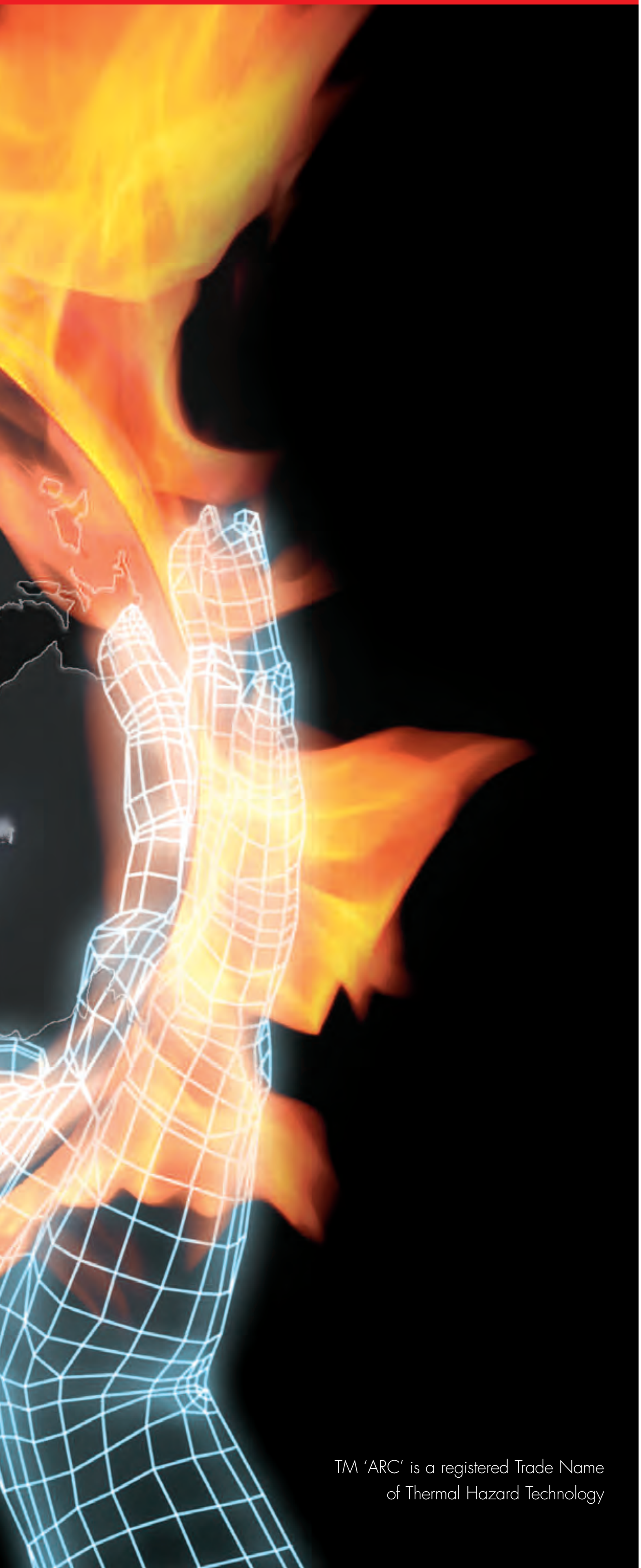
ES Enhanced Specification
Setting New Standards

thermal hazard technology

Offices in ENGLAND, USA, CHINA; Representation Worldwide

Enhanced Specification ARC™: Controlling the

elements



TM 'ARC' is a registered Trade Name
of Thermal Hazard Technology

Contents

Safety of Chemical Reactions and Processes

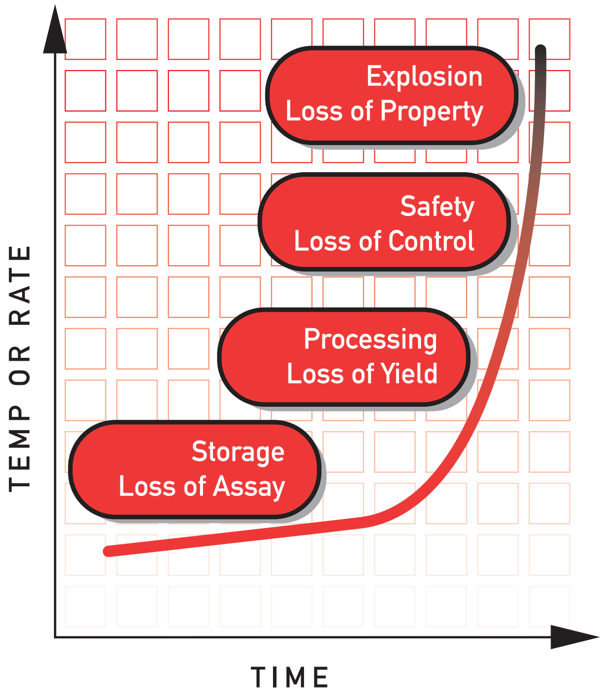
Heat, fire, explosion, pressure generation: all features of undesired reactions.

Reactive Chemicals and Materials, Monomers, Resins, Peroxides, API's Batteries and Explosives – all have the potential to produce heat by exothermic reactions, these typically are unwanted. 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 smaller scale with the aim to simulate the scenario of what can happen in real life on any larger industrial scale.

Such an understanding of energy release from chemical reactions and the potential for runaway reactions is vitally important in many branches of the Chemical & Allied Industries. When the heat generated by a chemical process is greater than the possible heat removal, the temperature will rise with perhaps catastrophic effect! It is an adiabatic calorimeter that can simulate such unknown exothermic runaway reactions, mimicking what can happen on large scale and giving worst case data; data obtained under zero-heat loss conditions.

The true ARC, originally developed by Dow Chemical in the USA, is the famous, the most well known and the world's most widely used adiabatic safety calorimeter. The ARC will provide full information on heat and pressure release showing the likelihood of self-heating, exothermic and the potential for a runaway reaction occurring. The ARC results will also enable optimum conditions to be employed to allow inherently safer operation. 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.



It must be realised that for reactions obeying classical kinetics the heat produced will increase EXPONENTIALLY with temperature, but heat loss from vessel will only increase LINEARLY with temperature.

What happens if a chemical or system self heats?

Initially (near onset of self-heating) this reaction will be slow. In chemicals this gives a loss of yield, a shelf life issue. At this stage heat loss is likely to pose little potential of a runaway and an explosion. However should the reaction accumulate heat it will accelerate and as temperature rises the rate of reaction will also increase. If the reaction is not kept under control, a safety problem will occur, which may result in explosion, loss of property, even human injury or death. It is necessary to remove this heat of reaction to control the reaction. To maintain control of the reaction the heat loss must be greater than the heat production.

Safety of Reactive Chemicals, Explosives, Lithium Batteries

Scales of Reaction

- R & D
- Process Development
- Manufacturing
- Transportation
- Storage

In the Chemical Industry, for all potential *Runaway Reactions*, heat loss possibility and environmental conditions are important, scale is important…

A small vessel will lose more heat than a large vessel; the large vessel is more adiabatic. A reactive material in a smaller vessel will be stable to a higher temperature than the same material in a larger vessel. The same sample may be safe in a beaker or drum – but may runaway in a tanker causing explosion. A battery may be stable as a single unit – but as a battery pack in a black cased Notebook alongside heat-producing electronic components heat output may raise the battery temperature causing disintegration and fire.

To simulate the real-life or large scale scenario, the sample under investigation must be in an environment without heat loss (or gain). The adiabatic environment best reproduced in the ARC.

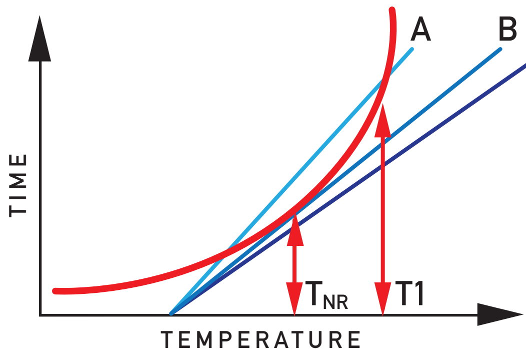
The temperature where the heat production exceeds the heat loss is the Temperature of No Return (T_{NR}). There is not just one T_{NR}, this value will change as heat loss potential changes. Vary the environment and the T_{NR} can be reduced significantly. Heat generation is quantified by the adiabatic calorimeter; the heat loss may be measured or calculated. ARC test data can then be linked with heat loss information giving T_{NR}, maximum pack size, SADT, maximum safe operating or storage temperature. This answers questions such as:

- Can the material be used safely?
- Should conditions be modified?
- Is your process safe? Is the storage safe?
- Should smaller containers be used?
- Is the material safe to transport in such scale in hot countries?
- Is the battery safe?

THERE IS A VITAL NEED FOR ADIABATIC SAFETY DATA FROM THE ARC TO ANSWER SUCH QUESTIONS.

Self-heating of a reaction and heat loss from 3 vessels, **A**, **B** and **C** is illustrated below.

A can control the sample to temp **T1**, **B** will control the sample at the critical temperature, $\mathbf{T_{NR}}$ and **C** cannot control the thermal runaway.



ARC technology was first devised 30 years ago, time has moved on – but the potential hazard of chemicals, intermediates, pharmaceuticals, monomer, and explosives remains. But new hazardous materials are now in use.

In addition one well-known new ARC application is Lithium Batteries. Lithium Batteries have the potential to runaway for more than one reason. Their chemistry is hazardous; lithium ions on carbon anodes, flammable electrolyte, unstable de-lithiated oxide materials (cathode) and a battery that will contain the highest charge density.

