CE 400 / CE 500

Process Safety Management

Lecture 16 Chemical Reactivity

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Chemical Reactivity

- Chemical reactions that are unintended or otherwise uncontrolled can lead to serious consequences
- Two main routes:
  - Exothermic reactions lead to large energy release generating rapid pressure build and possibility of explosion
  - Generation and release of unintended toxic or flammable materials
- From 1980 to 2001 there were 167 incidents related to chemical reactivity leading to 108 fatalities according to the Chemical Safety Board (CSB) in their 2002 report

Chemical Reactivity Hazards

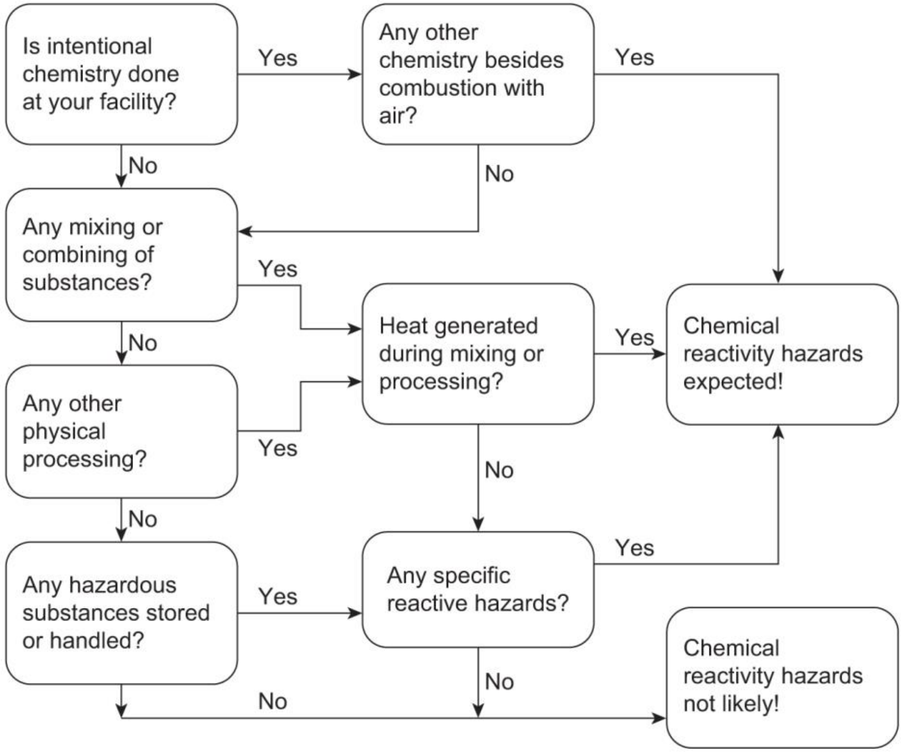
- Chemical Reaction Categories
  - Self Reacting Chemicals
    - Decomposition
    - Polymerization
  - Chemical Interactions
    - Between different chemicals
- Chemical Reaction Scenarios
  - Intended and Controlled Reactions
    - Products!
  - Intended but Uncontrolled Reactions
    - Process upsets lead to normal reactions proceeding at undesirable rates
  - Unintended Reactions
    - Process upsets or operating errors lead to unintended reactions occurring

Runaway Reaction

- Exothermic reaction leads to temperature increase
- Increased temperature leads to reaction rate increase
- Increased reaction rate leads to increased exotherm and therefore increase in rate of temperature increase
- Cooling system cannot overcome this spiraling effect
- Rapid temperature increase leads to rapid pressure increase
- Vessels fail leading to loss of containment
- Release of flammable or toxic material or explosion

Awareness and Identification

- I think it's a bit simpler than this…
- Do you handle chemicals that can react?
  - Either by themselves or with other chemicals
  - Do not limit yourself to combinations of chemicals you **intend** to introduce to one another, consider **ALL** combinations of the chemicals that you have
  - Do not limit yourself to the intended process conditions
- Also think about:
  - Would they release heat when they react?
  - Are any of the chemicals (including the products of ALL reactions identified) hazardous?



