CHARACTERIZATION OF REACTIVE CHEMICAL HAZARDS VIA CALORIMETRY

SAI SWETHA SATHANAPALLY
PROFESSIONAL MASTER'S STUDENT
DAVIDSON SCHOOL OF CHEMICAL ENGINEERING

PURDUE UNIVERSITY®

INTRODUCTION

- Time to Maximum Rate Under Adiabatic Conditions, **TMRad**, is a measure of probability of occurrence of a runaway.

- Adiabatic Temperature Rise ΔTad is a measure of consequence.

- Stoessel Criticality Index, risk is low at TMRad ≥ 24 hours and ΔTad ≤ 50 K.

- Temperature at which TMRad is 24 hours is called the **TD24**.

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

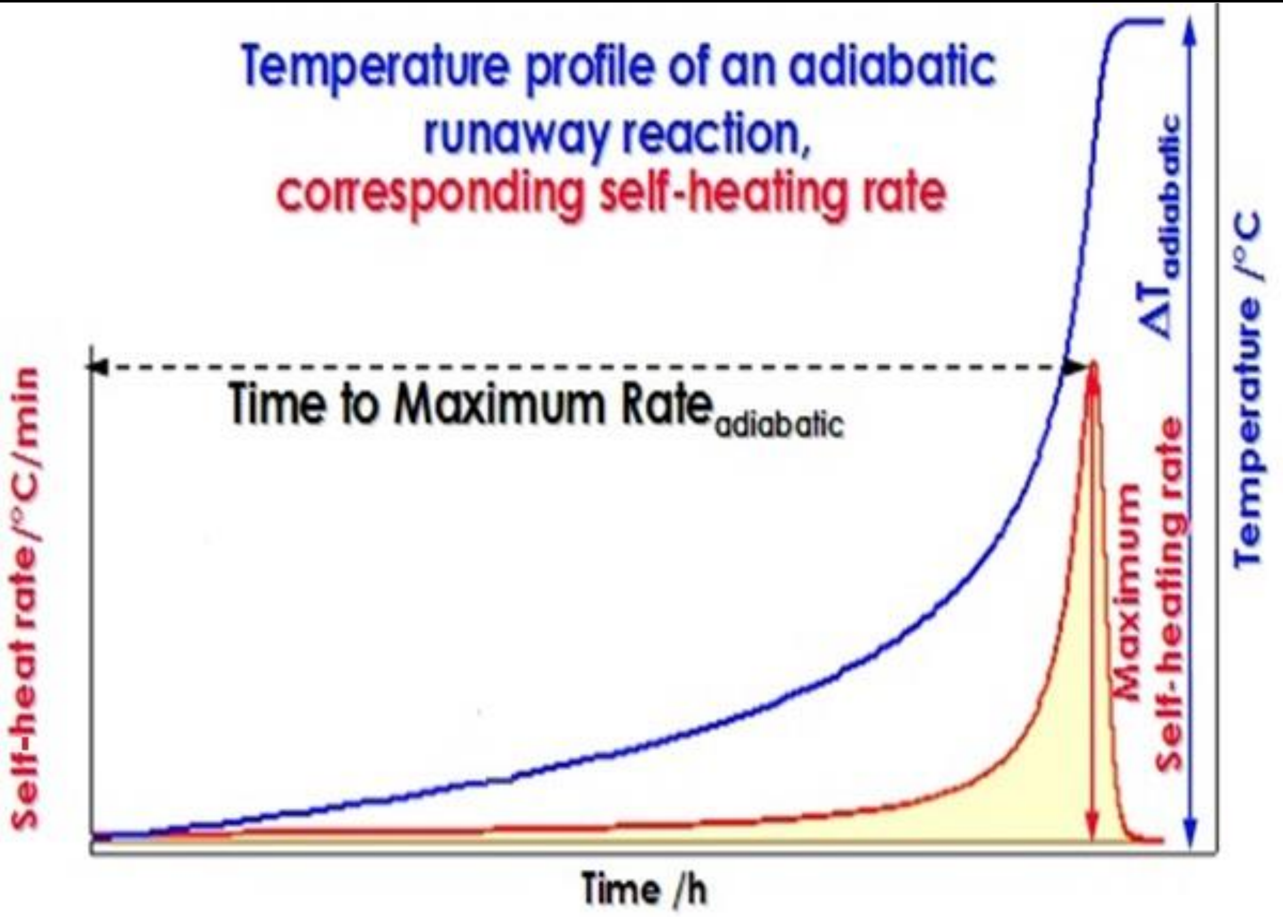

Figure 1: Temperature profile and the corresponding self-heat rate. (Source: AKTS Thermal Safety Software website)

PURDUE UNIVERSITY

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.

