

REACTIVE CHEMICALS TESTING AT THE DOW CHEMICAL COMPANY: AN INDUSTRIAL PERSPECTIVE

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REACTIVE CHEMICALS SUBJECT MATTER EXPERT

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Research Scientist, Reactive Chemicals Subject Matter Expert
The Dow Chemical Company
Freeport, TX

Expert in Reactive Chemicals hazard recognition, evaluation and associated utilization of small-scale calorimetric and flammability techniques to assess and quantify reactivity hazards.

- Define safe operating limits, determine what process operations are subject to thermal runaway & overpressure, RCIs
- Support multiple Dow businesses, including Packaging & Specialty Plastics, Amines, Oxygenated Solvents, & Core R&D

Passionate about safety, innovation and communication:

- Develop novel methods to couple hazard calorimetry to online analytical detection
- Lead for global R&D Dow initiative, R&D PSCE Prevention Project (R&D P3), to prevent lab-scale safety incidents
- American Institute of Chemical Engineers (AIChE)
 - Chair, 2022 Process Safety Management Mentoring Symposium for Spring AICHE meeting
 - Loss Prevention Symposium Committee member
- Dow industry representative: Purdue Process Safety & Assurance Center

Personal:

- Diversity, Inclusion & Equality
- Spending time outdoors and at the pool with family; exercise



OVERVIEW

- Reactive Chemicals Program at Dow
- Calorimetry and Calorimetric Testing
 - What is Calorimetry?
 - Overview Calorimetric Devices For Determining Process Heats Application
 - ✓ HOM
 - ✓ DSC
 - ✓ TSU (not a calorimeter)
 - ✓ ARC
 - ✓ VSP
- Key Takeaways



WHY BE CONCERNED WITH CHEMICAL REACTIVITY?

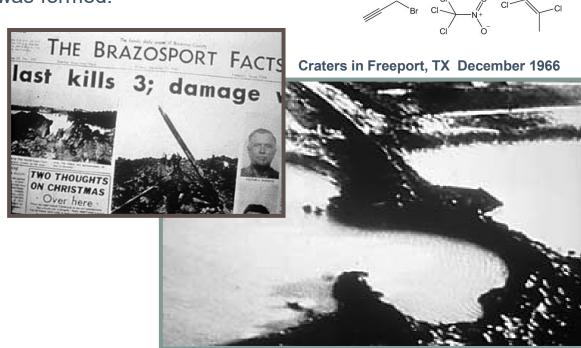
Explosions occurred due to mixing of chemicals using two railcars and a tank truck.

A shock sensitive compound was formed.

Three fatalities

Dow established the **Reactive Chemicals** Program following this event.

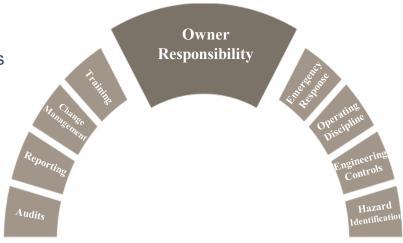
<u>Uncontrolled</u> chemical reactions could result in **injury**, **property damage**, or **environmental** harm.



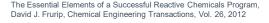
Dow's REACTIVE CHEMICALS PROGRAM

The Reactive Chemicals Program plays a key role in ensuring circumstances that put people, environment, equipment or businesses at risk are avoided

- Reactive chemicals hazards are identified.
- Protections are defined and in place
- Personnel is trained and knowledgeable about the hazards
- Incidents and near misses are reported
- Audits are completed in a timely manner
- All of the above is clearly documented



"Owner Responsibility" is the **keystone** of the Reactive Chemicals Program





PROCESS SAFETY & REACTIVE CHEMICALS:

ALLIES IN THE FIGHT AGAINST KINETICS & HEAT TRANSFER

Dow's Process Safety Group facilitates

- Process Hazard Analysis Reviews (PHA)
- Layers of Protection Analysis (LOPA)
- Loss Prevention Principles and Audits (LPP)

These require...

An <u>understanding</u> of thermal stability, flammability, and dust explosion hazards, and <u>expertise</u> in both chemistry and engineering

Laboratory



Scale-up



Pilot Plant



Soolo ...



