PRACTICAL CONSIDERATIONS IN THE APPLICATION OF CALORIMETRY FOR REACTIVE HAZARD ASSESSMENT

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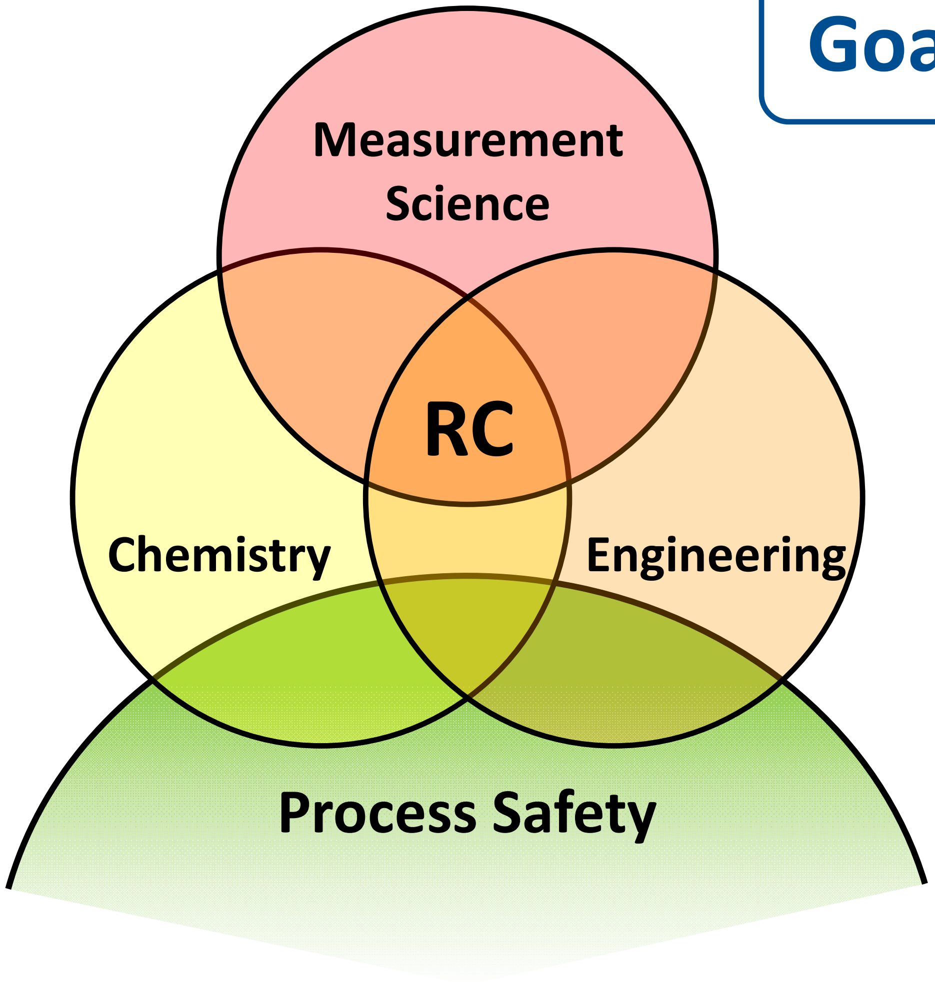
Outline

- The Reactive Chemicals discipline at Dow
- In general: calorimeters and their use cases in reactive hazard testing
- Discussion of applied calorimetry (and related methods), grounded in their thermodynamics and operating principles
  - Screening with differential scanning calorimetry (DSC)
    - ✓ Detection of autocatalysis by rapid screening vs. isothermal testing
  - Calorimeter-like screening alternatives (Thermal Screening Unit, TSu)
    - ✓ DSC + TSu as a substitute for more sophisticated calorimetry
  - Pseudo-adiabatic: Accelerating rate calorimetry (ARC)
    - ✓ The origins and importance of thermal inertia (ϕ)
    - ✓ Factors complicating use of ARC
  - Low thermal inertia: Vent Sizing Package (VSP2)

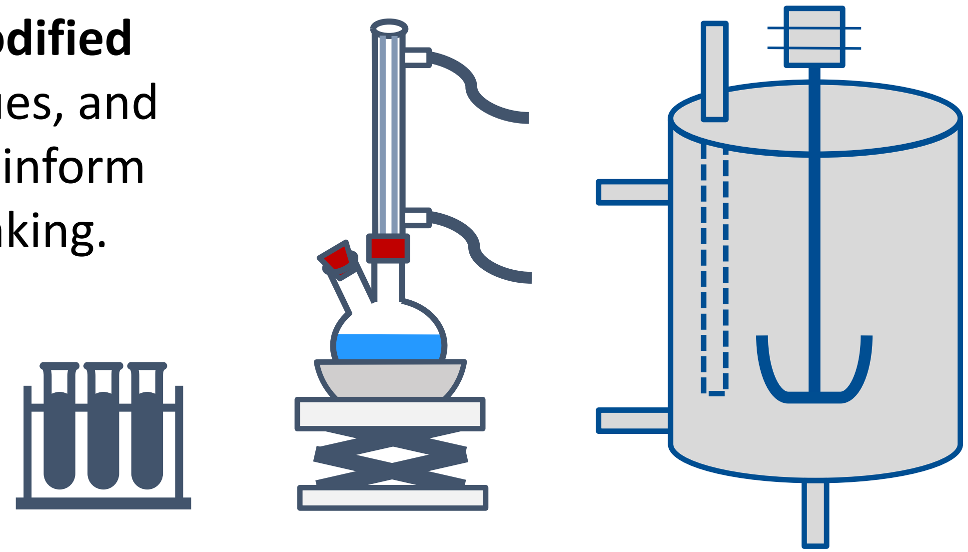
THE REACTIVE CHEMICALS (RC) DISCIPLINE AT DOW



Goal: Safe chemical processes at all scales

One global team provides **continuity of knowledge** across geographies, businesses, and stages of process maturity.

We leverage **standardized** test methods, **modified** analytical techniques, and **novel research** to inform safe decision making.

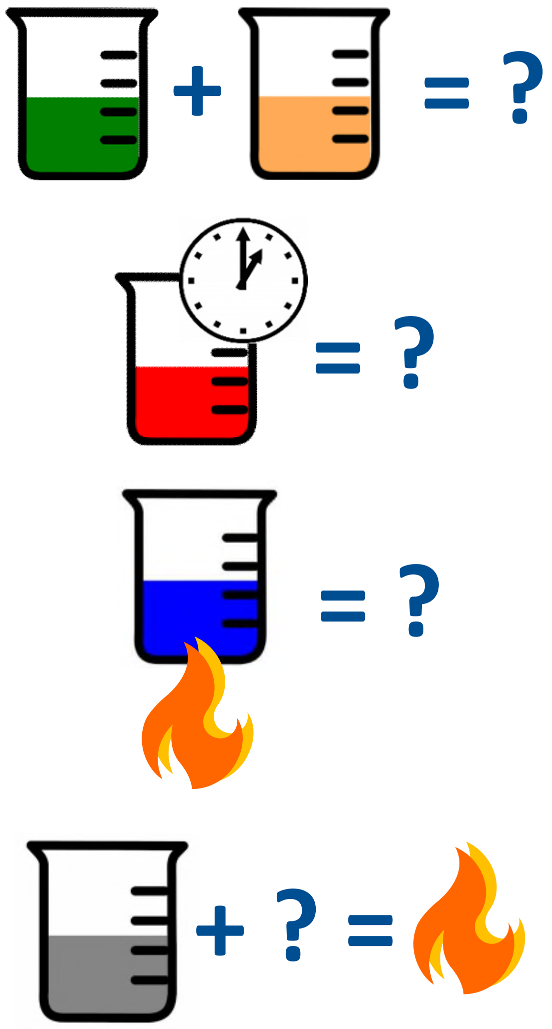


Why we use calorimetry to enable safe chemical synthesis

- Ensuring safe chemical synthesis requires we understand:
  - **Total energy release**
  - **Rate of energy release**

  ⟵ Calorimetry data

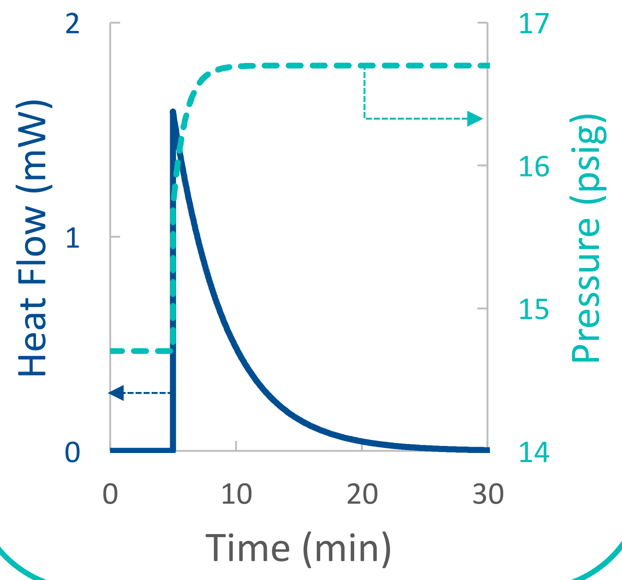
  - **Rate of energy removal** (closing the heat balance)
- We study these at **desired**, **upset**, and **failure** conditions
  - Think through possible "what if" scenarios:
    - ✓ Mixing, desired addition, undesired contamination, pooling
    - ✓ Effects of storage or thermal aging
    - ✓ Heating beyond intended operating conditions
    - ✓ What conditions lead to fire or explosion
- Calorimetry provides data essential for process design
  - **Thermodynamics** (vapor pressure, enthalpy of reaction)
  - **Energy release rates** (apparent kinetics)



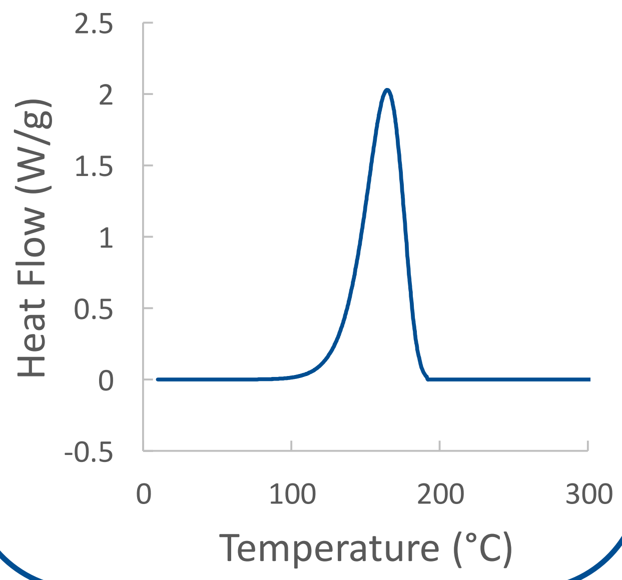
CALORIMETERS HELP US SAFELY STUDY HEAT (AND SOMETIMES PRESSURE)

What?	Why do we study it?	What causes this to occur?
Heat	"Universal chemical sensor"	Both desired and undesired reactions release heat
Pressure	Pressure causes vessels to rupture	Vapor pressure, thermal expansion, gas evolution

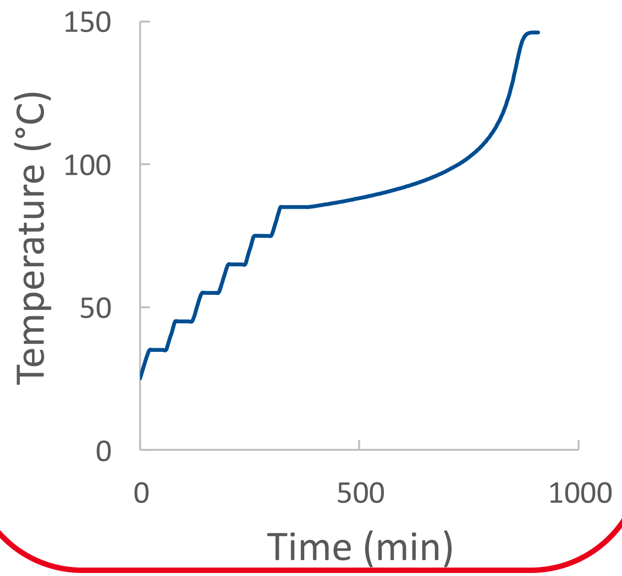
Isothermal (constant temperature)



Dynamic (varying temperature)



Pseudo-Adiabatic (thermal runaway)



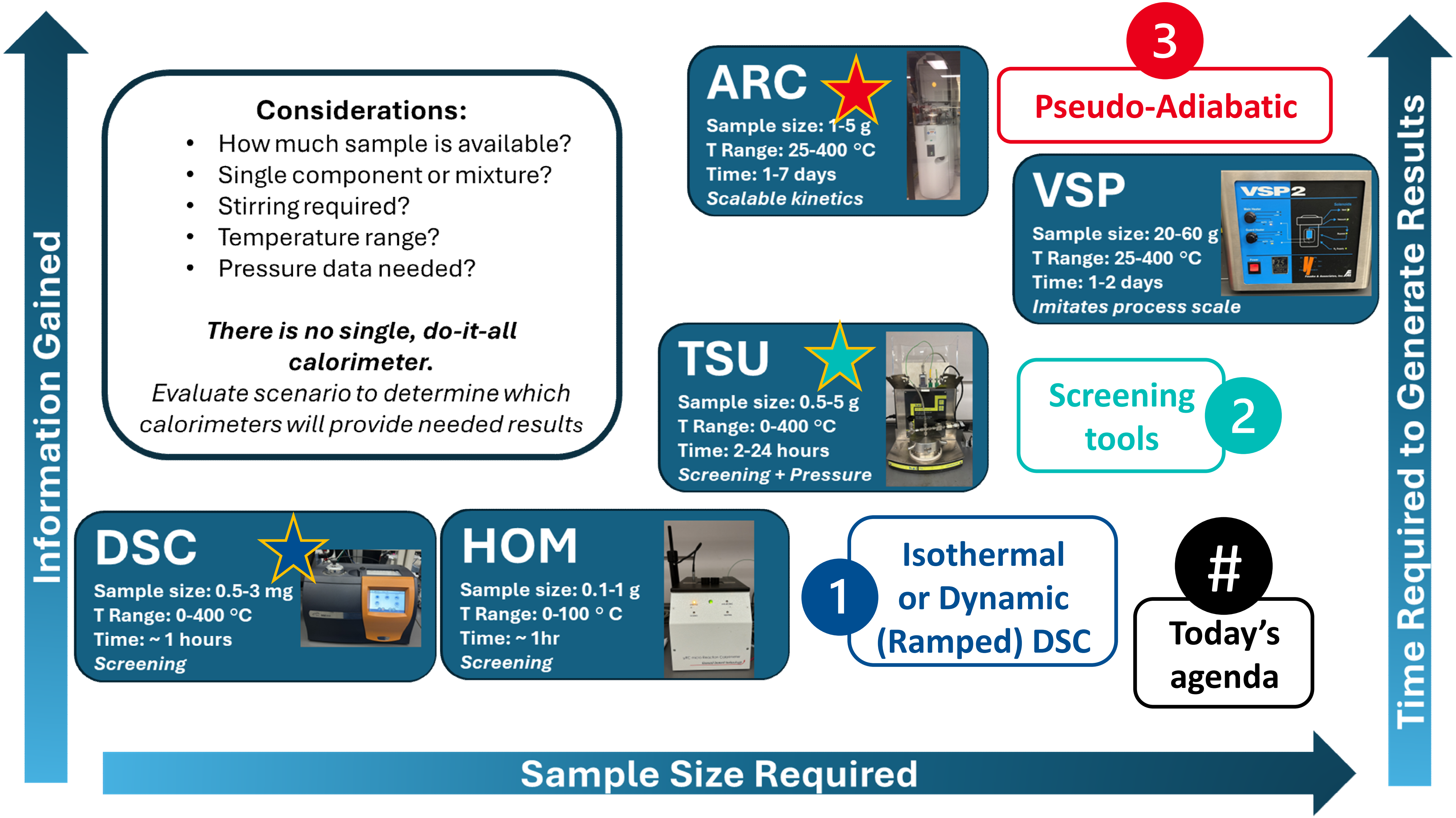
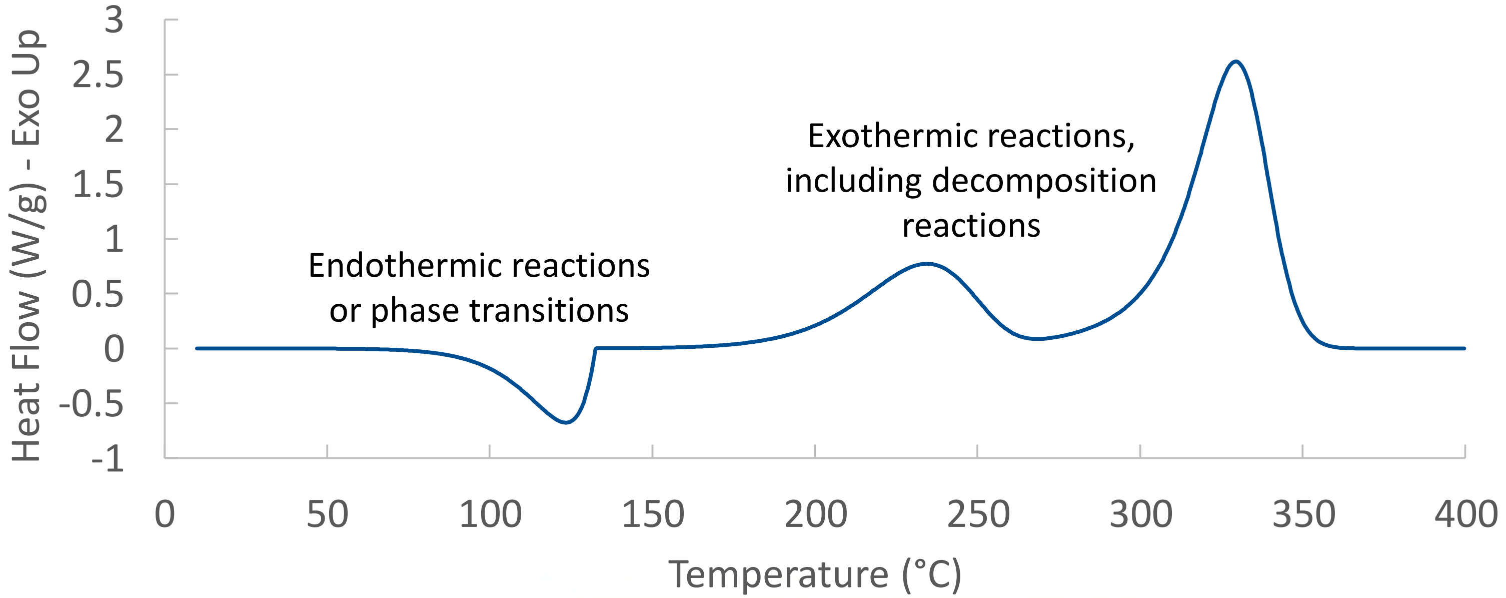


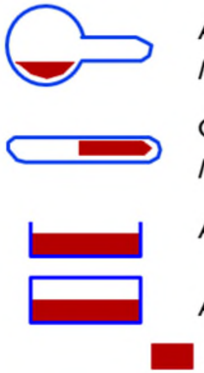
Figure from Sussman; Mulligan; Nichols, J. E. *ACS Chem. Heal. Saf.* **2025**, *32*, 600–611.
Photographs by K. Mulligan. Used with permission.