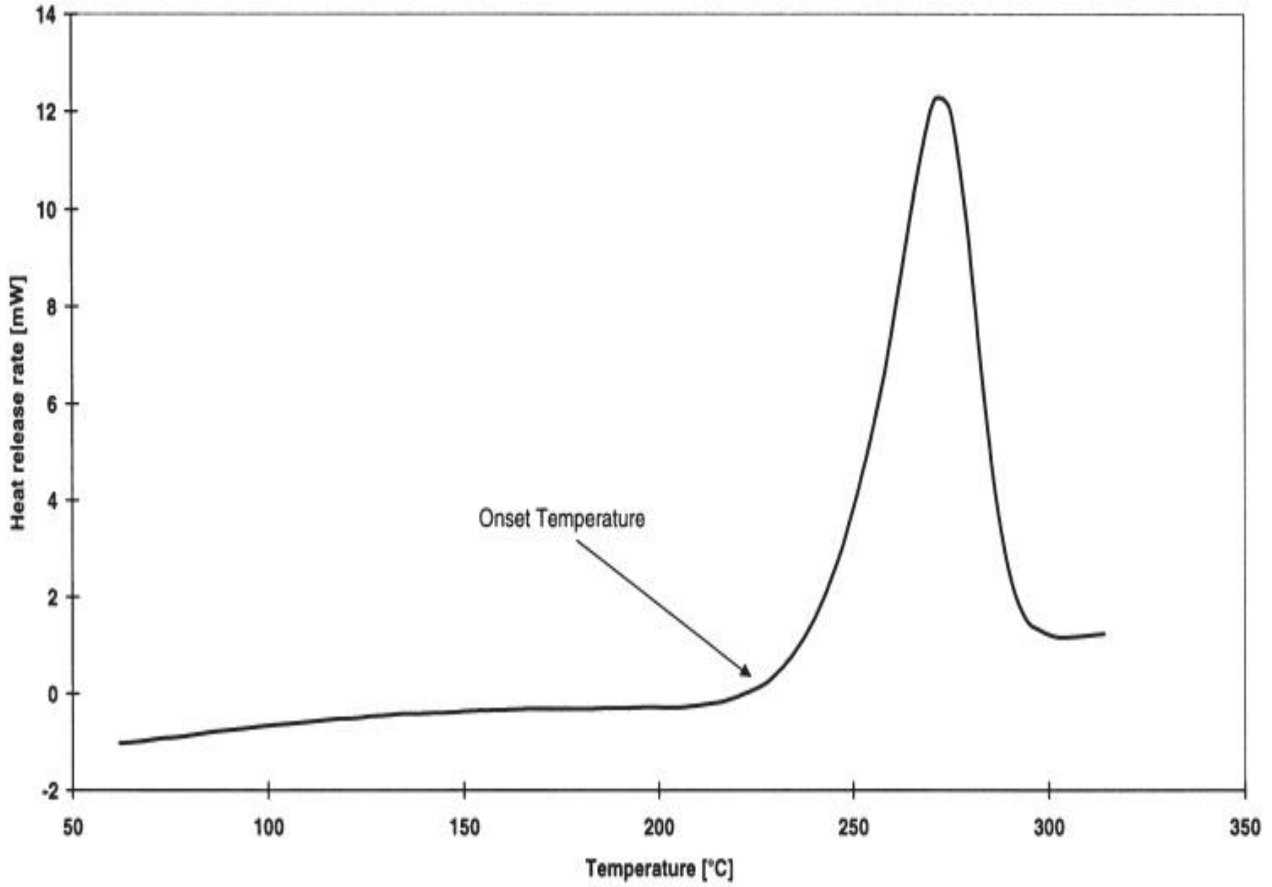

Figure 2: Dynamic DSC Experiment (Source: Crowl et.al, 2015)

PURDUE UNIVERSITY

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.

