Module 9 Exothermic Reactions
Section 3 and 4

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**

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

Section 3 – Characterizing Exothermic Reactions II

Module 9: Training Objectives – Section 3

Characterizing Exothermic Reactions:

Identify the parameters and data necessary to characterize exothermic reactions

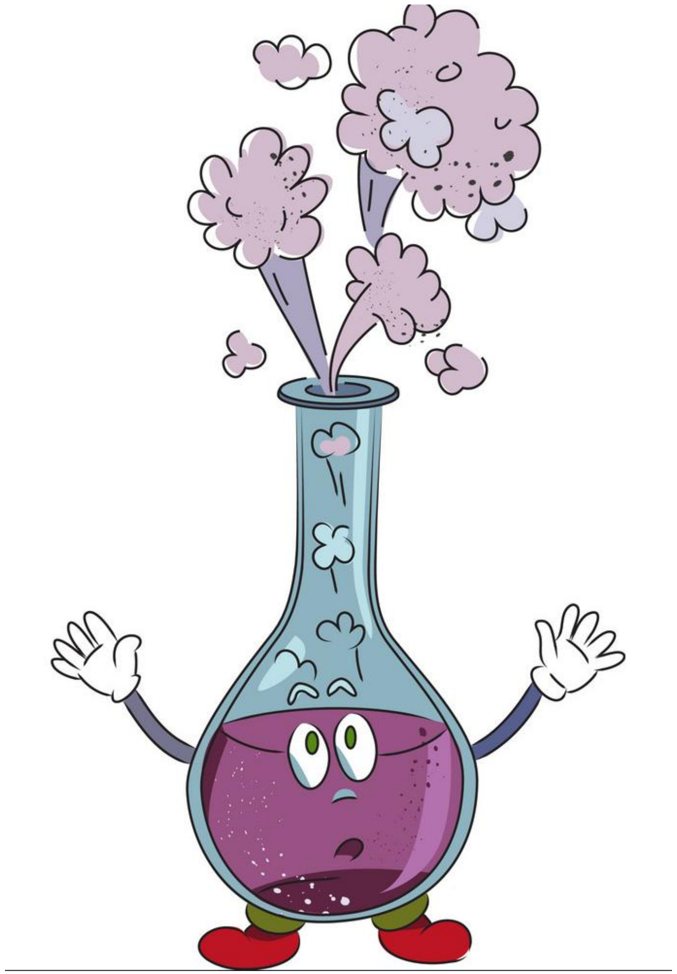
Review General Classifications of Familiar Exothermic and Endothermic Reactions

Chemical Reactivity Hazards

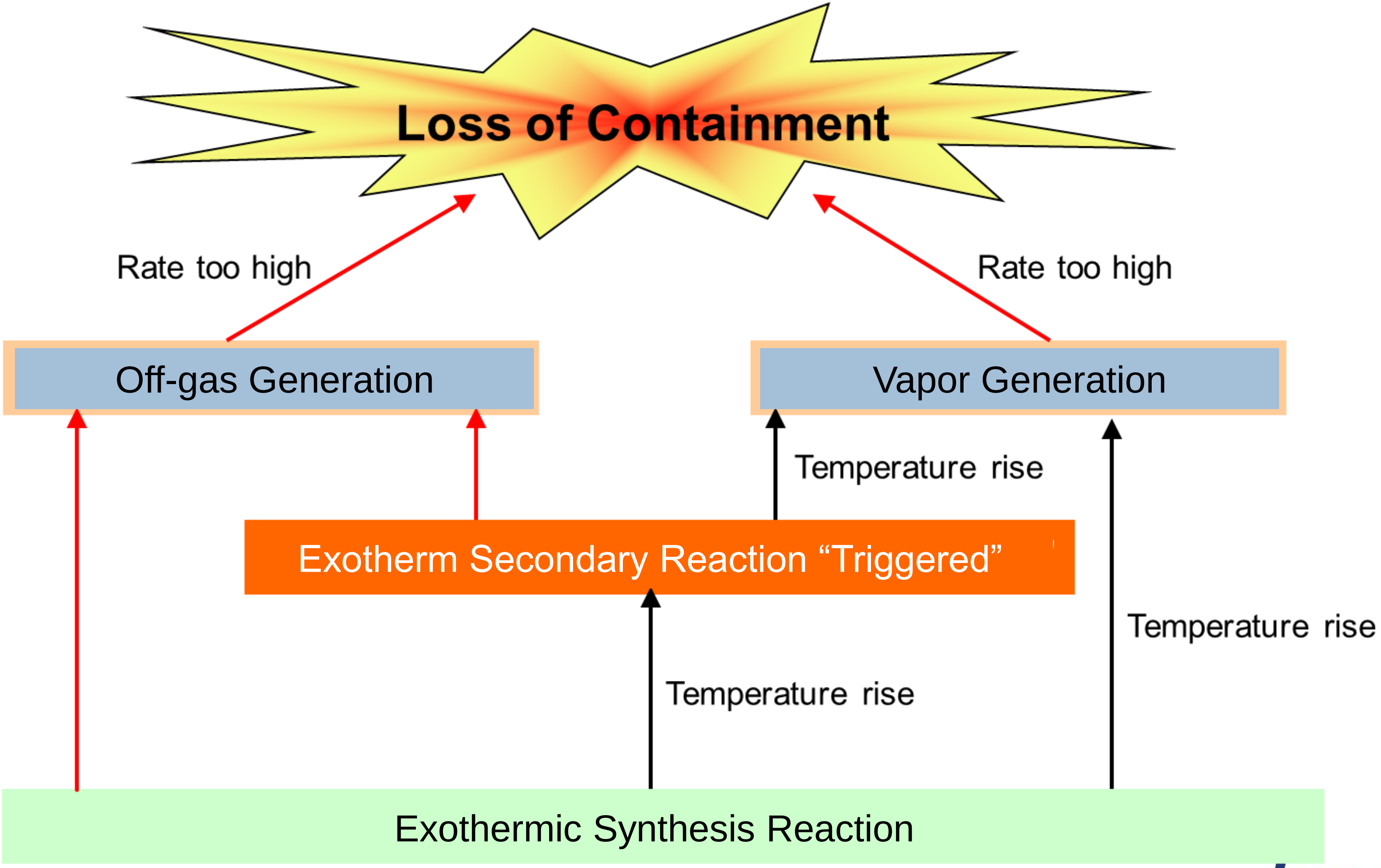
Self-Reacting or Unstable Chemicals

Runaway Reactions

Incompatibilities



Exothermic Reaction Hazards



Key Thermochemistry Information

Adiabatic Temperature Rise

Heat Capacity

Reaction Enthalpy

Heat Production Rate/Heat of Reaction

Accumulation

MTSR (Maximum Temperature of the Synthesis Reaction)

Desired Reaction, Undesired Reaction, Decomposition, Thermal Runaway

Inadvertent Mixing

Reactivity Assessment Depth

- Lab Scale
  - Literature
  - Theoretical Calculations
- Formulation Development
  - Screening Experiments
- Pilot Scale
  - Full Assess of Chemical Reaction Hazards
  - Full Set Experiments for Material Classifications
- Plant Scale
  - Assess Process Modifications
  - Optimization

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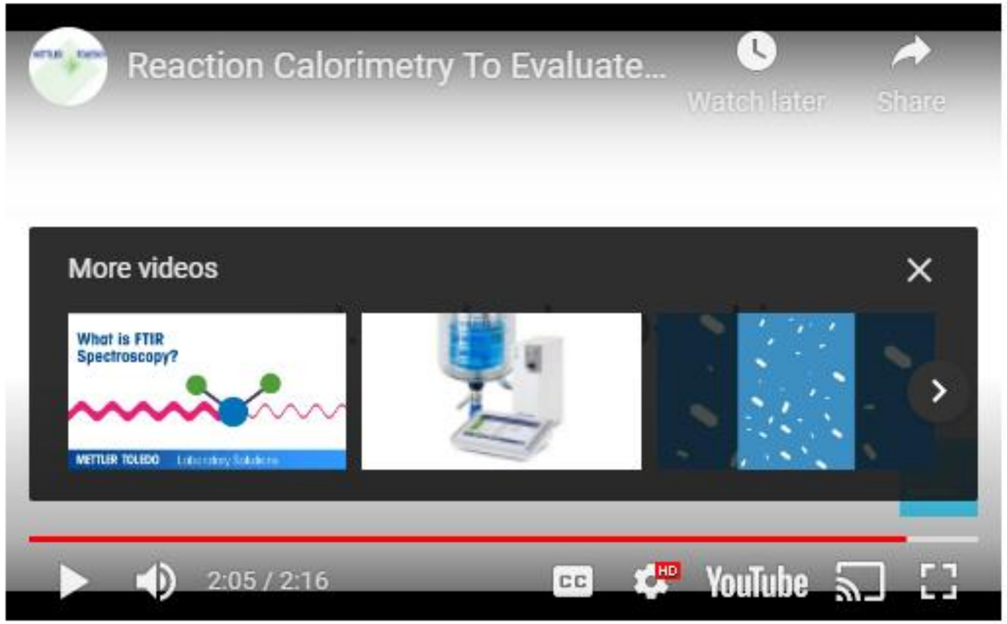
Adiabatic Temperature Rise

Dr. Francis Stossel – Presentation on Adiabatic Temperature Rise and RC1 Data



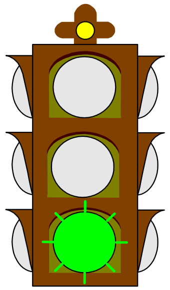
https://www.youtube.com/watch?v=uBMohkScxBg

Hazard Classification by ΔT_{ad}

$$\Delta T_{ad} = \frac{-\Delta H\ (J/g)}{C_p\ (J/g\ ^{o}C)}$$

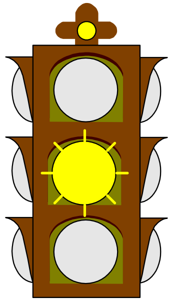
$\Delta T_{ad} < 50\ K$

Reaction in most cases can be considered safe



$150\ K > \Delta T_{ad} > 50\ K$

Reaction dynamics should be reviewed



$\Delta T_{ad} > 150\ K$

Danger!!

