The use of Criticality charts in process safety assessment

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HEL Group – 40 Years of Innovation in Process Safety

30+ Years Experience

Creating tools for healthier, sustainable, safer world

Global Presence

UK HQ with offices in US, China, India

Diverse Portfolio

Chemistry, safety, bioreactors, battery testing

Market Penetration

Trusted by labs worldwide – 2,500+ installations

1987 — Dr. Jasbir Singh founded H.E.L

- Carrying out hazard testing on behalf of customers

1990 — Development of the first Phi-TEC II

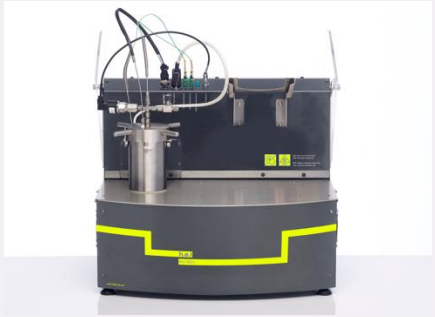
- Enable customers to conduct their own hazard screening.

1993 — The first Simular was developed

- Give fundamental data for safe Process Development.

2001 — TSU is added to the process safety portfolio

- Rapid screening of thermal and pressure



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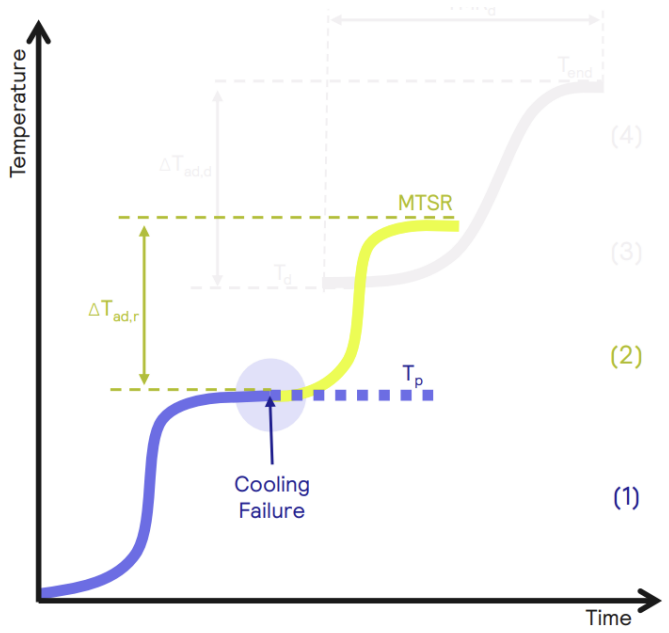
Criticality Classes – Understanding Reaction Risk

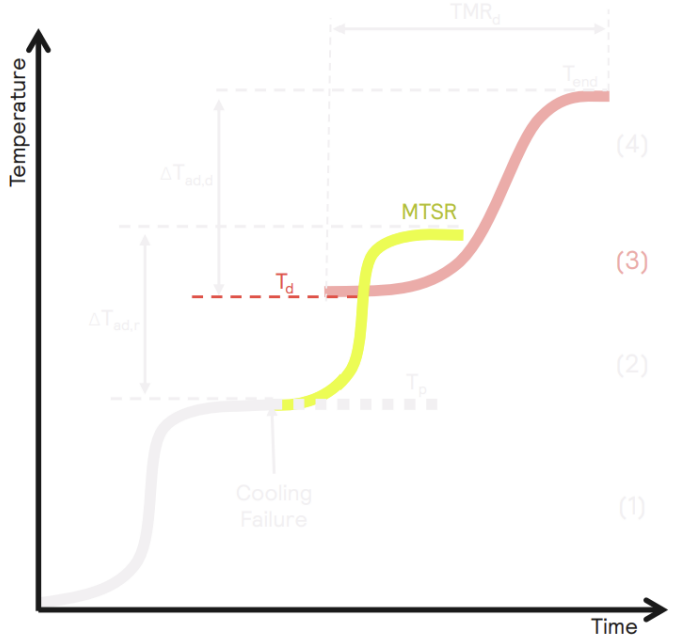
- Often used to categorize the risk level of **exothermic reactions**
- Five levels (1 to 5):
  - The higher the class, the more potential hazard, more caution and data are required
- Assesses:
  - Total **temperature rise** from the reaction
  - Risk of **secondary decomposition**
  - Possible **mitigation strategies**

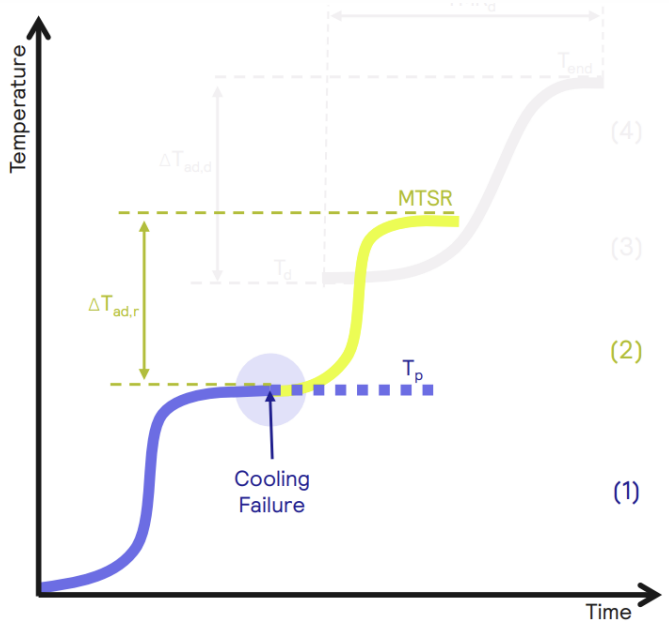
Parameters based on temperature – pressure is usually the real hazard

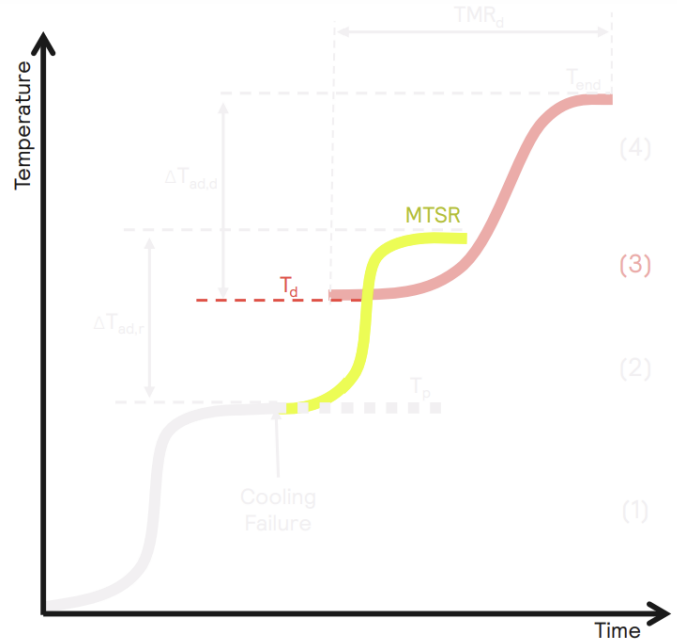
When things go wrong

1. **Cooling Loss**
   Control system failure
2. **Temperature Rise**
   Exothermic reaction accelerates
3. **Runaway**
   Heat generation exceeds cooling capacity
4. **Decomposition**
   Secondary reactions begin









Key Process Parameters

Process Temperature (Tp)

