APPLICATION **NOTE**

Is There a Way to Stop Thermal Runaway?

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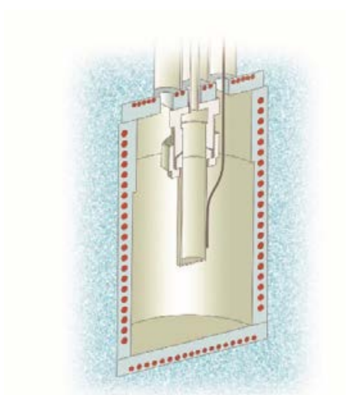
1 NETZSCH ARC® 254

Introduction

The NETZSCH ARC® 254 (fig. 1) is an accelerating rate calorimeter capable of carrying out so-called thermal runaway tests and worst-case scenario tests. The objective of this measurement technology is to find the hazardous potential with respect to the temperature of a sample or a reaction mixture under adiabatic conditions. Adiabaticity in particular means 'without any heat exchange'. If all the heat of reaction remains inside a reaction vessel and is not able to dissipate to the environment, the temperature will rise and thus cause the speed of reaction to increase. This will result in a self-accelerating reaction mechanism. By studying such scenarios, any real-world conditions – which are usually not fully adiabatic, but rather characterized by heat losses to the surroundings – can be calculated and classified.

The NETZSCH MMC 274 *Nexus*® is a multiple-module calorimeter offering three exchangeable modules: a coin-cell module for battery testing, a scanning module for thermal screening and an ARC module (figure 2) for thermal runaway testing as described above.

Although it is important to have laboratory instrumentation allowing for thermal runaway testing without damaging the measurement instrumentation, it is sometimes of interest to find only the temperature at which the thermal runaway starts (onset), without necessarily allowing it to run all the way through. Quite often, the question arises: Is it possible to stop thermal runaway once a reaction has started?



2 Cross-section of the ARC module of the NETZSCH MMC 274 *Nexus*®

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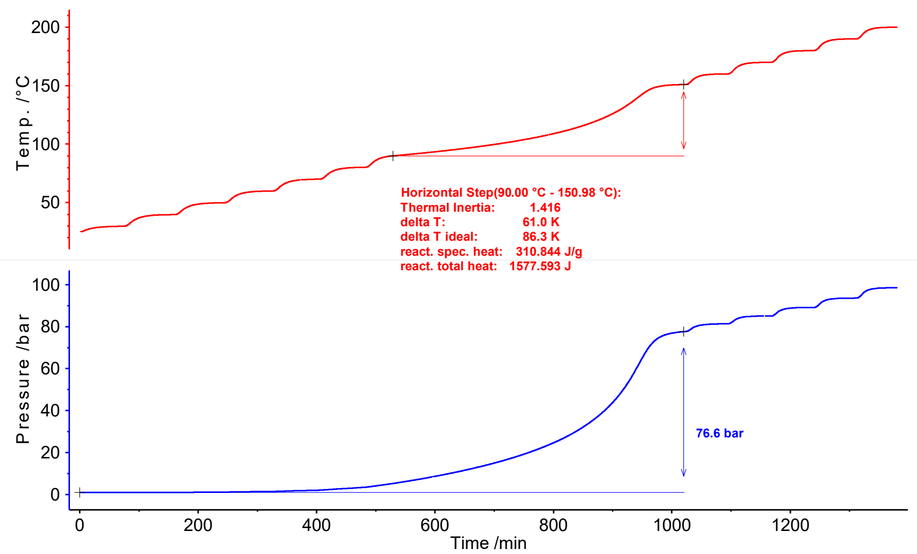
How to Detect the Beginning of an Exothermic Self-Decomposition Reaction

Both the NETZSCH ARC® 254 and the ARC module of the NETZSCH MMC 274 *Nexus*® can detect thermal runaway. To do so, the well-established heat-wait-search (HWS) temperature program is applied. It lifts the temperature stepwise, and at each isothermal temperature step it allows the whole system – sample and heaters – to equilibrate. At the end of the temperature equilibration, a search segment detects whether self-heating of the sample is occurring or not. As long as no self-heating is detected, the sequence of 'heat', 'wait' and 'search' will continue. As soon as a self-heating rate of 0.02 K/min is exceeded, the instrument will switch into the so-called adiabatic mode. This mode works to prevent heat losses to the sample environment by having all the heaters surrounding the sample track the sample temperature. If all heaters are at the same temperature as the sample, there will be no temperature gradient and without a temperature gradient, there will be no heat flow. This is the way the ARC ensures an adiabatic sample environment, which is essential for a worst-case scenario such as thermal runaway.

How to Measure a Thermal Runaway Reaction

Usually, when a thermal runaway reaction starts, it starts slowly. 0.02 K/min is a very low self-heating rate; it is just 1.2 K per hour. The self-heating reaction will start slowly, but it will continuously accelerate with increasing temperature until it reaches its maximum self-heating rate and finally the maximum temperature. Figure 3 shows the results for temperature (red) and pressure (blue) for an HWS test on a 17.5% hydrogen peroxide solution. 5.0575 g of the hydrogen peroxide solution were used inside a spherical titanium vessel (8.7 ml).

