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# The Role of Reaction Calorimetry in the Development of Safe, Efficient and Reliable Chemical Processes

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# Agenda

| | |
|---|---|
| 1 | What is Reaction Calorimetry? |
| 2 | Reasons to Perform Reaction Calorimetry |
| 3 | Technical Aspects |
| 4 | Our Reaction Calorimetry Market Offering |
| 5 | Appendix |

# Definitions& Concepts

In general, calorimetry is the measurement of heat.

Heat is thermal energy, which derives from the vibrations and movement of molecules

Heat is usually released when bonds are formed between atoms

The rate of heat release is proportional to the overall rate of the reaction

In the first instance, releasing heat increases the temperature of the reaction mixture

Calorimetry requires accurate control and measurement of temperature

METTLER TOLEDO AutoChem provides solutions for Reaction Calorimetry

Reaction calorimetry is a non-destructive, real-time technique that provides chemical process data. It is widely used by process and development chemists as well as dedicated process safety engineers. A reaction calorimeter accurately measures the enthalpy changes of chemical reactions ("reaction enthalpy")

# What Does Reaction Calorimetry Tell Us?

When does a reaction start?

When does a reaction stop?

What factors influence the reaction rate?

How much energy is released, and when?

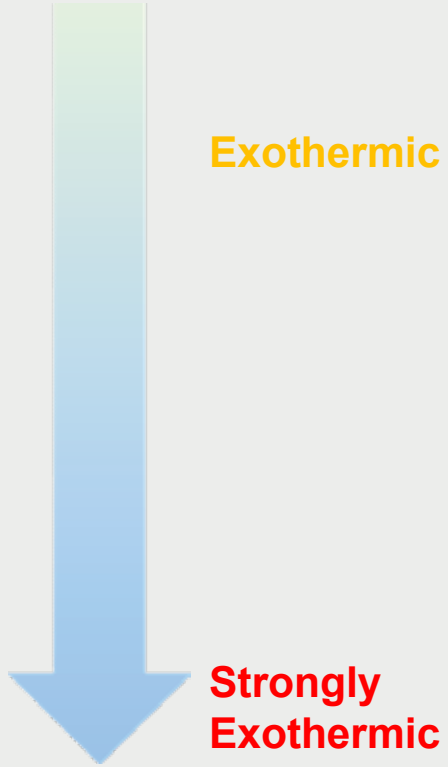
Calorimetry can also help to derive:

- Reaction mechanisms, pathways
- Reaction Kinetics
- Critical Process Parameters, CPP (dosing, mixing …)
- Scale up parameters (KJ/kg, cooling potential …)
- Safety Parameters (ΔTad, MTSR ...)

# Typical Reaction Enthalpies

**Reaction Enthalpies vary widely between reactions. It is obvious that the amount of energy released is directly linked to the potential damage in case of an accident.**

| Typical Example of Reaction Type | Energy H kJ.mol$^{-1}$ |
|---|---|
| Neutralization (HCl) | -55 |
| Hydrolysis (Acetic Anhydride) | -57 |
| Polymerization (Styrene) | -60 |
| Epoxidation | -100 |
| Neutralization (H2SO4) | -105 |
| Amination | -120 |
| Nitration | -130 |
| Sulphonation | -150 |
| Hydrogenation (Alkene) | -200 |
| Hydrogenation (Nitro) | -560 |

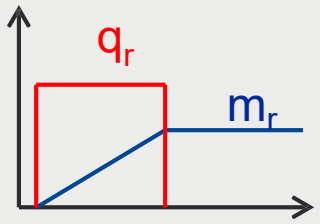


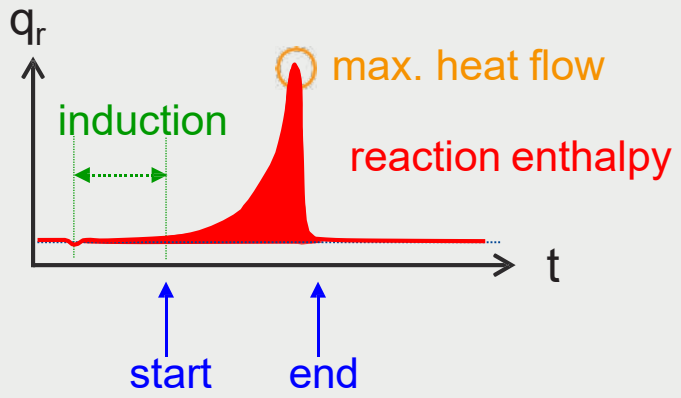
# Why is Reaction Calorimetry Critical?