Heat Capacity

Amount of energy required to increase the temperature of one (1) kilogram of material by one (1) degree Celsius

Units – kJ/kg.K-1

Direct Role

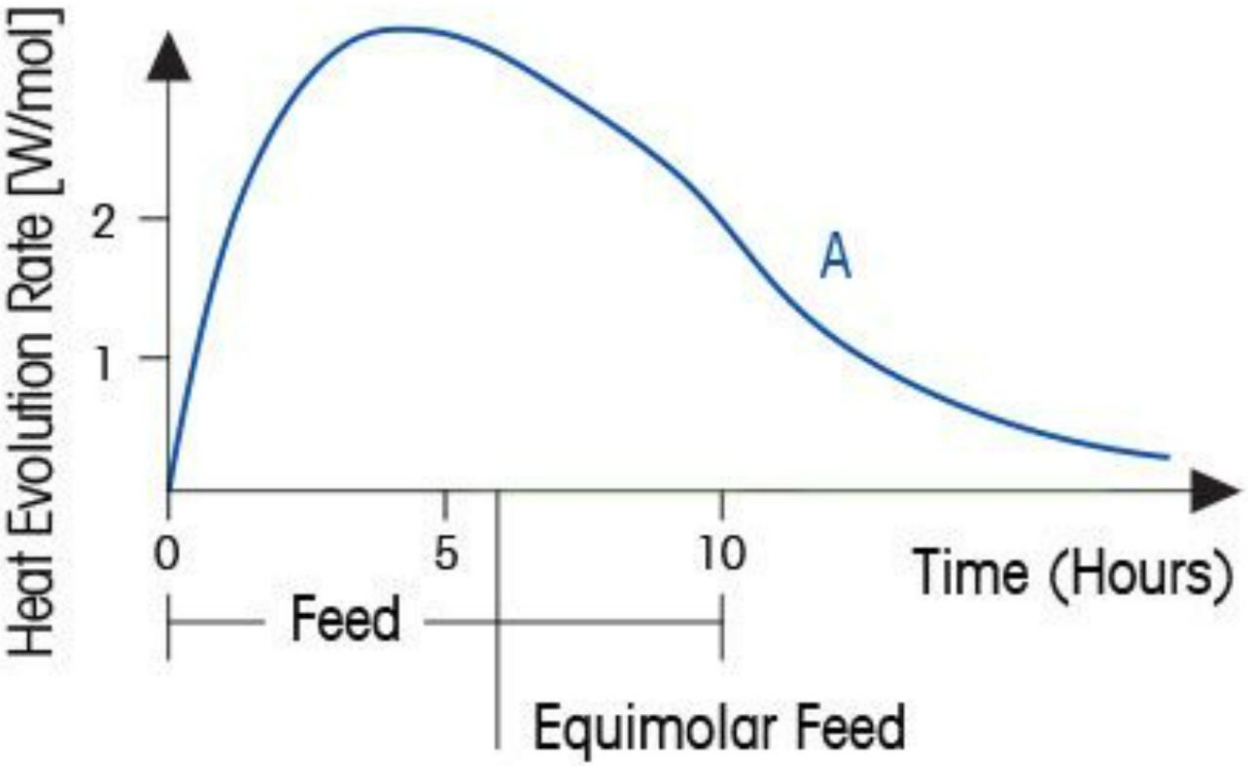
- Accumulated Heat
- Adiabatic Temperature Rise
- MTSR

Experimental Determination

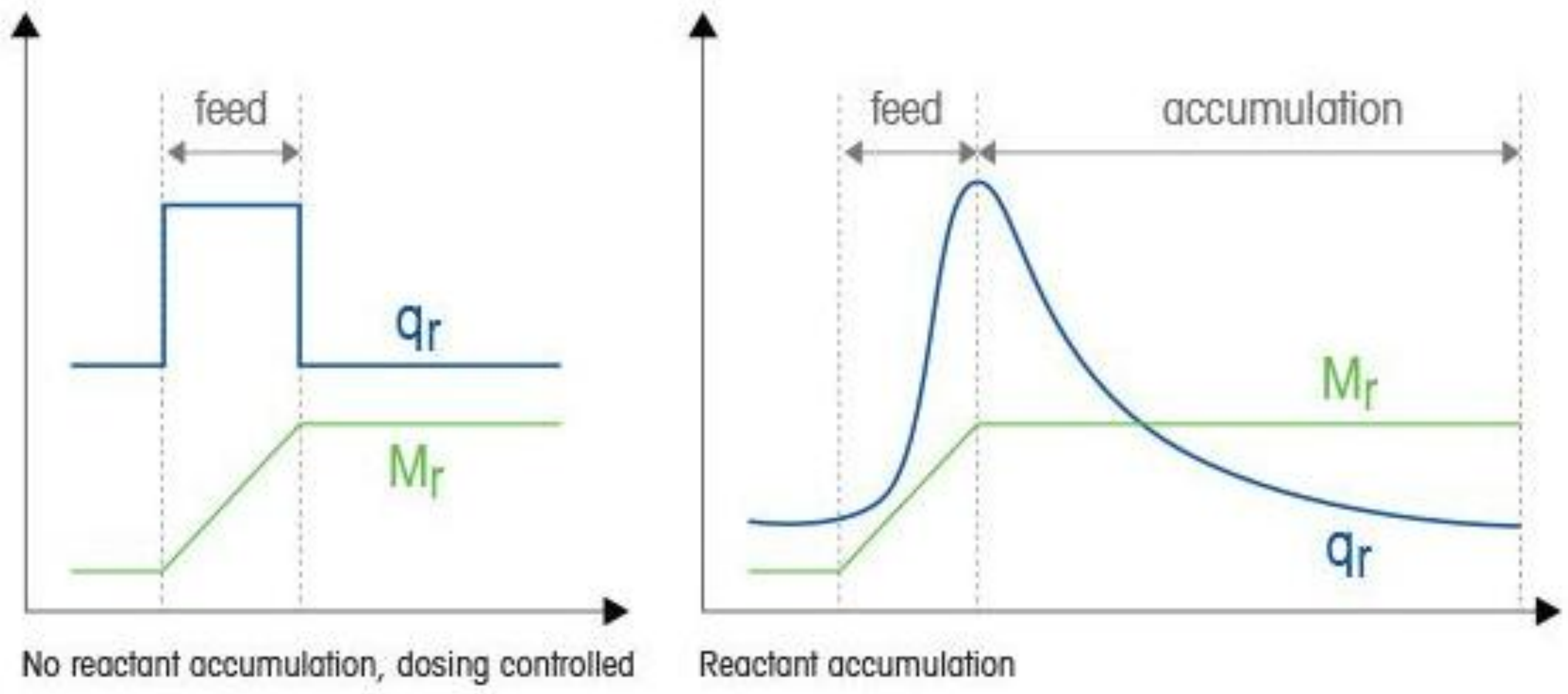
Used for overall energy (or heat) balance

