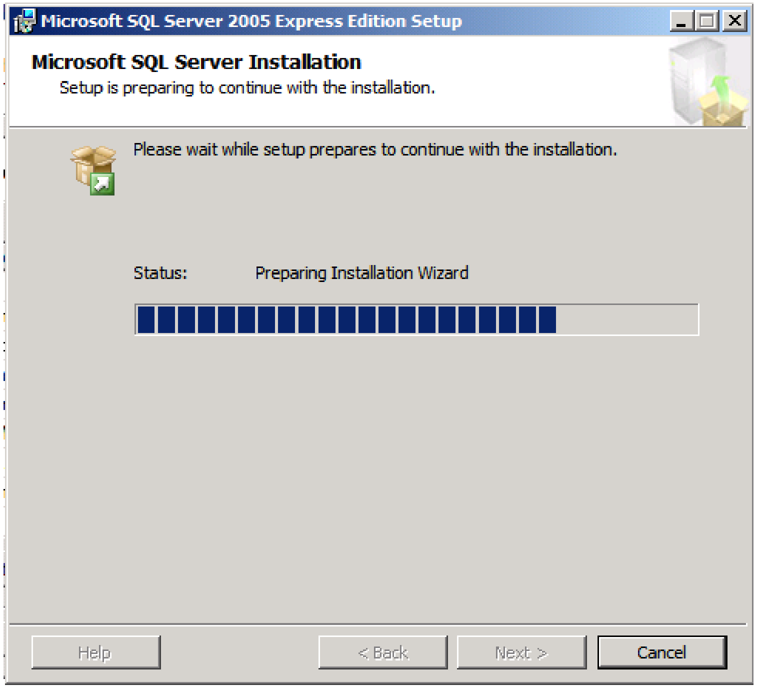
Success

12 Total
11 Success
0 Error
1 Warning

Details:

	Action	Status	Message
✓	SQL Server Edition Operating System ...	Success	
⚠	Minimum Hardware Requirement	Warning	Messages...
✓	Pending Reboot Requirement	Success	
✓	Default Installation Path Permission Re...	Success	
✓	Internet Explorer Requirement	Success	
✓	COM Plus Catalog Requirement	Success	
✓	ASP.Net Version Registration Require...	Success	
✓	Minimum MDAC Version Requirement	Success	

Press Next



Microsoft SQL Server Installation

Setup is preparing to continue with the installation.

Please wait while setup prepares to continue with the installation.

Status: Preparing Installation Wizard

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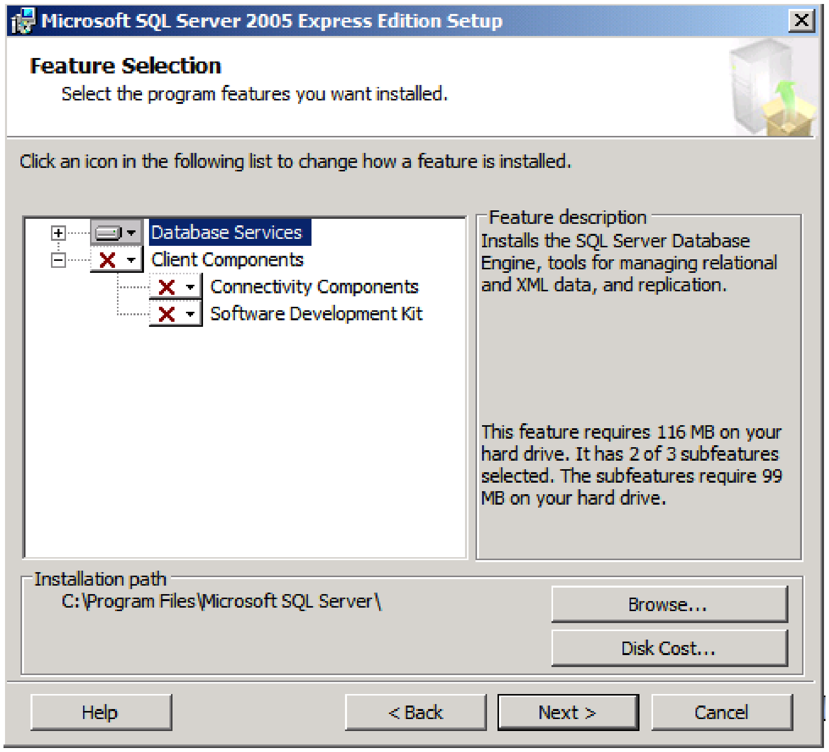
Your registration information will be requested. Press Next



Feature Selection

Select the program features you want installed.

Click an icon in the following list to change how a feature is installed.

- Database Services
- ☒ Client Components
  - ☒ Connectivity Components
  - ☒ Software Development Kit

Feature description

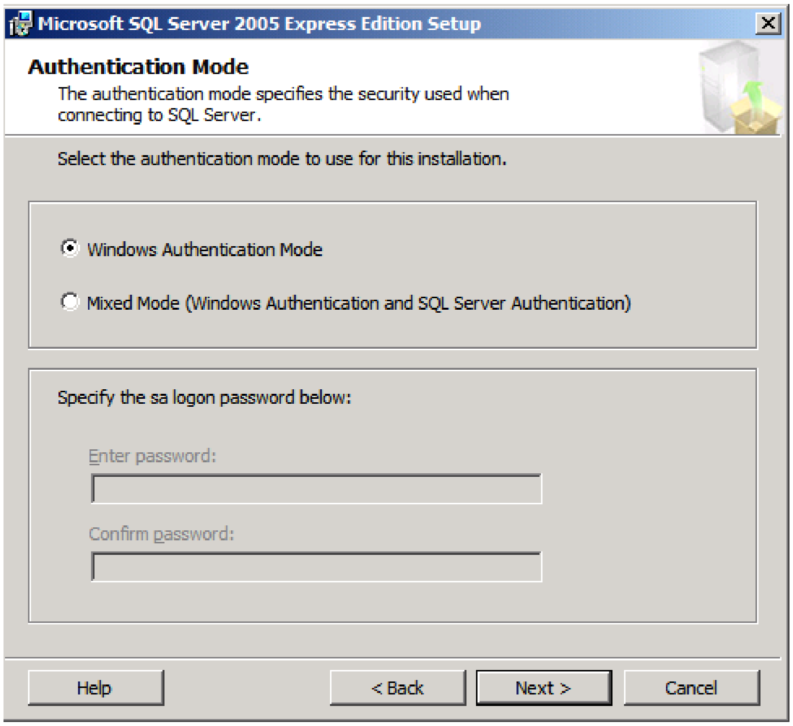
Installs the SQL Server Database Engine, tools for managing relational and XML data, and replication.

This feature requires 116 MB on your hard drive. It has 2 of 3 subfeatures selected. The subfeatures require 99 MB on your hard drive.

Installation path

C:\Program Files\Microsoft SQL Server\

Press next utilizing the default options



Authentication Mode

The authentication mode specifies the security used when connecting to SQL Server.

Select the authentication mode to use for this installation.

● Windows Authentication Mode

○ Mixed Mode (Windows Authentication and SQL Server Authentication)

Specify the sa logon password below:

Enter password:

Confirm password:

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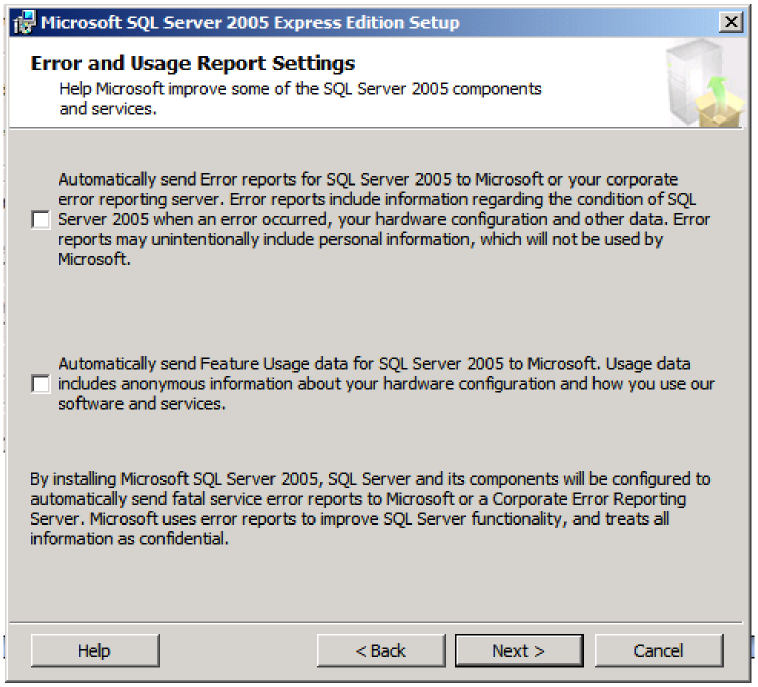
Press next utilizing the
Default settings



Error and Usage Report Settings

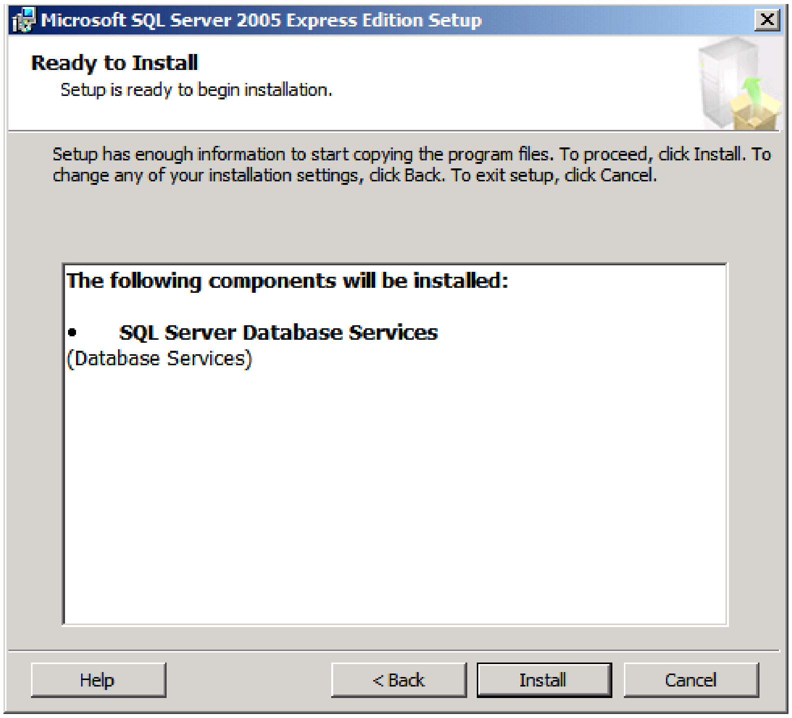
Help Microsoft improve some of the SQL Server 2005 components and services.

☐ Automatically send Error reports for SQL Server 2005 to Microsoft or your corporate error reporting server. Error reports include information regarding the condition of SQL Server 2005 when an error occurred, your hardware configuration and other data. Error reports may unintentionally include personal information, which will not be used by Microsoft.

☐ Automatically send Feature Usage data for SQL Server 2005 to Microsoft. Usage data includes anonymous information about your hardware configuration and how you use our software and services.

By installing Microsoft SQL Server 2005, SQL Server and its components will be configured to automatically send fatal service error reports to Microsoft or a Corporate Error Reporting Server. Microsoft uses error reports to improve SQL Server functionality, and treats all information as confidential.

Press Install utilizing
the default options.



Ready to Install

Setup is ready to begin installation.

Setup has enough information to start copying the program files. To proceed, click Install. To change any of your installation settings, click Back. To exit setup, click Cancel.

The following components will be installed:

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

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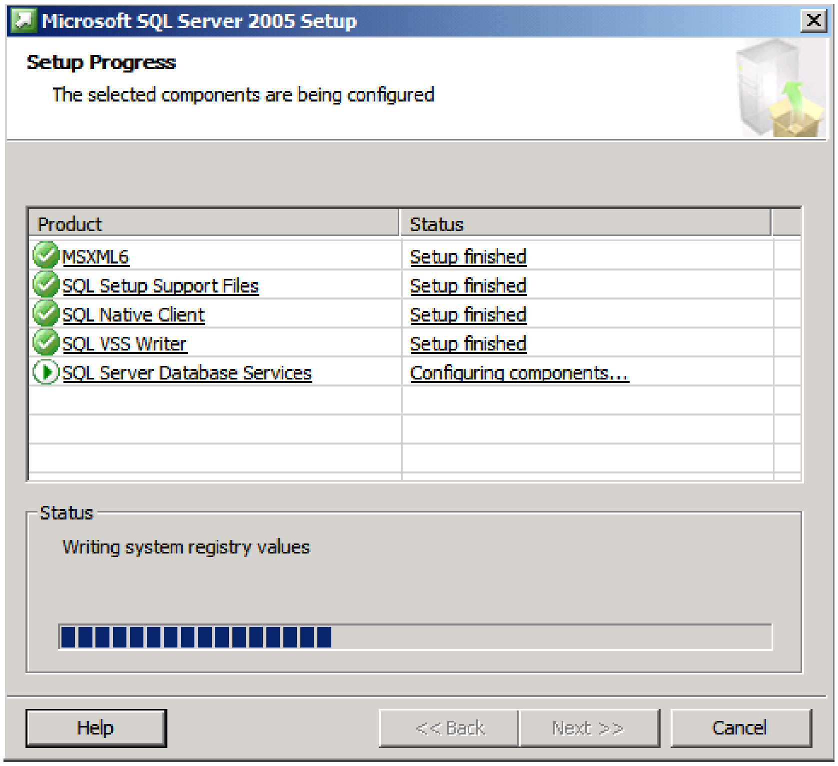
Press Next when the Install and configure is Complete.



Setup Progress

The selected components are being configured

Product	Status
MSXML6	Setup finished
SQL Setup Support Files	Setup finished
SQL Native Client	Setup finished
SQL VSS Writer	Setup finished
SQL Server Database Services	Configuring components...

Status

Writing system registry values

Finally press complete at the final information screen.

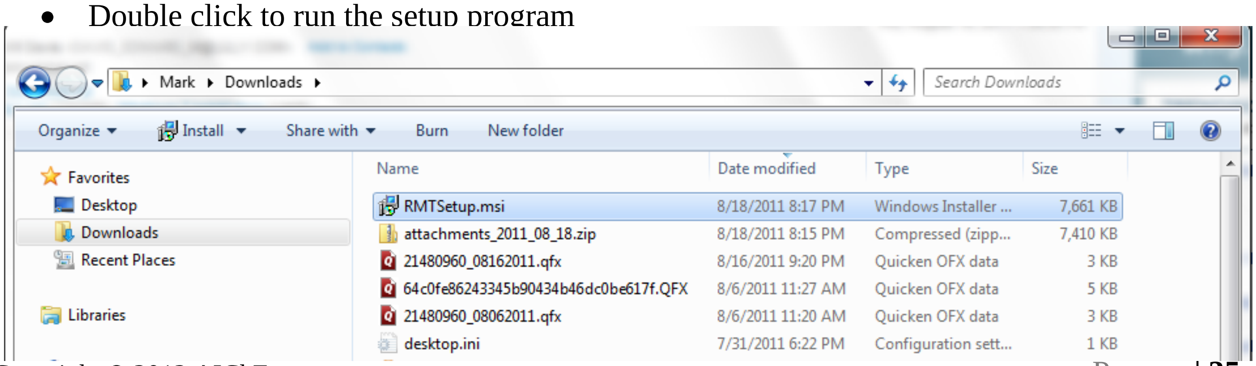
Reboot your computer now.
Go to the windows update and get all current updates for your computer to complete this installation.

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



Name	Date modified	Type	Size
RMTSetup.msi	8/18/2011 8:17 PM	Windows Installer ...	7,661 KB
attachments_2011_08_18.zip	8/18/2011 8:15 PM	Compressed (zipp...	7,410 KB
21480960_08162011.qfx	8/16/2011 9:20 PM	Quicken OFX data	3 KB
64c0fe86243345b90434b46dc0be617f.QFX	8/6/2011 11:27 AM	Quicken OFX data	5 KB
21480960_08062011.qfx	8/6/2011 11:20 AM	Quicken OFX data	3 KB
desktop.ini	7/31/2011 6:22 PM	Configuration sett...	1 KB

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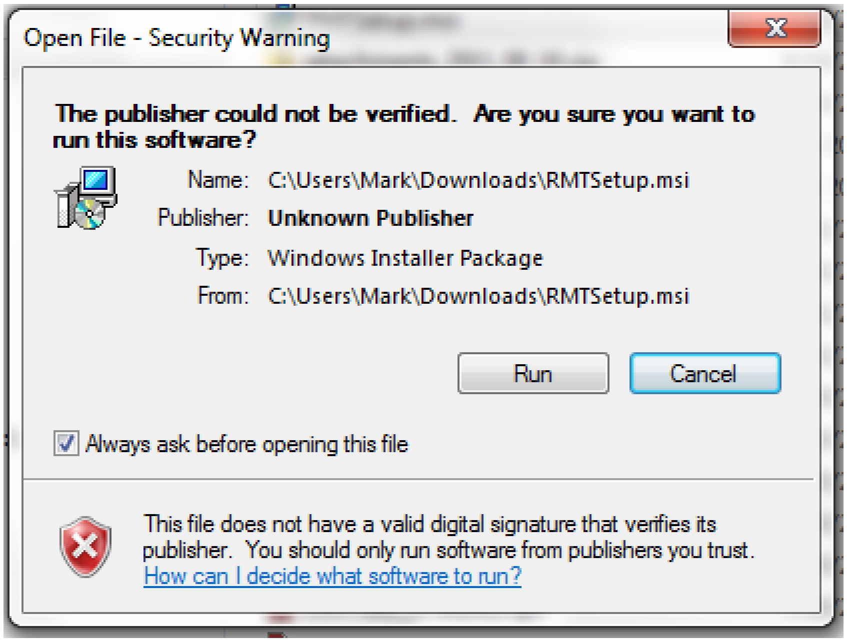
- Click Run

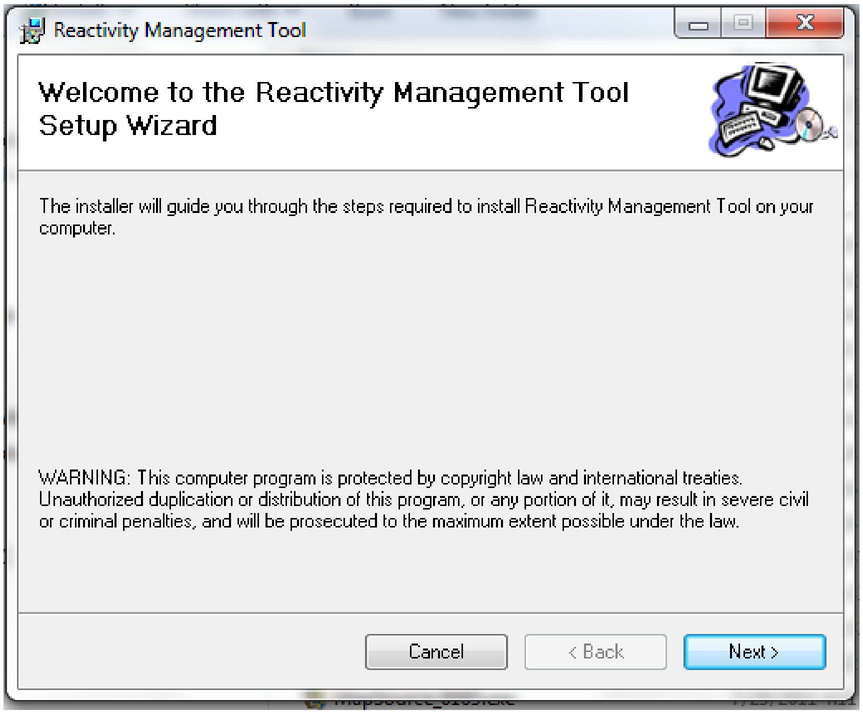


The publisher could not be verified. Are you sure you want to run this software?

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

☑ 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?

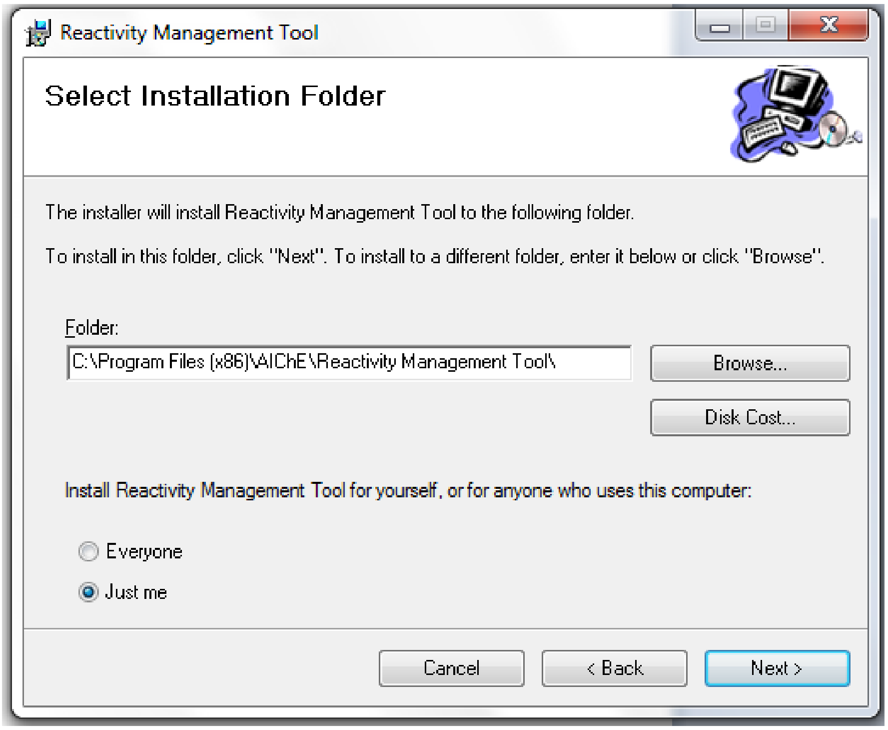


Welcome to the Reactivity Management Tool Setup Wizard

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.

- Click Next



Select Installation Folder

The installer will install Reactivity Management Tool to the following folder.

To install in this folder, click "Next". To install to a different folder, enter it below or click "Browse".

Folder: C:\Program Files (x86)\AIChE\Reactivity Management Tool\

Install Reactivity Management Tool for yourself, or for anyone who uses this computer:

○ Everyone
● Just me

- 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.

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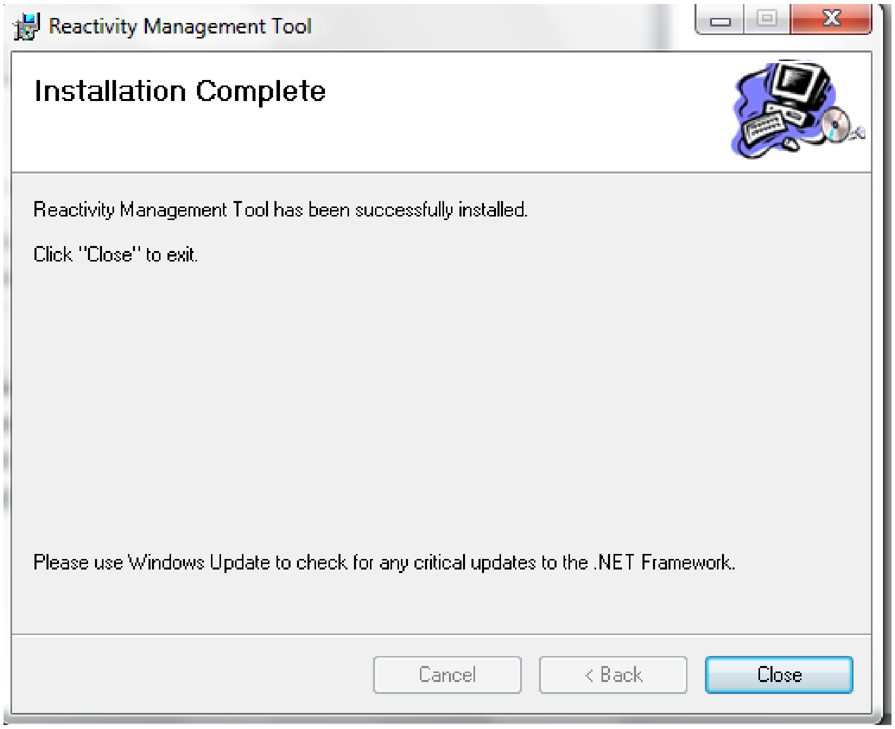


Installation Complete

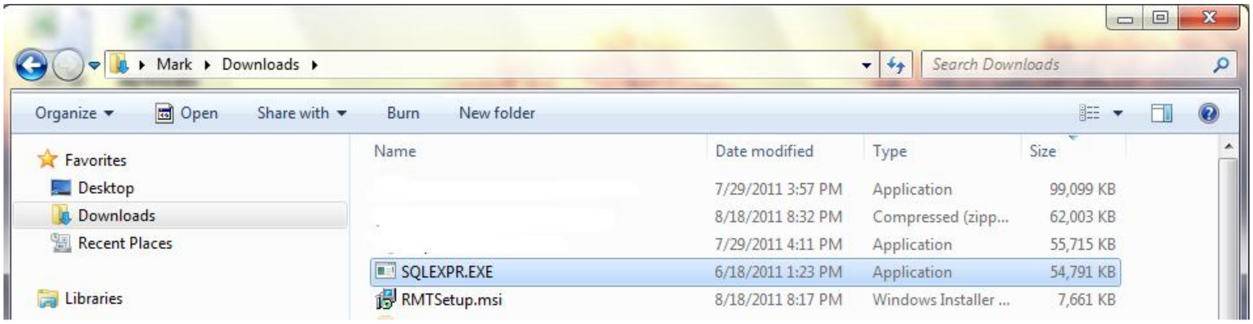
Reactivity Management Tool has been successfully installed.

Click "Close" to exit.

Please use Windows Update to check for any critical updates to the .NET Framework.

- 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



Name	Date modified	Type	Size
	7/29/2011 3:57 PM	Application	99,099 KB
	8/18/2011 8:32 PM	Compressed (zipp...	62,003 KB
	7/29/2011 4:11 PM	Application	55,715 KB
SQLEXPR.EXE	6/18/2011 1:23 PM	Application	54,791 KB
RMTSetup.msi	8/18/2011 8:17 PM	Windows Installer ...	7,661 KB

- 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.

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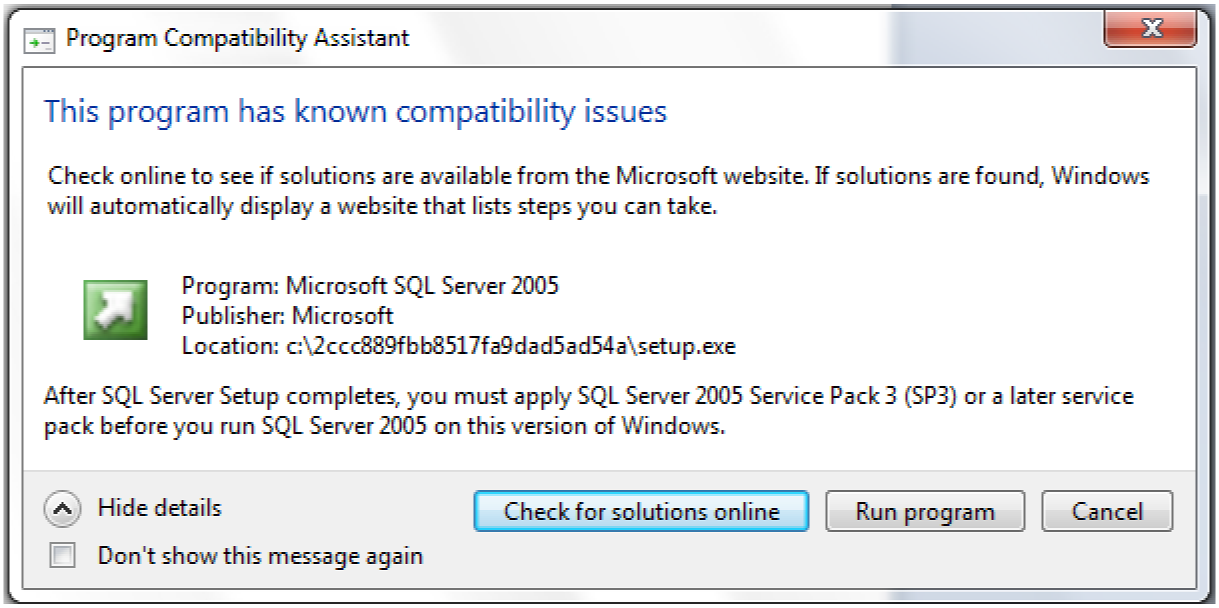
- Press run program



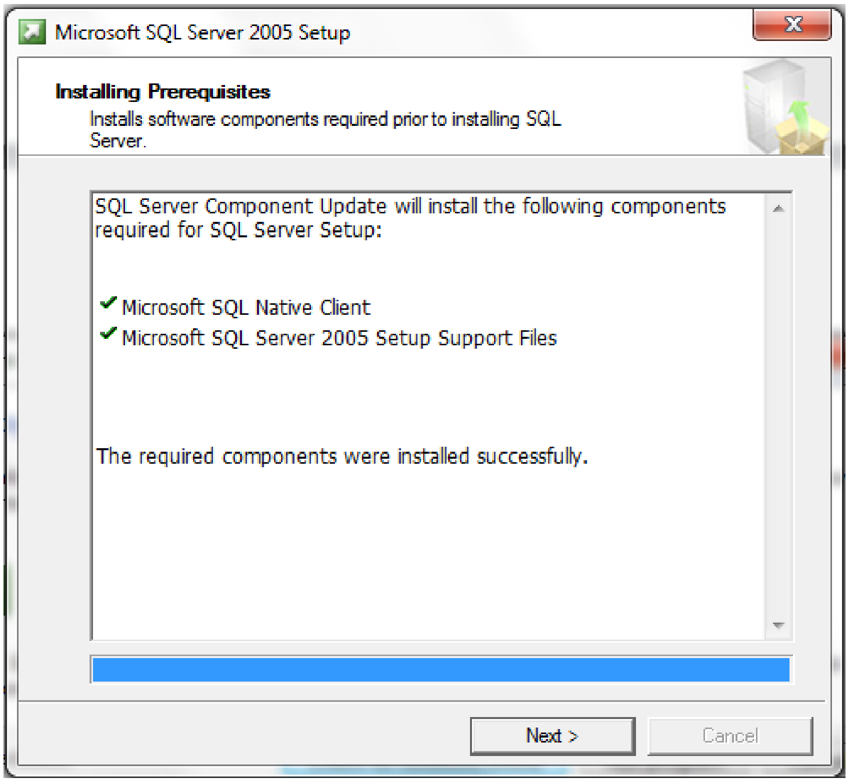
This program has known compatibility issues

Check online to see if solutions are available from the Microsoft website. If solutions are found, Windows will automatically display a website that lists steps you can take.

Program: Microsoft SQL Server 2005
Publisher: Microsoft
Location: c:\2ccc889fbb8517fa9dad5ad54a\setup.exe

After SQL Server Setup completes, you must apply SQL Server 2005 Service Pack 3 (SP3) or a later service pack before you run SQL Server 2005 on this version of Windows.

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



Installing Prerequisites

Installs software components required prior to installing SQL Server.

SQL Server Component Update will install the following components required for SQL Server Setup:

✓ Microsoft SQL Native Client
✓ Microsoft SQL Server 2005 Setup Support Files

The required components were installed successfully.

- Press next

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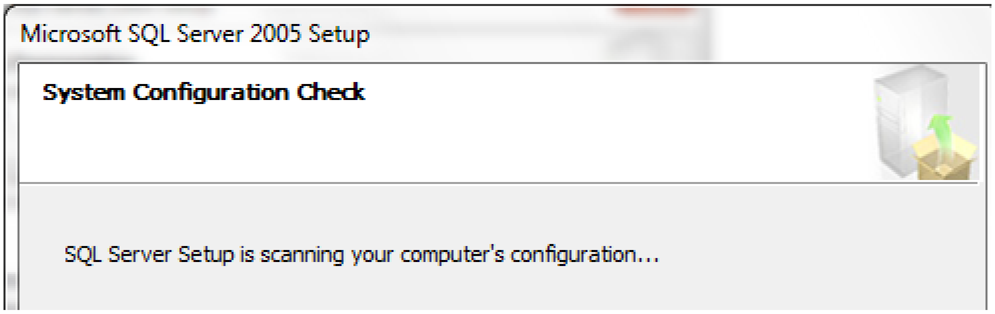
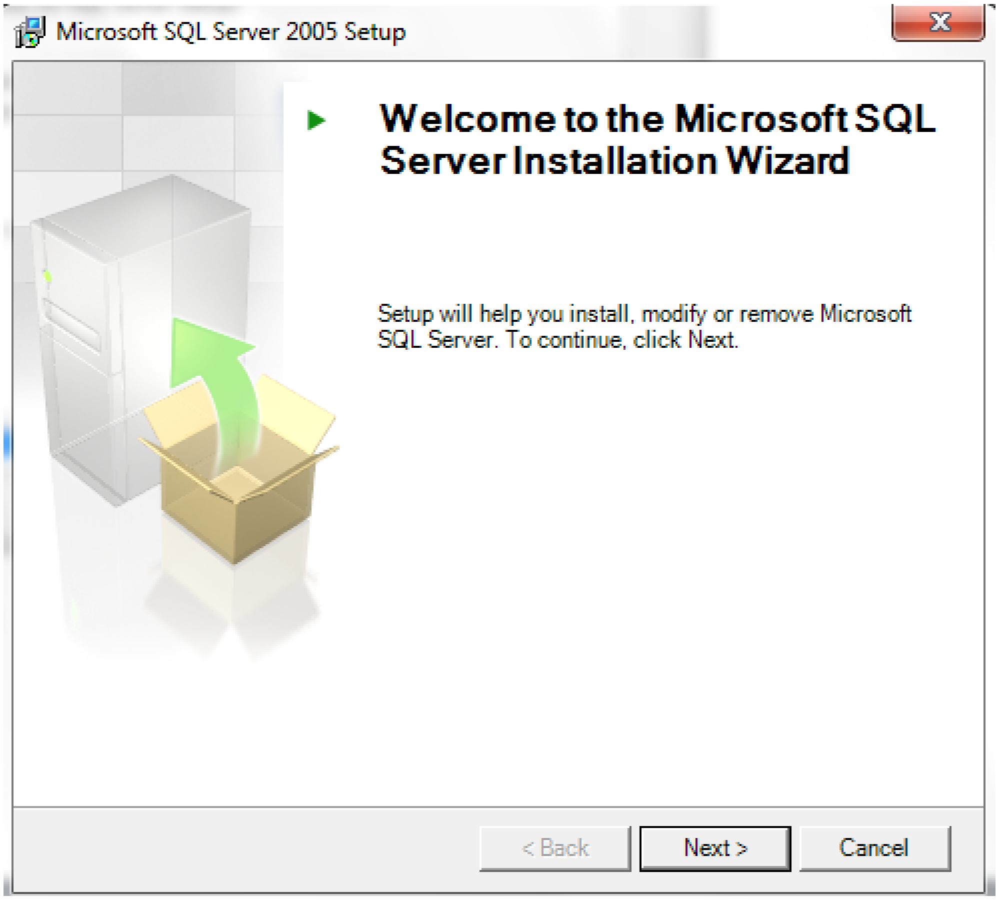


SQL Server Setup is scanning your computer's configuration...



Welcome to the Microsoft SQL Server Installation Wizard

Setup will help you install, modify or remove Microsoft SQL Server. To continue, click Next.

- Press Next

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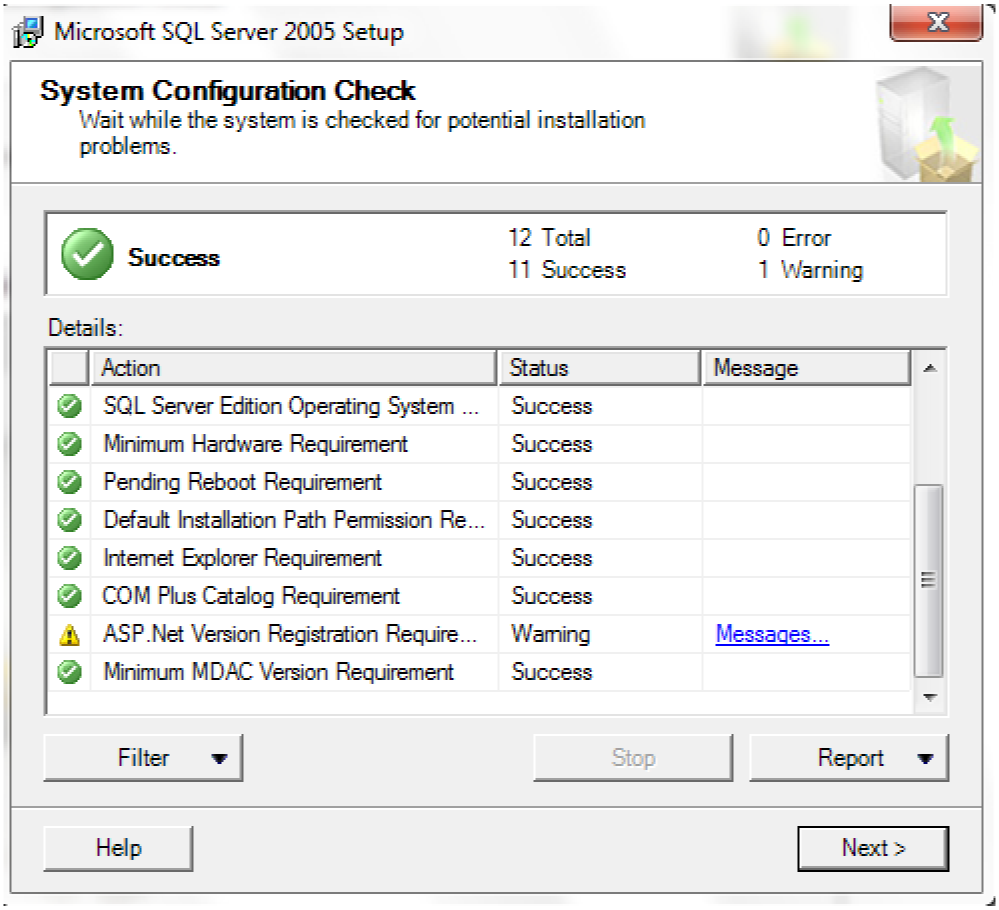


Microsoft SQL Server 2005 Setup

System Configuration Check

Wait while the system is checked for potential installation problems.

Success

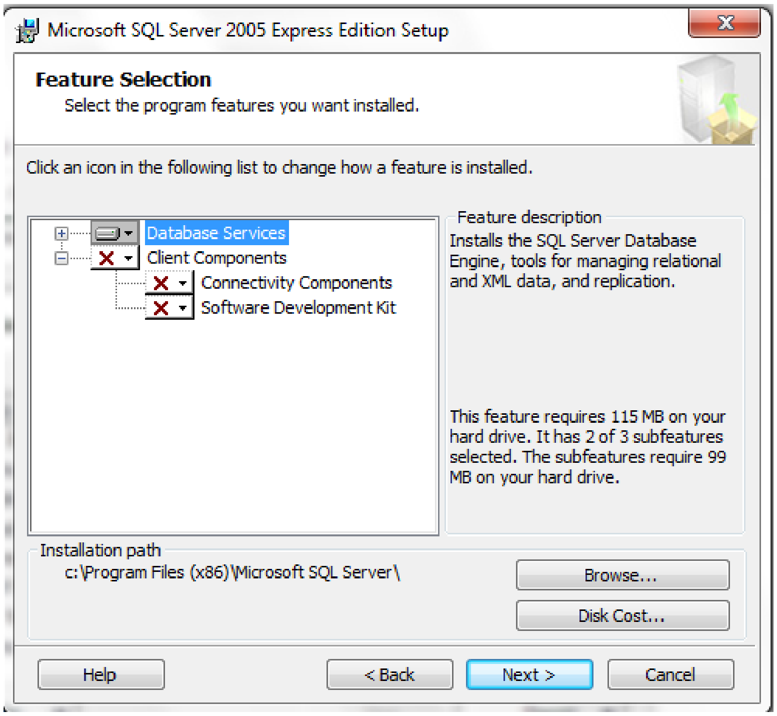
12 Total
11 Success

0 Error
1 Warning

Details:

	Action	Status	Message
✓	SQL Server Edition Operating System ...	Success	
✓	Minimum Hardware Requirement	Success	
✓	Pending Reboot Requirement	Success	
✓	Default Installation Path Permission Re...	Success	
✓	Internet Explorer Requirement	Success	
✓	COM Plus Catalog Requirement	Success	
⚠	ASP.Net Version Registration Require...	Warning	Messages...
✓	Minimum MDAC Version Requirement	Success	

- Press next
- Enter your registration information and press next



Microsoft SQL Server 2005 Express Edition Setup

Feature Selection

Select the program features you want installed.

Click an icon in the following list to change how a feature is installed.

- Database Services
- Client Components
  - Connectivity Components
  - Software Development Kit

Feature description

Installs the SQL Server Database Engine, tools for managing relational and XML data, and replication.

This feature requires 115 MB on your hard drive. It has 2 of 3 subfeatures selected. The subfeatures require 99 MB on your hard drive.

Installation path

c:\Program Files (x86)\Microsoft SQL Server\

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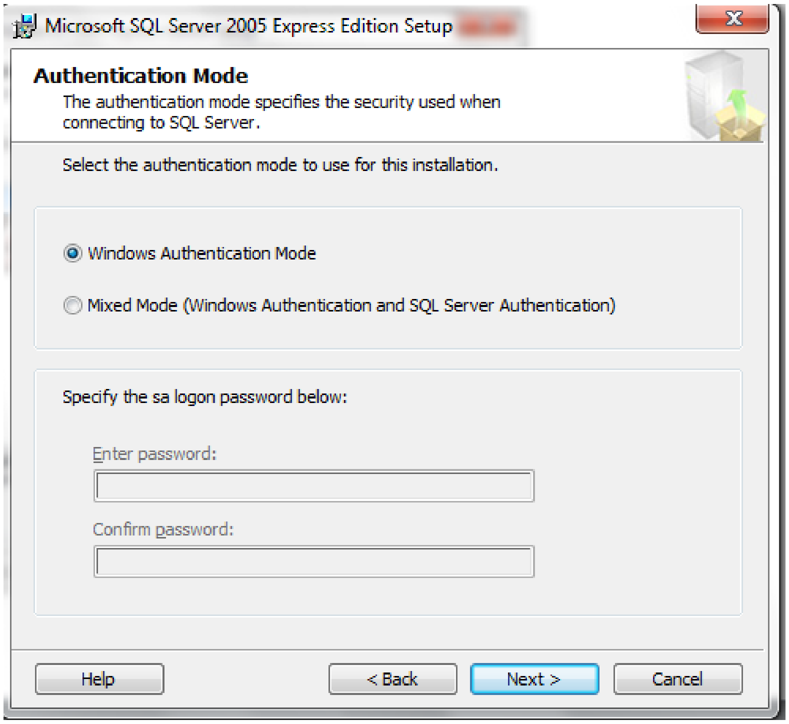
- Accept the default settings and press next


Microsoft SQL Server 2005 Express Edition Setup

Authentication Mode

The authentication mode specifies the security used when connecting to SQL Server.

Select the authentication mode to use for this installation.

● Windows Authentication Mode

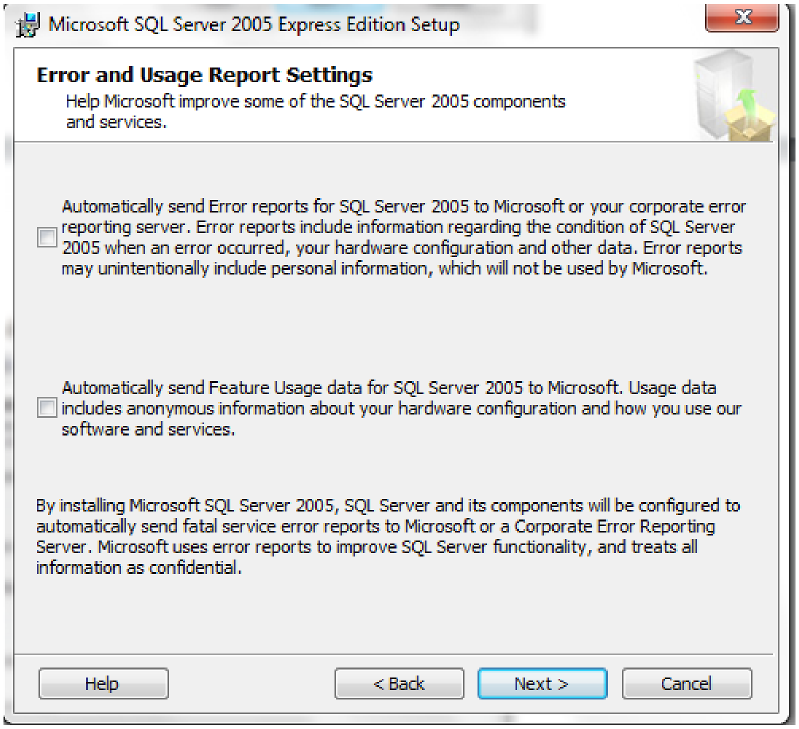
○ Mixed Mode (Windows Authentication and SQL Server Authentication)

Specify the sa logon password below:

Enter password:

Confirm password:

- Press next without entering a password


Microsoft SQL Server 2005 Express Edition Setup

Error and Usage Report Settings

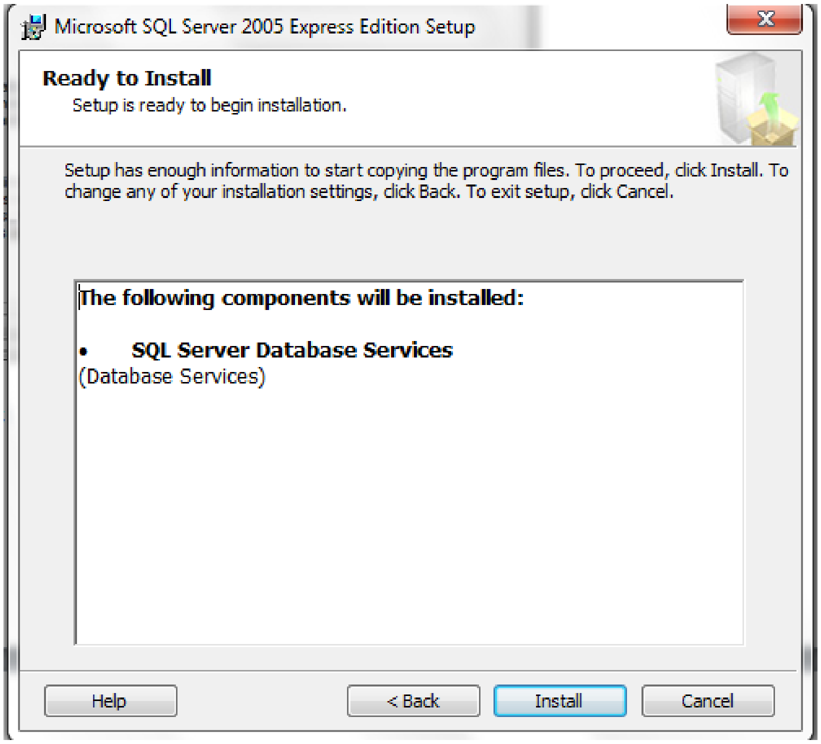
Help Microsoft improve some of the SQL Server 2005 components and services.

☐ Automatically send Error reports for SQL Server 2005 to Microsoft or your corporate error reporting server. Error reports include information regarding the condition of SQL Server 2005 when an error occurred, your hardware configuration and other data. Error reports may unintentionally include personal information, which will not be used by Microsoft.

☐ Automatically send Feature Usage data for SQL Server 2005 to Microsoft. Usage data includes anonymous information about your hardware configuration and how you use our software and services.

By installing Microsoft SQL Server 2005, SQL Server and its components will be configured to automatically send fatal service error reports to Microsoft or a Corporate Error Reporting Server. Microsoft uses error reports to improve SQL Server functionality, and treats all information as confidential.

- Press Next



Ready to Install

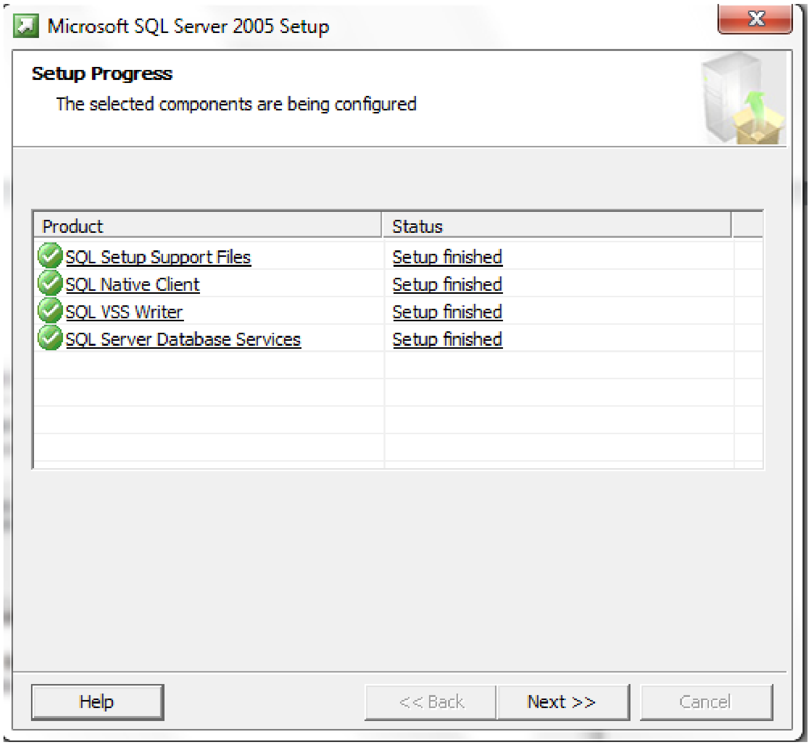
Setup is ready to begin installation.

Setup has enough information to start copying the program files. To proceed, click Install. To change any of your installation settings, click Back. To exit setup, click Cancel.

The following components will be installed:

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

- Press install



Setup Progress

The selected components are being configured

Product	Status
✓ SQL Setup Support Files	Setup finished
✓ SQL Native Client	Setup finished
✓ SQL VSS Writer	Setup finished
✓ SQL Server Database Services	Setup finished

- Press next when the install is finished
- Press finish on the final screen

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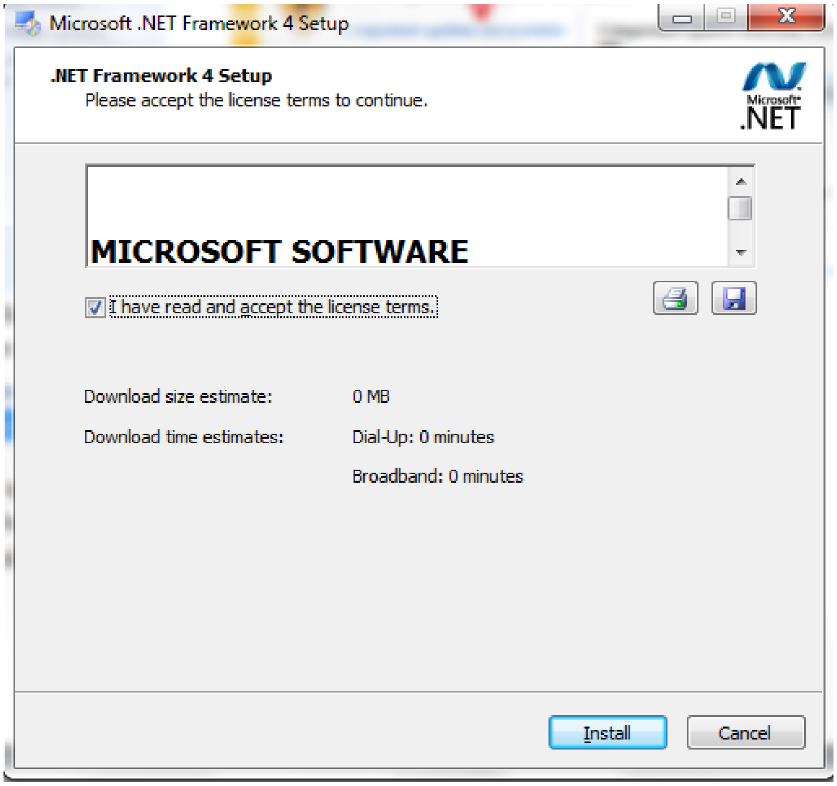
- Download the .NET framework file
- Run dotNetFx40_Full_x86_x64.exe
- Press yes at the windows security warning

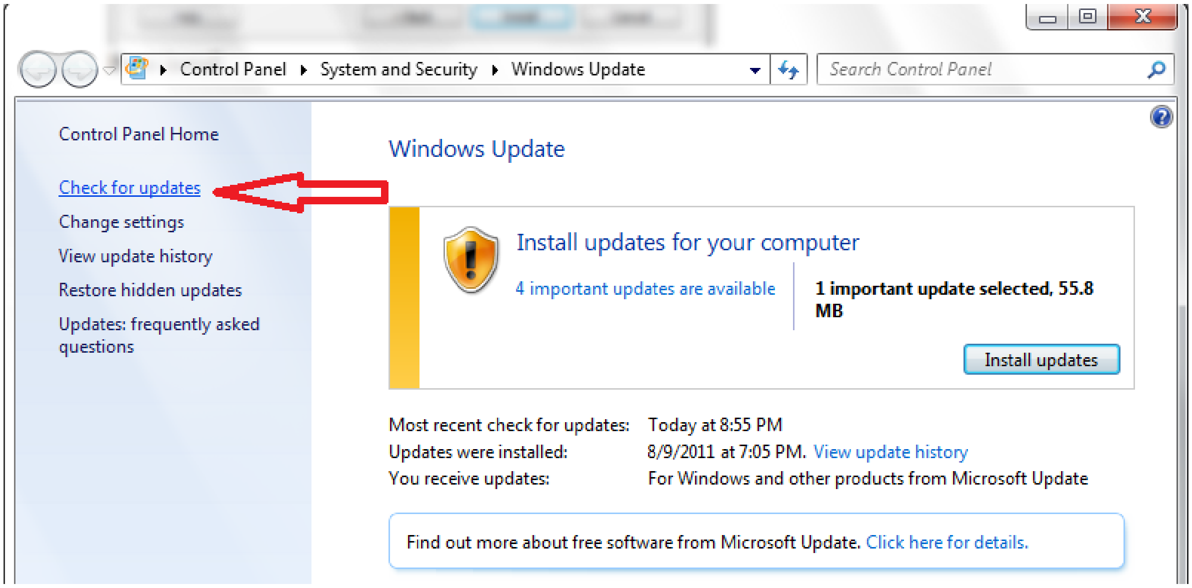


☑ I have read and accept the license terms.

Download size estimate: 0 MB
Download time estimates: Dial-Up: 0 minutes
Broadband: 0 minutes

- 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.



1 important update selected, 55.8 MB

Most recent check for updates: Today at 8:55 PM
Updates were installed: 8/9/2011 at 7:05 PM. View update history
You receive updates: For Windows and other products from Microsoft Update

Find out more about free software from Microsoft Update. Click here for details.

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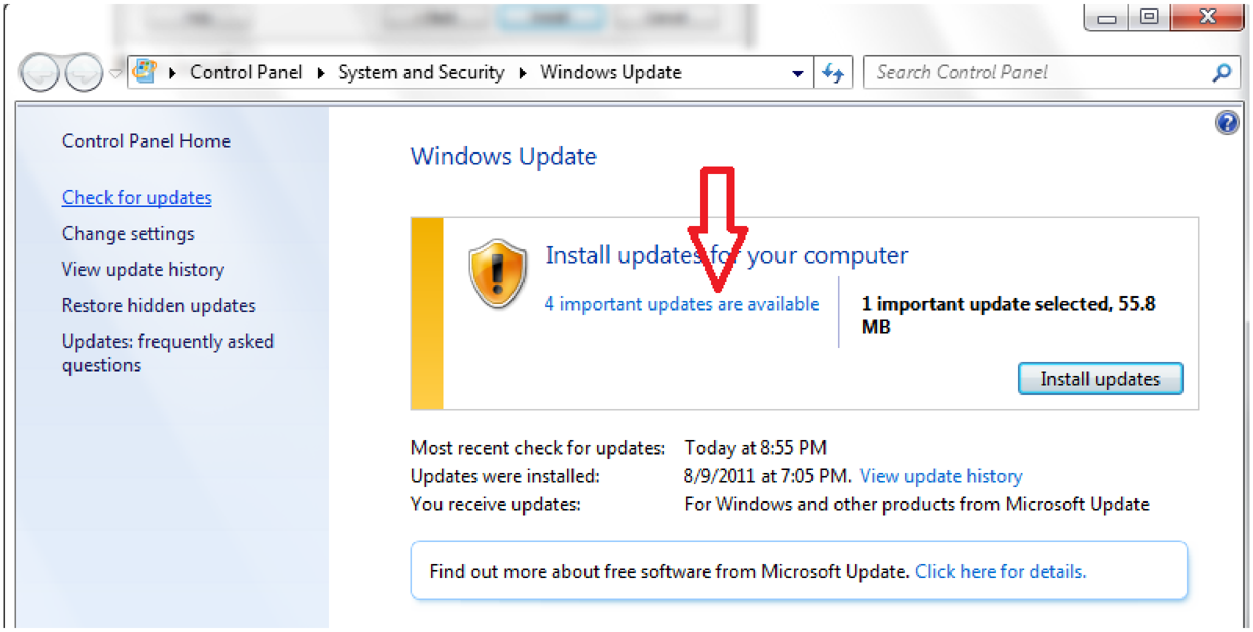
- Click on the link below the arrow



Windows Update

Install updates for your computer

4 important updates are available

1 important update selected, 55.8 MB

Most recent check for updates:	Today at 8:55 PM
Updates were installed:	8/9/2011 at 7:05 PM. View update history
You receive updates:	For Windows and other products from Microsoft Update

Find out more about free software from Microsoft Update. Click here for details.

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

SQL Server 2005 (1)

☑ Microsoft SQL Server 2005 Express Edition Service Pack 4 (KB2463332) 55.8 MB

- 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.

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3.2 Step by Step Program Instructions

Link To Full TOC

Table of Contents

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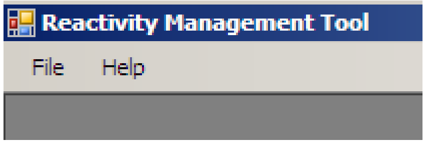
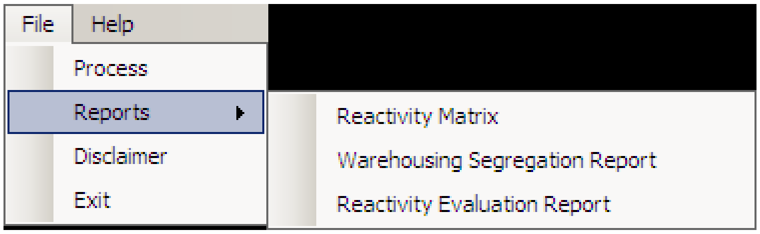
3.2.0 Starting the program

- 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

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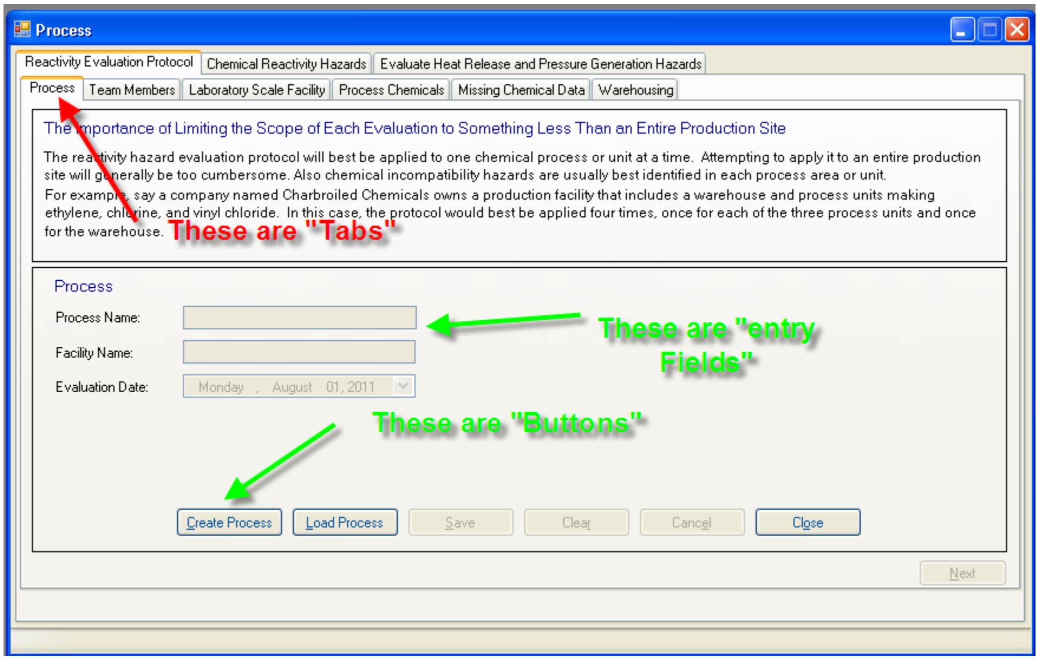
3.2.2 Navigation Within The Process Window

Definitions:



The Importance of Limiting the Scope of Each Evaluation 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. Also chemical incompatibility hazards are usually best identified in each process area or unit.

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.

Process

Process Name:

Facility Name:

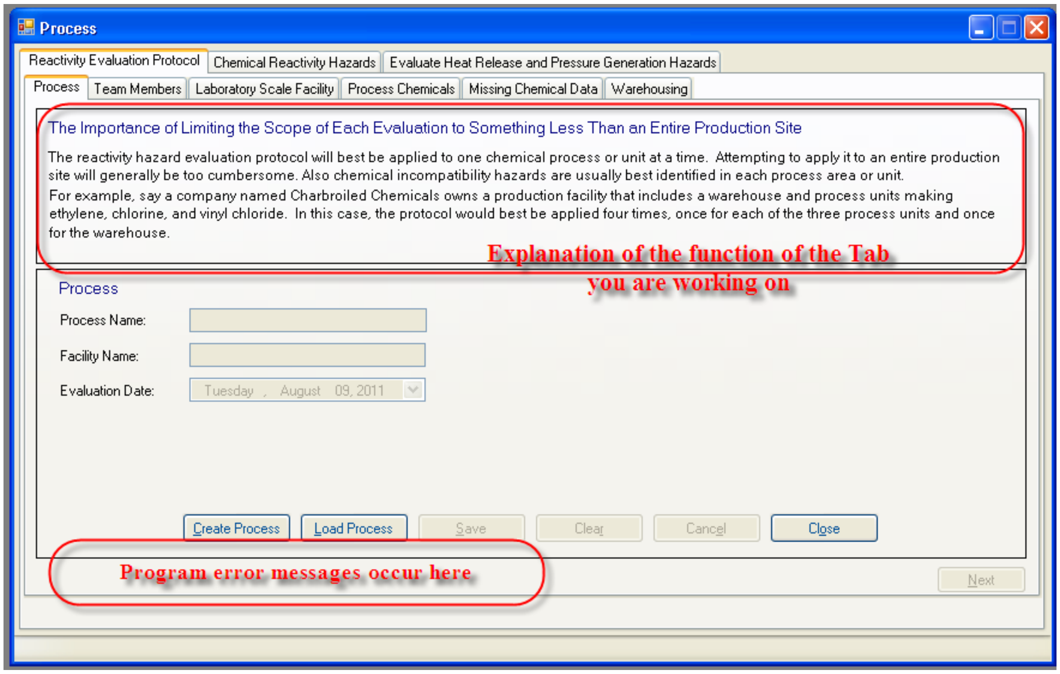
Evaluation Date: Monday , August 01, 2011

These are "Tabs"

These are "entry Fields"

These are "Buttons"

Information windows appear in the areas highlighted below.



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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.

Process

Process Name:

Facility Name:

Evaluation Date: Tuesday , August 09, 2011

Explanation of the function of the Tab you are working on

Program error messages occur here

Helpful Hint 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.

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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.

Pitfall alert

    - 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.

Helpful Hint

- **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

Helpful Hint

- 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

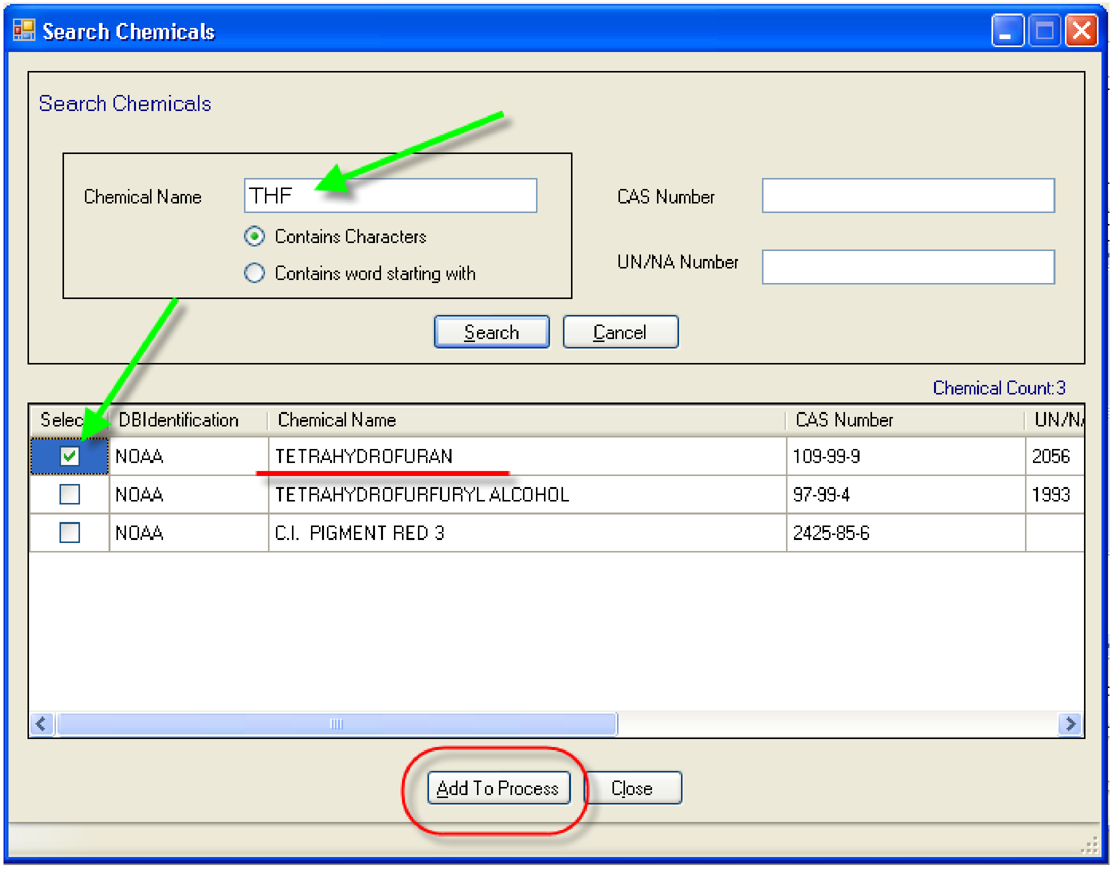
3.2.6.1 Searching for chemicals

- 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.

