“The Accelerating Rate Calorimeter is unique for its unparalleled adiabacity, its sensitivity and its sample universality. Coupled to this its ease of use and simple data analysis make it accessible and usable by all”

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An understanding of the energy release from chemical reactions and the potential for runaway reactions is vitally important in the chemical industry. When the heat generated by a chemical process is greater than the possible heat removal, the temperature will rise with perhaps catastrophic effect. Most chemical reactions proceed with heat release but the amount of heat release, the rate of release and the temperature of onset are very important parameters. Only in an adiabatic calorimeter can such a runaway reaction be reliably evaluated by simulating what can happen on a large scale by mimicking the worst case zero-heat loss conditions.

The Accelerating Rate Calorimeter is the most well known and world's most widely used adiabatic calorimeter and will provide full information on the heat and pressure release showing the potential of a runaway occurring. This will also enable optimum conditions to be employed to allow inherently safe operation. Only when tests are conducted in a truly adiabatic system is it possible to scale-up from the laboratory scale.

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Accelerating Rate Calorimeter

The system is contained in a metal sphere 2.5cm in diameter, typically of Titanium or Hastelloy C. The sample mass is usually 2-8g but would depend upon the expected energy release and type of sample container (known as a bomb) used. The bomb is attached to the lid section on the calorimeter assembly by a pressure fitting and a pressure line leads to the pressure transducer. A fine thermocouple is attached to the outer surface of the bomb and the lid of the calorimeter then positioned on the base section. The calorimeter has three separate thermal zones. The top (lid section) contains two heaters and a thermocouple, the side zone of the base section contains four heaters and a thermocouple and the bottom zone at the base section contains two heaters and a thermocouple. After set up and connection, the calorimeter is sealed within an explosion proof containment vessel. After defining experimental conditions on the PC, the test can commence. The test conditions are a start and end temperature and choosing the size of 'heat steps', 'wait time' and detection sensitivity.

The system will firstly heat to the start temperature. To do this, a small heater in the calorimeter, the radiant heater, applies heat. This heats the sample, bomb and it's thermocouple. The calorimeter is cooler and this temperature difference is observed by the three calorimeter thermocouples. The system will then apply power to the calorimeter heaters to minimise the temperature difference. This will continue as the temperature rises to the start temperature. When this start temperature is reached the system will go into a wait period, during this time no heat is provided by the radiant heater. This allows the temperature differences within the calorimeter to be reduced to zero.

The calorimeter operates adiabatically allowing the -calorimeter temperature to track sample temperature. This wait period (typically 10-15 minutes) is followed by a seek or search period. Again during this period (typically 20 minutes) no heat is provided by the radiant heater, and any temperature drift, upwards or downwards, is observed. If there is upward temperature drift this is caused by a self-heating reaction. The heat-wait-seek procedure, the normal mode of operation of the Accelerating Rate Calorimeter, will continue until an upward temperature drift observes an exothermic reaction, greater than the selected sensitivity (normally 0.01-0.02°C/min). The system automatically switches to the exothermic mode; the system will apply heat to the calorimeter jacket to keep its temperature the same as the bomb/sample.

The adiabatic control is the key feature of the Accelerating Rate Calorimeter. The system continues in the exotherm mode until the rate of self-heating is less than the chosen sensitivity, at this stage the heat-wait-seek procedure resumes. When the end temperature is reached (or an end pressure is reached) the test automatically stops and cooling, by compressed air, begins. The aim of the Accelerating Rate Calorimeter is to complete the test to get a full time, temperature, and pressure profile of the exothermic reaction in a safe and controlled manner.

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The World’s Benchmark Adiabatic Calorimeter
has been Re-Engineered

Introducing…
the Low φ
Accelerating Rate Calorimeter

Continuity
Proven design, same bomb types, same mode of operation
Results will be the same as those obtained from older style instruments

Enhancement
Low Phi (φ = 1.05)...Fume Extraction...Cryogenic operation (Testing from -35°C)...
True Isothermal Age mode...Rapid track option...Heat and Gas generation plots, SADT and
tnr calculations ... Network-able... Industry standard hardware and software

Expansion
Vent Size Unit...Sample Stirring Unit...Sample Dosing Unit...Automated Gas Sampling Unit...
Gas Scrubbing and Safe Release Unit (manual or automatic...Cryogenic unit...Battery Safety
and Cycling Units – see separate brochures

“to assist scientists and engineers involved
with safety and hazard testing and analysis”

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The Re-Engineered Accelerating Rate Calorimeter
First available in 1978, but little changed since, full re-engineering of the Accelerating Rate Calorimeter had been overdue. However with many original systems in use and a worldwide acceptance of the data produced, the first need was for Continuity of the data, but with re-engineering there is the possibility of enhancement and expansion of this proven technology. The re-engineered instrument offered by Thermal Hazard Technology allows for all of these aspects. The original well thought out features have been retained but modern microprocessor technology and computer control have been adopted.

