

## Technical Information Sheet No 22

### The $\phi$ (Phi) Correction in Accelerating Rate Calorimetry

#### Adiabaticity

By definition an adiabatic environment is one in which enthalpy is neither lost from or given to a sample. Therefore when reactions that cause an enthalpy rise in the sample in such an environment (an exothermic event) this heat will be contained within the material and its temperature will rise.

In the chemical industry, during processing, storage or transportation, the large quantities of materials used are such that the environment in which the material is contained may be close to the adiabatic state. The larger the volume, the more adiabatic the system would usually be. There is less potential heat loss to the environment.

To investigate runaway exothermic reactions, which have all too often occurred with such major consequences, an adiabatic calorimeter is very often used. The popular adiabatic calorimeter being the Accelerating Rate Calorimeter. Investigations may be to prevent runaway reaction, to investigate a runaway reaction or to give information to aid process optimisation or as part of a hazard or safety assessment.

Adiabatic calorimetry aims to simulate what may happen on a large scale by testing a small sample in an 'adiabatic environment'. In this respect an adiabatic calorimeter is very different from a DSC. Adiabatic calorimetry data being a simulation will give data that may be directly used for any real life scenario.

However the adiabatic environment is a theoretical state, in laboratory scale testing this cannot be obtained but may only be approached. Deviation from the fully adiabatic state comes from two sources:

(1) The thermal inertia of the test system or heat lost into the sample container, which causes 'thermal dilution'. The sample must be held in a container and it is the container + sample which is held in the adiabatic environment.

(2) The loss of heat from the container itself to the environment. This reflects the 'operational adiabaticity' of the instrument and is a result of inherent design limitations.

Both errors need to be known (or minimised to a level of insignificance) and corrected for if data is to be called adiabatic. The thermal dilution can be compensated for by correction with the so-called  $\phi$ -factor. The  $\phi$ -factor is the same as the 'water equivalent' calculation carried out in bomb calorimetry. The error caused by operational adiabaticity is usually overlooked, but is a very major cause of error in some instruments, this will be discussed later.

#### Definition and Derivation of the Thermal Inertia, $\phi$ -factor

In an adiabatic experiment a sample is held in a container and there is at all times thermal equilibrium. The temperature rise observed at the container is then proportional to the temperature rise which would have been observed in the sample if no heat was lost into the container, this is the fully adiabatic 'containerless situation' or infinite sample state.  $\phi$ ,  $\phi$ , is a constant of proportionality.

$$\Delta T_{ad} \propto (\Delta T_{ad})_{sys}$$

$$\Delta T_{ad} = \phi (\Delta T_{ad})_{sys}$$

$$\phi = \Delta T_{ad} / (\Delta T_{ad})_{sys}$$

The minimum value of  $\phi$  for the fully adiabatic state is thus 1 and the larger the value of

$\phi$ , the smaller the temperature rise, measured.

*But it is important to appreciate that  $\phi$  is a correction factor, it does not relate to or define the adiabaticity of the experiment.*

To derive an expression to enable  $\phi$  to be calculated, the total heat energy generated,  $Q$ , must be considered,  $Q$  is the product of mass, specific heat and adiabatic temperature rise. In an adiabatic system without a container all the exothermic heat energy,  $Q$ , goes to produce the 'theoretical' sample adiabatic temperature rise according to the equation:

$$Q = M_s C_{ps} \Delta T_{ad}$$

In a test where the sample is held in a container but with a fully operationally adiabatic environment all the energy,  $Q$ , goes to heat the sample-container system thus:

$$Q = M_{sys} C_{psys} (\Delta T_{ad})_{sys}$$

This may be expanded to:

$$Q = [(MC_p)_s + (MC_p)_b] (\Delta T_{ad})_{sys}$$

(The subscript sys indicates system; s sample, and b sample container or bomb.)

The equation is only valid if there is thermal equilibrium within the bomb and sample system, i.e. they both show the same rise in temperature,  $(\Delta T_{ad})_{sys}$ . Equating these, we have;

$$M_s C_{ps} \Delta T_{ad} = (M_s C_{ps} + M_b C_{pb}) (\Delta T_{ad})_{sys}$$

or 
$$\Delta T_{ad} / (\Delta T_{ad})_{sys} = (M_s C_{ps} + M_b C_{pb}) / M_s C_{ps}$$

Therefore  $\phi$  by definition is given by:

$$\phi = 1 + (M_b C_{pb} / M_s C_{ps})$$

### The Effect of $\phi$ on Experimental Data.

By definition,  $\phi = 1$  must represent a containerless, 100% adiabatic system and thus is a theoretical limit, unless heat is added to a situation which could be the case in a fire scenario. If, for example,  $\phi = 2$ , the thermal capacity of the bomb equals that of the sample and therefore only 50% of the containerless adiabatic temperature rise would be measured. The greater the value of  $\phi$  the larger this correction and the smaller the observed temperature rise.

