thermal hazard technology

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Technical Information Sheet No 2

An Introduction to Accelerating Rate Calorimetry

The Accelerating Rate Calorimeter was developed by the Dow Chemical Co in the 1970's and the classic description is by Townsend and Tou (Ref 1). The Accelerating Rate Calorimeter is a highly adiabatic calorimeter designed to assess the safety of reactive chemicals and mixtures. It is a safety calorimeter designed originally for the Chemical Processing Industry.

The aim is to simulate a runaway reaction, those reactions that one does not want to occur or to quantify a process to optimise process conditions for reaction engineering. The Accelerating Rate Calorimeter provides a full time, temperature, pressure profile of the reaction within a period of approximately 24 hours. The accelerating rate calorimeter was designed to be fully automatic in use and safe to operate in a normal laboratory environment. The data is simple to interpret and can be applied to a range of common situations that exist in the Chemical Processing Industry. Accelerating rate calorimetry has been available commercially since 1980 and has become accepted world wide. The reasons for this are:

Universal sample types,   from high explosives to low energy materials
    Liquid, solid, slurries
    In differing gas environments and pressures

Ease of use

Simple data analysis

Versatility of operation and application

Reliability , validity and accuracy of results - due to very high adiabaticity.

The Accelerating Rate Calorimeter comprises in essence

A calorimeter assembly, within which is the sample

A pressure transducer for pressure measurement

A blast proof containment vessel

Control electronics

Computer and printer system

Ancillary connections and cables

The calorimeter assembly has two parts, a top or lid section and a lower or main section. The main section is a copper pot 2.5cm that which contains six rod heaters and two thermocouples. The top section has two heaters and one thermocouple and the main section has a side zone with four heaters and one thermocouple and a bottom zone with two heaters and one thermocouple. The calorimeter is surrounded by insulation and is contained in an outer aluminium container. The sample container is usually referred to as the bomb since the system is used sealed gives a pressure tight environment. The bomb is connected to the top section by a compression fitting, from here tubing leads to the pressure transducer. The pressure line may be varied to allow a burst disk or safety valve or it may be adapted for gas collection or pressurisation. A fourth thermocouple is normally sited on the outside wall of the bomb. The sample holder is normally spherical and of diameter 2.5cm. Usually it is made from titanium or Hastelloy C, a nickel alloy. This shown in Fig. 1 below