Continuity
The Thermal Hazard Technology Accelerating Rate Calorimeter operates in the proven heat-wait-seek method and has isothermal capabilities. The calorimeter assembly is of the same proven design and the sample containers commonly available may be used. The performance of the system and its main characteristics remain unaltered and sample data from this instrument mirrors that of the original, thus there is continuity of data.

Enhancement
The hardware and software components are built to international standards, using recognised platforms. The design is such to allow expansion. In addition, the calorimeter containment vessel is designed to allow for improved access, gas extraction and housing of additional equipment. 60ml containers mean f values to 1.05 are obtained. Software design has a user friendly GUI.

Expansion
Thermal Hazard Technology Accelerating Rate Calorimeter has therefore been designed to fulfil the requirements of an adiabatic calorimeter system but with the ability for ongoing enhancement and development. Options are available; a Vent Sizing Unit is available to allow low f testing, determination of reaction types and for blow-down tests for the determination of relief vent area. There is sample-stirring option, a sample dosing option, a gas collection option and a cryogenic option; there is a gas scrubber system to allow safe removal and disposal of potentially toxic gases.
### Accelerating Rate Calorimeter

#### Unparalleled Adiabaticity
Proven adiabatic environment around whole sample, with high precision tracking of exothermic reactions.

#### Exceptional Sensitivity
Detection of exotherm from 0.003°C/min self-heating, which may be 100W/tonne.

#### Universality of Sample
Sample range, very low energy to very high-energy reactions Sample range, liquids solids salts residues mixtures gases Sample hazard range, processing, storage, transportation.

#### Easy to Use
Internationally recognised technique - set-up time before and after a test of 10-20 minutes.

#### Simple Data Analysis
The data from a standard test is column and row data of time, temperature and pressure. From this raw experimental data the self-heat rate, pressure rate, time to maximum rate and all other data types are generated. The data analysis is semi-automated though may be fully analysed manually if preferred. Accelerating Rate Calorimeter data has always been considered straight forward to use and apply and this is also the case the Thermal Hazard Technology software. In addition the data analysis allows for input of reaction vessel information to enable maximum safe temperatures or sizes to be determined. There is provision for other types of data analysis, e.g. SADT determination and an automatic report generator is provided. This and the graphical outputs may be user modified to customise or the change. The data analysis allows for production of quality colour output in slide or transparency format.

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Di-Tertiary Butyl Peroxide is the chemical usually chosen to illustrate the data from an adiabatic calorimeter. Results obtained from the Thermal Hazard Technology Accelerating Rate Calorimeter are shown below. The data shown here is for illustrative purposes, it shows what may be obtained from a single Accelerating Rate Calorimetry test. The DTBP test is useful as it clearly shows the performance of the system the accuracy of the data and the ability of the system to operate adiabatically.

In this test 6g of 20% DTBP (98%) by weight in toluene (99.8%) is used. The bomb is a titanium bomb close to 6g in weight. Starting temperature is 90°C; end temperature 220°C the wait time 15 minutes the heat step 3°C and the onset sensitivity 0.01°C/min. Below and more importantly at temperatures above the exothermic reaction it is possible to see how well calibrated the system is and it can be noted that there is little if any drift. This indicates that there is little if any heat loss from the system - many other calorimeters allow considerable heat loss by refluxing on the cold upper surface of the sample container. Analysis of the exotherm itself can be carried out by determining temperature at which certain self-heat rates occur e.g. 0.1°C/min 0.2°C/min 0.5°C/min etc. These repeat to within 1-2°C. Also important to note is the maximum self-heat rate (though this can change with differences in void volume) the final temperature and the pressure rise.

