Module 9A Exothermic Reactions - Session 1 and 2

Last Revised – April 2024

PS Bootcamp Modules

- ✓ **Module 1: Introduction**
- ✓ **Module 2: Hazard Identification**
- ✓ **Module 3: Risk Matrix**
- ✓ **Module 4: Safeguard Concepts**
- ✓ **Module 5: Explosion/Fire Protection**
- ✓ **Module 6: Management of Change**
- ✓ **Module 7: Incident Investigation**
- ✓ **Module 8: Facility Siting**
- ✓ **Module 9: Exothermic Reactions**

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Module 9: Exothermic Reactions Agenda

✓ **Section 1 – Reactive Chemicals Lesson Sharing**

✓ **Section 2 - Characterizing Exothermic Reactions I**

❑ **Section 3 – Characterizing Exothermic Reactions II**

❑ **Section 4 – Techniques for Investigating Exothermic Reactions**

❑ **Section 5 – Analyzing Exothermic Reaction Stability**

❑ **Section 6 – Evaluating the Hazards of Exothermic Reactions**

❑ **Section 7 – Controlling Reactive Chemistry Hazards**

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Module 9: Overall Module Training Objectives

Emphasize how pervasive exothermic reactions are in the chemical industry

Increase awareness of methods to characterize exothermic behavior

Present approaches for identifying the potential hazards of exothermic behavior

Provide techniques to avoid and/or mitigate exothermic reaction hazards.

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Section 1 – Reactive Chemicals Lesson Sharing

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Module 9: Training Objectives – Section 1

Reactive Chemicals Lesson Sharing to:

Increase awareness of the pervasiveness of exothermic behavior in the chemical process industry

Introduce the terms used in describing exothermic behavior

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Significance of Exothermic Reactions

Most industrial chemical processes are exothermic

alkoxylation, nitration, oxidation, polymerization, hydrogenation**....**

Chemicals mostly react exothermically (e.g., *decompose or polymerize*) while stored or held for prolonged periods during processing

ethylene oxide, butadiene, acrylonitrile**....**

The consequences of uncontrolled exothermic reactions (Runaway Reactions) can be catastrophic

vessel and piping rupture, explosions, flying debris, shock waves, radiant heat from fire, chemical burns

personnel and public endangerment...

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CSB Video – Reactive Hazards

Reactive Hazards - Safety Videos - Multimedia | CSB

Bhopal – Start to 1:38 – Formation of CSB

Morganton, NC – Synthron Chemical Explosion – Acrylic Polymer

BP Amoco – Slow Decomposition of Nylon Plastic

MFG Chloride – Toxic Allyl Alcohol and Hydrochloric Acid

First Chemical Corporation – MNT Distillation Tower Explosion

Testimonials – 10:40 to 11:25

Reference Sources – 11:44

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TPC Explosion – 1,3 Butadiene

Butadiene reaction with oxygen to form "popcorn" polymer

Initial pipe rupture and LOC of 7,100 gallons flammable liquid, vapor cloud explosion

Second explosion launched debutanizer tower

Figure 9. Popcorn polymer in a manhole from another undisclosed butadiene unit, published in the Butadiene Popcorn Polymer Resource Book. (Credit: International Institute of Synthetic Rubber Producers Inc. [12, p. 261])

Erwin Seba/Reuters

A tower flies through the air during one of the explosions

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Baker Petrolite Alkoxylation Reactor
Runaway Reaction – October 12, 1999

- Six alkoxylation batch reactions with EO or PO; four had top entry agitators and two had external re-circulation loops.

- Each reactor protected by pressure relief burst disc and vent line routed independently to a common knockout pot.

- Knockout pot – 27 m^3 atmospheric rated vertical vessel in reactor building with 2000 kg of water (intended to provide a degree of quenching and dissolution of EO/PO).

- Knockout pot outlet 0.6 m dia., routed vertically to atmosphere through building roof discharged 10 m above grade.

- Reactors mounted on load cells; relief vents were linked to reactor via a sliding joint

- Incident on reactor V6 with external re-circulation loop

- Product was polypropylene glycol

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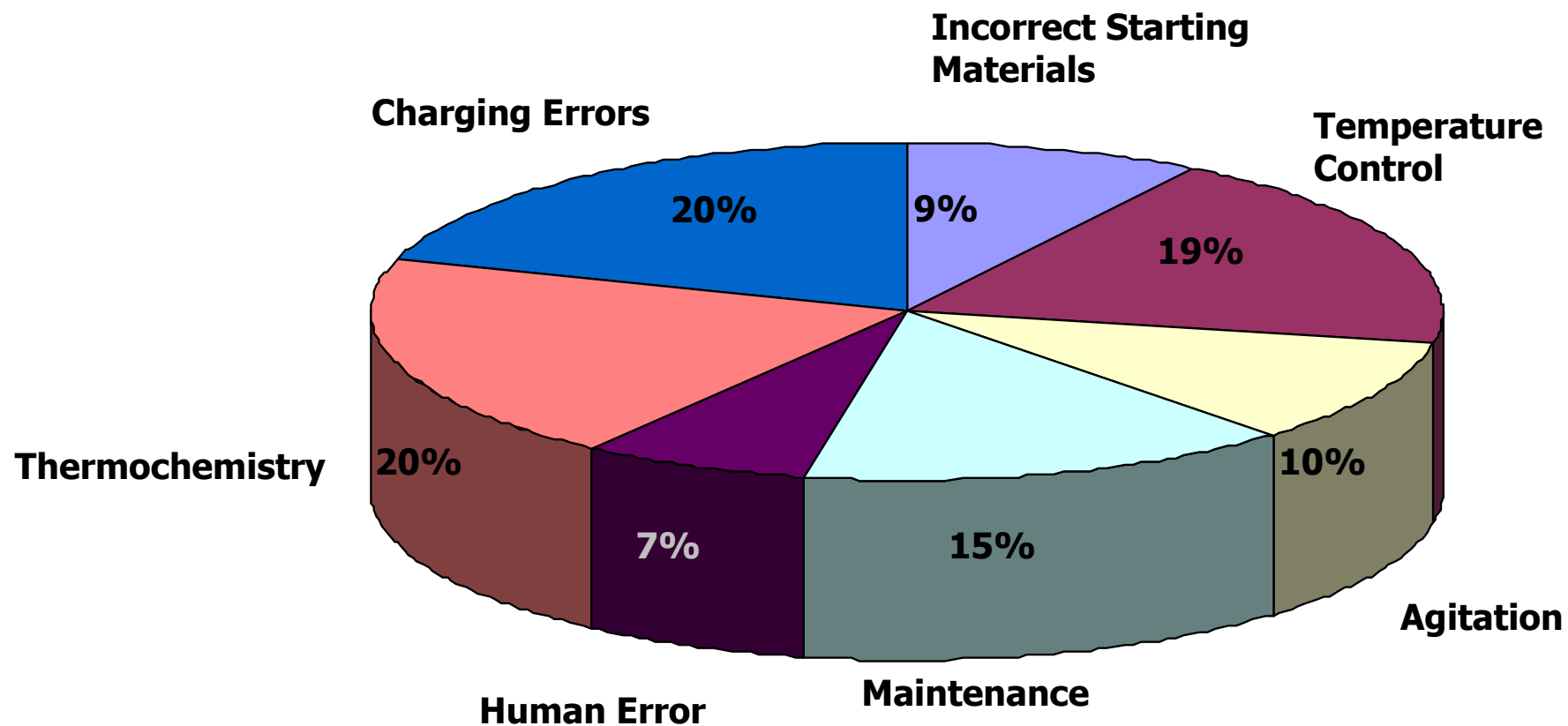
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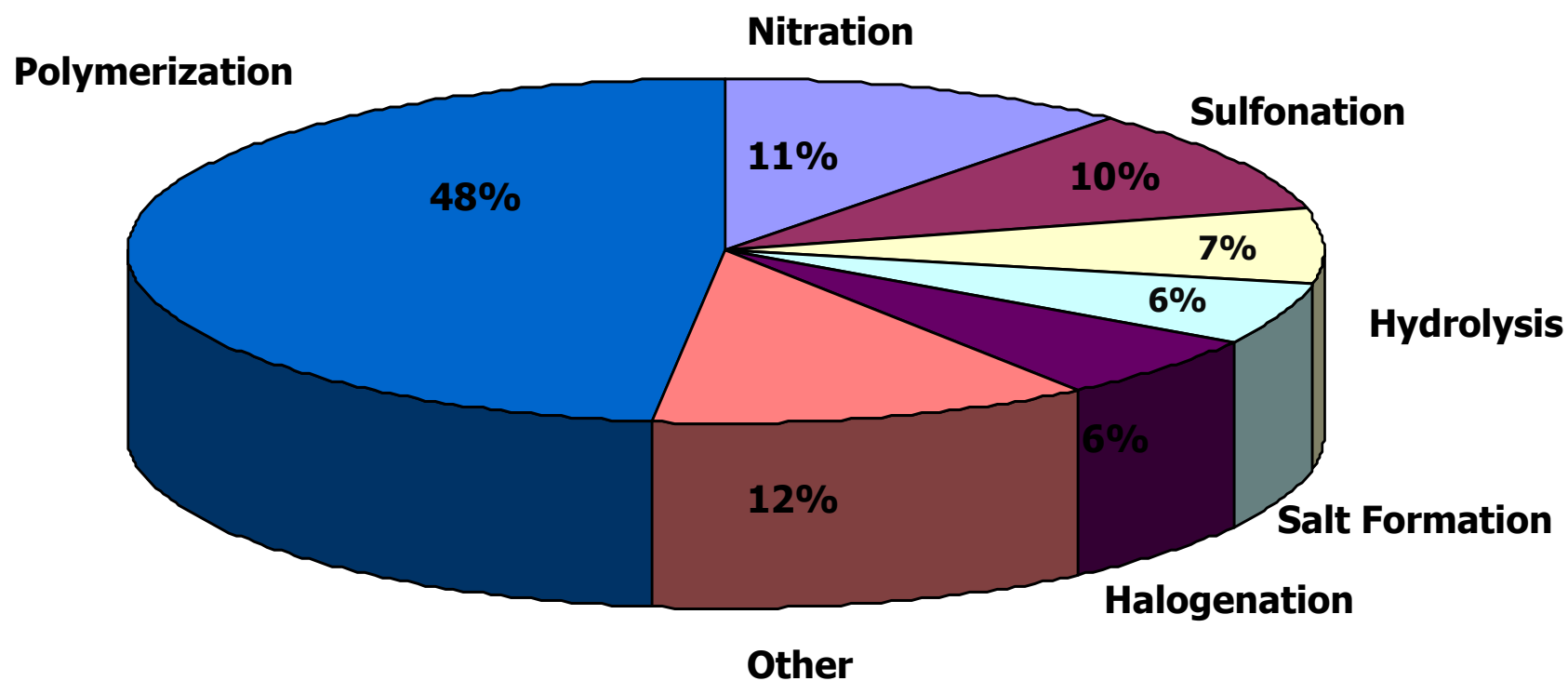# Baker Petrolite Alkoxylation Reactor Process Steps

