NETZSCH

Adiabatic & Reaction Calorimetry

Advanced Solution For Chemical Process Safety, Energetic Material, and Battery Development

Leading Thermal Analysis ∎

Best-in-Class Adiabatic Calorimetry

Adiabatic Calorimetry – A Key Tool to Understand Thermal Runaway

Adiabatic calorimetry has been the cornerstone of chemical process safety for the last 30 years. More recently, adiabatic calorimetry has been widely used in measuring the potential of thermal runaway of Li-ion cells. These cases are similar in that they require measuring both the amount of heat released (thermodynamics) and the rate at which the heat is released (kinetics). In both cases there can be a significant increase in the sample pressure and the combination of the temperature and pressure rise can lead to an explosion. Therefore adiabatic calorimeters are generally designed to be much more robust than many of other types of calorimeters.

ARC® 244

APTAC® 264

When looking at a thermal runaway, whether it is within a battery cell or part of a chemical process in a plant, the reaction produces heat which increases the temperature of the reaction and further increases the rate. There can come a point when the rate of heat release from the reaction exceeds the rate at which the heat can be lost to the surrounding environment- the point at which thermal runaway inevitable. Obviously the worst case is when there is little or no ability for the heat to be lost to the environment. Any heat, even small amounts of heat, cause the temperature to rise and accelerates the reaction producing even more heat. This is the adiabatic condition and it is this precise condition that adiabatic calorimeters can safely measure in the small scale. It is this same condition that can be found inside large processing vessels as well as inside a Li-ion pack running inside a laptop computer.

NETZSCH has taken adiabatic calorimetry to new levels. The instruments described herein are the best in their class. Building continuously on the original system developed by Dow in the late 1970's and commercialized by Columbia Scientific Industries and then ADL/TIAX (acquired by NETZSCH in 2009), NETZSCH continues its heritage of

taking the best technology and making it better. With the patented *VariPhi™* system, not only can adiabatic test be done more accurately but it also opens up new areas of calorimetry not possible with the original ARC® units. The systems have been enhanced to do more and answer more questions.
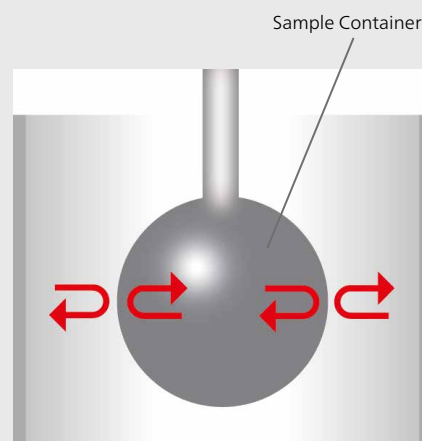
ARC® 254

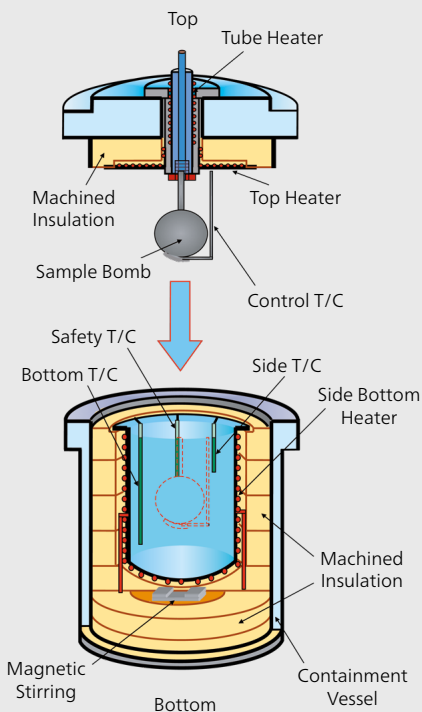# Understanding Adiabatic Reaction Calorimetry

Method

The energy release from chemical reactions (decomposition etc.) is a point of focus in chemical research, battery research and other industries. When energy is generated by a thermally induced chemical reaction and the heat transfer to the outside is smaller than the generated amount, runaway reactions can occur. In the worst case this can cause catastrophic effects (explosions). Adiabatic calorimeters are ideal tools for analyzing such questions as they simulate the worst case scenario with no heat exchange with the surroundings.

For decades accelerating rate calorimeters have been widely used by researchers in this field, offering the capability to measure temperatures, enthalpy changes and pressure changes quantitatively.

The use of adiabatic systems has the advantage that no heat loss is allowed from the sample; the behavior in real large scale chemical reactors can therefore be simulated (worst case scenario).

Sample Container

Adiabatic System: No heat in – no heat out

Technique

A sample (several grams) is placed in a spherical vessel. The vessel is surrounded by a sophisticated heating system. Depending on the working mode, the surroundings of the vessel are controlled to the same temperature as the sample. If there is no temperature difference between the heaters and the sample, then all the heat generated by the sample stays within the sample. This is the adiabatic condition.

Top
Tube Heater
Machined Insulation
Top Heater
Sample Bomb
Control T/C
Safety T/C
Bottom T/C
Side T/C
Side Bottom Heater
Machined Insulation
Magnetic Stirring
Containment Vessel
Bottom

