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Technical Information Sheet No 7

Pressure Hazards: Application of Accelerating Rate Calorimetry Data

The interpretation of pressure data available from the Accelerating Rate Calorimeter has been an area until now that has not been fully exploited. In many publications pressure data has been presented, but this has been simply the illustration of raw pressure values. There has always been a lack of interpretation.

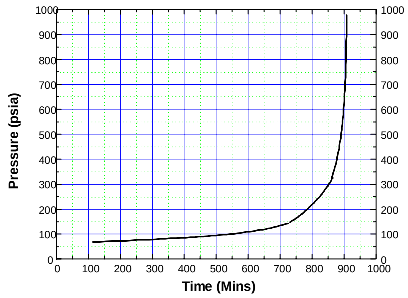
The majority of Accelerating Rate Calorimeter users have concentrated on the self-heat rate data and time to maximum rate data in their interpretation. However pressure information is of great concern in reaction engineering, to allow safe vessel design and to calculate vent requirements. It is of course the pressure and the pressure release that ultimately causes the damage which occurs in a runway reaction. The Thermal Hazard Technology Accelerating Rate Calorimeter will focus more in this area of data analysis.

However, it is simple to perform a qualitative analysis of the pressure data. Information gained might be

How big is the pressure rise?
Is the pressure rise associated with certain reactions?
Does the pressure rise occur at certain temperatures?
Is there pressure rise before the exothermic reaction?
What happens to the pressure on cooling?

It is a good idea to perform an accelerating rate calorimetry test at the ϕ of the real life situation, this is not as difficult to determine as it may appear. Similarly it is also a good idea to carry out the experiment with a sample volume to void volume in a similar proportion to that of the real-life situation to be simulated. In test results one can look for very rapid pressure rise, the rate of which outruns the self-heat rate, Fig. 1.

Fig. 1.



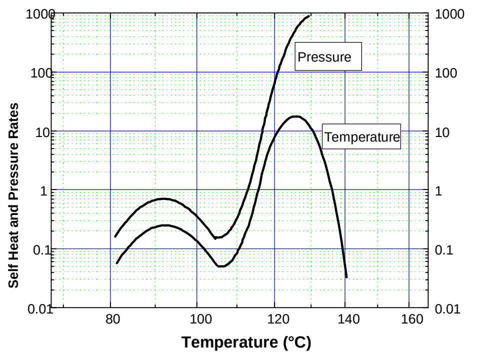
If ϕ simulation can be done, the pressure data becomes quantitative. Alternatively it is not difficult to normalise the pressure data to that of the real life situation. This can be done using the Thermal Hazard Technology software. In order to normalise the pressure data the void volume needs to be known in the test. This may be obtained by careful calculation or the system may be isolated, filled with liquid and the volume determined by weighing.

Assuming ideal gas laws the number of moles of gas formed per mole of reagent (N) is given by $N = \frac{P_f VD}{RMT_f}$. Where T_f and P_f are the final temperatures and pressures, D is the molecular weight and M the mass. R is the universal gas constant.

However in tests there may be error in the pressure data. There may be condensation in the pressure line above the heated zone of the calorimeter, there may be dissolution of gas in the silicone oil which is used to reduce the void volume. To overcome these, Thermal Hazard Technology can provide side-branch pressure tubes, minimising the cold void volume.

Although there have been no publications in this area, pressure data may be used to determine kinetics parameters. Simple reactions with a single reaction mechanism will give a pressure rate rise just as they do a self-heat rate rise which is related to the loss of concentration of reactant, Fig. 2.

Fig. 2.



Complications would arise if samples were tested in solution. For samples tested in solution, there is a competing pressure rise from the vapour pressure of the solvent and that of the gaseous products, which results from the reaction. Tests with DTBP/toluene reported in THT Technical Information Sheet No. 23, show similar pressure rises for different DTBP concentrations, the result indicating that when gaseous products of decomposition of DTBP are formed, there is an equal reduction in toluene vapour partial pressure.

A further aspect of the pressure hazard relates to the nature of the gaseous species that are produced. They may be flammable, flammable, flammable, toxic even explosive. Thermal Hazard Technology can provide pressure collection systems to allow analysis of gas produced and can provide a gas scrubber unit for the safe release of gaseous products.

But more detailed analysis of the pressure generation can be done to allow vent sizing determination. This requires specific tests to be carried out and to do this a "vent size option" is also available from Thermal Hazard Technology. Specific tests have to be carried out to do vent sizing. These are detailed in separate documentation.