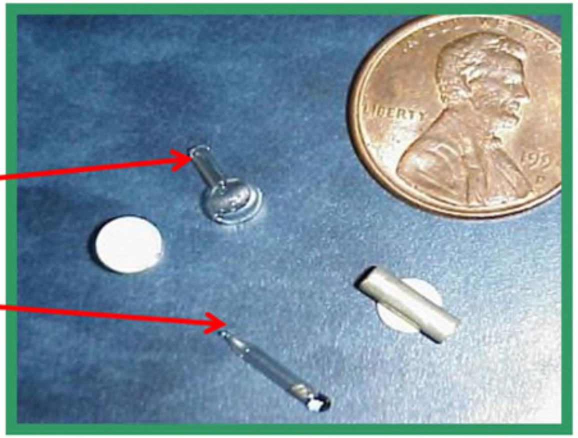
DIFFERENTIAL SCANNING CALORIMETRY (DSC) FOR RC TESTING



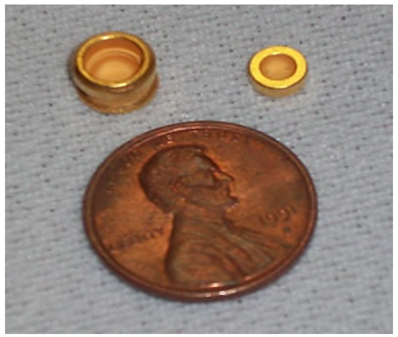
Advantages:

- Dynamic or isothermal (identifying autocatalysis)
- Small sample size (mg)
- Fast screening (<1 hr)
- Apparent thermokinetics
- Glass capillary or ampoule, with lower risk of instrument damage (vs. crucible or pan)





Gold-plated Crucible



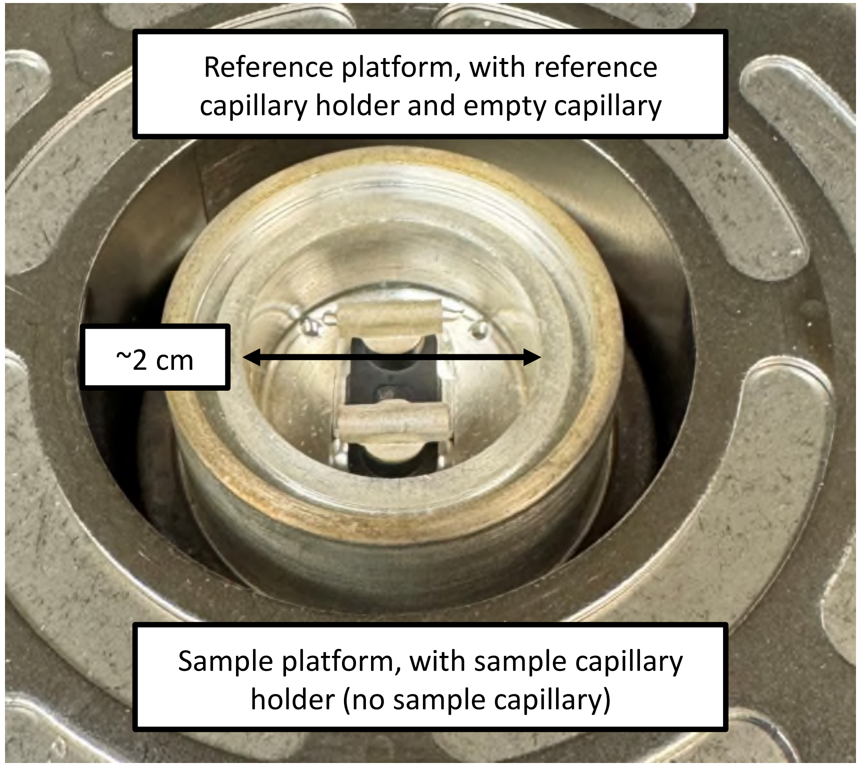
Disadvantages:

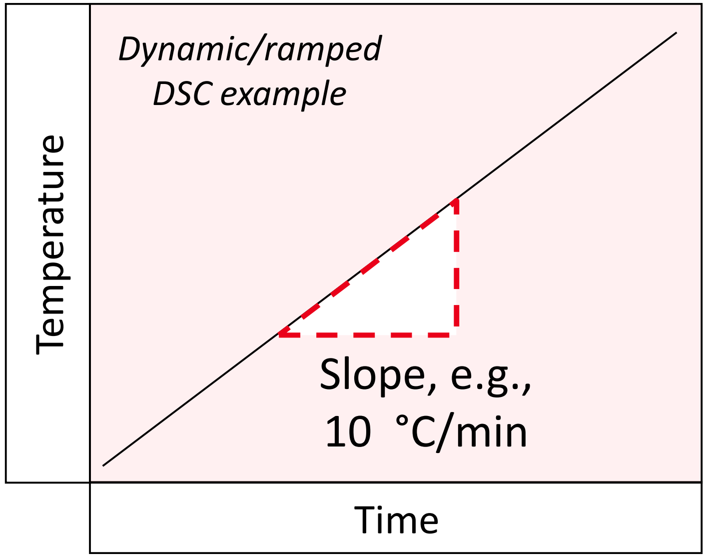
- No stirring/agitation/mixing
- No pressure measurement (except rupture)
- Chemistry-blind, with limited post-test options
- Direct application of data can be challenging

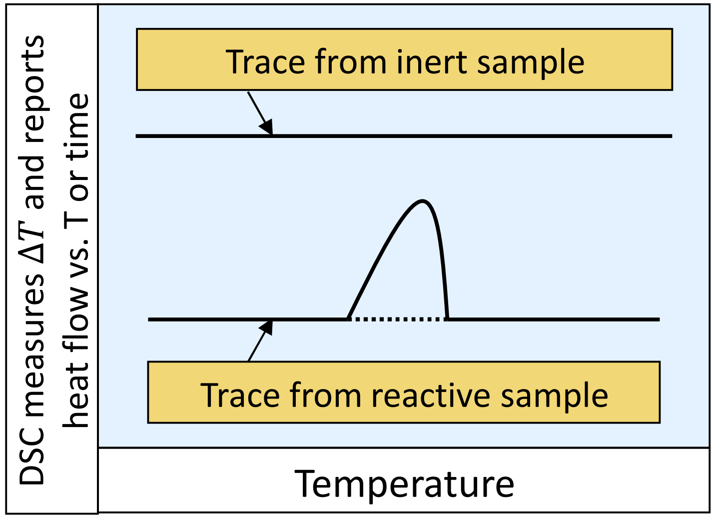
See also: Sheng et al. *Org Process Res Dev* **2019**, 23, 2200-2209

DSC OPERATING PRINCIPLES

Heat flux DSC measures heat flow during an imposed temperature change. Heat flow is determined by ΔT between sample and reference.

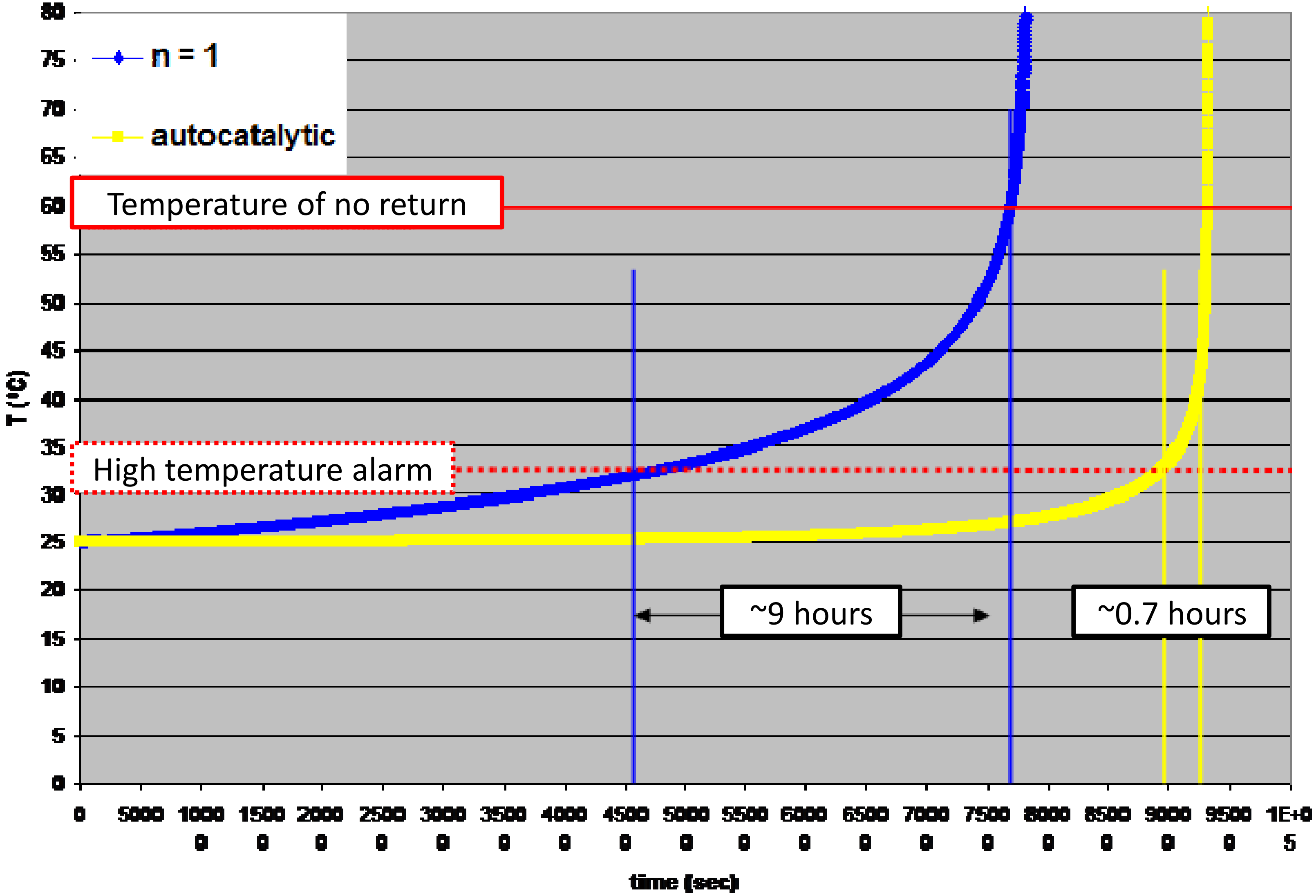






Advantage of capillary testing vs. traditional high-pressure pans or crucibles: Lower probability of instrument damage.

A CAUTIONARY NOTE ON AUTOCATALYSIS: WHY THE MECHANISM MATTERS

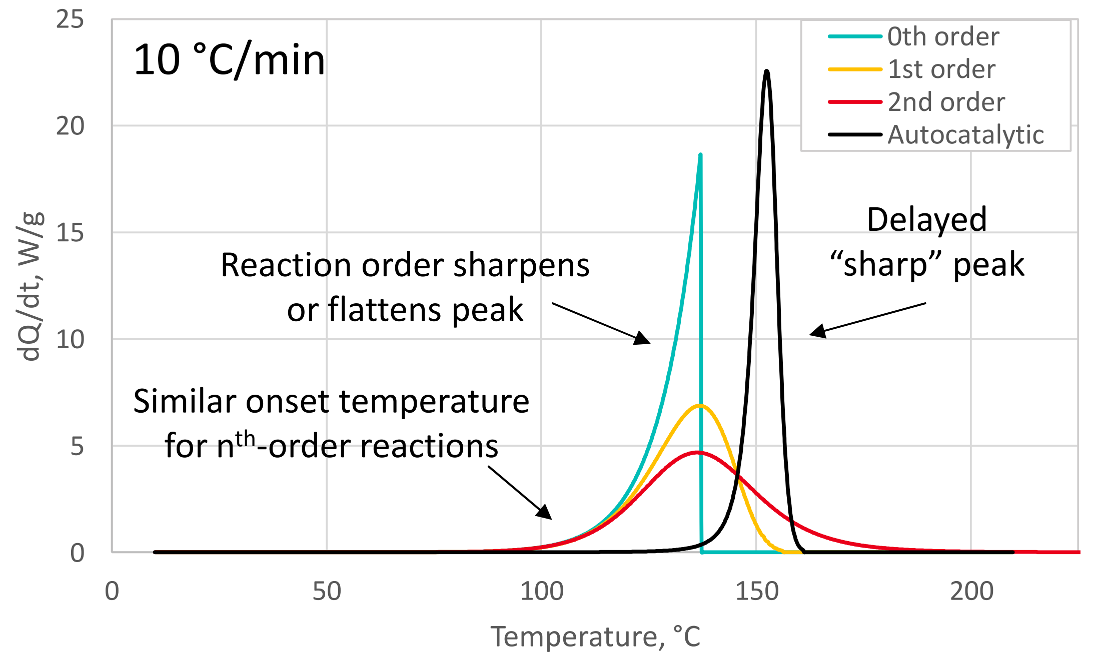


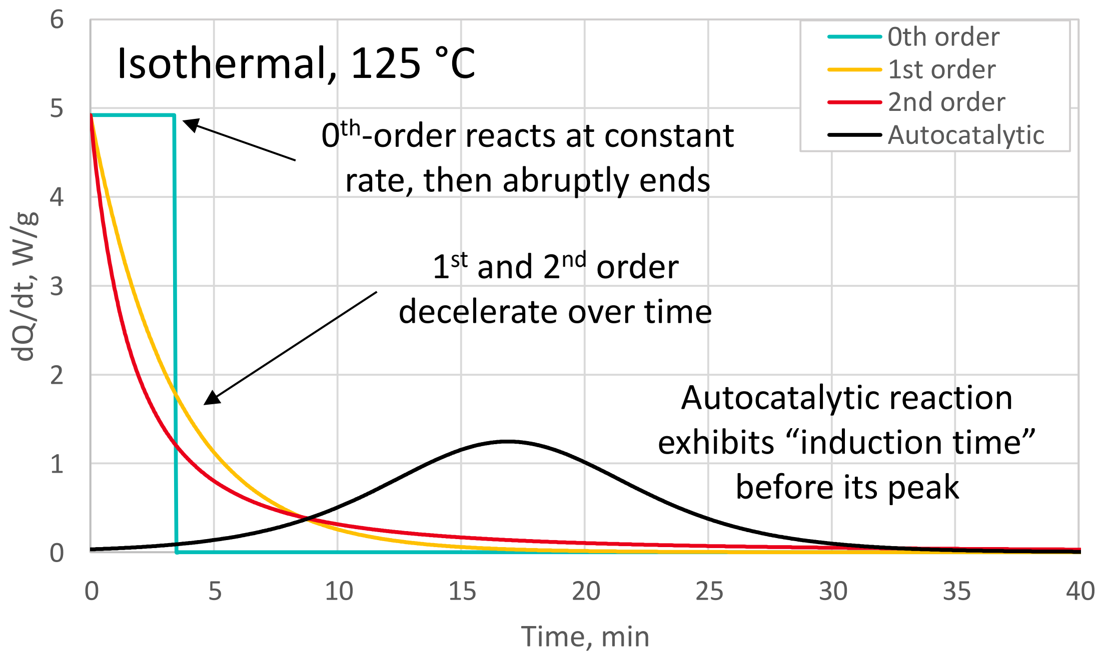
If protections are designed based on invalid assumptions, they can be wildly inadequate.

ALWAYS consider the mechanism of a reaction (or reaction<u>s</u>!) during design and validation of safeguards

Simulation by S. Horsch

The DSC thermogram: Ramped vs. isothermal





Most DSC testing is conducted in a ramped or dynamic mode.
Choose a maximum temperature well above range of interest!

