# Module 9 Exothermic Reactions
# Section 5, 6 and 7

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 5 – Analyzing Exothermic Reaction Stability

# Module 9: Training Objectives – Section 5

**Analyzing Exothermic Reaction Stability**

**Introduce the Seminov Diagram**

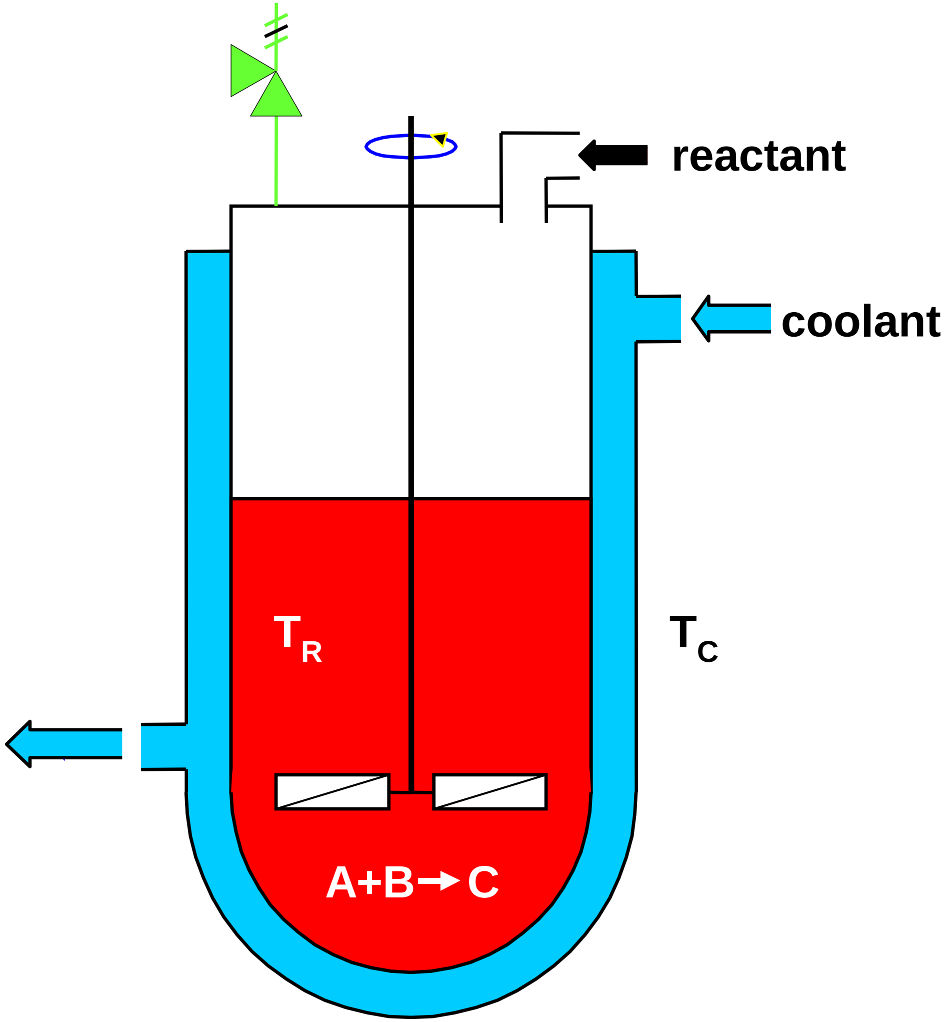
**Review Cooling System Capacity**

**Increase Understanding of Reaction Heat Generation**

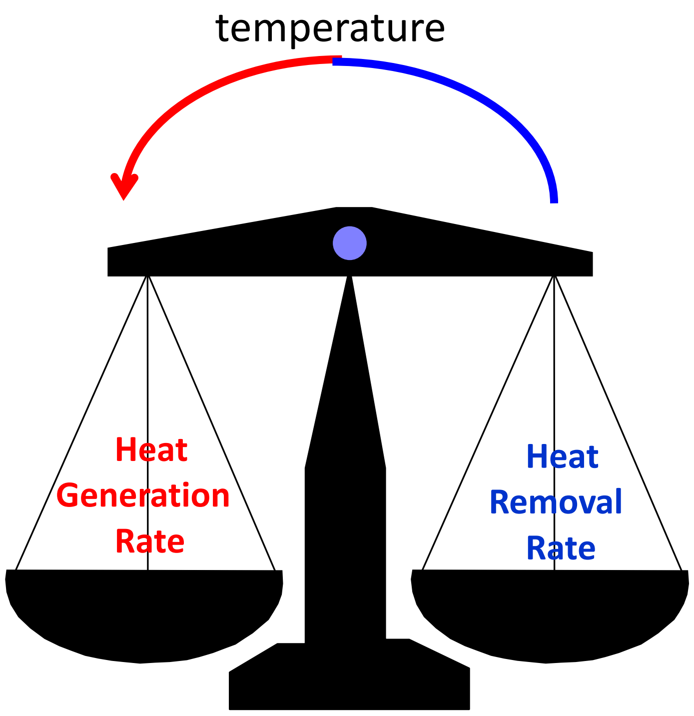
- Effects of Increased Heat of Reaction
- Effects of Fouling the Heat Exchanger
- Effects of Accumulating the Limiting Reactant

# Introduction to the Semenov Diagram

A typical reactor for
Exothermic reactions



# Introduction to the Semenov Diagram
# Balancing Energy Flows




$Q_R$ = heat generation rate, BTU/min
$\Delta H_{rxn}$ = Enthalpy of reaction, BTU/lbmole
C = reactant concentration, lbmole/ft$^3$
V = volume, ft$^3$
$A_r$ = pre-exponential constant, min$^{-1}$
E = activation energy, BTU/lbmole
$T_R$ = reactant temperature, $^oK$
R = gas constant, BTU/lbmole $^oK$
U = heat transfer coefficient, BTU/min ft$^2$ $^oK$
A = heat transfer area, ft$^2$
$T_C$ = temperature of cooling media, $^oK$

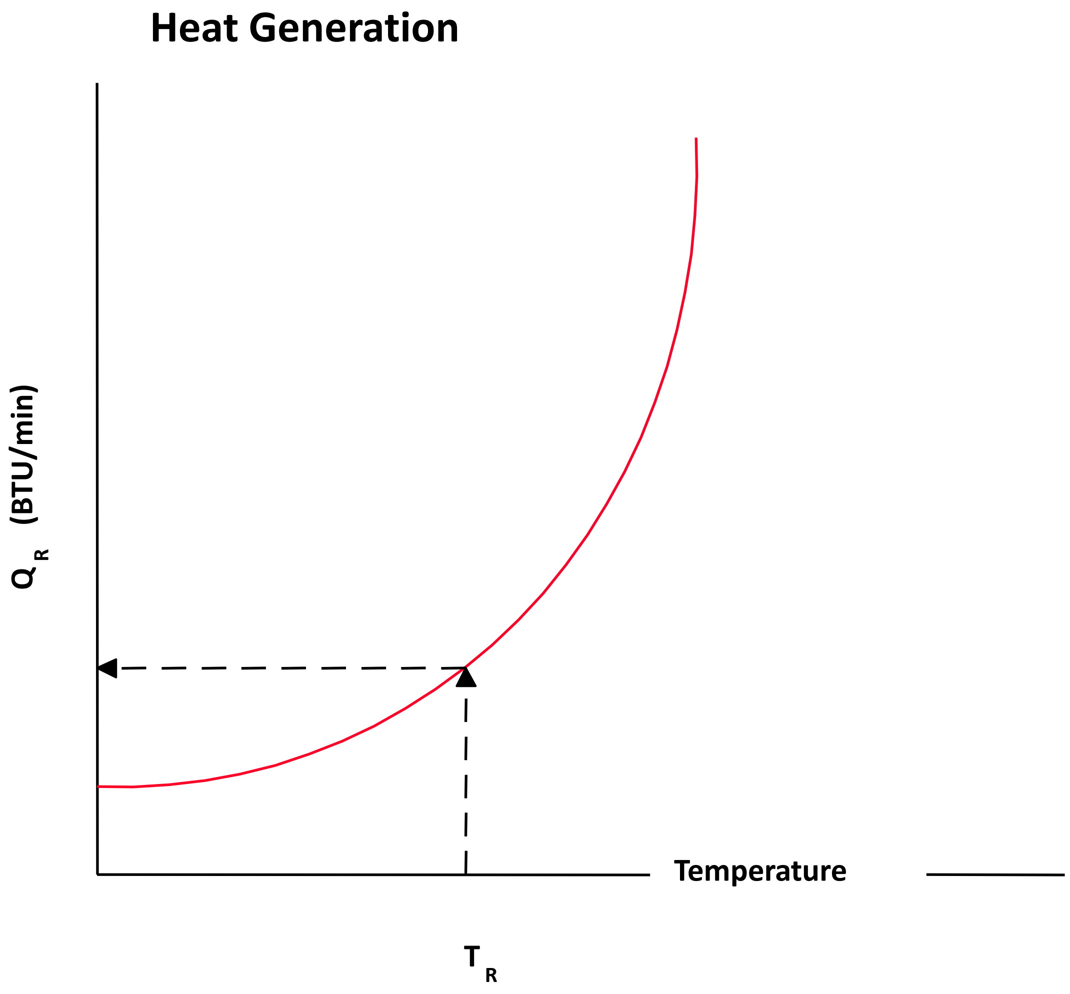
$$Q_R = -\Delta H_{rxn} \cdot C \cdot V \cdot A_r \cdot e^{-\frac{E}{R \cdot T_R}}$$