Full-Scale Production Plant



Increasing risk



REACTIVE CHEMICALS GROUP: UNITING DIVERSE TECHNICAL EXPERTISE FOR A SAFER DOW

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

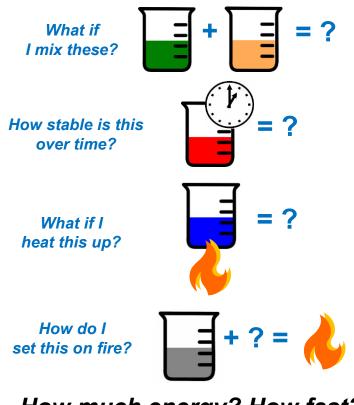
Measurement Science **RC** Chemistry **Engineering**

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

Ensure **safe** operation at all scales



How we accomplish this: The RC Toolbox



How much energy? How fast?

Screening techniques

Desktop estimations and calculations HOM – Heat of Mixing DSC – Differential Scanning Calorimetry TSu – Thermal Screening Unit

Testing thermal stability of materials

ARC – Accelerating Rate Calorimetry VSP – Vent Sizing Package

Numerous Modeling Capabilities

Flammability and explosion hazards

FP – Flash Point AIT – Auto-ignition temperature MIE – Minimum Ignition Energy LEL/UEL- Flammability Limits

MIE testing



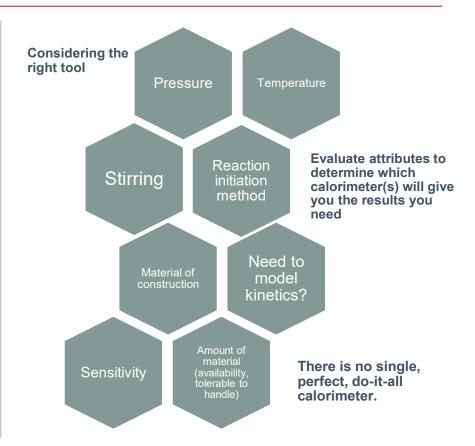
CALORIMETRY IN DOW REACTIVE CHEMICALS

What is calorimetry?

- Calorimetry is the science of measuring the heat generated by or heat transfer within a material when it undergoes a physical or chemical change.
- What can be determined by calorimetry?
 - Heats of reaction, kinetics
 - Phase-change heats
 - Heat capacity
 - Shelf-life stability
 - Reaction induction times.

Why do we need calorimetry?

- Safe operation requires understanding thermodynamics & kinetics of chemical reactions
 - Empirical methods for estimating, but not of sufficient accuracy for many processes.
 - Majority of the reactions we are interested in do not have published values.





CHEMICAL REACTIONS

- Chemical reactions involve energy changes
 - Exothermic reactions release energy
 - Endothermic reactions absorb energy
 - > For safety purposes: **pressure generating** reactions
 - ✓ Generation of (low) volatile components (CH₃OH, H₂O)
 - ✓ Generation or consumption of gases
 - ✓ Decomposition reactions
- Take notice: reactions do not start or stop at a certain temperature!
- Typically, the reaction rate increases with increasing temperature. When we detect them
 depends on the sensitivity of our instruments.
 - Your clothing is decomposing right now!
 - All the plastic around you is oxidizing!
 - The nails in the backyard fence are rusting (oxidation)!
 - Biochemical reactions occurring at the cellular level!

Don't worry, these exothermic processes are slow at ambient conditions!

If we had a calorimeter that is sensitive enough, we could detect these exothermic processes!



DEFINING REACTIVE CHEMICAL HAZARDS

 Kinetics (rate of heat release) are important if the worst-case energy release would result in severe consequences in a perfectly adiabatic system



Oxidation of iron is very high energy chemistry, and that energy is released even at room temperature...but can be very slow!



Polymerization of methacrylic acid is much less exothermic, but much faster and can result in serious consequences!