Screening flowchart for reactive chemical hazards. An answer of "yes" at any decision point moves more toward reactive chemistry. (Source: R. W. Johnson, S. W. Rudy, and S. D. Unwin. Essential Practices for Managing Chemical Reactivity Hazards (New York, NY: AICHE Center for Chemical Process Safety, 2003).)

Identifying Reactions

- First and foremost I recommend working with chemists who are knowledgeable in the classes of chemicals that you are handling
- Consulting the Safety Data Sheets (SDS) for each chemical will also alert you reactive hazards
- Some examples:
  - **Spontaneously Combustible**
    - Reacts with oxygen without needing an ignition source
  - **Peroxide forming**
    - Reacts with oxygen to form peroxides, also look for peroxides themselves
    - Peroxides are unstable and generate free radicals
  - **Water reactive**
  - **Oxidizers** – yields oxygen or other gas that readily promotes combustion
  - **Self Reactive** – substances that react on their own, not needing another chemical to interact with

Identifying Reactions

- Examining the chemical structure of the molecules can give insight
- If you see groups as shown in Table 8.3, the chemicals are prone to reactions
- Also look for vinyl groups (double bonded carbon) as they are likely to be polymerizable

Table 8-3 Reactive Functional Groups[a]

Azide	N_3
Diazo	$-N=N-$
Diazonium	$-N_2^+X^-$
Nitro	$-NO_2$
Nitroso	$-NO$
Nitrite	$-ONO$
Nitrate	$-ONO_2$
Fulminate	$-ONC$
Peroxide	$-O-O-$
Peracid	$-CO_3H$
Hydroperoxide	$-O-O-H$
Ozonide	O_3
N-haloamine	$-N(X)-Cl$
Amine oxide	$\equiv NO$
Hypohalites	$-OX$
Chlorates	ClO_3
Acetylides of heavy metals	$-C\equiv CM$

[a]Conrad Schuerch, "Safe Practice in the Chemistry Laboratory: A Safety Manual," in *Safety in the Chemical Laboratory*, v. 3, Norman V. Steere, ed. (Easton, PA: Division of Chemical Education, American Chemical Society, 1974), pp. 22–25.

Chemical Interaction Matrix

- Documents binary interactions of a group of chemicals
  - Extremely useful when evaluating consequences of process upsets in a Process Hazards Analysis
  - Document individual chemical hazards elsewhere
  - If there are any reactions requiring mixture of more than two chemicals they can be added as footnotes

	Chemical A	Chemical B	Chemical C	Chemical D
Chemical A	-	-	-	-
Chemical B	1	-	-	-
Chemical C	2	3	-	-
Chemical D	1	3	2, 4	-