The advantage of a low  $\phi$  is that there will be little thermal dilution and the experiment may be carried out at conditions near those encountered in real-life. The effect of  $\phi$  will be to reduce the magnitude of the adiabatic temperature rise and the self-heat rate at any temperature and the time to maximum rate at any temperature will be increased, *but by simple mathematical correction the effect of  $\phi$  may be removed.*

$\phi$  may influence a test and thus can play an important role in determining experimental conditions such that most appropriate data may be obtained. Consider testing of a highly exothermic material with a low  $\phi$ . This will cause the reaction to proceed with very fast self-heat values. With the thermal insulation necessary, an adiabatic calorimeter can not 'track' or follow self-heating above a certain rate, at self-heat rates above this limit some heat will be lost from the bomb and the calorimeter will not be operationally adiabatic. Indeed there will not be thermal equilibrium in the sample. In such a test, resulting thermodynamic parameters will be greatly underestimated.

With a low  $\phi$ , reliable onset and stability data may be obtained together with information important to storage situations. Also good Time to Maximum Rate data will be obtained. However, the full reaction may not be followed because maximum self-heat rates may exceed the maximum tracking capability of the calorimeter itself.

At a higher  $\phi$ , however, the reaction may be followed through its entirety, and high quality thermodynamic data will be obtained. However, larger correction will be needed, onset of self-heating is likely to be at a higher temperature and pressure data will be reduced in magnitude.

Before carrying out a thermal hazard evaluation experiment with an adiabatic calorimeter, therefore, the reactivity of the sample should be assessed. Also an understanding of what are the most important requirements from the test data must be agreed. This will lead to proper selection of experimental conditions and the versatility of the Accelerating Rate Calorimeter can be exploited.

It is therefore very important and useful to be able to vary  $\phi$  over a reasonable range for a particular sample. But the most important consideration is to *know that the sample and bomb are in thermal equilibrium* and to know that the system is in an operationally adiabatic environment.

#### The Accelerating Rate Calorimeter and Effect of $\phi$ .

During the development of the Accelerating Rate Calorimeter it was considered that the critical design principle was that the sample/bomb system had to be controlled in a very highly adiabatic environment, i.e. to obtain as good an operational adiabaticity as is achievable. By inspecting or recording the bomb-to-jacket temperature difference, during operation the Accelerating Rate Calorimeter can be seen to control to a temperature difference between calorimeter and sample-container to be hundredth's of a degree centigrade. It is this strict control which defines the Accelerating Rate Calorimeter's excellent operational adiabaticity and with this ability the instrument can be operated successfully over a range of  $\phi$  values.

Where possible, experiments would be carried out with a  $\phi$  value between 1.2 and 2.0 because this is the  $\phi$  range which occurs in real life situations. Using the standard sample containers Table 1 indicates that a  $\phi$  below 1.1 could be achieved, dependent upon sample density and specific heat, but as Fig. 1 indicates the correction for  $\phi = 1.2$  to  $\phi = 1.0$  is small and little advantage is to be gained trying to work at any lower  $\phi$ . Indeed, there are disadvantages in terms of heat transfer and with reaction at very fast self-heat rates as discussed earlier. However Thermal Hazard Technology have developed low- $\phi$  sample containers to allow specific experiments to be carried out at  $\phi$  values below 1.1.

Importantly, the opportunity that the Accelerating Rate Calorimeter provides to operate successfully with  $\phi$  above 2 is often very useful. Highly reactive materials, expensive research products or accident investigation often restrict the amount of sample that it is prudent or possible to use.

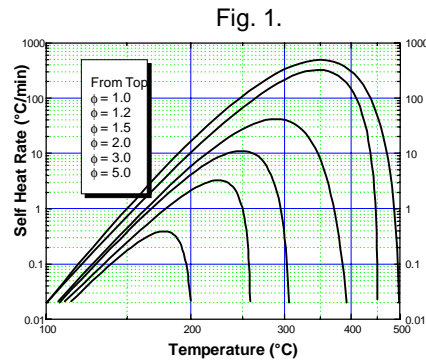


Fig. 1 shows self-heat rate curves constructed for a hypothetical reaction at represented at various values of  $\phi$  and thus the effect of  $\phi$  on the data, differences below  $\phi=1.2$  are small.

Table 1. Phi Calculations for a Range of Experimental Conditions.

Sample Mass (g)	Titanium 4g <sup>(1)</sup>		Titanium 8g <sup>(2)</sup>		Hastelloy 16g <sup>(3)</sup>	
	0.5*	0.25*	0.5*	0.25*	0.5*	0.25*
1	2.04	3.08	3.08	5.16	4.20	7.40
2	1.52	2.04	2.04	3.08	2.60	4.20
4	1.26	1.52	1.52	2.04	1.80	2.60
6	1.17	1.35	1.35	1.69	1.53	2.06
8	1.13	1.26	1.26	1.52	1.40	1.80
10	1.10	1.21	1.21	1.42	1.32	1.64

(1) Lightweight titanium bomb (2) Regular titanium bomb (3) Regular Hastelloy bomb

\* Specific heat in cal/g°C 0.5 = Organic liquids, 0.25 = Solids.

