



CREATING GROWTH, ENHANCING LIVES



**Technical Process Safety Seminar – Singapore**  
**Applying Functional Safety and Reaction Safety for Safety Cases**

# **Chemical Reaction Safety Workshop**

Shaik Salim/Paul Sharratt

19 Aug 2019



# Chemical Reaction Safety Workshop



## Introduction:

Seveso: Reaction Safety 3

Fundamentals of Chemical Reaction Safety 8

## Chemical Reaction Risk Assessment:

Chemical Hazard Evaluation 19

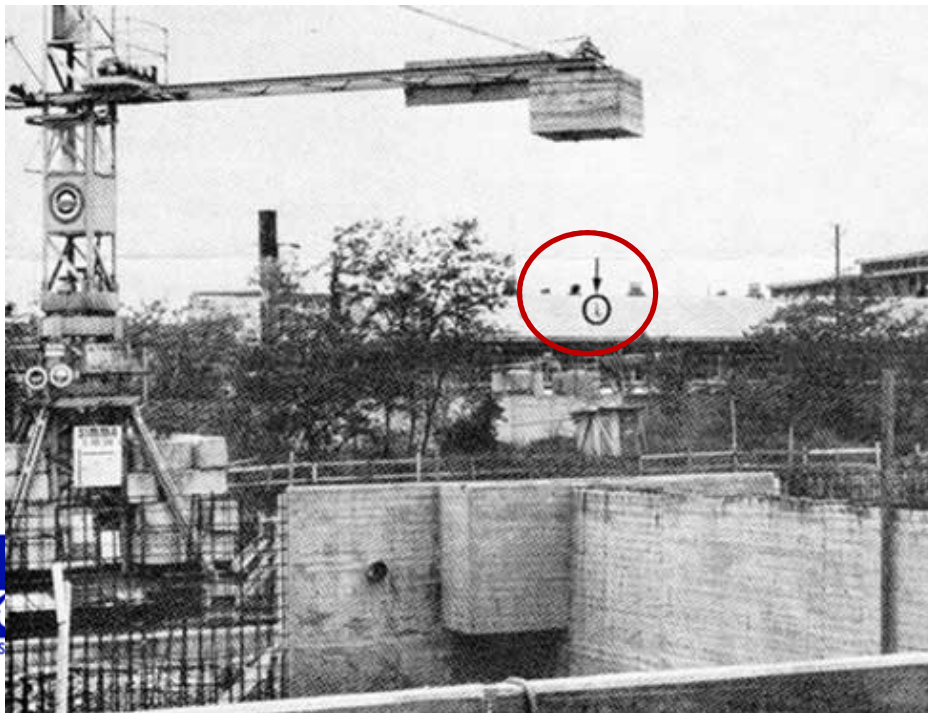
Desktop Screening 23

Experimental Techniques & Stoessel  
Criticality Class 36



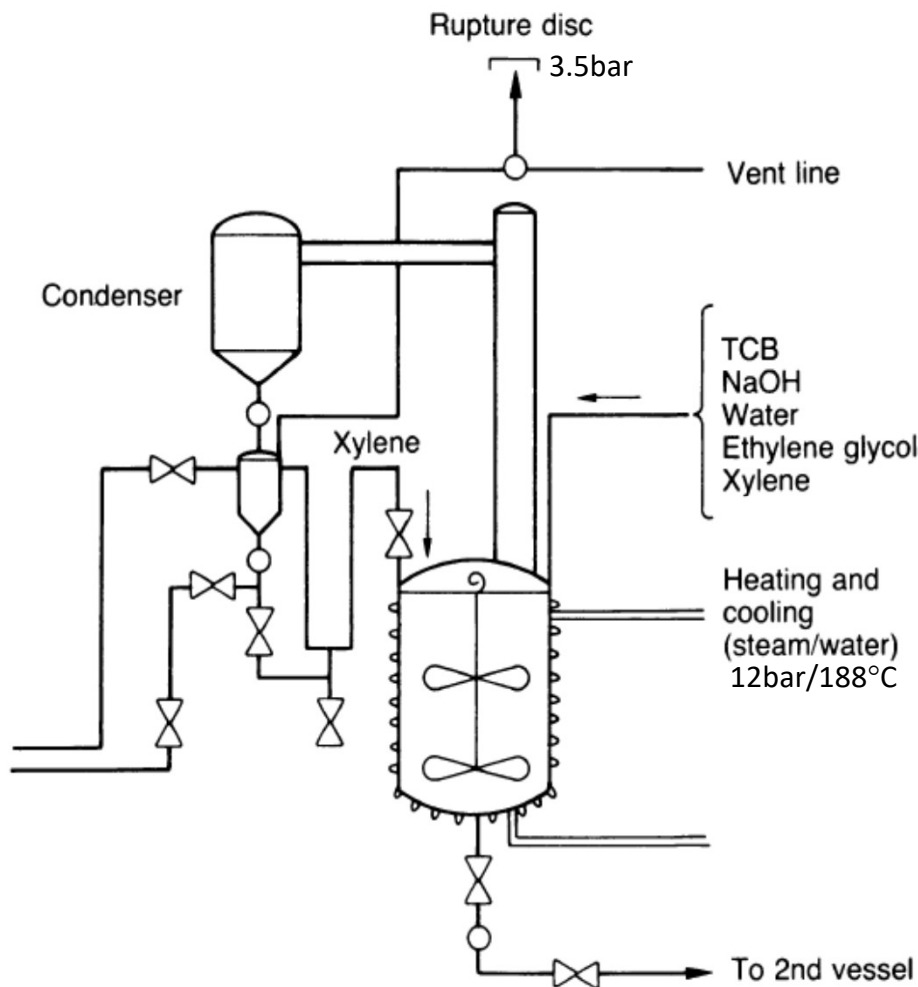
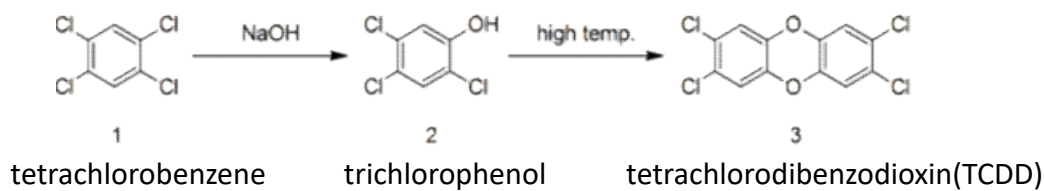
# Seveso: Toxic release

- Saturday 9 July 1976 a bursting disc ruptured on a chemical reactor at the works of the Icmesa Chemical Company at Meda near Seveso
- The start of the batch began at 16.00 on Friday 9 July. The batch process was interrupted prior to finishing the final step of removal of ethylene glycol by distillation, due to an Italian law requiring shutdown of plant operations over the weekend.
- This batch was stopped by isolating the steam, and turning off the stirrer.
- A runaway reaction occurred which led to the formation and release of tetrachlorodibenzodioxin (TCDD)
- A white cloud drifted from the works and some TCDD settled downwind.



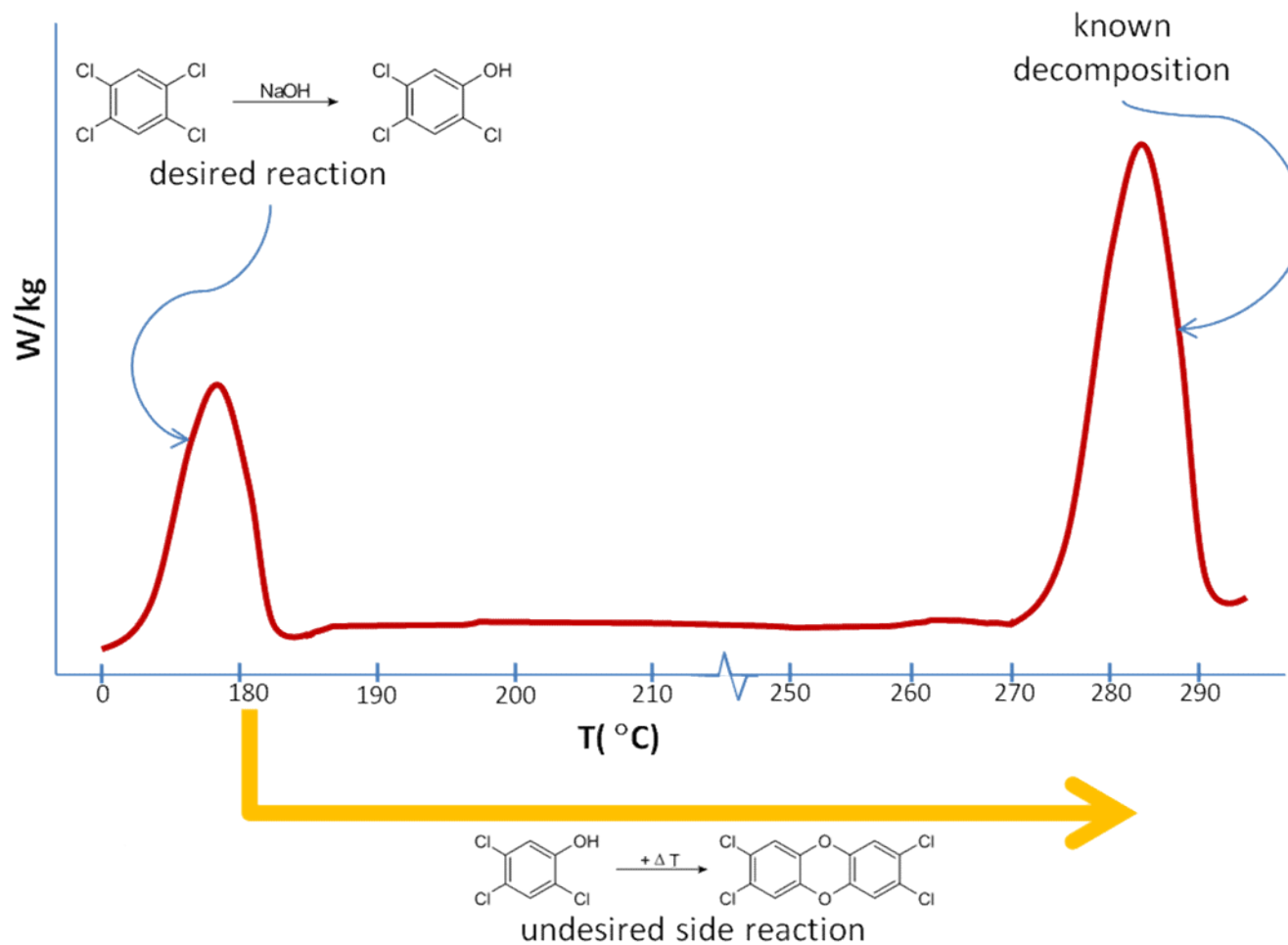
Icmesa chemical plant at Seveso, Italy. The vent pipe of the trichlorophenol reactor is shown ringed

# Seveso: The Process

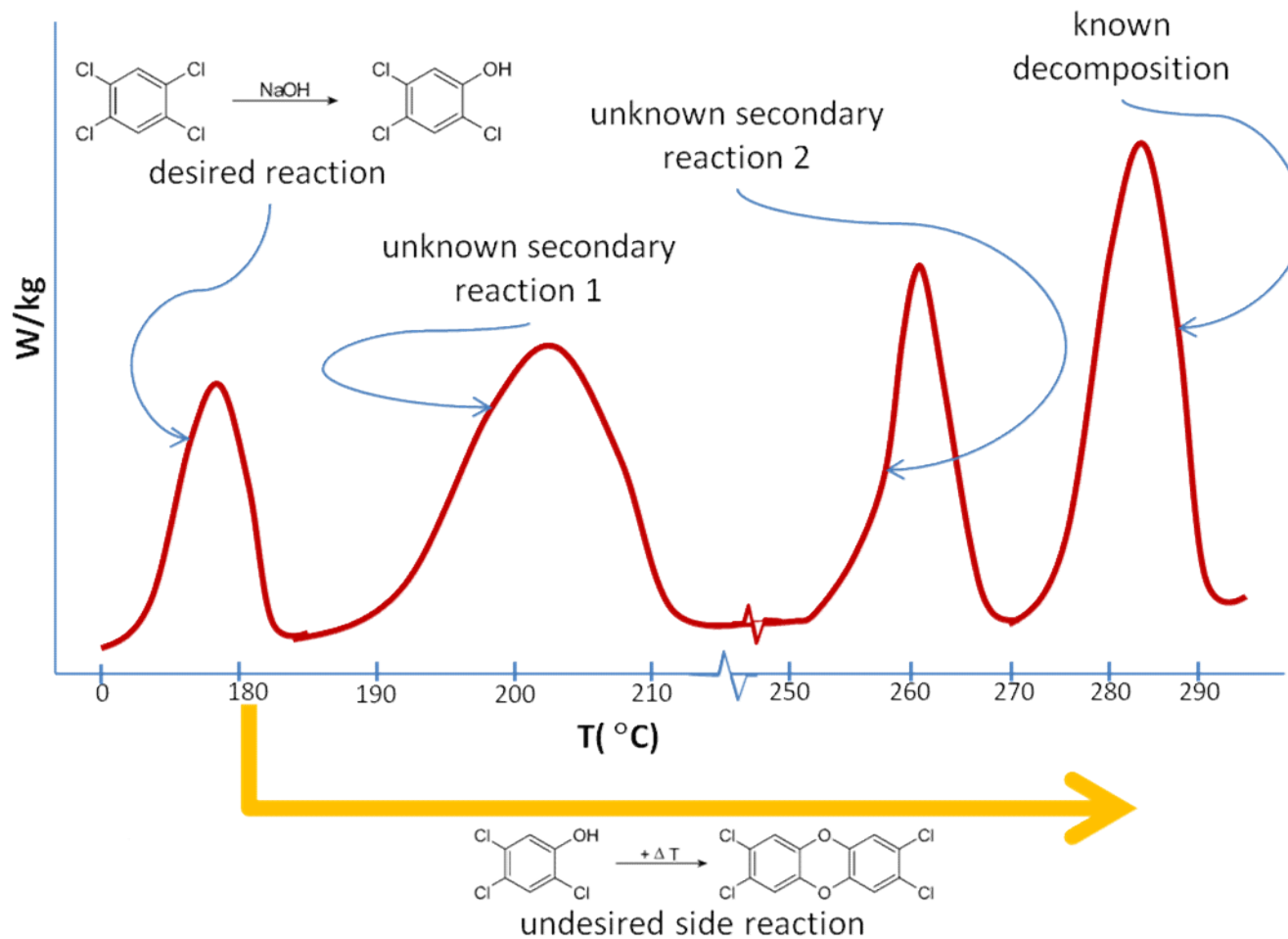


- the formation of small quantities of TCDD as a by-product is unavoidable. At a reaction temperature below 180°C the amount formed would be unlikely to exceed 1 ppm of TCP, but with prolonged heating in the temperature range 230±260°C it could increase a thousand-fold. The known decomposition exotherm starts at about 280°C
- There exists two (unknown) slow exotherms. One starts at about 185°C, the other starts at about 255°C
- The residual heat in the jacket then heated the upper layer of the mixture next to the wall to the critical temperature (ca. 180°C), starting a slow runaway decomposition, and after seven hours a rapid runaway reaction ensued when the temperature reached 230°C
- The relief valve eventually opened and 6 tonnes of material (1kg TCDD) were distributed over an area of 18 km<sup>2</sup>

# Seveso: Simulated Thermogram



# Seveso: Simulated Thermogram



# Seveso: Lessons

- Hazard of ultratoxic substances
- **Hazard of undetected exotherms**
- **Hazard of prolonged holding of reaction mass**
- **Inherently safer design of chemical processes**
- **Control and protection of chemical reactors**
- Adherence to operating procedures

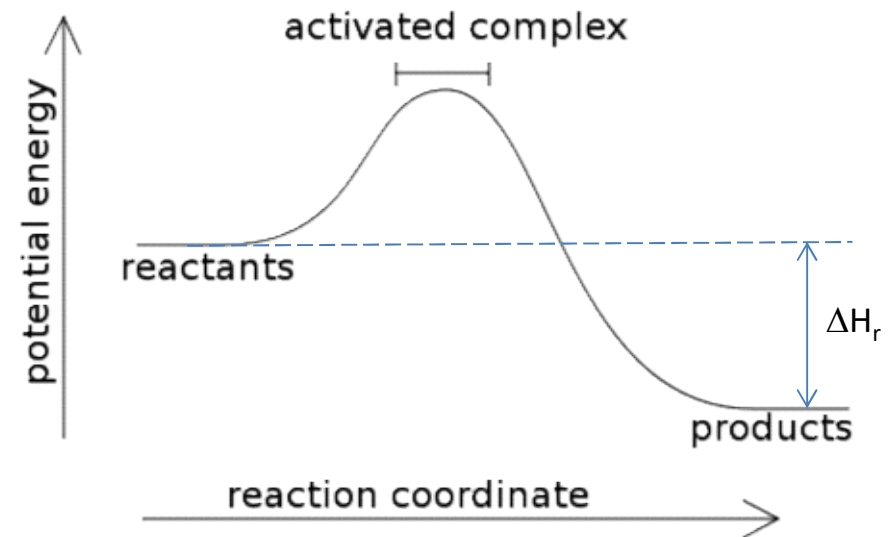
# Fundamentals of Chemical Reaction Safety





