A REACTIVE CHEMICALS WORKSHOP: PRACTICAL CONSIDERATAIONS OF THERMODYNAMIC AND KINETIC INFORMATION FROM CALORIMETRY FOR SAFE CHEMICAL OPERATIONS AT ALL SCALES

STEVE HORSCH
FELLOW
REACTIVE CHEMICALS / ANALYTICAL SCIENCES/CORE R&D
DOW

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Abstract

The *Reactive Chemicals Discipline* focuses on understanding the thermodynamic, transport phenomena, and kinetic information required to produce chemicals safely. This workshop will delve into the measurement science of lab-scale calorimeters and demonstrate how properly collected data can be used to determine heats of reaction, predict pressure generation, and develop a kinetic model to close the energy balance for process equipment.

Key Highlights:

- **Measurement Science:** Detailed overview of lab-scale calorimeters and their role in collecting accurate thermodynamic and kinetic data.
- **Data Utilization:** How to use collected data to determine heats of reaction, estimate pressure generation, and develop kinetic models.
- **Safety Applications:** Practical examples of applying these data to establish safe operating limits for chemical processes.

Where Does Reactive Chemicals at Dow Fit

Expertise in analytical **techniques** and experimental **design**

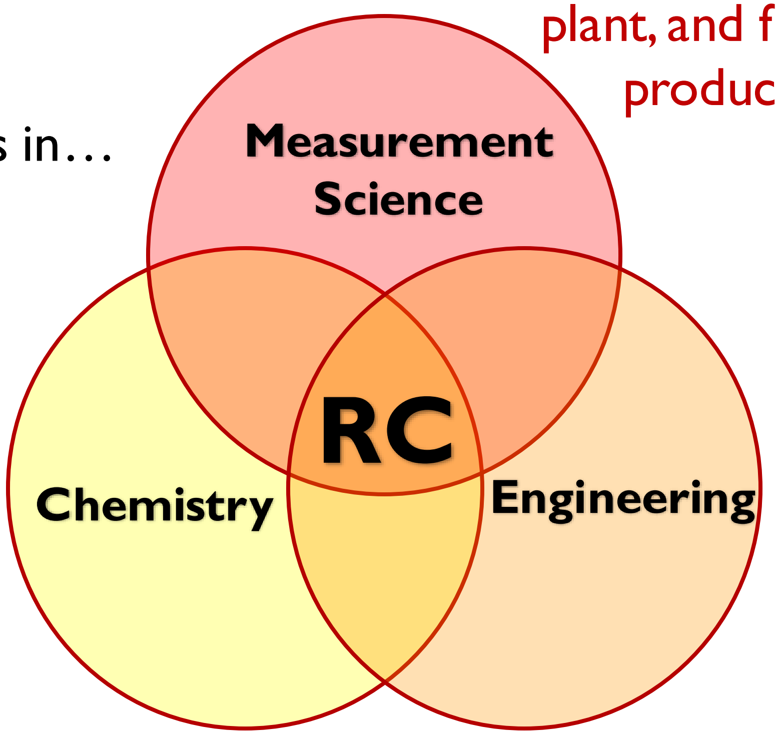
↳ Capability to **modify** and **develop** to meet changing needs and find new solutions

Subject-Matter Experts aligned with and experts in…

The **chemistry:** Physical, analytical, organic, and inorganic **chemists**

The **processes:** **Chemical engineers** with expertise in kinetic modeling, simulation, and energy balances

Continuity from experimental design through lab, pilot plant, and full-scale production



Ensure **safe** operation at **all** scales

Safe Chemical Synthesis (energy/rates)

What we need to know to set safe operating limits and design equipment

- Thermodynamics
  - Vapor pressure
    - Physical property data base/literature for simple mixtures, Estimation, or MEASURE
  - Heat of reaction
    - Calculate from heats of formation/estimate (group contributions method…) or MEASURE
- Energy release rates
  - Literature or MEASURE

Calorimetry can provide the needed Thermodynamic and Kinetic Data to do a safe process design

- Energy removal rates (other half of the energy balance)
  - CALCULATE/ESTIMATE or Measure

Adiabatic Calorimetry

Why Adiabatic Calorimetry

- Need to mimic process situation being studied
  - Many full-scale processes are insulated and large
    - Loss of process cooling results in near adiabatic conditions
  - Reaction trajectory of actual process partially mimicked when adiabatic is worst case
    - Adiabatic is not always the worst case (pooling of reactants due to external heat input or loss of agitation)
  - A single experiment provides reaction kinetics and thermodynamic data

Common Pseudo-Adiabatic Calorimeters in Use

ARC 244

ARC 254

esARC

ARC 2000

Phi-Tec 2

VSP II

Accelerating Rate Calorimetry (ARC)

Basic Information

- Start temperature: ambient temperature
- End temperature: 350-500°C
- Heat step: 5-10°C
- Wait time: 20-30 minutes (time for sample to equilibrate to calorimeter temperature)
- Search time: 15 minutes (comparing measured temperature rate to detection threshold)
- Exotherm detection threshold: 0.02 °C/min
- Maximum pressure: Dependent on pressure transducer and sphere burst pressure (2000-5000 psia)

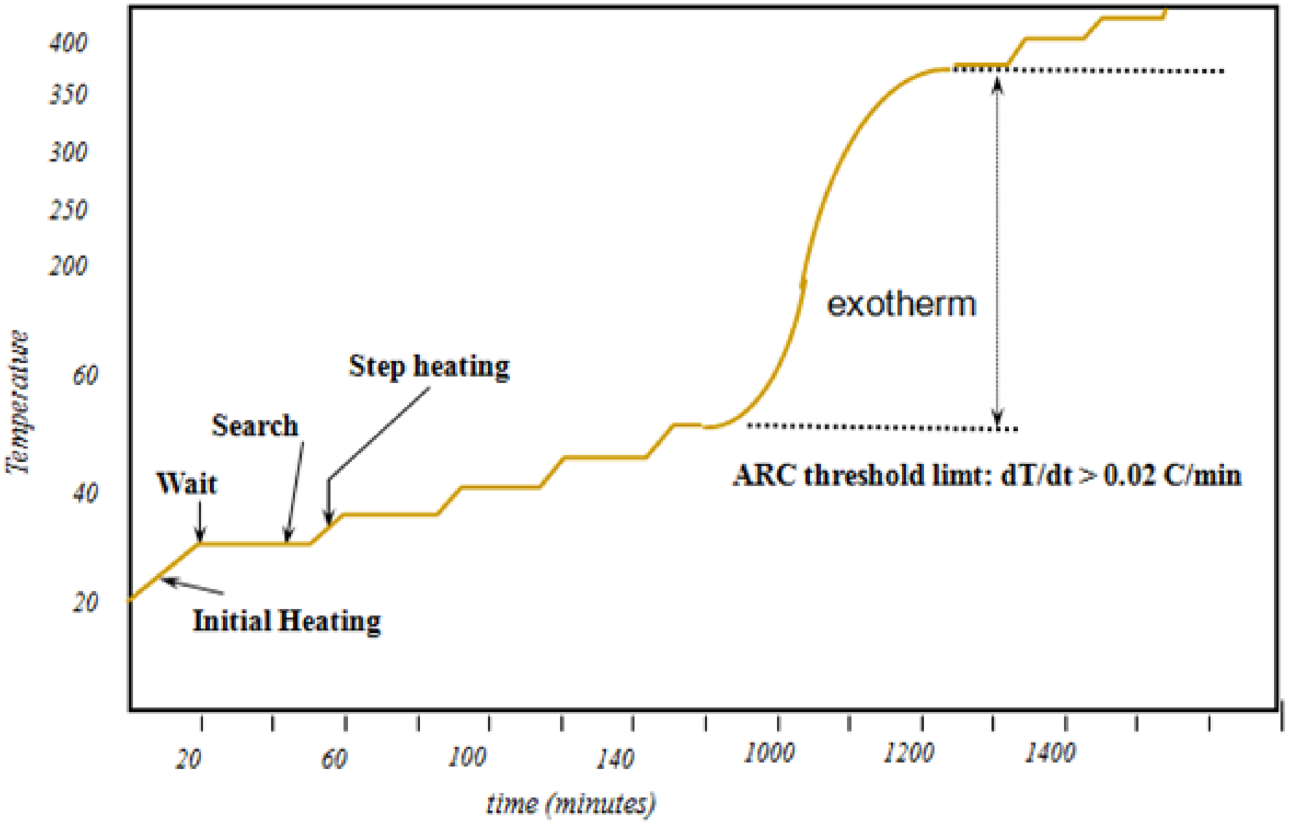
When to use or not use a standard ARC

- Use - low viscosity fully miscible system
- Use – high sensitivity needed
- Use - worst case scenario is adiabatic
- Use – collect data for formal kinetic modeling to simulate other scenarios
- Not Use – fine granulated solids that don't melt in temperature range of experiment
- Not Use - Emulsion polymerization or systems that require substantial mixing (gas/liquid phase reaction)

Key Principle - Control temperature is measured at the boundary of the sample container. Quality data requires minimal temperature and concentration gradients

Accelerating Rate Calorimetry (ARC)

Typical operation (Heat-Wait-Search)

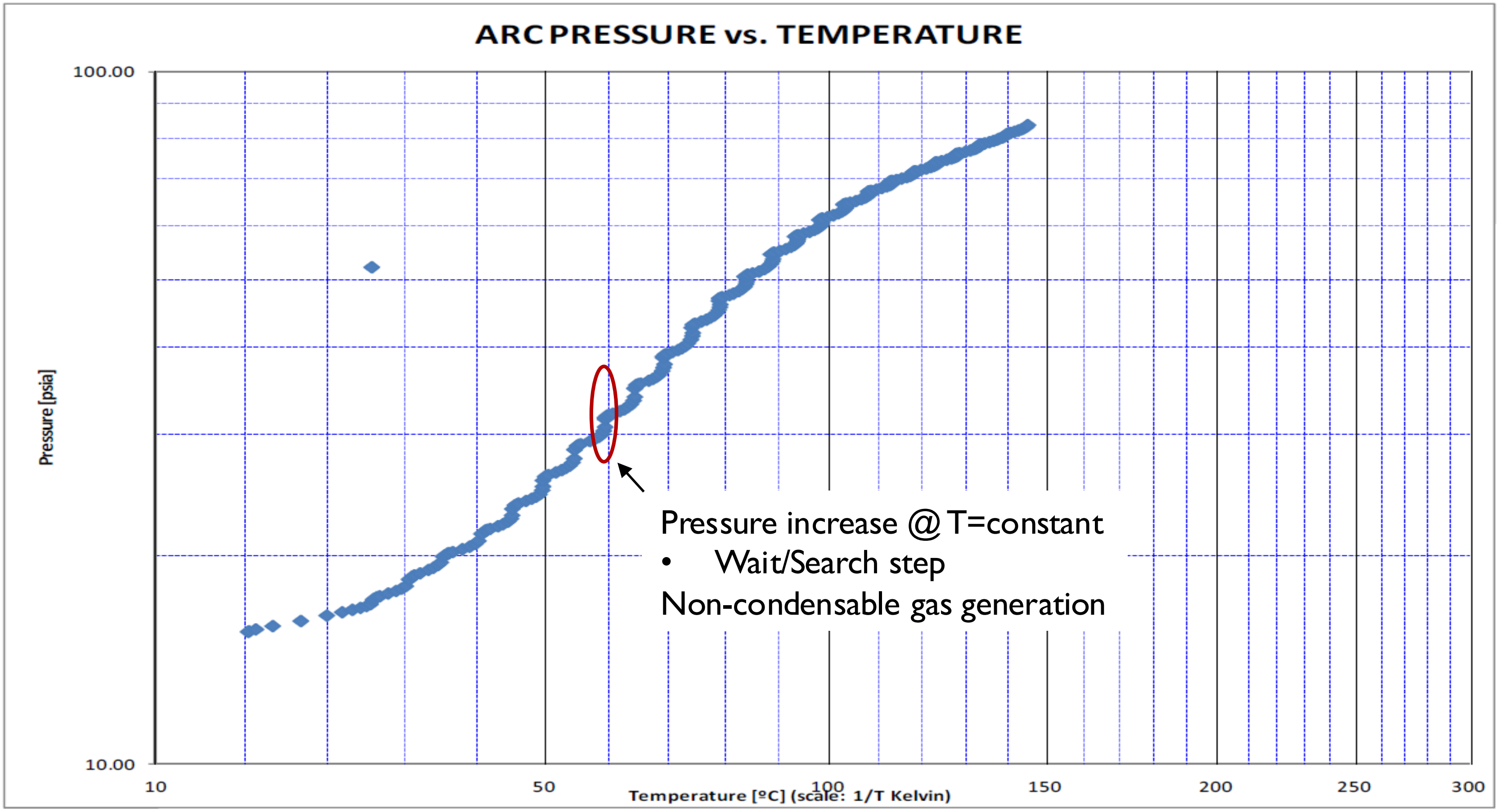


1) HEAT to desired Temperature
2) WAIT for Temperature to Equilibrate
3) SEARCH for Exotherm
    - Temp is constant during this part if there is no exotherm
4) Repeat until Exotherm is detected

Pressure Data from ARC

Pressure increase during search step indicates non-condensable gas generation

- Vapor pressure is fixed for a single temperature



Pressure increase @ T=constant

- Wait/Search step

Non-condensable gas generation

Heat of Reaction from ARC

ARC measures temperature and pressure. Need a relationship that allows heat of reaction to be calculated for a constant volume, variable pressure, adiabatic process in closed system

$\mathrm{dU} = Q + Qrxn$ Internal energy change with exothermic reaction (constant volume)

Q_{rxn}= energy from exothermic reaction, Q = energy crossing boundary in the form of heat

$\mathrm{dU} = \cancel{Q} + Qrxn = mC_v dT$ Constant volume adiabatic process

$\mathrm{Q_{rxn}} = mC_v dT$ Heat of reaction for ARC experiment!