Schematic of ARC® 254 Calorimeter Assembly

Measurement Results

A thermal runaway reaction is usually investigated with the Heat-Wait-Search mode (HWS). The temperature of reaction as well as the temperature and pressure increase are measured. Additionally, the temperature and pressure increase rates can be determined. These are important values in order to characterize the worst case scenario of a substance.
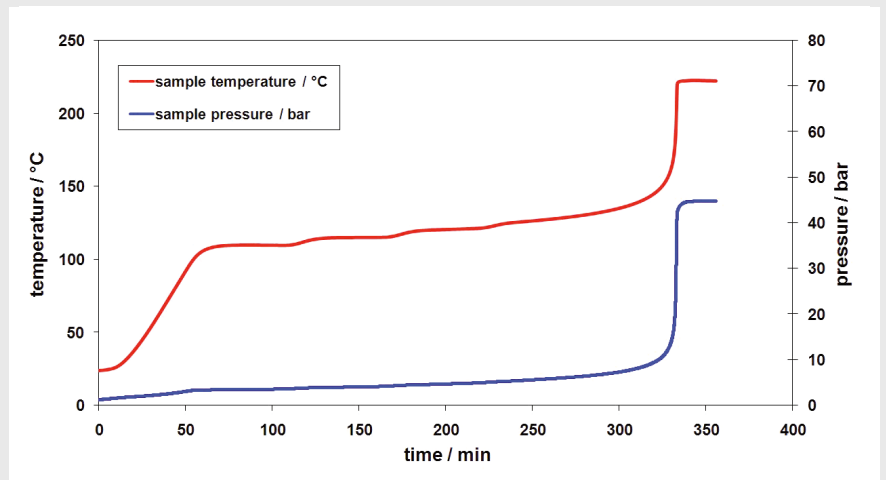
Thermal runaway reaction of a 20% solution of di-tert. butyl peroxide (DTBP) in toluene.

Accelerating Rate Calorimeter ARC® 244 –
The Original DOW Designed for Basic ARC® Testing

The cost-effective ARC® 244 is designed to safely measure the amount and rate of heat release associated with the processing or storage of chemicals with a sample volume of 0.5 ml to 7 ml. This is the only calorimeter which uses the same design as the first ARC® system developed by DOW for those customers interested in keeping the same platform.

The key features are high performance, safety, usability, and flexibility with data integrity and robustness in a temperature range from ambient to 500°C.

ARC® 244

Operating Modes

- Heat-Wait-Search test for thermal runaway reactions
- Iso-Fixed / Iso-Track for studying storage conditions/auto-catalytic reactions (iso-aging technique)
- Ramp mode for fast screening of unknown samples

Optionally with *VariPhi*™

Scanning and isothermal modes allow detection of exothermic and endothermic effects; similar to DSC method

ARC® 244 Calorimeter Assembly

Features	Advantages	Benefits
Over-Temperature Protection	One safety thermocouple monitor calorimeter temperatures and shut down the system independent of the software	Protects heaters and other instrument parts from runaways
Tube Heater	Heats the pressure transfer tube to the same temperature as the sample	Prevents refluxing and sample loss which can cause great underestimation of heats of reaction and temperature and pressure rates
Iso-Fixed™ Mode	Allows the user to run isothermal aging tests for many days with minimized drift	More accurate and reliable data
Automated Anneal, Temp. Calibration & Drift Tests	The user can quickly set-up the anneal-calibration-drift test sequence. The software will automatically go from one test to the next	No operator intervention necessary, improved efficiency

Accelerating Rate Calorimeter ARC® 254 – Advanced Technology for Specialized Testing

The advanced Accelerating Rate Calorimeter ARC® 254 helps engineers and scientists to identify potential hazards and tackle key elements of process optimization and thermal stability. As a highly versatile, miniature chemical reactor, sample can be stirred, material injected, and it can be used for vent studies.

ARC® 254

Operating Modes

- Heat-Wait-Search test for thermal runaway reactions of chemicals or battery samples
- Iso-Fixed / Iso-Track for studying storage/conditions/auto-catalytic reactions (iso-aging technique)
- Ramp mode for screening unknown samples

Optionally with *VariPhi*™

- Scanning and isothermal modes allow detection of exothermic and endothermic effects; similar to DSC method
- In-situ battery cycling using isothermal calorimeter much preferred over adiabatic

Features*	Advantages	Benefits
Motorized Headlift	Operator not required to lift calorimeter lid and can set working height based on personal preference	Easy for all operators to use safely and quickly
Temperature Tracking Rate up to 200 K/min	Fast reactions can be tracked without the need to increase thermal inertia	More reliable data and wider application range
Machined Gas-Tight Ceramic Insulation	Provides consistent insulation properties (i.e. density, geometry)	Constant insulation properties provide for accurate test results, easy cleaning
True Temperature Calibration	With *VariPhi*™ temperature measurements can be corrected to standards	More accurate onset temperature
Battery holder (D-cell, 18650, pouch cell)	Testing of battery or Charging/discharging battery	Easy testing of different batteries
Nail Penetration	contain any reaction or explosion, the gas around the battery , the temperature can be changed, and the pressure release can be measured	Flexible testing, safe operation

* in addition to ARC® 244 features

Automatic Pressure Tracking Adiabatic Calorimeter 264 – Premier Solution for Big Sample/High Pressure Testing

APTAC® 264 is a pressure balancing system for studying reactions with sample volumes of 5 ml to 80 ml. The pressure tracking rates can exceed 680 bar/min. As an adiabatic calorimeter, APTAC® 264 can detect and track exotherms at heat generation rates ranging from 0.02 K/min to 400 K/min.

This is the most advanced adiabatic calorimeter in the market today. It is able to run either as an ARC® or an APTAC®. Its ability to pressure balance effectively at low and high rates is unmatched by other low phi systems, and therefore best system for Emergency Relief System Design (ERSD).

APTAC® 264

Operating Modes

- Heat-Wait-Search test for thermal runaway reactions
- Iso-Fixed/Iso-Track for studying storage/conditions/auto-catalytic reactions (iso-aging technique)
- Ramp mode for screening unknown samples

Optionally with *VariPhi*™ (no pressure balancing)

- Scanning and isothermal modes allow detection of exothermic and endothermic effects; similar to DSC method
- Fire-exposure mode for simulation of thermodynamic and kinetic parameters of the reaction in a single test

Features*(all standard)	Advantages	Benefits
Automated needle valve used for pressure balancing control	Capability to change the pressure in small increments	- Improves calorimetric performance - Reduces noise - Allows the usage of very thin walled or fragile sample vessels
Temperature Tracking Rate max. 400 K/min	- Faster reactions can be tracked without the need to increase thermal inertia - Increased sample size	- More reliable data and wider application range - Better low-end thermal inertia and more accurate onset temperatures
Highest sensitivity (0.002 K/min)	Detection of smallest caloric effects even at lowest onset temperature	Extended range of applications
Injection, venting and stirring	Completely integrated into the hardware and software	No additional costs or space required
Numerous automated features	Easy to maintain and calibrate	- Low operation cost - Higher sample throughput

* in addition to ARC® 244/254 features

VariPhi™: A Patented Solution for Low Phi Operation and Reduced Testing Time

The basis of the *VariPhi™* is an additional controlled variable DC heater. With this option it is possible to define the thermal inertia in order to allow real-world thermal environment by compensating for heat lost from the sample to the vessel. By operating different modes such as isothermal or scanning, endothermic and exothermic transitions can be quantified, pressure data can be measured and the heat capacity of the sample can be determined.