CALORIMETRY AND REACTIVE CHEMICALS TESTING

If you already know the following, calorimetry may be unnecessary to inform safe process operation:

- 1. If materials will react under process conditions
- 2. What chemistry will occur at process conditions and at elevated temperatures
- 3. Heat of reaction for the chemistries that can occur
- 4. Reaction kinetics for the chemistry (desired and undesired)

For many desired and MOST undesired chemistries, this information is not known or available

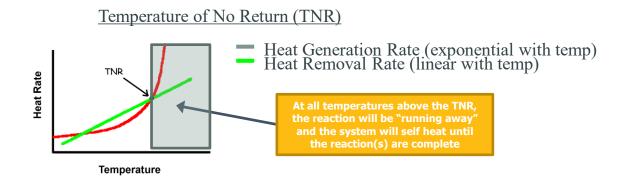
Calorimeters in Dow's Reactive Chemicals Capability





HEAT BALANCE DEFINES SAFE OPERATING CONDITIONS

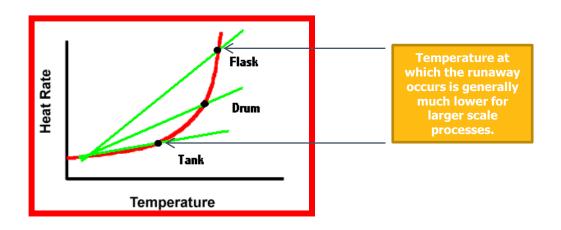
- Since pressure always rises with temperature, it is important for us to control our processes in such a way that the temperature will never rise out of control.
- Any time the rate heat is input into or generated by a system is faster than its capability to remove heat, the system is considered to be "running away."





THE IMPORTANCE OF SCALE

Heat is Lost From Different Vessels At Different Rates



Scale-up is one of the most common places for significant incidents because this is often overlooked or misunderstood!



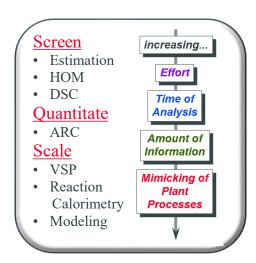
WHY SO MANY DIFFERENT TYPES OF CALORIMETERS?

Why calorimetric testing?

- > To look for side reactions or consecutive reactions
- > The sample may have unknown composition
- Look for reactivity at temperatures near the intended temperature range
 - Can the heat of reaction / loss of cooling initiate other reactions
- Estimated Heat of Reaction:
 - ✓ Tells nothing about presssure!
 - ✓ Tells nothing about the rate at which the energy is released.

Trying to balance many things:

- Sample size: Smaller is safer to test, larger increases sensitivity
- Resources: test supplies \$1-\$1000/test, Man hours 0.5-10+ /test
- Time: DSC, HOM: 0.5-2hr, ARC as long as a week
- Trying to best approximate process conditions/events:
 - DSC, TAM, and HOM can measure endothermic events, ARC and VSP cannot.



Amount of testing depends on the scale and hazards!

Larger scale → more testing More hazards → more testing



Screening Calorimeters



DIFFERENTIAL SCANNING CALORIMETRY (DSC)

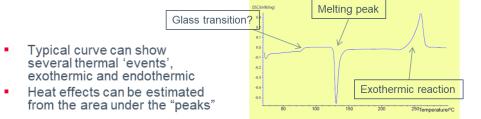
- Measures the difference in the amount of heat required to increase the temperature of a sample and reference as a function of temperature.
 - If the sample exhibits an exothermic reaction, less energy is needed to heat up the sample compared to the reference.
- Both the sample and reference are maintained at nearly the same temperature throughout the experiment.
- Accurate and reproducible thermodynamic results
- Versatile

Pros and cons of DSC testing

- Sample Size: 0.5-10mg
- Test Types: ramp, isothermal, others
- Temp Range: -70 to 500C
- Stirring: no
- Sensitivity: 0.2 μW
- Pressure measurement: no
- Avg. Test Time: <1 hr</p>
- Endotherm: yes
- Heats of mixing: no



DSC Thermogram





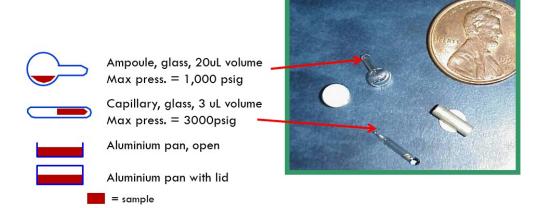
DSC SAMPLE CONTAINER CHOICE



At Dow we often use sealed glass capillaries or ampoules for RC testing to avoid evaporation (an endothermic effect)

Containers used for DSC

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





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)

Universal (gold plated) crucible can be used to mitigate sample incompatibility with materials of construction