Key Challenge - constant volume heat capacity not available over large temperature range for many compounds

Heat of Reaction from ARC

What is available? C$_P$

$$Q_{rxn} = dU = mC_P dT$$

Wouldn’t it be nice if…

$$\boxed{C_p \sim C_v}$$

How much error might be introduced for organic liquids:

$$dU_{rxn} = m_S C_{pS} dT_{ad}$$ *S: sample*

$$C_p \neq C_v$$

$$C_p - C_v = VT\frac{\alpha^2}{\beta_T}$$

Through application of engineering assumptions…

$$\frac{\alpha^2}{\beta_T} = \frac{\left(10^{-4}\ K^{-1}\right)^2}{10^{-5}\ bar^{-1}}\left(\frac{101325\ {}^{N}/_{m^2}}{1.01325\ bar}\right) = 100\ {}^{N/m^2}/_{K^2}$$

$$C_p - C_v = VT\frac{\alpha^2}{\beta_T} = \left(10^{-4}\ {}^{m^3}/_{mol}\right)(623\ K)100\ {}^{\frac{N}{m^2}}/_{K^2} = 6.23\ {}^{J}/_{mol\ K}$$

Butane (58 g/mol):

$$C_p - C_v = 0.1\ {}^{J}/_{g\ K}$$

Toluene (92 g/mol):

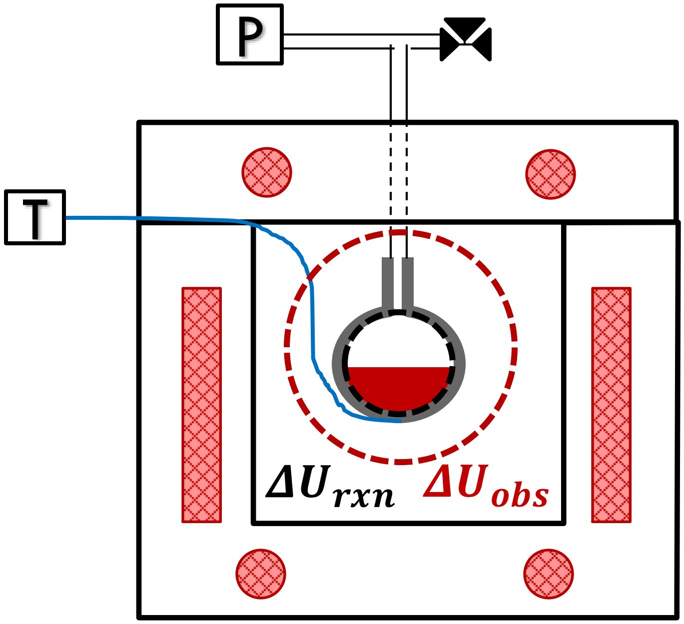
$$C_p - C_v = 0.067\ {}^{J}/_{g\ K}$$

Heat capacity of organic liquids is between 1.5-2.2 J/gK, typical error <10%

*Heat capacity is a function of temperature so taking an average heat capacity introduces additional error

Heat of Reaction from ARC

C_{pS} is average constant pressure heat capacity of sample: $\mathbf{Q_{rxn}} = \boldsymbol{m_S C_{pS} dT_{ad}}$



We **want** ΔT_{ad}, but we **get** ΔT_{obs}: $q_{rxn} = (MC_{pS})\Delta T_{obs}$

If we do a heat balance on the **ARC sphere** including the **sample**…

m_S: sample
m_B: sphere

$$q_{rxn} = m_S C_{pS} \Delta T_{ad} = \left(m_S C_{pS} + m_B C_{Bp}\right)\Delta T_{obs}$$

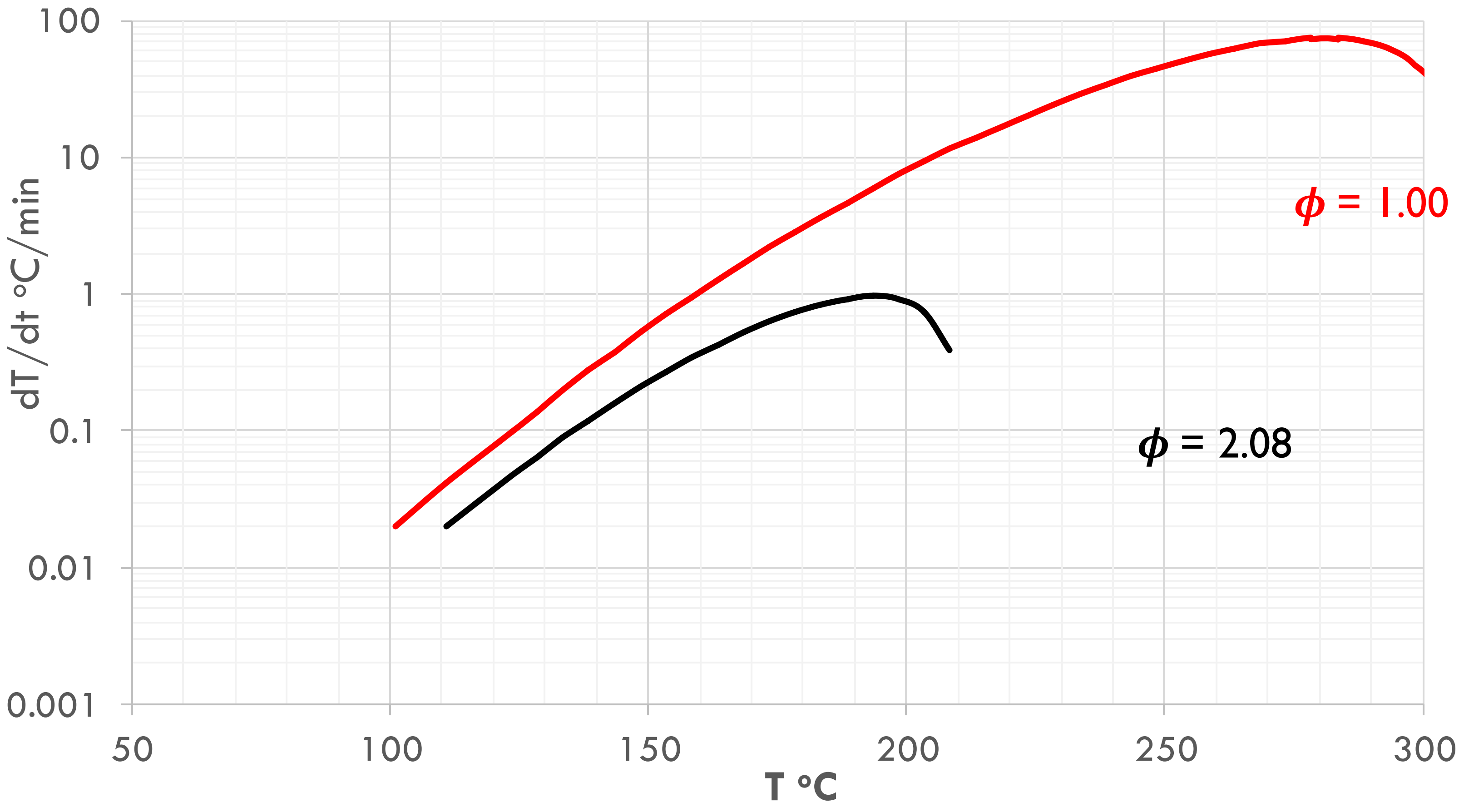
$$\frac{\Delta T_{ad}}{\Delta T_{obs}} = \frac{m_S C_{pS} + m_B C_{Bp}}{m_S C_{pS}} = \phi$$

PHI FACTOR, ϕ
or thermal inertia

$$\boldsymbol{q_{rxn} = \phi C_{pS} \Delta T_{obs}}$$

Impact of PHI in ARC Test

Example of simple first order reaction and impact of PHI



Note: X-axis is reciprocal absolute temperature but °C are superimposed for convenience

Kinetic data from ARC to close heat balance

E$_a$: activation energy
A: pre-exponential factor
n: reaction order

Key Kinetic Assumptions in ARC

- Heat of reaction (ΔT is related to change in concentration)

For an nth order reaction with one reactant… $\frac{dC}{dt} = -kC^n$

$$C = \frac{T_f - T}{\Delta T_{ad}} C_o = \frac{T_f - T}{\phi \Delta T_{obs}} C_o$$

Concentration of reactant at a given time
T_f: final temperature
T: temperature at time t
C_o: initial concentration

Differentiate with respect to time, and combine these two equations to get…

$$k^* = C_o^{n-1} k = \frac{\frac{dT}{dt}}{\left(\frac{T_f - T}{\phi \Delta T_{obs}}\right)^n (\phi \Delta T_{obs})}$$

Arrhenius kinetic parameters: $k = Ae^{\frac{-E_a}{RT}}$

$$\boxed{\ln k^* = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A^* \qquad A^* = C_o^{n-1} A}$$

$$\ln k^* = \ln\left(\frac{dT}{dt}\right) - n \ln\left(\frac{T_f - T}{\phi \Delta T_{obs}}\right) - \ln(\phi \Delta T_{obs})$$

Linear or Non-linear regression can be used to find E$_a$, A* and n

[2] Townsend and Tou, *Thermochim. Acta* **1980**, 37, 1-30

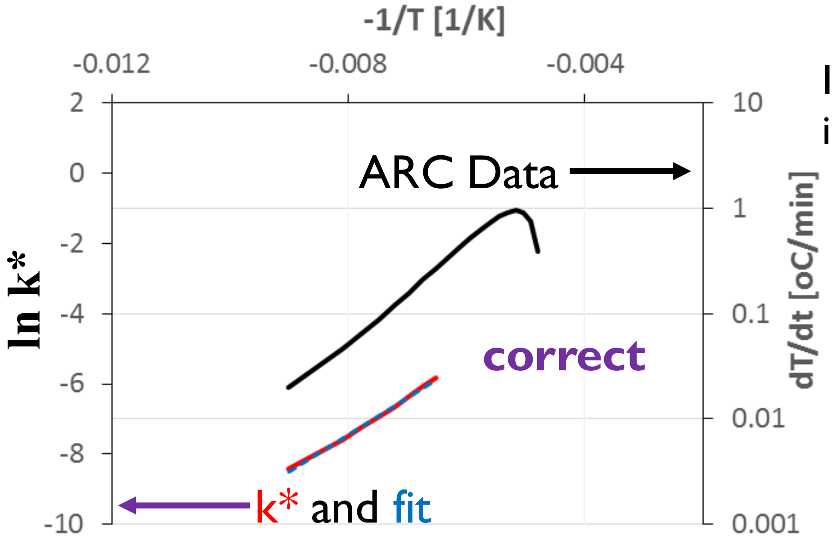
Reaction Kinetics from ARC

Linear regression to determine n

- Activation energy and pre-exponential can be determined via calculation

Arrhenius kinetic parameters: $k = Ae^{\frac{-E_a}{RT}}$

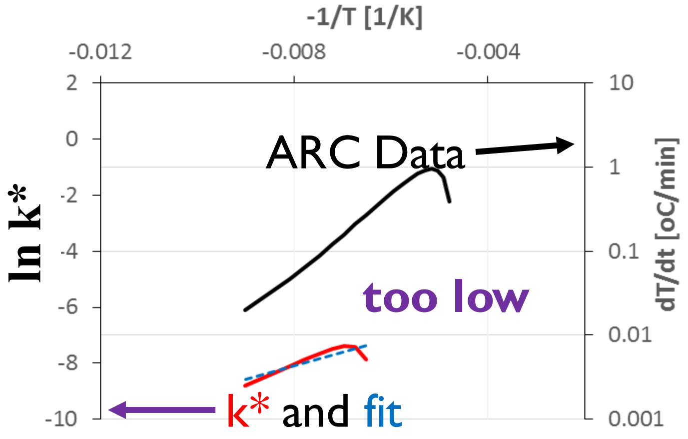
$$\boxed{\ln k^* = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A^* \qquad A^* = C_o^{n-1}A}$$

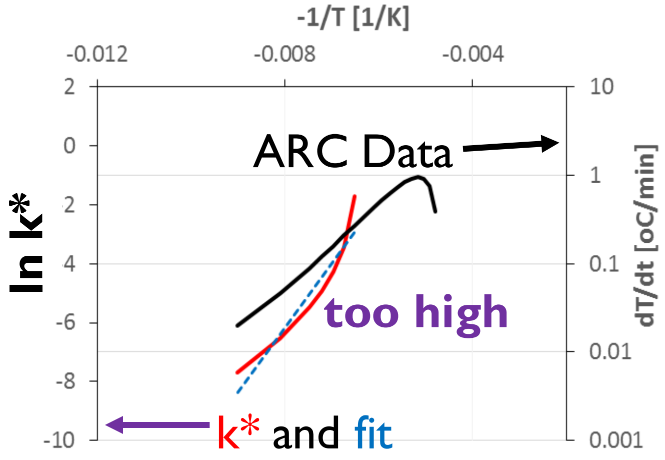


If the order of reaction is chosen correctly,

$$\ln k^* = a\frac{1}{T} + b$$

Solve for E_a,A





This approach is fast and typically accurate enough for a heat balance to determine TNR from temperature rate curve. Linear regression is NOT recommended to generate Temperature vs. Time curve.