Normal operating temperature

MTSR

Maximum temperature of synthesis reaction

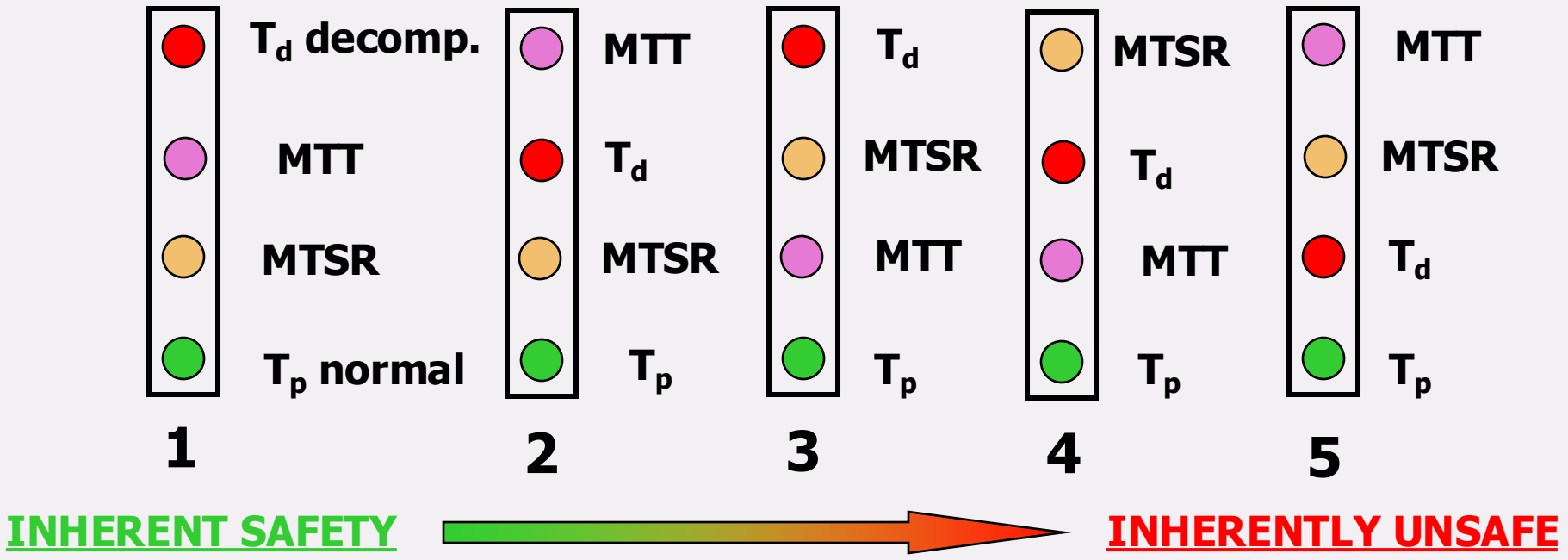
MTT

Maximum technical temperature limit

Td

Decomposition temperature

Stoessel Criticality Class Diagram



Maximum temperature of the synthesis reaction (MTSR)

- Process Temperature (Tp)
- MTSR
- MTT
- Td

Process temperature plus the adiabatic temperature rise associated with the heat of reaction

$$\Delta Tad = \frac{\Delta H_r}{Cp}$$

What is Cp? – of a reacting mixture, undergoing self heating

- So continually changing in both composition and temperature…
  What about effects of solvent boil off

Heat of reaction is often measured using a reaction calorimeter

Calculation assumes the chemistry is the same at normal process and runaway conditions

Maximum temperature for technical reasons (MTT)

- Process Temperature (Tp)
- MTSR
- MTT
- Td

- In an open system this could be as simple as the boiling point – if the temperature reaches that point, solvent will boil off and the temperature increase will stop.
- Effect of increasing reactant concentration with solvent boil off – decreasing heat sink effect of the solvent.
- What happens if all the solvent boils off leaving a more concentrated reaction mixture? – temperature may exceed MTT, changing class
- In a closed system it is harder. Generally taken as the temperature at the maximum possible pressure, often the relief set pressure.
- Pressure relief can cause cooling in some circumstances, but will not necessarily stop the reaction, which may continue to higher temperatures.
- If all that happens is some non-condensable gas is relieved, the reaction will continue to the decomposition phase, with potentially higher relief duty.

Decomposition temperature

- Process Temperature (Tp)
- MTSR
- MTT
- Td

Often taken as TMR24, TD24 etc

Empirical calculation methods generally assume Arrhenius kinetics and a “global” reaction mechanism. Usually done via adiabatic calorimetry or DSC

Not everything is as straightforward. Competing or sequential reactions each with differing kinetic rate/temperature profiles can occur. May not always get the same reaction

Previously, detected “onset” temperature was often used with an appropriate safety margin, based on the sensitivity apparatus

