ESARC Accelerating Rate Calorimeter
Enhanced Specification World Benchmark Calorimeter
The ARC simulates exothermic runaway reactions at safe laboratory scale.
Introduction

Adiabatic Calorimetry provides vital thermal and pressure data for safety of chemical reactions and processes.

Reactive Chemicals and Materials, Monomers, Resins, Peroxides, API's, Batteries and Explosives all have the potential to produce heat by exothermic reactions. If the heat is not removed there is the potential for a runaway reaction.

There is the need to understand the likelihood and to assess the impact of ‘undesired reactions’. This can be done in the laboratory on a small scale with the aim to simulate the worst case scenario of what can happen on larger industrial scale.

An adiabatic accelerating rate calorimeter (ARC) can replicate such potential exothermic runaway reactions, under zero-heat loss conditions. Only when tests are conducted in a truly adiabatic system (i.e. the ARC), is it possible to scale-up from the laboratory scale to any commercial scale.

The ARC was devised by the Dow Chemical Company in the 1970s and was commercialised in 1980. In operation, the calorimeter temperature aims to match the sample temperature while a reaction is occurring.

When the heat generated by a chemical process is greater than the possible heat removal, the temperature will rise leading to potentially catastrophic consequences.

As a sample self-heats and its temperature rises, so does the calorimeter temperature. There is minimal heat transfer between the sample and the surroundings. The “worst case” conditions are evaluated and a real life hazard scenario is understood.

The wide dynamic range allows for detection and measurement of very small heat release as well as the ability to quantify runaway explosive decompositions.

The ARC is robust and rugged enabling it to withstand explosive events and contain the significant energy released during thermal runaway.

For accurate detection of exothermic reactions the ARC employs a ‘heat-wait-seek’ (HWS) protocol which is slower, but far more accurate than a simple temperature scan. In HWS, small heat steps are applied and after a wait period for isothermal equilibrium, there is a seek period to detect heat release by temperature rise. When this occurs the system automatically switches to exotherm mode and tracks the heat release, accurately following and recording the temperature rise.
The eSARC

The world’s best selling and benchmark adiabatic calorimeter. Giving full adiabatic runaway information for both temperature and pressure events. The modular design allows extra features to be added as necessary without prohibitive upgrade costs. Standard safety features include, automatic door locking, fume extraction, a software independent heating fail-safe and blast-proof reinforced steel enclosure.

Heat-Wait-Seek procedure continues until, at a certain temperature, an upward temperature drift is observed. This is likely to be from self-heating of the sample; exothermic reaction. When this temperature rise is at a rate greater than the selected sensitivity the system automatically switches to Exotherm mode.

- World’s best-selling and benchmark adiabatic calorimeter
- On-set detection from 0.005°C/min
- Electronics housed in lower section with calorimeter sited in upper section blast box
- Working volume: 0.25m³

Detection of Exotherm

Tracking of Exotherm

eSARC records Time, Temperature and Pressure, allowing further analysis to be conducted.
### Specification

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
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</thead>
<tbody>
<tr>
<td>Chamber dimensions</td>
<td>9cm diameter 10cm depth</td>
</tr>
<tr>
<td>Temperature range</td>
<td>Ambient * to 600°C</td>
</tr>
<tr>
<td>Thermocouple specification</td>
<td>Resolution 0.001°C Precision &lt;0.2%</td>
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<tr>
<td></td>
<td>Accuracy 0.7%</td>
</tr>
<tr>
<td>No. of heaters</td>
<td>8</td>
</tr>
<tr>
<td>Pressure range</td>
<td>0-200bar</td>
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<tr>
<td>Sensitivity</td>
<td>0.005°C/min</td>
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<tr>
<td>Safety</td>
<td>0.25m³</td>
</tr>
<tr>
<td>Control modes</td>
<td>Adiabatic Ramping Isothermal Isoperibolic Step Isothermal</td>
</tr>
<tr>
<td>Control / Analysis Software</td>
<td>NI Labview based</td>
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<tr>
<td>Electrical requirement</td>
<td>200-250V, 16A 3.5kW</td>
</tr>
<tr>
<td>Dimensions (L x W x H)</td>
<td>Electronic s &amp; Blast Box 80cm x 70cm x 167cm</td>
</tr>
<tr>
<td></td>
<td>Blast Box (door open) 80cm x 150cm x 157cm</td>
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</table>

