Thermochimica Acta, 226 (1993) 211–220
Elsevier Science Publishers B.V., Amsterdam

Reliable scale-up of thermal hazards data using the PHI-TEC II calorimeter[1]

Jasbir Singh

Hazard Evaluation Laboratory Ltd., Fire Research Station Site, Melrose Avenue, Borehamwood, Hertfordshire WD6 2BL (UK)

(Received 16 November 1992; accepted 21 April 1993)

Abstract

This paper describes a recently developed calorimeter, the PHI-TEC II, which can provide direct data for large-scale application under conditions of practical interest. Applications of this device range from hazard screening (as with conventional instruments) to relief sizing and plant accident 'simulation'.

INTRODUCTION

Adiabatic calorimetry is one of the most common methods for testing exothermic chemical reactions in order to obtain information such as the detectable 'onset' temperature of reaction, the rates of subsequent pressure and temperature rises, the heat of reaction, and the kinetics.

The information derived from such tests is required to answer questions about the safe storage, transportation and processing of chemicals and mixtures. Selection of safe operating conditions, a knowledge of the gas generation rate following decomposition, and calculation of the relief capacity needed to prevent damage following a runaway are all possible using adiabatic calorimetry.

However, conventional instruments that attempt to provide exothermic reaction data fall substantially short of these requirements and rely on dangerous extrapolation or computer modelling before predictions about large-scale plant applications can be made. In addition, there are practical limitations in the way that tests can be conducted which often prevent realistic plant situations from being examined. Instruments typical of this include the *ARC (Columbia Scientific Industries) [1] and PHI-TEC I [2].

---

[1] Presented at the 21st annual NATAS Conference, Atlanta, GA, 13–16 September 1992.

ADIABATIC CALORIMETERS: GENERAL FEATURES

The main features of conventional adiabatic calorimeters for hazard assessment are shown in Fig. 1. The sample (a few grams), whose pressure and temperature are monitored, is placed between a set of electrical guard heaters (whose temperature is also monitored). Heat loss from the sample is prevented by maintaining a zero temperature difference between the sample and the guard heaters. A typical experiment involves heating the sample in steps until an exotherm is detected; after this, the sample is allowed to self-heat and the guard heaters track the temperature. Because the temperature of the guard heaters is equal to that of the sample, heat loss is prevented and adiabatic conditions ensured. In the case of both the *ARC and PHI-TEC I, three guard heaters are used, above and below the sample, plus a cylindrical one around it. The entire assembly of sample cell plus heaters is placed inside a large protective vessel (for safety). As the sample self-heats and the temperature rise accelerates, the guard heaters on the *ARC can track at rates of up to about 10–15°C min^{-1}, compared with about 200°C min^{-1} with PHI-TEC I. At self-heat rates higher than this, adiabatic conditions cannot be maintained.

It is commonly the case that as the sample temperature increases, the pressure will also rise. Therefore, the sample cell must be designed to hold a