#### Operational Adiabaticity of the Accelerating Rate Calorimeter and Other Calorimeters.

Without knowledge of operational adiabaticity, the reliability of the data produced would not be known. Thus in tests it is vital to monitor and know all differences between the sample container and the environment, if necessary corrections ought to be made.

In the Accelerating Rate Calorimeter, such differences are measured and may be recorded. In normal operation the temperature differences are so close to zero that the small error is normally negligible. However other calorimeters do not perform so well.

Low  $\phi$ , vent sizing calorimeters have been criticised for poor operational adiabaticity which is not accurately known and cannot be compensated or corrected. There have been reports of temperature differences in the order of 1-2°C in vent sizing calorimeters and these are known to have major heat loss at higher temperatures by reflux on the lid of the sample container. In addition such instruments utilize a pressure equalisation system

which means large volume of gas, often at room temperature, is added to the calorimeter during the test, a further cause of error in the operational adiabaticity of the system.

The better the operational adiabaticity, the smaller the sample size which may be reliably used. Indeed, only when a system has such adiabaticity as the Accelerating Rate Calorimeter can a sample size of a few grams be reliably used.

### Sensitivity and Adiabaticity, the Accelerating Rate Calorimeter and Other Calorimeters.

Sensitivity and adiabaticity go hand in hand. A poorly adiabatic system must be used at lower sensitivity than a system of high adiabaticity and such a system would require larger samples and it would detect onset at a relatively high self-heat rate, almost irrespective of  $\phi$ . In contrast to other instruments the Accelerating Rate Calorimeter's high operational adiabaticity combined with its sensitivity allows small samples to be tested reliably and in safety.

The result of this may be seen in Fig. 2. An Accelerating Rate Calorimeter test, detecting onset of exothermicity at  $0.02^{\circ}\text{C}/\text{min}$ , would show reaction starting in the range  $50\text{-}60^{\circ}\text{C}$ , dependent upon the  $\phi$  used. Now consider a system which detects at  $0.2^{\circ}\text{C}/\text{min}$ ; even if  $\phi$  was 1.0 with this instrument, onset of exothermicity would not be recorded until  $88^{\circ}\text{C}$ ! Even an Accelerating Rate Calorimeter test with  $\phi = 5$  shows an onset at  $75^{\circ}\text{C}$ .

Detecting at a lower sensitivity (at a rate of say,  $0.2^{\circ}\text{C}/\text{min}$ ) has other limitations. These are highlighted in Fig. 2.



Fig. 2.

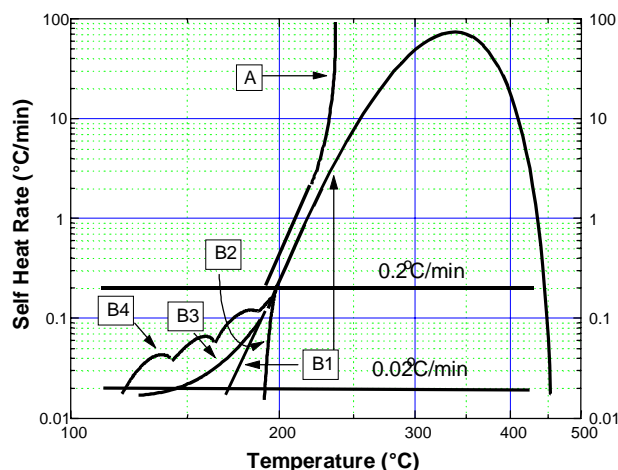


Fig. 2 shows data as given in Fig. 1 but Curve A showing reaction at  $\phi = 1$ , recorded from  $0.2^{\circ}\text{C}/\text{min}$ , Curves B illustrates alternatives as may be recorded from  $0.02^{\circ}\text{C}/\text{min}$ .  
B1 = Arrhenius reaction, B2 = autocatalytic reaction, B3 = trigger reaction,  
B4 = initial low exothermicity reaction.

It can be seen that detecting at a lower rate means that early information and data that may be vital is not recorded, detection. of autocatalysis (curve B2) or a trigger mechanism (curve B3) in the early stages of the reaction may be missed, even a complete, low exothermicity reaction (curve B4) may not be recorded. In addition to missing what could be considered to be the most important region of data, a test with detection at  $0.2^{\circ}\text{C}/\text{min}$  would not take long to complete. As such the time base of the data may well be insufficient to yield time to maximum rate information.

Because the Accelerating Rate Calorimeter is capable of using relatively small samples, reliable data may be obtained with solid samples. In contrast, techniques requiring larger samples might allow intolerably large temperature gradients within such samples because of their poor heat transfer properties or testing may have to be done in suspension using an inert liquid. Of course this raises the true  $\phi$  of the test to a very large value since the inert liquid simply acts as a heat absorber!