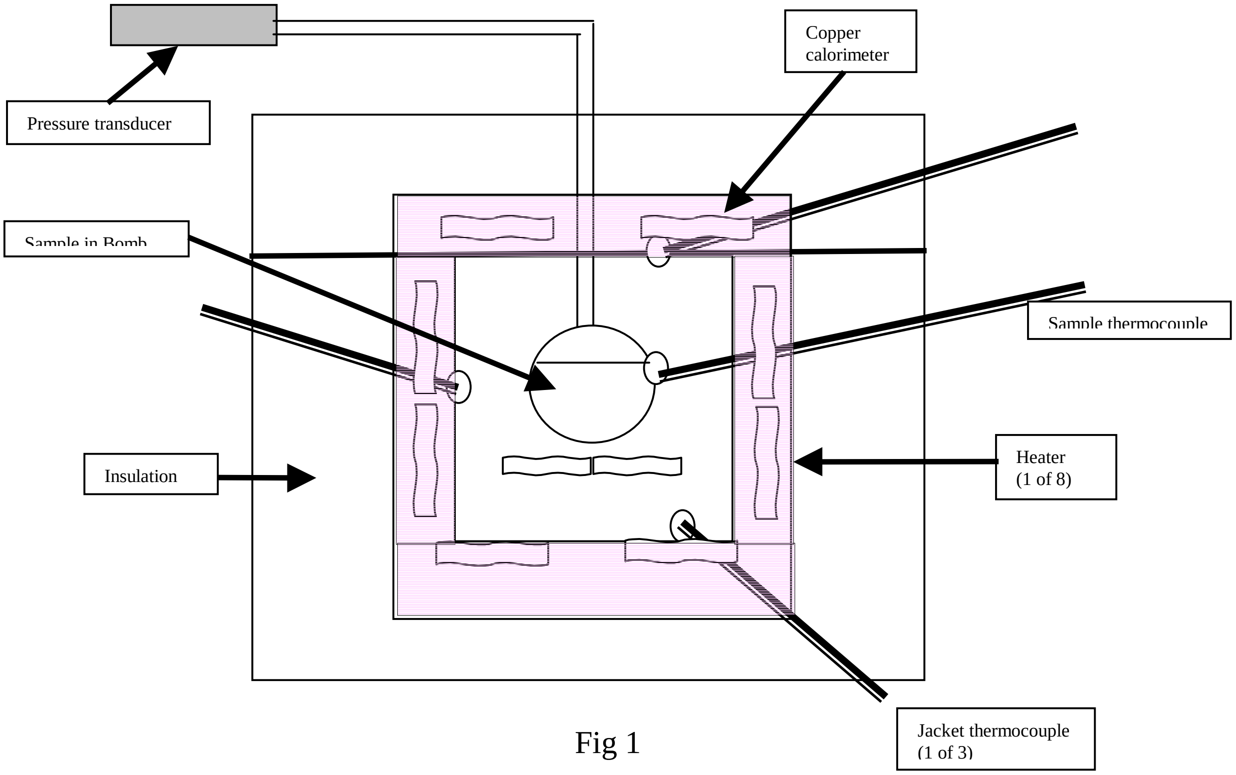


Fig 1

In use, the calorimeter and pressure transducer are housed in the containment vessel. This is an explosion proof container tough it is not a pressure vessel. The control electronics will control the experiment - i.e. the temperature of the calorimeter assembly. There is a PC that is the operator interface where the experimental conditions are input and the course of the experiment can be seen. This is shown in Fig. 2 overleaf.

Once the sample is in the bomb, this is connected to the lid and the lid is positioned on the lower section. The containment vessel is then shut and the experiment can begin

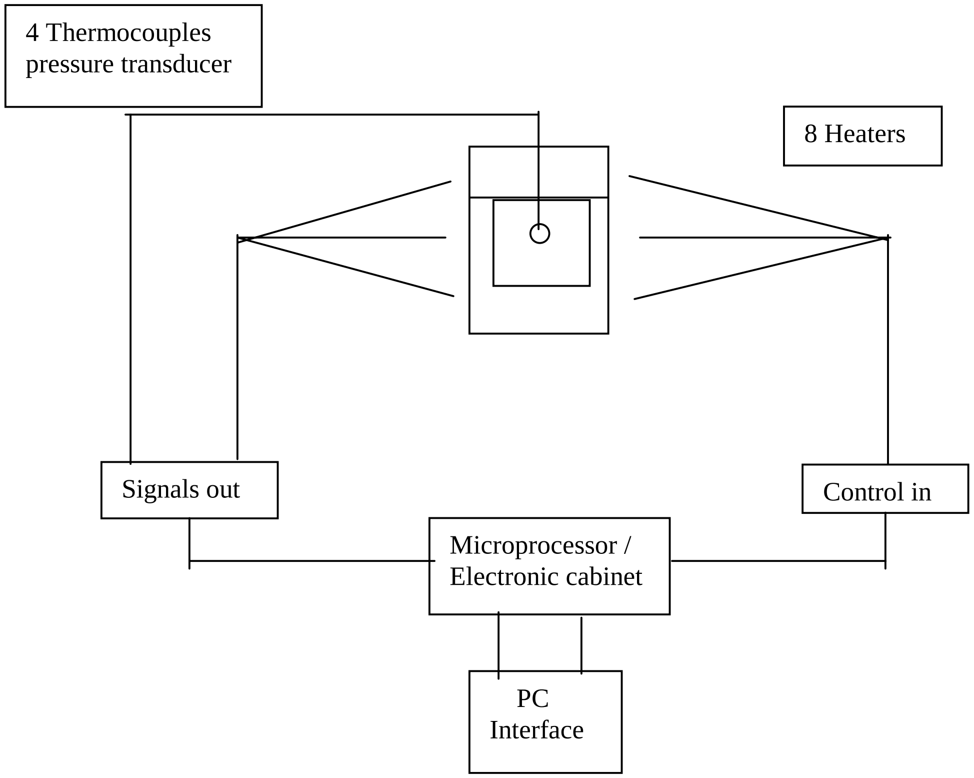


Fig. 2

For the test protocol a Start Temperature and an End Temperature must be specified, values for Heat Steps, Wait Time and Sensitivity (a self- heating rate above which exothermic reaction is defined) must also be selected. Typically, if nothing is known of the sample, the start and end temperature may be 50°C and 400°C, the heat steps 5°C centigrade the wait time 15 minutes and the sensitivity 0.02 °C/min. Therefore it is not difficult to define the experimental conditions, perhaps the only difficult decision is the amount of samples to use. Too little sample will mean too small reaction but too large sample may cause bomb rupture by a spontaneous explosive decomposition. The sample mass is important, and this should be considered with the type of bomb being used. In the test there will be heat lost to the bomb and this can be corrected by using the ϕ