1. Add starting polyol

2. Add 45% potassium hydroxide solution (catalyst)

3. Perform pressure test to approximately 60 psi

4. Heat to approximately 110˚C (230˚F) to dehydrate

5. Sample to check moisture

6. Apply nitrogen padding to reactor

7. Add propylene oxide at controlled rate

- PO addition rate controlled on temperature

- Cooling water added, when necessary, on manual control at time of the event

- PO feed was interrupted during batch. PO addition resumed at a time when reaction mixture had dropped to 60˚C (140˚F).
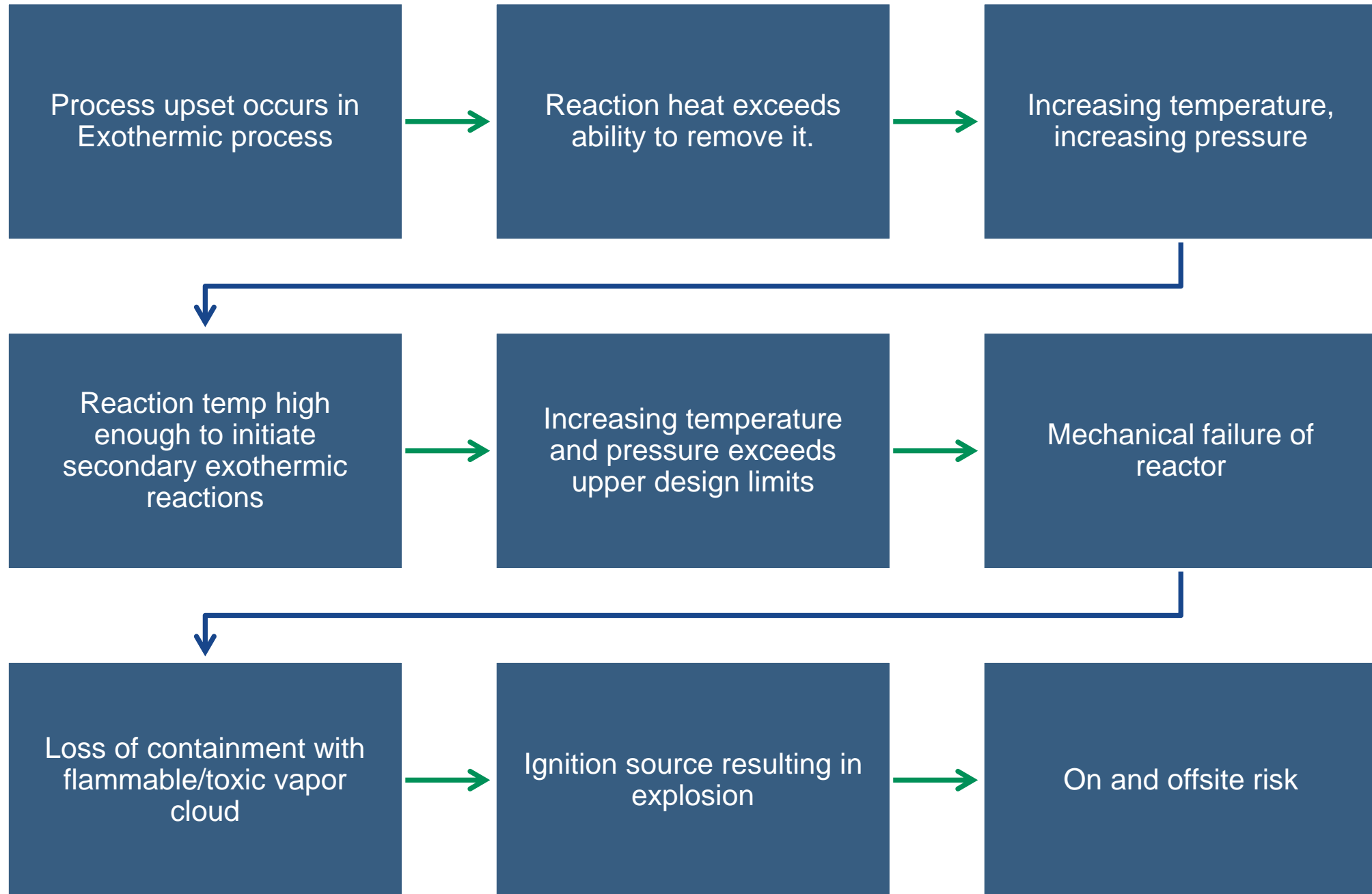
Unreacted PO or EO will pool if added to a reaction mixture that is too cold, then react at an accelerated rate when it reaches the onset temperature again.
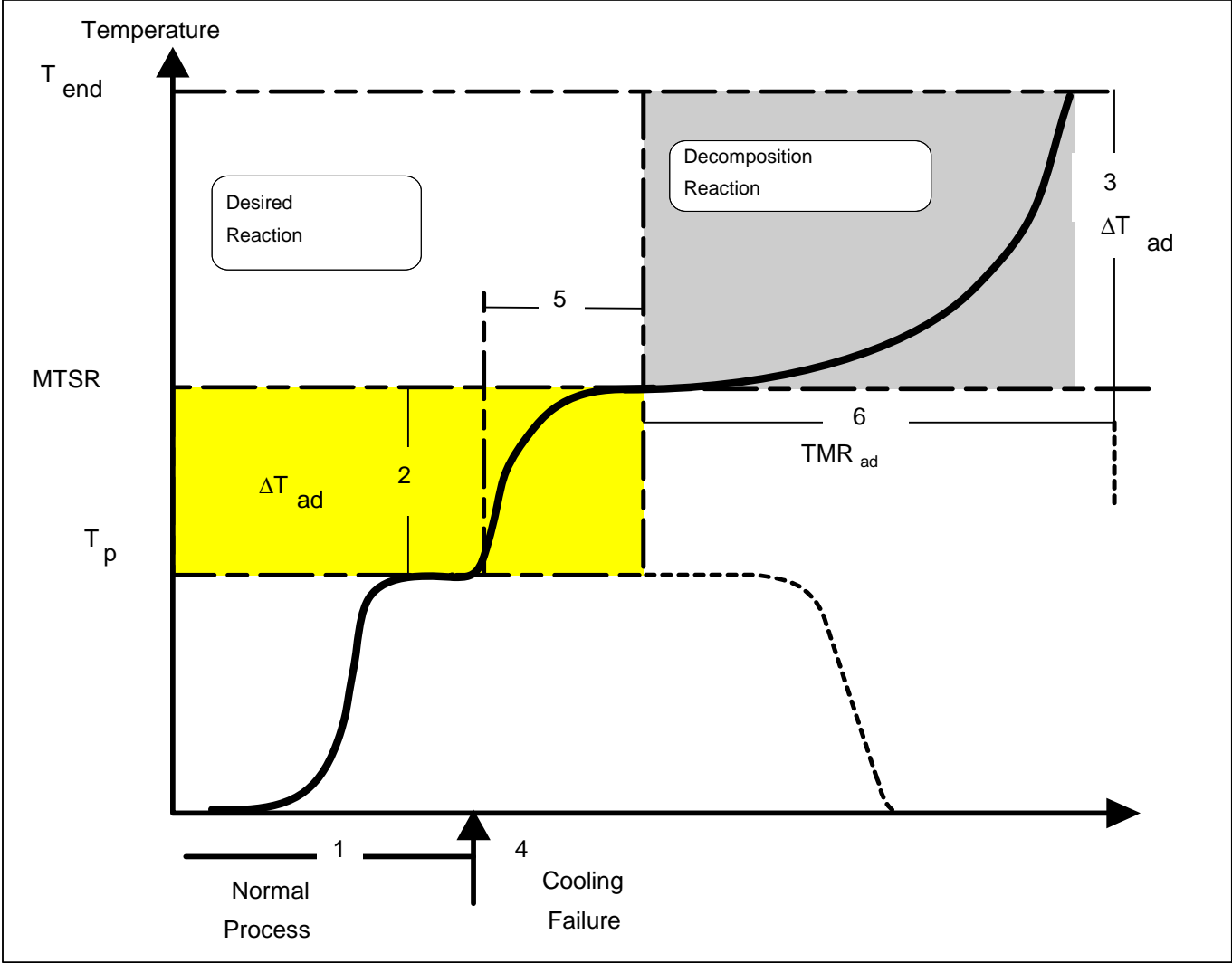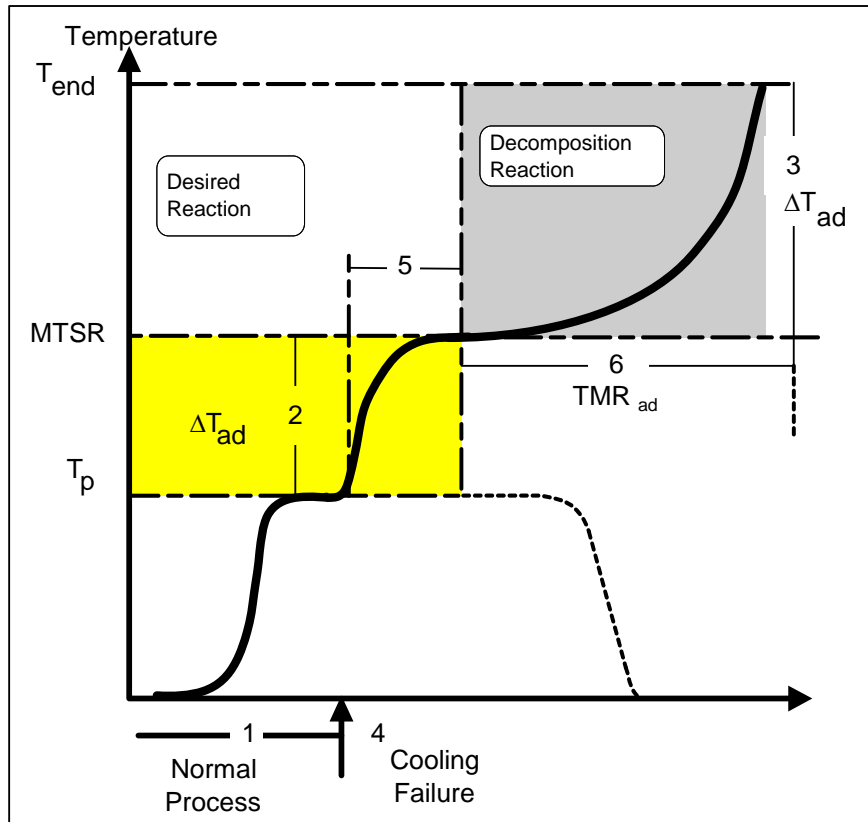
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Causes for Runaway Reactions

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Types of Reactions Involved in Runaways

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┌─────────────────────────┐      ┌─────────────────────────┐      ┌─────────────────────────┐
│  Process upset occurs in │ ───> │  Reaction heat exceeds  │ ───> │ Increasing temperature, │
│    Exothermic process    │      │  ability to remove it.  │      │   increasing pressure   │
└─────────────────────────┘      └─────────────────────────┘      └─────────────────────────┘
                                                                                │
                  ┌─────────────────────────────────────────────────────────────┘
                  v
┌─────────────────────────┐      ┌─────────────────────────┐      ┌─────────────────────────┐
│   Reaction temp high    │      │  Increasing temperature │      │   Mechanical failure of │
│   enough to initiate    │ ───> │  and pressure exceeds   │ ───> │         reactor         │
│  secondary exothermic   │      │   upper design limits   │      │                         │
│        reactions        │      │                         │      │                         │
└─────────────────────────┘      └─────────────────────────┘      └─────────────────────────┘
                                                                                │
                  ┌─────────────────────────────────────────────────────────────┘
                  v
┌─────────────────────────┐      ┌─────────────────────────┐      ┌─────────────────────────┐
│  Loss of containment with│      │   Ignition source       │      │   On and offsite risk   │
│   flammable/toxic vapor  │ ───> │  resulting in explosion │ ───> │                         │
│         cloud            │      │                         │      │                         │
└─────────────────────────┘      └─────────────────────────┘      └─────────────────────────┘
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Runaway Reaction Scenario

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Risk Assessment Questions for Reactor

Can the process temperature be controlled by the cooling system?

What temperature can be attained after runaway of the desired reaction?

What temperature can be reached after runaway triggering a secondary decomposition reaction?

At which moment does the cooling failure have the worst-case consequences?

How fast is the runaway of the desired reaction?

How fast is the runaway of the decomposition starting at MTSR?