### Options

<table>
<thead>
<tr>
<th>Options</th>
<th>Details</th>
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<tbody>
<tr>
<td>CSU</td>
<td>For temperature application, -40°C start temperature</td>
</tr>
<tr>
<td>SSM</td>
<td>Manual sample system for gas collection</td>
</tr>
<tr>
<td>SSS</td>
<td>Single sample gas collection during or after test into collection vessel, up to 4 litre sample</td>
</tr>
<tr>
<td>SSU</td>
<td>Gas collection, 4 samples – automatic collection at any time, temperature or pressure</td>
</tr>
<tr>
<td>PSU</td>
<td>Pneumatic raising and lowering of calorimeter lid</td>
</tr>
<tr>
<td>UPS</td>
<td>Maintains operation for up to 1hr in the event of power failure, includes smart shutdown routine</td>
</tr>
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</table>

*-40°C with LNFO option
DTBP: Di-tertiary butyl peroxide

DTBP is an organic peroxide that has been used over many years as the standard sample to evaluate the performance of the ARC. This sample gives a simple decomposition that is well characterised. The sample is diluted with toluene to a concentration of 20wt%.

20% DTBP Data

Two data files are generated, the real time (*.dat) file contains all data and the exotherm only data file (*.exo). Real time datasets are used to evaluate the entire run, with exotherm files used for analysis.

The four graphs show temperature and pressure data plot against time, with calorimeter zone temperatures also plotted. The data both before and after the exothermic reaction can be seen.

At lower temperatures, reaction below the exothermic threshold may be noted and at higher temperatures the calibration accuracy of the instrument can be confirmed. By noting the pressure before and after the exotherm any indication of a leak can be observed – or it may be that there is pressure generated from a non-exothermic process.

The simple 20% DTBP test illustrates the quality of the data and performance of the instrument.
DTBP: Di-tertiary butyl peroxide

Time to Maximum Rate, TMR, is a key graph obtained from the ARC test which indicates time available prior to explosion. From this graph, with phi correction, and with knowledge of heat loss from the container or vessel, maximum safe temperate or vessel size can be determined. Further analysis allows Temperature of No Return (TNR) and self-accelerating decomposition temperature (SADT) to be determined. Kinetic Model graphs and associated tabular data can be calculated when the data obeys classical kinetics. This allows Activation Energy, Order of Reaction, and Heat of Reaction to be obtained.

Raw Data; Temperature and Pressure

Calculated Data, Phi-Corrected Time to Explosion

Phi (φ) Correction

In any adiabatic test, heat is lost into the sample container. Correction can be made to the fully adiabatic situation using a phi (φ) correction. A key advantage of the ARC is the ability to test a much wider range of sample types than other calorimeters.

\[ \phi = 1 + \left( \frac{m_b}{m_s} \cdot \frac{C_p_b}{C_p_s} \right) \]

Where ‘b’ = ‘bomb’ sample container and ‘s’ = sample

Tests may be carried out with low energy samples in large volume, φ may be 1.10, tests can be carried out with energetic samples; liquids, solids, slurries etc, with smaller sample mass where φ may be 2, 5, 10, even higher. This is very important for explosive materials.

The ability of the ARC to test such a wide range of φ values make it unique and give the technology unrivalled flexibility and versatility.

Phi corrected Temperature and Pressure

Phi corrected Temperature and Pressure Rate
Reactive Chemicals

Peroxides, azo dyes, nitro compounds and others with reactive groups, plus intermediates and additives that contain potentially more than two or three reactive groups are the major types of sample tested in the ARC. Data is shown here for AIBN (an Azo initiator), Benzoyl Peroxide and NMTS, the original sample tested and reported by Dow Chemical.