DSC- MATERIAL OF CONSTRUCTION



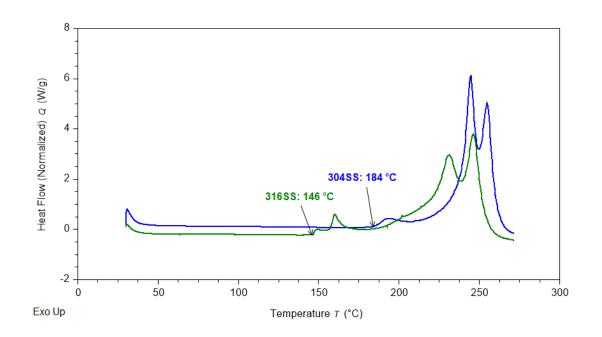
Can use DSC to assess if reactive chemical(s) thermal behavior is affected by material of construction

Sealed glass capillary





Metal shavings/filings



HEAT OF MIXING CALORIMETERS

Measure heat release when 2 materials come in contact under isothermal conditions

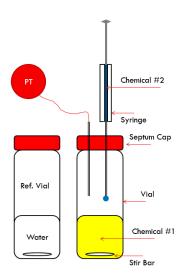
- Heat of reaction
- Heats of solution/dilution
- Heats of adsorption (gas-solid/liquid-solid)
- Inexpensive, Portable
- Sample Size:0.5-10 mL
- Test Types: Isothermal
- Temp Range:10 to 60C
- Stirring: Yes (magnetic, low viscosity)
- Sensitivity: 0.02mW
- Pressure measurement: Qualitative
- Avg. Test Time: <1hr</p>
- Endotherm: Yes
- Heats of mixing: Yes



Super CRC

Micro RC

2-Drop

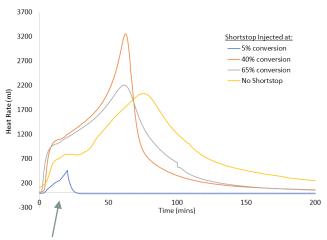




HEAT OF MIXING CALORIMETRY EXAMPLE

Identifying Effective Shortstopping Parameters

Inject shortstopping agent into polymerizing monomer to determine the conditions under which the shortstop will work



Add shortstop early in polymerization for best outcome



Thermal Screening Unit (TSU)



THERMAL SCREENING UNIT (TSU)

Sample Size: ~5ml

Test Types: Ramp, Isothermal

Temp Range: Ambient to 400C

Thermocouple in the sample

Stirring: No

Sensitivity: Depends on ramp rate

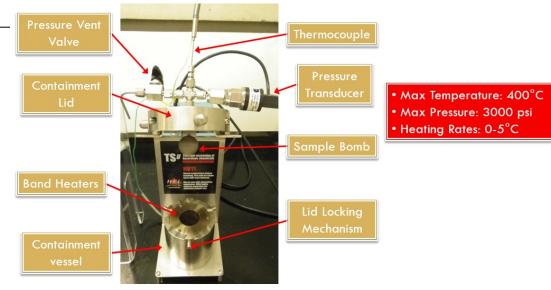
Pressure: Yes, up to 3000psi

Avg. Test Time: 2-4 hr

Endotherm: No

Heats of mixing: No

TSU is not a true calorimeter but is still useful for screening!



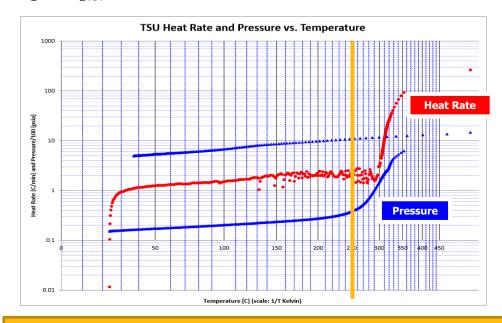
- □ Screening a material for heat or gas generating reactions
 - not for quantifying heat release or kinetics
- Screening a larger number of samples to narrow down which would be worst case and will require more advanced testing
- □ If direct thermocouple contact with sample is important (powdery solids)
- Determining the amount of gas generated during a specific isothermal timeframe



TSU EXAMPLE

Isocyanate + water, premixed at ambient T

RNCO + $H_2O \rightarrow RNH_2 + CO_2(g)$ + heat



TSU can detect the gas generation at lower temperatures than it can the heat release

Adiabatic Calorimeters



ADIABATIC CALORIMETRY- WHY?