Clearly the need to assess safety of chemicals, materials, systems and even batteries for their potential to self-heat has never been greater. There has never been a time when there is greater need for data obtained by adiabatic calorimetry as supplied by the THT ARC, the world benchmark Adiabatic Safety Calorimeter.

ESARC

Devised by Dow Chemical Company in the 1970's, an explosion at a Dow UK site led to commercialisation of ARC technology. The Chemical Processing Industry has been safer from its first availability in 1980! The ARC has specific features and advantages that make it unique and preferable to all other technologies that were available at this time – and today 30 years later this technology is still the number one choice for most people focusing in this area of quantifying exothermic reactions, effect of heat upon materials and simulating runaway reactions.

THT has played the major role in ARC technology development and THT has continuously kept ARC technology in manufacture.

THT has produced up-to-date instruments and has extended and enhanced the technology as requested, by users. THT has worked with users worldwide to understand their needs and to develop new products and opportunities.

Key Aspects of the ARC:

- Excellent Adiabatic Control
- Universal Sample Type
- Ultimate Sensitivity
- Ease of Use
- Simplified Data Analysis
- Widespread acceptance of ARC Data worldwide
- Safe in Use

And Latest Features:

- Greater Stability, Higher Sensitivity
- Wider Temperature Range
- More Versatile Isothermal Modes
- Remote Operation worldwide
- Virtual Technician
- Endotherms/Exotherms
- Zero Reflux
- Gas Flow
- Low Phi containers

Plus

- Additional Larger Calorimeters
- Options for Battery Applications

In use the sample is contained in a holder often a metal ARC Bomb, a sphere 2.5cm in diameter of Titanium or Hastelloy C. The sample mass is typically 2-8g but the amount of sample used depends upon the expected energy release and type of sample container used. The bomb is attached to the lid section on the calorimeter assembly by a pressure fitting and a line leads to the pressure transducer. A thermocouple is attached to the outer surface of the bomb. The lid section of the calorimeter rests on the base section. The calorimeter has three separate controlled zones. The top (lid section) contains two heaters and a thermocouple, the side zone contains four heaters and a thermocouple and the bottom zone in the calorimeter base contains two heaters and a thermocouple. After set up and connection, the calorimeter is sealed inside an explosion proof containment vessel. Test set up is simple; the hardware is ready to go. Experimental conditions are entered into the controller, a current specification workstation, this takes only 2 or 3 minutes then the test can be commenced. There are few test conditions that have to be specified – a Start Temperature and an End Temperature, plus the 'Heat Steps' (usually 3°C or 5°C), the 'Wait Time' (typically 10-30 minutes) and 'Detection Sensitivity' (usually 0.01°C/min or 0.02°C/min).

The system will at first 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 its 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 at all times in a quasi-adiabatic mode; the calorimeter temperature tracks the sample temperature. This Wait period is followed by the Seek period. Again during this period (typically 20 minutes) no heat is provided by the radiant heater, and any temperature drift, upwards or downwards, is recorded.

If there is no upward temperature drift, the unit will implement a Heat step. This **Heat-Wait-Seek** procedure is the normal mode of operation of the ARC. It will continue 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 the Exotherm mode.

The system will then apply heat to the calorimeter jacket to keep its temperature the same as the bomb/sample – i.e. the calorimeter tracks the exothermic temperature rise adiabatically.

This adiabatic control and the ability to maintain the calorimeter to hundredths of a degree similar to the bomb is the key feature of the ARC. The system continues in the Exotherm mode until the rate of self-heating reduces and becomes less than the chosen sensitivity. At this stage the Heat-Wait-Seek procedure will resume. When the End Temperature is reached (or an End Pressure is reached) the test automatically stops. Rapid cooling, by compressed air, will begin. The aim of the ARC is to complete the test to get a full time, temperature, and pressure profile of the exothermic reaction in a safe and controlled manner, typically within a time period of 24 hours.

ESARC

THT ARC Hallmarks...

Continuity

Enhancement

Expansion

Safe in Use

- 1 Cubic Metre Containment Vessel
- 3mm Reinforced Steel
- Door Interlock
- Proximity Switch
- Software Shut Down Facilities
- Fume Extraction Automated
- All Explosions Contained
- Rugged and Robust Construction

Ease of Use

- 10 Minute Set Up
- Intuitive Labview Software
- Large Working Volume

Versatile in Use

- Any Sample Type
- Many Sample Holders
- Exotherms, Endotherms
- Isothermal, Isoperibolic
- Gas Atmosphere, Vacuum

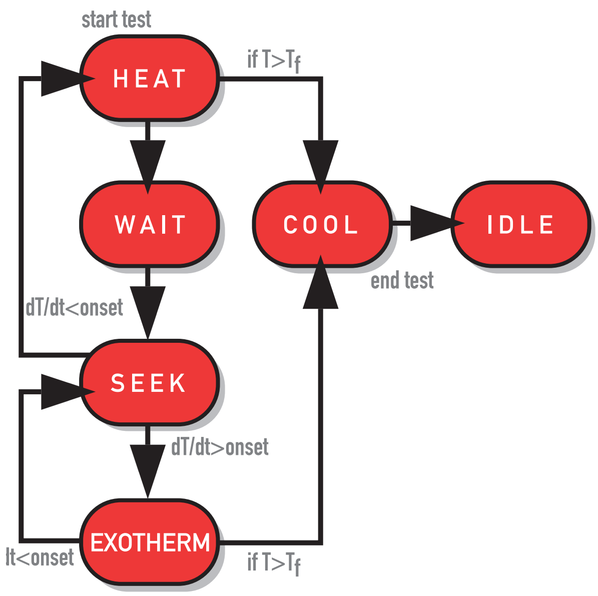
Real Time Operations Software
Set Up, Control and On-the-Fly Changing

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 and then the test conditions. Most are 'default values', minimizing data entry. Click Start Test and the test will commence. At any time conditions may be changed (on-the-fly); at any time the Mode may be manually changed. Data is immediately seen on the screen in all graphical and tabular forms. There is a Messages file that records all appropriate test information. The software allows start delay, and the set up of any number of tests to start at the click of a button. The control workstation can be made dormant and the control switched to any allowed PC anywhere in the world. The current data can be broadcast to any number of networked computers. The data is in column and row format. After the test, the shut down is similarly simple, cooling and fume extraction will come on automatically. The ESARC has latest user-friendly real time software.

ARC Operation – has never been so easy and elegant

Operation of the ARC

Heat Wait Seek Operation; Adiabatic Control



The logic of Heat-Wait-Seek operation is shown, at all stages the system controls adiabatically.

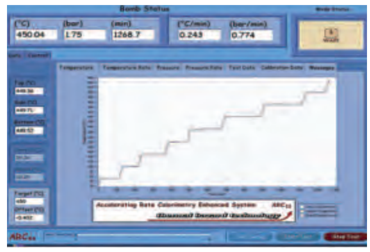
With conditions of NO HEAT LOSS or gain, the data from an exotherm reaction is 'WORST CASE' DATA. In this way the ARC gives a SIMULATION of what can happen.

This worst case data may then be extrapolated reliably to any industrial or commercial larger scale.

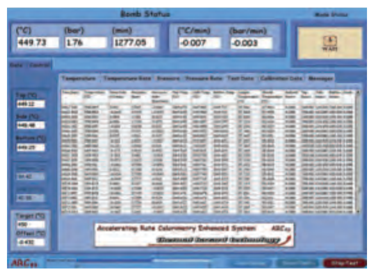
As there is no heat loss, the data can be used in any simulation, to determine the possibility of what can happen for any heat loss scenario.

The three Screen illustrations show the Real Time Software of the ESARC. There are two main 'Tabs'. The top illustration shows the Control Tab; here the 'virtual instrument' is displayed. All temperatures and pressure are shown, there are heater lights that flash and all useful experimental information is given. From here conditions can be changed during the test. The Data Tab, lower two illustrations, has several 'sub-Tabs'. Shown here are the Temp-Time display and the Tabulated Data display. Here the data can be inspected during the test.

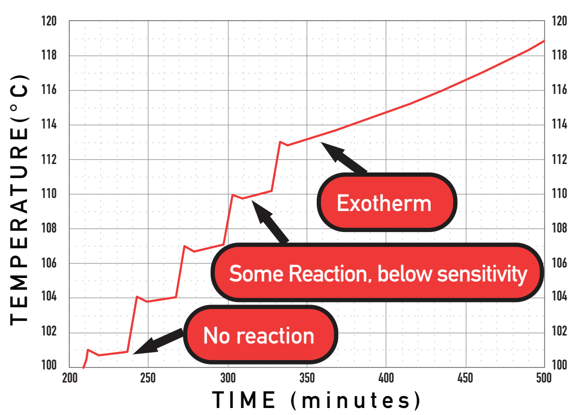
As the test proceeds The Control Tab shows the Test Status and all test information – with options for manual modifications etc.



As the test proceeds all data can be viewed. Note the 'Sub Tabs'…for Temp Rate, Pressure, Tabulated Data, Messages etc.



As the test proceeds typically exothermic reaction commences. This is shown in the annotated illustration. At low temperatures there is no reaction, the temperature in the Seek period is constant, i.e. no reaction. When reaction commences there is indication of temperature increase in the Seek period; initially the rate of self-heating, as indicated, will be below the onset Sensitivity. At a higher temperature, when the self-heating is faster than the sensitivity, the ARC switches automatically to Exotherm mode.