Reaction Kinetics from ARC

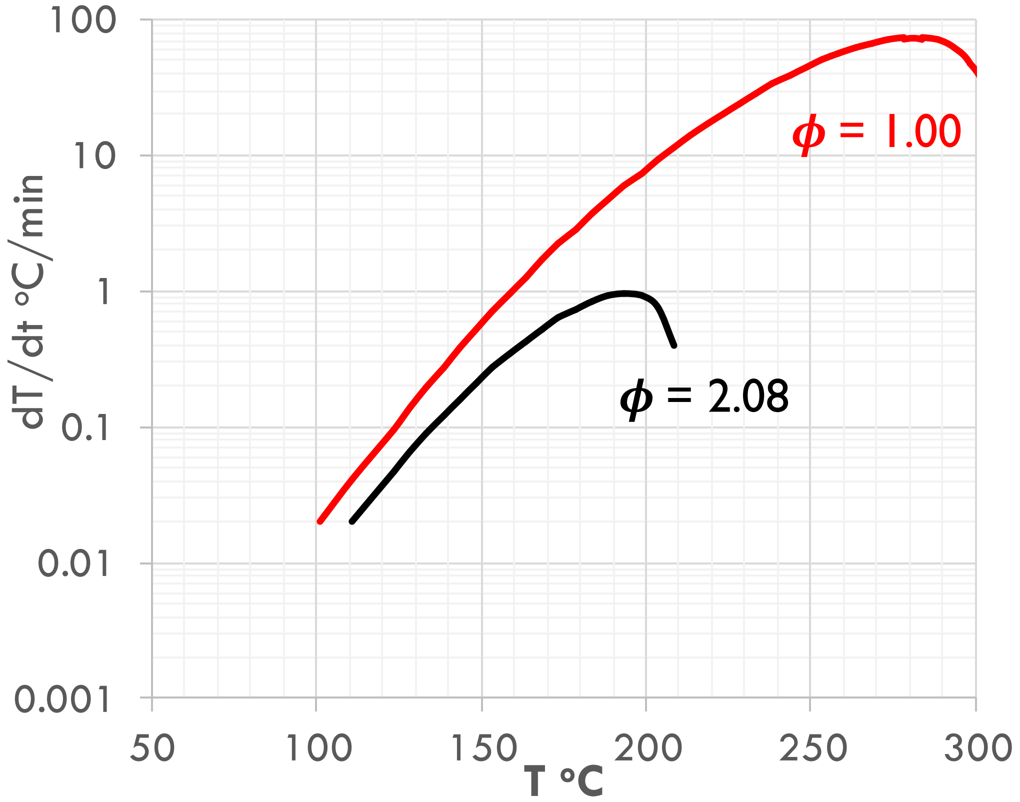
Once the activation energy is known, we can correct the full range of ARC data using the Fisher equation:

$$\left.\frac{dT}{dt}\right|_{\phi=1} = \phi \exp\left(\frac{E_a}{R}\left(\frac{1}{T_m} - \frac{1}{T_a}\right)\right)\left.\frac{dT}{dt}\right|_{\phi>1}$$

$$T_a = T_o + \phi(T_m - T_o)$$

T_m: measured temperature

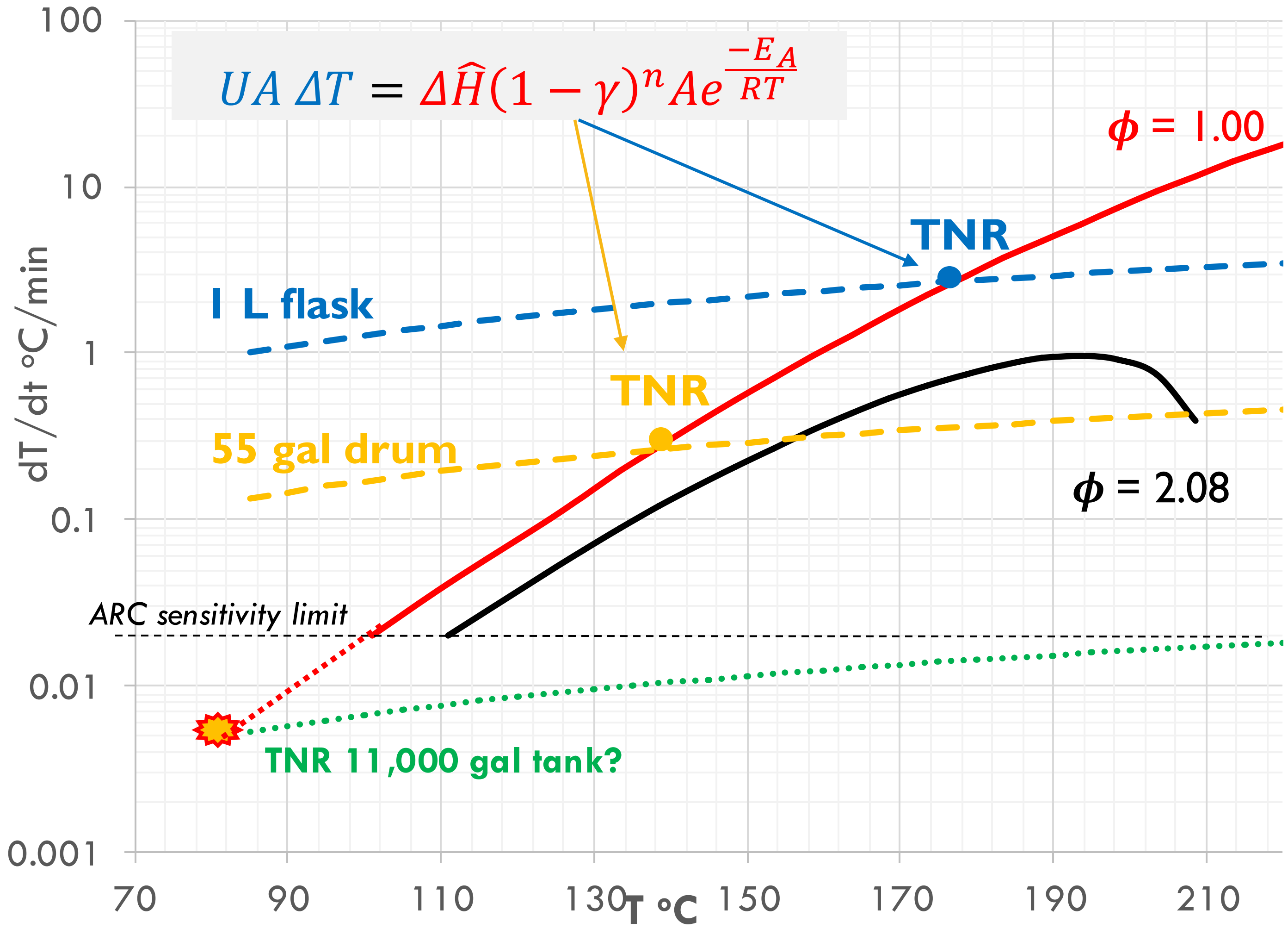
Note: the above equation should NOT be integrated to create the Temperature vs. Time curve



[3]Kossoy, Singh, and Koludarova, *J. Loss Prev. Proc. Ind.*, **2015**, 33, 88-100

Reaction Kinetics from ARC

The TNR can now be estimated (ex. below assumes heat transfer limitation at boundary (Q=UAΔT)



1. Plot ARC data with ϕ = 1.00

2. Plot heat removal rate
   - 1 L flask
   - 55 gal drum
   - 11,000 gal

3. Intersection = Temperature of No Return

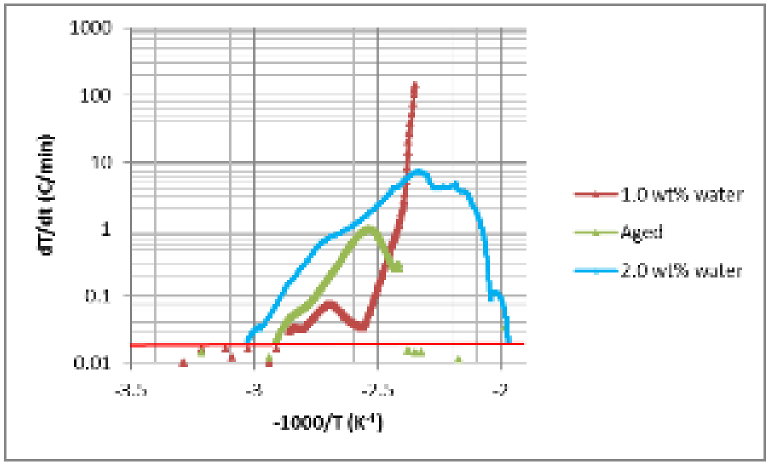
ϕ-corrected data are essential for accurate, safe predictions

More sophisticated modeling approaches may be necessary for other chemistries.

Complex heat balance (no convection)

System in internally heat transfer limited (Kinetic parameters from Linear or Non-linear regression)

- Frank-Kamenetskii approach



$$\delta = \frac{\Delta H}{k}\frac{E}{RT_w^2}x_o^2\,\rho A e^{\frac{-E}{RT_w}} \qquad \delta > \delta_c$$

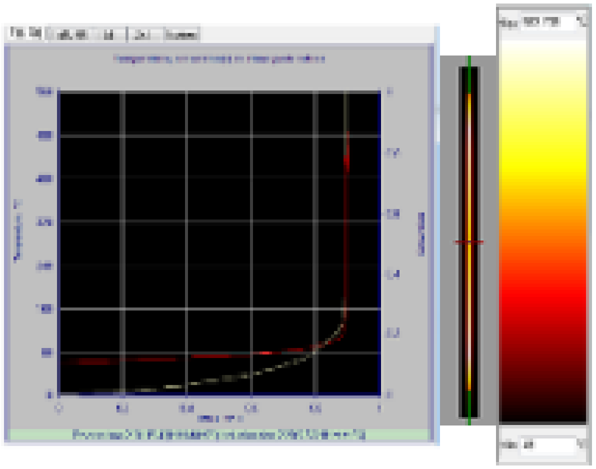
$$\partial_{slab} = 0.88, \partial_{sphere} = 3.32, \partial_{cylinder} = 2.00$$

Critical diameter of vessel exceeded = Thermal Runaway!

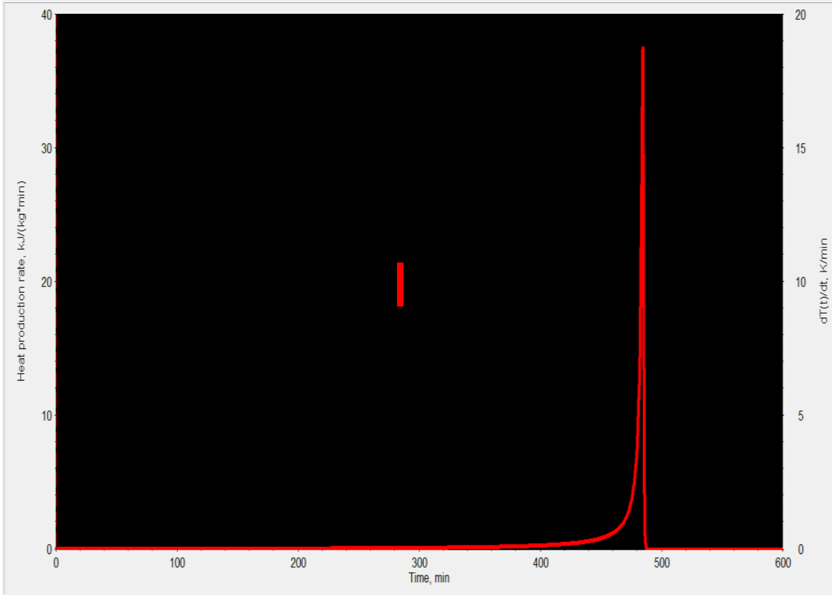
Need spacial and temporal temperature information

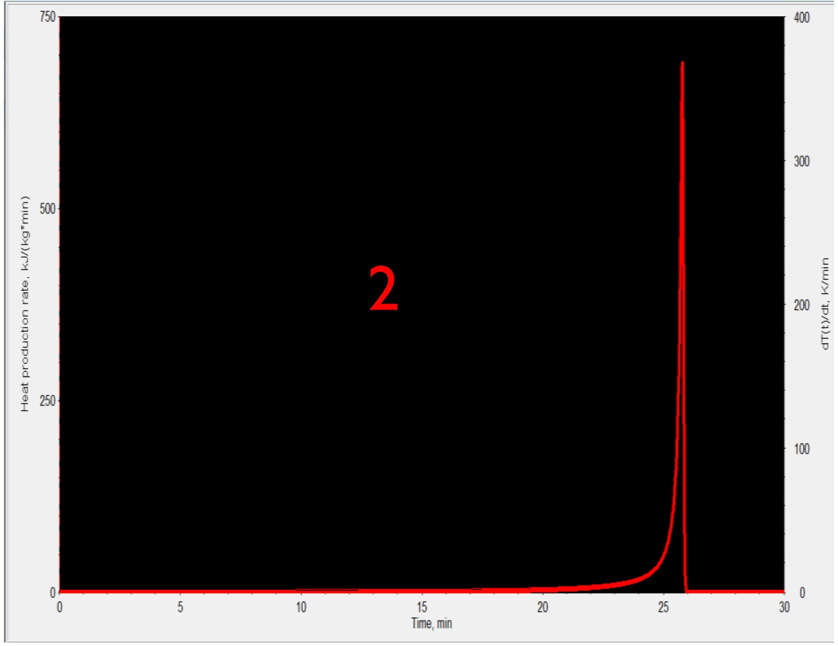
- Finite analysis method (Comsol and others)
- Method of Lines (TSS software)
  - cannot be used on elliptical PDE’s

$$\left(C_{pb}\rho_b\frac{\partial T}{\partial t} + C_{pg}\rho_g v.\nabla T\right) = (\nabla\cdot k\nabla T) + \sum\left\{-\Delta H_{rx}C^n A e^{\frac{-E_a}{RT}}\right\}_j$$



External Heat Input and Pooling Effect





Adiabatic Reaction Trajectory

- Heat of reaction = -250 J/g
- Order of reaction = 1
- Activation energy = 120 kJ/mol
- Ln A = 26 s^{-1}
- dQ/dt_{max} ~ 38 J/(g*min)

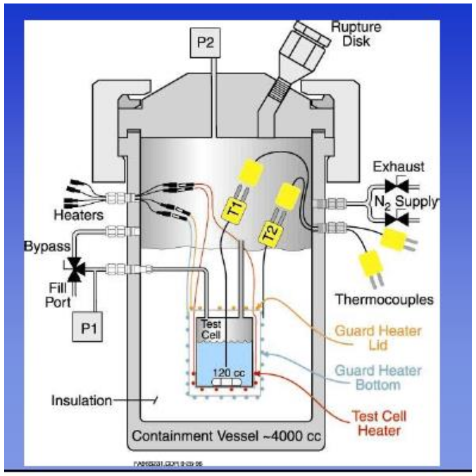
2°C/min Heat Input Rate and No Energy Loss (Fire scenario where vessel is engulfed)