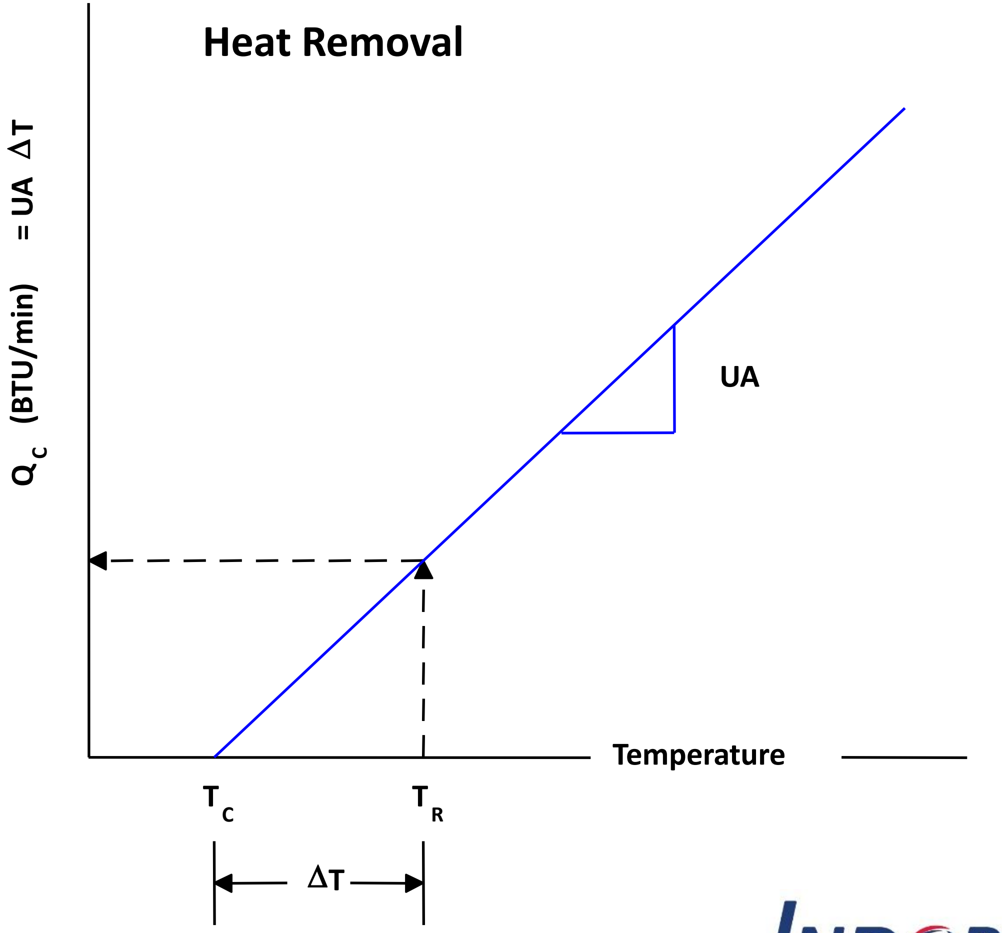
Heat generation rate: an <u>exponential</u> function of reaction temperature $T_R$

$$Q_C = U \cdot A \cdot (T_R - T_C)$$

Heat removal rate: a <u>linear</u> function of $\Delta T = T_R - T_C$

# Introduction to the Semenov Diagram
## *Heat Flow vs. Temperature Plots*

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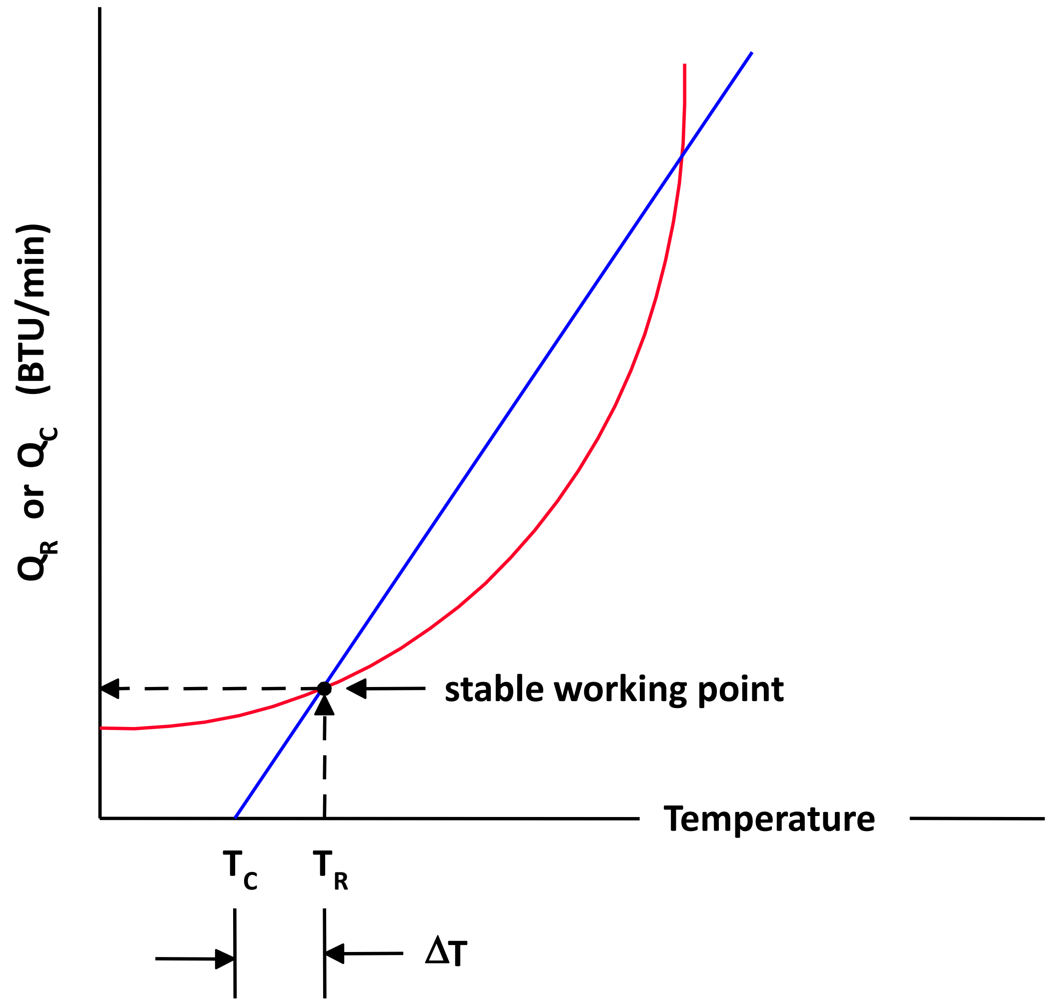
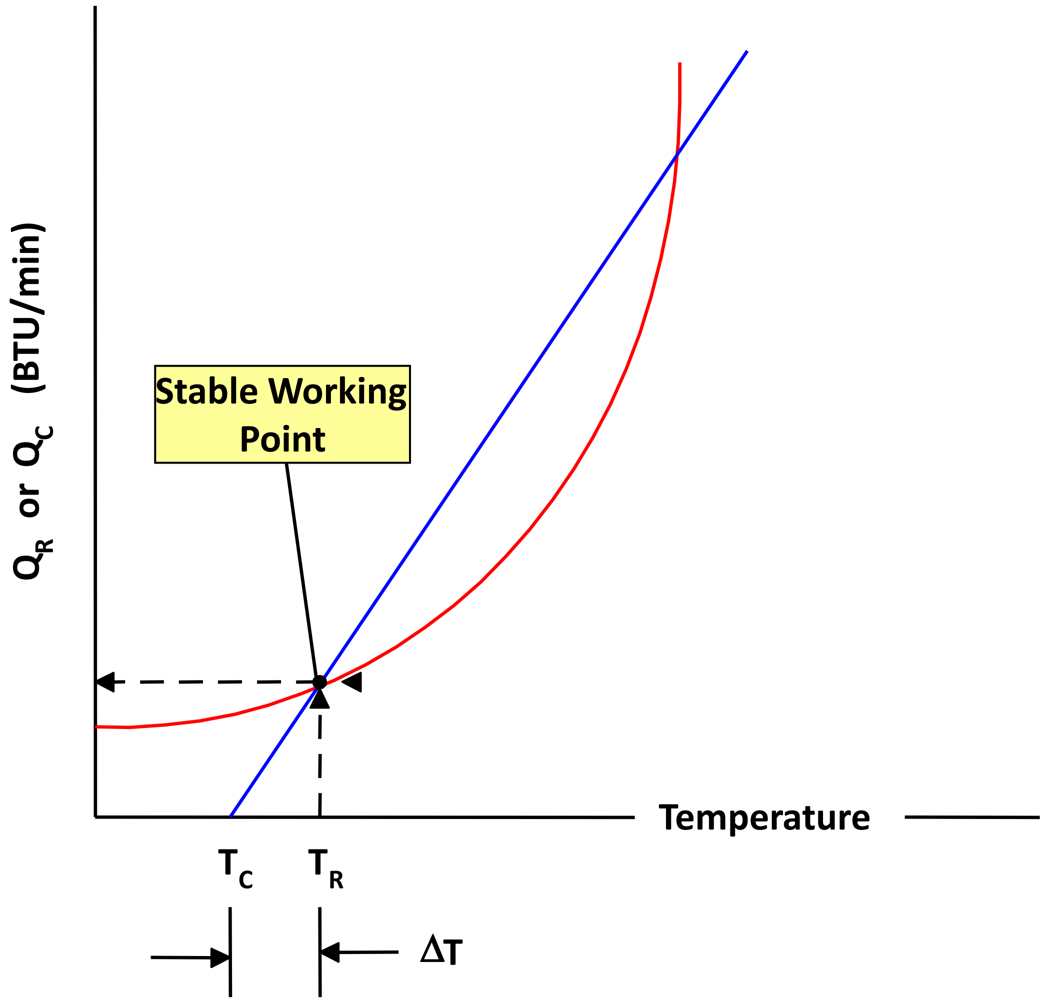
# The Semenov Diagram
# A picture of system stability