# Fundamentals of chemical reaction safety:

- When considering reaction hazards, temperature is rarely a hazard on its own. Overpressure due to temperature rise on the system is much more important. The three potential sources of overpressure are:



- **Gas Generation** from the normal process
- **Vapour pressure** effects as a consequence of heat on the normal process
- **Secondary reactions** at elevated temperature due to heat from the normal process causing gas and/or vapour effects

# Fundamentals of chemical reaction safety: Thermal Hazards

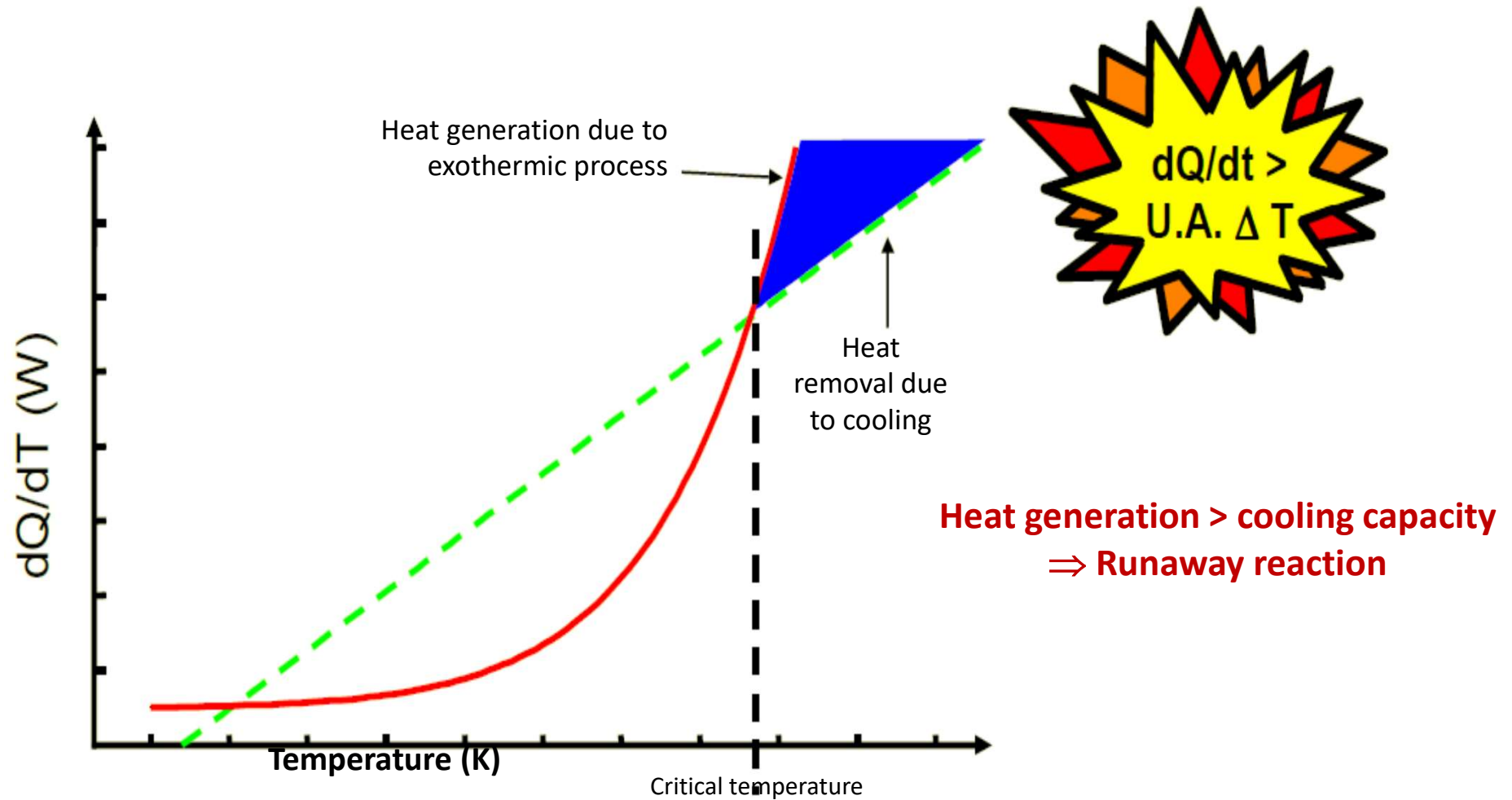
## Examples of exothermic reactions and their severity

Reaction Type	Severity	$\Delta H_r$ (cal/g)
Oxidation	Highly exothermic	>300
Nitration	Highly exothermic	>300
Halogenation	Highly exothermic	>300
Organometallics	Highly exothermic	>300
Diazotization	Highly exothermic	>300
Hydrogenation	Highly exothermic	>300
Thermal decomposition	Highly exothermic/Exothermic	100 to >300
Polymerization	Highly exothermic/Exothermic	100 to >300
Sulfonation	Exothermic/Moderately exothermic	20 to 300
Condensation	Exothermic/Moderately exothermic	20 to 300

Reaction Type	Severity	$\Delta H_r$ (cal/g)
Amination	Moderately exothermic	20 to 100
Esterification	Moderately exothermic	20 to 100
Methylation	Mildly exothermic	<20
Alkylation	Mildly exothermic	<20
Hydrolysis	Mildly exothermic	<20
Salt formation	Mildly exothermic	<20
Reduction	Slightly exothermic	<20
Electrolysis	Slightly exothermic	<20
Isomerization	Slightly exothermic	<20
Cyclization	Slightly exothermic	<20

# Fundamentals of chemical reaction safety: Thermal Hazards

## Thermal Runaway



# Fundamentals of chemical reaction safety: Thermal Hazards

## Thermal Runaway

### Desired Reaction → Heat of reaction

- Heat generation not a problem if vessel correctly designed and vented
- Safety systems will contain or allow controlled release of pressure

Beware assuming simple kinetics for:

- Autocatalytic reactions
- Heterogeneous reactions
  - Mass transfer may be rate determining
  - Phase transfer agents may dictate rate
- Complex reactions (multi steps/routes)

### Secondary Decompositions → Heat of decomposition

- May be initiated at high temperatures
- If not considered during vessel design may cause overpressurisation

Rapid, simple screening methods can determine severity & likelihood of problem

# Fundamentals of chemical reaction safety: Thermal Hazards

## Adiabatic temperature rise

- When a reactive system cannot exchange energy with its surroundings, adiabatic conditions prevail.
- All energy released by the reaction is used to increase the system's temperature
- Adiabatic temperature rise is a commonly used criterion to assess the severity of a reaction

**Adiabatic temperature rise:** 
$$\Delta T_{ad} = \frac{(-\Delta H_r)C_{A0}}{\rho c_p'} = \frac{Q_r'}{c_p'}$$

$\Delta H_r$  : Molar enthalpy, kJ/mol

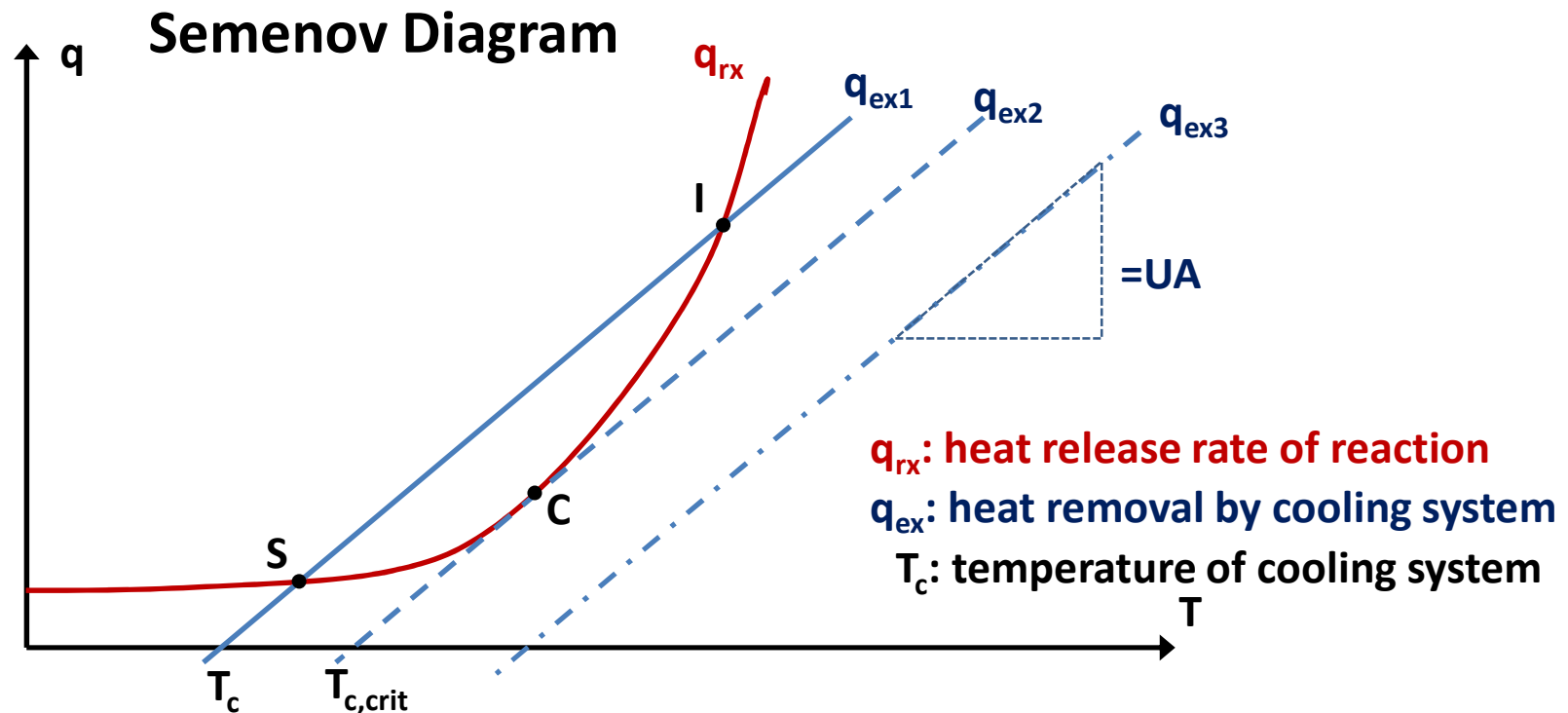
$C$  : concentration, mol/m<sup>3</sup>

$\rho$  : specific weight, kg/m<sup>3</sup>

$Q_r'$  : specific energy, kJ/kg

$c_p'$  : specific heat capacity, kJ/kgK

# Fundamentals of chemical reaction safety: Thermal Hazards



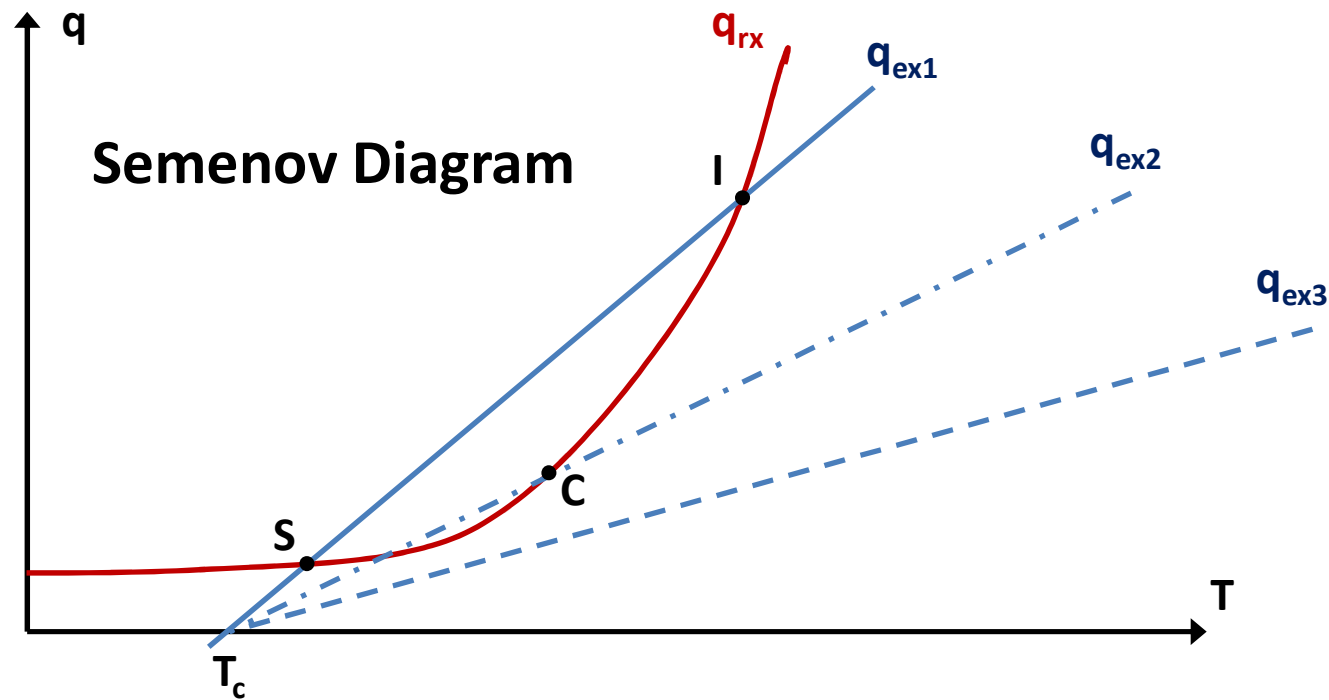
Heat balance when  $q_{rx} = q_{ex}$  (at S, I, C)

I is the instable point:

- If  $T \uparrow$  heat generation dominates and runaway condition develops
- If  $T \downarrow$  heat removal dominates and temperature decreases to point S

S is the stable point  
C is the critical point

# Fundamentals of chemical reaction safety: Thermal Hazards

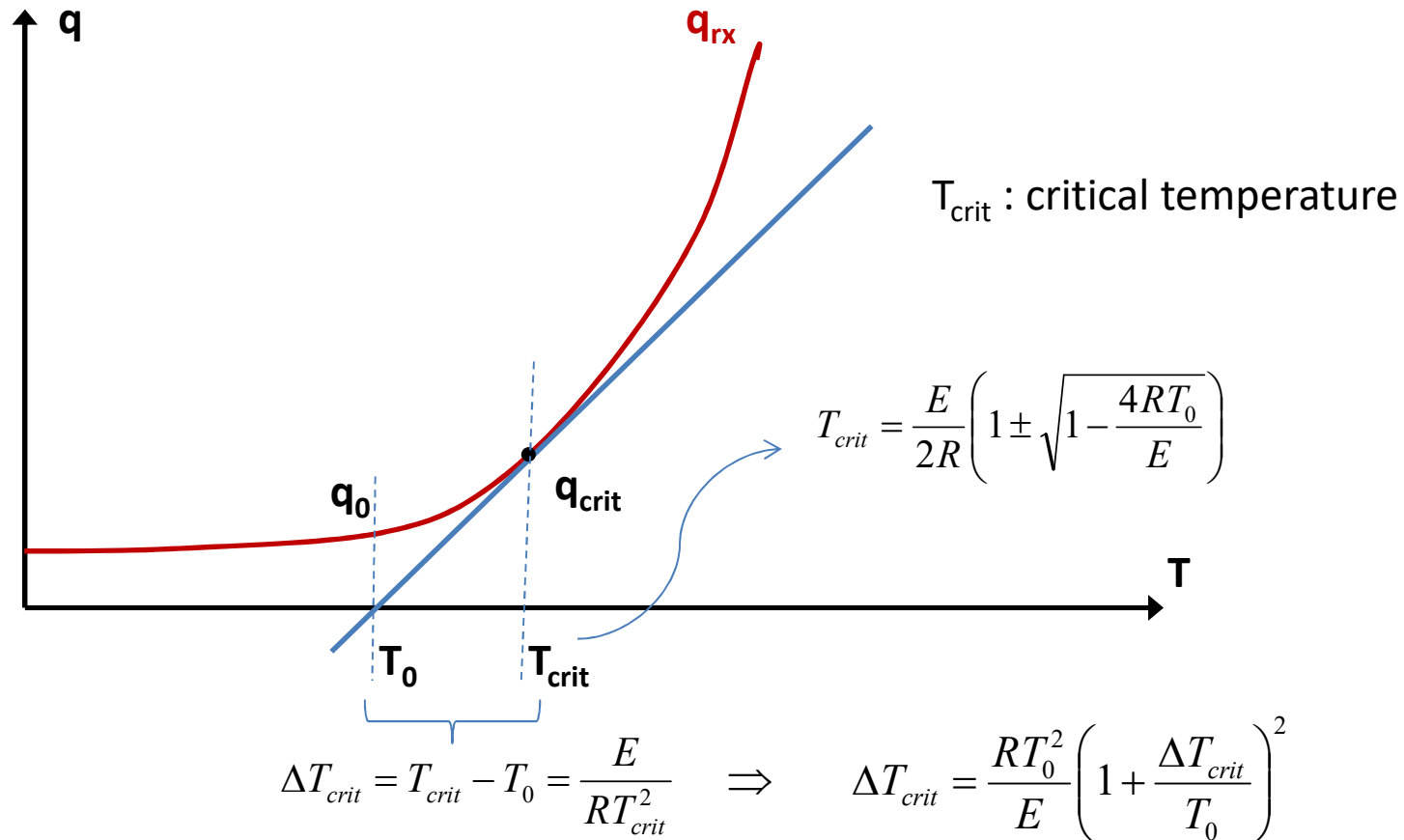


If heat transfer coefficient ( $U$ ) or the surface area ( $A$ ) of the cooling system is changed, a similar shift to a critical point will occur.

