thermal hazard technology

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Technical Information Sheet No 21

Heat Losses and Errors in Accelerating Rate Calorimetry

Heat losses in the Accelerating Rate Calorimeter may be divided into two types. Heat lost into the bomb (the phi correction) and heat lost from the bomb. The latter, the ϕ correction is discussed in detail in THT Technical Information Sheets No 22, 23, 24.

In the Accelerating Rate Calorimeter, the ϕ correction is the only correction necessary to carried out with the sample data to get excellent adiabatic data. In experiments a full simulation of the potentially undesired chemical reaction is carried out. When this is done under conditions which do not lead to self-heating rates so high that the accurate tracking or following of the bomb/sample by the calorimeter is lost there are no errors in the data. There is a limit of maximum heating of the calorimeter and of course if the self-heating of the sample/bomb exceed this, then there is a divergence in temperature and the possibility of heat loss from the sample/bomb system. Ie a loss of operational adiabaticity.

Heat lost from the sample bomb and heat transfer along the stem of the bomb were comprehensively evaluated prior to the launch of the Accelerating Rate Calorimeter. Much work was done within Dow Chemical and calculations showed that heat loss must be less than 0.001°C/min (Ref 1).

When tests are carried out at lower ϕ the reaction may proceed at rates above 50°C/min where significant heat loss could occur. The rate may further accelerate and then may rapidly shoot up to 100 - 1000 °C/min, indicating a spontaneous, explosive type decomposition. The Accelerating Rate Calorimeter data may be similar to that shown in Fig. 1, Fig. 2 and Fig. 3.

Fig. 1.

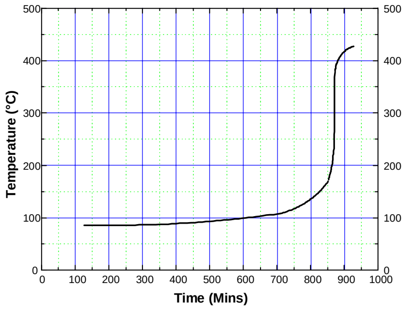


Fig. 2.

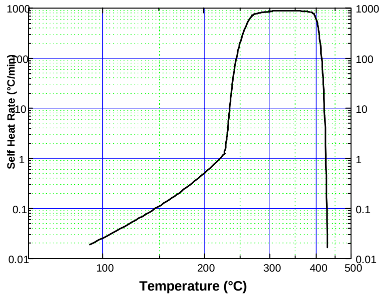
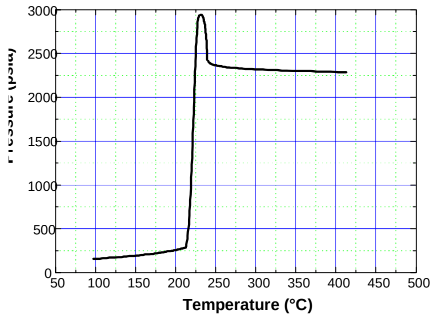


Fig. 3.



At a temperature above 200°C the rate suddenly increases. The effect may be very large or may not be easy to discern.

However at this temperature /time/ pressure there has been a spontaneous reaction, the reaction being completed in perhaps just a few micro seconds. The temperature data above this is simply an artefact of the heat transfer through and out of the system to the rather slow responding thermocouple. The temperature rise may take 1-2 minutes. The rate then becomes negative and a heat step will occur.

The fact that the reaction is over exceedingly rapidly is shown much more clearly in the pressure data. Assuming there is no bomb rupture at this point and this is quite likely, the pressure will show a pressure wave. The pressure will rise to a maximum in a few seconds and the pressure will then fall over a period of perhaps one minute. This is caused by the pressure wave impacting on the pressure transducer measuring surface and also by some gas dissolution in the silicone oil which hopefully is present and occupies some void volume not just to reduce the head space but also to protect the pressure transducer itself. What actually happens in the system is illustrated in Fig. 4 and Fig. 5 below.

Fig. 4.

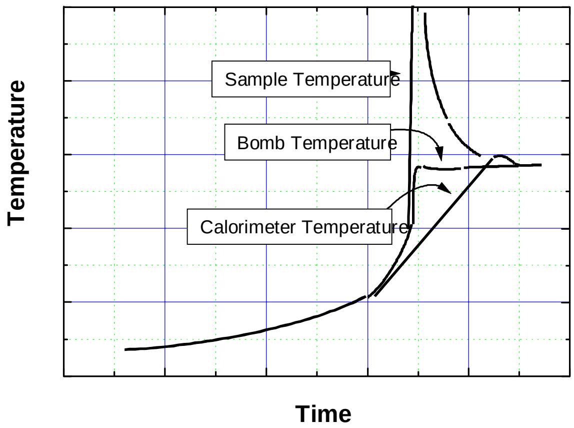
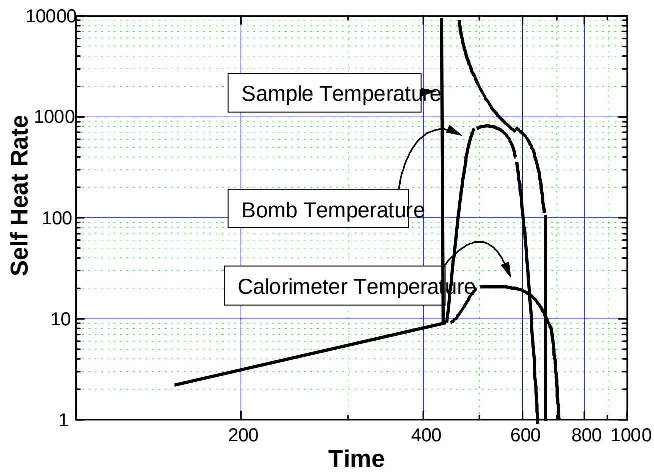


Fig. 5.



Such tests will certainly lead to serious under prediction of heat of reaction, they may lead to bomb rupture and can even destroy the pressure transducer. Therefore in setting up conditions for an Accelerating Rate Calorimeter test, the reason for the test and purpose of the data must be considered very carefully such that not too much sample is used and such a spontaneous reaction occurs. Only then will the best performance of the instrument be produced but also the best data will be obtained.