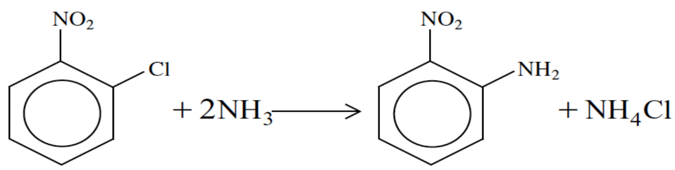
Reaction Engineering and Design

[i]**Safety Module 2a:** *Monsanto Runaway Reaction*[†]

This module is based on Example 13-2 in the 2nd edition of *Essentials of Chemical Reaction Engineering* and the 5th edition of *Elements of Chemical Reaction Engineering*.

Problem Statement: A serious accident occurred at the Monsanto plant in Sauget, Illinois, on August 8, 1969, at 12:18 AM. (see Figure E13-2.1). (Sauget (pop. 200) is the home of the 1988 Mon-Clar League Softball Champions.) The blast was heard as far as 10 miles away in Belleville, Illinois, where people were awakened from their sleep. The explosion occurred in a batch reactor that was used to produce nitroaniline and ammonium chloride from ammonia and o-nitrochlorobenzene (ONCB) in the presence of water:



$$A + 2B \xrightarrow[H_2O(W)]{} C + D$$

This reaction is normally carried out isothermally at 175°C and about 500 psi. The ambient temperature of the cooling water in the heat exchanger is 25°C. By adjusting the coolant rate, the reactor temperature could be maintained at 175°C. At the maximum coolant rate, the ambient temperature is 25°C throughout the heat exchanger. Let me tell you something about the operation of this reactor. Over the years, the heat exchanger would fail from time to time, but the technicians would be "Johnny on the Spot" and run out and get it up and running within 10 minutes or so, and there was never any problem. It is believed that one day someone in management looked at the reactor and said, "It looks as if your reactor is only a third full and you still have room to add more reactants and to make more product and more money. How about filling it up to the top so we could triple production?" They did and started the reactor up at 9:45 PM. As before, the heat exchanger went down at 10:30 PM. The reaction continued until around midnight when the reactor exploded. The aftermath is shown in the following figure.

Figure E13-2.1. Aftermath of the explosion. (St. Louis Globe/Democrat photo by Roy Cook. Courtesy of St. Louis Mercantile Library.)

[†] Adapted from the problem by Ronald Willey, Seminar on a Nitroaniline Reactor Rupture. Prepared for SAChE, Center for Chemical Process Safety, American Institute of Chemical Engineers, New York (1994). Also see Process Safety Progress, vol. 20, no. 2 (2001), pp. 123–129. The values of ΔH_{Rx} and UA were estimated from the plant data of the temperature–time trajectory in the article by G. C. Vincent, Loss Prevention, 5, 46–52.

The model equations and parameter values are given in Example 13-2 of the textbook. One added note: As long as Q_g is less than the maximum value of Q_r a temperature controller can maintain the temperature at 175°C. Consequently, any temporary upset due to heat exchange failure where the temperature will be returned to 175°C provided the maximum value for Q_r is greater than Q_g.

While a Chemical Safety Board video of incident does not exist for the Monsanto explosion, a parallel incident with similar circumstances and concepts ($Q_g > Q_r$) can be found in the Synthron Explosion. The Chemical Safety Board video can be helpful for understanding parallels between explosions, however, note that the situations are **different**, and the problems that follow are **only** regarding the Monsanto situation.

Synthron Video: (*https://www.youtube.com/watch?v=sRuz9bzBrtY*) *Note:* Only relevant from 2:00-7:00

Synthron Incident Report: (*https://www.csb.gov/file.aspx?DocumentId=5619*)

Monsanto Runaway Power Point: (*http://umich.edu/~safeche/assets/pdf/Ch9Explosion.ppt*)
Note: This PowerPoint also served as an introduction to Chemical Reaction Engineering, so only slides 1-15 are relevant for this module.