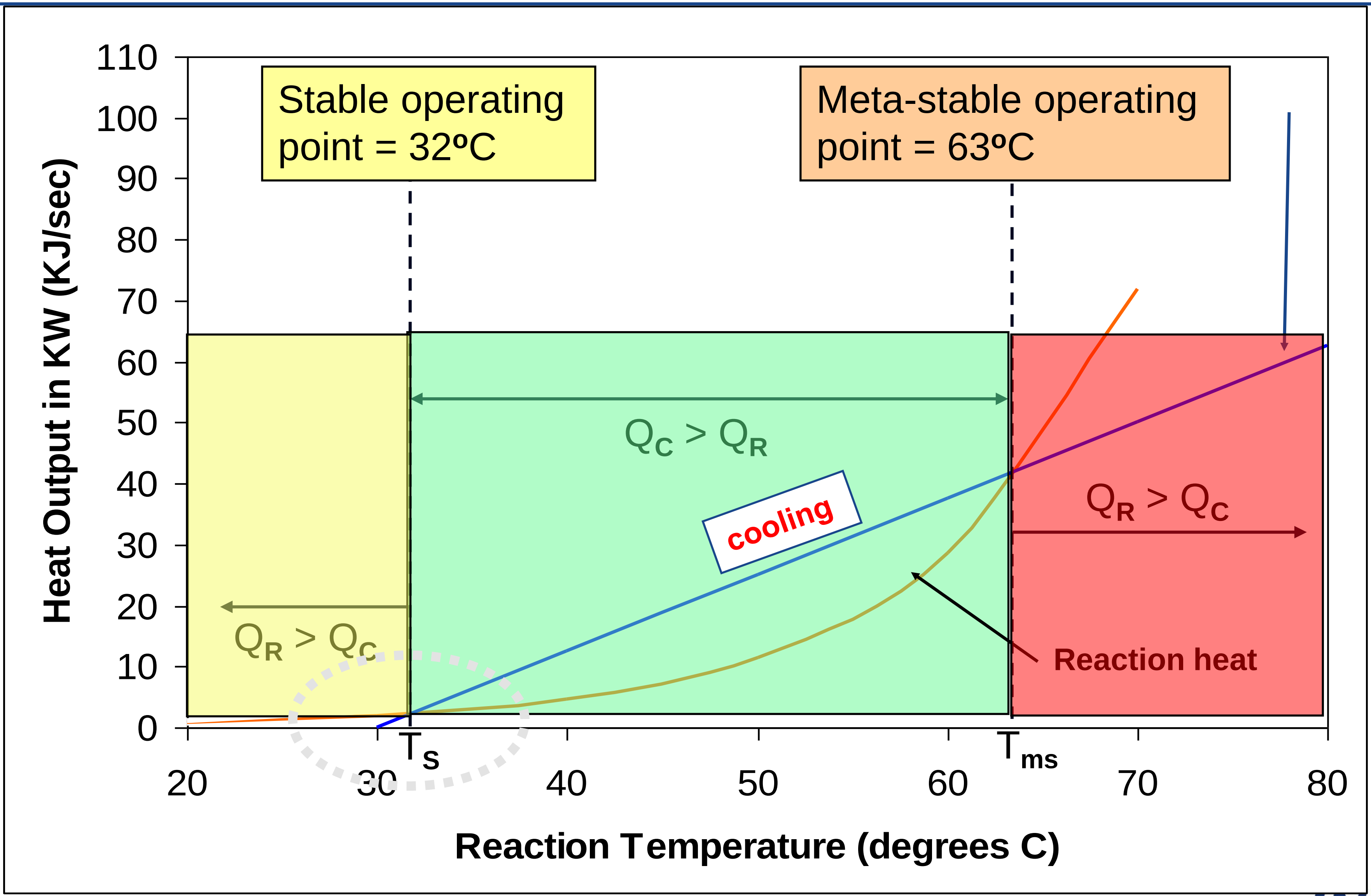

***Combining the two heat flow plots yields the "Semenov Diagram"***

# The Semenov Diagram
# Why is this Point Stable?

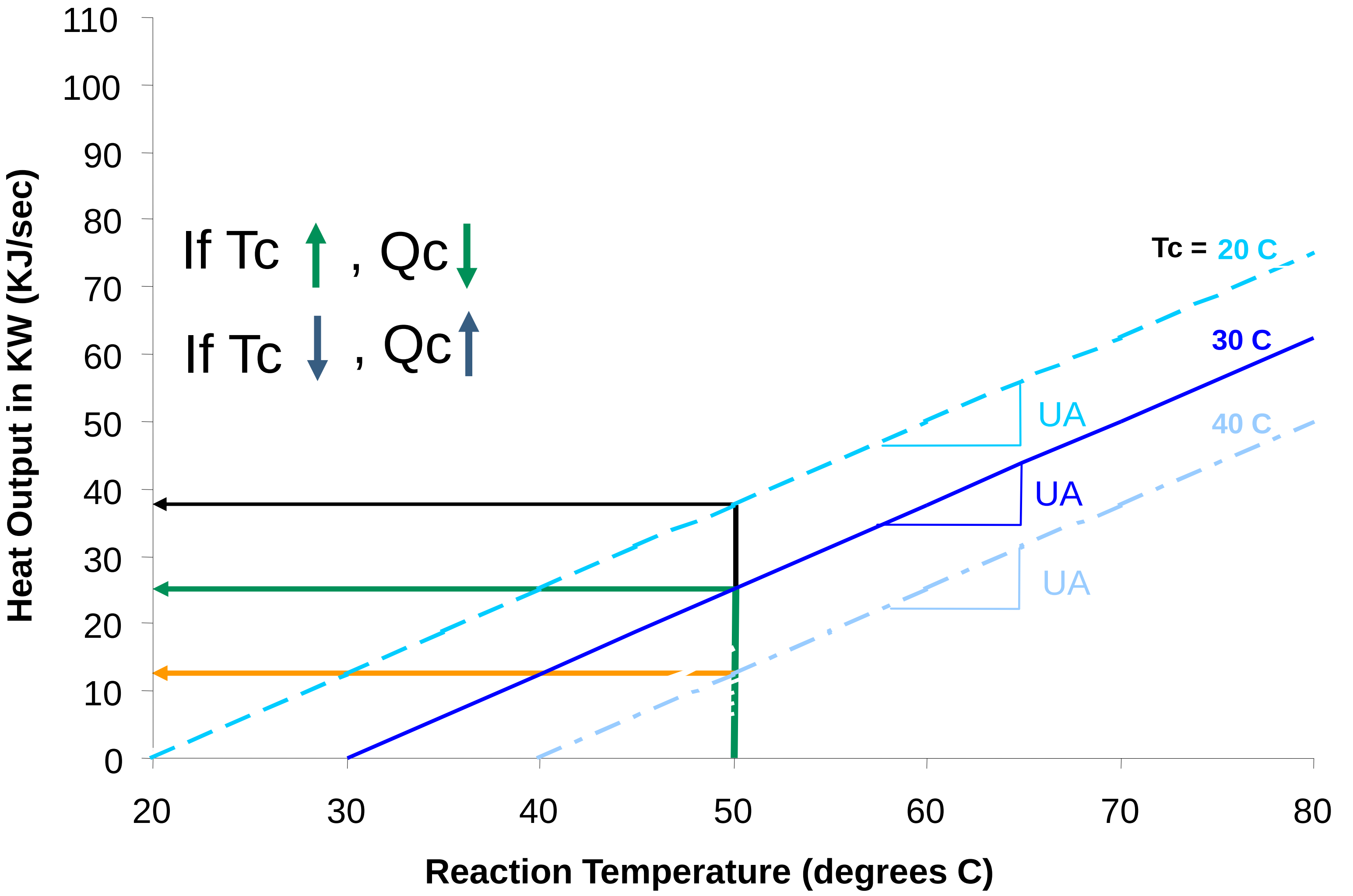



- The energy flows are ________________.
- The temperature is ___________________.