Helpful Hint

- 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



Search Chemicals

Search Chemicals

Chemical Name: THF

● Contains Characters

○ Contains word starting with

CAS Number:

UN/NA Number:

Chemical Count:3

Selec	DBIdentification	Chemical Name	CAS Number	UN/N
☑	NOAA	TETRAHYDROFURAN	109-99-9	2056
☐	NOAA	TETRAHYDROFURFURYL ALCOHOL	97-99-4	1993
☐	NOAA	C.I. PIGMENT RED 3	2425-85-6	

- 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

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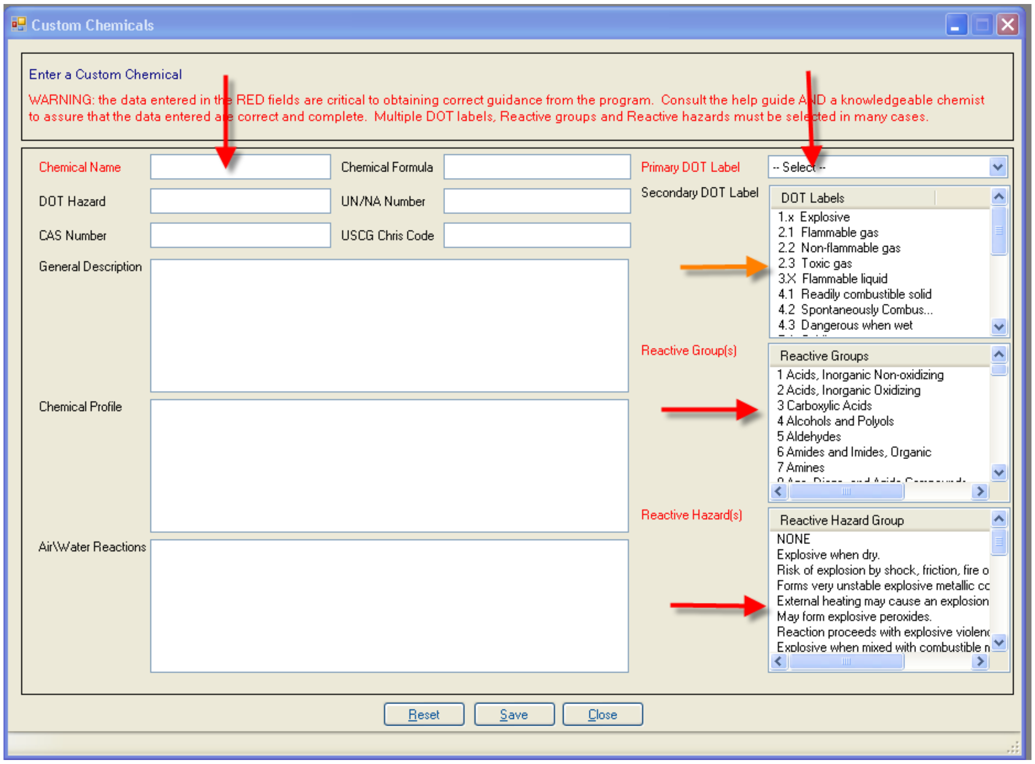
3.2.6.2 Custom Chemicals entry and editing pop-up form

- 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

Helpful Hint



WARNING: the data entered in the RED fields are critical to obtaining correct guidance from the program. Consult the help guide AND a knowledgeable chemist to assure that the data entered are correct and complete. Multiple DOT labels, Reactive groups and Reactive hazards must be selected in many cases.

Pitfall alert

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.

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- 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**

Helpful Hint

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**.

Pitfall alert

- 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.**

Pitfall alert

- 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”**

Helpful Hint

- 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

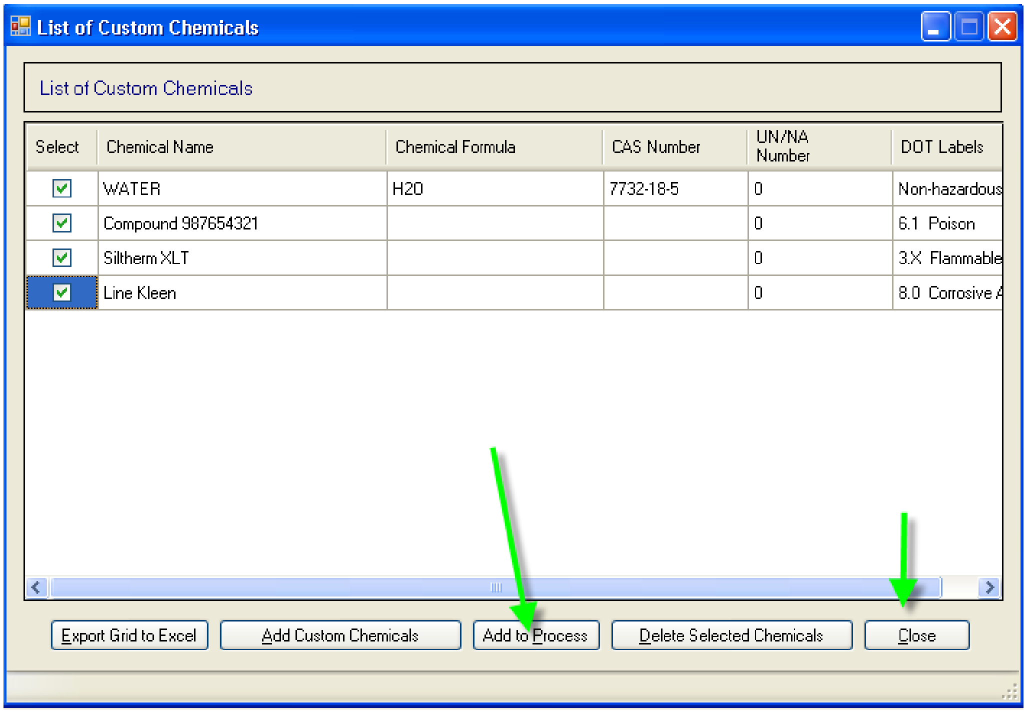
3.2.6.4 Adding custom chemicals to the process

- 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.

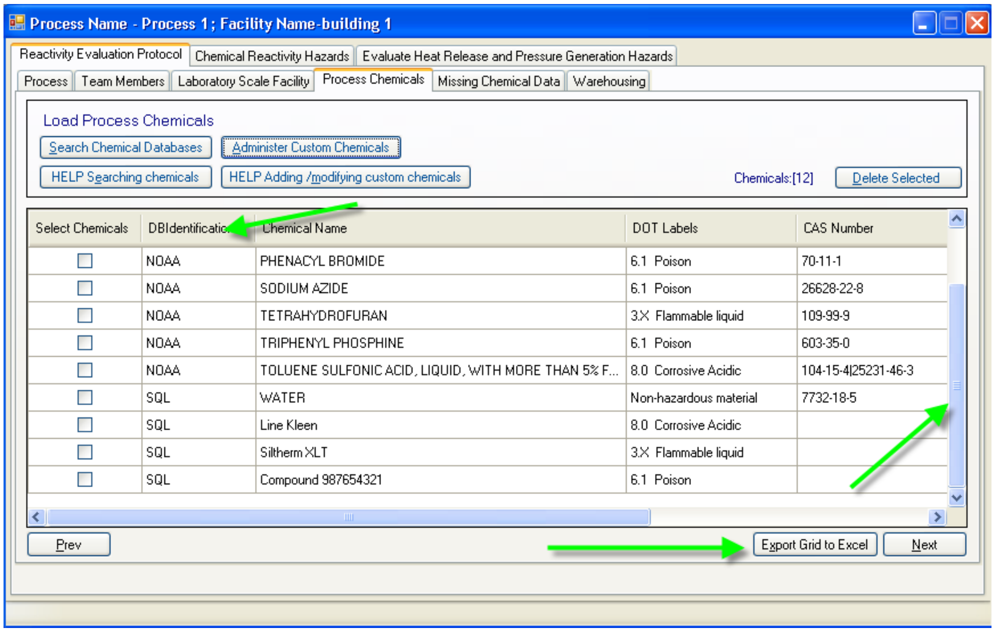
  2) From the Administer Custom Chemicals pop-up (see screen shot next page)

- Check the box in front of the name of the chemical(s) you wish to add
- Press the "A**dd to Process**" button
- Press the "**close**" button to close the pop-up and return you to the **Process Chemicals tab**



Select	Chemical Name	Chemical Formula	CAS Number	UN/NA Number	DOT Labels
☑	WATER	H2O	7732-18-5	0	Non-hazardous
☑	Compound 987654321			0	6.1 Poison
☑	Siltherm XLT			0	3.X Flammable
☑	Line Kleen			0	8.0 Corrosive A

3.2.6.5 Viewing and Navigation



Select Chemicals	DBIdentificatio	Chemical Name	DOT Labels	CAS Number
☐	NOAA	PHENACYL BROMIDE	6.1 Poison	70-11-1
☐	NOAA	SODIUM AZIDE	6.1 Poison	26628-22-8
☐	NOAA	TETRAHYDROFURAN	3.X Flammable liquid	109-99-9
☐	NOAA	TRIPHENYL PHOSPHINE	6.1 Poison	603-35-0
☐	NOAA	TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% F...	8.0 Corrosive Acidic	104-15-4|25231-46-3
☐	SQL	WATER	Non-hazardous material	7732-18-5
☐	SQL	Line Kleen	8.0 Corrosive Acidic	
☐	SQL	Siltherm XLT	3.X Flammable liquid	
☐	SQL	Compound 987654321	6.1 Poison	

- Use the scroll bar to view all the chemicals entered for the process.
- Use "Export to Excel" to data check all entries.

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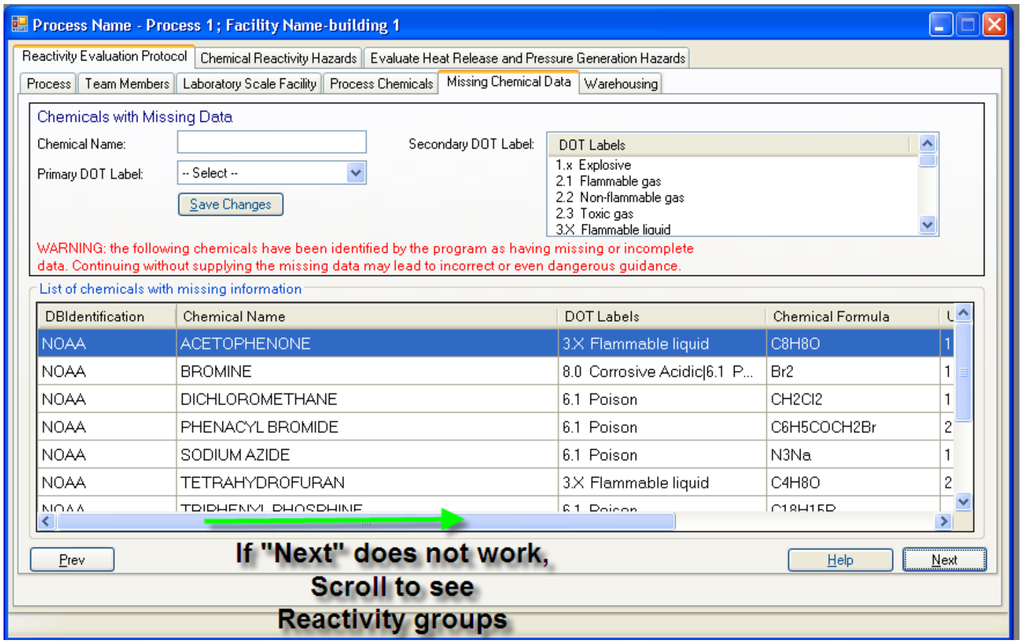
- The form tells you where the chemical information resides under **DB identification**
- When satisfied with all entries, press “next”

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.



Chemicals with Missing Data

Chemical Name:

Primary DOT Label: -- Select --

Secondary DOT Label:

DOT Labels
1.x Explosive
2.1 Flammable gas
2.2 Non-flammable gas
2.3 Toxic gas
3.X Flammable liquid

WARNING: the following chemicals have been identified by the program as having missing or incomplete data. Continuing without supplying the missing data may lead to incorrect or even dangerous guidance.

List of chemicals with missing information

DBIdentification	Chemical Name	DOT Labels	Chemical Formula	U
NOAA	ACETOPHENONE	3.X Flammable liquid	C8H8O	1
NOAA	BROMINE	8.0 Corrosive Acidic|6.1 P...	Br2	1
NOAA	DICHLOROMETHANE	6.1 Poison	CH2Cl2	1
NOAA	PHENACYL BROMIDE	6.1 Poison	C6H5COCH2Br	2
NOAA	SODIUM AZIDE	6.1 Poison	N3Na	1
NOAA	TETRAHYDROFURAN	3.X Flammable liquid	C4H8O	2
NOAA	TRIPHENYL PHOSPHINE	6.1 Poison	C18H15P	

If "Next" does not work,
Scroll to see
Reactivity groups

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. See section 4.2 for how to determine the proper DOT codes.

Pitfall alert

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.

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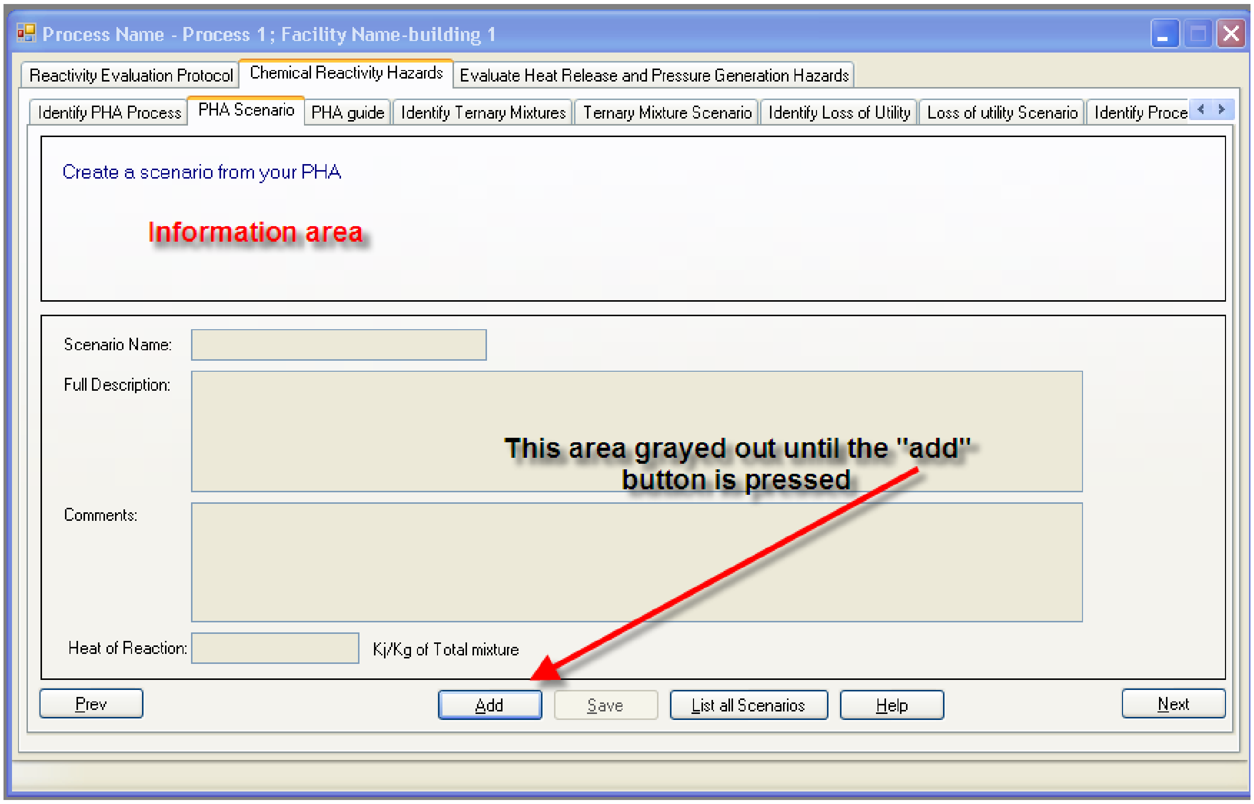
3.2.9 Reactivity and Failure Scenarios

Pitfall alert

- 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.



Create a scenario from your PHA

Information area

Scenario Name:

Full Description:

Comments:

Heat of Reaction: Kj/Kg of Total mixture

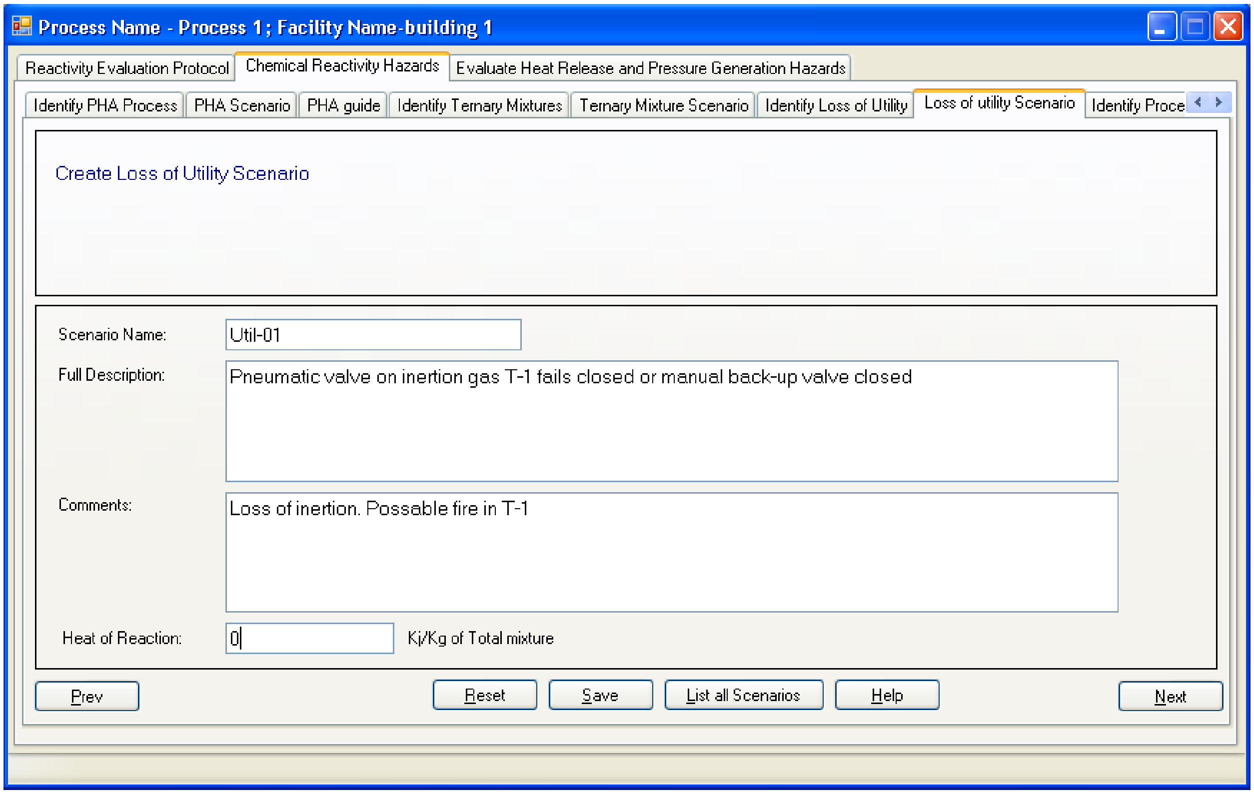
This area grayed out until the "add" button is pressed

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.

Helpful Hint

- 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.



Create Loss of Utility Scenario

Scenario Name: Util-01

Full Description: Pneumatic valve on inertion gas T-1 fails closed or manual back-up valve closed

Comments: Loss of inertion. Possable fire in T-1

Heat of Reaction: 0 Kj/Kg of Total mixture

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.

Pitfall alert

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

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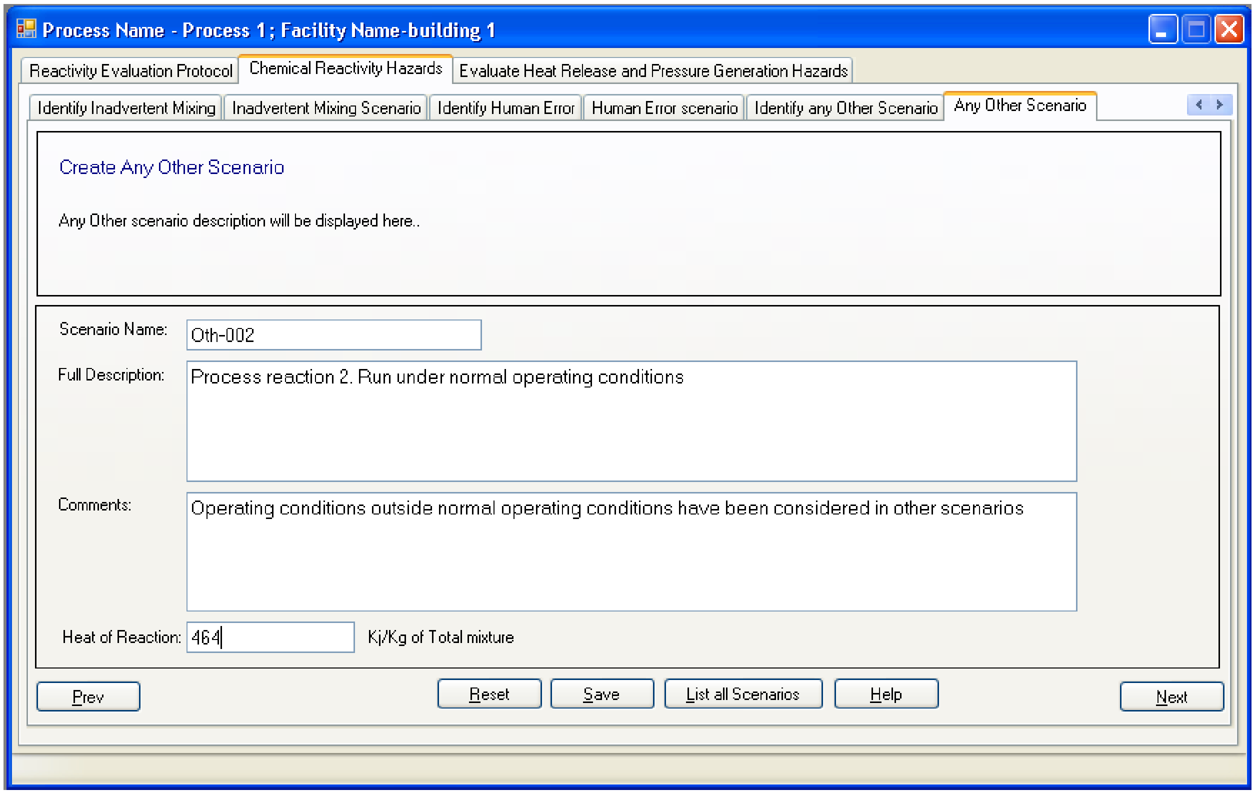
distinguished by their name such as “Rxn 1” for step 1 Or Bin-001 for a chemical incompatibility.

Pitfall alert

Note that **Exothermic** reaction energies are entered as **positive number.**
Note the units: **Kilojoules per kilogram of total reaction mixture**



Create Any Other Scenario

Any Other scenario description will be displayed here..

Scenario Name: Oth-002

Full Description: Process reaction 2. Run under normal operating conditions

Comments: Operating conditions outside normal operating conditions have been considered in other scenarios

Heat of Reaction: 464 Kj/Kg of Total mixture

3.2.9.2 Scenario management- viewing and editing

Helpful Hint

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.

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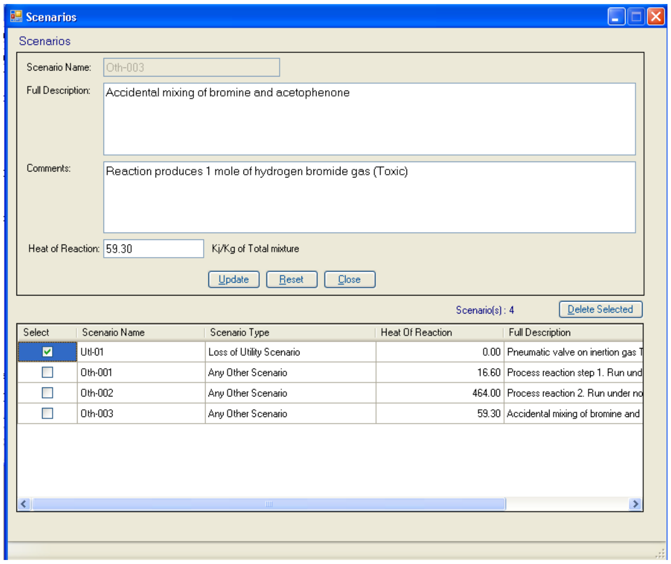
- Check the box in from of the scenario and press delete to remove it from the process



Scenarios

Scenario Name: Oth-003

Full Description: Accidental mixing of bromine and acetophenone

Comments: Reaction produces 1 mole of hydrogen bromide gas (Toxic)

Heat of Reaction: 59.30 Kj/Kg of Total mixture

Scenario(s) : 4

Select	Scenario Name	Scenario Type	Heat Of Reaction	Full Description
☑	Utl-01	Loss of Utility Scenario	0.00	Pneumatic valve on inertion gas T
☐	Oth-001	Any Other Scenario	16.60	Process reaction step 1. Run und
☐	Oth-002	Any Other Scenario	464.00	Process reaction 2. Run under no
☐	Oth-003	Any Other Scenario	59.30	Accidental mixing of bromine and

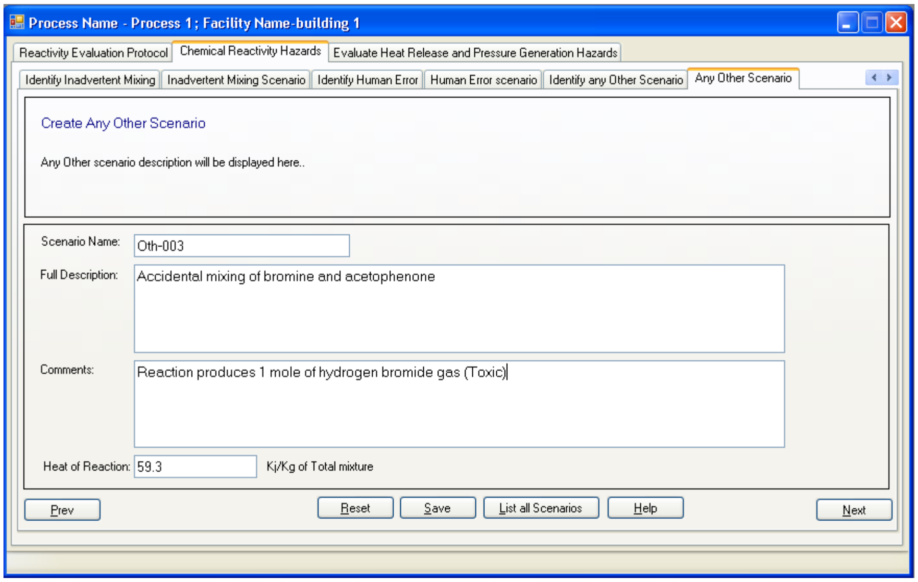
3.2.9.3 Identifying significant chemical interactions

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



Create Any Other Scenario

Any Other scenario description will be displayed here..

Scenario Name: Oth-003

Full Description: Accidental mixing of bromine and acetophenone

Comments: Reaction produces 1 mole of hydrogen bromide gas (Toxic)

Heat of Reaction: 59.3 Kj/Kg of Total mixture

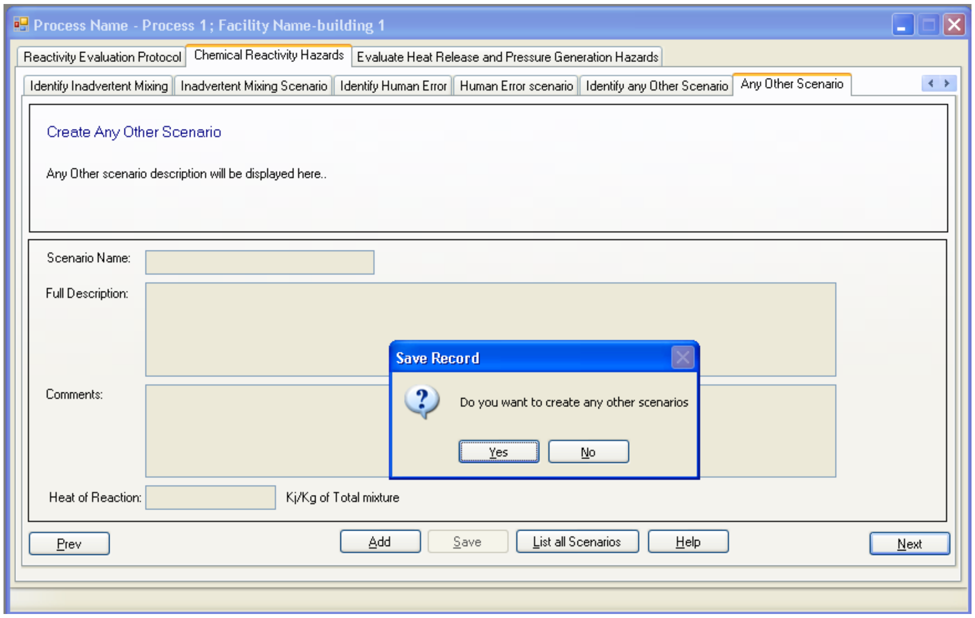
Helpful Hint

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

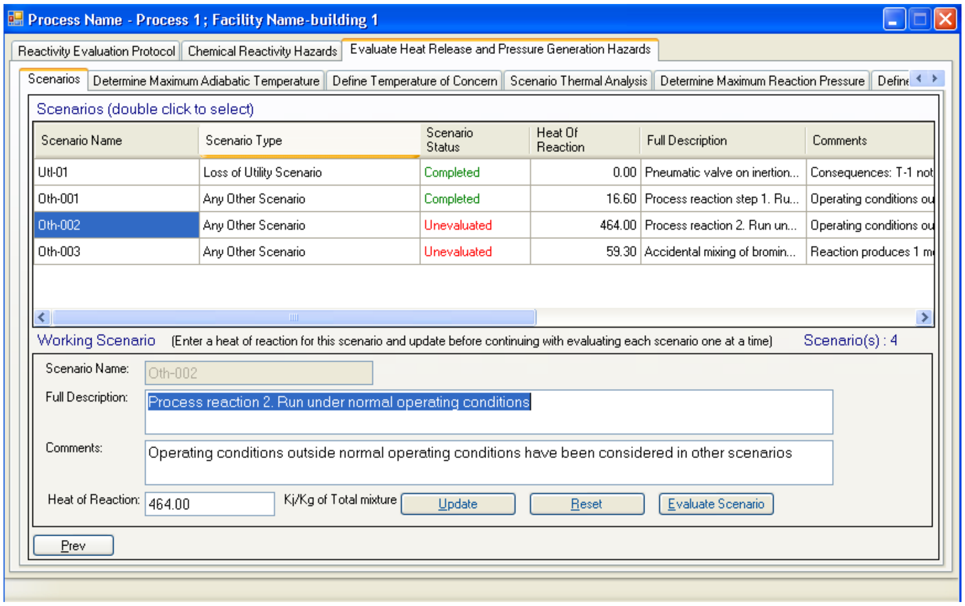
3.2.10.1 Scenarios Tab

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.



Any Other scenario description will be displayed here..

Do you want to create any other scenarios



Scenario Name	Scenario Type	Scenario Status	Heat Of Reaction	Full Description	Comments
Utl-01	Loss of Utility Scenario	Completed	0.00	Pneumatic valve on inertion...	Consequences: T-1 not
Oth-001	Any Other Scenario	Completed	16.60	Process reaction step 1. Ru...	Operating conditions ou
Oth-002	Any Other Scenario	Unevaluated	464.00	Process reaction 2. Run un...	Operating conditions ou
Oth-003	Any Other Scenario	Unevaluated	59.30	Accidental mixing of bromin...	Reaction produces 1 m

(Enter a heat of reaction for this scenario and update before continuing with evaluating each scenario one at a time)

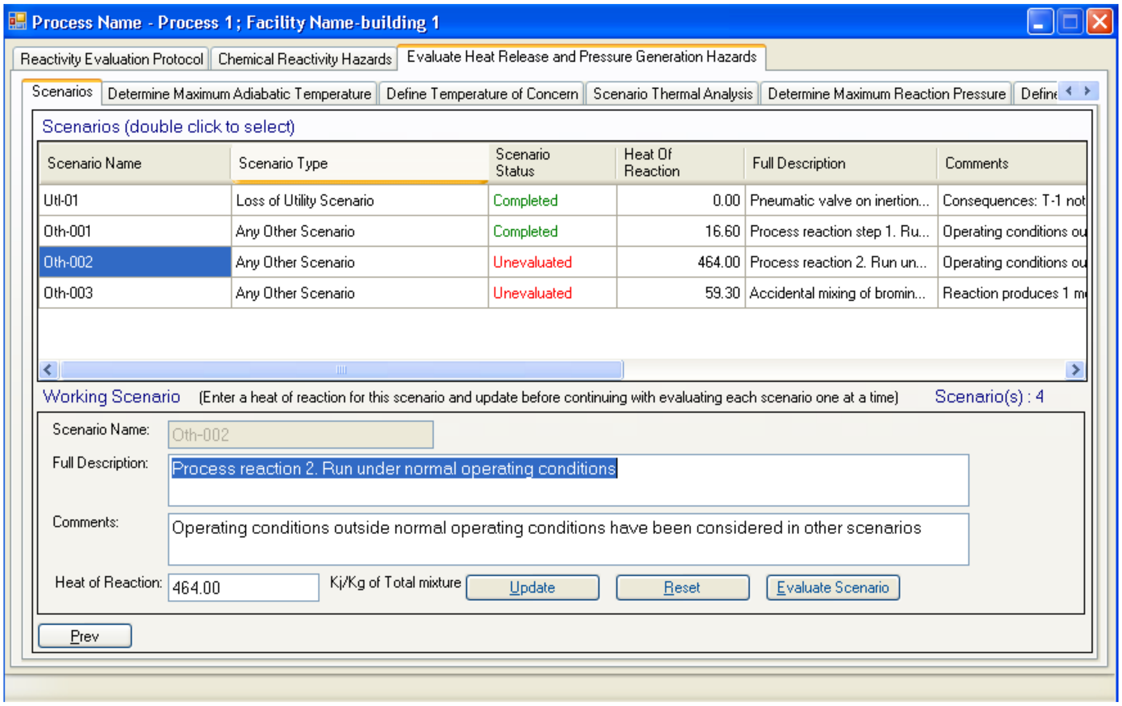
Scenario Name: Oth-002

Full Description: Process reaction 2. Run under normal operating conditions

Comments: Operating conditions outside normal operating conditions have been considered in other scenarios

Heat of Reaction: 464.00 Kj/Kg of Total mixture

- 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.



Scenarios (double click to select)

Scenario Name	Scenario Type	Scenario Status	Heat Of Reaction	Full Description	Comments
Utl-01	Loss of Utility Scenario	Completed	0.00	Pneumatic valve on inertion...	Consequences: T-1 not
Oth-001	Any Other Scenario	Completed	16.60	Process reaction step 1. Ru...	Operating conditions ou
Oth-002	Any Other Scenario	Unevaluated	464.00	Process reaction 2. Run un...	Operating conditions ou
Oth-003	Any Other Scenario	Unevaluated	59.30	Accidental mixing of bromin...	Reaction produces 1 m

Working Scenario (Enter a heat of reaction for this scenario and update before continuing with evaluating each scenario one at a time) Scenario(s) : 4

Scenario Name: Oth-002

Full Description: Process reaction 2. Run under normal operating conditions

Comments: Operating conditions outside normal operating conditions have been considered in other scenarios

Heat of Reaction: 464.00 Kj/Kg of Total mixture

- 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

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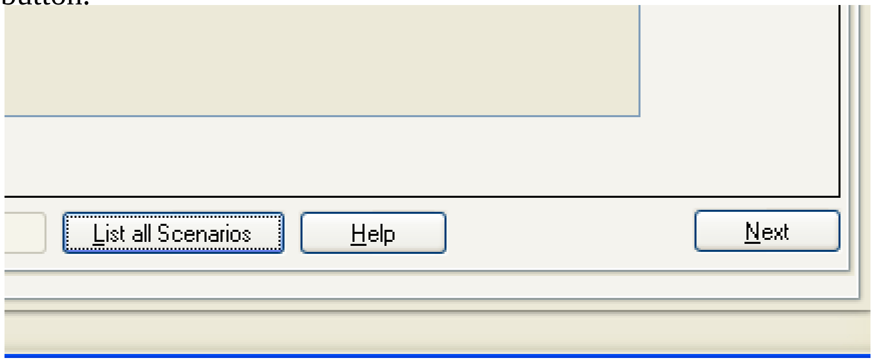
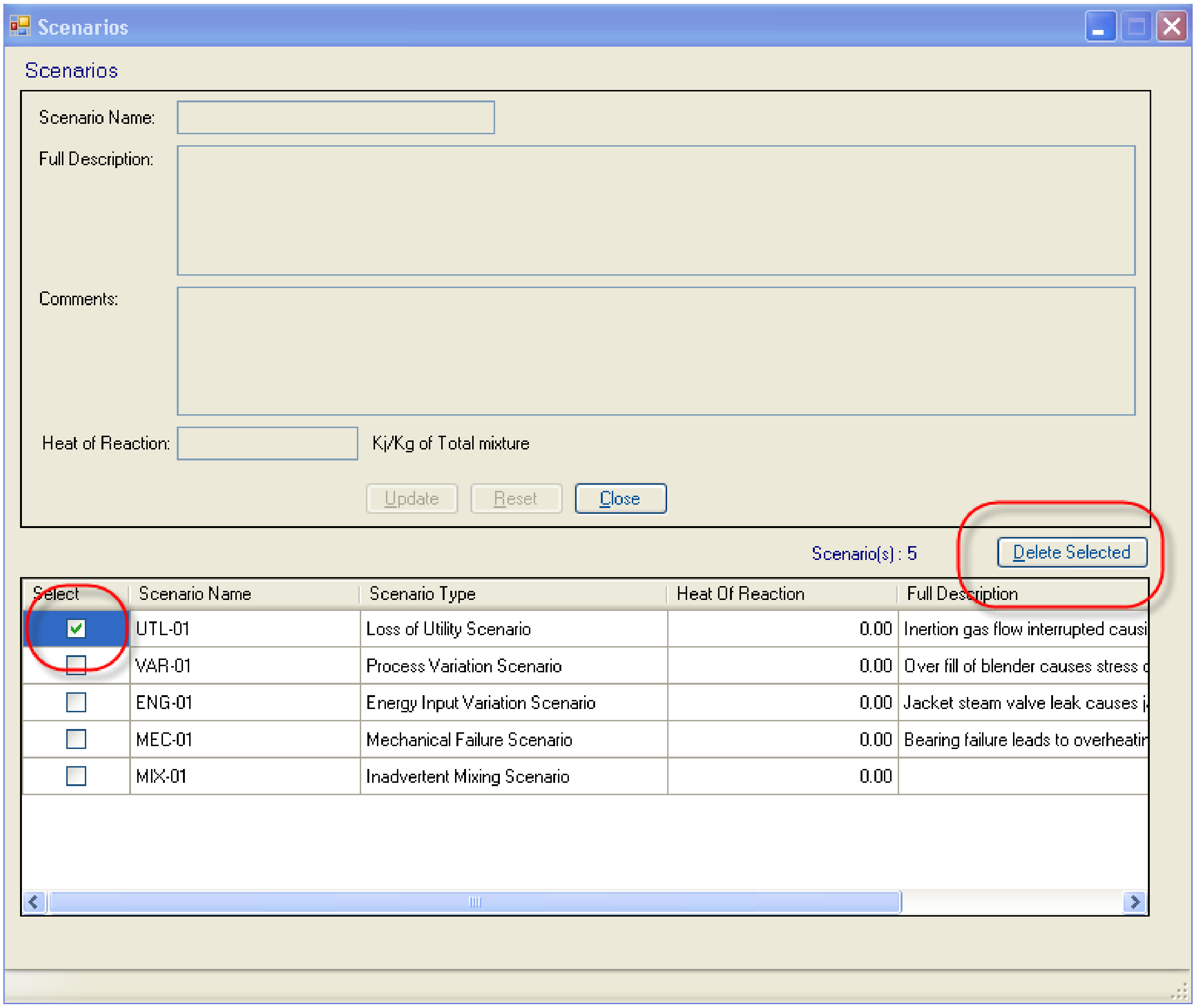
To delete or edit a scenario, go back to any Scenario entry tab. Press the “list all Scenarios” button.



The following pop-up box appears.

Check the box in front of the scenarios you wish to delete and press “delete selected”



Scenario(s) : 5

Select	Scenario Name	Scenario Type	Heat Of Reaction	Full Description
☑	UTL-01	Loss of Utility Scenario	0.00	Inertion gas flow interrupted causi
☐	VAR-01	Process Variation Scenario	0.00	Over fill of blender causes stress
☐	ENG-01	Energy Input Variation Scenario	0.00	Jacket steam valve leak causes
☐	MEC-01	Mechanical Failure Scenario	0.00	Bearing failure leads to overheati
☐	MIX-01	Inadvertent Mixing Scenario	0.00	

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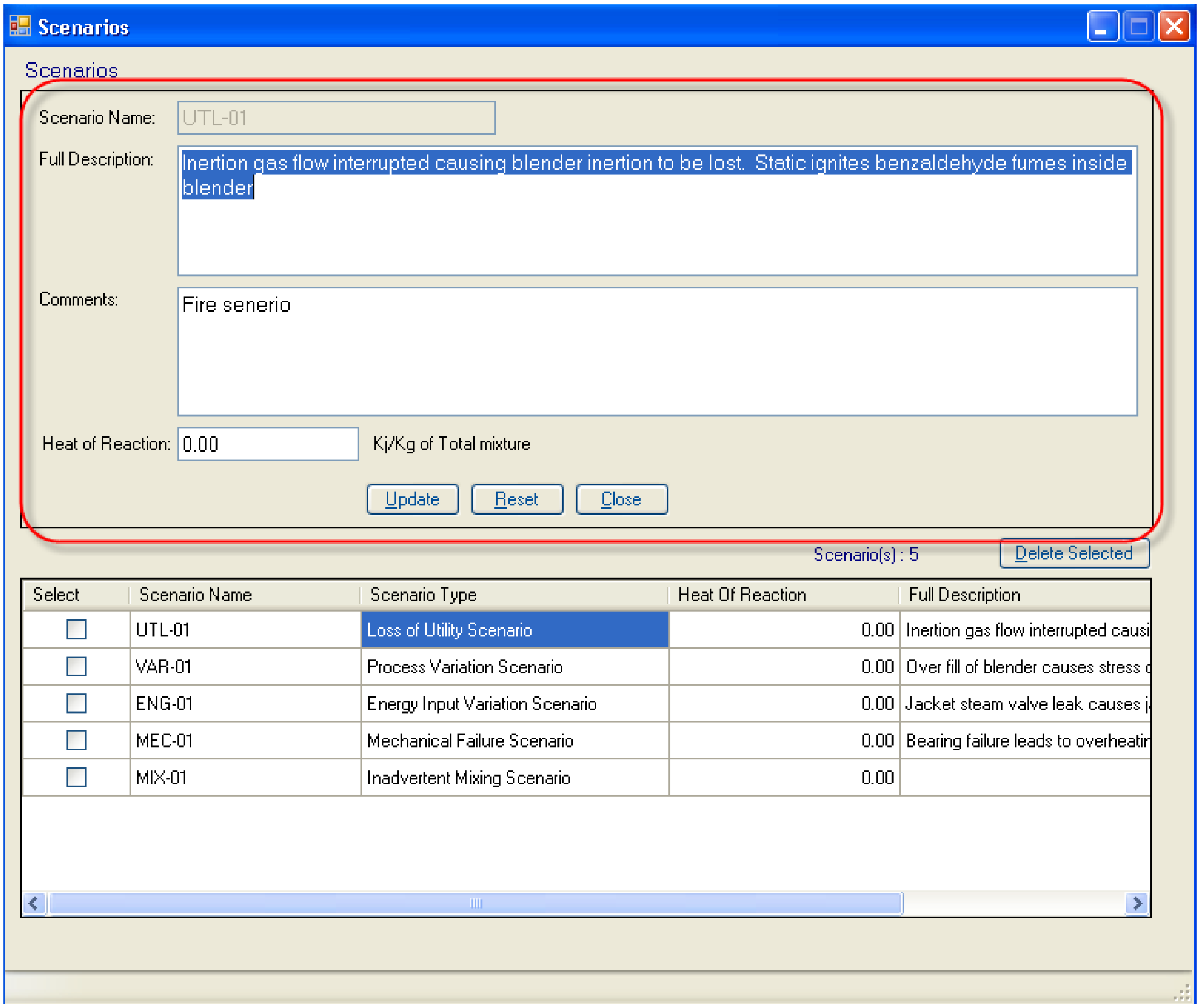
Note that you can edit a scenario from this pop-up form. Double click on the scenario and the scenario will be editable in the top half.



Scenario Name: UTL-01

Full Description: Inertion gas flow interrupted causing blender inertion to be lost. Static ignites benzaldehyde fumes inside blender

Comments: Fire senerio

Heat of Reaction: 0.00 Kj/Kg of Total mixture

Scenario(s) : 5

Select	Scenario Name	Scenario Type	Heat Of Reaction	Full Description
☐	UTL-01	Loss of Utility Scenario	0.00	Inertion gas flow interrupted causi
☐	VAR-01	Process Variation Scenario	0.00	Over fill of blender causes stress c
☐	ENG-01	Energy Input Variation Scenario	0.00	Jacket steam valve leak causes j
☐	MEC-01	Mechanical Failure Scenario	0.00	Bearing failure leads to overheatin
☐	MIX-01	Inadvertent Mixing Scenario	0.00	

Helpful Hint Because of the database structure of the program, there is no way to edit the scenario name once entered – choose wisely.

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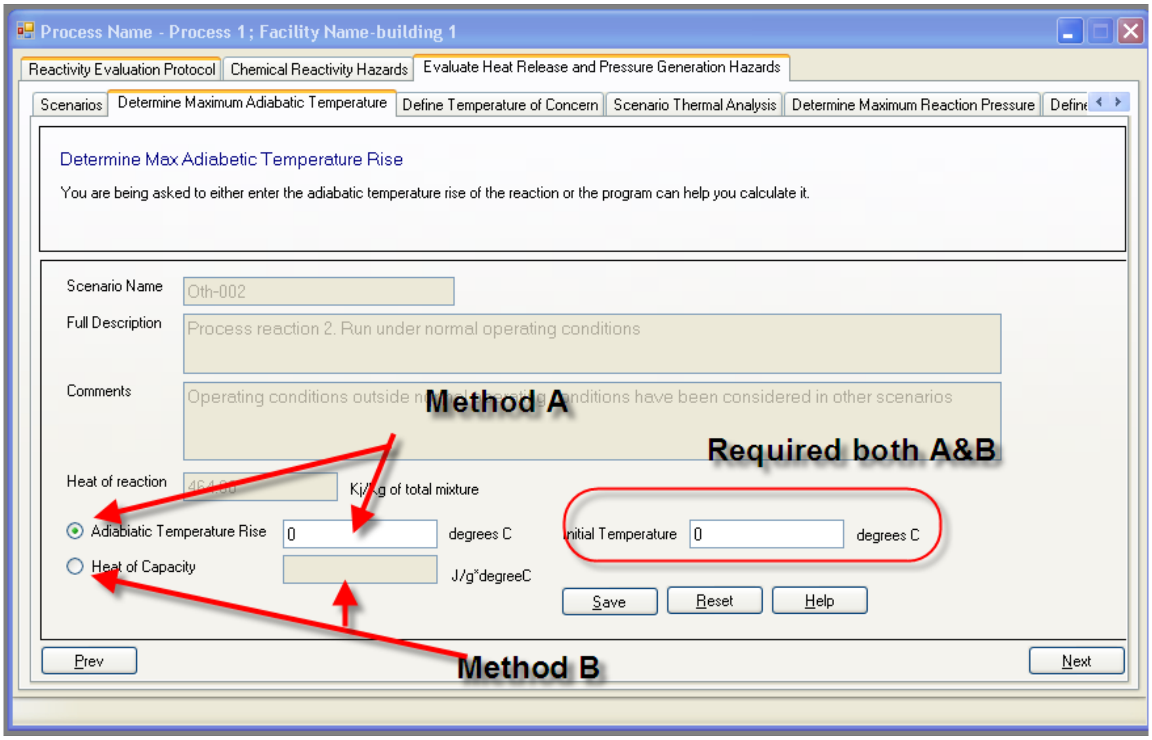
3.2.10.3 Determine Maximum Adiabatic Temperature Tab



Process Name - Process 1; Facility Name-building 1

Determine Max Adiabetic Temperature Rise

You are being asked to either enter the adiabatic temperature rise of the reaction or the program can help you calculate it.

Scenario Name: Oth-002

Full Description: Process reaction 2. Run under normal operating conditions

Comments: Operating conditions outside normal operating conditions have been considered in other scenarios

Heat of reaction: 464.00 Kj/Kg of total mixture

● Adiabatic Temperature Rise: 0 degrees C

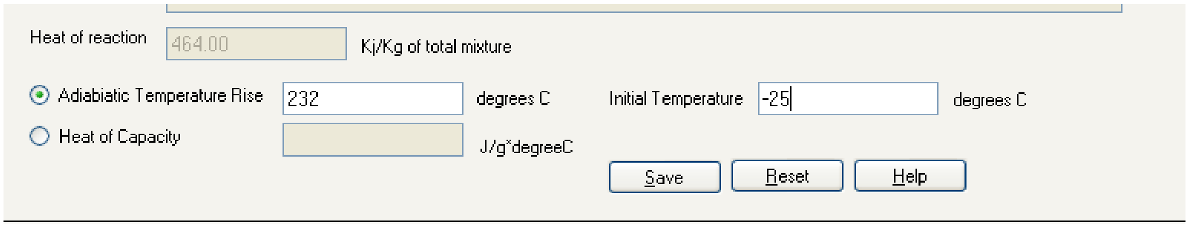
○ Heat of Capacity: J/g*degreeC

Initial Temperature: 0 degrees C

There are two methods of data entry here.

Method A

- You can enter the adiabatic heat rise directly



Heat of reaction: 464.00 Kj/Kg of total mixture

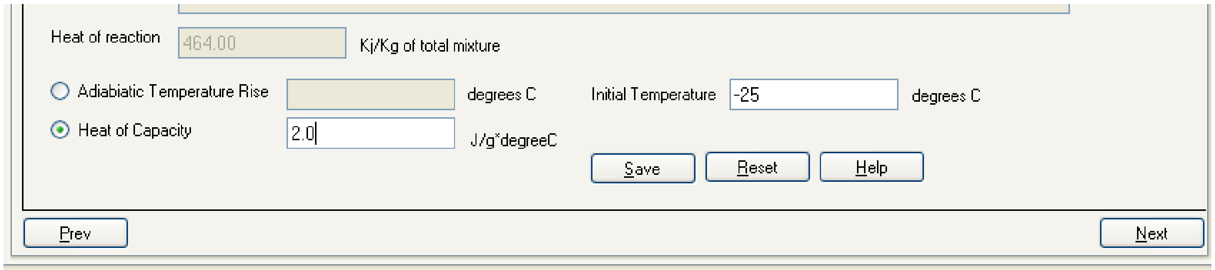
● Adiabatic Temperature Rise: 232 degrees C

Initial Temperature: -25 degrees C

○ Heat of Capacity: J/g*degreeC

Method B

- The program will calculate it for you from the heat of reaction and heat capacity of the mixture



Heat of reaction: 464.00 Kj/Kg of total mixture

○ Adiabatic Temperature Rise: degrees C

Initial Temperature: -25 degrees C

● Heat of Capacity: 2.0 J/g*degreeC

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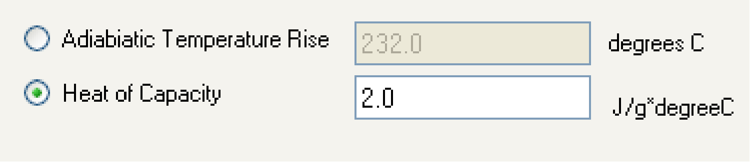
Helpful Hint

For organic reactions a heat capacity of 2j/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

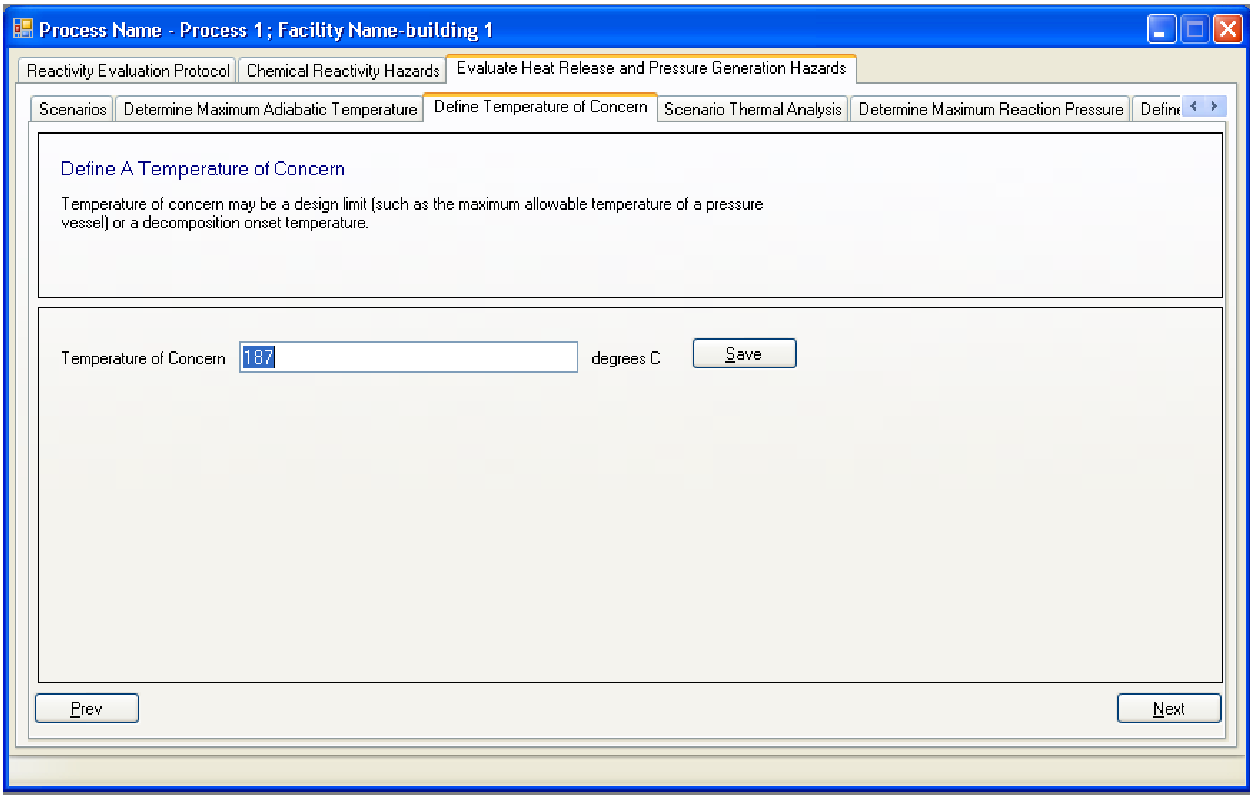


○ Adiabatic Temperature Rise 232.0 degrees C

● Heat of Capacity 2.0 J/g*degreeC

3.2.10.4 Define Temperature of Concern Tab

- Press the Next button



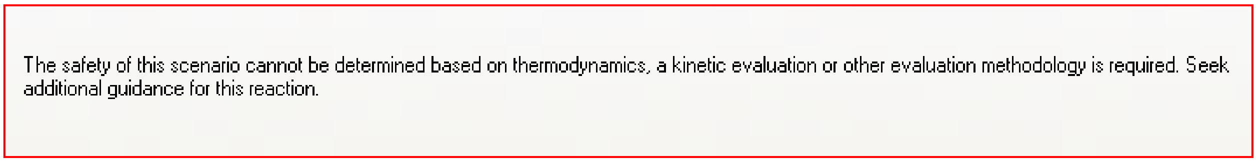
Define A Temperature of Concern

Temperature of concern may be a design limit (such as the maximum allowable temperature of a pressure vessel) or a decomposition onset temperature.

Temperature of Concern 187 degrees C

- 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.

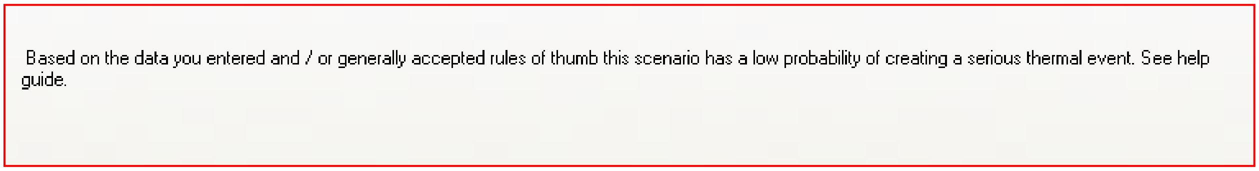
The program will now display one of two messages:



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

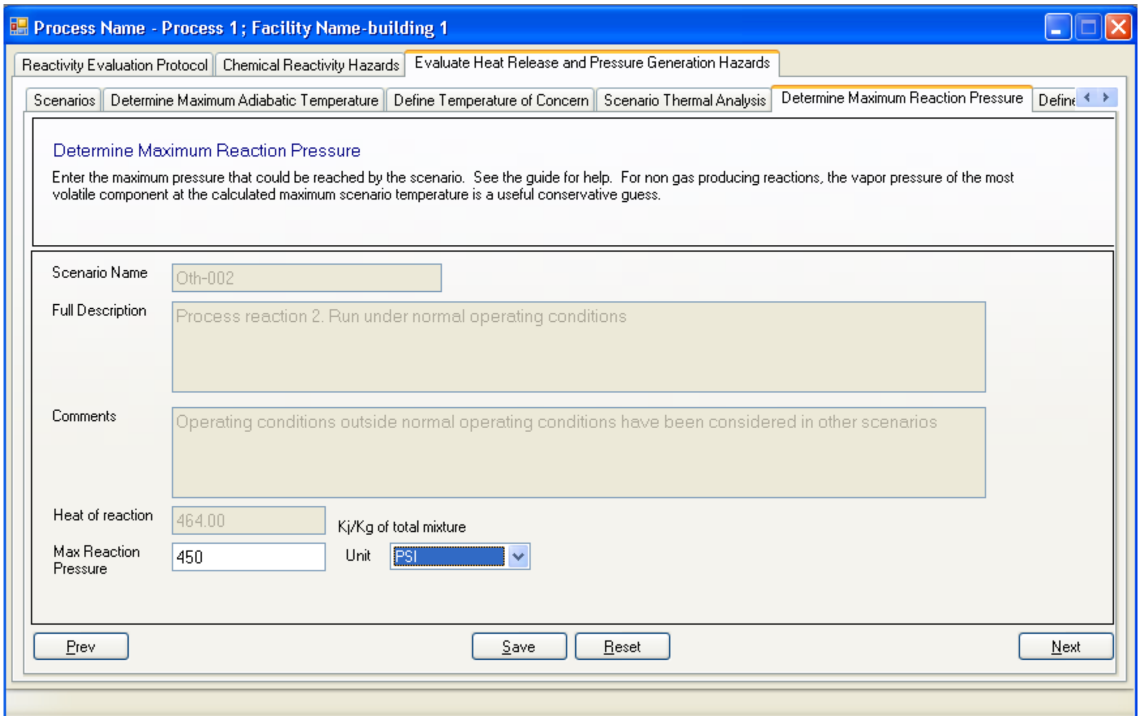


Based on the data you entered and / or generally accepted rules of thumb this scenario has a low probability of creating a serious thermal event. See help guide.

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



Determine Maximum Reaction Pressure

Enter the maximum pressure that could be reached by the scenario. See the guide for help. For non gas producing reactions, the vapor pressure of the most volatile component at the calculated maximum scenario temperature is a useful conservative guess.

Scenario Name: Oth-002

Full Description: Process reaction 2. Run under normal operating conditions

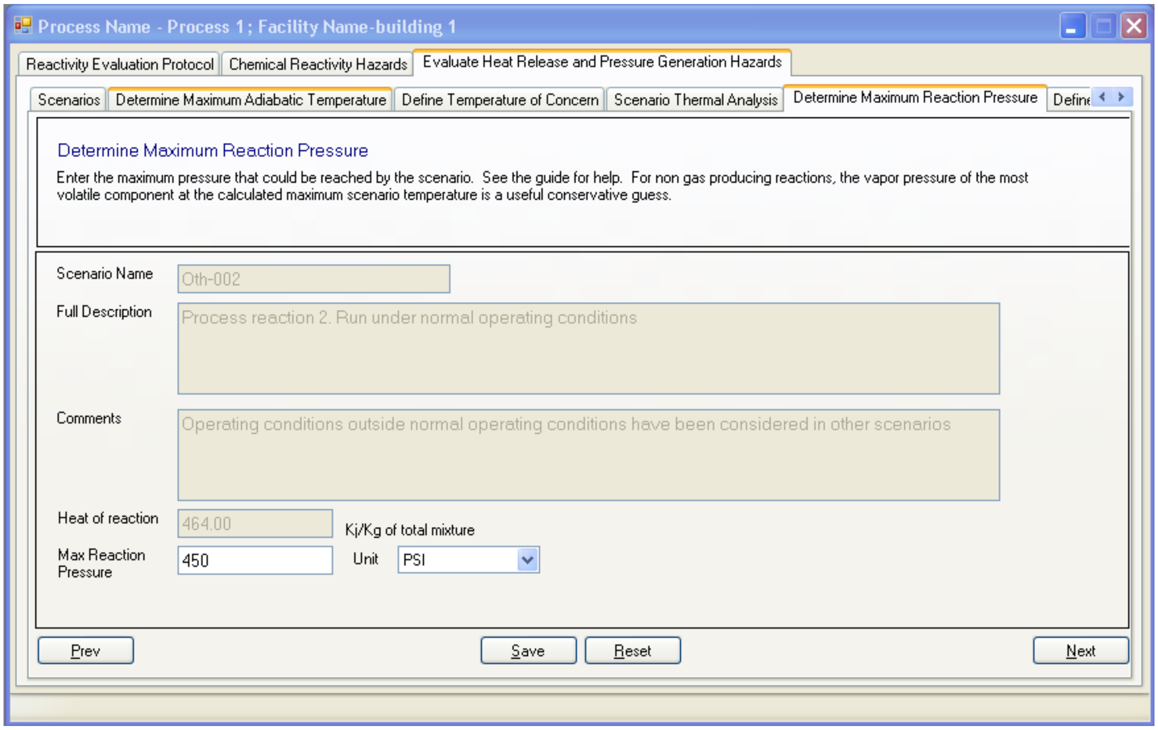
Comments: Operating conditions outside normal operating conditions have been considered in other scenarios

Heat of reaction: 464.00 Kj/Kg of total mixture

Max Reaction Pressure: 450 Unit: PSI

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



Determine Maximum Reaction Pressure

Enter the maximum pressure that could be reached by the scenario. See the guide for help. For non gas producing reactions, the vapor pressure of the most volatile component at the calculated maximum scenario temperature is a useful conservative guess.

Scenario Name: Oth-002

Full Description: Process reaction 2. Run under normal operating conditions

Comments: Operating conditions outside normal operating conditions have been considered in other scenarios

Heat of reaction: 464.00 Kj/Kg of total mixture

Max Reaction Pressure: 450 Unit: PSI

- Choose your pressure units from the drop-down menu.
- Press save then Next

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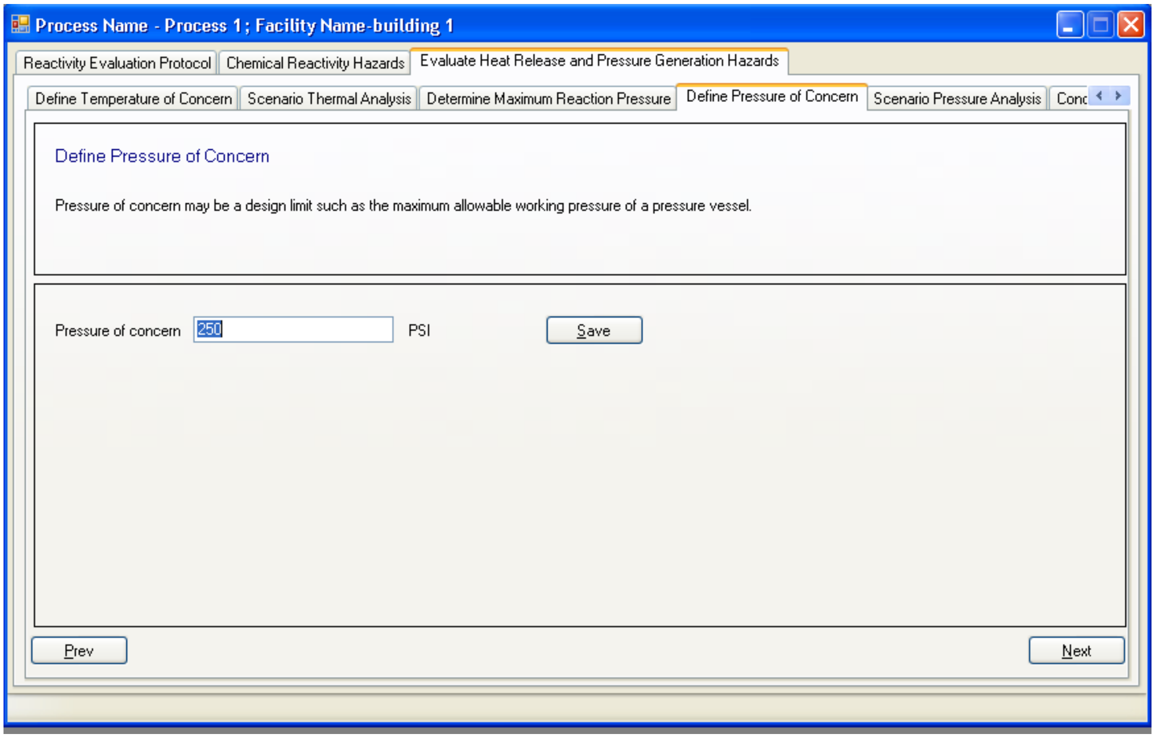
3.2.10.6 Determine Pressure of Concern Tab

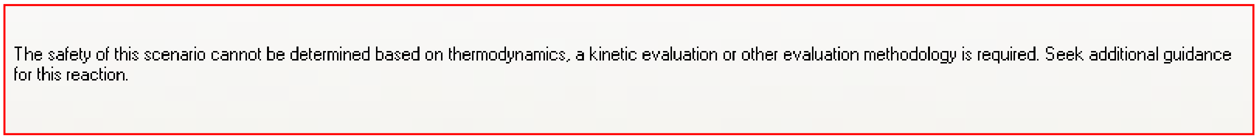


Define Pressure of Concern

Pressure of concern may be a design limit such as the maximum allowable working pressure of a pressure vessel.

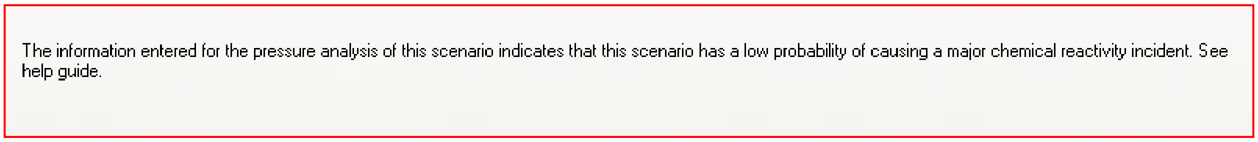
Pressure of concern 250 PSI

- 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 this scenario has a low probability of causing a major chemical reactivity incident. See help guide.

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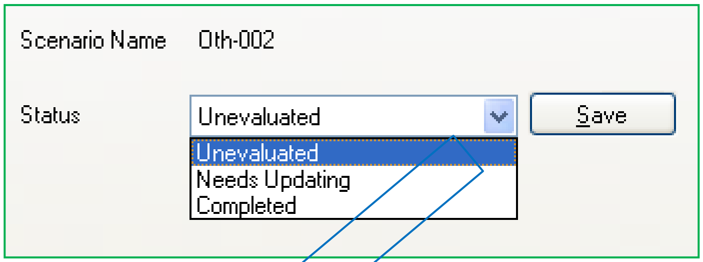
- In this case the user should check all data entries and also fully understand the limitations of this program before judging the scenario “safe”.

