NETZSCH

Analyzing & Testing
Business Unit

Adiabatic Reaction Calorimetry

Method, Technique, Applications

Leading Thermal Analysis.

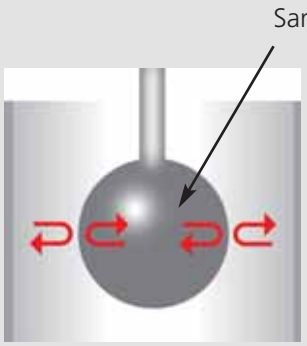
Adiabatic Reaction Calorimetry

Method

The energy release from chemical reactions (decomposition etc.) is a point of focus in chemical research and related 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.

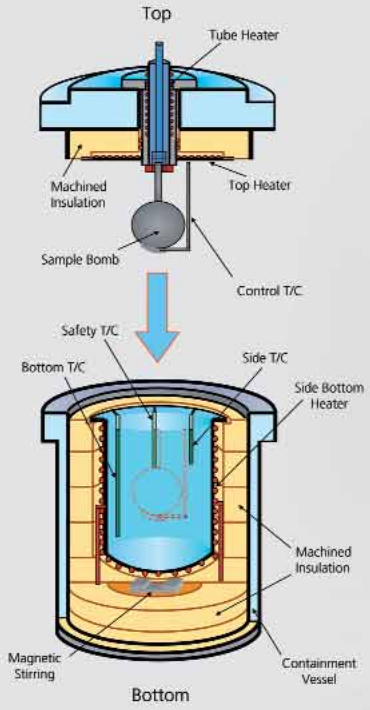
The use of adiabatic systems has the advantage that no heat loss is allowed from the sample; the behavior in real large scale chemical reactors can therefore be simulated (worst case scenario).



Adiabatic System: No heat in - no heat out

Technique

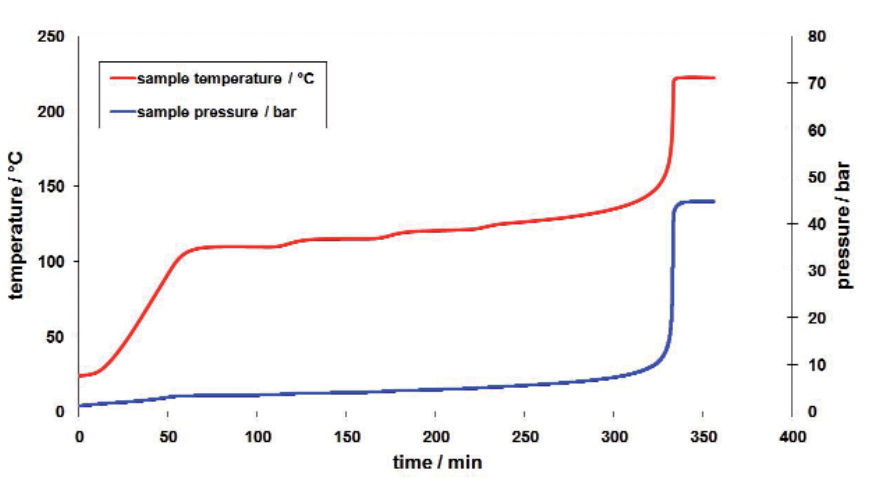
A sample (several grams) is placed in a spherical vessel. The vessel is surrounded by a sophisticated heating system. Depending on the working mode, the surroundings of the vessel are controlled to the same temperature as the sample. If there is no temperature difference between the heaters and the sample,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



Schematic of ARC 254 Calorimeter Assembly

Measurement Results

A thermal runaway reaction is usually investigated with the patented 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 244

Model 244

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

Model 244 Calorimeter Assembly

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

Features	Advantages	Benefits
Over-Temperature Protection	Two redundant safety thermocouples 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 254

The advanced Accelerating Rate Calorimeter 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, it allows tests even at subambient temperature.

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*™:

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

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
Electrical Connection Management	Separation of electrical connections and measuring part	Easier maintenance

* in addition to Model 244 features

Automatic Pressure Tracking Adiabatic Calorimeter 264

APTAC™ 264 is a pressure balancing system for studying reactions with sample volumes of 5 ml to 75 ml. The pressure tracking rates amount to max. 680 bar/min. As an adiabatic calorimeter, APTAC™ 264 can detect and track exotherms at heat generation rates ranging from 0.04 K/min to 400 K/min.