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

Common Adiabatic Calorimeters





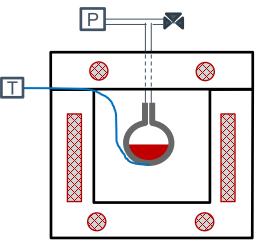
ACCELERATING RATE CALORIMETRY

Pressure and adiabatic* calorimetry data

- Critical for understanding RC hazards
- Heats of reaction
- Vapor pressure data







Left: Thermal Hazard Technology

Detects 0.02°C/min (vs. 0.4°C/min using DSC)

- Up to 100°C/min
- 2500 psia max pressure
- High pressure cells
 - Designed to handle 2g TNT
- Use: low viscosity, fully miscible systems, adiabatic worst case, kinetic modeling needed

Unfortunately...

- Poor agitation
- No sub-ambient testing
- *Adiabatic up to 10-25°C/min
- 14+ hours
- Applying data at scale requires accounting for the PHI factor
- Do not use: systems that require substantial mixing, solids that don't melt during experiment



ACCELERATING RATE CALORIMETER

Sample Size: 5ml

Test Types: Adiabatic HWS, Adiabatic temp hold (isothermal)

Temp Range: Ambient to 500C

Mixing: Yes (magnetic)

Sensitivity: 0.02 C/min

Pressure: Yes (up to 3000psi)

Avg. Test Time: 18 hrs - 4 days

Endotherm: No

Heats of mixing: Poor (limited capability)



- □ Scenario involves potential adiabatic runaway reaction.
- Understanding of potential pressure generation is required.
- Reaction kinetics/kinetic modeling is required
- Material of construction issues are being investigated
- Higher sensitivity to onset temperatures is needed than the DSC can provide
 - E.g. a process is running very "close" to where an onset is detected in DSC
- Need to evaluate a reaction with unusual headspace composition
 - Chlorine, hydrogen, HF, HCI, ethylene, etc.
- If some amount of stirring during the test is necessary

Open Cup ARC

Need to understand potential for runaway oxidation reactions of solids or wetted solids (e.g. Insulation or Sawdust with Isocyanates)



DSC TESTING IDENTIFIES HAZARDS DURING SAFETY REVIEW

- Researcher planned to run small-scale synthesis reactions
- Neat reaction (no solvent) in molten state at 150°C

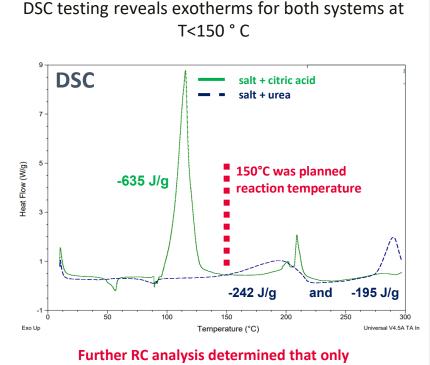
What will happen when these materials are combined & heated?

Chemistry #1: Oxidizing salt + urea

Chemistry #2: Oxidizing salt + citric acid

SDS for the nitrate salt: hazard phrase H272

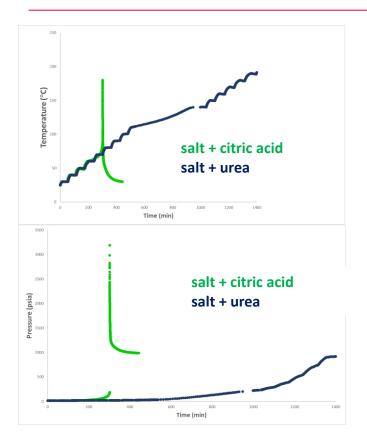




Further RC analysis determined that only Chemistry #1 (urea + oxidizing salt) could safely proceed!



ARC TESTING PROVIDES FURTHER INSIGHT



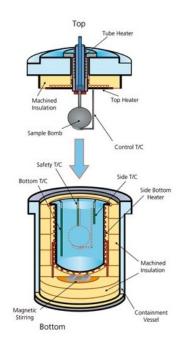
- The reaction between salt and citric acid deemed unsafe due to very rapid heat and gas generation
 - Rapid rates of heat (>2800 °C/min) and gas generation
 - Heat release cannot be controlled

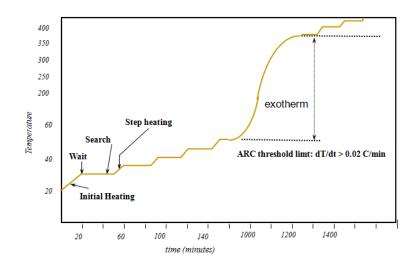
- The reaction between salt and urea deemed safe with controls
 - "Mild" rates of heat and gas generation
 - Heat release can be controlled and pressure contained in chosen reactor



CALORIMETRY TO GATHER KINETICS

Accelerating Rate Calorimetry (ARC)





Staged heating of chemical(s) inside closed sphere with high MAWP.