**Reaction Calorimetry provides the basic information to create safe and scalable processes**

Provides information about progress reaction

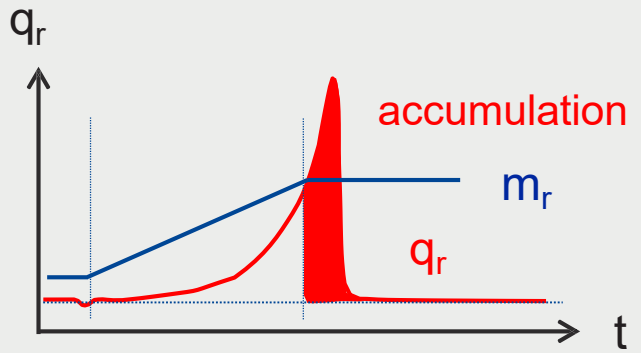
- Induction time
- Start and End of reaction
- Maximum heat flow
- Reaction enthalpy
- Heat flow in function of dosing




Provides information about potential safety issues

- Accumulation of reactants
- Non-scalable conditions

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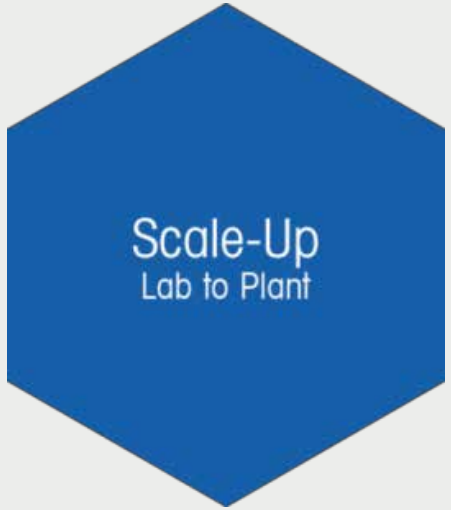
# Where and When is Reaction Calorimetry Applied?

## The Three Pillars of Application


Improve the understanding of a chemical reaction from the thermal behavior point of view