APTAC™ 264

Lithium-ion battery

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*™:

- 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*	**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 Model 244 / 254 features

VariPhi™

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

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

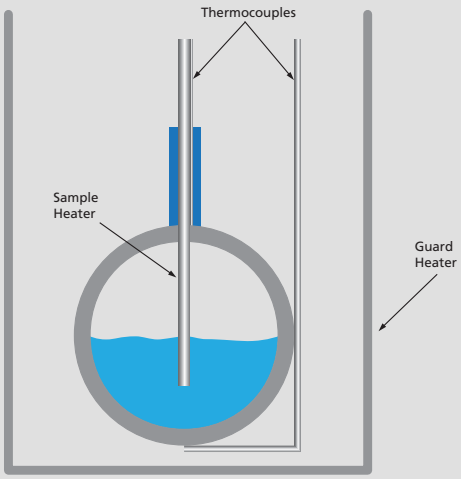


Diagram of the *VariPhi*™

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
- Sample heat capacity can be measured as a function of time
- Endothermic transition can be analyzed

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 analyzed

Fire-Exposure Mode

- Simulation of additional heat to the sample

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

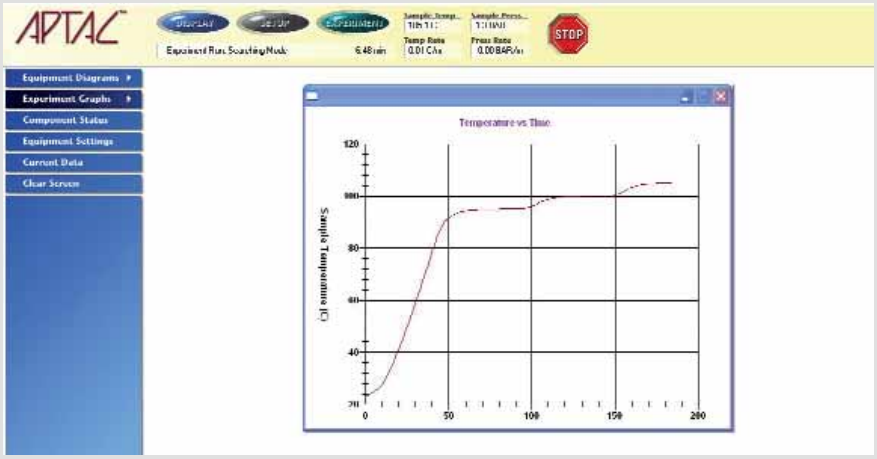
Most important features of the three adiabatic calorimeters

Technical Features

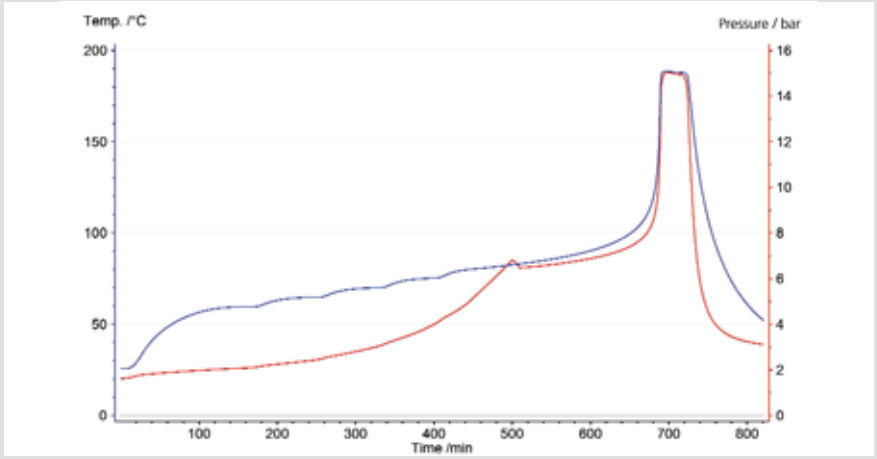
Calorimeter Type	**244**	**254**	**264**
Temperature range	RT to 500°C	<RT to 500°C	RT to 500°C
Pressure range (Standard)	0 bar to 200 bar	0 bar to 200 bar	0 bar to 140 bar
Lift mechanism	Manual	Motorized	Motorized
Sample volume	0.5 ml to 7 ml	0.5 to 7 ml	5 ml to 75 ml
Max. tracking rate	20 K/min	200 K/min	400 K/min
Temperature accuracy	0.1 K	0.1 K	0.1 K
VariPhi™	Optional	Optional	Optional
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	Not available	Optional	Standard
Pressure compensation	No	No	Yes
Accessory for battery test	Basic system available	Further options available	Further options available
Low Φ factor	Yes, pressure-dependent	Yes, pressure-dependent	Optimum 1.05, pressure independent
Kinetics software	Optional	Optional	Optional