- Heat of reaction = -250 J/g
- Order of reaction = 1
- Activation energy = 120 kJ/mol
- Ln A = 26 s^{-1}
- dQ/dt_{max} ~ 710 J/(g*min)

Vent Sizing Package (VSP)

Why VSP

- Significant stirring capability (test cell & agitator can be made to specifications)
- Can simulate an external heat input (mimic a fire or steam valve failure in real process)…pooling effect will be accounted for and real reaction trajectory measured instead of adiabatic trajectory
- Low phi factor device (*data does not need to be corrected for scale)
- Adiabatic to very high heat rates
- Determination of vent flow type (blow down test)



Key disadvantages

- Higher cost per test
- Less sensitive

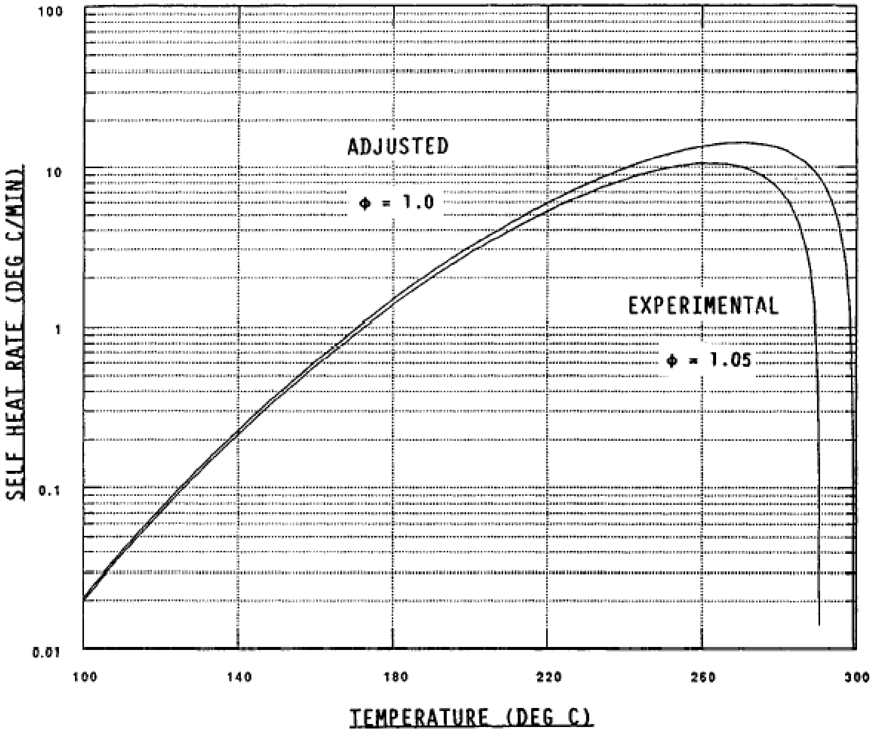


FIGURE VI-A2. Sample kinetics — self-heat rate versus temperature [33].

Preferred calorimeter for relief sizing at Dow

Pressure Data from Adiabatic Calorimetry

Pressure Data should be plotted as log of pressure vs. reciprocal absolute temperature

- Allows for rapid detection of non-condensable gas formation
- Clausius-Clapeyron space (vapor pressure should be straight line until critical point is approached

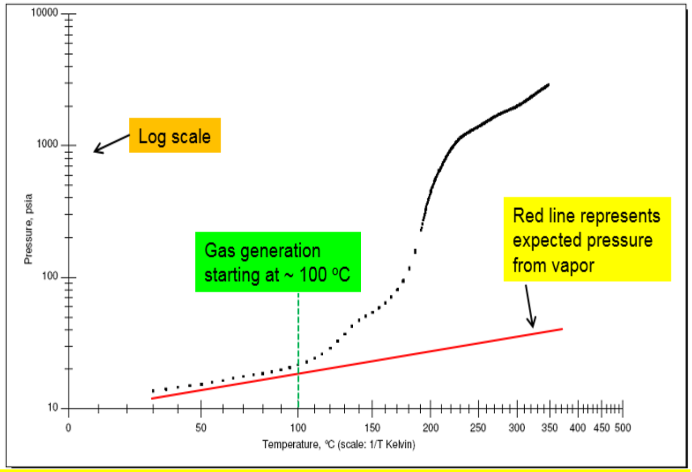
$$\frac{d\ln P}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

Assumes molar volume of gas much greater than liquid (good assumption far from the critical temperature). Assumes vapor phase can be approximated by ideal gas law.

$$\int d\ln P = \frac{\Delta H_{vap}}{R} \int \frac{1}{T^2} dT \longrightarrow \ln P = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C$$

<u>Assumes heat of vaporization is constant :</u> weak function of temperature until near critical point where it exponentially approaches 0

$$y = mx + b$$



Log scale

Gas generation starting at ~ 100 °C

Red line represents expected pressure from vapor

HINT: look for pressure changes during search steps, temperature is constant so pressure changes should be from gas generation not vapor pressure

NOTE: if pad gas pressure is initially much higher than vapor pressure a change in slope maybe due to vapor pressure starting to dominate

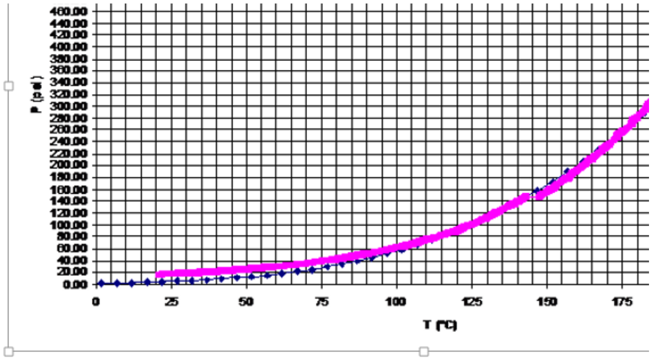
Antoine Coefficients from Adiabatic Data

Low Vapor Pressure Material

- Pull vacuum on ARC sphere to remove non-condensable gas (typically air or nitrogen)
- Perform ARC test and plot pressure on log scale vs. reciprocal absolute temperature
- Use linear portion of curve near beginning of test calculate Antoine coefficients

High Vapor Pressure Material

- After loading ARC sphere heat sample slightly so pressure exceeds ambient
- Vent ARC sphere for 15 seconds which will remove non-condensable gas
  - Alternatively, calculate pad gas pressure and subtract from data
- Perform ARC test and plot pressure on log scale vs. reciprocal absolute temperature
- Use linear portion of curve near beginning of test calculate Antoine coefficients



Purple is calculated pressure from ARC
Blue is from physical property database

Pressure data from ARC and three point method can be used to determine the parameters for the Antione Equation.
This method is outlined in:
Stull, D.; Westrum, Jr. E.; Sinke, G. (1987)
THE CHEMICAL THERMODYNAMICS OF ORGANIC COMPOUNDS,
Malabar, FL: Robert E. Krieger Publishing Company Inc.

Antoine – Equation

$$Log_{10}P = A - \frac{B}{T+C}$$

where;

$$C = \left(\frac{T_3 - T_1}{\left[1 - \left(\frac{y_3 - y_2}{y_2 - y_1} \right) \left(\frac{T_2 - T_1}{T_3 - T_2} \right) \right]} \right) - T_3$$

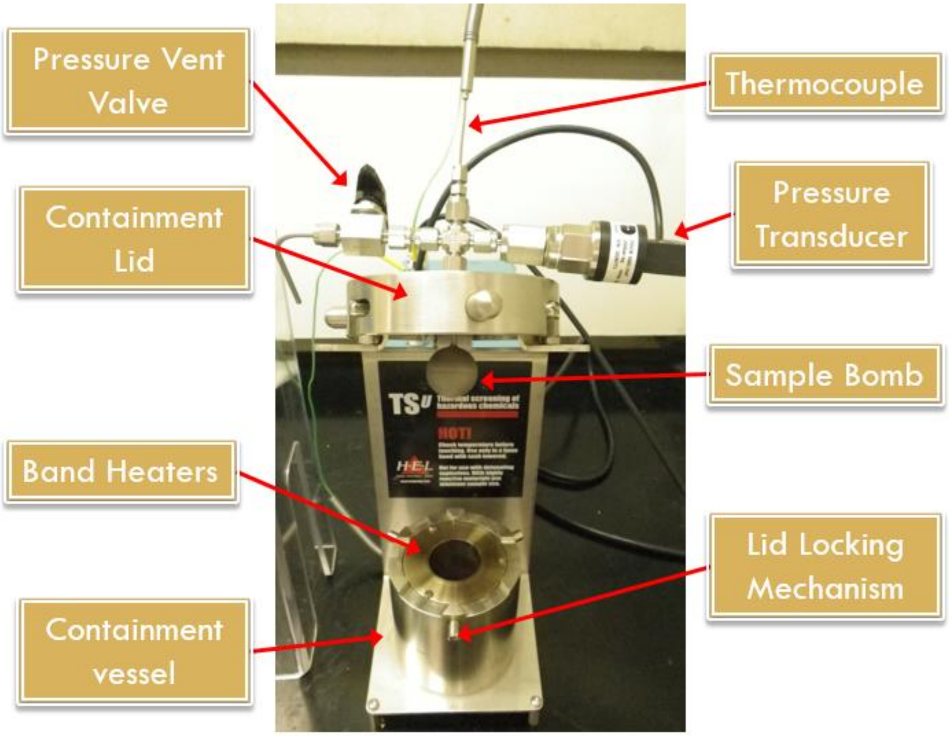
$$B = \left(\frac{y_3 - y_1}{T_3 - T_1} \right) (T_1 + C)(T_3 + C)$$

$$A = y_2 + \frac{B}{T_2 + C}$$

Thermal Screening Unit (TSu)

Why use TSu

- Fast and Easy
- Provides Pressure Data
  - What temperature does non-condensable gas generation become significant
  - Measure gas generation under pseudo-isothermal conditions
  - Larger sample size so compliments Differential Scanning Calorimetry
- Sensitivity close to an ARC



When to use or not use TSu

•Use - low viscosity fully miscible system

•Use – high sensitivity needed

•Use – fine granulated solids that melt in temperature range of experiment

•Use – pressure data is needed

•Use - screening many different reaction mixtures

•Not Use – small quantity of highly volatile reaction component

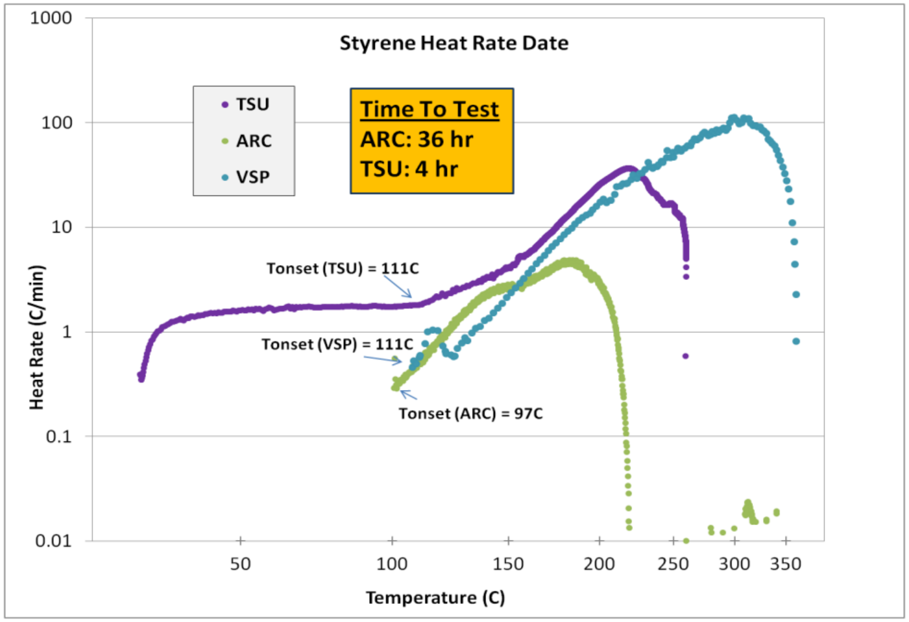
•Not Use – trying to determine reaction kinetics and heats of reaction

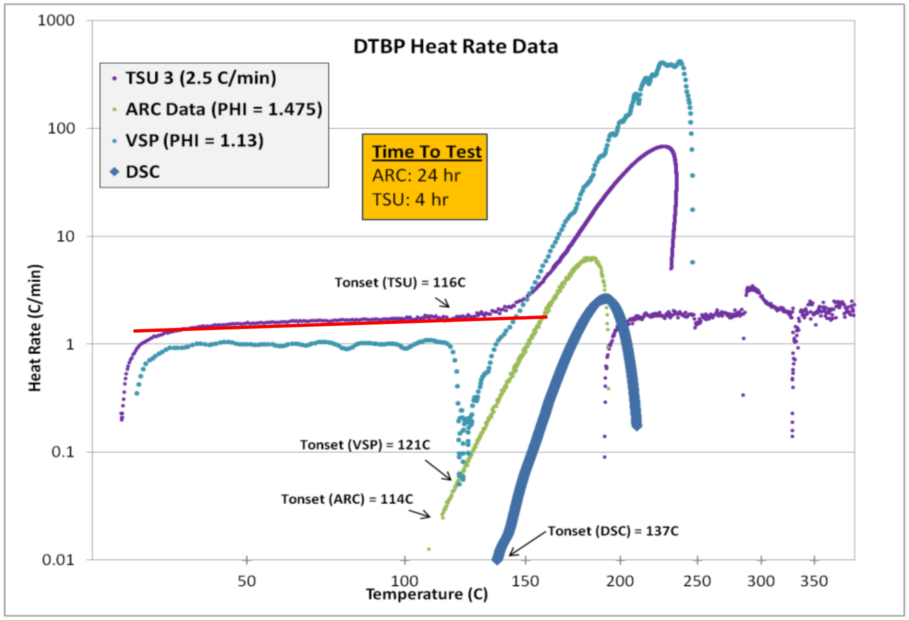
- Max Temperature: 400°C
- Max Pressure: 3000 psi
- Heating Rates: 0-5°C