# The Semenov Diagram



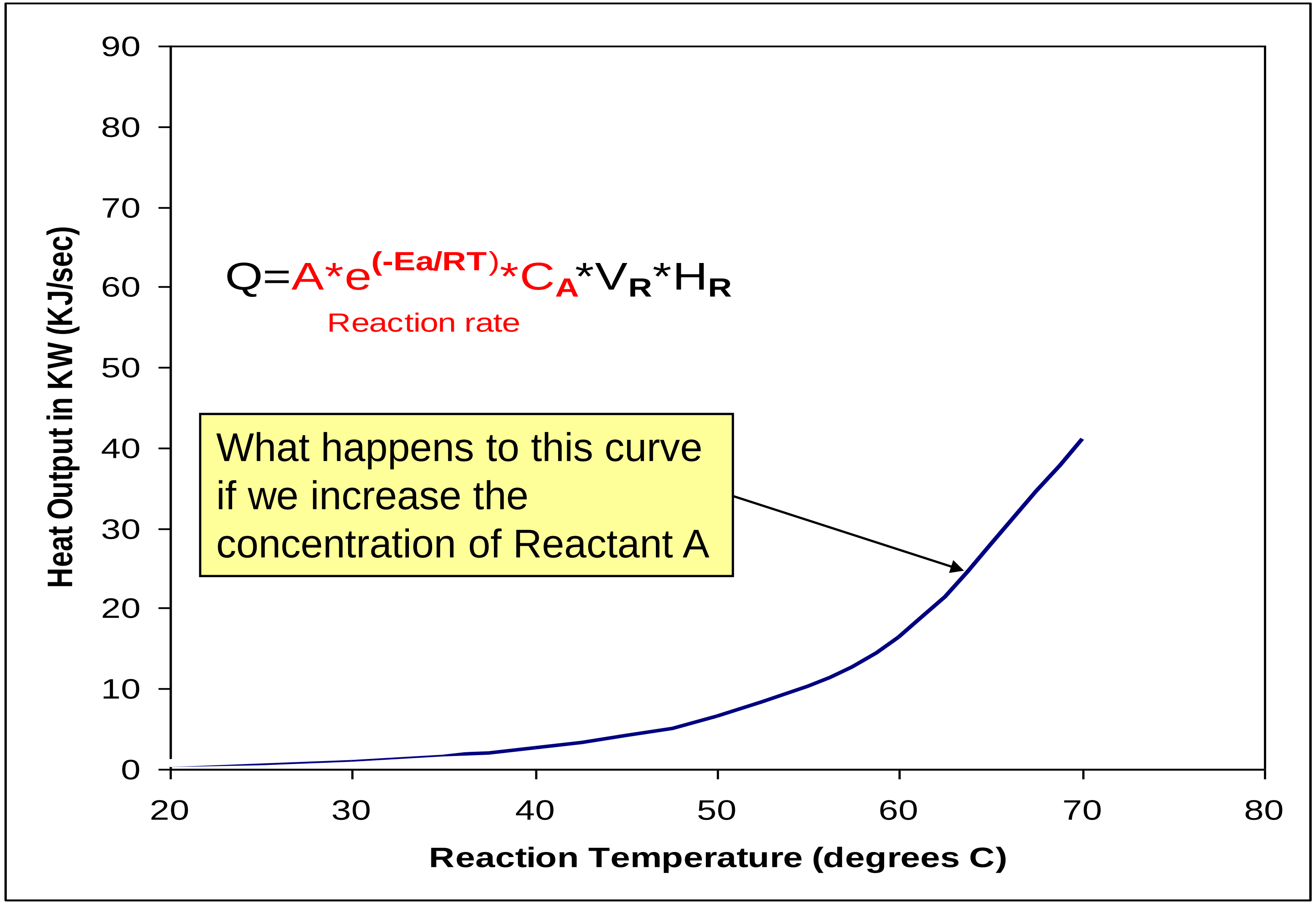
# Cooling System Capacity as a function of Coolant Temperature