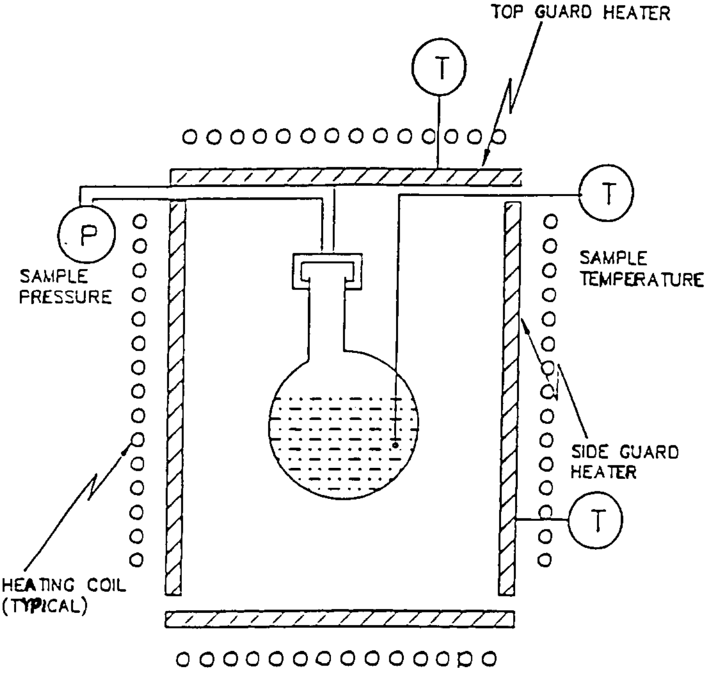

Fig. 1. Basic components of an adiabatic calorimeter.

significant pressure which makes it relatively heavy. This design feature is important because the cell acts as a heat sink, absorbing part of the heat from the sample. This is often expressed in terms of the phi-factor

$$\phi = 1 + \frac{M_c C_{pc}}{M_s C_{ps}}$$

where M is mass and C_p specific heat (subscript c for test cell and s for sample). The ϕ-factor is a direct measure of the fraction of heat released by the reaction which is used to heat up the cell. Typically, the *ARC and PHI-TEC I cells have a ϕ-factor of around 2. This means that about half the heat is absorbed by the cell, suppressing the rise in pressure and temperature from the true value under plant conditions where $\phi \approx 1$.

In addition to the ϕ-factor limitation, the use of small test cells confined in large protective covers imposes other practical difficulties. The most important of these are: poor sample agitation; difficulty with addition of solids and viscous liquids; realistic operating conditions cannot be simulated, e.g. addition of reactants, initiators, etc., after the test cell is in the protective cover is not generally possible.

DESCRIPTION OF PHI-TEC II

Main features of the design

A diagram of the PHI-TEC II is shown in Fig. 2 [3]. The general principle is similar to that in Fig. 1 where adiabatic conditions are achieved by a set of guard heaters surrounding the chemical to be tested.

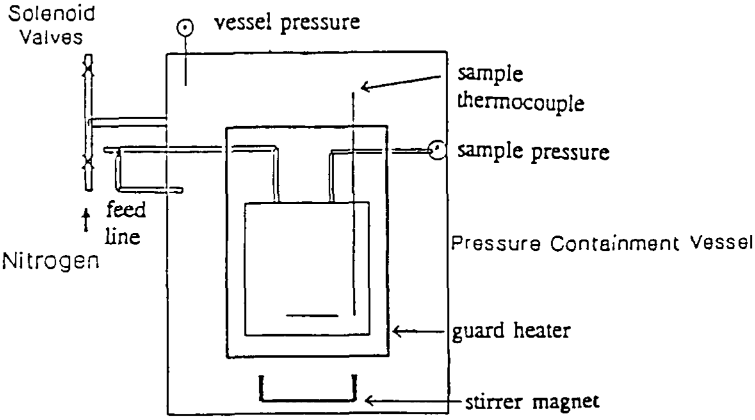

Fig. 2. The PHI-TEC II calorimeter for the assessment of reactive materials.

The sample cell plus heaters are placed inside a pressure vessel to which two solenoid valves plus another pressure transducer are attached. The solenoids control the pressure inside the vessel, i.e. outside the test cell, by injection/venting of nitrogen so as to track the sample pressure. In this way pressure differences across the walls of the cell are minimized, so that high pressures can be contained with a thin-walled (≈0.15 mm) test cell.

Typically, the ϕ-factor for PHI-TEC II is about 1.05–1.08, acceptably close to that of a large-scale plant. Therefore, when exothermic reactions occur in the low ϕ-factor test cells, the data can be expected to mimic results expected from a plant incident, without the need for extrapolation.

These design characteristics ensure that in achieving a low ϕ-factor, sensitivity is not compromised, compared with the ARC (trademark of Columbia Scientific Industries) or PHI-TEC I devices.

