thermal hazard technology

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Technical Information Sheet No 1

Hazards, the Safety of Reactive Chemicals & Adiabatic Calorimetry

The chemical industry has become a more and more hazardous environment. Since the 1950's the chemical industry has made larger quantities of more dangerous and more reactive materials. There has been a huge increase in the number of different chemicals produced and in addition, there has been the need to produce these materials both faster and cheaper.

However, there have always been dangers with chemical production. Years ago the chemical products manufactured were inorganic and coal-based and most incidents were with the manufacture of explosives. By the 20th century chemical production was beginning on a large scale, and perhaps the worst and well-known accident occurred in Germany in 1921 when an explosion left 509 people dead. This was an explosion of 4500 tons of fertiliser which was being blasted with dynamite. This may now seem not a good idea, but the process had been carried out 30,000 times without incident.

A great change occurred in the 1950's and 1960's. The chemical processing industry was using oil as the basic feed stock and this led to the great diversity of chemical production. The larger companies recognised the hazards and, since commercial equipment was not available, developed their own in-house tests for safety. Instrumental techniques for testing safety were crude or inappropriate.

There are various hazards associated with chemicals: flammability, oxidation, toxicity, shock and friction sensitivity, dust explosions and, of course, self-heating. In addition, these hazards may be caused by many problems: equipment failure, poor material evaluation, mis-charging of materials, bad process design, lack of process knowledge etc. The hazard may result from the intended reaction, in distillation, drying, mixing or the hazard may be in storage and transportation, or as is often the case, there may be an unintentional reaction. Self-heating is a major hazard in the chemical industry, and assessment of reactive chemical hazards is the area of adiabatic calorimetry because uniquely this allows a safe simulation of the hazard using laboratory scale testing.

Self-heating is unique in that the energy involved is solely available from the material, chemical or chemicals themselves. No other species is required. Also when self-heating occurs the whole of the mass increases in temperature at a uniform rate. Of course, many reactions required in the chemical industry release energy though most reactions release energy that is easily dissipated.

A reaction that gives out heat is called an exothermic reaction. Self-heating occurs with a temperature rise if the heat produced is not removed. Early methods used to assess self-heating included simple oven tests, tests with vacuum containers, or Dewar flasks and differential thermal analysis (DTA). It was because these techniques were considered restrictive, that some large companies designed and developed their own test equipment. What was needed was to simulate on the small (but safe) laboratory scale what can happen on the large industrial scale (reactions which may be processing, storage or transportation). What was required was an adiabatic calorimeter. The calorimeter measures heat and an adiabatic environment is one where no heat is lost (or gained) from the sample.

In an adiabatic calorimeter the data may be extrapolated from the small scale to any larger real-life scale.

During the 1970’s Dow Chemical in Midland, Michigan, USA developed an adiabatic calorimeter. This they called the Accelerating Rate Calorimeter (in introduction to accelerating rate calorimetry is given in THT Technical Information Sheet No 2). But in

1975 there was an incident in England and as a result it was concluded that the Accelerating Rate Calorimeter should be used widely within Dow Chemical, and thus this technique was made commercially available. In the incident report from the UK Health and Safety Executive of 1976, there is the first mention of the Accelerating Rate Calorimeter and the first result is published. Assessment of the safety of chemicals or chemical reactions must involve many areas of investigation. There may be several potential hazards with the material, chemical or with the chemical process. If there are flammability, oxidation or sensitivity problems these would be investigated by techniques designed for this purpose. Information on the equipment to be used for processing or storage must be obtained and finally a hazard and operability study of the full process.

Thus a large range of practical tests and investigation needs to be carried out. Their description outside the scope of this document.

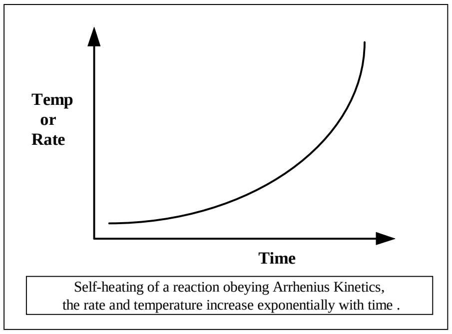
To evaluate the potential pressure and thermal hazard of the substance, its risk of runaway, again a number of investigations will be necessary, not just accelerating rate calorimetry.

Initial investigation of the safety or hazard potential may be gained from non-experimental investigation. This may be a literature search or by using a hazard rating scheme. Two such schemes are CHETAH and the Reaction Hazard Index. Hazard rating schemes have value but limitations. Many assumptions are made. The CHETAH programme is purely thermodynamic and the Reaction Hazard Index links thermodynamics and kinetics. After this, screening tests may be used to quickly gain an insight into exothermic reactions. For example, DSC with closed pans and other in-house tests may be carried out to study the hazard. After this adiabatic calorimetry testing would be carried out to give a full simulation of the hazard and the data of time, temperature and pressure analysed fully. The adiabatic calorimetry data would allow onset of reaction to be easily determined. The magnitude of the hazard, the number of reactions (whether it was a simple or complex process), the speed of rise of the reaction, the reaction rate at any temperature, the time to maximum rate and all associated pressure information. The latter is important because it is the pressure that causes the explosion. If the exothermic reaction is simple, it will be easier to get a full thermokinetic evaluation. By comparing the adiabatic calorimetry data with the information on the process vessel, it will be possible to get information specifically for real-life optimisation e.g., maximum safe temperature or maximum safe size. However, a strategy for testing of self-heating hazards is normally employed. This is discussed in more detail in THT Technical Information Sheet No 30.