Beware of autocatalytic or induction time effects

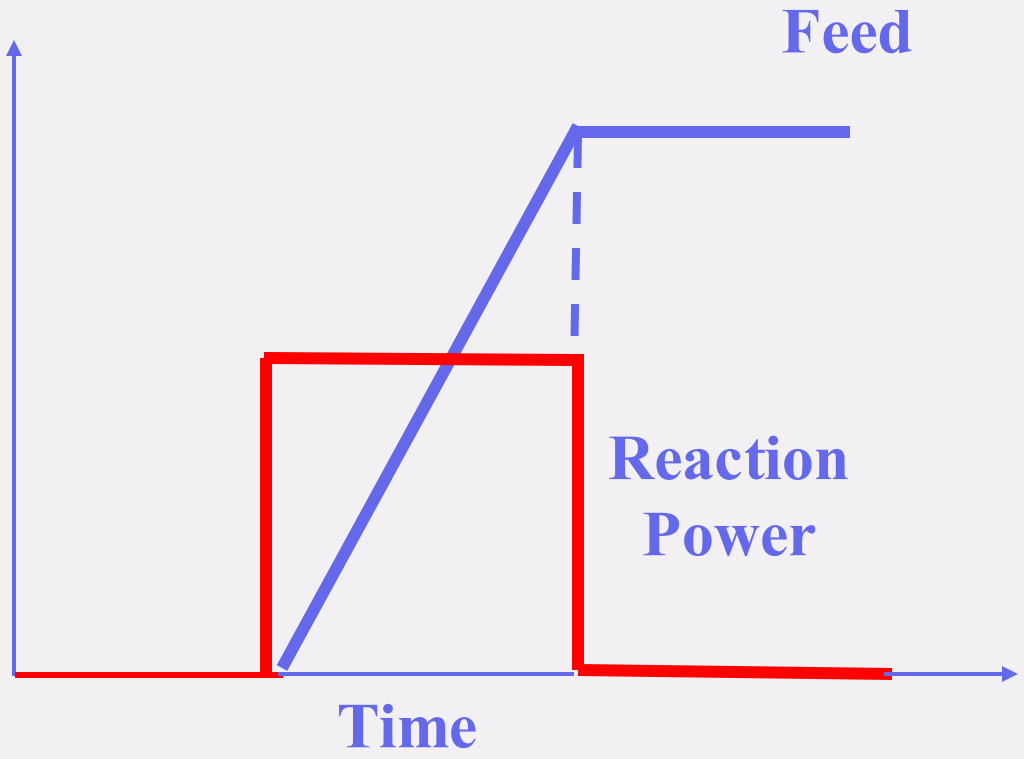
Reaction Calorimetry

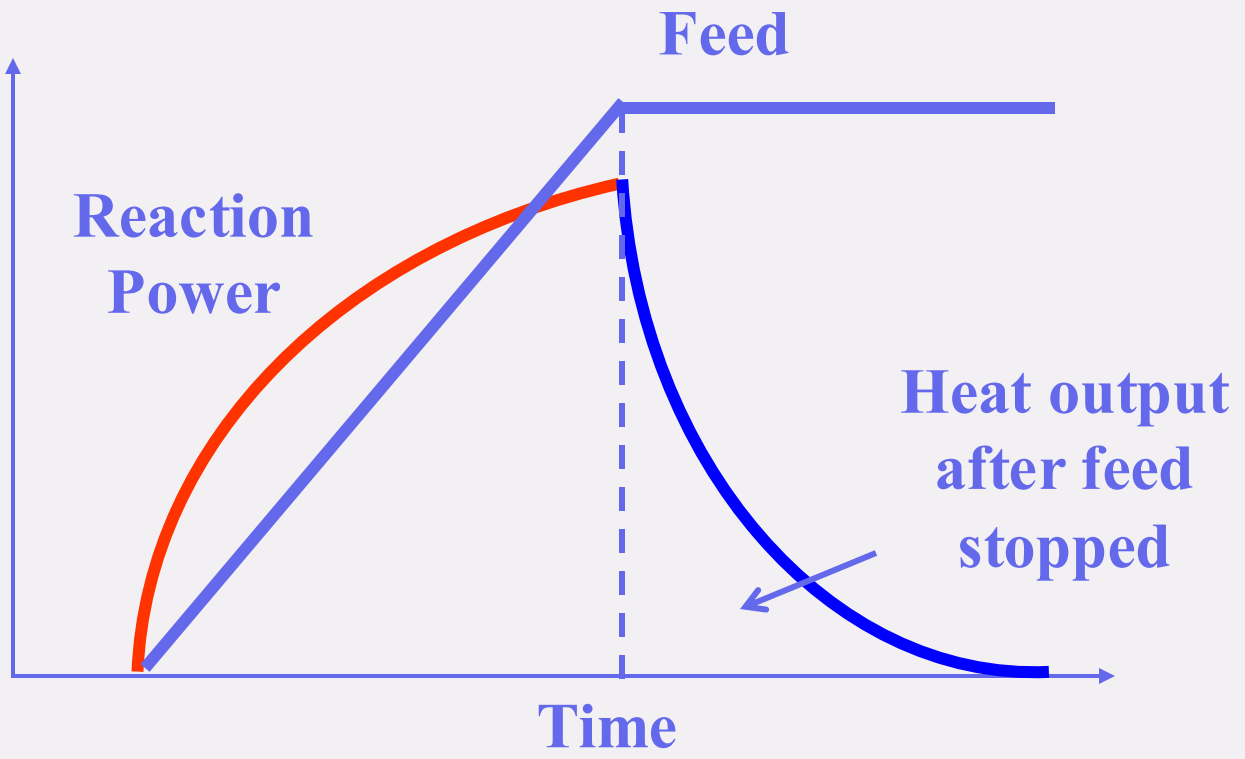
Data obtained:

- Power of reaction (hence cooling requirement)
- Heat of reaction
- Heat capacity of material (at beginning and end)
- Kinetic information – is the reaction feed rate limited or kinetically controlled

- Allows us to estimate MTSR

Feed rate vs Kinetically Limited Reaction

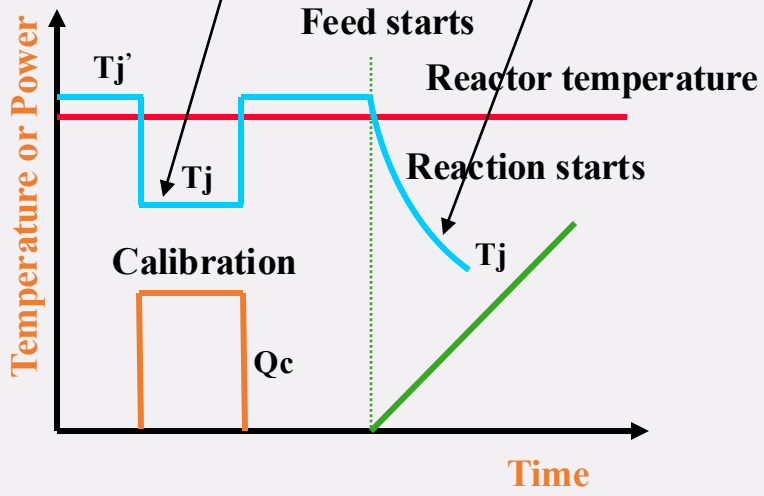


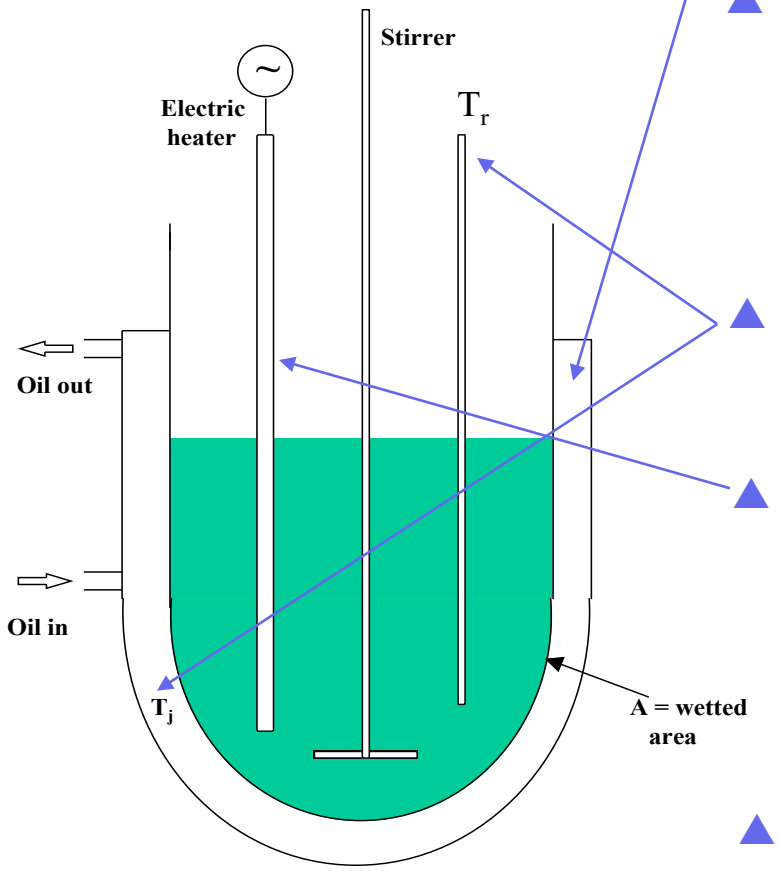


Heat Flow

$$UA = \frac{Qc}{(Tj' - Tj)}$$

$$Qr = UA\,(Tj' - Tj)$$





Hardware setup

Heater used for calibration only

- Reaction temperature is controlled through adjustable-temperature oil circulating into a jacket
- Energy (enthalpy) and power exchanged by reactive mass is (mainly) calculated through heat flow across wall between reactor and jacket:

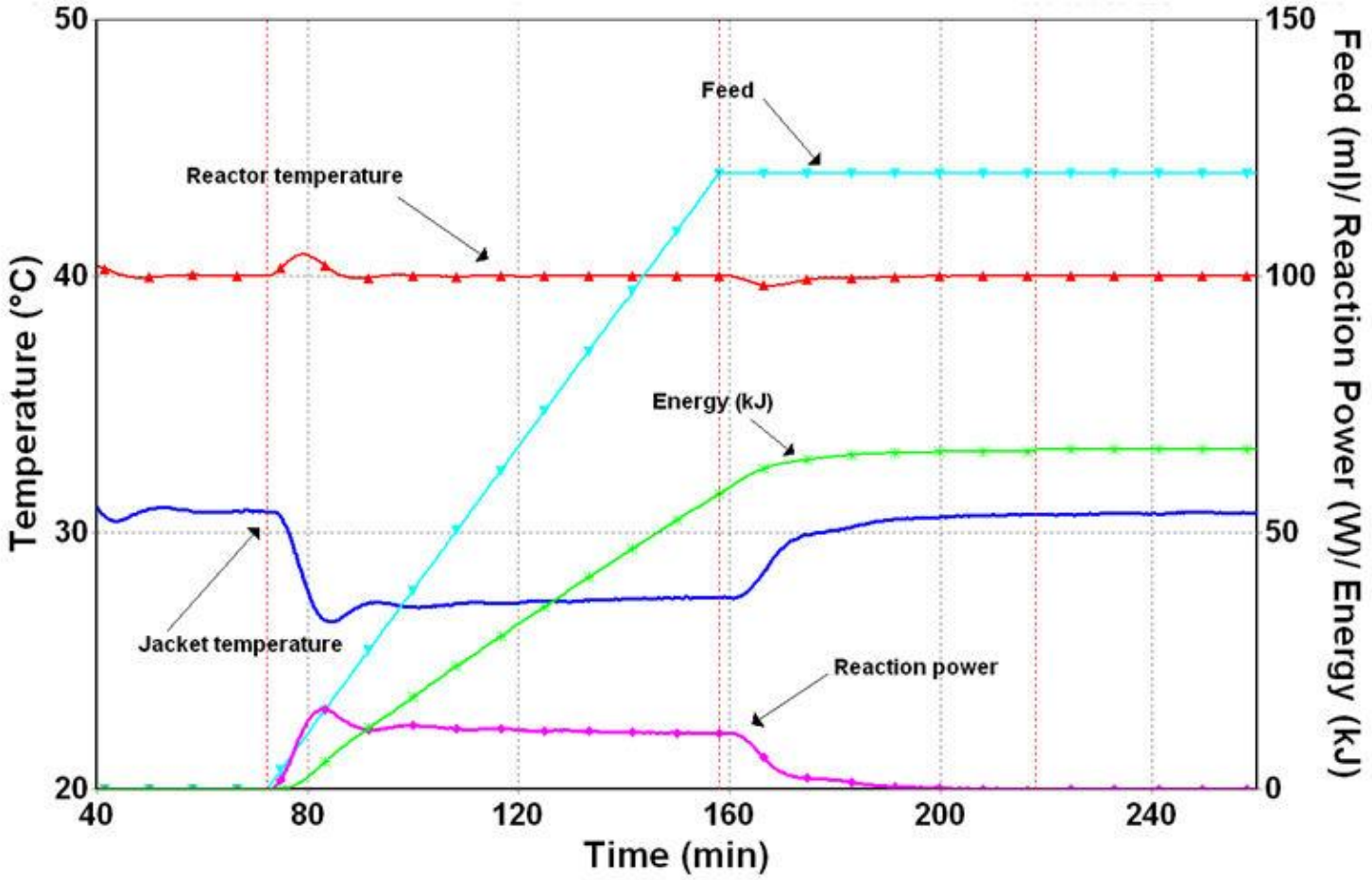
$$Q = UA\,(T_r - T_j)$$

- T_r and T_j are constantly measured but heat transfer characteristics, UA, must be evaluated in order to calculate Q
- This is done by keeping reactor in a stable condition (baseline state),then activating a calibration heater providing a known power and applying the above equation in baseline state and after heater activation
- UA often changes during process being affected by fill level, agitation, viscosity… Hence UA determination is needed before and after experiment with results interpolation

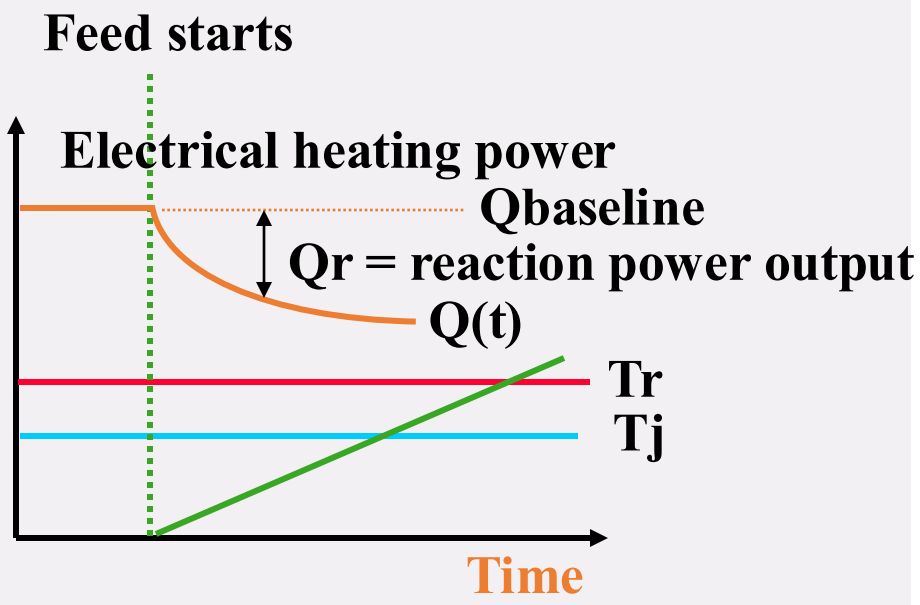
Heat Flow

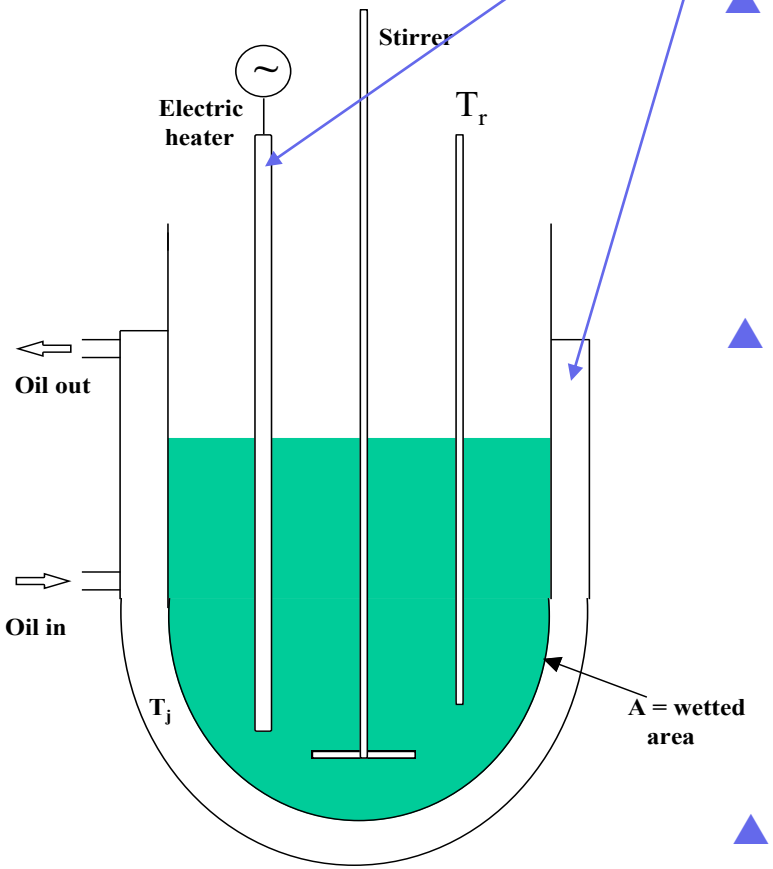
Heat flow calorimetry typical plot

Note drop in jacket temperature during reaction (ΔT is used to calculate power output)