This may happen due to fouling of the cooling system

If reactor is operated with a cooling medium temperature close to the critical cooling medium temperature, small variations of  $T_c$ ,  $U$  and  $A$  may result in a runaway situation

# Fundamentals of chemical reaction safety: Thermal Hazards



For a given reaction characterised by its thermo-kinetic constants ( $k$ ,  $E$ ,  $Q_r$ ) processed in a given reactor and characterised by its heat exchange parameters ( $U$ ,  $A$ ,  $T_0$ ) there is a minimum temperature difference required for stable reactor performance:

$$\Delta T_{crit} = T - T_0 \geq \frac{RT_{crit}^2}{E}$$



# Fundamentals of chemical reaction safety: Thermal Hazards

## Time of No Return – TNR

- TNR: time required to reach the critical temperature  $T_{\text{crit}}$  from the initial temperature from which the thermal explosion develops  $T_0$ .
- After this time has elapsed under adiabatic conditions, even if the cooling system has recovered, it is impossible to cool the reactor
- TNR is an important feature of an emergency cooling system designed to cope with an imminent runaway reaction – i.e. It has to be effective in a time less than the TNR

$$TNR = 0.632 \frac{c_p' R T_0^2}{q_0 E}$$

$q_0$  : heat release rate at initial conditions  $T_0$ , J/s

$E$  : activation energy, J/mol

$c_p'$  : specific heat capacity of reaction mixture, J/gK

# Fundamentals of chemical reaction safety: Thermal Hazards

## Time frame of thermal explosion – $TMR_{ad}$ concept

- $TMR_{ad}$ : time to maximum rate under adiabatic conditions is the time a thermal explosion takes to develop under adiabatic conditions

$$TMR_{ad} = \frac{c'_p RT_0^2}{q_0 E}$$

- $TMR_{ad}$  is a function of the reaction kinetics
- $q_0$  is an exponential function of temperature thus  $TMR_{ad}$  decreases exponentially with temperature and decreases with increasing activation energy

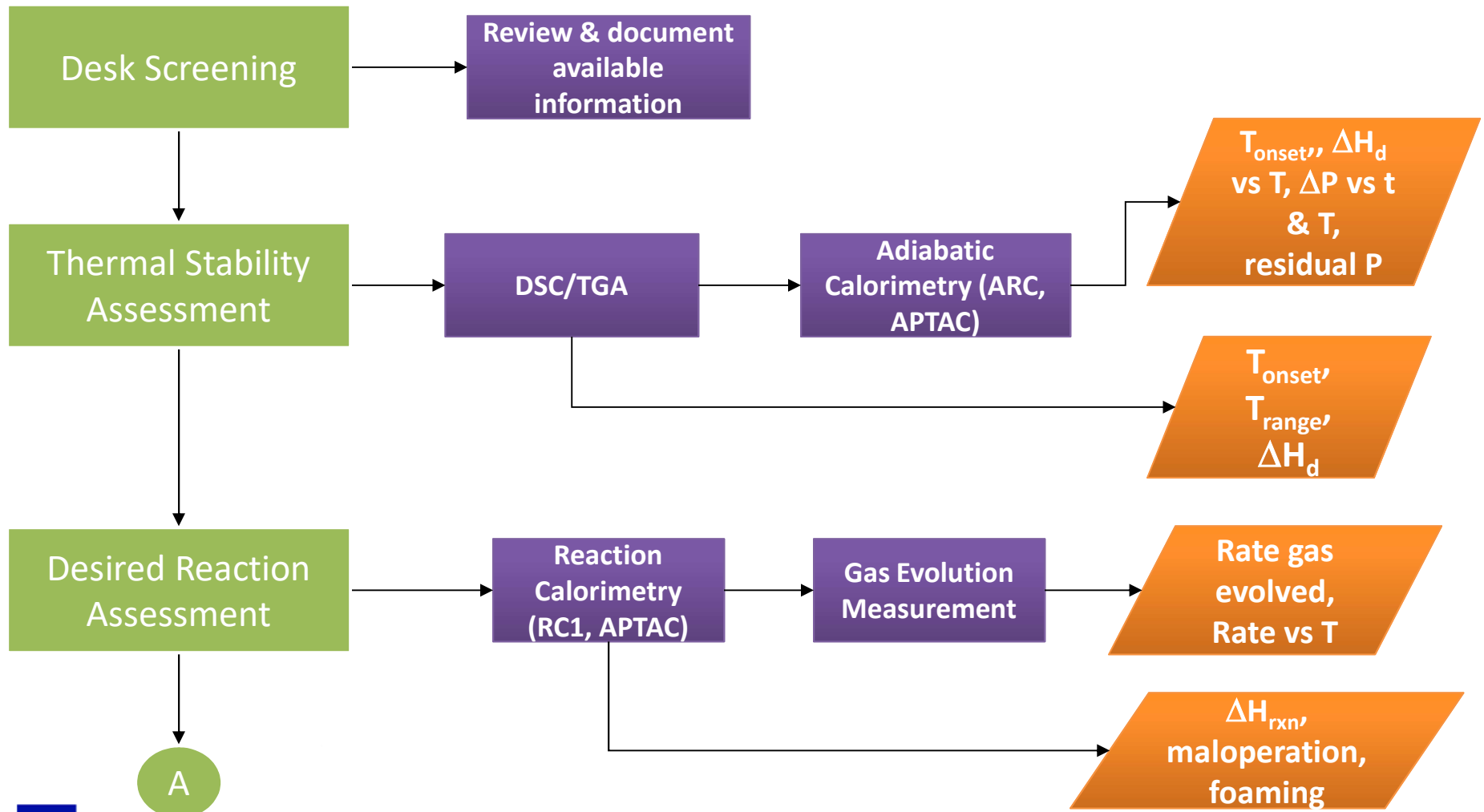
$$TMR_{ad}(T) = \frac{c'_p RT_0^2}{q_0 e^{-E/RT_0} E}$$



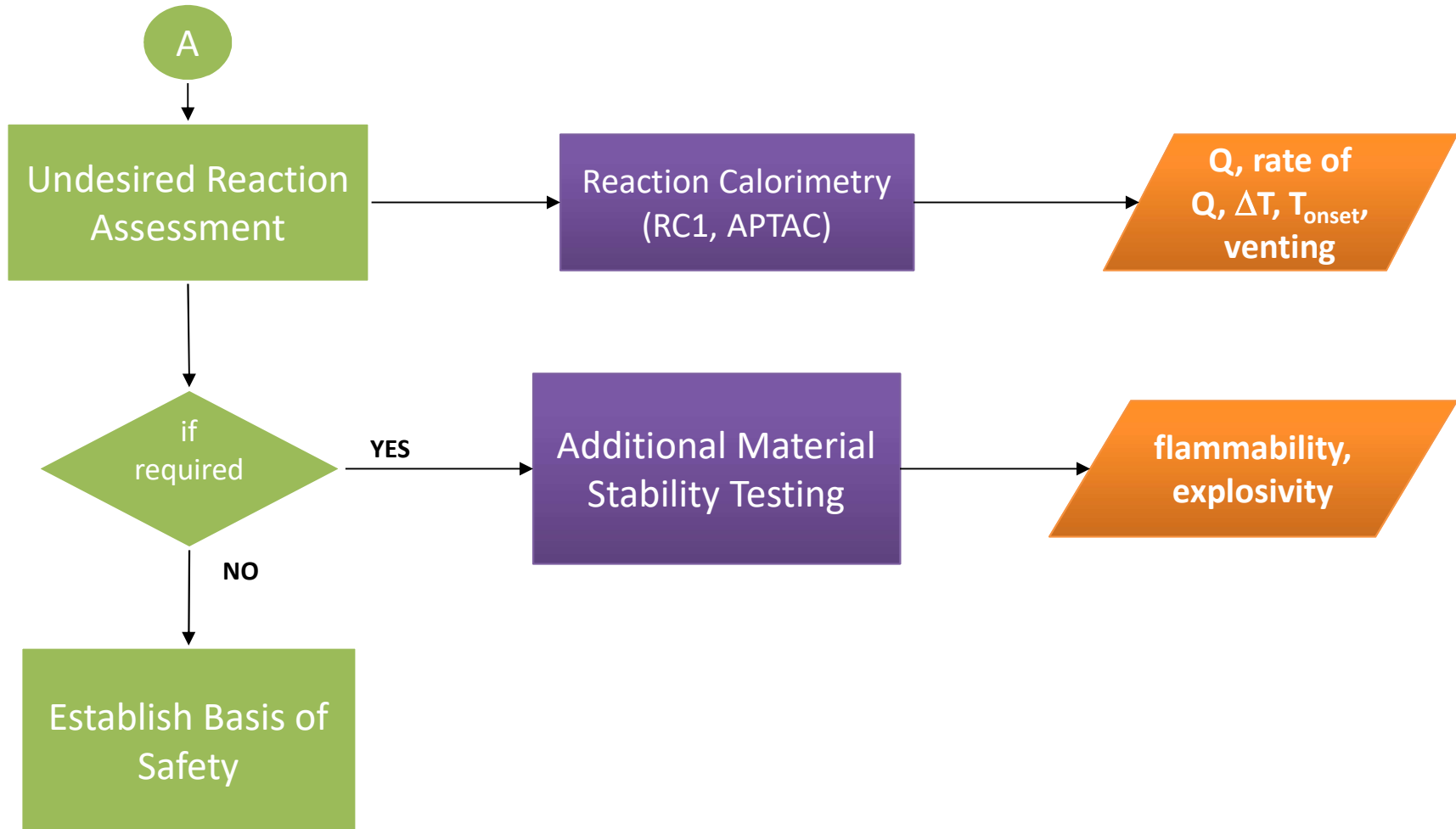
## Chemical Reaction Risk Assessment

- Chemical Hazard Evaluation

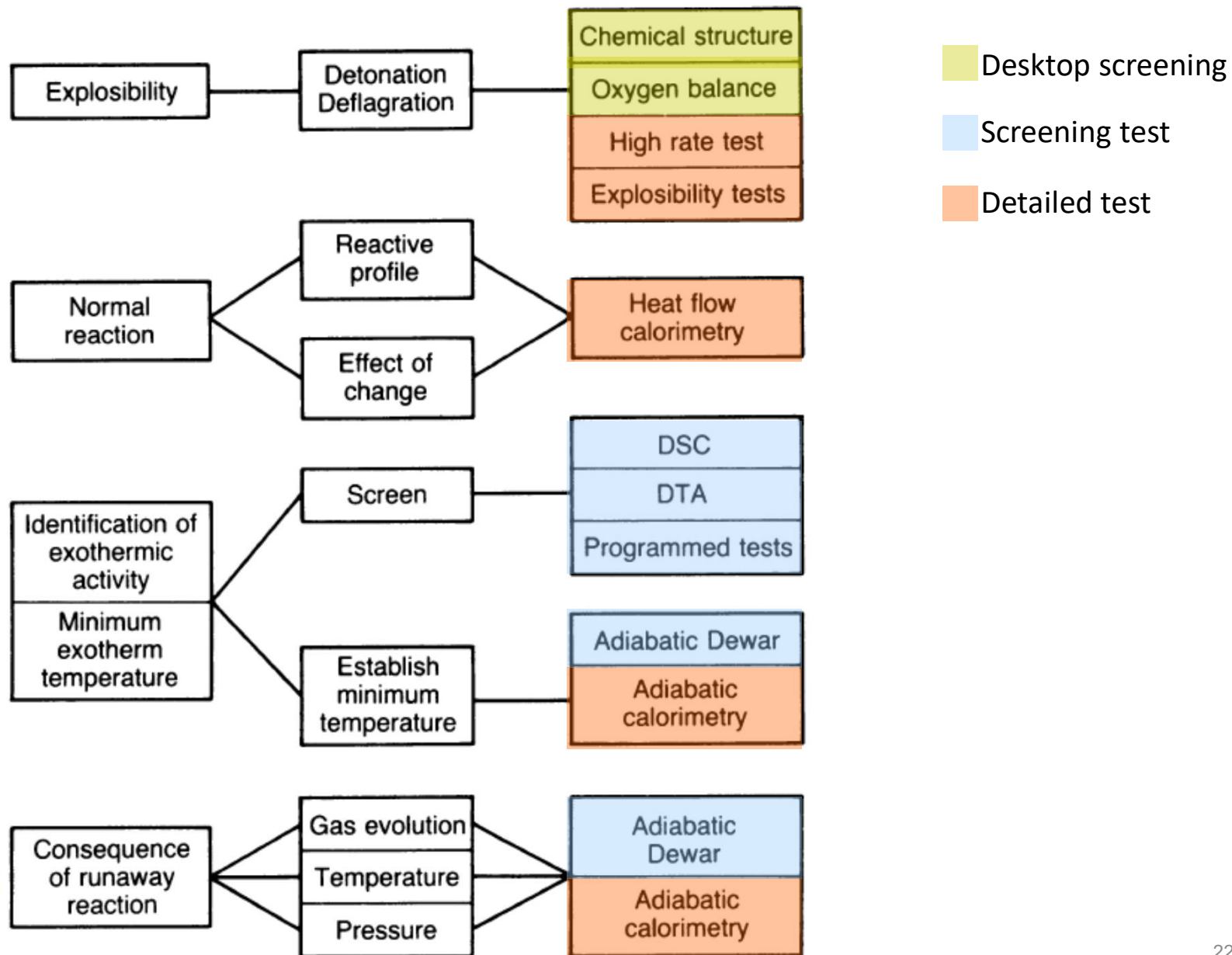
# Chemical Hazard Evaluation Flow Chart



# Chemical Hazard Evaluation Flow Chart



# Chemical Reaction Risk Assessment: Reaction Hazard Evaluation



# Chemical Reaction Risk Assessment

## Reaction Hazard Evaluation

- Desktop Screening



# Reaction Hazard Evaluation: Desktop Screening

Important physical and chemical properties for initial evaluation

General properties	Molecular structure Freezing point Vapour pressure, boiling point Critical pressure, temperature, volume Vapour density, specific heat, viscosity, thermal conductivity Liquid density, specific heat, viscosity, thermal conductivity Latent heats of vaporization and fusion Dielectric constant, electrical conductivity
Flammability	Flammability limits Flash point Autoignition temperature Minimum ignition energy Maximum experimental safe gap Self-heating
Corrosion	Corrosiveness to materials of construction Incompatibility with particular materials
Polymerization, decomposition	Polymerization characteristics Decomposition, hydrolysis characteristics
Impurities	Impurities in: raw material plant material Mutual solubilities with water
Reaction, explosion	Heats of formation, combustion, decomposition Energy hazard potential Thermal stability Impact sensitivity
Toxicity	Threshold limit values, emergency exposure limits Lethal concentration LC <sub>50</sub> , lethal dose LD <sub>50</sub> Exposure effects (inhalation, ingestion, skin and eye contact) Long-term low exposure effects Warning levels (smell)
Radioactivity	Radiation survey $\alpha$ -particle, $\beta$ -, $\gamma$ -ray exposures



# Reaction Hazard Evaluation: Desktop Screening

## Typical High Energy Molecular Structures

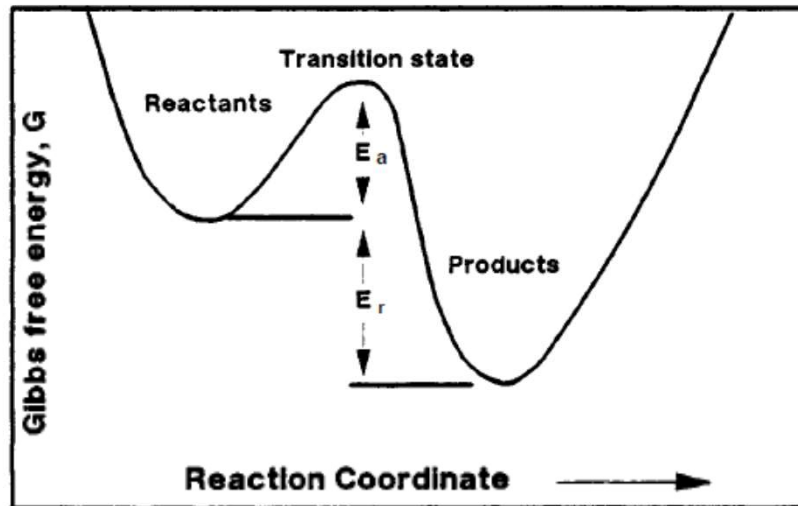
<i>Definition</i>	<i>Bond Grouping</i>	<i>Definition</i>	<i>Bond Grouping</i>
acetylenic compounds	$-\text{C}\equiv\text{C}-$	tetrazoles; high nitrogen-containing compounds	$-\text{N}=\text{N}-\text{N}=\text{N}-$
haloacetylene derivatives	$-\text{C}\equiv\text{C}-\text{X}$	triazines (R=H, -CN, -OH, -NO)	$-\text{C}-\text{N}=\text{N}-\underset{\text{R}}{\text{N}}-\text{C}-$
metal acetylides	$-\text{C}\equiv\text{C}-\text{M}$	alkyl hydroperoxides; peroxyacids	$-\text{C}-\text{O}-\text{O}-\text{H}$
azo compounds	$-\text{C}-\text{N}=\text{N}-\text{C}-$	peroxides (cyclic, diacyl, dialkyl); peroxyesters	$-\text{C}-\text{O}-\text{O}-\text{C}-$
diazo compounds	$-\text{C}=\text{N}^+=\text{N}^-$	metal peroxides; peroxyacid salts	$-\text{O}-\text{O}-\text{M}$
diazeno compounds	$-\text{C}-\text{N}=\text{NH}$	amine chromium peroxocomplexes	$\text{N} \rightarrow \text{Cr}-\text{O}_2$
nitroso compounds	$-\text{C}-\text{N}=\text{O}$	azides	$-\text{N}_3$
nitroalkanes	$-\text{C}-\text{NO}_2$	halogen azides; N-halogen compounds; N-haloimides	$-\text{N}-\text{X}$
polynitro alkyl compounds; polynitro aryl compounds	$-\text{C}-\text{NO}_2$ $\text{LNO}_2$	diazonium sulfides and derivatives; "Xanthates"	$-\text{C}-\text{N}=\text{N}^+ \text{S}^-$
acyl or alkyl nitrates	$-\text{C}-\text{O}-\text{NO}_2$	diazonium carboxylates and salts	$-\text{C}-\text{N}=\text{N}^+ \text{Z}^-$

