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THE ARC IN CHEMICAL HAZARD EVALUATION

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ABSTRACT

The ARC studies the decomposition of compounds under fully adiabatic conditions in a sealed bomb. Data relating temperature pressure and time is generated. This paper describes the application of this instrument to hazard evaluation in a medium-sized company manufacturing organic chemicals.

INTRODUCTION

In a relatively short time the ARC has become one of the most useful diagnostic methods for the determination of thermal stability and other reaction parameters. Users range from chemical producers to weapons manufacturers.

Thermal stability testing need not be restricted to materials that are to be heated directly as part of a chemical reaction. Peripheral operations such as drying, distillation, milling and even shipment to hot countries must all be considered as potential initiators of uncontrollable decomposition reactions.

THE ACCELERATING RATE CALORIMETER

The design of the ARC is by now quite familiar. Its important features are summarised in Fig 1. The sample is contained in a small spherical bomb of titanium or hastalloy that has an approximate capacity of 10g. This is connected, by capillary tubing, to a pressure transducer reading to 2500 psi. The bomb is suspended inside a heavy vessel of nickel plated copper that has heaters and thermocouples in its bottom, side and top. The vessel temperature is always controlled in order to create conditions of no heat loss from the bomb. A run is normally carried out by a step-wise temperature programme the parameters of which are all user variable.

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At each step the instrument waits to see if any self-heating is detected before proceeding to the next set point. When self-heating in excess of 0.02°C/min is detected the instrument follows the rise whilst recording the elapsed time, temperature and pressure at set intervals of 1°C.

TIME TO MAXIMUM RATE PLOT

One of the most useful relationships is that between the sample temperature and the time taken to reach a maximum rate of decomposition where:

$$\text{Time to max. rate} = \frac{RT^2C}{E_a \; H_R k_T} \qquad (1)$$

C = Specific heat, Ea = Arnhenius activation energy,
H_R = Heat of reaction, k_T = Rate constant

A good straight line is normally obtained of I/T versus time to maximum rate for the early part of an exotherm (see Fig 2).

This plot is readily understood by people with no knowledge of the ARC. It gives a clear indication of the temperature of first exotherm and of the increase in temperature required for decomposition to become rapid. It is possible, therefore, to set temperature alarms on reactor vessels at levels which give good operability to the process yet still give sufficient time for corrective measures to be taken.

FIG 1

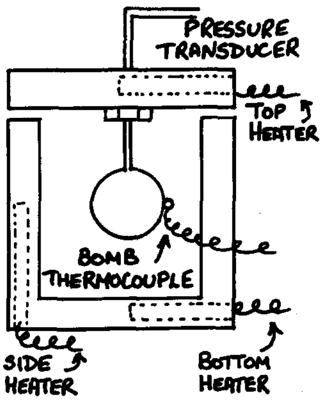
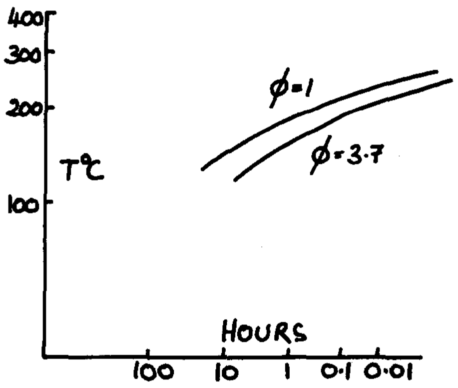


FIG 2



As long as reasonable care is taken the experimental data can be extrapolated in order to decide on safe storage temperatures. This is particularly important for materials that are stored in bulk in the molten state. Fig 2 shows the data from an aromatic polybromo-compound that was to be vacuum distilled. Decomposition begins at 145°C but extrapolation suggests that 48h stability can only be obtained at 115°C. Seven day stability requires temperatures below 105°C. Our approach was, therefore, to install a microprocessor which automatically limited the time that the distillation vessel could spend in excess of 120°C to 16 hours. After this time a mandatory instruction ensured that the vessel contents were cooled to below 105°C and ultimately destroyed.

AUTOCATALYSIS

It is important to identify this behaviour at the outset as it can lead to misleading judgements about a materials stability. Fortunately autocatalysis is typified by a lag-phase whilst the catalyst, a decomposition or reaction product, reaches the required concentration. In cases of autocatalysis the thermal history of a compound plays a very important part in deciding its decomposition behaviour. Fig 3 shows the effect of autocatalysis on the time to maximum rate plot. In such cases it is best to perform isothermal runs at various temperatures around the point of interest. In this way the highest temperature which gives extended stability can be directly observed and not obtained from extrapolation.

FIG 3

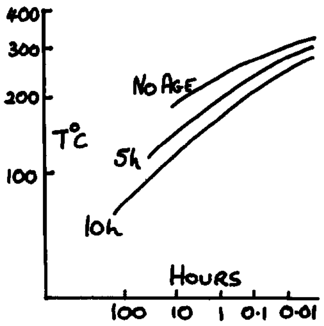
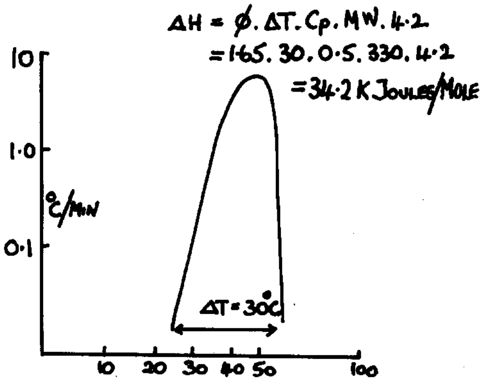


FIG 4



HEAT OF REACTION

This is often quite simply performed by the use of the ARC. However three prerequisites must be satisfied.

1. It must be possible to prevent reaction by cooling in order to allow all reactants to be charged to the bomb.
2. The reaction must be homogeneous (unless stirring option is available).
3. The reaction must be exothermic.

Using the established practise of equating temperature change with concentration change the following relationship is obtained:

$$\phi \times \Delta T = \frac{\Delta H}{Cp} \qquad (2)$$

Where ϕ = Thermal dilution factor of bomb, ΔT = Temperature change ΔH = Heat of reaction, Cp = Heat capacity.

From this equation the value of ΔH can be calculated using data from the plot of self heat rate against temperature. This is the fundamental plot performed by the ARC. An example of data from an aromatic bromination is shown in Fig 4. The ARC gives a summation of all heat producing phenomena which is particularly useful to the chemical engineer. Moreover it is possible to judge at what stages of the reaction most heat is produced.

CONCLUSION

The aim of this paper has been to briefly demonstrate some of the uses of the ARC. There are, of course, many more. One area in particular is the calculation of emergency vent sizes from the pressure versus time data. As the instrument is adiabatic its results always represent the worst case scenario. This is important as the intention of our hazard evaluation work is to design processes which are intrinsically safe.

The instrument is somewhat slow compared to other methods such as DSC and Sikarex and it does require a reasonable level of interpretation skill. It is, though, very accurate and when properly calibrated gives results which are highly reproducible.

REFERENCES

1 Smith, D.W., Chemical Engineering, Dec 13, 1982.
2 ASTM DS 51 The ASTM Chemical thermodynamic and energy release evaluation program 1974.