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Process Safety Decisions using RC1e™, RTCal™, iC Safety™ and Criticality Classes

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Abstract:

Reaction calorimetry is an essential part of the process information required to develop and understand chemical processes. For the more forward-thinking organisation, reaction calorimetry, and safety generally, is an intrinsic part of the process development process. Leaving safety to chemical engineers, after development, is a recipe for cost inefficiency and delays. Techniques for reaction calorimetry have improved over a 30 year period and today's commercial environment is as competitive as ever with an increasing number of vendors offering equipment with increasing levels of complexity, accuracy and versatility.

This paper discusses improvements in techniques to gain reaction calorimetry information (specifically, the advent of the Mettler-Toledo RTCal™ concept) and discusses the uses of the resulting data in safety decisions. iC Safety™ and the criticality class concept are discussed and exemplified with specific real-life examples. The importance of "good data" is highlighted as is the significance of a robust and detailed hazard assessment procedure to determine potential failure scenarios. The use of reaction calorimetry and thermal stability data in qualitatively assessing the consequences of identified process deviations is discussed.

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Introduction

The safety of reactions is of paramount importance at any scale and companies should have a strategy in place for developing safety information during the entire process lifecycle. Specifically, safety should not be left until just prior to scale-up as is unfortunately common in some organisations. The consequence of this approach is that processes are developed which are inherently more hazardous than they should be. This results in a higher risk at scale-up or requires remedial work (with associated cost and resource requirement) to mitigate the risk.

The strategy for assessing exothermic reaction and instability hazards of chemical processes is displayed in Figure 1.

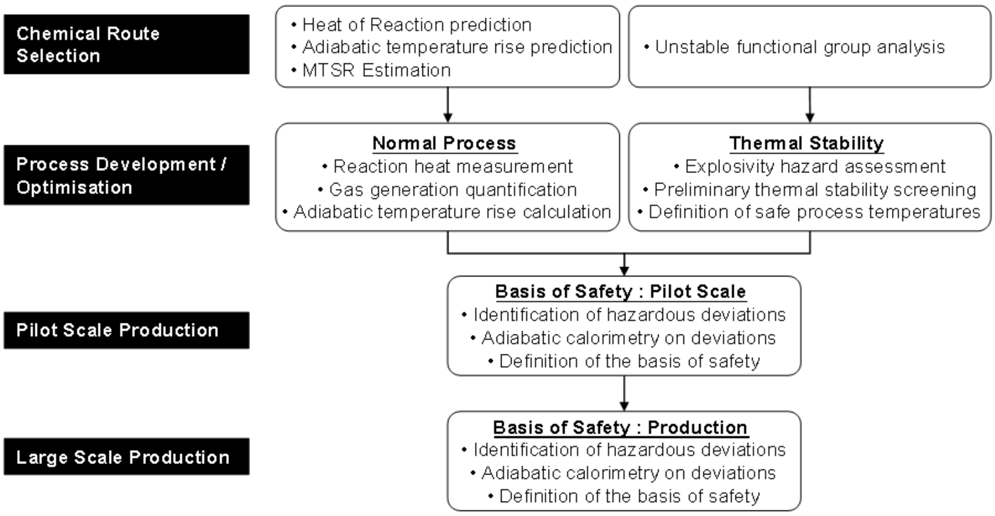

Figure 1
Stages of Safety Assessment

This paper focuses on the development of safer processes and the data requirements to quantify safety. Whilst touching on the importance of safety in Chemical Route Selection, the majority of the paper relates to "Normal Process" characterisation, thermal stability assessment and the decisions that are made with the resulting data.
The advantages of the novel RTCal™ system from Mettler-Toledo are discussed as compared to other types of reaction calorimeter. An example of a process where the RTCal™ system provides invaluable accuracy is detailed.

The saying "It's not what you've got, it's what you do with it" is almost universally relevant. Even with the best equipped laboratory in the world, the ability to generate data does not provide a competitive advantage. The key is converting this data to information. The iC Safety™ software now available from Mettler extends the data available from the RC1e calorimeter. This welcome extension provides a critical information link between reaction calorimetry data and its place in the overall safety assessment strategy. A further extension to the "Criticality Class" concept is briefly discussed.

Understanding the Normal Reaction

Prediction and estimation of reaction heats and potential thermal stability risks presented by a process should be considered right from the conceptual route selection stage. The importance of this cannot be understated. The decisions in the route selection stage will define the intrinsic risk presented by the process. Whilst a risk can be mitigated by careful process design, the need for this may be avoidable if ″safer process routes″ are selected.