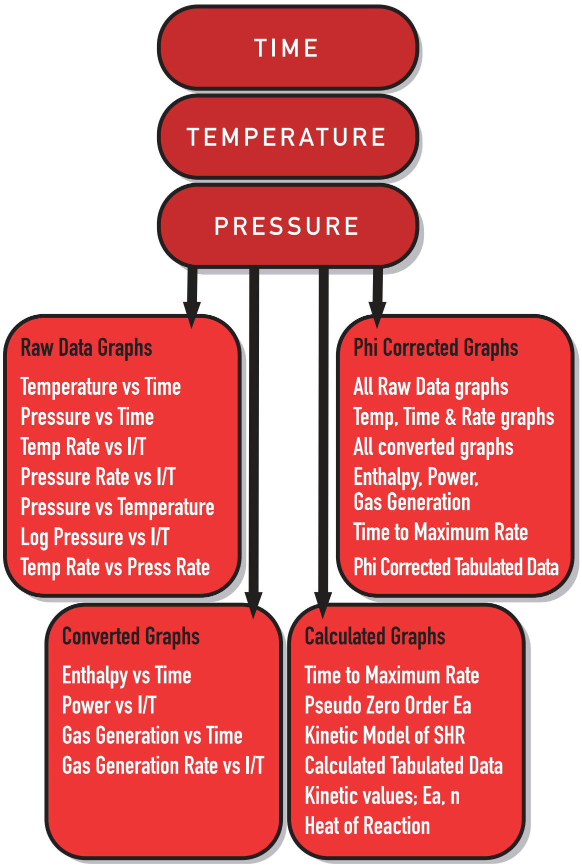


Operation of the ARC

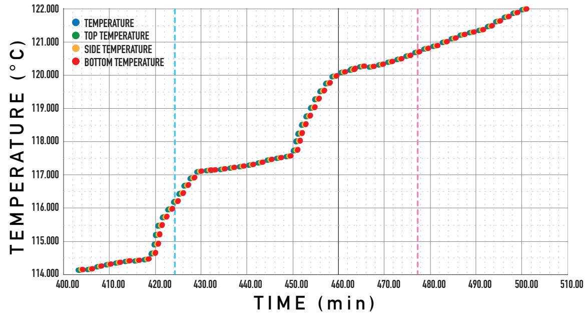
During the test, Time, Temperature, Pressure Data is stored... together with the 14 further columns of data (e.g. calorimeter jacket temperature, mode, heater power)

As an exothermic reaction proceeds the sample temperature increases, the bomb thermocouple senses a temperature higher than that of the calorimeter. The signals are fed-back and when the calorimeter temperatures are found to be low, heat is supplied to the calorimeter heaters. The calorimeter follows the bomb/sample adiabatically; tracking is to 0.01°C – an adiabaticity higher than in any other technology, making the ESARC the benchmark safety calorimeter.

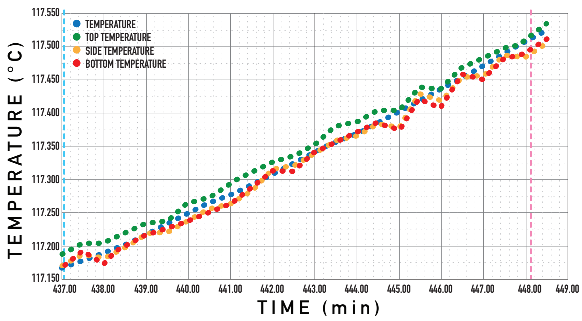
The data is Time, Temperature and Pressure, but from this many potential data analyses are possible. From one ARC test the information is very extensive as listed below; Raw data, Converted data, Phi Corrected data, Calculated data (Time to Explosion), Thermokinetic data; Applied data.



Detection of Exotherm



Tracking of Exotherm



One ARC test will answer many questions...

The questions

- Is there a thermal hazard?
- At what temperature does it begin?
- How many processes;
- Simple or complex mechanism?
- Is there an effect of impurity or additive?
- How fast does it occur? (The kinetics).
- How big an event is it? (The thermodynamics).
- At what temperature will all control be lost?
- What time is there before explosion?
- How much pressure develops?
- At what rate does pressure increase?

The conclusions

- How to control the process.
- How to regain control if this is lost.
- How much time is there for corrective action?
- How much time is there for evacuation?
- Which temperature should alarms be set.
- What is the Temperature of No Return.
- What is the Time to Explosion.
- What is the critical radius of storage vessel.
- Evaluation of catalyst, inhibitor, accelerator, impurity.
- Determination of reaction kinetics and thermodynamics.
- Information for relief vent sizing.

Data; Standard Sample 20% DTBP

DTBP, di-tertiary butyl peroxide, 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 characterized. The sample is diluted with toluene to a concentration of 20%. Standard conditions are employed, e.g. 6 grams mass. The result can be simply analysed – there are two files to consider; the real time data file (*.dat) that contains all data and the exotherm only data file (*.exo). Typically real time datasets are used to consider instrument performance, exotherm files are used for analysis.

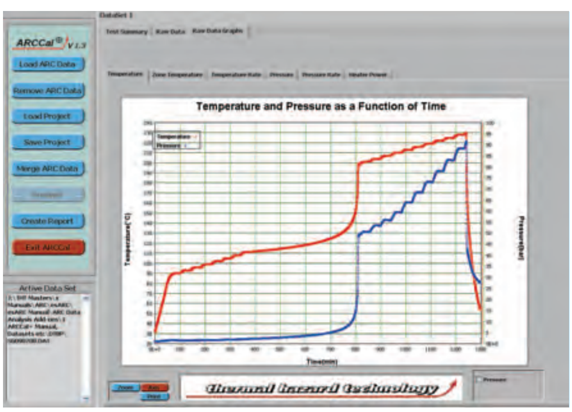
All further analysis is carried out with the exotherm data file. The illustrations below are 'screen shots' from a test and illustrate the software features.

The data shows the course of the experiment with time. The data both before and after the exothermic reaction can be seen. At low temperature, 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 below the exotherm (and above) any indication of a leak can be observed – or it may be that there is pressure generated from a non-exothermic process.

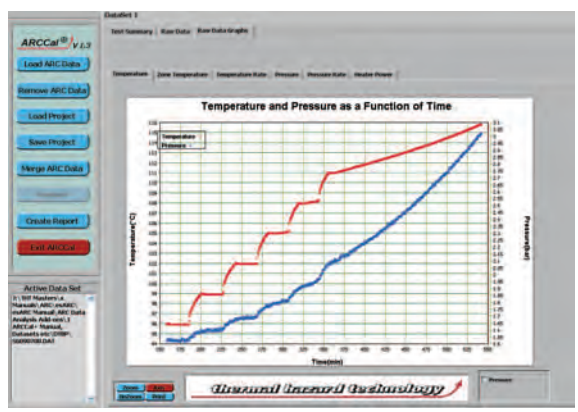
Real Time Data

Data Analysis software is based upon National Instruments Labview™. The four graphs illustrate temperature and pressure data plot against time, with calorimeter zone temperatures. This is the information that illustrates the test completely and shows the quality of the data and performance of the instrument.

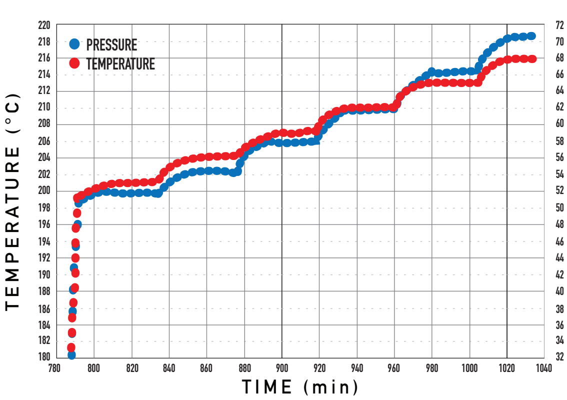
The Complete Data Illustrated



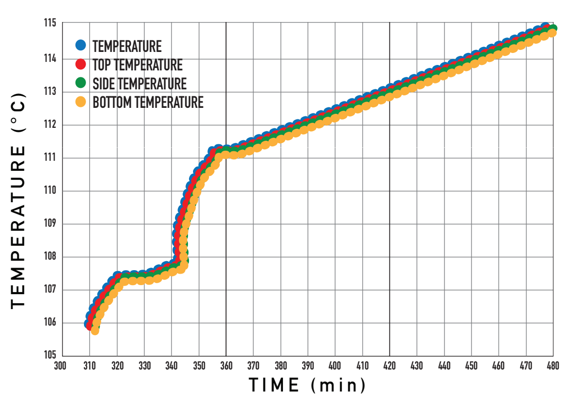
Zoomed to show 'Onset' of Exotherm



Zoomed to show Data After Exotherm



Tracking of Exotherm



Data; Standard Sample 20% DTBP

Exotherm Data

Analysis of Exotherm data can generate many graphs. Data is also available in Tabular form and there is the possibility to merge data sets. Results of all analyses can then be written to a Report; this may be Microsoft Word, Excel or html format.

Raw Data Graphs

These are Temperature and Pressure, Self-Heat Rate, Pressure Rate Graphs: The self-heat rate and pressure graphs are those most used for analysis; they show all features illustrated on other raw data graphs and much more, e.g. onset of reaction, rate at any temperature, its magnitude and complexity, single or multiple reactions, autocatalysis, maximum rate. By knowing the rate at any temperature first knowledge is obtained on cooling requirements, by knowing pressure rise the potential for explosion can be realised.

Converted Graphs

Conversion of the measured units to Enthalpy, Power, Gas generation allow the reaction to be assessed in units that are well known and have more specific relevance.

Calculated Graphs

Time to Maximum Rate is a key graph obtained from the ARC test; this indicates time available prior to explosion and from this graph, phi corrected, and with knowledge of heat loss from the container or vessel, maximum safe temperate or vessel size can be determined. From this graph the SADT can be determined and Temperature of No Return values calculated. Kinetic Model graphs and associated tabular data can be calculated when the data obeys classical kinetics. This allows Activation Energy, Order of Reaction, Heat of Reaction to be obtained with a graph that indicates the quality of the kinetic fit and thus the reliability of the result.