Reaction Enthalpy and Heat of Reaction

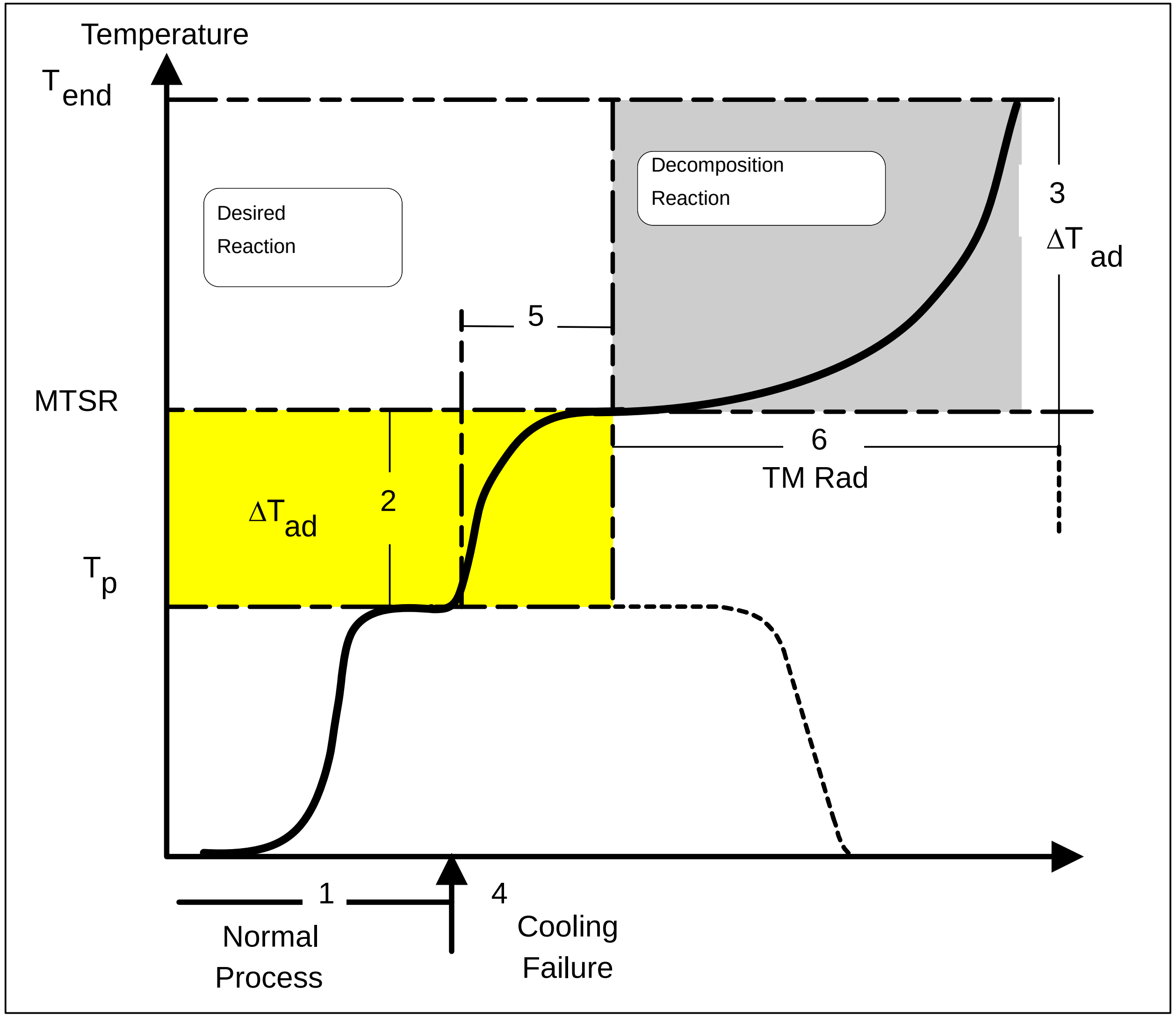
Enthalpy is calculated by integrating the Heat of Reaction trend over time.



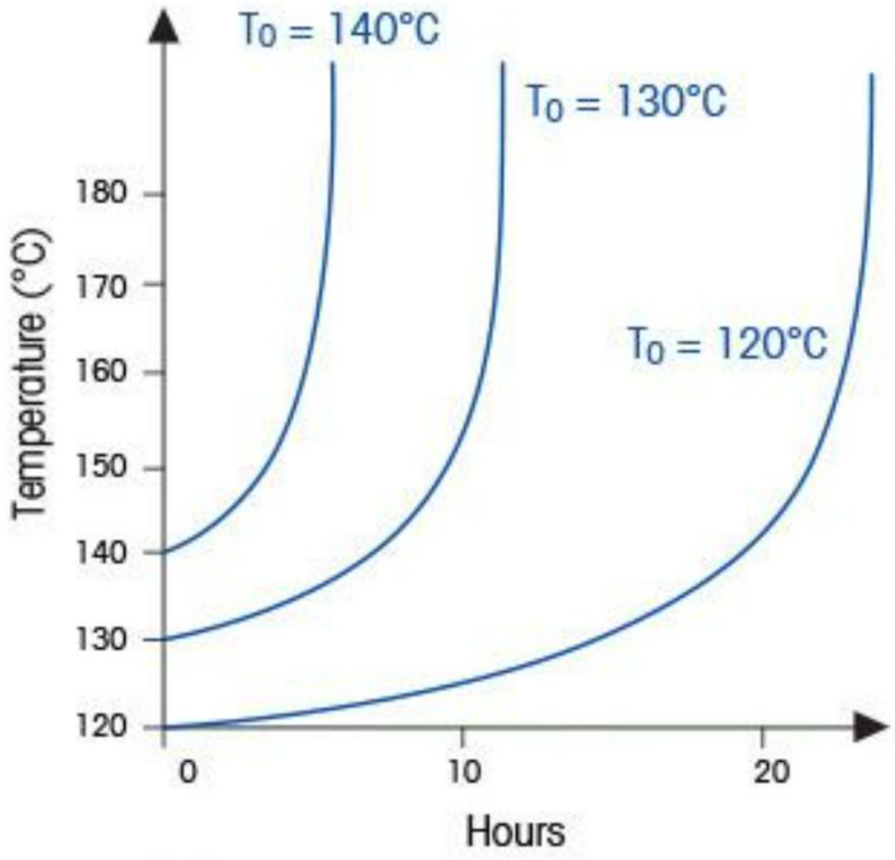
Accumulation



Maximum Temperature of the Synthesis Reaction



Desired Reaction, Undesired Reaction, Decomposition, Thermal Runaway



Adiabatic runaway curves.

Inadvertent Mixing

Assess the potential for mixing whether intentional or not

- Mixing calorimeter can determine if significant heat can be released either by heat of mixing or chemical reaction
- Develop a chemical interaction matrix (HS1-d)
- Develop a materials interaction matrix (HS1-e)

Inadvertent mixing may occur at the following:

- Unloading spots
- Manifolds
- Reactor vessels
- Multi-product storage tanks
- Vent systems
- Clean up

Inadvertent Mixing Matrix

Interactions between chemicals

Title / Project:	**Testproduct**		Project-No.
Location:		Building:	Proc. Dated:
Author:		Issue:	Date:

		2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	Chemicals	Hydrochloric Acid	Formaldehyde													
1	Epichlorhydrin	X2	X2													
2	Hydrochloric Acid		X2													
3	Formaldehyde															
4																
5																
6																
7																
8																
9																
10																
11																
12																
13																

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HS1-d

Evaluating the Reactive Hazard

Step One: Determine if the net flow of energy (heat) is into or out of the process.

Endothermic: An endothermic reaction is a reaction where energy (heat) is absorbed during the process.

Exothermic: An exothermic reaction is a reaction where energy (heat) is released during the process.

Which of the following processes is endothermic?

A. Boiling water

B. Burning wood

C. Iron rusting

D. Setting cement

Endothermic	Exothermic
Energy IN	Energy OUT
COOLER than surrounding	WARMER than surrounding

Things to keep in mind…..

Most chemical reactions are exothermic, i.e., produce heat

All reactions are progressing. Only the rate of reaction varies

Chemical reactions accelerate with increasing temperature. This rate increase is exponentially

Decomposition reactions often generate a lots of heat, with likely gas generation and accelerate strongly with temperature

Reactions can be significantly affected by contaminants, e.g., iron salts strongly accelerate the decomposition of hydroxylamine

Process times (heat up, drying, addition etc.,) tend get longer with increasing scale

Cooling and venting capacity of vessels reduces with increasing scale

Overall mixing tends to get worse with increasing scale

Consequences of an incident get more severe with increasing scale

Reactive Chemistry at Indorama

Chemistry	Products	Ankleshwar	Botany	Dayton	Port Neches	Clear Lake	Chocolate Bayou	Lake Charles	Camaçari	Coatzacoalcos	Guadalajara	Maua	Montevideo	Pasadena	San Juan Del Rio	Suzano	Tremembe	Triunfo
Acid Neutralization	Heavy Fuel Oil						X											
Alkoxylation	Alkoxylates	X		X	X				X	X	X	X		X				
Alkylation	EO Derivatives/ Synthetic Organics	X	X							X		X		X				
	Amines, Ethanolamines (MEA, DEA, TEA)				X				X									
	Nonylphenol									X								
Alkylation, Ethoxylation, Propoxylation	Surfactants, Surfactant Intermediates	X	X	X	X				X	X	X	X		X				
Cracking	Ethylene				X			X										
Cracking, Oxidation, Hydrolysis	Propylene, Propylene Oxide, Propylene Glycol				X													
Dehydrogenation	Linear Olefins						X											
	MEK																	X
Epoxidation	Ethylene Oxide MTBE				X													
Esterification	Phosphate Esters	X		X								X		X				
Esterification	Lactylates										X							
	Glyceryl Esters										X							
	Sorbitan Esters										X					X		
	PEG Esters										X							
Esterification/Hydrolysis	Sec-butanol																	X
HF – Adsorption	Water/AlF3						X											
HF – Alkylation	Alkylbenzene						X					X						
Hydrolysis	Glycols (MEG, DEG, TEG)		X		X	X			X			X						
Hydrogenation	Ethylene							X										
Methanation	Methane																	
Oxidation	Ethylene Oxide				X	X	X		X			X						
	Amine Oxides													X				
	Amine Oxides																X	
Polymerization	Polyacrylates																X	
	Polyethers	X		X						X	X	X		X				
Sulfonation, sulfation	Anionic surfactants (sulfated)												X		X	X	X	