# Reaction Hazard Evaluation: Desktop Screening

## Typical High Energy Molecular Structures

<i>Definition</i>	<i>Bond Grouping</i>	<i>Definition</i>	<i>Bond Grouping</i>
acyl or alkyl nitrites	$\text{-C-O-N=O}$	amine metal oxo salts	$(\text{N} \rightarrow \text{M})^+ \text{Z}^-$
1, 2-epoxides	$\begin{array}{c} \text{-C-C-} \\   \quad   \\ \text{O} \end{array}$	N-metal derivatives	$\text{-N-M}$
metal fulminates	$\text{-C=N-O-M}$	halo-aryl metal compounds	$\text{Ar-M-X}$
aci-nitro salts	$\text{HO-(O=)N=}$	hydroxyammonium salts	$\text{-N}^+ \text{-OH} \text{Z}^-$
N-nitroso compounds	$\text{-N-N=O}$	arenediazoates	$\text{-C-N=N-O-C-}$
N-nitro compounds	$\text{-N-NO}_2$	arenediazo aryl sulfides	$\text{-C-N=N-S-C-}$
fluoro dinitromethyl compounds	$\begin{array}{c} \text{F-C-NO}_2 \\   \\ \text{NO}_2 \end{array}$	bis-arenediazo oxides	$\text{-C-N=N-O-N=N-C-}$
difluoro amino compounds; N,N,N-trifluoroalkylimidines	$\text{-N-F}_2$	bis-arenediazo sulfides	$\text{-C-N=N-S-N=N-C-}$
N-azolium nitroimidates	$\begin{array}{c}   \\ \text{-N}^+ \text{-N}^- \text{-NO}_2 \\    \end{array}$		

# Reaction Hazard Evaluation: Desktop Screening



$$G = U - TS + pV \quad \textcircled{1}$$

U: internal energy of the system, T: absolute temperature, S: entropy, p: pressure, V: volume

*for reaction at constant temperature and pressure:*

$$\Delta G_r = \Delta U_r - T\Delta S_r + p\Delta V_r \quad \textcircled{2}$$

Since the entropy change of an exothermic reaction is small ( $\approx 0.1 \text{ kJ/mol} \cdot ^\circ\text{C}$ ) relative to  $\Delta U_r$ ,  $T\Delta S_r$  can be omitted.

$$\Delta U_r = \sum_{\text{products}} (U_f)_{\text{products}} - \sum_{\text{reactants}} (U_f)_{\text{reactants}} \quad \textcircled{3}$$

*for reaction at constant pressure:*

$$\Delta H_r = \Delta U_r + p\Delta V_r \quad \textcircled{4}$$

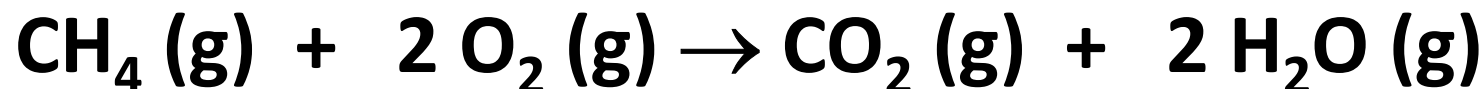
Under isobaric conditions, a small amount of energy is consumed or released by expansion or contraction of the system, and  $\Delta H_r$  is the observed (i.e., net) heat dissipated or absorbed. The enthalpy released or absorbed in an isobaric process can be described in a manner similar to Equation (3) for constant volume conditions

$$\Delta H_r = \sum_{\text{products}} (H_f)_{\text{products}} - \sum_{\text{reactants}} (H_f)_{\text{reactants}} \quad \textcircled{5}$$

# Reaction Hazard Evaluation: Desktop Screening

## Worked Example

The reaction/combustion of methane gas in oxygen is represented by the reaction:



The calculation for the heat of reaction (combustion) for methane is then:

$$\begin{aligned}\Delta H &= \sum \Delta H_{f, \text{products}} - \sum \Delta H_{f, \text{reactants}} \\ \Delta H &= (\Delta H_{f, \text{CO}_2} + 2 \Delta H_{f, \text{H}_2\text{O}}) - (\Delta H_{f, \text{CH}_4} + 2 \Delta H_{f, \text{O}_2}) \\ \Delta H &= [-393.5 \text{ kJ} + 2 \times (-241.8 \text{ kJ})] - [-74.8 \text{ kJ} + 2 \times (0 \text{ kJ})] \\ &\quad \underline{\Delta H = - 802.3 \text{ kJ}}\end{aligned}$$

So, the heat of combustion, that is, the heat of reaction, is - 802.3 kJ per mole of methane.

Notice that the value is negative, so the reaction gives off heat as expected for a combustion reaction.

# Reaction Hazard Evaluation: Desktop Screening

## Oxygen balance

The oxygen balance is the amount of oxygen, expressed as weight percent, liberated as a result of complete conversion of the material  $C_xH_yO_zN_q$  to  $CO_2$ ,  $H_2O$ ,  $SO_2$ ,  $N_2$ , and other relatively simple oxidized molecules.

(Note: the nitrogen is assumed to evolve as  $N_2$ )

$$OB = \frac{-1600(2x + (y/2) - z)}{MW}$$

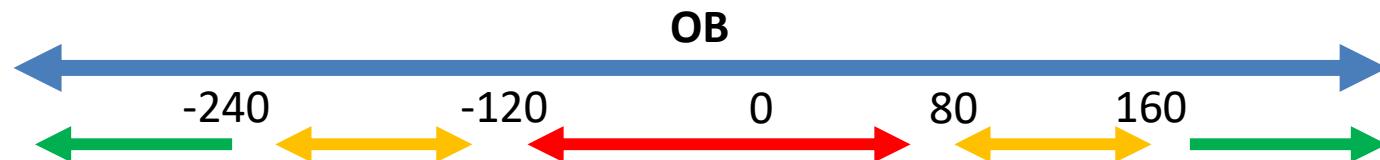
X : number of atoms of carbon

Y : number of atoms of hydrogen

Z : number of atoms of oxygen

M: number of atoms of metal

- substance lacking sufficient oxygen has a negative OB value, and one containing excess oxygen has a positive OB value
- the power of explosives increases as the OB increases and approaches a value of zero



# Reaction Hazard Evaluation: Desktop Screening

## $\gamma$ Criterion – hazard potential classification

$$\gamma_{\text{criterion}} = \frac{10Q^2(MW)}{N}$$

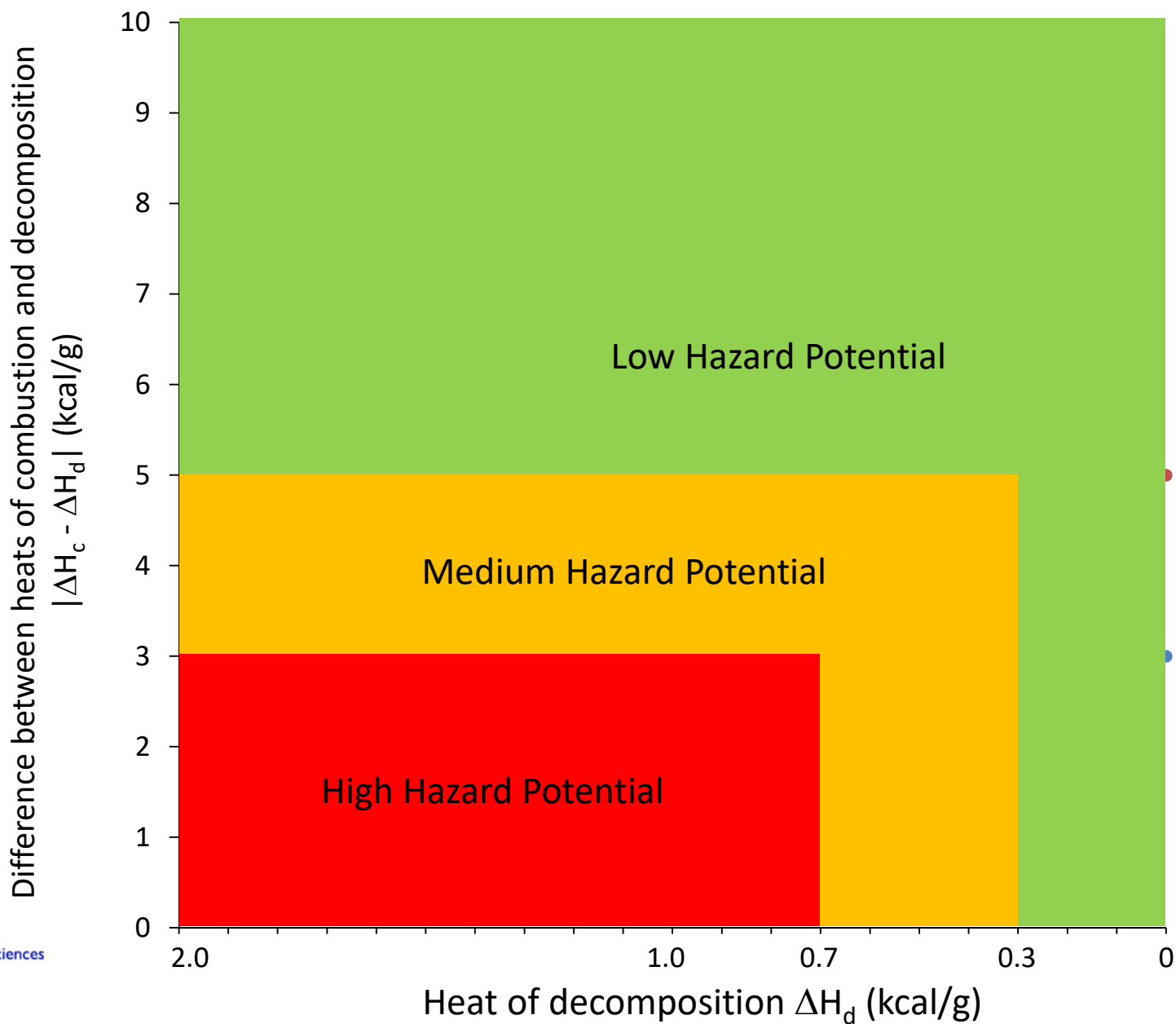
$\gamma$ : energy release evaluation (ERE) value

$Q$ : decomposition energy in kcal/g (with positive sign for heat released),

$MW$ : molecular weight

$N$ : number of atoms in the composition.

# Reaction Hazard Evaluation: Desktop Screening



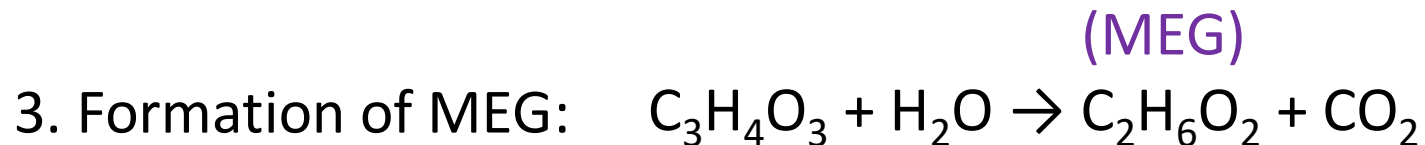
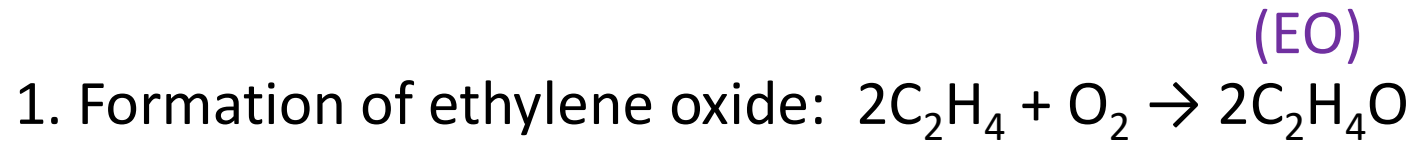
# Reaction Hazard Evaluation: Desktop Screening

Criterion	Energy Hazard Potential		
	Low	Medium	High
1	$\Delta H_d > -1255\text{J/g}$	$-2929 < \Delta H_d < -1255\text{J/g}$	$\Delta H_d < -2929\text{J/g}$
2	<i>Refer to relationship between heats of combustion and decomposition</i>		
3	OB < -240 OB > 160	-240 < OB < -120 80 < OB < 160	-120 < OB < 80
4	$\gamma < 30$	$30 < \gamma < 110$	$\gamma > 110$

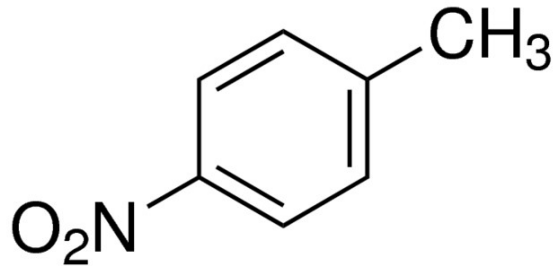


## Activity: Heat of Reaction

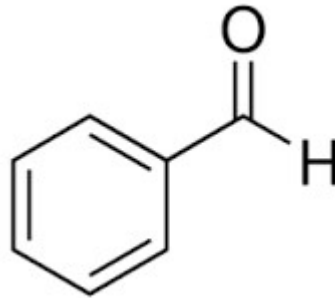
The OMEGA process is a process by Shell that is used to produce ethylene glycol from ethylene. This process comprises two steps, the controlled oxidation of ethylene to ethylene oxide, and the net hydrolysis of ethylene oxide to monoethylene glycol (MEG) as follows:



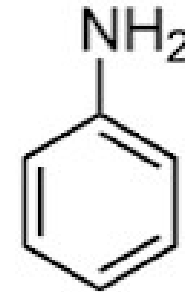
# Exercise 1: Desktop Screening - Reaction Hazard Evaluation



nitrotoluene:  $C_7H_7NO_2$



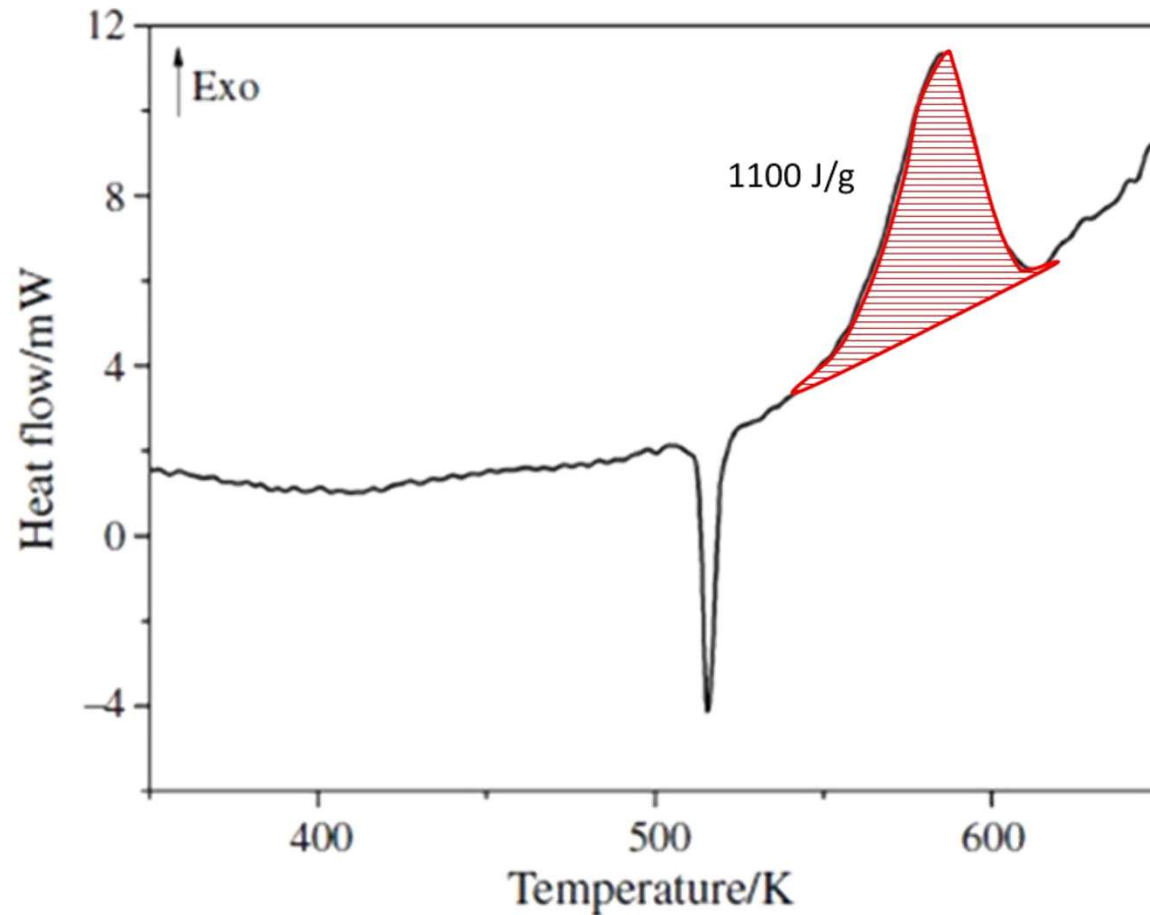
Benzaldehyde:  $C_7H_6O$



Aniline:  $C_6H_5NH_2$

1. Determine the heat of combustion
2. Determine the heat of decomposition
3. Calculate oxygen balance
4. Calculate  $\gamma$
5. Classify compounds