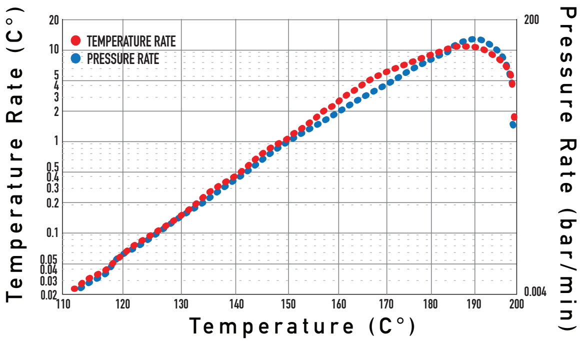
Phi (Φ) Corrected Graphs

When kinetic modelling is achieved, the model is used to perform phi correction. Φ corrected graphs are available for all raw data graphs and all converted graphs. The Φ corrected result can be plotted on the same graph as the raw data illustrating the effect of heat loss into the Bomb during the ARC test.

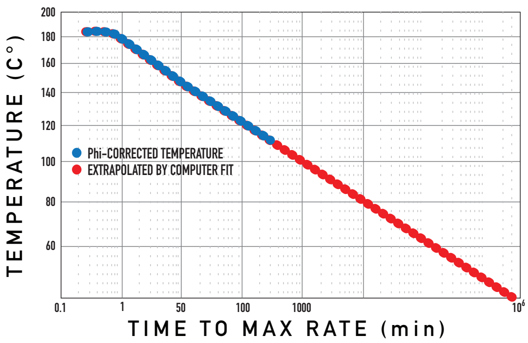
Merged Data Graphs

ARCCal+ the data analysis software from THT, will allow up to 9 data sets to be opened in any one application; from all of these 3 separate analyses are possible. It is then possible to select any or all of the data sets to be merged and carry out such merging 3 times to produce 3 separate merge data sets. Subsequent to this the work can be saved as a Project or Reports may be generated incorporating any number of the open datasets.

Raw Data; Temperature and Pressure Rate



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, the phi correction. A key advantage of the ARC is the ability to test a much wider range of sample types than other calorimeters.

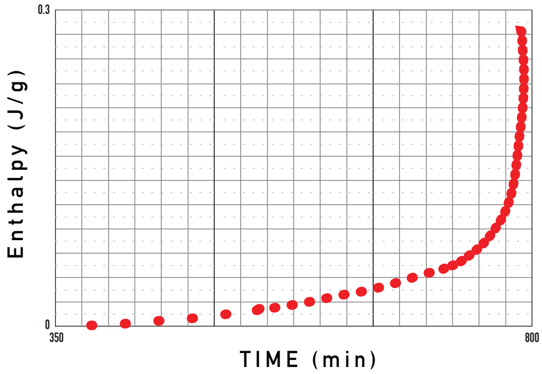
$$\Phi = 1 + (m_b\, Cp_b \,/\, m_s\, Cp_s)$$

Tests may be carried out with low energy samples in large volume containers, 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.

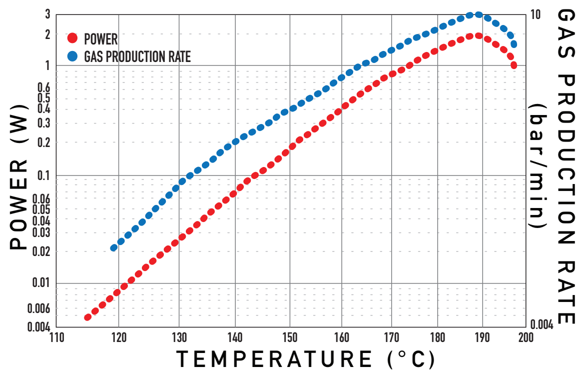
The ability of the ARC to test such a wide range of Φ values make it unique and gives the technology unrivalled flexibility and versatility.

Two Converted Data Graphs

Enthalpy as a Function of Time

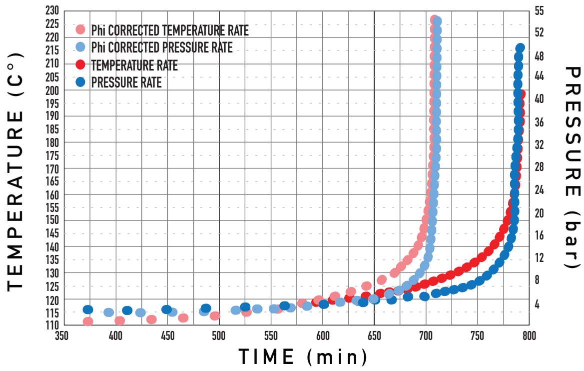


Power & Gas Production Rate as a Function of Temperature

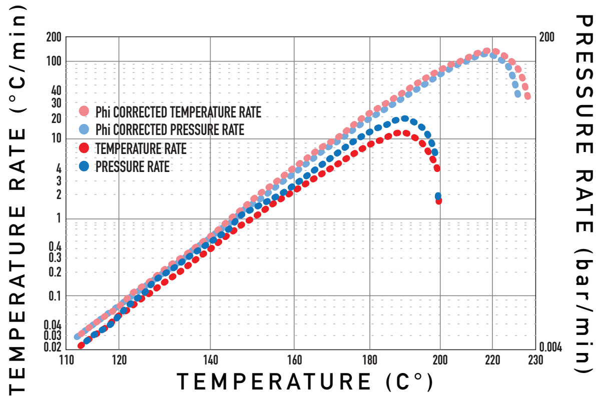


Two Φ Corrected Data Graphs

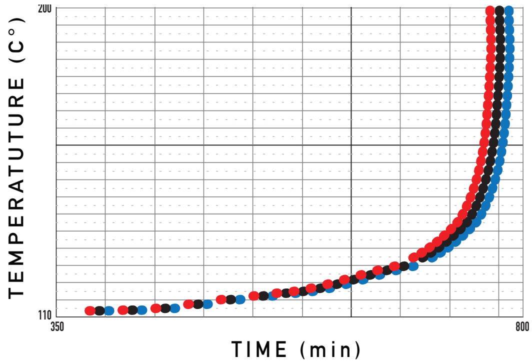
Phi corrected Temperature and Pressure

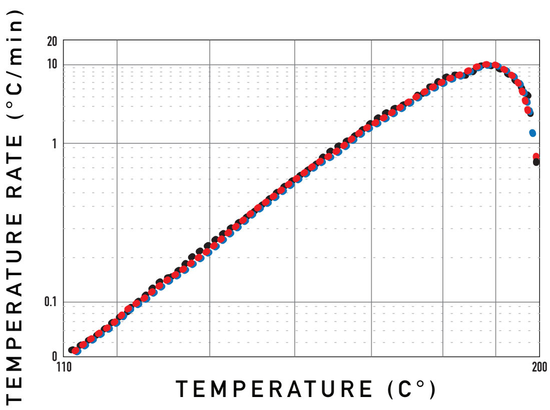


Phi corrected Temperature Rate and Pressure Rate



Two Merged Data Graphs (3 data sets)





Applications of the ARC

ORGANIC CHEMICALS

FINE CHEMICALS

PHARMACEUTICALS

BLEACHES MONOMERS

HIGH EXPLOSIVES, PROPELLANTS, PYROTECHNICS

BATTERIES

RESINS

PEROXIDES

DETERGENTS

DYESTUFFS

FERTILIZERS

BULK CHEMICALS

ADDITIVES

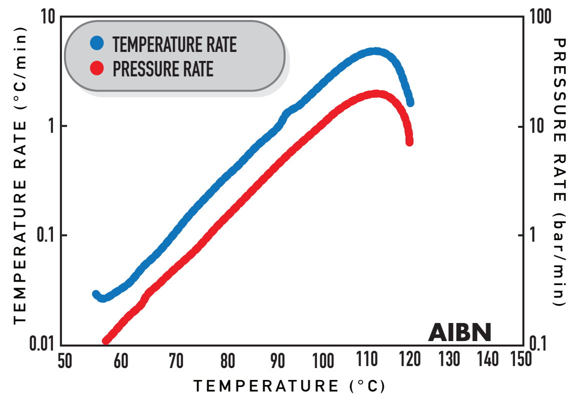
INTERMEDIATES

OIL (SHALE, CRUDE)

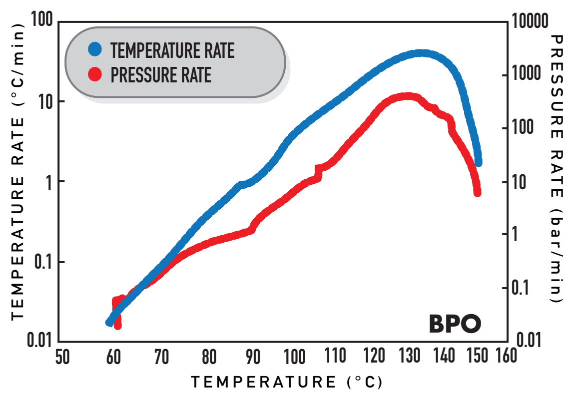
Reactive Chemicals

Peroxides, azo dyes, nitro compounds and others with reactive groups, plus intermediates and additives that contain potentially more than 2 or 3 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.