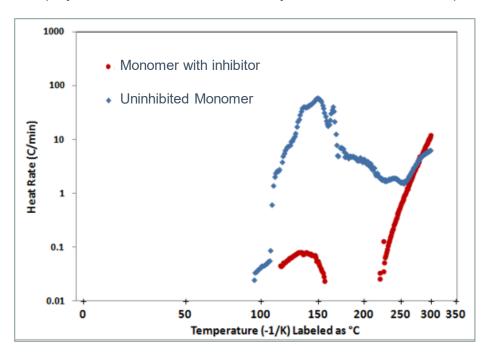
If an exotherm is detected, the sample is held under pseudo-adiabatic conditions and the chemical reaction is monitored.

Limit: No way to provide constant air flow and measure oxidation kinetics.

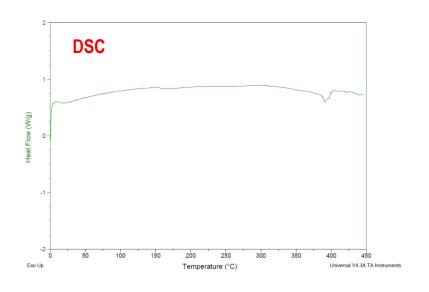


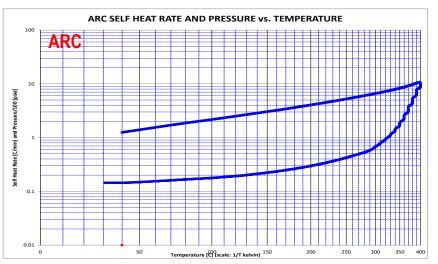
ARC Example - Evaluation of Monomer Polymerization Inhibition

- Can 200 ppm of polymerization inhibitor phenothiazine sufficiently inhibit the polymerization at 100C?
 - > ARC result supports that polymerization is inhibited, and only dimerization occurs at specified T with inhibitor



DSC vs. ARC: THERMAL STABILITY OF LIQUID AMINE AT T>300 °C





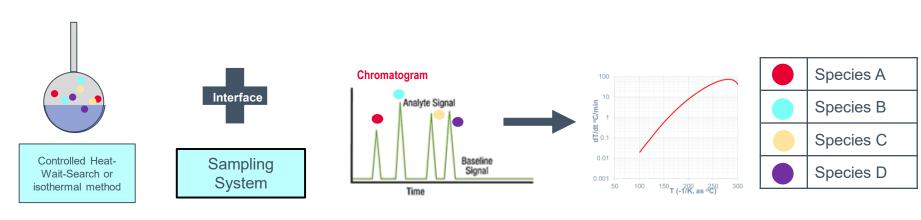
- DSC: no thermal activity to 450 °C
- ARC: no exotherm detected
 - 'thermo-neutral' decomposition: gas generation (blue trace) but no exotherm
 - Non-condensable gas generation detected at ~ 320 °C

One calorimeter may not provide all the information necessary to assess the scenario



ACCELERATING RATE CALORIMETRY (ARC) X GC-MS

- Prior to ARCxGC-MS, analytical characterization of gas-phase reaction effluent from ARC experiments has often been carried out off-line.
- Cooling the system before sampling allows for possibility of plugged lines, condensation of low-volatile species, gas
 diffusion outside of gas collection container, and potential for exposure when sampling unknown species.



1. Collect ARC data

2. Safe, online collection of sphere headspace (desired T, P)

3. Separation and analysis of headspace using GC-MS

ARC x GC-MS

Extend ARC thermal capability to provide **online effluent analysis** of gas-evolving reactive systems
(not commercially available)





APPLY ARC, BUT FEED THE (POSSIBLE?) FIRE

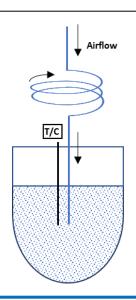


Well-known phenomenon: Powdery solid oxidation can result in runaway (fire)



Open-cup Accelerating Rate Calorimetry (OC-ARC)





Solution: Staged heating of chemical inside open cup with constant pre-heated airflow.