Theory
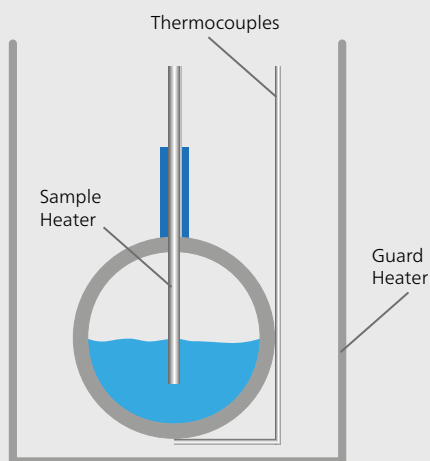
Diagram of the *VariPhi™*

Sample holders absorb some of the energy from the reaction. How much heat is absorbed depends upon the mass and heat capacity of the sample container. The ratio between the product of the sample mass and heat capacity to the product of the container mass and heat capacity is what is known as thermal inertia.

When the sample mass is large compared to the container mass, the thermal inertia approaches one. These tests are often called "low phi" tests. They are important because most industrial scale processing or storage conditions are low thermal inertia conditions. The mass of a large storage container is very small compared to

the mass of the stored material. Since this is not always true it is important to be able to run multiple tests at varying thermal inertia. The *VariPhi™* gets its name because the user can quickly and easily run low and high thermal inertia (˝Phi˝) tests in the same calorimeter using a small and inherently safer sample size.

Formula for thermal inertia (Φ-factor):

$$\Phi = 1 + \frac{m_c \times C_{p,c}}{m_s \times C_{p,s}}$$

m_c = mass of the container
$C_{p,c}$ = heat capacity of the container
m_s = mass of the sample
$C_{p,s}$ = heat capacity of the sample

Standard Modes such as Heat-Wait-Search, Iso-Fixed or Iso-Track

■ Compensation for heat lost to the sample container during test
■ Thermal inertia or Phi (Φ) factor can be defined
■ Low Phi testing with small samples

Scanning Mode

■ Reduces test time by 75% or more without loss of sensitivity
■ Sample heat capacity can be measured as a function of temperature
■ Endothermic transition can be accurately measured

Fire-Exposure Mode

Simulation of additional heat to the sample during external fire scenario

Isothermal Mode

■ True isothermal calorimeter is possible on chemical samples and battery cells
■ 3D battery sensors are available based on the *VariPhi™* concept. They allow the study of charge/discharge of battery inside calorimeter

Testing Vessels for the Accelerating Rate Calorimeters

A broad variety of testing vessels are available to meet different test requirements. Tube-type vessels are available for running smaller APTAC® samples or energetic materials and for use with solids and pastes in the *VariPhi™*. For battery testing, specific holders are designed for common commercial sizes. Custom vessels can also be designed.

Materials

■ Spherical vessels with a wall thickness between 0.4 mm and 5.1 mm are made of glass, Hastelloy, Inconel, stainless steel, tantalum and titanium
■ Tube-type vessels with a wall thickness of 0.4 mm and 0.7 mm are made of stainless steel and titanium

Volume

■ 1 ml to 130 ml for spherical vessels
■ 0.1 ml to 9 ml for tube-type vessels

Pressure

■ Up to 1000 bar for spherical vessels
■ Up to 200 bar for tube-type vessels

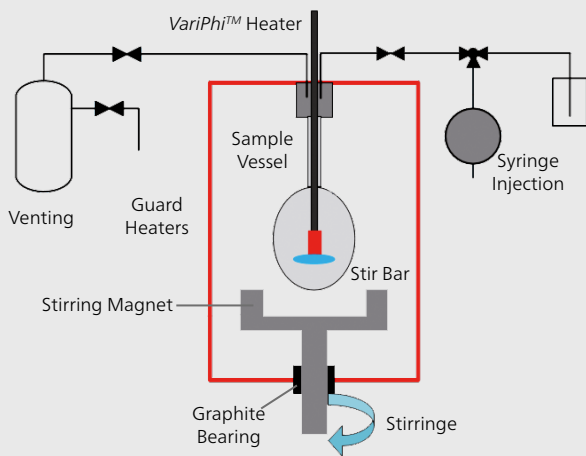# Selecting the Best Calorimetry for Your Applications