Power Compensation





Hardware setup

same as HF, heater used for T control

- Reaction temperature is controlled through oil jacket and electrical heater
- Oil Jacket is kept at a temperature (usually 10-20°) lower than desired setpoint. Process reactive mass temperature is achieved by adding extra power trough a controlled heater, called “baseline power”
- Energy (enthalpy) and power exchanged by reactive mass is directly measured by change in power needed for heater to keep the system at constant temperature

$$Q = Q_{\text{in reaction}} - Q_{\text{baseline}})$$

Intuitive live data interpretation during experiment

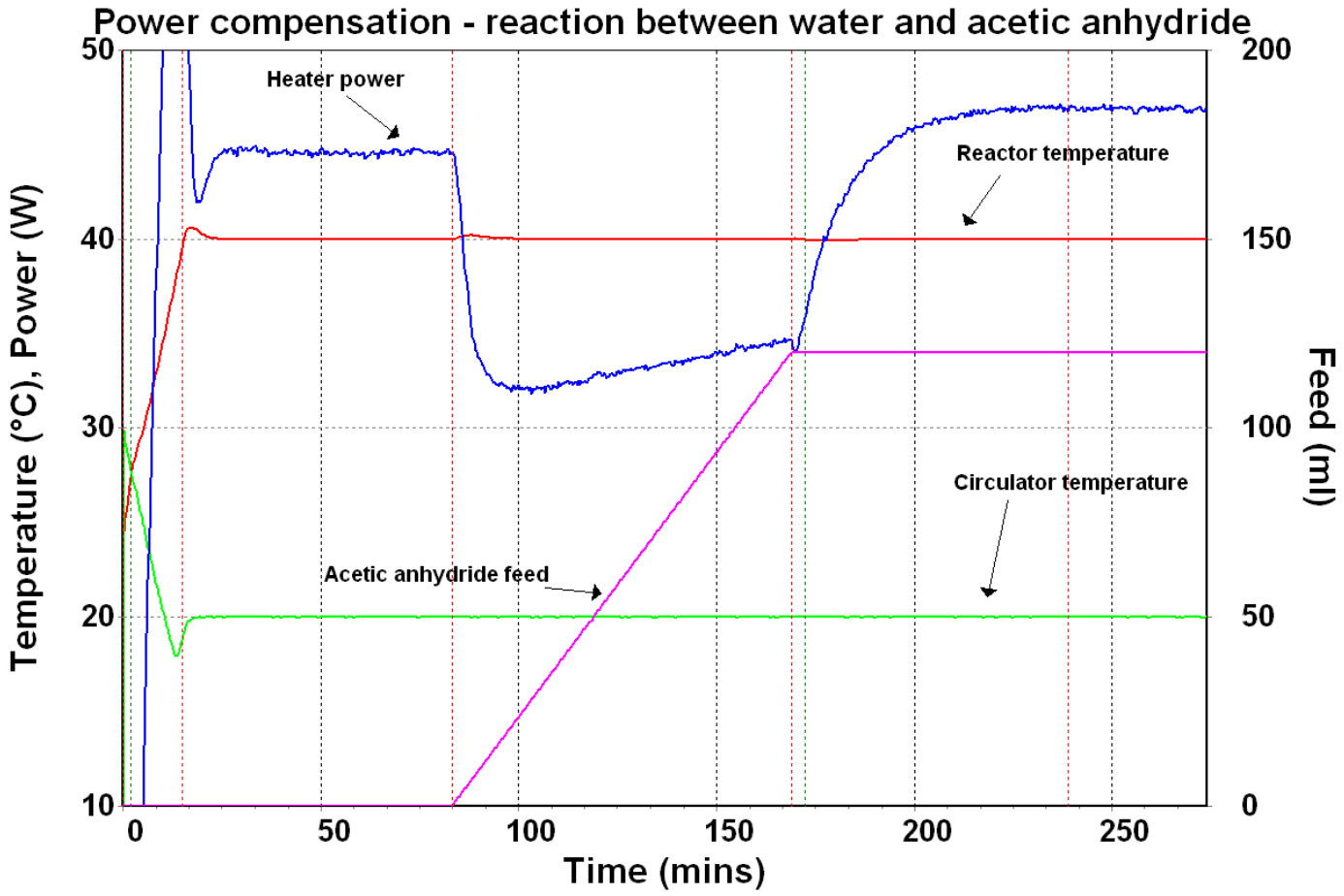
- UA (as well as Cp) determination still possible but not needed.

Power Compensation

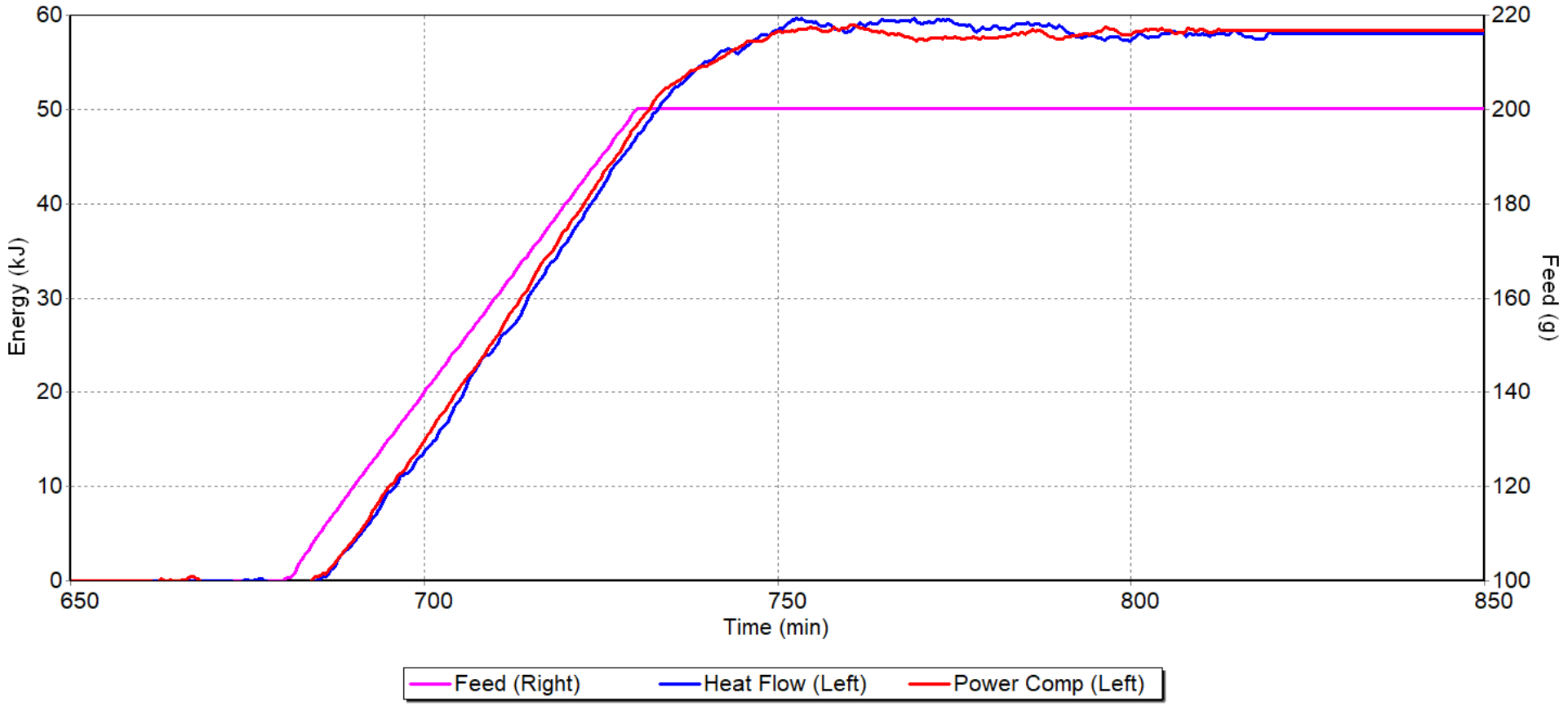
Power compensation calorimetry typical plot