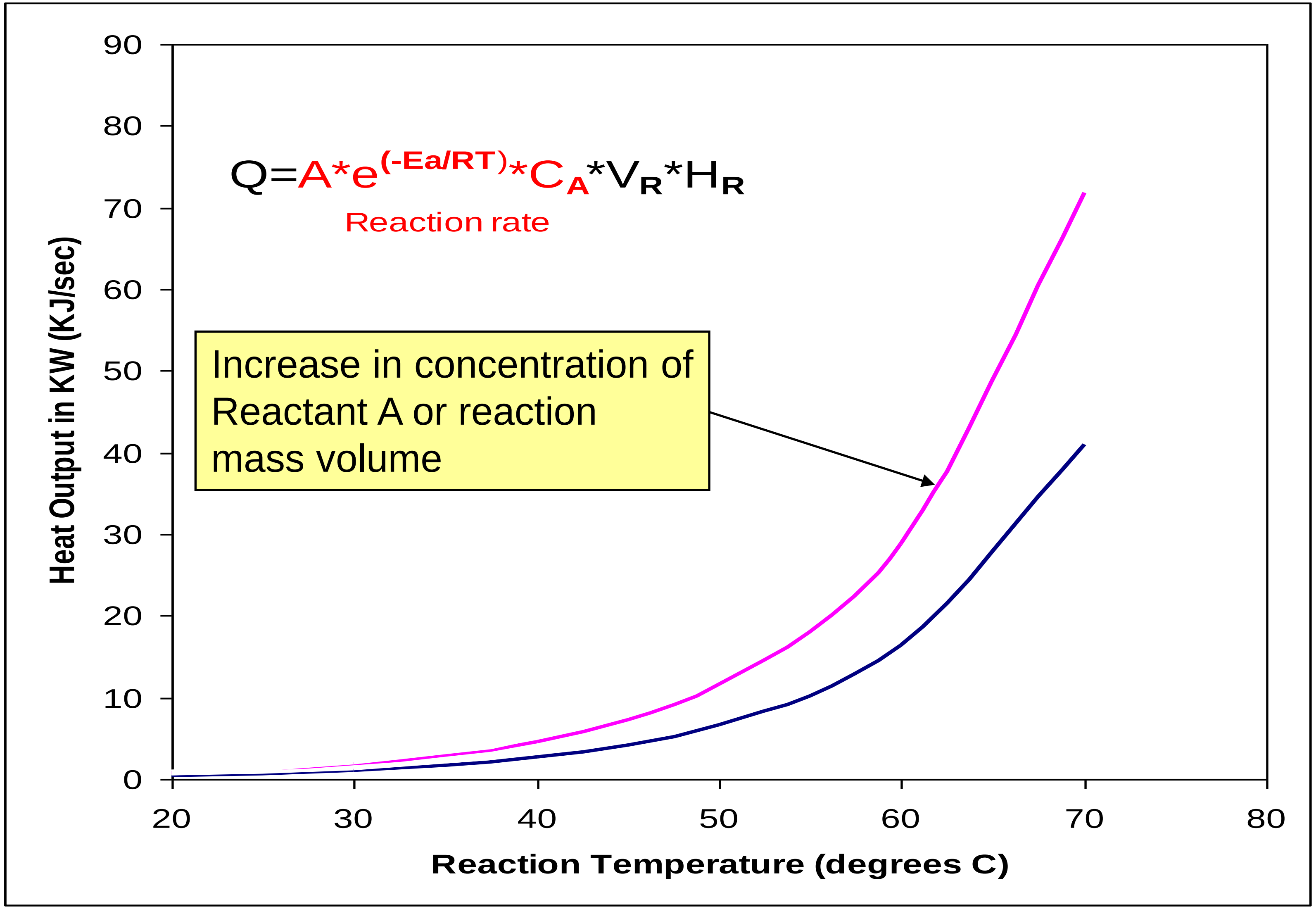

$$Q_C = U \cdot A \cdot (T_R - T_C)$$

**Heat removal rate: a <u>linear</u> function of $\Delta T = T_R - T_C$**

# Reaction Heat Generation

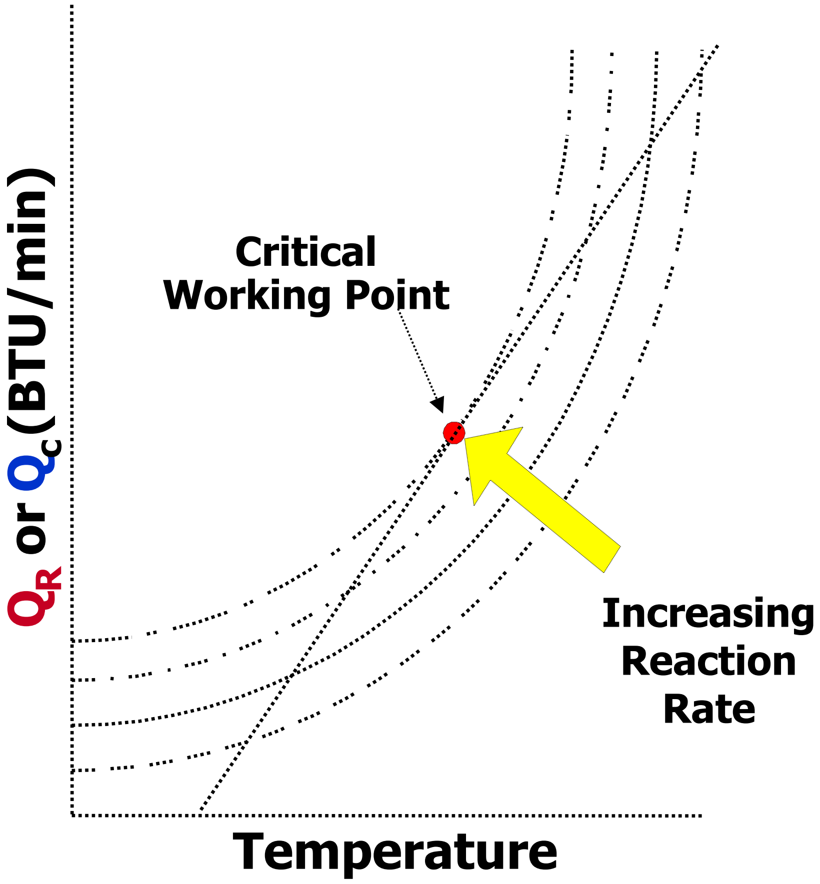


# Reaction Heat Generation



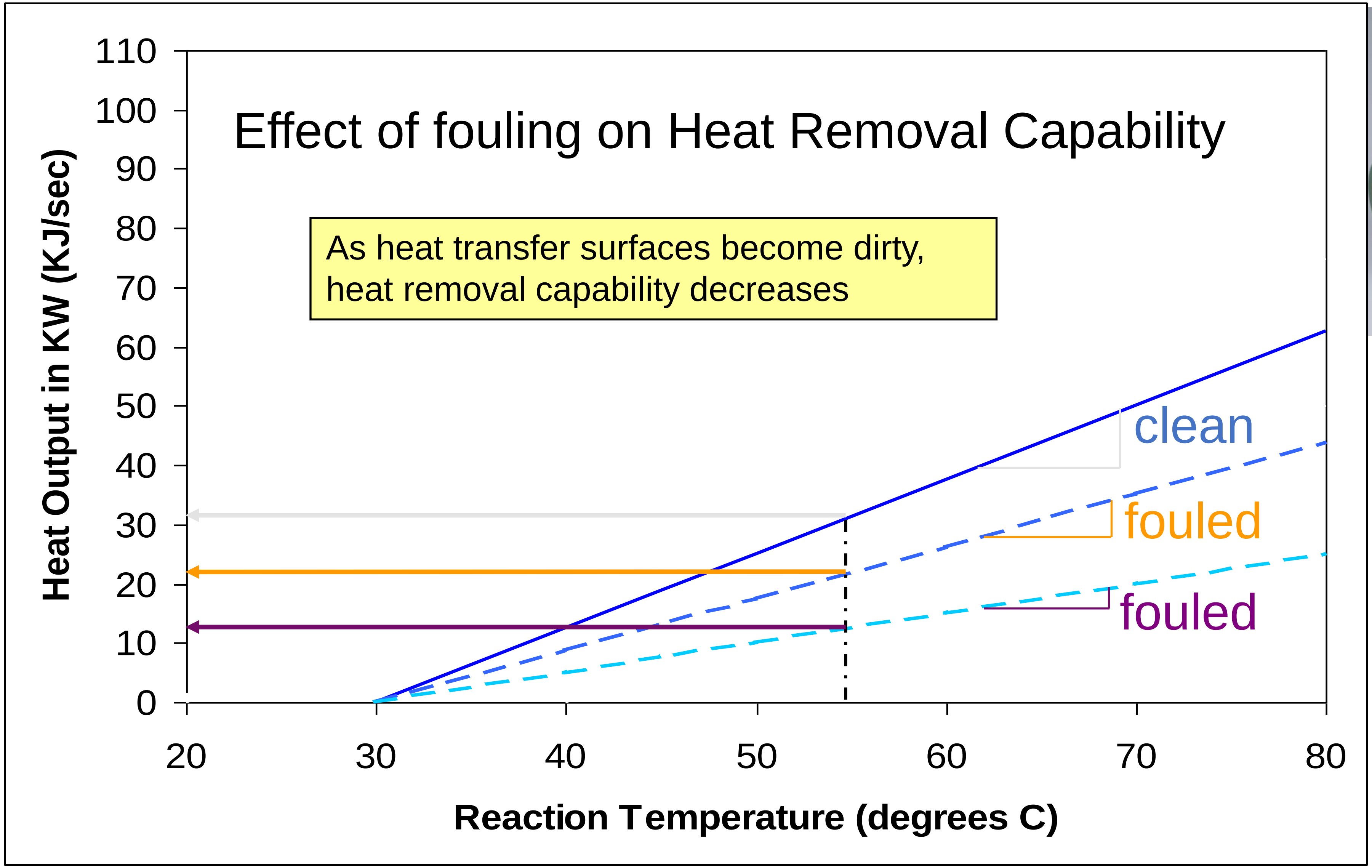
# Semenov Diagram –
# Effects of Increased Heat of Reaction

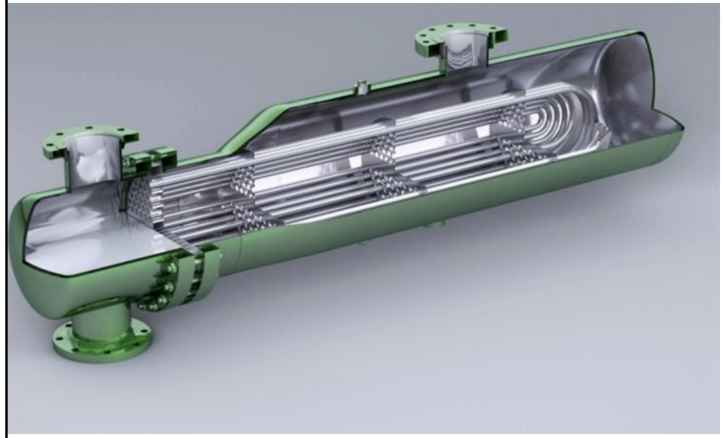
Typical Causes of approaching the Critical Working Point




- Reactant concentration too high
- Reactant feed rate too high
- Wrong catalyst or excess catalyst
- Charging error (wrong material, wrong sequence….)
- Secondary reactions
- …