1 No reaction

2 Exothermic Reaction, may generate heat and/or cause pressurization

3 Combination liberates toxic gaseous products

4 Generation of corrosive liquid

Example of Chemical Interaction Hazard of Unintended Mixing

- https://www.csb.gov/videos/mixed-connection-toxic-result/

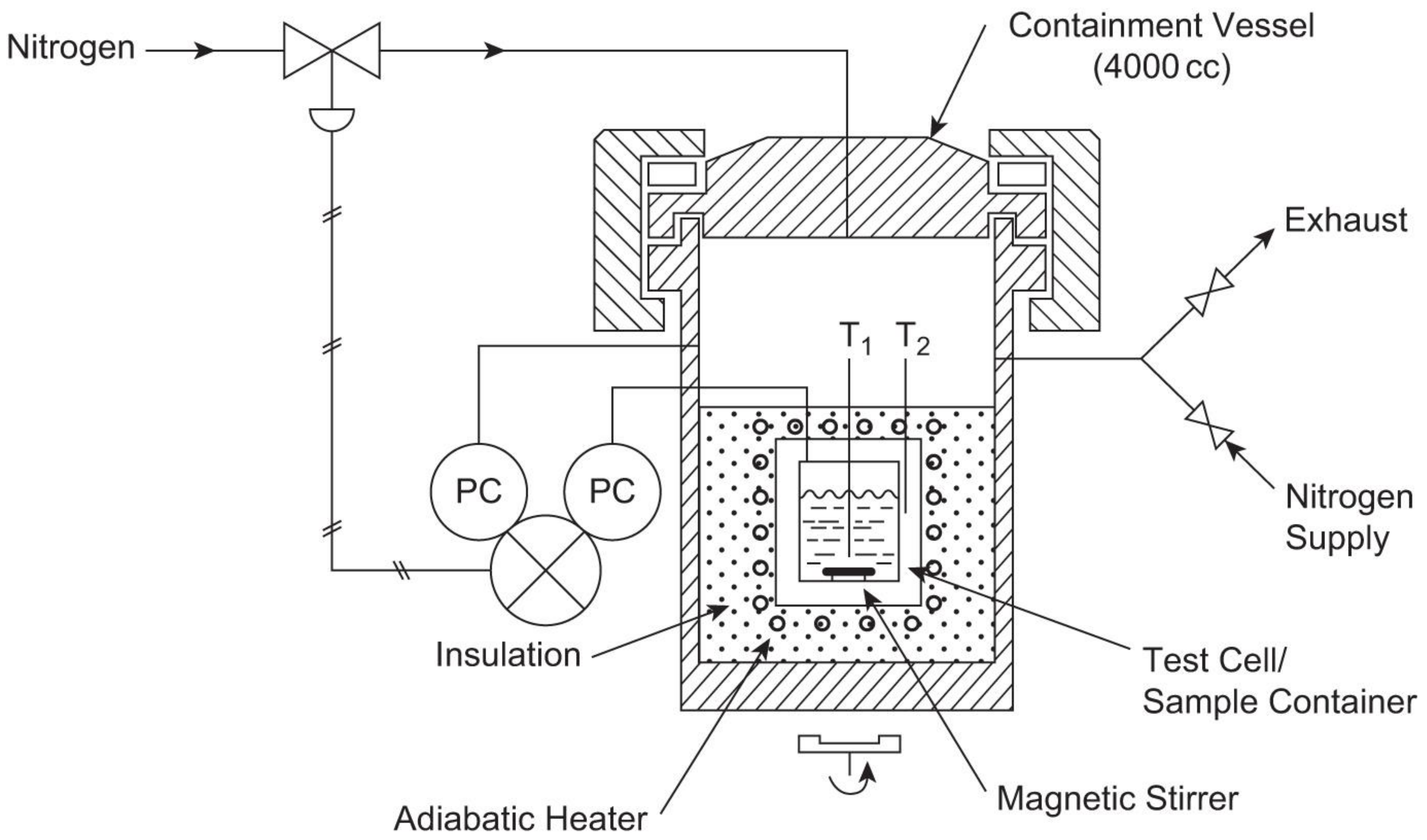
Characterization of Reactive Chemical Hazards

- At what temperature does significant reaction rate begin to occur?
- What is maximum rate of temperature increase?
  - Important information for the design of process cooling system
- What is maximum rate of pressure increase?
  - Is this due to increased vapor pressure of the liquid or generation of gaseous products
- Do other reactions kick in as temperature increases?
  - Do we reach unexpected temperatures that now start off new reactions?