Used within Dow Reactive Chemicals group to assess risk of oxidative thermal runaway.



VENT SIZING PACKAGE (VSP)

COMPARISON WITH ARC

- Larger sample (lower phi; >50g)
- 10-fold less sensitive (although smaller phi makes up for some of that)
- > Higher temperature / lower pressure limits
- Adiabatic to very high heat rates
- Better agitation

STRENGTHS

- Addition of small amounts of volatile, reactive, air-sensitive reagents
- Heterogeneous reactions
- High temperature / high pressure reactions
- Accurately tracks high rates of temperature / pressure rise
- Specialized testing for vent relief sizing
- Low phi factor device (*data does not need to be corrected for scale)



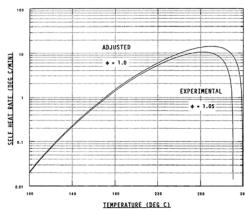


FIGURE VI-A2. Sample kinetics - self-heat rate versus temperature [33].

- Generate data for Reactive Relief Vent Sizing calculations
- Sample/scenario requires good stirring to acquire thermal stability and/or pressure generation data
- System is difficult to model (scaled simulation of scenario)
- Specific scenario involves a constant heat input
- Reaction is expected to have very high heat rates
- Good agitation is required



VENT SIZING PACKAGE (VSP)



Typical test cells

- Type I (closed test cell)
 - High vapor pressure (HVP)
 - Gassy and HVP
- Type II (vented test cell)
 - Tempering test
 - Flow regime determination
 - Liquid venting
- Type III (vented direct vent sizing)
 - Vent scaled to represent real vessel

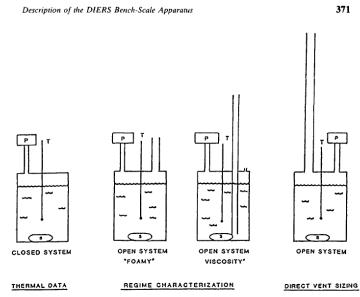


FIGURE VI-4. Test cell configurations.



VENT SIZING PACKAGE (VSP)



Why VSP?

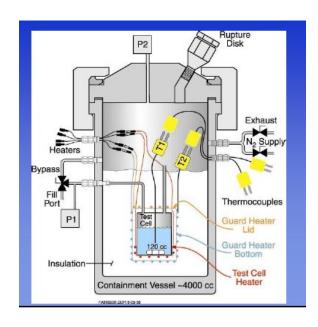
- Significant stirring capability (test cell & agitator can be made to specifications)
- Can simulate an external heat input (mimic a fire or steam valve failure in real process)
- Low phi factor device (*data does not need to be corrected for scale)
- Adiabatic to very high heat rates
- Determination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

Why VSP?

Significant stirring capability (test cell & agitator can be made to specifications)

Key disadvantages

Higher cost per test Less sensitive than ARC



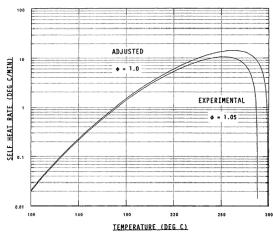


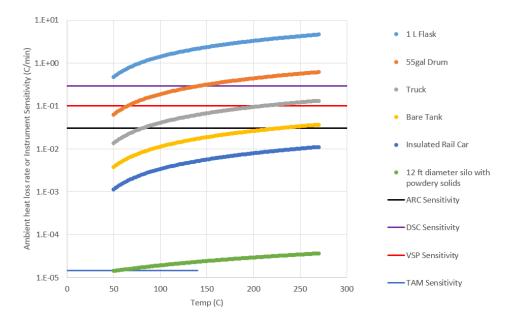
FIGURE VI-A2. Sample kinetics - self-heat rate versus temperature [33].