(a) It is important that chemical engineers understand what the accident was, why it happened and how it could have been prevented in order ensure similar accidents may be prevented. Applying a safety algorithm to the accident will help achieve this goal. In order to become familiar with a strategy for accident awareness and prevention, re-read the background information on the Monsanto explosion and fill out the following Safety Algorithm for the Monsanto incident. See definitions on the last page.

Safety Analysis of Monsanto Incident

Activity: ____

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Hazard: ____

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Incident: ____

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Initiating Event: ____

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Preventative Actions and Safeguards: ____

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Contingency Plan/ Mitigating Actions: ____

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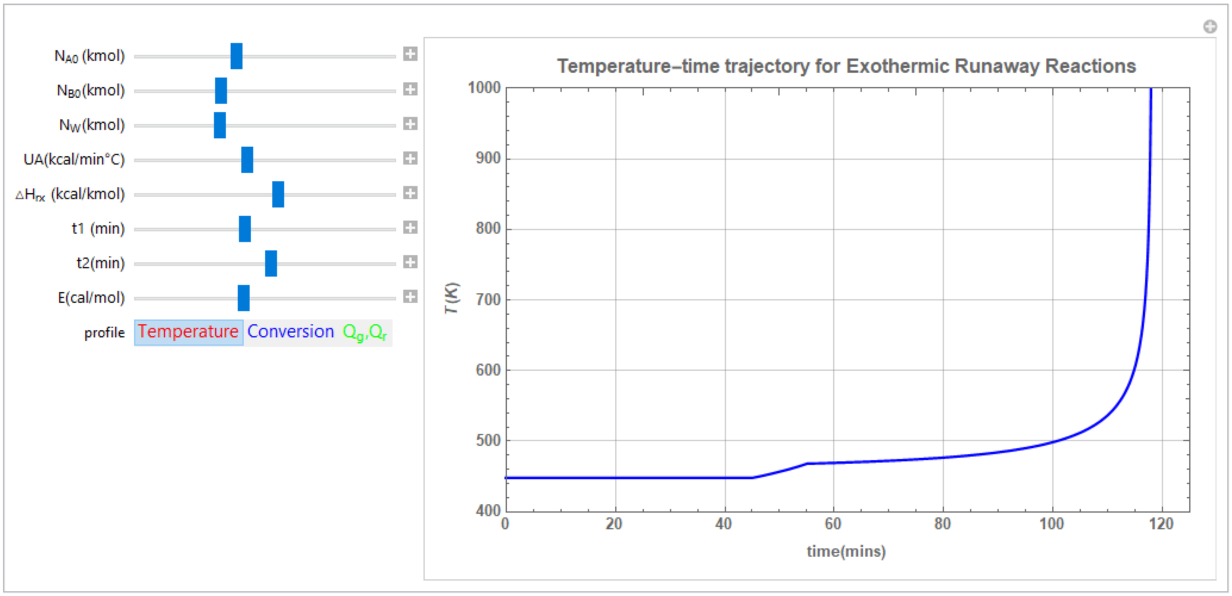
Lessons Learned: ____

For Parts (b)-(e), go to Living Example Problems in Chapter 13 of Elements or Essentials of Chemical Reaction Engineering and load Example 13-2 using Wolfram.

http://www.umich.edu/~elements/5e/tutorials/Wolfram_tutorials.html

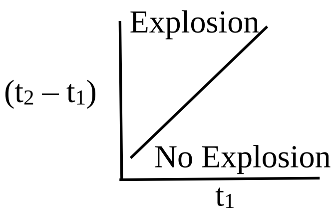
You can download Wolfram on your computer for free, just follow the instructions at the bottom of the LEP web page (*http://www.umich.edu/~elements/5e/13chap/live.html*).



(b) In the Wolfram file, t_1 is defined as the time after the start of the reaction when the heat exchanger fails, and t_2 is defined as the time when heat exchange is restored. Given $t_1 = 45$ minutes and $t_2 = 55$ minutes, show that the explosion would not have occurred if the ONCB amount had not been increased from its original recipe value.

(c) Show the explosion would not have occurred for triple production (i.e. an increase from $N_{A0} = 3.17$ kmol to $N_{A0} = 9.04$ kmol) if the heat exchanger had not failed.