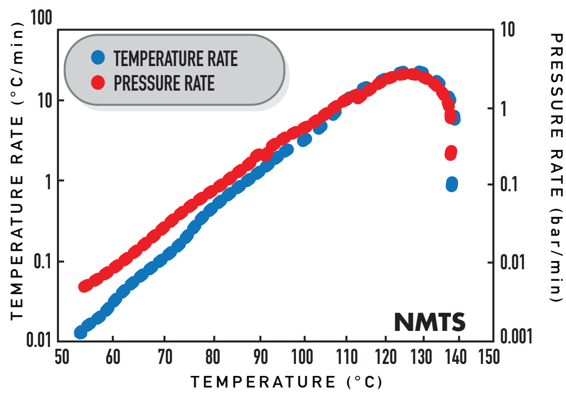
Temperature Rate and Pressure Rate as a Function of Temperature



Temperature Rate and Pressure Rate as a Function of Temperature



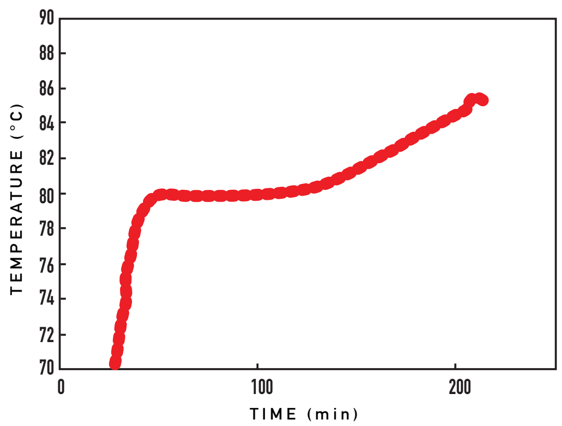
Temperature Rate and Pressure Rate as a Function of Temperature



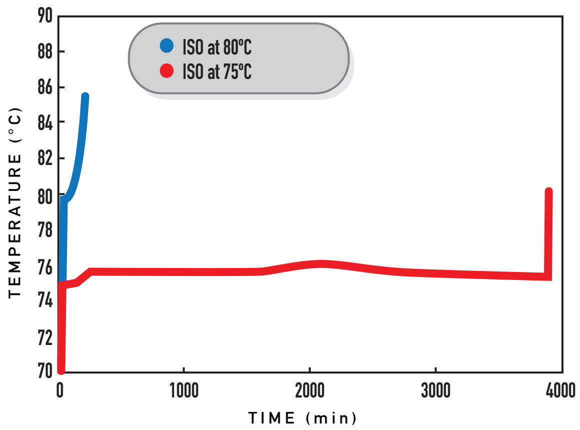
Monomers

Polymerisation reactions can be studied in the ARC. In this application area, the reaction is controlled by using inhibitors, accelerators and other additives. This is an area of application where isothermal testing is often employed. 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, at 80°C the reaction occurred after 2 hours.

Temperature as a Function of Time



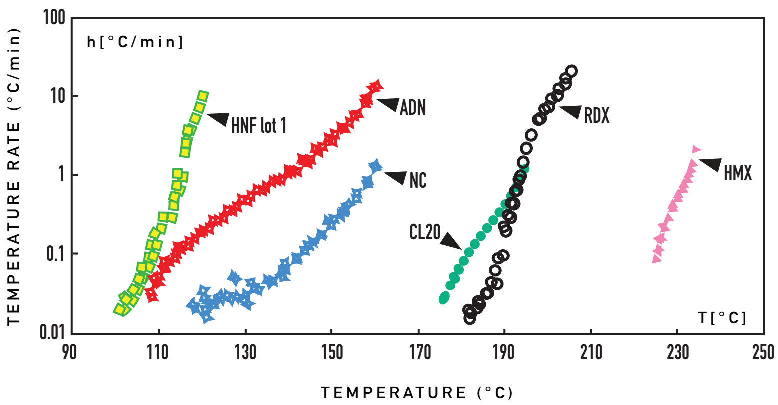
Temperature as a Function of Time



Explosives

Stability, onset of reaction, batch-to-batch variation, compatibility, ageing, all areas of interest in Civilian and Military explosives. This is an application area 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.

Adiabatic Self Heating of Some Energetic Substances



Applications of the ARC

In the variety of sample types that can be tested, the versatility of the ARC is unrivalled. The ARC is uniquely able to assess the Chemical Reactivity and Runaway potential of materials from low to high energies. Sample may be tested in the solid form, liquid form or slurries, pastes and mixtures – from sub gram to above 100 gram samples. Reaction of gas to liquids and solids and testing at high pressures, testing with a flow of gas is possible, with stirring and with dosing, measuring pressure as well as temperature.

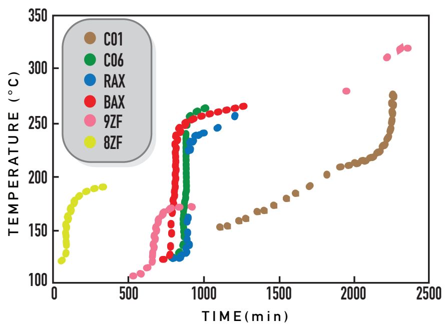
Intermediate Selection

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 effect 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.

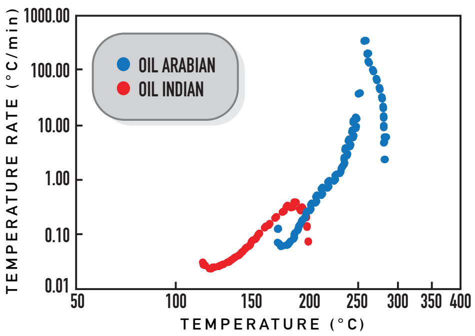
Oil (Oxidation)

The characteristics of oil samples are important, particularly when Enhanced Oilfield Recovery techniques are being used such as 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 oils and their interactions.

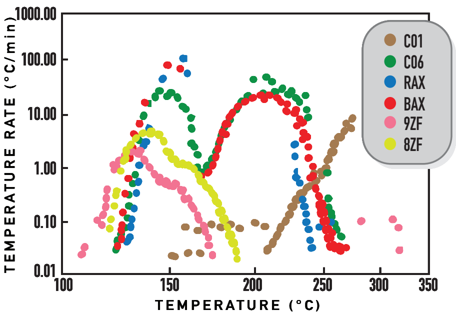
Temperature as a Function of Time



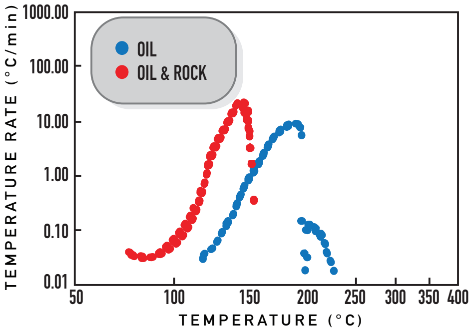
Temperature Rate as a Function of Temperature



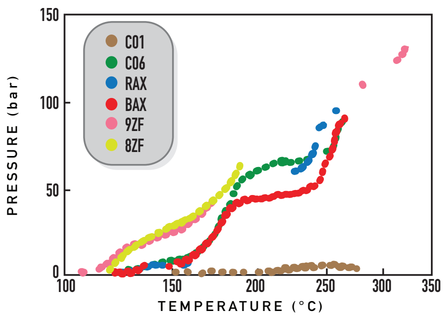
Temperature Rate as a Function of Temperature



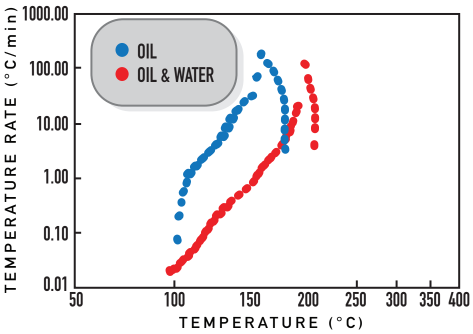
Temperature Rate as a Function of Temperature



Pressure as a Function of Temperature

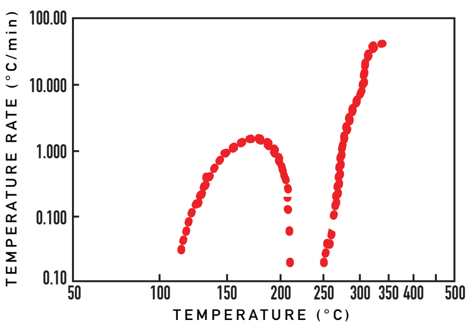


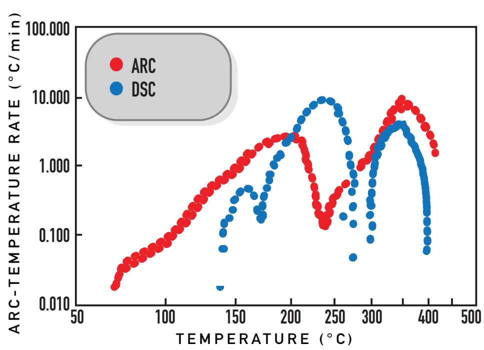
Temperature Rate as a Function of Temperature

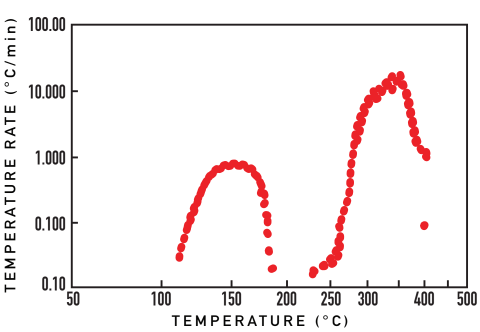


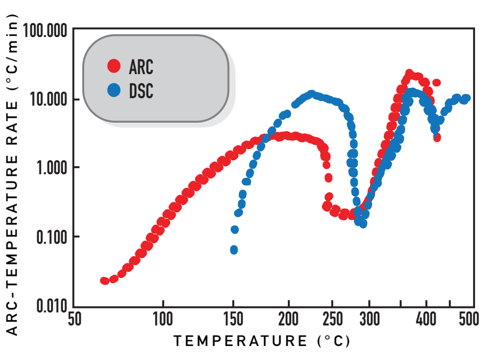
Epoxy Resins – and Comparison with DSC Data

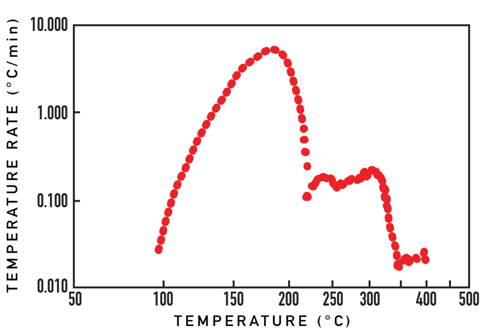
Epoxy resins are used universally and manufactured in bulk by many well known name companies: Ciba, Cytec, Hexcel, Shell. The results from 6 commercially available resins are shown, three have DSC data superimposed. All show a curing reaction followed by a decomposition. The ARC results illustrate the 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.