Go deeper into the thermodynamics before the geometrical scale-up

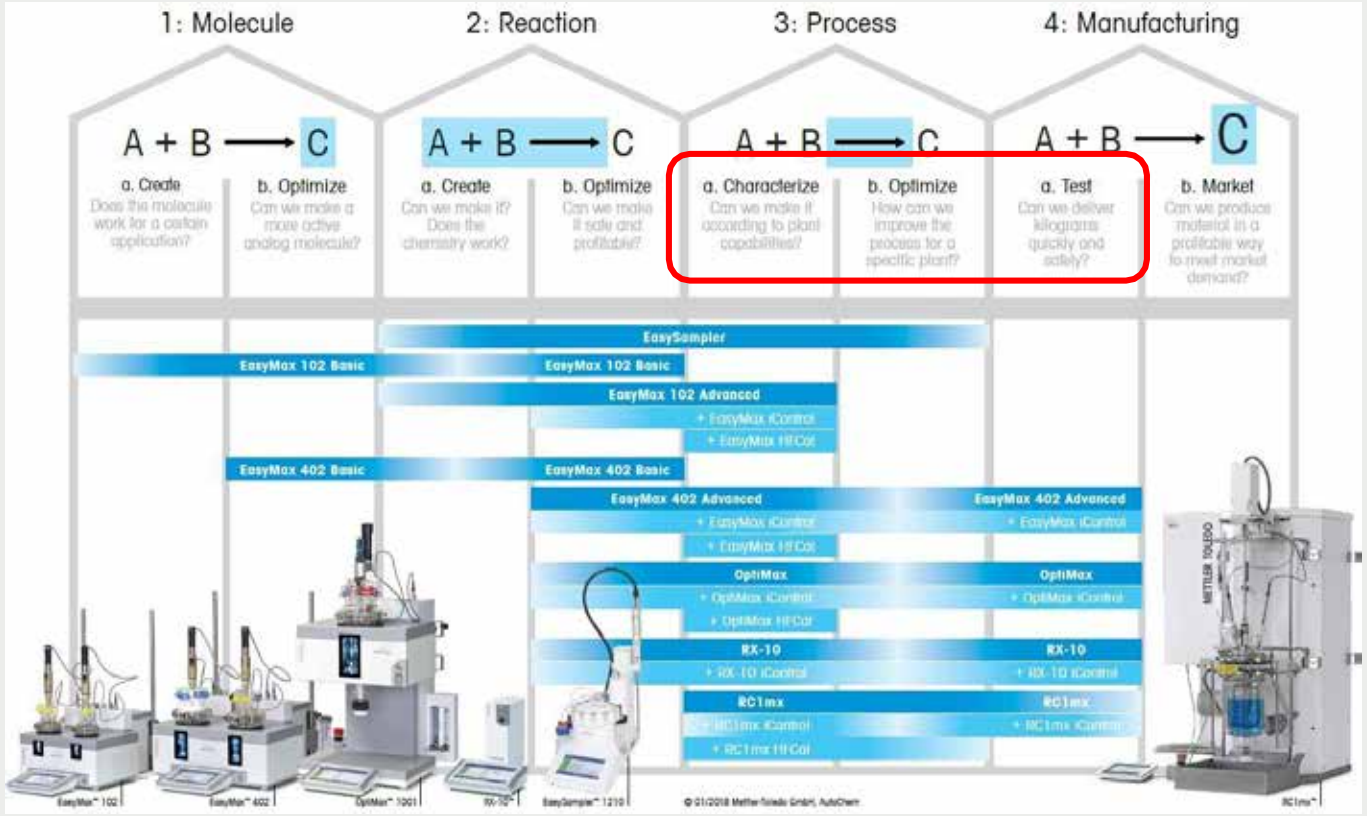

Quantify the process risks

Safely explore a wide range of conditions and process upsets

# Where Does MT AutoChem Offer Solutions?

MT calorimeters are optimized primarily for liquid-phase reactions

The focus on process safety, scale up and process understanding (see ▭ )

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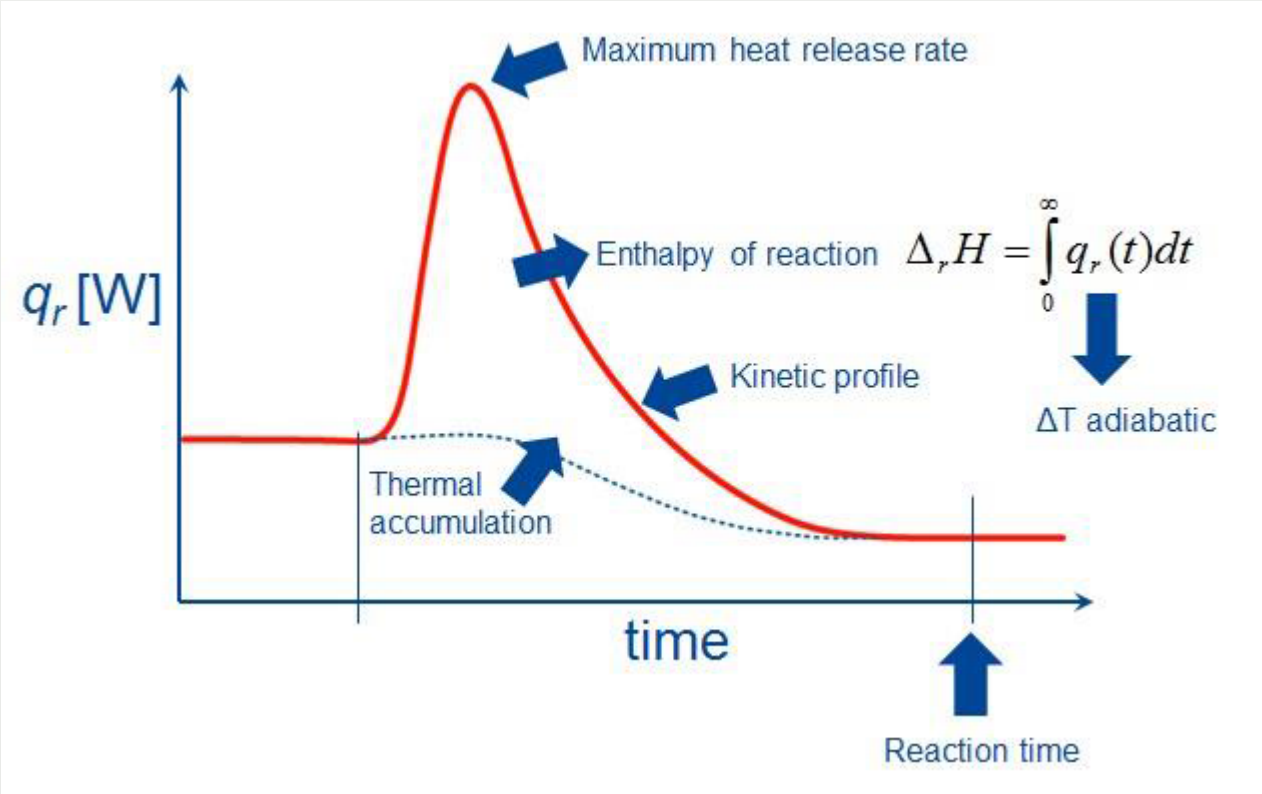
# Reasons to Perform Calorimetry in R&D