# Shell & Tube Heat Exchangers
# Effects of Fouling



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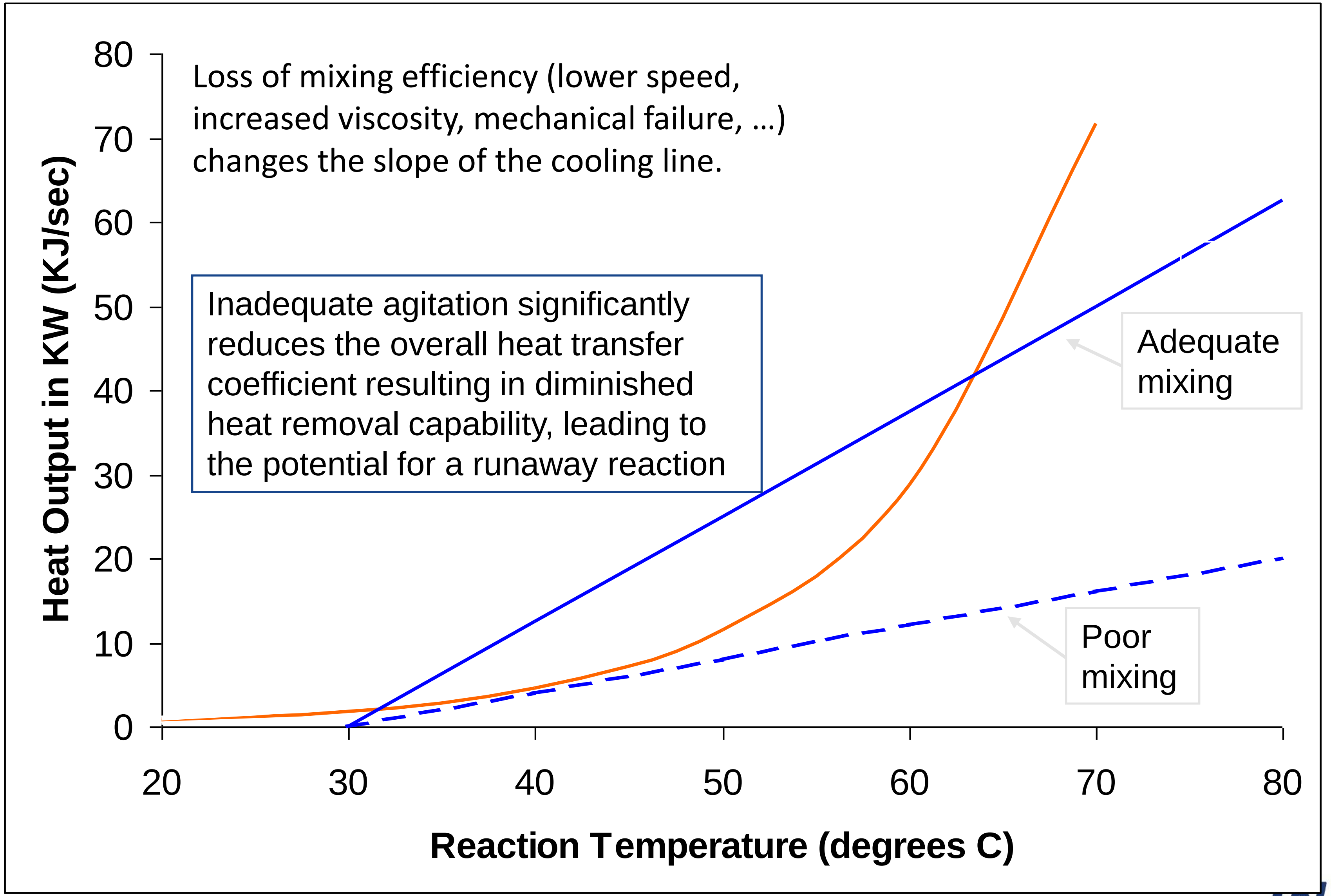
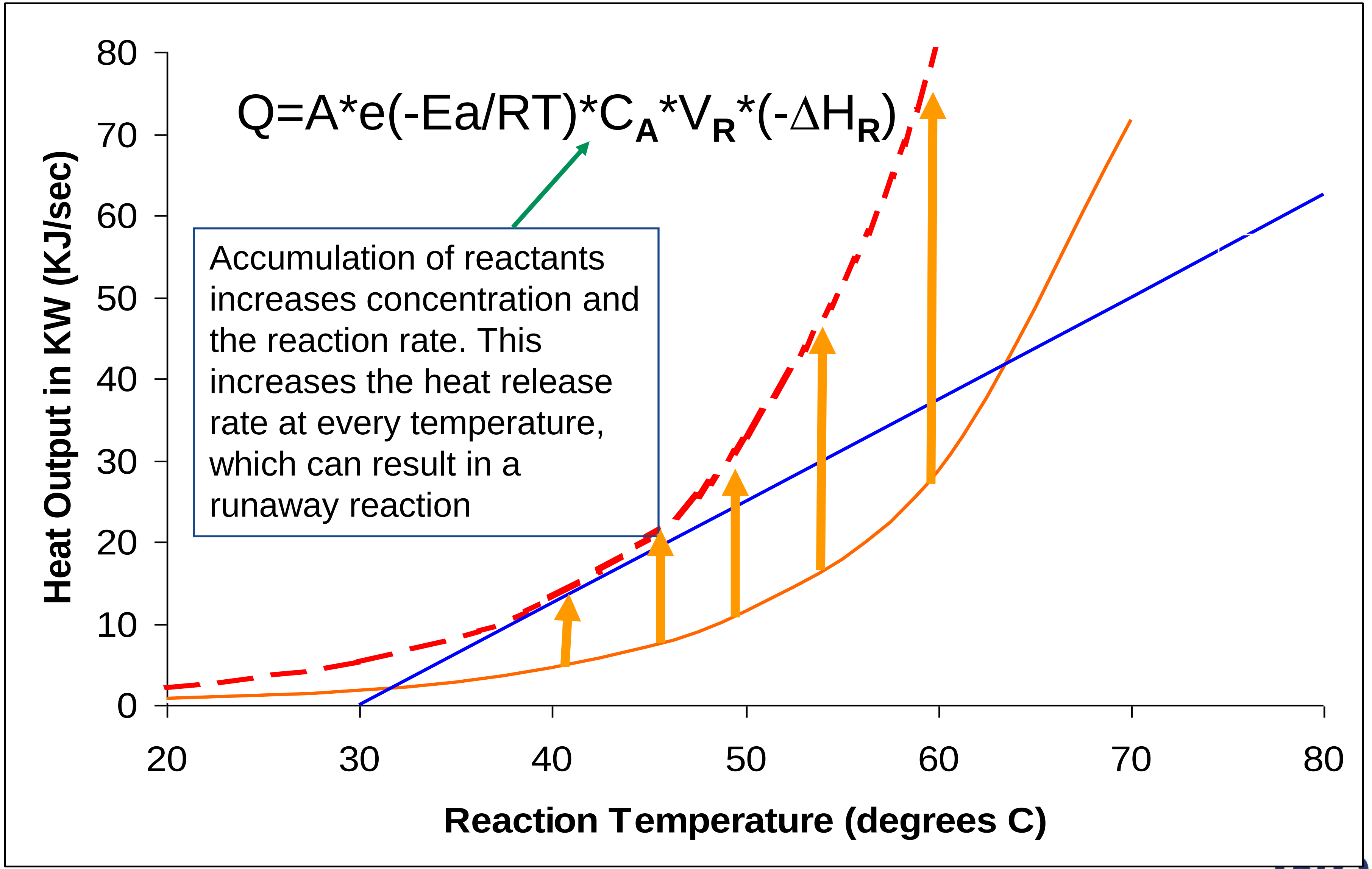
# Runaway Reaction because of Installing an Unsuitable Agitator



# Effects of Accumulating a Reactant



# Knowledge Check

The Semenov Diagram is an illustration of the Reactor Stability

It combines the plots of Heat Generation and Heat Removal

Stable working point is where the heat generation equals the heat removal with no net gain

As temp of coolant decreases, heat transfer increases.

As fouling increases, heat transfer decreases, temp increases

Loss of agitation decreases heat transfer, increases reactor temp

Increasing the concentration of Reactant A increases the reaction rate

Increasing the reaction rate with constant cooling capacity increases temp

**Increasing temperature has potential for runaway reaction!**

# Section 6 – Evaluating the Hazards of Exothermic Reactions

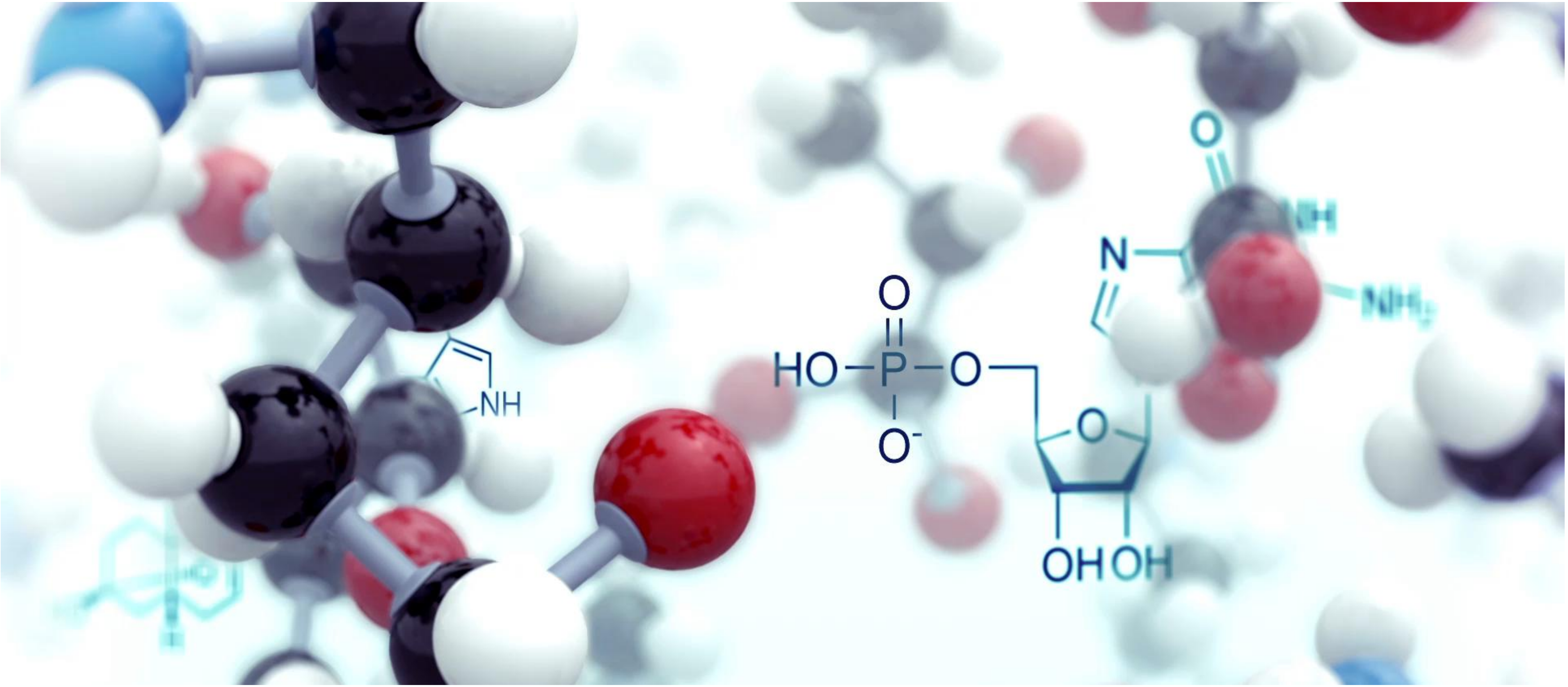
# Module 9: Training Objectives – Section 6