Sample size: 1-7 g
Sample container: ARC sphere
Mode of operation:

- Isothermal
- Scanning

Comparing TSu Data with ARC, VSP and DSC





Styrene (low activation energy system)

- ARC detected onset 97 °C
- TSu detected onset 111 °C
- VSP detected onset 111 °C

20 wt% DTBP in Toluene Typical activation energy system

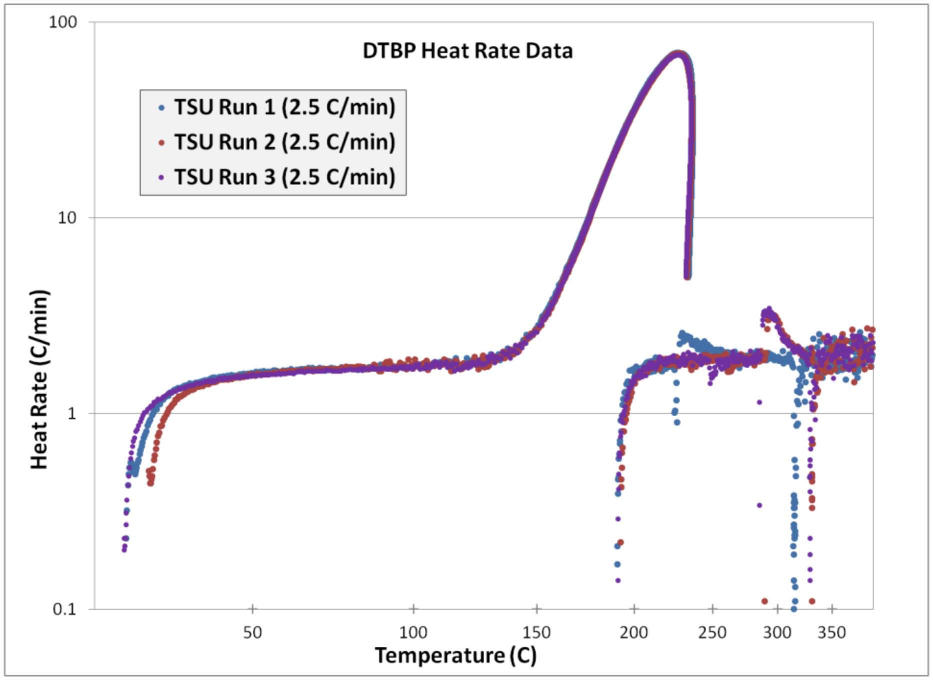
- ARC detected onset114 °C
- TSu detected onset 116 °C
- VSP detected onset 121 °C
- DSC detected onset 137 °C

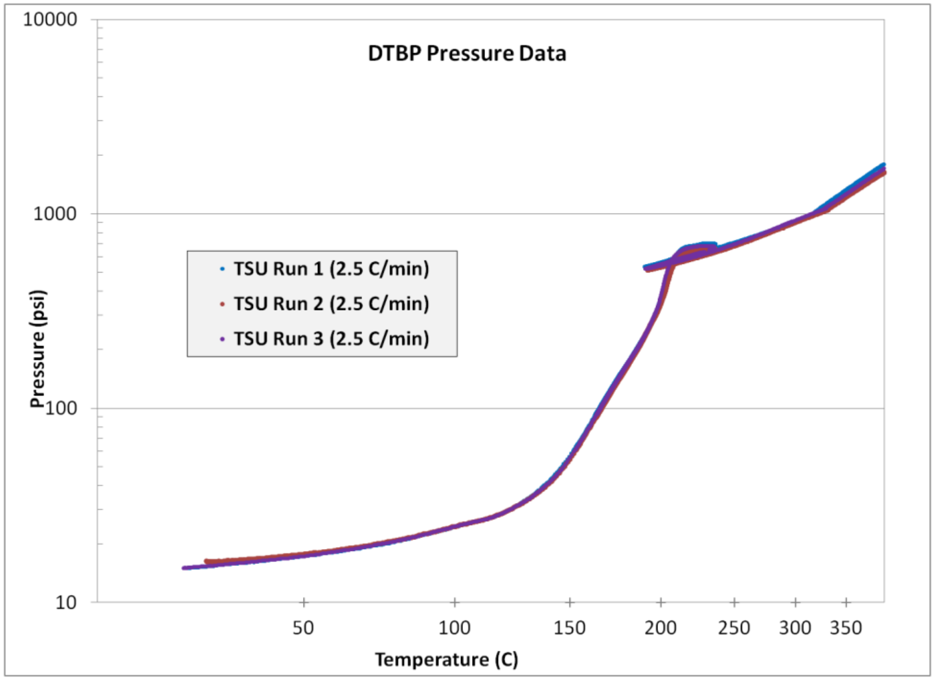
Not a calorimeter but has good sensitivity to detect exotherms!

TSu

20 wt% DTBP in Toluene

- Good reproducibility



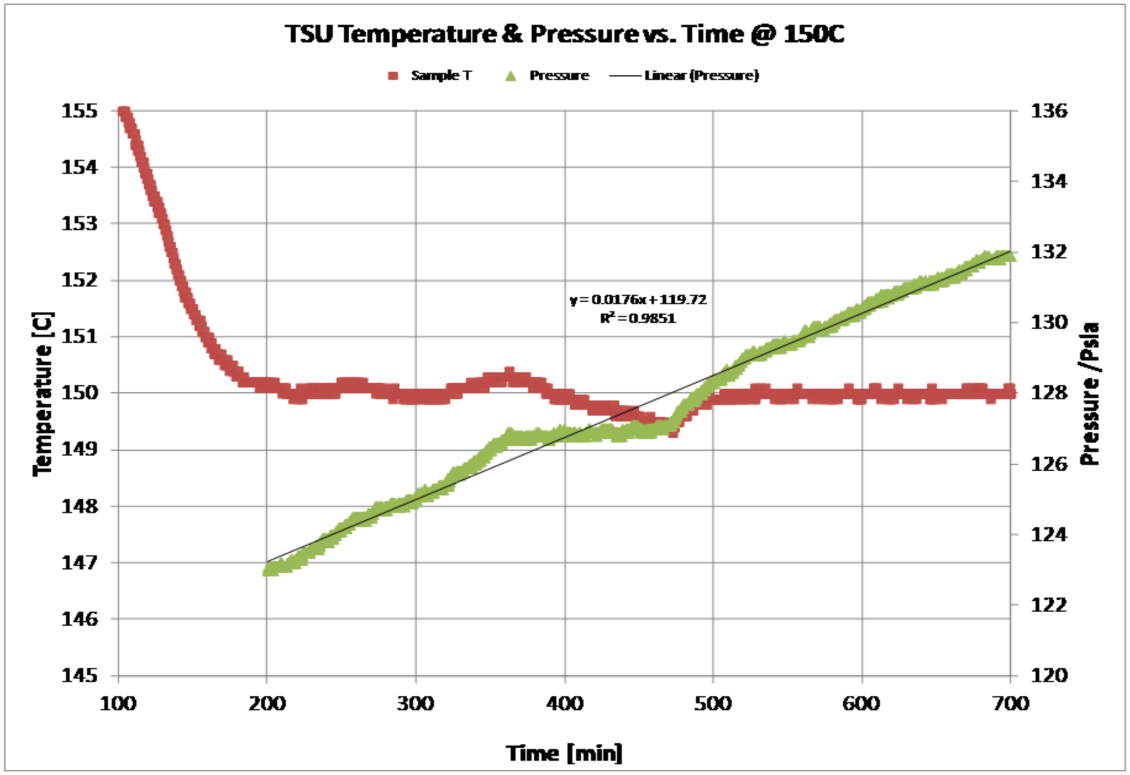


Not a calorimeter but has good sensitivity to detect exotherms!

Isothermal TSu to Determine Gas Generation Rate

Constant oven temperature TSu

- Gas generation frequently occurs lower than where exotherm is noticeable
- Some reactions generate gas and are endothermic (entropically driven reactions)
- Even slow gas generation rates are important to understand in large vessels
- Gas generation rates can be quantified on a mol/(g*time) basis which can be scaled
- Often good to choose a temperature 10 °C to 20 °C higher than actual conditions
    - Solubility of non-condensable gases decreases
    - Provides more conservative results (reactions are exponential functions of temperature)

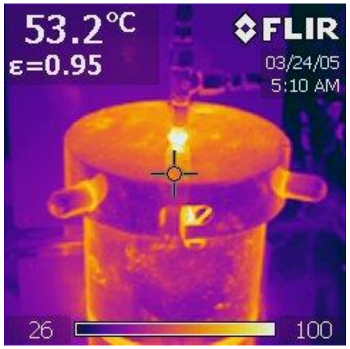


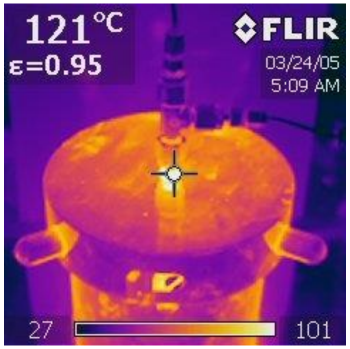
Vapor Pressure in TSu

Vapor pressure issues in TSu

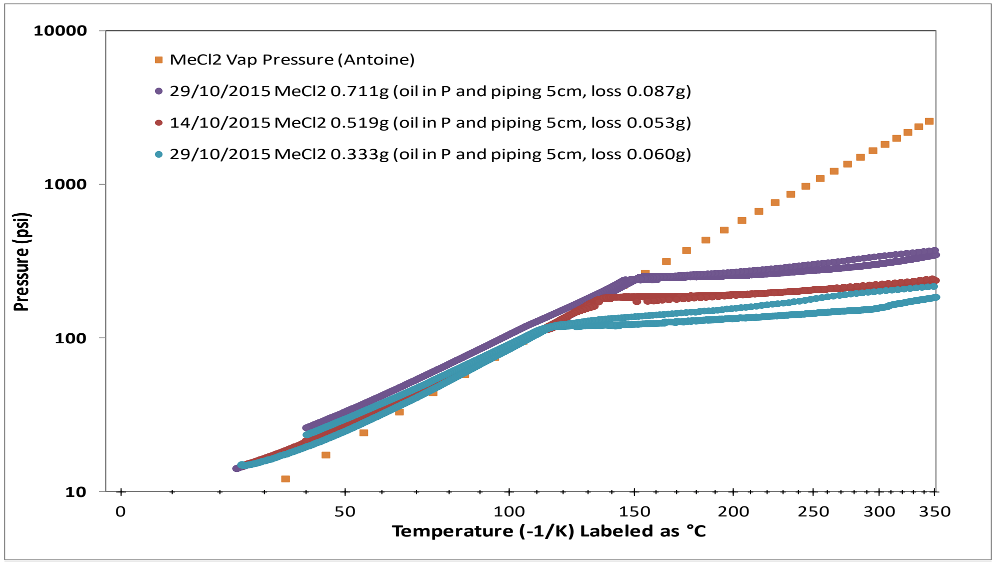
- Condensation in external tubing and valves
- Reflux in neck of TSu
- May result in loss of a volatile reaction component
- When prevalent results in large temperature gradient between sample and oven
  - Typically results in a false exotherm

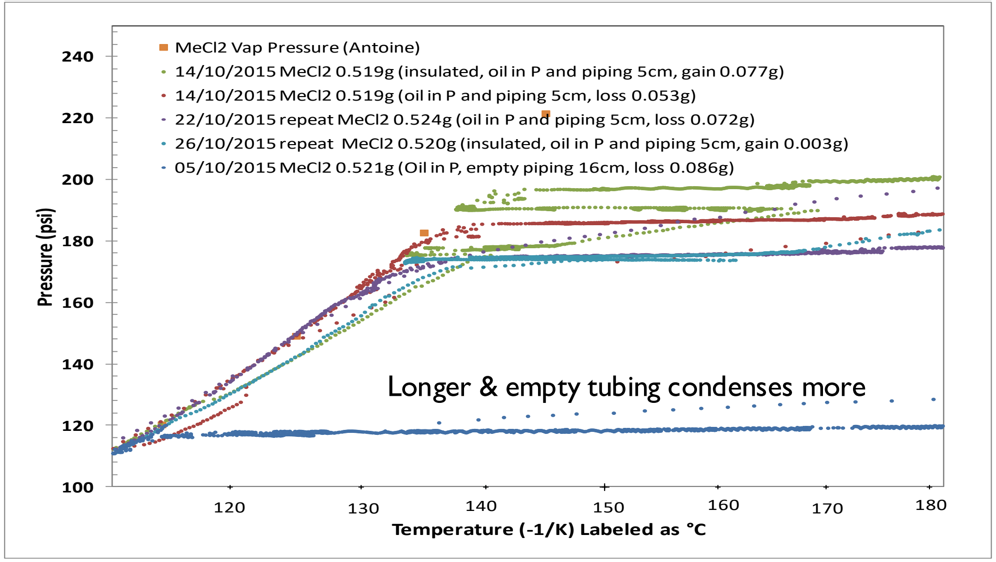
Why





The sample sphere is at 250 °C, the lid and the pass through are much cooler resulting in condensation/reflux. If the sample contains low level of volatile, this is a big issue.