General Classifications - Exotherms

Mild Exotherms:

- **Hydrogenation**
- **Hydrolysis**
- **Isomerization**
- **Sulfonation**
- **Neutralization**

Moderate Exotherms:

- **Alkylation**
- **Esterification**
- **Addition Reactions (Inorganic acids & unsaturated hydrocarbons)**
- **Oxidation**
- **Polymerization**
- **Condensation**

Critical to Control Exotherms:

- **Halogenation**

Sensitive Exotherms:

- **Nitration**

Ref: Dow Fire & Explosion Index

General Classifications - Endotherms

Calcination

Electrolysis

Pyrolysis or Cracking

Ref: Dow Fire & Explosion Index

Questions/Comments

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Section 4 – Techniques for Investigating Exothermic Reactions

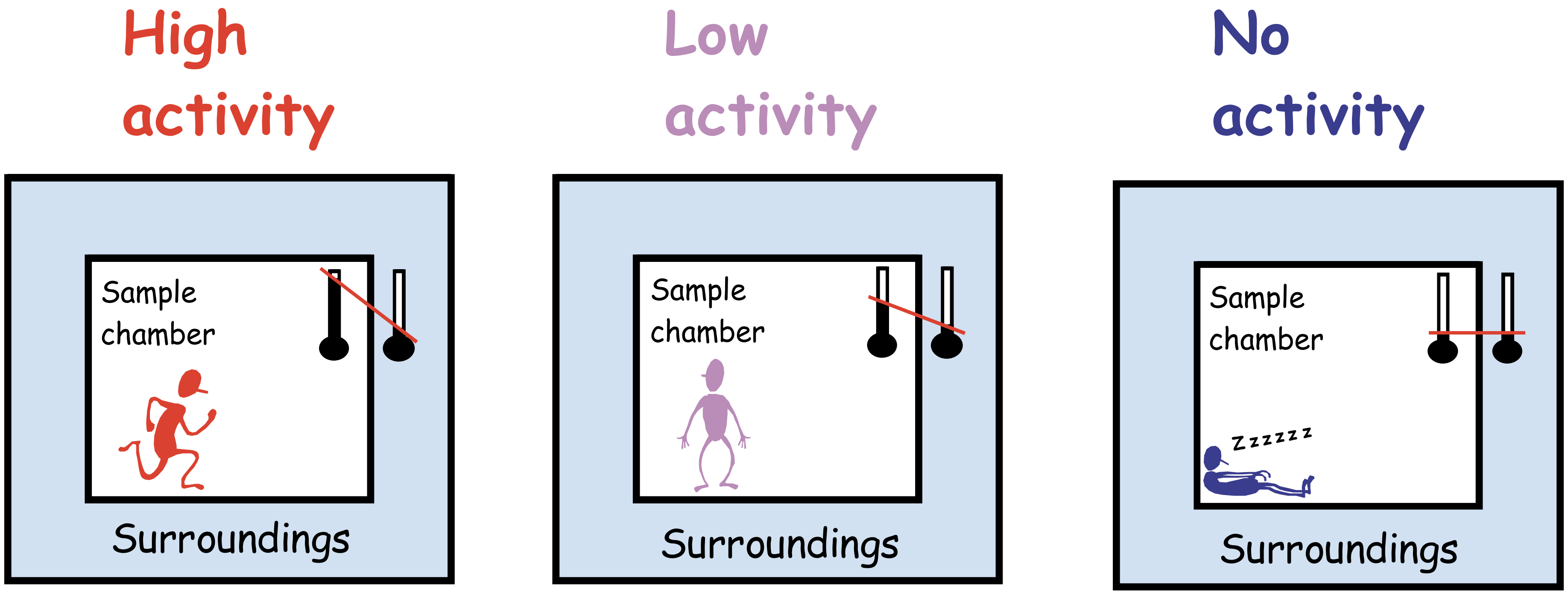
Module 9: Training Objectives – Section 4

Techniques for Investigating Exothermic Reactions:

Increase awareness of the analytical techniques for developing reactive chemistry information

Calorimetric Principle

If the sample temperature is higher than the reference temperature, then this indicates thermal activity in the sample.



Calorimetric Testing Devices

Adiabatic Calorimetry

Differential Scanning Calorimetry (DSC)

Vent Sizing Package (VSP2)

Automatic Pressure Tracking Adiabatic Calorimeter (APTAC)

Druckewarmestau-Apparatur (DWS) Pressure-Heat Accumulation A

Reaction Calorimetry (Semi-Batch)

Mixing Calorimetry

Adiabatic Calorimetry
Measurement of Thermal Runaway

Adiabatic = no heat loss from the sample

Adiabatic conditions are realized by:

Insulation of the sample (such as in a Dewar vessel)

Maintaining the environment temperature the same as the sample temperature

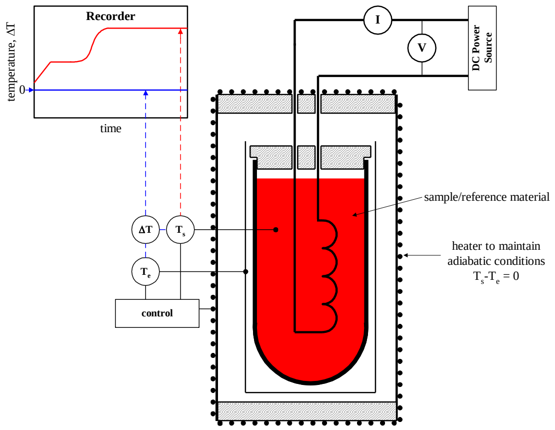
Indication for adiabatic tests

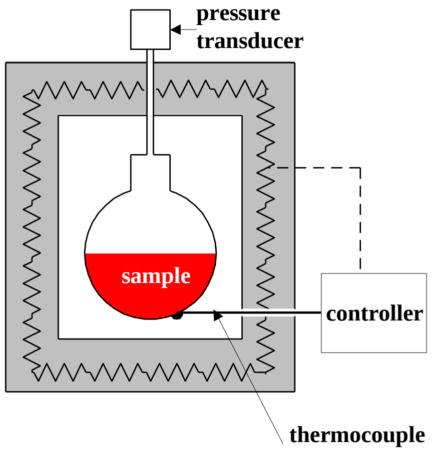
Determination of P_{max} and T_{max}

Design of pressure relief system (dp/dt, dT/dt)

Direct determination of adiabatic induction time

Development of a kinetic model





Adiabatic Calorimetry
Measurement of Thermal Runaway

Information?

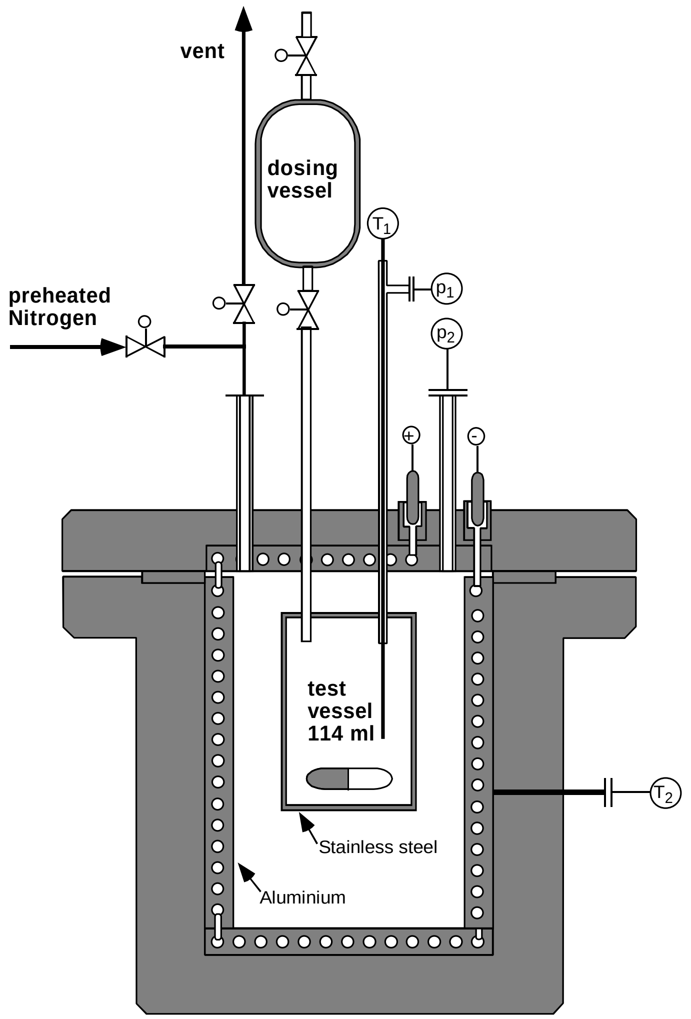
- temperature as f(time) and T_{max}
- pressure as f(time) and P_{max}
- dp/dt, rate of gas evolution
- dT/dt, self-heating rate

What is to be tested?