Calorimetry

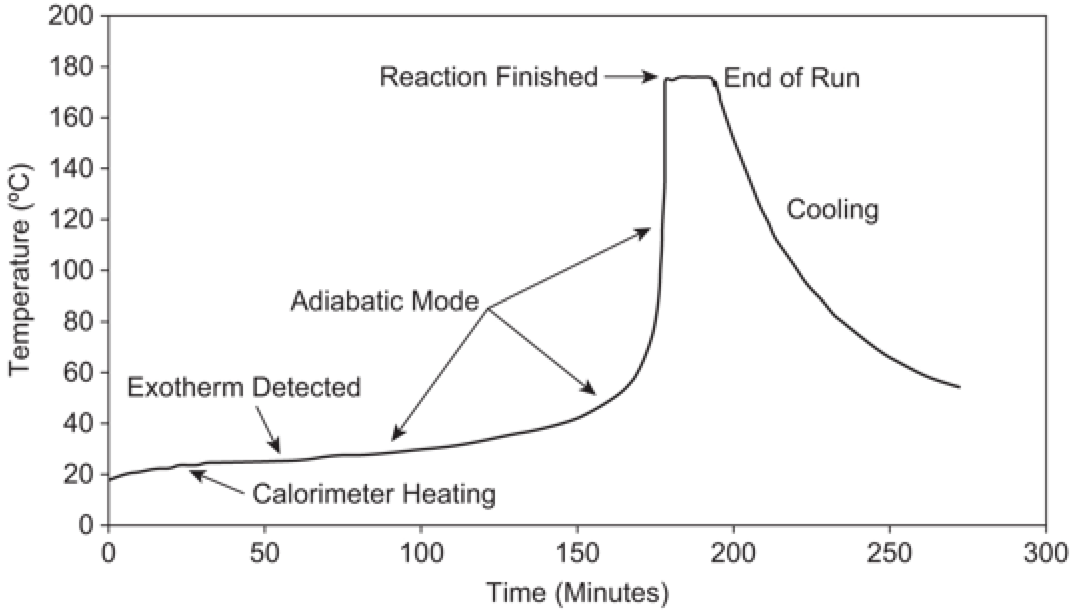
- Allows safe determination of reaction rates / heat generation rates / pressure build using small quantities in the lab
- Two modes of operation
  - Thermal Scan Mode
    - Heats sample at a constant temperature increase rate
    - Continues until calorimeter detects heat generation from reaction
    - Detects that it requires less heat input from calorimeter to maintain constant rate of temperature increase
  - Heat-Wait-Search Mode
    - Heats sample to a fixed temperature and then waits to see if self-heating from reaction occurs

Chemical Reactivity



Vent Sizing Package (VSP2) showing the control system to equalize the pressure between the sample cell and the containment vessel.

Example of Calorimetry Data



Calorimetry Data Analysis

- Convert raw data of Temperature versus Time into rate of temperature rise versus time
- Plot dT/dt versus -1000/T on a semi-log plot
- Onset Temperature is point where the dT/dt versus time plot becomes a straight line
  - This is the temperature where the reaction self accelerates
- Final Temperature is that temperature where the plot drops off rapidly
  - This is more or less as hot as the contents will get, as reactants are now consumed