Technical Features

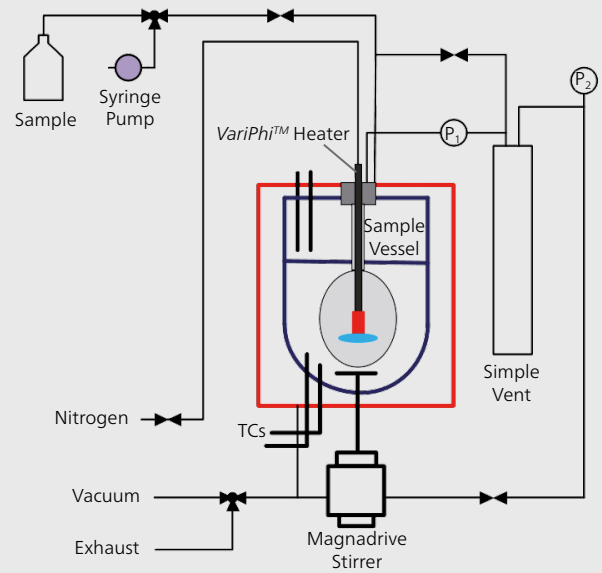| Calorimeter Type	ARC® 244	ARC® 254	APTAC® 264
Temperature range	RT to 500°C	RT to 550°C	RT to 500°C
Pressure range (Standard)	0 bar to 200 bar	0 bar to 200 bar	0 bar to 140 bar
Lift mechanism	motorized	motorized	motorized
Typical sample volume*	0.5 ml to 7 ml	0.5 ml to 7 ml	5 ml to 80 ml
Max. tracking rate	20 K/min	200 K/min	400 K/min
Temperature reproducibility	0.1 K	0.1 K	0.1 K
VariPhi™	Optional	Optional	Optional, in ARC® mode only
Operating mode	Heat-Wait-Search constant heating rate isothermal	Heat-Wait-Search constant heating rate isothermal	Heat-Wait-Search constant heating rate isothermal; fire test
Stirring	Optional	Optional	Standard
Injection collection vessel for reaction gas	Optional	Optional	Standard
Venting	Optional	Optional	Standard
Pressure compensation	No	No	Yes
Accessory for battery test	thermal runaway	thermal runaway; isothermal; cycling; nail penetration	thermal runaway; isothermal; cycling; nail penetration
Low Φ factor	Yes, pressuredependent	Yes, pressuredependent	optimum 1.05, pressuredependent
Kinetics software	Optional	Optional	Optional
Applications	Process Safety; Comparison to legacy data	Process Safety; Battery; Energetic Material	ERSD; Operate as ARC® 254

* Sample volumes shown are typical and not limits. Sample vessels for the ARCs and APTAC are interchangeable.
  The choice of sample vessels can influence test results. See product manual or spare parts list for more details.

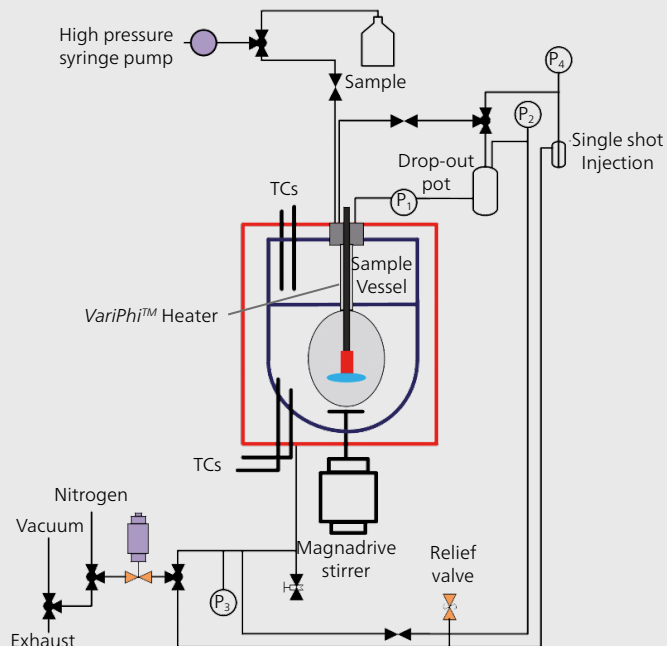# Configurable Options to Match Testing Needs

ARC®244 options

VariPhi™ Heater

Sample Vessel

Syringe Injection

Venting

Guard Heaters

Stirring Magnet

Stir Bar

Graphite Bearing

Stirringe

ARC®254 options

Sample

Syringe Pump

VariPhi™ Heater

P_1

P_2

Sample Vessel

Simple Vent

Nitrogen

TCs

Vacuum

Exhaust

Magnadrive Stirrer

APTAC® 264 with syringe injection option

High pressure syringe pump

Sample

P_4

P_2

Single shot Injection

Drop-out pot

TCs

P_1

Sample Vessel

VariPhi™ Heater

TCs

Nitrogen

Vacuum

Magnadrive stirrer

Relief valve

P_3

Exhaust

The schematics show the different options available to the product line.

Intelligent Software Solutions

Measurement Task

The measurement software for the Accelerating Rate Calorimeters and the APTAC® offers easy setup of a measurement, selection of the measurement mode and follow-up of the test progress. All raw data signals are accessible on the screen, switches can be set with one mouse click and simple plots of the running measurements can be generated. The software stores data in binary and ASCII formats, making it easy to load results into other software packages for advanced analysis.

- Software automatically customizes itself to the instrument and application
- Intuitive Windows set-up of testing methods with input checks to reduce typos
- Methods can be saved and recalled for later use
- On-line help, comprehensive and easy to understand, available throughout the software
- Data is automatically saved to hard-drive throughout the run
- Intelligent Firmware monitors the status and health of key operating sensors and active components
- Safety integrated with hardware and firmware controls
- Seamless integration of data files to *Proteus®*
- Analysis, NETZSCH Advanced Software Tools or 3rd party software
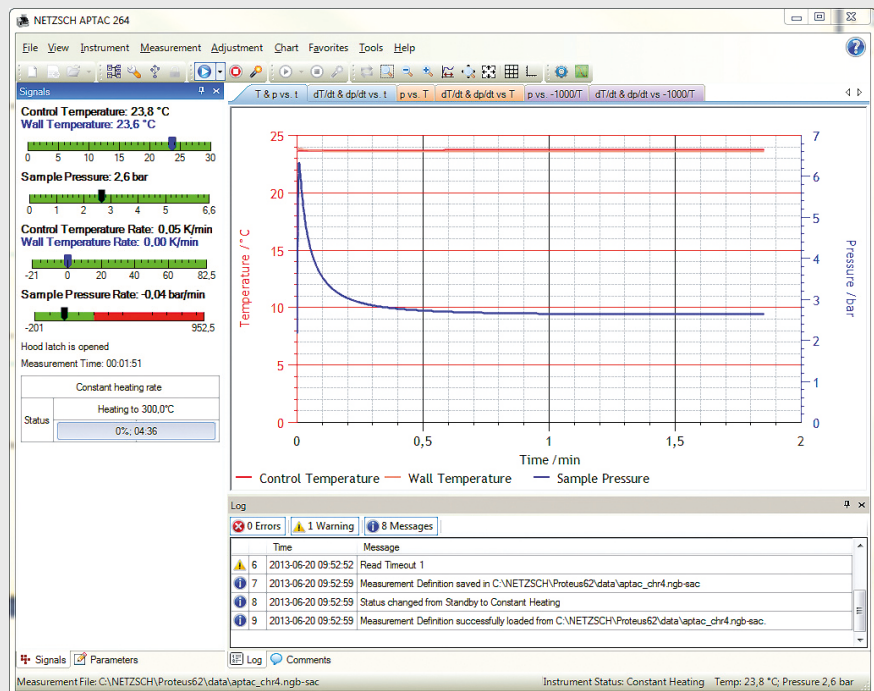
Software screenshot for APTAC® 264