Once a process route is selected, it is normal to conduct reaction calorimetry to ″characterise″ the thermodynamics and kinetics of the reaction under controlled conditions. The Mettler-Toledo RC1*e*™ reaction calorimeter is the most well known method for heat of reaction determination. The system continues to undergo development and extension to improve accuracy, ″user friendliness″ and versatility.

The RC1*e*™ system works using a heat flow measurement principle according to the classical equation, $Q = U.A.\Delta T$, where Q is the heat flow (W), U is the overall heat transfer coefficient ($W.m^{-2}.K^{-1}$), A is the (wetted) area for heat transfer (m^2) and ΔT is the temperature difference between the jacket and reaction mass (K).

The method of heat flow calorimetry involves conducting a reaction (measuring A and ΔT), and having a value of U available from electrical calibrations conducted before and after the reaction. If the U value does not change significantly, then the measured heat flow is likely to be highly accurate. However, if the U value changes significant at some stage during the reaction, then there is a need to interpolate the U value through the reaction period to get an accurate value of heat flow.

The interpolation of U can be achieved by proportioning it to a range of potential process variables. The most likely cause of a significant change in U is a significant change in viscosity. This can occur in a wide variety of chemical processes including dissolution, crystallisation, polymerisation and digestion.

The most common variables to which U can be proportioned include:

- Virtual volume (Vv) – the apparent volume of contents in the reactor
- Torque (Rt) – measured from the stirrer and, in theory, proportional to viscosity for Newtonian fluids
- Conversion – a derived value to reflect the extent of completion of the reaction by integration of the heat flow.

Whilst it is usually possible to use one of these parameters to good effect, they are not always available or reliable. Virtual volume only provides a good indicator if the reaction is instantaneous and the viscosity changes due to the addition. Torque is normally a very valuable indicator and is widely used for proportioning U. However, if the torque of the stirrer gland is relatively high, this may not give any usable signal for U interpolation.

Conversion is a derived term and assumes that the viscosity change will be directly proportional to the extent of reaction that has occurred. In many systems, this will also not be reliable. Some polymerisation processes, for example, the viscosity climbs only in the very final stages of conversion.

To overcome these deficiencies in interpolating U, an "add-on" was offered in 1999 for the RC1e called "SmartCal". This was based on the principle of online U interpolation using Oscillating Reaction Calorimetry (see [1]). This was subsequently discontinued as an add-on. However, the recently introduced RTCal™ system offers an alternative type of measurement and has been purchased, and used very successfully, by Chilworth Technology.

RTCal™ Overview

The 500 mL RTCal™ vessel (Figure 2), incorporates a three walled vessel with and outer vacuum jacket, as well as the normal internal heat transfer fluid jacket. The vessel has a horizontal heat flux sensor band around the circumference. Temperature gradients cause a voltage change across the band which is directly proportional to heat flow. Thee vertical band measures the wetted area. The sensor band is factory calibrated and, critically, the heat flow measurement is independent of the reactor contents or any changes thereof. The system can be used simultaneously with conventional calorimetry.

Figure 2
RTCal™ vessel

RTCal™ Example

A client's process involved a solution polymerisation of a high molecular weight acrylate monomer in toluene using AZDN as initiator. The reaction was performed by adding the initiator solution to the reactor containing the solvent / monomer mixture at 80 °C. The polymerisation was likely to result in a significant viscosity change, hence U change. The experimental results confirmed this (Figure 3 and Table 1).