## 1. Reaction / Process Understanding – Points of Interest

Scalability
Start/Stop
Accumulation
Reagent, Solvents
Catalysts
General conditions
CPPs (Kinetics,
Thermal accumulation...)

Process Understanding R&D

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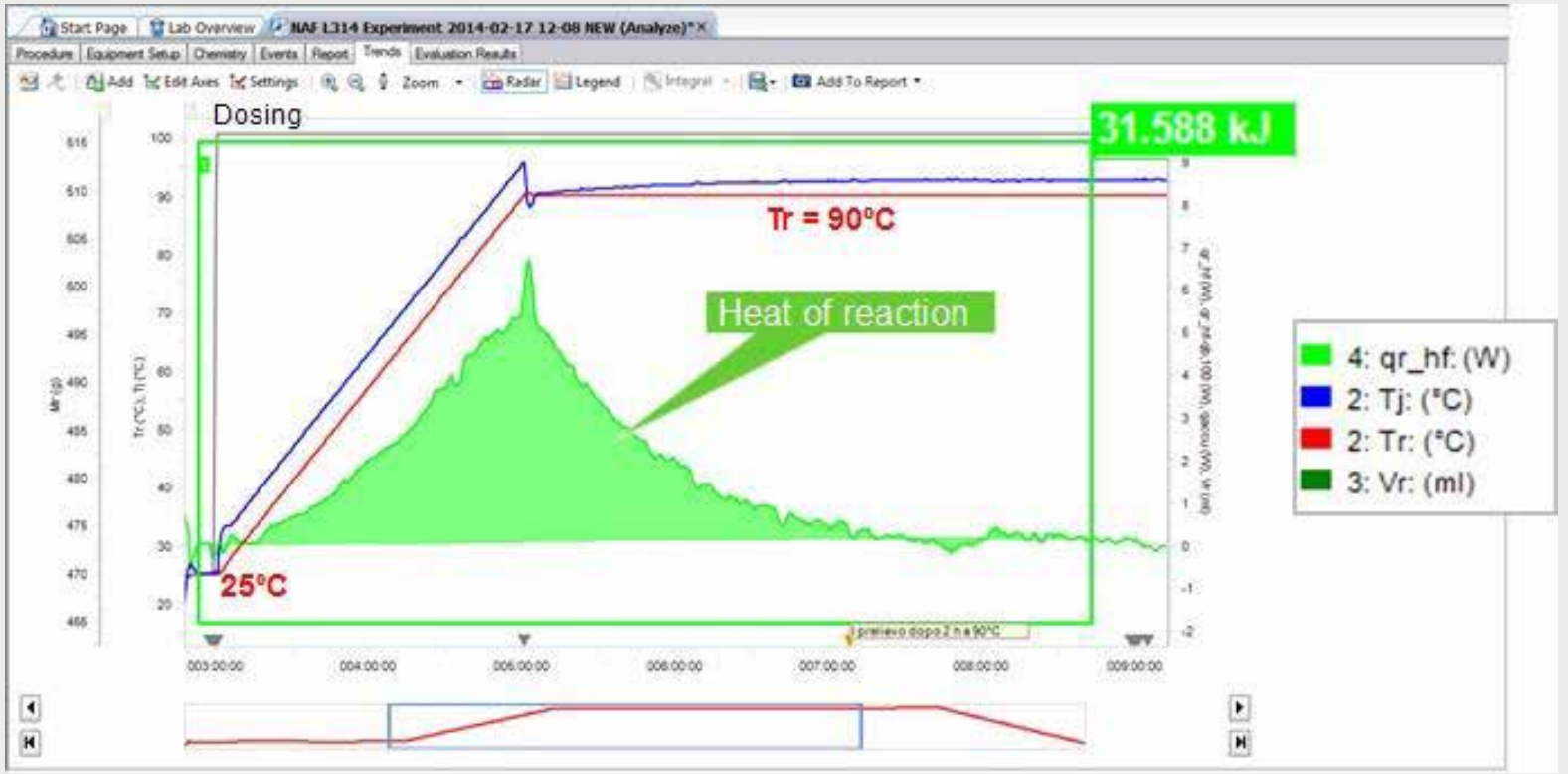
# Reaction and Process Understanding