Software Solutions

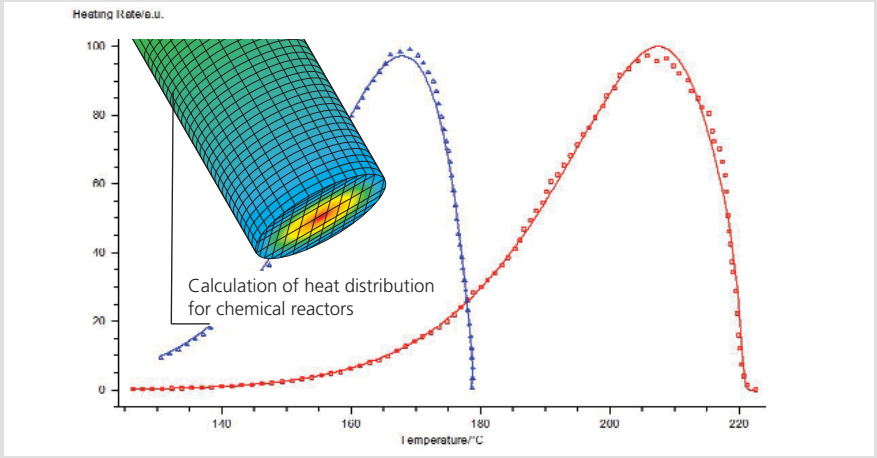
The Accelerating Rate Calorimeters and APTAC™ run under a 32-bit Windows® software package which includes everything needed to carry out a measurement. The combination of easy-to-understand menus and automated routines makes this software very user friendly.



Screenshot of the measurement software



Screenshot of the *Proteus*® evaluation software



Comparison of measured and calculated data for different phi-factors

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.

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.

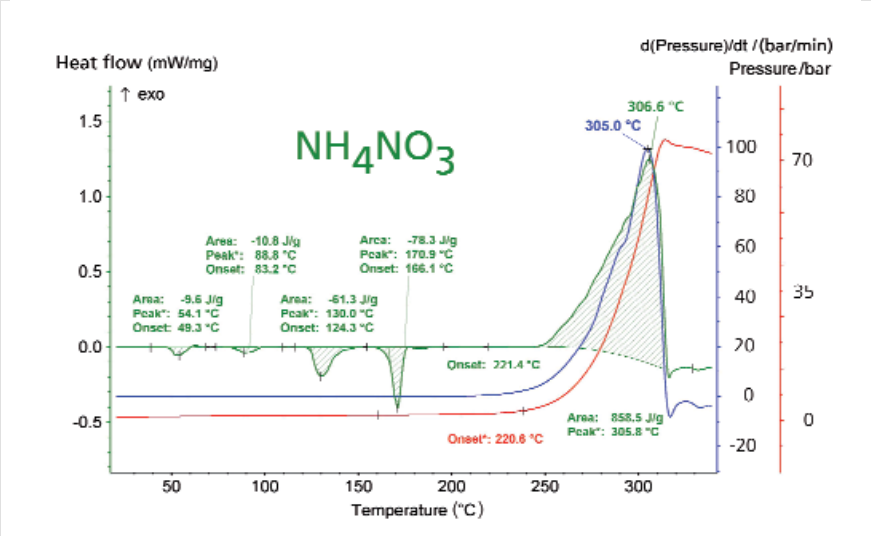
Advanced Thermokinetic and Thermal Simulation
Most decomposition reactions cannot be explained by simple kinetic approaches. In most cases the nature of a reaction is based on various steps (consecutive, parallel or competitive reactions). Multiple-step reactions (up to 6 different steps) with more than 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.

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

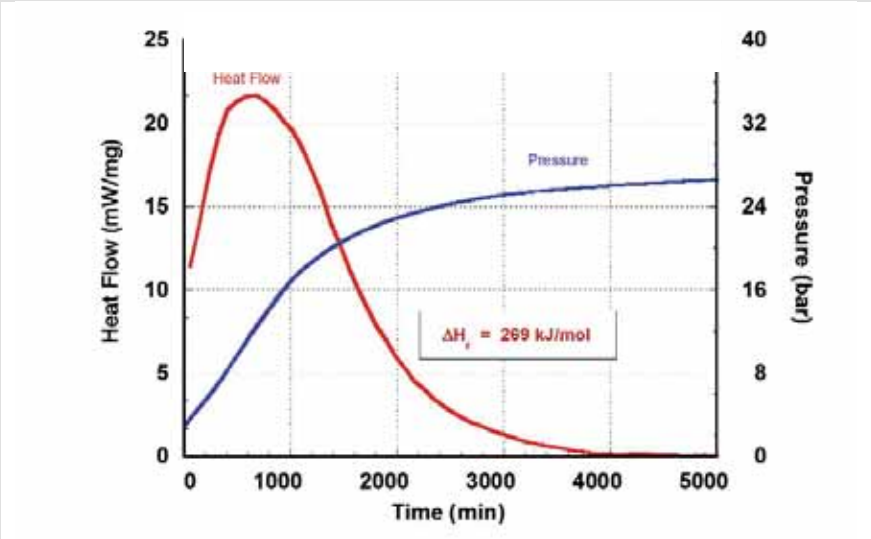
Ammonium nitrate is a base material for various applications, such as fertilizers. Measured here are solid-state phase transitions and melting (at 166°C) as well as the decomposition behavior, starting at 221°C. Such tests are crucial for safety studies on such highly energetic materials.