Arrhenius-type model:
$\ln(k_0) = 40$ ln(1/s)
$E_a = 150$ kJ/mol
$n = 0$, 1, or 2
-1000 J/g reaction

Generalized autocatalysis model:
$\ln(k_0) = 40$ ln(1/s) $\ln(z_0) = -2$ ln(1/s)
$E_a = 150$ kJ/mol $E_z = 10$ kJ/mol
$n_1 = 1$ $n_2 = 1$
-1000 J/g reaction

Simulated DSC results by J. Nichols

Under isothermal conditions:

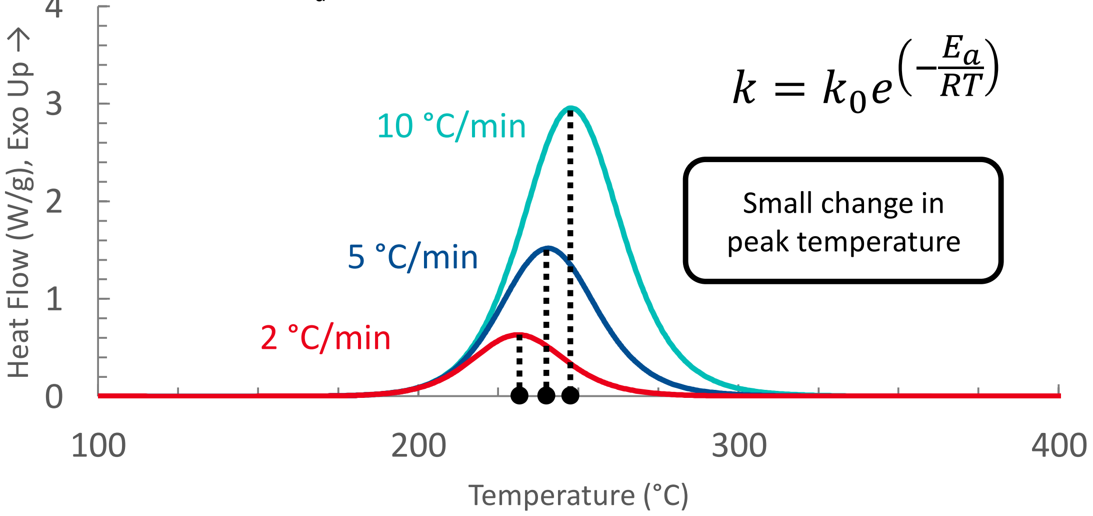
$$\frac{dQ}{dt} = \Delta H\, k_0 e^{-\frac{E_a}{RT}}$$
Constant rate: 0^{th} order

$$\frac{dQ}{dt} = \Delta H\, k_0 e^{-\frac{E_a}{RT}} (1-\alpha)^n$$
Deceleration: n^{th} order

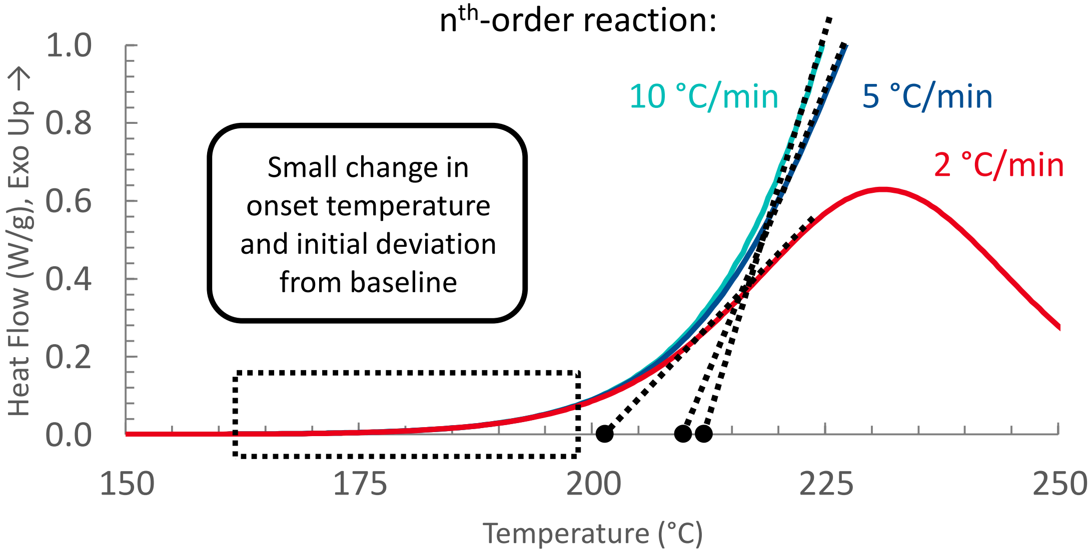
$$\frac{dQ}{dt} = \Delta H\, k_0 e^{-\frac{E_a}{RT}} (1-\alpha)^{n_1} \left(z_0 e^{-\frac{E_z}{RT}} + \alpha^{n_2}\right)$$
Acceleration: Autocatalytic

USING DSC SCAN RATE TO SCREEN FOR POTENTIAL AUTOCATALYSIS

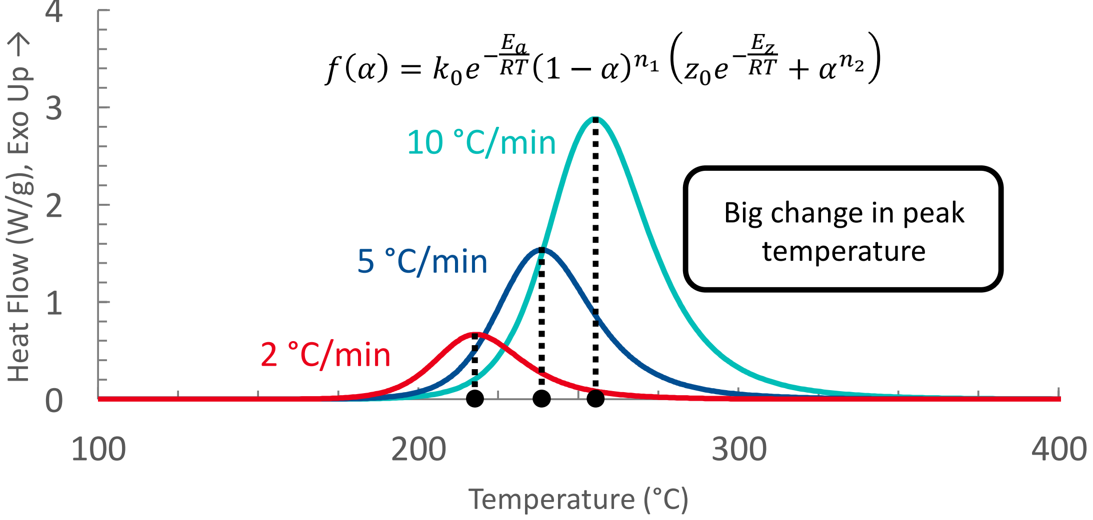
High E_a n^{th}-order reaction (Arrhenius-type)



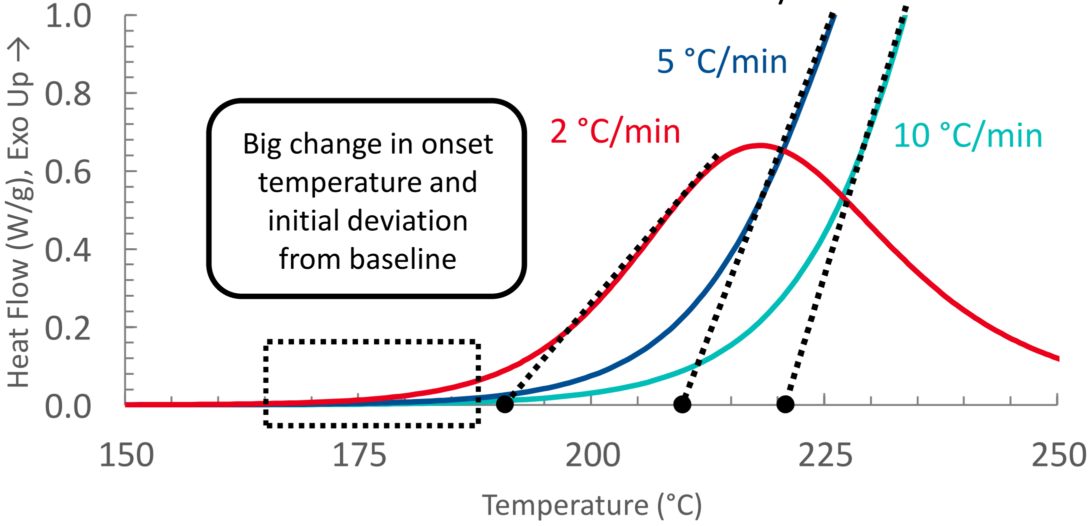
n^{th}-order reaction:



Generalized autocatalysis, e.g., for pseudo-species α:



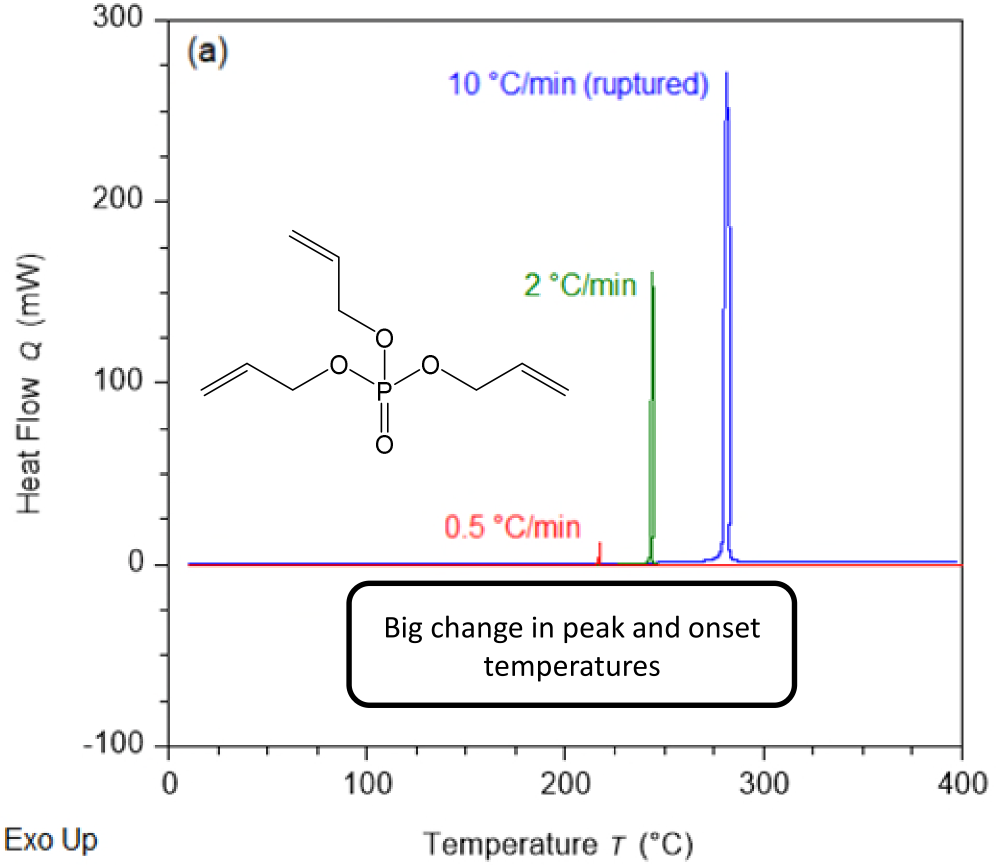
Generalized autocatalysis:



Simulated DSC results by J. Nichols

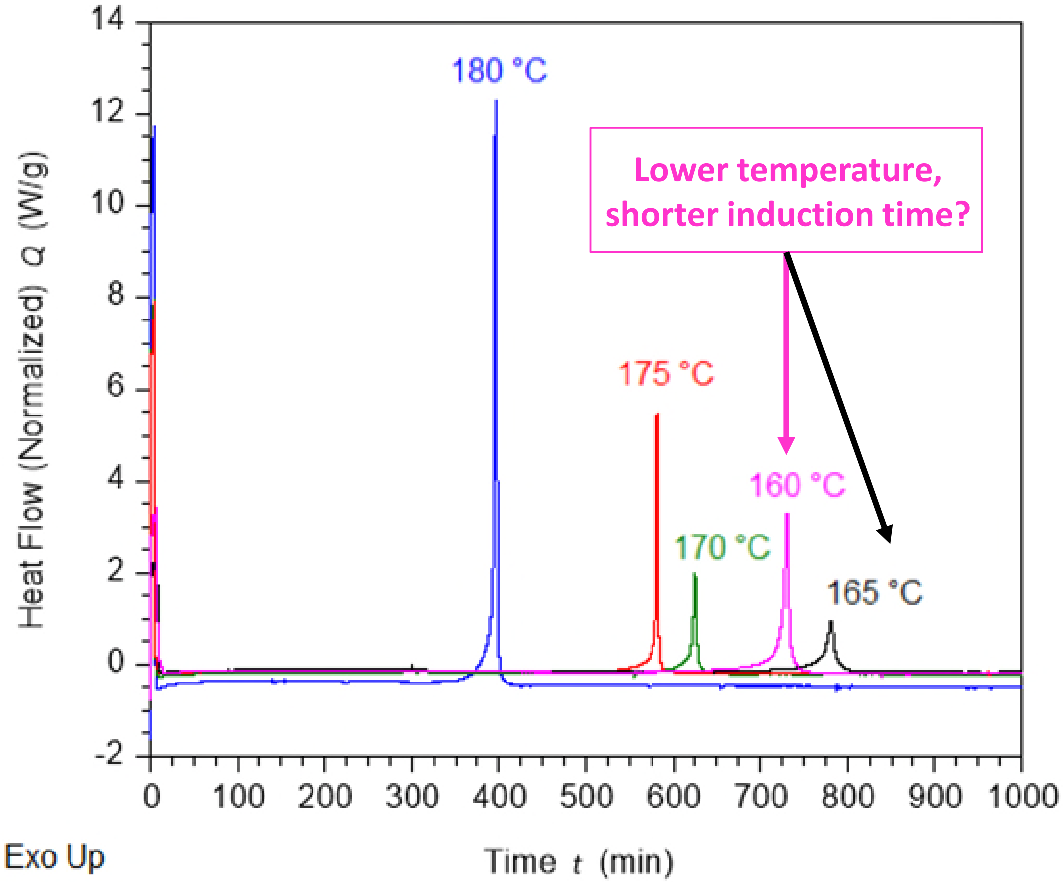
ADDITIONAL CONSIDERATIONS FOR AUTOCATALYSIS SCREENING

Initial screening by scan rate suggests autocatalysis; isothermal testing confirms it



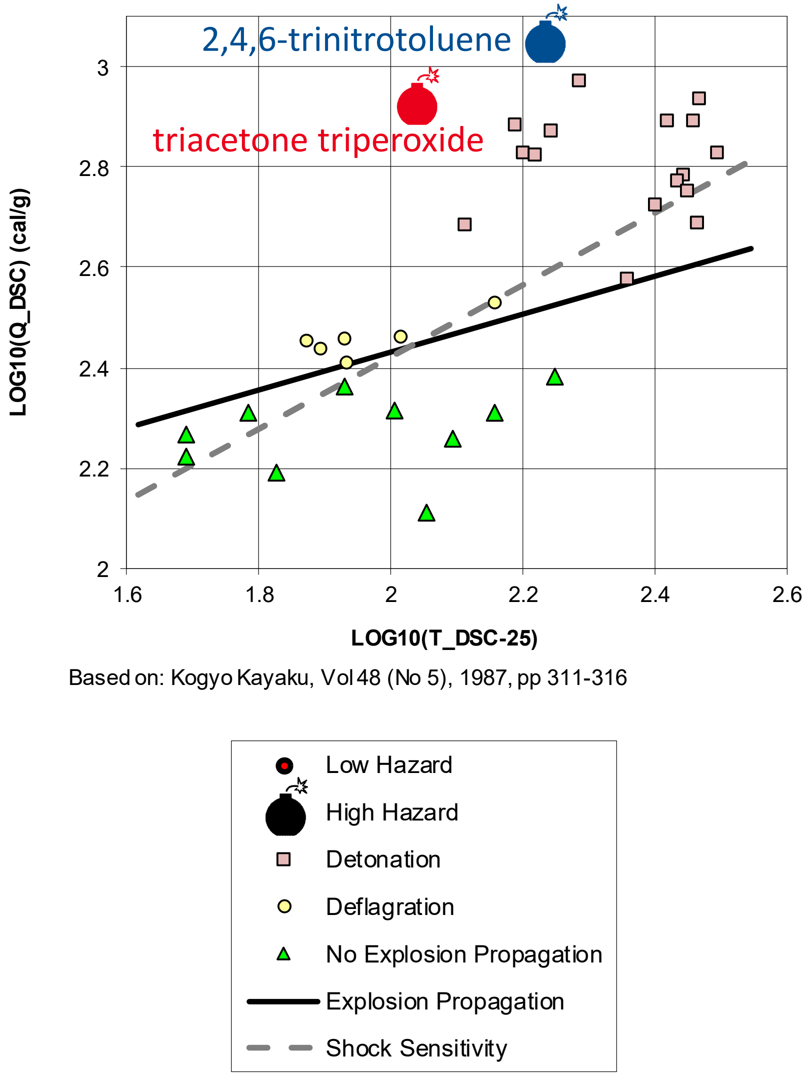
Data: T. Scholtz, E. Cayo, J. Nichols.
See also: Nichols, Scholtz, Horsch. *Chemical Engineering Progress* **2025**, 40–45.