Preferred calorimeter for relief sizing at Dow



CALORIMETER SENSITIVITY AND PROCESS SCALE

- Calorimeter sensitivity important consideration when deciding how to test reactive systems
 - > Plot shows rate of heat losses to ambient for a variety of vessels along with calorimeter sensitivities



If heat losses are lower than the sensitivity of the instrument, the data must be extrapolated or modeled to determine the TNR



KEY TAKEAWAYS ON REACTIVITY AND FLAMMABILITY

- Defining safe operating conditions, credible worst-case scenarios and consequence requires knowledge of the energy release potential and flammable properties of the chemicals that are handled
- Understanding the process is a requirement to ensure the proper experiment is performed
- Understanding measurement science is required to collect quality data
- The data collected and used to drive decisions must be appropriate for the <u>specific scenario</u> of concern
 - Example: If you have flammability data at ambient conditions but operate at 5,000 psi and 200C, this data will not reflect the hazard
 - Example: If your well insulated system operates at 150C and the detected onset of decomposition in DSC is at 200C, it is still possible that your system could runaway at 150C!



Dow's Reactive Chemicals Program

- Recognized by many as "Best in Class" and backed up by performance!
- Industry benchmark
- Active support of external activities
 - > AIChE, CCPS, ACC Responsible Care
 - CCPS Process Safety Faculty Workshops
 - Undergraduate Process Safety Learning Initiative
- Academic collaboration
 - Purdue Process Safety & Assurance Center (P2SAC)
 - Michigan Tech endowed chair
 - Texas A&M Mary Kay O'Connor Process Safety Center (MKOPSC)
- Program documents publicly available from CCPS
 - Chemical Reactivity Worksheet (CRW4)
 - Risk Analysis Screening Tool (RAST) and Chemical Hazard Engineering Fundamentals (CHEF)



REFERENCES AND USEFUL LINKS

Selection of Dow-authored papers:

- Guidelines for Chemical Reactivity Evaluation and Application to Process Design Update after Twenty Years. M.S. Holsinger, S.H. Horsch, S. Tipler, K. Shaughnessy. 2016 AIChE Spring Meeting & 12th Global Congress on Process Safety, 50th Annual Loss Prevention Symposium (LPS). Center for Chemical Process Safety
- Losing Your Heat Balance: Insights into Thermal Hazard Assessments,
 Robert Bellair & Soham Dutta, Chemical Engineering Progress, 2022, 27.
- The Essential Elements of a Successful Reactive Chemicals Program David J. Frurip, Chemical Engineering Transactions, Vol. 26, 2012
- Thermal Hazard Evaluation by an Accelerating Rate Calorimeter D.I. Townsend & J.C. Tou, Thermochimica Acta, 37 (1980) 1-30
- Hazard evaluation of polymerizable compounds
 D.J. Frurip, A. Chakrabarti, T.C. Hofelich, S.J. Martinez and L.F. Whiting Process Safety Progress, Vol. 14, No.2, 79
- Effective Use of Differential Scanning Calorimetry in Reactive Chemicals Hazard Evaluation, David J. Frurip and Tim Elwell, Process Safety Progress, Vol. 26, No.1, 51
- Selection of the Proper Calorimetric Test Strategy in Reactive Chemicals Hazard Evaluation, D.J. Frurip, Organic Process Research & Development, 12(6) (2008), 1287.

Selection of useful resources and websites:

- Guidelines for Hazard Evaluation Procedures, 3rd ed., Center for Chemical Process Safety, New Jersey: John Wiley & Sons, Inc. (2008). The public version of Dow's Reactive Chemicals Program is provided on CDROM. See also sections 3 – Hazard Identification Methods (utilizing existing material properties and developing compatibility charts).
- CRW4 Chemical Reactivity Workbook A handy tool to develop compatibility charts http://www.aiche.org/ccps/resources/crw-overview
- Bretherick's Handbook of Reactive Chemicals Hazards, 8th Edition, 2017, Published by Elsevier
- CCPS (Center for Chemical Process Safety)
 - Books and free downloads
 - http://www.aiche.org/ccps
- CSB US Chemical Safety Board website
 - Large collection of videos on incidents with detailed descriptions and investigation reports http://www.csb.gov/
- SACHE (AIChE group, training modules)
 - http://www.aiche.org/ccps/community/technological-communities/safety-and-chemical-engineering-education-sache
- ECHA European Chemicals Agency
 - Information on regulations like REACH and CLP
 - https://echa.europa.eu/
- Cefic the European Chemistry Industry Council <u>http://www.cefic.org/</u>





Seek

Together^m