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Energy of Reaction vs Severity

$$\Delta T\,ad = \frac{Q_R}{C_p}$$

with:

ΔTad	adiabatic temperature rise	[Degrees Kelvin (Absolute); K]
Q_R	energy of reaction	[kJ/kg]
C_p	specific heat capacity	[kJ/kg/K]

Reaction	Desired	Decomposition
Energy	100 kJ/kg	2000 kJ/kg
Adiabatic Temperature Rise	50 K	1000 K
Evaporation of Methanol per kg of Reaction Mixture	0.1 kg	1.8 kg

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Knowledge Check

All processes must be examined

Process safety information (PSI) should address both intended and unintended (or secondary) reactive chemistry

Ethylene Oxides is highly reactive

Understanding the reactive hazards of the process enables PHA/LOPA teams to identify appropriate safeguards

Many Indorama sites are dealing with same reactive hazards for lesson learning

Reaction Temperature/Time Curve provides valuable data

Severity of a Runaway Reaction is proportional to the energy released

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Section 2 – Characterizing Exothermic Reactions I

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Characterizing Exothermic Reactions I:

Increase familiarity and understanding of:

- Exothermic Reactors
  - Discuss the mass & energy flows for an exothermic reactor
  - Review the importance of heat transfer for safe exothermic reactor operation
  - Review scale-up impact on exothermic reactor operation
- Semenov Diagram
  - Discuss a graphical approach to analyzing exothermic reactor stability
  - Evaluate the stability of an exothermic batch reactor
  - Evaluate a change to the operation of a batch reactor

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Mass & Energy Balance

$M_{in}, C_{i,in}$

dc_R/dt

C_R M_R Q

ρ_R V_R

dT_R/dt

$M_{out}, C_{i,out}$
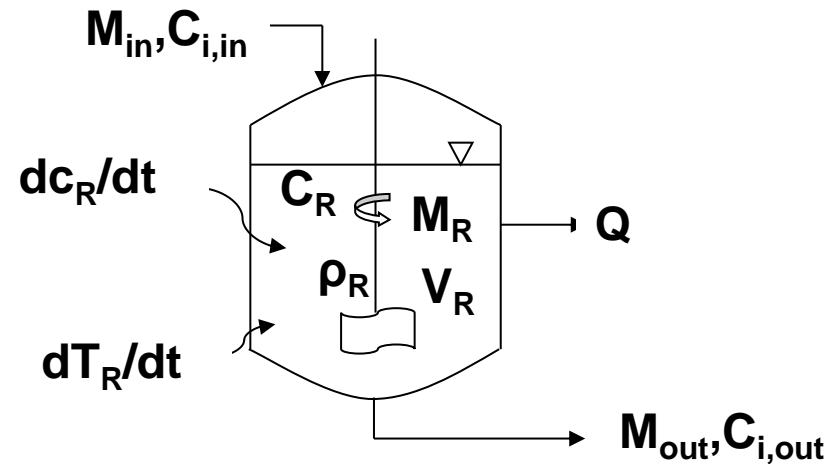
Mass Balance

Component i feed per unit time		Component i outlet per unit time		Component i formed /consumed per unit time		Accumulation of Component i per unit time
	$-$		$\pm$		$=$	

$$(c_{i,in} * M_{in}) \quad - \quad (C_{i,out} * M_{out}) \quad \pm \quad (r * M_R) \quad = \quad (M_R * dc_i/dt)$$

Energy Balance

Feed heat per unit time		Outlet heat per unit time		Reaction heat per unit time		Heat removed by cooling per unit time		Heat accumulation per unit time
	$-$		$+$		$-$		$=$	

$$(M_{in} * c_p * T_{in}) \quad - \quad (M_{out} * c_p * T_{out}) \quad + (r * \rho_R V_R * (-\Delta H_R)) - (U * A * \Delta T) \quad = \quad (M_R * c_p * dT/dt)$$

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Characterizing Chemical Reactions

$$a\mathbf{A} + b\mathbf{B} \rightarrow c\mathbf{C} + d\mathbf{D} \qquad -\Delta H_R$$

Reactants   Products   Heat of Reaction

What **do** we know from this?

Characterizing Chemical Reactions (Answer Key)

$$aA + bB \rightarrow cC + dD \qquad -\Delta H_R$$

Reactants   Products   Heat of Reaction

What **do** we know from this?

1. **100% completion the A and B molecules are fully reacted to C and D molecules**
2. **No heat or catalyst required to drive the reaction**
3. **Heat of Reaction is negative, so it is releasing heat into the surroundings (exothermic).**

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Characterizing Chemical Reactions

$$a\textbf{A} + b\textbf{B} \rightarrow c\textbf{C} + d\textbf{D} \qquad -\Delta H_R$$

Reactants   Products   Heat of Reaction

What **don't** we know from this?

Characterizing Chemical Reactions (Answer Key)

$$aA + bB \rightarrow cC + dD \qquad -\Delta H_R$$

Reactants   Products   Heat of Reaction

What **don't** we know from this?

1. **Limiting reactant**
2. **Rate of Reaction/Reaction Kenetics**
3. **Maximum Temperature Rise**
4. **Potential for Secondary Reactions**
5. **Physical properties of the products (e.g., offgassing)**

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Characterizing Chemical Reactions

Heat Release vs Conversion

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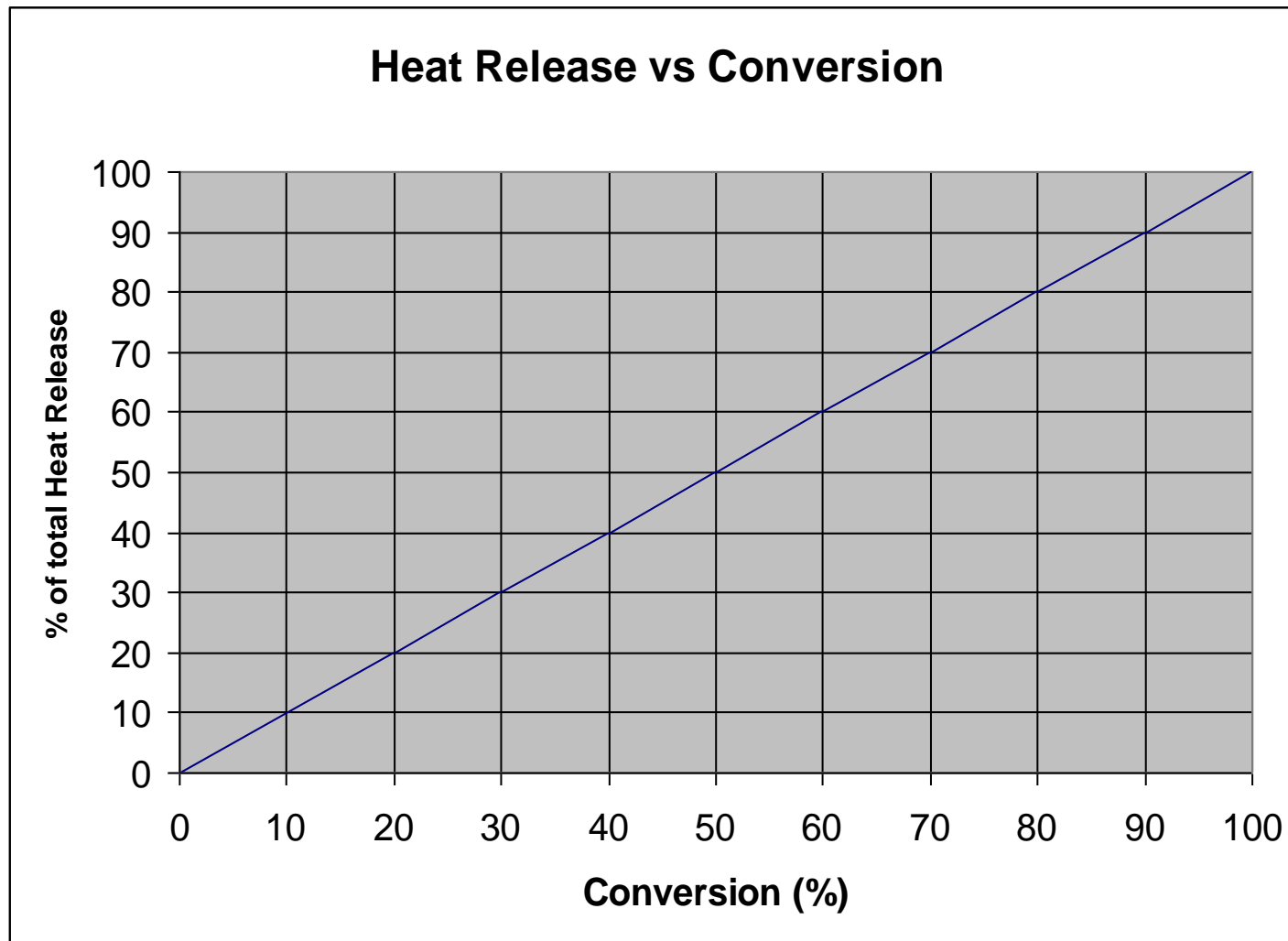
Characterizing Chemical Reactions

To ensure the safe design and control of an exothermic reaction process

Knowing reaction kinetics is essential.