Many self-heating exothermic reactions are easily controlled. They are often necessary to initiate a chemical reaction. The hazard potential is described by the speed of the reaction, the kinetics and the amount of energy released, the thermodynamics.

When a thermal energy starts the heat generated is greater than the heat loss. The system is past its ‘temperature of no return’. The heat generation is a property of the material; the heat loss is a property of the vessel. The latter will change depending on ambient temperature and other considerations.

An elegant way to visualise runway reactions is in the plots often referred to as Semenov plots, since the mathematics of Semenov theory of adiabatic reactions is essentially illustrated.
Fig. 1 and Fig. 2 illustrate how the rate of a reaction varies with temperature or time if the situation is adiabatic. The rate increases exponentially as described in the Arrhenius theory. But the heat loss from the vessel, Fig. 3, will increase linearly with temperature

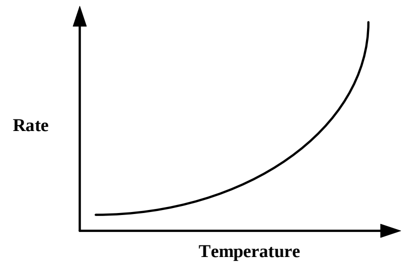


Self-heating of a reaction obeying Arrhenius Kinetics,
the rate and temperature increase exponentially with time .

Fig 1.

Linking these, Fig. 4 for example, this material in this vessel would have an equilibrium temperature at A. If the material was charged into the vessel at any temperature below T, the temperature would fall to A.

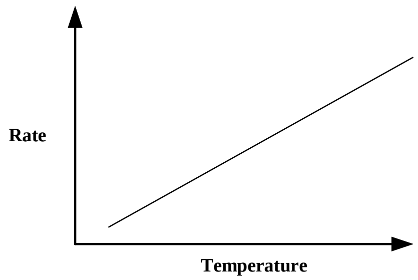
Filling at any temperature above T will lead to runaway and possibly explosion.



Self-heating of a reaction obeying Arrhenius Kinetics, the rate increases exponentially with temperature.

Fig. 2

But the same vessel may be subjected to another ambient temperature. In Fig. 5 it is shown that the heat loss line will move in a parallel direction. As the ambient temperature increases, the equilibrium temperature increases and the maximum safe temperature decreases. If the ambient temperature rises to B, both temperatures are the same and this critical equilibrium temperature is called the 'Temperature of No Return'.

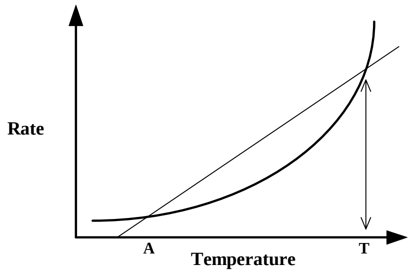


Heat loss from a vessel, the rate increases linearly with temperature.

Fig. 3

The temperature B is called the self- accelerating decomposition temperature, SADT.

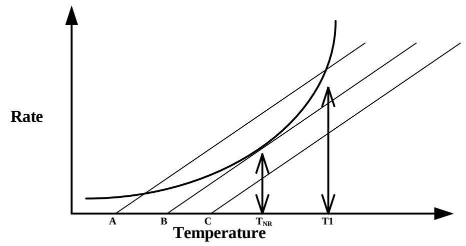
At temperatures above B this mass of sample is not safe in this vessel. This therefore defines the maximum safe storage temperature or critical operating temperature.



Self-heating of a reaction and heat loss from a vessel . Temp A is the equilibrium temperature, temp T is the max safe temperature.

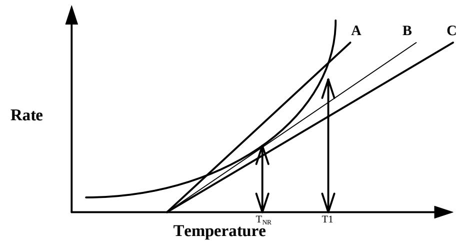
Fig. 4

In Fig. 6, 3 vessels A, B and C are considered they are illustrated at the same ambient temperature. Vessel B can lose less heat than A, and C less than B. Maybe C is better insulated or it is larger. Alternatively A might be a storage drum, B might be a 2 dimensional packing of drums and C a 3 dimensional packing. Quite simply as the vessel or scenario becomes more adiabatic its heat loss line swings and the equilibrium temperature increases and the maximum safe temperature decreases until again the critical temperature of no return is reached. This illustrates the. maximum pack size or critical radius of vessel that may be used.



Self-heating of a reaction and heat loss from a vessel, at 3 ambient temps, A, B and C. A can control the sample to temp T1, B is at the critical temperature T_{NR} and C cannot control the thermal runaway.

Fig. 5



Self-heating of a reaction and heat loss from 3 vessels, A, B and C. A can control the sample to temp T1, B is at the critical temperature T_{NR} and C cannot control the thermal runaway.

Fig. 6