Longer & empty tubing condenses more

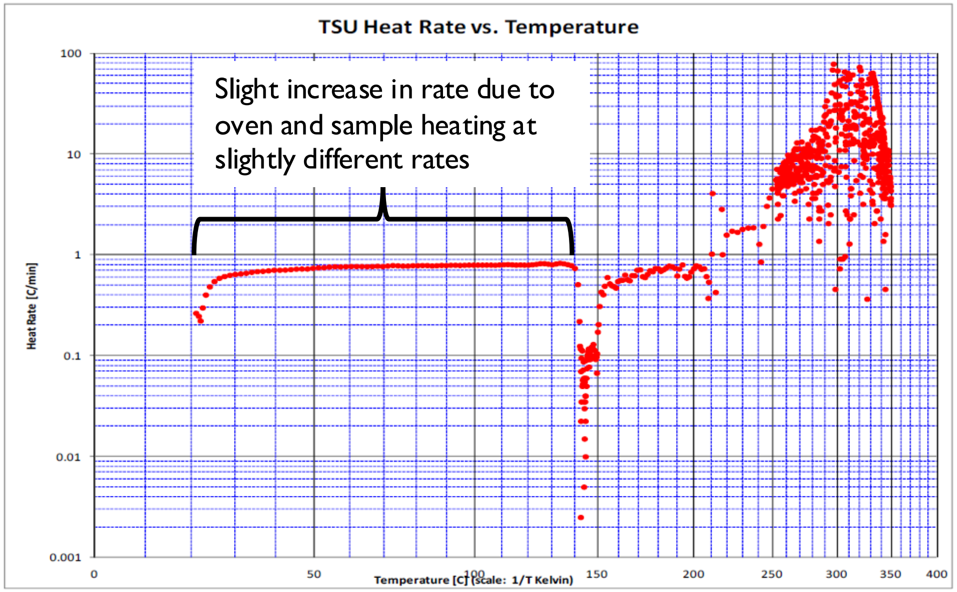
* Data collected by Min Sheng

False Exotherm TSu

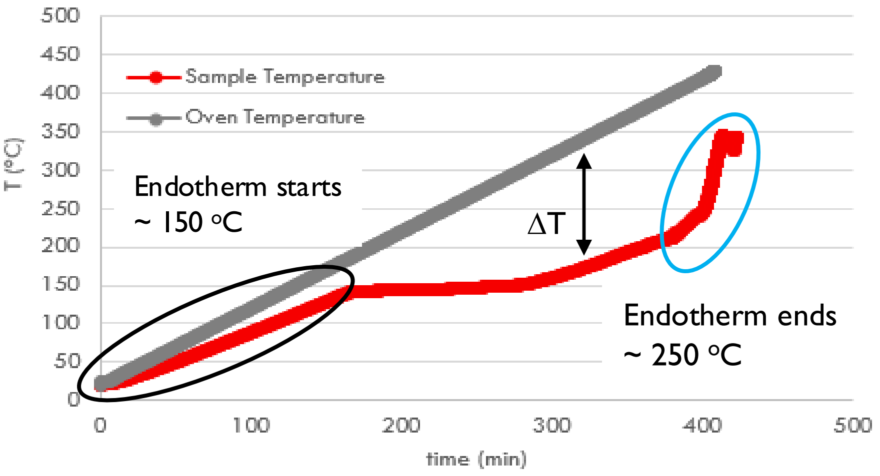
Target heat rate = 2 °C/min

- From starting temp to 150 °C oven and sample have only slightly different rates (appears as a small positive slope in heat rate)
- At 150 °C there is an endothermic event that lasts until approximately 250 °C
- There is a large temperature gradient between sample and oven as a result
- When endotherm ends the large temperature gradient results in a much more rapid heating of the sample
- The rapid heating appears as an exotherm but it is a heat transfer phenomenon NOT a chemical reaction!

Using inserts from HEL helps but will not eliminate
Minimizing external volume helps but will not eliminate
Heating of Lid is likely the best approach but not easy to do



Slight increase in rate due to oven and sample heating at slightly different rates



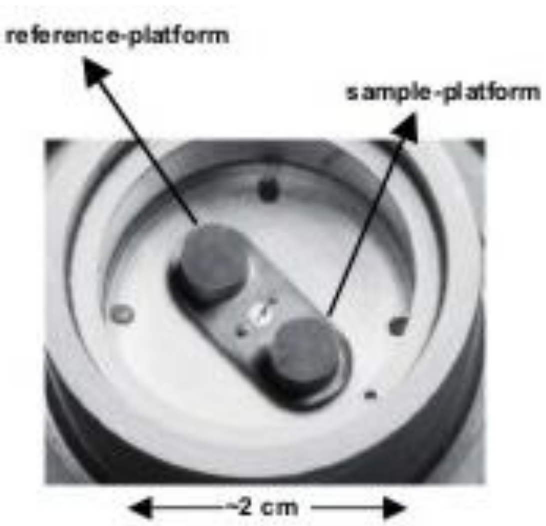
Endotherm starts ~ 150 °C

Endotherm ends ~ 250 °C

Differential Scanning Calorimetry

Why use DSC

- Rapid results
- Excellent heat of reaction for homogeneous systems
- Provides good thermo-kinetic data for energy balance
- True isothermal testing capability
- Temperature scanning capability (-90 to 500°C)



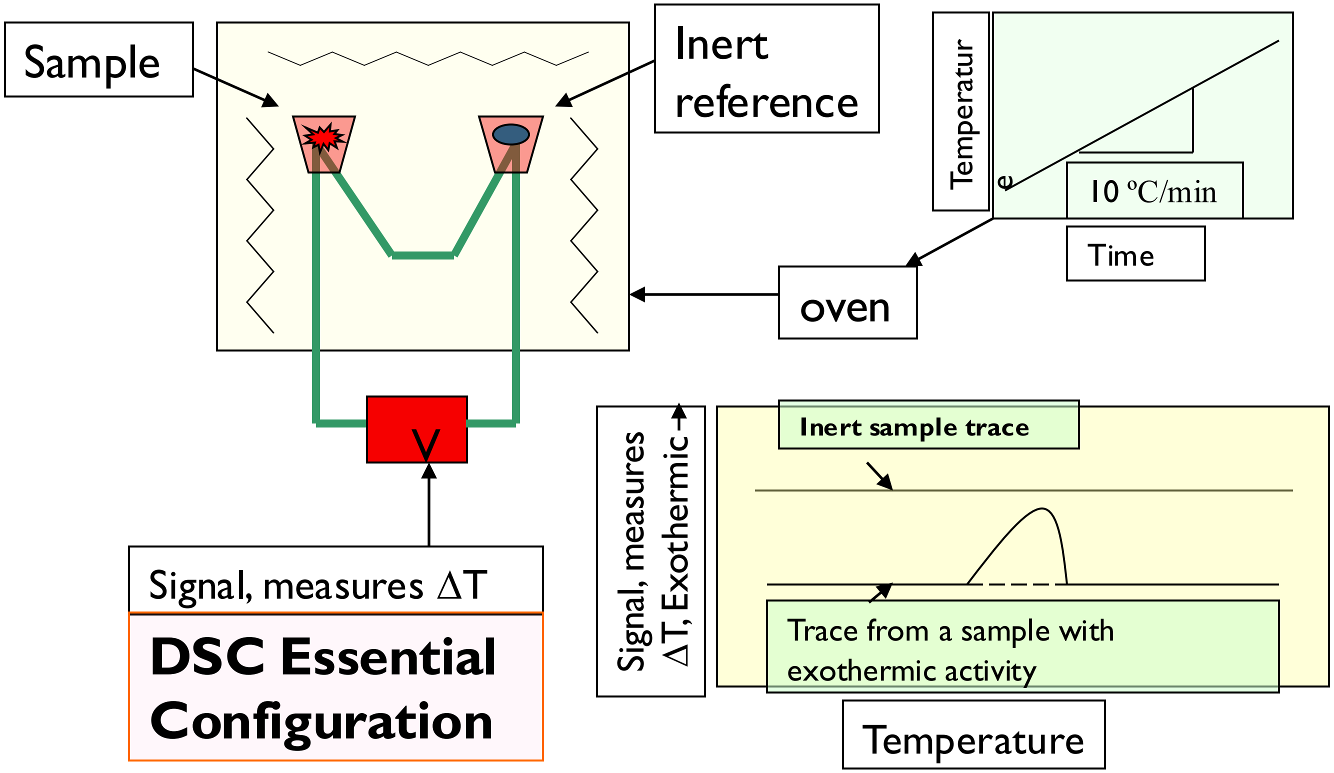
When to use or not use DSC

- Use – heat of reaction homogeneous system
- Use – screening
- Use – thermo-kinetic data for homogeneous systems
- Use – screening or validating autocatalysis
- Not use – pressure data is needed (TSu/DSC combination will work well in this situation)
- Not use – inhomogeneous systems

Differential Scanning Calorimetry

DSC Fundamentals

- Heat flow vs sample temperature compared with heat flow vs reference temperature
- Heat flux DSC, like Q2000, have a single silver heating block in direct contact with a precisely machined sensor and thermocouples under the sample and reference are used to determine heat flow
- DSC does not directly measure sample temperature
- Response time of the instrument, thermal properties of sample, type of sample container and container contact with sensor impact shape of thermogram



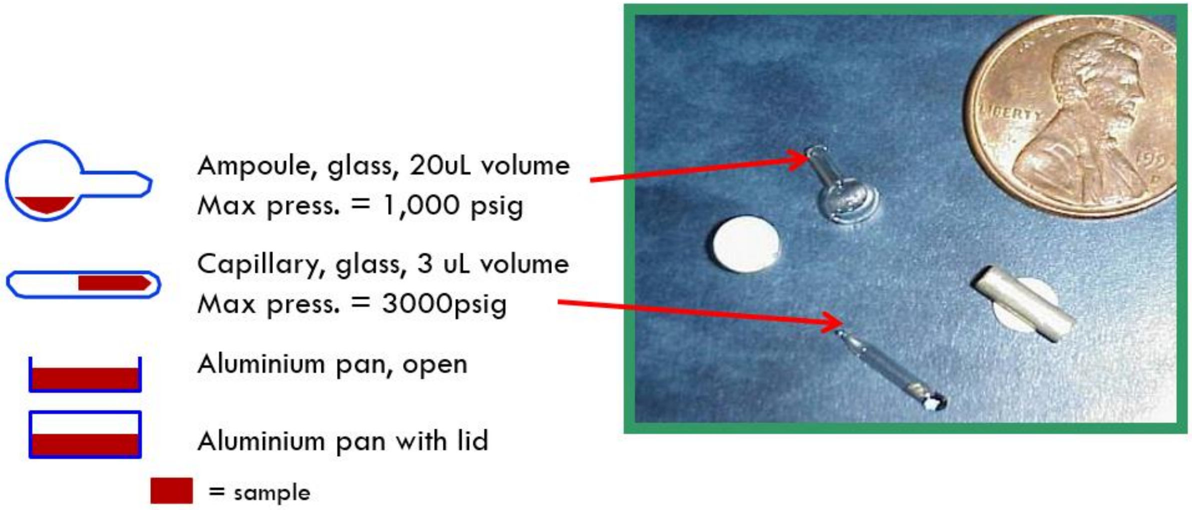
DSC Essential Configuration

Heat flow vs time and Temperature vs time are impacted by instrument and need deconvolution for good kinetic modeling results

DSC Sample Container Choice

Containers used for reactive chemical analysis as Dow

- Borosilicate glass capillary (most common)
- Borosilicate glass ampoule
- Crimped high pressure gold pans



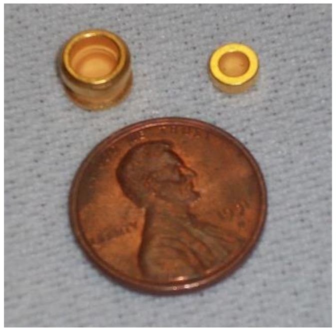
Ampoule, glass, 20uL volume
Max press. = 1,000 psig

Capillary, glass, 3 uL volume
Max press. = 3000psig

Aluminium pan, open

Aluminium pan with lid

🟥 = sample



Universal (gold plated) Crucible
Mass: 0.98 g; height: 4.5 mm; Diameter: 7.0 mm; Volume: 20 microliters
Tested up to 200 bar (2900 psi) at 400°C (tested with supercritical water pressure)

<u>Universal (gold plated) crucible can be used to avoid sample incompatibility with materials of construction</u>

DSC Thermograms

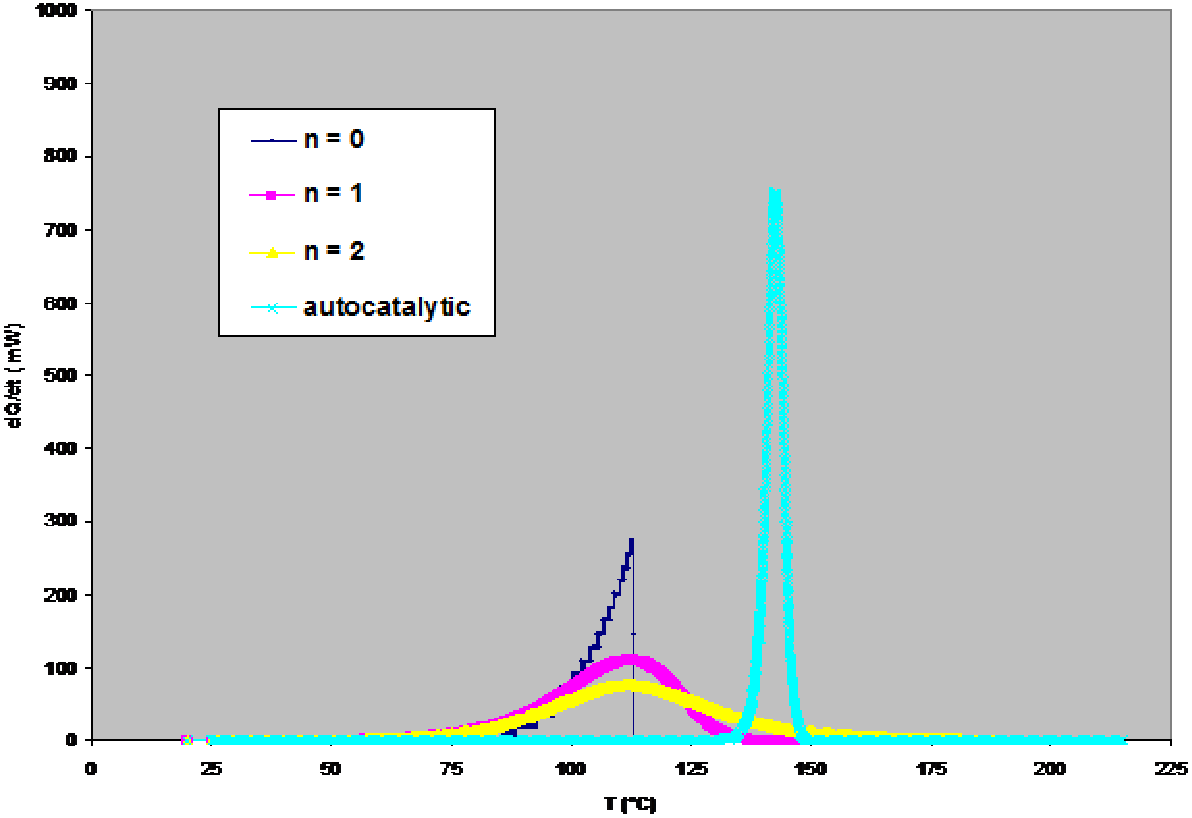
Reaction order and type on shape of thermogram