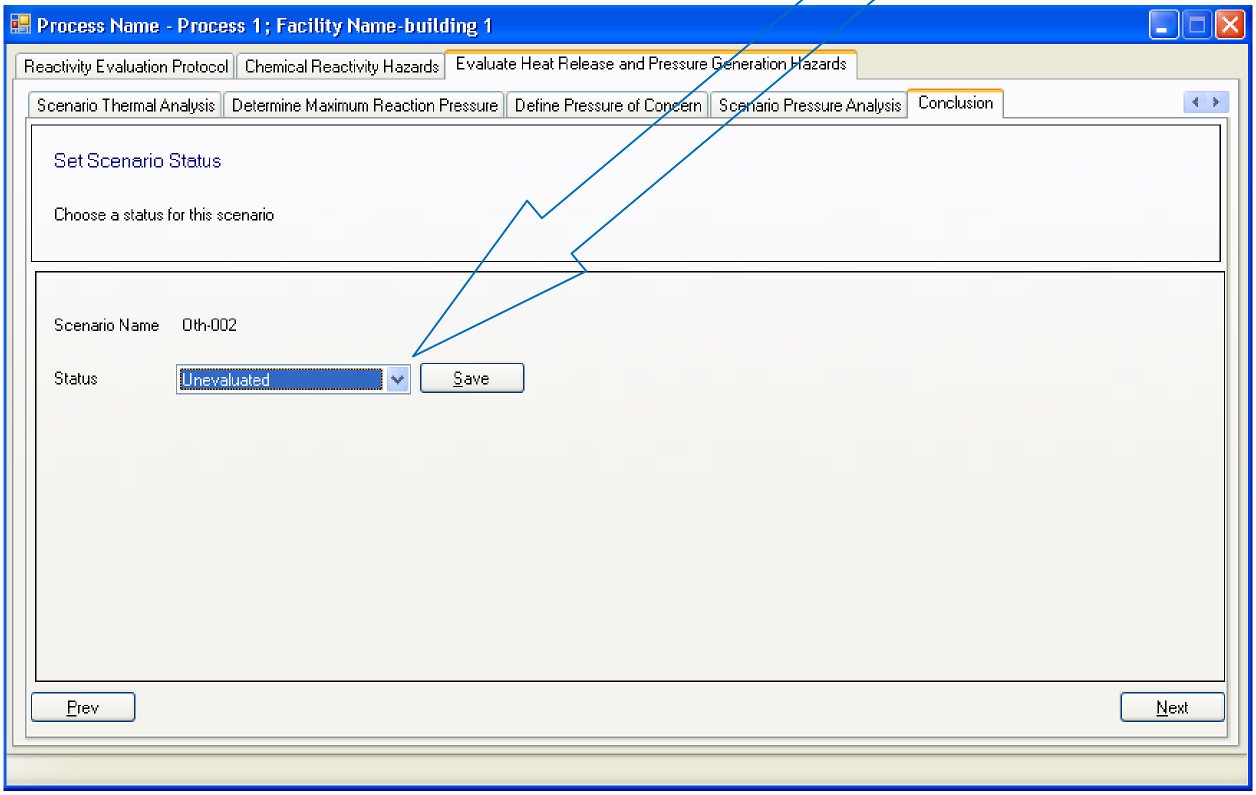
3.2.10.7 Conclusion Tab – setting scenario status

- 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



Scenario Name Oth-002

Status Unevaluated



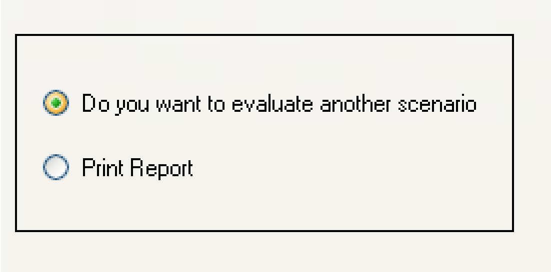
Set Scenario Status

Choose a status for this scenario

Scenario Name Oth-002

Status Unevaluated

- Press save and next
- The box below may appear below the status in the above screen shot



● Do you want to evaluate another scenario

○ Print Report

- The first choice takes you back to the Scenarios tan 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.

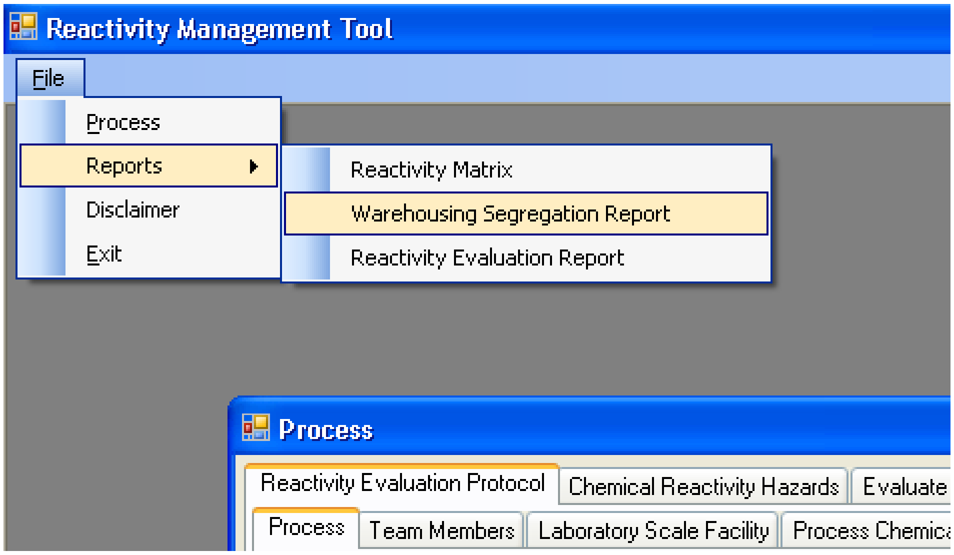
3.2.11 Reports

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.

Helpful Hint

3.2.11.1 Warehousing Segregation Report

Select: File – Reports-Warehousing Segregation report



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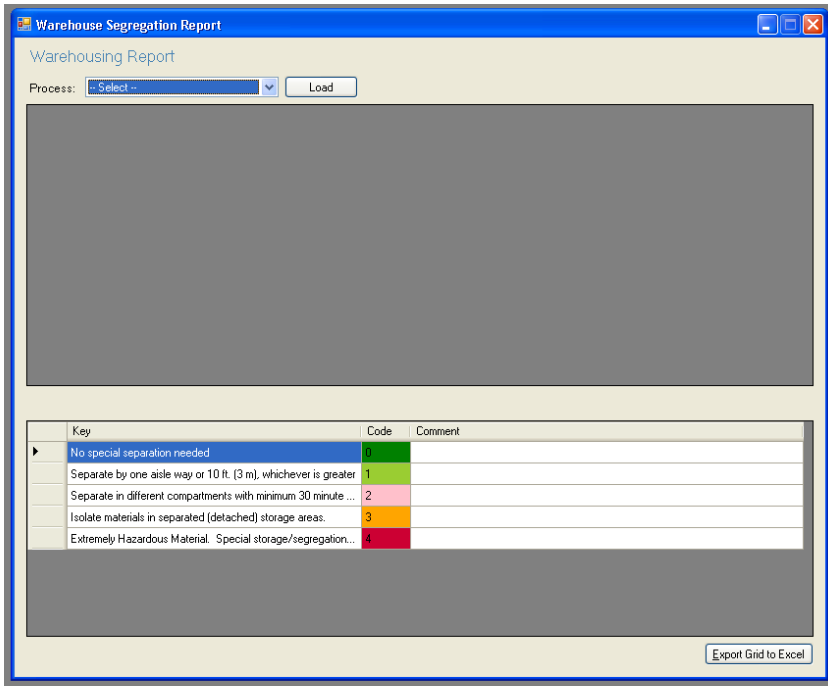
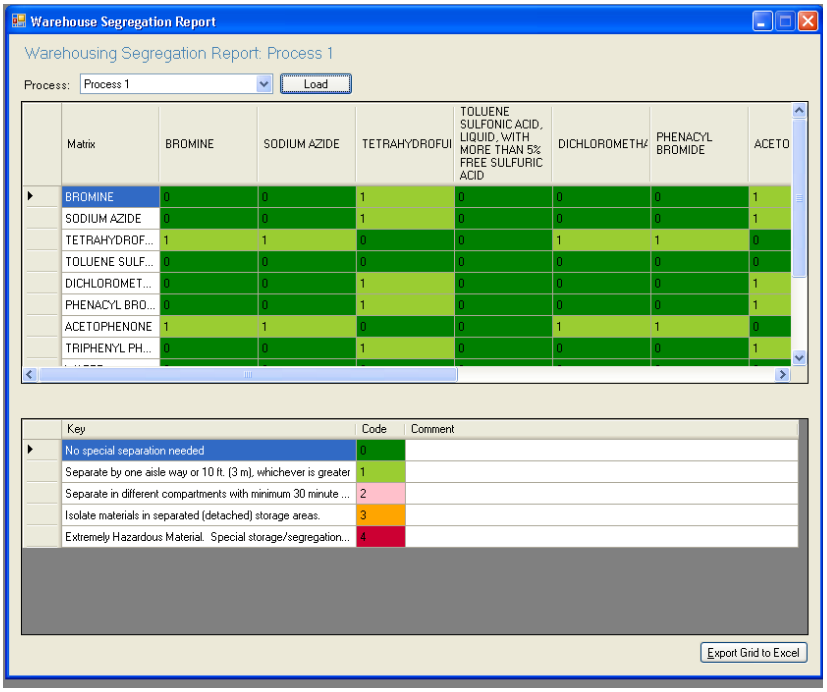
Selecting this report opens up the pop-up window shown below



	Key	Code	Comment
▸	No special separation needed	0	
	Separate by one aisle way or 10 ft. (3 m), whichever is greater	1	
	Separate in different compartments with minimum 30 minute ...	2	
	Isolate materials in separated (detached) storage areas.	3	
	Extremely Hazardous Material. Special storage/segregation...	4	

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



Process: Process 1

	Matrix	BROMINE	SODIUM AZIDE	TETRAHYDROFUI	TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID	DICHLOROMETH/	PHENACYL BROMIDE	ACETO
▸	BROMINE	0	0	1	0	0	0	1
	SODIUM AZIDE	0	0	1	0	0	0	1
	TETRAHYDROF...	1	1	0	0	1	1	0
	TOLUENE SULF...	0	0	0	0	0	0	0
	DICHLOROMET...	0	0	1	0	0	0	1
	PHENACYL BRO...	0	0	1	0	0	0	1
	ACETOPHENONE	1	1	0	0	1	1	0
	TRIPHENYL PH...	0	0	1	0	0	0	1

	Key	Code	Comment
▸	No special separation needed	0	
	Separate by one aisle way or 10 ft. (3 m), whichever is greater	1	
	Separate in different compartments with minimum 30 minute ...	2	
	Isolate materials in separated (detached) storage areas.	3	
	Extremely Hazardous Material. Special storage/segregation...	4	

- 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.

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Pitfall alert

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.

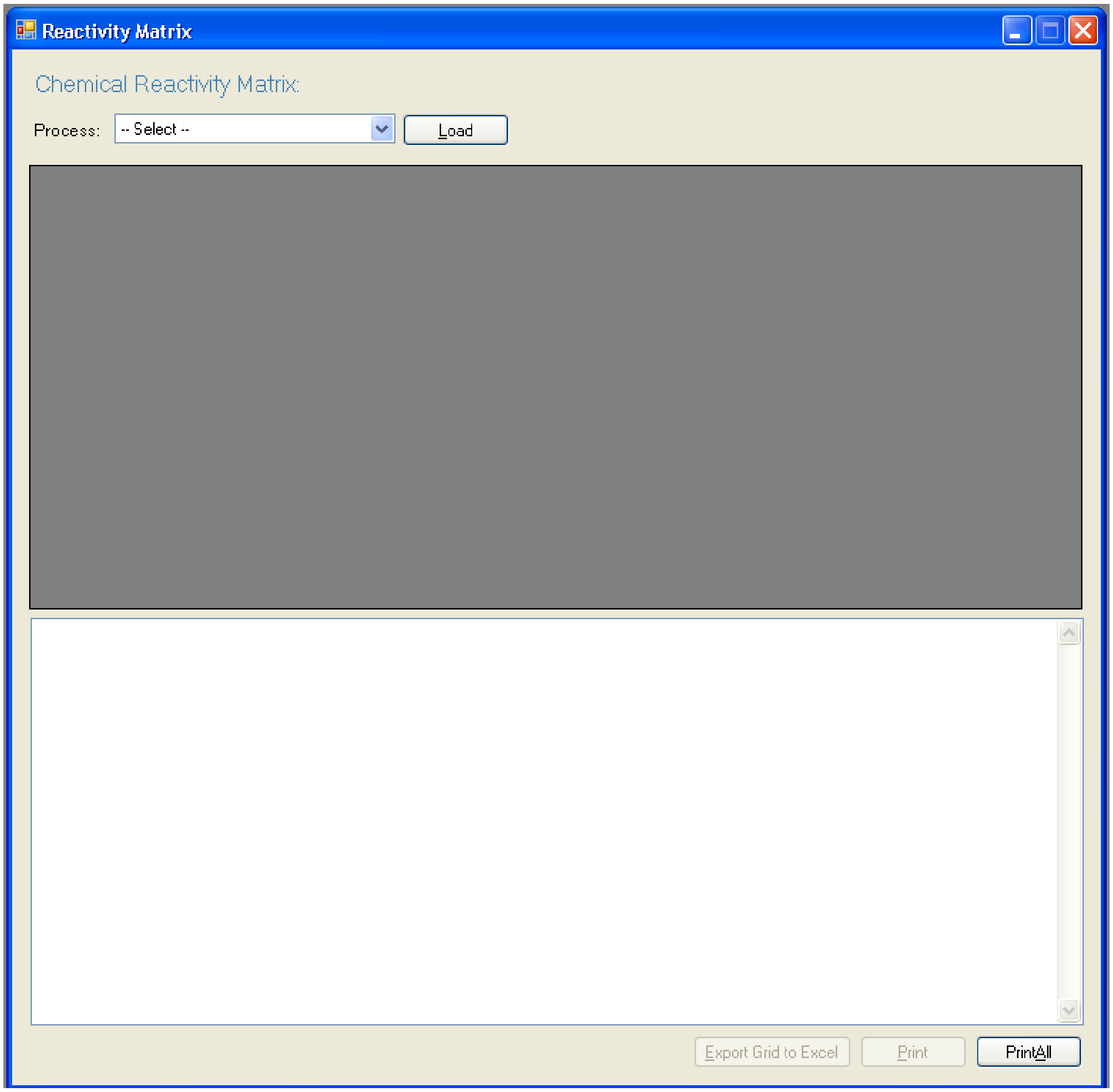
3.2.11.2 Reactivity matrix

The reactivity matrix report is accessed through the file menu

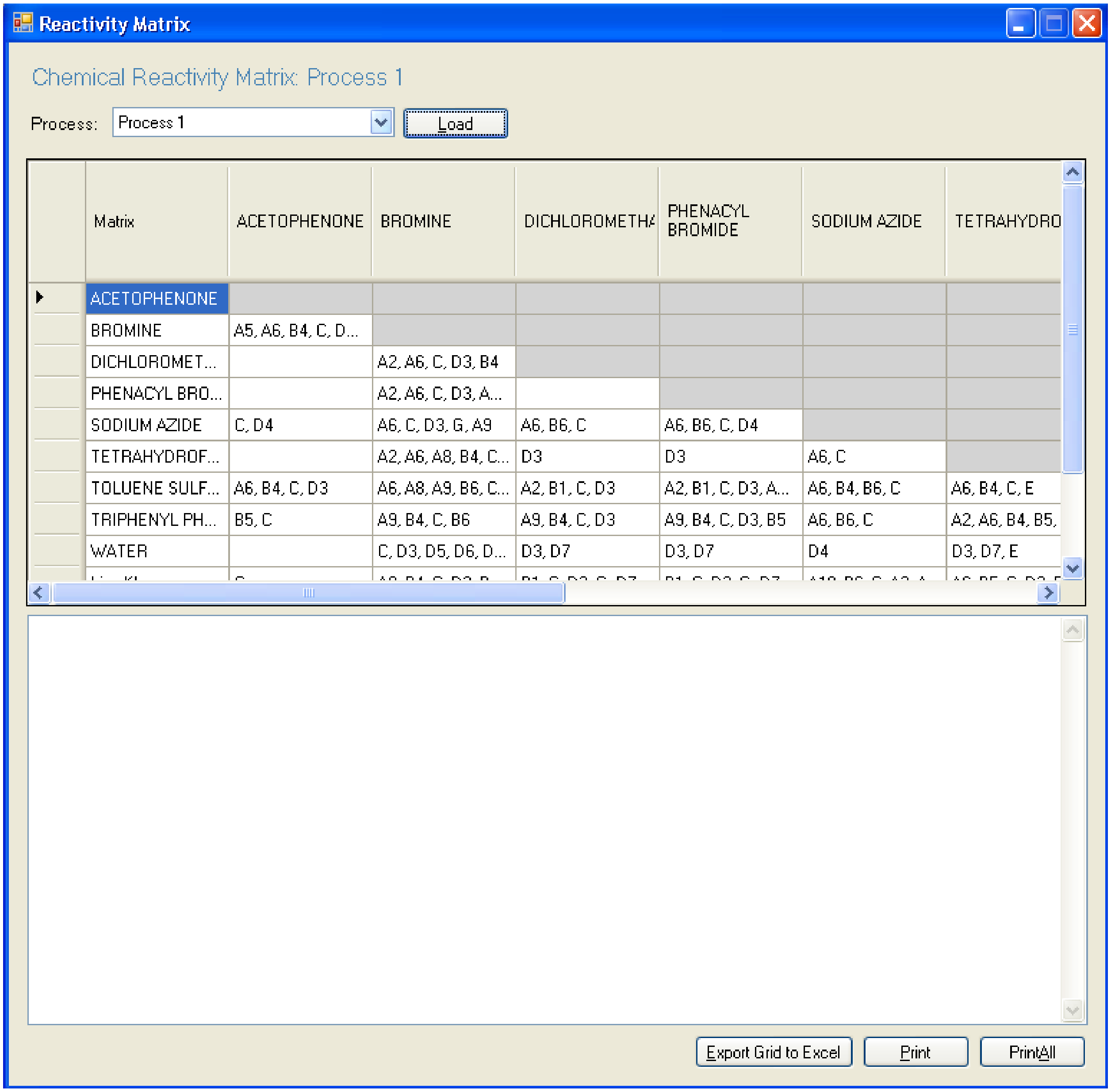
Select: File – Reports-Reactivity matrix

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



Chemical Reactivity Matrix: Process 1

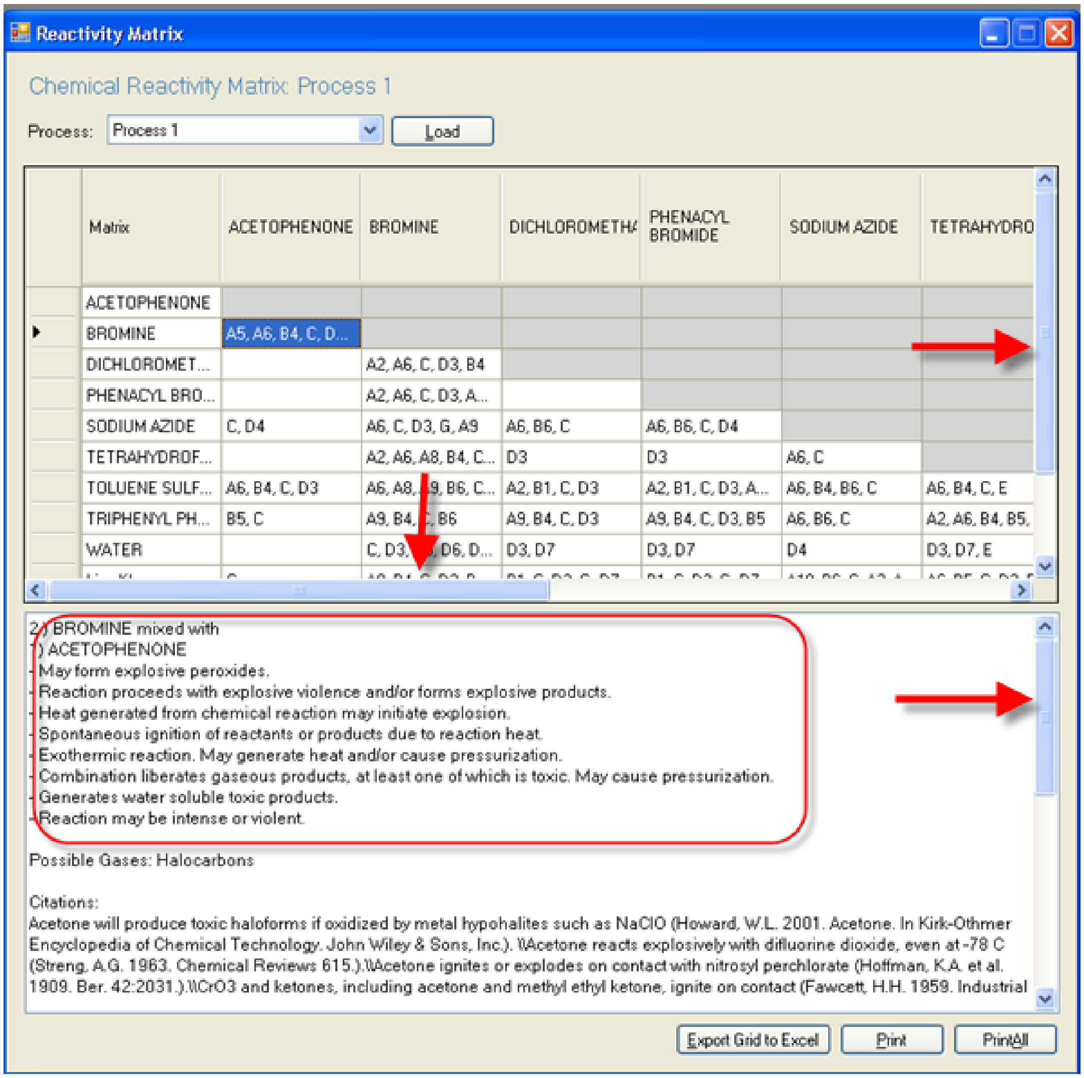
Process: Process 1

Matrix	ACETOPHENONE	BROMINE	DICHLOROMETHA	PHENACYL BROMIDE	SODIUM AZIDE	TETRAHYDRO
ACETOPHENONE						
BROMINE	A5, A6, B4, C, D...					
DICHLOROMET...		A2, A6, C, D3, B4				
PHENACYL BRO...		A2, A6, C, D3, A...				
SODIUM AZIDE	C, D4	A6, C, D3, G, A9	A6, B6, C	A6, B6, C, D4		
TETRAHYDROF...		A2, A6, A8, B4, C...	D3	D3	A6, C	
TOLUENE SULF...	A6, B4, C, D3	A6, A8, A9, B6, C...	A2, B1, C, D3	A2, B1, C, D3, A...	A6, B4, B6, C	A6, B4, C, E
TRIPHENYL PH...	B5, C	A9, B4, C, B6	A9, B4, C, D3	A9, B4, C, D3, B5	A6, B6, C	A2, A6, B4, B5,
WATER		C, D3, D5, D6, D...	D3, D7	D3, D7	D4	D3, D7, E

- 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.



Chemical Reactivity Matrix: Process 1

Process: Process 1

Matrix	ACETOPHENONE	BROMINE	DICHLOROMETHA	PHENACYL BROMIDE	SODIUM AZIDE	TETRAHYDRO
ACETOPHENONE						
BROMINE	A5, A6, B4, C, D...					
DICHLOROMET...		A2, A6, C, D3, B4				
PHENACYL BRO...		A2, A6, C, D3, A...				
SODIUM AZIDE	C, D4	A6, C, D3, G, A9	A6, B6, C	A6, B6, C, D4		
TETRAHYDROF...		A2, A6, A8, B4, C...	D3	D3	A6, C	
TOLUENE SULF...	A6, B4, C, D3	A6, A8, [illegible]9, B6, C...	A2, B1, C, D3	A2, B1, C, D3, A...	A6, B4, B6, C	A6, B4, C, E
TRIPHENYL PH...	B5, C	A9, B4, [illegible], B6	A9, B4, C, D3	A9, B4, C, D3, B5	A6, B6, C	A2, A6, B4, B5,
WATER		C, D3, [illegible], D6, D...	D3, D7	D3, D7	D4	D3, D7, E

2) BROMINE mixed with
1) ACETOPHENONE
- May form explosive peroxides.
- Reaction proceeds with explosive violence and/or forms explosive products.
- Heat generated from chemical reaction may initiate explosion.
- Spontaneous ignition of reactants 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.
- Generates water soluble toxic products.
- Reaction may be intense or violent.

Possible Gases: Halocarbons

Citations:
Acetone will produce toxic haloforms if oxidized by metal hypohalites such as NaClO (Howard, W.L. 2001. Acetone. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.). \\Acetone reacts explosively with difluorine dioxide, even at -78 C (Streng, A.G. 1963. Chemical Reviews 615.).\\Acetone ignites or explodes on contact with nitrosyl perchlorate (Hoffman, K.A. et al. 1909. Ber. 42:2031.).\\CrO3 and ketones, including acetone and methyl ethyl ketone, ignite on contact (Fawcett, H.H. 1959. Industrial

- Use the **Export to Excel** button to export a printable reactivity matrix into Excel.
    - The matrix will look like the top half of the window
- 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.

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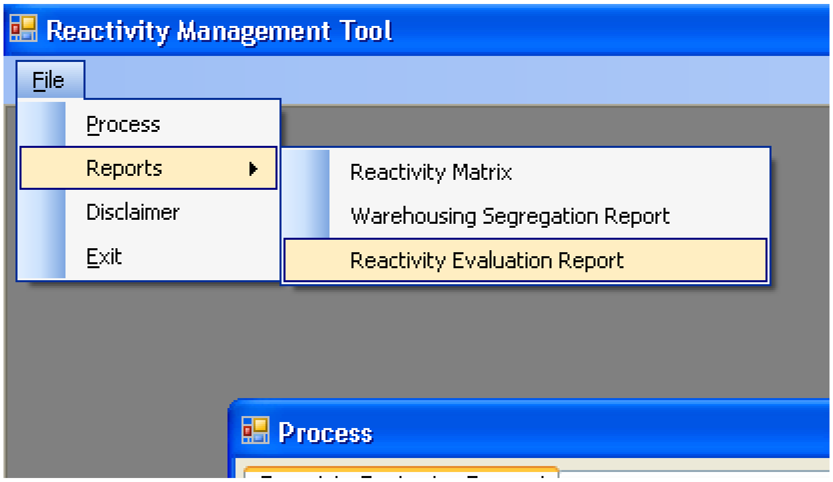
3.2.11.3 Chemical reactivity evaluation report

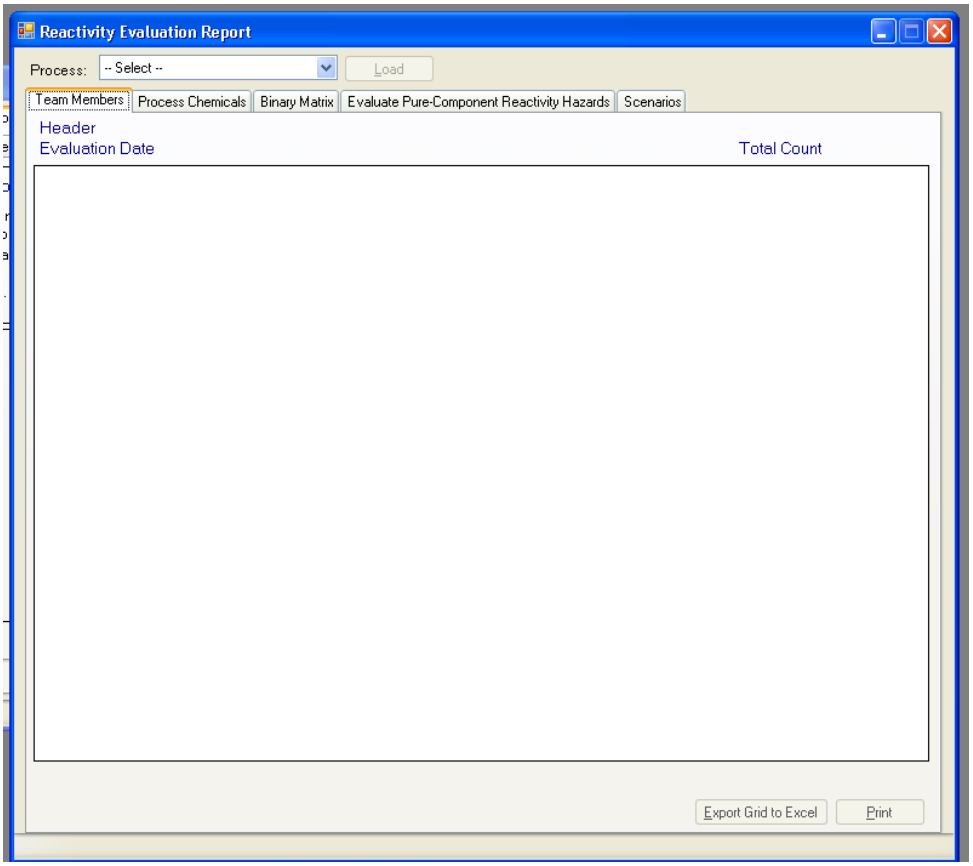
This report displays all of the scenarios along with their evaluation data

File – Reports – Reactivity Evaluation report



Displays a blank form.

Select your process from the drop-down menu and press **Load**



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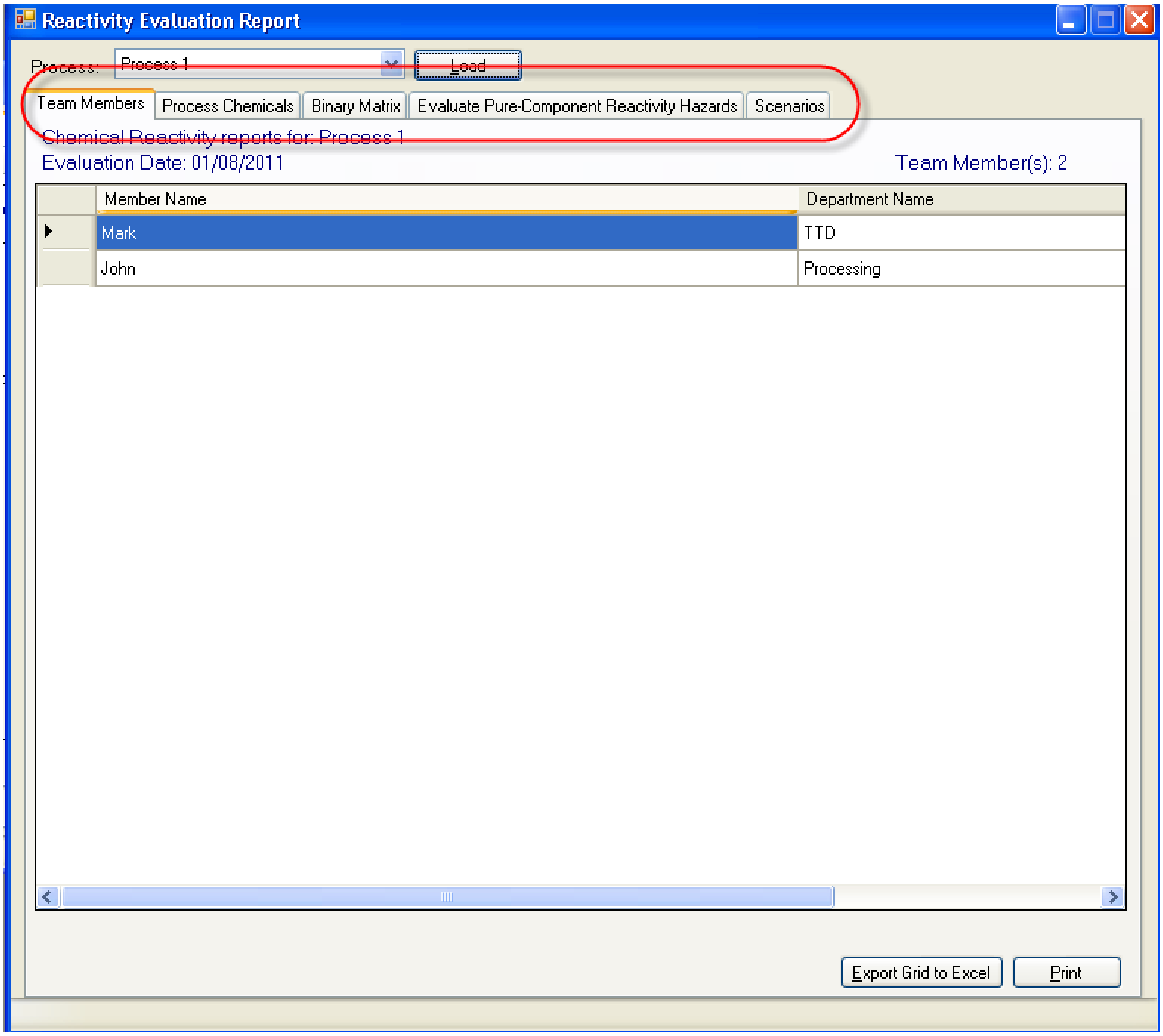

Chemical Reactivity reports for: Process 1

Evaluation Date: 01/08/2011

Team Member(s): 2

Member Name	Department Name
Mark	TTD
John	Processing

Note the Tabs. Each tab bust be printed or exported separately for a complete report.

Helpful Hint

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.

Helpful Hint

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

Helpful Hint

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.

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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.

Pitfall alert 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.

Pitfall alert 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

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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.[7] 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

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[7] http://www.phmsa.dot.gov/hazmat/library Under the link for "Hazardous Materials Table (HMT)"

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4.3 Guidance on Selected Pure Componant Hazards

Link To Full TOC

Table of Contents

4.3.0 General Guidance

Sections 4.3 is edited from the AIChE/CCPS Guide Book Essential Practices for Managing Chemical Reactivity Hazards.[8] 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.

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[8] R.W. Johnson, S.W. Rudy and S.D. Unwin, Essential Practices for Managing Chemical Reactivity Hazards, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (2003); www.aiche.org/ccps

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.*

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Examples of Pyrophoric Materials [9]

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

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;

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[9] Bretherick, 1986, 71-72: Britton, 1989; Cardillo and Nebuloni, 1992; National Research Council, 1983, 240-241; Sax & Lewis, 1987, 985

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 nay 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

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- 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[10]

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

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[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[11].

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

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

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[11] Includes material extracted from NFPA 49, 1994 edition, amended 2001

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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

Acetylenic Compounds, especially polyacetylenes, haolacetylenes and heavy metal salts of Acetylenes (copper, silver, and mercury salts are especially sensitive);
Acyl Nitrates
Alkyl Nitrates, particularly polyol nitrates such as nitrocellulose and nitro glycerin
Alkyl and **Acyl Nitrites**
Alkyl Perchlorates
Amminemetal Oxosalts: metal compounds with coordinated ammonia, hydrazine, or similar nitrogenous donors and ionic perchlorate, nitrite, permanganate, or other oxidizing group
Azides, including metal, nonmetal, and organic azides
Chlorite salts of metals, such as silver chlorite ($AgClO_2$) and Mercury chlorite ($Hg(ClO_2)_2$)
Diazo compounds such as diazomethane (CH_2N_2)
Diazonium salts, such as benzenediazonium chloride ($Ar\text{-}N\equiv N^+Cl^-$), when dry
Nitrides, such as silver nitride (Ag_3N);
Hydrogen peroxide (H_2O_2) 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);
N-Halogen compounds such as difluoroamino compounds and halogen azides;
N-Nitro compounds such as N-nitromethylamine, nitrourea, nitroguanidine, nitric amide;
Oxo salts of nitrogenous bases: perchlorates, dichromates, nitrates, iodates, chlorites, chlorates, and permanganates of ammonia, amines, guanidide, etc.;
Perchlorate salts; most metal, nonmetal and amine perchlorates can be detonated and may undergo violent reaction in contact with combustible materials;
Peroxides and **hydroperoxides**, organic;
Peroxides (solid) that crystallize from or are left from evaporation of peroxidizable solvents;
Peroxides, transition metals salts
Picrates, 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;
Polynitroalkyl compounds such as tetranitromethane and dinitroacetonitrile;
Polynitroaromatic compounds, especially polynitro hydrocarbons, phenols, and amines.

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;

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- 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, CO_2, CL2, H_2, HCl, and SO_2. 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;

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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

4.3.3.1 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).

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Typical Oxidizers [12] (Johnson et al., 2003)

Ammonium dichromate	Lead dioxide	Silver peroxide
Ammonium nitrate	Lead perchlorate	Sodium bromate
Ammonium perchlorate	Lithium chlorate	Sodium carbonate peroxide
Ammonium permanganate	Lithium hypochlorite	Sodium chlorate
Ammonium persulfate	Lithium perchlorate	Sodium chlorite
Amyl nitrate	Lithium peroxide	Sodium dichloro-*s*-triazinetrione (sodium dichloroisocyanurate)
Barium bromate	Magnesium bromate	Sodium dichloro-*s*-triazinetrione dihydrate
Barium chlorate	Magnesium chlorate	Sodium dichromate
Barium hypochlorite	Magnesium perchlorate	Sodium perborate (anhydrous)
Barium perchlorate	Magnesium peroxide	Sodium perborate monohydrate
Barium permanganate	Manganese dioxide	Sodium perborate tetrahydrate
Barium peroxide	Mercurous chlorate	Sodium percarbonate
Bromine pentafluoride	Monochloro-*s*-triazinetrione acid	Sodium perchlorate
Bromine trifluoride	Mono-(trichloro)-tetra-(monopotassium dichloro)-penta-*s*-triazinetrione	Sodium perchlorate monohydrate
1-Bromo-3-chloro-5,5-dimethylhydantoin (BCDMH)	Nitric acid and fuming nitric acid	Sodium permanganate
Calcium chlorate	Nitrites, inorganic	Sodium peroxide
Calcium chlorite	Nitrogen oxides (NO_x)	Sodium persulfate
Calcium hypochlorite	Oxygen	Strontium chlorate
Calcium perchlorate	Peracetic acid	Strontium perchlorate
Calcium permanganate	Perchloric acid solutions	Strontium peroxide
Calcium peroxide	Potassium bromate	Tetranitromethane
Chloric acid (10 percent maximum concentration)	Potassium chlorate	Thallium chlorate
Chlorine	Potassium dichloro-*s*-triazinetrione (potassium dichloroisocyanurate)	Trichloro-*s*-triazinetrione (trichloroisocyanuric) (acid all forms)
Chlorine trifluoride	Potassium percarbonate	Urea hydrogen peroxide
Chlorosulfonic acid	Potassium perchlorate	Zinc bromate
Chromium trioxide (chromic acid)	Potassium permanganate	Zinc chlorate
Copper chlorate	Potassium peroxide	Zinc permanganate
Guanidine nitrate	Potassium persulfate	Zinc peroxide
Halane (1,3-dichloro-5,5-dimethylhydantoin)	Potassium superoxide	
Hydrogen peroxide solutions	*n*-Propyl nitrate	

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.

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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 ~~W~~ 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, alkylnon-metal halides, complex hydrides, metal halides, metal hydrides, metal oxides, non-metal halides (and their oxides), non-metal oxides[13]. 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

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

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[13] Bretherick's Reactive Chemical Hazards

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Some Materials That React with Water

Acetic Anhydride	Diethylaluminum hydride	Phosphorus oxychloride
Acetyl chloride	Diethylzinc	Phosphorus pentachloride
Alkyl aluminums	Diketene	Phosphorus pentasulfide
Allyl trichlorosilane	Diisobutylaluminum hydride	Phosphorus tribromide
Dipropylaluminum hydride	Dimethyldichlorosilane	Phosphorus trichloride
Aluminum chloride (anhydrous)	Diphenyldichlorosilane	Potassium, metal
Aluminum phosphide	1,2-Ethanediol Diformate	Potassium-sodium alloys
Amyl trichlorosilane	Ethyl Chloroformate	Propionic anhydride
Benzoyl chloride	Ethyldichlorosilane	Propionyl chloride
Boron tribromide	Ethyl oxalate	Propyltrichlorosilane
Boron trifluoride	Ethyl silicate	Silicon tetrachloride
Boron trifluoride etherate	Ethyl trichlorosilane	Silicon tetrafluoride
Bromine pentafluoride	Ethylaluminum dichloride	Sodium, metal
Bromine trifluoride	Ethylaluminum sesquichloride	Sodium dichloro-*s*-triazinetrion dihydrate
Butylacrylate	Fluorine	Sodium hydride
n-Butyl isocyanate	Gallium arsenide	Sodium hydrosulfite
Butylithium	Gallium phosphide	Sulfuric acid
Butyric anhydride	Germane	Sulfur chloride
Calcium, metal	Isobutyric anhydride	Sulfur dichloride
Calcium carbide	Isophorone diisocyanate	Sulfuryl chloride
Calcium chloride	Lithium, metal	Tetraethyl lead
Caprylyl chloride	Lithium aluminum hydride	Tetramethyl lead
Chlorine trifluoride	Lithium hydride	Titanium tetrachloride
2-Chloropropionyl chloride	Thionyl chloride	Tributyl phosphite
Chlorosilanes	Methylaluminum sesquibromide	Trichlorosilane
Chlorosulfonic acid	Toluene-2,4-diisocyanate	Triethylaluminum
Chromium oxychloride	Methylaluminum sesquichloride	Triethylborane
Cyanamide	Methyl borate	Trihexyl phosphite
Decaborane	Methyldichlorosilane	Triisobutylaluminum
Diborane	Methyl isocyanate	Trimethylaluminum
Dichloroacetyl chloride	Methylenediisocyanate	Trimethylchlorosilane
Dichlorosilane	Methyl lactate	Tripropylaluminum
Diethylaluminum chloride	Methylpentaldehyde	Vanadium tetrachloride
2-(Diethylamino)ethyl Acrylate	Methyltrichlorosilane	Vinyl trichlorosilane
Diethyl carbamyl chloride	Monochloro-*s*-triazinetrion acid	Zirconium tetrachloride
Diethyl telluride	Mono-(trichloro)tetra-(monopotassiumdichloro)-penta-*s*-triazinetrione	
Diethylaluminum chloride	Octadecyltrichlorosilane	

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 Oxychloride. 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.

Refer to the CCPS guideline book entitled *Guidelines for Hazard Evaluation Procedures, Third Edition*[14] for a detailed description of process hazard analysis methods.

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

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[14] CCPS (2008). Guidelines for Hazard Evaluation Procedures (3rd Edition).. CCPS/AIChE. Online version available at: www.knovel.com

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 over pressuring 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

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[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:

Pitfall alert

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 xperimental 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

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- 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 mist 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

Raw Data Table

Time (sec)	temperature
0	22
30	23
60	25
90	28
120	35
150	50
180	60
187	62.5
200	60

ΔT_{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 * 2 kJ/°C*kg = 81kJ/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.

Pitfall alert

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

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- 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[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 stoichiometery 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 stoichiometery is straight forward. 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 Pmax 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°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 forktruck 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.

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Thus the blender charge would be:
Thus the blender charge would be:
•5400 lb = 2115.5 kg $Na_2S_2O_3$ molecular weight 158g/mole

2,115,500g / 158 g/mole = 13,389 moles $Na_2S_2O_3$

Each mole of decomposing $Na_2S_2O_3$ 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_2CO_3 molecular weight 138 g/mole

335.9000g / 138 g/mole = 2434 moles

Each mole of decomposing K_2CO_3 gives off 1 mole of CO_2 thus 2434 moles of CO_2 are released on complete decomposition.

P=nRT/V

- R= 0.083 bar*L/mole*K
- T= 779K :7293K (20°C starting temp) + 486 (adiabatic heat rise)
- V Assumed from drawling in CSB report that head volume is roughly equal to the fill volume of 6 m3 = 6 m3 = 6,000L
- n = 9,948 = 8354 moles $Na_2S_2O_3$ + 1594 moles CO_2

P=0.083*15823*779/6000=175 bar or 2572.5 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.

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4.10 Determining the Validity of Information from Matrix Reports

Pitfall alert

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.

Pitfall alert

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

[Link To Full TOC](#)

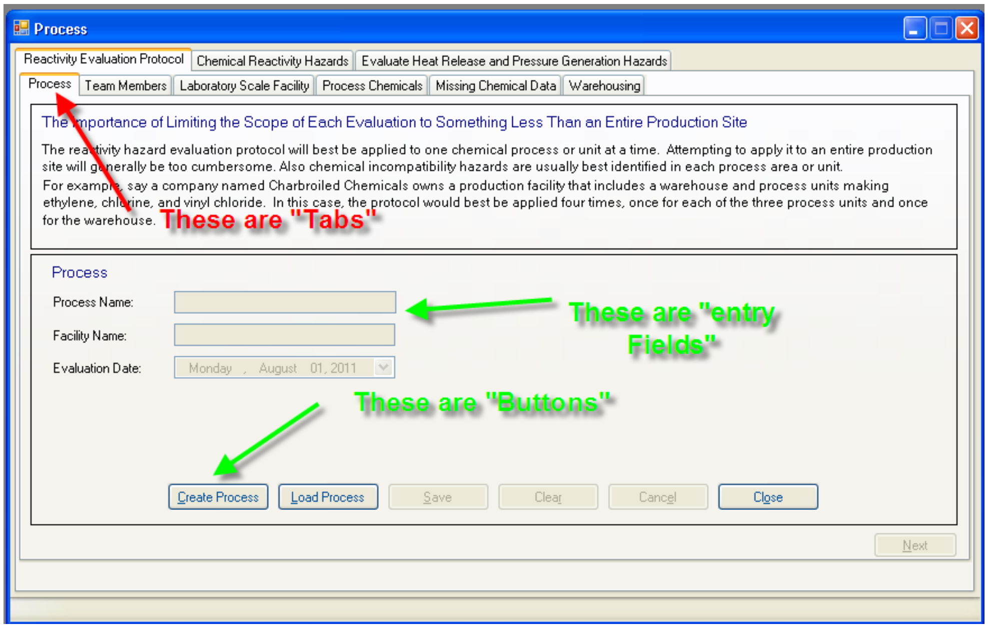
Table of Contents

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.



The Importance of Limiting the Scope of Each Evaluation 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. Also chemical incompatibility hazards are usually best identified in each process area or unit.
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.

Process Name:
Facility Name:
Evaluation Date: Monday , August 01, 2011

These are "Tabs"

These are "entry Fields"

These are "Buttons"

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- 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

Helpful Hint

- 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.

Helpful Hint

- 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”

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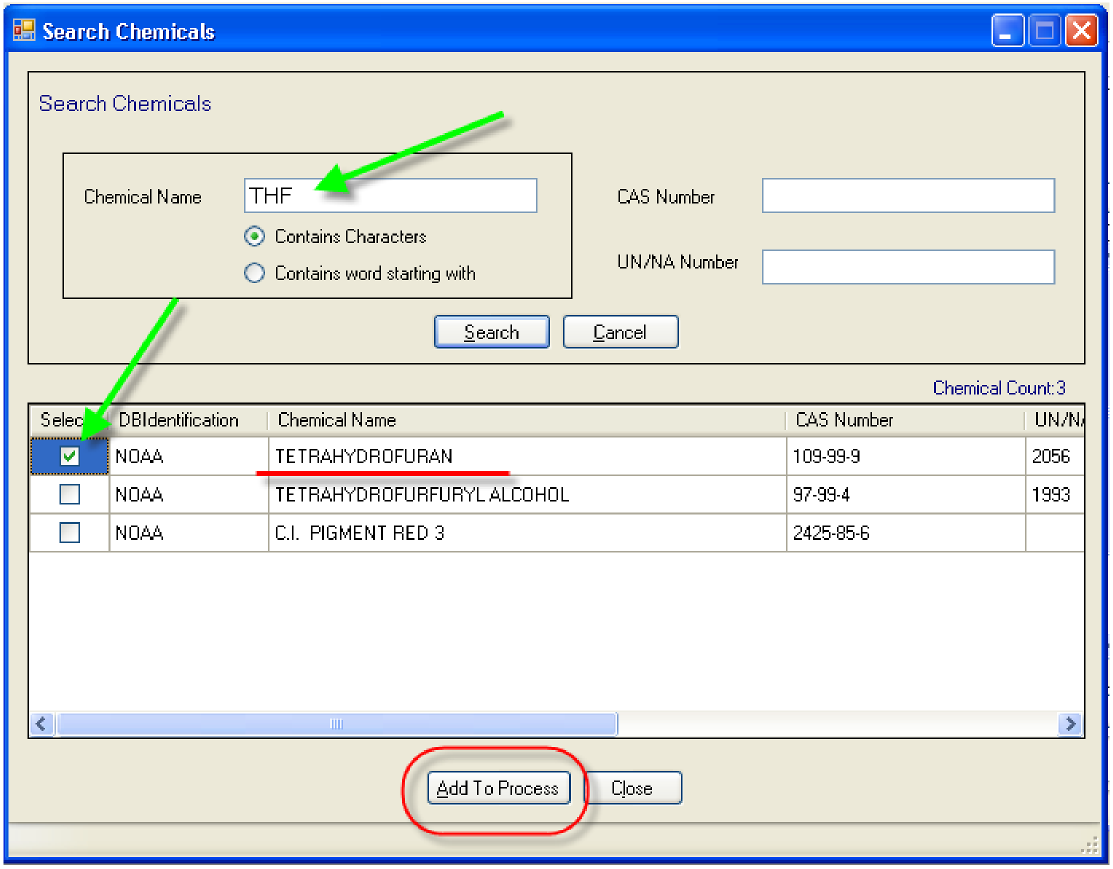
- Search through your hits for your desired chemical. Check the box in front of the name. (you may make multiple selections.) them press the Add to process" button



Chemical Name: THF

● Contains Characters

○ Contains word starting with

CAS Number:

UN/NA Number:

Chemical Count:3

Selec	DBIdentification	Chemical Name	CAS Number	UN/N
☑	NOAA	TETRAHYDROFURAN	109-99-9	2056
☐	NOAA	TETRAHYDROFURFURYL ALCOHOL	97-99-4	1993
☐	NOAA	C.I. PIGMENT RED 3	2425-85-6	

- 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.
    - "Export to Excel" data dumps your 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.

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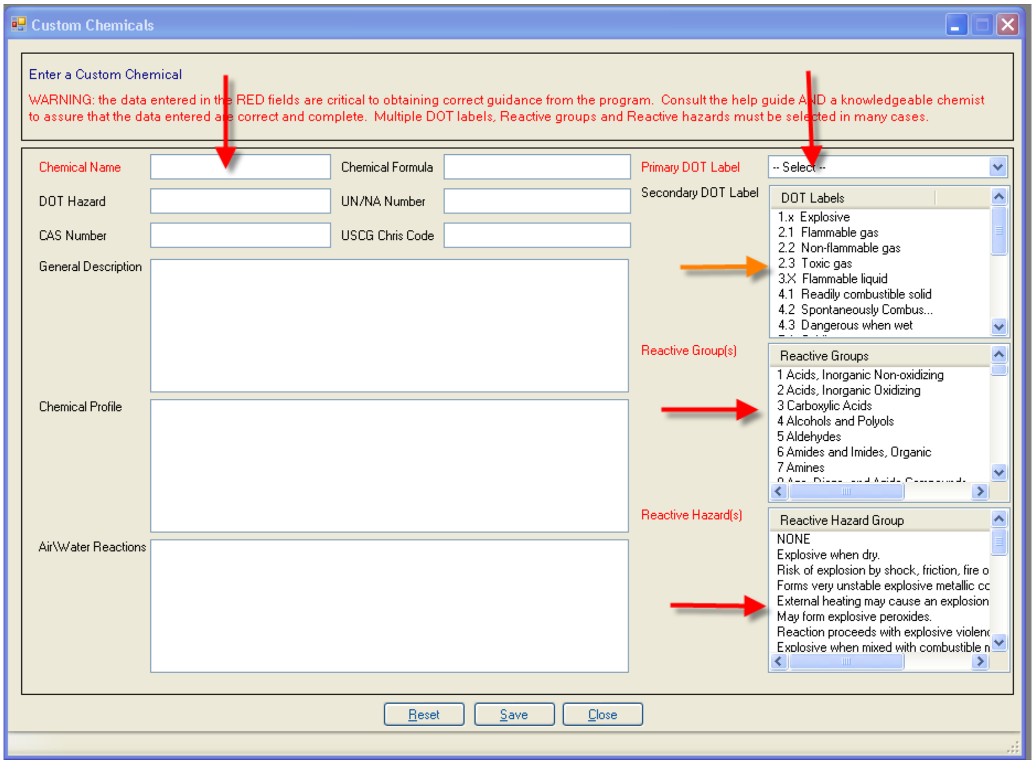
Helpful Hint

  - "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


Custom Chemicals

Enter a Custom Chemical

WARNING: the data entered in the RED fields are critical to obtaining correct guidance from the program. Consult the help guide AND a knowledgeable chemist to assure that the data entered are correct and complete. Multiple DOT labels, Reactive groups and Reactive hazards must be selected in many cases.

Primary DOT Label: -- Select --

Pitfall alert

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

Pitfall alert

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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.**

Pitfall alert

  - 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.

Helpful Hint

- 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

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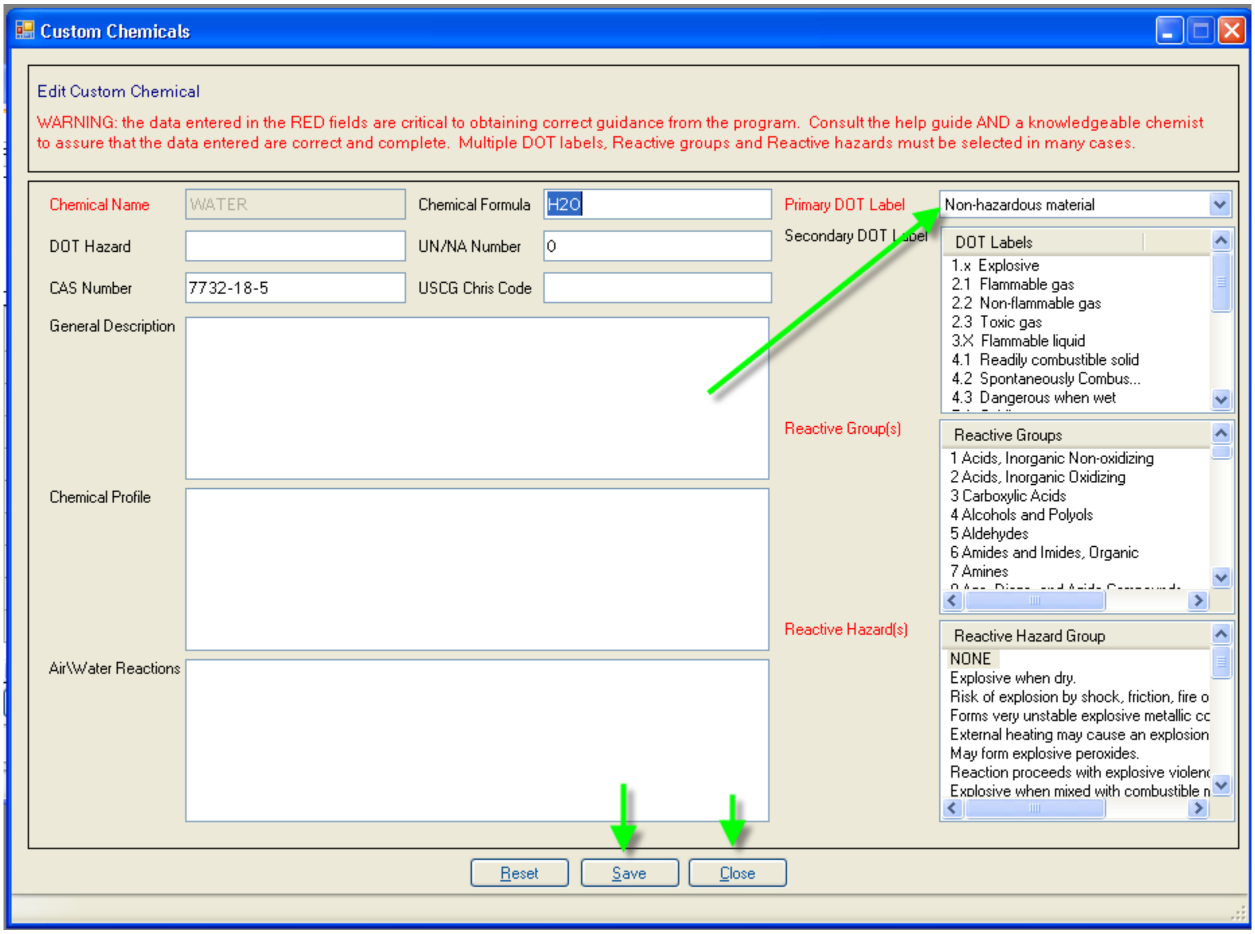


Edit Custom Chemical

WARNING: the data entered in the RED fields are critical to obtaining correct guidance from the program. Consult the help guide AND a knowledgeable chemist to assure that the data entered are correct and complete. Multiple DOT labels, Reactive groups and Reactive hazards must be selected in many cases.

Chemical Name: WATER

Chemical Formula: H2O

Primary DOT Label: Non-hazardous material

DOT Hazard:

UN/NA Number: 0

CAS Number: 7732-18-5

USCG Chris Code:

General Description:

Chemical Profile:

Air\Water Reactions:

Secondary DOT Label:

DOT Labels
1.x Explosive
2.1 Flammable gas
2.2 Non-flammable gas
2.3 Toxic gas
3.X Flammable liquid
4.1 Readily combustible solid
4.2 Spontaneously Combus...
4.3 Dangerous when wet

Reactive Group(s):

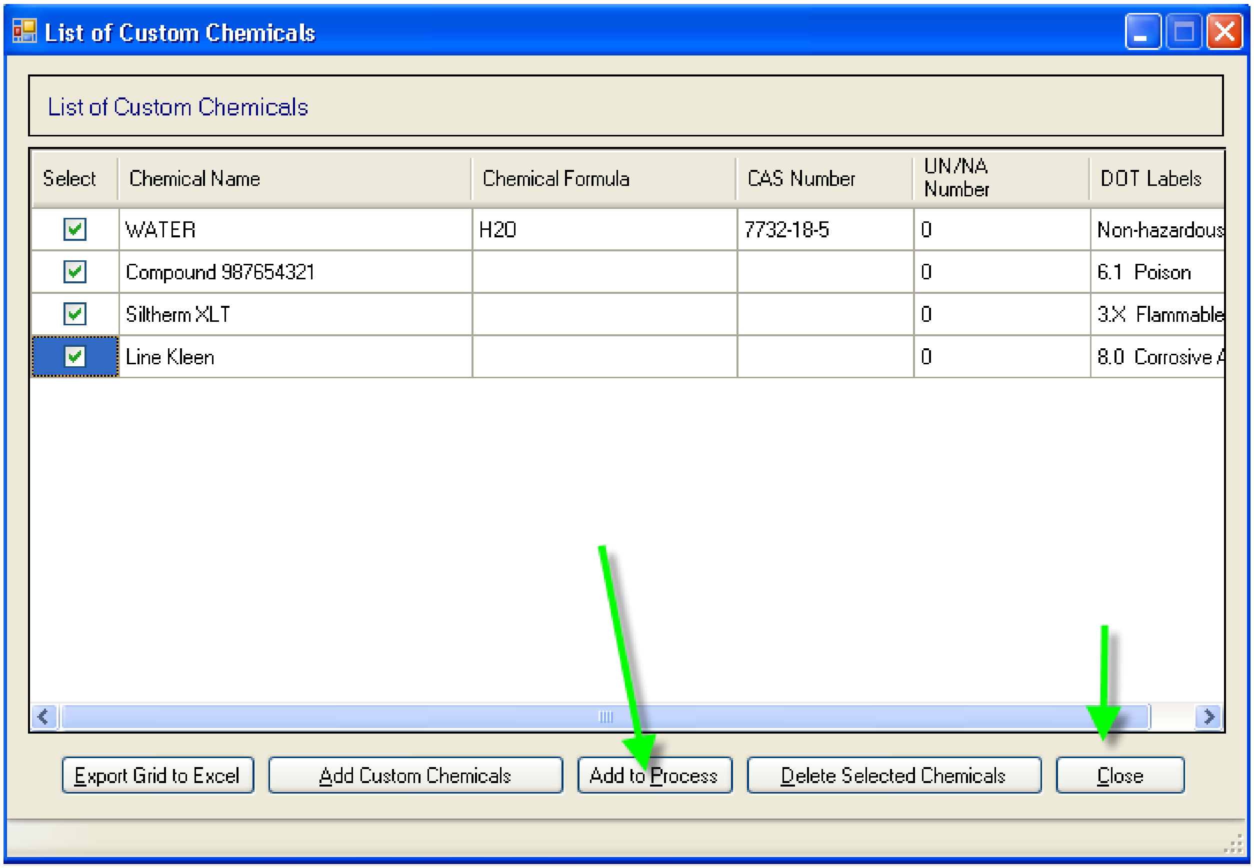
Reactive Groups
1 Acids, Inorganic Non-oxidizing
2 Acids, Inorganic Oxidizing
3 Carboxylic Acids
4 Alcohols and Polyols
5 Aldehydes
6 Amides and Imides, Organic
7 Amines

Reactive Hazard(s):

Reactive Hazard Group
NONE
Explosive when dry.
Risk of explosion by shock, friction, fire o
Forms very unstable explosive metallic cc
External heating may cause an explosion
May form explosive peroxides.
Reaction proceeds with explosive violenc
Explosive when mixed with combustible n

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.



Select	Chemical Name	Chemical Formula	CAS Number	UN/NA Number	DOT Labels
☑	WATER	H2O	7732-18-5	0	Non-hazardous
☑	Compound 987654321			0	6.1 Poison
☑	Siltherm XLT			0	3.X Flammable
☑	Line Kleen			0	8.0 Corrosive A

- Press the “Add to Process” button then close the pop-up. This will return you to the **Process Chemicals tab**

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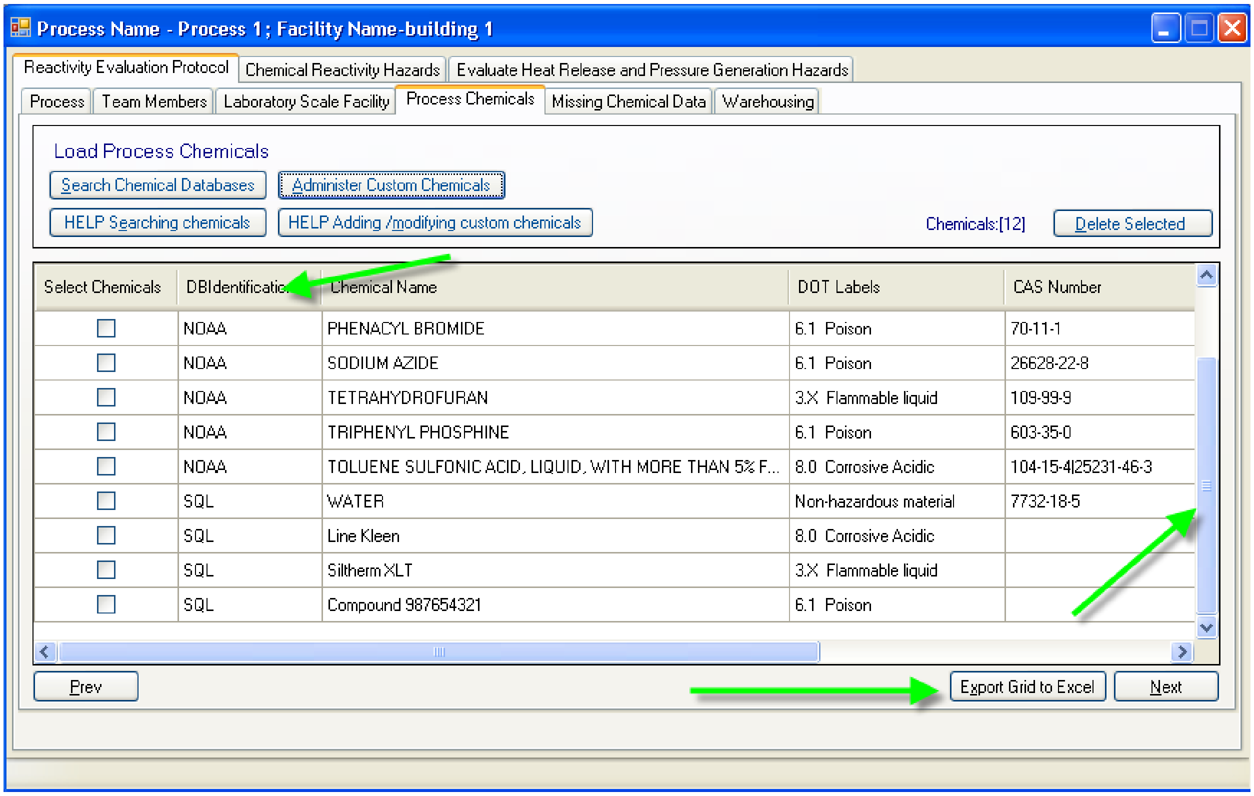

Chemicals:[12]

Select Chemicals	DBIdentificatio	Chemical Name	DOT Labels	CAS Number
☐	NOAA	PHENACYL BROMIDE	6.1 Poison	70-11-1
☐	NOAA	SODIUM AZIDE	6.1 Poison	26628-22-8
☐	NOAA	TETRAHYDROFURAN	3.X Flammable liquid	109-99-9
☐	NOAA	TRIPHENYL PHOSPHINE	6.1 Poison	603-35-0
☐	NOAA	TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% F...	8.0 Corrosive Acidic	104-15-4|25231-46-3
☐	SQL	WATER	Non-hazardous material	7732-18-5
☐	SQL	Line Kleen	8.0 Corrosive Acidic	
☐	SQL	Siltherm XLT	3.X Flammable liquid	
☐	SQL	Compound 987654321	6.1 Poison	

- 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.

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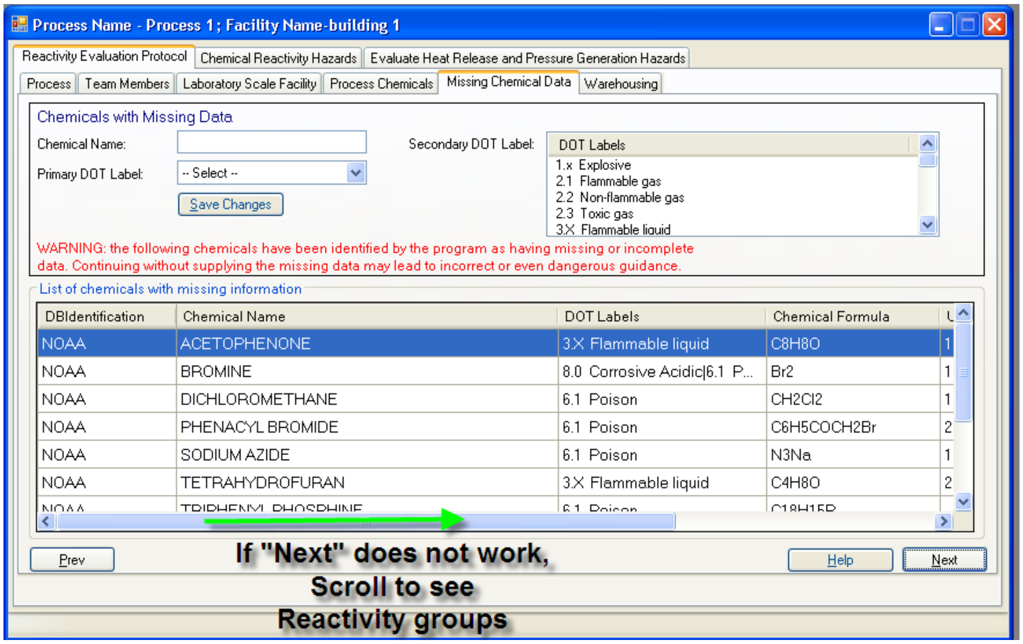
Pitfall alert If the next button does not work recheck that at least a primary DOT code and at least one reactivity group has been entered for each chemical. Use the scroll bar on the bottom to scroll right to see the reactivity group column.



Chemicals with Missing Data

Chemical Name:

Primary DOT Label: -- Select --

Secondary DOT Label:

DOT Labels
1.x Explosive
2.1 Flammable gas
2.2 Non-flammable gas
2.3 Toxic gas
3.X Flammable liquid

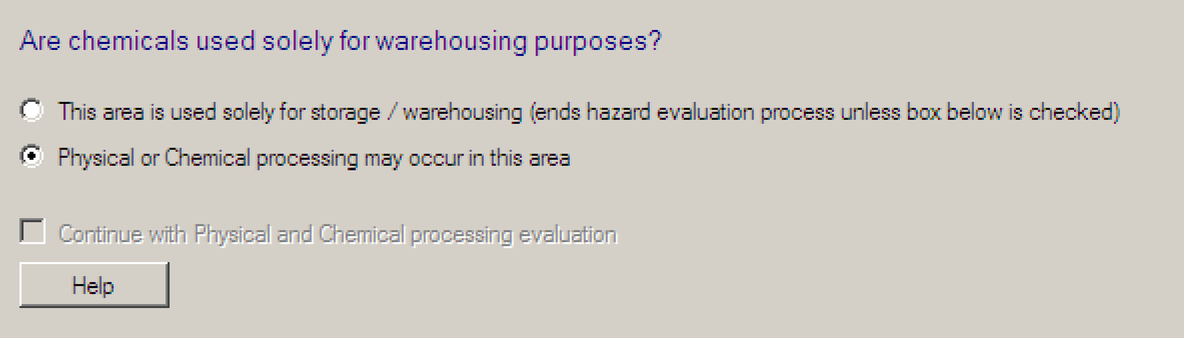
WARNING: the following chemicals have been identified by the program as having missing or incomplete data. Continuing without supplying the missing data may lead to incorrect or even dangerous guidance.

List of chemicals with missing information

DBIdentification	Chemical Name	DOT Labels	Chemical Formula	
NOAA	ACETOPHENONE	3.X Flammable liquid	C8H8O	1
NOAA	BROMINE	8.0 Corrosive Acidic|6.1 P...	Br2	1
NOAA	DICHLOROMETHANE	6.1 Poison	CH2Cl2	1
NOAA	PHENACYL BROMIDE	6.1 Poison	C6H5COCH2Br	2
NOAA	SODIUM AZIDE	6.1 Poison	N3Na	1
NOAA	TETRAHYDROFURAN	3.X Flammable liquid	C4H8O	2
NOAA	TRIPHENYL PHOSPHINE	6.1 Poison	C18H15P	

If "Next" does not work,
Scroll to see
Reactivity groups

5.0.9 Warehousing vs. Chemical Processing



Are chemicals used solely for warehousing purposes?

○ This area is used solely for storage / warehousing (ends hazard evaluation process unless box below is checked)

● Physical or Chemical processing may occur in this area

☐ Continue with Physical and Chemical processing evaluation

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.