Beware **hidden variables**: for this chemical induction time was sensitive to **internal system volume** and sample age



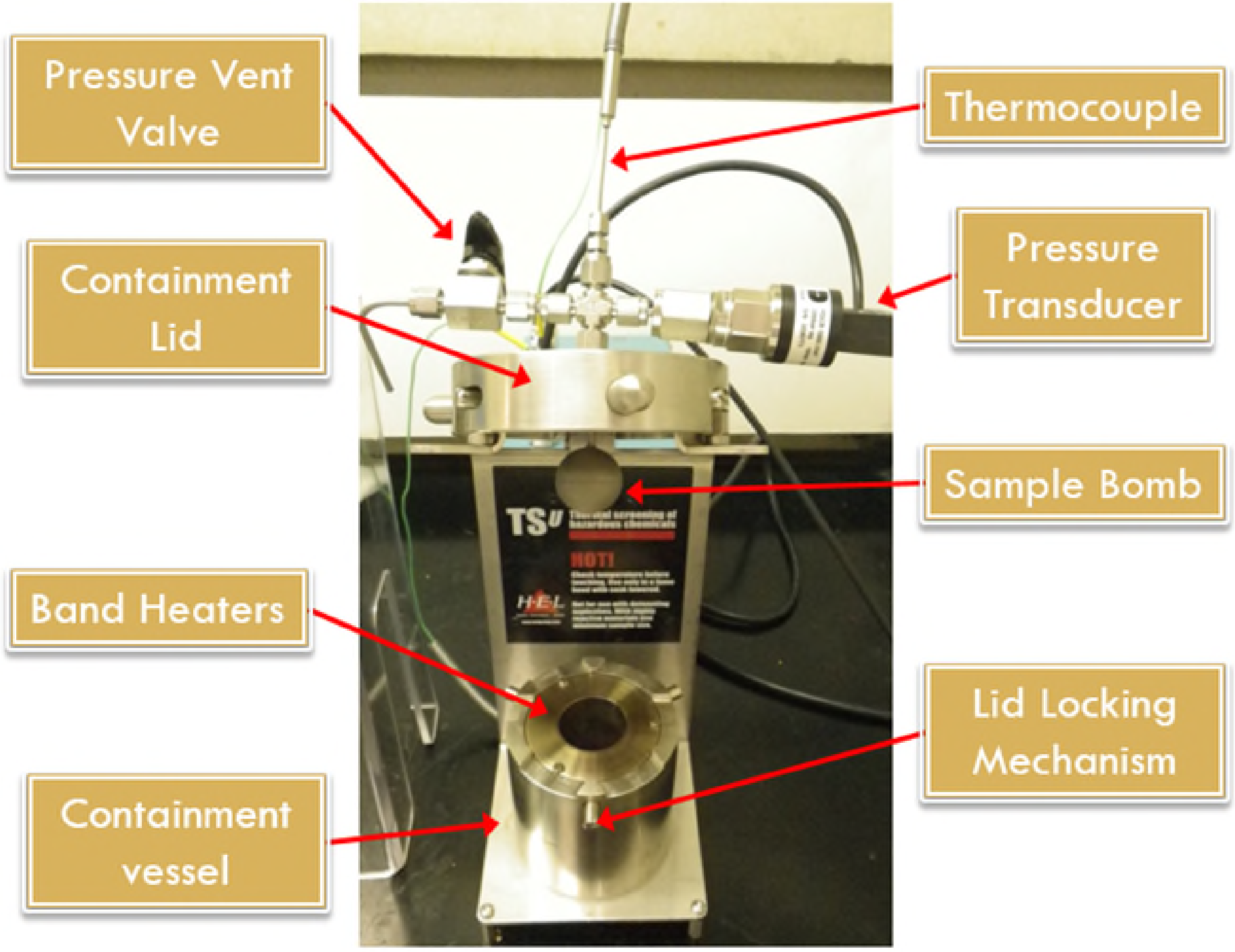
SCREENING FOR SENSITIVE ENERGETIC BEHAVIOR BY DSC

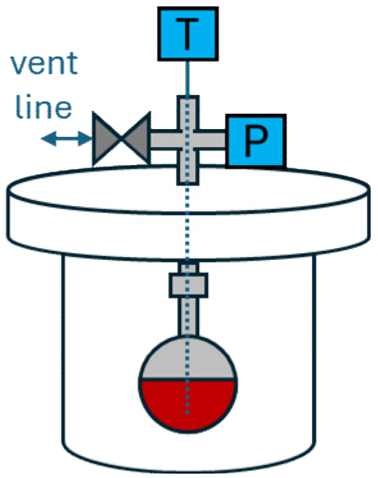
- DSC data can be correlated with sensitivity to shock and ability to propagate explosions, such as by Yoshida's correlation
  - ✓ Yoshida et al. *Kogyo Kayaku* **1987**, *48*, 311–316.
  - ➢ **Caution**: "Shock sensitive" has a specific definition in hazard assessment and in explosives science
  - ➢ Sensitivity to other stimuli (friction or impact) is harder to predict from DSC
  - ➢ Suggested reading:
    - ✓ Oxley, Smith, & Marimaganti, *J. Therm. Anal. Calorim.*, **2010**, 102, 597–603.



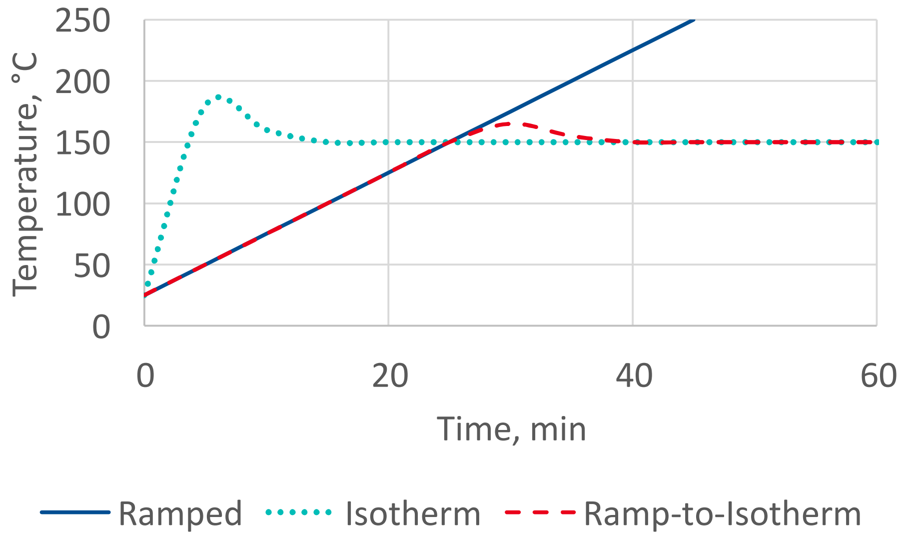
Based on: Kogyo Kayaku, Vol 48 (No 5), 1987, pp 311-316

Screening for heat and gas: Thermal Screening Unit (TSu)



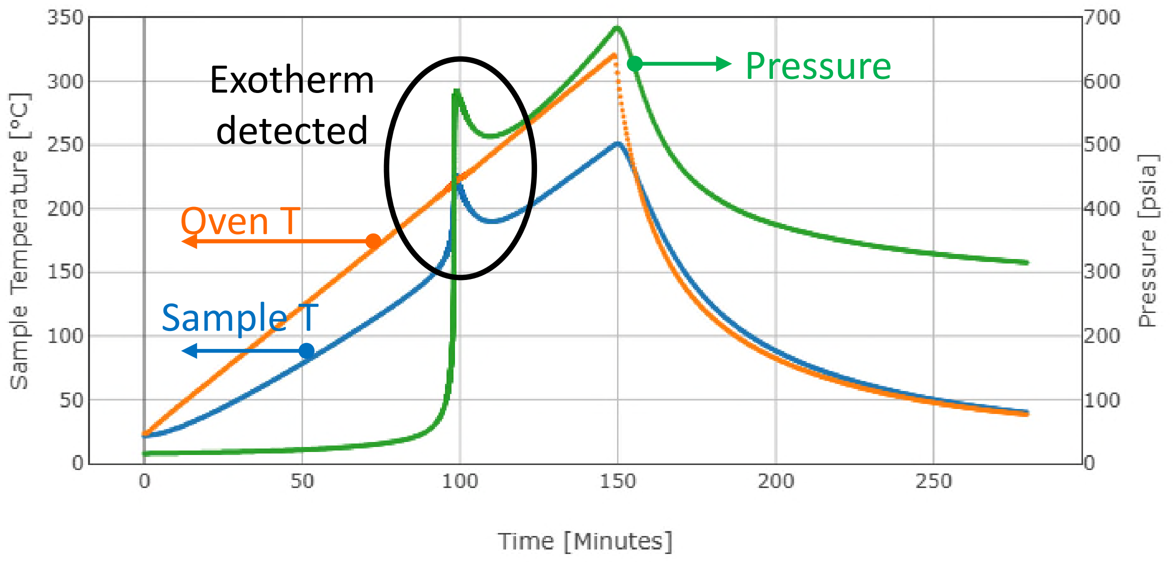


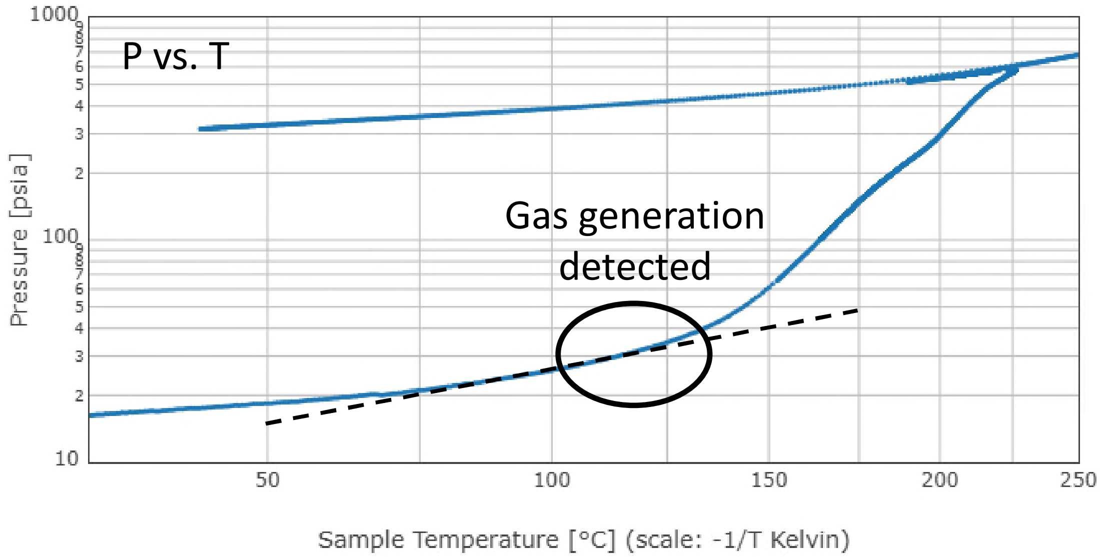
TSu is **not a calorimeter,** but it provides valuable **screening** data for both heat and gas evolution.

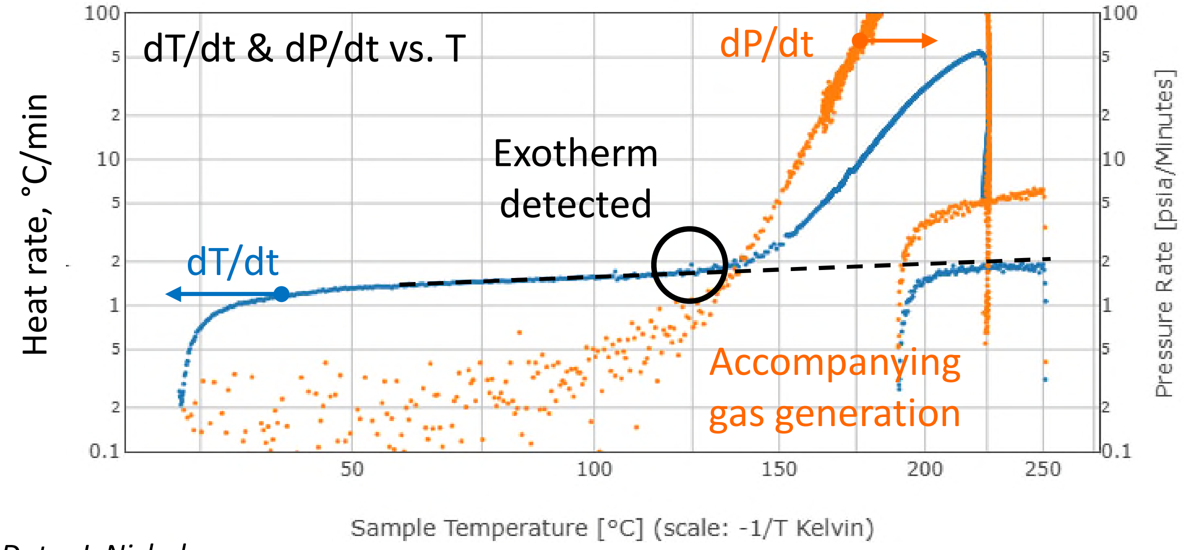


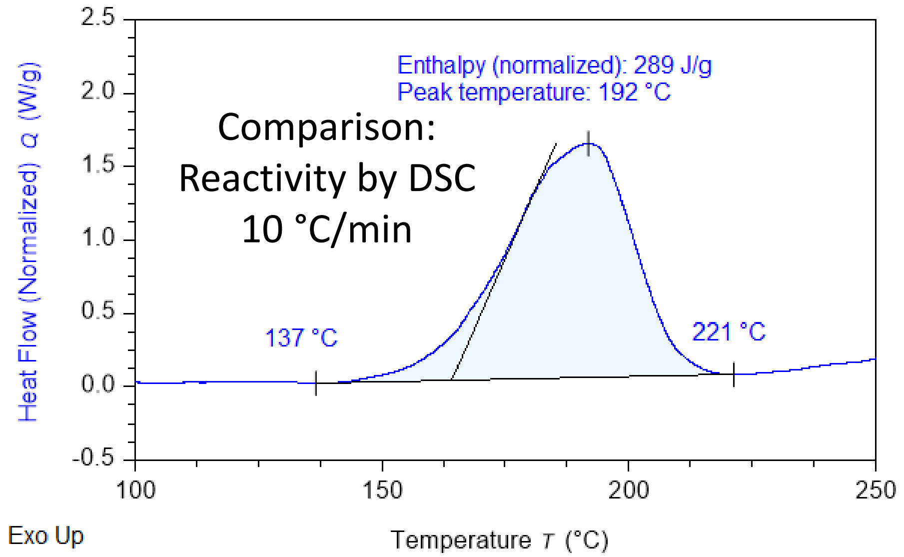
Simplified example of temperature vs. time

USE OF RAMPED TSU TO SCREEN FOR REACTIVITY (COMBINED WITH DSC)



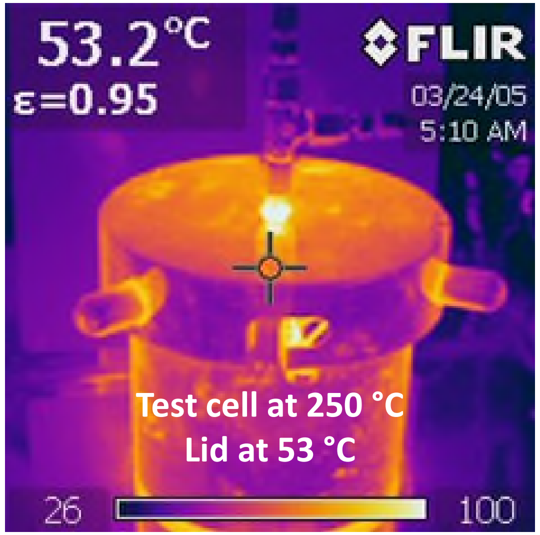






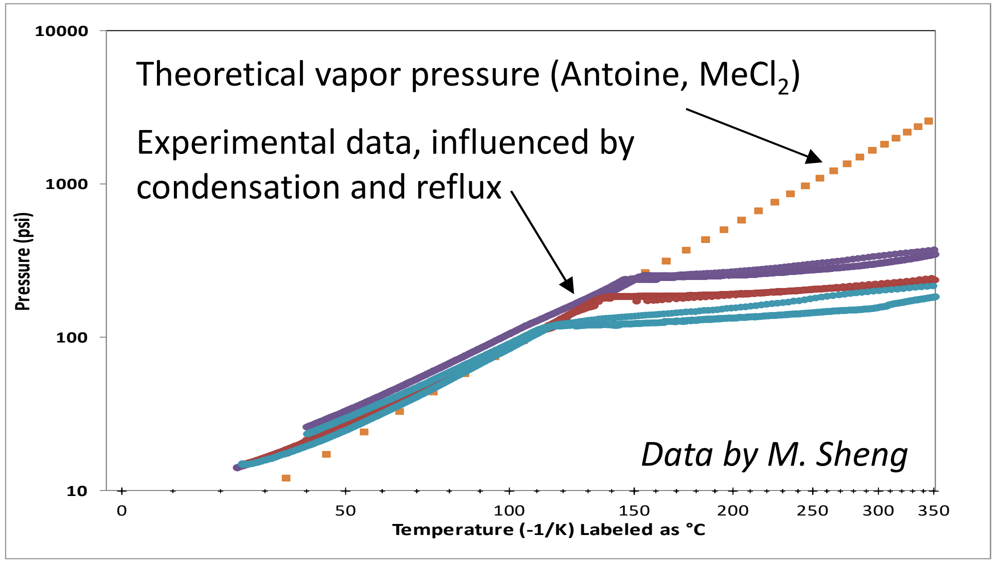
Data: J. Nichols.