- Check behaviour of process at small scale (100ml or less)
- Assess scalability (heat release)
- Identify critical process steps
- Rapid screening of process parameters
- Parallel reactions

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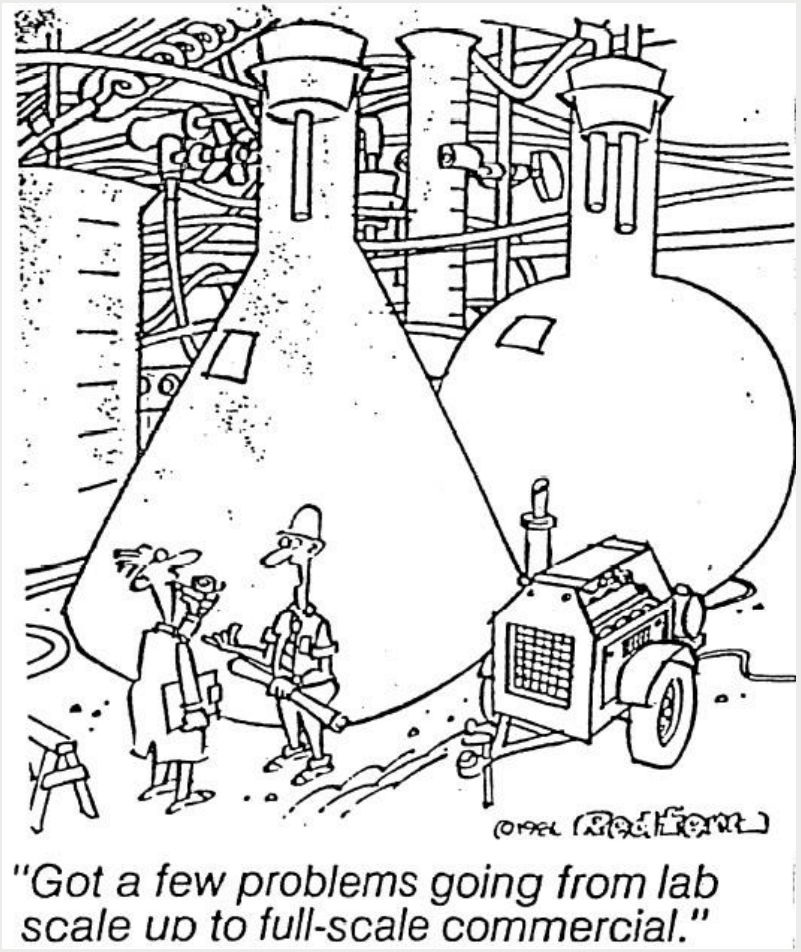
# Reasons to Perform Calorimetry: Scale-up