Evaluation Software

Analysis of the measurements is done using the well-known *Proteus®* Thermal Analysis software. Presentation of measurement results such as various temperatures, heat generation rates or the pressure development can be done in one plot. Evaluation of characteristic temperatures onsets, peaks, end temperatures) can be done on each signal curve. Direct evaluation of decomposition enthalpies and standard kinetic analysis is possible.
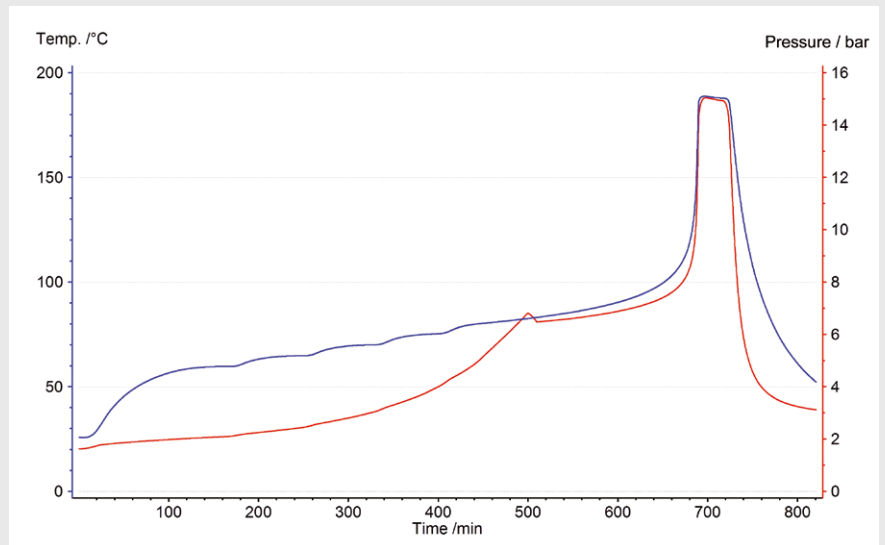
Screenshot of the *Proteus®* evaluation software

Advanced Thermokinetic and Thermal Simulation

Most decomposition reactions cannot be explained by simple kinetic approaches. In such cases the nature of a reaction is based on various steps (consecutive, parallel or competitive reactions). Multiplestep reactions (up to 6 different steps) with more than 15 different reaction types can be used in NETZSCH Thermokinetics for the analysis of the results. This is the ideal tool for understanding the real chemistry and kinetics behind a reaction.
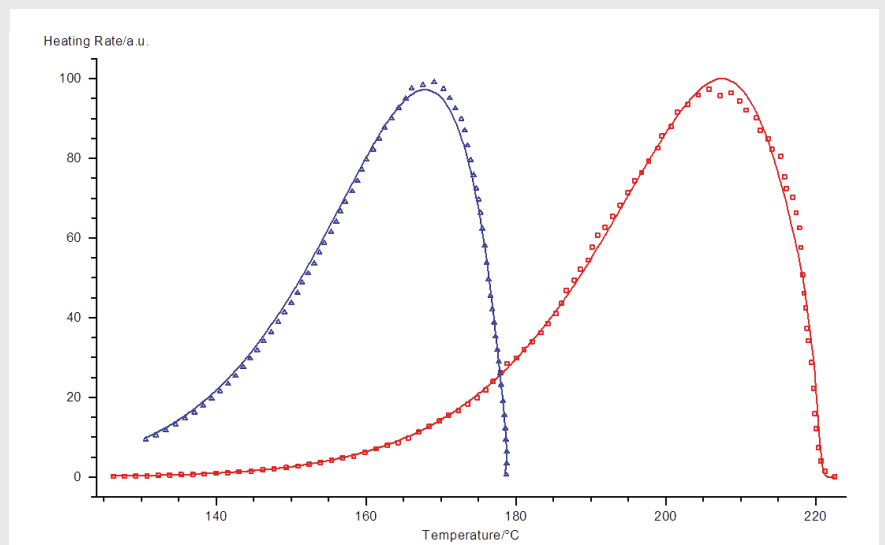

Comparison of measured and calculated data for different phi-factors

Typical Applications

Accelerating Rate Calorimeters by NETZSCH can be used for the thermal analysis of solid or liquid chemicals or for gas/liquid, liquid/liquid, gas/solid, and liquid/solid mixtures. They can also be used for process simulation of batch and semi-batch reactions, fire exposures, emergency relief venting, and physical properties measurement.