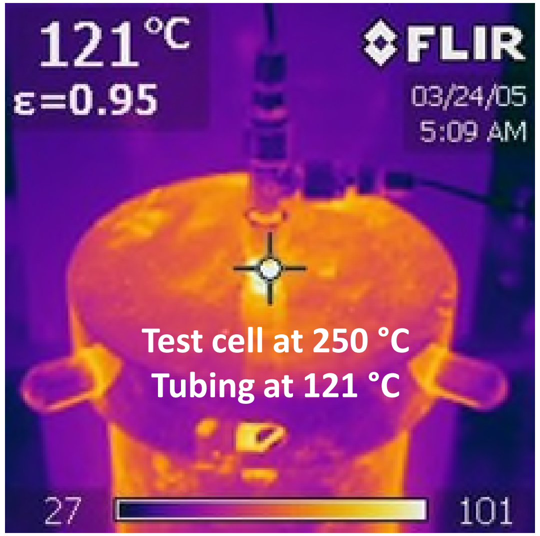
TSu: Cautionary note on vapor pressure and condensation

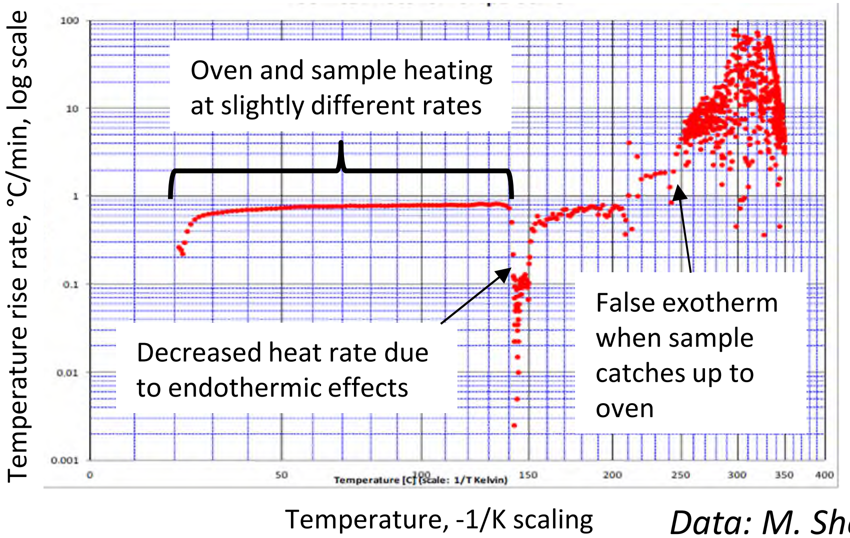


Condensation can occur in the external tubing and valves, with reflux occurring in the neck of the sample sphere.

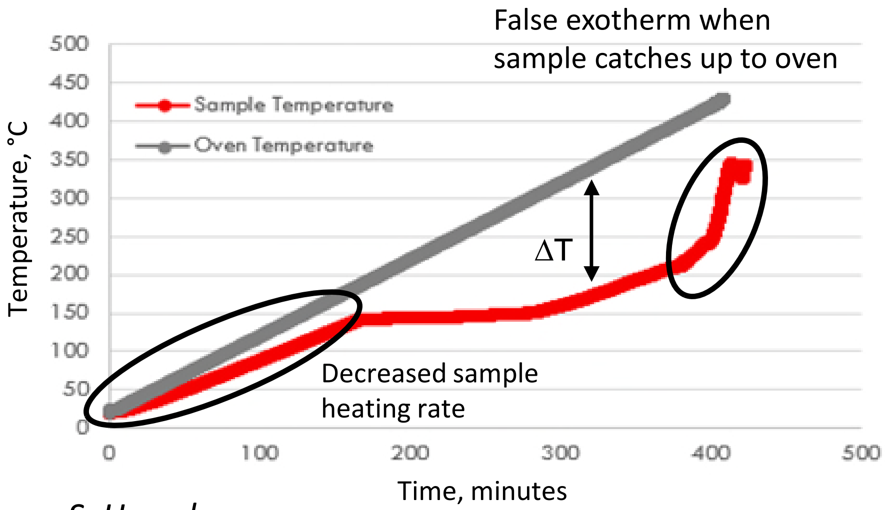
The resulting large temperature gradient between sample and oven can yield poor-quality vapor pressure data and **false "exotherms."**







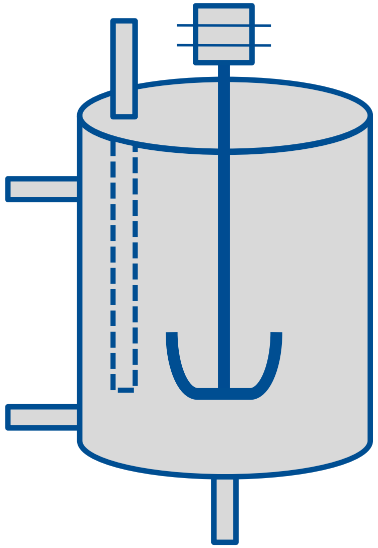
Data: M. Sheng, S. Horsch

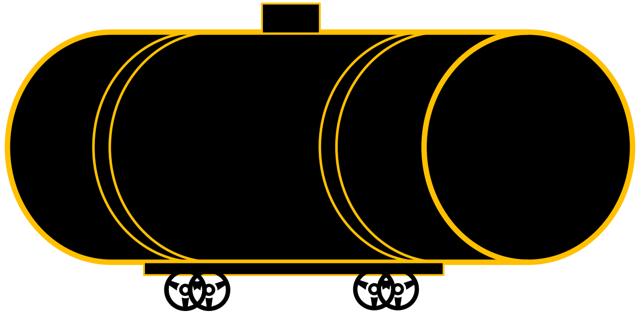


WE OFTEN PREFER (PSEUDO)-ADIABATIC CALORIMETRY

Adiabatic experiments usually yield superior predictions of uncontrolled production-scale exothermic reactions

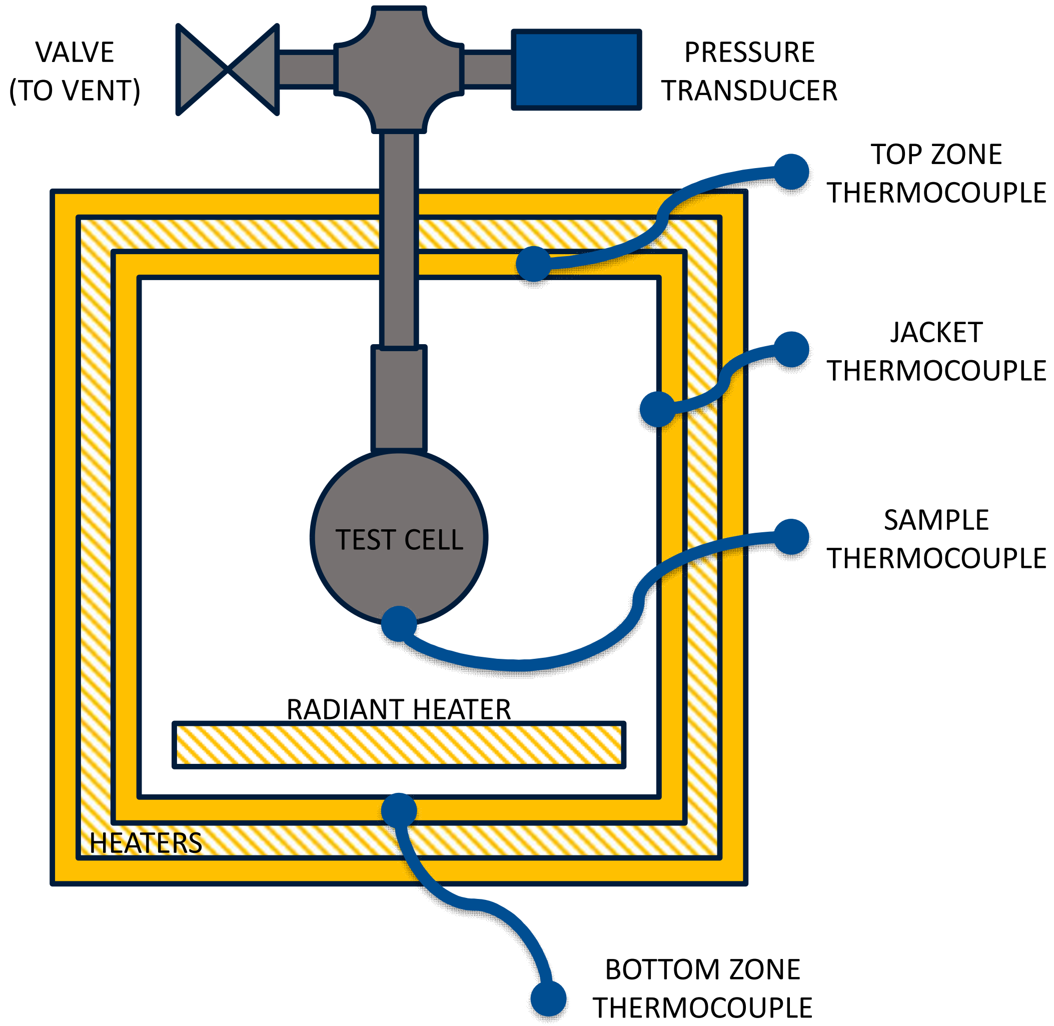
Large vessels usually have poor heat transfer to their surroundings, by design (insulation) or due to surface area/volume ratio





- We prefer experiments that mimic the reaction trajectories likely to occur during a process upset
  - Adiabatic is **not always** worst-case
  - External heat inputs or other reagent pooling can exacerbate reaction rates
- A single pseudo-adiabatic experiment can provide:
  - Apparent reaction kinetics
  - Thermodynamic and pressure data
- These are useful even when adiabatic is not worst-case

ACCELERATING RATE CALORIMETRY (ARC)



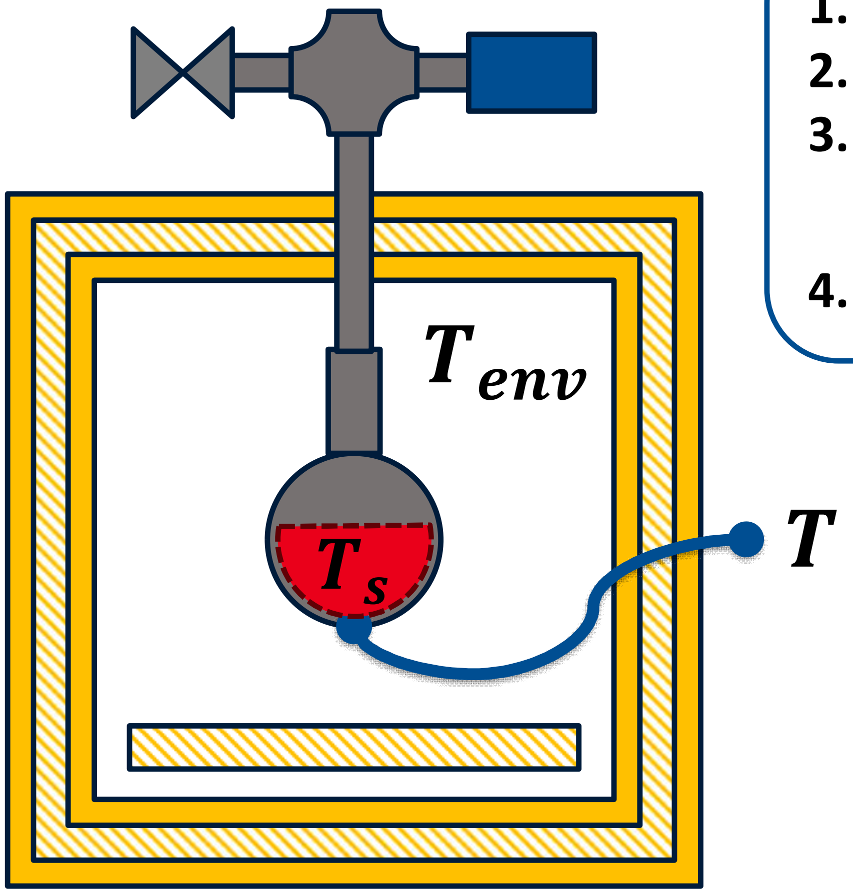
Based on ASTM E1981-22 and on Townsend & Tou, *Thermochim. Acta* **1980**, 37, 1-30

ARCs exist in a variety of form factors from different manufacturers; these are examples of common ARC equipment.

NETZSCH ARC 244 inside a walk-in enclosure

Soham Dutta, Dow RC SME, with a THT esARC

ARC FUNDAMENTALS: HEAT-WAIT-SEARCH (HWS)



1. **Heat** to desired temperature
2. **Wait** for temperature to equilibrate
3. **Search** for exotherm:

   If $\frac{dT}{dt} > 0.02\ °C/min$, track exotherm
4. **Else, repeat** until exotherm detected

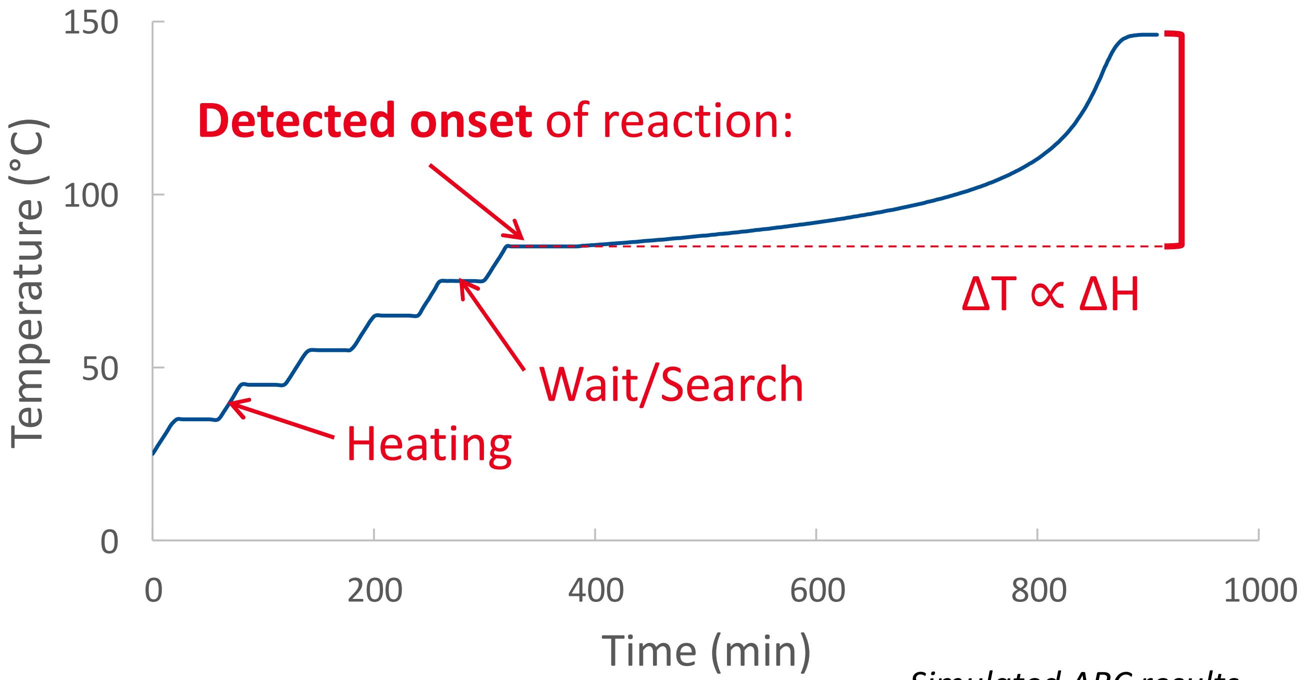
The reaction remains adiabatic if

$T_s = T_{env}$

as controlled by

$T = T_{env}$

Required: $T = T_s$



Simulated ARC results

Townsend & Tou, *Thermochim. Acta* **1980**, 37, 1-30

ARC FUNDAMENTALS: GENERAL INFORMATION AND USE

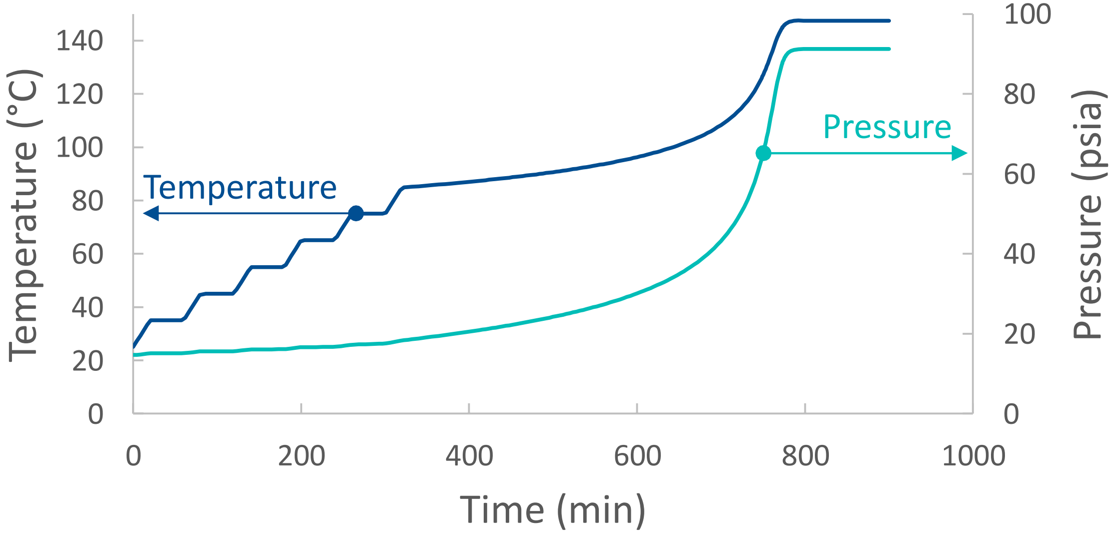
ARC: adiabatic if
$T_s = T_{env}$
as controlled by
$T = T_{env}$