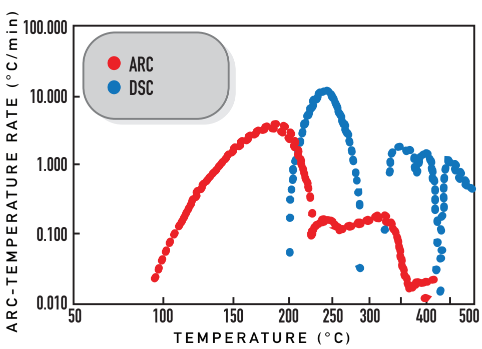












Options for the ARC

For the first 15 years the ARC saw little development and few options added. THT however has worked with a variety of users to develop Options and Kits to extend the use of the ARC and make it more flexible and versatile.

Options may be passive or active. Active options are under Workstation control.

Kits are simpler, they are hardware add-ons that have particular use and relevance in specific areas of application. Some options are detailed here.

Low Phi and Fast Tracking

The most simple addition to increase application of the ARC was the development of alternative sample containers. THT have designed and produced a range of 65ml lightweight test cells. These are manufactured from 316-Stainless Steel and provide users with several testing options. These containers are often used with the 'Burst Disk Assembly' designed to relieve pressure and discharge to an in-built catch pot in the event of rapid pressurisation.

To extend the maximum rate of adiabatic tracking, THT introduced the 'Fast Tracking Calorimeter with an ability to follow exotherms to 150°C/min. The Fast Tracking Calorimeter looks identical to the standard Dow Patent design, but consists of thinner wall construction and fast acting heaters. It is most important in any adiabatic safety calorimeter to be able to test over a range of phi values. Standard ARC bombs are applicable for the vast majority of tests; for solids, for high energy samples phi is 1.2 or above. Lower phi values are useful for vent sizing or low energy samples. Phi is 1.05 or above. The ARC has the ability to test all sample types, many other adiabatic calorimeters do not. It also must be realised that the most important data is obtained near the onset where there is possibility for remedial action.

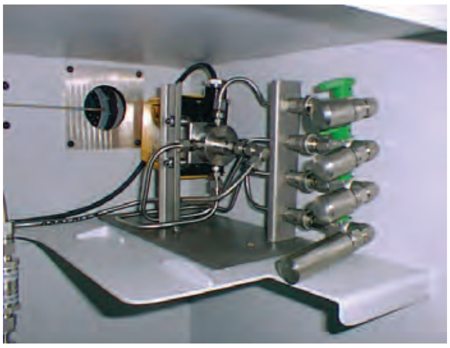
Cryogenic Operation

With more processes being developed utilizing sub-zero operating temperatures there has been a need for low temperature testing. The CSU Option is a passive unit that attaches directly on to the ARC.

The CSU option reduces the temperature of the containment vessel and calorimeter and sample to -40°C allowing testing from this temperature. This is a unique option to the THT ARC.

Gas Collection and Safe Gas Release

THT have developed several options. These range from a simple manual gas release system (SSM) through to a system allowing 4 samples to be automatically taken during the course of the test (SSU). An intermediate system (SSS), where the gas is released and automatically collected at the end of the test is offered. For collection a variety of vessels are available; for safe release the supplied scrubber tank may be filled with appropriate neutralising material.



Dosing

THT offer two options to enable dosing; The Manual Dosing Unit (MDU) achieves addition by manual dosing at ambient pressure with a glass syringe at the start of the test. This passive unit can be viewed as a low cost experimental option. The computer-controlled Automated Dosing Unit (ADU) is fully controlled to enable dosing at any time during the test. Dosing can be made at elevated pressure. A stainless steel high pressure syringe and specific dosing sample containers are used.

Stirring and Agitation

Stirring is important for reaction mixtures and non-homogeneous materials. In some applications it is necessary to test such samples within a stirred environment. This is typically the realm of a reaction calorimeter, rather than a adiabatic calorimeter. But for those customers who have this requirement THT offer the ASU option. Stirring is continuous mixing in one direction; agitation has varied direction stirring.

Vent Sizing

THT offer manual and automated options to allow closed vessel tests, tempering and hydrodynamic tests. Such tests typically require additional options; stirring, low phi and the fast track calorimeter may be needed.

These are options to further extend the versatility of ARC testing.

High Pressure Flow Option

For in-situ combustion applications, a high pressure/low flow rate gas supply is often required to simulate oil reservoir conditions. To meet this requirement, THT have developed the High Pressure Flow Option, providing accurate thermal and pressure measurement as well as controlled flue gas analysis capability.

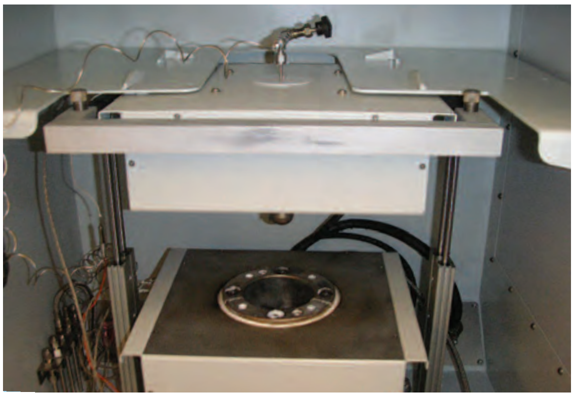
Fume Extraction

The esARC has in-built capability for fume extraction. A fan in the ceiling of the containment vessel operates automatically in conjunction with the test conditions and software. However in some application areas there may be need for significant additional extraction. This may be the case when specific materials are to be tested within the Pharmaceutical Industry.

The Fume Hood Unit (FHU) incorporates a very high speed extraction fan and additional door cover to give a gas extraction rate in excess of Fume Cupboards. This is an option to further enhance safe operations.

Automated Lid Lifting

The calorimeter lid can be raised and lowered automatically with the Pneumatic Rising Unit (PRU). This has been made available for users for whom lifting of the calorimeter lid can be difficult.This is an option to further enhance ease of use.



Kits

Kits have been developed by THT to facilitate specific testing in the ARC where hardware modifications are appropriate. These include **Explosive Test Kit** (containing low volume sample holders, high volume feed through tube, burst disk assembly), **Side Branch Kit** (containing alternative pressure feed-through tubes and a Burst Disk Assembly; this prohibits any 'reflux' of sample or solvent and avoids need for any 'tube heater'), and **Low Phi Kit** (containing low phi containers, special feed through tubes and burst disk assembly).

ARC Testing of Lithium Batteries

Safety of Lithium Batteries is of Major Global Concern

In the past 10 years rechargeable lithium batteries have been introduced to the market, initially in specialist uses but today commonly applied. Lithium batteries have excellent use characteristics, including the highest charge density. However the chemistry (initially involving lithium ions being intercalated on carbon based anodes, delithiated spinel cathodes and flammable electrolytes), led to instability and potential for flammable disintegration. There have been many reports of notebooks and phones catching fire. Batteries may be affected by heat and also will produce heat upon discharge. Huge effort has been put in to development of safer chemistries as well as improved performance. In smaller batteries relative heat loss capacity is good – but as the battery gets larger (or is used as a pack) the battery becomes more adiabatic. Today there is the aim to 'scale up', to incorporate lithium batteries into power tools, planes, cars and buses. In addition newer applications are more demanding, power tools and vehicles require fast discharge – producing more heat output. There is the need for safe batteries – and the ARC is the calorimeter of choice for this application.

There are 5 Categories of Application of ARC to Lithium Batteries

- Battery components testing and development of new battery chemistries
- Complete batteries and packs for safety studies
- Battery heat output under use and abuse conditions
- Battery heat output under normal conditions for heat output, efficiency and lifecycle studies
- Battery performance and the temperature distribution over the surface of the battery

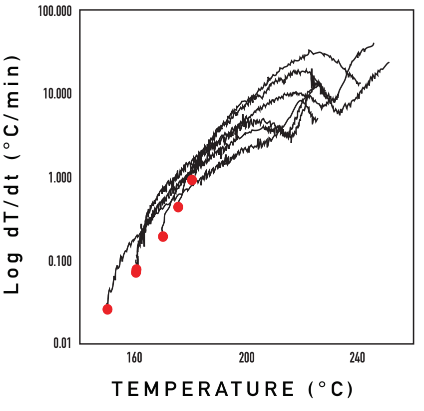
Battery Components

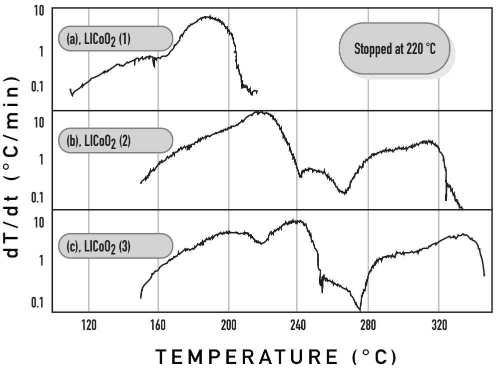
Many groups, mainly in academic environments, are using the ARC to study battery materials either separately or in combination. The aim is to develop new battery chemistries and configurations.