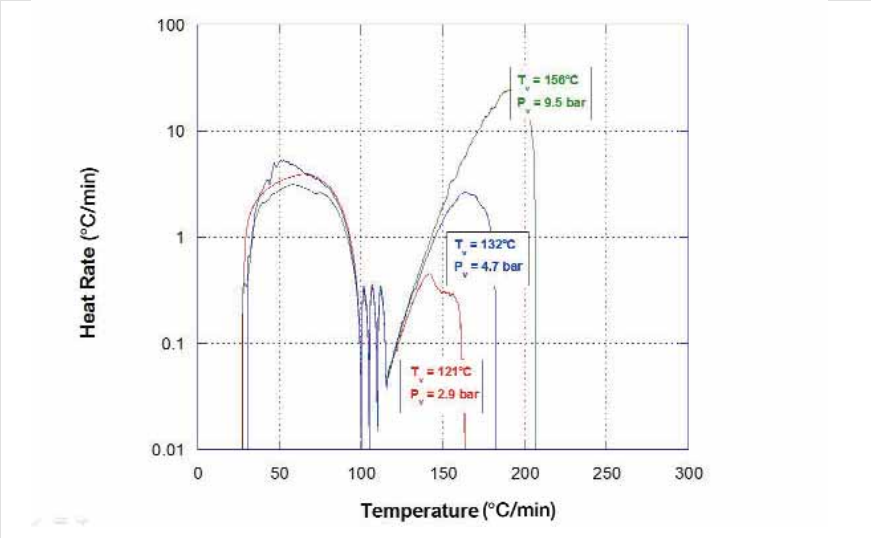
Analysis of the phase changes and decomposition behavior of ammonium nitrate using the *VariPhi*™-option

Autocatalytic Behavior

3-methyl 4-nitrophenol displays autocatalytic behavior when heated to decomposition temperatures. This may 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.



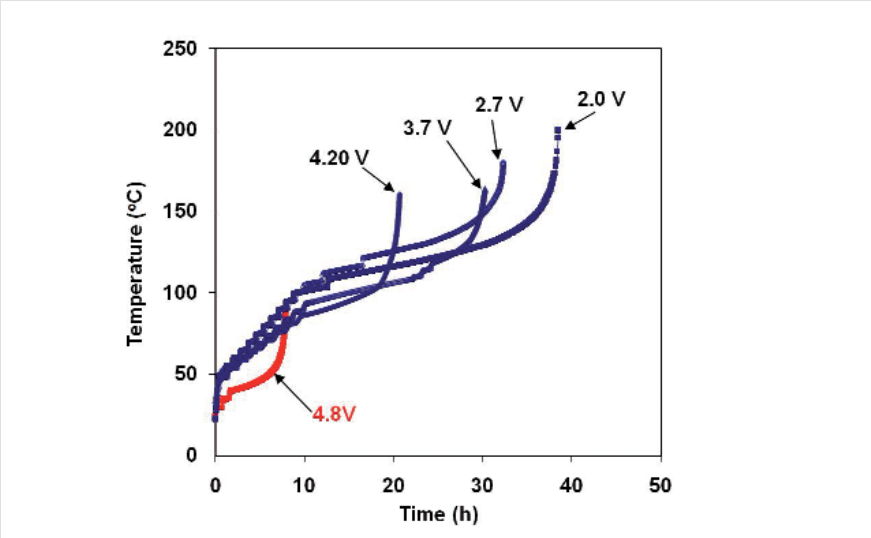
Autocatalytic behavior of 3g 3-methyl 4-nitrophenol at 180°C (isothermal)



3 vented tests showing increasing tempering as the vent set pressure is reduced

Vented Tests

The instrument 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 drop-out 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.



Effect of state-of-charge on the thermal stability

Battery Testing

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.

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