Sample agitation

The ability to stir the test sample adequately is important, particularly when there is more than one phase. This may be done either by means of

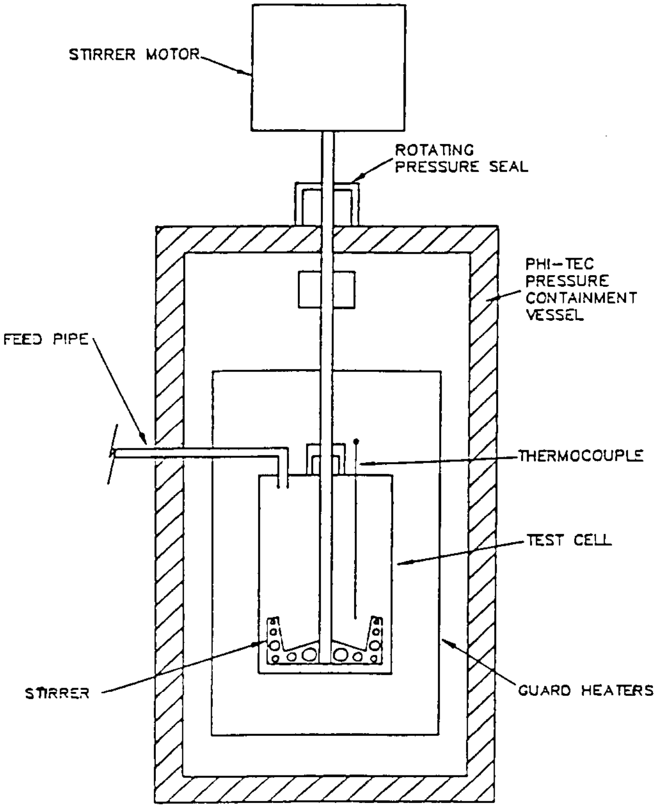

Fig. 3. Direct agitation of sample.

magnetic coupling (as shown in Fig. 2) or, optionally, a small impeller can be placed inside the cell and driven by an electric motor (see Fig. 3).

Replication of plant conditions

The test cell used in PHI-TEC II is about 120 cm^3, which makes it relatively easy to add reactants, catalysts, etc., after the cell is in the protective cover. In fact, liquids can be added when the cell is at an elevated pressure or temperature. This permits tests to be carried out in a manner closely resembling plant operation. The unit can be used essentially as a hazard simulator.

Another feature that can be important is the use of thin glass test cells instead of the normal metal ones. The pressure compensation facility allows glass cells to be used at high pressure.

Gas generation rate measurement

An important parameter describing a decomposition reaction is the rate at which gas is generated. The gas rate can be calculated from a knowledge of the pressure rise using the gas law. However, in the small test cells used in conventional calorimeters, the gas space is so small that the pressure rise due to gas production cannot be separated from that due to liquid expansion alone. The gas pressure can become very high leading to significant departure from the ideal gas law and solubility of the gas in the liquid can introduce further complications. These effects are very difficult to estimate. Also, if the gas generation rate is high, test cells frequently leak. Using the larger test cells, the gas rate can be more reliably measured. For high gas rates it is also possible to allow the gas to vent directly into the containment vessel (whose pressure is measured), thereby preventing explosive rupture and avoiding the solubility and non-ideality problems.

Relief and disposal system analysis

An important consequence of the low ϕ-factor is that it is possible to obtain relief sizing data. The methodology developed in the DIERS research project [4] is directly applicable to the data from PHI-TEC II. Additionally, it is possible to extend the applications to the design of disposal units, downstream of reactor vents. Thus, data for a complete combination of reactor and downstream facilities may be generated [5].

DATA COMPARISON FROM A SIMPLE DECOMPOSITION REACTION

The typical form of data from an exothermic reaction under adiabatic runaway conditions is shown in Fig. 4, where the temperature rise is plotted against time. The data refer to NMTS (*N*-nitroso-*n*-methyl-*p*-toluenesulphonamide) which starts to decompose at about 71°C. The data compare the results for $\phi = 1.067$ (PHI-TEC II) and $\phi = 1.56$ (*ARC or PHI-TEC I type). The same information is expressed in the form of self-heating rate (dT/dt) against temperature in Fig. 5.