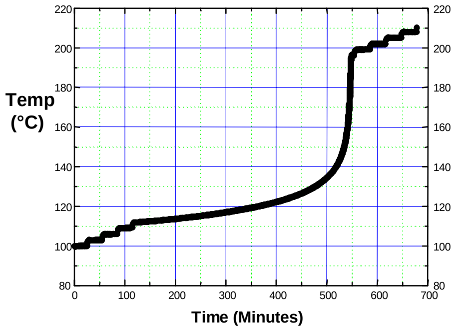
correction. THT Technical Information Sheet No 22 discusses this in detail. Setting up the test will take about 20 minutes.

The temperature range of the Accelerating Rate Calorimeter is 0-500°C, the pressure range 0-150 bars, though using other pressure transducers a wider range may be achieved. The samples mass usually will be a few grams of solid, liquid, slurry or mixture or the sample may be a reactive gas or gas-solid or gas-liquid.

At the start of the test, the system will be heated to the start temperature. Then during the wait time the system will come to isothermal equilibrium, the temperature differences between the bomb thermocouple and the three jacket thermocouples that control the three heated zones of the calorimeter will be reduced towards zero. Then there will be a seek period where should the temperature rise an exothermic reaction will be detected. If there is no temperature rise (greater than the selected sensitivity) the first small heat step will automatically occur. After this there will again be a wait time and a further seek period. This heat-wait-seek procedure will continue until an exothermic is determined detected. Detection is by a continuous temperature rise at a rate greater than the selected sensitivity. The system will enter the exothermic mode automatically and as the temperature of the bomb increases the calorimeter temperature will also increase, the system keeping the temperature differences between the sample bomb and a three separate calorimeter zones as small as possible. The system will continue in the exotherm mode until the self-heating rate decreases below the selective sensitivity, then the heat-wait-seek process will commence again. When the temperature reaches the end temperature the test will automatically terminate. There is an automatic cooling procedure whereby compressed air will cool the calorimeter to a chosen ‘Cool Temperature’. Throughout the test and until cool down the containment door cannot be opened.

During the test, data comprising time, temperature and pressure values will be stored at the user defined intervals. Of most use is the time temperature and pressure data relating to the exothermic reactions. However other data is useful, even the cooling data. Fig. 3 indicates data from a typical test.

Fig. 3.



After the test and cooling the containment door can be opened and the sample bomb removed. The operation of the Accelerating Rate Calorimeter is very simple and the total operator time for each test is typically less than one hour. In addition the amount of samples needed is small but representative.

The Accelerating Rate Calorimeter can use any type of sample, this may be made 100 milligrams of an explosive or 10 or more grams of a formulated detergent, it may be a pure chemical or sample mixture in solvent. Or for example it may be a residue from the bottom of a still. The sample may be a monomer or a slurry, it is possible to start with a high pressure of reactive or inert gas.

Over the past 20 years the Accelerating Rate Calorimeter has become established as the benchmark adiabatic safety system. There are systems in use in the majority of major chemical processing companies and pharmaceutical companies in the USA, in Europe and in Japan. There are systems also in use in South America, Africa, India and other S E Asian countries.

To summarise, the acceptance of the Accelerating Rate Calorimeter has been due not only to its high unrivalled adiabaticity which leads to excellent sensitivity and reliability and reproducibility of data but also its ease of use and its versatility with a large range of samples The acceptance has also been due to the uniformity of data, for example data obtained in one country will be the same as that obtained anywhere else in the world.

The exothermic data is a table of time, temperature and pressure columns. From this data it is possible to get simple plots of raw data but also data plots based upon calculation.

The raw data plots are:

- Temperature against time
- Pressure against time self-heating rate against time
- Pressure against temperature
- Self-heating rate against temperature
- Pressure rate against temperature
- Self-heating rate against pressure rate

Calculated plots (and tables of data) are available for

- Time to maximum rate against temperature
- Activation energy determination
- Kinetic modeling
- Thermodynamic heat of reaction determination

A set of data plots from di-Tertiary Butyl Peroxide is shown.   The temperature and pressure plotted against time are shown in Fig. 4 and Fig. 5. They show the

Fig. 4.