Unlike very many samples DTBP is completely reliable as a standard. The other way to analyse is to perform a thermokinetic analysis; the software can do this. There are very many literature reports of DTBP in toluene heat of decomposition and activation energy. These centre on a heat of reaction near 170KJ/mol and activation energy near 160KJ/mol. Typically the Accelerating Rate Calorimeter working correctly will reproduce these values to ±2-3%. Getting such results clearly indicates the quality of the techniques and the correct operation of the system in use.
Accelerating Rate Calorimeter

Real Time Data Plot: This shows the temperature against time for the complete test. In addition to showing the course of the experiment with time, the exothermic reaction temperature and magnitude of the reactions the data both before and after the exothermic reaction can be seen. At low temperature, reactions below the exothermic threshold may be noted and at higher temperatures the calibration accuracy of the instrument can be confirmed. By noting the pressure below the exotherm (and above) any indication of leak can be observed - or it may be that there is pressure generated from a non-exothermic process. (see previous page for examples)

Temperature and Pressure Plot: The temperature and pressure data are plotted against time to show the onset of reaction, the magnitude of the reaction and as a comparison it can be seen how much pressure is produced over which reaction or temperature range. It can be noted that much of the time of the reaction is in the first few degrees of temperature rise. (shown right)

Self-Heat Rate Plot: The Self-Heat Rate is a key presentation of the results. The onset of reaction can be seen, as can the size, the magnitude, the complexity and number of reactions. The self-heat rate at any temperature is shown as is the maximum self-heat rate. By knowing the self-heat rate at an operating temperature for instance the amount of cooling required can be determined. By comparing the pressure rate with the self-heat rate further important information about the reaction can be obtained. (shown right)
Self-Heat Rate Analysis: Mathematical analysis of the self-heat rate plot can determine heat of reaction, activation energy and other kinetic parameters. The latter is carried out by an automated curve fitting procedure. With the model result this may be used to back-extrapolate the data to get results below the onset of reaction, including time to maximum rate data from the modelled reaction at low temperatures.

Pressure and Pressure Rate Temperature Plots: Pressure may be plotted on linear axes or as logarithm of the pressure against reciprocal temperature (Kelvin). Should the data produce a linear plot on linear axes the pressure rise is that of a non-condensable gas, if the plot is linear on log-reciprocal axes the pressure rise is likely to that due to vapour pressure increase. In addition a plot of pressure rate and against temperature rate may be produced, a straight line here indicates a single reaction - when heat is pro-

Time to Maximum Rate: After selecting the temperature of maximum rate this important curve may be generated. With knowledge of activation energy, the plot may be corrected to worst case. If the model reaction has been determined the time to maximum rate curve may be generated to lower temperatures. This presentation of data shows immediately the amount of time available from any temperature to runaway, possible disaster - in the worst case. The plot may also be used to determine maximum safe temperatures or size of storage vessels; the data may be used to determine SADT.
Operations Software

The Set-up of a test is carried out by entry of information into user-friendly screens. This will include information on the sample and the bomb. All information entered here and data from the test result will link directly to the Microsoft Word Report that can be automatically generated after the test. It is possible to manually override the test conditions and run mode during the test. During the test the screen graphical user interface shows clearly the current status. The software can be networked such that the user can view run information remote from the instrument.
Accelerating Rate Calorimeter

Vent Sizing

THT's Unique VSU (Vent Sizing Unit) utilizes DIERS technology to perform: Closed vessel, Tempering, and Blow-down tests. THT have experience in all aspects of process design and safety. The use of modern instrumentation and advanced software modelling allow THT to provide rapid and accurate thermal safety assessment.

Options and other products from Thermal Hazard Technology:

Uniquely THT have developed the Accelerating Rate Calorimeter to extend its operation and usefulness: Low Phi, Vent Sizing, Cryogenic Operation, Sample Gas Collection, Sample Gas Safe Release, Sample Stirring and Dosing.

THT have also developed the Battery Safety Calorimeter to allow use and abuse testing to be carried out with 1 instrument.

System Specifications:
Sample sizes: mg-grams (>50g with low-phi test cell)
Phi Range: 1.05 and higher
Operating Temperature Range: Ambient - 500 °C (absolute max 600 °C) (Sub-zero with cryogenic option)
Maximum Sensitivity: 0.005 °C/min (typical power equivalent 30mW/g)
Maximum Isothermal Stability (in Isothermal mode) 0.002°C over 24 hours, onset detection from 0.002°C/min
Maximum Heat Rate (in Ramp mode) 10°C/min
Pressure Limit 200bar (higher value transducers available)
Mains Supply: Voltage: 100, 110, 120, 200, 220, 240 V AC / Frequency: 50, 60 Hz / Power: 2.5 kW
Cooling: Dry Air @ 2 - 10 bar (6 mm ID flexible tube)