- Reactants
- Reaction products
- Reaction mixture (also semi-batch processes)

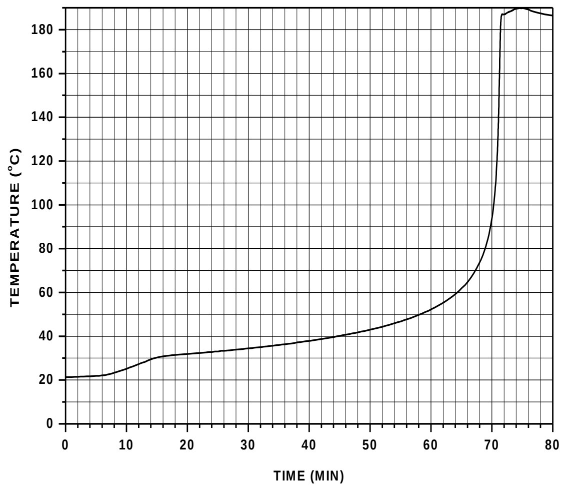
Standard Experimental Conditions:

- P_{max} : 50 bar
- Temperature range: 30 °C < T < 350 °C
- Materials of measurement cell: stainless steel, HC

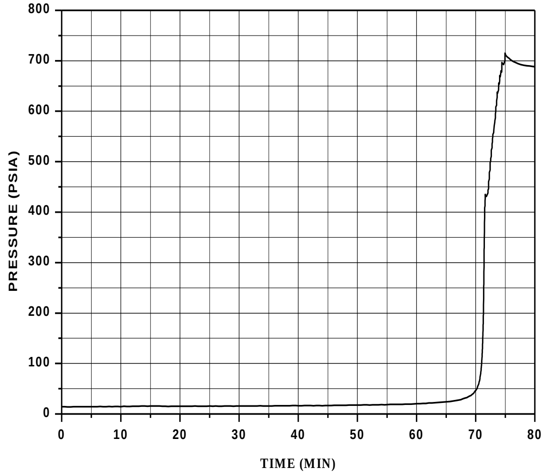


Information from Adiabatic Calorimeters

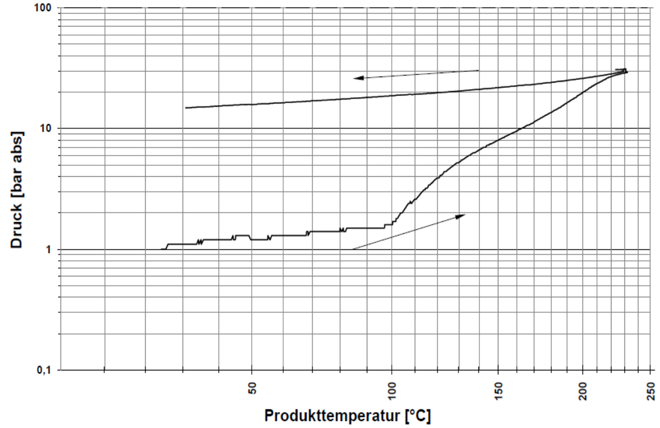
Temperature/Time



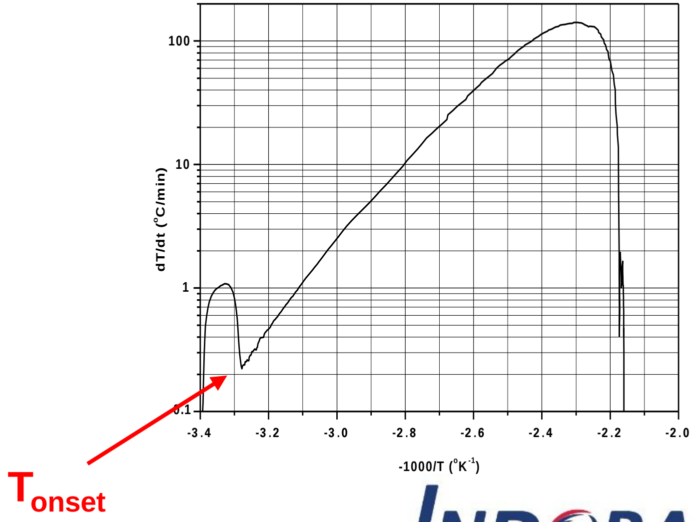
Pressure/Time



Vapor Pressure

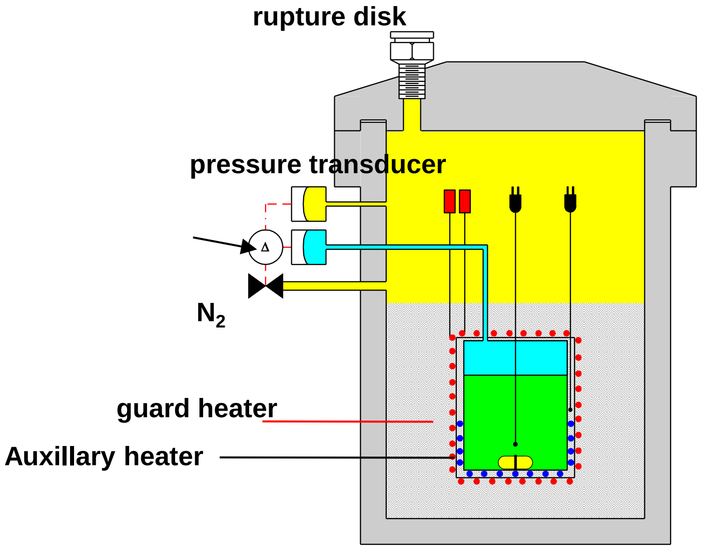


Self Heat Rate



Vent Sizing Package (VSP2)

- A low phi (Φ) factor adiabatic calorimeter.
- Designed to characterize the T and P characteristics of runaway reactions for sizing Emergency Relief Systems (ERS) using the DIERS methodology.
- The temperature and pressure behavior in the VSP is the same as that which would be observed in a plant vessel.
- Additional information that can be obtained from VSP data are:
  - heats of reaction, $-\Delta H_r$
  - adiabatic temperature rise, ΔT_{ad}
  - reaction kinetics



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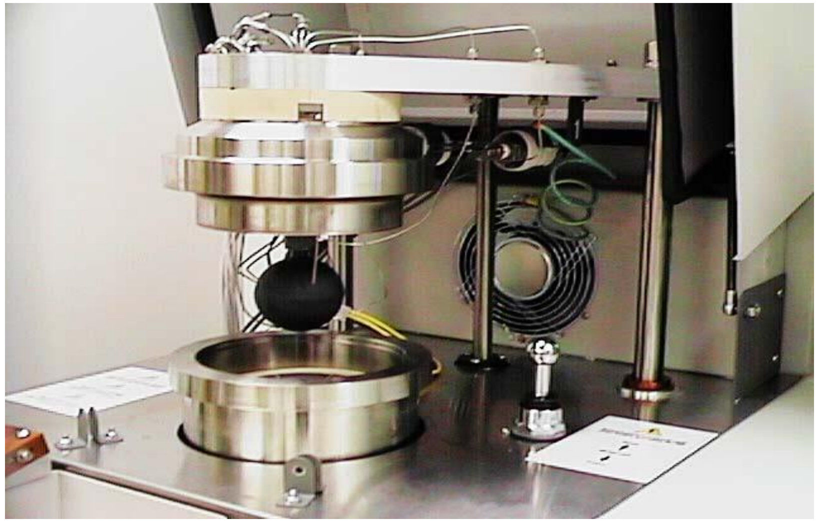
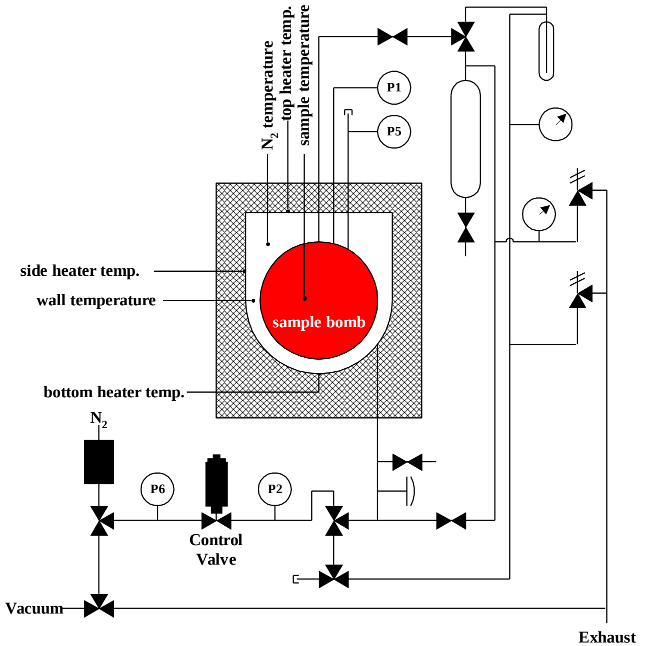
Automatic Pressure Tracking Adiabatic Calorimeter (APTAC)