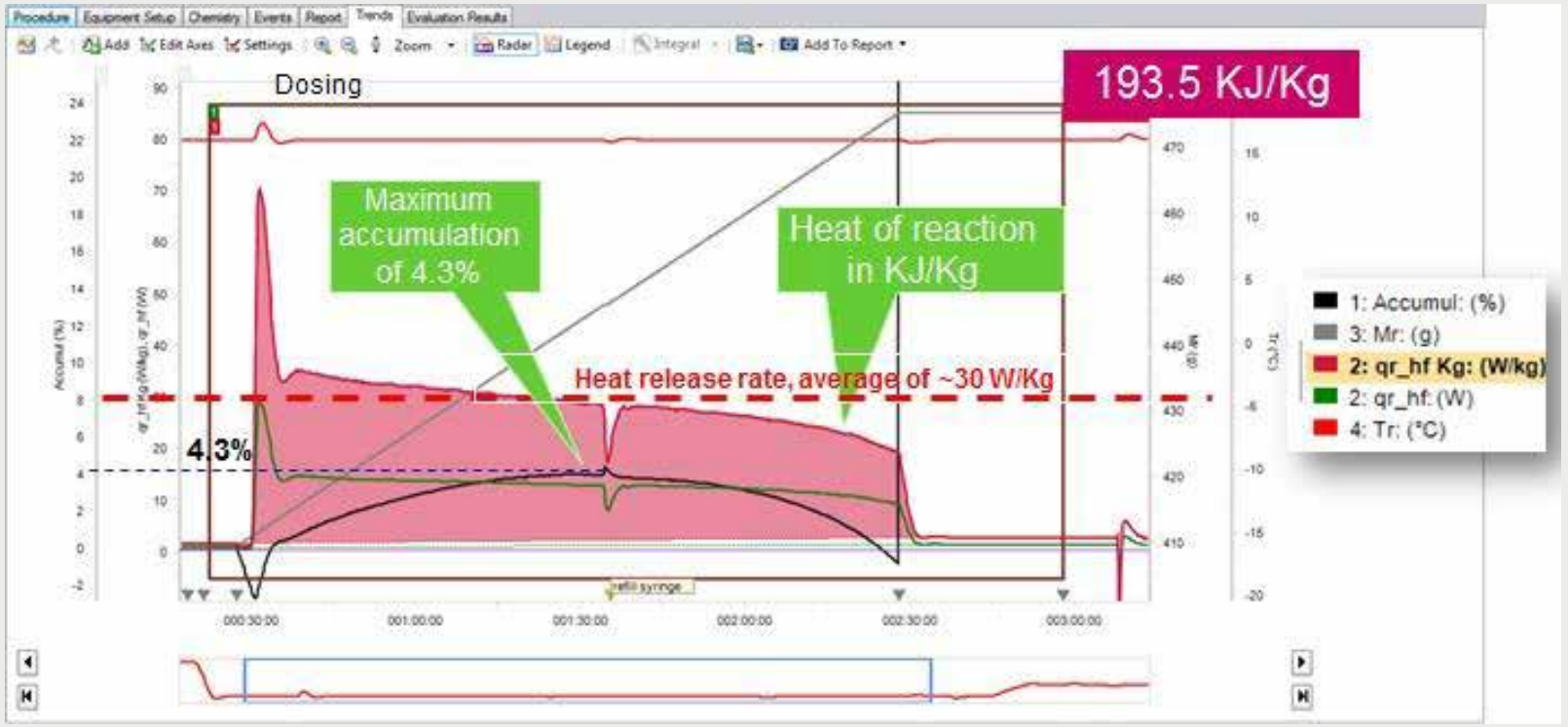
## 2. Process Scale-Up – Points of Interest

- Energy balance
- Temperature Profile
- Cooling Requirement
- Mixing / Mass Transfer
- Dosing profile
- Yield / Quality
- Optimization
- Fit to Plant

"Got a few problems going from lab scale up to full-scale commercial."

# Process Scale– Up




- Assessment of Enthalpy, Heat Capacity, Heat Transfer & Mass Transfer under **Process-Like Conditions** (up to 1 litre scale)
- Develop dosing and temperature profiles
- Optimize critical process steps

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# Reasons to Perform Calorimetry in Safety

## 3. Process Safety – Points of Interest

- Ensure safety of process
- Understand limits
- Evaluate risks
- Avoid disasters
- Protect the environment
- Save lives