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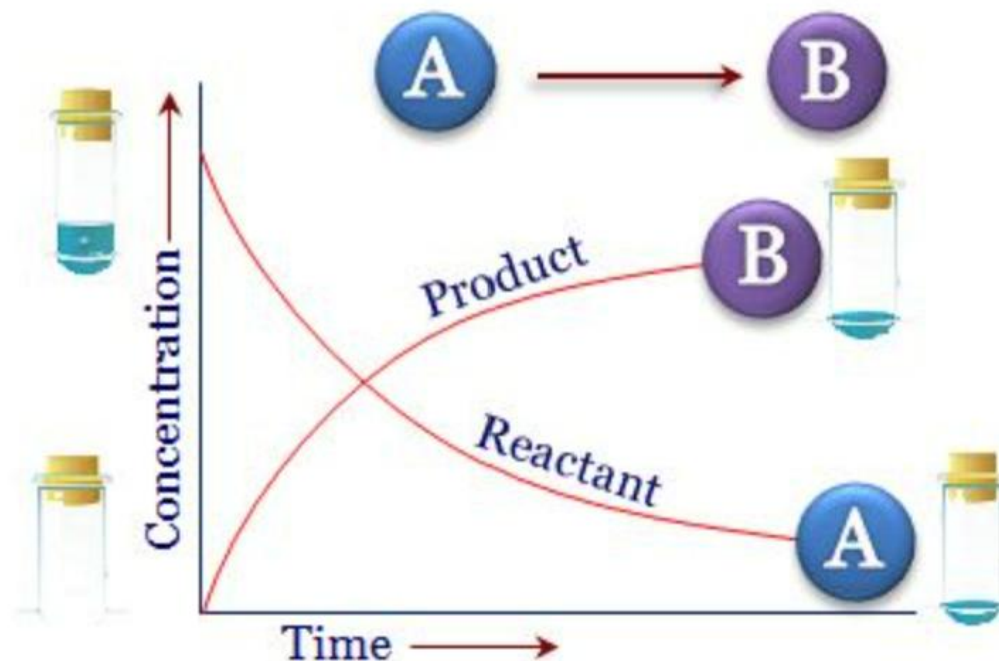
For the reaction aA + bB → cC + dD

Reaction Rate, $r = -dc_A/dt = kc_A^x c_B^y$

** C_A and C_B are the concentrations of components A and B in the system, x and y are the order of the reaction for that component and **k** is the rate constant

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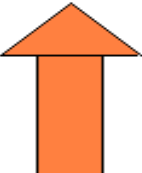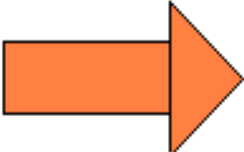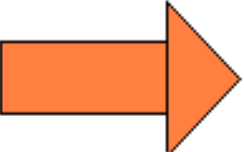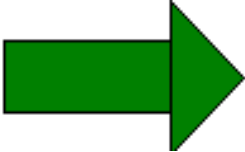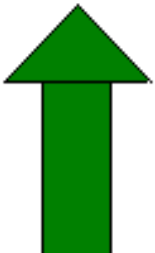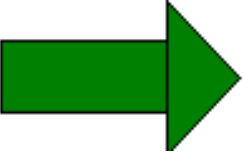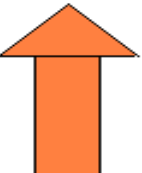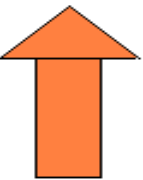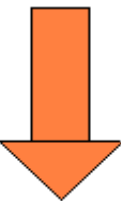
- **experimentally determined**
- **a strong function of reaction temperature**

The Reaction Rate is:

❖ $k = A * e^{(-E_a/RT)}$ (this is the Arrhenius equation)
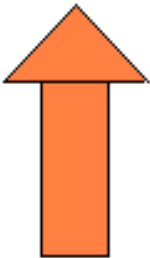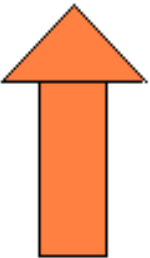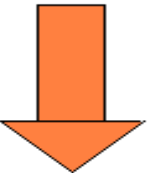
- **A is the Arrhenius constant**
- **E_a is the activation energy for the reaction,**
- **R is the gas constant**
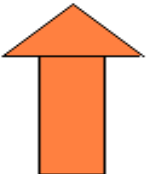- **T is the temperature.**

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Characterizing Chemical Reactions

Concentration and Temperature Effects

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Characterizing Chemical Reactions

T	⬆	⬇	⬆	⬇
C$_{(A\ or\ B)}$	⬆	⬇	⬇	⬆
r,Q	⬆	⬇	**?**	**?**

Concentration and Temperature Effects

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Characterizing Chemical Reactions

The two parameters that most directly impact the heat release rate from an exothermic reaction:

1. Reactant concentration
2. Reaction temperature

Thus, feed control and heat removal are both key for exothermic reaction safety.

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Process Description

Exothermic semibatch reaction:

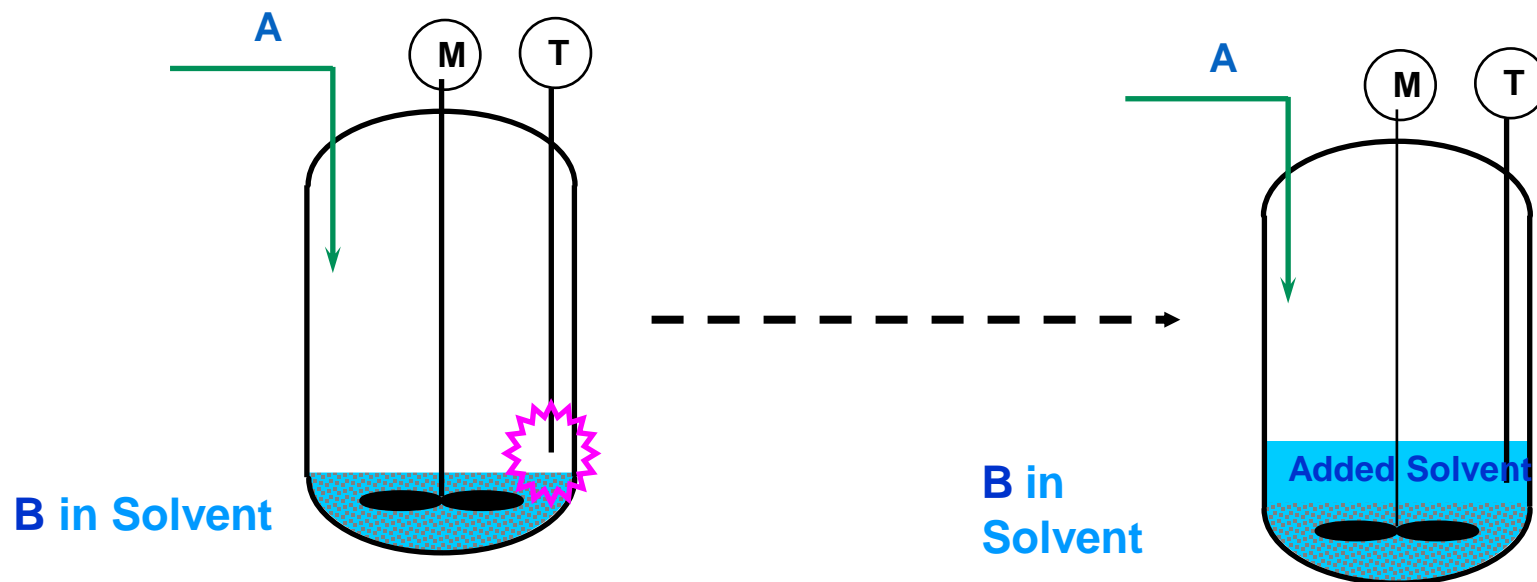the reactive component A is fed into compound B in an inert organic solvent at low temperature (< 0° C)