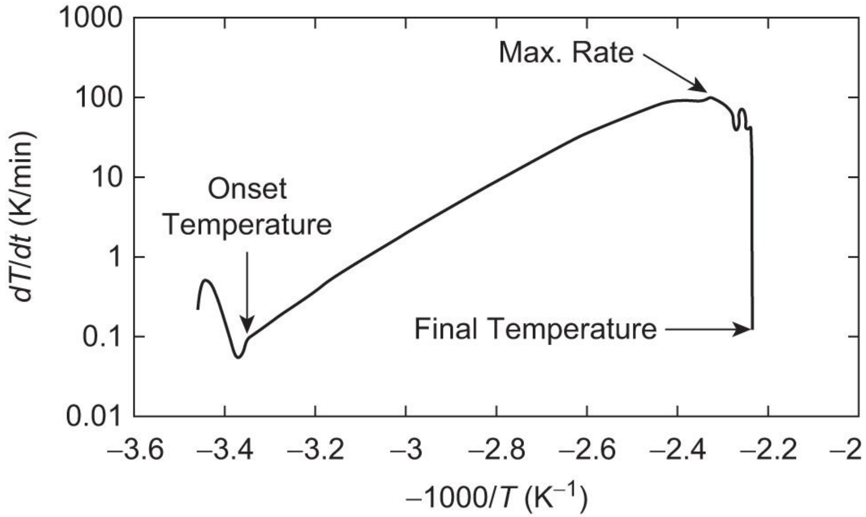


Figure 8-11 Graphical procedure to estimate the detected onset and final temperatures.

Calorimetry Data Analysis

- For a First Order Reaction:

$$\frac{dC}{dt} = -k(T)C$$

Where:

C is the concentration of our reactant

$k(T)$ is the temperature dependent reaction rate coefficient

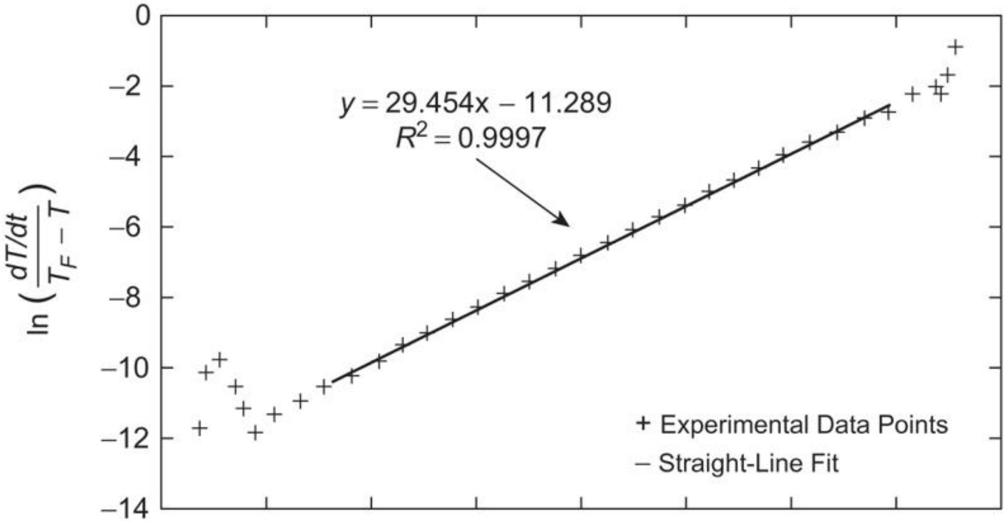
$$k(T) = Ae^{-E_a/RT}$$

- For a First Order Reaction:

$$ln\left[\frac{dT/dt}{T_F - T}\right] = ln\,A - \frac{E_a}{RT}$$

Calorimetry Data Analysis

- If we plot $\ln\left[\frac{dT/dt}{T_F-T}\right]$ versus $\frac{-1000}{RT}$ and obtain a straight line we confirm that we have a First order Reaction



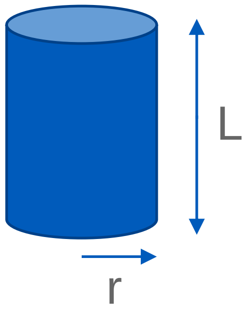
- Get a trendline on the portion of the plot that is a straight line
  - The slope is E_a in kJ/mol
  - The intercept is $-\ln A$ where A is in s^{-1}
  - Use $R = 8.314\ \frac{J}{K\,mol}$, time in seconds, temperature in Kelvin

Some Applications of Calorimeter Data

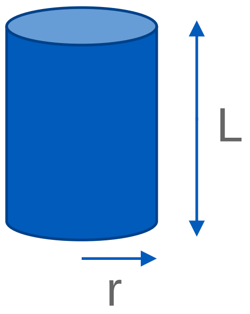
- Heat Exchanger Duty required for cooling reactor
- Maximum concentrations of reactants allowed to avoid overpressure in reactor
- Reactor vessel size and required pressure rating
- Relief System sizing
- Reactor temperature control design