**Evaluating the Hazards of Exothermic Reactions**

**Learn the process for identifying reaction hazards**

**Discuss ‘rules’ for establishing safe operating margins and process safety times**

# Consider a Reactive Chemical Hazards Pre-screen Prior to the PHA



# Evaluating Upsets

## Potential Deviations in Chemical Processes

- **Product changes -** **contamination w/ catalytic effects, inhibitors, increasing/ decreasing concentration, byproducts**
- **Loss of component(s) -** **solvent missing, solvent recovery, initiator**
- **Charging failure -** **wrong material, wrong sequence, wrong ratio, wrong rate of charging**
- **Reaction conditions -** **pH deviations, pressure, temperature, residence time**
- **Mixing loss -** **equipment failure, separation of solids / catalysts, loss of energy transfer**

# Evaluating Upsets

## Potential Deviations in Technical Plant Operation

- **Heating / cooling -** exceeding or not meeting temperatures needed for safe operation, loss of...
- **Interruption of a material stream -** wrong material used, pumping loss, control loss (valve / transmitter / controller)
- **Agitation -** loss of, energy input (mechanical) due to higher viscosity, change in rotation speed or direction
- **Level -** overfilling, release from bottom outlet, backflow to another plant section
- **Materials of construction**
- **Material contact to / from heat transfer system**
- **Loss of utilities (including total loss)**

# Loss of Cooling Upset

## Causes:

Loss of booster pump

Loss of cooling medium

Loss of agitation / reduced mixing performance

Fouling

Reduction in active exchange area

## Or Increase in Heat Generation Due to:

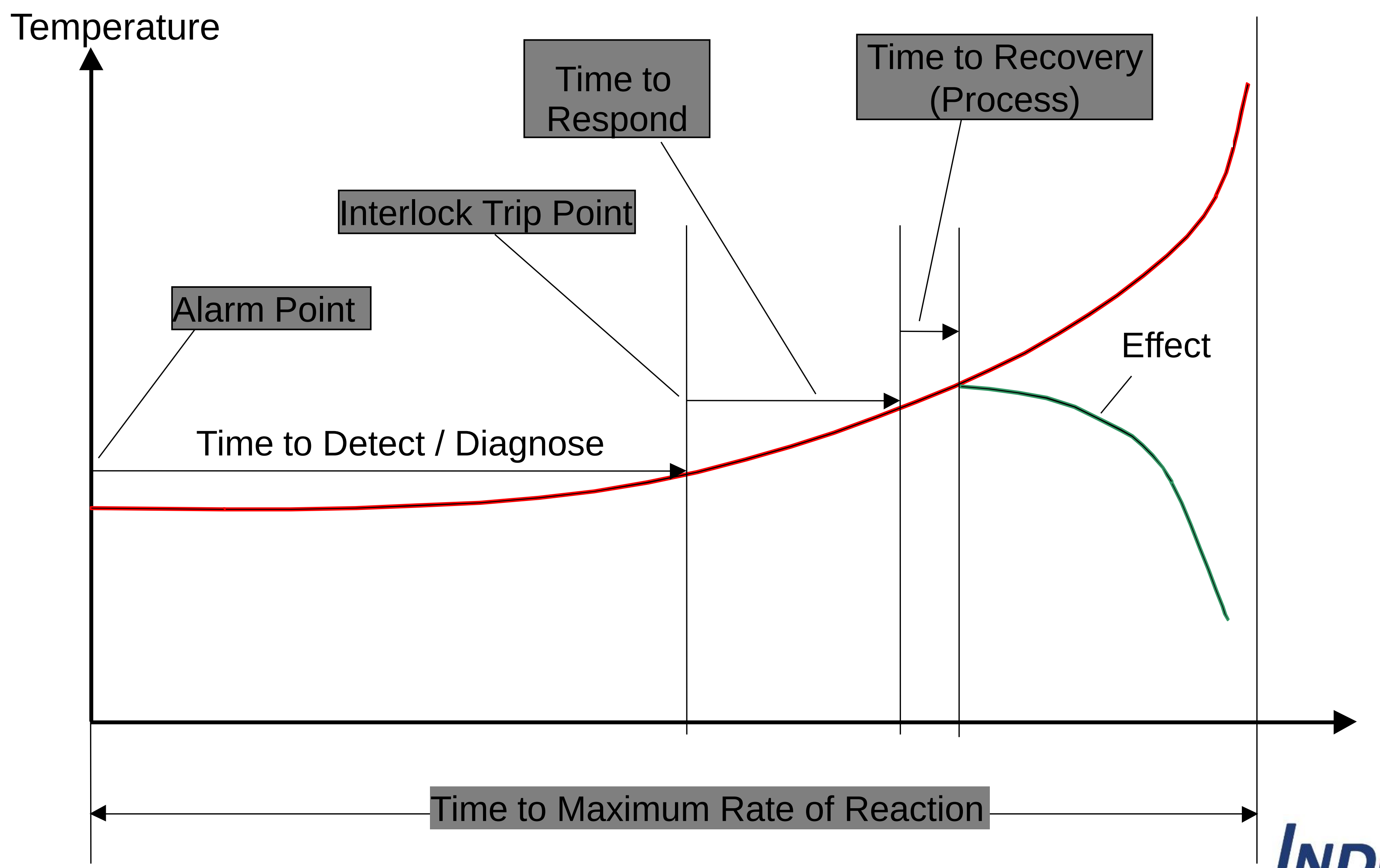
Late addition of forgotten catalyst

Feed control failure

Addition of wrong chemical

**Loss of temperature control is the MOST critical case!**

# Process Response Time



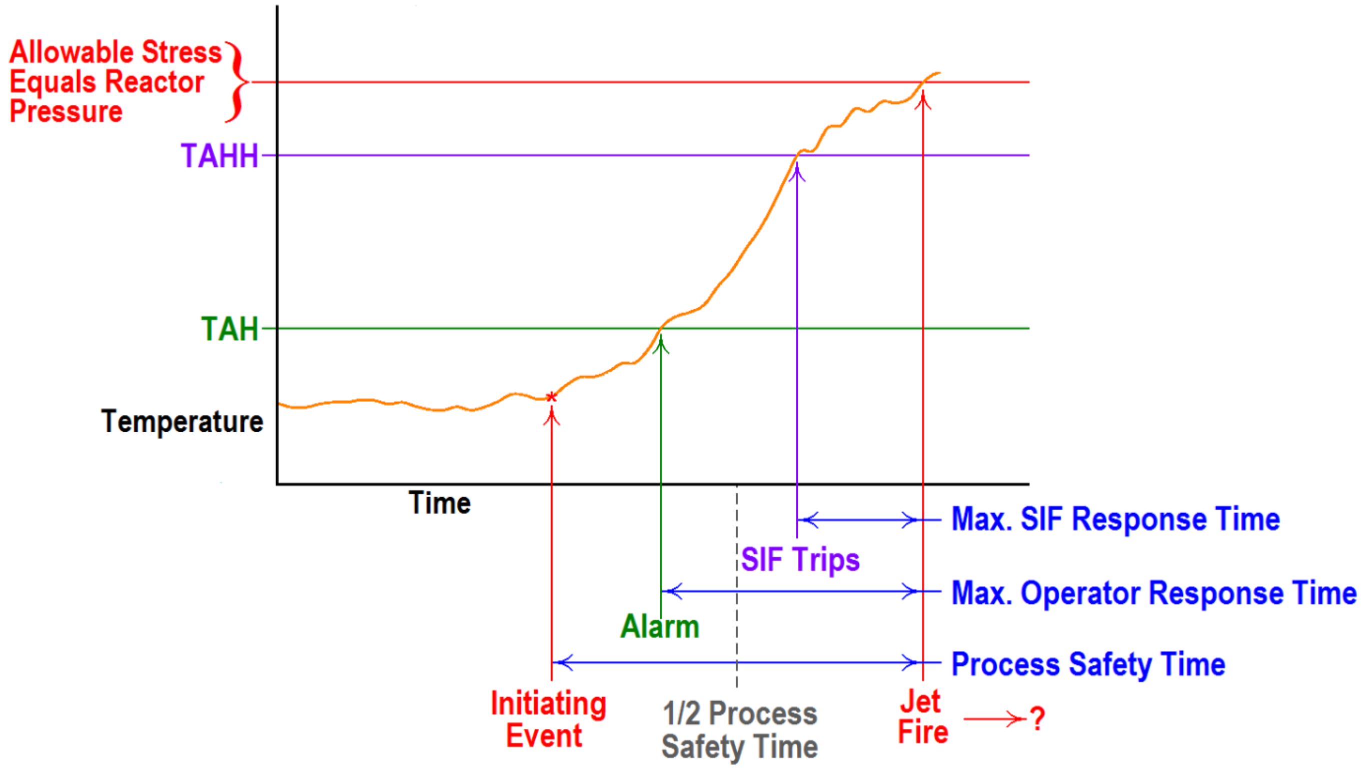
# Process Safety Time & Response Time

## Process Safety Time (PST)

- Starts when Initiating Event occurs
- Stop when the Consequence cannot be averted