After time controlled addition of A, the reaction mass is warmed up to ambient temperature in order to complete conversion

B in Solvent
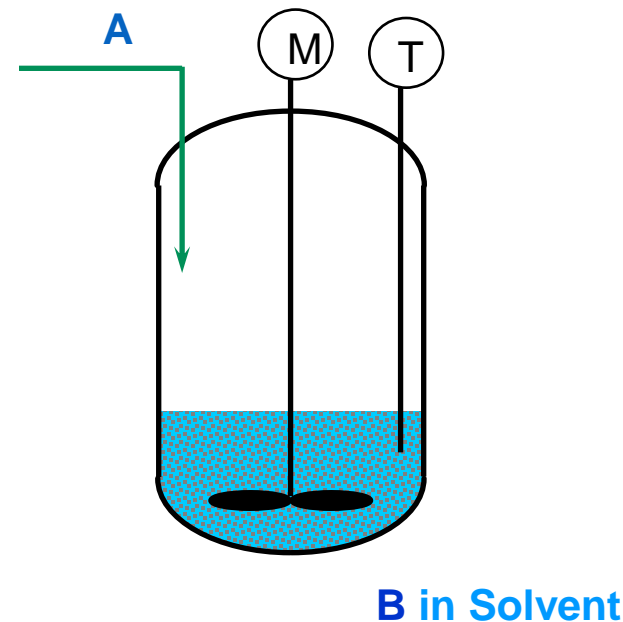
Case Study 1
Meeting the Customer's Needs

In order to satisfy an increased short term customer demand for the product, the batch size had to be increased. Only a significantly oversized reactor was available. After charging **B** and the solvent, the operator observed that the temperature probe was not immersed in the liquid. In a quick decision to solve the problem, additional solvent was added to increase the liquid level and immerse the temperature element. As a result the quantity of solvent charged was doubled. All other conditions were maintained. **A** was charged over the standard batch time.

A

M   T

B in Solvent

A

M   T

Added Solvent

B in Solvent

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Case Study 1
The Surprise

During the warming up step of the process, a sudden unexpected temperature rise was observed, which led to overpressure and the rupture of a glass venting line.

Large amounts of the reaction mixture and solvent vapors were released into the production building.

Fortunately there were no effective ignition sources present.

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Case Study 1 –
The Temperature Trace

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What went wrong?

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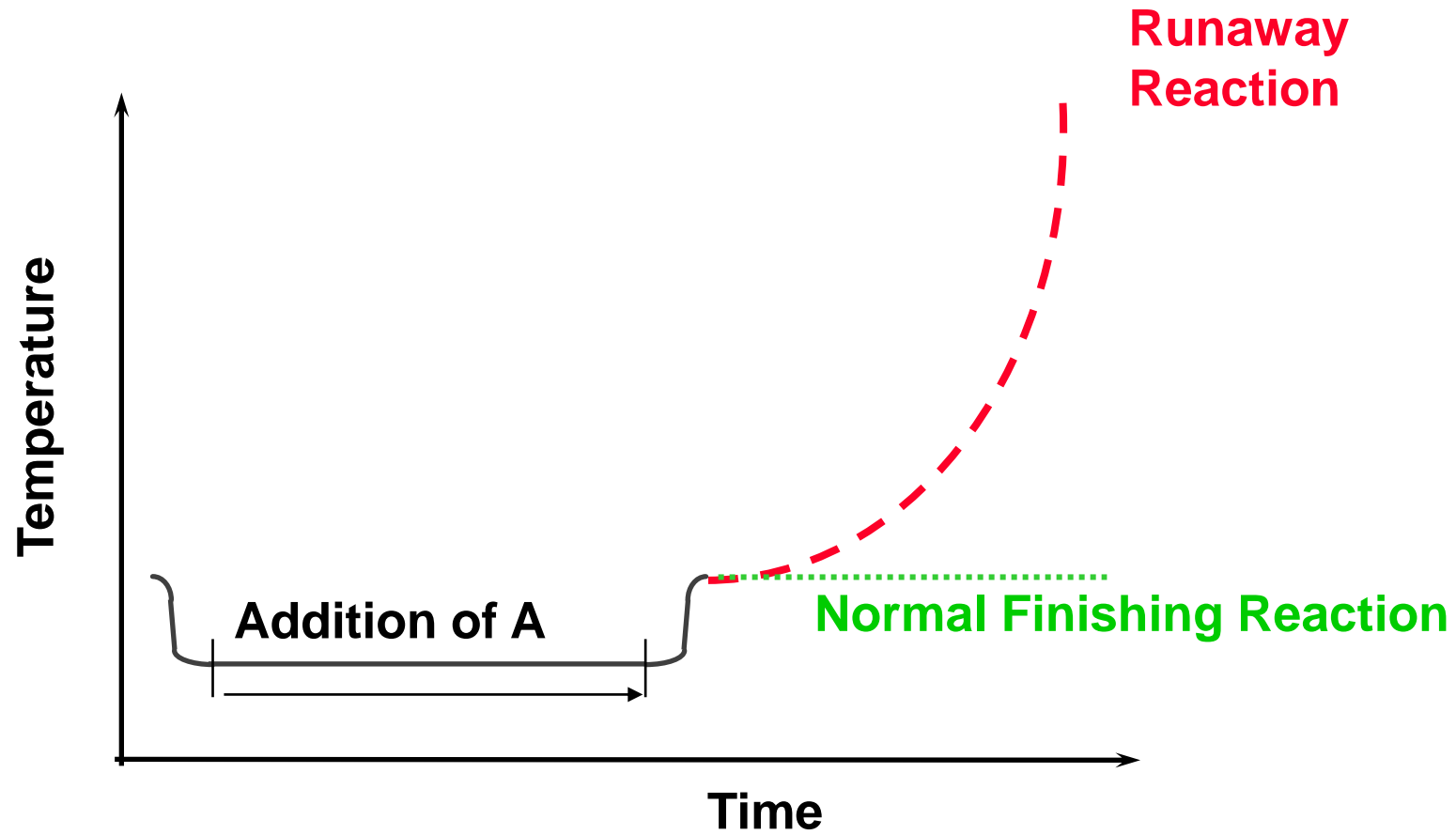
Case Study 1
The Usual Suspects & the Culprits

Starting concentration wrong

Variable mixing rate of A and B

Wrong temperature of the process or feed

Wrong temperature or set point of the cooling medium

Wrong catalyst, absence or excess of catalyst

Charging error (wrong material, wrong sequence...)

Secondary reactions........

Different Safe Upper and Lower Operating Limits require Management of Change

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Van't Hoff's Rule of Thumb

Thermal Runaway Sequence **(thermal explosion)**

In one quarter of the time to t_{ad}, the temperature increases another 10ºC (to 20ºC) and the reaction rate doubles again

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Heat Transfer through Vessel Walls