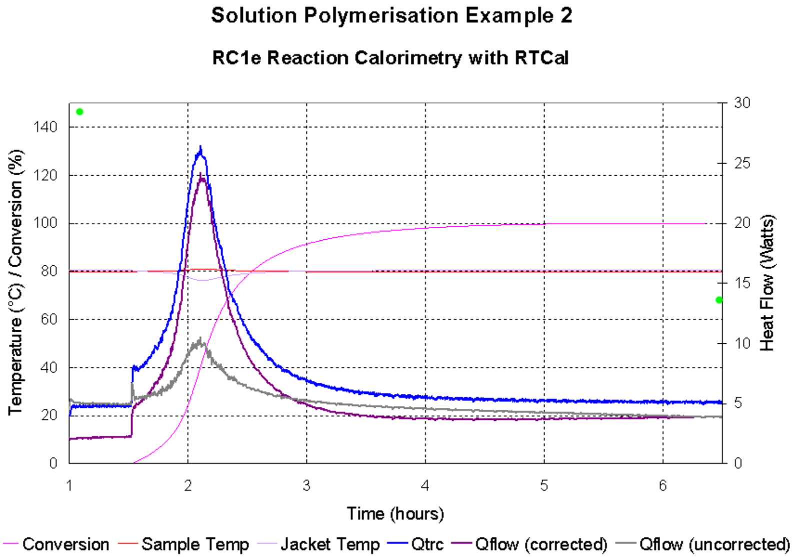

Figure 3
Experimental Data using Conventional Calorimetry and RTCal™

For the conventional calorimetric data, the uncorrected U value was, by default, proportional to Vv, resulting in an extreme underestimate of the overall heat flow and heat of reaction. Proportioning U to conversion (after much "fiddling" with the data) resulted in a more realistic heat flow. In this case, it must be considered that the overall heat flow is estimated and limited by the accuracy of the U proportionality. RTCal™ however, provides a real-time, accurate measure of heat flow.

Calorimetric Method	Qflow	Qflow	Qrtc
Type of integration baseline	Proportional to		
Vv	Proportional to conversion	Proportional to conversion	
Calculated Cp	1857 J.kg^{-1}.K^{-1}	1857 J.kg^{-1}.K^{-1}	1857 J.kg^{-1}.K^{-1}
U value (first calibration)	149.8 W.m^{-2}.K^{-1}	149.8 W.m^{-2}.K^{-1}	--
U value (second calibration)	74.1 W.m^{-2}.K^{-1}	74.1 W.m^{-2}.K^{-1}	--
Calculated ΔH	18 kJ	42 kJ	46.5 kJ
Adiabatic temperature rise	27.3 K	63.7 K	71.5 K

Table 1
Conventional Calorimetry and RTCal™ Results

RTCal™ Appraisal

There are a number of benefits of the RTCal system, many of which have already been realised at Chilworth:

- No interpolation of U required therefore excellent accuracy for reactions with changing viscosity (polymerisation, crystallisation, dissolution, digestion, etc)
- Seamless interchange with other vessels and can use RTCal™ and conventional calorimetry together in the same experiment to validate results
- Correlates with Q_{flow} reliably within 3 % for reference reactions
- Eliminates need for calibrations (saves time and permits "back-to-back" operations)
- Provides real-time heat flow measurement for feedback experiment control
- Virtual volume measurement is automated (but still requires manual values before and after additions due to extrapolation issues)
- Stirrer speed impact on heat flow can be measured in real-time.
- External vacuum jacket prevents condensation / ice formation on out wall allowing clear view of reaction mass at all temperatures (even sub-zero)

Minor limitations exist including a temperature limit of 160 °C, vortexing or foam generation interfering with A measurement and limited stirrer design options. Overall, however, the system provides a superb addition to the RC1*e*™.

Converting Data to Information using iC Safety™ and Criticality Classes

Reaction calorimetry, specifically its application in process safety studies, provides important data to describe the overall risk of the process but it cannot be used in isolation.

Criticality Classes

The thermal safety of a reaction can be crudely, but very effectively, described by knowledge of four key temperatures, and their relation to one another (described in more detail in [2]). These are the:

- Normal process temperature (TP)
- Maximum Temperature of the Synthesis Reaction (MTSR)
  - The MTSR is the maximum temperature which could be achieved if the exothermic reaction occurs with no heat loss (for example, in the event of a complete loss of cooling). This is the sum of the normal process temperature and the adiabatic temperature rise of the reaction (ΔTad). The ΔTad assumes that there are no secondary reactions or side-reactions at elevated temperatures
- Maximum Temperature for Technical reasons (MTT)
  - The MTT is the temperature at which the vapour pressure of the mixture poses a potential risk to the integrity of the vessel. For an open reactor (or low pressure vessel), the MTT would be taken as the boiling point of the mixture. For a closed pressure vessel, the MTT would typically be the temperature equivalent to either the relief device set pressure or the design pressure of the reactor. It is conservative, and easier, to define the MTT as the boiling point of the mixture at atmospheric pressure.
- The onset temperature of decomposition or secondary reaction (Tdec)
  - The Tdec is the onset temperature of secondary or decomposition reactions. This data can be determined through thermal stability screening tests or more sensitive adiabatic calorimetry. If thermal screening tests are used, then it would be necessary to correct the measured onset temperature of a reaction using an appropriate and conservative safety margin. This is necessary to account for the nature of the test (ramped, heat-wait-search or isothermal) and the sensitivity of the test method. It is common, for example, to find safety margins of up to 100 °C applied to measured onset temperatures from Differential Scanning Calorimetry tests. If much more sensitive adiabatic techniques are used to determine the onset temperature of decomposition, then smaller margins can be applied. In such cases, it is possible to calculate the temperature from which it takes 24 hours for the reaction to reach its maximum rate (referred to as T_{D24}). This value can be used directly as Tdec.