Energetic Materials

Ammonium nitrate is a base material for various applications, such as fertilizers. Measured here are solid-state phase transitions and melting (at 166°C) as well as the decomposition behavior, starting at 221°C. Such tests are crucial for safety studies on such highly energetic materials.
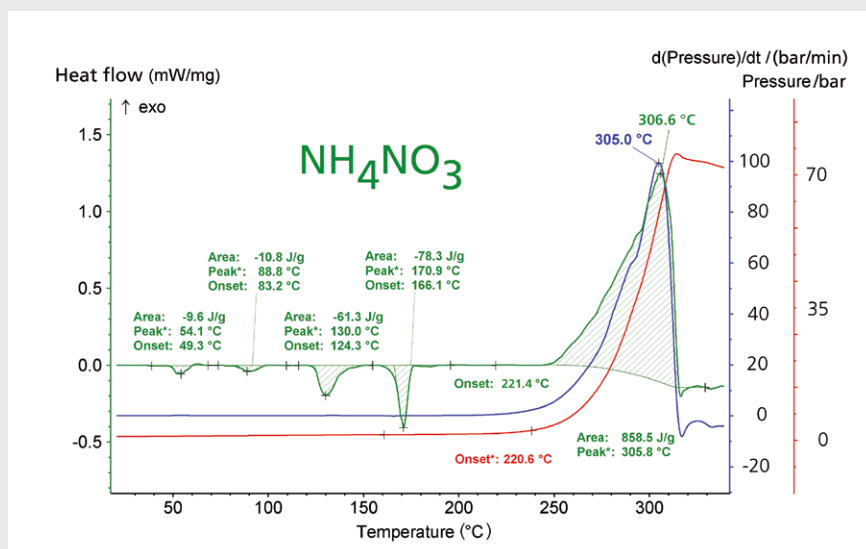

Analysis of the phase changes and decomposition behavior of ammonium nitrate using the *VariPhi™*-option

Autocatalytic Behavior

3-methyl 4-nitrophenol displays autocatalytic behavior when heated to decomposition temperatures. Thismay be studied using the Iso-Track or Iso-Fixed feature of the calorimeter-control software. Using the *VariPhi™* option allows measurement of the sample under true isothermal conditions. The plot shows the autocatalytic nature of the material where the sample heat flux initially increases and then decreases due to consumption of reactant. The total heat release during the decomposition is simply obtained by integration of the heat flux signal.
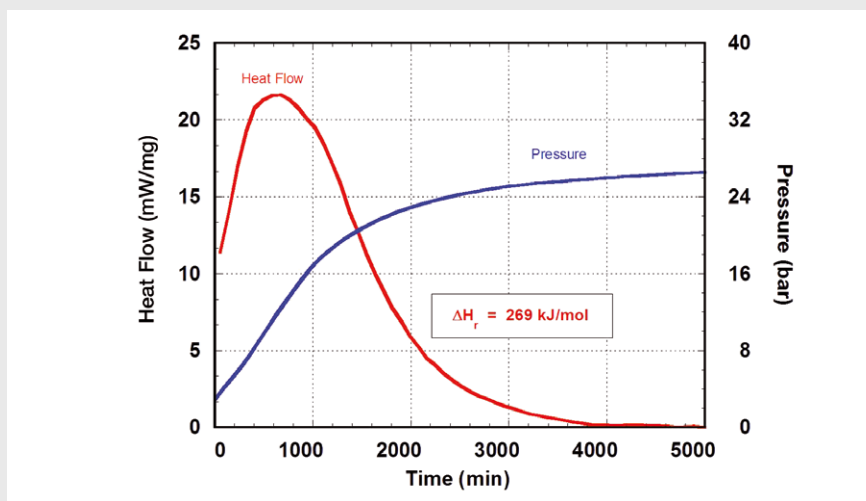

Autocatalytic behavior of 3g 3-methyl 4-nitrophenol at 180°C (isothermal)
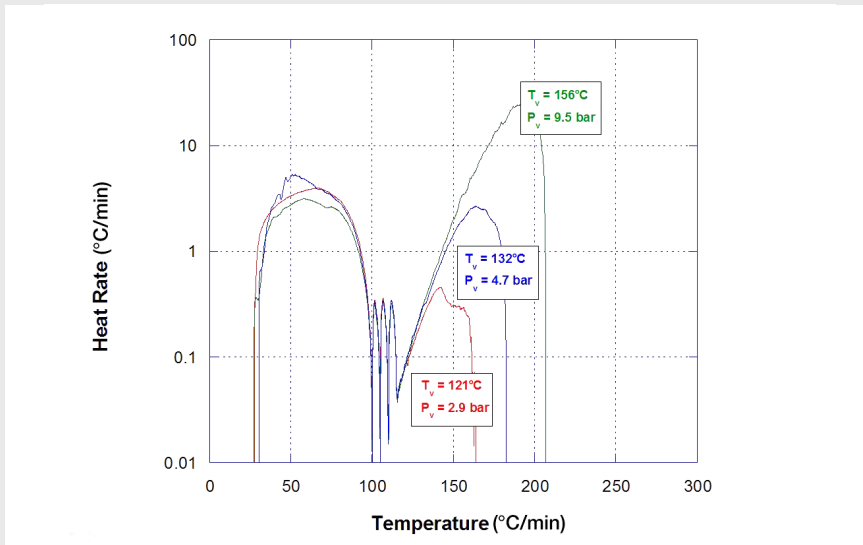
Vented tests showing increasing tempering as the vent set pressure is reduced