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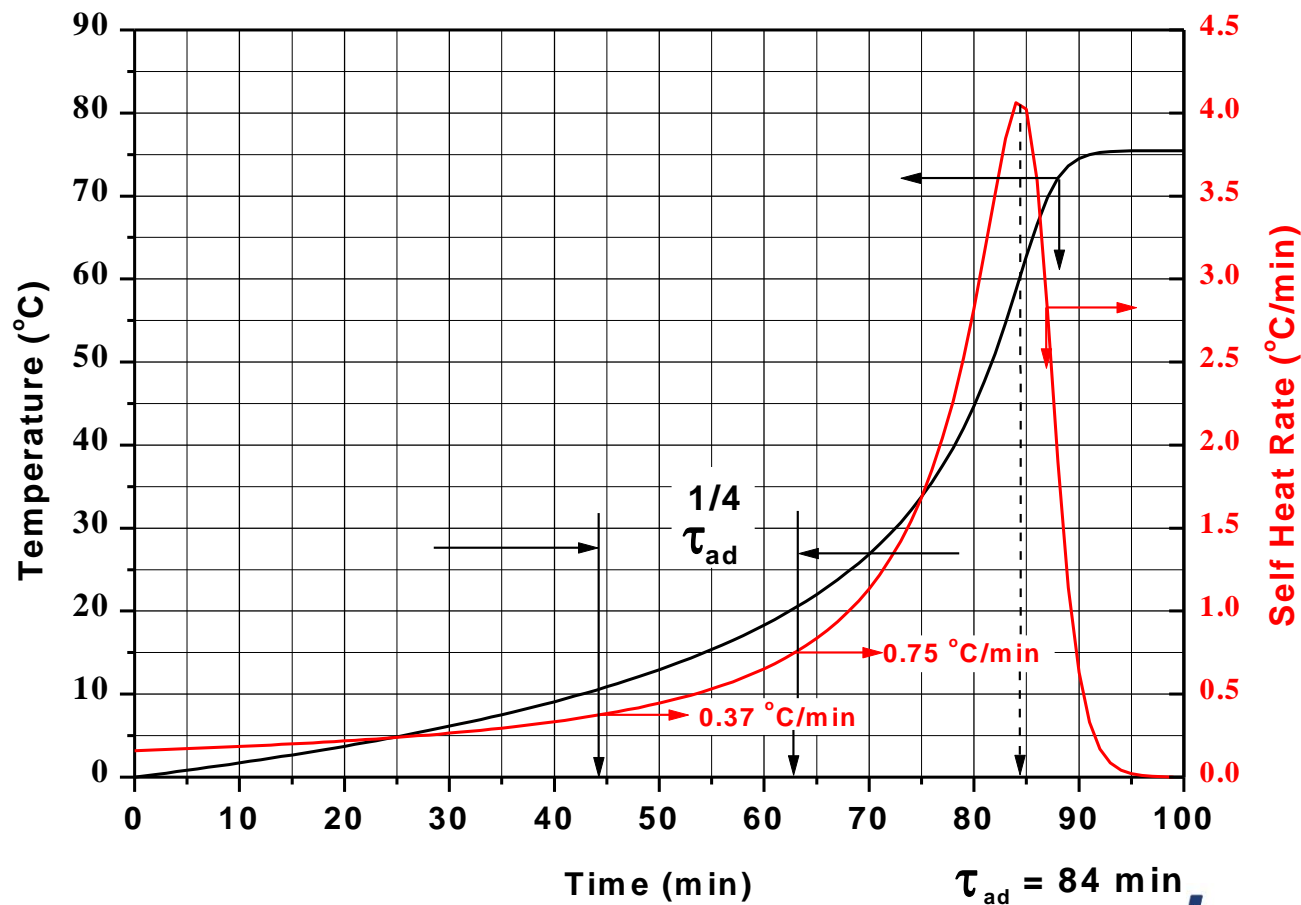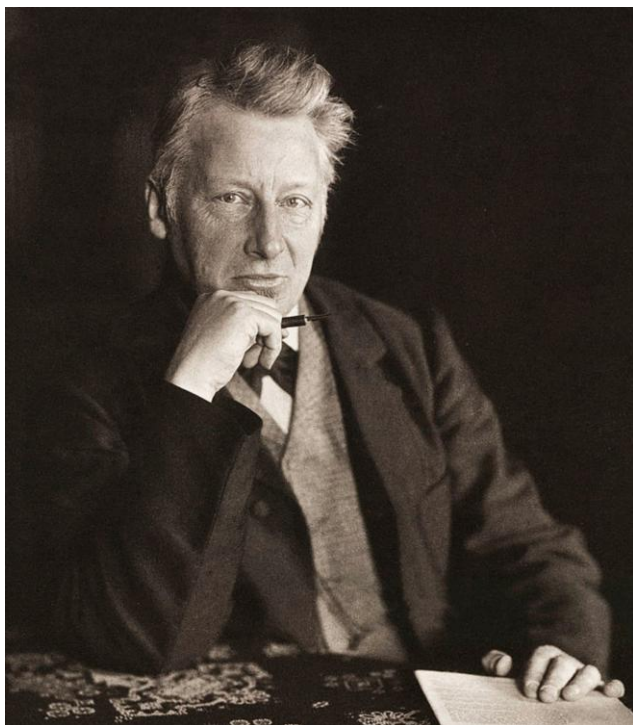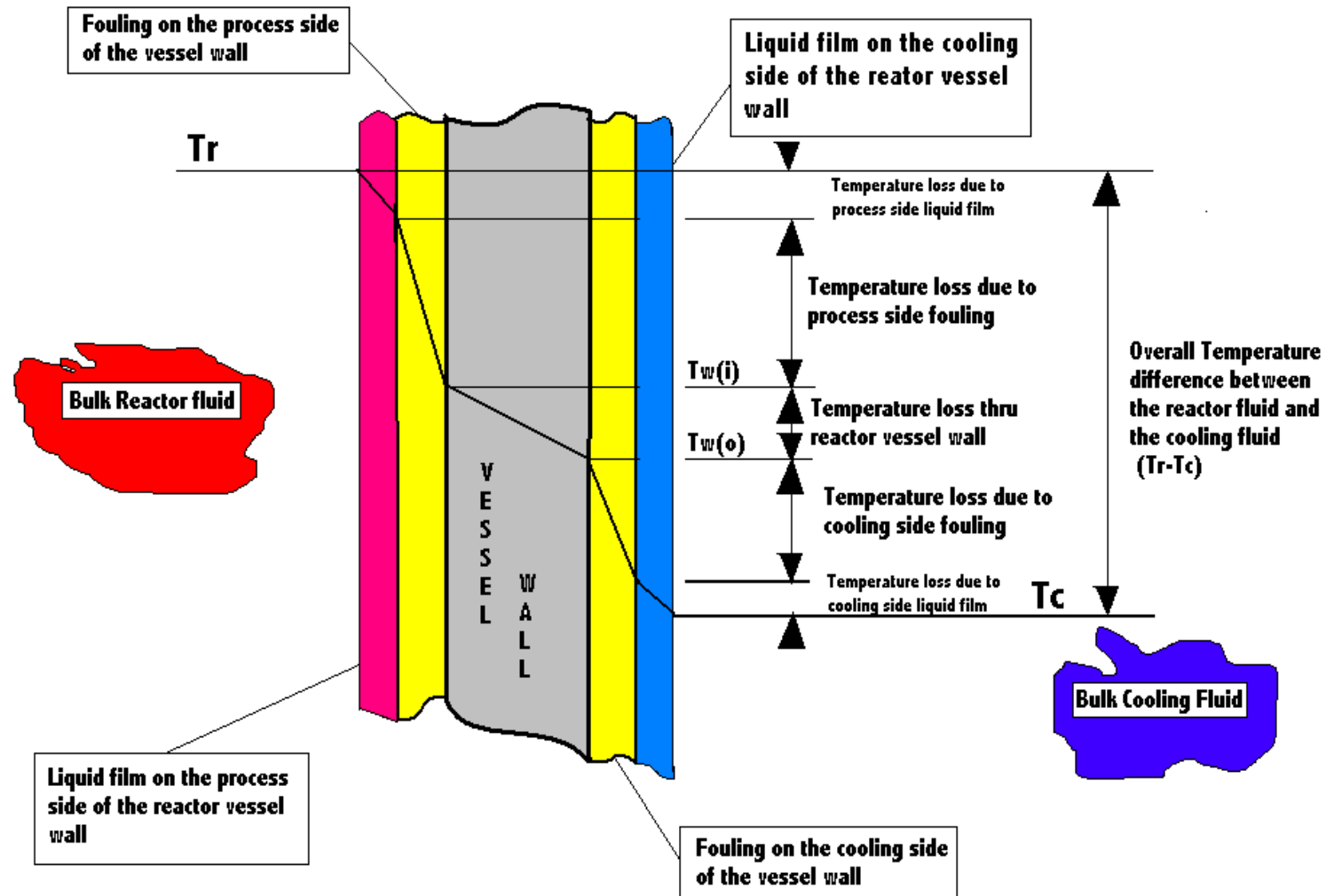
Heat Transfer through Vessel Walls

Overall Heat Transfer Coefficient

To simplify for practical heat transfer applications, a single coefficient (U) is used to describe the overall process

