CHARACTERIZATION OF REACTIVE CHEMICAL HAZARDS VIA CALORIMETRY

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• Time to Maximum Rate Under Adiabatic Conditions, $T_{MRad}$, is a measure of probability of occurrence of a runaway.

• Adiabatic Temperature Rise $\Delta T_{ad}$ is a measure of consequence.

• Stoessel Criticality Index, risk is low at $T_{MRad} \geq 24$ hours and $\Delta T_{ad} \leq 50$ K.

• Temperature at which $T_{MRad}$ is 24 hours is called the TD24.

• Calorimetric techniques are used for the evaluation of these parameters.

**Figure 1:** Temperature profile and the corresponding self-heat rate. (Source: AKTS Thermal Safety Software website)
CALORIMETRIC TECHNIQUES

- Various Calorimeters: Differential Scanning Calorimetry (DSC), Accelerating Rate Calorimeter, Reaction Calorimeter, Thermal Activity Monitor, Advanced Reactive System Screening Tool, Vent Sizing Package 2, Automatic Pressure Tracking Adiabatic Calorimeter.

- DSC is the most commonly used technique in safety laboratories.

- Onset Temperature, Temperature Vs Time and Self-Heat Rate Vs Temperature data can be obtained from calorimetric experiments.

Figure 2: Dynamic DSC Experiment (Source: Crowl et.al, 2015)
ANALYSIS OF CALORIMETRIC DATA

The steps to determine the TMRad and the TD24 are as follows:
1. Evaluation of the Kinetics of the Reaction
2. Correction of Experimental Data
3. Estimation of the TMRad

**Note:** The standard approach is meant for simple non-autocatalytic reactions. It gives a more conservative estimate of the TMRad. For all complex reactions, the expert approach gives more reliable results.

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<th><strong>THE STANDARD APPROACH</strong></th>
<th><strong>THE EXPERT APPROACH</strong></th>
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<td><strong>Arrhenius Linearization Method</strong></td>
<td><strong>Complex non-linear optimization methods</strong></td>
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<td>( \ln \frac{d \alpha}{dT} = \ln k_0 + n(1 - \alpha) - \frac{E}{RT} )</td>
<td><strong>Model Free Kinetics</strong></td>
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<td><strong>Enhanced Fisher’s Method</strong></td>
<td><strong>Behavior of reacting system simulated under adiabatic conditions</strong></td>
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<td>• Correcting temperature vs time data for ( \Phi )</td>
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<td><strong>Frank Kamenetskii Method</strong></td>
<td><strong>Estimate TMRad using simulation</strong></td>
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<td>• Zero order kinetics assumption</td>
<td>• Software packages are available</td>
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<td>( TMR_{\text{ad}} = \frac{c_p R T_0^2}{q_0 E} )</td>
<td><strong>Source:</strong> Kossoy et.al, 2015</td>
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ADVANCED KINETICS TECHNOLOGY SOLUTIONS THERMAL SAFETY SOFTWARE

• Requires about 3-4 dynamic DSC runs.

• Evaluates kinetics assuming the differential iso-conversional approach.

• Simulates reacting system behavior under adiabatic conditions and for extended temperature ranges.

• It has a module for the prediction of the TMRad and the TD24. Capable of predicting the Self Accelerating Decomposition Temperature (SADT).

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• Kinetics based simulation approach.

• Consists of a module to predict the TMRad and the SADT.
• 50 K or 100 K below the onset temperature is considered as the safe handling process temperature.

• Onset temperature detected by a calorimeter depends on a number of factors such as experimental conditions, sample mass used, and sensitivity. TD24 is based on reaction kinetics and therefore, scientifically more accurate.

• ADT24 is the temperature at which TMRad is 24 hours derived from adiabatic storage tests.

\[ T_{D24}^{[K]} = 0.65T_{\text{onset}}^{[K]} + 50 \]

Figure 3: Comparison of ADT24, TD24, 100 K and 50 K rules,
(Source: Pastre et.al, 2000)
CONCLUSIONS

• From a safety perspective, TMRad is the time within which an emergency cooling system must be effective in order to cope with an imminent runaway reaction.

• TD24 means that an intervention is possible within 24 hours.

• TD24 is scientifically more accurate than the 100 K and 50 K rules.

• Run dynamic DSC tests, analyze experimental data to predict the TMRad and TD24: (1) Standard Approach (2) Expert Approach

• Adiabatic experiments (~24 hrs) to confirm the validity of the predictions.
Questions?