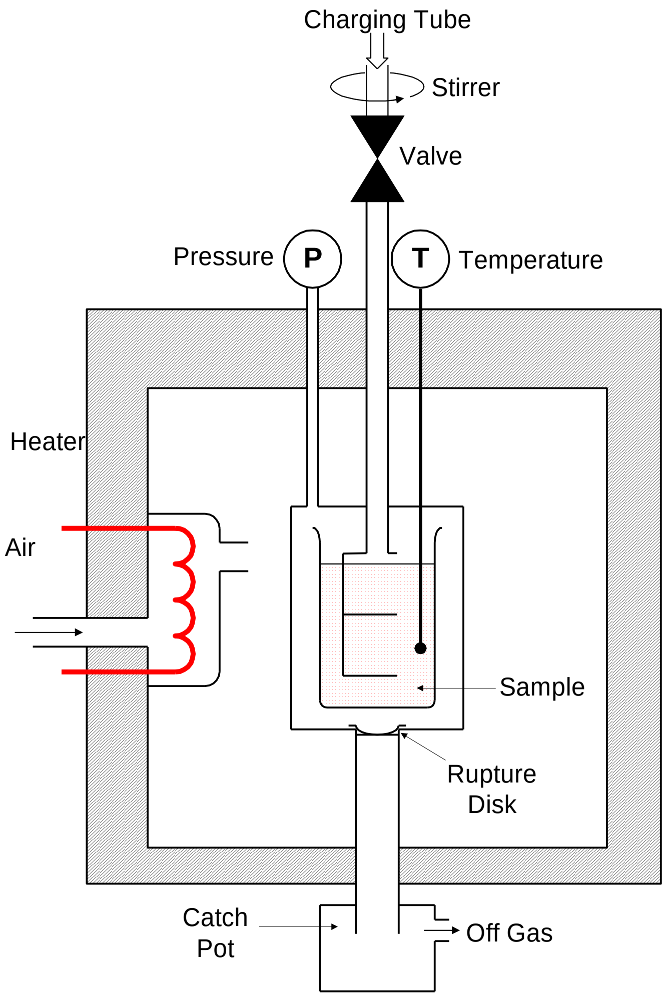
- A low phi (Φ) factor adiabatic calorimeter
- Capable of detecting and tracking exotherms at self-heat rates < 0.04 to > 400 oC/min.
- Sample bombs are prevented from bursting by pressurizing the containment vessel to keep a constant differential pressure across the wall of the sample bomb.
- Operates from full vacuum to 1,200 psig and is capable of tracking pressures of about 10,000 psi/min. Principally used for characterizing runaway reactions and obtaining data required for sizing Emergency Relief Systems (ERS) using the DIERS methodology.





Druckwarmestau-Apparatur (DWS) Pressure-Heat Accumulation Apparatus

- Consists of a 750 ml stainless steel autoclave located in a hot air furnace.
- The oven temperature is maintained the same as the sample temperature.
- Pressures greater than ~580 psi are relieved through a rupture disk.
- Pressures and temperatures are recorded as a function of time.
- Induction times from three storage tests plotted logarithmically versus 1/T result in a straight line from which induction times at any storage temperature may be determined.
- The results may be applied directly to amounts up to 100 lb_m



Adiabatic Calorimetry with Low -Factor Benefits and Constraints

Benefits

- Relatively small quantities of sample
- Fewer limitations with respect to agitation and charging compared to the DSC
- Pressure and vapor pressure data can be generated
- Can examine time dependent behavior
- Can characterize upset conditions

Constraints

- Cost
- Temperature limitations
- Difficult to simulate steady state process conditions
- Agitation capabilities are limited

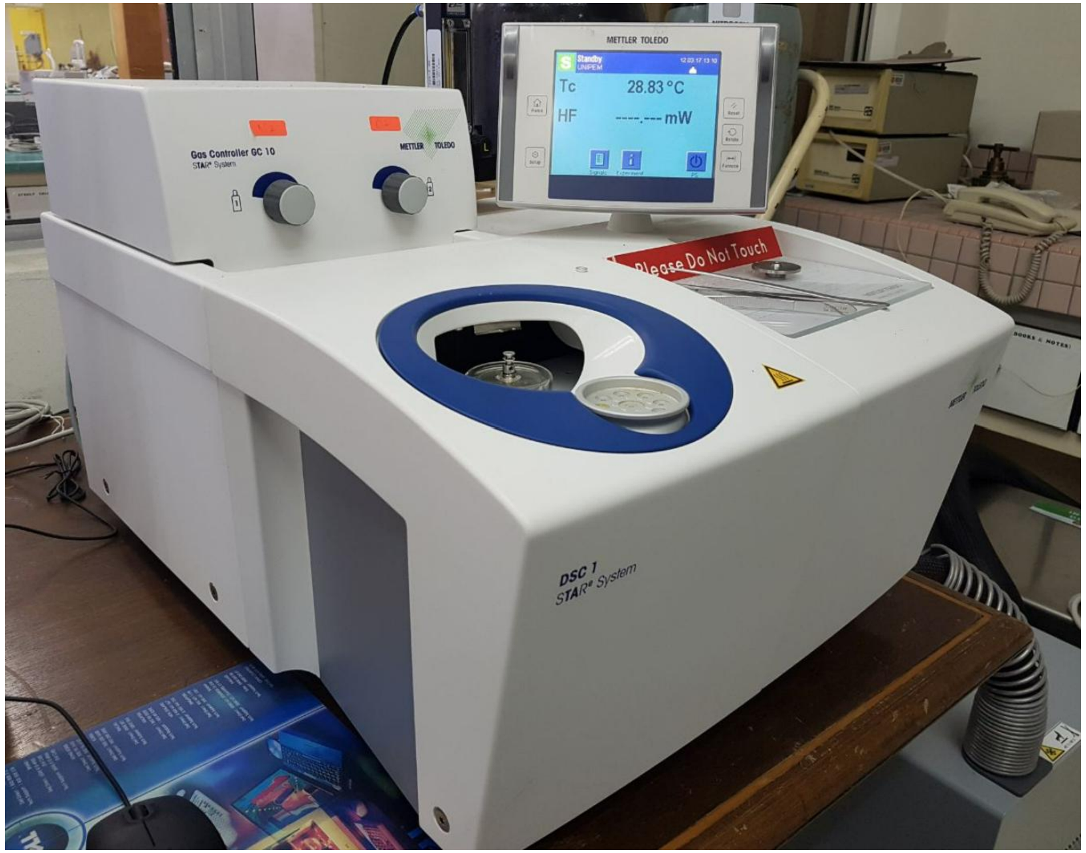
Differential Scanning Calorimetry

Most common thermal hazards screening tool

- Fast and inexpensive
- Safe, small sample size (approx. 10 mg)

Provides information on

- Exothermic onset temperatures
- Heats of Reaction
- Melting points, glass transitions



Principle of DSC Measurements

T_{onset} = Lowest temperature at which exothermic activity is detected

Determination Method:

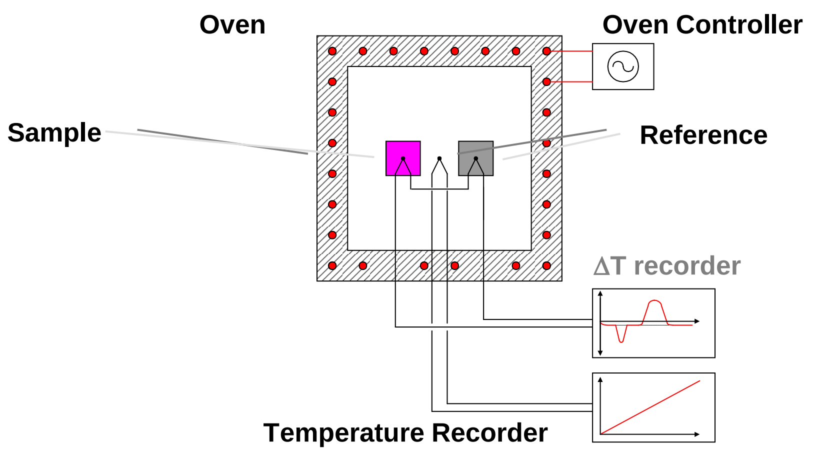
Heat generation can be detected using small amounts of sample (~10 mg)

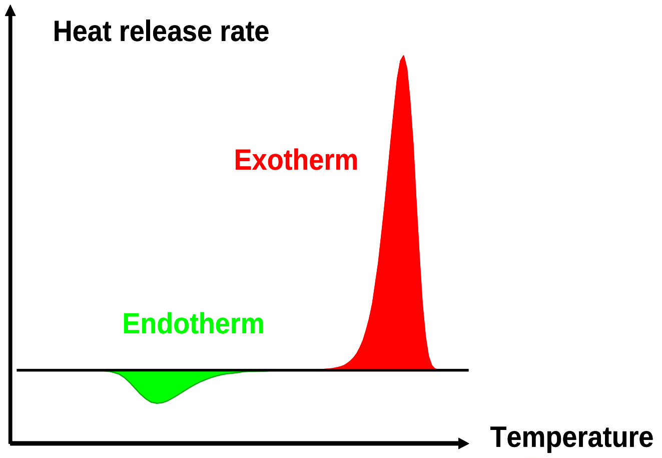
The sample and a reference substance are heated simultaneously.