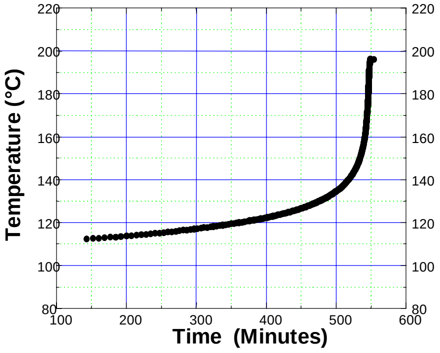
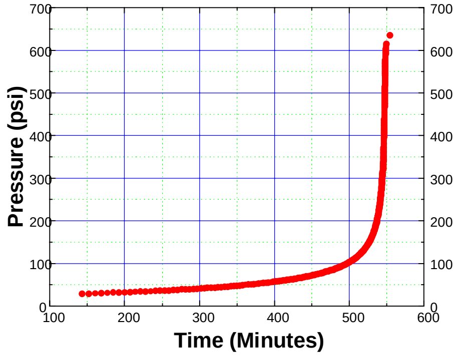


Fig. 5.



course of the reaction in real time. The onset of reaction, the end of reaction and the final pressure may be observed. However data presented this way does not reveal as clearly and as usefully as data presented in terms of self-heat rate and pressure rate plotted against temperature, Fig. 6 and Fig. 7.

Fig. 6.

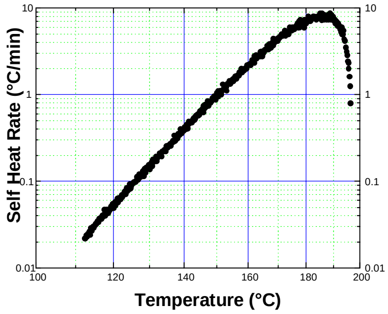
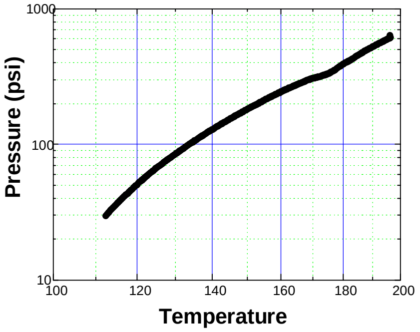


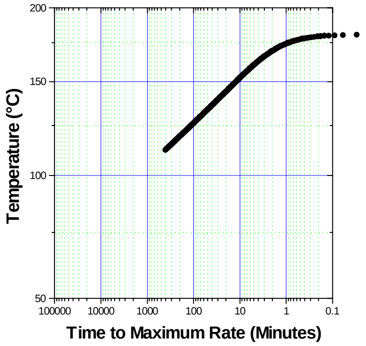
Fig. 7.



From the self-heat rate plot the onset is seen clearly, the heat rate at any temperature, the temperature of maximum rate and the type and number of reactions can be observed. Perhaps there are several overlapping reactions. The pressure rate plot clearly shows how the pressure develops. More detail of interpretation is given in THT Technical Information Sheet No 3.

The Time to Maximum Rate plot, Fig. 8, is a plot of temperature against the time that must elapse to get to the time when the self-heating rate is a maximum. This shows the 'Time to Explosion' at all temperature and is discussed in detail in THT Technical Information Sheet No 4.

Fig. 8.



Analysis of self-heat rate data and modeling the curve (if possible) will allow a full thermokinetic evaluation. THT Technical Information Sheet No 8, 9 and 20 detail this interpretation.

However it is clear that a single Accelerating Rate Calorimeter test produces data that in full analysis aims to answer many questions:

Is there a thermal hazard?
At what temperature does it begin?
Are there small low temperature reactions?
At each temperature, what is the self-heating rate?
What is the temperature of maximum self-heating?
What is the temperature of no return?
What is the time of explosion?
How many reactions, simple or complex?
How fast is the reaction (kinetics)?
How big is the reaction (thermodynamics)?
What pressure develops?
How rapid is the pressure rise?

Therefore....

How to optimise the process
How to keep control of the process
How to maximise process yields
How to regain control, if this is lost
How much time for corrective action
How much time for evacuation
Temperature to set alarms
Reaction rate, order, mechanism
Impurity catalyst inhibitor evaluation
Reactor design, heat exchanger info
Relief vent sizing

Ref 1. Townsend D I and Tou J C, Thermochimica Acta 37, 1 (1980).