- Activation energy = 120 kJ/mol
- Heat of reaction = 500 J/g
- Ln A = 26 s^{-1}
- Order of reaction for autocatalytic reaction = 1
- Scan rate = 10 °C/min

Peak shape is impacted by reaction order

Detected onset temperature is not impacted by reaction order

Autocatalytic reactions have an induction time where little to no heat is released



DSC Thermograms

Scan rate impact on thermogram

- Activation energy = 120 kJ/mol
- Heat of reaction = 500 J/g
- Ln A = 26 s^{-1}
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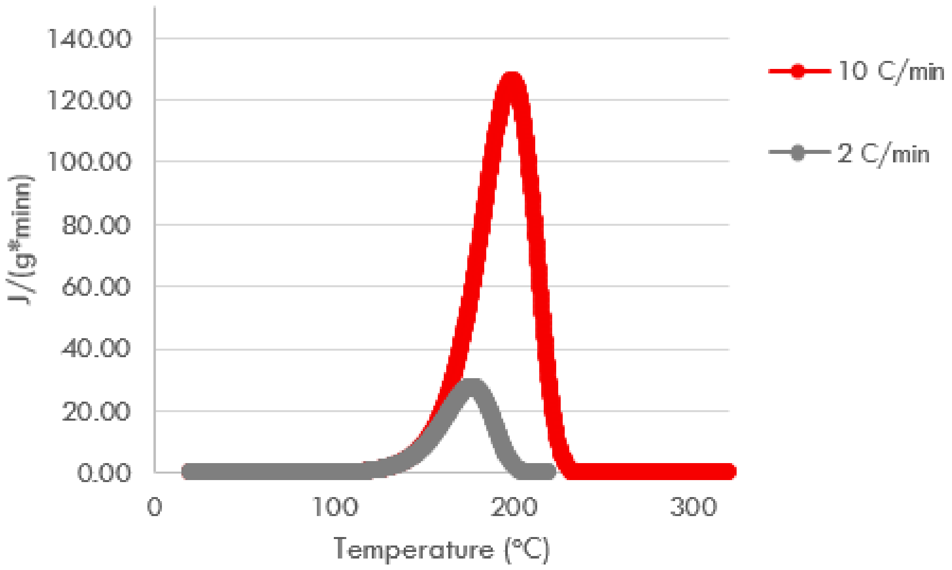
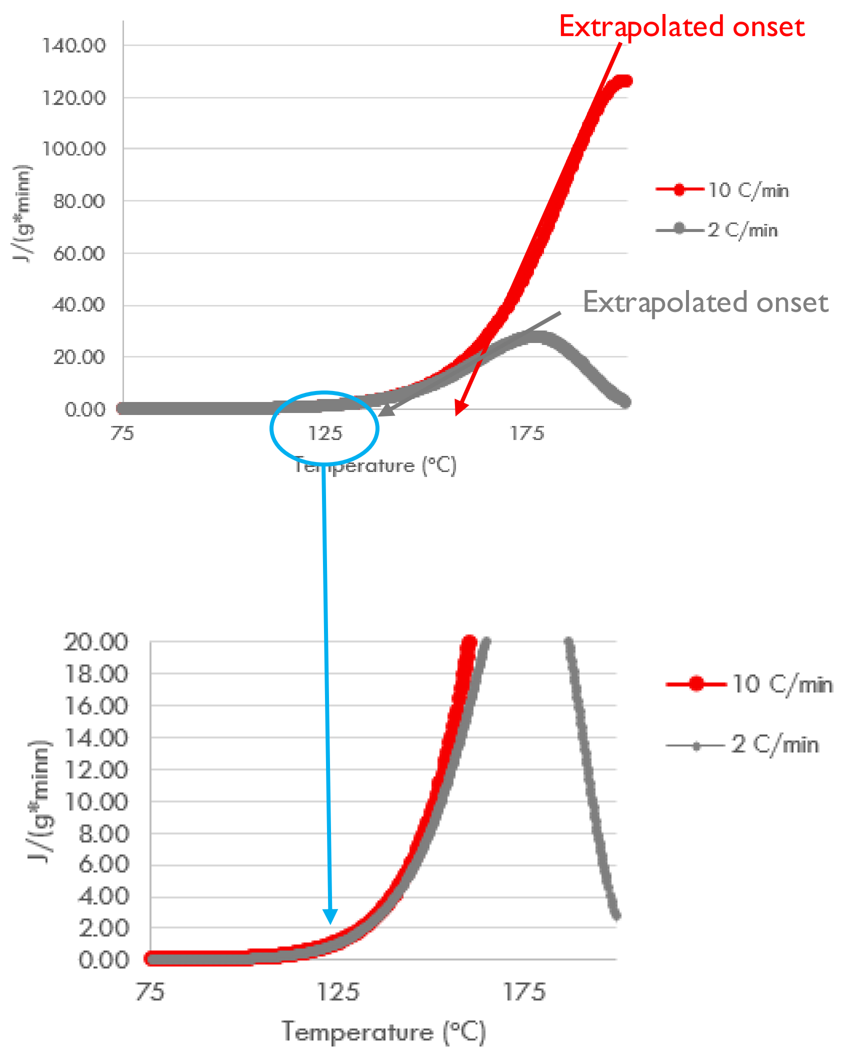


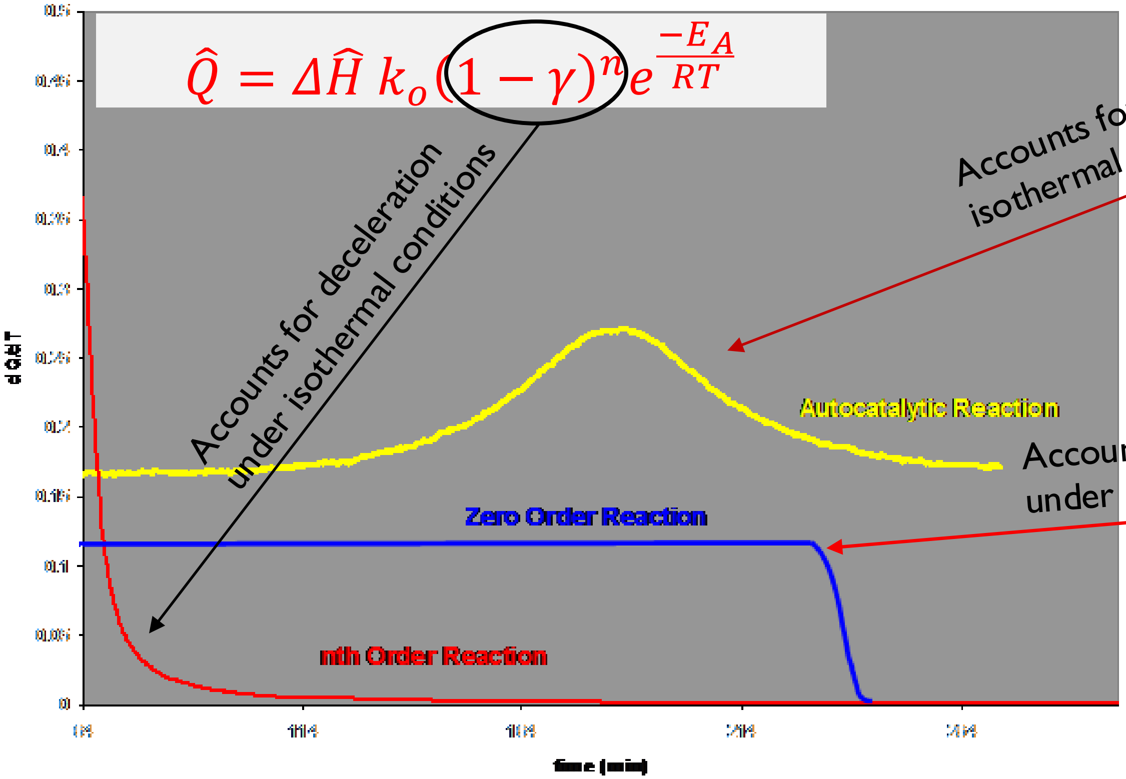


DSC Isothermal Thermogram

Autocatalysis

- Activation energy = 120 kJ/mol
- Heat of reaction = 500 J/g
- Ln A = 26 s^{-1}

$$\hat{Q} = \Delta\hat{H}\, k_o (1-\gamma)^{n1} e^{\frac{-E_A}{RT}} \left(Z_0 e^{\frac{-E_Z}{RT}} + \gamma^{n2} \right)$$



$$\hat{Q} = \Delta\hat{H}\, k_o (1-\gamma)^{n} e^{\frac{-E_A}{RT}}$$

Accounts for deceleration under isothermal conditions

Accounts for acceleration under isothermal conditions

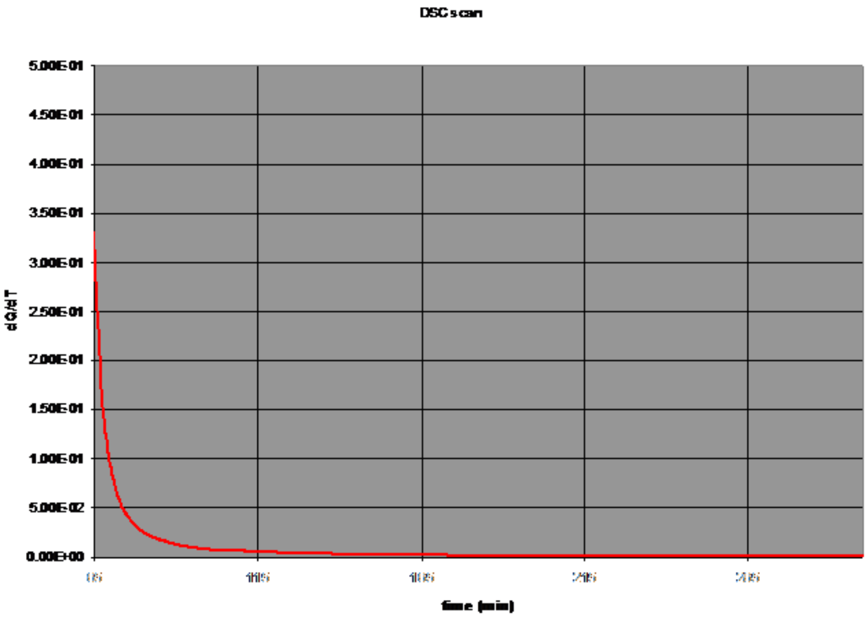
Accounts for constant rate under isothermal conditions

$$\hat{Q} = \Delta\hat{H} e^{\frac{-E_A}{RT}}$$

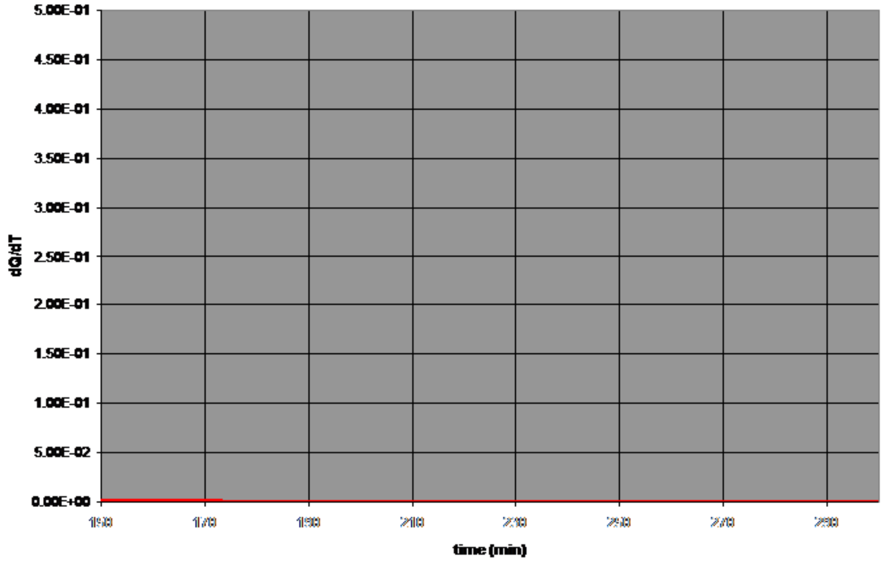
DSC Isothermal Thermogram

Autocatalysis

- What happens if isothermal temperature and time are not adequate



Induction time exceeded while bringing DSC to isothermal temperature

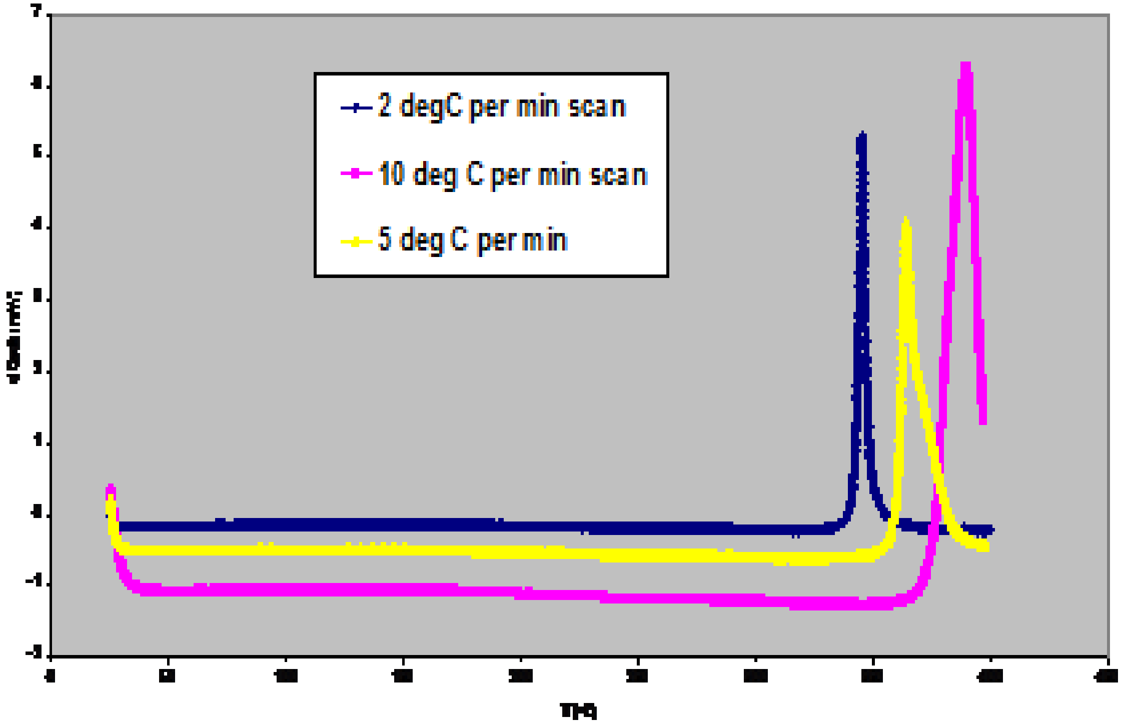


Induction time never exceeded because time chosen for the given isothermal temperature was too short