Monomers

Polymerisation reactions are studied in the ARC. The reaction is controlled by using inhibitors, accelerators and other additives. This is an area of application where ARC isothermal testing is often employed to good effect.

The two illustrations below show a styrene monomer sample held isothermally at 80°C (left) and at 75°C (right). At 75°C the reaction occurred after 65 hours, whereas at 80°C the reaction occurred after 2 hours.
Explosives

Stability, onset of reaction, batch-to-batch variation, compatibility, and ageing are all areas of interest for Civilian and Military explosives. This is an application well suited to the ARC and where the ARC is extensively used worldwide. The illustration, used with permission, illustrates a number of well-known high explosives.

Intermediate Selection

In production processes there is often a choice of intermediates and there may be various catalysts or other additives that can be used.

The stability of all choices and their impact on the reaction has to be determined. The ARC is a good choice; illustrated by a comparative set of six different materials. It can be seen that self-heat rate and pressure are good parameters for comparison, temperature-time is less appropriate.
Oil (Oxidation)

The characteristics of oil samples are important, particularly when Enhanced Oilfield Recovery techniques are being used which incorporates in situ combustion. Oils have low and high temperature oxidation regions. ARC testing is typically carried out at very high initial pressure (e.g. 100bar). Testing is carried out with the oil alone or with rock and water. Graphs below indicate differing oil samples.

Epoxy Resins
Comparison with DSC Data

Epoxy resins are used universally and manufactured in bulk by many well known large chemical companies.

The results from three commercially available resins are shown with DSC data superimposed. All show a curing reaction followed by a decomposition. The ARC results illustrate the thermal differences in onset, heat release and rate of heat release.

Comparing ARC with DSC illustrates the benefit of ARC testing; the clearest and most striking conclusion is that DSC shows reaction onset at significantly higher temperature.
Options under software control require the OSU within the electronics cabinet.
Options

THT has worked with a variety of users to develop options to extend the use of the ARC and make it more flexible and versatile. Options may be manual or automatic. Automatic options are under ARC software control.

Fast Tracking

**FTO** Fast Tracking Option

- A thin metal alloy shield and fast acting heater to extend adiabatic control to rates of upto 400°C/min.

- Useful for vent sizing assessment and tests where it may be necessary and important to get reliable data from fast reacting system.

- Typically used with low phi sample holders. The burst disk assembly may also be used.

**Cryogenic Option**

**CSU** Cryogenic System Unit.

- Cooling unit to reduce temperature of containment vessel, calorimeter and sample to -40°C

- Passive unit fitted directly to esARC

- Once sub-ambient temperature is reached standard heat-wait-seek (or isothermal test) may be conducted.
Dosing

- **MDU** Manual Dosing Unit for addition at ambient pressure via 10ml glass syringe at start of test
- **ADU** Automatic Dosing Unit. Software controlled addition during test at elevated temperature and pressure

Syringe options
- 10ml syringe (50µL - 10ml/min) up to 300bar
- 20ml syringe (100µL - 20ml/min) up to 150bar

Stirring and Agitation

- **ASU** Automatic Stirring Unit.
- **MSU** Manual Stirring Unit.

- Magnetically coupled stirring with software controlled speed from 120-540rpm
- Fixed speed of 260rpm with MSU
- Agitation achieved by varied directional stirring at user defined time interval
- Test cells pre-loaded with magnet, available from THT.

Data above shows polymerisation of vinyl acetate. The sample was a 1:1 mix of water and vinyl acetate. Total heat release similar, speed of heat release is an order of magnitude greater in stirred sample due to dispersion. Stirred data 7°C/min compared with 0.7°C/min for non-stirred.
Gas Collection

- **SSM** Sample System Manual for gas collection after test to 50ml cylinder.

- **SSS** Single Sampling System, software controlled collection of gas after the test or at a specified temperature prior to the end of the test. 50ml cylinder as standard.