Pitfall alert 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.

Helpful Hint

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.

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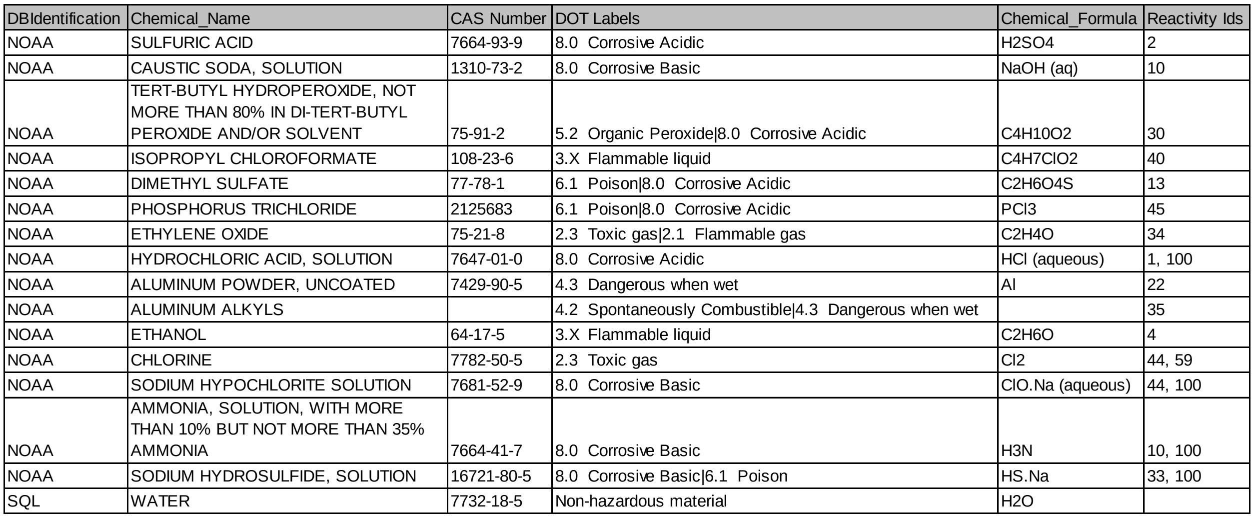
The list of chemicals for this warehouse example is as follows:

Chemical	Primary DOT	Secondary DOT(s)
Sulfuric Acid, 93%	8 Corrosive acidic	
Sodium Hydroxide, 50% solution	8 Corrosive basic	
tert-Butyl Hydroperoxide, 70%	5.2 Organic Peroxide	8 Corrosive acidic
Sodium Hydrosulfide, 18-22%	8 Corrosive basic	6.1 poison
Isopropyl Chloroformate	3.x Flammable Liquid	
Dimethyl Sulfate	6.1 poison	8 Corrosive acidic
Phosphorus Trichloride, 90 - 100%	6.1 poison	8 Corrosive acidic
Ethylene Oxide	2.3 Toxic gas	2.1 Flammable gas
Hydrochloric Acid, 33 - 40%	8 Corrosive acidic	
Water	Non-hazardous	
Aluminum, powder	4.3 Dangerous when wet	
Triethyl Aluminum	4.2 spontaneously combustible	4.3 Dangerous when wet
Ethanol, denatured, 200 proof	3.x Flammable Liquid	
Chlorine	2.3 Toxic gas	
Sodium Hypochlorite, 5-15% solution	8 Corrosive basic	
Aqueous Ammonia, 10% solution	8 Corrosive basic	

Helpful Hint

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,



DBIdentification	Chemical_Name	CAS Number	DOT Labels	Chemical_Formula	Reactivity Ids
NOAA	SULFURIC ACID	7664-93-9	8.0 Corrosive Acidic	H2SO4	2
NOAA	CAUSTIC SODA, SOLUTION	1310-73-2	8.0 Corrosive Basic	NaOH (aq)	10
NOAA	TERT-BUTYL HYDROPEROXIDE, NOT MORE THAN 80% IN DI-TERT-BUTYL PEROXIDE AND/OR SOLVENT	75-91-2	5.2 Organic Peroxide|8.0 Corrosive Acidic	C4H10O2	30
NOAA	ISOPROPYL CHLOROFORMATE	108-23-6	3.X Flammable liquid	C4H7ClO2	40
NOAA	DIMETHYL SULFATE	77-78-1	6.1 Poison|8.0 Corrosive Acidic	C2H6O4S	13
NOAA	PHOSPHORUS TRICHLORIDE	2125683	6.1 Poison|8.0 Corrosive Acidic	PCl3	45
NOAA	ETHYLENE OXIDE	75-21-8	2.3 Toxic gas|2.1 Flammable gas	C2H4O	34
NOAA	HYDROCHLORIC ACID, SOLUTION	7647-01-0	8.0 Corrosive Acidic	HCl (aqueous)	1, 100
NOAA	ALUMINUM POWDER, UNCOATED	7429-90-5	4.3 Dangerous when wet	Al	22
NOAA	ALUMINUM ALKYLS		4.2 Spontaneously Combustible|4.3 Dangerous when wet		35
NOAA	ETHANOL	64-17-5	3.X Flammable liquid	C2H6O	4
NOAA	CHLORINE	7782-50-5	2.3 Toxic gas	Cl2	44, 59
NOAA	SODIUM HYPOCHLORITE SOLUTION	7681-52-9	8.0 Corrosive Basic	ClO.Na (aqueous)	44, 100
NOAA	AMMONIA, SOLUTION, WITH MORE THAN 10% BUT NOT MORE THAN 35% AMMONIA	7664-41-7	8.0 Corrosive Basic	H3N	10, 100
NOAA	SODIUM HYDROSULFIDE, SOLUTION	16721-80-5	8.0 Corrosive Basic|6.1 Poison	HS.Na	33, 100
SQL	WATER	7732-18-5	Non-hazardous material	H2O	

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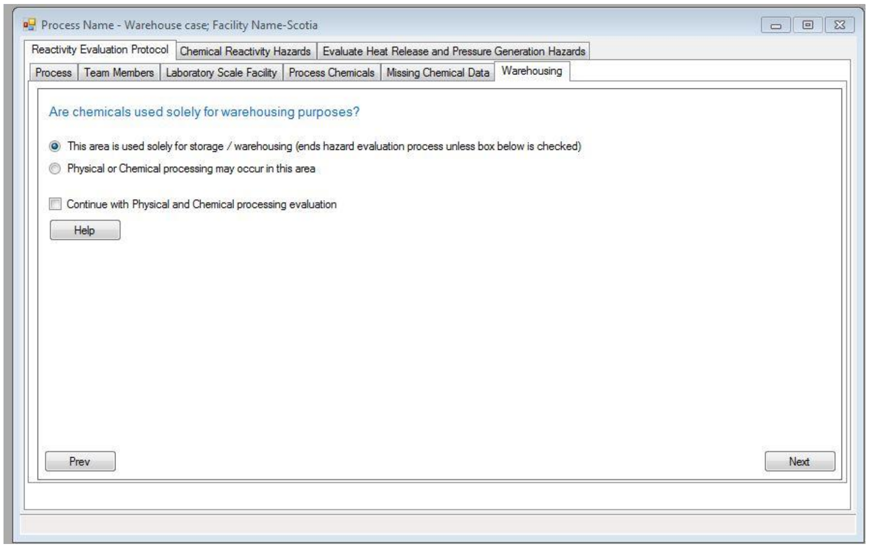
The user can now proceed to the warehouse evaluation part of the program.

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



Are chemicals used solely for warehousing purposes?

● This area is used solely for storage / warehousing (ends hazard evaluation process unless box below is checked)
○ Physical or Chemical processing may occur in this area

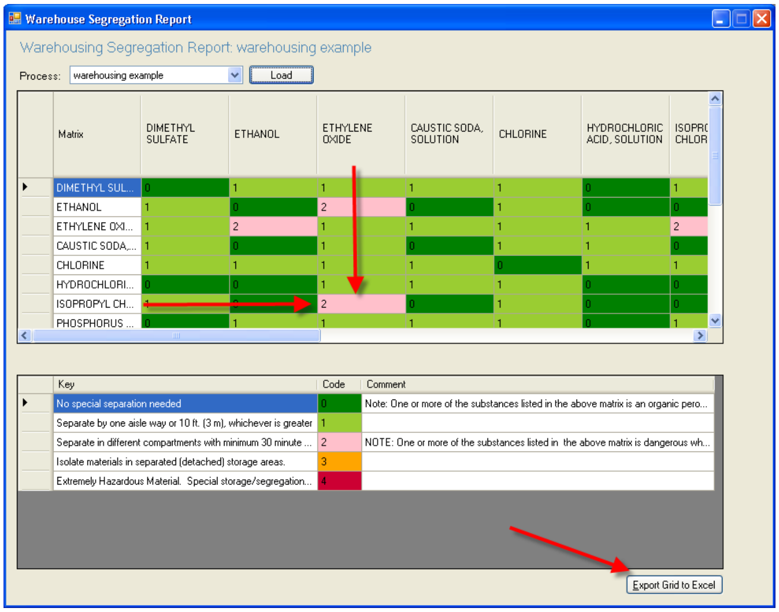
☐ Continue with Physical and Chemical processing evaluation

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 screen shot 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".



Warehousing Segregation Report: warehousing example

Process: warehousing example

Matrix	DIMETHYL SULFATE	ETHANOL	ETHYLENE OXIDE	CAUSTIC SODA, SOLUTION	CHLORINE	HYDROCHLORIC ACID, SOLUTION	ISOPRC CHLOR
DIMETHYL SUL...	0	1	1	1	1	0	1
ETHANOL	1	0	2	0	1	0	0
ETHYLENE OXI...	1	2	1	1	1	1	2
CAUSTIC SODA,...	1	0	1	0	1	1	0
CHLORINE	1	1	1	1	0	1	1
HYDROCHLORI...	0	0	1	1	1	0	0
ISOPROPYL CH...	1	0	2	0	1	0	0
PHOSPHORUS ...	0	1	1	1	1	0	1

Key	Code	Comment
No special separation needed	0	Note: One or more of the substances listed in the above matrix is an organic pero...
Separate by one aisle way or 10 ft. (3 m), whichever is greater	1	
Separate in different compartments with minimum 30 minute ...	2	NOTE: One or more of the substances listed in the above matrix is dangerous wh...
Isolate materials in separated (detached) storage areas.	3	
Extremely Hazardous Material. Special storage/segregation...	4	

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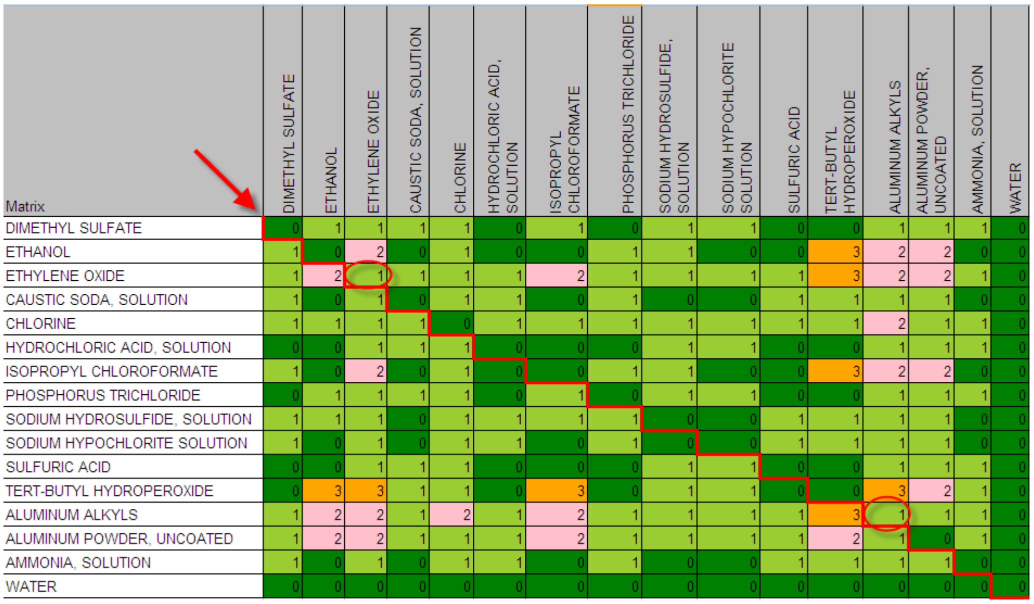
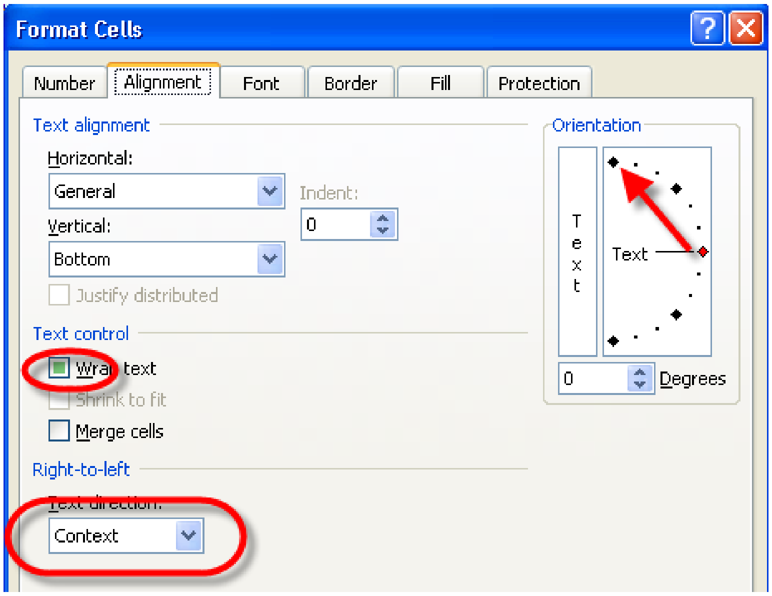
The displayed color-coded report can also be printed by pressing the "export grid to Excel" as sown below:



Matrix	DIMETHYL SULFATE	ETHANOL	ETHYLENE OXIDE	CAUSTIC SODA, SOLUTION	CHLORINE	HYDROCHLORIC ACID, SOLUTION	ISOPROPYL CHLOROFORMATE	PHOSPHORUS TRICHLORIDE	SODIUM HYDROSULFIDE, SOLUTION	SODIUM HYPOCHLORITE SOLUTION	SULFURIC ACID	TERT-BUTYL HYDROPEROXIDE	ALUMINUM ALKYLS	ALUMINUM POWDER, UNCOATED	AMMONIA, SOLUTION	WATER
DIMETHYL SULFATE	0	1	1	1	1	0	1	0	1	1	0	0	1	1	1	0
ETHANOL	1	0	2	0	1	0	0	1	1	0	0	3	2	2	0	0
ETHYLENE OXIDE	1	2	1	1	1	1	2	1	1	1	1	3	2	2	1	0
CAUSTIC SODA, SOLUTION	1	0	1	0	1	1	0	1	0	0	1	1	1	1	0	0
CHLORINE	1	1	1	1	0	1	1	1	1	1	1	1	2	1	1	0
HYDROCHLORIC ACID, SOLUTION	0	0	1	1	1	0	0	0	1	1	0	0	1	1	1	0
ISOPROPYL CHLOROFORMATE	1	0	2	0	1	0	0	1	1	0	0	3	2	2	0	0
PHOSPHORUS TRICHLORIDE	0	1	1	1	1	0	1	0	1	1	0	0	1	1	1	0
SODIUM HYDROSULFIDE, SOLUTION	1	1	1	0	1	1	1	1	0	0	1	1	1	1	0	0
SODIUM HYPOCHLORITE SOLUTION	1	0	1	0	1	1	0	1	0	0	1	1	1	1	0	0
SULFURIC ACID	0	0	1	1	1	0	0	0	1	1	0	0	1	1	1	0
TERT-BUTYL HYDROPEROXIDE	0	3	3	1	1	0	3	0	1	1	0	0	3	2	1	0
ALUMINUM ALKYLS	1	2	2	1	2	1	2	1	1	1	1	3	1	1	1	0
ALUMINUM POWDER, UNCOATED	1	2	2	1	1	1	2	1	1	1	1	2	1	0	1	0
AMMONIA, SOLUTION	1	0	1	0	1	1	0	1	0	0	1	1	1	1	0	0
WATER	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

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.



Format Cells

Text alignment

Horizontal: General

Indent: 0

Vertical: Bottom

☐ Justify distributed

Text control

☑ Wrap text

☐ Shrink to fit

☐ Merge cells

Right-to-left

Text direction: Context

Orientation

0 Degrees

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.

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Pitfall alert

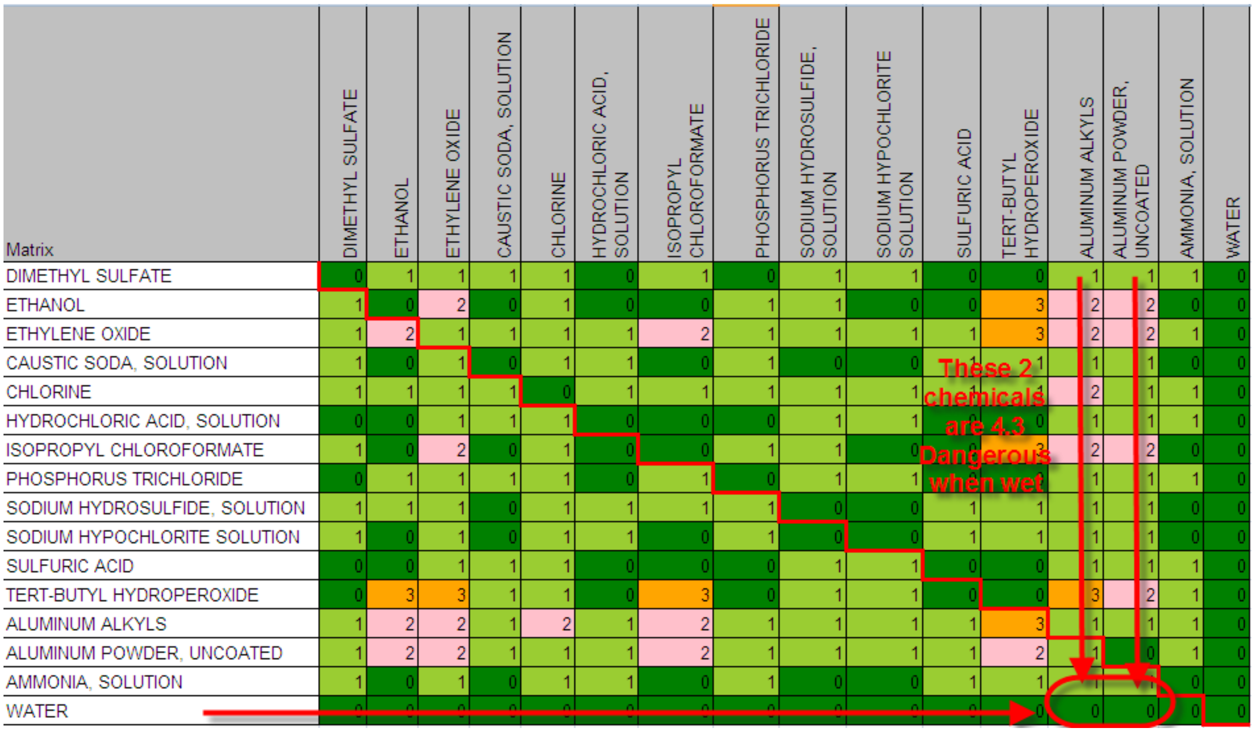
Remember that in order to store items together on the same isle they ALL must have a zero separation from each other. The numbers on the grid only determine compatibility for storage of the pair on who's intersection they lay.

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.



Matrix	DIMETHYL SULFATE	ETHANOL	ETHYLENE OXIDE	CAUSTIC SODA, SOLUTION	CHLORINE	HYDROCHLORIC ACID, SOLUTION	ISOPROPYL CHLOROFORMATE	PHOSPHORUS TRICHLORIDE	SODIUM HYDROSULFIDE, SOLUTION	SODIUM HYPOCHLORITE SOLUTION	SULFURIC ACID	TERT-BUTYL HYDROPEROXIDE	ALUMINUM ALKYLS	ALUMINUM POWDER, UNCOATED	AMMONIA, SOLUTION	WATER
DIMETHYL SULFATE	0	1	1	1	1	0	1	0	1	1	0	0	1	1	1	0
ETHANOL	1	0	2	0	1	0	0	1	1	0	0	3	2	2	0	0
ETHYLENE OXIDE	1	2	1	1	1	1	2	1	1	1	1	3	2	2	1	0
CAUSTIC SODA, SOLUTION	1	0	1	0	1	1	0	1	0	0	1	1	1	1	0	0
CHLORINE	1	1	1	1	0	1	1	1	1	1	1	1	2	1	1	0
HYDROCHLORIC ACID, SOLUTION	0	0	1	1	1	0	0	0	1	1	0	0	1	1	1	0
ISOPROPYL CHLOROFORMATE	1	0	2	0	1	0	0	1	1	0	0	3	2	2	0	0
PHOSPHORUS TRICHLORIDE	0	1	1	1	1	0	1	0	1	1	0	0	1	1	1	0
SODIUM HYDROSULFIDE, SOLUTION	1	1	1	0	1	1	1	1	0	0	1	1	1	1	0	0
SODIUM HYPOCHLORITE SOLUTION	1	0	1	0	1	1	0	1	0	0	1	1	1	1	0	0
SULFURIC ACID	0	0	1	1	1	0	0	0	1	1	0	0	1	1	1	0
TERT-BUTYL HYDROPEROXIDE	0	3	3	1	1	0	3	0	1	1	0	0	3	2	1	0
ALUMINUM ALKYLS	1	2	2	1	2	1	2	1	1	1	1	3	1	1	1	0
ALUMINUM POWDER, UNCOATED	1	2	2	1	1	1	2	1	1	1	1	2	1	0	1	0
AMMONIA, SOLUTION	1	0	1	0	1	1	0	1	0	0	1	1	1	1	0	0
WATER	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

These 2 chemicals are 4.3 Dangerous when wet

Pitfall alert

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)

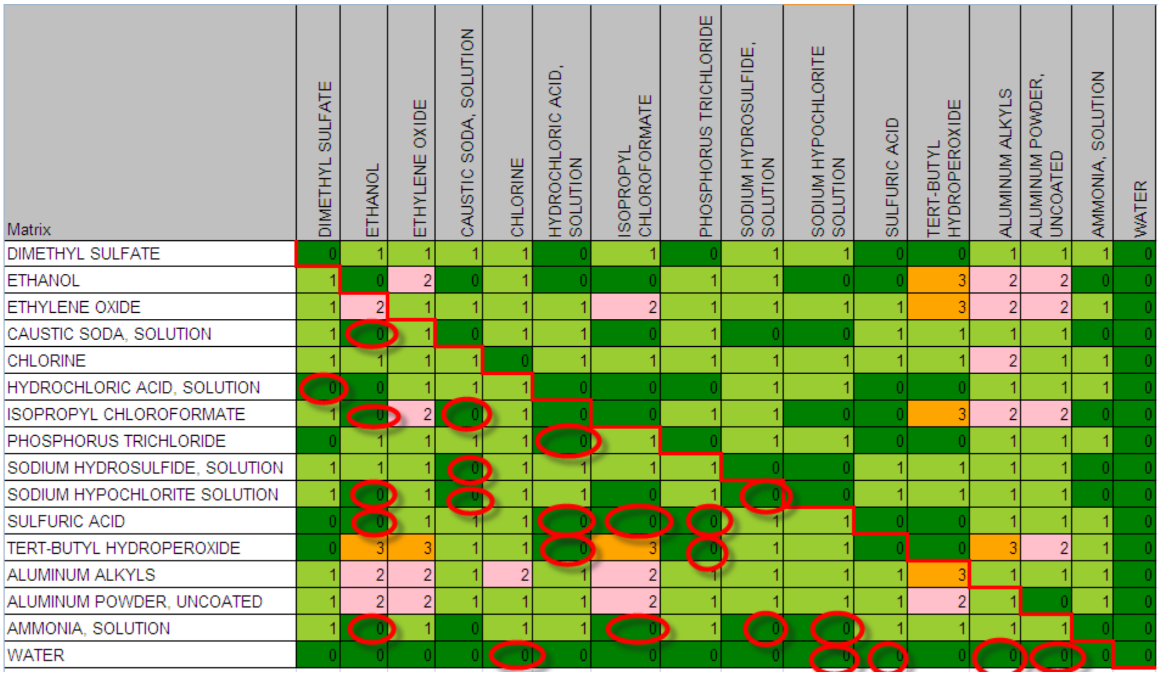
Pitfall alert

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.

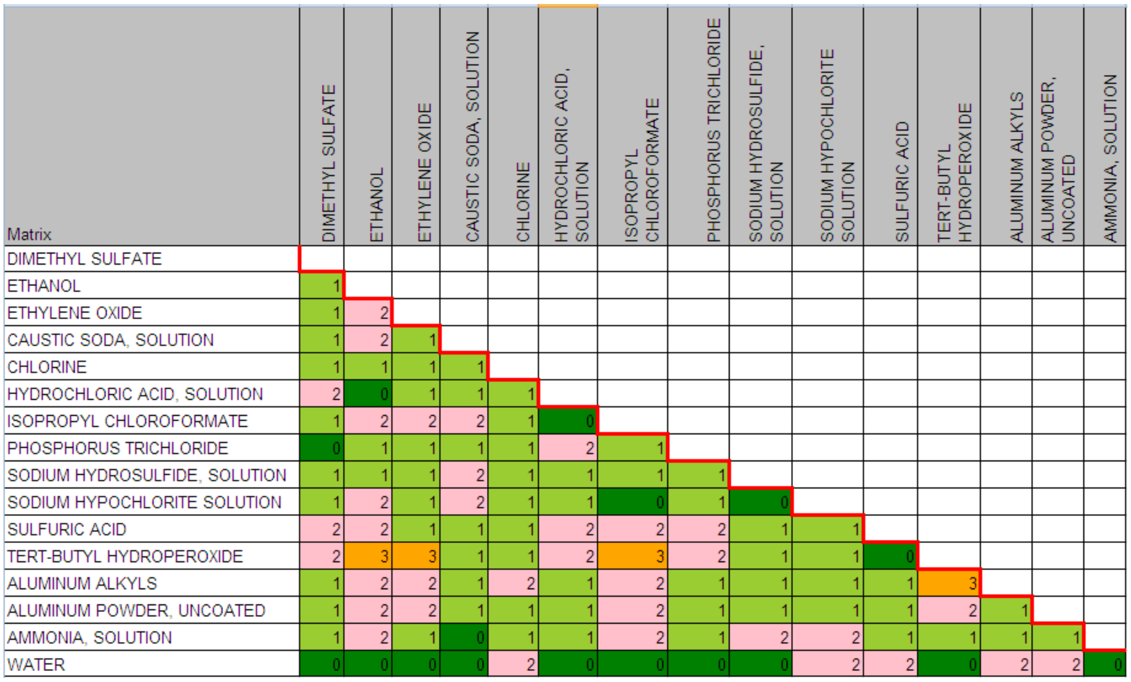
Look for any code A, B1, B3, B4, D1, G these indicate a serious reactivity issue that require segregation. In addition any other code starting with B, C or D not listed above may pose a serious risk to your warehouse under certain conditions.

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



Matrix	DIMETHYL SULFATE	ETHANOL	ETHYLENE OXIDE	CAUSTIC SODA, SOLUTION	CHLORINE	HYDROCHLORIC ACID, SOLUTION	ISOPROPYL CHLOROFORMATE	PHOSPHORUS TRICHLORIDE	SODIUM HYDROSULFIDE, SOLUTION	SODIUM HYPOCHLORITE SOLUTION	SULFURIC ACID	TERT-BUTYL HYDROPEROXIDE	ALUMINUM ALKYLS	ALUMINUM POWDER, UNCOATED	AMMONIA, SOLUTION	WATER
DIMETHYL SULFATE	0	1	1	1	1	0	1	0	1	1	0	0	1	1	1	0
ETHANOL	1	0	2	0	1	0	0	1	1	0	0	3	2	2	0	0
ETHYLENE OXIDE	1	2	1	1	1	1	2	1	1	1	1	3	2	2	1	0
CAUSTIC SODA, SOLUTION	1	0	1	0	1	1	0	1	0	0	1	1	1	1	0	0
CHLORINE	1	1	1	1	0	1	1	1	1	1	1	1	2	1	1	0
HYDROCHLORIC ACID, SOLUTION	0	0	1	1	1	0	0	0	1	1	0	0	1	1	1	0
ISOPROPYL CHLOROFORMATE	1	0	2	0	1	0	0	1	1	0	0	3	2	2	0	0
PHOSPHORUS TRICHLORIDE	0	1	1	1	1	0	1	0	1	1	0	0	1	1	1	0
SODIUM HYDROSULFIDE, SOLUTION	1	1	1	0	1	1	1	1	0	0	1	1	1	1	0	0
SODIUM HYPOCHLORITE SOLUTION	1	0	1	0	1	1	0	1	0	0	1	1	1	1	0	0
SULFURIC ACID	0	0	1	1	1	0	0	0	1	1	0	0	1	1	1	0
TERT-BUTYL HYDROPEROXIDE	0	3	3	1	1	0	3	0	1	1	0	0	3	2	1	0
ALUMINUM ALKYLS	1	2	2	1	2	1	2	1	1	1	1	3	1	1	1	0
ALUMINUM POWDER, UNCOATED	1	2	2	1	1	1	2	1	1	1	1	2	1	0	1	0
AMMONIA, SOLUTION	1	0	1	0	1	1	0	1	0	0	1	1	1	1	0	0
WATER	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

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



Matrix	DIMETHYL SULFATE	ETHANOL	ETHYLENE OXIDE	CAUSTIC SODA, SOLUTION	CHLORINE	HYDROCHLORIC ACID, SOLUTION	ISOPROPYL CHLOROFORMATE	PHOSPHORUS TRICHLORIDE	SODIUM HYDROSULFIDE, SOLUTION	SODIUM HYPOCHLORITE SOLUTION	SULFURIC ACID	TERT-BUTYL HYDROPEROXIDE	ALUMINUM ALKYLS	ALUMINUM POWDER, UNCOATED	AMMONIA, SOLUTION
DIMETHYL SULFATE															
ETHANOL	1														
ETHYLENE OXIDE	1	2													
CAUSTIC SODA, SOLUTION	1	2	1												
CHLORINE	1	1	1	1											
HYDROCHLORIC ACID, SOLUTION	2	0	1	1	1										
ISOPROPYL CHLOROFORMATE	1	2	2	2	1	0									
PHOSPHORUS TRICHLORIDE	0	1	1	1	1	2	1								
SODIUM HYDROSULFIDE, SOLUTION	1	1	1	2	1	1	1	1							
SODIUM HYPOCHLORITE SOLUTION	1	2	1	2	1	1	0	1	0						
SULFURIC ACID	2	2	1	1	1	2	2	2	1	1					
TERT-BUTYL HYDROPEROXIDE	2	3	3	1	1	2	3	2	1	1	0				
ALUMINUM ALKYLS	1	2	2	1	2	1	2	1	1	1	1	3			
ALUMINUM POWDER, UNCOATED	1	2	2	1	1	1	2	1	1	1	1	2	1		
AMMONIA, SOLUTION	1	2	1	0	1	1	2	1	2	2	1	1	1	1	
WATER	0	0	0	0	2	0	0	0	0	2	2	0	2	2	0

5.2 Napp Technologies - Physical Processing

Jump to Common Preliminary Step section 5.0

Start with section 5.0 before completing these steps

Table of Contents

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*[17], a gold precipitating agent." [18]

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

---

[17] TM Technic Inc, Cranston RI

[18] Based on EPA/OSHA Joint Chemical Accident Investigation Report, Napp Technologies, inc. Lodi, NJ EPA 550-R-97-002, October 1997

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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 m^3 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

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5.2.4.3 Entering Missing Chemical Information

See Section 5.0 for detailed instructions

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

Helpful Hint

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.

Helpful Hint

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.

Chemical Name	Special Hazard
ALUMINUM POWDER, UNCOATED, ISOPROPANOL,ACR 9031 GPA	Highly Flammable
ALUMINUM POWDER, UNCOATED, SODIUM HYDROSULFITE, ACR 9031 GPA	Water-Reactive
SODIUM HYDROSULFITE	Air-Reactive
ALUMINUM POWDER, UNCOATED, ACR 9031 GPA	Pyrophoric
ISOPROPANOL	Peroxidizable Compound

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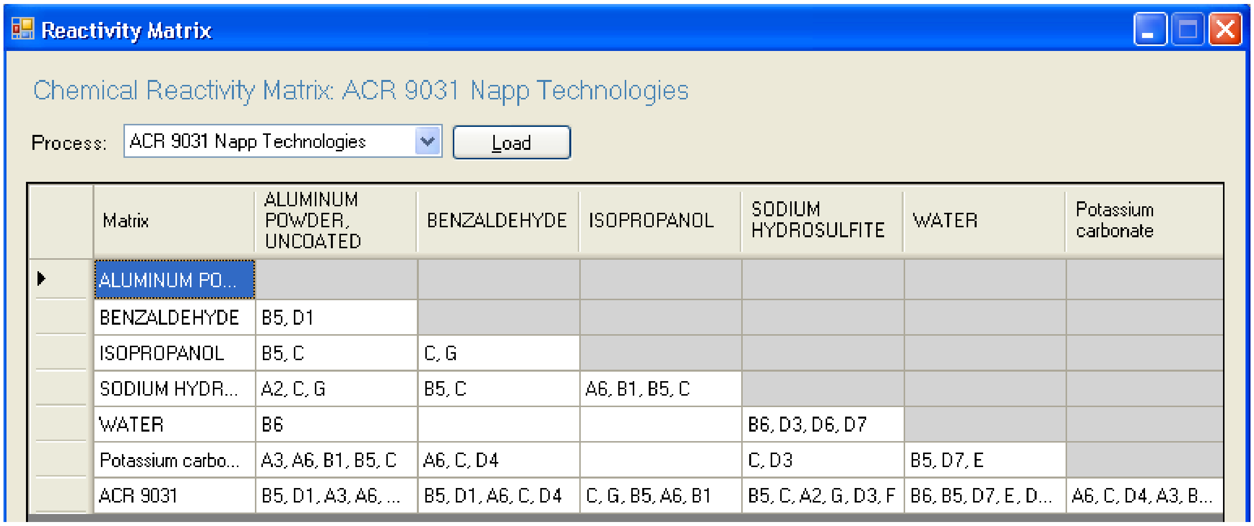
5.2.6 Displaying the binary chemical interactions

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.



Chemical Reactivity Matrix: ACR 9031 Napp Technologies

Process: ACR 9031 Napp Technologies

Matrix	ALUMINUM POWDER, UNCOATED	BENZALDEHYDE	ISOPROPANOL	SODIUM HYDROSULFITE	WATER	Potassium carbonate
ALUMINUM PO...						
BENZALDEHYDE	B5, D1					
ISOPROPANOL	B5, C	C, G				
SODIUM HYDR...	A2, C, G	B5, C	A6, B1, B5, C			
WATER	B6			B6, D3, D6, D7		
Potassium carbo...	A3, A6, B1, B5, C	A6, C, D4		C, D3	B5, D7, E	
ACR 9031	B5, D1, A3, A6, ...	B5, D1, A6, C, D4	C, G, B5, A6, B1	B5, C, A2, G, D3, F	B6, B5, D7, E, D...	A6, C, D4, A3, B...

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

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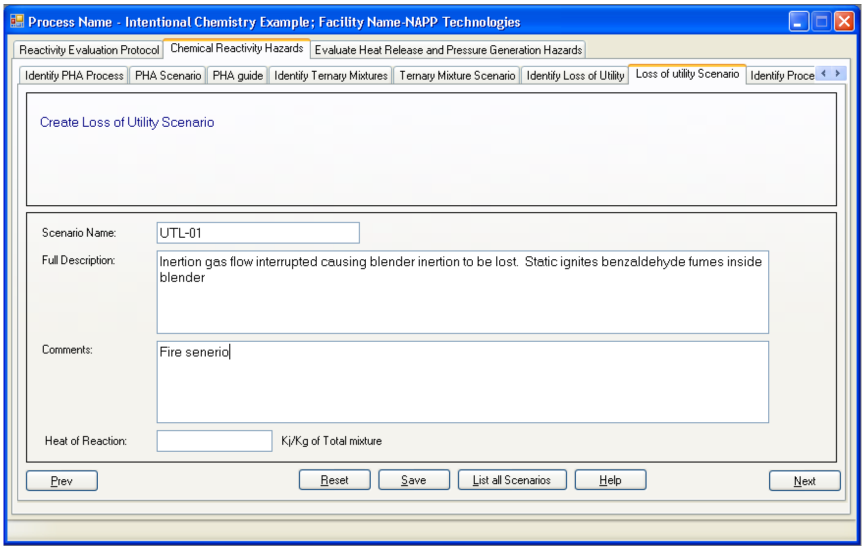
- Water + sodium hydrosulfite
- Water + GPA
    - Sweating – pipes or perspiration – drum filling
    - Fire suppression system
    - Cleaning operations near-by
    - Humidity during charging or dispensing
    - Blender water wet from cleaning
    - Header pipes have trapped water
    - Residual GPA in blender during cleaning
    - Potassium carbonate wet from improper storage
    - Water in inerting gas line
- Water + Al
    - →Combustion of aluminum
    - Hydrogen build-up in mixer with static ignition

For illustration purposes we will only enter a few of the scenarios from the list above. In practice you would enter all scenarios generated.

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”



Scenario Name: UTL-01

Full Description: Inertion gas flow interrupted causing blender inertion to be lost. Static ignites benzaldehyde fumes inside blender

Comments: Fire senerio

Heat of Reaction: Kj/Kg of Total mixture

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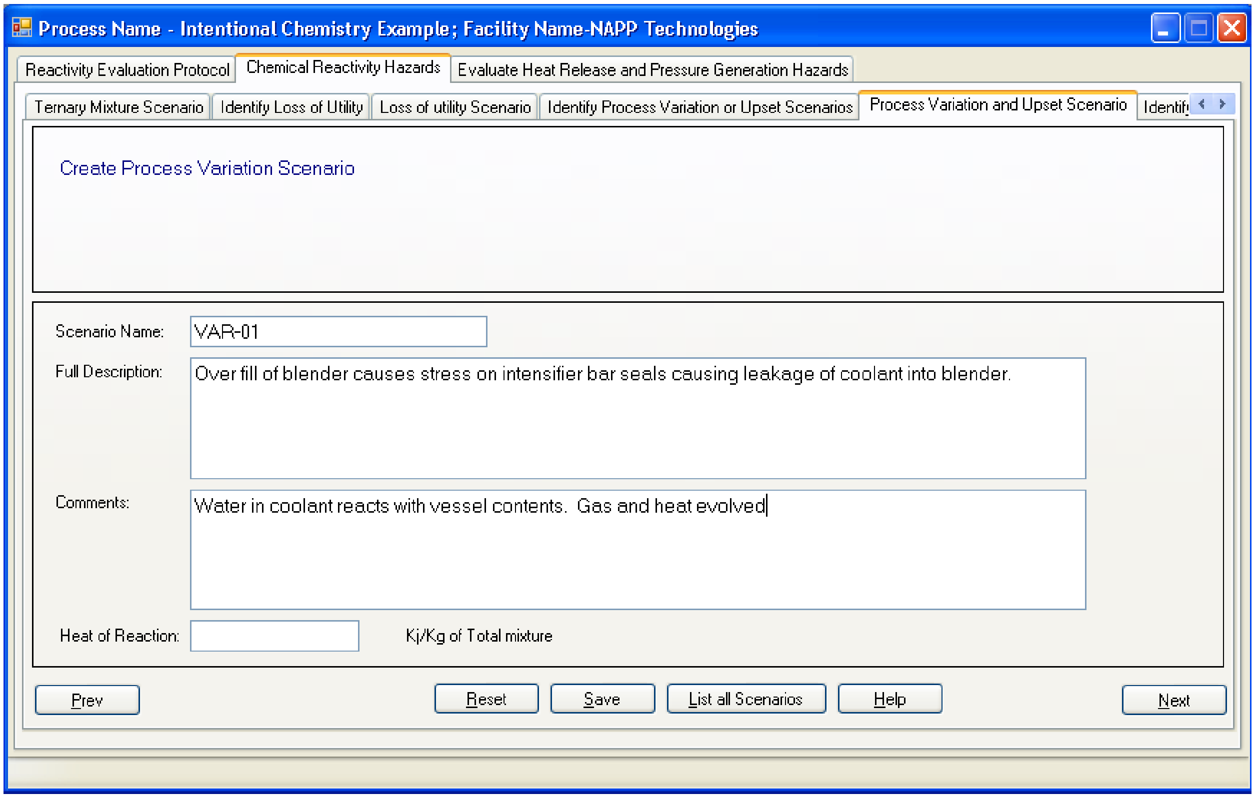
5.2.7.2 Process variation or upset example

Over fill of blender causes stress on intensifier bar seals causing leakage of coolant into blender.

- Enter the information below



Scenario Name: VAR-01

Full Description: Over fill of blender causes stress on intensifier bar seals causing leakage of coolant into blender.

Comments: Water in coolant reacts with vessel contents. Gas and heat evolved

Heat of Reaction: Kj/Kg of Total mixture

- 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.

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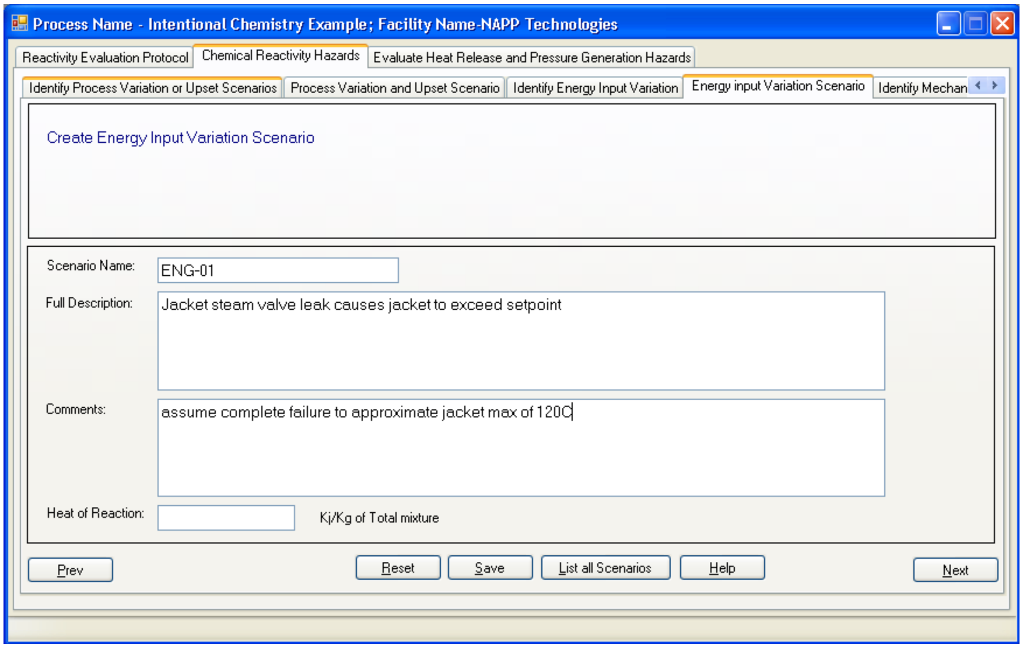
- Enter the information shown below



Scenario Name: ENG-01

Full Description: Jacket steam valve leak causes jacket to exceed setpoint

Comments: assume complete failure to approximate jacket max of 120C

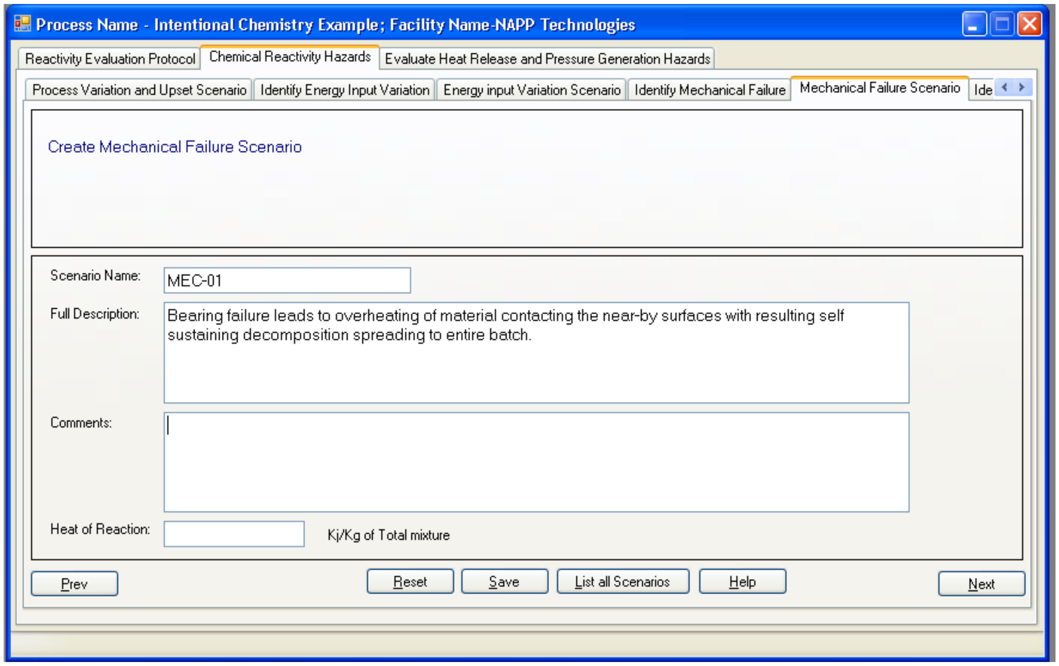
Heat of Reaction: Kj/Kg of Total mixture

- 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



Scenario Name: MEC-01

Full Description: Bearing failure leads to overheating of material contacting the near-by surfaces with resulting self sustaining decomposition spreading to entire batch.

Comments:

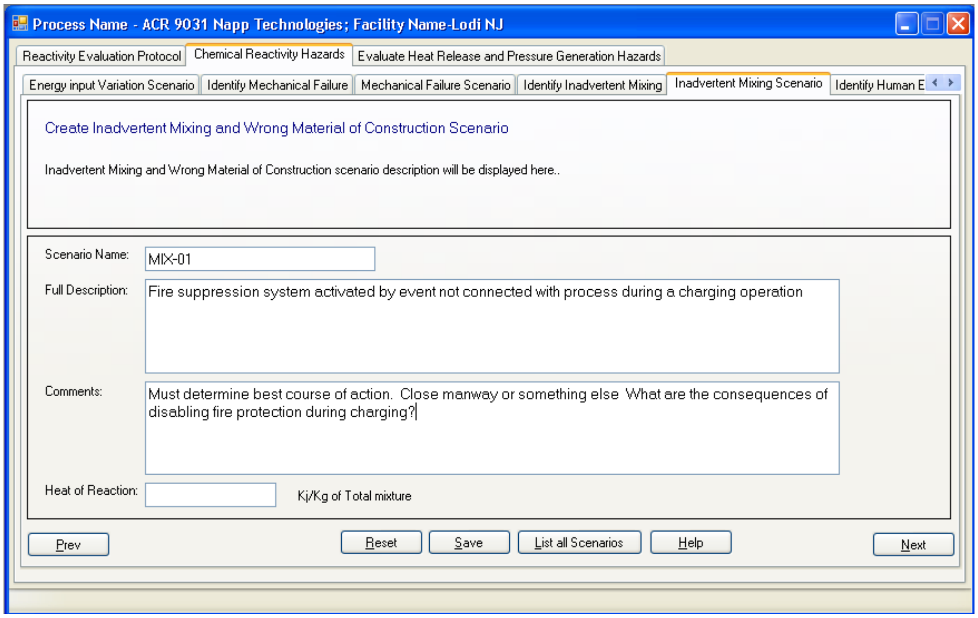
Heat of Reaction: Kj/Kg of Total mixture

- 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



Create Inadvertent Mixing and Wrong Material of Construction Scenario

Inadvertent Mixing and Wrong Material of Construction scenario description will be displayed here..

Scenario Name: MIX-01

Full Description: Fire suppression system activated by event not connected with process during a charging operation

Comments: Must determine best course of action. Close manway or something else What are the consequences of disabling fire protection during charging?

Heat of Reaction: Kj/Kg of Total mixture

We have completed entering scenarios in this example.

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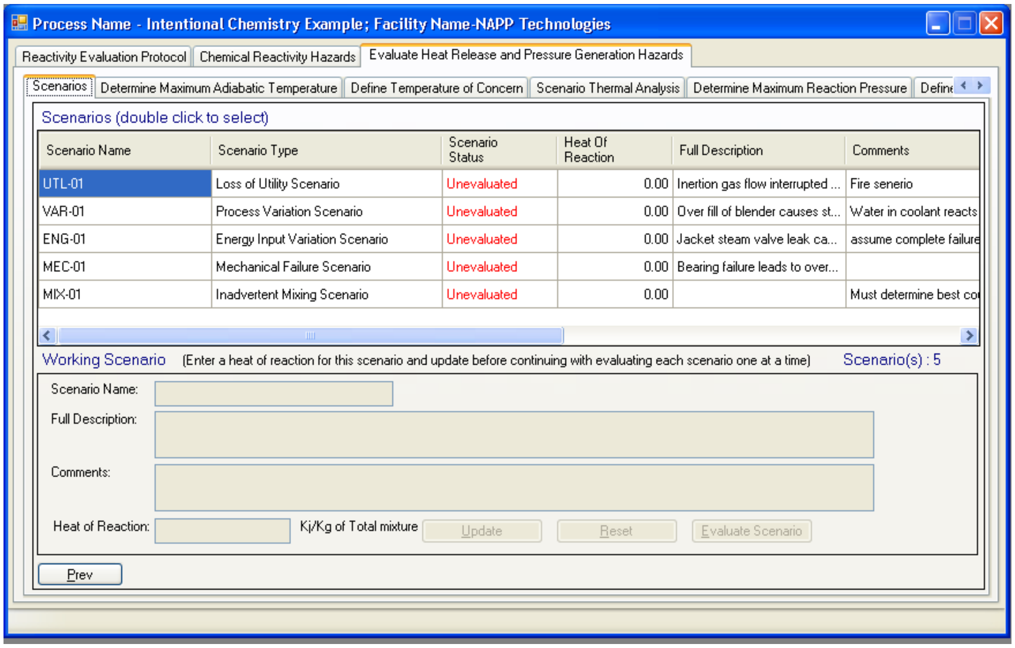
5.2.8 Evaluating the Scenarios

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.



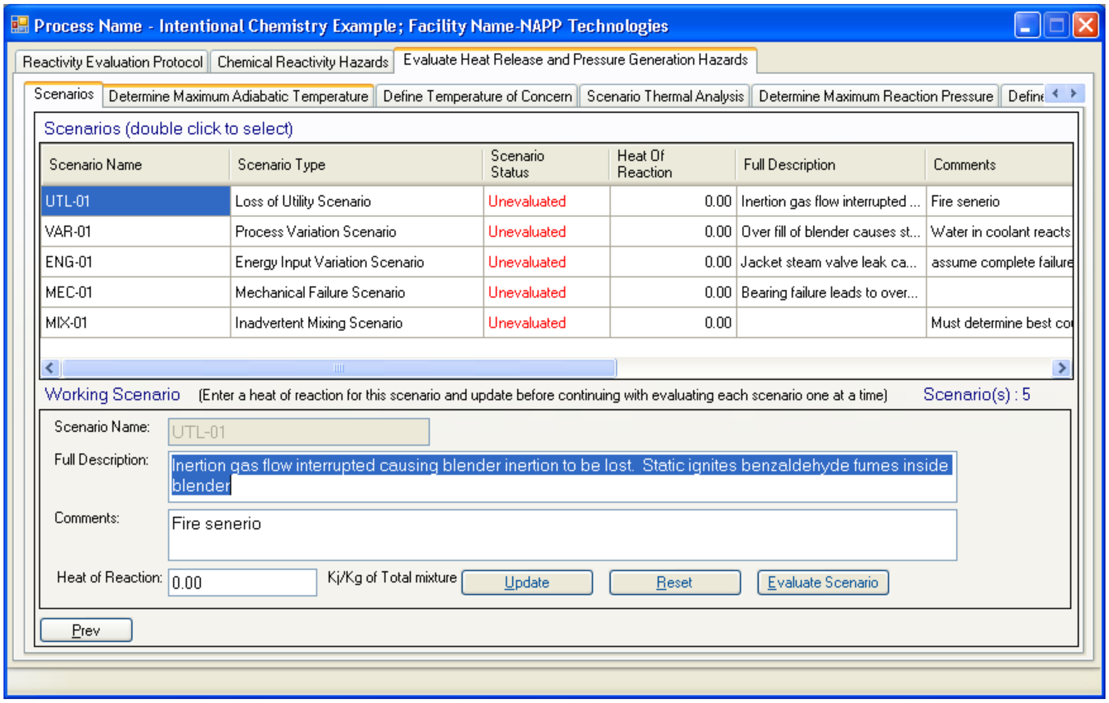
Scenarios (double click to select)

Scenario Name	Scenario Type	Scenario Status	Heat Of Reaction	Full Description	Comments
UTL-01	Loss of Utility Scenario	Unevaluated	0.00	Inertion gas flow interrupted ...	Fire senerio
VAR-01	Process Variation Scenario	Unevaluated	0.00	Over fill of blender causes st...	Water in coolant reacts
ENG-01	Energy Input Variation Scenario	Unevaluated	0.00	Jacket steam valve leak ca...	assume complete failure
MEC-01	Mechanical Failure Scenario	Unevaluated	0.00	Bearing failure leads to over...	
MIX-01	Inadvertent Mixing Scenario	Unevaluated	0.00		Must determine best co

Working Scenario (Enter a heat of reaction for this scenario and update before continuing with evaluating each scenario one at a time) Scenario(s) : 5

Scenario Name:
Full Description:
Comments:
Heat of Reaction: Kj/Kg of Total mixture

- Double click on a scenario
- The information entered thus far appears in editable format



Scenarios (double click to select)

Scenario Name	Scenario Type	Scenario Status	Heat Of Reaction	Full Description	Comments
UTL-01	Loss of Utility Scenario	Unevaluated	0.00	Inertion gas flow interrupted ...	Fire senerio
VAR-01	Process Variation Scenario	Unevaluated	0.00	Over fill of blender causes st...	Water in coolant reacts
ENG-01	Energy Input Variation Scenario	Unevaluated	0.00	Jacket steam valve leak ca...	assume complete failure
MEC-01	Mechanical Failure Scenario	Unevaluated	0.00	Bearing failure leads to over...	
MIX-01	Inadvertent Mixing Scenario	Unevaluated	0.00		Must determine best co

Working Scenario (Enter a heat of reaction for this scenario and update before continuing with evaluating each scenario one at a time) Scenario(s) : 5

Scenario Name: UTL-01
Full Description: Inertion gas flow interrupted causing blender inertion to be lost. Static ignites benzaldehyde fumes inside blender
Comments: Fire senerio
Heat of Reaction: 0.00 Kj/Kg of Total mixture

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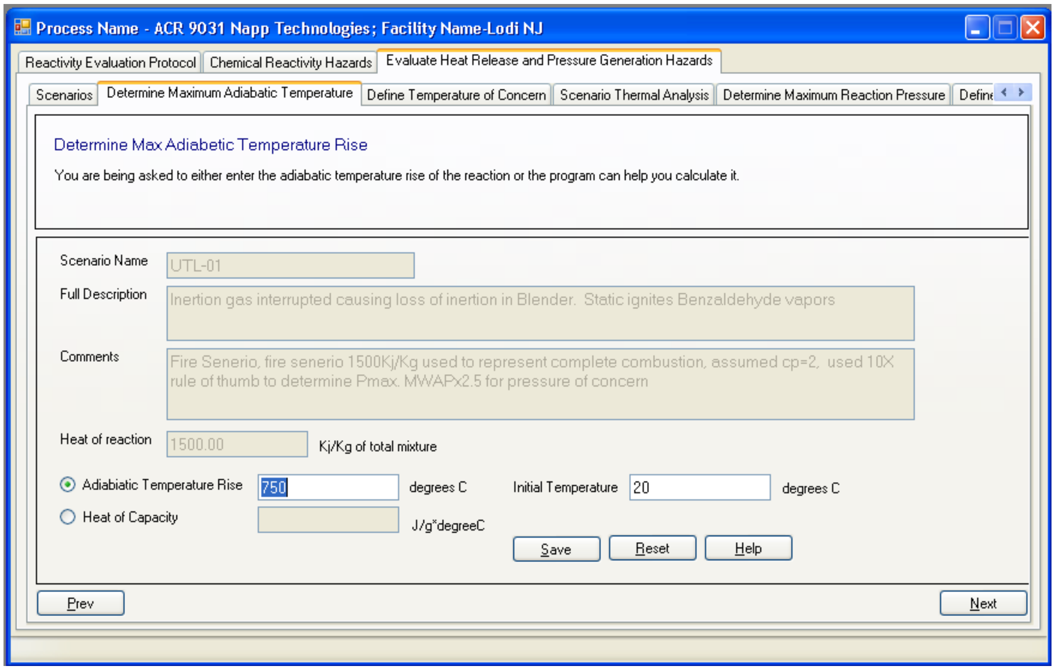
- Make any changes necessary. You must enter a heat of reaction in kJ/kg of reaction mixture at this time
- Since this is a fire scenario enter any large number or calculate the heat of combustion.
- Press Update and Evaluate scenario



Determine Max Adiabetic Temperature Rise

You are being asked to either enter the adiabatic temperature rise of the reaction or the program can help you calculate it.

Scenario Name: UTL-01

Full Description: Inertion gas interrupted causing loss of inertion in Blender. Static ignites Benzaldehyde vapors

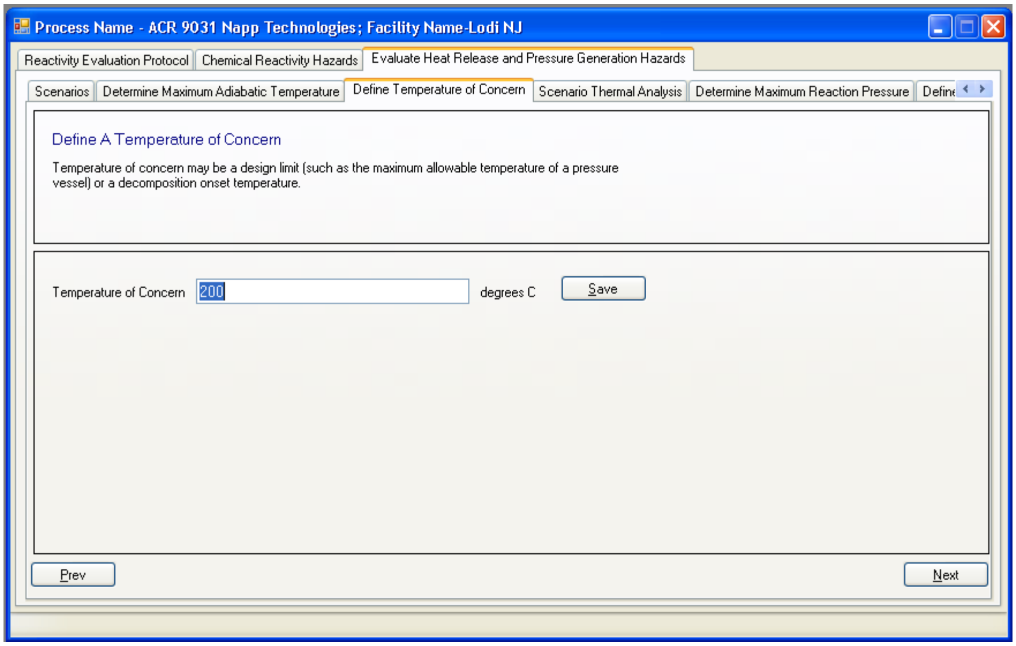
Comments: Fire Senerio, fire senerio 1500Kj/Kg used to represent complete combustion, assumed cp=2, used 10X rule of thumb to determine Pmax. MWAPx2.5 for pressure of concern

Heat of reaction: 1500.00 Kj/Kg of total mixture

● Adiabatic Temperature Rise: 750 degrees C Initial Temperature: 20 degrees C

○ Heat of Capacity: J/g*degreeC

- 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

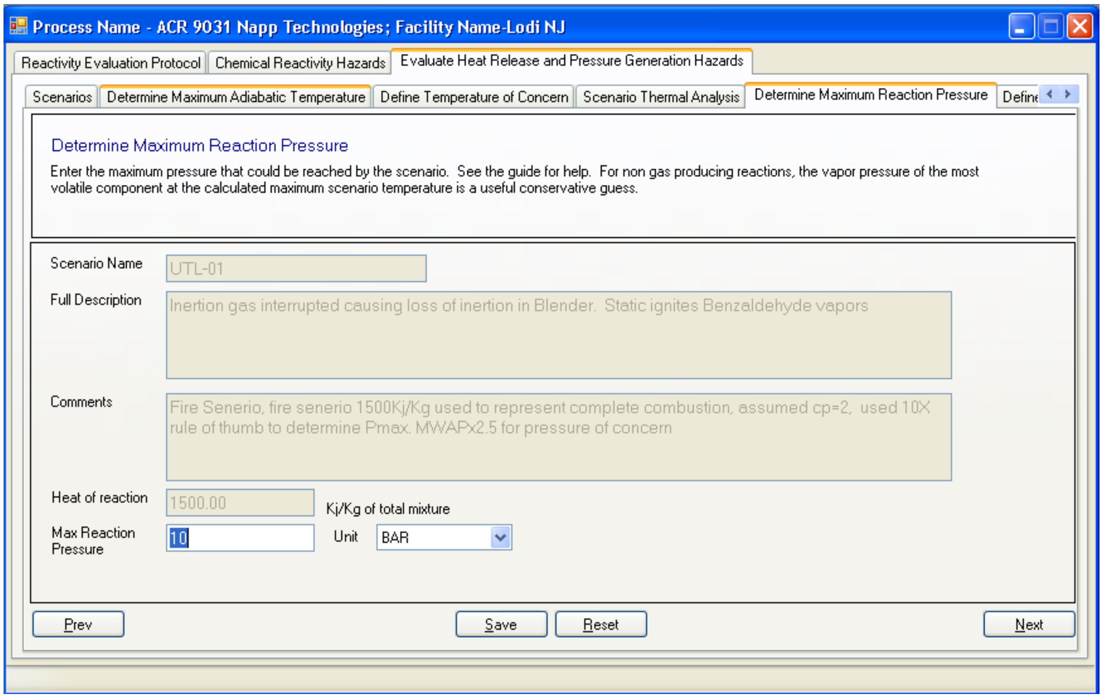


Define A Temperature of Concern

Temperature of concern may be a design limit (such as the maximum allowable temperature of a pressure vessel) or a decomposition onset temperature.

Temperature of Concern: 200 degrees C

- 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



Determine Maximum Reaction Pressure

Enter the maximum pressure that could be reached by the scenario. See the guide for help. For non gas producing reactions, the vapor pressure of the most volatile component at the calculated maximum scenario temperature is a useful conservative guess.

Scenario Name: UTL-01

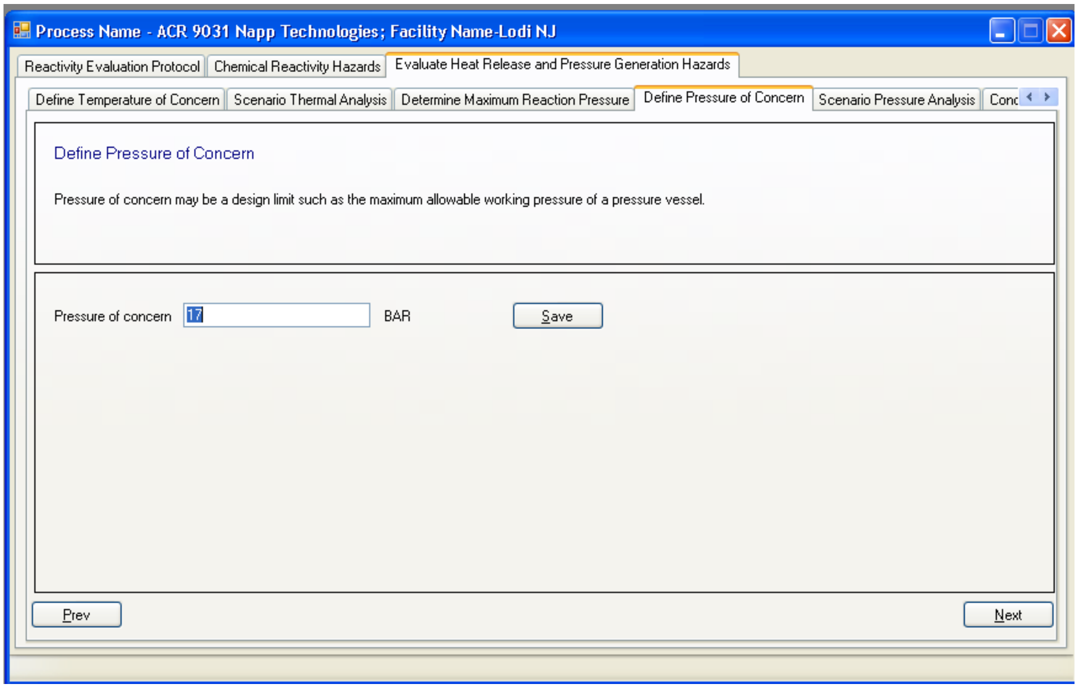
Full Description: Inertion gas interrupted causing loss of inertion in Blender. Static ignites Benzaldehyde vapors

Comments: Fire Senerio, fire senerio 1500Kj/Kg used to represent complete combustion, assumed cp=2, used 10X rule of thumb to determine Pmax. MWAPx2.5 for pressure of concern

Heat of reaction: 1500.00 Kj/Kg of total mixture

Max Reaction Pressure: 10 Unit: BAR

- Press ‘save” then “Next”



Define Pressure of Concern

Pressure of concern may be a design limit such as the maximum allowable working pressure of a pressure vessel.

Pressure of concern 17 BAR

- 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”

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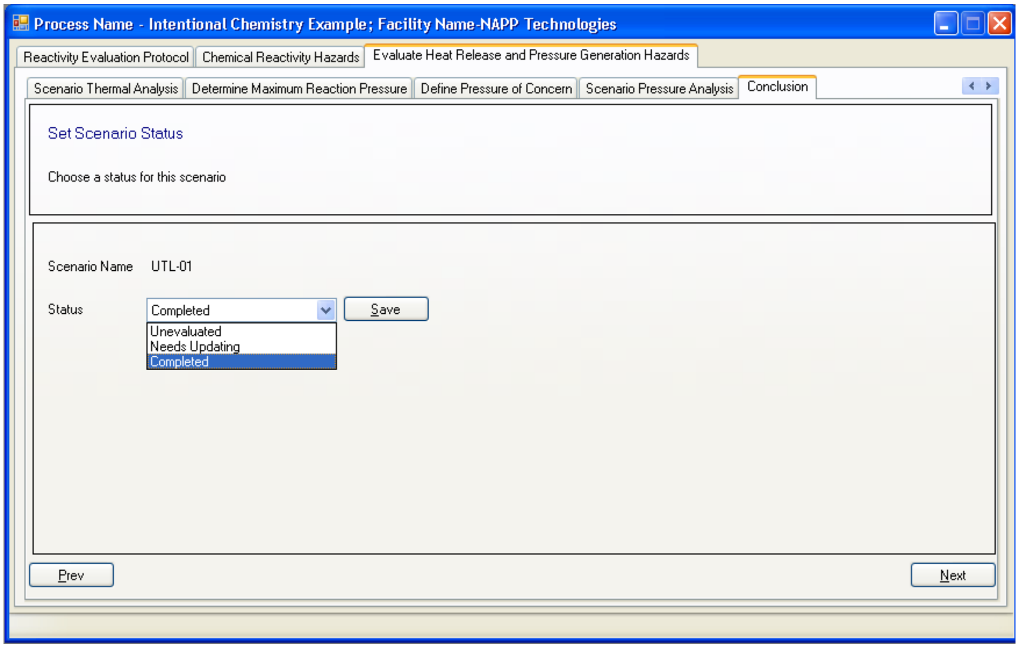
- Choose "completed"



Process Name - Intentional Chemistry Example; Facility Name-NAPP Technologies

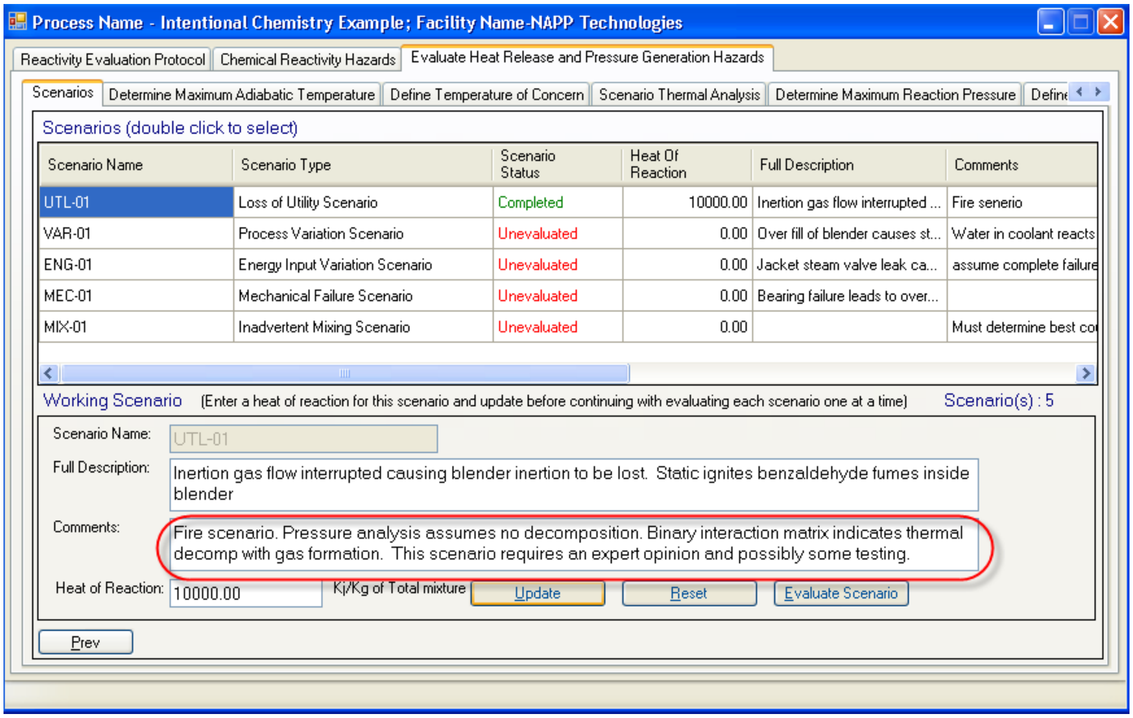
Set Scenario Status

Choose a status for this scenario

Scenario Name UTL-01

Status 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.