Magnablend, Waxahachie TX, October 2011

# Safety Concept Assessment

***Chemical reaction***

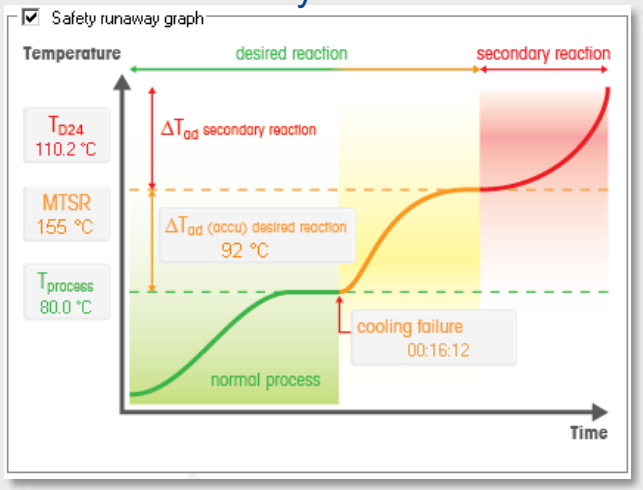
- Heat of reaction?
- Can the heat be removed ?
- Is the boiling point triggered ?
- Gas involved ?
- Heat capacity
- Delta T adiabatic

**CALORIMETRY**

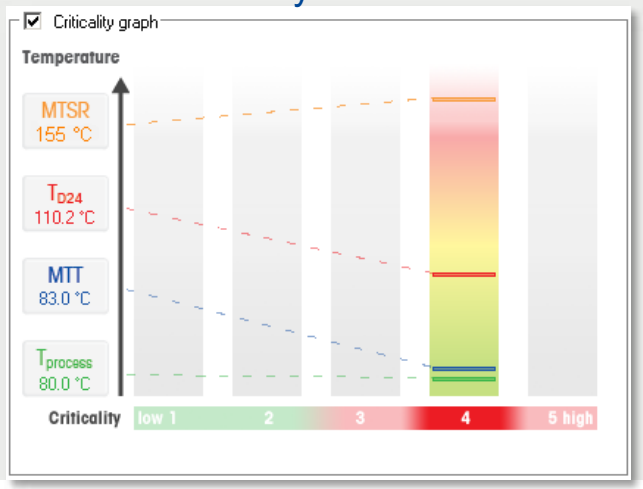
***Decomposition reaction***

- Heat of reaction?
- Heat capacity?
- Boiling point triggered?
- Gas involved?
- Final temperature triggered?

Runaway scenario




Criticality scenario

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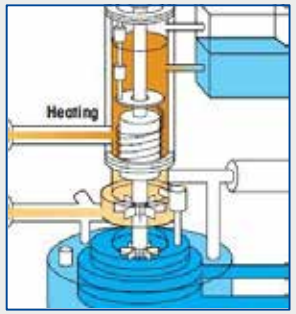
# Why Perform Risk Assessment?

**The 6 questions that help to develop the runaway scenario and provide guidance for the determination of data required for the risk assessment:**




### Question 1

Can the process temperature be controlled by the cooling system?


### Question 2

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


### Question 3

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


### Question 4

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


### Question 5

How fast is the runaway of the desired reaction?