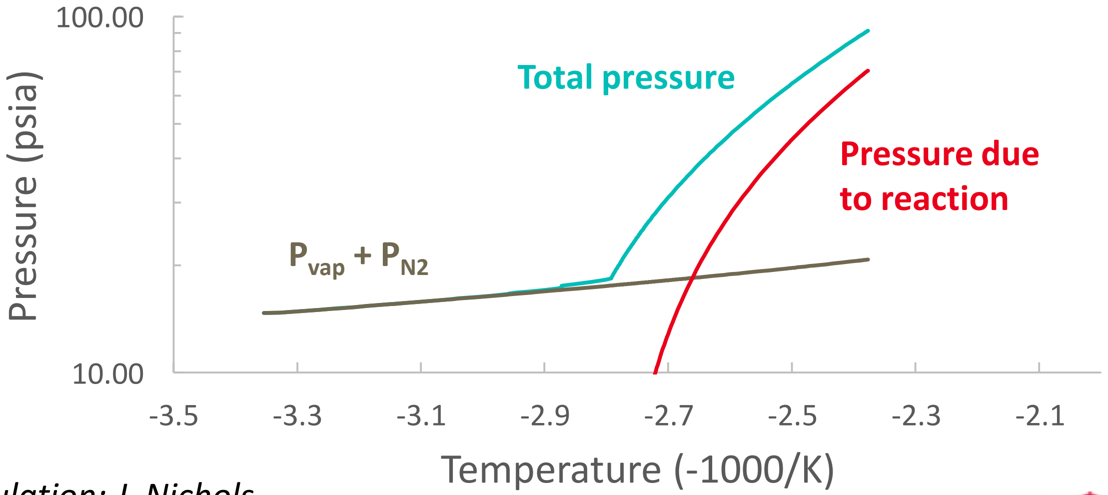
- **Typical operating limits:**
  - Temperature:
    - Minimum: Ambient (unless refrigerated)
    - Maximum: **350-500 °C**
  - Pressure, as limited by equipment:
    - Pressure transducer, fittings, valves, and ARC sphere burst pressure
- **Common test parameters:**
  - Detection threshold: **0.02 °C/min**
  - Heat step: **5-10 °C**
  - Wait time: **20-30 minutes**
    - Depends on time required for equilibration
    - Varies with heat step size and other factors
  - Search time: **15 minutes**
    - Time spent comparing measured temperature rise rate to detection threshold

- **Requirement:** $T = T_s$
- Good use cases for ARC:
  - Inviscid, miscible systems
  - A high sensitivity is desired
  - Worst-case scenario is adiabatic thermal runaway
  - Data will be used for formal thermokinetic modeling or to simulate other scenarios
- Cases where ARC may become unreliable:
  - Samples that are likely to have poor internal heat and/or mass transfer
    - Fine granulated solids that will not melt
    - Pellets or chunks with poor heat transfer
    - Viscous, immiscible systems
  - Samples requiring substantial mixing
    - Emulsions
    - Gas/liquid reactions

ARC FUNDAMENTALS: PRESSURE DATA WITH AND WITHOUT GAS EVOLUTION

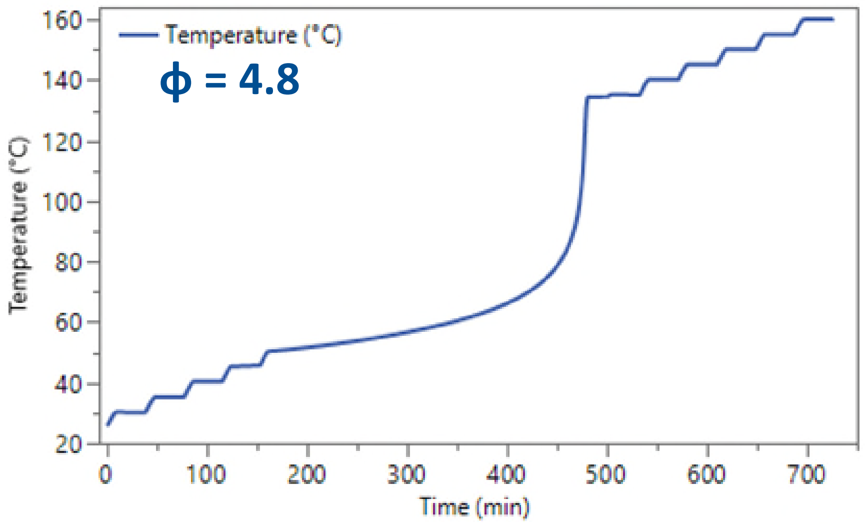
Gas-generating system (A + B → C + D + E + F + G + …)

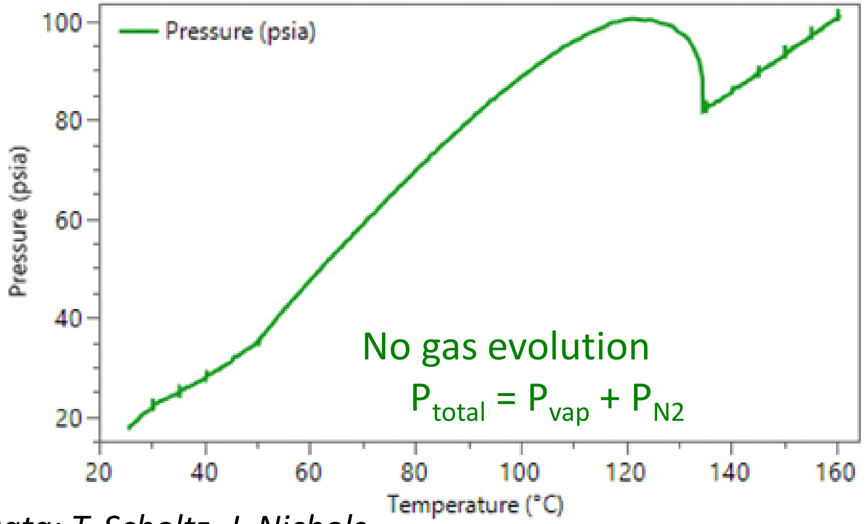




Simulation: J. Nichols

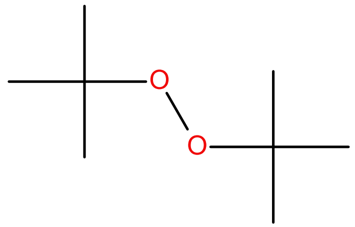
Non-gassy system, building molecular weight (A + B → C)



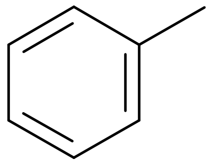


Data: T. Scholtz, J. Nichols

ARC EXAMPLE: START-TO-FINISH ARC TEST DATA, "WELL-BEHAVED" SAMPLE

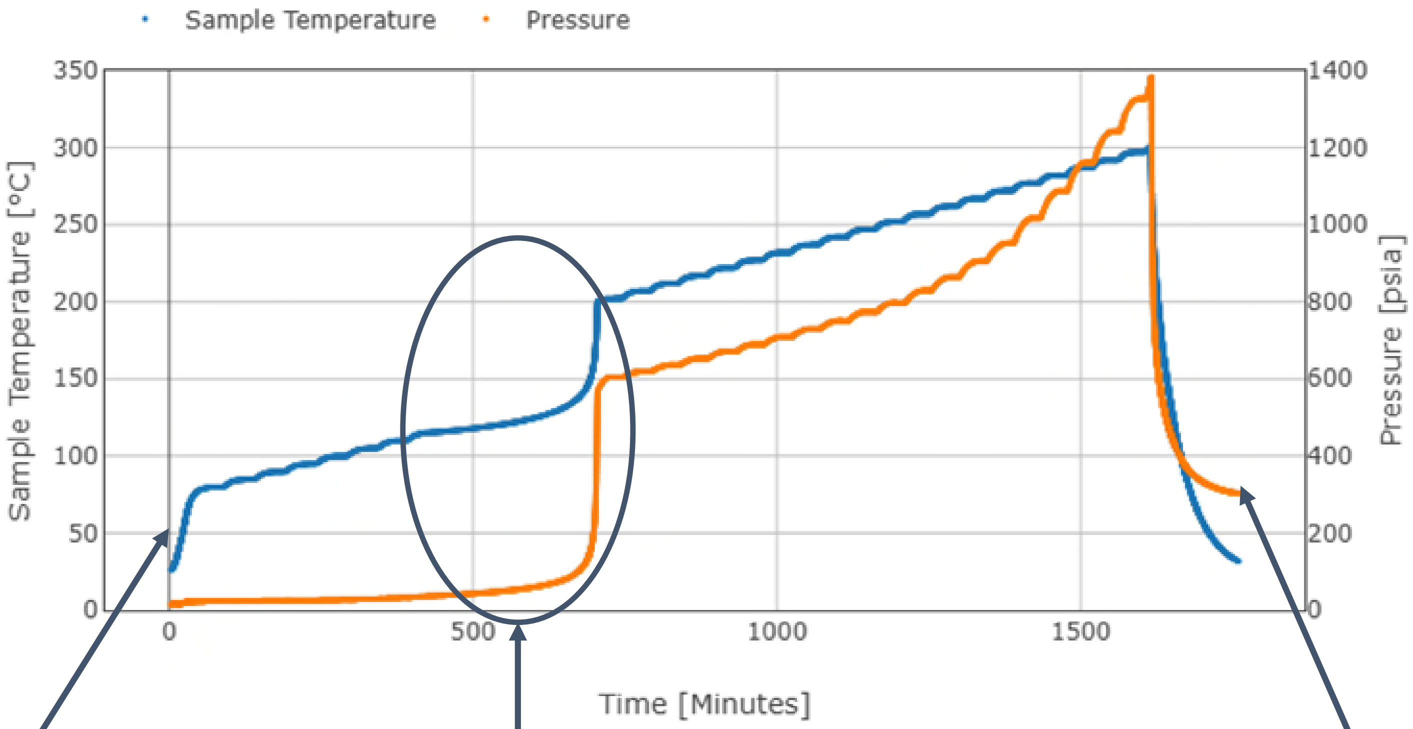


20% di-tert butyl peroxide



80% toluene

5.26 g sample
10.1 g ARC sphere (Ti)
ϕ = 1.50



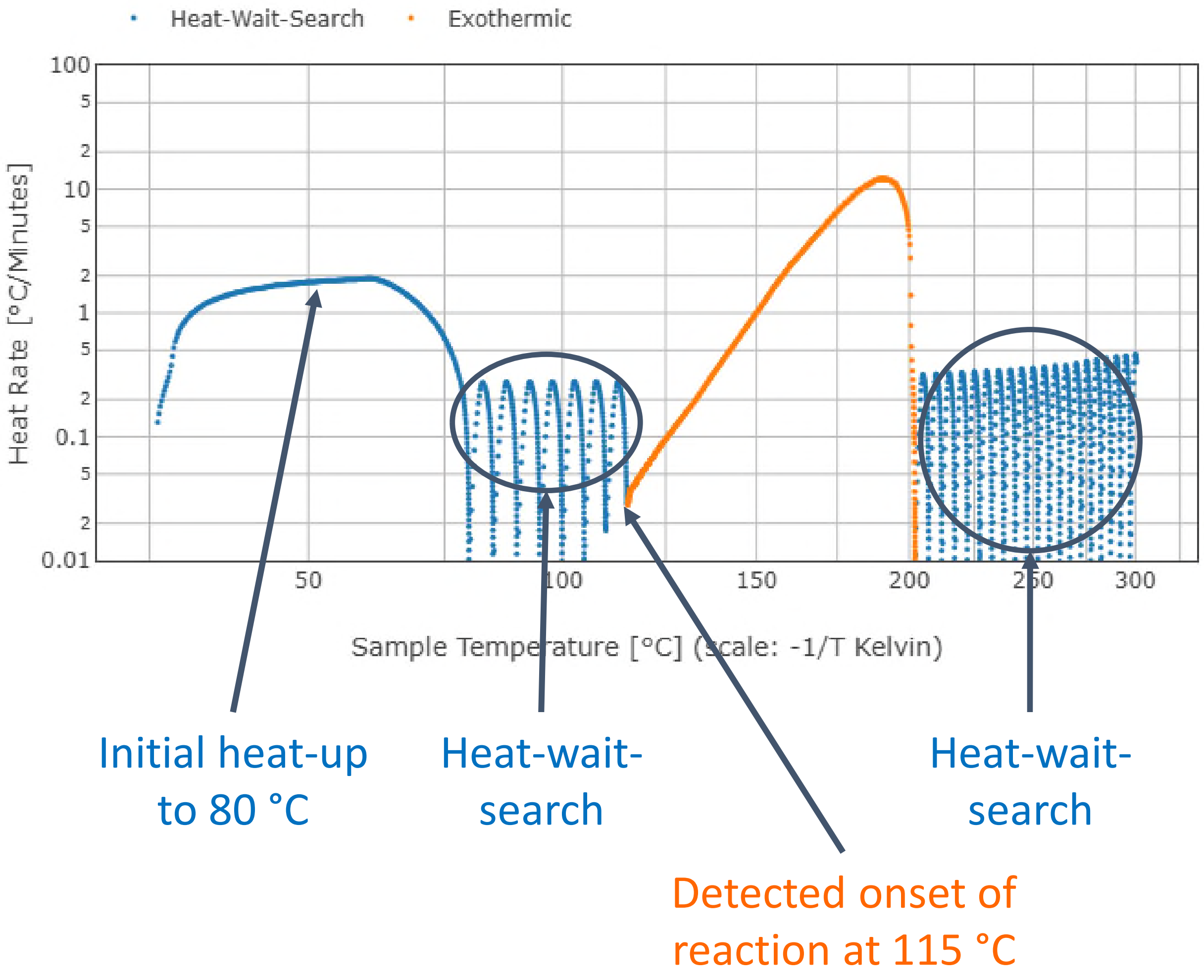
Initial heat-up to 80 °C ("jump-starting" well-known chemistry)

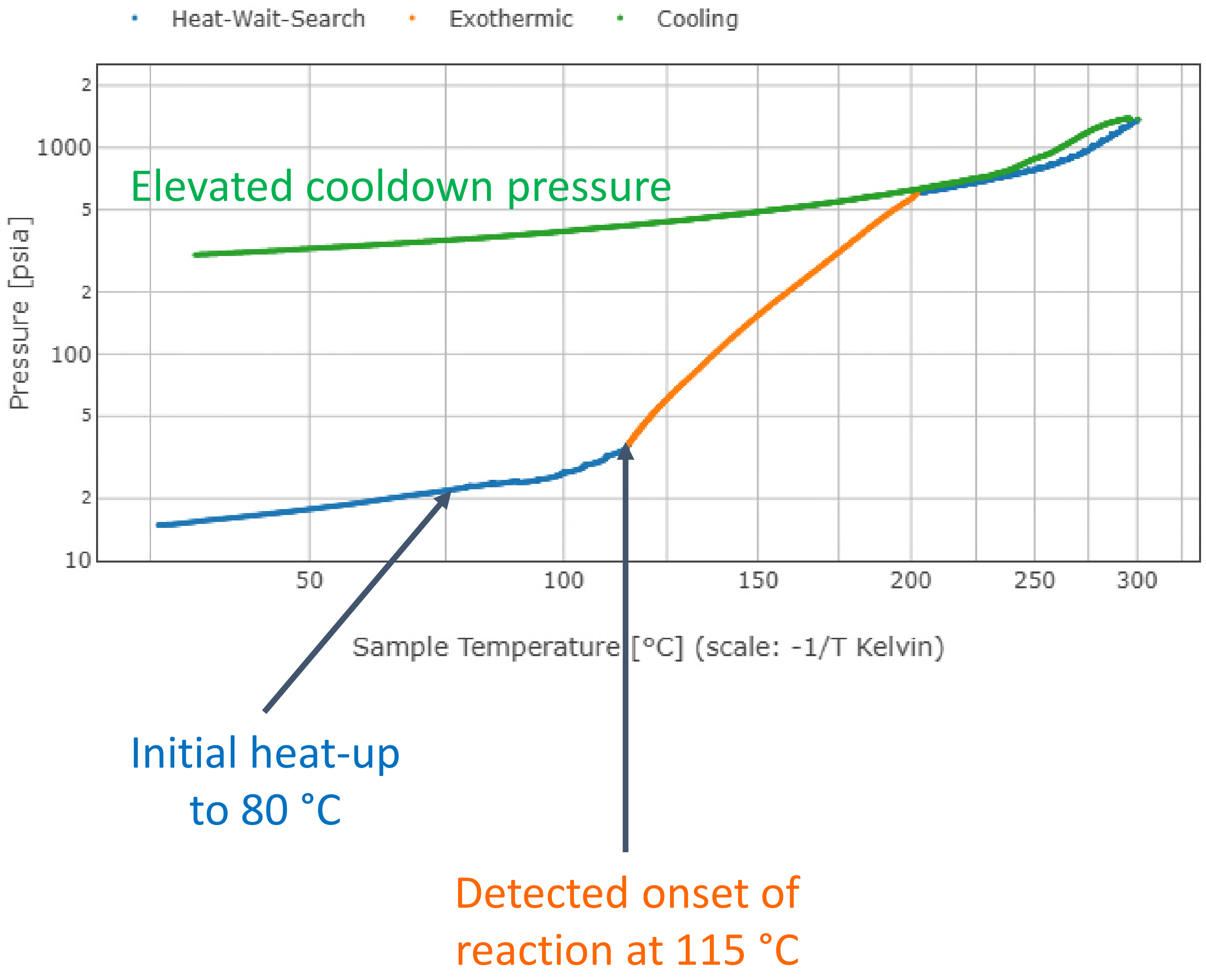
Exothermic reaction generating heat and pressure

Elevated pressure after cooldown indicating non-condensable gas

Data: A. de Decker

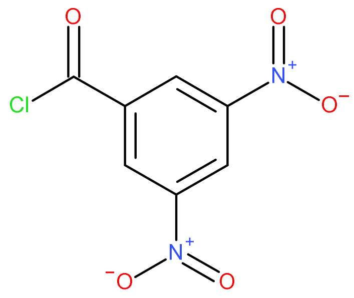
ARC EXAMPLE: 20% DTBP IN TOLUENE, A "WELL-BEHAVED" SAMPLE