Process Name - Intentional Chemistry Example; Facility Name-NAPP Technologies

Scenarios (double click to select)

Scenario Name	Scenario Type	Scenario Status	Heat Of Reaction	Full Description	Comments
UTL-01	Loss of Utility Scenario	Completed	10000.00	Inertion gas flow interrupted ...	Fire senerio
VAR-01	Process Variation Scenario	Unevaluated	0.00	Over fill of blender causes st...	Water in coolant reacts
ENG-01	Energy Input Variation Scenario	Unevaluated	0.00	Jacket steam valve leak ca...	assume complete failure
MEC-01	Mechanical Failure Scenario	Unevaluated	0.00	Bearing failure leads to over...	
MIX-01	Inadvertent Mixing Scenario	Unevaluated	0.00		Must determine best co

Working Scenario (Enter a heat of reaction for this scenario and update before continuing with evaluating each scenario one at a time) Scenario(s) : 5

Scenario Name: UTL-01

Full Description: Inertion gas flow interrupted causing blender inertion to be lost. Static ignites benzaldehyde fumes inside blender

Comments: Fire scenario. Pressure analysis assumes no decomposition. Binary interaction matrix indicates thermal decomp with gas formation. This scenario requires an expert opinion and possibly some testing.

Heat of Reaction: 10000.00 Kj/Kg of Total mixture

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- Continue to evaluate the scenarios one at a time using the following data

Scenario	Heat kJ/kg	Adiabatic temp rise	Heat capacity	Temp of concern	Starting temp	Max pressure	Pressure of concern
UTL-01	5000		2	200	20	10bar	17.2bar
VAR-01	972	486		200	20	175bar *	17.2bar
ERG-01	972	486		200	20	175bar	17.2 bar
MEC-01	972	486		200	20	175bar	17.2bar
MIX-01	5000		2	200	20	unknown[19]	17.2

***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 $Na_2S_2O_3$ molecular weight 158g/mole

  2,115,500g / 158 g/mole = 13,389 moles $Na_2S_2O_3$

  Each mole of decomposing $Na_2S_2O_3$ 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_2CO_3 molecular weight 138 g/mole

  335900g / 138 g/mole = 2,434 moles

  Each mole of decomposing K_2CO_3 gives off 1 mole of CO_2 thus 2434 moles of CO_2 are released on complete decomposition.

-

- R= 0.083 bar*L/mole*K
- T= 779K :7293K (20°C starting temp) + 486 (adiabatic heat rise)
- V[20] = 6 m^3 = 6,000L
- n = 15823 = 13389 moles SO_2 + 2434 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

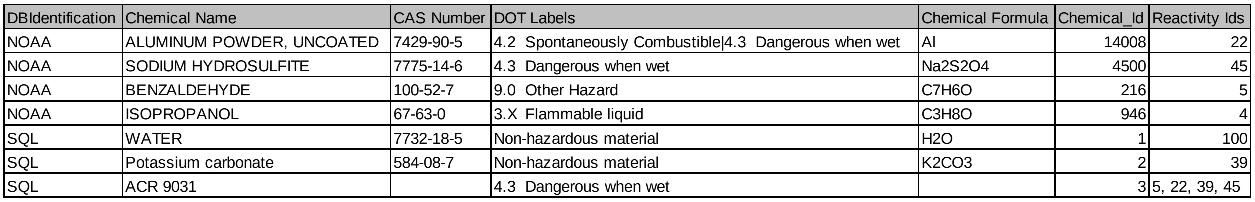
5.2.9 Reporting and Proof Reading

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.

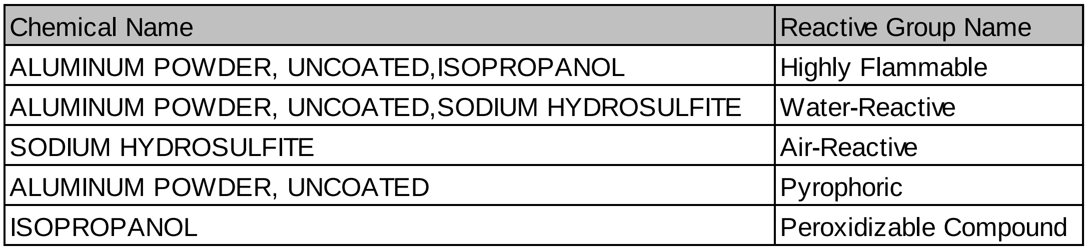
Selected screen shots of reports:

Chemicals report exported to Excel:



DBIdentification	Chemical Name	CAS Number	DOT Labels	Chemical Formula	Chemical_Id	Reactivity Ids
NOAA	ALUMINUM POWDER, UNCOATED	7429-90-5	4.2 Spontaneously Combustible|4.3 Dangerous when wet	Al	14008	22
NOAA	SODIUM HYDROSULFITE	7775-14-6	4.3 Dangerous when wet	Na2S2O4	4500	45
NOAA	BENZALDEHYDE	100-52-7	9.0 Other Hazard	C7H6O	216	5
NOAA	ISOPROPANOL	67-63-0	3.X Flammable liquid	C3H8O	946	4
SQL	WATER	7732-18-5	Non-hazardous material	H2O	1	100
SQL	Potassium carbonate	584-08-7	Non-hazardous material	K2CO3	2	39
SQL	ACR 9031		4.3 Dangerous when wet		3	5, 22, 39, 45

Pure component hazards



Chemical Name	Reactive Group Name
ALUMINUM POWDER, UNCOATED,ISOPROPANOL	Highly Flammable
ALUMINUM POWDER, UNCOATED,SODIUM HYDROSULFITE	Water-Reactive
SODIUM HYDROSULFITE	Air-Reactive
ALUMINUM POWDER, UNCOATED	Pyrophoric
ISOPROPANOL	Peroxidizable Compound

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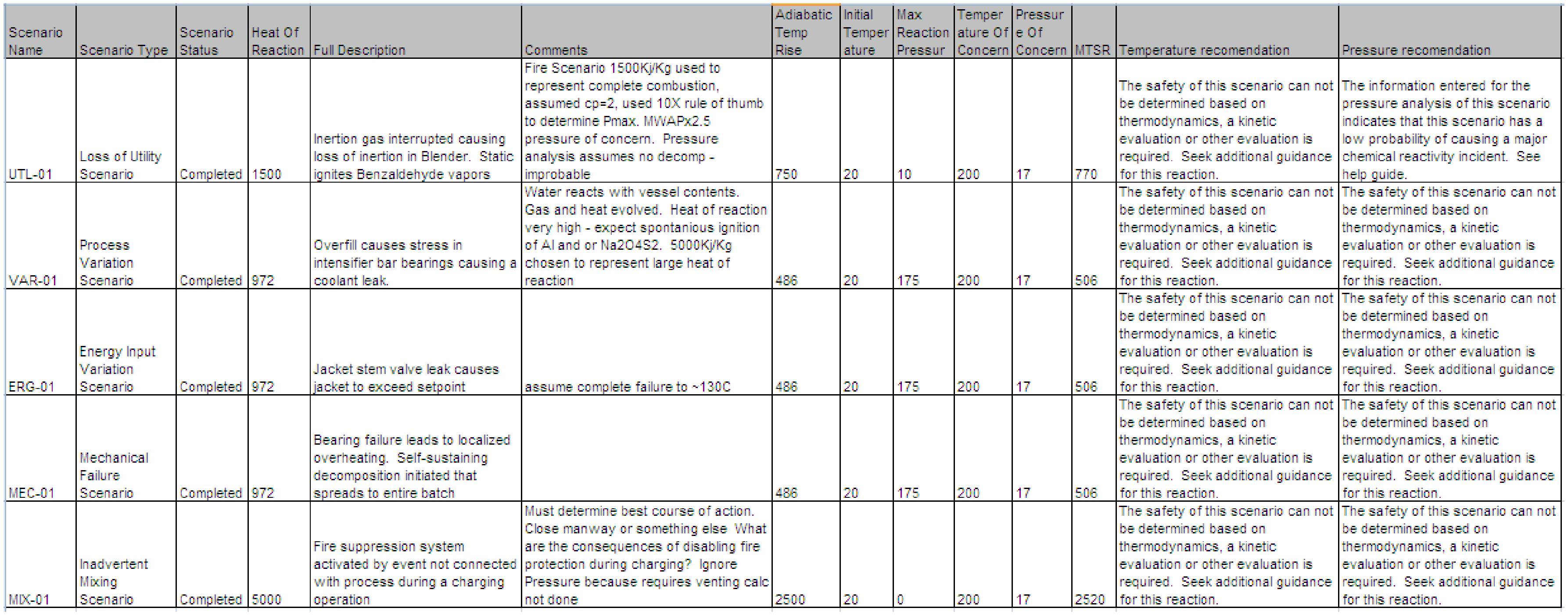
Binary interaction matrix reformatted in Excel for readability

Matrix	ALUMINUM POWDER, UNCOATED	BENZALDEHYDE	ISOPROPANOL	SODIUM HYDROSULFITE	WATER	Potassium carbonate
BENZALDEHYDE	B5, D1					
ISOPROPANOL	B5, C	C, G				
SODIUM HYDROSULFITE	A2, C, G	B5, C	A6, B1, B5, C			
WATER	B6			B6, D3, D6, D7		
Potassium carbonate	A3, A6, B1, B5, C	A6, C, D4		C, D3	B5, D7, E	
ACR 9031	B5, D1, A3, A6, B1, C, A2, G	B5, D1, A6, C, D4	C, G, B5, A6, B1	B5, C, A2, G, D3, F	B6, B5, D7, E, D3, D6	A6, C, D4, A3, B1, B5, D3

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:



Scenario Name	Scenario Type	Scenario Status	Heat Of Reaction	Full Description	Comments	Adiabatic Temp Rise	Initial Temperature	Max Reaction Pressur	Temperature Of Concern	Pressure Of Concern	MTSR	Temperature recomendation	Pressure recomendation
UTL-01	Loss of Utility Scenario	Completed	1500	Inertion gas interrupted causing loss of inertion in Blender. Static ignites Benzaldehyde vapors	Fire Scenario 1500Kj/Kg used to represent complete combustion, assumed cp=2, used 10X rule of thumb to determine Pmax. MWAPx2.5 pressure of concern. Pressure analysis assumes no decomp - improbable	750	20	10	200	17	770	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.	The information entered for the pressure analysis of this scenario indicates that this scenario has a low probability of causing a major chemical reactivity incident. See help guide.
VAR-01	Process Variation Scenario	Completed	972	Overfill causes stress in intensifier bar bearings causing a coolant leak.	Water reacts with vessel contents. Gas and heat evolved. Heat of reaction very high - expect spontanious ignition of Al and or Na2O4S2. 5000Kj/Kg chosen to represent large heat of reaction	486	20	175	200	17	506	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.
ERG-01	Energy Input Variation Scenario	Completed	972	Jacket stem valve leak causes jacket to exceed setpoint	assume complete failure to ~130C	486	20	175	200	17	506	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.
MEC-01	Mechanical Failure Scenario	Completed	972	Bearing failure leads to localized overheating. Self-sustaining decomposition initiated that spreads to entire batch		486	20	175	200	17	506	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.
MIX-01	Inadvertent Mixing Scenario	Completed	5000	Fire suppression system activated by event not connected with process during a charging operation	Must determine best course of action. Close manway or something else What are the consequences of disabling fire protection during charging? Ignore Pressure because requires venting calc not done	2500	20	0	200	17	2520	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.

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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.

Table of Contents

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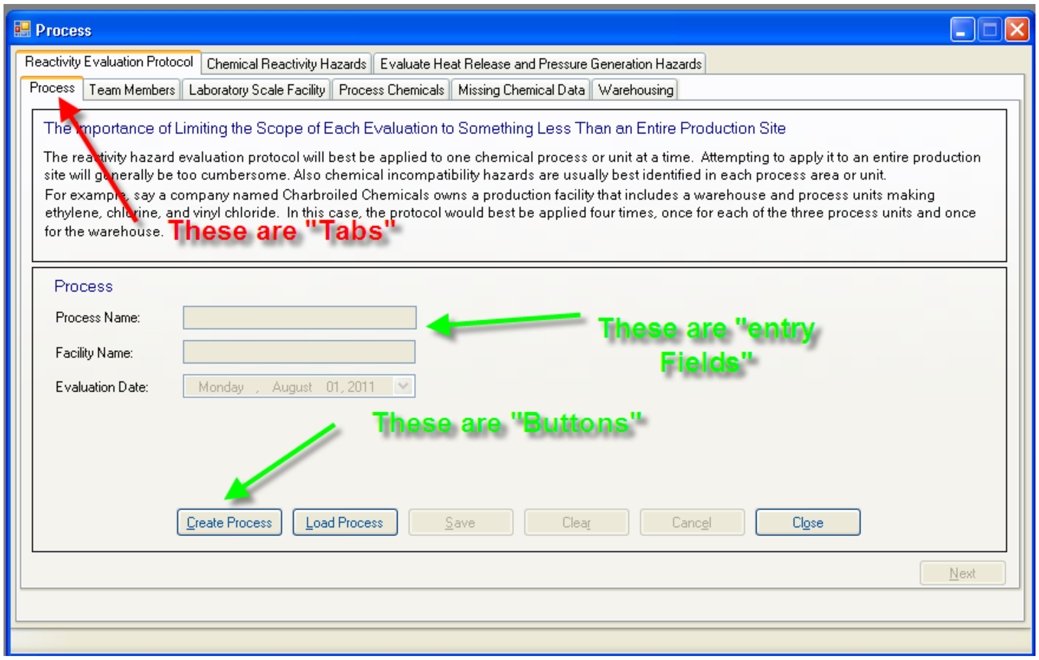
Jump to Common Preliminary Steps

Sections 5.3.1 through 5.3.6 are abbreviated instructions for detailed instructions use the link above.

5.3.1 Process Tab

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



The Importance of Limiting the Scope of Each Evaluation 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. Also chemical incompatibility hazards are usually best identified in each process area or unit.
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.

Process

Process Name:

Facility Name:

Evaluation Date: Monday , August 01, 2011

- 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.) them press the Add to process” button

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Production area chemical list	Hazard codes for custom entry	DOT Codes (MSDS sect.14)	Reactive Hazard
acetophenone	in NOAA DB	3.2	in NOAA DB
bromine	in NOAA DB	8A,6.1	in NOAA DB
dichloromethane	in NOAA DB	6.1	in NOAA DB
2-bromo-1-phenylethanone	in NOAA DB	6.1	in NOAA DB
sodium azide	in NOAA DB	6.1	in NOAA DB
tetrahydrofuran	in NOAA DB	3.1	in NOAA DB
triphenylphosphine	in NOAA DB	6.1	in NOAA DB
4-methylbenzenesulfonic acid	in NOAA DB	8A	in NOAA DB
compound 987654321	6,38	6.1	none
Ubiquitous chemicals			
Water	in NOAA DB	non-haz	none
Syltherm XLT®	28	3	none
Line Kleen®	1,38, 100	8A	none

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.

Name	Primary DOT	Secondary DOT	Reactive Groups	React hazards
Compound 987654321	3	none	6 , 38	none
Syltherm XLT	8A	none	28	none

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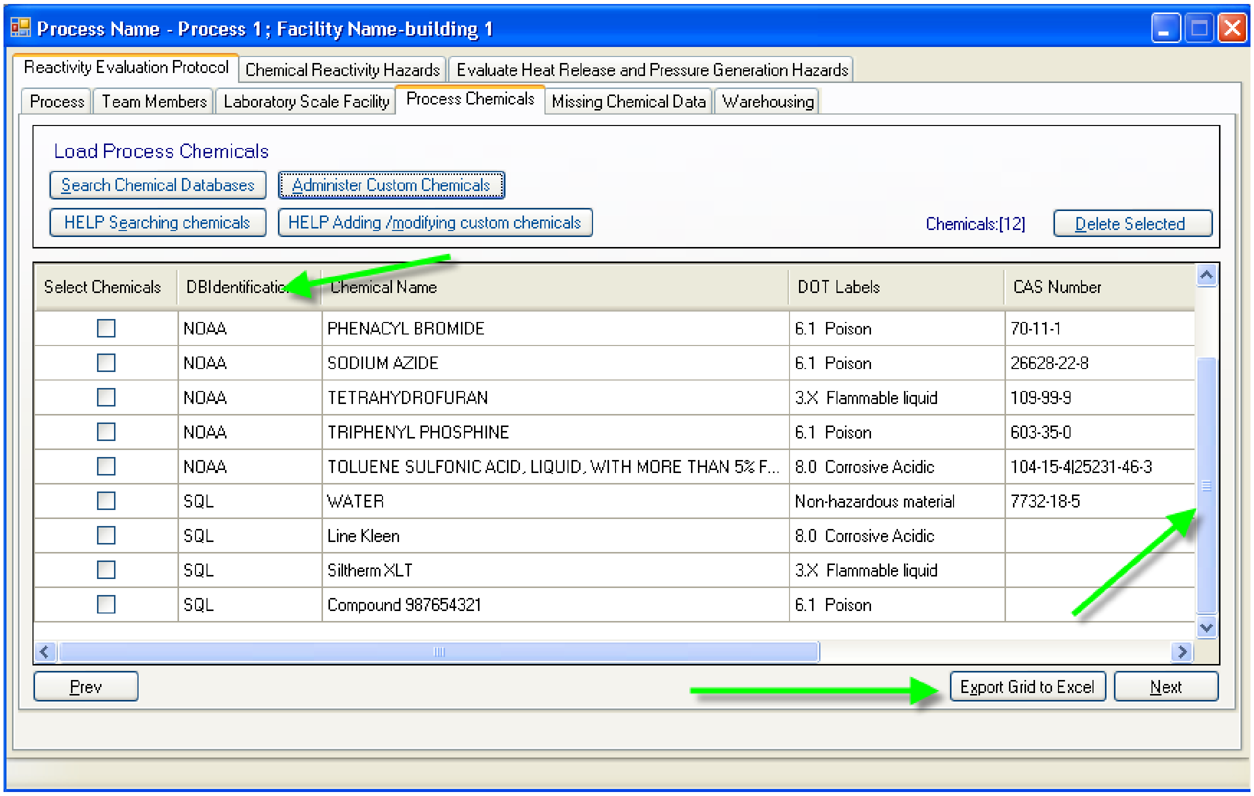

Select Chemicals	DBIdentificatio	Chemical Name	DOT Labels	CAS Number
☐	NOAA	PHENACYL BROMIDE	6.1 Poison	70-11-1
☐	NOAA	SODIUM AZIDE	6.1 Poison	26628-22-8
☐	NOAA	TETRAHYDROFURAN	3.X Flammable liquid	109-99-9
☐	NOAA	TRIPHENYL PHOSPHINE	6.1 Poison	603-35-0
☐	NOAA	TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% F...	8.0 Corrosive Acidic	104-15-4|25231-46-3
☐	SQL	WATER	Non-hazardous material	7732-18-5
☐	SQL	Line Kleen	8.0 Corrosive Acidic	
☐	SQL	Siltherm XLT	3.X Flammable liquid	
☐	SQL	Compound 987654321	6.1 Poison	

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.

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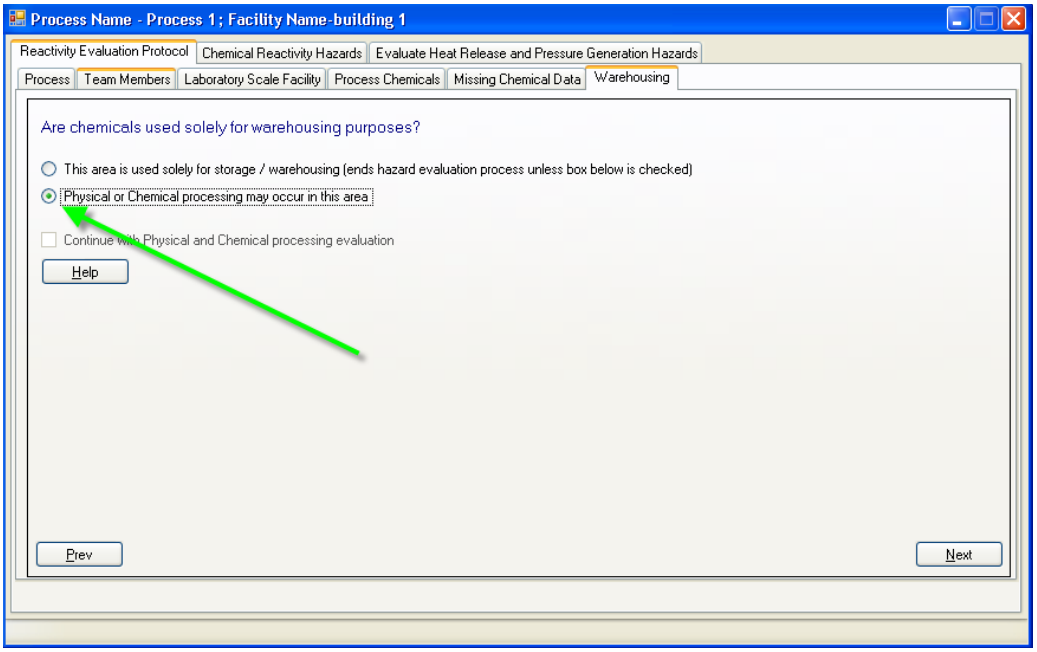
- For this example we are reacting chemicals in a chemical reactor and therefore we shall select the answer: **Physical or Chemical processing may occur in this area.**



Are chemicals used solely for warehousing purposes?

○ This area is used solely for storage / warehousing (ends hazard evaluation process unless box below is checked)

● Physical or Chemical processing may occur in this area

☐ Continue with Physical and Chemical processing evaluation

- 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.

Helpful Hint

- 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.

Helpful Hint

- 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

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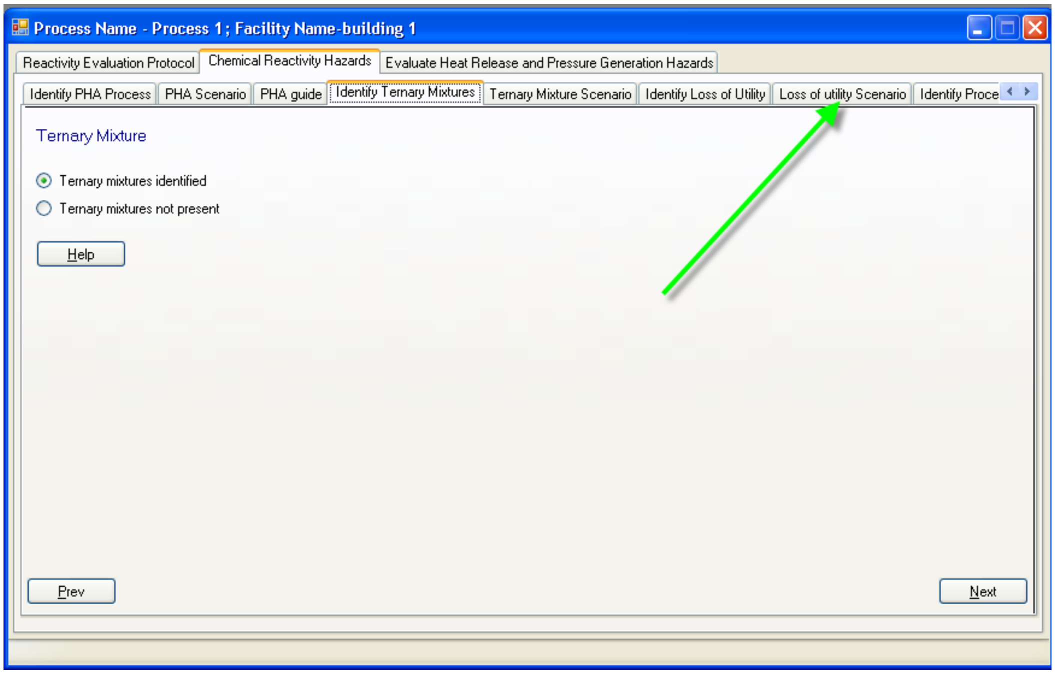
consecutive numbers. Ex TER-001 for the first scenario built under the Ternary mixtures tab.

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

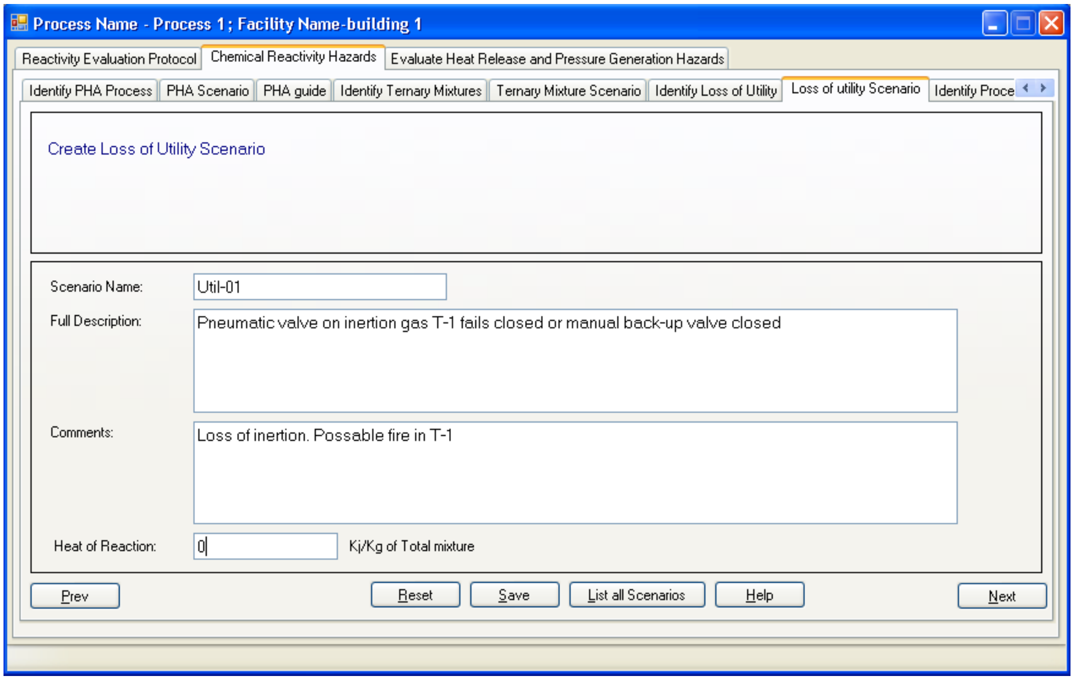


● Ternary mixtures identified
○ Ternary mixtures not present

- Click the "add" button
- Enter the data as shown below

Helpful Hint

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.



Scenario Name: Util-01

Full Description: Pneumatic valve on inertion gas T-1 fails closed or manual back-up valve closed

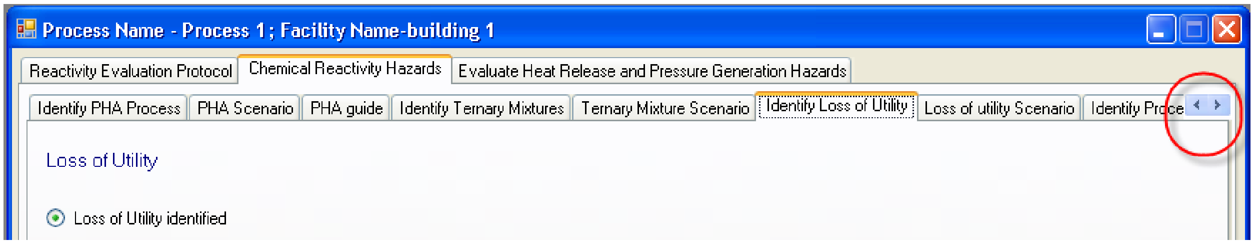
Comments: Loss of inertion. Possable fire in T-1

Heat of Reaction: 0 Kj/Kg of Total mixture

- 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

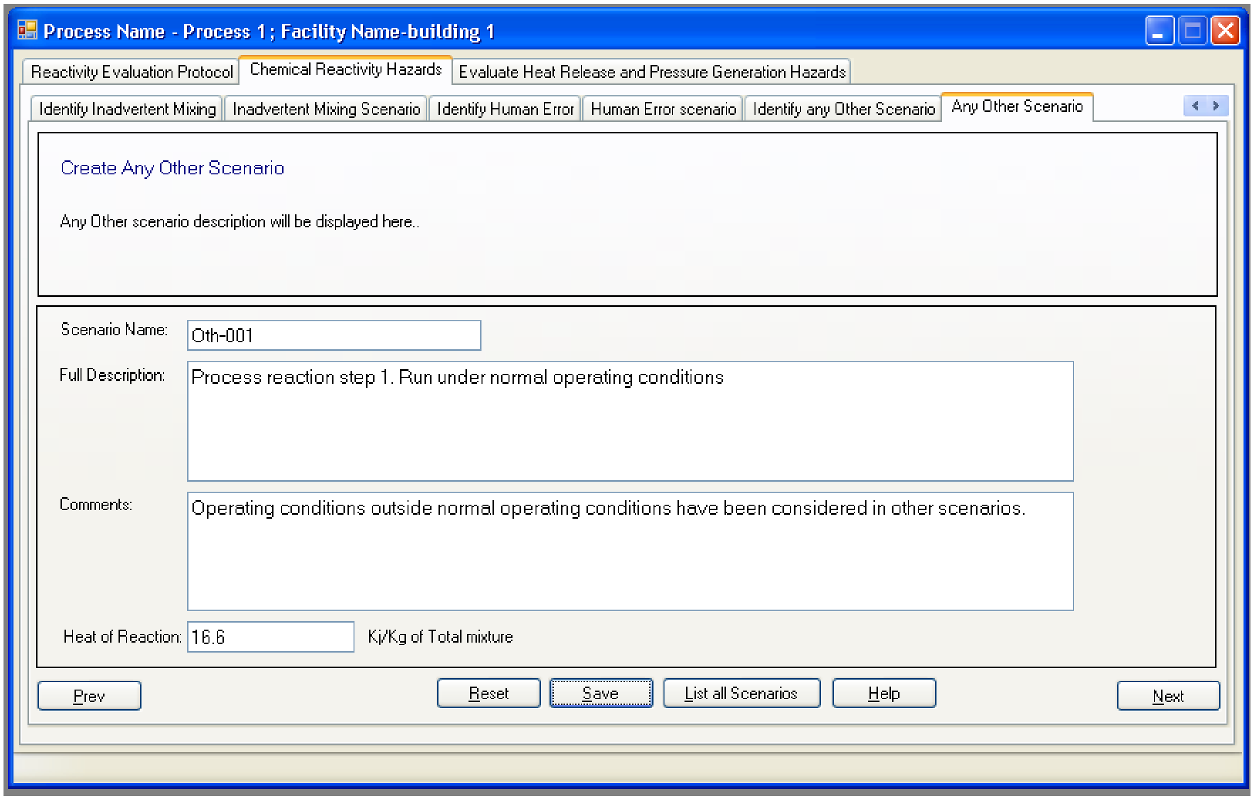
Select the “Any Other Scenario” tab. To view this tab you must use the arrows in the upper right corner of the process window.



● Loss of Utility identified

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:



Any Other scenario description will be displayed here..

Scenario Name: Oth-001

Full Description: Process reaction step 1. Run under normal operating conditions

Comments: Operating conditions outside normal operating conditions have been considered in other scenarios.

Heat of Reaction: 16.6 Kj/Kg of Total mixture

Note that the -16.6kJ/kg reaction energy (exothermic) is entered as positive number.

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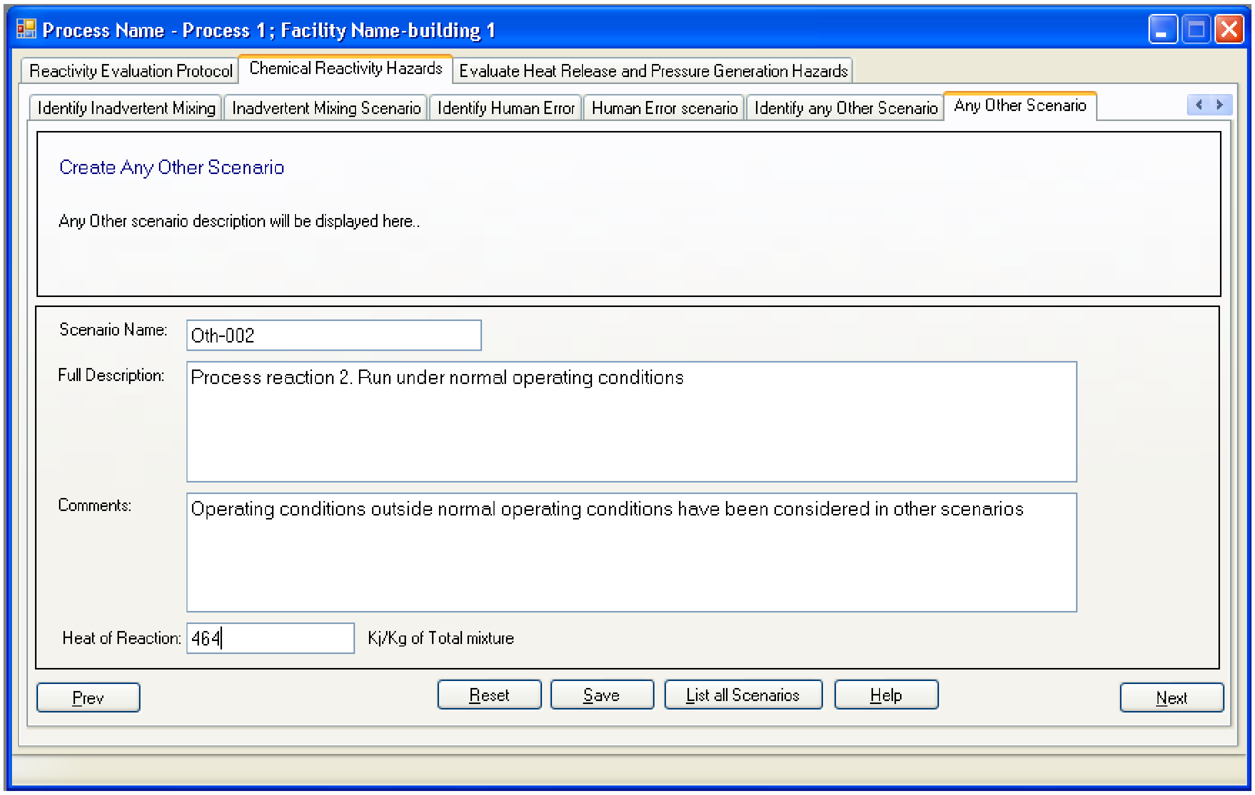
Press the save button and enter the next Reaction as shown. With a heat of reaction = 464kJ/kg



Create Any Other Scenario

Any Other scenario description will be displayed here..

Scenario Name: Oth-002

Full Description: Process reaction 2. Run under normal operating conditions

Comments: Operating conditions outside normal operating conditions have been considered in other scenarios

Heat of Reaction: 464 Kj/Kg of Total mixture

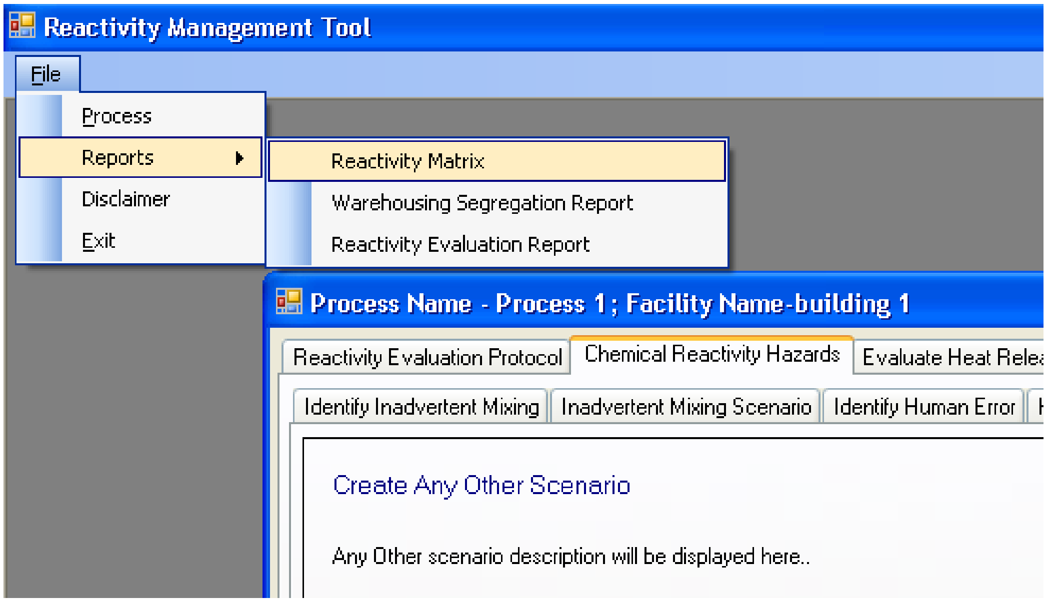
Press Save.

5.3.7.2 Identifying significant Binary interactions

We will now search for any binary chemical interactions identified by the program

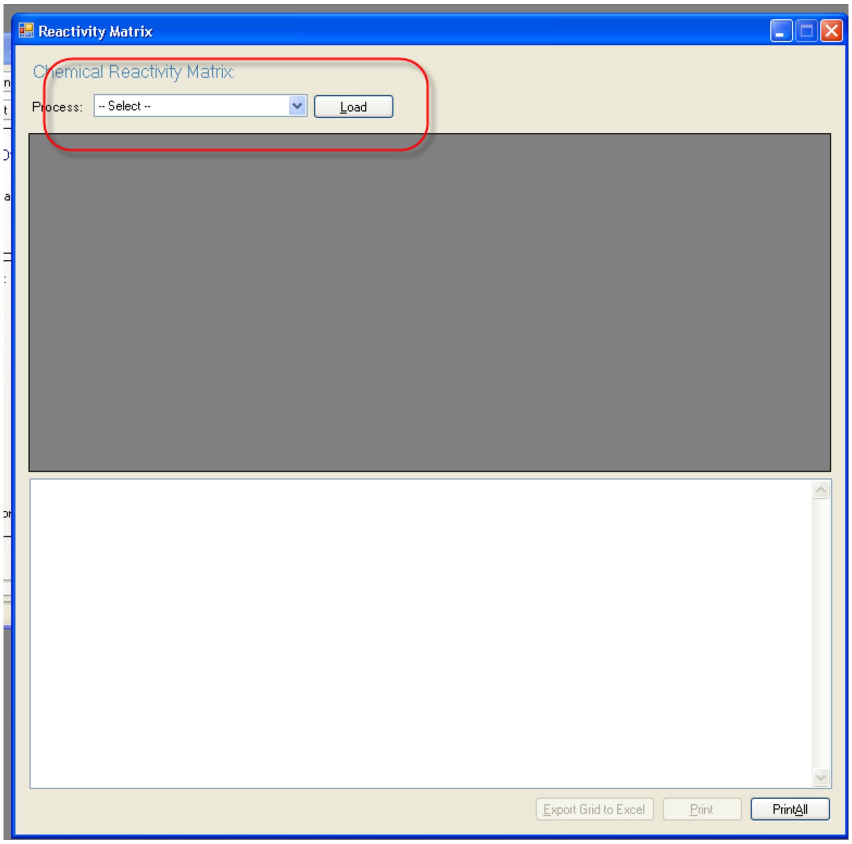
Under the “File” menu select reports; Reactivity Matrix

This opens a blank report window.



Any Other scenario description will be displayed here..

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.

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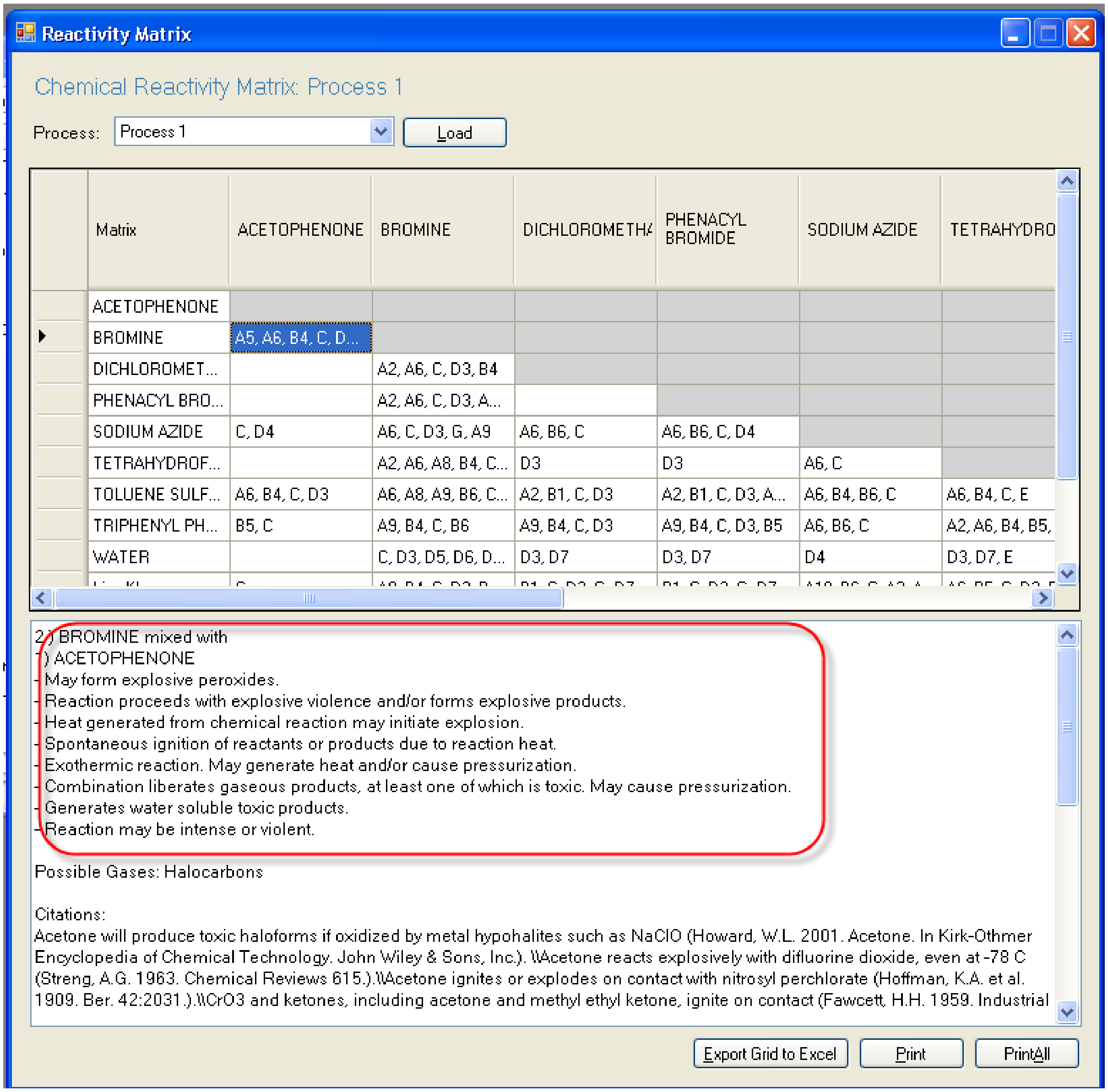

Chemical Reactivity Matrix: Process 1

Process: Process 1

	Matrix	ACETOPHENONE	BROMINE	DICHLOROMETHA	PHENACYL BROMIDE	SODIUM AZIDE	TETRAHYDRO
	ACETOPHENONE						
▶	BROMINE	A5, A6, B4, C, D...					
	DICHLOROMET...		A2, A6, C, D3, B4				
	PHENACYL BRO...		A2, A6, C, D3, A...				
	SODIUM AZIDE	C, D4	A6, C, D3, G, A9	A6, B6, C	A6, B6, C, D4		
	TETRAHYDROF...		A2, A6, A8, B4, C...	D3	D3	A6, C	
	TOLUENE SULF...	A6, B4, C, D3	A6, A8, A9, B6, C...	A2, B1, C, D3	A2, B1, C, D3, A...	A6, B4, B6, C	A6, B4, C, E
	TRIPHENYL PH...	B5, C	A9, B4, C, B6	A9, B4, C, D3	A9, B4, C, D3, B5	A6, B6, C	A2, A6, B4, B5,
	WATER		C, D3, D5, D6, D...	D3, D7	D3, D7	D4	D3, D7, E

2) BROMINE mixed with
1) ACETOPHENONE
- May form explosive peroxides.
- Reaction proceeds with explosive violence and/or forms explosive products.
- Heat generated from chemical reaction may initiate explosion.
- Spontaneous ignition of reactants 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.
- Generates water soluble toxic products.
- Reaction may be intense or violent.

Possible Gases: Halocarbons

Citations:
Acetone will produce toxic haloforms if oxidized by metal hypohalites such as NaClO (Howard, W.L. 2001. Acetone. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.). \\Acetone reacts explosively with difluorine dioxide, even at -78 C (Streng, A.G. 1963. Chemical Reviews 615.).\\Acetone ignites or explodes on contact with nitrosyl perchlorate (Hoffman, K.A. et al. 1909. Ber. 42:2031.).\\CrO3 and ketones, including acetone and methyl ethyl ketone, ignite on contact (Fawcett, H.H. 1959. Industrial

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 → Bromoacetophenone + HBr into CHETAH® results in a ΔH_{rxn} value of -3.96Kcal/mole. This converts to -16.6 kJ/mole

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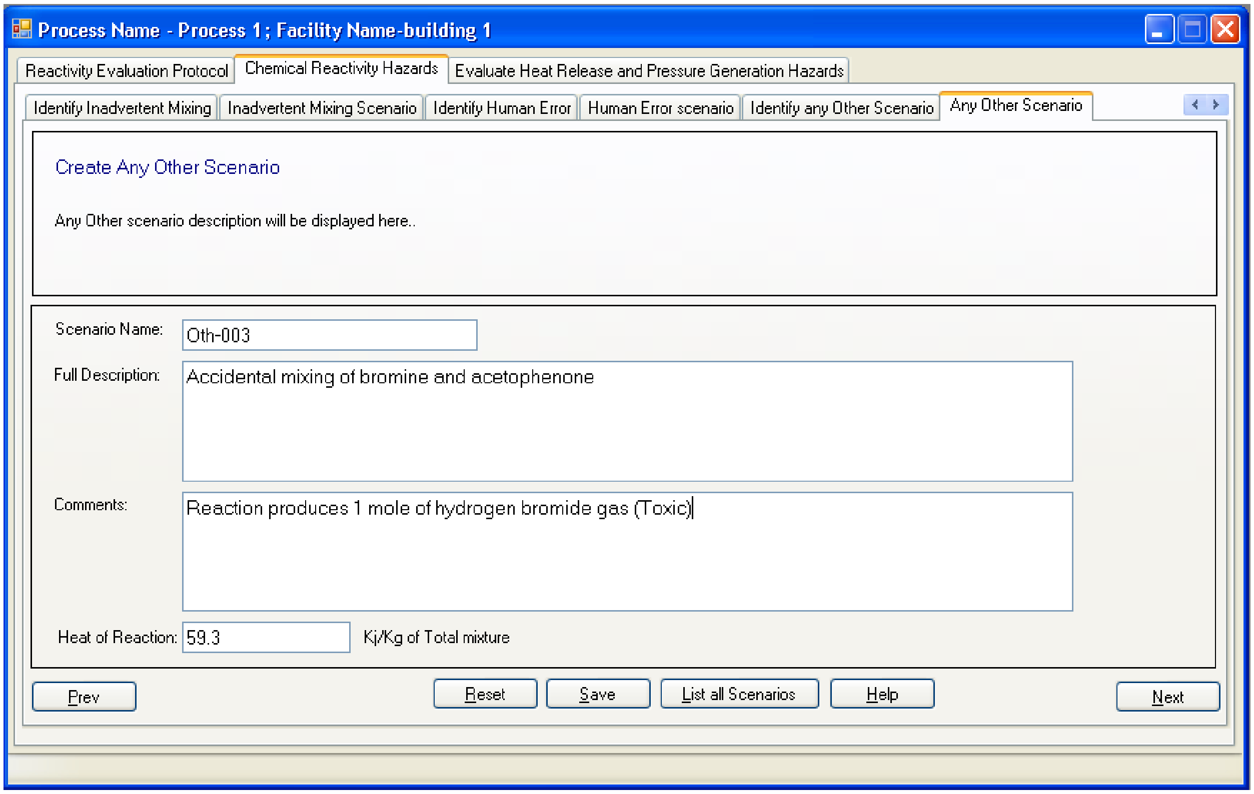
The molecular weight of acetophenone = 120.2g.mole
The molecular weight of bromine is 159.8g/mole

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



Create Any Other Scenario

Any Other scenario description will be displayed here..

Scenario Name: Oth-003

Full Description: Accidental mixing of bromine and acetophenone

Comments: Reaction produces 1 mole of hydrogen bromide gas (Toxic)

Heat of Reaction: 59.3 Kj/Kg of Total mixture

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.

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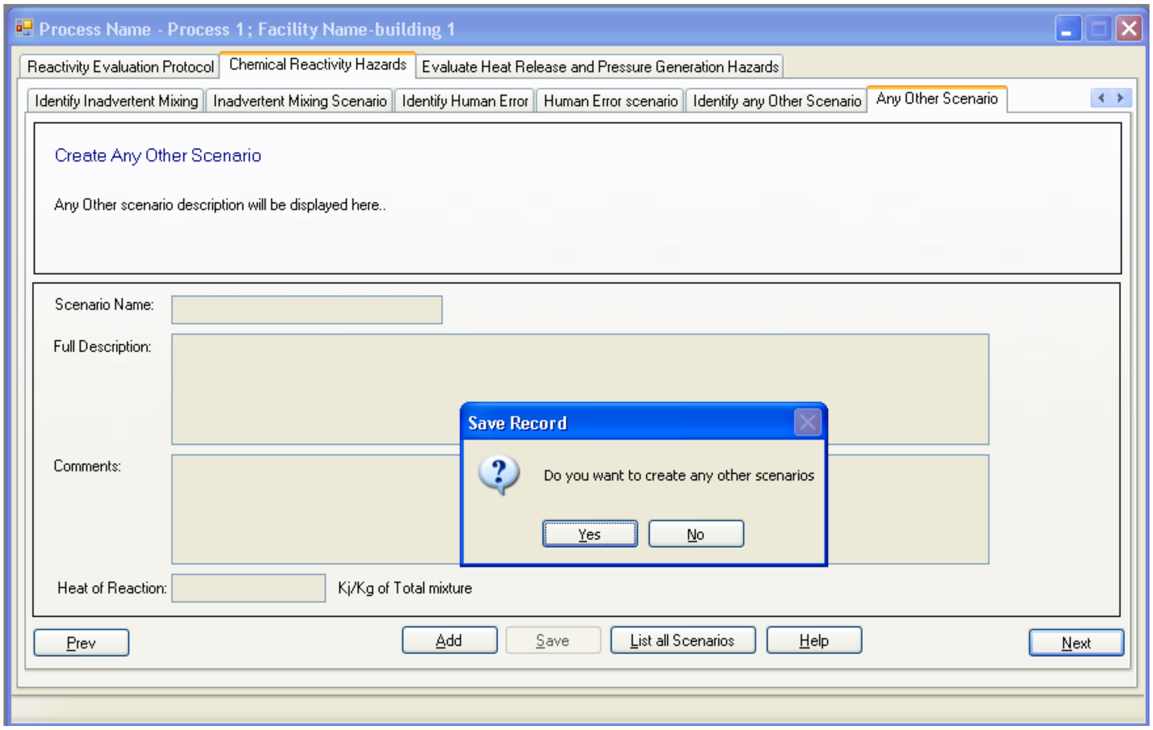
5.3.8 Evaluation of Scenarios

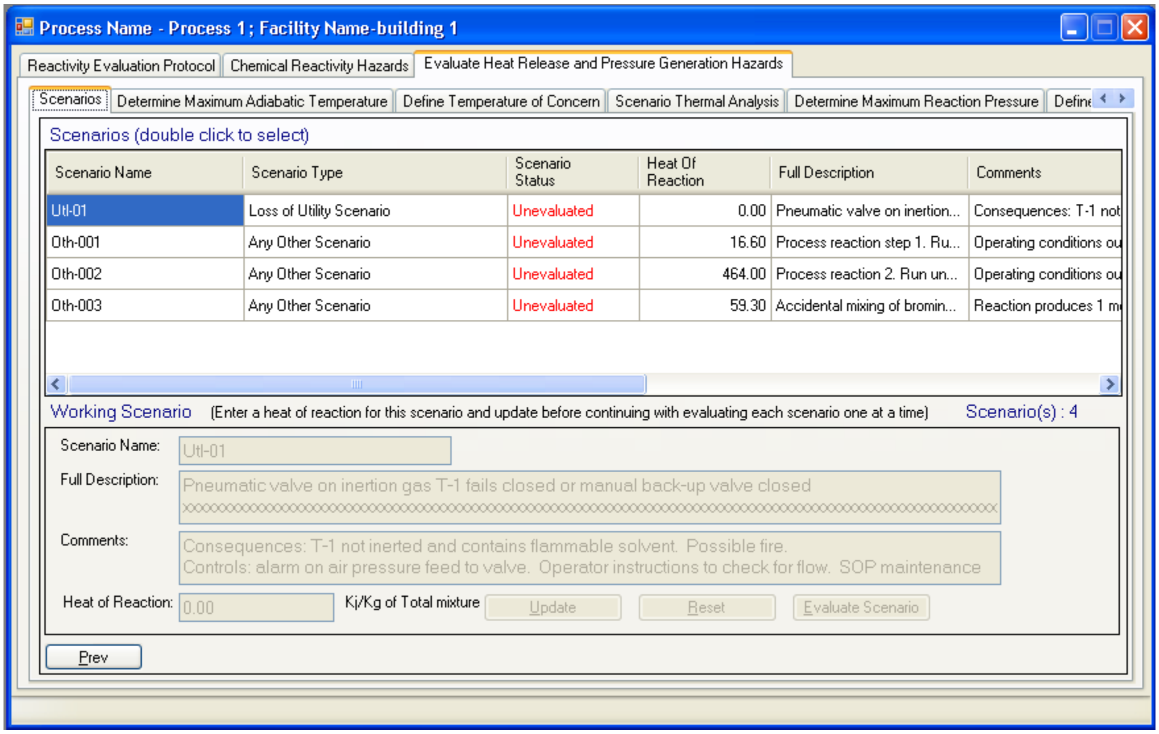
Upon saving your last scenario press the next button. The program will pop-up a box asking if you want to create any more scenarios. Answer NO to move to the scenario evaluation phase. Alternately use the tabs to navigate to scenario evaluation.



Create Any Other Scenario

Any Other scenario description will be displayed here..

Do you want to create any other scenarios



Scenarios (double click to select)

Scenario Name	Scenario Type	Scenario Status	Heat Of Reaction	Full Description	Comments
Utl-01	Loss of Utility Scenario	Unevaluated	0.00	Pneumatic valve on inertion...	Consequences: T-1 not
Oth-001	Any Other Scenario	Unevaluated	16.60	Process reaction step 1. Ru...	Operating conditions ou
Oth-002	Any Other Scenario	Unevaluated	464.00	Process reaction 2. Run un...	Operating conditions ou
Oth-003	Any Other Scenario	Unevaluated	59.30	Accidental mixing of bromin...	Reaction produces 1 m

Working Scenario (Enter a heat of reaction for this scenario and update before continuing with evaluating each scenario one at a time) Scenario(s) : 4

Scenario Name: Utl-01

Full Description: Pneumatic valve on inertion gas T-1 fails closed or manual back-up valve closed
xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx

Comments: Consequences: T-1 not inerted and contains flammable solvent. Possible fire.
Controls: alarm on air pressure feed to valve. Operator instructions to check for flow. SOP maintenance

Heat of Reaction: 0.00 Kj/Kg of Total mixture

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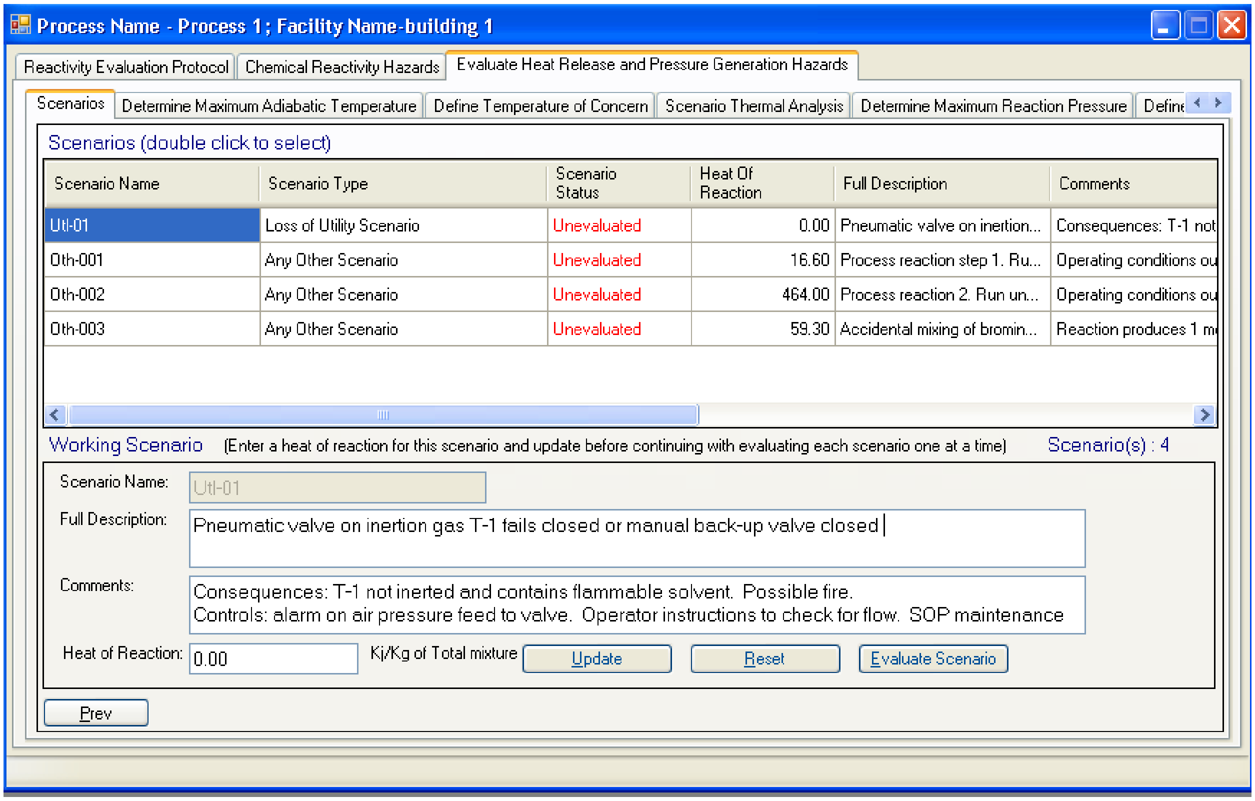
5.3.8.1 Evaluation of Utl-01

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



Scenarios (double click to select)

Scenario Name	Scenario Type	Scenario Status	Heat Of Reaction	Full Description	Comments
Utl-01	Loss of Utility Scenario	Unevaluated	0.00	Pneumatic valve on inertion...	Consequences: T-1 not
Oth-001	Any Other Scenario	Unevaluated	16.60	Process reaction step 1. Ru...	Operating conditions ou
Oth-002	Any Other Scenario	Unevaluated	464.00	Process reaction 2. Run un...	Operating conditions ou
Oth-003	Any Other Scenario	Unevaluated	59.30	Accidental mixing of bromin...	Reaction produces 1 m

Working Scenario (Enter a heat of reaction for this scenario and update before continuing with evaluating each scenario one at a time) Scenario(s) : 4

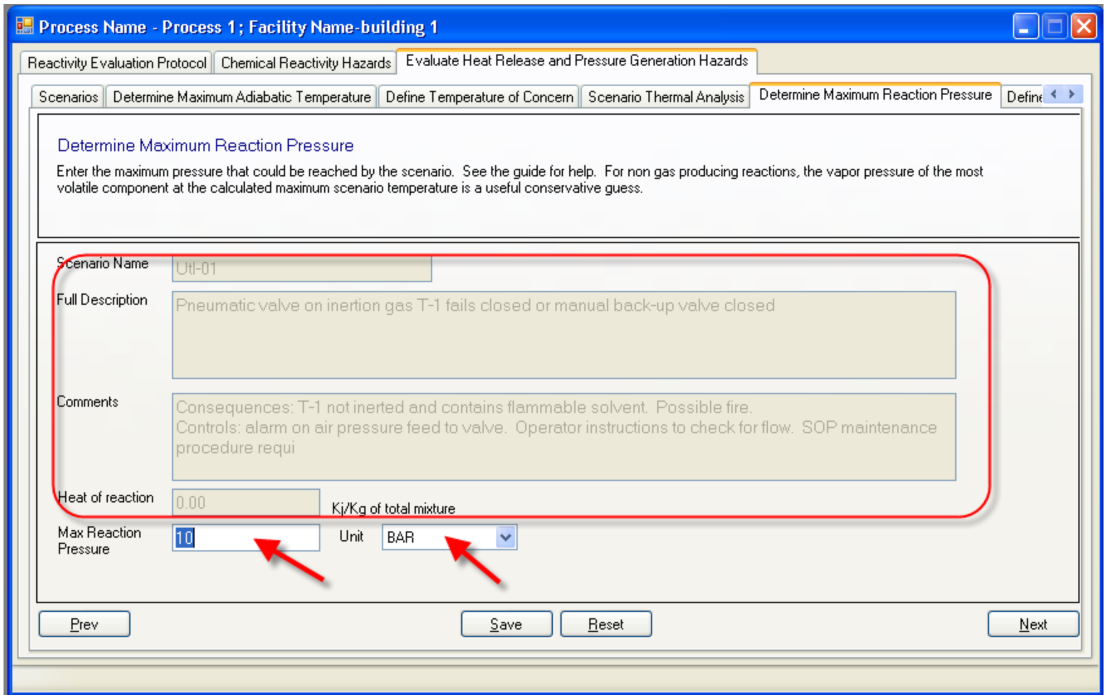
Scenario Name: Utl-01

Full Description: Pneumatic valve on inertion gas T-1 fails closed or manual back-up valve closed

Comments: Consequences: T-1 not inerted and contains flammable solvent. Possible fire.
Controls: alarm on air pressure feed to valve. Operator instructions to check for flow. SOP maintenance

Heat of Reaction: 0.00 Kj/Kg of Total mixture

Press the “Evaluate scenario” button



Determine Maximum Reaction Pressure

Enter the maximum pressure that could be reached by the scenario. See the guide for help. For non gas producing reactions, the vapor pressure of the most volatile component at the calculated maximum scenario temperature is a useful conservative guess.

Scenario Name: Utl-01

Full Description: Pneumatic valve on inertion gas T-1 fails closed or manual back-up valve closed

Comments: Consequences: T-1 not inerted and contains flammable solvent. Possible fire.
Controls: alarm on air pressure feed to valve. Operator instructions to check for flow. SOP maintenance procedure requi

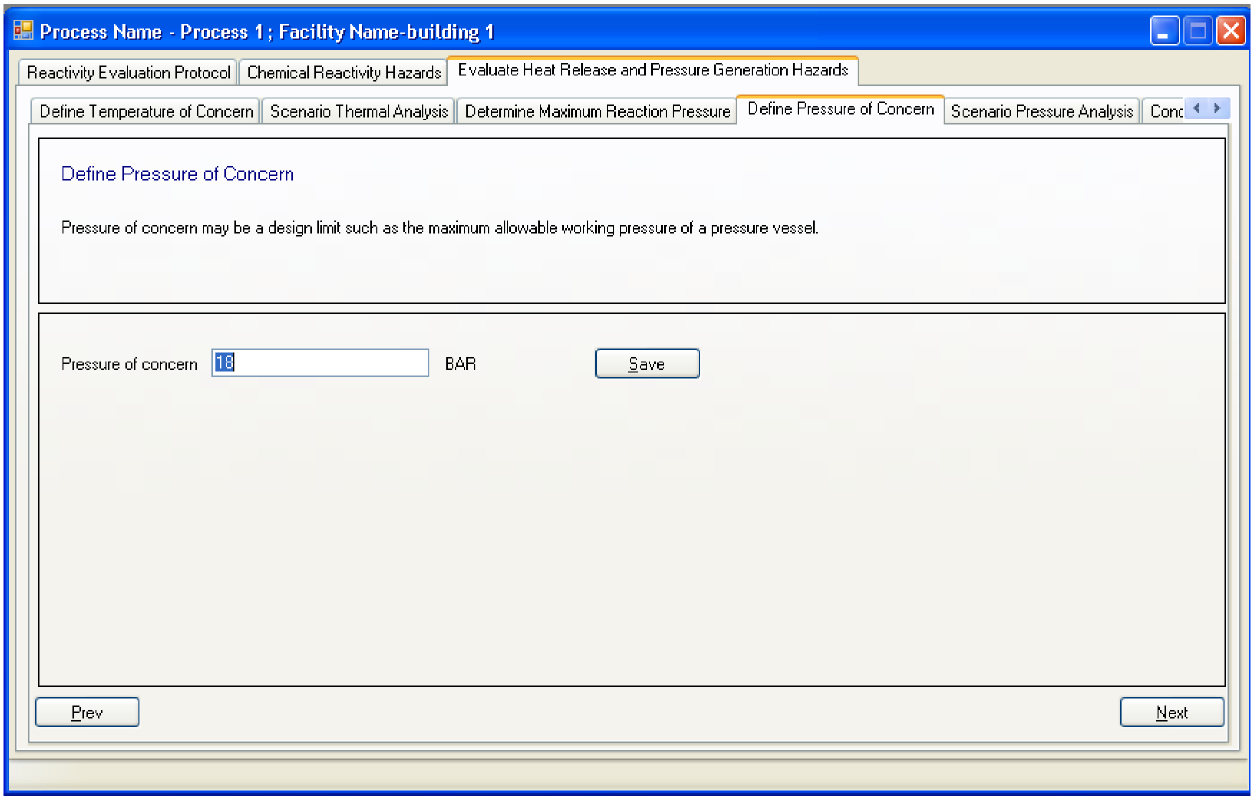
Heat of reaction: 0.00 Kj/Kg of total mixture

Max Reaction Pressure: 10 Unit: BAR

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



Define Pressure of Concern

Pressure of concern may be a design limit such as the maximum allowable working pressure of a pressure vessel.

Pressure of concern 18 BAR

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.

Helpful Hint

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.