(d) Plot the down time ($t_2 - t_1$) versus time since the start of the reaction that the heat exchanger fails (t_1). Explain how the plot could help in identifying regions where the explosion will and will not occur.



HINT: Choose t_1 and then find the largest t_2 for which the reaction will not run away. Choose another larger value of t_1 and repeat. Continue in this manner to construct your plot.

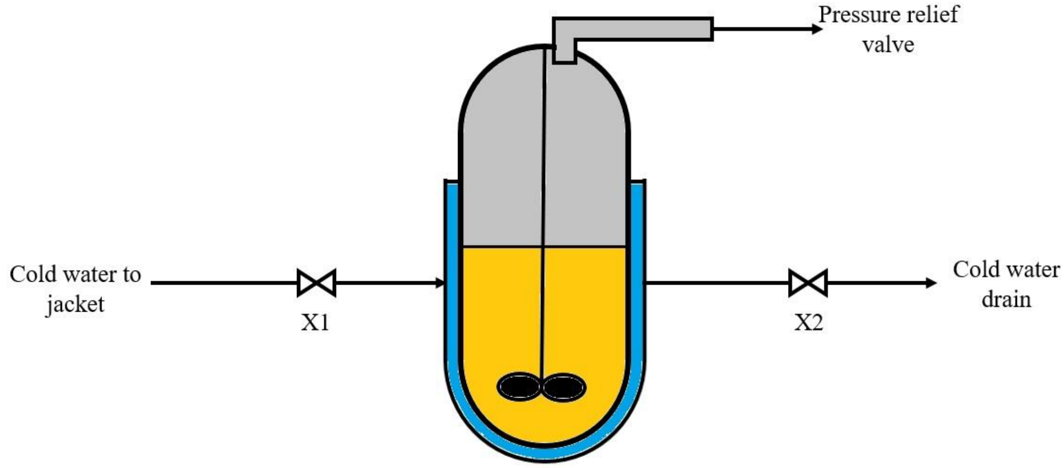
(e) Vary other Wolfram parameters and write a set of conclusions.

Parts (f)-(h) are based on industry practices used to assess process safety. For more information on process safety and its importance in chemical engineering, please visit the University of Michigan SafeChE website here. *It is recommended that professors only assign 1-2 of the following parts due to the similar nature of the questions.*

(f) Review the explanation of the components of a BowTie diagrams found here. After reviewing the information, create a BowTie diagram for the Monsanto incident.

(g) A HAZOP study is structured analysis of process design to identify potential vulnerabilities in a facility. Review the background on how to conduct a HAZOP study here before completing one for the following system. It is important to note that not all guidewords and parameters will be relevant for different systems. Some information is given here for guidance:

System to consider: The batch reactor used to produce nitroaniline and ammonium chloride from ammonia and ONCB, which is an exothermic reaction. The reactor is normally maintained at a constant temperature of 175 °C by a cooling jacket and a pressure of about 500 psi.



Process parameters to consider: Temperature, Pressure, Level, Composition

(i) Fill out the HAZOP chart as shown in the tutorial. Some other information has been filled out here for you.

Guideword + Parameter = Deviation	**Causes**	**Consequences**	**Safeguards**	**Recommendations**
More (Higher) Temperature	Heat exchange failure			
More (Higher) Pressure	Continuous temperature increase			
More Level				
Other Composition *Than* Usual				

(ii) When conducting a HAZOP, you will often find combinations of guidewords and parameters that describe a possible situation for the system that is not hazardous. For the given process parameters, give an example, explain why the situation is not hazardous, and describe another consequence that could occur. *HINT*: Consider the effect of an overworking heat exchanger.

(iii) Write a short conclusion on some takeaways from completing a HAZOP for this system and recommendations you would make.