Data: A. de Decker

ARC EXAMPLE: START-TO-FINISH ARC TEST DATA, "NAUGHTY" SAMPLE

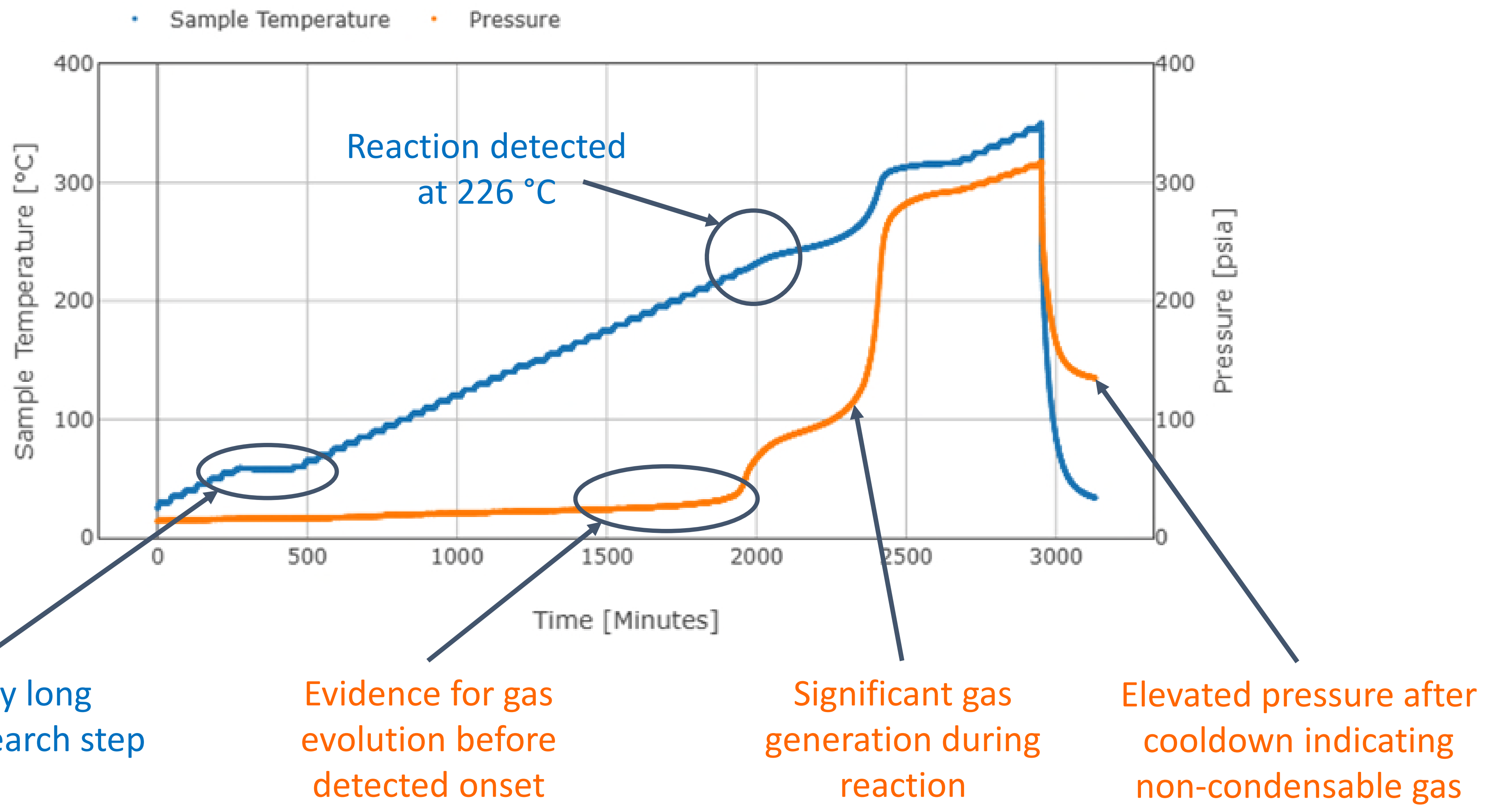


3,5-dinitrobenzoyl chloride

261 mg sample
20.6 g ARC sphere
(Hast-C276)

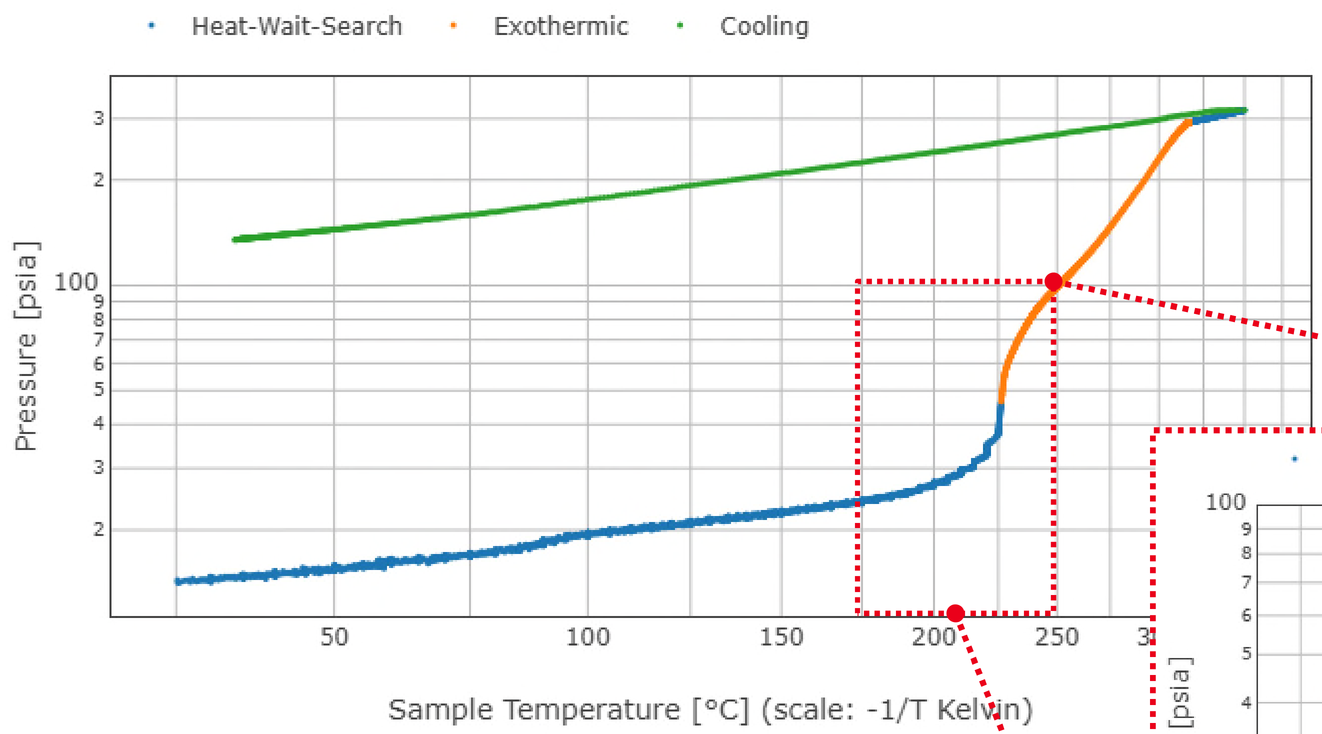
m.p. 68-69 °C

ϕ ≈ 31

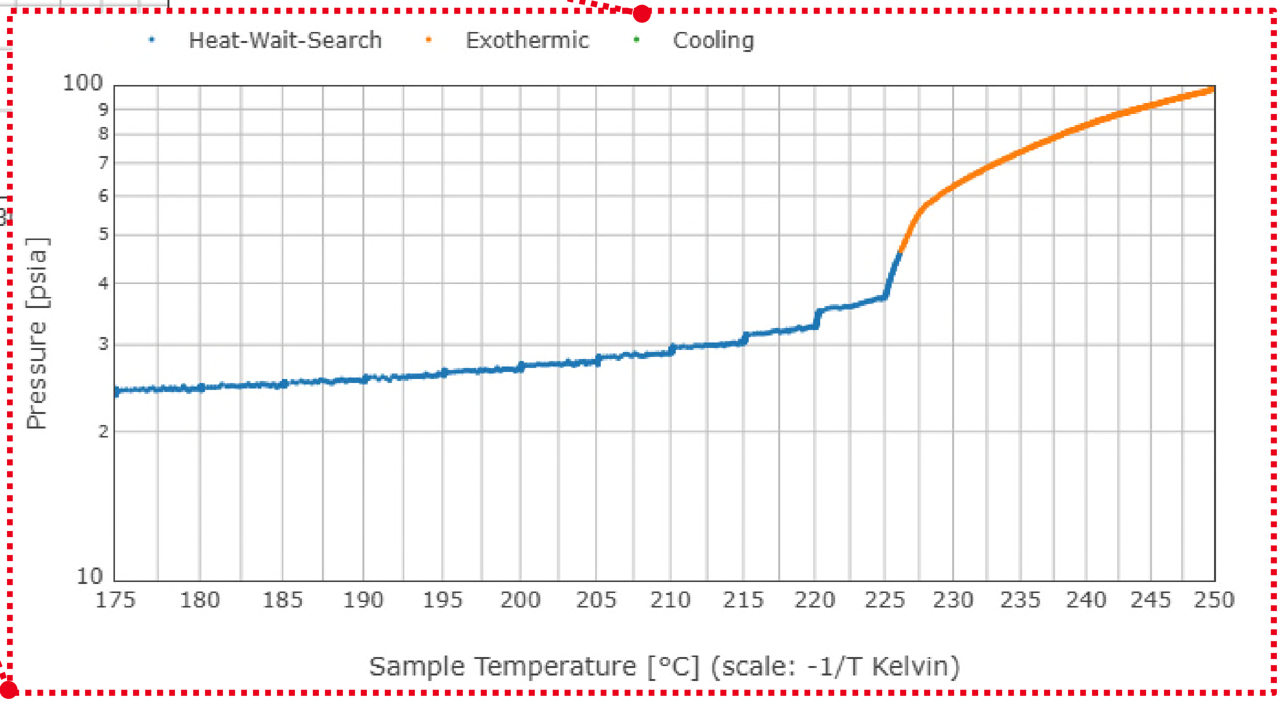


Data: T. Scholtz, J. Nichols

ARC EXAMPLE: GAS GENERATION BEFORE EXOTHERM



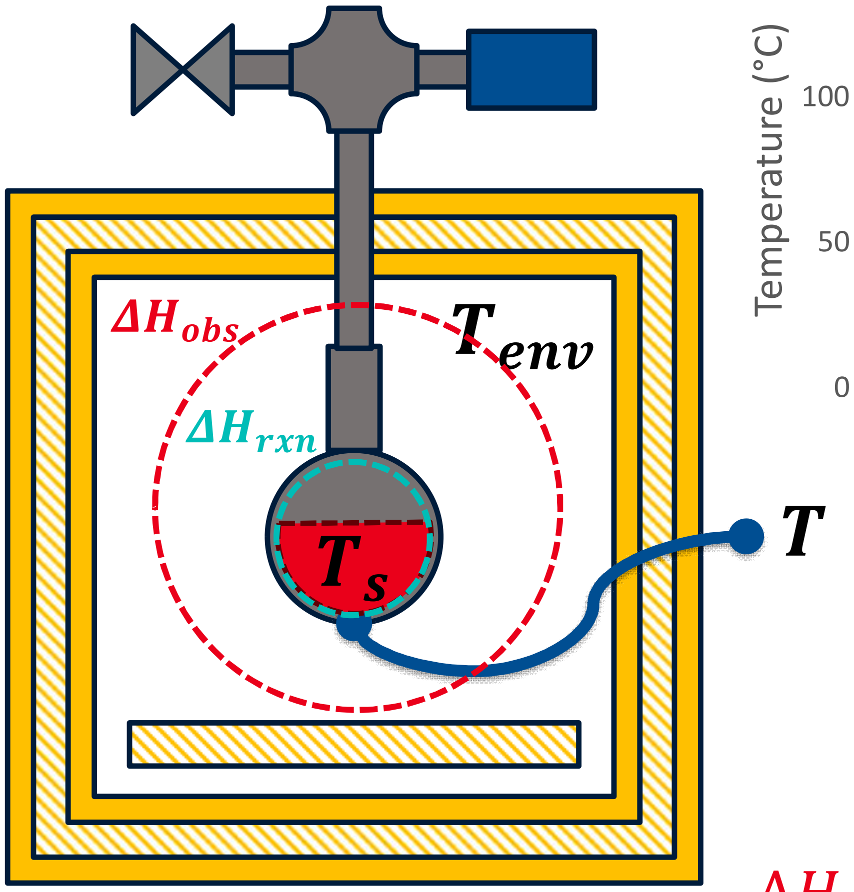
Evidence of gas generation, either from exothermic reactions occurring below the detection limit, or from endothermic processes, is **commonly observed during wait-search**

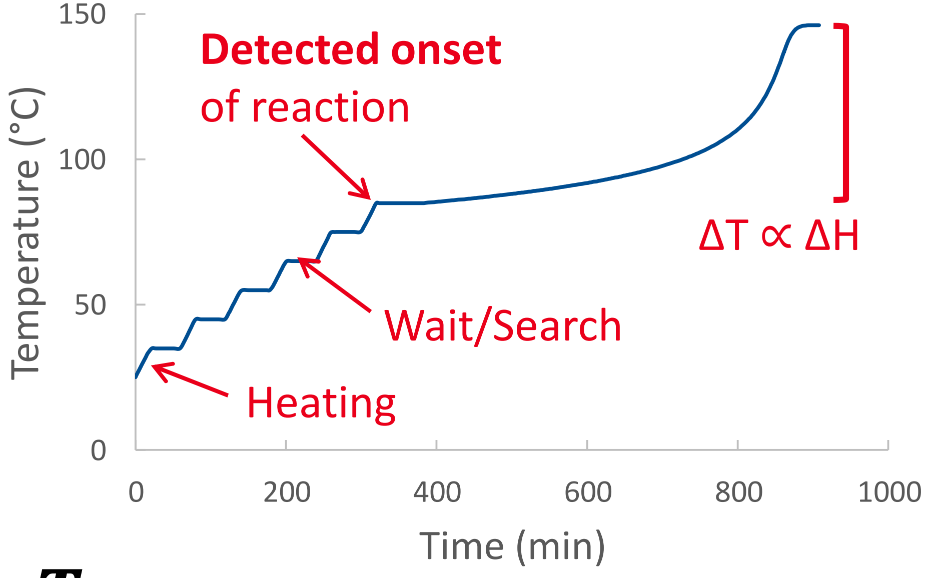


ARC pressure data can be impacted by vapor pressure, thermal expansion, gas generation, volatile species consumption, and pad gas expansion

Data: T. Scholtz, J. Nichols

ARC FUNDAMENTALS: ENTHALPY AND REACTION KINETICS





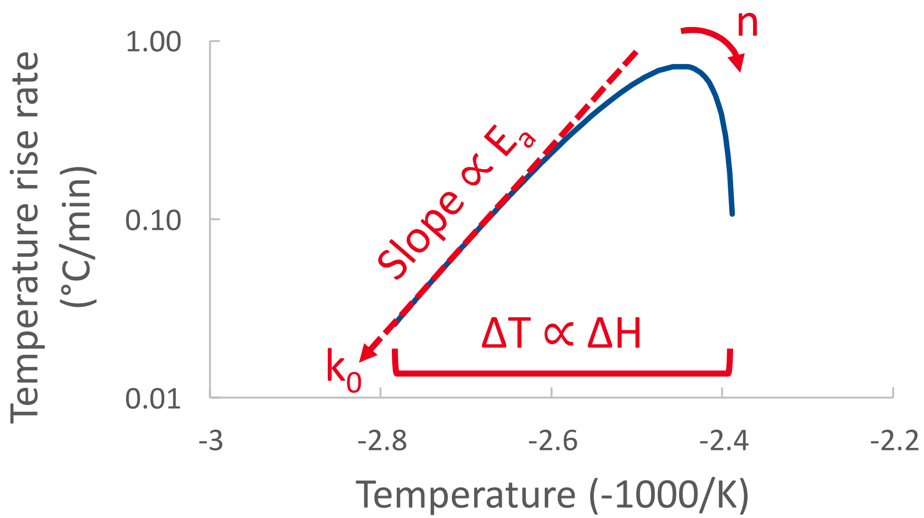
Example mathematical model:

$$r_{rxn} = k_0 e^{\frac{-E_A}{RT}} (1-\alpha)^n$$

$$\log r_{rxn} = \log k_0 + \frac{E_a}{\ln(10) R}\left(\frac{-1}{T}\right) + n \log(1-\alpha)$$

$$\frac{dT}{dt} \propto r_{rxn}$$

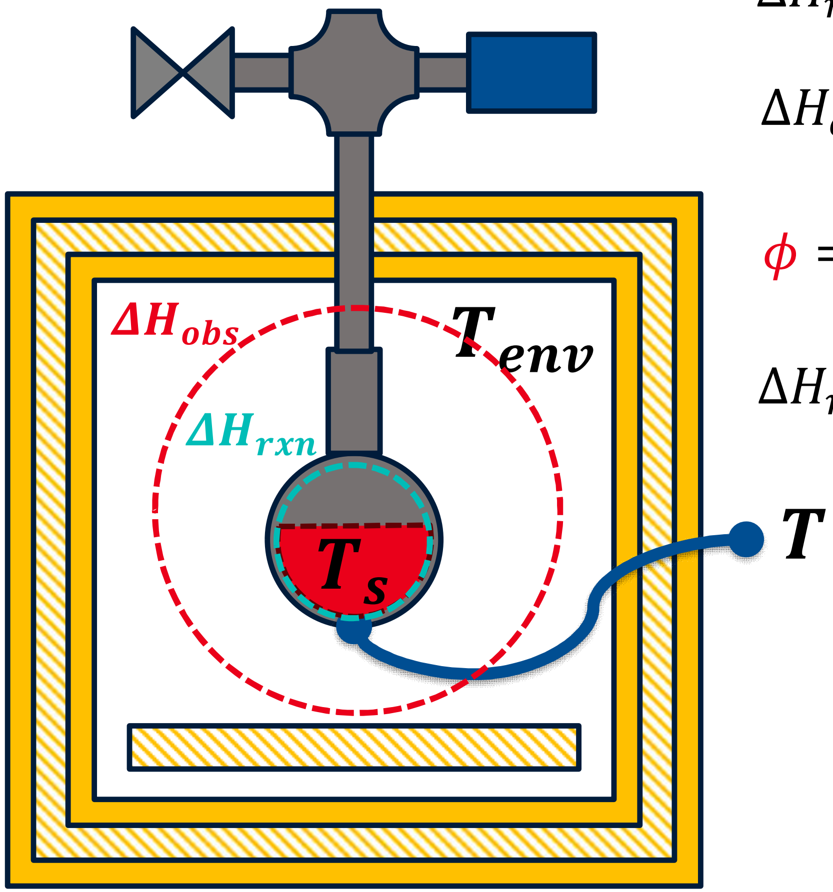
$$\Delta H_{rxn} = mC\Delta T_{adiabatic}$$