The temperature increase is controlled and linear (1 to 10 oC/min).

The ΔT between the sample and reference is measured and recorded

When the Cp of the two materials are the same heat capacity, the Δ T at any instance is proportional to the heating rate of the reaction.





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Thermal Stability Testing by DSC

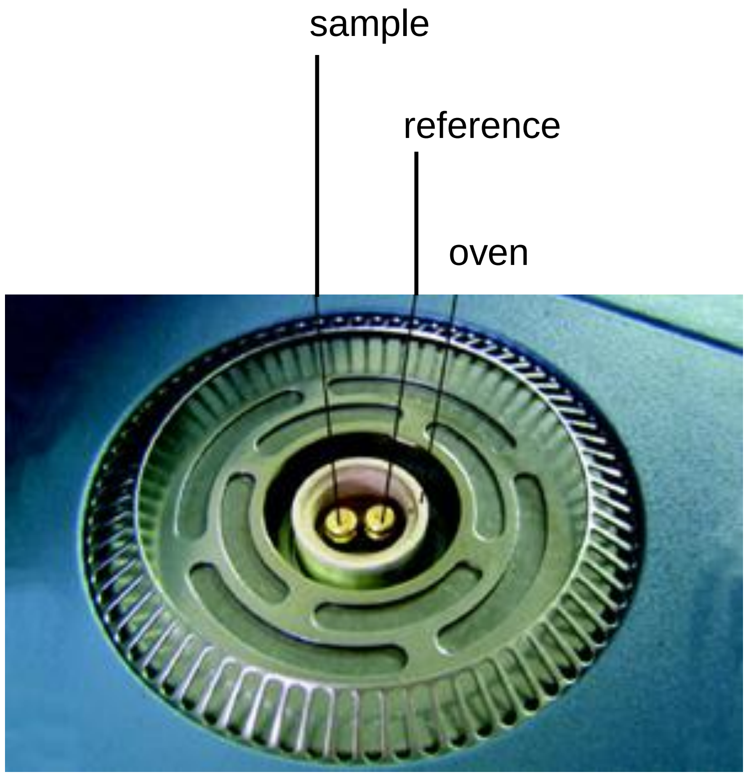
Information?

- ✓ Time and temperature dependent heat production rate
- ✓ Onset temperature, heat of decomposition/reaction
- ✓ Need of further tests for explosion hazard?

  ($-\Delta H > 500$ J/g (deflagration), $-\Delta H > 800$ J/g (detonation))
- ✓ Need of further classification tests for commercial products?

  (e.g., UN 4.1 ($-\Delta H > 300$ J/g))
- ✓ Basis for formal kinetic modelling of decomposition reaction,

  (e.g., estimation of degradation rate and heat flow



What is to be tested?

Reactants

Reaction products

Reaction mixture (batch process)

Differential Scanning Calorimetry (DSC)
Benefits and Constraints

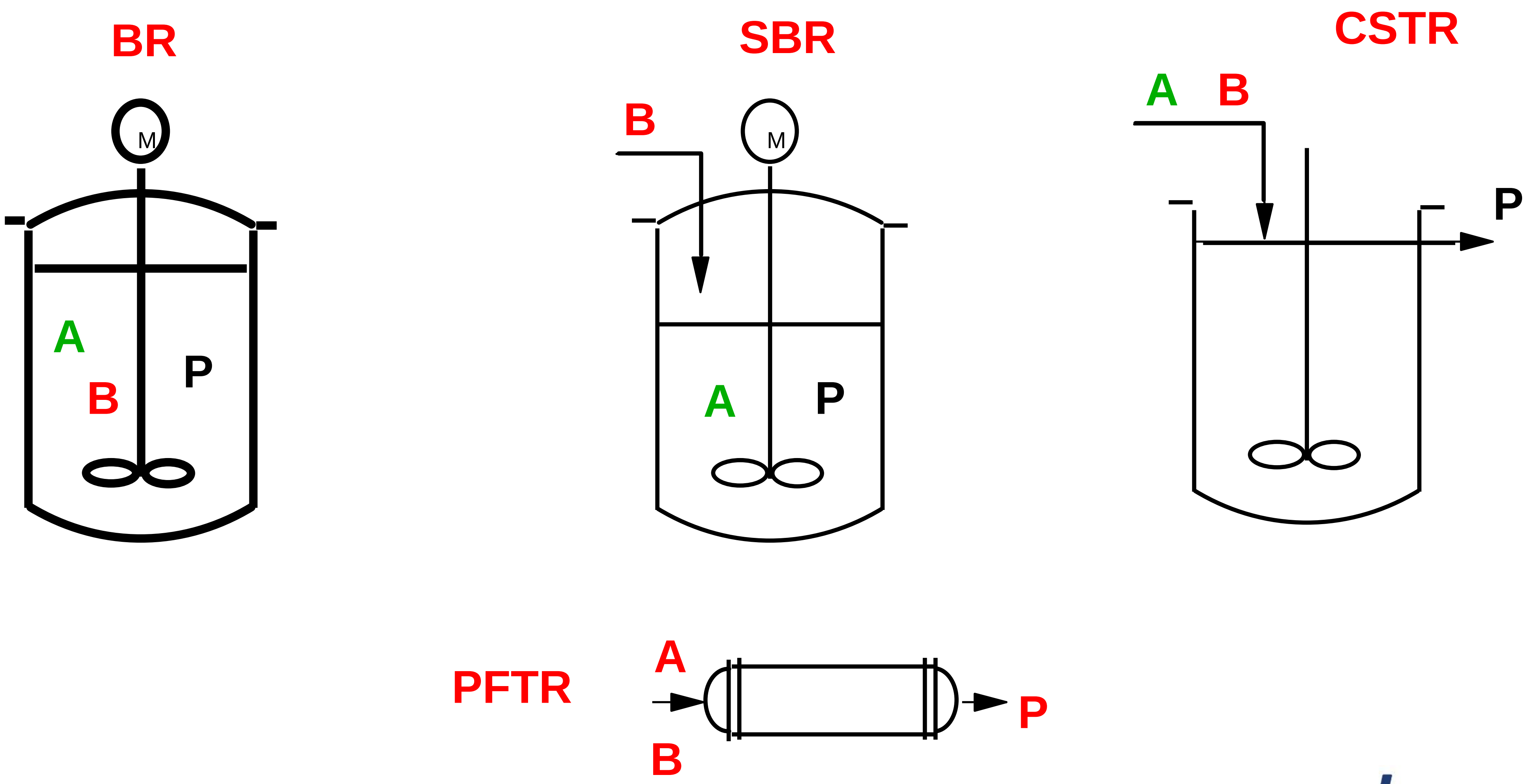
Benefits

- Quick, inexpensive
- Safe-small sample size
- Provides overview information
- Easy to screen autocatalytic effects

Constraints

- No mixing
- Closed test cell
- High surface to volume ratio can factor into results
- Not adiabatic
- Not as sensitive as other adiabatic techniques
- No pressure/gas info
- Cell pressure limitations

Ideal Reactors



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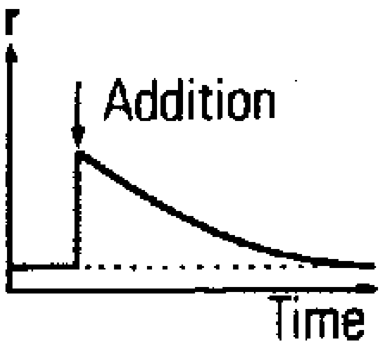
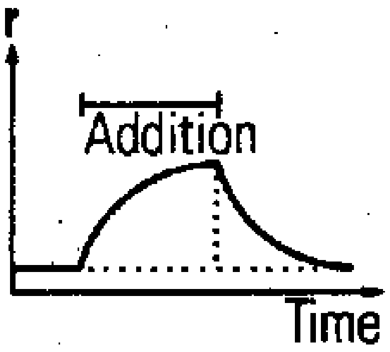
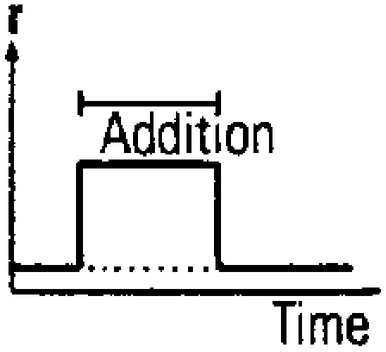
Semibatch Process
Dosing controlled vs. kinetic controlled reaction