- **SSU** System Sampling Unit provides four sampling cylinders (3x 10ml; 1x 25ml). Collection is software triggered on basis of either temperature, pressure, time, temperature change, pressure change or onset of exotherm.

Gas Scrubbing System

- **GSS** automatically vents toxic or corrosive gasses through a scrubber tank at the end of the test.

  - Automatic activation once test has been completed and calorimeter cooled to user defined temperature.

Fume Hood Unit

- **FHU** converts the ARC blast box info a fume hood. Consists of top-mounted fan extraction unit and front Perspex access panel.

  - Linear face velocity matches that of dedicated fume cupboards. Capable of replacing the volume of the containment vessel 120 times per minute.

  - Automated operation commences at end of ARC test and ceases once idle mode is reached. Manual operation also possible.
Gas Flow Options

THT offer several different gas flow options at varying levels of pressure.

- **HPFO** High pressure flow option
  - flow up to 400 bar
- **MPFO** Medium pressure flow option
  - flow up to 200 bar
- **APFO** Ambient pressure flow option
  - no excess pressure

![Composite Oil Sample](image)

Data shows HWS of 6g composite oil sample. Tests under 20.6 bar of pressure with and without flow. Data from 10ml/min (air) detects onset at 165°C

Automated Lid Lifting

- **PRU** Pneumatic Rising Unit

- Automatic raising and lowering of calorimeter lid by compressed air.
- Enhanced ease of use during sample bomb fixing and removal.
Vent Sizing Unit

- Facilitates low phi closed vent sizing tests, tempering tests and hydrodynamic blow down tests.

- Tempering is the ability to slow down and stop the exothermic reaction by endothermic boil off of solvent.

- Blow down means loss of sample by its ejection from its vessel, determining the hydrodynamics of the mix.

VSU allows simulation tests that aid vent sizing.

Spares and Consumables

THT stock a comprehensive range of spares and consumables.

- Spherical test cells or ‘bombs’ are the main consumable. Accommodating a wide range of samples these vary in material of construction, wall thickness and loading stem diameter.

- Titanium test cells have a lower thermal capacity, which may allow closer modelling of the conditions encountered during commercial scale operation,

- Hastelloy cells are very resistant to interaction with corrosive chemicals and have high strength; they also withstand higher pressures at high temperature.

- Different stem diameters are available to accommodate liquids, solids, pastes or mixtures. Other types of sample containers are available such as glass and high volume / low phi.

- Test cells, replacement feed through tubes, thermocouples and radiant heaters can all be ordered at online at www.arcspares.com.
Test cells are available in a variety of materials, wall thickness and stem diameter.
History

Accelerating rate calorimetry has a long history of being the favoured technology for process development, process optimisation and safety.

The true ARC, originally developed in the 1970s by Dow Chemical in the USA, is well known and the world's most widely used adiabatic safety calorimeter. THT have been working with the ARC since the 1980s and developed our first system in 1996.

ARC calorimetry is our passion and core business as the industry has evolved, so have our products. THT has worked with a variety of users to develop options to extend the use of the ARC and make it more flexible and versatile.

Today, THT is considered to be a leader in design, manufacture and supply of the ARC. Globally more than 100 of the world's leading pharmaceutical and chemical companies, government laboratories and universities are using THT products.

THT products are supported from its four main offices located in the UK, USA, India and China and by a network of qualified and experienced distributor network.

“ARC calorimetry is our passion and core business”

As well as instrument sales we offer a full range consultancy options. From simple sample tests to full consultancy. THT are committed to working together with companies to provide solutions for their process and safety needs.

Into the future THT has a full programme of innovation and development; this will keep THT products at the forefront of technology and address the challenges of today's scientist.
Selected Users of THT ARC

Our accelerating rate calorimeter is utilised in the majority of the world's pharmaceutical and chemical companies as well as government laboratories and universities.

Service & Support

THT offer expert training with lifetime email and telephone support. Operating to ISO9001 THT enjoys an exceptional reputation amongst leading scientific and industrial organisations worldwide.