## Experimental Data



Sample DSC - benzaldehyde

Similarly:

Aniline =  $\Delta H_d = - 820 \text{ J/g}$

Nitrotoluene =  $\Delta H_d = - 3520 \text{ J/g}$



## Chemical Reaction Risk Assessment

### Reaction Hazard Evaluation

- Experimental Techniques
- Stoessel Criticality Class

# Reaction Hazard Evaluation: Experimental Techniques

## Comparison of different common calorimetric methods used in safety laboratories

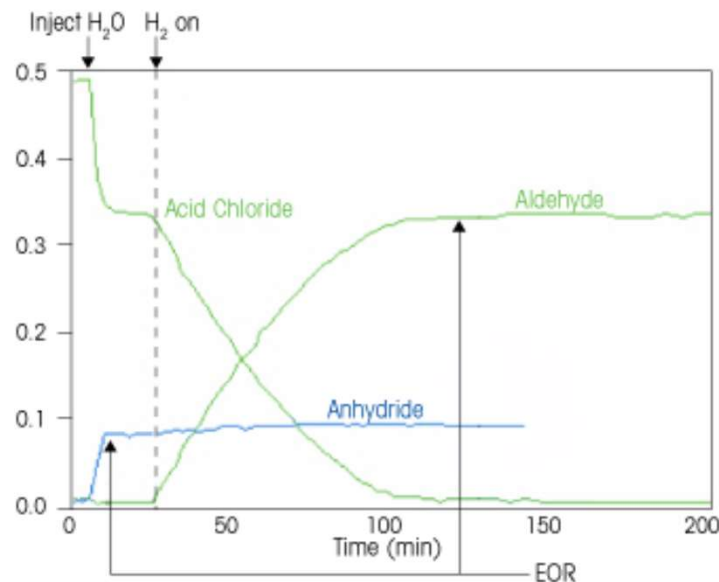
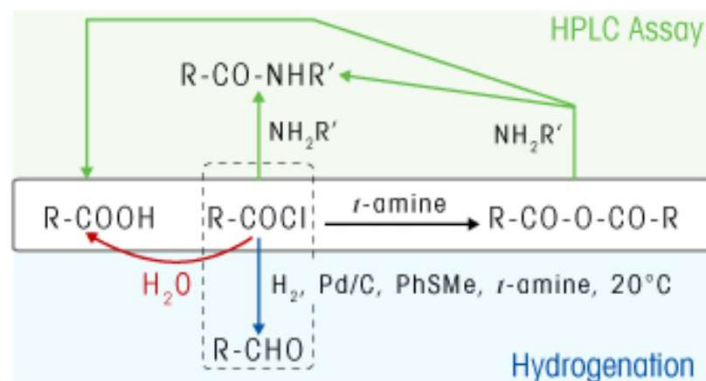
Method	Measuring principles	Application range	Sample size	Temperature range	Sensitivity W kg <sup>-1</sup>
DSC differential scanning calorimetry	Differential, ideal flux, or isoperibolic	Screening, secondary reactions	1-50mg	-50 to 500°C	2 to 10
Calvet	Differential, ideal flux	Main and secondary reactions	0.5-3 g	30 to 300°C	0.1
ARC accelerating rate calorimeter	Ideal accumulation	Secondary reactions	0.5-3 g	30 to 400°C	0.5
SEDEX sensitive detector of exothermal processes	Isoperibolic, adiabatic	Secondary reactions, storage stability	2-100g	0 to 400°C	0.5
RADEX	Isoperibolic	Screening, secondary reactions	1.5-3 g	20 to 400°C	1
SIKAREX	Ideal accumulation, isoperibolic	Secondary reactions	5-50g	20 to 400°C	0.25
RC1 reaction calorimeter	Ideal flux	Main reactions	300-2000g	-40 to 250°C	1
TAM thermal activity monitor	Differential, ideal flux	Secondary reactions, storage stability	0.5-3 g	30 to 150°C	0.01
Dewar	Ideal accumulation	Main reactions and thermal stability	100-1000g	30 to 250°C	varies

# Reaction Hazard Evaluation : Experimental Techniques

## Reaction calorimetry - desired reaction



Reaction Calorimeter



# Reaction Hazard Evaluation : Experimental Techniques

## Adiabatic calorimetry – undesired reaction

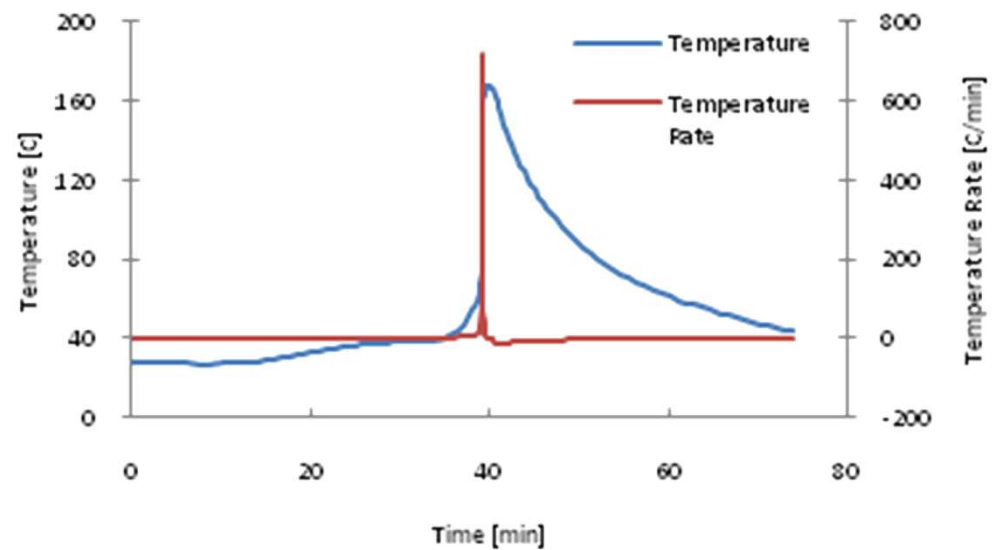
APTAC



New ARC



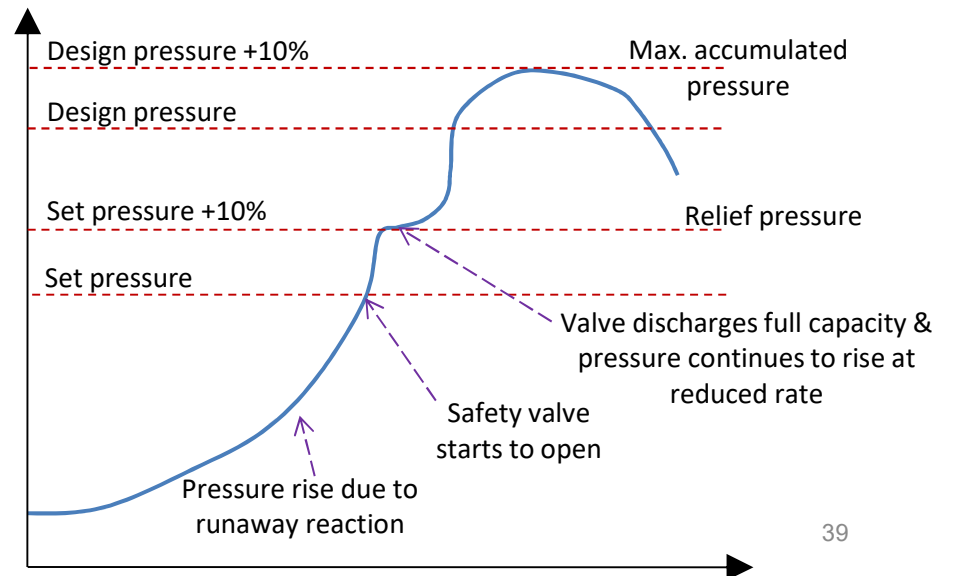
Temperature Profile



Vent Sizing package -VSP2



Adiabatic Calorimeters



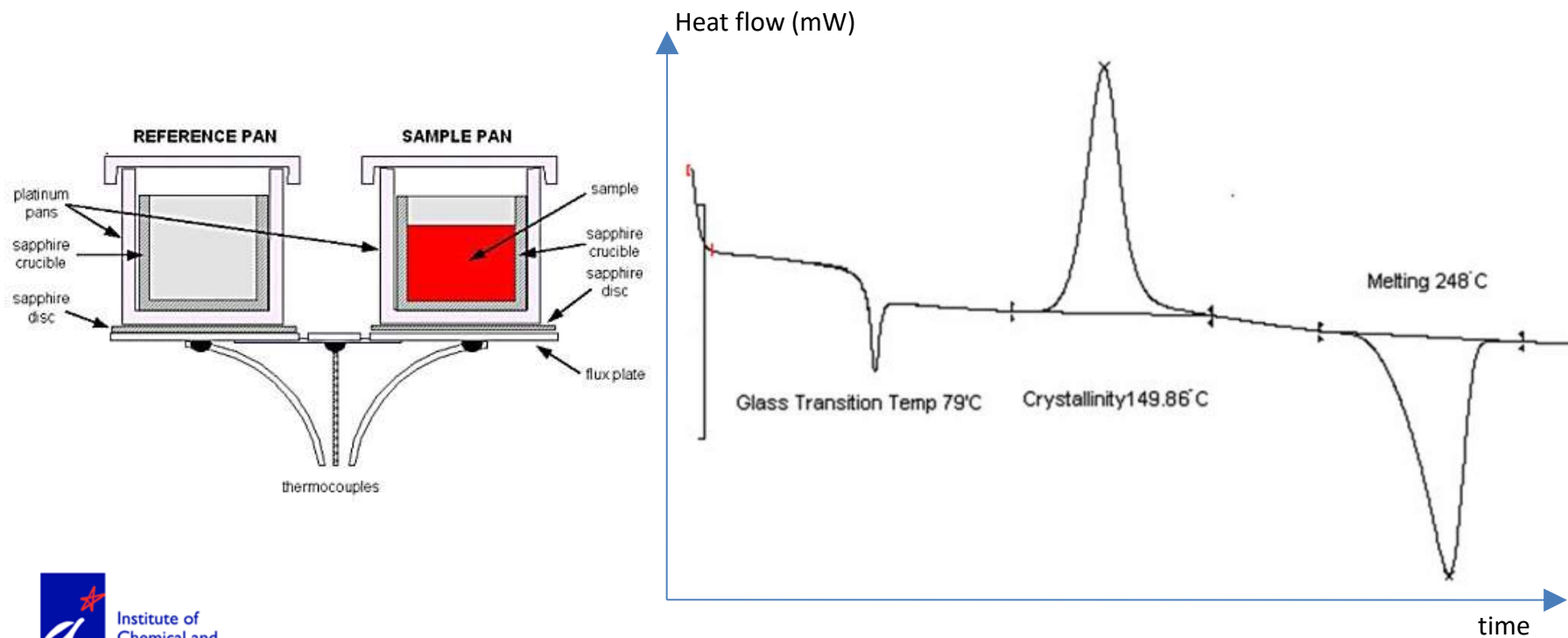
# Reaction Hazard Evaluation : Experimental Techniques

## Differential scanning calorimetry – undesired reaction



DSC measures the energy required to keep both the reference and the sample at the same temperature

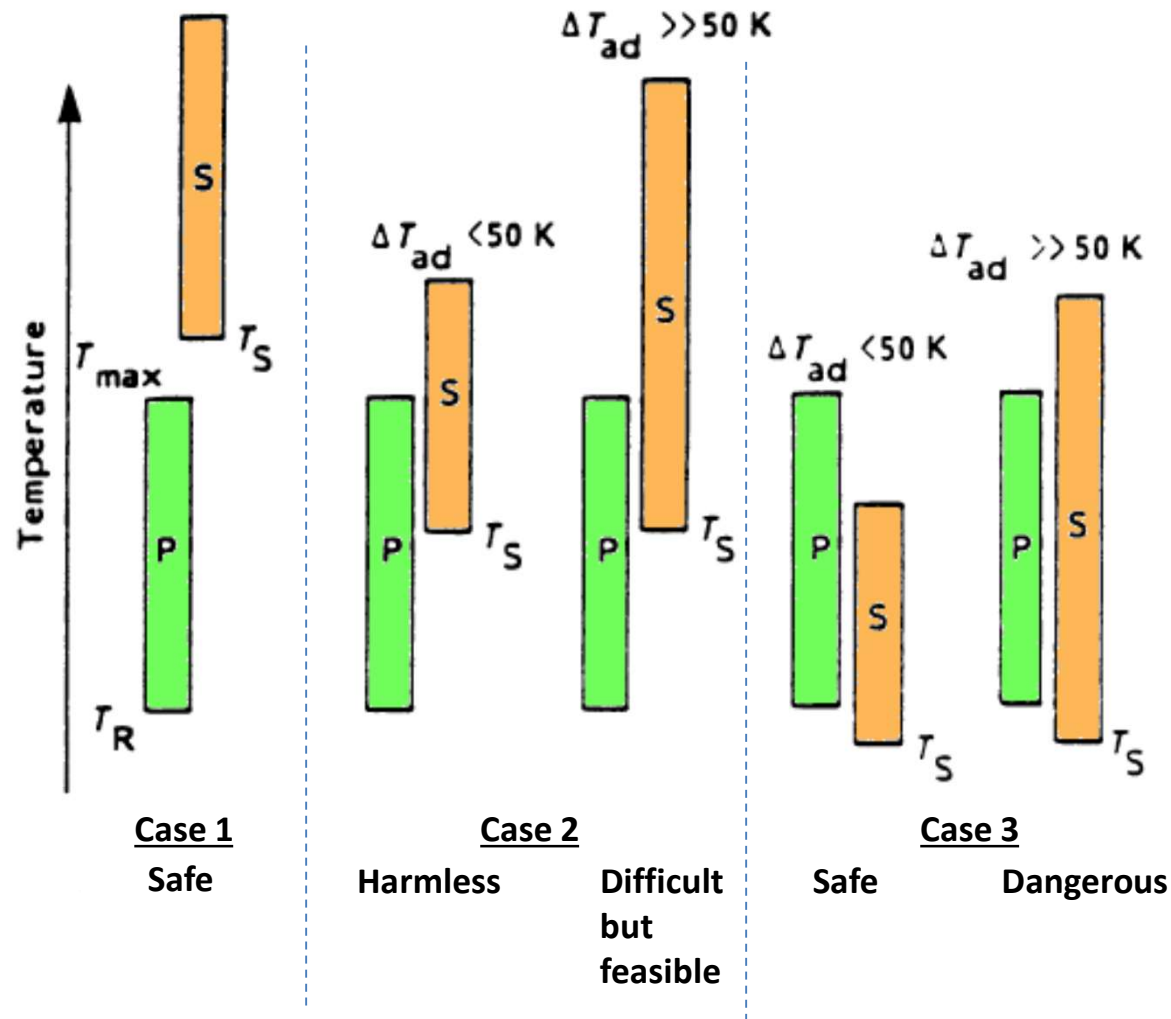
DTA measures the difference in temperature between the sample and the reference