	"Batch"	"Semibatch" partially feed controlled	"Semibatch" feed controlled
Reaction rate (r) Typical profile			
Dependency	temperature dependent	temperature and feed dependent	feed dependent
Accu (t) at maximum	1	between 0 and 1	0

Types of discontinuous reaction control

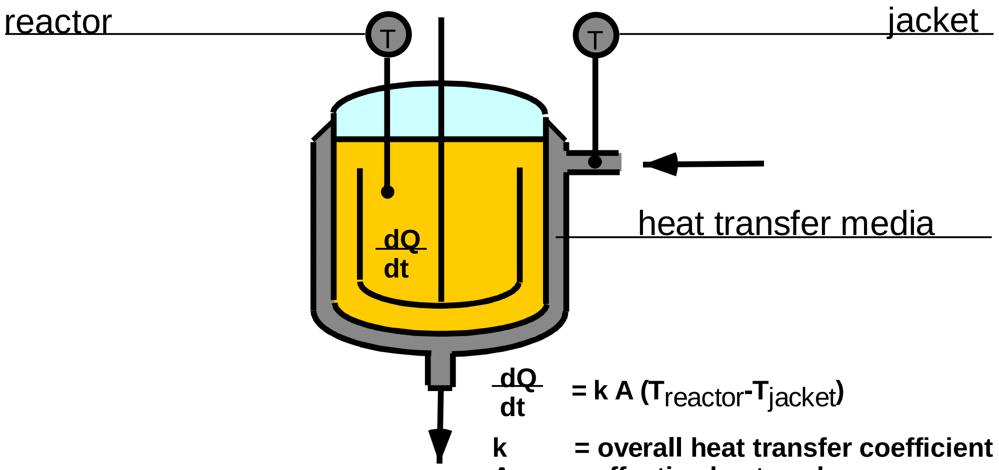
Semibatch Process Reaction Calorimetry

Experimental Conditions:

0.5 kg < mass < 2.0 kg,

-20 °C < Temperature < +250 °C

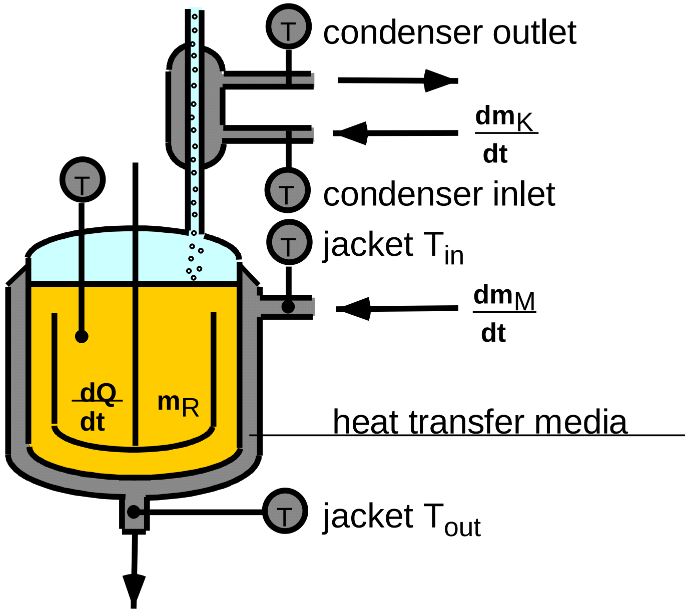
heat flow calorimeter



$$\frac{dQ}{dt} = k\,A\,(T_{reactor} - T_{jacket})$$

k = overall heat transfer coefficient
A = effective heat exchange area
k A = calibration factor

heat balance calorimeter



$$\frac{dQ}{dt} = \underbrace{m_R\, c_{pR} \frac{dT_R}{dt}}_{\text{heat accumulation}} + \underbrace{\frac{dm_M}{dt}\, c_{pM}\,(T_{out} - T_{in})_M}_{\text{jacket balance}} + \underbrace{\frac{dm_K}{dt}\, c_{pK}\,(T_{out} - T_{in})_K}_{\text{condenser balance}}$$

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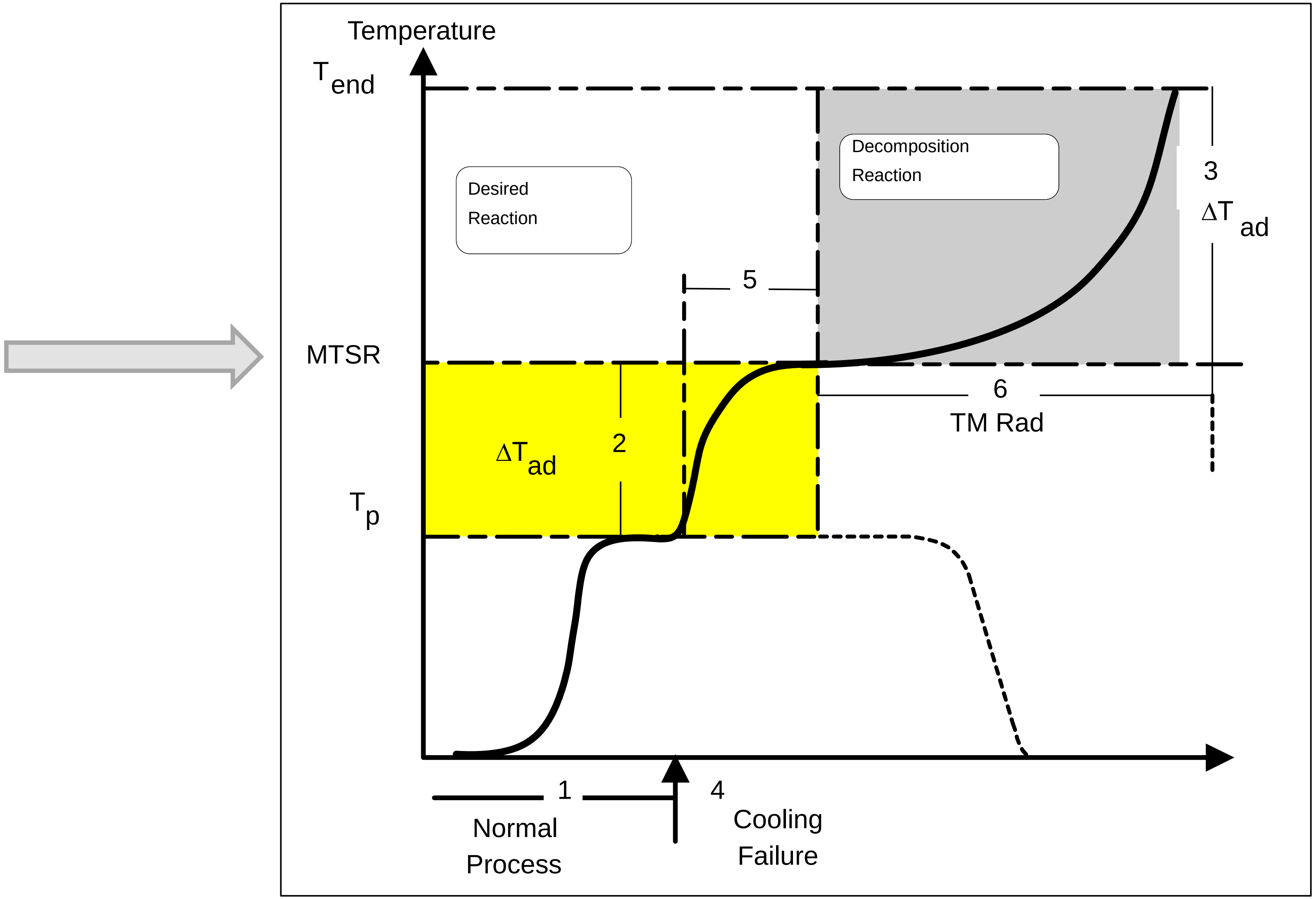
INDORAMA VENTURES

Maximum Temperature of the Synthesis Reaction (MSTR)



Inherent Safety Principles

Normal Operating Condition

Cooling Capacity

$Q_{rxn} < Q_{cooling}$

Case of Cooling Failure

Accumulation

$MTSR < T_{exo}$

T_{exo} < (T_{onset} - 50 K), depending on activation energy and T_{onset}

Knowledge Check

Method used for screening for autocatalytic (secondary reaction) properties

Method for data required for sizing Emergency Relief Systems using DIERS

Method used to determine MTSR – maximum temperature synthesis reaction

APTAC and VSP2

Reaction Calorimetry

Differential Scanning Calorimetry

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Questions/Comments