As expected, the rise in temperature is lowered for $\phi = 1.56$ compared with the low ϕ-factor data due to the different amounts of heat retained by

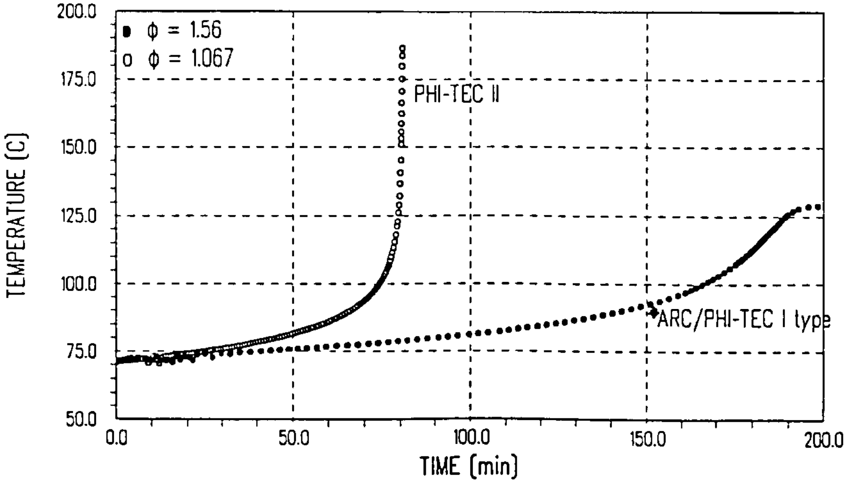

Fig. 4. Decomposition of NMTS [20%] in dioxane: temperature vs. time.

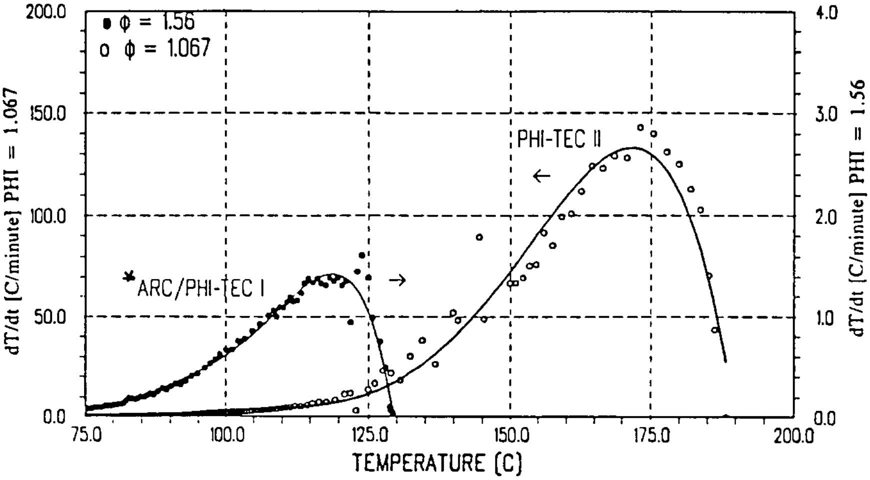

Fig. 5. Decomposition of NMTS (20%) in dioxane: rate of temperature rise vs. temperature.

the test cell. Rather surprising information emerges from Fig. 5 where the rates of temperature rise are compared. Changing the ϕ-factor from 1.56 to 1.067, increases the maximum self-heating rate from about 1.4°C min^{-1} to over 140°C min^{-1}. This order of difference is quite typical for exothermic reactions.

This illustrates one of the major drawbacks of measuring data in an apparatus with an undesirably high ϕ-factor: the level of hazard can be totally understated by seemingly small changes in ϕ.