Simulated ARC results

Townsend & Tou, *Thermochim. Acta* **1980**, 37, 1-30

ARC OPERATING PRINCIPLES: THERMAL INERTIA (ϕ)



$$\Delta H_{rxn} = m_{sample} C_{sample} \Delta T_{adiabatic}$$

$$\Delta H_{obs} = (m_{sample} C_{sample} + m_{sphere} C_{sphere}) \Delta T_{observed}$$

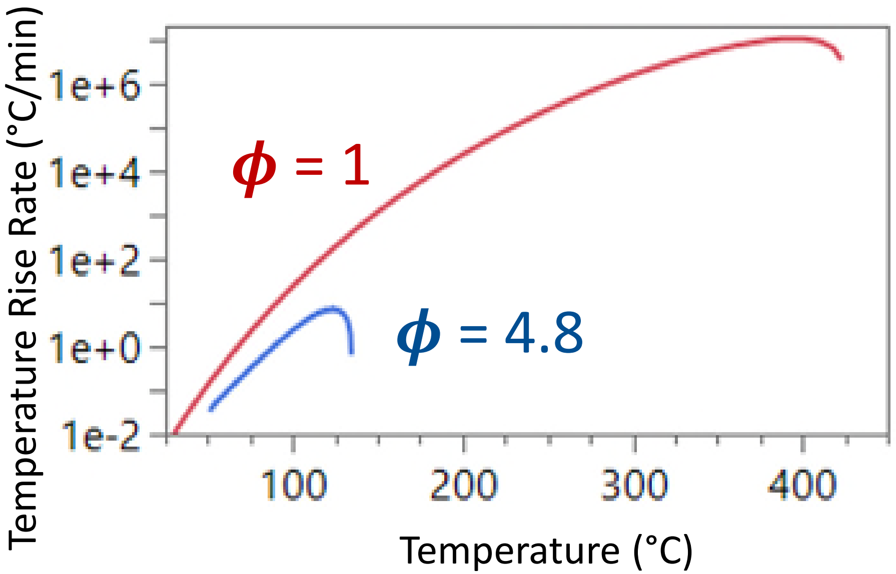
$$\phi = \frac{\Delta T_{adiabatic}}{\Delta T_{observed}} = \frac{m_{sample} C_{sample} + m_{sphere} C_{sphere}}{m_{sample} C_{sample}}$$

$$\Delta H_{rxn} = \phi \, m_{sample} C_{sample} \Delta T_{observed}$$

ϕ : thermal inertia, "phi"

Correcting for this effect is nontrivial:

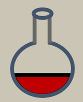
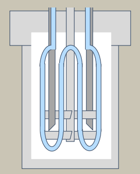
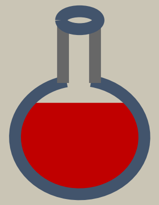
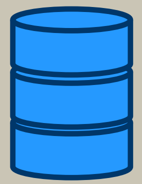
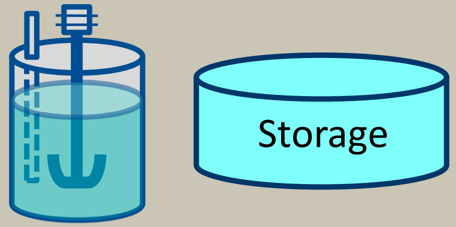
<u>Do not</u> apply ARC data without accounting for ϕ



Data: T. Scholtz; Simulated ϕ *= 1 by J. Nichols*

Townsend & Tou, *Thermochim. Acta* **1980**, 37, 1-30

THERMAL INERTIA AND THE EFFECTS OF SCALE

Container	ARC test (10 mL)	1 L Metal Reactor	1 L Glass Flask	55 gal Drum	11,000 gal insulated tank
					
Surface area	<20 cm^2	0.05 m^2	0.05 m^2	1.8 m^2	51 m^2
Volume	<10 mL	0.001 m^3	0.001 m^3	0.21 m^3	42 m^3
Mass of chemical	0.5 – 8 g	<1 kg	<1 kg	180 kg	34700 kg
Mass of container	10 – 30 g	8 kg	0.2 kg	9 – 37 kg	1500 kg
h_{ext}	-	10 – 1000 W/m^{2}K	15 W/m^{2}K	11 W/m^{2}K	1.4 W/m^{2}K
$\phi = \frac{mC + m_s C_s}{mC}$	**1.5 – 30+**	**3.0 – 5.0**	**1.1 – 1.5**	**1.05 – 1.2**	**1.0 – 1.1**

These values determined for representative vessels containing a representative organic liquid with:

Density: 0.8 kg *Specific heat capacity: 1.6 J/gK*

Heat transfer parameters (h_{ext}) estimated for representative systems.

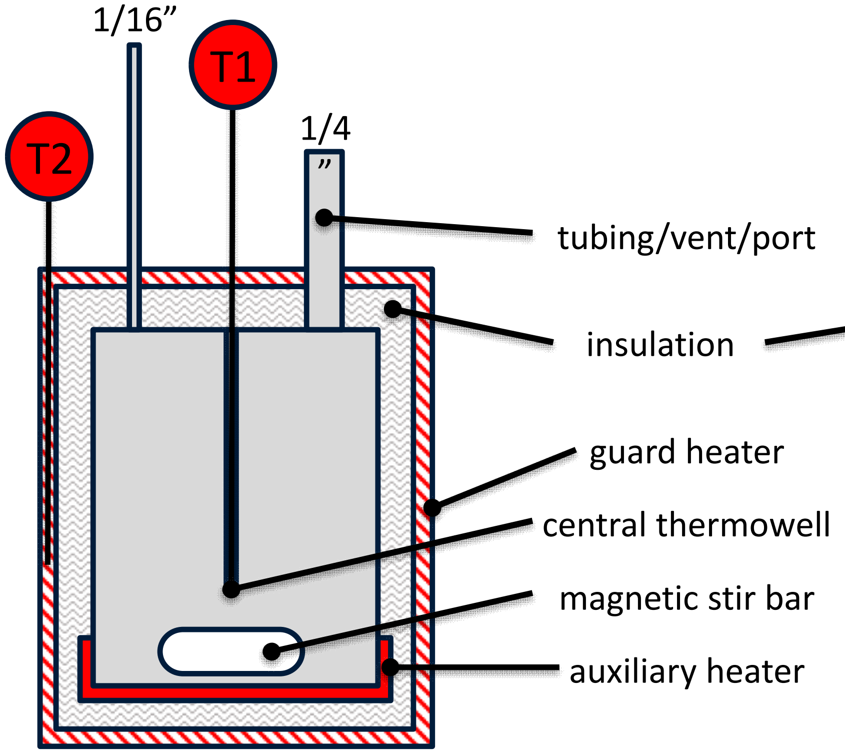
VENT SIZING PACKAGE (VSP, VSP2) FOR LOW THERMAL INERTIA TESTING

The **guard heater** around the test cell assembly maintains an adiabatic condition if:

$$T_1 = T_2$$

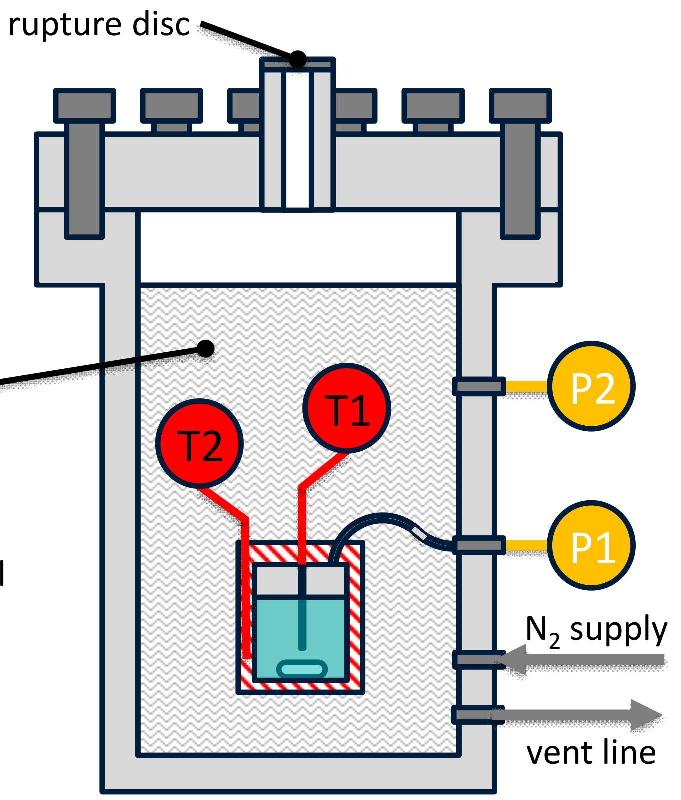
Option: External heat input during otherwise adiabatic control via **auxiliary heater**

VSP test cells can be made with a variety of vents/ports, agitators, thermowells, etc.



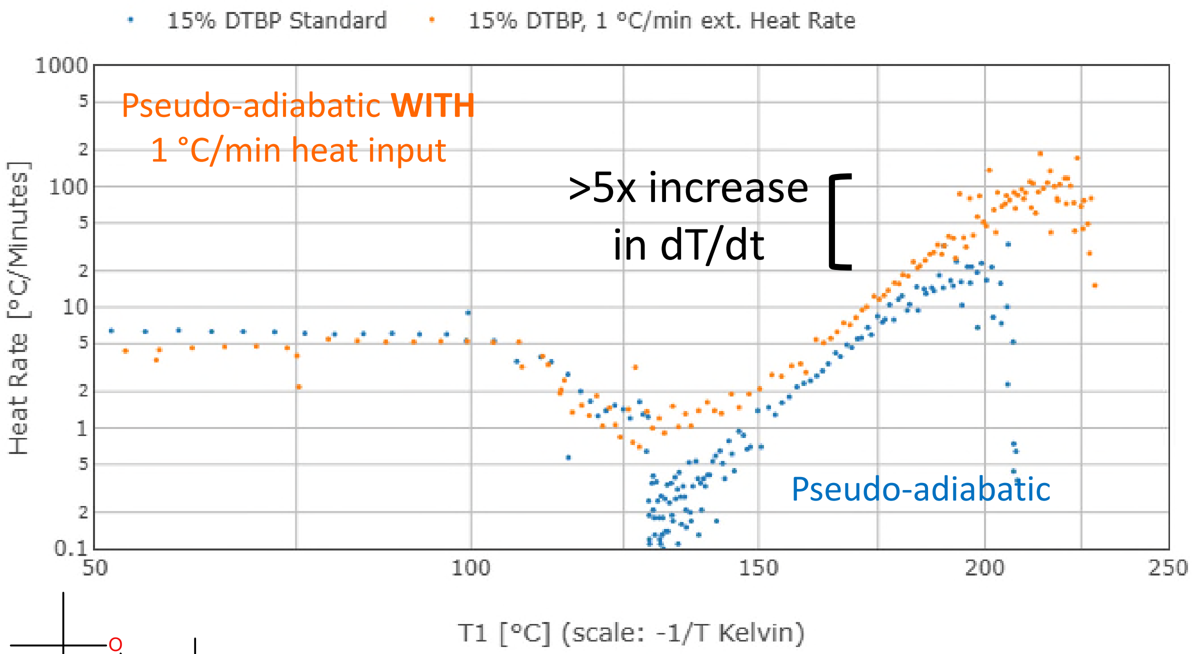
Test cell inside heater assembly

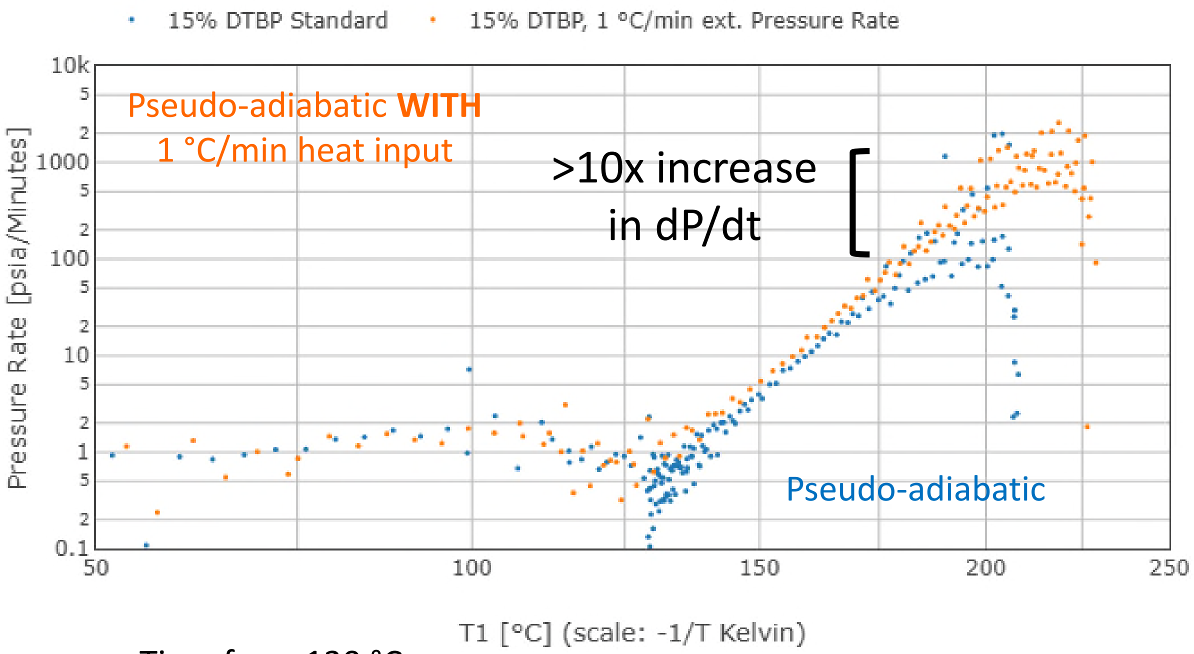
VSP is a **pressure-balancing** adiabatic calorimeter

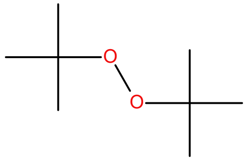


VSP containment vessel

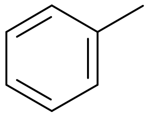
EXAMPLE: EXTERNAL HEAT INPUT "POOLING" EFFECT IN VSP TESTING







15% di-tert butyl peroxide



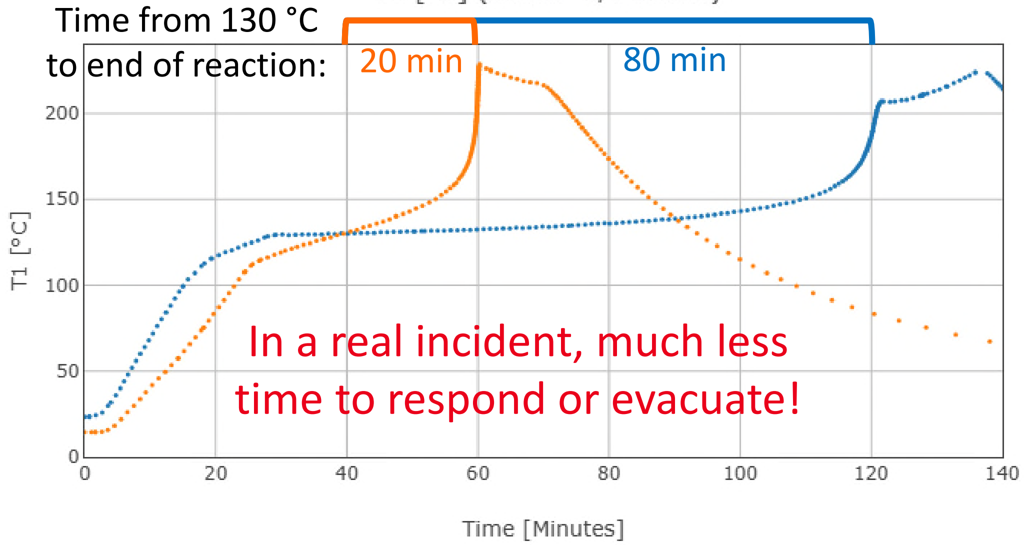
85% toluene

Same sample volume
in same test cell
ϕ ~ 1.2

Data: J. Nichols

An adiabatic reaction trajectory is **not** worst-case if an external heat input is possible:

- ❑Pool fire under vessel
- ❑Steam valve stuck open
- ❑Heater control fails on



Closing remarks on the application of calorimetry to safety

- Understand **the process AND the measurement science**
  - Match the process need to the proper experiment and calorimeter
  - Different methods have different strengths and weaknesses
  - Understanding fundamental operating principles enables:
    - ✓ Quality data collection and interpretation
    - ✓ Identification of atypical results
    - ✓ Appropriate formulation and falsification of hypotheses

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Thank you, P2SAC!

- Check and question your assumptions: **Are they appropriate?**

- Cultivate the expertise to **match theory to data**
  - Expert chemical engineers and chemists (or those willing to learn)

References

- **Thanks to**: Steve Horsch, Travis Scholtz, Min Sheng, Anja de Decker, Katie Mulligan, Soham Dutta, E. Cayo

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