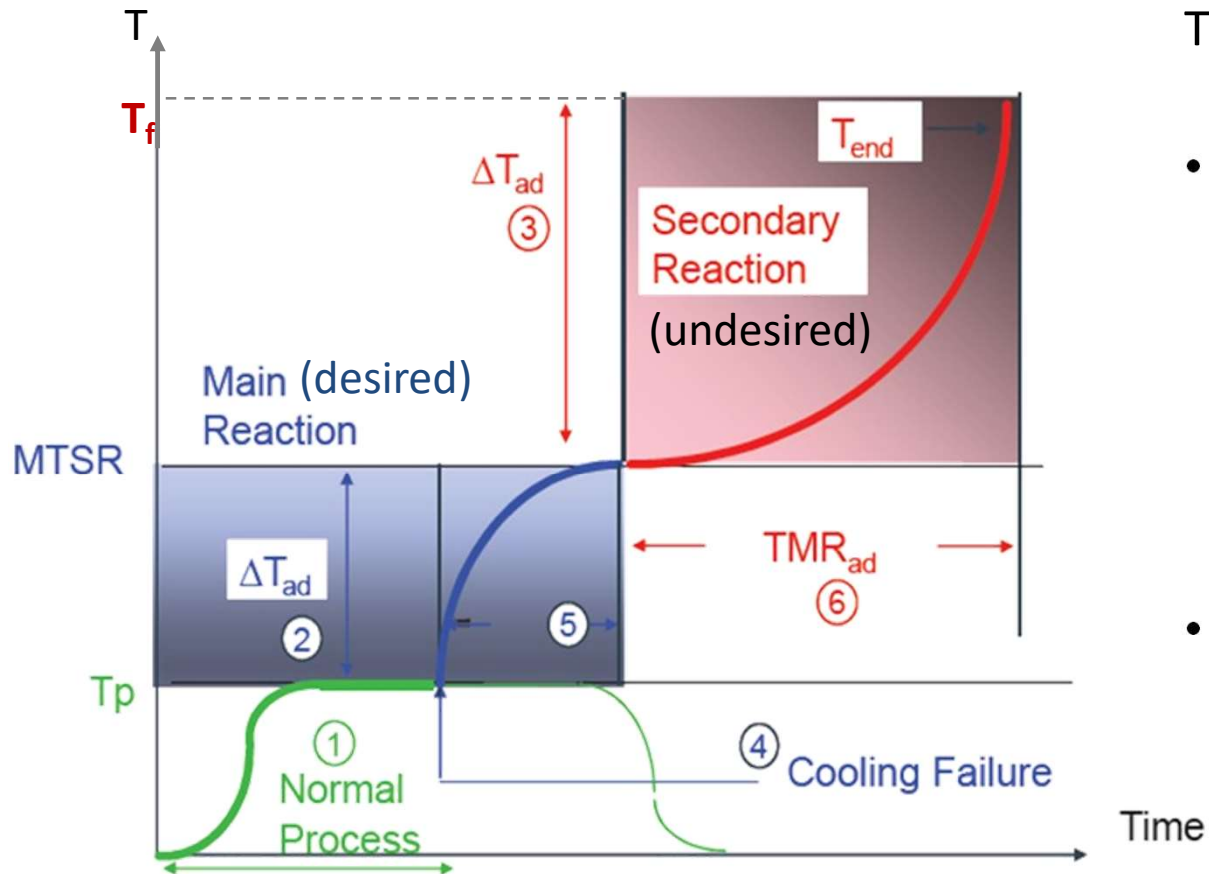


# Chemical Reaction Risk Assessment: Reaction Hazard Evaluation

## Hazards of side reactions



# Chemical Reaction Risk Assessment: Stoessel Criticality Class



This **runaway scenario** works as follows:

- if a cooling failure occurs while the reactor is at the process temperature ( $T_p$ ), it reaches a level called the maximum temperature of the synthesis reaction (**MTSR**)
- a secondary decomposition reaction may then be initiated and the heat produced by this reaction may lead to a further increase in temperature reaching the final temperature ( $T_f$ )

The cooling failure scenario was developed for the systematic assessment of thermal risks linked with exothermal chemical reactions

# Chemical Reaction Risk Assessment: Stoessel Criticality Class

- **Question 1: Can the process temperature be controlled by the cooling system?**
  - The power of the cooling system must be sufficient to remove the heat released in the reactor
- **Question 2: What temperature can be attained after runaway of the desired reaction?**
  - Upon cooling failure, unconverted reactants still present in reactor will react uncontrollably leading to an adiabatic temperature rise
  - The available energy is proportional to the accumulated (unreacted) fraction,  $X_{ac}$
  - Maximal Temperature of Synthesis Reaction (MTSR):

$$MTSR = T_p + X_{ac} \cdot \Delta T_{ad, reaction}$$

# Chemical Reaction Risk Assessment: Stoessel Criticality Class

- **Question 3: What temperature can be attained after runaway of the secondary reaction**

- If the MTSR is higher than the intended process temperature, secondary reactions may be triggered
- A further runaway due to uncontrolled secondary reaction (e.g. decomposition) will further increase the temperature

$$T_{end} = MTSR + \Delta T_{ad,secondary}$$

- **Question 4: At which moment does the cooling failure have the worst consequences?**

- The worst instance is when accumulation is maximum and/or thermal stability of reaction mixture is critical

# Chemical Reaction Risk Assessment: Stoessel Criticality Class

- **Question 5: How fast is the runaway of the desired reaction?**

- The duration of the main reaction runaway may be estimated using the initial heat release rate and  $TMR_{ad}$ :

$$TMR_{ad} = \frac{c'_p R T_p^2}{q_{(T_p)} E}$$

- **Question 6: How fast is the runaway of the decomposition starting at MTSR?**

- If secondary reactions are triggered:

$$TMR_{ad} = \frac{c'_p R T_{MTSR}^2}{q_{(MTSR)} E}$$

# Chemical Reaction Risk Assessment: Stoessel Criticality Class

## • Severity

- The adiabatic temperature rise can be calculated by dividing the energy of the reaction by the specific heat capacity:

$$\Delta T_{ad} = \frac{Q'}{c'_p}$$

- Q' represents the specific energy of desired reaction or of the secondary (decomposition) reaction.
- The higher the final temperature, the worse the consequences of the runaway
- The temperature increase may cause components of the reaction mixture (e.g. solvents) to vapourise or the decomposition may produce gasses causing pressure increase

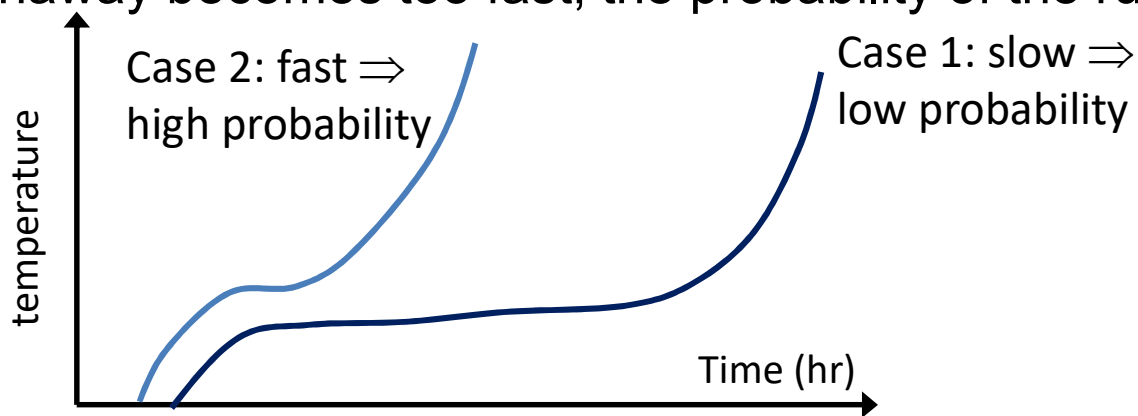
Simplified	Extended	$\Delta T_{ad}$	Q' (kJ/kg)
High	Catastrophic	>400	>800
	Critical	200-400	400-800
Medium	Medium	50-100	100-400
Low	Negligible	<50	<100

Assessment criteria for severity of a runaway reaction

# Chemical Reaction Risk Assessment: Stoessel Criticality Class

## • Probability

- The probability can be evaluated using the time scale: If after a cooling failure, there is enough time left to take emergency measures before the runaway becomes too fast, the probability of the runaway will remain low



Simplified	Extended	TMR <sub>ad</sub> (hr)
High	Frequent	<1
	Probable	1-8
Medium	Occasional	8-24
Low	Seldom	24-50
	Remote	50-100
	Almost impossible	>100

Assessment criteria for probability of a runaway reaction

# Chemical Reaction Risk Assessment: Stoessel Criticality Class

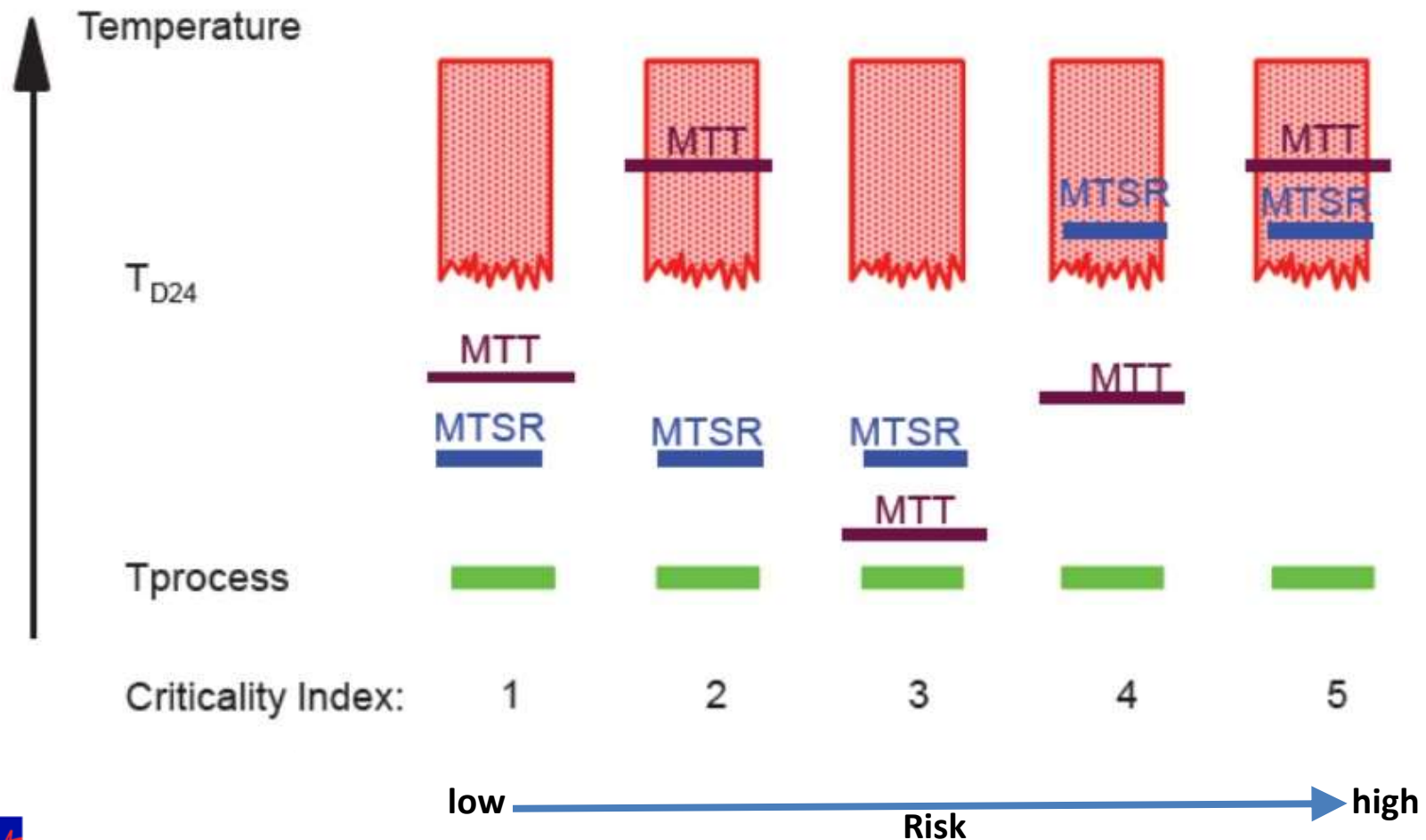
Risk Matrix for Reaction Hazard Assessment

Severity	High	$\Delta T_{ad} > 200K$			
	Medium	$50K < \Delta T_{ad} < 200K$			
	Low	$\Delta T_{ad} < 50K$ no pressure increase			
			$TMR_{ad} \cdot 24h$	$8h < TMR_{ad} < 24$	$TMR_{ad} \cdot 8h$
			Low	Medium	High
			Probability		



# Chemical Reaction Risk Assessment: Stoessel Criticality Class

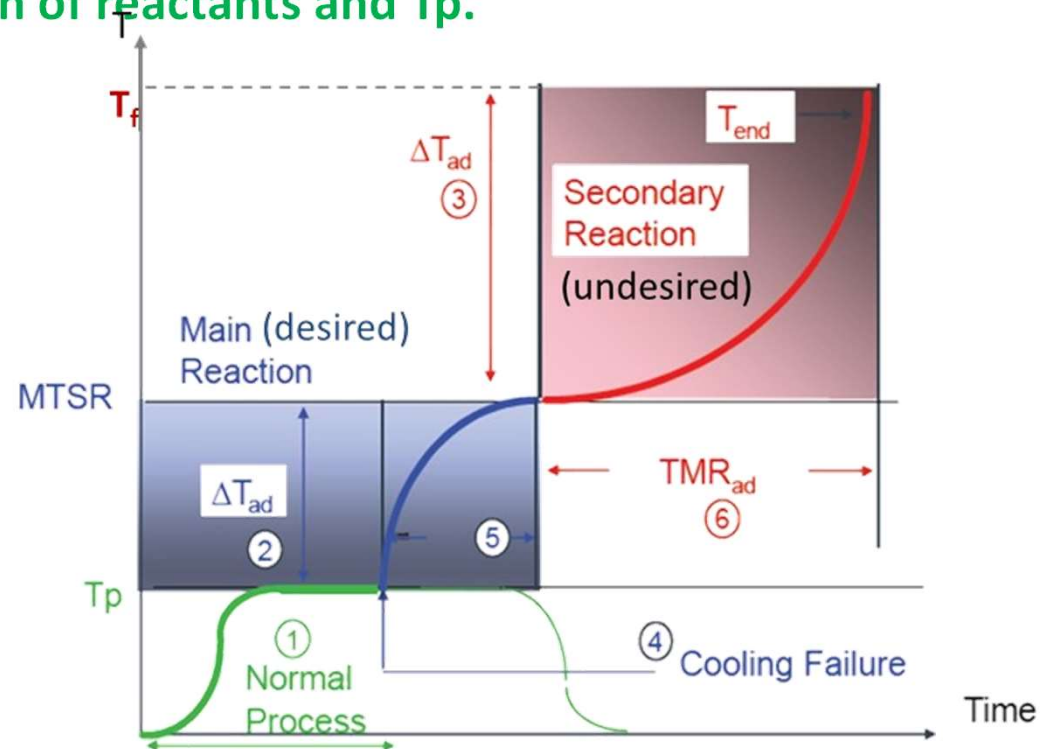
## Stoessel Criticality Class



# Chemical Reaction Risk Assessment: Stoessel Criticality Class

## KEY PARAMETERS

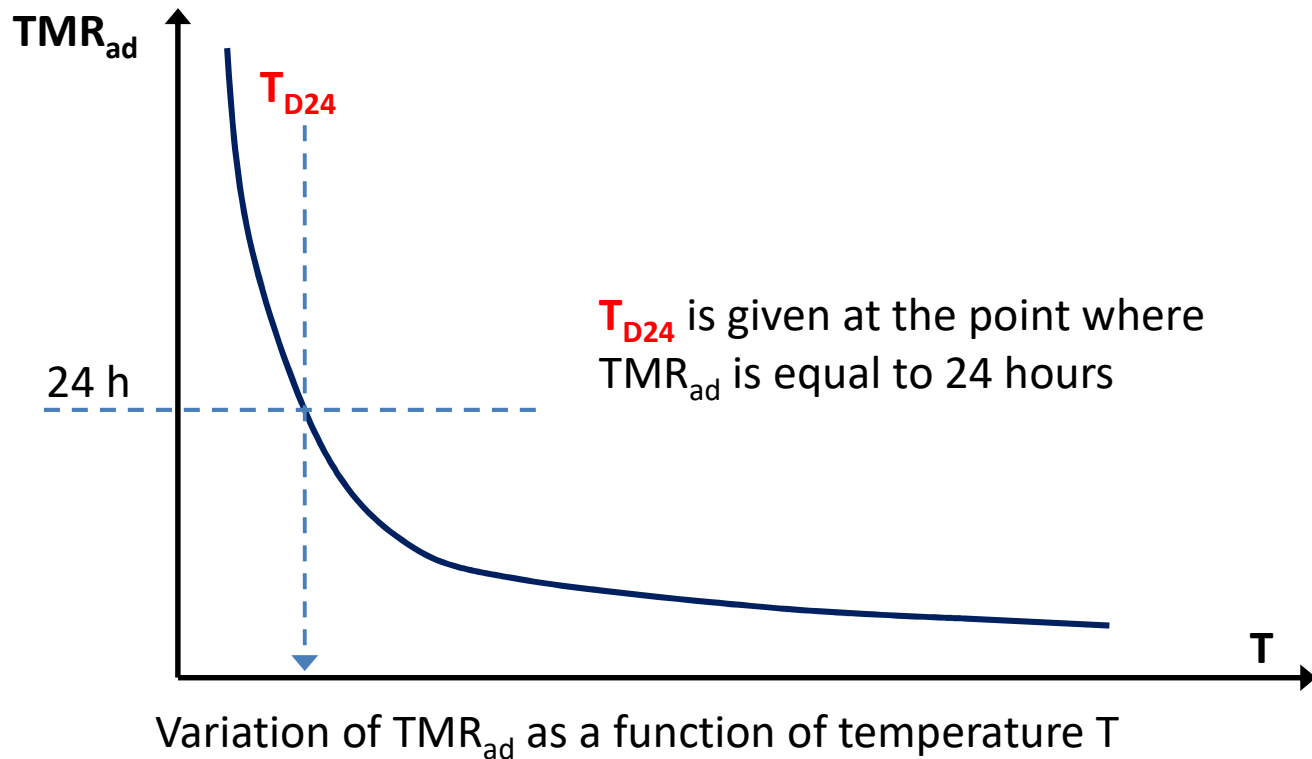
- **Process temperature ( $T_p$ ):** The initial temperature in the cooling failure. For non-isothermal processes, the initial temperature will be taken at the instant when cooling failure has the worst consequences. **Defined by the mode of operation.**
- **Maximum temperature of the synthesis reaction (MTSR):** This temperature depends on the degree of accumulation of unconverted reactants. **Defined by the accumulation of reactants and  $T_p$ .**