Using these four conceptually simple temperatures, the relative thermal risk of a process can be classified in to one of five "Criticality Classes" (see Figure 4).

The Criticality Classes are based on thermal effects only and do not consider gas generation directly. However, this aspect must be considered in the overall safety assessment. The Criticality Class concept can be used to define the relative risk of a reaction and make decisions regarding safety measures and procedures.

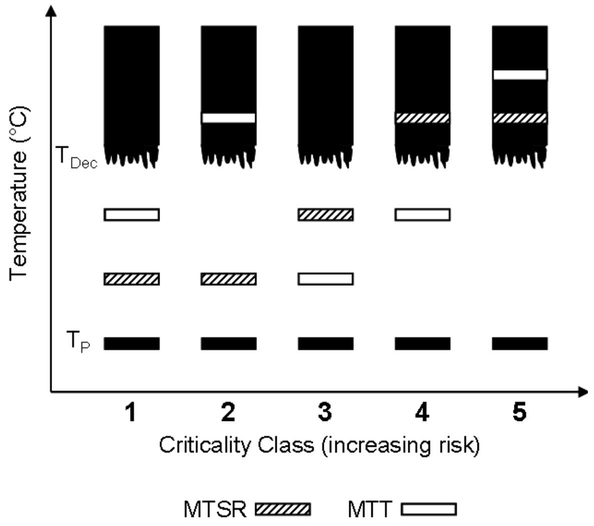

Figure 4
Risk Ranking of Reactions using Criticality Classes

iC Safety™

The iC Safety™ software available from Mettler-Toledo provides a welcome add-on to the iControl™ software to convert basic RC1*e*™ data into usable information for safety assessment. An example is provided in Figure 5 relating to the methanol / acetic anhydride reaction (stoichiometric & acid catalysed) at 20 °C.

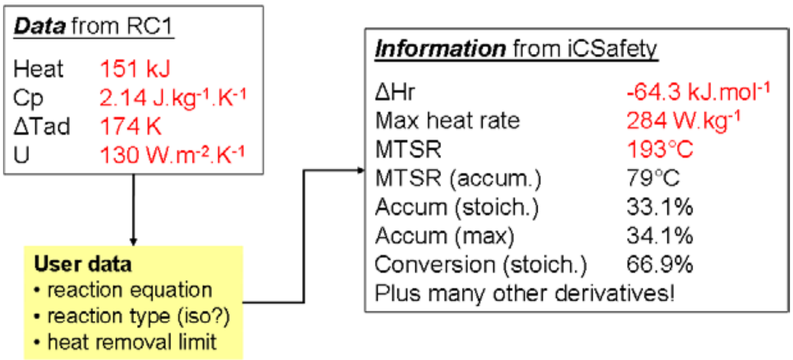

Figure 5
Data to Information using iCSafety
(Methanol / Acetic Anhydride Data)

The software is a valuable addition which automates the process of deriving information from data for safety application of RC1e data. The most valuable information relates to maximum reaction power output, MTSR (for the full reaction and accumulated heat only) and extent of accumulation / conversion during the process.

The software alludes to the criticality class concept. However, it should ideally be extended to allow users to enter MTT and T_{dec} data thus allowing the criticality class to be displayed.
In addition, it could be extended to include more sophisticated cooling assessment for plant reactors thus providing a near simulation package.

References

[1] Bou-Diab, L, "On-line Determination of the Global Heat Transfer Coefficient for Continuous Calibration in Chemical and Biochemical Calorimetry", 9th RC User Forum, Berne, 1999 (Mettler Toledo).

[2] Stoessel, F., "Thermal Safety of Chemical Processes", Wiley-VCH Verlag GmbH, 2008, ISBN 978-3-527-31712-7.