Note mantle (jacket) temperature almost constant and drop in heater power during reaction

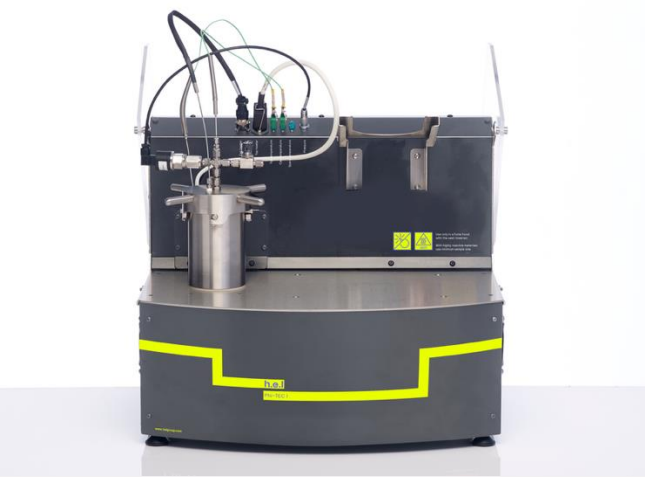
In a pressurized reactor using power compensation, this poses no issues due to huge metal mass of reactor as it is not directly heated



Data Comparison



Adiabatic Calorimetry

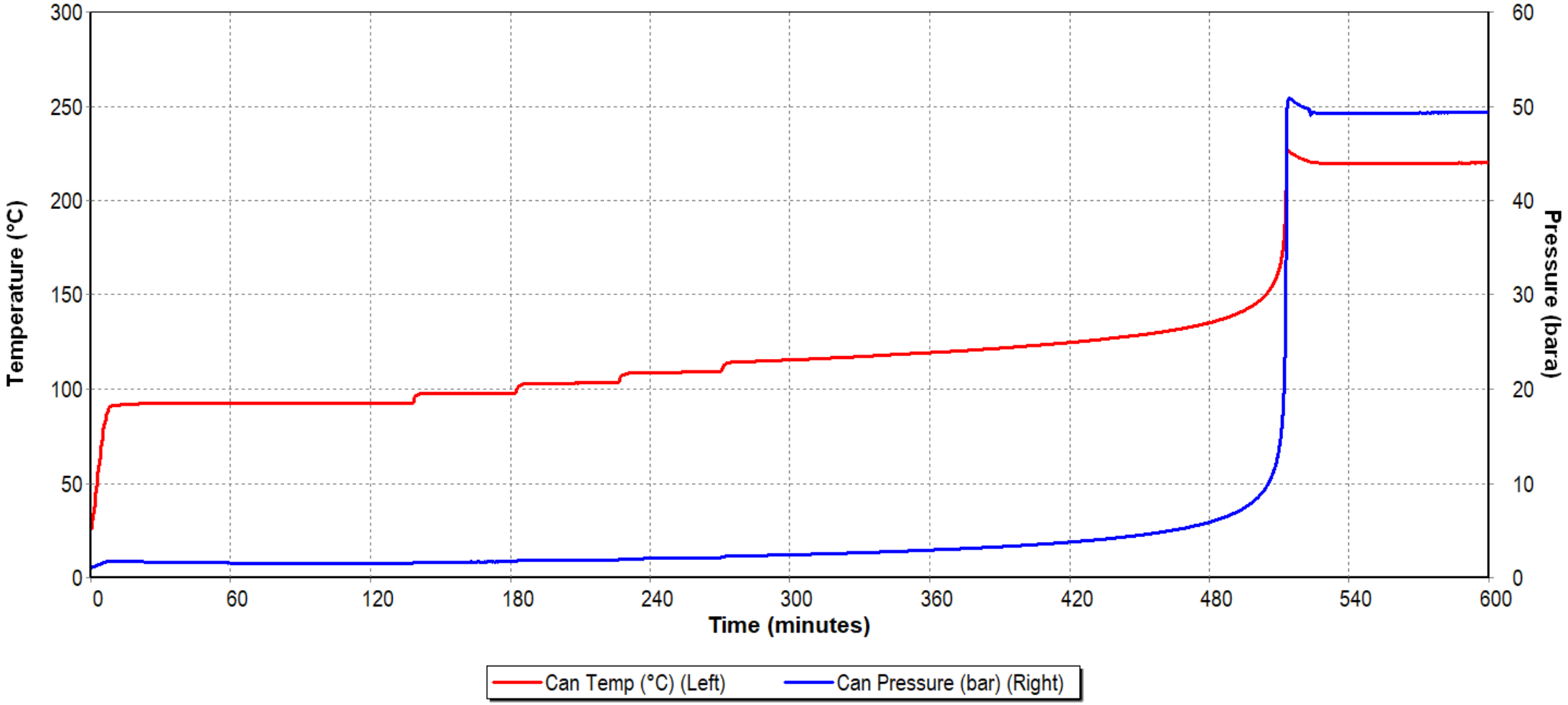


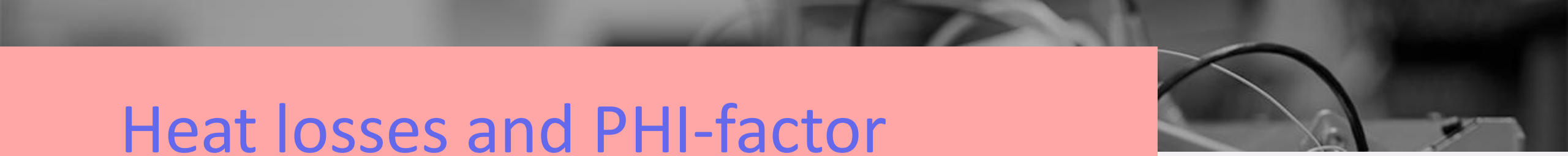
Phi-TEC I

Phi-TEC II

- Exotherms can be tracked to eliminate heat loss
- Data Obtained:
- “onset” temperature
- Adiabatic temperature rise (Phi corrected)
- Heat of reaction, based on heat capacity…
- Kinetic parameters – activation energy etc *(where a kinetic fit can be applied to the data)*

Typical Heat –Wait –Search Graph





Heat losses and PHI-factor

- Heat losses on a small scale are proportionately much larger than on plant scale
- Eliminate heat losses so that all the heat of reaction goes into heating the sample *and the test cell*.
- Track the sample temperature using oven heaters.

What is the Phi-Factor?