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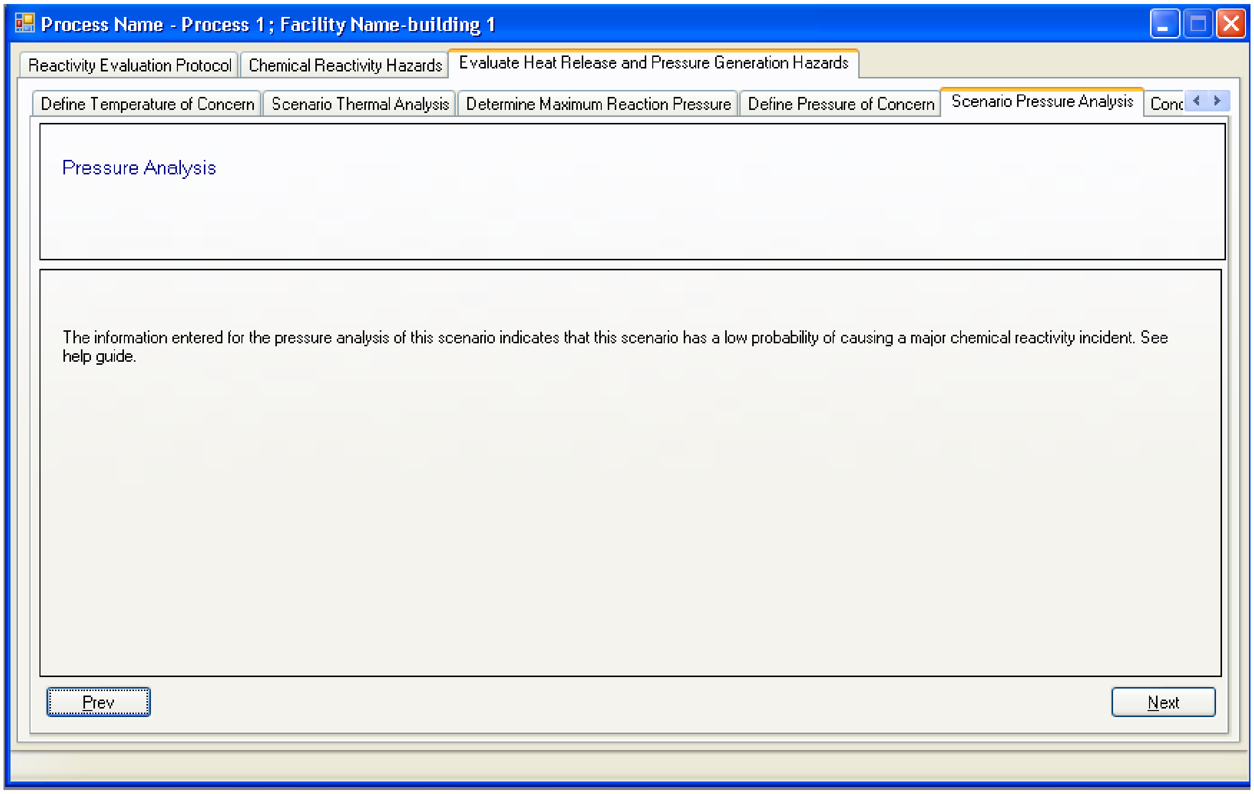

The information entered for the pressure analysis of this scenario indicates that this scenario has a low probability of causing a major chemical reactivity incident. See help guide.

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.

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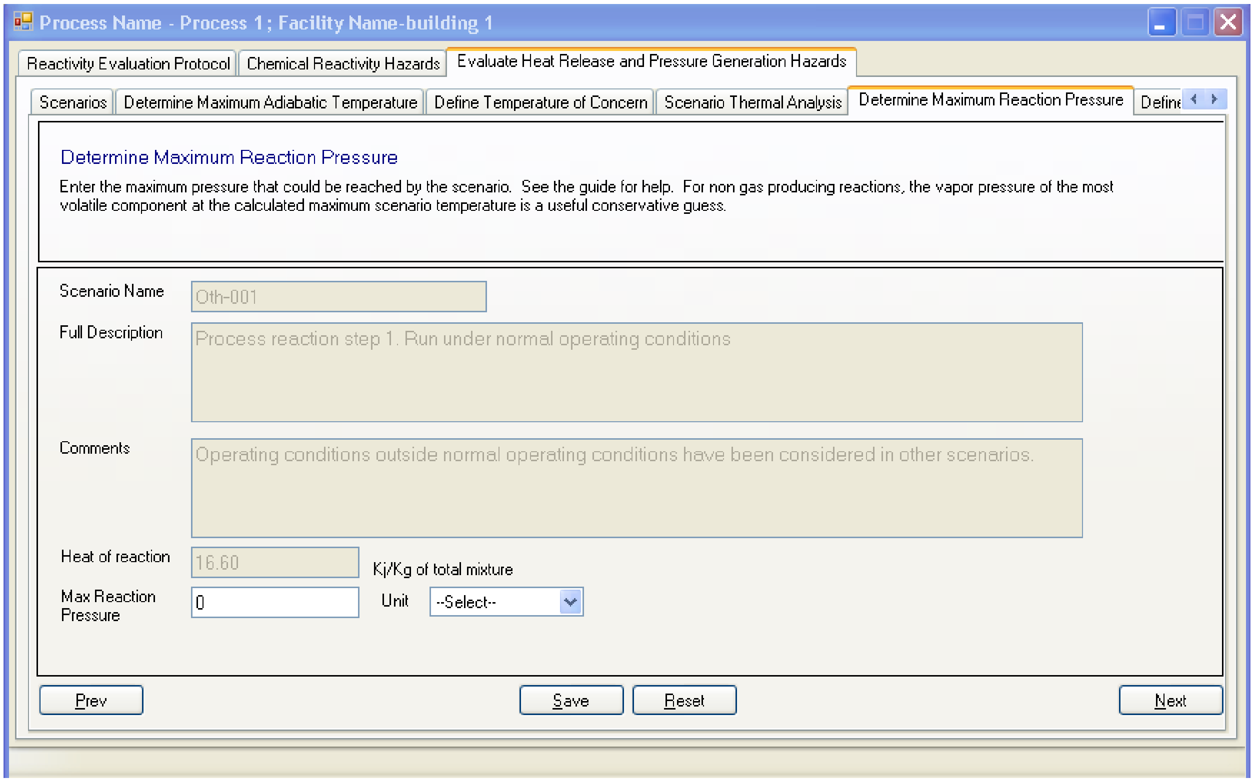
5.3.8.2 Evaluation of Reaction step 1 (Oth-001)

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



Determine Maximum Reaction Pressure

Enter the maximum pressure that could be reached by the scenario. See the guide for help. For non gas producing reactions, the vapor pressure of the most volatile component at the calculated maximum scenario temperature is a useful conservative guess.

Scenario Name: Oth-001

Full Description: Process reaction step 1. Run under normal operating conditions

Comments: Operating conditions outside normal operating conditions have been considered in other scenarios.

Heat of reaction: 16.60 Kj/Kg of total mixture

Max Reaction Pressure: 0 Unit: --Select--

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.

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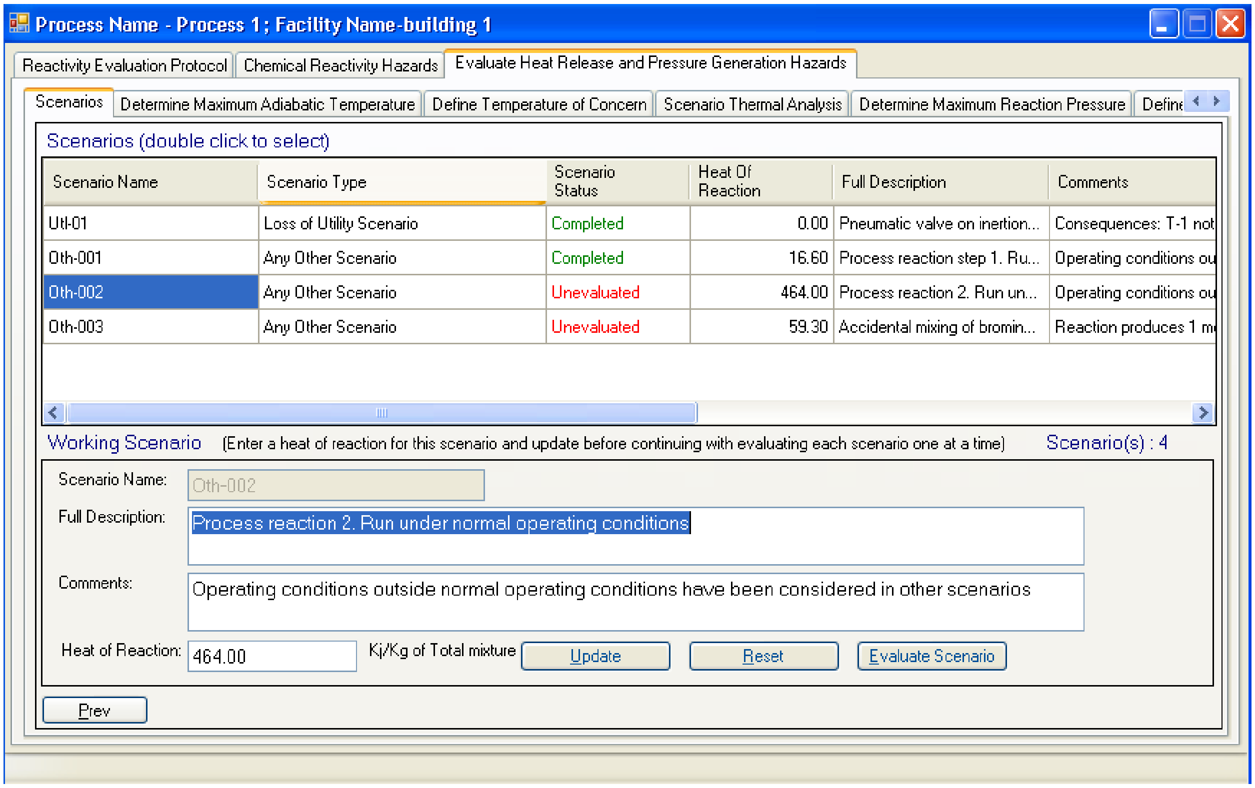
Go back to the scenario evaluation area by choosing evaluate another scenario.

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



Scenario Name	Scenario Type	Scenario Status	Heat Of Reaction	Full Description	Comments
Utl-01	Loss of Utility Scenario	Completed	0.00	Pneumatic valve on inertion...	Consequences: T-1 not
Oth-001	Any Other Scenario	Completed	16.60	Process reaction step 1. Ru...	Operating conditions ou
Oth-002	Any Other Scenario	Unevaluated	464.00	Process reaction 2. Run un...	Operating conditions ou
Oth-003	Any Other Scenario	Unevaluated	59.30	Accidental mixing of bromin...	Reaction produces 1 m

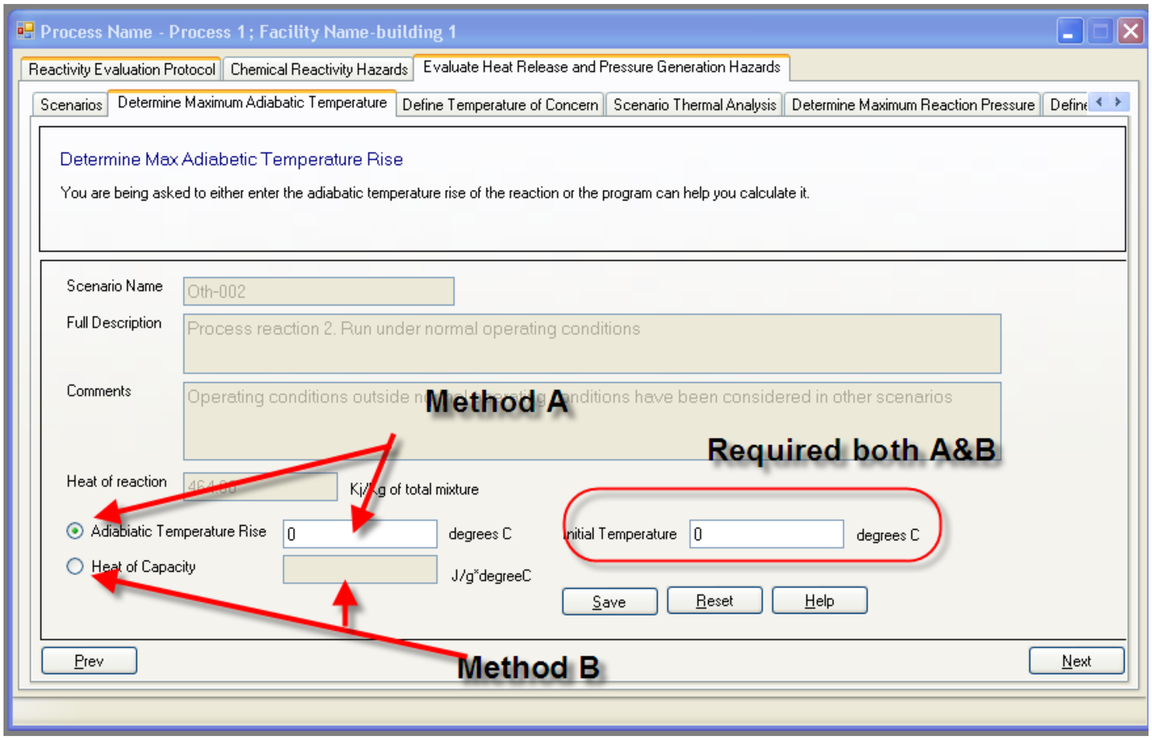
Scenario Name: Oth-002

Full Description: Process reaction 2. Run under normal operating conditions

Comments: Operating conditions outside normal operating conditions have been considered in other scenarios

Heat of Reaction: 464.00 Kj/Kg of Total mixture

This time the program asks for more information for assessing the thermal hazard of the process.



Determine Max Adiabetic Temperature Rise

You are being asked to either enter the adiabatic temperature rise of the reaction or the program can help you calculate it.

Scenario Name: Oth-002

Full Description: Process reaction 2. Run under normal operating conditions

Comments: Operating conditions outside normal operating conditions have been considered in other scenarios

Heat of reaction: 464.00 Kj/Kg of total mixture

● Adiabatic Temperature Rise: 0 degrees C

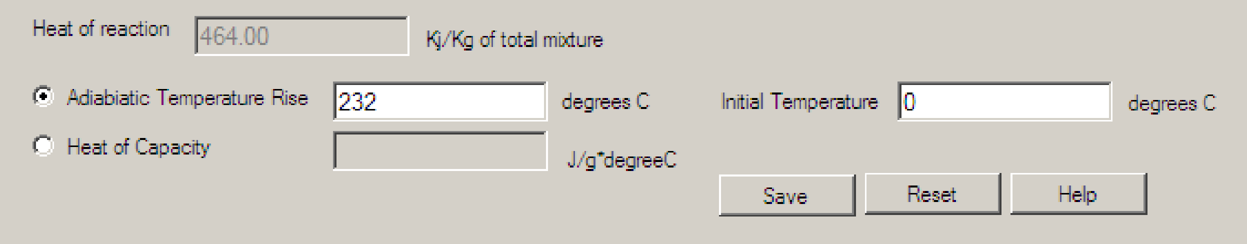
Initial Temperature: 0 degrees C

○ Heat of Capacity: J/g*degreeC

There are two methods of data entry here.

Method A

You can enter the adiabatic heat rise directly



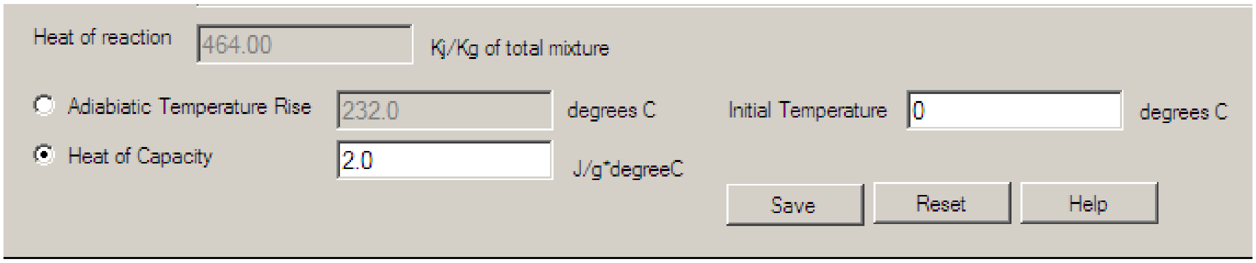
Heat of reaction: 464.00 Kj/Kg of total mixture

● Adiabiatic Temperature Rise: 232 degrees C

Initial Temperature: 0 degrees C

○ Heat of Capacity: J/g*degreeC

Method B
The program will calculate it for you from the heat of reaction and heat capacity of the mixture.



Heat of reaction: 464.00 Kj/Kg of total mixture

○ Adiabiatic Temperature Rise: 232.0 degrees C

Initial Temperature: 0 degrees C

● Heat of Capacity: 2.0 J/g*degreeC

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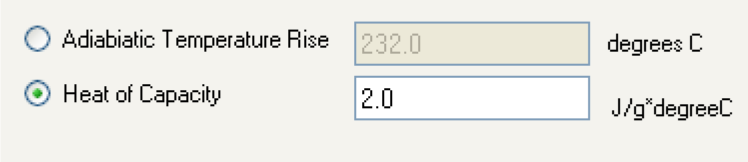
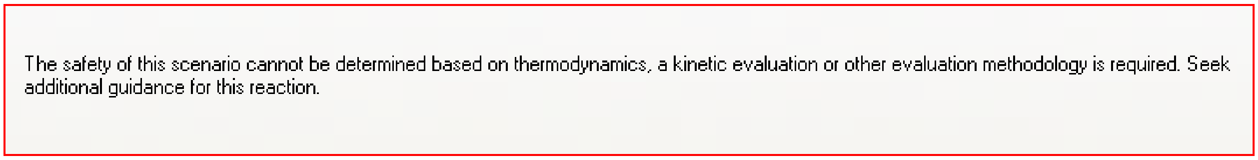
In this case we have a reaction mixture with a heat capacity of 2j/g°C which is typical for an organic reaction mixture. Our reaction starts at 0°C.

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



○ Adiabatic Temperature Rise 232.0 degrees C
● Heat of Capacity 2.0 J/g*degreeC

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°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.

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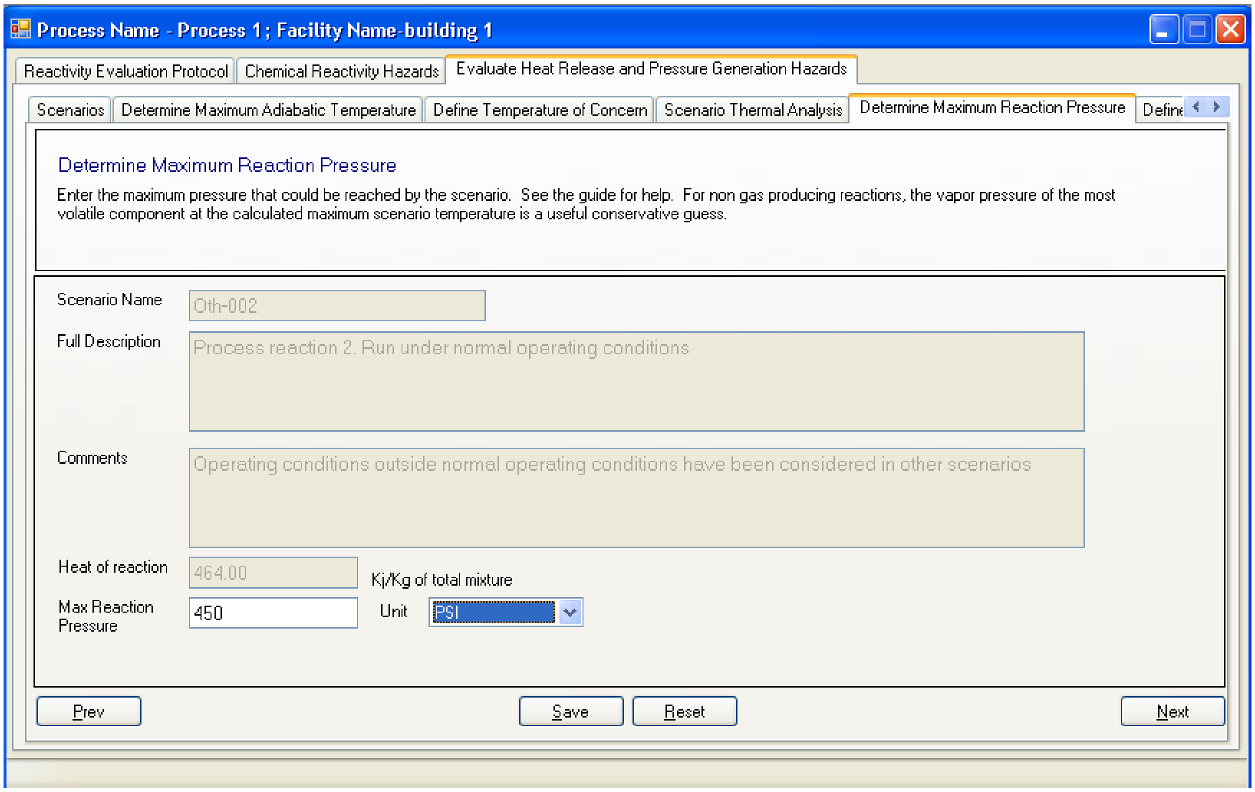
The program will now evaluate the Pressure hazard

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 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.



Determine Maximum Reaction Pressure

Enter the maximum pressure that could be reached by the scenario. See the guide for help. For non gas producing reactions, the vapor pressure of the most volatile component at the calculated maximum scenario temperature is a useful conservative guess.

Scenario Name: Oth-002

Full Description: Process reaction 2. Run under normal operating conditions

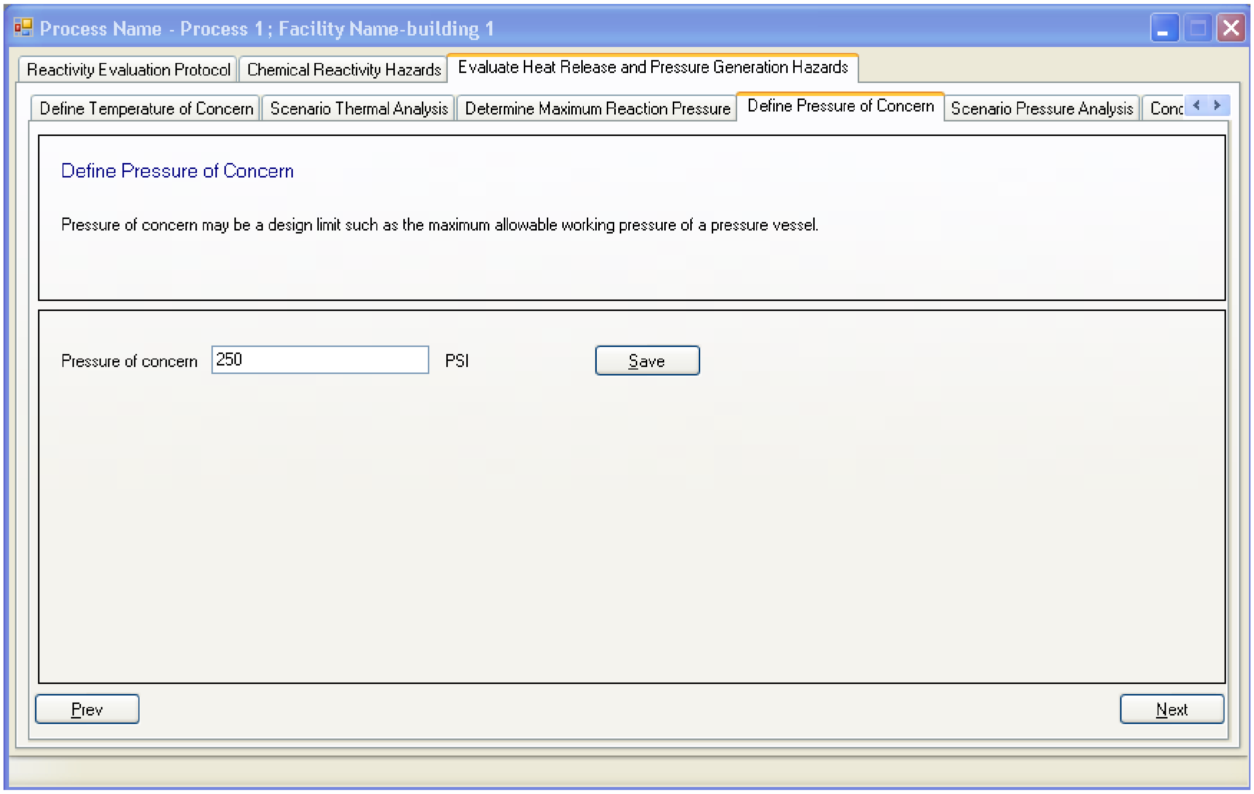
Comments: Operating conditions outside normal operating conditions have been considered in other scenarios

Heat of reaction: 464.00 Kj/Kg of total mixture

Max Reaction Pressure: 450 Unit: PSI

Press save and next

Recall our MAWP times 2.5 was 250psi so this becomes our temperature of concern

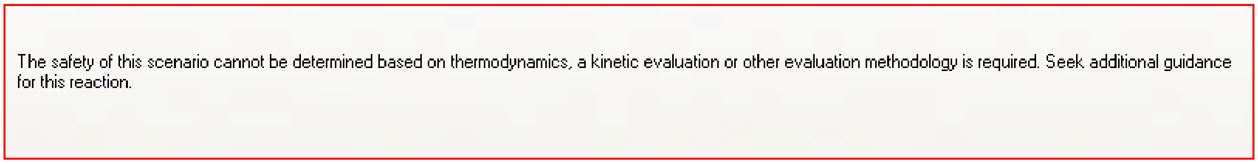


Define Pressure of Concern

Pressure of concern may be a design limit such as the maximum allowable working pressure of a pressure vessel.

Pressure of concern 250 PSI

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.

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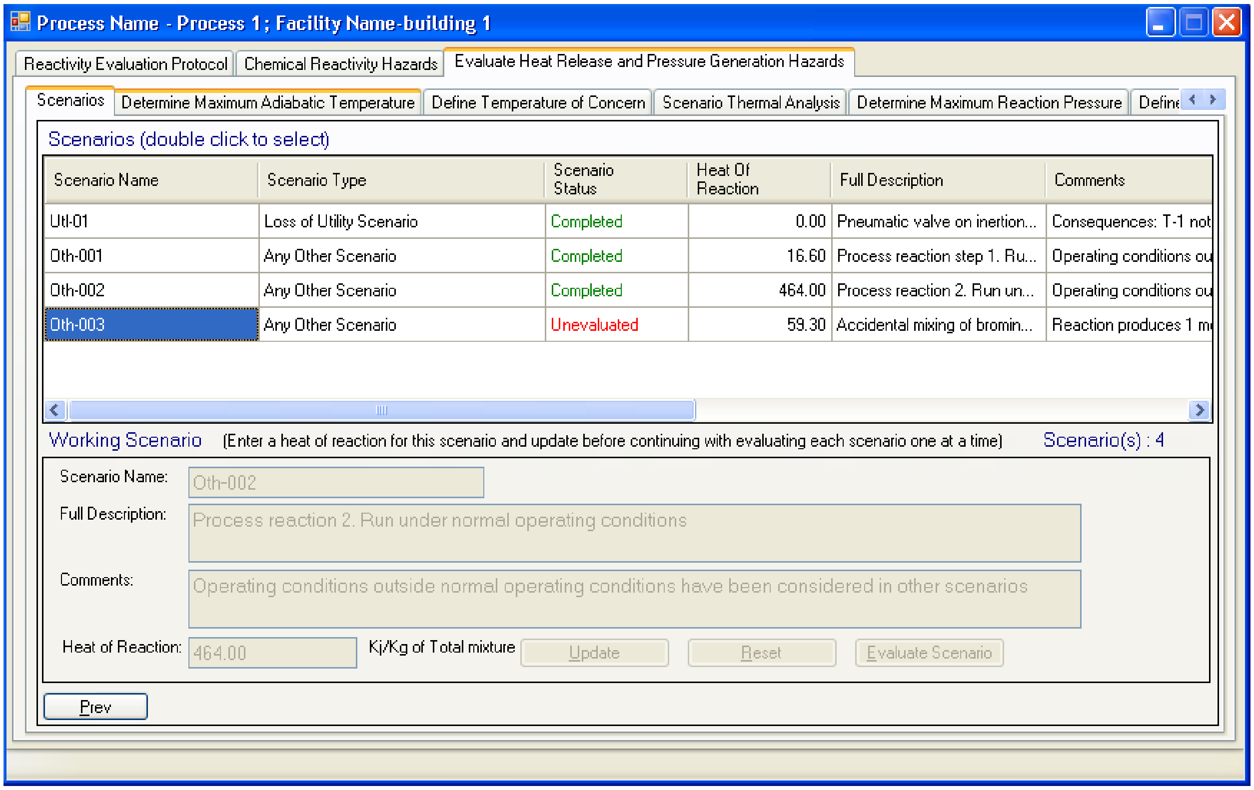


Scenarios (double click to select)

Scenario Name	Scenario Type	Scenario Status	Heat Of Reaction	Full Description	Comments
Utl-01	Loss of Utility Scenario	Completed	0.00	Pneumatic valve on inertion...	Consequences: T-1 not
Oth-001	Any Other Scenario	Completed	16.60	Process reaction step 1. Ru...	Operating conditions ou
Oth-002	Any Other Scenario	Completed	464.00	Process reaction 2. Run un...	Operating conditions ou
Oth-003	Any Other Scenario	Unevaluated	59.30	Accidental mixing of bromin...	Reaction produces 1 m

Working Scenario (Enter a heat of reaction for this scenario and update before continuing with evaluating each scenario one at a time) Scenario(s) : 4

Scenario Name: Oth-002

Full Description: Process reaction 2. Run under normal operating conditions

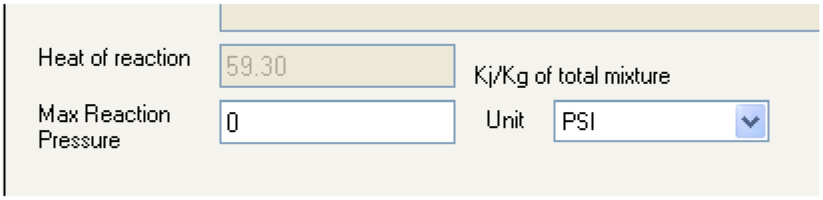
Comments: Operating conditions outside normal operating conditions have been considered in other scenarios

Heat of Reaction: 464.00 Kj/Kg of Total mixture

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.

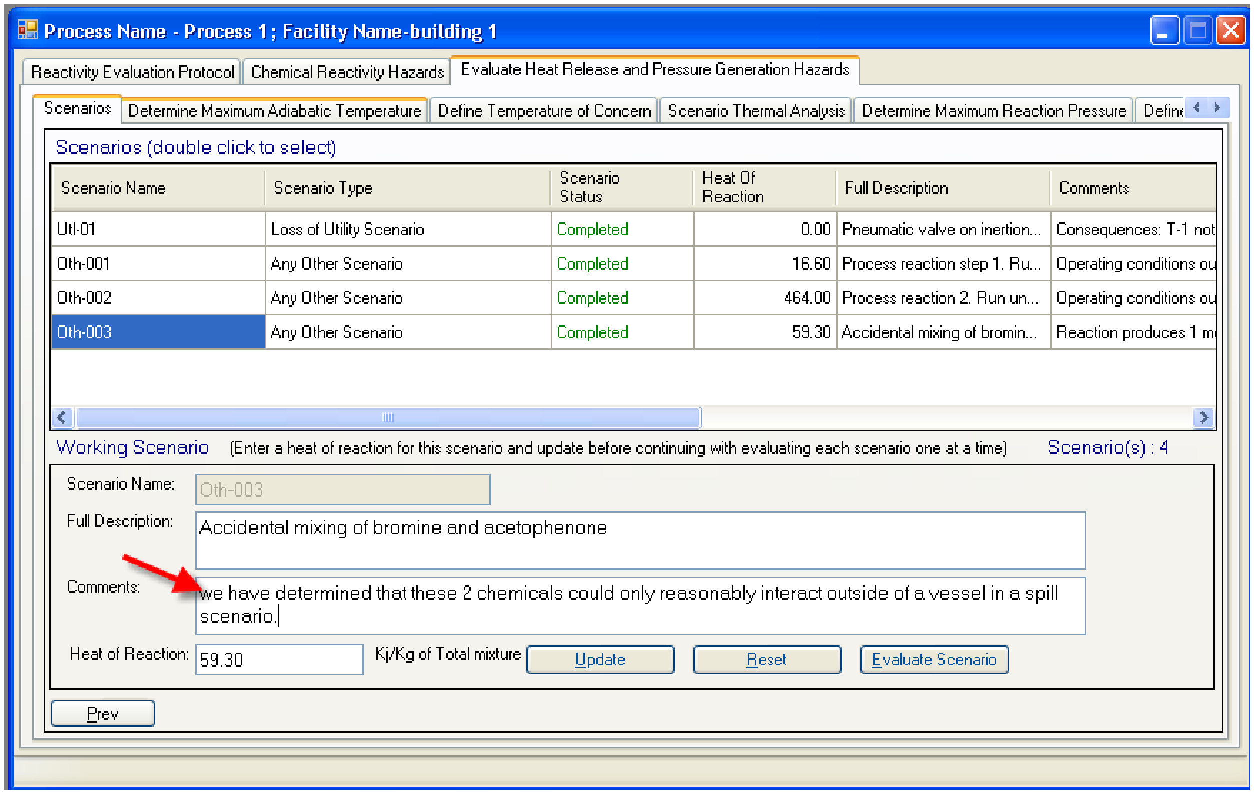


Heat of reaction: 59.30 Kj/Kg of total mixture

Max Reaction Pressure: 0 Unit: PSI

Pressure of concern: 0 PSI

To enter the comment navigate back to the list scenarios screen



Scenarios (double click to select)

Scenario Name	Scenario Type	Scenario Status	Heat Of Reaction	Full Description	Comments
Utl-01	Loss of Utility Scenario	Completed	0.00	Pneumatic valve on inertion...	Consequences: T-1 not
Oth-001	Any Other Scenario	Completed	16.60	Process reaction step 1. Ru...	Operating conditions ou
Oth-002	Any Other Scenario	Completed	464.00	Process reaction 2. Run un...	Operating conditions ou
Oth-003	Any Other Scenario	Completed	59.30	Accidental mixing of bromin...	Reaction produces 1 m

Working Scenario (Enter a heat of reaction for this scenario and update before continuing with evaluating each scenario one at a time) Scenario(s) : 4

Scenario Name: Oth-003

Full Description: Accidental mixing of bromine and acetophenone

Comments: we have determined that these 2 chemicals could only reasonably interact outside of a vessel in a spill scenario.

Heat of Reaction: 59.30 Kj/Kg of Total mixture

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)

Matrix	ACETOPHENONE	BROMINE	DICHLOROMETHANE	PHENACYL BROMIDE	SODIUM AZIDE	TETRAHYDROFURAN	TOLUENE SULFONIC ACI	TRIPHENYL PHOSPHINE	WATER	Line Kleen	Siltherm XLT
BROMINE	A5, A6, B4, C, D3, E, G, A9										
DICHLOROMETHANE	🟩	A2, A6, C, D3, B4									
PHENACYL BROMIDE	🟩	A2, A6, C, D3, A5, B4, E, G, A9	🟩								
SODIUM AZIDE	C, D4	A6, C, D3, G, A9	A6, B6, C	A6, B6, C, D4							
TETRAHYDROFURAN	🟩	A2, A6, A8, B4, C, D3, G	D3	D3	A6, C						
TOLUENE SULFONIC ACID, LIQUID, \	A6, B4, C, D3	A6, A8, A9, B6, C, B4, D3	A2, B1, C, D3	A2, B1, C, D3, A6, B4	A6, B4, B6, C	A6, B4, C, E					
TRIPHENYL PHOSPHINE	B5, C	A9, B4, C, B6	A9, B4, C, D3	A9, B4, C, D3, B5	A6, B6, C	A2, A6, B4, B5, C	A6, A9, B4, B5, C				
WATER	🟩	C, D3, D5, D6, D7, G	D3, D7	D3, D7	D4	D3, D7, E	D6, D7	B4, B5, D3, D6, D7, G			
Line Kleen	C	A9, B4, C, D3, B6, D5, D6, D7, G, A6	B1, C, D3, G, D7	B1, C, D3, G, D7	A10, B6, C, A3, A6, D4	A6, B5, C, D3, D7, E	A9, B1, B6, C, D6, D7	A6, B1, B5, C, B4, D3, D6, D7, G	D3, D6, D7, B5, E		
Siltherm XLT	🟩	A5, A6, B1, C, D1, A9, B4, D3	🟩	🟩	C	🟩	A6, B3, C, D3	A6, B5, C, D1	🟩	C	
Compound 987654321	🟩	A6, B4, C, D3, B6	C, G	C, G	A10, A3, A6, C, D4	🟩	B1, B6, C	A9, B6, C, B1, B5	B5, D3, D6, D7, E	C, D3, D6, G, B6, B5, D7, E	🟩

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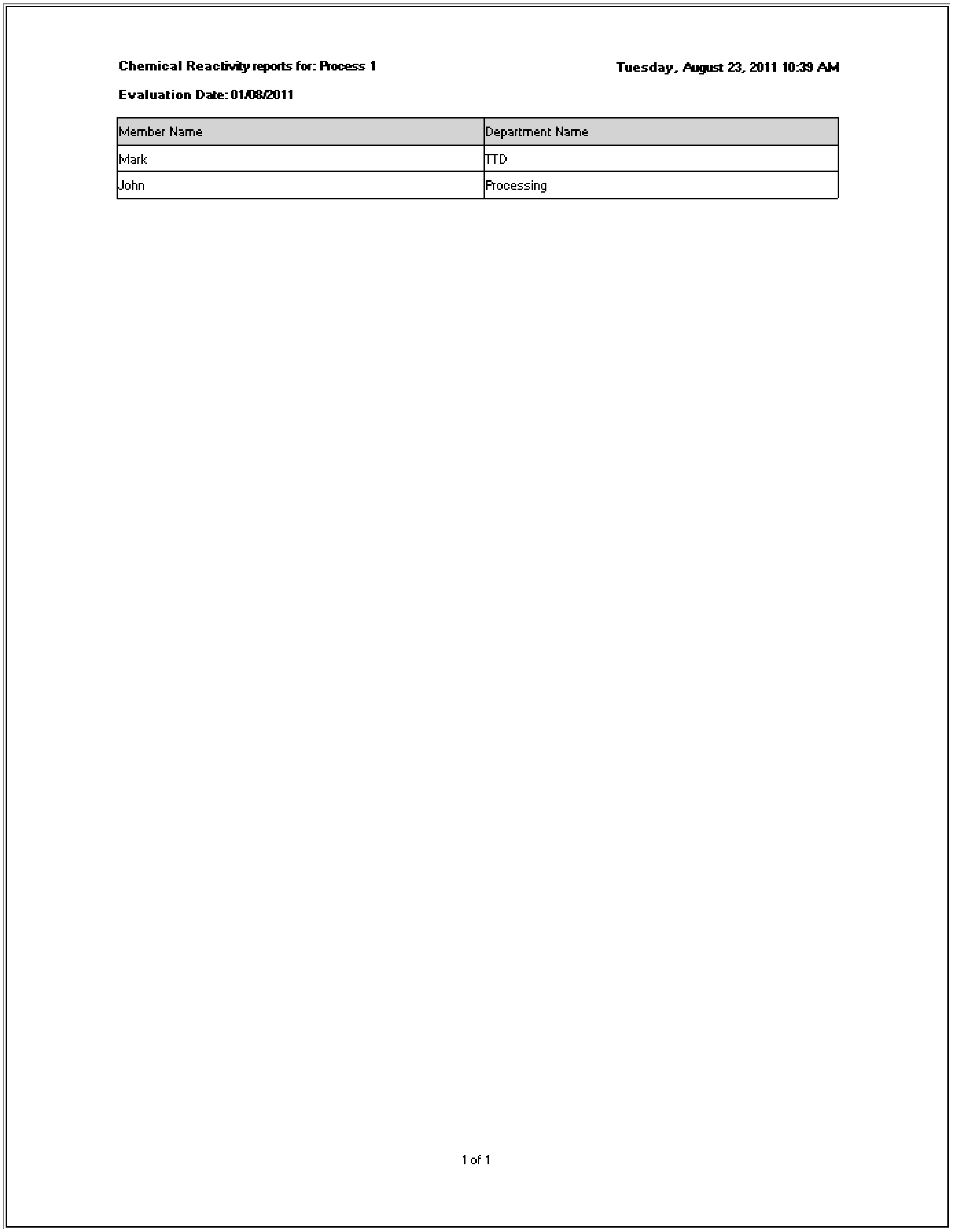
5.3.9.3 Chemical reactivity evaluation Report

5.3.9.3.1 Team tab



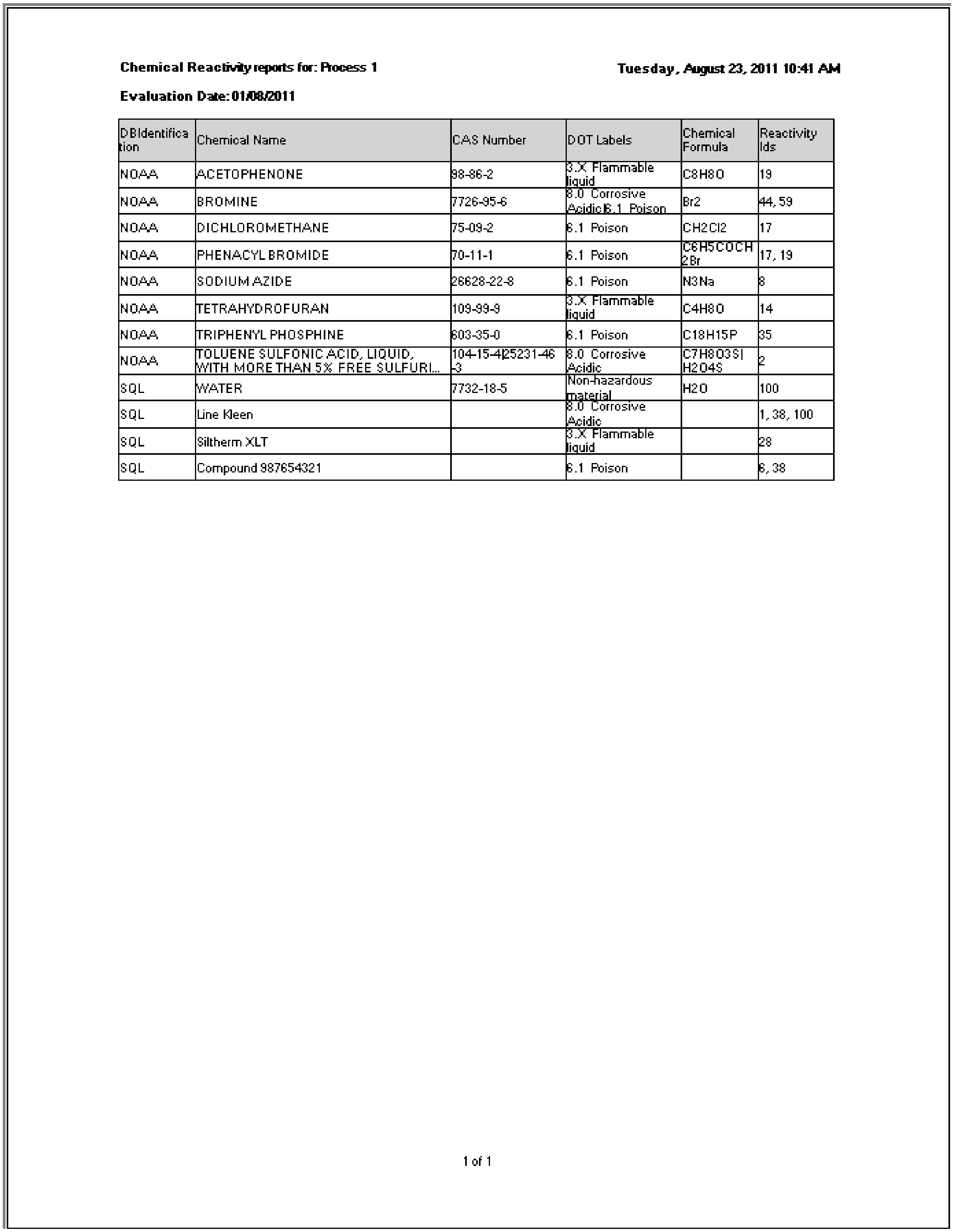
Chemical Reactivity reports for: Process 1 **Tuesday, August 23, 2011 10:39 AM**

Evaluation Date: 01/08/2011

Member Name	Department Name
Mark	TTD
John	Processing

1 of 1

5.3.9.3.2 Chemicals tab



Chemical Reactivity reports for: Process 1 **Tuesday, August 23, 2011 10:41 AM**

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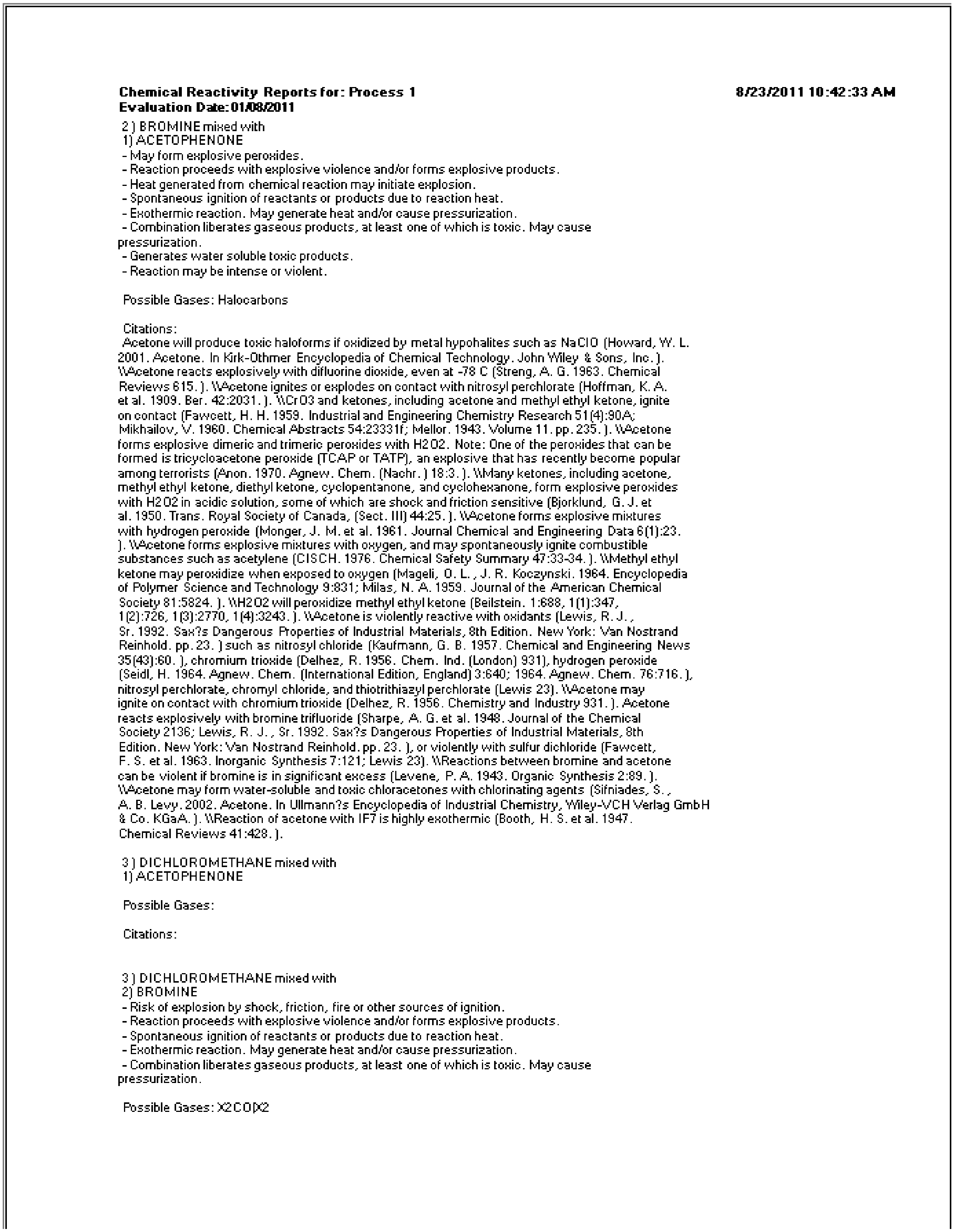
DBIdentification	Chemical Name	CAS Number	DOT Labels	Chemical Formula	Reactivity Ids
NOAA	ACETOPHENONE	98-86-2	3.X Flammable liquid	C8H8O	19
NOAA	BROMINE	7726-95-6	8.0 Corrosive Acidic|6.1 Poison	Br2	44, 59
NOAA	DICHLOROMETHANE	75-09-2	6.1 Poison	CH2Cl2	17
NOAA	PHENACYL BROMIDE	70-11-1	6.1 Poison	C6H5COCH2Br	17, 19
NOAA	SODIUM AZIDE	26628-22-8	6.1 Poison	N3Na	8
NOAA	TETRAHYDROFURAN	109-99-9	3.X Flammable liquid	C4H8O	14
NOAA	TRIPHENYL PHOSPHINE	603-35-0	6.1 Poison	C18H15P	35
NOAA	TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURI...	104-15-4|25231-46-3	8.0 Corrosive Acidic	C7H8O3S|H2O4S	2
SQL	WATER	7732-18-5	Non-hazardous material	H2O	100
SQL	Line Kleen		8.0 Corrosive Acidic		1, 38, 100
SQL	Siltherm XLT		3.X Flammable liquid		28
SQL	Compound 987654321		6.1 Poison		6, 38

1 of 1

5.3.9.3.3 Binary Matrix tab



Chemical Reactivity Reports for: Process 1 **8/23/2011 10:42:33 AM**
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2) BROMINE mixed with
1) ACETOPHENONE
- May form explosive peroxides.
- Reaction proceeds with explosive violence and/or forms explosive products.
- Heat generated from chemical reaction may initiate explosion.
- Spontaneous ignition of reactants 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.
- Generates water soluble toxic products.
- Reaction may be intense or violent.

Possible Gases: Halocarbons

Citations:
Acetone will produce toxic haloforms if oxidized by metal hypohalites such as NaClO (Howard, W. L. 2001. Acetone. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.). \\Acetone reacts explosively with difluorine dioxide, even at -78 C (Streng, A. G. 1963. Chemical Reviews 615.). \\Acetone ignites or explodes on contact with nitrosyl perchlorate (Hoffman, K. A. et al. 1909. Ber. 42:2031.). \\CrO3 and ketones, including acetone and methyl ethyl ketone, ignite on contact (Fawcett, H. H. 1959. Industrial and Engineering Chemistry Research 51(4):90A; Mikhailov, V. 1960. Chemical Abstracts 54:23331f; Mellor. 1943. Volume 11. pp. 235.). \\Acetone forms explosive dimeric and trimeric peroxides with H2O2. Note: One of the peroxides that can be formed is tricycloacetone peroxide (TCAP or TATP), an explosive that has recently become popular among terrorists (Anon. 1970. Agnew. Chem. (Nachr.) 18:3.). \\Many ketones, including acetone, methyl ethyl ketone, diethyl ketone, cyclopentanone, and cyclohexanone, form explosive peroxides with H2O2 in acidic solution, some of which are shock and friction sensitive (Bjorklund, G. J. et al. 1950. Trans. Royal Society of Canada, (Sect. III) 44:25.). \\Acetone forms explosive mixtures with hydrogen peroxide (Monger, J. M. et al. 1961. Journal Chemical and Engineering Data 6(1):23.). \\Acetone forms explosive mixtures with oxygen, and may spontaneously ignite combustible substances such as acetylene (CISCH. 1976. Chemical Safety Summary 47:33-34.). \\Methyl ethyl ketone may peroxidize when exposed to oxygen (Mageli, O. L., J. R. Koczynski. 1964. Encyclopedia of Polymer Science and Technology 9:831; Milas, N. A. 1959. Journal of the American Chemical Society 81:5824.). \\H2O2 will peroxidize methyl ethyl ketone (Beilstein. 1:688, 1(1):347, 1(2):726, 1(3):2770, 1(4):3243.). \\Acetone is violently reactive with oxidants (Lewis, R. J., Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 23.) such as nitrosyl chloride (Kaufmann, G. B. 1957. Chemical and Engineering News 35(43):60.), chromium trioxide (Delhez, R. 1956. Chem. Ind. (London) 931), hydrogen peroxide (Seidl, H. 1964. Agnew. Chem. (International Edition, England) 3:640; 1964. Agnew. Chem. 76:716.), nitrosyl perchlorate, chromyl chloride, and thiotrithiazyl perchlorate (Lewis 23). \\Acetone may ignite on contact with chromium trioxide (Delhez, R. 1956. Chemistry and Industry 931.). Acetone reacts explosively with bromine trifluoride (Sharpe, A. G. et al. 1948. Journal of the Chemical Society 2136; Lewis, R. J., Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 23.), or violently with sulfur dichloride (Fawcett, F. S. et al. 1963. Inorganic Synthesis 7:121; Lewis 23). \\Reactions between bromine and acetone can be violent if bromine is in significant excess (Levene, P. A. 1943. Organic Synthesis 2:89.). \\Acetone may form water-soluble and toxic chloracetones with chlorinating agents (Sifniades, S., A. B. Levy. 2002. Acetone. In Ullmann?s Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA.). \\Reaction of acetone with IF7 is highly exothermic (Booth, H. S. et al. 1947. Chemical Reviews 41:428.).

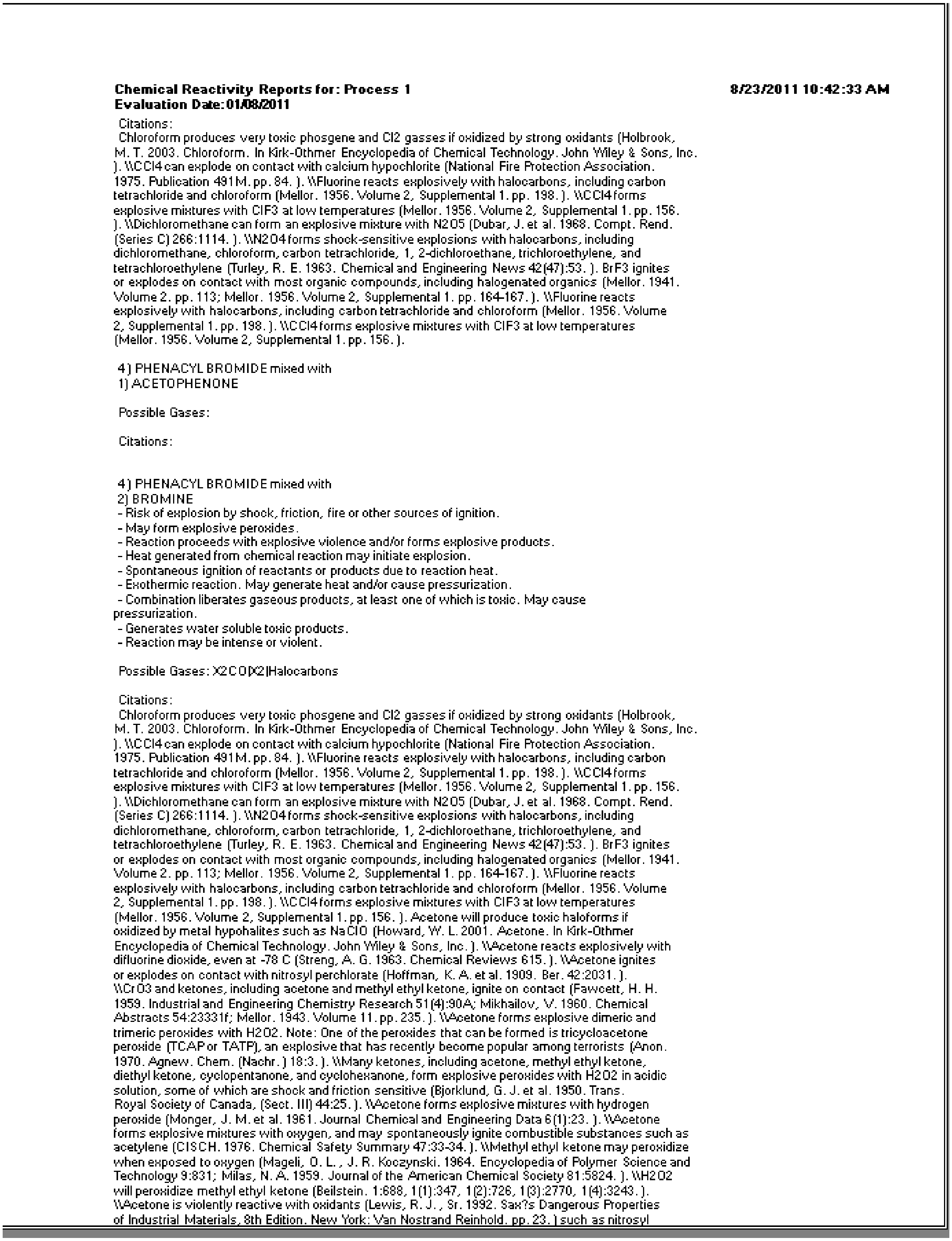
3) DICHLOROMETHANE mixed with
1) ACETOPHENONE

Possible Gases:

Citations:

3) DICHLOROMETHANE mixed with
2) BROMINE
- Risk of explosion by shock, friction, fire or other sources of ignition.
- Reaction proceeds with explosive violence and/or forms explosive products.
- Spontaneous ignition of reactants 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: X2CO|X2



Chemical Reactivity Reports for: Process 1 **8/23/2011 10:42:33 AM**
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Citations:

Chloroform produces very toxic phosgene and Cl2 gasses if oxidized by strong oxidants (Holbrook, M. T. 2003. Chloroform. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.). \\CCl4 can explode on contact with calcium hypochlorite (National Fire Protection Association. 1975. Publication 491M. pp. 84.). \\Fluorine reacts explosively with halocarbons, including carbon tetrachloride and chloroform (Mellor. 1956. Volume 2, Supplemental 1. pp. 198.). \\CCl4 forms explosive mixtures with ClF3 at low temperatures (Mellor. 1956. Volume 2, Supplemental 1. pp. 156.). \\Dichloromethane can form an explosive mixture with N2O5 (Dubar, J. et al. 1968. Compt. Rend. (Series C) 266:1114.). \\N2O4 forms shock-sensitive explosions with halocarbons, including dichloromethane, chloroform, carbon tetrachloride, 1, 2-dichloroethane, trichloroethylene, and tetrachloroethylene (Turley, R. E. 1963. Chemical and Engineering News 42(47):53.). BrF3 ignites or explodes on contact with most organic compounds, including halogenated organics (Mellor. 1941. Volume 2. pp. 113; Mellor. 1956. Volume 2, Supplemental 1. pp. 164-167.). \\Fluorine reacts explosively with halocarbons, including carbon tetrachloride and chloroform (Mellor. 1956. Volume 2, Supplemental 1. pp. 198.). \\CCl4 forms explosive mixtures with ClF3 at low temperatures (Mellor. 1956. Volume 2, Supplemental 1. pp. 156.).

4) PHENACYL BROMIDE mixed with
1) ACETOPHENONE

Possible Gases:

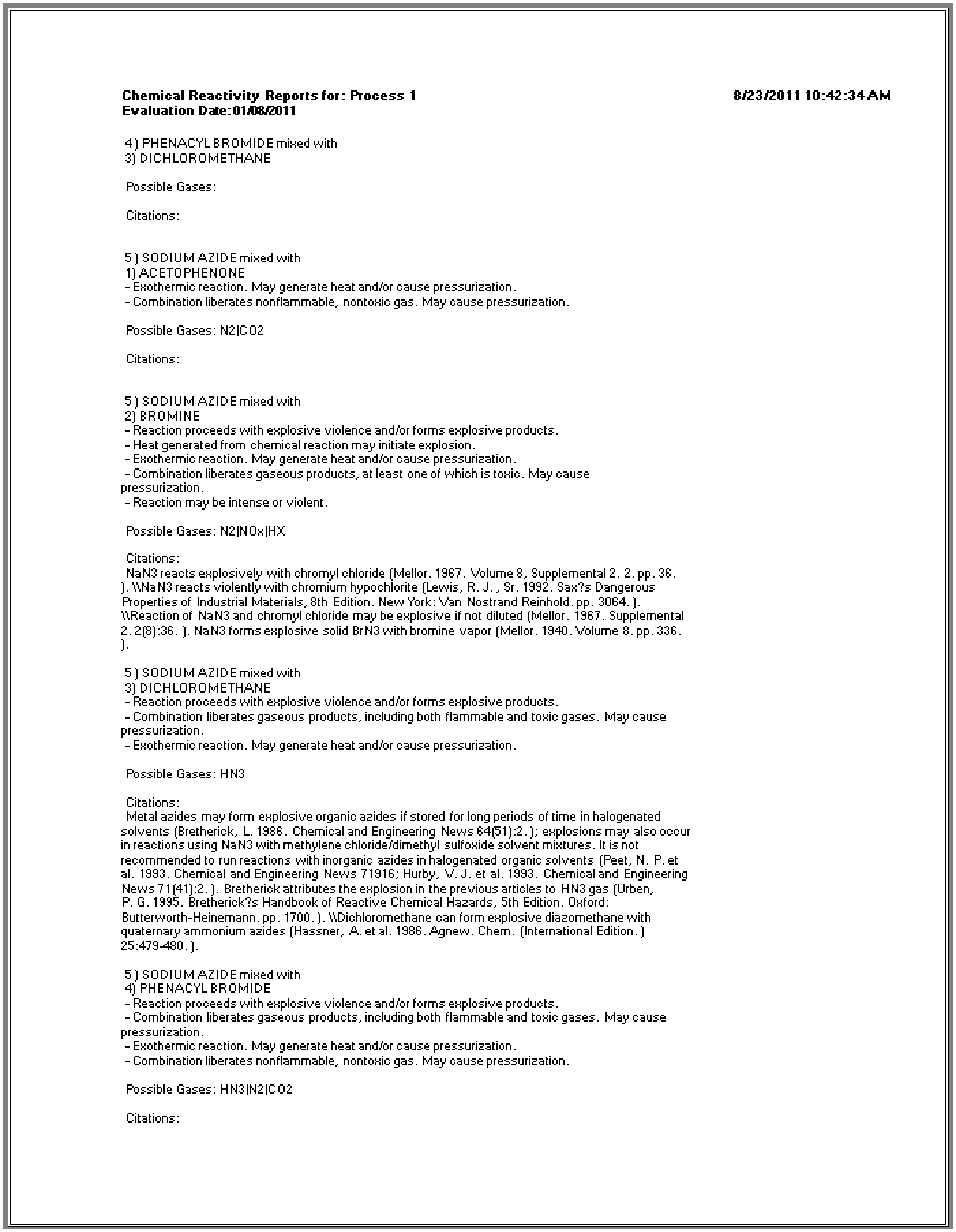
Citations:

4) PHENACYL BROMIDE mixed with
2) BROMINE
- Risk of explosion by shock, friction, fire or other sources of ignition.
- May form explosive peroxides.
- Reaction proceeds with explosive violence and/or forms explosive products.
- Heat generated from chemical reaction may initiate explosion.
- Spontaneous ignition of reactants 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.
- Generates water soluble toxic products.
- Reaction may be intense or violent.

Possible Gases: X2CO|X2|Halocarbons

Citations:

Chloroform produces very toxic phosgene and Cl2 gasses if oxidized by strong oxidants (Holbrook, M. T. 2003. Chloroform. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.). \\CCl4 can explode on contact with calcium hypochlorite (National Fire Protection Association. 1975. Publication 491M. pp. 84.). \\Fluorine reacts explosively with halocarbons, including carbon tetrachloride and chloroform (Mellor. 1956. Volume 2, Supplemental 1. pp. 198.). \\CCl4 forms explosive mixtures with ClF3 at low temperatures (Mellor. 1956. Volume 2, Supplemental 1. pp. 156.). \\Dichloromethane can form an explosive mixture with N2O5 (Dubar, J. et al. 1968. Compt. Rend. (Series C) 266:1114.). \\N2O4 forms shock-sensitive explosions with halocarbons, including dichloromethane, chloroform, carbon tetrachloride, 1, 2-dichloroethane, trichloroethylene, and tetrachloroethylene (Turley, R. E. 1963. Chemical and Engineering News 42(47):53.). BrF3 ignites or explodes on contact with most organic compounds, including halogenated organics (Mellor. 1941. Volume 2. pp. 113; Mellor. 1956. Volume 2, Supplemental 1. pp. 164-167.). \\Fluorine reacts explosively with halocarbons, including carbon tetrachloride and chloroform (Mellor. 1956. Volume 2, Supplemental 1. pp. 198.). \\CCl4 forms explosive mixtures with ClF3 at low temperatures (Mellor. 1956. Volume 2, Supplemental 1. pp. 156.). Acetone will produce toxic haloforms if oxidized by metal hypohalites such as NaClO (Howard, W. L. 2001. Acetone. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.). \\Acetone reacts explosively with difluorine dioxide, even at -78 C (Streng, A. G. 1963. Chemical Reviews 615.). \\Acetone ignites or explodes on contact with nitrosyl perchlorate (Hoffman, K. A. et al. 1909. Ber. 42:2031.). \\CrO3 and ketones, including acetone and methyl ethyl ketone, ignite on contact (Fawcett, H. H. 1959. Industrial and Engineering Chemistry Research 51(4):90A; Mikhailov, V. 1960. Chemical Abstracts 54:23331f; Mellor. 1943. Volume 11. pp. 235.). \\Acetone forms explosive dimeric and trimeric peroxides with H2O2. Note: One of the peroxides that can be formed is tricycloacetone peroxide (TCAP or TATP), an explosive that has recently become popular among terrorists (Anon. 1970. Agnew. Chem. (Nachr.) 18:3.). \\Many ketones, including acetone, methyl ethyl ketone, diethyl ketone, cyclopentanone, and cyclohexanone, form explosive peroxides with H2O2 in acidic solution, some of which are shock and friction sensitive (Bjorklund, G. J. et al. 1950. Trans. Royal Society of Canada, (Sect. III) 44:25.). \\Acetone forms explosive mixtures with hydrogen peroxide (Monger, J. M. et al. 1961. Journal Chemical and Engineering Data 6(1):23.). \\Acetone forms explosive mixtures with oxygen, and may spontaneously ignite combustible substances such as acetylene (CISCH. 1976. Chemical Safety Summary 47:33-34.). \\Methyl ethyl ketone may peroxidize when exposed to oxygen (Mageli, O. L., J. R. Koczynski. 1964. Encyclopedia of Polymer Science and Technology 9:831; Milas, N. A. 1959. Journal of the American Chemical Society 81:5824.). \\H2O2 will peroxidize methyl ethyl ketone (Beilstein. 1:688, 1(1):347, 1(2):726, 1(3):2770, 1(4):3243.). \\Acetone is violently reactive with oxidants (Lewis, R. J., Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 23.) such as nitrosyl



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Chemical Reactivity Reports for: Process 1                                8/23/2011 10:42:34 AM
Evaluation Date: 01/08/2011

 4) PHENACYL BROMIDE mixed with
 3) DICHLOROMETHANE

 Possible Gases:

 Citations:


 5 ) SODIUM AZIDE mixed with
 1) ACETOPHENONE
 - Exothermic reaction. May generate heat and/or cause pressurization.
 - Combination liberates nonflammable, nontoxic gas. 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 gaseous products, at least one of which is toxic. May cause
pressurization.
 - Reaction may be intense or violent.

 Possible Gases: N2|NOx|HX

 Citations:
 NaN3 reacts explosively with chromyl chloride (Mellor. 1967. Volume 8, Supplemental 2. 2. pp. 36.
). \\NaN3 reacts violently with chromium hypochlorite (Lewis, R. J., Sr. 1992. Sax?s Dangerous
Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 3064. ).
\\Reaction of NaN3 and chromyl chloride may be explosive if not diluted (Mellor. 1967. Supplemental
2. 2(8):36. ). NaN3 forms explosive solid BrN3 with bromine vapor (Mellor. 1940. Volume 8. pp. 336.
).

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

 Possible Gases: HN3

 Citations:
 Metal azides may form explosive organic azides if stored for long periods of time in halogenated
solvents (Bretherick, L. 1986. Chemical and Engineering News 64(51):2. ); explosions may also occur
in reactions using NaN3 with methylene chloride/dimethyl sulfoxide solvent mixtures. It is not
recommended to run reactions with inorganic azides in halogenated organic solvents (Peet, N. P. et
al. 1993. Chemical and Engineering News 71916; Hurby, V. J. et al. 1993. Chemical and Engineering
News 71(41):2. ). Bretherick attributes the explosion in the previous articles to HN3 gas (Urben,
P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford:
Butterworth-Heinemann. pp. 1700. ). \\Dichloromethane can form explosive diazomethane with
quaternary ammonium azides (Hassner, A. et al. 1986. Agnew. Chem. (International Edition.)
25:479-480. ).

 5 ) SODIUM AZIDE mixed with
 4) PHENACYL BROMIDE
 - Reaction proceeds with explosive violence and/or forms explosive products.
 - 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, nontoxic gas. May cause pressurization.