Vented Tests

All ARC®s/APTAC® may be operated in vented or open vessel mode. For vented tests a computer-controlled valve is opened which allows material to flow to a 500 ml dropout pot. If the pressure in the reaction vessel ceases to rise and the sample temperature remains flat or is tempered, then the reaction may be classified as a vapor system. The pressure in the reaction vessel may continue to rise, but at a reduced rate because of the increase in the head space of the reaction vessel. At the end of the test, the contents of the drop-out pot are available for analysis.
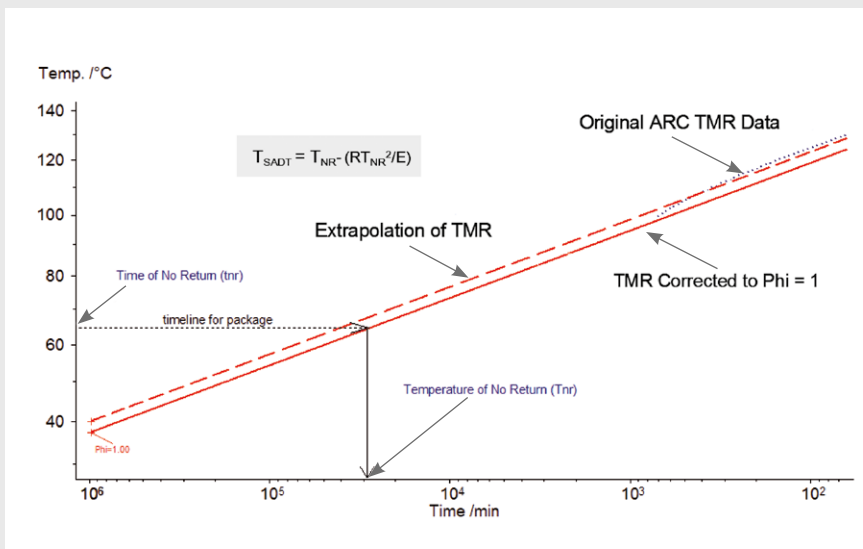

Determining SADT Using ARC® Data

SADT or Self-Accelerating Decomposition Temperature, is a UN testing requirement to determine if packages need to be refrigerated during shipment to prevent a runaway reaction from occurring during international shipments. Many countries have similar requirements as well. Using ARC® data to determine SADT is well established and has been accepted as a substitute for direct testing of packages. From the self-heat rate curve measured during an ARC® test the phicorrected Time-to-Maximum-Rate (TMR) curve can be determined as well as the activation energy, Ea. Using the package time constant and the TMR curve the TNR (temperature of no return), SADT can be determined.

Typical Battery Applications
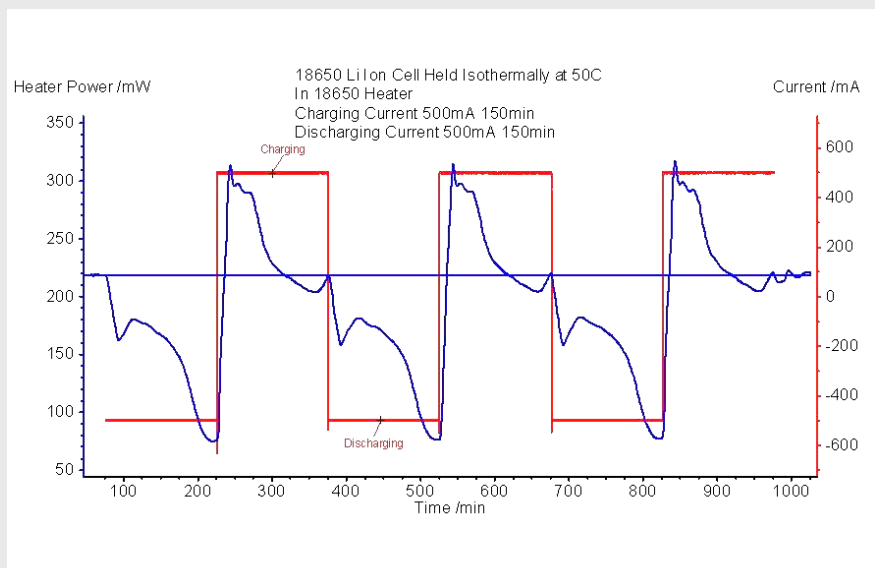
Battery Thermal Runaway

Adiabatic reaction calorimeters allow the researcher the ability to test full cells in an adiabatic environment to determine how well they perform in real and exaggerated conditions. Cells can be charged and discharged while inside the calorimeter so many use scenarios can be tested. With the *VariPhi™* option, cells can be held isothermally during the charge and discharge process in order to get important data on heat energy management.
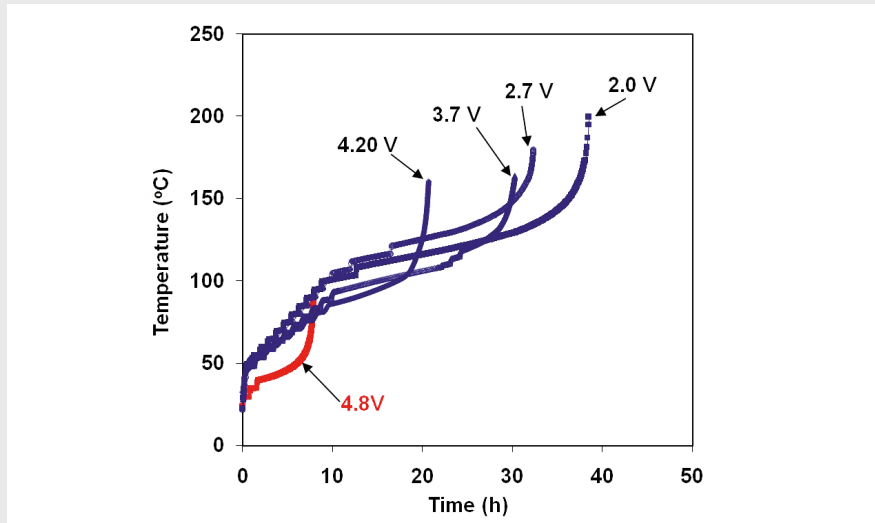
Effect of state-of-charge on the thermal stability of a prototype 18650 lithium ion batteries

Battery Cycling – isothermal

Battery cycling inside a calorimeter can provide insight into the underlying phenomena occurring in the cell. Furthermore the necessary data to design thermal management systems for battery packs can be determined at normal and exaggerated operating conditions.