The easily-measured $(T_R - T_C)$ can then be used, and the overall heat transfer process is simply described by

$$\text{Total Heat Flow} = Q = U*A*\Delta T_{LM}$$

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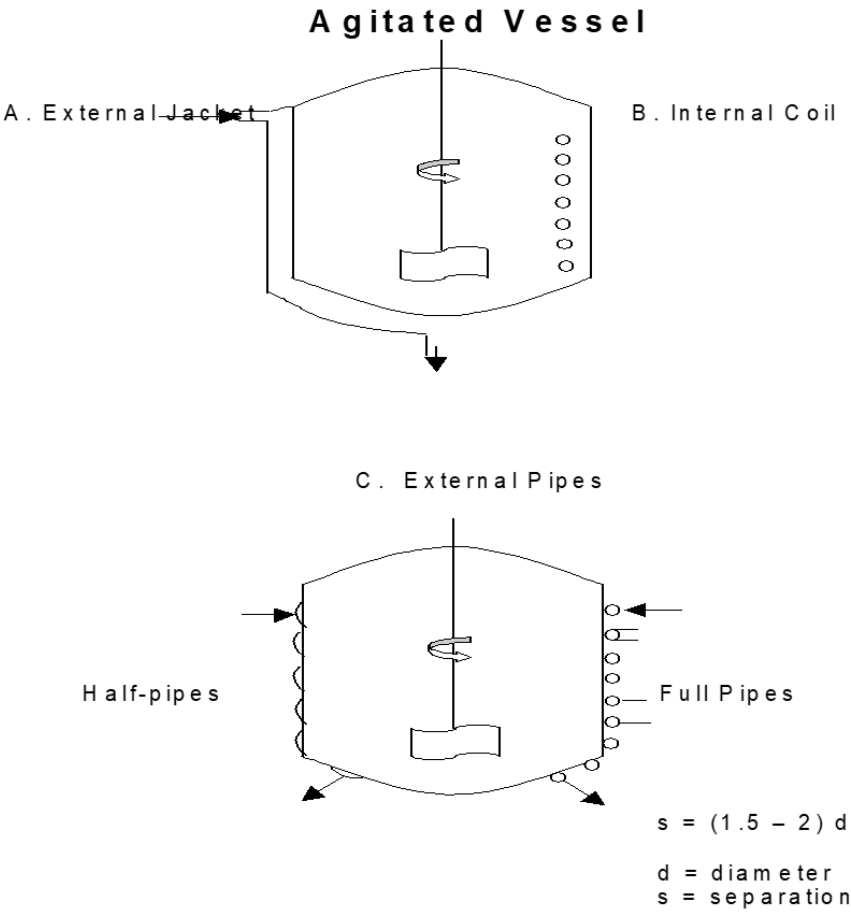# Estimating U, Overall Heat Transfer Coefficient

Estimated Heat Transfer Coefficients for Individual Heat Transport Design Techniques		VDI Heat Atlas 5th Edition, 1988	
Design Technique		Transport Conditions	Estimated U [BTU/hr/ft2/F]
Agitated Vessel A. External Jacket B. Internal Coil C. External Pipes Half-pipes Full Pipes s = (1.5 – 2) d d = diameter s = separation		External jacket Condensing steam outside and liquid inside the vessel	87 to 266
		Condensing steam outside and boiling liquid inside the vessel	124 to 302
		Cooling water or brine on the outside and liquid inside the vessel	27 to 62
		Internal Coil Condensing steam inside the coil and liquid inside the vessel	124 to 443
		Condensing steam inside the coil and boiling liquid inside the vessel	213 to 621
		Cooling water or brine inside the coil and liquid inside the vessel	87 to 213
		External Pipe welded to the Vessel Condensing steam inside the heating channel and liquid inside the vessel	87 to 302
		Condensing steam inside the heating channel and boiling liquid inside the vessel	124 to 408
		Cooling water or brine inside the cooling channel and liquid inside the vessel	62 to 160

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Scale-up: Heat Transfer Impacts

Basis: Heat of Reaction = 100 W/kg, T_R = 500 K, Cooling Water T_C = 300 K
= 155 BTU/lb/hr,   = 440 F,   =   80 F

	Laboratory 1 liter, Glass	Pilot Plant 100 liters, Metal	Production 10 m^3, Metal	
Surface Area [m²]	0.048	0.8	18.7	
		16.7	*390*	*23*
Reaction Heat [Btu/hr]	340	34000	3,400,000	
		100	*10,000*	*100*
Cooling Capability [Btu/hr]	5800	270,000	6,500,000	
		17	8	1.9
Natural Convection [Btu/hr]	340	3820	81,550	
	1		0.1	0.02
Radiant Heat Removal [Btu/hr]	305	5050	118,000	
	<1		0.15	0.04
Ratio of Total Cooling to Reaction Heat	19	8	2	

Some Exothermic Reaction Rules

Avoid accumulation of reactive potential

- continuous instead of semi-batch where possible
- semi-batch instead of batch where possible
- operate with charge control not kinetic control
- know the minimum temperature for reaction

Maintain a safe margin from "onset" temperature of secondary reactions (*decomposition and polymerization, ...*)

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Some Exothermic Reaction Rules

Know the reactive behavior of your system

- especially side reactions and autocatalytic behavior, and for other than normal reaction conditions

Take utmost care with process changes

- know exactly what the influence and consequence of the change is, arrange for advice / investigations from specialists

Avoid unacceptable residence times

Keep in mind, that storage may be <u>as</u> hazardous as reaction

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Questions/Comments

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Backup Slides

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BP Amoco Thermal Decomp

Accident Description

Accident: BP Amoco Thermal Decomposition Incident

Location: Location: Augusta, GA

Accident Occured On: 03/13/2001 | **Final Report Released On:** 05/20/2002

Accident Type: Oil and Refining - Reactive Incident

Investigation Status: The final report on this investigation was approved on May 20, 2002.

On March 13, 2001, three people were killed as they opened a process vessel containing hot plastic at the BP Amoco Polymers plant in Augusta, Georgia. They were unaware that the vessel was pressurized. The workers were killed when the partially unbolted cover blew off the vessel, expelling hot plastic. The force of the release caused some nearby tubing to break. Hot fluid from the tubing ignited, resulting in a fire.

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Synthron Chemical Explosion

Accident Description

Accident: Synthron Chemical Explosion

Location: Location: Morganton, NC

Accident Occured On: 01/31/2006 | **Final Report Released On:** 07/31/2007

Accident Type: Reactive Incident

Investigation Status: The CSB's final report was issued at a news conference in Charlotte, North Carolina on July 31, 2007

One worker was fatally burned and about a dozen others were injured when a powerful explosion devastated the Synthron Inc. chemical manufacturing facility. CSB investigators believe the explosion was related to the process inside a 1500-gallon batch reactor at the plant, which contained butyl acrylate along with the flammable solvents toluene and cyclohexane.

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First Chemical Corp Reactive Chemical Explosion

Accident Description

Accident: First Chemical Corp. Reactive Chemical Explosion

Location: Location: Pascgoula, MS

Accident Occured On: 10/13/2002 | **Final Report Released On:** 10/15/2003

Accident Type: Reactive Incident

Investigation Status: The final CSB report on this investigation was approved at a Board public meeting in Pascagoula on October 15, 2003.

On October 13, 2002, a violent explosion occurred in a chemical distillation tower at First Chemical Corporation in Pascagoula, Mississippi, sending heavy debris over a wide area. Three workers in the control room were injured by shattered glass. One nitrotoluene storage tank at the site was punctured by explosion debris, igniting a fire that burned for several hours.

TPC Explosion – 1,3 Butadiene

Butadiene reaction with oxygen to form "popcorn" polymer

Initial pipe rupture and LOC of 7,100 gallons flammable liquid, vapor cloud explosion

Second explosion launched debutanizer tower

Figure 9. Popcorn polymer in a manhole from another undisclosed butadiene unit, published in the Butadiene Popcorn Polymer Resource Book. (Credit: International Institute of Synthetic Rubber Producers Inc. [12, p. 261])

Erwin Seba/Reuters

A tower flies through the air during one of the explosions

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