# Chemical Reaction Risk Assessment: Stoessel Criticality Class

- **Temperature at which  $TMR_{ad}$  is 24h ( $T_{D24}$ ):** the highest temperature at which the thermal stability of the reaction mass is unproblematic. **Defined by the thermal stability of reaction mass.**

$$TMR_{ad} = \frac{c'_p R T_p^2}{q(T_p) E}$$

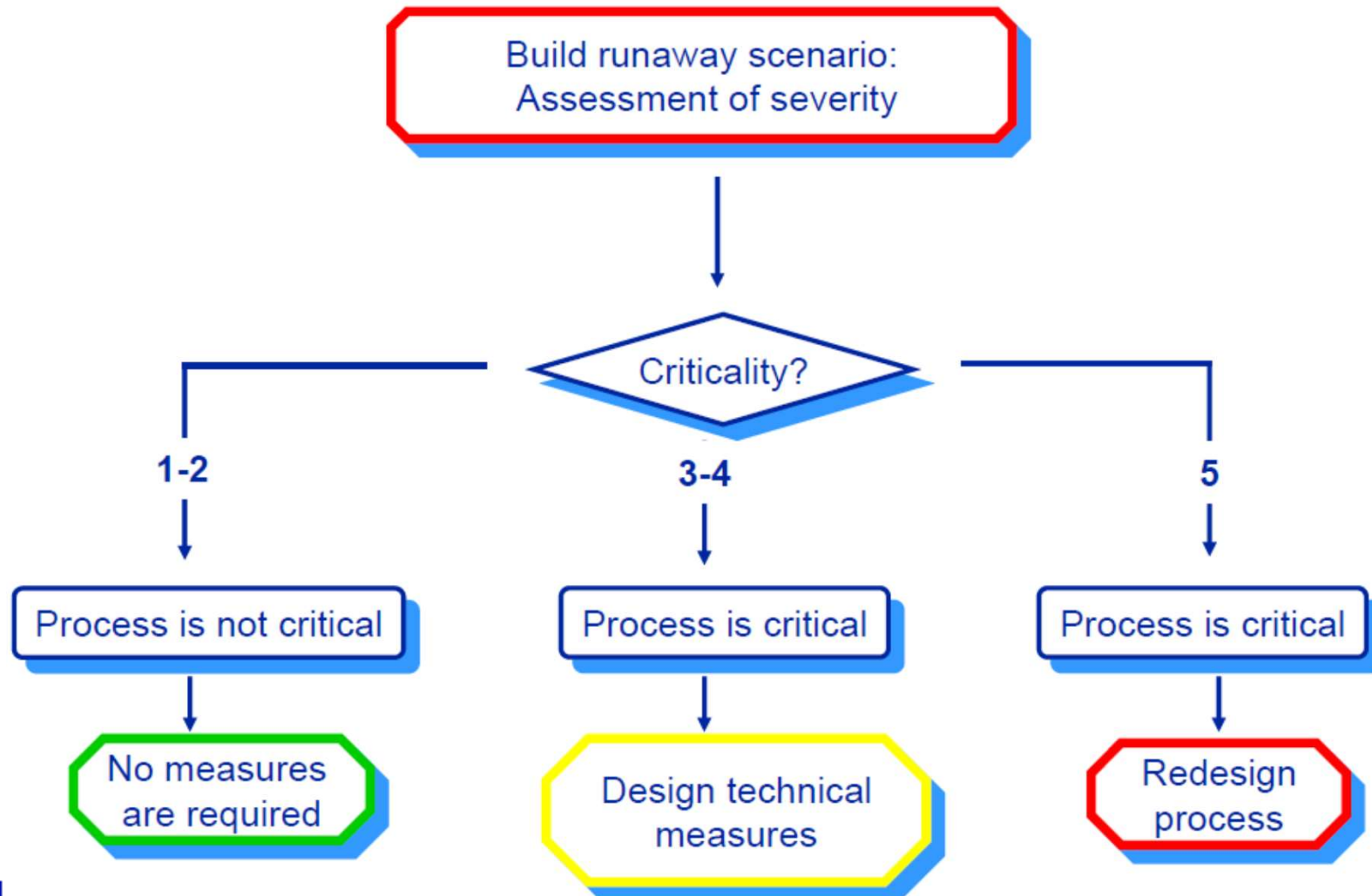


# Chemical Reaction Risk Assessment: Stoessel Criticality Class

## KEY PARAMETERS

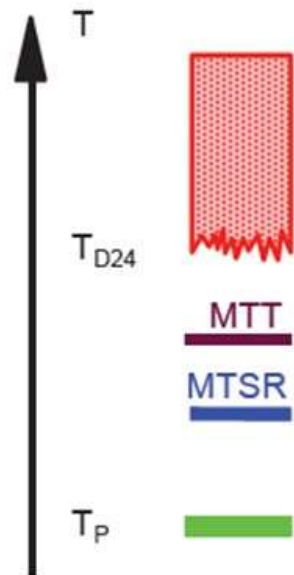
- **MTT:** maximum temperature for technical reasons (e.g. construction materials, reactor permissible design temperature and permissible design pressure). **Defined by the equipment.**
  - open reacting system, i.e. Operated at atmospheric pressure, the boiling point is used
  - closed system, operated under pressure, the temperature at which the pressure reaches the set pressure of the pressure relief system or a shutdown pressure for a protection system

# Chemical Reaction Risk Assessment: Stoessel Criticality Class



# Chemical Reaction Risk Assessment: Stoessel Criticality Class

## • Criticality Class 1



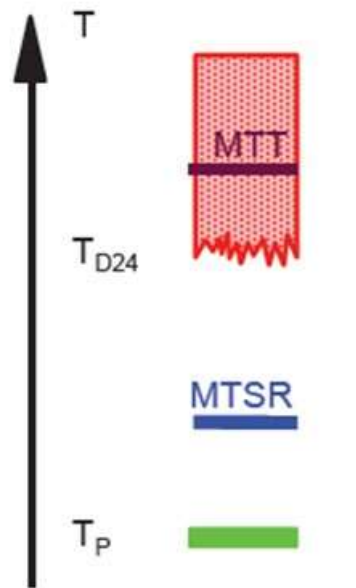
Decomposition is not triggered.  
MTT is not reached

- After loss of control of synthesis reaction the technical limit ( $MTSR < MTT$ ) cannot be reached and decomposition cannot be triggered ( $MTSR < T_{D24}$ )
- Process presents a low thermal risk
- No special measures required but reaction mass should not be held for a long time under heat accumulation condition
- Evaporative cooling (i.e. boiling point) or emergency pressure relief could serve as a safety barrier

# Chemical Reaction Risk Assessment: Stoessel Criticality Class

- **Criticality Class 2**

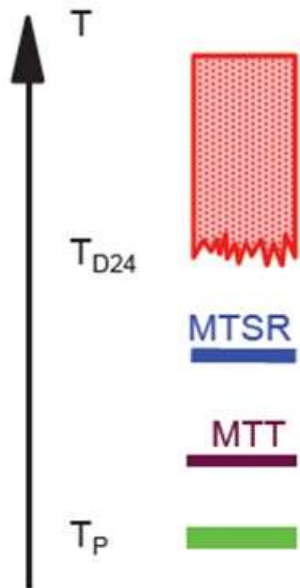
- After loss of control of synthesis reaction the technical limit (MTSR < MTT) cannot be reached and decomposition cannot be triggered (MTSR <  $T_{D24}$ )
- Situation similar to Class 1 but MTT >  $T_{D24}$ , hence is reaction mass held for long time under heat accumulation condition decomposition can be triggered and reach MTT
- Process presents a low thermal risk
- No special measures required if heat accumulation is avoided
- Evaporative cooling or emergency pressure relief could serve as a safety barrier
- Boiling point could not serve as a safety barrier.



Decomposition is not triggered.

MTT is not reached

# Chemical Reaction Risk Assessment: Stoessel Criticality Class



Decomposition is not triggered.  
MTT is reached

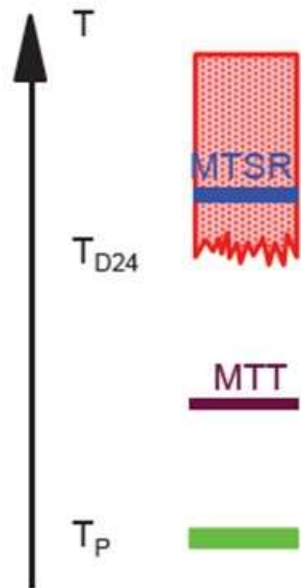
## • Criticality Class 3

- After loss of control of synthesis reaction the technical limit will be reached ( $MTSR > MTT$ ) but decomposition cannot be triggered ( $MTSR < T_{D24}$ )
- Safety of this process depends on the heat release rate of the synthesis reaction at the MTT
- Risk reducing measures are required.
- Evaporative cooling, controlled depressurisation, backup cooling, dumping of the reaction mass or quenching may be used
- Alternatively a pressure relief system could also serve as a safety barrier



# Chemical Reaction Risk Assessment: Stoessel Criticality Class

- **Criticality Class 4**



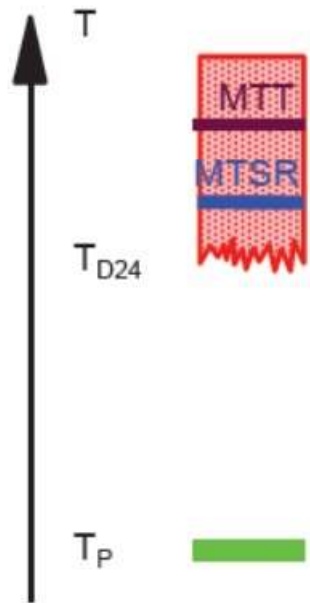
Decomposition could be triggered.  
MTT is reached

- After loss of control of synthesis reaction the technical limit will be reached ( $MTSR > MTT$ ) and decomposition could theoretically be triggered ( $MTSR > T_{D24}$ )
- Safety of this process depends on the heat release rate of both the synthesis and decomposition reactions at the MTT
- Risk reducing measures are required.
- This scenario is similar to Class 3 with the difference being that if control measures fail, the secondary reaction will be triggered
- Evaporative cooling or pressure relief system may serve as a safety barrier

# Chemical Reaction Risk Assessment: Stoessel Criticality Class

- **Criticality Class 5**

- After loss of control of synthesis reaction the decomposition reaction will be triggered ( $MTSR > T_{D24}$ ) and the technical limit will be reached during the runaway of the secondary reaction.
- The heat release rate of the secondary reaction at MTT may be too high resulting in a critical pressure increase.
- Thus there is no safety barrier between the main and secondary reactions.
- In this case, neither evaporative cooling or pressure relief system can serve as a safety barrier. Only quenching or dumping can be used.
- Worthwhile to consider alternative process design (e.g. change from batch to semi-batch)



Decomposition is triggered.  
MTT is reached

# Chemical Reaction Risk Assessment: Stoessel Criticality Class

## Worked example

A ketone is to be hydrogenated to the corresponding alcohol at 30°C in an aqueous solution at a concentration of 0.1mol/l and at a pressure of 2 barg in a reactor protected against overpressure by a safety valve with a set pressure of 3.2 barg. The molecule presents no other reactive functional groups.

**Assess the thermal risks linked to this hydrogenation reaction**

*Data:*

Similar reactions have an enthalpy of 200kJ/mol.

The specific heat capacity of the reaction mass is  $c_p' = 3.6 \text{ kJ/kgK}$

*Solution:*

This example shows that with only sparse thermal data it is sometimes possible to assess thermal risks. This is possible due to the low concentration used in this hydrogenation. The reaction is performed in a diluted aqueous solution. Thus, its density can be assumed to be 1000kg/m<sup>3</sup>. Then, the specific heat of reaction is:

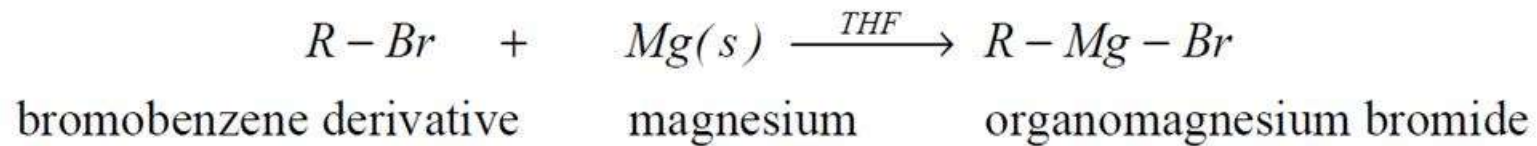
$$Q_r' = \frac{C(-\Delta H_r)}{\rho} = \frac{0.1 \text{ mol} \cdot \text{l}^{-1} \times 200 \text{ kJ} \cdot \text{mol}^{-1}}{1 \text{ kg} \cdot \text{l}^{-1}} = 20 \text{ kJ} \cdot \text{kg}^{-1}$$

Therefore, the corresponding adiabatic temperature rise is:

$$\Delta T_{ad} = \frac{Q_r'}{c_p'} = \frac{20 \text{ kJ} \cdot \text{mol}^{-1}}{3.6 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}} \approx 6 \text{ K}$$

Such a weak adiabatic temperature rise cannot lead to a thermal explosion. The severity is low. In case of malfunction of the reactor cooling system, the reaction, providing it is not stopped, will lead to an immediate temperature rise by 6 K reaching the MTSR of 36°C. The thermal risk linked to this hydrogenation reaction is low.

# Activity: Grignard Reagent Formation



$$\Delta H_r = (270 \pm 6) \text{ kJ/mol}$$

Reaction mixture density,  $\rho = ?? \text{ kg/m}^3$

Specific heat capacity,  $C_p = 123 \text{ J/mol.K}$

Activation energy,  $E_A = 9.7 \text{ kJ/mol}$

If initial concentration of R-Br is 2 moles, what is the adiabatic temperature rise?