Scale Up Issues

- One must be aware that cooling capacity does not scale directly
- Heat generation scales as volume whereas cooling capacity scales as surface area
- Cylindrical tank with $\frac{L}{r} = \epsilon$
- Volume: $V = \pi r^2 L = \pi r^3 \epsilon$
- Surface Area: $SA = \pi r^2 + 2\pi r L = \pi r^2 + 2\pi r^2 \epsilon$
- Surface to Volume: $StV = \frac{\pi r^2 + 2\pi r^2 \epsilon}{\pi r^3 \epsilon} = \frac{1+2\epsilon}{r\epsilon}$



Scale Up Issues



- Assume that $\frac{L}{r} = \epsilon$ is to be held constant
- Increasing the volume from V_0 to V
- $\frac{V}{V_0} = k = \frac{\pi r^3 \epsilon}{\pi r_0^3 \epsilon} = \frac{r^3}{r_0^3}$
- $\frac{r_0}{r} = k^{-1/3}$
- The relative surface to volume ratios of the production equipment to the lab apparatus is

$$\frac{StV}{StV_0} = \frac{\frac{1+2\epsilon}{r\epsilon}}{\frac{1+2\epsilon}{r_0\epsilon}} = \frac{r_0}{r} = k^{-1/3}$$

Scale Up Issues

- The relative surface to volume ratios of the production equipment to the lab apparatus is

$$\frac{StV}{StV_0} = \frac{\frac{1+2\epsilon}{r\epsilon}}{\frac{1+2\epsilon}{r_0\epsilon}} = \frac{r_0}{r} = k^{-1/3}$$

- If you increase the volume by a factor or 10 ($\frac{V}{V_0} = k = 10$), the surface to volume ratio scales by a factor of $10^{-1/3} = 0.46$
- The ability to remove heat relative to heat generation is only 46% that of the test apparatus
- What seemed safe in the lab can be disastrous in the production unit

Controlling Reactive Hazards – Inherently Safer

- Use less hazardous chemicals
- Use reaction pathway (steps or process conditions) that are less energetic
- Use smaller inventories of reactive chemicals in process and in storage
- Use lower concentrations or add inert solvent to temper reaction
- Control stoichiometry or charge of reactor so that runaway reaction does not lead to a pressure that exceeds vessel rating

Controlling Reactive Hazards – Passive Methods

- Ensure that incompatible materials are always separated
- Provide adequate separation distances between storage vessels, reactors, and other process equipment using reactive chemicals
- Provide passive engineering controls to control reactive chemical spills
  - Dikes
  - Berms
- Passive Fire Protection
  - Insulation of equipment containing reactive chemicals
  - Thermal coating of mechanical supports
- Locate plant with adequate separation from local community

Controlling Reactive Hazards – Active Methods

- Identify reactive chemical hazards and obtain experimental calorimetric data
- Provide properly designed control systems to control reactions in process
- Use quench, stop, or dump systems to quickly stop out-of-control reactions
  - The chemicals involved in these systems can present their own hazards
- Provide reliable mixing systems with mixing problem detection
- Relief systems designed to prevent over-pressurization due to reactive chemistry
- Provide inhibitor and ensure proper levels to self-reactive materials
- Provide adequate cooling systems and method to detect proper function

Controlling Reactive Hazards - Procedural

- Review and document chemical reactivity risks
- Communicate and train all personnel on chemical reactivity hazards
- Implement Management of Change procedures to ensure operations do not evolve in an unsafe manner
- Investigate all chemical reactivity incidents
- Provide Quality Control procedures to ensure that all reactive chemicals received are correct chemicals at correct concentrations and without hazardous impurities