An experienced group is in Dalhousie University, Nova Scotia; headed by Professor Jeff Dahn. The data shown below is from his laboratory and reproduced with his permission.

Battery material testing has been carried out on anode and cathode materials, electrolytes and their mixtures. Testing has been performed on battery component material after battery charging, it is then removed giving complex products.

Family of Battery Components





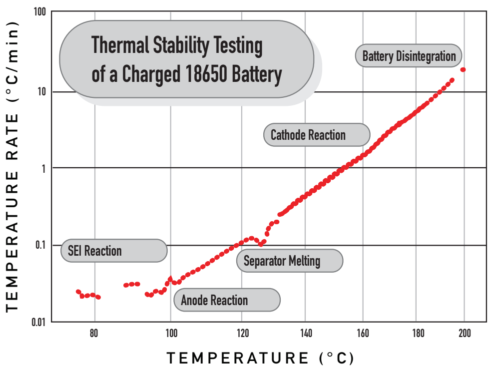
ARC data is complex. Typically several reactions occur that overlap.

The application of the ARC in the field of lithium batteries is wide. Only an overview is given here. Contact THT for a separate detailed Brochure: ARC-Battery Applications.

Safety Testing of Batteries

The ARC calorimeter can accommodate smaller batteries; coin cell, AA, 4/5A, 18650, 26650, prismatics and lithium polymer pouch batteries. A big advantage of any battery is that it may be tested in an open environment. As the battery has its own case, this reduces phi to one. The battery can be positioned within the calorimeter in several ways. Data from an 18650 battery is illustrated.

Temperature Rate as a Function of Temperature



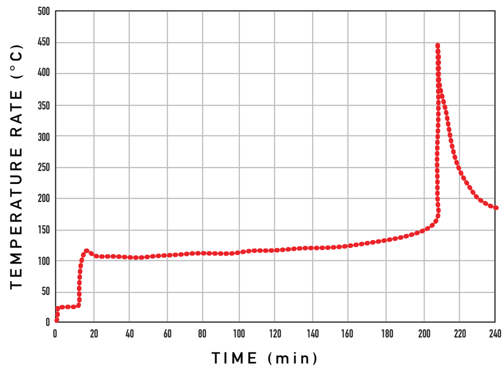
With batteries, the simplest test is 'effect of heat upon the battery', but it is also possible to connect cables to the battery for 2 or 4 wire measurement, e.g. of voltage during test. Batteries can be tested at any State of Charge or at any age to determine variation in stability. Aside from onset the ARC test will determine self heating at all temperatures – and thus gives much more information than 'Hot Box' and other empirical tests. The final potential of the battery to remain intact or disintegrate is important. Ejection of battery components will be associated with fire as the lithium reacts with air.

Internal pressure can be measured during temperature increase and exothermic reaction. The battery can be held in a pressure tight chamber inside the calorimeter. The pressure rise when the battery vents can be recorded and the gas released can be later analysed. Batteries develop significant pressure and therefore care must be taken in carrying out pressure contained tests.

Testing of Batteries under Abuse Conditions

The ARC is ideal for testing heat effects associated with battery abuse. Such tests are rapid and commence typically near ambient temperature. Simply by connecting the battery to cables, external shorting tests can be carried out. The battery temperature is likely to rise 100°C – the battery then may or may not further react and disintegrate. In addition with the battery connected to a power supply the effect of overvoltage charging or discharging can be determined. Other tests include nail penetration, crush, even tests to simulate water immersion have been attempted. These tests allow a quantitative determination of heat release from internal short. Such tests can be implemented with the THT BSU Option.

Temperature as a Function of Time

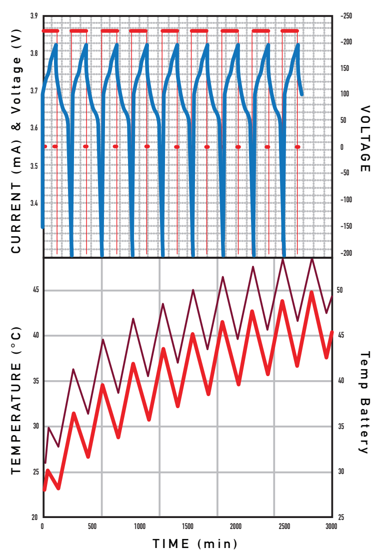


Testing of Batteries under Use Conditions

Testing of batteries under use conditions requires connection to a battery cycler. The battery can be connected to leads to allow 2 or 4 wire measurement. To facilitate this THT offer a range of single channel cyclers that integrate with the ARC software to allow control by the ARC and a synchronised single data set to be obtained.

This allows voltage and current measure-ments during charging, discharging, cycling and shorting and other abuse tests to be carried out in-situ within the ARC.

The tests may be carried out at various discharge/charge rates to measure heat release under these conditions. Continual cycling (or testing with batteries that have been subject to multiple cycles externally) will allow information on lifecycle and efficiency to be determined.



THT's Battery Options (BSU and KSU) allow computer controlled use and abuse tests.

The EVARC, Double & Triple Systems

The EVARC is unique to THT and has a calorimeter 25cm in diameter and 50cm deep. This has been designed to accommodate larger batteries and battery packs as may be used in Electric Vehicles, Satellites and other similar applications. The EVARC can do all that the standard ARC can do – but with bigger batteries. The EVARC can accommodate the same THT Battery Options.

The EV calorimeter is constructed from aluminium and like the standard calorimeter contains 8 heaters built into the metal. This design enables the calorimeter to function with the same electronics (and software) as the standard ESARC. The EVARC will heat more slowly and typically in tests a longer wait time is required – to allow thermal stability. Pressure measurement is the same.

It should be realised that with large batteries there is increased risk. Typically batteries are not contained in sealed containers and therefore should a battery disintegrate with large gas release there is no likelihood of explosion. However there will be significant release of flammable material and fire. Typically tests ought not be carried out to completion with a large and energy laden battery or battery pack.

It is not normally the aim not to take such large batteries to full runaway. It must also be realised that tests will take longer since longer times must be allowed for thermal equilibration. In addition it must be realised that large batteries will equilibrate thermally more slowly and heat gradients will occur within such large samples as the self-heating rate increases.

There are limitations – but the EVARC offers potential to carry out all battery safety and cycling tests with large batteries – generating data that cannot be obtained with any other calorimeter.

The EVARC has safety features built in that are the same as those in the ESARC, including proximity switch and automated gas extraction. In addition the software features will restrict the functioning to give shut down and quench cooling to slow and stop self-heating, preventing battery disintegration.

Batteries come in all shapes and sizes and often it is necessary to test both small and large batteries. To facilitate this, the EVARC was designed to utilise all electronics and software of the ESARC. Because of this, it is possible, for modest cost to have a 'Double System' with both EV and standard calorimeters. The calorimeters are exchanged in a few moments and set up is very rapid – offering the functionality of both calorimeters and the ability to test from Coin Cells to EV Batteries.

Battery Performance, MultiPoint™ & CryoCool™

Rapid Discharge

Power packs for Electric Vehicles and power tools are

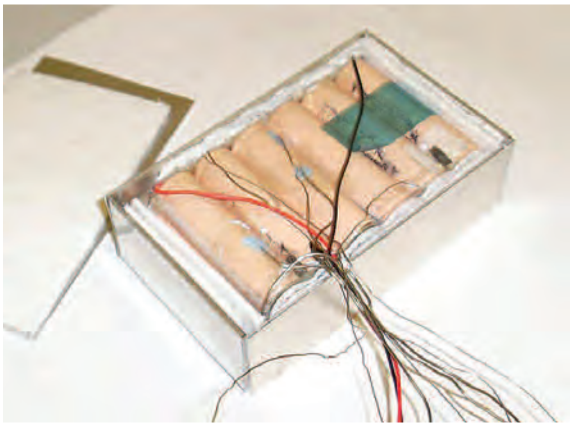
- Large or very large in size
- Designed to give fast, high power discharge

Battery chemistry is tailored to minimise heat release during multi-kW, short time discharge.

Information is needed not specifically for safety, but on the 'spatial heat release' to allow appropriate 'Thermal Management' and to determine 'Battery Performance'.

To address these needs, THT have developed a third Calorimeter, the Battery Performance Calorimeter, or BPC. This is larger than the EV Calorimeter, but is accommodated within the EV Blast Box and uses the same electronics and software of EV and ES systems.

The BPC can test very large batteries and packs in the same way as the EV or standard calorimeter.



MultiPoint™ Option

The MultiPoint option may be used with any THT ARC system, but is appropriate when rapid discharge tests are to be carried out. This option allows multiple thermocouples to be positioned on and around the battery. The temperature at all points is recorded, the ARC can be controlled from any of these. Tests are started at a chosen isothermal temperature and heat release causes temperature rise. Surface temperatures are recorded during the charge/discharge test.