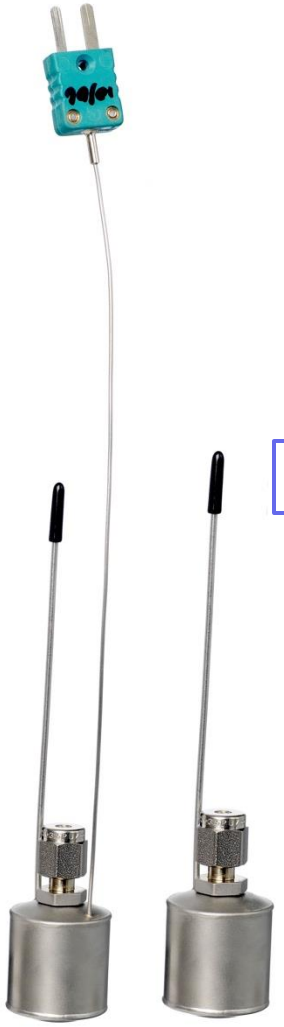
- During self-heating, the reactor or container is heated as well as the reacting materials.
- Phi factor can be described as a measure of how much of this heat is used to heat the container

$$\phi = \frac{(\text{Mass} \times \text{specific heat})_{\text{sample}} + (\text{Mass} \times \text{specific heat})_{\text{container}}}{(\text{Mass} \times \text{specific heat})_{\text{sample}}}$$