DSC Thermogram

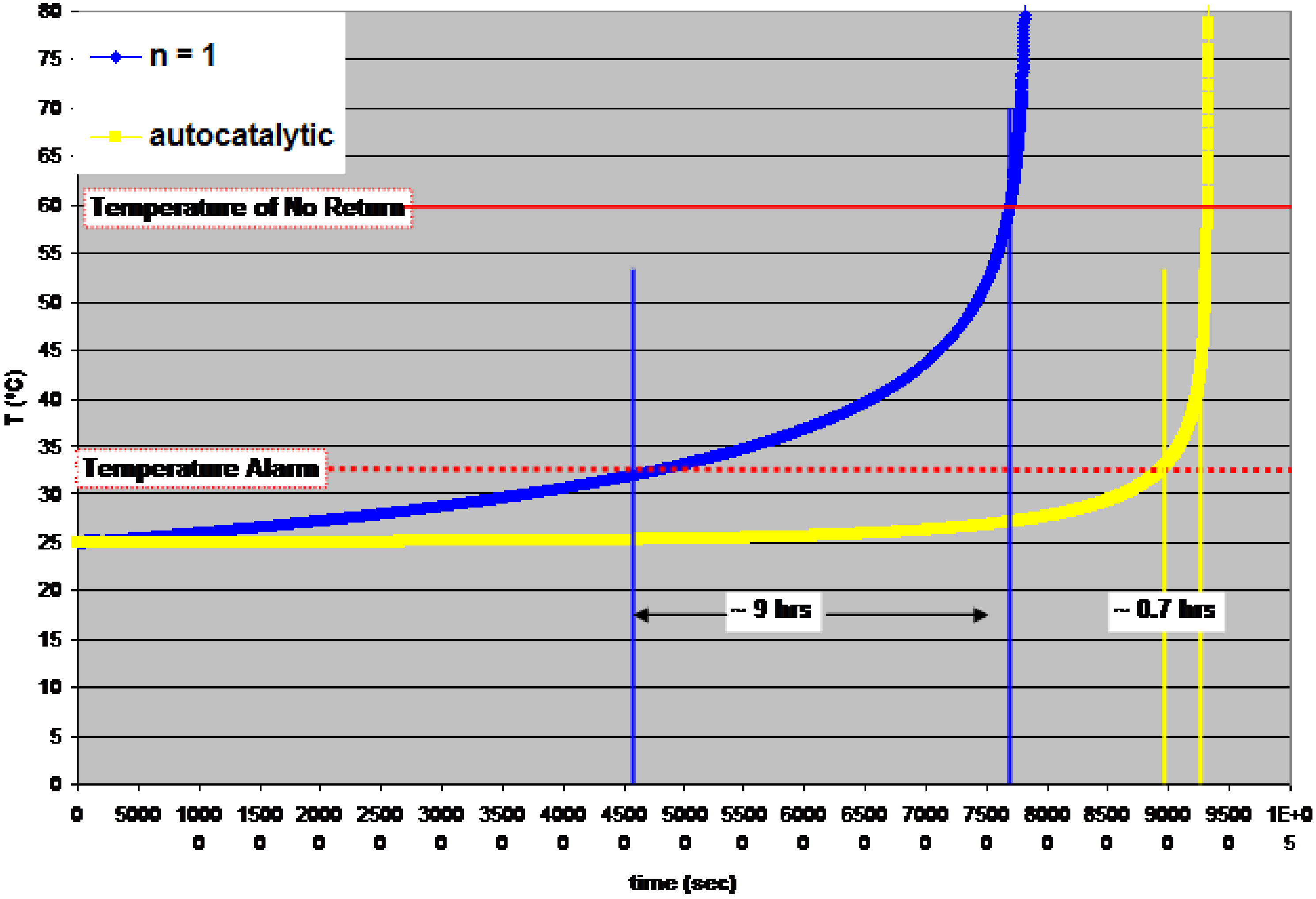
Scan rate and autocatalysis

- Slower scan rates result in lower detected onset temperature
- Incrementally longer time at each temperature results in more catalyst at each temperature. This results in critical concentration being reached at lower temperature
- Faster and more direct way to identify autocatalysis
- Eliminates challenges with choosing the right T&t
    - Wrong selection of temperature and time potentially results in misidentification of reaction type



DSC is an excellent calorimeter to determine autocatalysis!

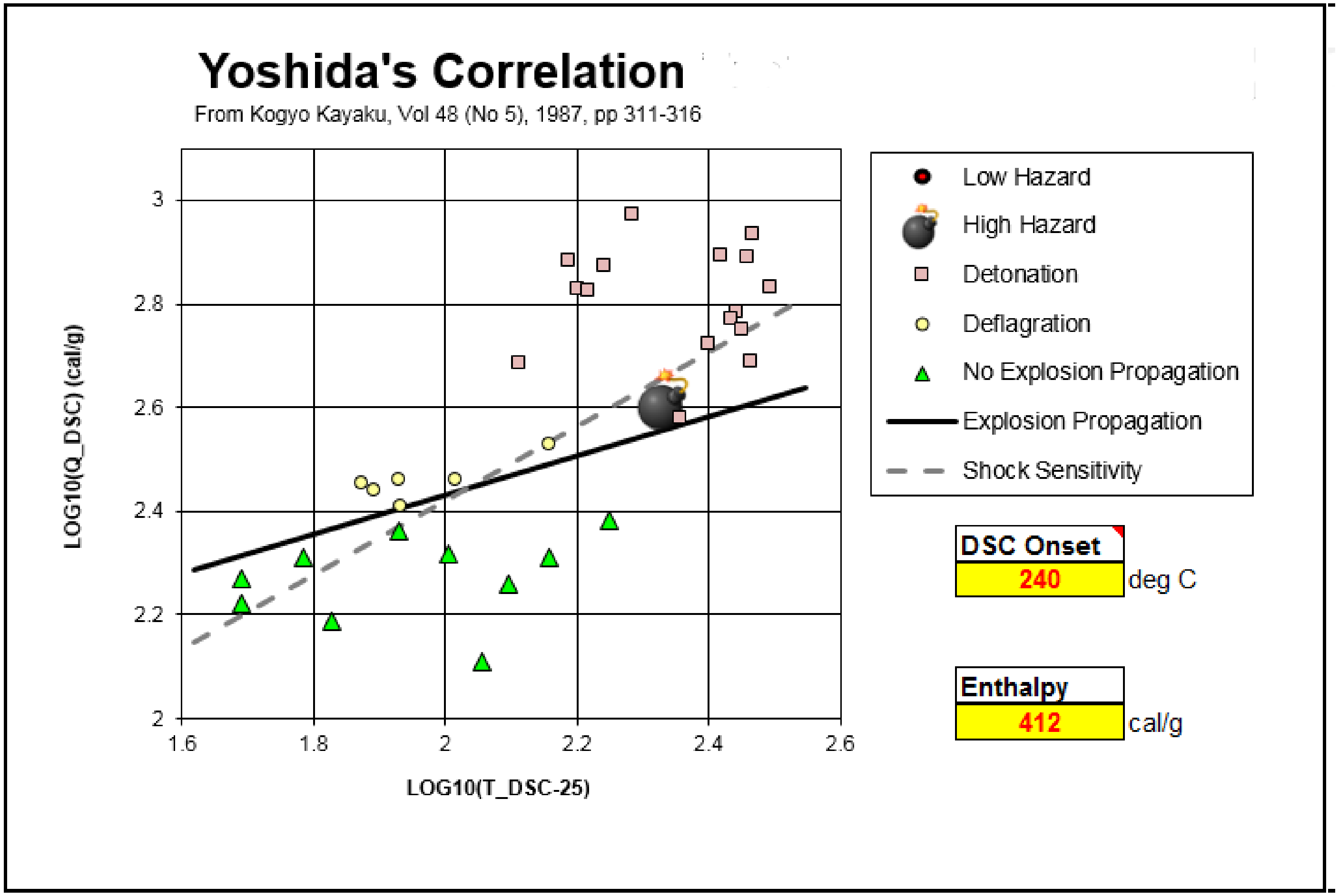
Why it is Important to Identify Autocatalysis



High temperature alarms may not allow adequate response time!

DSC and shock sensitivity

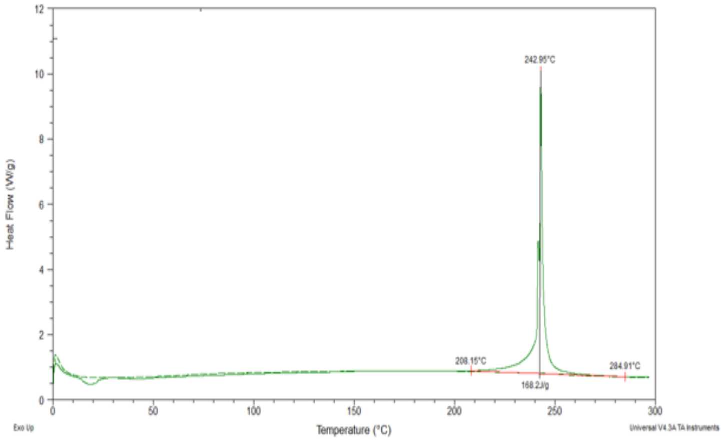
DSC can provide insight into whether something is likely to be shock sensitive or not



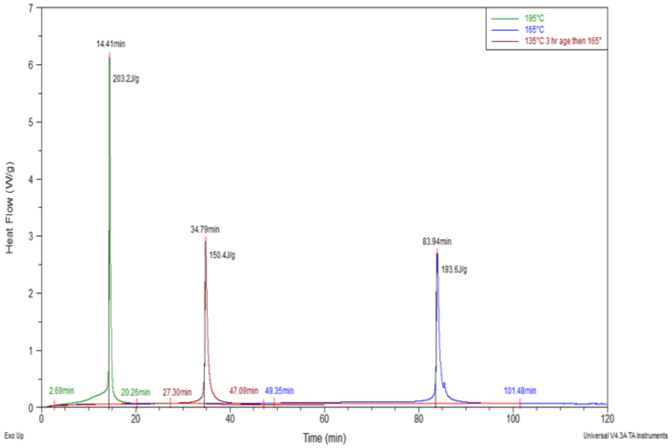
Too Large of Headspace in DSC Sample Container

Isothermal test validates autocatalysis

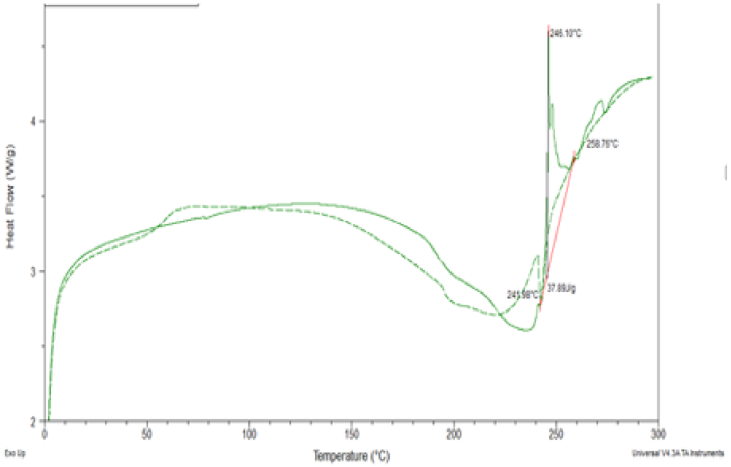
- Capillary shows clear chemical reaction
- Ampoule shows no significant exotherm
    - Scan and rescan look almost identical
    - Determined that required catalyst quantities were very small and fugacity drove most of the catalyst into the headspace
- Make sure to understand how headspace volume impacts results



Dynamic scan in capillary



Isothermal test in capillary



Dynamic scan in ampoule

Conclusions

Understanding the process is a requirement to ensure the proper experiment is performed

Understanding measurement science is required to collect the correct data and ensure quality data

Matching the data to theory requires a scientist (typically chemist or chemical engineer)

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