THE STANDARD APPROACH	THE EXPERT APPROACH
Arrhenius Linearization Method $\ln\frac{d\propto}{dT} = \ln k_0 + n(1-\propto) - \frac{E}{RT}$	• Complex non-linear optimization methods • Model Free Kinetics
Enhanced Fisher's Method • Correcting temperature vs time data for Ø	• Behavior of reacting system simulated under adiabatic conditions
Frank Kamenetskii Method • Zero order kinetics assumption $TMR_{ad} = \frac{c_p R T_0^2}{q_0 E}$	• Estimate TMRad using simulation • Software packages are available Source: Kossoy et.al, 2015

COMMERICALLY AVAILABLE SOFTWARE

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).

CHEMINFORM ST. PETERSBURG THERMAL SAFETY SERIES

- Kinetics based simulation approach.
- Consists of a module to predict the TMRad and the SADT.

PURDUE
UNIVERSITY

TD24 Vs 100 K & 50 K RULES

- 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.

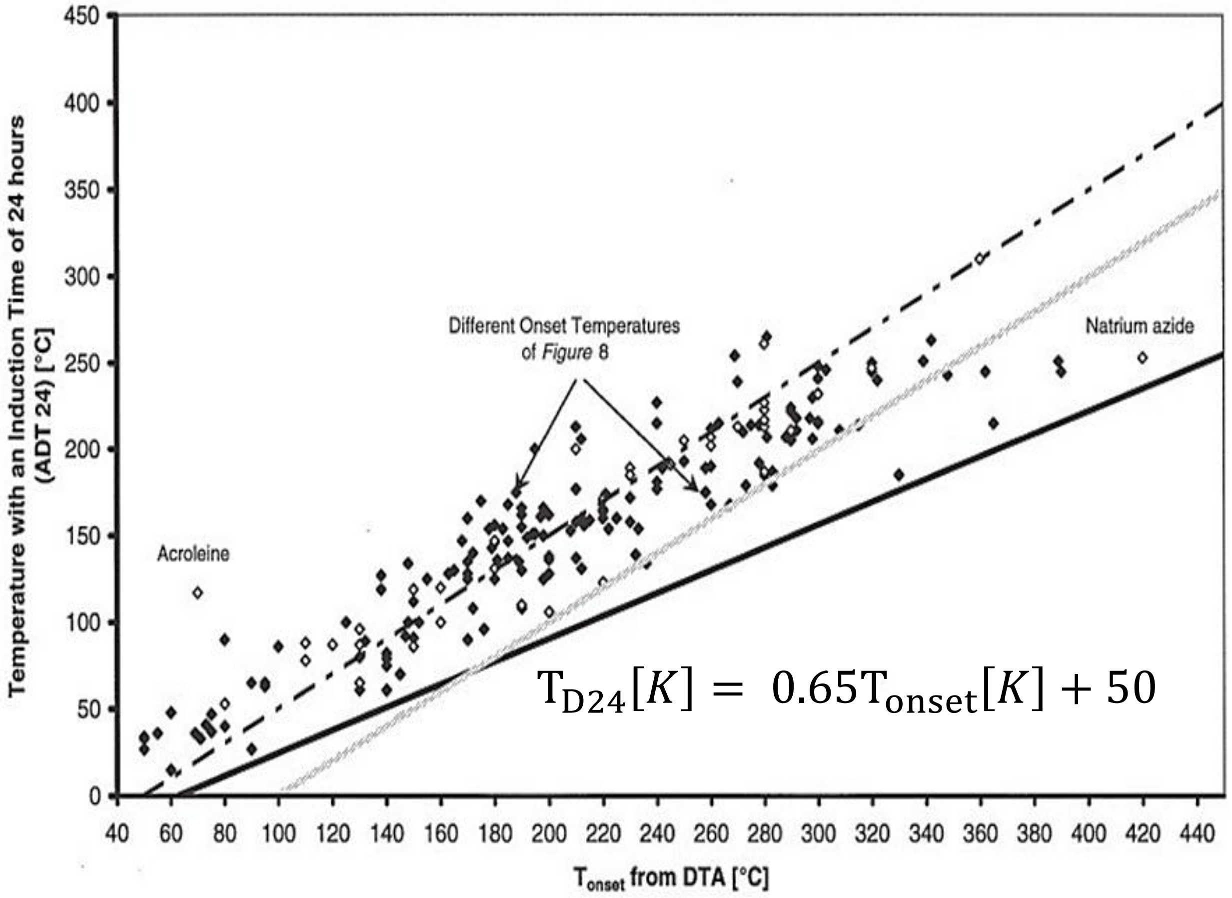

Figure 3: Comparison of ADT24, TD24, 100 K and 50 K rules, (Source: Pastre et.al, 2000)

PURDUE UNIVERSITY

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?