Large Scale Equipment $1 < \phi < 1.05$

Laboratory Scale Equipment $1.05 < \phi < 10$

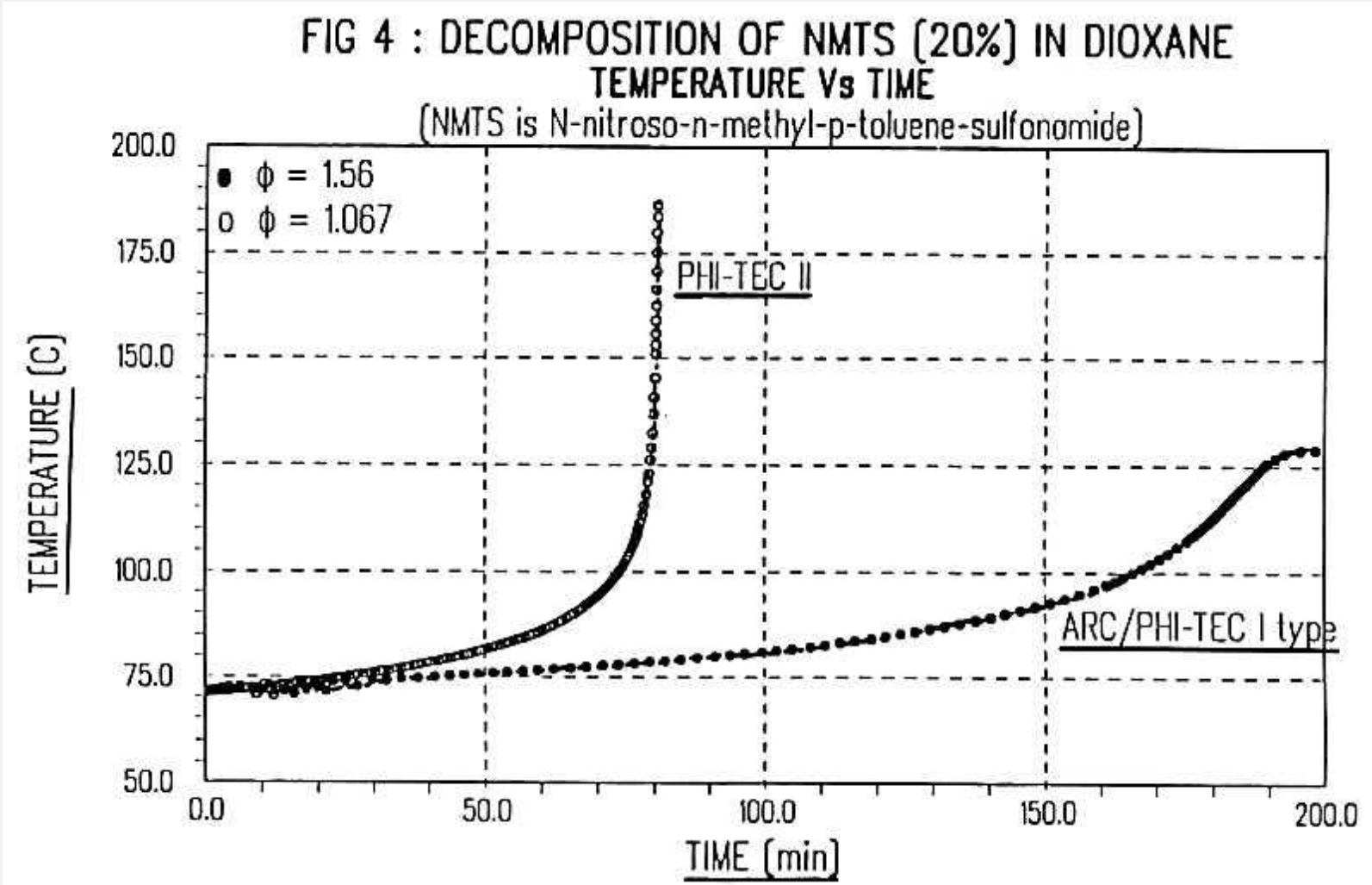
Test Cells



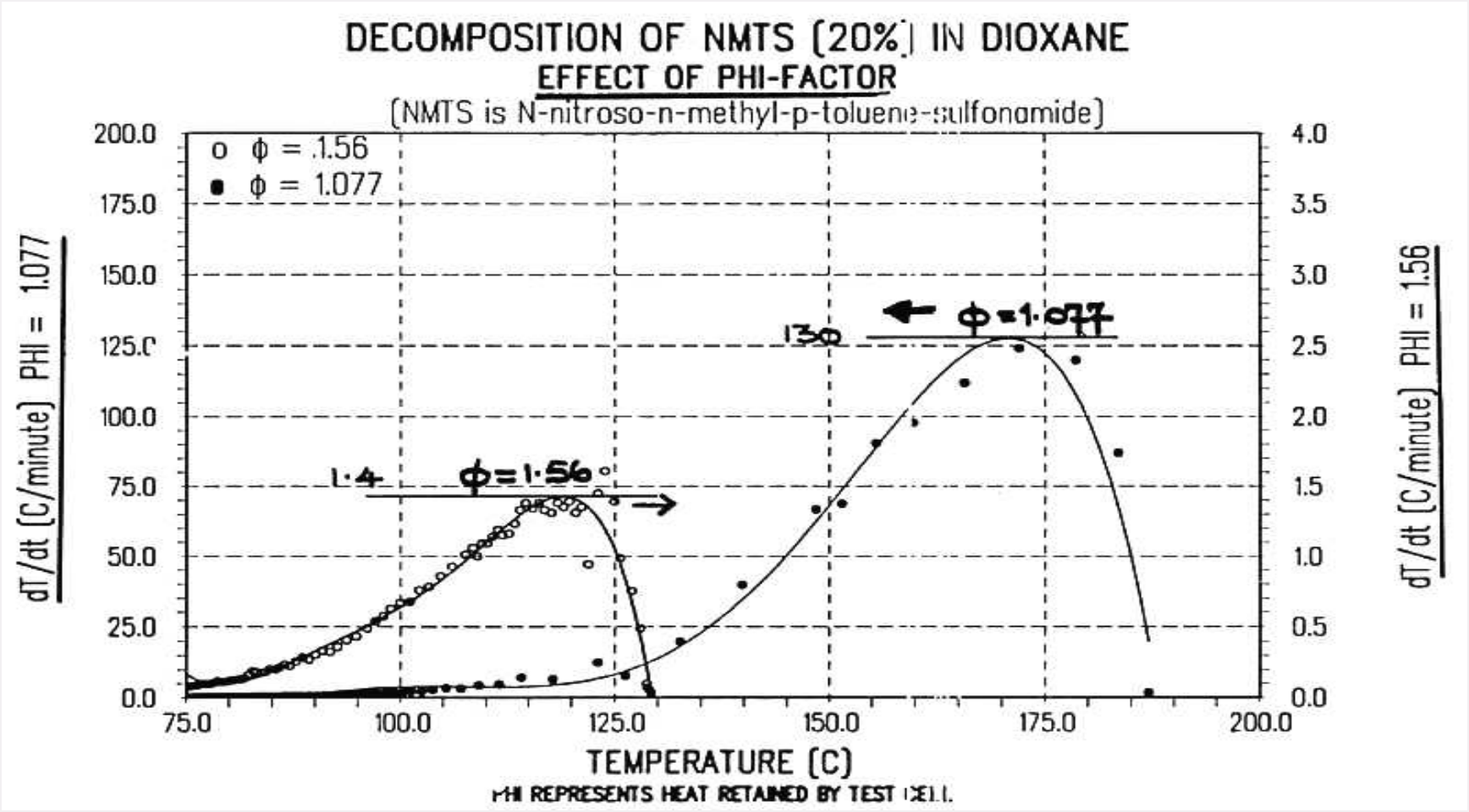
Examples of high Φ test cells

Examples of low Φ test cells

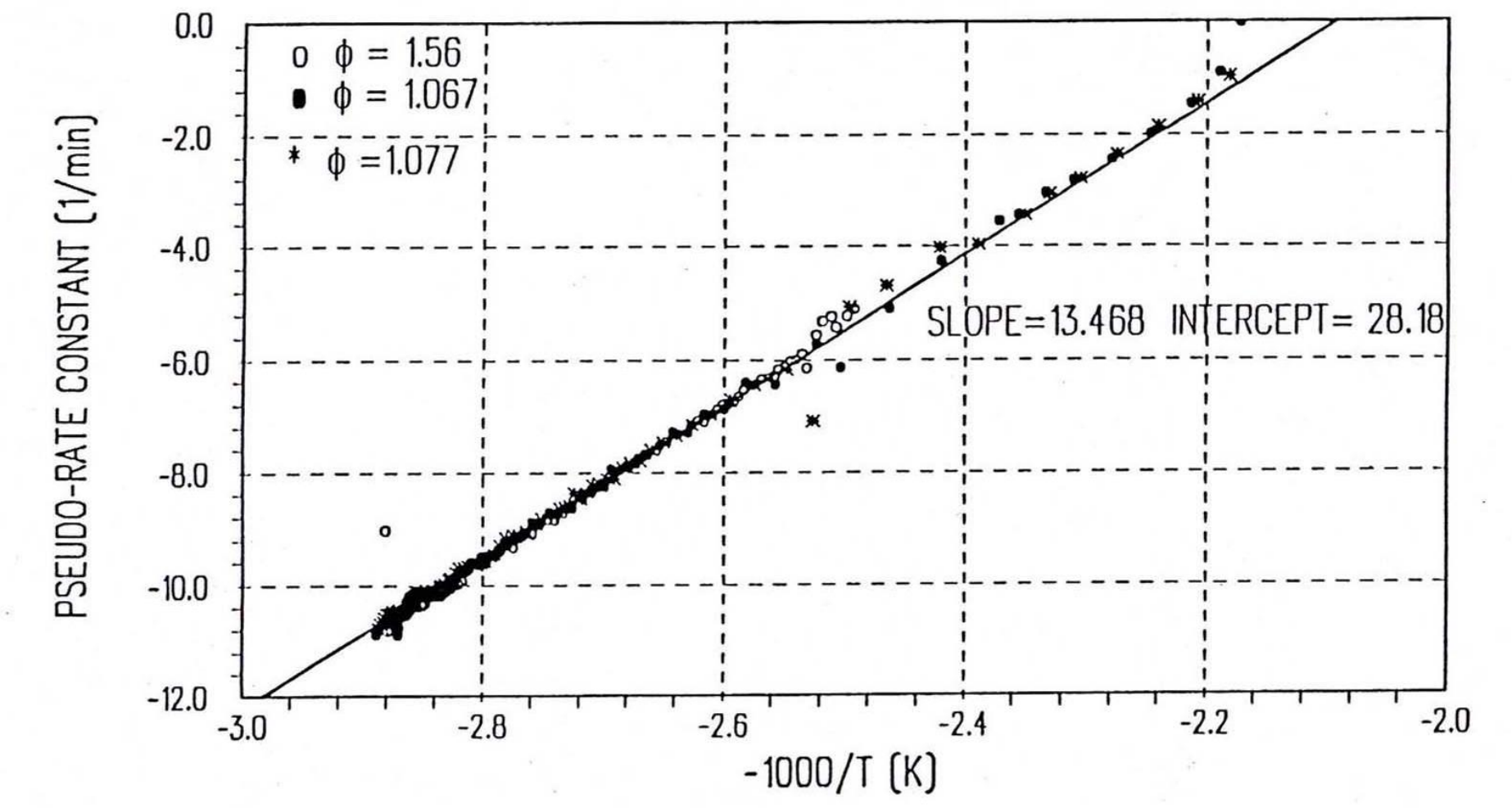
Effects of PHI factor



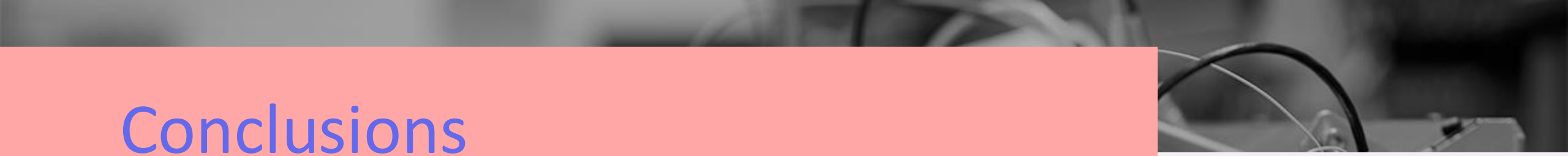
Heat rates


DECOMPOSITION OF NMTS (20%) IN DIOXANE
EFFECT OF PHI-FACTOR
(NMTS is N-nitroso-n-methyl-p-toluene-sulfonamide)
o ϕ = 1.56
● ϕ = 1.077
dT/dt (C/minute) PHI = 1.077
dT/dt (C/minute) PHI = 1.56
TEMPERATURE (C)
PHI REPRESENTS HEAT RETAINED BY TEST CELL
200.0
175.0
150.0
125.0
100.0
75.0
50.0
25.0
0.0
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
75.0
100.0
125.0
150.0
175.0
200.0
1.4
ϕ=1.56
13ϕ
ϕ=1.077

Kinetic data



Data at different phi factors can often be described by a single kinetic model



Conclusions

- Criticality charts are extremely useful in reviewing process hazards and defining bases of safety
- There may be further considerations to be made - Some situations may fall outside the strict definitions
- Beware when parameters are close in value
- Some assumptions are inevitable when dealing with reacting mixtures of changing composition and temperature.
- Different apparatus is needed to get the various parameters
- **Understanding the data and what it means, what might happen is always important.**

Thank you for listening

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