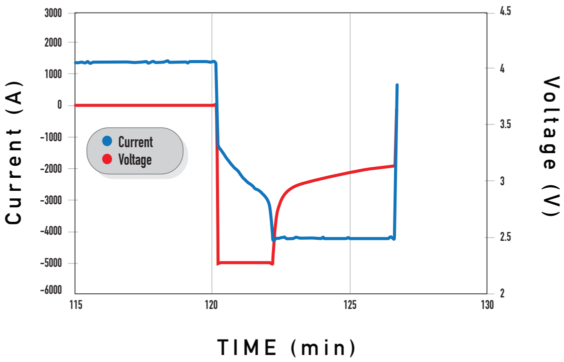
CryoCool™

Such battery performance tests are typicallly commenced at ambient environmental temperature. These may be below 0°C. To allow this, the MultiPoint option includes CryoCool. This is a simple method to reduce the calorimeter temperature with liquid nitrogen and cold nitrogen gas.

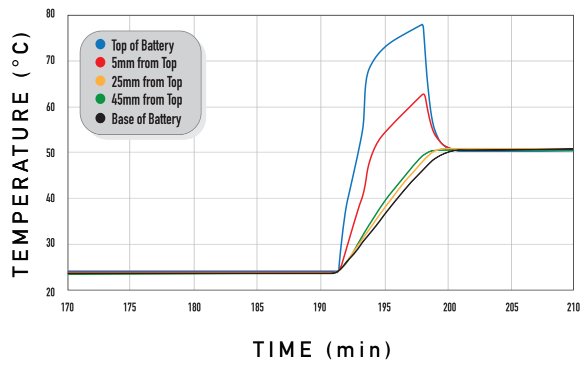
The BPS with MultiPoint may be used in conjunction with ultra-rapid discharge single channel cycler supplied either by THT or the user. The MultiPoint can be used externally from any THT calorimeter, i.e. directly in a power plant within a vehicle.

The graphical illustrations show a simple multipoint test.

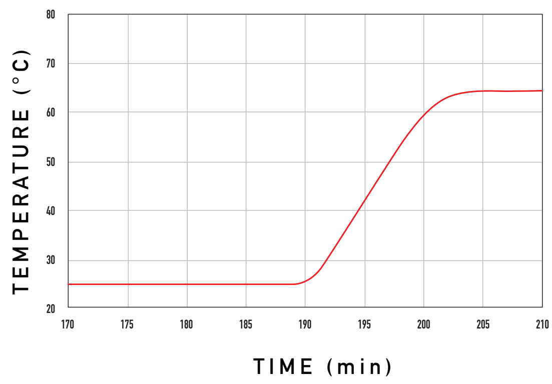
Cycler Data



Spatial Temperature of Battery



Control Temperature as a Function of Time



Support & Service

THT staff have been supporting ARC systems for an unbroken period of over 25 years! THT offer unparalleled technical knowledge and support in the area of chemical safety. THT offer an ongoing free of charge email and phone support at all times over the lifetime of the instrument.

THT's focus in this area and their worldwide reputation is unique.

Support

THT offers support for all users of ARC systems manufactured by all companies. This includes provision of Calorimeter Assemblies for CSI ARC users. This also includes parts for non-THT manufactured instruments. THT also offers a full range of spares and consumables for all instruments and a repair and service facility. First line support is undertaken from all THT Offices and qualified distributors. Such support is typically phone and email response, THT commit to provide this without cost throughout the lifetime of the instrument.

Where appropriate THT will supply upgrades either to older ARC systems or to those trading from standard to EV size. Software and electronic upgrades are available from THT irrespective of age of instrument. To aid users of original CSI systems THT maintain a small supply of pre-used modules.

Service

THT have offices and trained service & support personnel worldwide. THT offer service contracts tailored to user demand.

Consistency

THT have worked with such specialist safety calorimeters for over 25 years. Competitor products have been passed from company to company every few years!

Why the ARC? Why THT?

Why the ARC?

- World Benchmark Safety Calorimeter
- Most Widely Used and Understood Technology
- Unrivalled Sensitivity, Versatility and Flexibility

Why THT?

- Unsurpassed, Continous ARC Experience
- Unparalleled Technical Expertise and Knowlege
- Uniquely Focused in Safety Calorimetry

THT currently offer the ESARC, the EVARC and double and triple systems and upgrade instruments. THT also manufacture other instrumentation in the area of calorimetry. THT is proud to be the premier manufacturer of safety calorimeters with an enviable reputation. THT is the World leader and strives to maintain this position.

THT has a clear Mission Statement: Assisting Chemists and Engineers Working in the Area of Safety and with Hazardous and Reactive Materials.

The brochure highlights **tangible** benefits of these instruments; as important as this are **intangible** benefits; aspects that are not visible; reliability, experience, support and back up.

Tangible Benefits

- Highest Sensitivity
- Complete Specification
- Greatest Range of Applications
- Latest Hardware
- Latest Software
- Most Options
- 3 Worldwide Offices: England, USA, China

Intangible Benefits

- Lifetime Support (e-mail and phone free of charge)
- Highly Experienced Personnel
- Unrivalled Manufacturing Experience
- Largest Technical Group
- Largest Customer Base
- Worldwide Operation

Who's Who of Users - using THT ARC systems

Partial Users List:

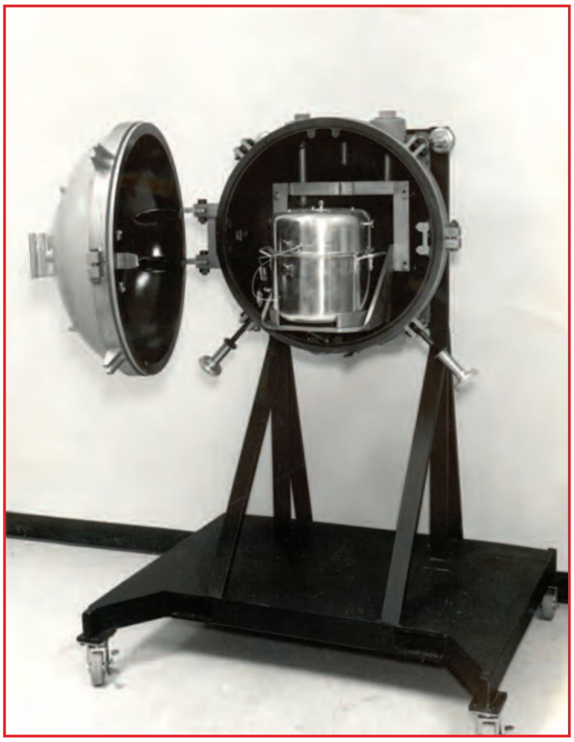
Pharmaceutical	Chemical	National Labs	Battery
GSK	Dow	NASA	Sanyo
Pfizer	Bayer	Sandia	Sony
AstraZeneca	Rhodia	HSE	Lishen
Roche	Henkel	Qinetiq	ATL
Sanofi Aventis	Rohm & Haas	ITRI	BAK
Schering Plough	Ciba	CEA	Panasonic
BMS	Sumitomo	NREL	Samsung
Amgen	Solvay	DSTL	LG

History

The ARC has been the unique adiabatic calorimeter of choice from the late 1970's to today. The ARC is used in the safety laboratory of most major Chemical and Pharmaceutical companies, many National Laboratories having responsibility for safety, the major Defence Laboratories of most developed countries and is used by the majority of Battery Manufacturers.

Several THT staff have been working in technical sales, support and development continuously for 15-25 years. THT is proud of its contribution to this area.

Past



Present

Specification

Fully compliant to the American National Standards Institute: ASTM E1981 (E27 all revisions)

Design
Calorimeter design to Dow Patents of 1980 and 1984; 2.5cm thick copper, 8 heaters.
6 measuring, control and safety thermocouples

Temperature
0-600°C temperature range (-40°C to 500°C with CSU option)

Sensitivity
0.002°C/min exotherm onset detection to 200°C; 0.01C/min to 500°C; 0.002°C/min in isothermal mode
Temperature resolution 0.001°C; precision 0.2%, accuracy 0.1°C; thermocouples external and internal of sample

Pressure
Vacuum to 200 bar pressure range (to 2000 bar with alternative transducers)
Pressure resolution 0.005bar; precision 0.02%; accuracy 0.05%

Control Modes
Adiabatic; quasi Isothermal; true isothermal; isoperibolic, ramping
Adiabatic control to 0.01°C, Ability to track exotherms; to follow endotherms

Operation
in air, vacuum, inert gas, reactive gas, flowing gas

Sample holders
ARC Bombs: Titanium, steel, Hastelloy, glass, aluminum and variants

Phi Range
from 1.05 with 65cm^3 holders; from 1.2 with ARC Bombs

Adiabatic Tracking
20°C/min Dow Patent Calorimeter; 150°C/min Fast Tracking Calorimeter

Safety
1 cubic meter containment vessel (allows options); reinforced 3mm steel; proximity switch, door interlock
Reflux Guard; side branch pressure line prohibits reflux (avoid need for tube heaters)

Networking
Worldwide access and use
Workstation with Microsoft Windows and National Instruments (NI) Labview; 19 inch flat screen monitor keyboard and mouse

Software
Data Analysis software in Labview with ability that includes

- Graphical and tabulation of raw data including Phi Corrected TMR plots
- Data Conversion to Enthalpy, Power, Gas Generation; Temperature of No Return
- Kinetic Modeling for thermodynamic and kinetic data analysis
- Phi Correction through kinetic modelling
- Report generation in Microsoft Word, Excel, html
- Analysis of 9 data sets; 3 analyses on each, 3 merge dataset

Real Time software in Labview that includes on-the-fly condition modification and full control; remote operation and data transfer.

Options
Stirring and agitation 0-500rpm with ASU Option
Dosing; Manual or Automated with MDU or ADU options
Gas collection with SSS and SSU options
Lid lifting with PRU option
Vent sizing options
Cryogenic option
Lifetime e-mail and phone support, 1 Year warranty

Contact THT for more information on options

The following are thanked for the right to use information: Professor Jeff Dahn, Dr Manfred Bohn, Professor Malcolm Greaves

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thermal hazard technology

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