## SIF Response Time

- Starts when Process condition meets Trip Threshold
- Stops when the SIF has achieved the Safe State




**Loss of Containment**

# Knowledge Check

**There are abnormal chemical processing events that can result in a runaway reaction**

**There are abnormal technical plant operations and equipment failures that can result in a runaway reaction**

**Loss of cooling and temperature control is typically the MOST critical event!**

**Defining the process safety time of an event provides:**

- Maximum Operator Response Time to an Alarm
- Maximum Instrumented Trip Response Time  (BPCS/SIS)
- Safety Basis for the Alarm and Trip Setpoints

# Section 7 – Controlling Reactive Chemistry Hazards

# Module 9: Training Objectives – Section 7

Controlling Reactive Chemical Hazards

Managing Chemical Storage Reactions

Managing Batch Reactions

Managing Continuous Reactions

PHA Pitfalls of Chemical Reactivity Analysis

# Chemical Storage Reactions

**Physical and Chemical properties from SDS and HS1**

**Incompatibilities (e.g., acids, bases, oxidizers) and Water Reactivity**

**Self-heating properties (Differential Scanning Calorimeter to check)**

**Inhibitors for reactive monomers**

**Turnover time – shelf life, storage temperatures**

**Inerting of vapor space to keep oxygen from forming peroxides or other potentially hazardous contaminates**

**Tanks venting into a common vent system have contamination potential that must be evaluated**

# Chemical Storage Controls

Inherently safer design of unloading station locations and fittings

Inherently safer design – Materials of Construction

Specifications and Manifesting

Temperature monitoring prior to unloading and in storage

Dedicated Railcar Service and Cleaning Procedures

Nitrogen Pad and Transfer

Refrigeration

Cavitated and Deadheaded Pump Trips

Pressure and Temperature Sensing, Alarms and Trips on Storage Tanks

High Level trip of tank vent valves to Caustic Scrubbers

# Batch Reactions

**Attachment G of IVL EHSG-403-04 addresses the Chemical and Thermal Risk Assessments and the Thermal Safety of Bulk Materials**

**Most commercial batch reactions are exothermic**

**Reactor cooling systems must be able to dissipate the heat for normal and abnormal situations produced in the reactor**

- Alkoxylation Reactors - Loss of cooling is a credible worst-case scenario

**Experienced chemists from process development within the business should be utilized when evaluating the chemical and thermal hazards of reactor systems**

# Batch Reaction Controls

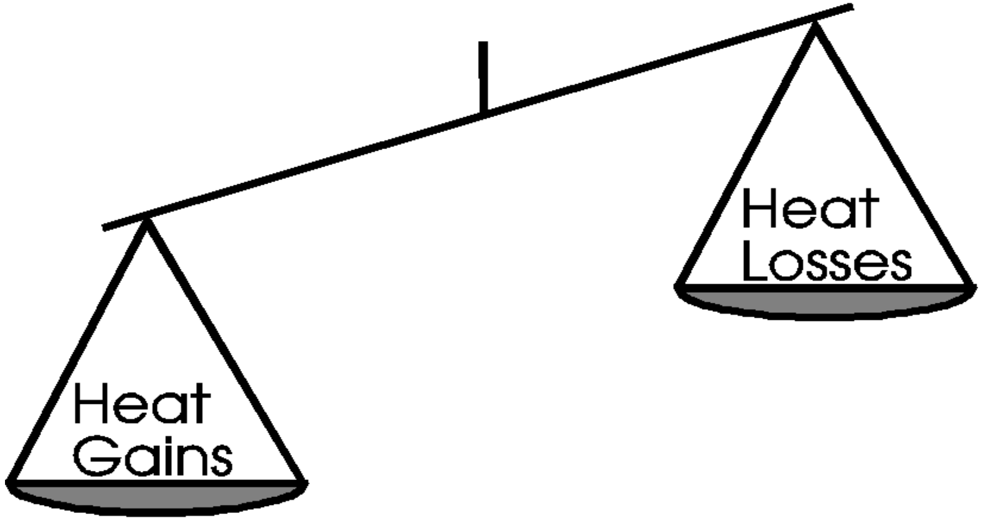
Feed Permissive on Valve Line Ups
Pmax Reactor Dosing Trip (Control below decomp range in vapors)
Test Charge on Alkoxylation Reactions
High/Low Temperature Safety Interlocks
High Pressure Safety Interlocks
Loss of Cooling Safety Interlocks
Loss of Agitation Safety Interlocks
Hot Agitator Bearing Safety Interlocks
Loss of EO Header Pressure Trip of Feed Valve
Purge Pocket Design
Pump Deadhead and Cavitation Safety Interlocks

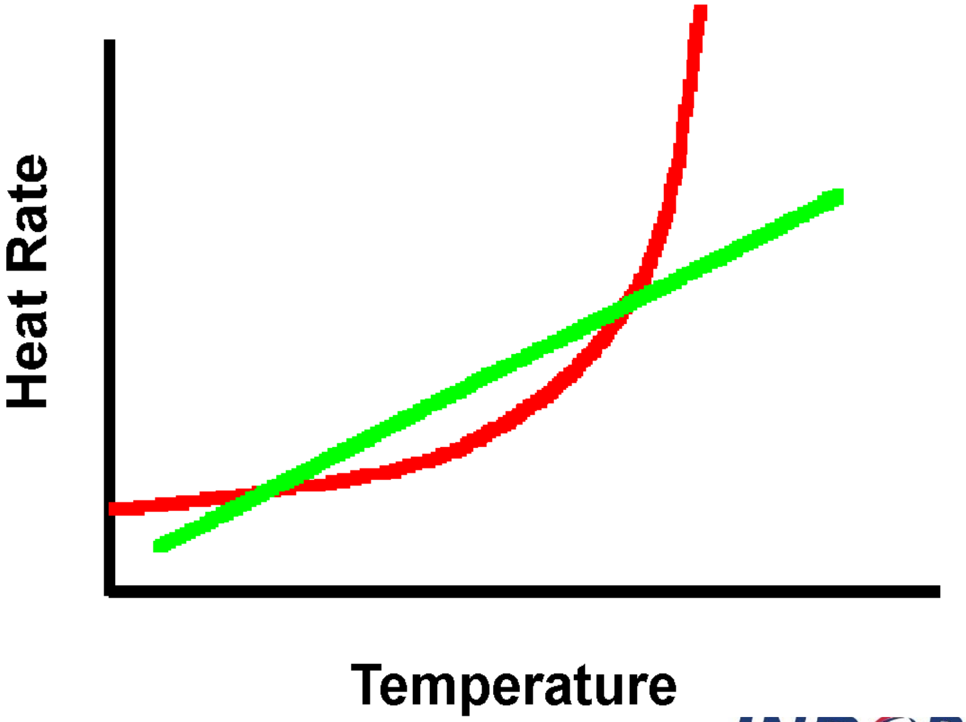
# Continuous Reaction Processes

**Define Heat Gains**

**Define Heat Losses**

**Put these together to define operating windows for scale up & plant operations**



# Controls for Continuous Reactive Processes

Oxygen Concentration Monitoring and Safety Interlocks

Temperature and Pressure Safety Interlocks

TBA Concentration Monitoring and Safety Interlocks

High Level Safety Interlocks

Pump Deadhead and Cavitation Safety Interlocks

Sampling and Water Analysis Procedures

# PHA Pitfalls of Chemical Reactivity Analysis

Lack of understanding chemical kinetics and thermodynamics

Inadequate process design

Problems with procedures

Misconceptions about chemical reactivity ratings

Insufficient consideration of chemicals with low reactivity ratings

Incomplete safety data sheets (SDSs)

Incomplete list of sources of chemical reactivity hazards

Neglecting chemical reactivity hazards that develop over time

Misunderstanding the importance of runaway reactions

**Complete a Chemical Reactivity Hazard Screening prior to the PHA.**

# Questions/Comments