 Possible Gases: HN3|N2|CO2

 Citations:
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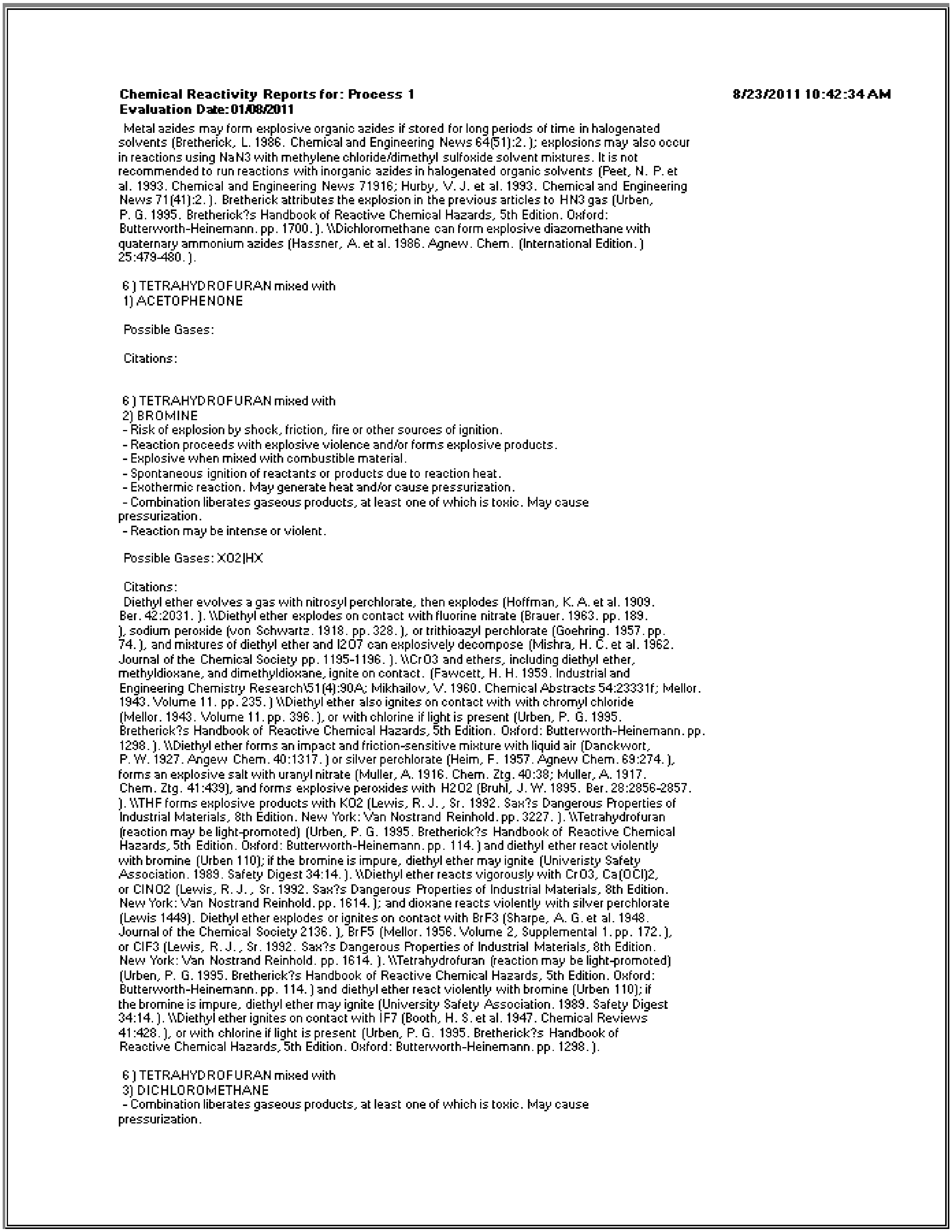

Chemical Reactivity Reports for: Process 1 **8/23/2011 10:42:34 AM**
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Metal azides may form explosive organic azides if stored for long periods of time in halogenated solvents (Bretherick, L. 1986. Chemical and Engineering News 64(51):2.); explosions may also occur in reactions using NaN3 with methylene chloride/dimethyl sulfoxide solvent mixtures. It is not recommended to run reactions with inorganic azides in halogenated organic solvents (Peet, N. P. et al. 1993. Chemical and Engineering News 71916; Hurby, V. J. et al. 1993. Chemical and Engineering News 71(41):2.). Bretherick attributes the explosion in the previous articles to HN3 gas (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 1700.). \\Dichloromethane can form explosive diazomethane with quaternary ammonium azides (Hassner, A. et al. 1986. Agnew. Chem. (International Edition.) 25:479-480.).

6) TETRAHYDROFURAN mixed with
1) ACETOPHENONE

Possible Gases:

Citations:

6) TETRAHYDROFURAN mixed with
2) BROMINE
- Risk of explosion by shock, friction, fire or other sources of ignition.
- Reaction proceeds with explosive violence and/or forms explosive products.
- Explosive when mixed with combustible material.
- Spontaneous ignition of reactants 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.
- Reaction may be intense or violent.

Possible Gases: XO2|HX

Citations:
Diethyl ether evolves a gas with nitrosyl perchlorate, then explodes (Hoffman, K. A. et al. 1909. Ber. 42:2031.). \\Diethyl ether explodes on contact with fluorine nitrate (Brauer. 1963. pp. 189.), sodium peroxide (von Schwartz. 1918. pp. 328.), or trithioazyl perchlorate (Goehring. 1957. pp. 74.), and mixtures of diethyl ether and I2O7 can explosively decompose (Mishra, H. C. et al. 1962. Journal of the Chemical Society pp. 1195-1196.). \\CrO3 and ethers, including diethyl ether, methyldioxane, and dimethyldioxane, ignite on contact. (Fawcett, H. H. 1959. Industrial and Engineering Chemistry Research\51(4):90A; Mikhailov, V. 1960. Chemical Abstracts 54:23331f; Mellor. 1943. Volume 11. pp. 235.) \\Diethyl ether also ignites on contact with with chromyl chloride (Mellor. 1943. Volume 11. pp. 396.), or with chlorine if light is present (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 1298.). \\Diethyl ether forms an impact and friction-sensitive mixture with liquid air (Danckwort, P. W. 1927. Angew Chem. 40:1317.) or silver perchlorate (Heim, F. 1957. Agnew Chem. 69:274.), forms an explosive salt with uranyl nitrate (Muller, A. 1916. Chem. Ztg. 40:38; Muller, A. 1917. Chem. Ztg. 41:439), and forms explosive peroxides with H2O2 (Bruhl, J. W. 1895. Ber. 28:2856-2857.). \\THF forms explosive products with KO2 (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 3227.). \\Tetrahydrofuran (reaction may be light-promoted) (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 114.) and diethyl ether react violently with bromine (Urben 110); if the bromine is impure, diethyl ether may ignite (Univeristy Safety Association. 1989. Safety Digest 34:14.). \\Diethyl ether reacts vigorously with CrO3, Ca(OCl)2, or ClNO2 (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 1614.); and dioxane reacts violently with silver perchlorate (Lewis 1449). Diethyl ether explodes or ignites on contact with BrF3 (Sharpe, A. G. et al. 1948. Journal of the Chemical Society 2136.), BrF5 (Mellor. 1956. Volume 2, Supplemental 1. pp. 172.), or ClF3 (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 1614.). \\Tetrahydrofuran (reaction may be light-promoted) (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 114.) and diethyl ether react violently with bromine (Urben 110); if the bromine is impure, diethyl ether may ignite (University Safety Association. 1989. Safety Digest 34:14.). \\Diethyl ether ignites on contact with IF7 (Booth, H. S. et al. 1947. Chemical Reviews 41:428.), or with chlorine if light is present (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 1298.).

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

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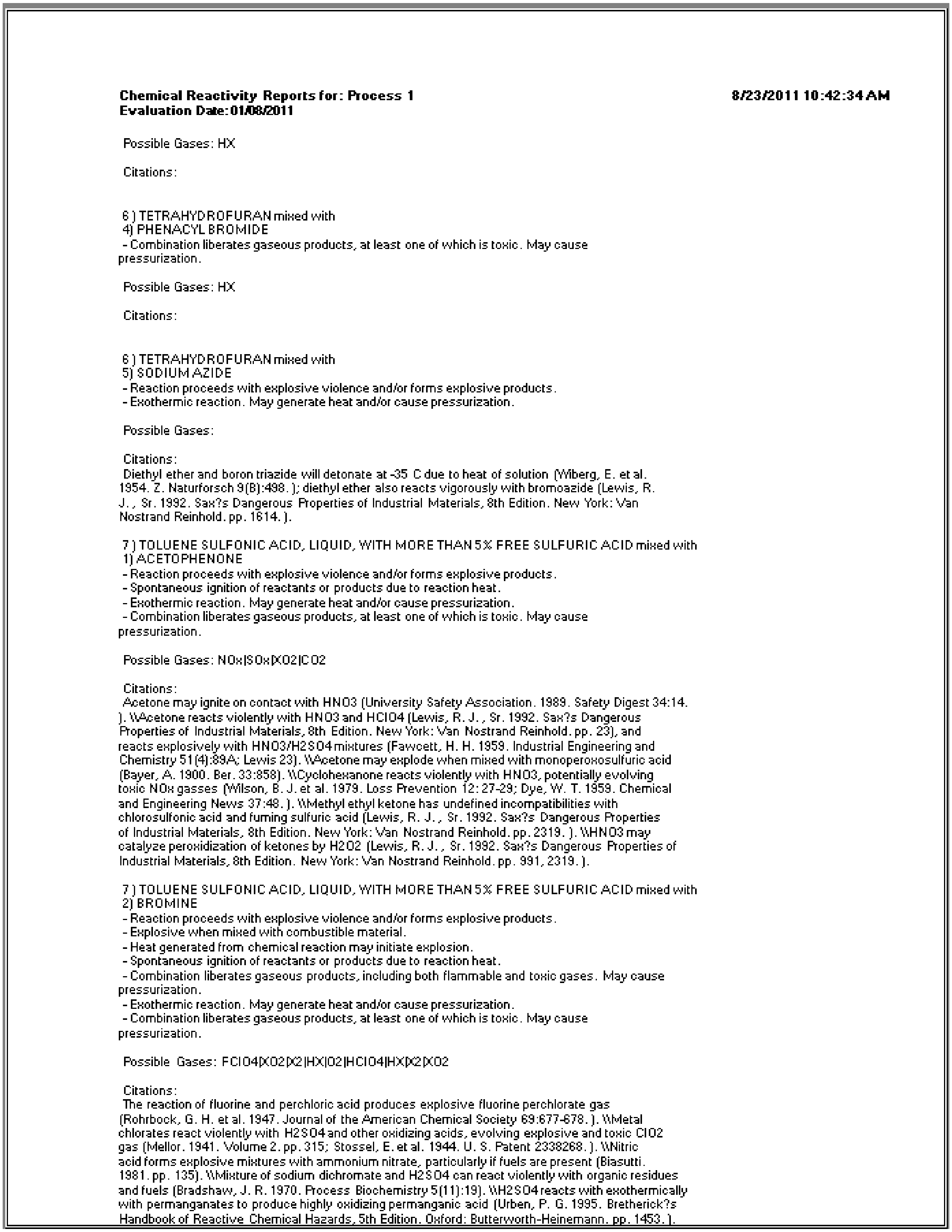

Chemical Reactivity Reports for: Process 1 **8/23/2011 10:42:34 AM**
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Possible Gases: HX

Citations:

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

Possible Gases: HX

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:
Diethyl ether and boron triazide will detonate at -35 C due to heat of solution (Wiberg, E. et al. 1954. Z. Naturforsch 9(B):498.); diethyl ether also reacts vigorously with bromoazide (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 1614.).

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 reactants 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|SOx|XO2|CO2

Citations:
Acetone may ignite on contact with HNO3 (University Safety Association. 1989. Safety Digest 34:14.). \\Acetone reacts violently with HNO3 and HClO4 (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 23), and reacts explosively with HNO3/H2SO4 mixtures (Fawcett, H. H. 1959. Industrial Engineering and Chemistry 51(4):89A; Lewis 23). \\Acetone may explode when mixed with monoperoxosulfuric acid (Bayer, A. 1900. Ber. 33:858). \\Cyclohexanone reacts violently with HNO3, potentially evolving toxic NOx gasses (Wilson, B. J. et al. 1979. Loss Prevention 12: 27-29; Dye, W. T. 1959. Chemical and Engineering News 37:48.). \\Methyl ethyl ketone has undefined incompatibilities with chlorosulfonic acid and fuming sulfuric acid (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 2319.). \\HNO3 may catalyze peroxidization of ketones by H2O2 (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 991, 2319.).

7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID mixed with
2) BROMINE
- Reaction proceeds with explosive violence and/or forms explosive products.
- Explosive when mixed with combustible material.
- Heat generated from chemical reaction may initiate explosion.
- Spontaneous ignition of reactants 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.

Possible Gases: FClO4|XO2|X2|HX|O2|HClO4|HX|X2|XO2

Citations:
The reaction of fluorine and perchloric acid produces explosive fluorine perchlorate gas (Rohrbock, G. H. et al. 1947. Journal of the American Chemical Society 69:677-678.). \\Metal chlorates react violently with H2SO4 and other oxidizing acids, evolving explosive and toxic ClO2 gas (Mellor. 1941. Volume 2. pp. 315; Stossel, E. et al. 1944. U. S. Patent 2338268.). \\Nitric acid forms explosive mixtures with ammonium nitrate, particularly if fuels are present (Biasutti. 1981. pp. 135). \\Mixture of sodium dichromate and H2SO4 can react violently with organic residues and fuels (Bradshaw, J. R. 1970. Process Biochemistry 5(11):19). \\H2SO4 reacts with exothermically with permanganates to produce highly oxidizing permanganic acid (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 1453.).

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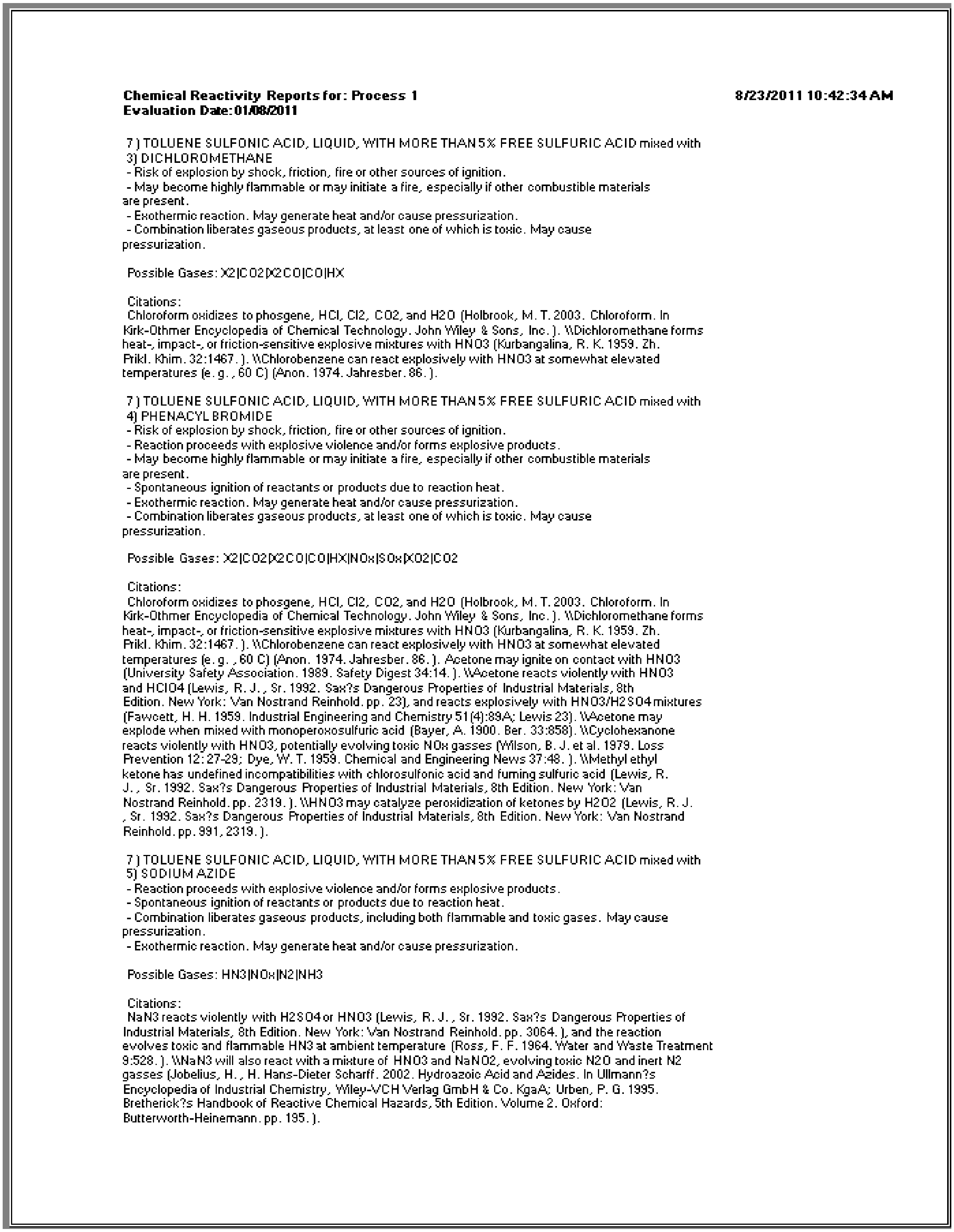

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7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID mixed with
3) DICHLOROMETHANE
- Risk of explosion by shock, friction, fire or other sources of ignition.
- May become highly flammable or may initiate a fire, especially if other 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: X2|CO2|X2CO|CO|HX

Citations:

Chloroform oxidizes to phosgene, HCl, Cl2, CO2, and H2O (Holbrook, M. T. 2003. Chloroform. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.). \\Dichloromethane forms heat-, impact-, or friction-sensitive explosive mixtures with HNO3 (Kurbangalina, R. K. 1959. Zh. Prikl. Khim. 32:1467.). \\Chlorobenzene can react explosively with HNO3 at somewhat elevated temperatures (e. g. , 60 C) (Anon. 1974. Jahresber. 86.).

7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID mixed with
4) PHENACYL BROMIDE
- Risk of explosion by shock, friction, fire or other sources of ignition.
- 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.
- Combination liberates gaseous products, at least one of which is toxic. May cause pressurization.

Possible Gases: X2|CO2|X2CO|CO|HX|NOx|SOx|XO2|CO2

Citations:

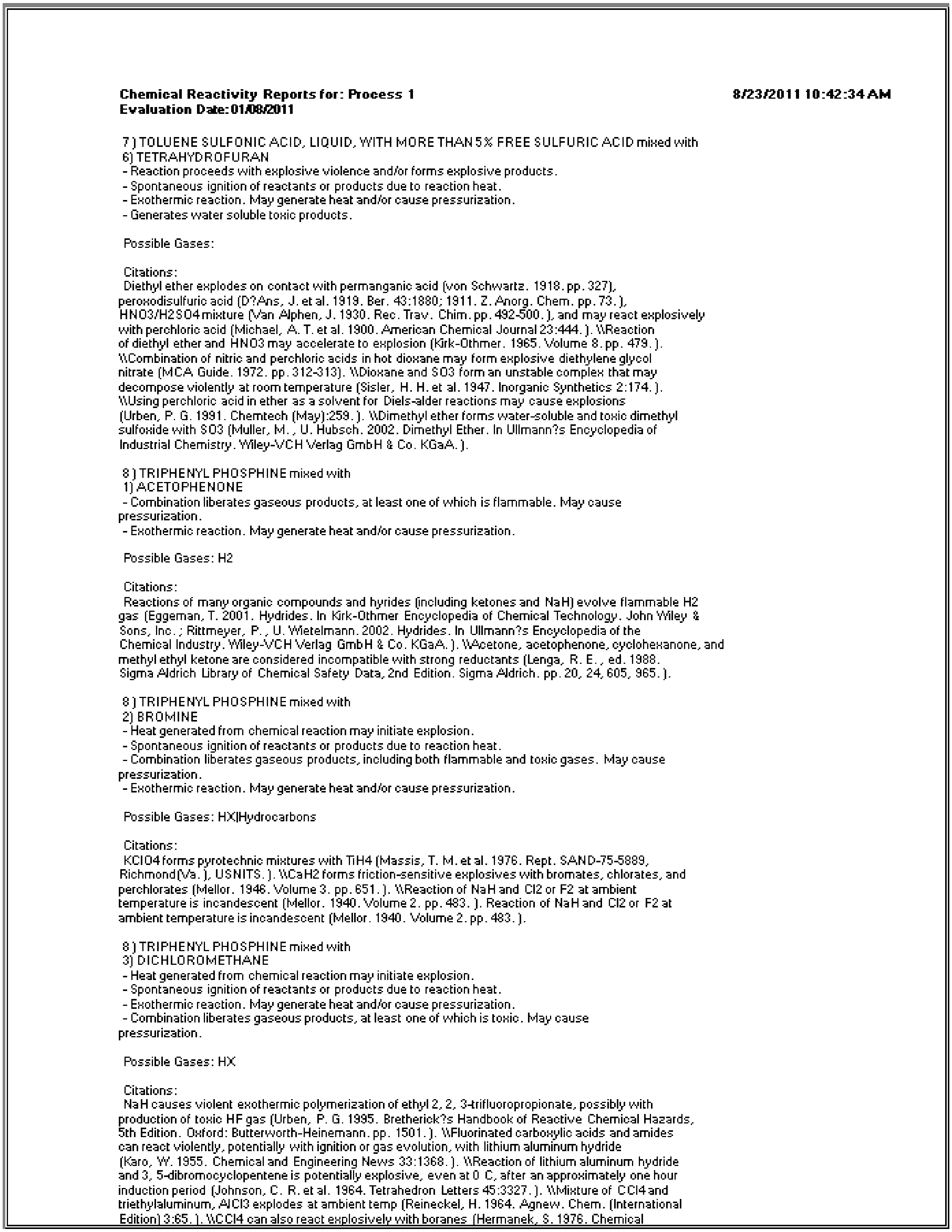
Chloroform oxidizes to phosgene, HCl, Cl2, CO2, and H2O (Holbrook, M. T. 2003. Chloroform. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.). \\Dichloromethane forms heat-, impact-, or friction-sensitive explosive mixtures with HNO3 (Kurbangalina, R. K. 1959. Zh. Prikl. Khim. 32:1467.). \\Chlorobenzene can react explosively with HNO3 at somewhat elevated temperatures (e. g. , 60 C) (Anon. 1974. Jahresber. 86.). Acetone may ignite on contact with HNO3 (University Safety Association. 1989. Safety Digest 34:14.). \\Acetone reacts violently with HNO3 and HClO4 (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 23), and reacts explosively with HNO3/H2SO4 mixtures (Fawcett, H. H. 1959. Industrial Engineering and Chemistry 51(4):89A; Lewis 23). \\Acetone may explode when mixed with monoperoxosulfuric acid (Bayer, A. 1900. Ber. 33:858). \\Cyclohexanone reacts violently with HNO3, potentially evolving toxic NOx gasses (Wilson, B. J. et al. 1979. Loss Prevention 12: 27-29; Dye, W. T. 1959. Chemical and Engineering News 37:48.). \\Methyl ethyl ketone has undefined incompatibilities with chlorosulfonic acid and fuming sulfuric acid (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 2319.). \\HNO3 may catalyze peroxidization of ketones by H2O2 (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 991, 2319.).

7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID mixed with
5) SODIUM AZIDE
- Reaction proceeds with explosive violence and/or forms explosive products.
- Spontaneous ignition of reactants 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.

Possible Gases: HN3|NOx|N2|NH3

Citations:

NaN3 reacts violently with H2SO4 or HNO3 (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 3064.), and the reaction evolves toxic and flammable HN3 at ambient temperature (Ross, F. F. 1964. Water and Waste Treatment 9:528.). \\NaN3 will also react with a mixture of HNO3 and NaNO2, evolving toxic N2O and inert N2 gasses (Jobelius, H. , H. Hans-Dieter Scharff. 2002. Hydroazoic Acid and Azides. In Ullmann?s Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KgaA; Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Volume 2. Oxford: Butterworth-Heinemann. pp. 195.).



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

 Possible Gases:

 Citations:
 Diethyl ether explodes on contact with permanganic acid (von Schwartz. 1918. pp. 327),
peroxodisulfuric acid (D?Ans, J. et al. 1919. Ber. 43:1880; 1911. Z. Anorg. Chem. pp. 73. ),
HNO3/H2SO4 mixture (Van Alphen, J. 1930. Rec. Trav. Chim. pp. 492-500. ), and may react explosively
with perchloric acid (Michael, A. T. et al. 1900. American Chemical Journal 23:444. ). \\Reaction
of diethyl ether and HNO3 may accelerate to explosion (Kirk-Othmer. 1965. Volume 8. pp. 479. ).
\\Combination of nitric and perchloric acids in hot dioxane may form explosive diethylene glycol
nitrate (MCA Guide. 1972. pp. 312-313). \\Dioxane and SO3 form an unstable complex that may
decompose violently at room temperature (Sisler, H. H. et al. 1947. Inorganic Synthetics 2:174. ).
\\Using perchloric acid in ether as a solvent for Diels-alder reactions may cause explosions
(Urben, P. G. 1991. Chemtech (May):259. ). \\Dimethyl ether forms water-soluble and toxic dimethyl
sulfoxide with SO3 (Muller, M. , U. Hubsch. 2002. Dimethyl Ether. In Ullmann?s Encyclopedia of
Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA. ).

 8 ) TRIPHENYL PHOSPHINE mixed with
 1) ACETOPHENONE
 - Combination 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:
 Reactions of many organic compounds and hyrides (including ketones and NaH) evolve flammable H2
gas (Eggeman, T. 2001. Hydrides. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley &
Sons, Inc. ; Rittmeyer, P. , U. Wietelmann. 2002. Hydrides. In Ullmann?s Encyclopedia of the
Chemical Industry. Wiley-VCH Verlag GmbH & Co. KGaA. ). \\Acetone, acetophenone, cyclohexanone, and
methyl ethyl ketone are considered incompatible with strong reductants (Lenga, R. E. , ed. 1988.
Sigma Aldrich Library of Chemical Safety Data, 2nd Edition. Sigma Aldrich. pp. 20, 24, 605, 965. ).

 8 ) TRIPHENYL PHOSPHINE mixed with
 2) BROMINE
 - Heat generated from chemical reaction may initiate explosion.
 - Spontaneous ignition of reactants 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.

 Possible Gases: HX|Hydrocarbons

 Citations:
 KClO4 forms pyrotechnic mixtures with TiH4 (Massis, T. M. et al. 1976. Rept. SAND-75-5889,
Richmond(Va. ), USNITS. ). \\CaH2 forms friction-sensitive explosives with bromates, chlorates, and
perchlorates (Mellor. 1946. Volume 3. pp. 651. ). \\Reaction of NaH and Cl2 or F2 at ambient
temperature is incandescent (Mellor. 1940. Volume 2. pp. 483. ). Reaction of NaH and Cl2 or F2 at
ambient temperature is incandescent (Mellor. 1940. Volume 2. pp. 483. ).

 8 ) TRIPHENYL PHOSPHINE mixed with
 3) DICHLOROMETHANE
 - Heat generated from chemical reaction may initiate explosion.
 - Spontaneous ignition of reactants 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: HX

 Citations:
 NaH causes violent exothermic polymerization of ethyl 2, 2, 3-trifluoropropionate, possibly with
production of toxic HF gas (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards,
5th Edition. Oxford: Butterworth-Heinemann. pp. 1501. ). \\Fluorinated carboxylic acids and amides
can react violently, potentially with ignition or gas evolution, with lithium aluminum hydride
(Karo, W. 1955. Chemical and Engineering News 33:1368. ). \\Reaction of lithium aluminum hydride
and 3, 5-dibromocyclopentene is potentially explosive, even at 0 C, after an approximately one hour
induction period (Johnson, C. R. et al. 1964. Tetrahedron Letters 45:3327. ). \\Mixture of CCl4 and
triethylaluminum, AlCl3 explodes at ambient temp (Reineckel, H. 1964. Agnew. Chem. (International
Edition) 3:65. ). \\CCl4 can also react explosively with boranes (Hermanek, S. 1976. Chemical
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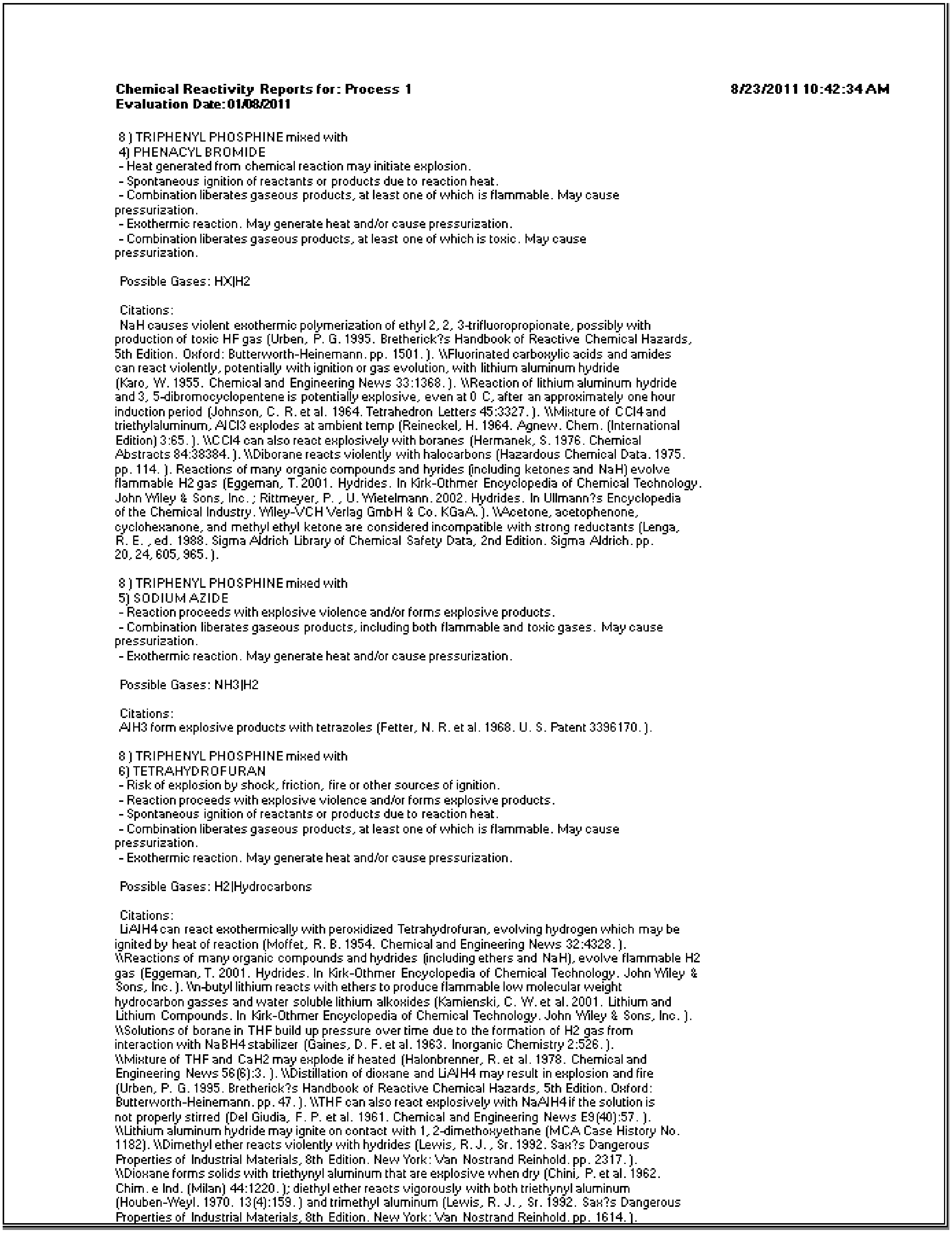

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Chemical Reactivity Reports for: Process 1                                         8/23/2011 10:42:34 AM
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 8 ) TRIPHENYL PHOSPHINE mixed with
 4) PHENACYL BROMIDE
 - Heat generated from chemical reaction may initiate explosion.
 - Spontaneous ignition of reactants or products due to reaction heat.
 - 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.

 Possible Gases: HX|H2

 Citations:
 NaH causes violent exothermic polymerization of ethyl 2, 2, 3-trifluoropropionate, possibly with
production of toxic HF gas (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards,
5th Edition. Oxford: Butterworth-Heinemann. pp. 1501. ). \\Fluorinated carboxylic acids and amides
can react violently, potentially with ignition or gas evolution, with lithium aluminum hydride
(Karo, W. 1955. Chemical and Engineering News 33:1368. ). \\Reaction of lithium aluminum hydride
and 3, 5-dibromocyclopentene is potentially explosive, even at 0 C, after an approximately one hour
induction period (Johnson, C. R. et al. 1964. Tetrahedron Letters 45:3327. ). \\Mixture of CCl4 and
triethylaluminum, AlCl3 explodes at ambient temp (Reineckel, H. 1964. Agnew. Chem. (International
Edition) 3:65. ). \\CCl4 can also react explosively with boranes (Hermanek, S. 1976. Chemical
Abstracts 84:38384. ). \\Diborane reacts violently with halocarbons (Hazardous Chemical Data. 1975.
pp. 114. ). Reactions of many organic compounds and hyrides (including ketones and NaH) evolve
flammable H2 gas (Eggeman, T. 2001. Hydrides. In Kirk-Othmer Encyclopedia of Chemical Technology.
John Wiley & Sons, Inc. ; Rittmeyer, P. , U. Wietelmann. 2002. Hydrides. In Ullmann?s Encyclopedia
of the Chemical Industry. Wiley-VCH Verlag GmbH & Co. KGaA. ). \\Acetone, acetophenone,
cyclohexanone, and methyl ethyl ketone are considered incompatible with strong reductants (Lenga,
R. E. , ed. 1988. Sigma Aldrich Library of Chemical Safety Data, 2nd Edition. Sigma Aldrich. pp.
20, 24, 605, 965. ).

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

 Possible Gases: NH3|H2

 Citations:
 AlH3 form explosive products with tetrazoles (Fetter, N. R. et al. 1968. U. S. Patent 3396170. ).

 8 ) TRIPHENYL PHOSPHINE mixed with
 6) TETRAHYDROFURAN
 - Risk of explosion by shock, friction, fire or other sources of ignition.
 - Reaction proceeds with explosive violence and/or forms explosive products.
 - Spontaneous ignition of reactants or products due to reaction heat.
 - Combination 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|Hydrocarbons

 Citations:
 LiAlH4 can react exothermically with peroxidized Tetrahydrofuran, evolving hydrogen which may be
ignited by heat of reaction (Moffet, R. B. 1954. Chemical and Engineering News 32:4328. ).
\\Reactions of many organic compounds and hydrides (including ethers and NaH), evolve flammable H2
gas (Eggeman, T. 2001. Hydrides. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley &
Sons, Inc. ). \\n-butyl lithium reacts with ethers to produce flammable low molecular weight
hydrocarbon gasses and water soluble lithium alkoxides (Kamienski, C. W. et al. 2001. Lithium and
Lithium Compounds. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc. ).
\\Solutions of borane in THF build up pressure over time due to the formation of H2 gas from
interaction with NaBH4 stabilizer (Gaines, D. F. et al. 1963. Inorganic Chemistry 2:526. ).
\\Mixture of THF and CaH2 may explode if heated (Halonbrenner, R. et al. 1978. Chemical and
Engineering News 56(6):3. ). \\Distillation of dioxane and LiAlH4 may result in explosion and fire
(Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford:
Butterworth-Heinemann. pp. 47. ). \\THF can also react explosively with NaAlH4 if the solution is
not properly stirred (Del Giudia, F. P. et al. 1961. Chemical and Engineering News E9(40):57. ).
\\Lithium aluminum hydride may ignite on contact with 1, 2-dimethoxyethane (MCA Case History No.
1182). \\Dimethyl ether reacts violently with hydrides (Lewis, R. J. , Sr. 1992. Sax?s Dangerous
Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 2317. ).
\\Dioxane forms solids with triethynyl aluminum that are explosive when dry (Chini, P. et al. 1962.
Chim. e Ind. (Milan) 44:1220. ); diethyl ether reacts vigorously with both triethynyl aluminum
(Houben-Weyl. 1970. 13(4):159. ) and trimethyl aluminum (Lewis, R. J. , Sr. 1992. Sax?s Dangerous
Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 1614. ).
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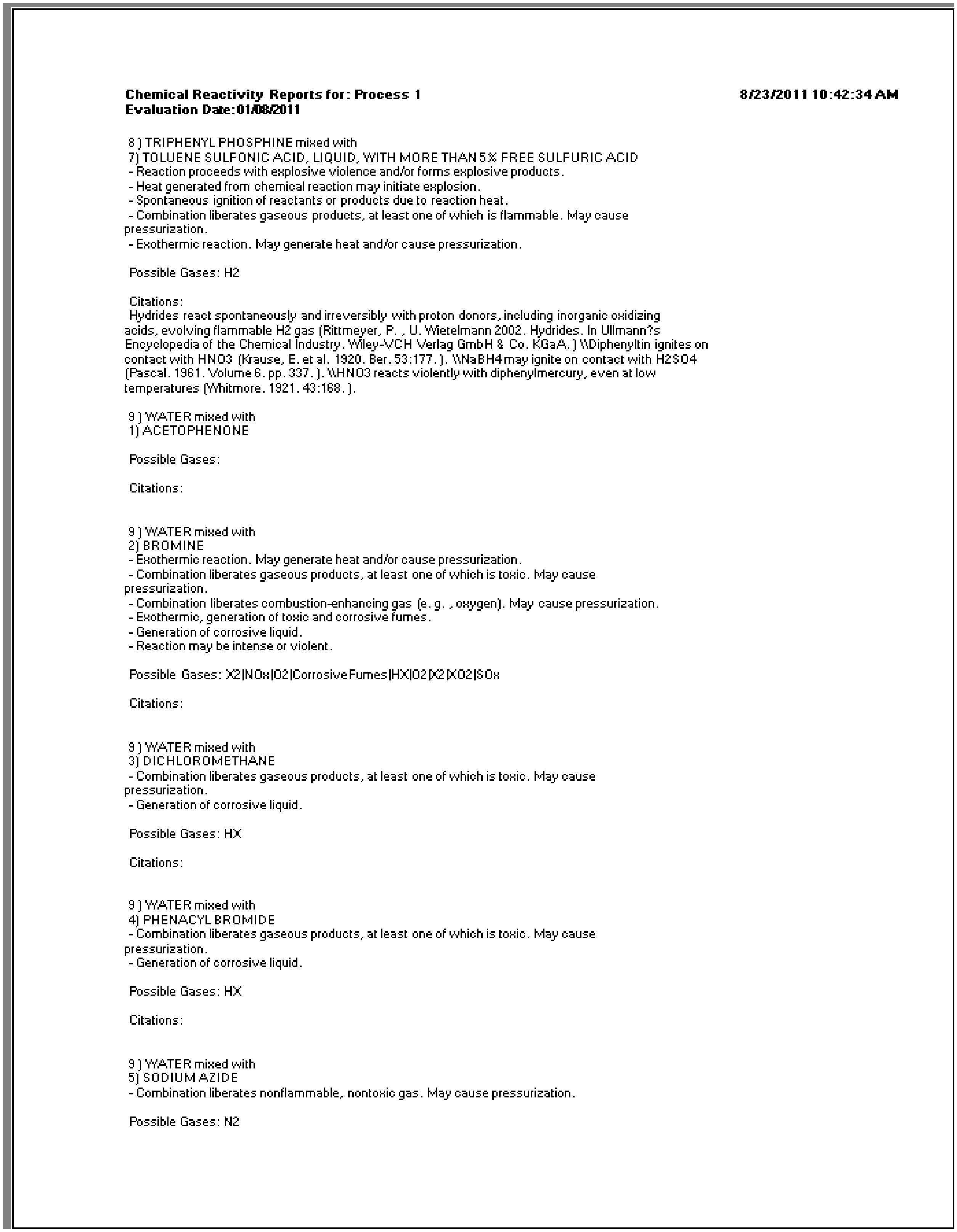

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8) TRIPHENYL PHOSPHINE mixed with
7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID
- Reaction proceeds with explosive violence and/or forms explosive products.
- Heat generated from chemical reaction may initiate explosion.
- Spontaneous ignition of reactants or products due to reaction heat.
- Combination 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:
Hydrides react spontaneously and irreversibly with proton donors, including inorganic oxidizing acids, evolving flammable H2 gas (Rittmeyer, P. , U. Wietelmann 2002. Hydrides. In Ullmann?s Encyclopedia of the Chemical Industry. Wiley-VCH Verlag GmbH & Co. KGaA.) \\Diphenyltin ignites on contact with HNO3 (Krause, E. et al. 1920. Ber. 53:177.). \\NaBH4 may ignite on contact with H2SO4 (Pascal. 1961. Volume 6. pp. 337.). \\HNO3 reacts violently with diphenylmercury, even at low temperatures (Whitmore. 1921. 43:168.).

9) WATER mixed with
1) ACETOPHENONE

Possible Gases:

Citations:

9) WATER mixed with
2) BROMINE
- 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: X2|NOx|O2|CorrosiveFumes|HX|O2|X2|XO2|SOx

Citations:

9) WATER mixed with
3) DICHLOROMETHANE
- Combination 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
- Combination 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
- Combination liberates nonflammable, nontoxic gas. May cause pressurization.

Possible Gases: N2

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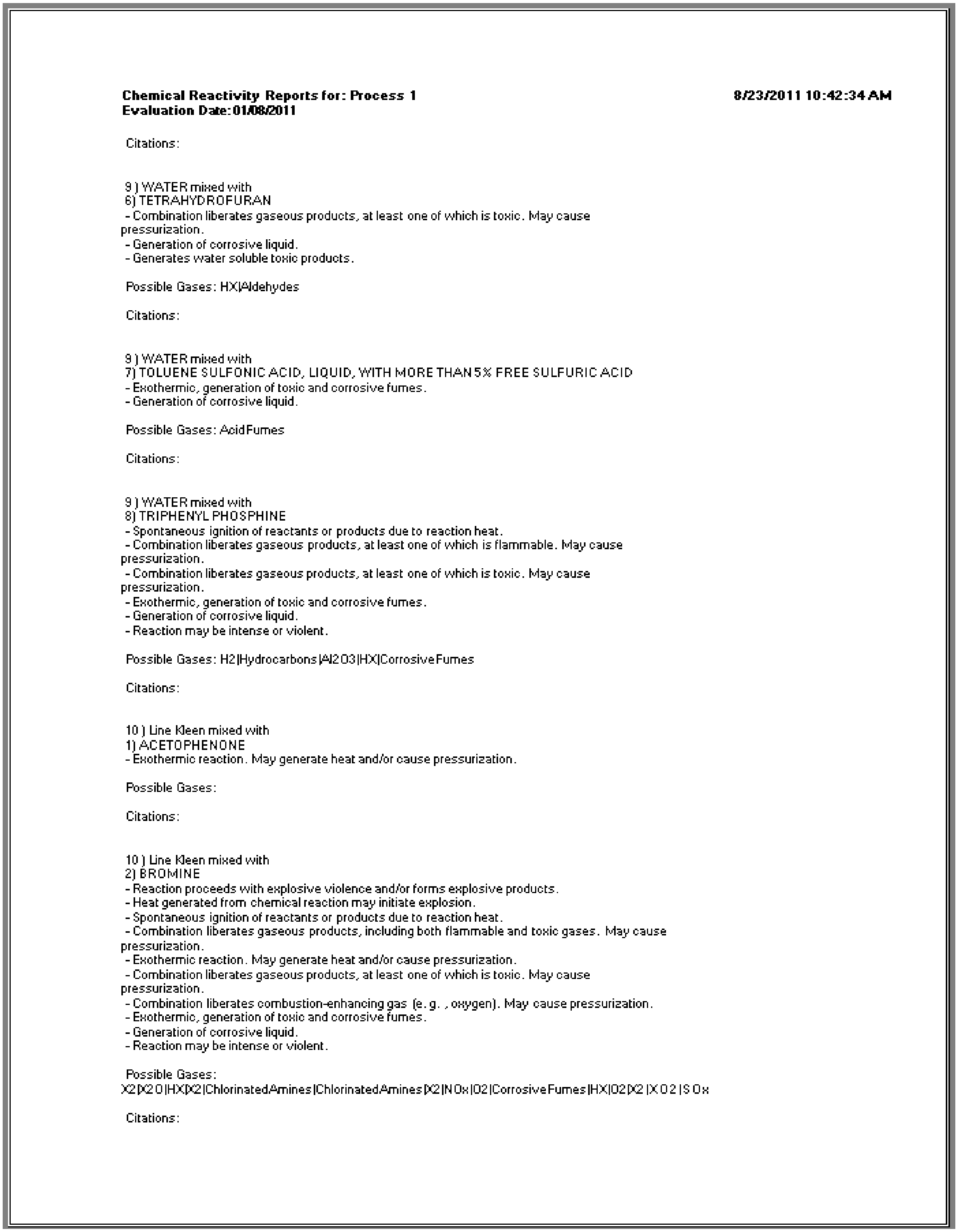

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 Citations:


 9 ) WATER mixed with
 6) TETRAHYDROFURAN
 - 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: HX|Aldehydes

 Citations:


 9 ) WATER mixed with
 7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID
 - Exothermic, generation of toxic and corrosive fumes.
 - Generation of corrosive liquid.

 Possible Gases: AcidFumes

 Citations:


 9 ) WATER mixed with
 8) TRIPHENYL PHOSPHINE
 - Spontaneous ignition of reactants 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|Al2O3|HX|CorrosiveFumes

 Citations:


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

 Possible Gases:

 Citations:


 10 ) Line Kleen mixed with
 2) BROMINE
 - Reaction proceeds with explosive violence and/or forms explosive products.
 - Heat generated from chemical reaction may initiate explosion.
 - Spontaneous ignition of reactants 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:
X2|X2O|HX|X2|ChlorinatedAmines|ChlorinatedAmines|X2|NOx|O2|CorrosiveFumes|HX|O2|X2|XO2|SOx

 Citations:
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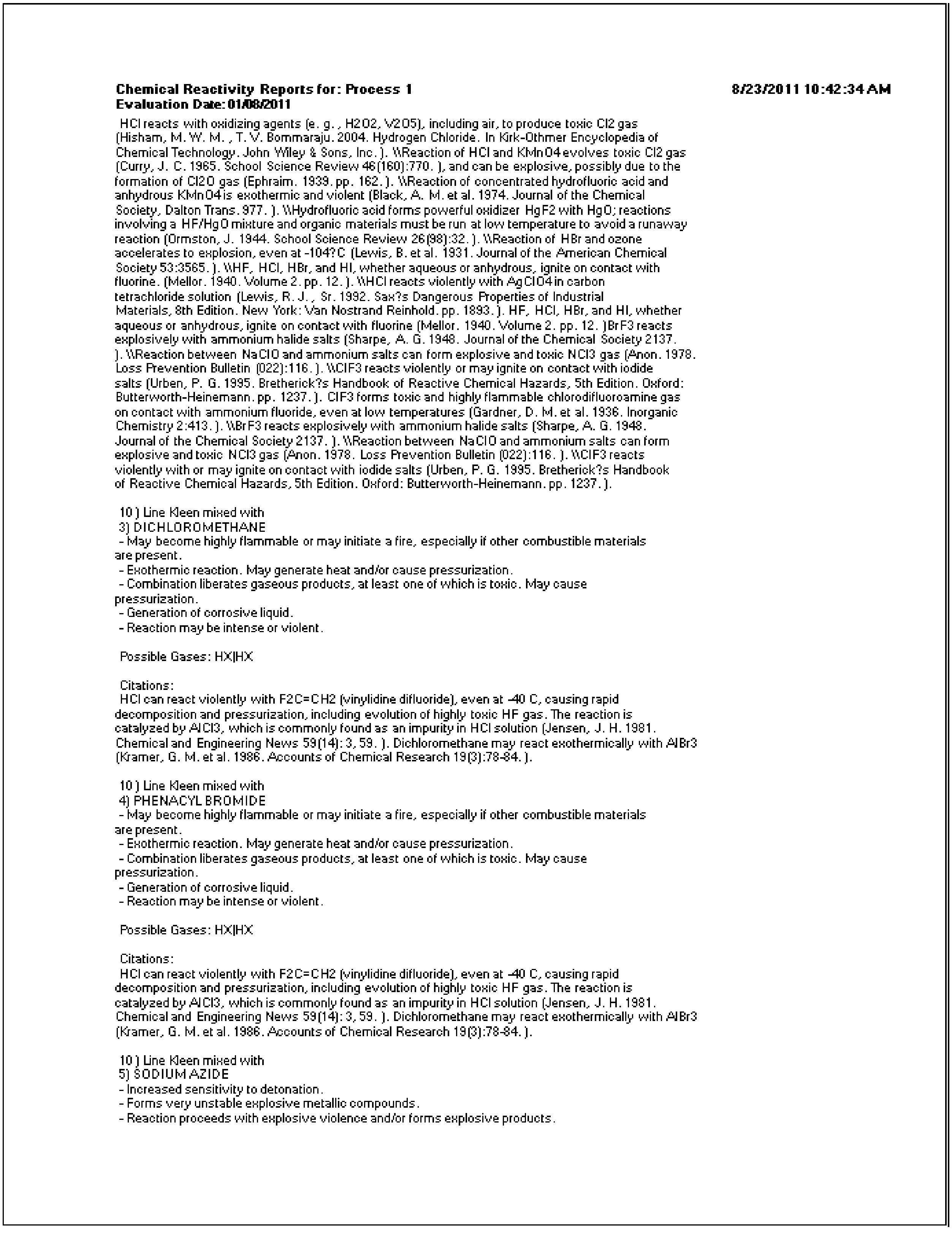

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HCl reacts with oxidizing agents (e. g. , H2O2, V2O5), including air, to produce toxic Cl2 gas (Hisham, M. W. M. , T. V. Bommaraju. 2004. Hydrogen Chloride. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.). \\Reaction of HCl and KMnO4 evolves toxic Cl2 gas (Curry, J. C. 1965. School Science Review 46(160):770.), and can be explosive, possibly due to the formation of Cl2O gas (Ephraim. 1939. pp. 162.). \\Reaction of concentrated hydrofluoric acid and anhydrous KMnO4 is exothermic and violent (Black, A. M. et al. 1974. Journal of the Chemical Society, Dalton Trans. 977.). \\Hydrofluoric acid forms powerful oxidizer HgF2 with HgO; reactions involving a HF/HgO mixture and organic materials must be run at low temperature to avoid a runaway reaction (Ormston, J. 1944. School Science Review 26(98):32.). \\Reaction of HBr and ozone accelerates to explosion, even at -104?C (Lewis, B. et al. 1931. Journal of the American Chemical Society 53:3565.). \\HF, HCl, HBr, and HI, whether aqueous or anhydrous, ignite on contact with fluorine. (Mellor. 1940. Volume 2. pp. 12.). \\HCl reacts violently with AgClO4 in carbon tetrachloride solution (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 1893.). HF, HCl, HBr, and HI, whether aqueous or anhydrous, ignite on contact with fluorine (Mellor. 1940. Volume 2. pp. 12.)BrF3 reacts explosively with ammonium halide salts (Sharpe, A. G. 1948. Journal of the Chemical Society 2137.). \\Reaction between NaClO and ammonium salts can form explosive and toxic NCl3 gas (Anon. 1978. Loss Prevention Bulletin (022):116.). \\ClF3 reacts violently or may ignite on contact with iodide salts (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 1237.). ClF3 forms toxic and highly flammable chlorodifluoroamine gas on contact with ammonium fluoride, even at low temperatures (Gardner, D. M. et al. 1936. Inorganic Chemistry 2:413.). \\BrF3 reacts explosively with ammonium halide salts (Sharpe, A. G. 1948. Journal of the Chemical Society 2137.). \\Reaction between NaClO and ammonium salts can form explosive and toxic NCl3 gas (Anon. 1978. Loss Prevention Bulletin (022):116.). \\ClF3 reacts violently with or may ignite on contact with iodide salts (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 1237.).

10) Line Kleen mixed with
3) DICHLOROMETHANE
- 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.
- Generation of corrosive liquid.
- Reaction may be intense or violent.

Possible Gases: HX|HX

Citations:
HCl can react violently with F2C=CH2 (vinylidine difluoride), even at -40 C, causing rapid decomposition and pressurization, including evolution of highly toxic HF gas. The reaction is catalyzed by AlCl3, which is commonly found as an impurity in HCl solution (Jensen, J. H. 1981. Chemical and Engineering News 59(14): 3, 59.). Dichloromethane may react exothermically with AlBr3 (Kramer, G. M. et al. 1986. Accounts of Chemical Research 19(3):78-84.).

10) Line Kleen mixed with
4) PHENACYL BROMIDE
- 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.
- Generation of corrosive liquid.
- Reaction may be intense or violent.

Possible Gases: HX|HX

Citations:
HCl can react violently with F2C=CH2 (vinylidine difluoride), even at -40 C, causing rapid decomposition and pressurization, including evolution of highly toxic HF gas. The reaction is catalyzed by AlCl3, which is commonly found as an impurity in HCl solution (Jensen, J. H. 1981. Chemical and Engineering News 59(14): 3, 59.). Dichloromethane may react exothermically with AlBr3 (Kramer, G. M. et al. 1986. Accounts of Chemical Research 19(3):78-84.).

10) Line Kleen mixed with
5) SODIUM AZIDE
- Increased sensitivity to detonation.
- Forms very unstable explosive metallic compounds.
- Reaction proceeds with explosive violence and/or forms explosive products.

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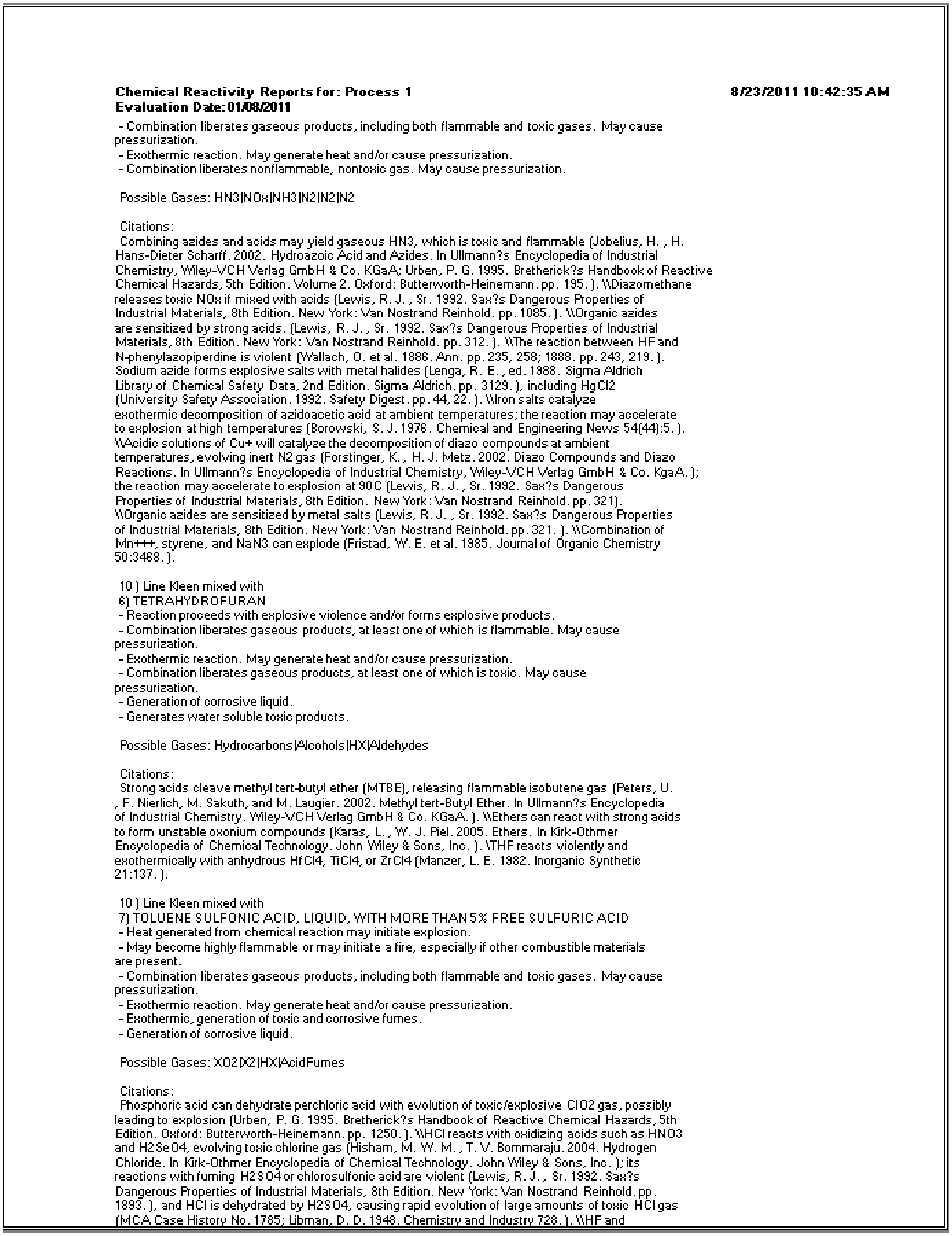

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Chemical Reactivity Reports for: Process 1                                    8/23/2011 10:42:35 AM
Evaluation Date:01/08/2011
 - Combination liberates gaseous products, including both flammable and toxic gases. May cause
pressurization.
 - Exothermic reaction. May generate heat and/or cause pressurization.
 - Combination liberates nonflammable, nontoxic gas. May cause pressurization.

 Possible Gases: HN3|NOx|NH3|N2|N2|N2

 Citations:
 Combining azides and acids may yield gaseous HN3, which is toxic and flammable (Jobelius, H. , H.
Hans-Dieter Scharff. 2002. Hydroazoic Acid and Azides. In Ullmann?s Encyclopedia of Industrial
Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA; Urben, P. G. 1995. Bretherick?s Handbook of Reactive
Chemical Hazards, 5th Edition. Volume 2. Oxford: Butterworth-Heinemann. pp. 195. ). \\Diazomethane
releases toxic NOx if mixed with acids (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of
Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 1085. ). \\Organic azides
are sensitized by strong acids. (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial
Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 312. ). \\The reaction between HF and
N-phenylazopiperdine is violent (Wallach, O. et al. 1886. Ann. pp. 235, 258; 1888. pp. 243, 219. ).
Sodium azide forms explosive salts with metal halides (Lenga, R. E. , ed. 1988. Sigma Aldrich
Library of Chemical Safety Data, 2nd Edition. Sigma Aldrich. pp. 3129. ), including HgCl2
(University Safety Association. 1992. Safety Digest. pp. 44, 22. ). \\Iron salts catalyze
exothermic decomposition of azidoacetic acid at ambient temperatures; the reaction may accelerate
to explosion at high temperatures (Borowski, S. J. 1976. Chemical and Engineering News 54(44):5. ).
\\Acidic solutions of Cu+ will catalyze the decomposition of diazo compounds at ambient
temperatures, evolving inert N2 gas (Forstinger, K. , H. J. Metz. 2002. Diazo Compounds and Diazo
Reactions. In Ullmann?s Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KgaA. );
the reaction may accelerate to explosion at 90C (Lewis, R. J. , Sr. 1992. Sax?s Dangerous
Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 321).
\\Organic azides are sensitized by metal salts (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties
of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 321. ). \\Combination of
Mn+++, styrene, and NaN3 can explode (Fristad, W. E. et al. 1985. Journal of Organic Chemistry
50:3468. ).

 10 ) Line Kleen mixed with
 6) 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|Aldehydes

 Citations:
 Strong acids cleave methyl tert-butyl ether (MTBE), releasing flammable isobutene gas (Peters, U.
, F. Nierlich, M. Sakuth, and M. Laugier. 2002. Methyl tert-Butyl Ether. In Ullmann?s Encyclopedia
of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA. ). \\Ethers can react with strong acids
to form unstable oxonium compounds (Karas, L. , W. J. Piel. 2005. Ethers. In Kirk-Othmer
Encyclopedia of Chemical Technology. John Wiley & Sons, Inc. ). \THF reacts violently and
exothermically with anhydrous HfCl4, TiCl4, or ZrCl4 (Manzer, L. E. 1982. Inorganic Synthetic
21:137. ).

 10 ) Line Kleen mixed with
 7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID
 - Heat generated from chemical reaction may initiate explosion.
 - May become highly flammable or may initiate a fire, especially if other combustible materials
are present.
 - Combination liberates gaseous products, including both flammable and toxic gases. 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: XO2|X2|HX|AcidFumes

 Citations:
 Phosphoric acid can dehydrate perchloric acid with evolution of toxic/explosive ClO2 gas, possibly
leading to explosion (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th
Edition. Oxford: Butterworth-Heinemann. pp. 1250. ). \\HCl reacts with oxidizing acids such as HNO3
and H2SeO4, evolving toxic chlorine gas (Hisham, M. W. M. , T. V. Bommaraju. 2004. Hydrogen
Chloride. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc. ); its
reactions with fuming H2SO4 or chlorosulfonic acid are violent (Lewis, R. J. , Sr. 1992. Sax?s
Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp.
1893. ), and HCl is dehydrated by H2SO4, causing rapid evolution of large amounts of toxic HCl gas
(MCA Case History No. 1785; Libman, D. D. 1948. Chemistry and Industry 728. ). \\HF and
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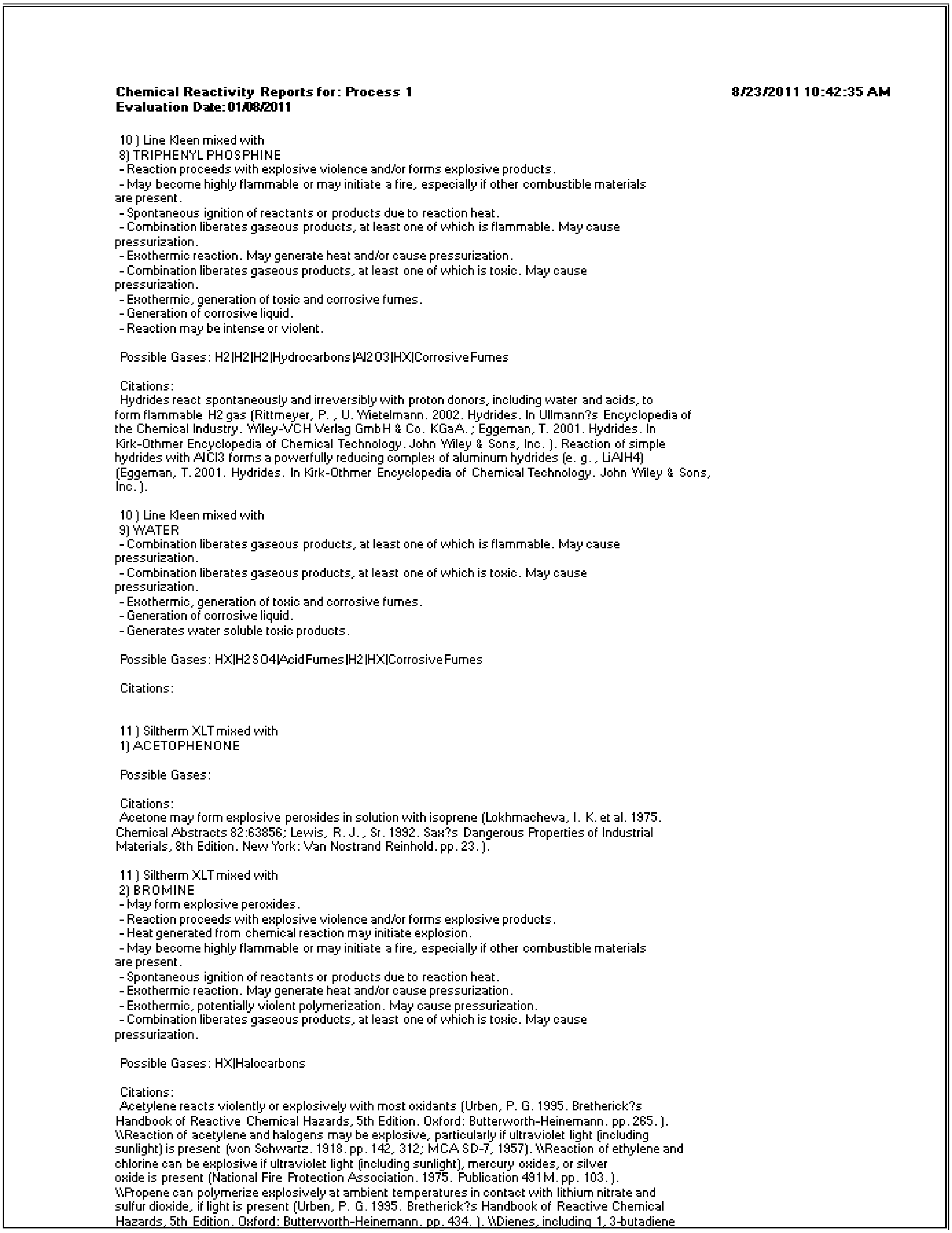

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Chemical Reactivity Reports for: Process 1                                    8/23/2011 10:42:35 AM
Evaluation Date: 01/08/2011

 10 ) Line Kleen mixed with
 8) TRIPHENYL PHOSPHINE
 - 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.
 - 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.
 - Exothermic, generation of toxic and corrosive fumes.
 - Generation of corrosive liquid.
 - Reaction may be intense or violent.

 Possible Gases: H2|H2|H2|Hydrocarbons|Al2O3|HX|Corrosive Fumes

 Citations:
 Hydrides react spontaneously and irreversibly with proton donors, including water and acids, to
form flammable H2 gas (Rittmeyer, P. , U. Wietelmann. 2002. Hydrides. In Ullmann?s Encyclopedia of
the Chemical Industry. Wiley-VCH Verlag GmbH & Co. KGaA. ; Eggeman, T. 2001. Hydrides. In
Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc. ). Reaction of simple
hydrides with AlCl3 forms a powerfully reducing complex of aluminum hydrides (e. g. , LiAlH4)
(Eggeman, T. 2001. Hydrides. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons,
Inc. ).

 10 ) Line Kleen mixed with
 9) WATER
 - 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.
 - Generates water soluble toxic products.

 Possible Gases: HX|H2SO4|Acid Fumes|H2|HX|Corrosive Fumes

 Citations:


 11 ) Siltherm XLT mixed with
 1) ACETOPHENONE

 Possible Gases:

 Citations:
 Acetone may form explosive peroxides in solution with isoprene (Lokhmacheva, I. K. et al. 1975.
 Chemical Abstracts 82:63856; Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial
 Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 23. ).

 11 ) Siltherm XLT mixed with
 2) BROMINE
 - May form explosive peroxides.
 - Reaction proceeds with explosive violence and/or forms explosive products.
 - Heat generated from chemical reaction may initiate explosion.
 - 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.
 - Combination liberates gaseous products, at least one of which is toxic. May cause
pressurization.

 Possible Gases: HX|Halocarbons

 Citations:
 Acetylene reacts violently or explosively with most oxidants (Urben, P. G. 1995. Bretherick?s
 Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 265. ).
\\Reaction of acetylene and halogens may be explosive, particularly if ultraviolet light (including
sunlight) is present (von Schwartz. 1918. pp. 142, 312; MCA SD-7, 1957). \\Reaction of ethylene and
chlorine can be explosive if ultraviolet light (including sunlight), mercury oxides, or silver
oxide is present (National Fire Protection Association. 1975. Publication 491M. pp. 103. ).
\\Propene can polymerize explosively at ambient temperatures in contact with lithium nitrate and
sulfur dioxide, if light is present (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical
 Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 434. ). \\Dienes, including 1, 3-butadiene
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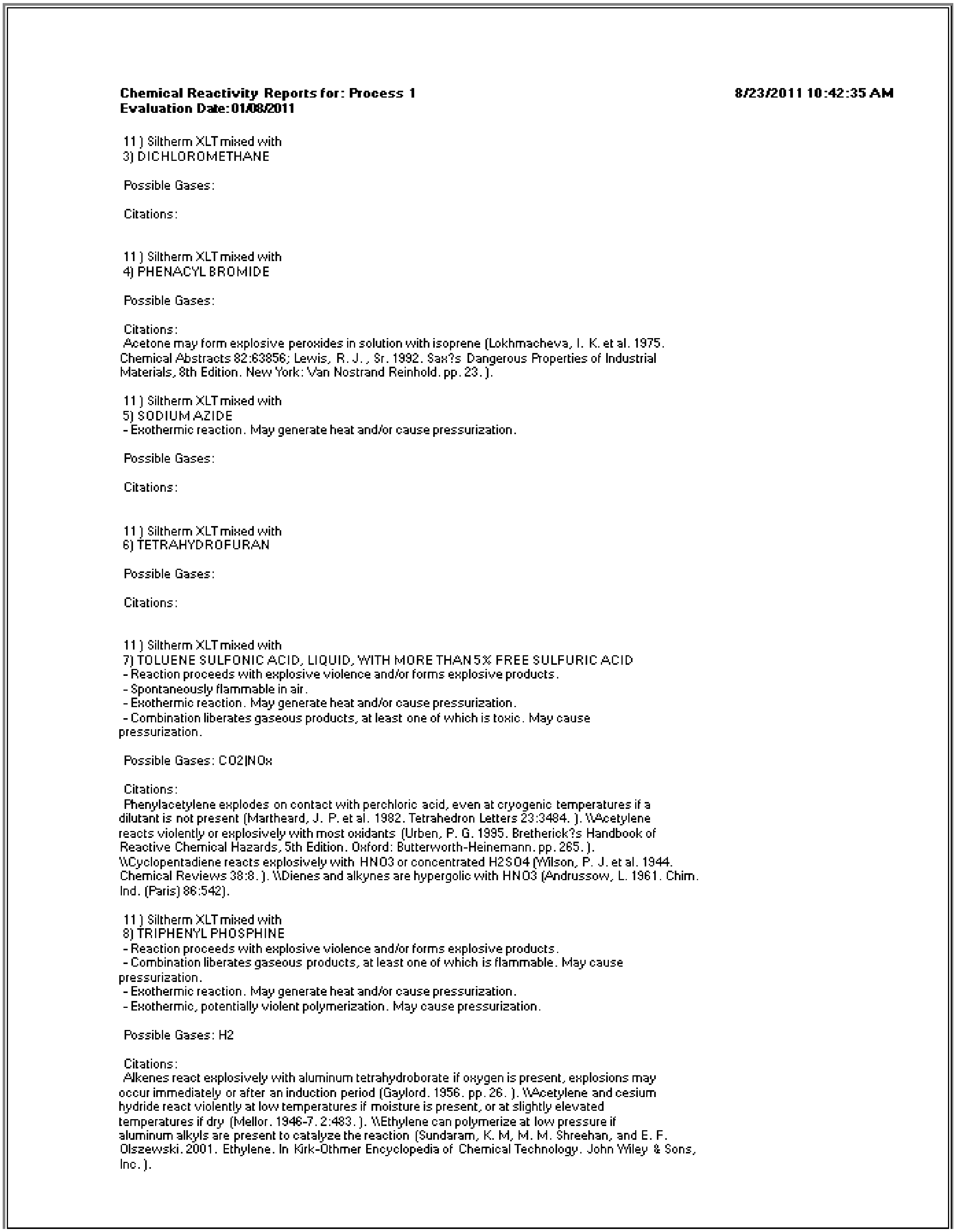

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Chemical Reactivity Reports for: Process 1                                    8/23/2011 10:42:35 AM
Evaluation Date:01/08/2011

 11 ) Siltherm XLT mixed with
 3) DICHLOROMETHANE

 Possible Gases:

 Citations:


 11 ) Siltherm XLT mixed with
 4) PHENACYL BROMIDE

 Possible Gases:

 Citations:
 Acetone may form explosive peroxides in solution with isoprene (Lokhmacheva, I. K. et al. 1975.
Chemical Abstracts 82:63856; Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial
Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 23. ).