As mentioned earlier, a self-heating rate of more than 0.02 K/min will trigger the recognition of an exothermic event. Here, the exothermic reaction was detected at 90°C and the exothermic sample reaction made the temperature rise to 151°C. During the decomposition reaction, the pressure inside the sample vessel increased to 76.6 bar.



3 HWS results for hydrogen peroxide (17.5%), temperature (red) and pressure (blue)

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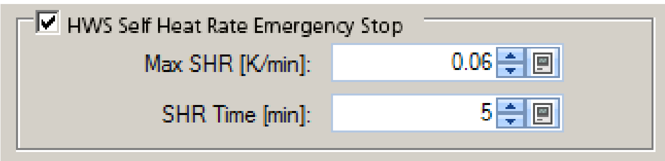
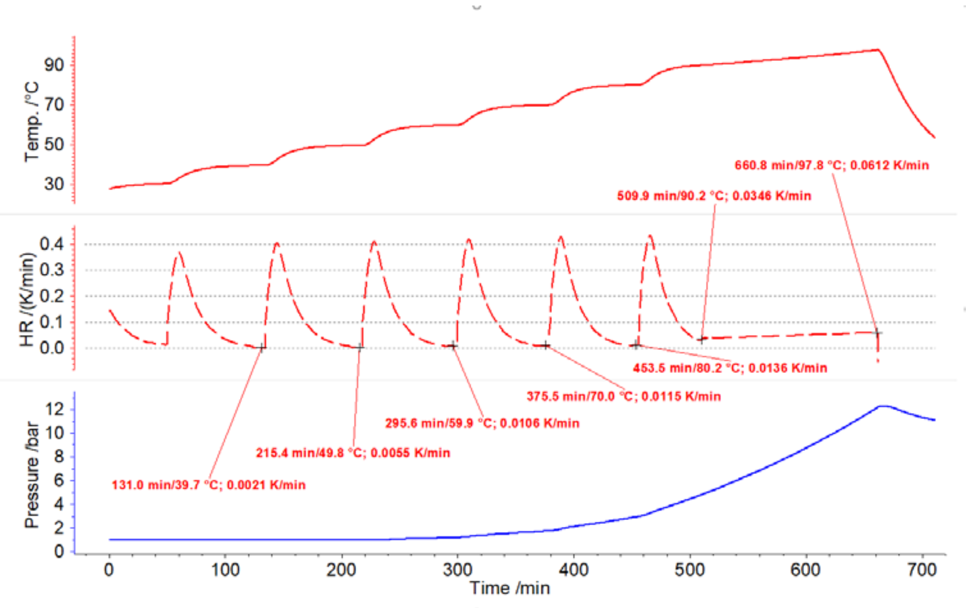
How to Stop a Thermal Runaway Reaction?

The question as to whether the thermal runaway reaction can be stopped or not is, of course, strongly related to the self-heating rate. It is necessary to detect the thermal runaway, but maybe it is not always desirable to allow the thermal runaway reaction to fully run its course. In this case, it would be nice to have a criterion for stopping the thermal runaway at a certain point. Again, the self-heating rate is a meaningful criterion for determining whether it is possible to halt the runaway of a decomposition reaction. When the heaters are stopped from tracking the sample temperature, the sample environment is no longer adiabatic. The temperature around the sample will decline and the temperature gradient will allow the reaction heat from the sample to dissipate. It is obvious that the earlier the adiabatic sample environment is removed, the easier it will be to stop the reaction. Therefore, it is useful to set the self-heating function in such a way that the heaters switch off when the rate is slightly higher than the exothermic detection rate of 0.02 K/min. Figure 4 shows how easily a self-heating emergency stop can be programmed. Figure 5 depicts the results of a measurement under conditions similar to those shown in figure 3, but applying the self-heating emergency stop at a rate of 0.06 K/min. The self-heating rate, evaluated during the search segment of each temperature step, rose slowly with temperature but remained below the exothermic threshold of 0.02 K/min up to 80°C. At 90°C, self-heating was detected to be 0.035 K/min; this is why the ARC changed from HWS mode into the adiabatic tracking mode. At 97.8°C, the self-heating rate exceeded the self-heating emergency stop value of 0.06 K/min; the tracking was thus terminated, and the heaters stopped heating. The sample temperature dropped and the runaway reaction was stopped.



4 NETZSCH *Proteus*® measurement software: Self-heating rate emergency stop



5 HWS results for hydrogen peroxide (17.5%), temperature (top), self-heating rate (middle) and pressure (bottom)

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Conclusion

At a certain point, thermal runaway reactions proceed out of control and cannot be stopped. If, however, an exothermic event is detected using high sensitivity at a relatively low self-heating rate, the reaction can be stopped using a clever software feature called a 'self-heating emergency stop'. This function allows for removing the adiabatic environment around the sample (here at a self-heating rate of 0.06 K/min). It allows the sample to dissipate heat and, as shown in the example above, prevents the sample reaction from running out of control.

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