Cell Heater Power and Cell Current versus Time for an Isothermal Battery Cycling Test on ARC® 254

Lithium-ion battery
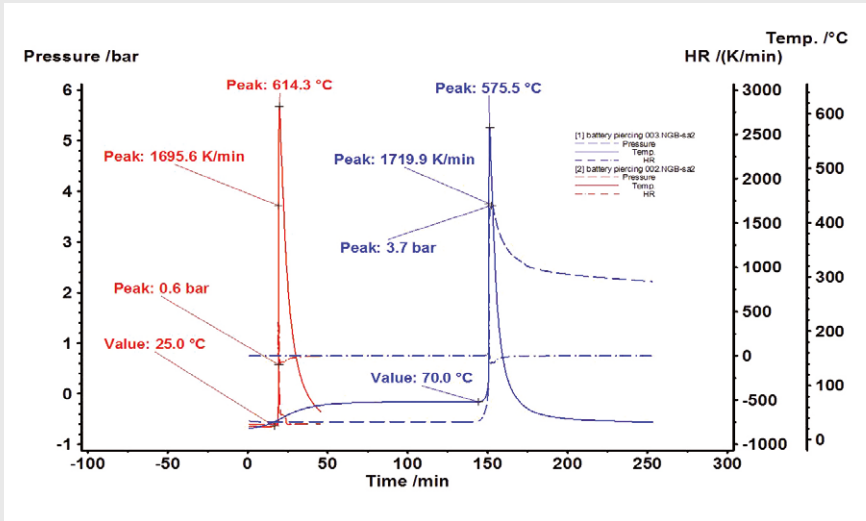
The pressure, temperature and self-heat rate verses time for a nail pentration test conducted at 25 °C and 70 °C on ARC® 254

Nail Penetration

Nail penetration tests have been used extensively as an indicator of battery safety. When nail penetrates the battery, a strong exothermic reaction starts which leads to combustion of the organic vapors released from the system.
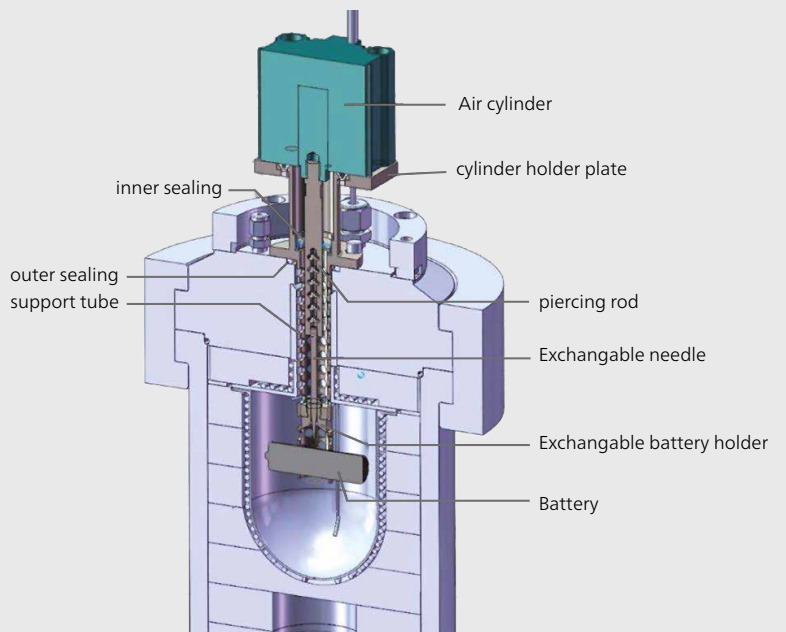The advantage of running these types of tests inside a calorimeter is the ability to contain any reaction or explosion, the gas around the battery can be changed, the temperature at which the test is done can be changed, and the pressure release can be measured.

18650 cell and its *VariPhi*™ 3D sensor

D cell and its *VariPhi*™ 3D sensor

Nail Penetration set up diagram

Expertise in Service

Our Expertise – Service

All over the world, the name NETZSCH stands for comprehensive support and expert, reliable service, before and after sale. Our qualified personnel from the technical service and application departments are always available for consultation.

In special training programs tailored for you and your employees, you will learn to tap the full potential of your instrument.

To maintain and protect your investment, you will be accompanied by our experienced service team over the entire life span of your instrument.

Summary of Our Services

- Installation and commissioning
- Hotline service
- Preventive maintenance
- Calibration service
- On-site repairs with emergency service for NETZSCH components
- Moving / exchange service
- Technical information service
- Spare parts assistance

Our Expertise – Applications Laboratories

The NETZSCH Thermal Analysis applications laboratories are a proficient partner for nearly any Thermal Analysis issue. Our involvement in your projects begins with proper sample preparation and continues through meticulous examination and interpretation of the measurement results. Our diverse methods and over 50 different state-of-the-art measuring stations will provide ready-made solutions for all your thermal needs.

Within the realm of thermal analysis and the measurement of thermo-physical properties, we offer you a comprehensive line of the most diverse analysis techniques for materials characterization (solids, powders and liquids).

Measurements can be carried out on samples of the most varied of geometries and configurations. You will receive high-precision measurement results and valuable interpretations from us in the shortest possible time. This will enable you to precisely characterize new materials and components before actual deployment, minimize risks of failure, and gain decisive advantages over your competitors.

For production problems, we can work with you to analyze concerns and develop solutions. The minimal investment in our testing and services will reward you with reduced down time and reject rates, helping you optimize your processes across the board.

NETZSCH

The NETZSCH Group is a mid-sized, family-owned German company engaging in the manufacture of machinery and instrumentation with worldwide production, sales, and service branches.

The three Business Units – Analyzing & Testing, Grinding & Dispersing and Pumps & Systems – provide tailored solutions for highest-level needs. Over 3,300 employees at 210 sales and production centers in 35 countries across the globe guarantee that expert service is never far from our customers.

When it comes to Thermal Analysis, Adiabatic Reaction Calorimetry and the determination of Thermophysical Properties, NETZSCH has it covered. Our 50 years of applications experience, broad state-of-the-art product line and comprehensive service offerings ensure that our solutions will not only meet your every requirement but also exceed your every expectation.

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