# Exercise 2: Thermal Hazard Assessment

## Chemistry

- Reaction:  $A + B \rightarrow P \rightarrow S$  at process temperature = 80 °C
- Where: A, B: reactants, P: desired product , S: decomposition product

## Experimental Data – Reactants A & B

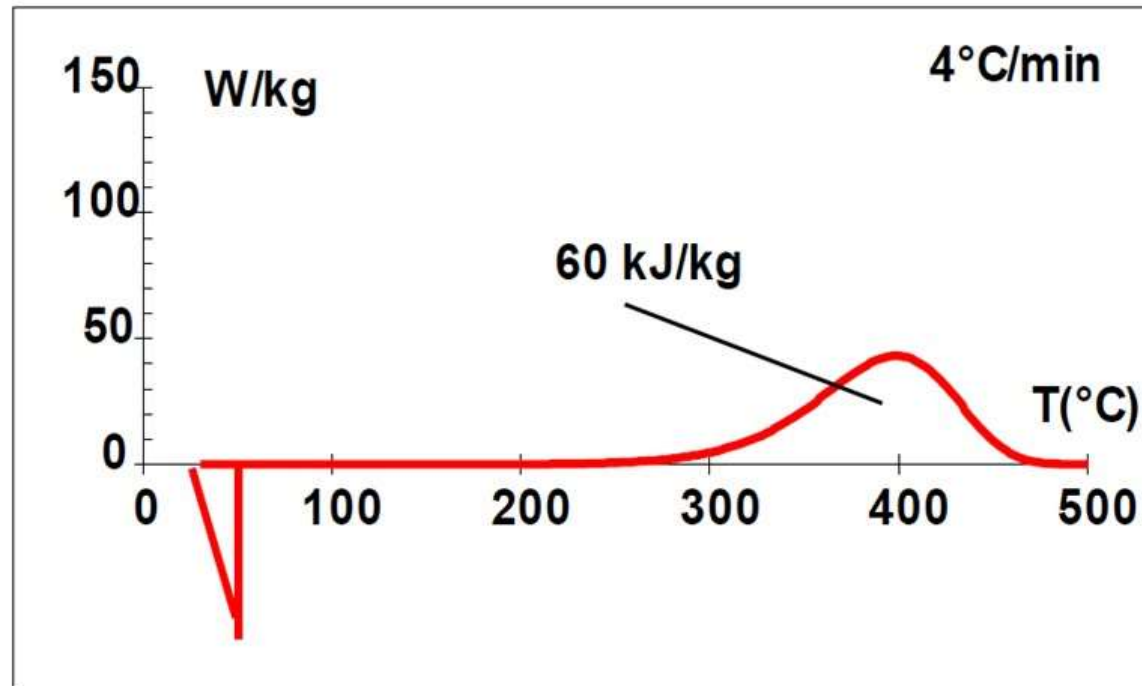


Figure 1: DSC Thermogram of Reactant A

**NOTE: Reactant B shows no exotherm below 500°C**

## Experimental Data – Final Reaction Mass

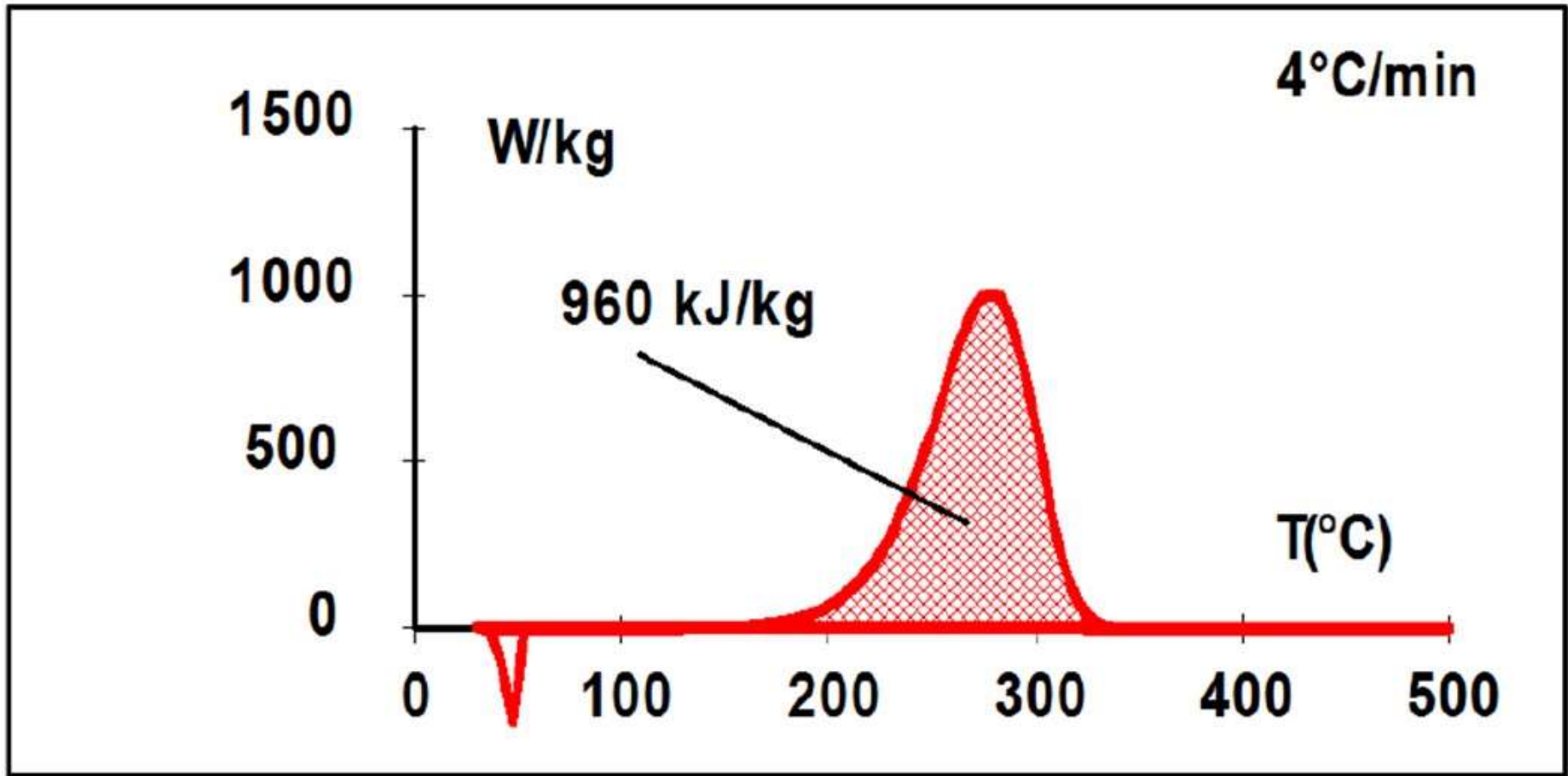


Figure 2: DSC Thermogram of the final reaction mass (A+B+P but mostly P)

### Further Information:

- The specific heat capacity of the reaction mass is 1.7 kJ/(kg.K)
- The boiling point of the reaction mass is below 200°C.
- No gases are formed during the reaction.

## Experimental Data – Whole Reaction Mass

Both reactants A and B were mixed at the ambient in a pressure resistant gold plated steel cell which was then heated linearly in the DSC apparatus.

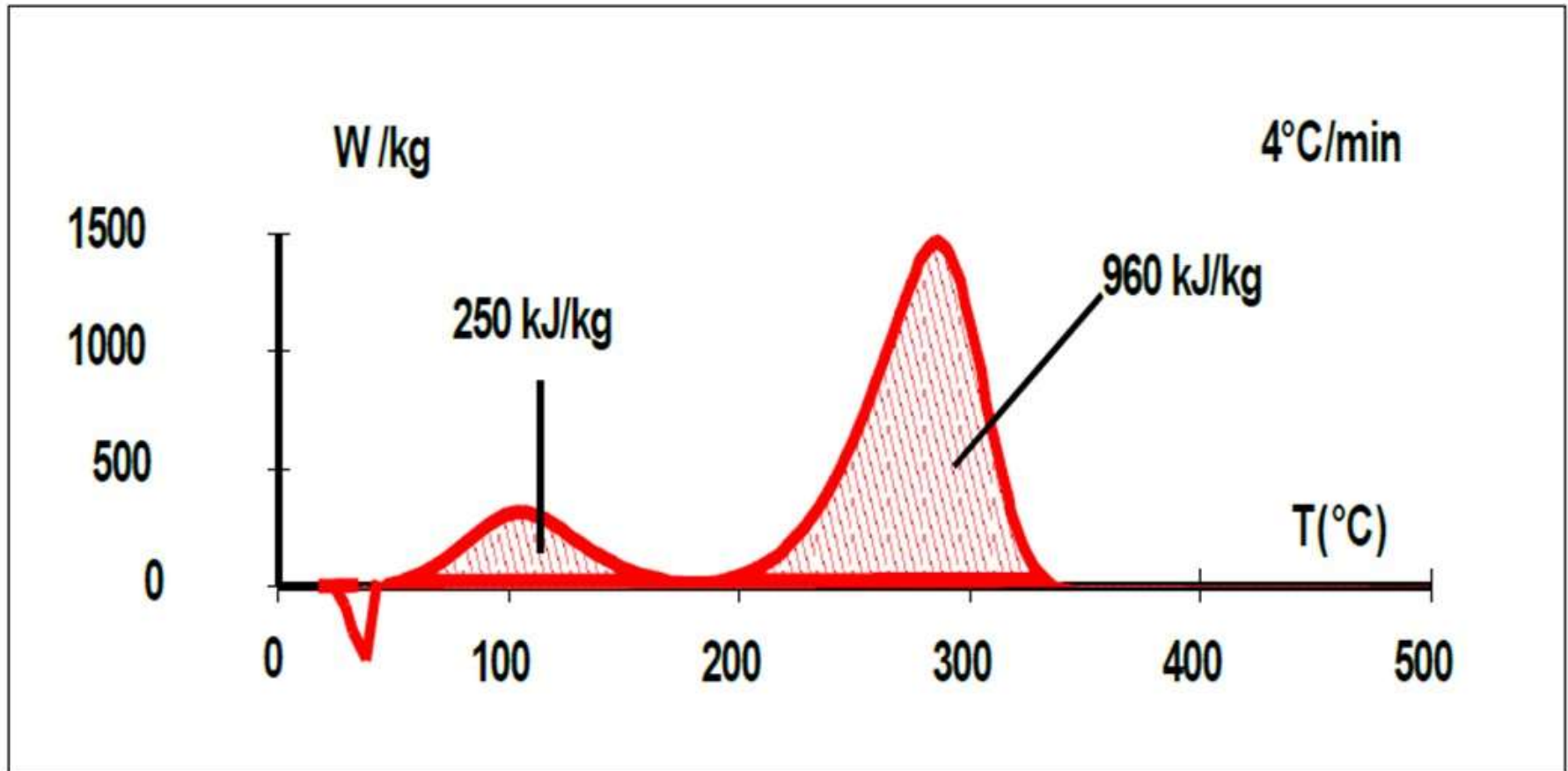


Figure. 3: DSC Thermogram of the Cold Mixed Reactants (A+B)

## Experimental Data – Kinetics

A series of isothermal DSC measurements at different temperatures allow determining the maximum heat flow as a function of temperature. The analysis of the flow by using Arrhenius law leads to the activation energy of the decomposition.

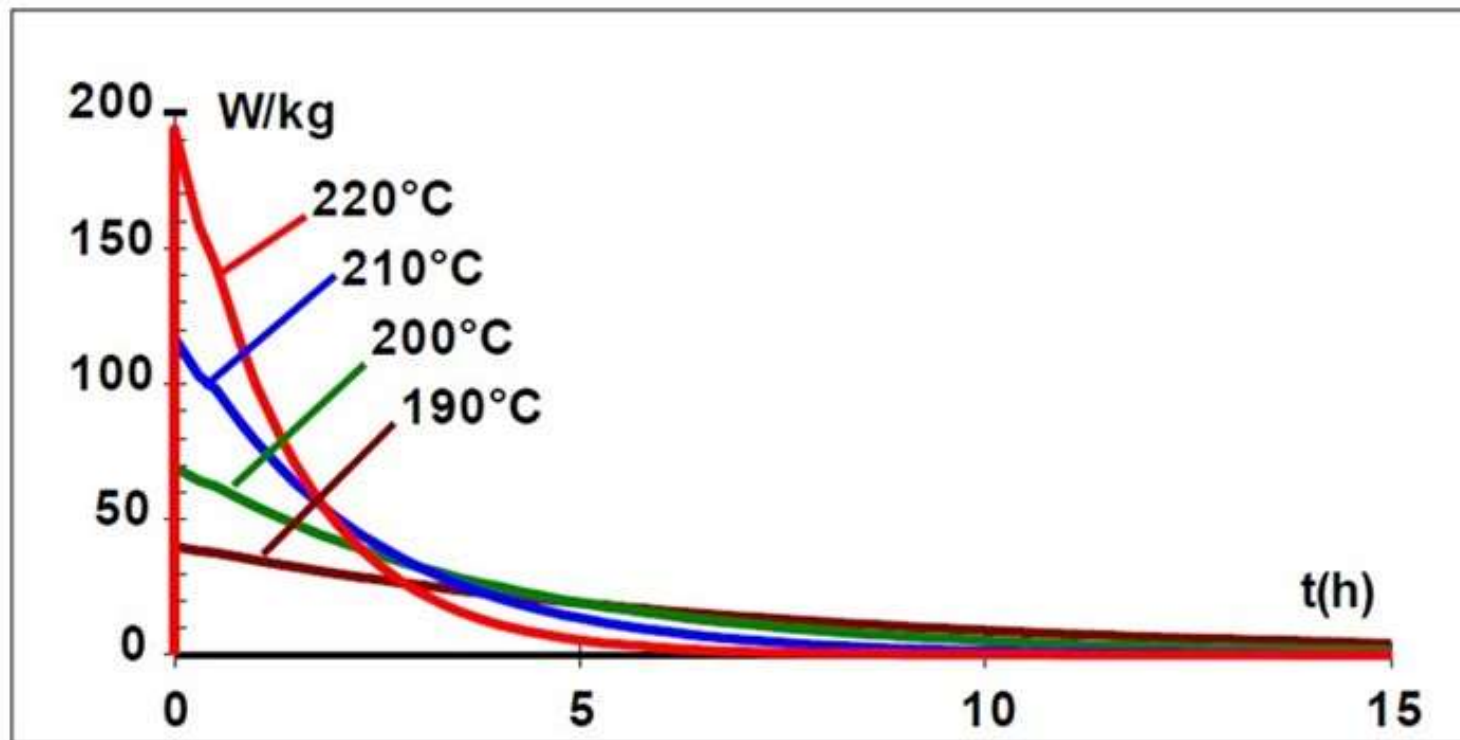


Figure 5: Isothermal DSC Thermograms of the Final Reaction Mass

Table 1: Maximum Heat Release Rates (from isothermal DSC experiments)

T (°C)	190	200	210	220
$q_{\max}$ (W/kg)	40	70	120	190



## Exercise 2: Thermal Hazard Assessment

### QUESTIONS

#### *A. Desired Reaction*

- i. Is Reactant A likely to decompose under normal process conditions?
- ii. What is the adiabatic temperature rise ( $\Delta T_{ad}$ ) of the primary reaction?
- iii. What is the final temperature?
- iv. Can the decomposition temperature be triggered by the desired reaction?
- v. If so, what will be the final temperature?

## Exercise 2: Thermal Hazard Assessment

### B. Undesired Reaction

- i. Calculate the activation energy  $E_a$  of the secondary (undesired) reaction based on the data in Table 1 and using:

$$E_a = \frac{R \ln(q_1/q_2)}{\frac{1}{T_2} - \frac{1}{T_1}}$$

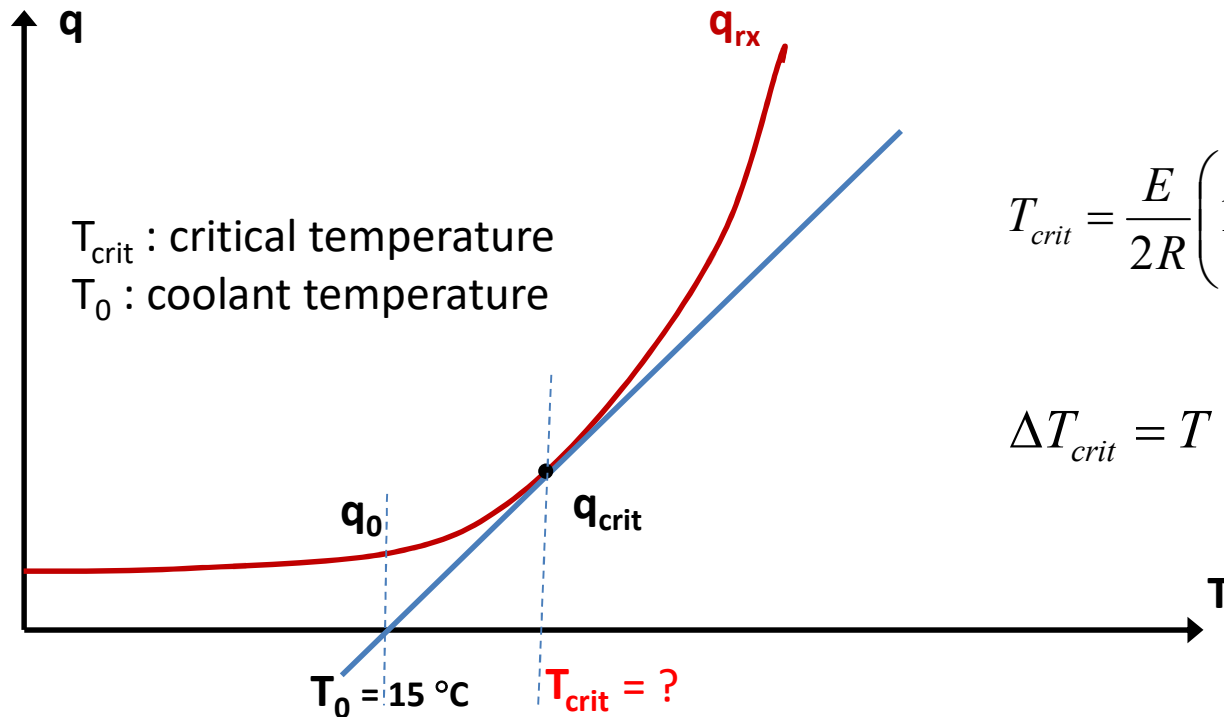
- ii. Determine  $TMR_{ad}$  using:

$$TMR_{ad} = \frac{C_p R T^2}{q E_a}$$

- iii. What is the temperature when the time to maximum rate ( $TMR_{ad}$ ) is 24hrs (i.e.  $T_{D24}$ )

- iv. What is the Stoessel Criticality Class?

## Exercise 3: Reactor stability - critical temperature



$$T_{crit} = \frac{E}{2R} \left( 1 \pm \sqrt{1 - \frac{4RT_0}{E}} \right)$$

$$\Delta T_{crit} = T - T_0 \geq \frac{RT_{crit}^2}{E}$$

1. What is the minimum temperature difference between the cooling medium and reaction mixture required for stable reactor performance?
2. What is the maximum temperature of the cooling medium that will allow for a stable reactor if the required process temperature is 80 °C?

**End**

# Contact us

## **Paul Sharratt**

Institute of Chemical & Engineering Sciences

Principal Scientist

## **Shaik Salim**

Institute of Chemical & Engineering Sciences

Principal Specialist

Tel: +65-67963950

Email: [shaik\\_salim@ices.a-star.edu.sg](mailto:shaik_salim@ices.a-star.edu.sg)



CREATING GROWTH, ENHANCING LIVES



**Thank you**