(h) A Layers of Protection Analysis (LOPA) is a semi-quantitative study to identify available safeguards and determine if the safeguards sufficiently protect against a given risk. Review the background on how to conduct a LOPA study here before filling the table out for the system described in this module. Some information is given for guidance:

- Assume that the plant can only accept a moderate risk
- Assume that the nitroaniline reaction is carried out 100 times per year
- The explosion caused severe plant damage and put the lives of all operators in danger

LOPA Study for Monsanto Runaway Explosion		
Initiating Event	Cause:	Operator Error (charging more feed than normal)
	Consequence:	Unexpected increase of heat release and reaction runaway that can lead to an explosion
	FOIE:	
IPL(s)	Description of IPL_1, IPL_2, ...	
	$PFD = PFD_1 \times PFD_2 \times ...$	
MCF	MCF = FOIE x PFD	
	Category of MCF:	
Severity	Impact:	Potential for multiple fatalities, extensive damage
	Category:	
Risk	Type of risk:	
	Acceptable / Unacceptable?	
If risk evaluated above is unacceptable, please continue below:		
Proposed IPL(s) (P-IPL(s))	Description of P-IPL_1, P-IPL_2, ...	
	$P\text{-}PFD = P\text{-}PFD_1 \times P\text{-}PFD_2 \times ...$	
MCF	MCF = FOIE x PFD x P-PFD	
	Category of MCF:	

Risk	Type of risk:	
	Acceptable / Unacceptable?	

(i) Describe what was the most unsettling to you about this incident.

Additional Information:

Rate law: $-r_{ONCB} = kC_{ONCB}C_{NH_3}$

With $k = 0.00017 \frac{m^3}{kmol \cdot min}$ at 188°C (461K) and $E = 11.273 \frac{cal}{mol}$

The reaction volume for the new charge of 9.0448 kmol of ONCB:
V = 3.265 m^3 ONCB/NH_3 + 1.854 m^3 H_2O = 5.119 m^3

The reaction volume for the previous charge of 3.17 kmol of ONCB: V = 3.26 m^3

$$\Delta H_{Rx} = -5.9 \times 10^5 \frac{kcal}{kmol}$$

$$C_{P_{ONCB}} = C_{P_A} = 40 \frac{cal}{mol \cdot K}$$

$$C_{P_{H_2O}} = C_{P_W} = 18 \frac{cal}{mol \cdot K}$$

$$C_{P_{NH_3}} = C_{P_B} = 8.38 \frac{cal}{mol \cdot K}$$

Assume that $\Delta C_P \approx 0$

$$UA = 35.85 \frac{kcal}{min \cdot °C} \; with \; T_A = 298K$$

Definitions

Activity: The process, situation, or activity for which risk to people, property or the environment is being evaluated.

Hazard: A chemical or physical characteristic that has the potential to cause damage to people, property, or the environment.

Incident: What happened? Description of the event or sum of the events along with the steps that lead to one or more undesirable consequences, such as harm to people, damage to property, harm to the environment, or asset/business losses.

Initiating Event: The event that triggers the incident, (e.g., failure of equipment, instrumentation, human actions, flammable release, etc.). Could also include precursor events, (e.g., no flow from pump, valve closed, inadvertent human action, ignition). The root cause of the sum events in causing the incident.

Preventative Actions and Safeguards: Steps that can be taken to prevent the initiating event from occurring and becoming an incident that causes damage to people, property, or the environment. Brainstorm all problems that could go wrong and then actions that could be taken to prevent them from occurring.

Contingency Plan/ Mitigating Actions: These actions occur after the initiating event. They are steps that reduce or mitigate the incident after the preventative action fails and the initiating event occurred.

Lessons Learned: What we have learned and can pass on to others that can prevent similar incidents from occurring

BowTie Diagram: A qualitative hazard analysis tool through which potential problems and consequences associated with a hazard are studied through a pictorial representation. Necessary preventive and mitigating barriers are determined to reduce the process safety risk.

Hazard and Operability Study (HAZOP): A qualitative hazard analysis tool that uses a set of guide words to determine whether deviations from design or operating intent can lead to undesirable consequences. The existing safeguards are evaluated and if required, actions are recommended to mitigate the consequences.

Layer of Protection Analysis (LOPA): A semi-quantitative study that determines initiating event frequency, consequence severity, and likelihood of failure of independent protection layers (IPLs) to calculate the risk of a scenario. If the existing risk is intolerable, then additional IPLs are suggested to bring down risk to an acceptable level.

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[i] In collaboration with Zach Gdowski, University of Michigan