### Question 6

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

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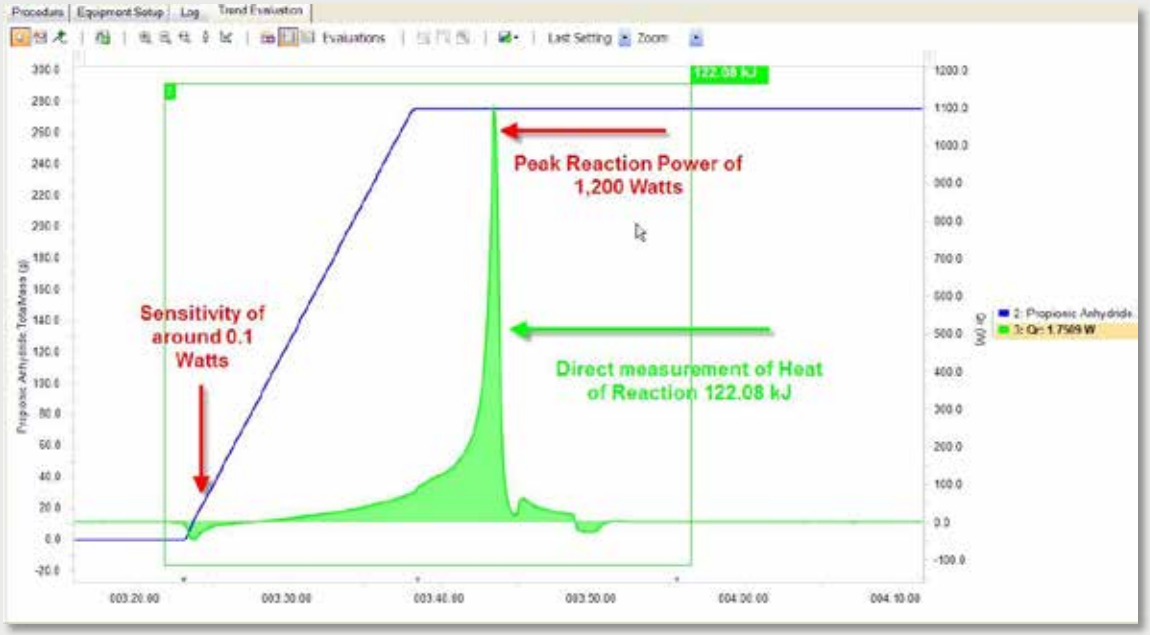
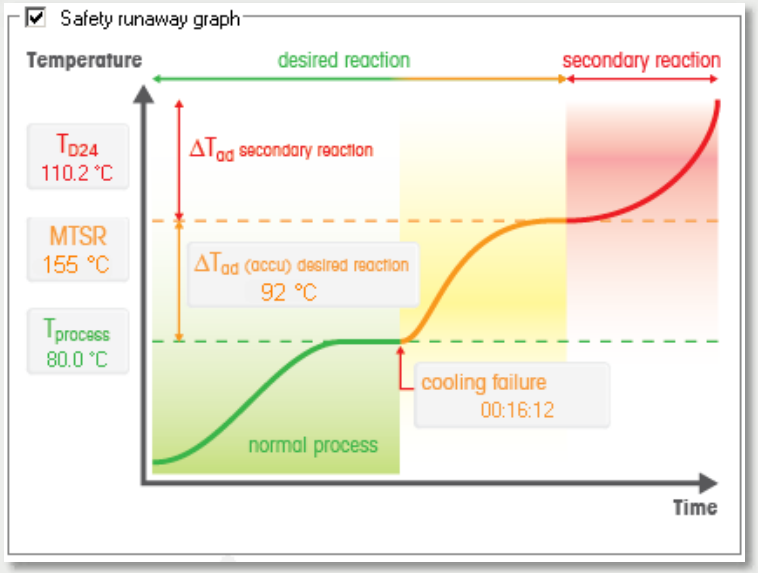
# Process Safety





- Assessment of Enthalpy, Heat Capacity, Heat Transfer, Mass Transfer under **Process-Like Conditions**
- Safely explore wide range of conditions and process upsets
- Quantify the process risk

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# What Bad Calorimetry Data Means

**Bad Calorimetry Data = Lack of understanding of thermochemistry**
**Potential risk for accidents**

For the User

- Difficulty interpreting the results equates to a waste of time
- Inaccurate results
- Risk of personnel injuries

For the Management

- No trust in data  Plant cannot be run in an optimal way
- Need to apply large "safety buffers" resulting in a less efficient process
- Risk of accidents

For the Company

- Environmental consequences
- Monetary and reputation loss

# What Good and Reliable Calorimetry Data Means

**Accurate and Precise results will allow you to design a better and safer process at lower cost (when you need it most!)**

An integrated thermostat will

- have better and faster control
- ensure that system can be run isothermally
- Provide heat capacity (Cp) data and good results under non-isothermal conditions
- be safer in case of emergency

"Simple experiments" will work with most systems, however …

Calorimetry with external circulator/cryostat will be more difficult if the reaction

- is highly exothermic
- is non-isothermal
- has large changes in Heat Transfer properties (viscosity, precipitation etc.)

For challenging experiments, the accuracy of the RC1mx is much better

The RC1mx will get good results for reactions under difficult but real conditions

- close to boiling temperature
- under reflux

# Our Reaction Calorimetry Market Offering

**Mettler-Toledo AutoChem provides you with:**

- Global Support and Service with local contacts
- Over 30 years of Applications Know-How and Experience
- Over 1000 satisfied users across the chemical industry
- Web support, User Meetings, International Conferences
- AutoChem Community Website
- A comprehensive range of options and accessories
- Continuous research and development of new technologies
- Unique RTCal Real Time Calorimetry – save time and money
- Modern, reliable hardware and software – maximum utilization rates
- Proven ROI – case studies available

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