 11 ) Siltherm XLT mixed with
 5) SODIUM AZIDE
 - Exothermic reaction. May generate heat and/or cause pressurization.

 Possible Gases:

 Citations:


 11 ) Siltherm XLT mixed with
 6) TETRAHYDROFURAN

 Possible Gases:

 Citations:


 11 ) Siltherm XLT mixed 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.
 - Combination liberates gaseous products, at least one of which is toxic. May cause
pressurization.

 Possible Gases: CO2|NOx

 Citations:
 Phenylacetylene explodes on contact with perchloric acid, even at cryogenic temperatures if a
dilutant is not present (Martheard, J. P. et al. 1982. Tetrahedron Letters 23:3484. ). \\Acetylene
reacts violently or explosively with most oxidants (Urben, P. G. 1995. Bretherick?s Handbook of
Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 265. ).
\\Cyclopentadiene reacts explosively with HNO3 or concentrated H2SO4 (Wilson, P. J. et al. 1944.
Chemical Reviews 38:8. ). \\Dienes and alkynes are hypergolic with HNO3 (Andrussow, L. 1961. Chim.
Ind. (Paris) 86:542).

 11 ) Siltherm XLT mixed with
 8) TRIPHENYL PHOSPHINE
 - 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.
 - Exothermic, potentially violent polymerization. May cause pressurization.

 Possible Gases: H2

 Citations:
 Alkenes react explosively with aluminum tetrahydroborate if oxygen is present, explosions may
occur immediately or after an induction period (Gaylord. 1956. pp. 26. ). \\Acetylene and cesium
hydride react violently at low temperatures if moisture is present, or at slightly elevated
temperatures if dry (Mellor. 1946-7. 2:483. ). \\Ethylene can polymerize at low pressure if
aluminum alkyls are present to catalyze the reaction (Sundaram, K. M, M. M. Shreehan, and E. F.
Olszewski. 2001. Ethylene. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons,
Inc. ).
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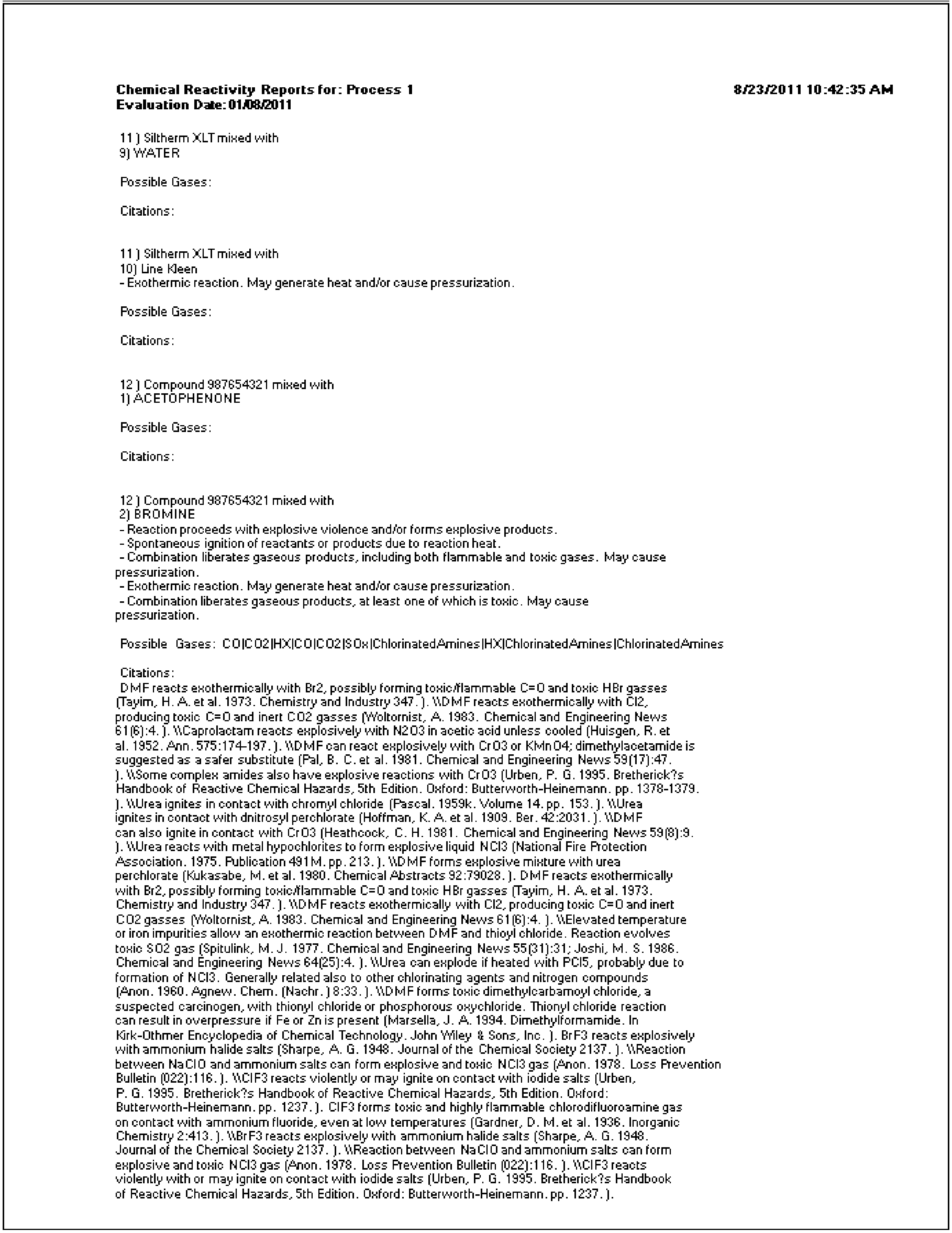

Chemical Reactivity Reports for: Process 1 **8/23/2011 10:42:35 AM**
Evaluation Date: 01/08/2011

11) Siltherm XLT mixed with
9) WATER

Possible Gases:

Citations:

11) Siltherm XLT mixed with
10) Line Kleen
- Exothermic reaction. May generate heat and/or cause pressurization.

Possible Gases:

Citations:

12) Compound 987654321 mixed with
1) ACETOPHENONE

Possible Gases:

Citations:

12) Compound 987654321 mixed with
2) BROMINE
- Reaction proceeds with explosive violence and/or forms explosive products.
- Spontaneous ignition of reactants 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.

Possible Gases: CO|CO2|HX|CO|CO2|SOx|ChlorinatedAmines|HX|ChlorinatedAmines|ChlorinatedAmines

Citations:
DMF reacts exothermically with Br2, possibly forming toxic/flammable C=O and toxic HBr gasses (Tayim, H. A. et al. 1973. Chemistry and Industry 347.). \\DMF reacts exothermically with Cl2, producing toxic C=O and inert CO2 gasses (Woltornist, A. 1983. Chemical and Engineering News 61(6):4.). \\Caprolactam reacts explosively with N2O3 in acetic acid unless cooled (Huisgen, R. et al. 1952. Ann. 575:174-197.). \\DMF can react explosively with CrO3 or KMnO4; dimethylacetamide is suggested as a safer substitute (Pal, B. C. et al. 1981. Chemical and Engineering News 59(17):47.). \\Some complex amides also have explosive reactions with CrO3 (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 1378-1379.). \\Urea ignites in contact with chromyl chloride (Pascal. 1959k. Volume 14. pp. 153.). \\Urea ignites in contact with dnitrosyl perchlorate (Hoffman, K. A. et al. 1909. Ber. 42:2031.). \\DMF can also ignite in contact with CrO3 (Heathcock, C. H. 1981. Chemical and Engineering News 59(8):9.). \\Urea reacts with metal hypochlorites to form explosive liquid NCl3 (National Fire Protection Association. 1975. Publication 491M. pp. 213.). \\DMF forms explosive mixture with urea perchlorate (Kukasabe, M. et al. 1980. Chemical Abstracts 92:79028.). DMF reacts exothermically with Br2, possibly forming toxic/flammable C=O and toxic HBr gasses (Tayim, H. A. et al. 1973. Chemistry and Industry 347.). \\DMF reacts exothermically with Cl2, producing toxic C=O and inert CO2 gasses (Woltornist, A. 1983. Chemical and Engineering News 61(6):4.). \\Elevated temperature or iron impurities allow an exothermic reaction between DMF and thioyl chloride. Reaction evolves toxic SO2 gas (Spitulink, M. J. 1977. Chemical and Engineering News 55(31):31; Joshi, M. S. 1986. Chemical and Engineering News 64(25):4.). \\Urea can explode if heated with PCl5, probably due to formation of NCl3. Generally related also to other chlorinating agents and nitrogen compounds (Anon. 1960. Agnew. Chem. (Nachr.) 8:33.). \\DMF forms toxic dimethylcarbamoyl chloride, a suspected carcinogen, with thionyl chloride or phosphorous oxychloride. Thionyl chloride reaction can result in overpressure if Fe or Zn is present (Marsella, J. A. 1994. Dimethylformamide. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.). BrF3 reacts explosively with ammonium halide salts (Sharpe, A. G. 1948. Journal of the Chemical Society 2137.). \\Reaction between NaClO and ammonium salts can form explosive and toxic NCl3 gas (Anon. 1978. Loss Prevention Bulletin (022):116.). \\ClF3 reacts violently or may ignite on contact with iodide salts (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 1237.). ClF3 forms toxic and highly flammable chlorodifluoroamine gas on contact with ammonium fluoride, even at low temperatures (Gardner, D. M. et al. 1936. Inorganic Chemistry 2:413.). \\BrF3 reacts explosively with ammonium halide salts (Sharpe, A. G. 1948. Journal of the Chemical Society 2137.). \\Reaction between NaClO and ammonium salts can form explosive and toxic NCl3 gas (Anon. 1978. Loss Prevention Bulletin (022):116.). \\ClF3 reacts violently with or may ignite on contact with iodide salts (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 1237.).

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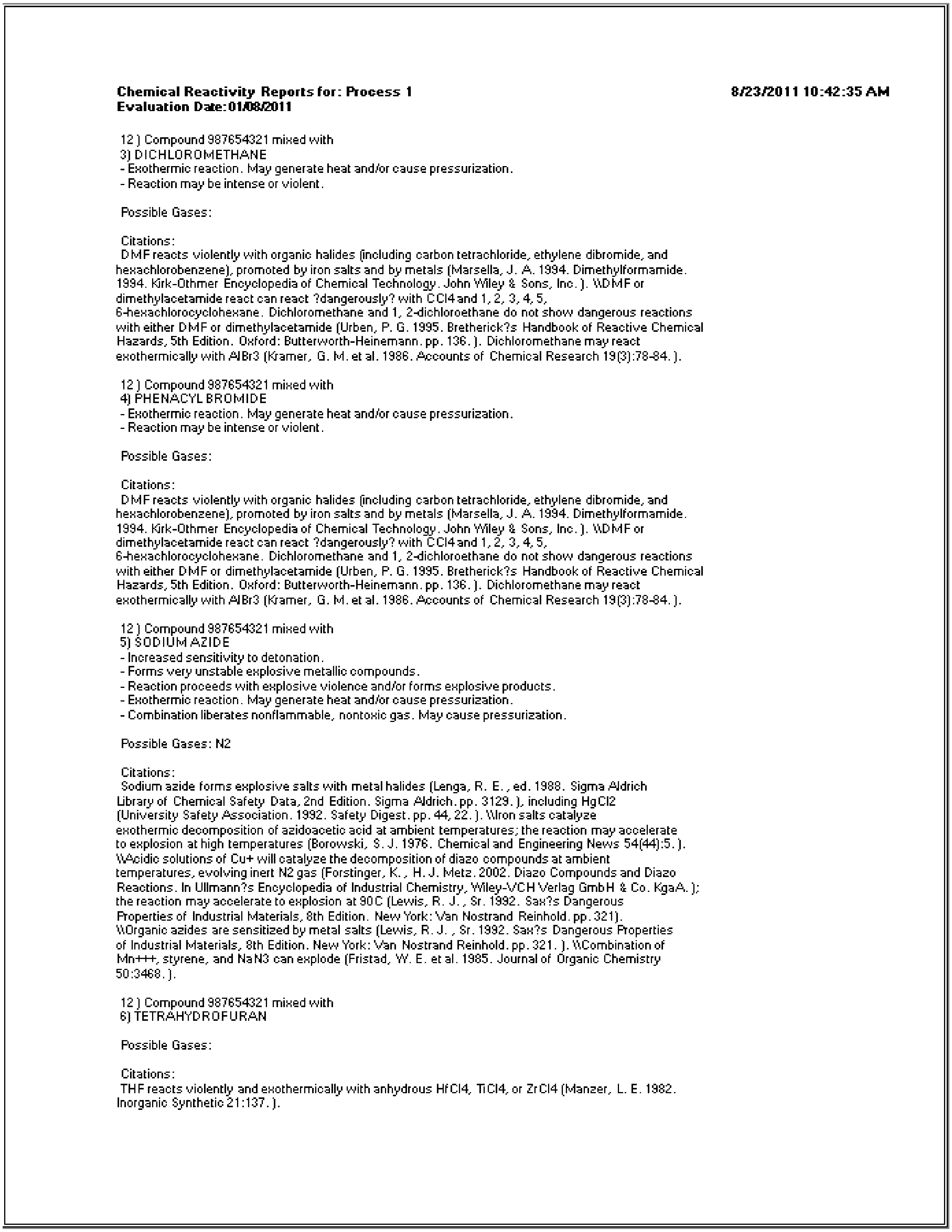

Chemical Reactivity Reports for: Process 1 **8/23/2011 10:42:35 AM**
Evaluation Date:01/08/2011

12) Compound 987654321 mixed with
3) DICHLOROMETHANE
- Exothermic reaction. May generate heat and/or cause pressurization.
- Reaction may be intense or violent.

Possible Gases:

Citations:
DMF reacts violently with organic halides (including carbon tetrachloride, ethylene dibromide, and hexachlorobenzene), promoted by iron salts and by metals (Marsella, J. A. 1994. Dimethylformamide. 1994. Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.). \\DMF or dimethylacetamide react can react ?dangerously? with CCl4 and 1, 2, 3, 4, 5, 6-hexachlorocyclohexane. Dichloromethane and 1, 2-dichloroethane do not show dangerous reactions with either DMF or dimethylacetamide (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 136.). Dichloromethane may react exothermically with AlBr3 (Kramer, G. M. et al. 1986. Accounts of Chemical Research 19(3):78-84.).

12) Compound 987654321 mixed with
4) PHENACYL BROMIDE
- Exothermic reaction. May generate heat and/or cause pressurization.
- Reaction may be intense or violent.

Possible Gases:

Citations:
DMF reacts violently with organic halides (including carbon tetrachloride, ethylene dibromide, and hexachlorobenzene), promoted by iron salts and by metals (Marsella, J. A. 1994. Dimethylformamide. 1994. Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.). \\DMF or dimethylacetamide react can react ?dangerously? with CCl4 and 1, 2, 3, 4, 5, 6-hexachlorocyclohexane. Dichloromethane and 1, 2-dichloroethane do not show dangerous reactions with either DMF or dimethylacetamide (Urben, P. G. 1995. Bretherick?s Handbook of Reactive Chemical Hazards, 5th Edition. Oxford: Butterworth-Heinemann. pp. 136.). Dichloromethane may react exothermically with AlBr3 (Kramer, G. M. et al. 1986. Accounts of Chemical Research 19(3):78-84.).

12) Compound 987654321 mixed with
5) SODIUM AZIDE
- Increased sensitivity to detonation.
- Forms very unstable explosive metallic compounds.
- Reaction proceeds with explosive violence and/or forms explosive products.
- Exothermic reaction. May generate heat and/or cause pressurization.
- Combination liberates nonflammable, nontoxic gas. May cause pressurization.

Possible Gases: N2

Citations:
Sodium azide forms explosive salts with metal halides (Lenga, R. E. , ed. 1988. Sigma Aldrich Library of Chemical Safety Data, 2nd Edition. Sigma Aldrich. pp. 3129.), including HgCl2 (University Safety Association. 1992. Safety Digest. pp. 44, 22.). \\Iron salts catalyze exothermic decomposition of azidoacetic acid at ambient temperatures; the reaction may accelerate to explosion at high temperatures (Borowski, S. J. 1976. Chemical and Engineering News 54(44):5.). \\Acidic solutions of Cu+ will catalyze the decomposition of diazo compounds at ambient temperatures, evolving inert N2 gas (Forstinger, K. , H. J. Metz. 2002. Diazo Compounds and Diazo Reactions. In Ullmann?s Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KgaA.); the reaction may accelerate to explosion at 90C (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 321). \\Organic azides are sensitized by metal salts (Lewis, R. J. , Sr. 1992. Sax?s Dangerous Properties of Industrial Materials, 8th Edition. New York: Van Nostrand Reinhold. pp. 321.). \\Combination of Mn+++, styrene, and NaN3 can explode (Fristad, W. E. et al. 1985. Journal of Organic Chemistry 50:3468.).

12) Compound 987654321 mixed with
6) TETRAHYDROFURAN

Possible Gases:

Citations:
THF reacts violently and exothermically with anhydrous HfCl4, TiCl4, or ZrCl4 (Manzer, L. E. 1982. Inorganic Synthetic 21:137.).

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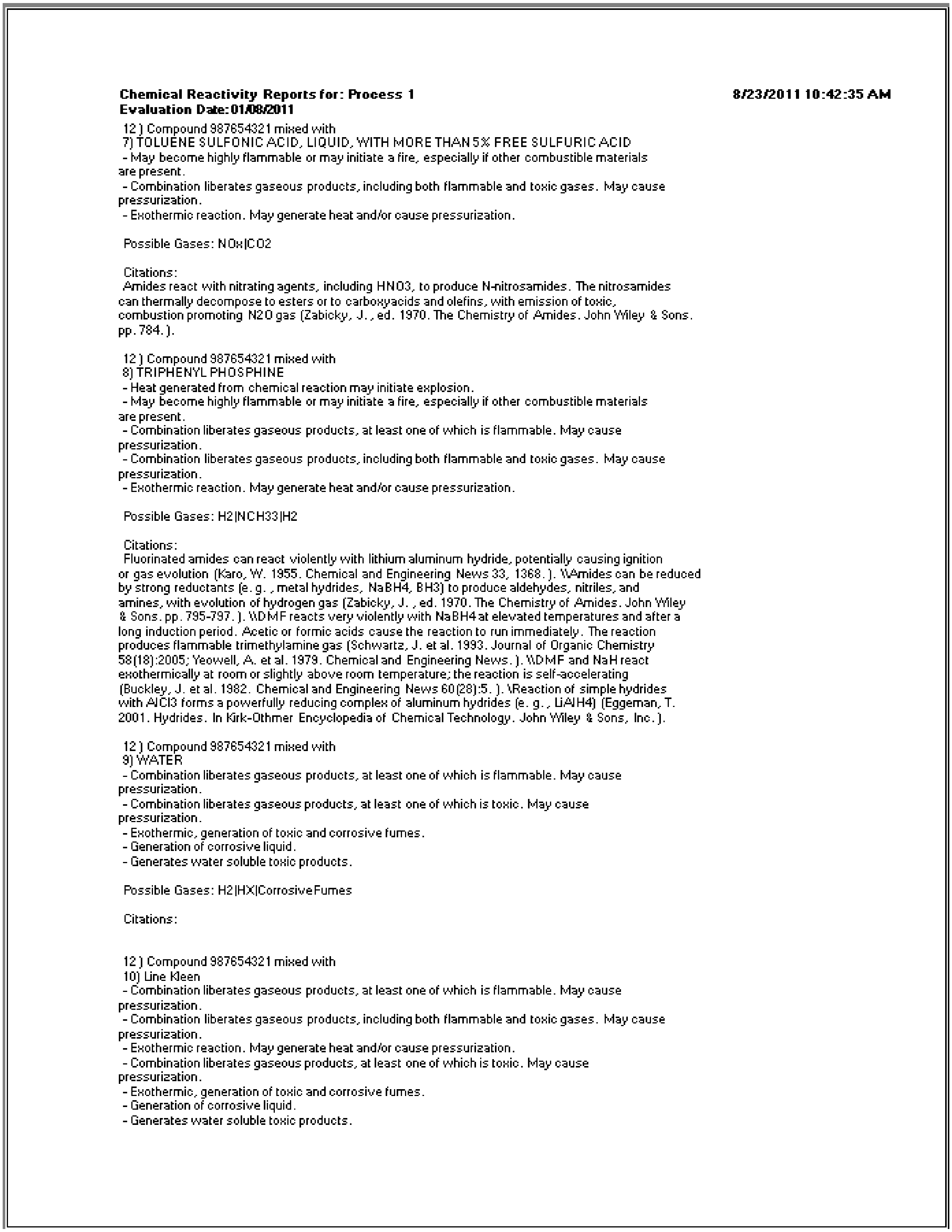

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Chemical Reactivity Reports for: Process 1                                   8/23/2011 10:42:35 AM
Evaluation Date:01/08/2011
 12 ) Compound 987654321 mixed with
 7) TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID
 - May become highly flammable or may initiate a fire, especially if other combustible materials
are present.
 - Combination 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:
 Amides react with nitrating agents, including HNO3, to produce N-nitrosamides. The nitrosamides
can thermally decompose to esters or to carboxyacids and olefins, with emission of toxic,
combustion promoting N2O gas (Zabicky, J., ed. 1970. The Chemistry of Amides. John Wiley & Sons.
pp. 784.).

 12 ) Compound 987654321 mixed with
 8) TRIPHENYL PHOSPHINE
 - Heat generated from chemical reaction may initiate explosion.
 - May become highly flammable or may initiate a fire, especially if other combustible materials
are present.
 - Combination liberates gaseous products, at least one of which is flammable. May cause
pressurization.
 - Combination liberates gaseous products, including both flammable and toxic gases. May cause
pressurization.
 - Exothermic reaction. May generate heat and/or cause pressurization.

 Possible Gases: H2|NCH33|H2

 Citations:
 Fluorinated amides can react violently with lithium aluminum hydride, potentially causing ignition
or gas evolution (Karo, W. 1955. Chemical and Engineering News 33, 1368.). \\Amides can be reduced
by strong reductants (e.g., metal hydrides, NaBH4, BH3) to produce aldehydes, nitriles, and
amines, with evolution of hydrogen gas (Zabicky, J., ed. 1970. The Chemistry of Amides. John Wiley
& Sons. pp. 795-797.). \\DMF reacts very violently with NaBH4 at elevated temperatures and after a
long induction period. Acetic or formic acids cause the reaction to run immediately. The reaction
produces flammable trimethylamine gas (Schwartz, J. et al. 1993. Journal of Organic Chemistry
58(18):2005; Yeowell, A. et al. 1979. Chemical and Engineering News.). \\DMF and NaH react
exothermically at room or slightly above room temperature; the reaction is self-accelerating
(Buckley, J. et al. 1982. Chemical and Engineering News 60(28):5.). \Reaction of simple hydrides
with AlCl3 forms a powerfully reducing complex of aluminum hydrides (e.g., LiAlH4) (Eggeman, T.
2001. Hydrides. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.).

 12 ) Compound 987654321 mixed with
 9) WATER
 - 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.
 - Generates water soluble toxic products.

 Possible Gases: H2|HX|CorrosiveFumes

 Citations:


 12 ) Compound 987654321 mixed with
 10) Line Kleen
 - Combination liberates gaseous products, at least one of which is flammable. May cause
pressurization.
 - 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.
 - Exothermic, generation of toxic and corrosive fumes.
 - Generation of corrosive liquid.
 - Generates water soluble toxic products.
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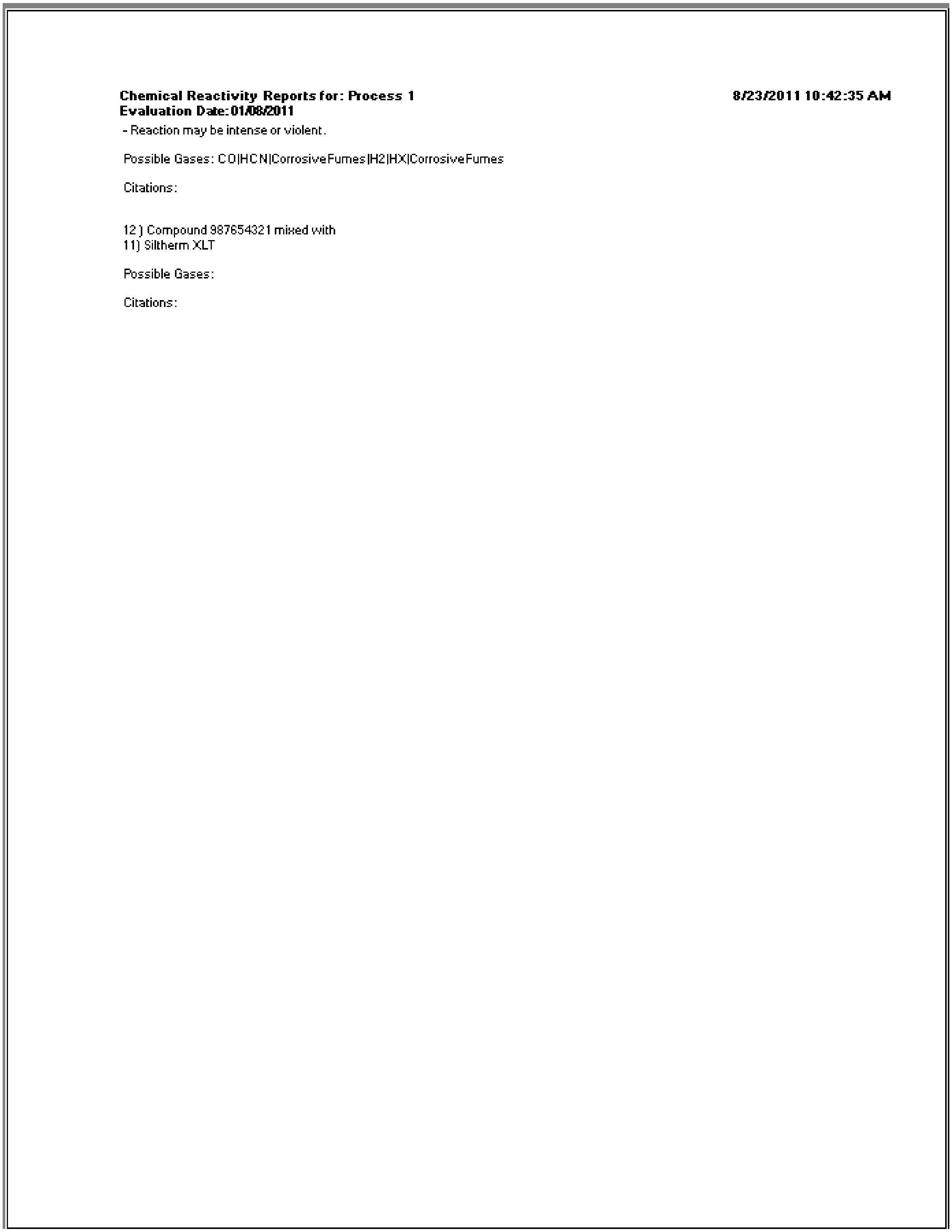

Chemical Reactivity Reports for: Process 1 **8/23/2011 10:42:35 AM**
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- Reaction may be intense or violent.

Possible Gases: CO|HCN|CorrosiveFumes|H2|HX|CorrosiveFumes

Citations:

12) Compound 987654321 mixed with
11) Siltherm XLT

Possible Gases:

Citations:

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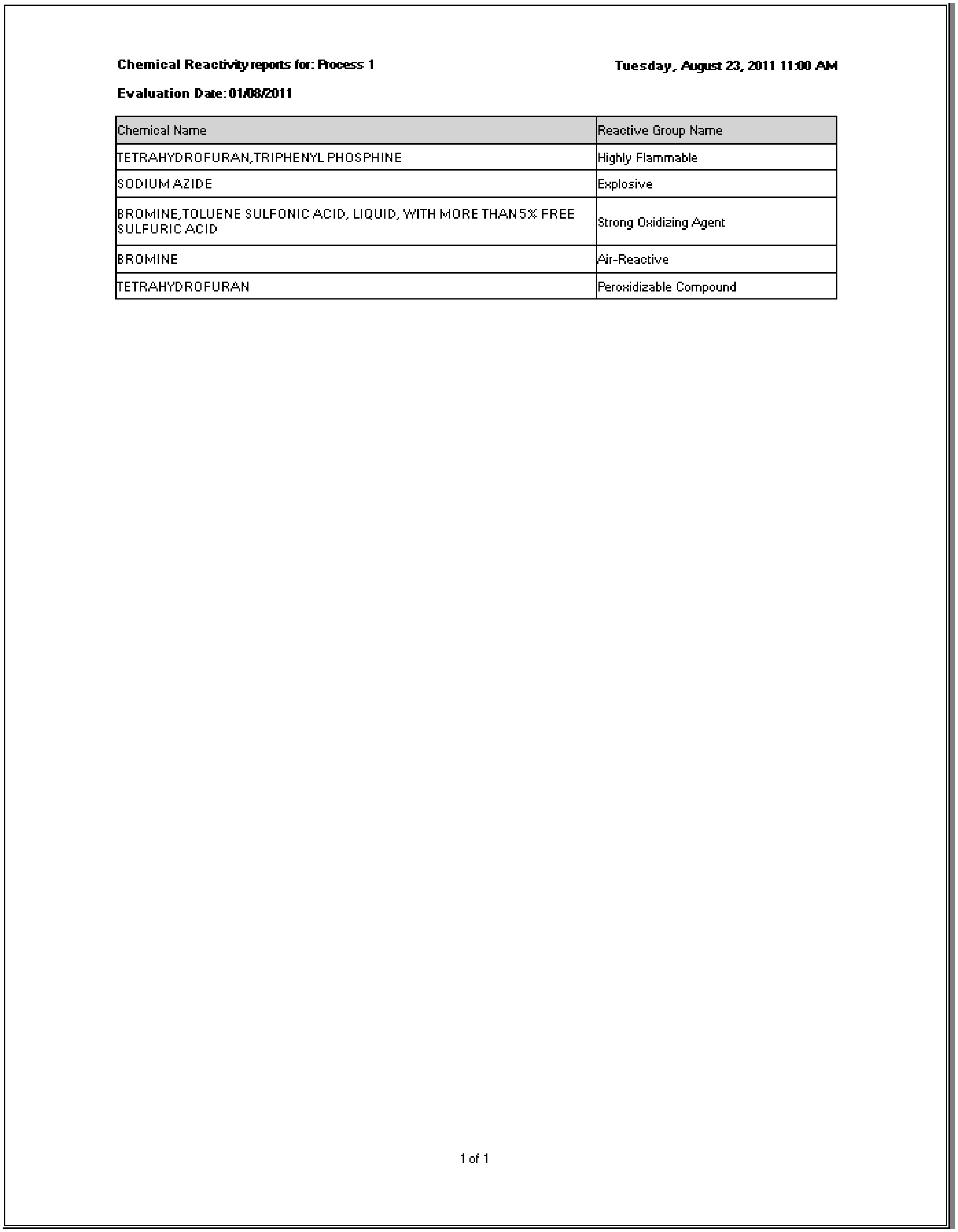
5.3.9.3.4 Pure Component Hazards Tab



Chemical Reactivity reports for: Process 1 **Tuesday, August 23, 2011 11:00 AM**

Evaluation Date: 01/08/2011

Chemical Name	Reactive Group Name
TETRAHYDROFURAN,TRIPHENYL PHOSPHINE	Highly Flammable
SODIUM AZIDE	Explosive
BROMINE,TOLUENE SULFONIC ACID, LIQUID, WITH MORE THAN 5% FREE SULFURIC ACID	Strong Oxidizing Agent
BROMINE	Air-Reactive
TETRAHYDROFURAN	Peroxidizable Compound

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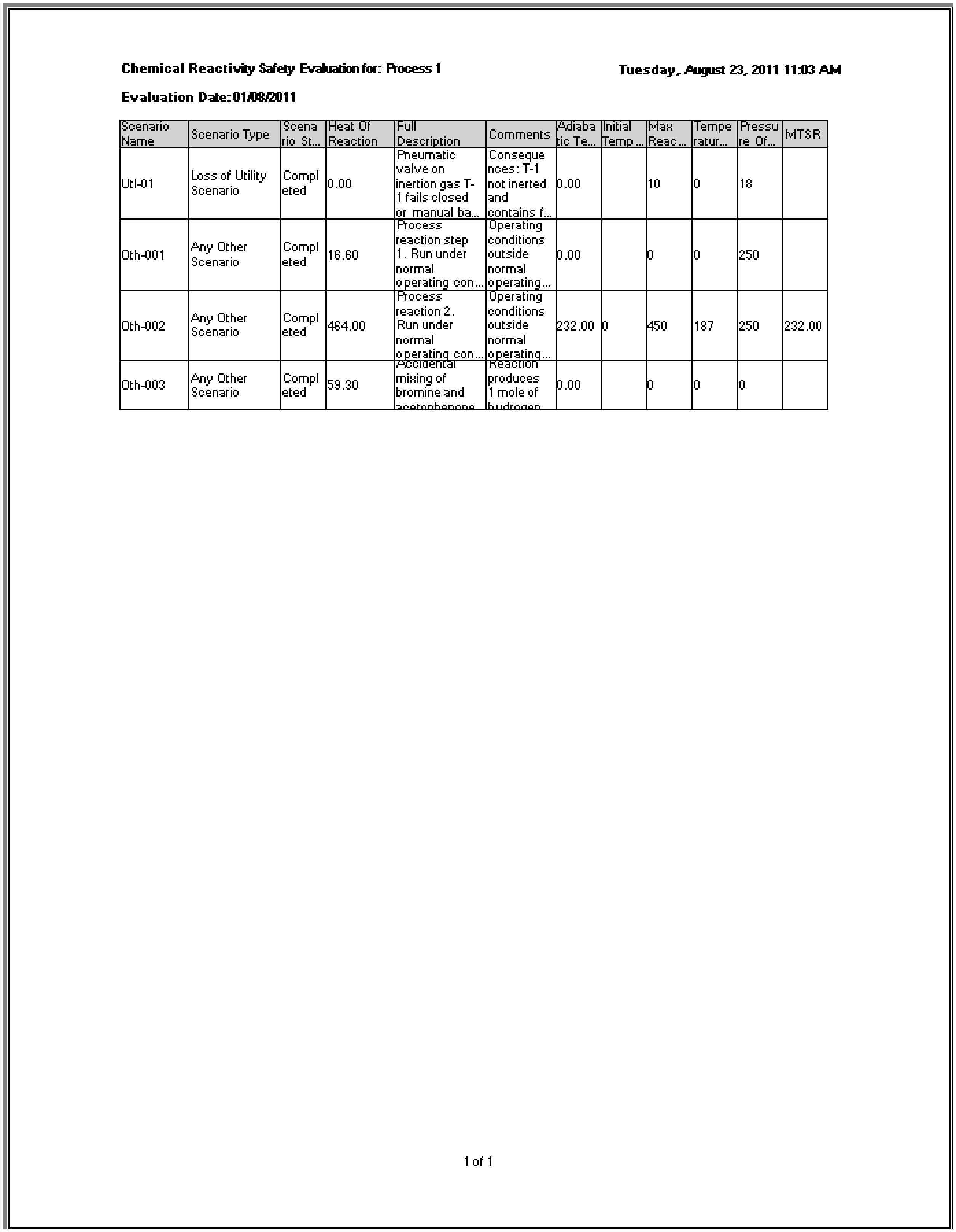
5.3.9.3.5 Scenario Evaluation Tab

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



Chemical Reactivity Safety Evaluation for: Process 1 **Tuesday, August 23, 2011 11:03 AM**

Evaluation Date: 01/08/2011

Scenario Name	Scenario Type	Scenario St...	Heat Of Reaction	Full Description	Comments	Adiabatic Te...	Initial Temp ...	Max Reac...	Temperatur...	Pressure Of...	MTSR
Utl-01	Loss of Utility Scenario	Completed	0.00	Pneumatic valve on inertion gas T-1 fails closed or manual ba...	Consequences: T-1 not inerted and contains f...	0.00		10	0	18	
Oth-001	Any Other Scenario	Completed	16.60	Process reaction step 1. Run under normal operating con...	Operating conditions outside normal operating...	0.00		0	0	250	
Oth-002	Any Other Scenario	Completed	464.00	Process reaction 2. Run under normal operating con...	Operating conditions outside normal operating...	232.00	0	450	187	250	232.00
Oth-003	Any Other Scenario	Completed	59.30	Accidental mixing of bromine and acetophenone	Reaction produces 1 mole of hydrogen	0.00		0	0	0	

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APPENDICES

Appendix A: Program Code Keys

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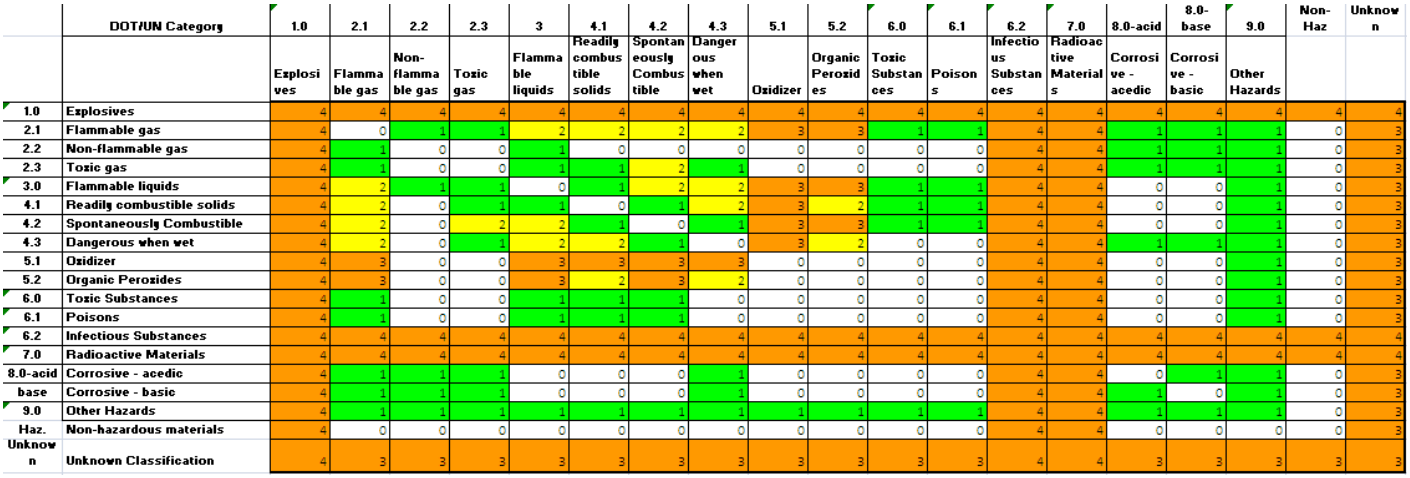
A.1 DOT Segregations

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.



	DOT/UN Category	1.0	2.1	2.2	2.3	3	4.1	4.2	4.3	5.1	5.2	6.0	6.1	6.2	7.0	8.0-acid	8.0-base	9.0	Non-Haz	Unknown
		Explosives	Flammable gas	Non-flammable gas	Toxic gas	Flammable liquids	Readily combustible solids	Spontaneously Combustible	Dangerous when wet	Oxidizer	Organic Peroxides	Toxic Substances	Poisons	Infectious Substances	Radioactive Materials	Corrosive - acedic	Corrosive - basic	Other Hazards		
1.0	Explosives	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
2.1	Flammable gas	4	0	1	1	2	2	2	2	3	3	1	1	4	4	1	1	1	0	3
2.2	Non-flammable gas	4	1	0	0	1	0	0	0	0	0	0	0	4	4	1	1	1	0	3
2.3	Toxic gas	4	1	0	0	1	1	2	1	0	0	0	0	4	4	1	1	1	0	3
3.0	Flammable liquids	4	2	1	1	0	1	2	2	3	3	1	1	4	4	0	0	1	0	3
4.1	Readily combustible solids	4	2	0	1	1	0	1	2	3	2	1	1	4	4	0	0	1	0	3
4.2	Spontaneously Combustible	4	2	0	2	2	1	0	1	3	3	1	1	4	4	0	0	1	0	3
4.3	Dangerous when wet	4	2	0	1	2	2	1	0	3	2	0	0	4	4	1	1	1	0	3
5.1	Oxidizer	4	3	0	0	3	3	3	3	0	0	0	0	4	4	0	0	1	0	3
5.2	Organic Peroxides	4	3	0	0	3	2	3	2	0	0	0	0	4	4	0	0	1	0	3
6.0	Toxic Substances	4	1	0	0	1	1	1	0	0	0	0	0	4	4	0	0	1	0	3
6.1	Poisons	4	1	0	0	1	1	1	0	0	0	0	0	4	4	0	0	1	0	3
6.2	Infectious Substances	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
7.0	Radioactive Materials	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
8.0-acid	Corrosive - acedic	4	1	1	1	0	0	0	1	0	0	0	0	4	4	0	1	1	0	3
base	Corrosive - basic	4	1	1	1	0	0	0	1	0	0	0	0	4	4	1	0	1	0	3
9.0	Other Hazards	4	1	1	1	1	1	1	1	1	1	1	1	4	4	1	1	1	0	3
Haz.	Non-hazardous materials	4	0	0	0	0	0	0	0	0	0	0	0	4	4	0	0	0	0	3
Unknown	Unknown Classification	4	3	3	3	3	3	3	3	3	3	3	3	4	4	3	3	3	3	3

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A.2 Reactivity Matrix Interaction Codes [21]

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

---

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

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A.3 Reactive Groups

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

Continued on next page

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

Reactive group #	**Reactive Group description**
101	Highly Flammable
102	Explosive
103	Polymerizable
104	Strong Oxidizing Agent
105	Strong Reducing Agent
107	Water-Reactive
108	Air-Reactive
109	Pyrophoric
111	Peroxidizable Compound
400	Radioactive Material

A.4 Special Hazards choices

Select One or More [21]
None
Highly Flammable
Explosive
Polymerizable
Strong Oxidizing Agent
Strong Reducing Agent
Water-Reactive
Air-Reactive
Pyrophoric
Peroxidizable Compound
Radioactive Material

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A.5 DOT Codes

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

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

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Appendix B: FAQ

Link To Full TOC

List of Topics

1.) Deselect a secondary DOT code

2.) Chemical adds twice

3.) Next button not available or program will not advance

4.) Navigation tabs grayed out

5.) Importing chemicals and processes from other users

6) My reactivity matrix predicts severe reactivity where I know it does not exist

7) Program Freezes

8) Error message "Unable to add due to some technical problem…"

9) Reactivity groups for custom chemicals shown in the Process Chemicals window are missing or different than those entered.

10) The Special Hazards entered for a custom chemical do not show up in the "Evaluate Pure-componant reactivity hazards" tab of the report.

11) Updated custom chemical data does not appear in process window.

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.

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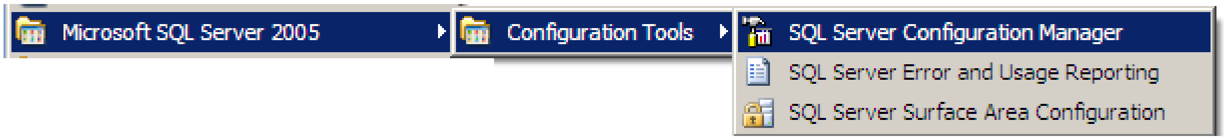
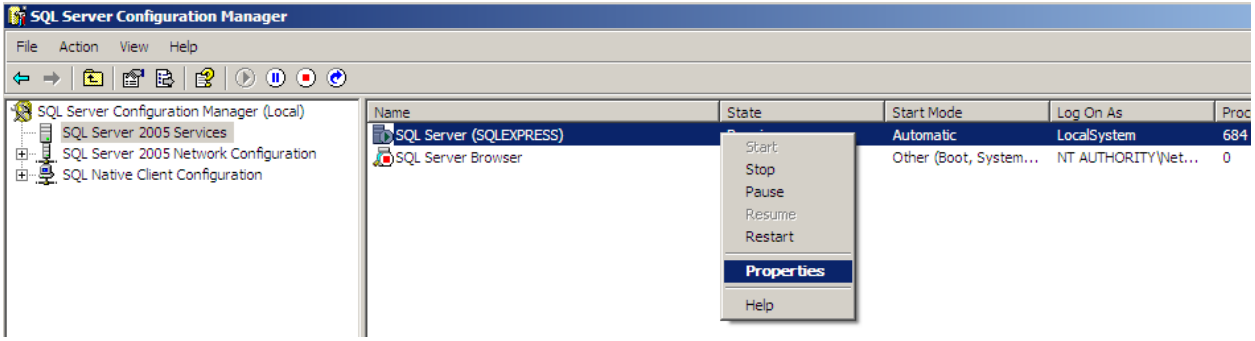
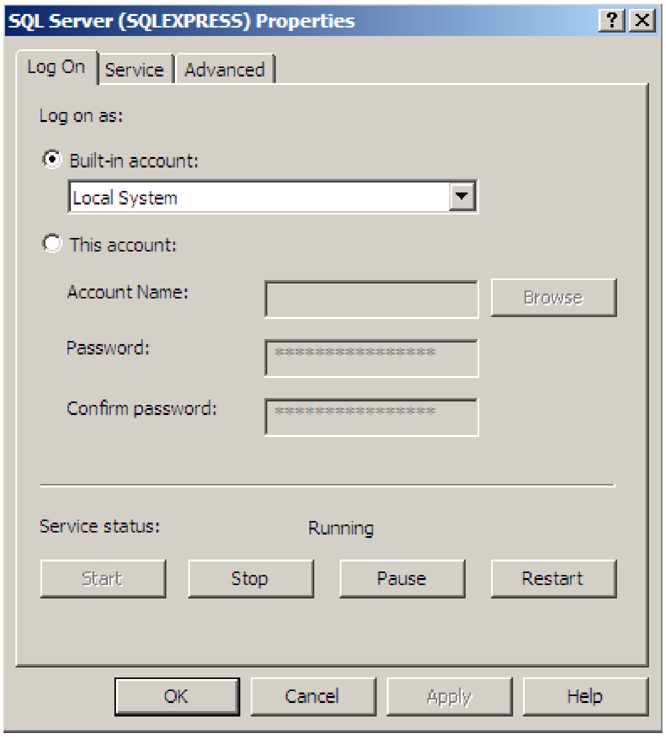
8) Error message “Unable to add due to some technical problem…”
This is a database error. Make sure you have the files RMTDB.mdf and RMTDB_log.ldf in your program directory (see section 3.1.6 Executable and Database File location and descriptions for location). Next check that you have SQL express 2005 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.





Name	State	Start Mode	Log On As	Proc
SQL Server (SQLEXPRESS)		Automatic	LocalSystem	684
SQL Server Browser		Other (Boot, System…	NT AUTHORITY\Net…	0

From the left menu select “SQL Server 2005 services” and right click on “SQL Server (SQLEXPRESS)” and select properties.



Log on as:

● Built-in account: Local System

○ This account:

Account Name:

Password: ******************

Confirm password: ******************

Service status: Running

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.

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Appendix C: Abbreviations and Acronyms

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

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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

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[22] CCPS (2003). Essential Practices for Managing Chemical Reactivity Hazards. AIChE/CCPS. ISBN 978-0-8169-0896-7. The content of this book is available free of charge at www.knovel.com

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 1

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

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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.

Term	Definition
Accelerating rate calorimetry (ARC)	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.)
Activation energy	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.
Adiabatic	No heat transfer occurs to or from the environment surrounding the sample, including the sample container.
Adiabatic temperature rise	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.
Air-reactive	A chemical that reacts with some component of ambient air (usually water or oxygen) to form heat and or gas. Also see Pyrophoric
Arrhenius equation	$k = Z e^{-E/RT}$ 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.
Autocatalysis	The increase of the rate of reaction due to the catalyzing effect of the reaction products.

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Term	Definition
Auto decomposition	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.
Auto decomposition temperature	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.
Autoxidation	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.
Catalyst	A chemical substance that accelerates the rate of a chemical reaction by lowering the energy of activation required for the chemical reaction to occur.
Chemical	Any element, chemical compound, or mixture of elements and/or compounds.
chemical reactivity	The tendency of substances to undergo chemical change.
Chemical reactivity hazard	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.
Compatibility	The ability of materials to exist in contact without specified (usually hazardous) consequences under a defined scenario.

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Term	Definition
Cool-flame ignition	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.
Critical half thickness	An estimation of the half thickness of a sample in an *unstirred container*, 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.
Decomposition	To undergo chemical breakdown, separating into constituent parts or elements or into simpler compounds.
Decomposition energy	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.
Decomposition temperature	See *auto decomposition temperature.*
deflagration	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 *explosive deflagration* may be used.
Detonation	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.
Differential thermal analysis (DTA)	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.
Differential scanning calorimetry (DSC)	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.
Disproportionation	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.

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Term	Definition
Endothermic	A physical or chemical change that requires or is accompanied by the absorption of heat.
Exothermic	A process or chemical reaction that is accompanied by release of heat.
Explosion	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.
Explosive	A chemical that causes a sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden shock, pressure, or high temperature.
Extrinsic factor	As used in this publication, a factor that is not an intrinsic property of a material being handled (see *intrinsic property*).
Flammable gas	(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.
Flammable liquid	Any liquid that has a closed-cup flash point below 100ºF (37.8ºC), as determined by the test procedures described in NFPA 30 and a Reid vapor pressure not exceeding 40 psia (2068.6 mm Hg) at 100ºF (37.8ºC), 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: (a) Class IA liquids shall include those liquids that have flash points below 73ºF (22.8ºC) and boiling points below 100ºF (37.8ºC). (b) Class IB liquids shall include those liquids that have flash points below 73ºF (22.8ºC) and boiling points at or above 100ºF (37.8ºC). (c) Class IC liquids shall include those liquids that have flash points at or above 73ºF (22.8ºC), but below 100ºF (37.8ºC). (NFPA 30)
Hazard	A chemical or physical condition that has the potential for causing damage to people, property, or the environment.
Hazardous chemical	Any chemical that is a physical hazard or a health hazard.

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Term	Definition
Hazardous material	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.
Health hazard	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.
Heat of reaction	The total quantity of thermal energy liberated or absorbed during a chemical reaction. (see section 4.5)
Highly flammable liquid	See Flammable Liquid Class 1A
Hot-flame ignition	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.
Hydration	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.
Hypergolic	Hypergolic behavior is characterized by immediate, spontaneous ignition of an oxidation reaction upon mixing of two or more substances.
Incompatible	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.
Inhibitor	A chemical substance used to prevent or stop a chemical reaction, such as polymerization, from occurring.
Instability	The degree of intrinsic susceptibility of a material to release energy through self-reaction (polymerizing, decomposing, or rearranging).
Intentional chemistry	The mixing or blending of chemicals designed to produce a chemical reaction.
Intrinsic property	In relation to materials, a property of the material itself, regardless of use or environmental conditions.

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Term	Definition
Isomerization	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 C_2H_4O) and butane to isobutane (both C_4H_{10}).
Isoperibolic system	A system in which the controlling external temperature is kept constant.
Isothermal	A system condition in which the temperature remains constant.
Laboratory scale	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.
Minimum ignition energy (MIE)	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.
Monomer	A simple molecule that is capable of combining with a number of other molecules to form a polymer.
MTSR	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)
Near miss	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.
Onset temperature	The temperature at which a deflection from the established baseline is first observed.

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Term	Definition
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.
Oxidizing agent	See definition for *oxidation.*
Partial oxidation	The combination of oxygen with a material in an oxygen-deficient atmosphere that generally results in carbon monoxide being one of the combustion products.
Peroxide	A chemical compound that contains the peroxy (–O–O–) group, which may be considered a derivative of hydrogen peroxide (HOOH).
Peroxide former	A material that reacts with oxygen or hydrogen peroxide to produce a peroxide of the reactant.
Peroxidizable compound	A material that reacts with oxygen or hydrogen peroxide to produce a peroxide of the reactant. l
Physical hazard	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.
Physical processing	The transfer, blending, mixing, grinding, sampling or other handling of open packages of chemicals where no chemical reaction is expected to occur.
Polymer	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.

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Term	Definition
Polymerizable	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
Polymerization	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.
Pressure of concern	The pressure above which unacceptable consequences occur (see section 4.9)
Pyrophoric	A chemical that will ignite spontaneously in air at a temperature of 130°F (54.4°C) or below. Note that definitions of *pyrophoric* from other sources may specify a time frame, usually seconds or minutes, within which ignition must be observed.
Quenching	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.
Radioactive material	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.
Reaction	Any transformation of material accompanied by a change of enthalpy which may be endothermic or exothermic.
Reaction induction time (RIT) value	The time a chemical compound or mixture may be held under isothermal conditions until it exhibits a specific exothermic reaction.
Reactive chemical	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.
Reactive group	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.

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Term	Definition
Reactivity Management System	A complete and comprehensive system for dealing with chemical reactivity hazards both legally and responsibly (See Appendix D)
Reactivity, chemical	See *chemical reactivity.*
Rearrangement	Disproportionation, isomerization, or tautomerization.
Runaway reaction	A reaction that is out of control because the rate of heat generation by an exothermic chemical reaction exceeds the rate of cooling available.
Scenario	In the context of identifying incompatibilities: A detailed physical description of the process whereby a potential inadvertent combination of materials may occur.
Self-accelerating decomposition temperature (SADT)	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.
Self-reactive	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.
Shock sensitive	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.

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Term	Definition
Spontaneously combustible	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.
Stable materials	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.
Strong oxidizing agent	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.
Strong reducing agent	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, "Oxidizing Agent" **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
Tautomerizing	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.
Temperature of concern	The temperature above which unacceptable consequences occur (see section 4.7)
Temperature of no return	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.

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Term	Definition
Thermally unstable	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.
Time to thermal runaway (TMR)	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.
Toll manufacturer	Contract manufacturer (external manufacturer).
Unstable material	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.
Warehousing	The handling of sealed packages of chemicals for the sole purposes of storage and distribution.
Water reactive	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.

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Appendix F: Bibligraphy: Suggested Referances for Further Reading

Link To Full TOC

Table of Contents

F.1 Foundational Process Safety Textbooks and Publications

CCPS (2003). ***Essential Practices for Managing Chemical Reactivity Hazards***. AIChE/CCPS. ISBN 978-0-8169-0896-7. The content of this book is available free of charge at www.knovel.com

CCPS (2009). ***Inherently Safer Chemical Processes: A Life Cycle Approach 2nd ed***. CCPS/AIChE. ISBN 978-0471-77892-9

Crowl, Daniel A., Louvar, Joseph F. (2008) ***Chemical Process Safety: Fundamentals with Applications 2nd ed ,*** Upper Saddle River NJ, Prentice Hall ISBN 0-13-018176-5

CSB (2002). ***Hazard Investigation. "Improving Reactive Hazard Management."*** Report No. 2001-01-H. Washington, D.C.: U.S. Chemical Safety and Hazard Investigation Board. October. 2001

Sanders, Roy E. (1999) ***Chemical Process Safety: Learning from Case Histories***, Boston MA, Butterworth Heinemann ISBN 0-7506-7022-3

F.2 Topical Guidebooks and Publications

Barton, John (2002) ***Dust Explosion: Prevention and Protection***, Rugby UK, IChemE ISBN 0-85295-410-7

CCPS (1994). ***Guidelines for Implementing Process Safety Management Systems***. CCPS/AIChE.

CCPS (1995), ***Guidelines for Chemical Reactivity Evaluation and Applications to Process Design***, 1995, New York, American Institute of Chemical Engineers-Center for Chemical Process Safety. ISBN 0-8169-0479-0.

CCPS (1995). ***Guidelines for Process Safety Documentation***. CCPS/AIChE.

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CCPS (1995). *Guidelines for Safe Storage and Handling of Reactive Materials*, 1995, New York, CCPS / AIChE

CCPS (1999). ***Guidelines for Process Safety in Batch Reaction Systems***. CCPS/AIChE.

CCPS (2001). ***Revalidating Process Hazard Analyses***. CCPS/AIChE.

CCPS (2001). ***Layer of Protection Analysis - Simplified Process Risk Assessment***. CCPS/AIChE.

CCPS (2003). ***Essential Practices for Managing Chemical Reactivity Hazards***. AIChE/CCPS. ISBN 978-0-8169-0896-7. The content of this book is available free of charge at www.knovel.com

CCPS (2006). ***Safe Design and Operation of Process Vents and Emission Control.*** CCPS/AIChE.

CCPS (2007). ***Guidelines for Risk Based Process Safety***. CCPS/AIChE.

CCPS (2008). ***Guidelines for Hazard Evaluation Procedures (3rd Edition)***. CCPS/AIChE.

CCPS (2009). ***Inherently Safer Chemical Processes: A Life Cycle Approach 2nd ed.*** CCPS/AIChE. ISBN 978-0471-77892-9

CCPS (2011), ***Guidelines for Engineering Process Safety Design, Second Edition***, 2011, New York, , American Institute of Chemical Engineers- Center for Chemical Process Safety (CCPS)

David Leggett, ***Chemical reaction hazard identification and evaluation: Taking the first steps***, Process Safety Progress, March 2004,Volume 23, No. 1, AIChE

Davies, A.G. (1961) ***Organic Peroxides***. London: Butterworths.

Lewis, R.J. (2004). ***Sax's Dangerous Properties of Industrial Materials, 11th Edition***. New York: Wiley-Interscience. ISBN 978-0471476627.

NOAA (2009). ***Chemical Reactivity Worksheet, Version 2.0.2***. Washington, D.C.: U.S. National Oceanic and Atmospheric Administration

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

Perry, Judy; ***Strategy for Managing Reactivity Hazards, An ioMosaic Corporation Whitepaper***; available free of charge (registration required) http://www.iomosaic.com

Urben, Peter G. (2007). ***Bretherick's Handbook of Reactive Chemical Hazards, Volumes 1-2 (7th Edition)***. *Elsevier.*

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F.3 Pertinent References on Common Pure Componant Hazards

F.3.1 Safe Storage and Handling of Spontaneously Combustible Materials

Gudelines for the Safe Storage and Handling of Reactive Materials, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (1995); www.aiche.org/ccps
Essential Practices for Managing Reactivity Hazards, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (1995); www.aiche.org/ccps
Guidelines for Chemical Reactivity Evaluation and Application to Process Design; Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (1995); www.aiche.org/ccps
Guidelines for Engineering Design for Chemical Process Safety, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (2003); www.aiche.org/ccps
Guidelines For The Safe Handling of Powers and Bulk Solids; Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (2005); www.aiche.org/ccps
Organoaluminum Compounds; J. Mole and EA Jeffery (1972); Elsevier Publishing Company, Amsterdam, The Netherlands
Hazardous Chemicals Handbook; PA Carson and CJ Mumford (1994); Elsevier Publishing Company, Amsterdam, The Netherlands
Loss Prevention in the Process Industries, Frank P. Lees, Third Edition; Elsevier –Butterworth-Heinmann, Burlingtom, MA (2005); www.elsevier.com
NFPA 400 *Hazardous Chemicals Code*, National Fire Protection Association, Quincy MA; www.nfpa.org
NFPA 15 *Standard for Water Spray Fixed Systems for Fire Protection*, National Fire Protection Association, Quincy MA; www.nfpa.org
NFPA 432 *Code for the Storage of Organic Peroxide Formulations*; National Fire Protection Association, Quincy MA; www.nfpa.org
NFPA 484 *Standard for Combustible Metals*; National Fire Protection Association, Quincy MA; www.nfpa.org
NFPA 654 *Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids*; National Fire Protection Association, Quincy MA; www.nfpa.org
NFPA 654, *Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids*, National Fire Protection Association, Quincy MA; www.nfpa.org
Fire Protection Handbook; National Fire Protection Association, Quincy MA; www.nfpa.org

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Primer on Spontaneous Heating and Pyrophoricity; US Department of Energy, Washington, DC; www.doe.gov
Handling Procedures for Organometalics; Albemarle Corporation, Baton Rouge, LA; www.albemarle.com
Creating the Right Chemistry - Metal Alkyls from Akzo Nobel; Akzo Nobel Polymer Chemicals, Chicago, IL (2003); www.akzonobel-polymerchemicals.com
Personal Protective Equipment for Handling Metal Alkyals; Akzo Nobel Polymer Chemicals, Chicago, IL (2003); www.akzonobel-polymerchemicals.com
Metal Alkyals and Their Burning Properties; Akzo Nobel Polymer Chemicals, Chicago, IL (2003); www.akzonobel-polymerchemicals.com
Pyrophoricity of Metal Alkyals; Akzo Nobel Polymer Chemicals, Chicago, IL (2003); www.akzonobel-polymerchemicals.com
Unloading Procedure for Metal Alkyals in C-Type Portable Tanks; Akzo Nobel Polymer Chemicals, Chicago, IL (2003); www.akzonobel-polymerchemicals.com
Control of Metal Alkyl Fires; Akzo Nobel Polymer Chemicals, Chicago, IL (2003); www.akzonobel-polymerchemicals.com
Metal Alkyls and Their Solutions; Akzo Nobel Polymer Chemicals, Chicago, IL (2003); www.akzonobel-polymerchemicals.com
UnloadingProcedures for Metal Alkyls in ISO Portable Tanks; Akzo Nobel Polymer Chemicals, Chicago, IL (2003); www.akzonobel-polymerchemicals.com
Disposal of Metal Alkyl Residues; Akzo Nobel Polymer Chemicals, Chicago, IL (2003); www.akzonobel-polymerchemicals.com

F.3.2 Safe Storage and Handling of Self Reacting Materials

Guidelines for the Safe Storage and Handling of Reactive Materials, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (1995); www.aiche.org/ccps
Essential Practices for Managing Reactivity Hazards, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (1995); www.aiche.org/ccps
Guidelines for Chemical Reactivity Evaluation and Application to Process Design; Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (1995); www.aiche.org/ccps
Guidelines for Engineering Design for Chemical Process Safety, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (2003); www.aiche.org/ccps
Hazardous Chemicals Handbook; PA Carson and CJ Mumford (1994); Elsevier Publishing Company, Amsterdam, The Netherlands

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Loss Prevention in the Process Industries, Frank P. Lees, Third Edition; Elsevier –Butterworth-Heinmann, Burlingtom, MA (2005); www.elsevier.com

NFPA 400 *Hazardous Chemicals Code*, National Fire Protection Association, Quincy MA; www.nfpa.org

NFPA 15 *Standard for Water Spray Fixed Systems for Fire Protection*, National Fire Protection Association, Quincy MA; www.nfpa.org

NFPA 68, *Standard on Explosion Protection by Deflagration Venting*, National Fire Protection Association, Quincy MA; www.nfpa.org

NFPA 69, *Standard on Explosion Prevention Systems*, National Fire Protection Association, Quincy MA; www.nfpa.org

NFPA 432 Code for the Storage of Organic Peroxide Formulations, National Fire Protection Association, Quincy MA; www.nfpa.org

NFPA 35 Standard for the Manufacture of Organic Coatings, National Fire Protection Association, Quincy MA; www.nfpa.org

Popcorn Polymer Resource Book, 1,3-Butadiene; International Institute of Synthetic Rubber Producers, Inc. (1995; www.iisrp.com

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

Guidelines for the Safe Storage and Handling of Reactive Materials, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (1995); www.aiche.org/ccps

R.W. Johnson, S.W. Rudy and S.D. Unwin, Essential Practices for Managing Chemical Reactivity Hazards, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (2003); www.aiche.org/ccps

Guidelines for Chemical Reactivity Evaluation and Application to Process Design; Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (1995); www.aiche.org/ccps

Guidelines for Engineering Design for Chemical Process Safety, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (2003); www.aiche.org/ccps

Hazardous Chemicals Handbook; PA Carson and CJ Mumford (1994); Elsevier Publishing Company, Amsterdam, The Netherlands

S. Mannan (ed.), Loss Prevention in the Process Industries, Third Edition; Elsevier –Butterworth-Heinmann, Burlingtom, MA (2005); www.elsevier.com

NFPA 400, *Hazardous Chemicals Code*, National Fire Protection Association, Quincy MA; www.nfpa.org

NFPA 15 *Standard for Water Spray Fixed Systems for Fire Protection*, National Fire Protection Association, Quincy MA; www.nfpa.org

NFPA 68, *Standard on Explosion Protection by Deflagration Venting*, National Fire Protection Association, Quincy MA; www.nfpa.org

NFPA 69, *Standard on Explosion Prevention Systems*, National Fire Protection Association, Quincy MA; www.nfpa.org

NFPA 430, Code for the Storage of Liquid and Solid Oxidizers, National Fire Protection Association, Quincy MA; www.nfpa.org

NFPA 432, Code for the Storage of Organic Peroxide Formulations, National Fire Protection Association, Quincy MA; www.nfpa.org

NFPA 35, Standard for the Manufacture of Organic Coatings, National Fire Protection Association, Quincy MA; www.nfpa.org

Popcorn Polymer Resource Book, 1,3-Butadiene; International Institute of Synthetic Rubber Producers, Inc. (1995; www.iisrp.com

F.3.4 Safe Storage and Handling of Water reactives

Guidelines for the Safe Storage and Handling of Reactive Materials, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (1995); www.aiche.org/ccps

R.W. Johnson, S.W. Rudy and S.D. Unwin, Essential Practices for Managing Chemical Reactivity Hazards, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (2003); www.aiche.org/ccps

Guidelines for Chemical Reactivity Evaluation and Application to Process Design; Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (1995); www.aiche.org/ccps

Guidelines for Engineering Design for Chemical Process Safety, Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York, NY (2003); www.aiche.org/ccps

Hazardous Chemicals Handbook; PA Carson and CJ Mumford (1994); Elsevier Publishing Company, Amsterdam, The Netherlands

S. Mannan (ed.), Loss Prevention in the Process Industries, Third Edition; Elsevier –Butterworth-Heinmann, Burlingtom, MA (2005); www.elsevier.com

Kapias, T., R. F. Griffiths, and C. Stefanidis (2001). "REACTPOOL: a Code Implementing a New Multi-Compound Pool Model That Accounts for Chemical Reactions and Changing Composition for Spills of Water Reactive Chemicals." *Journal of Hazardous Materials* A81, 1-18

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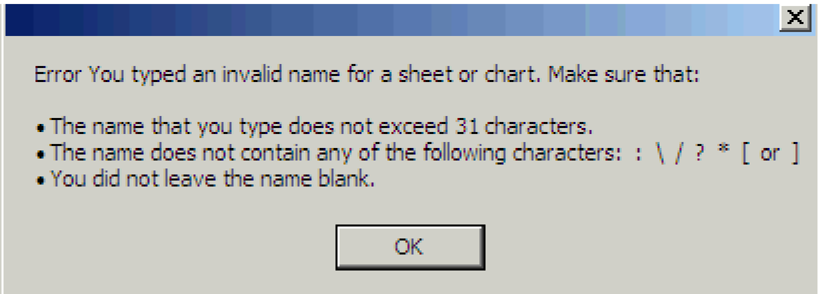
Appendix G: Known Programming Bugs

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:


Error You typed an invalid name for a sheet or chart. Make sure that:

- The name that you type does not exceed 31 characters.
- The name does not contain any of the following characters: : \ / ? * [or]
- You did not leave the name blank.

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.

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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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vs. Chemical Processing