It should be noted, however, that the two sets of data in Figs. 4 and 5 are quite consistent. This can be illustrated by replotting the data in terms of a pseudo-rate constant k for a first-order reaction against reciprocal temperature [1], where k is defined as

$$k = \frac{\mathrm{d}T/\mathrm{d}t}{(T_\mathrm{m} - T)/(T_\mathrm{m} - T_\mathrm{o})}$$

where T_o is the initial (onset) temperature, T_m the maximum temperature and $\mathrm{d}T/\mathrm{d}t$ the rate of temperature rise at temperature T.

Such a plot is shown in Fig. 6 using the data in Fig. 5: it is clear that both sets of data fall on the same straight line. The slope of the line is proportional to E, the activation energy for the reaction.

Simplified equations for conversion of high ϕ-factor data to $\phi \approx 1$ have been suggested, which make use of the activation energy [1,6]. However, these equations often give differing results and rarely agree with experimental data for $\phi \approx 1$ [7]. Even if such discrepancies can be tolerated, it is not always possible to obtain a value of E because most real reactions do not follow a simple Arrhenius dependence on temperature. Morover, there

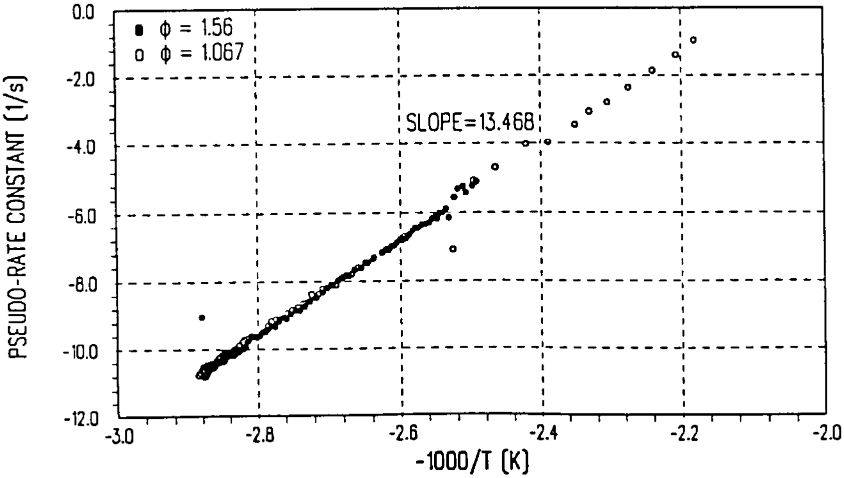

Fig. 6. Decomposition of NMTS (20%) in dioxane: pseudo-rate constant vs. reciprocal temperature.

is no reliable way to extrapolate the pressure, particularly where decomposition is involved or large volatility changes take place as the reaction proceeds. In many cases, a knowledge of pressure is more important than that of temperature for safety assessments.

COMPARISON OF COMPLEX INDUSTRIAL REACTIONS

Most industrially important exothermic reactions involve mixtures of reactants which must be brought together under the correct conditions, rather than a single compound. Also, the reactions are rarely simple, first-order, Arrhenius-type throughout the exothermic range and therefore extrapolation of high ϕ-factor data is quite impossible.

An example which illustrates this is the reaction between formaldehyde and a cyanide, initiated by an amine. The resulting exotherm is shown in Fig. 7, temperature against time, for three different values of ϕ. For $\phi = 1.05$ corresponding to the "real" plant situation, the reaction occurs immediately upon injection of the initiator (clearly necessitating the need for remote injection!). The temperature rises to over 300°C in about 5 min; the corresponding pressure rise (not shown) was over 100 bar. If the ϕ-factor is raised to 1.35, the initial reaction is observed as before but the subsequent temperature rise is much slower, taking about 100 min to reach ≈250°C. In the case of $\phi = 2.47$, the initial temperature rise is again evident but no subsequent reaction occurs. (This is presumably because the maximum temperature at the end of the first exotherm, with the high ϕ-factor, is too low to initiate the subsequent reactions. Further heating of the sample in the high ϕ-factor test would presumably show up subsequent exotherms. However, this would still not give the correct impression of the hazard which is that in a plant-scale situation, the reaction can runaway to

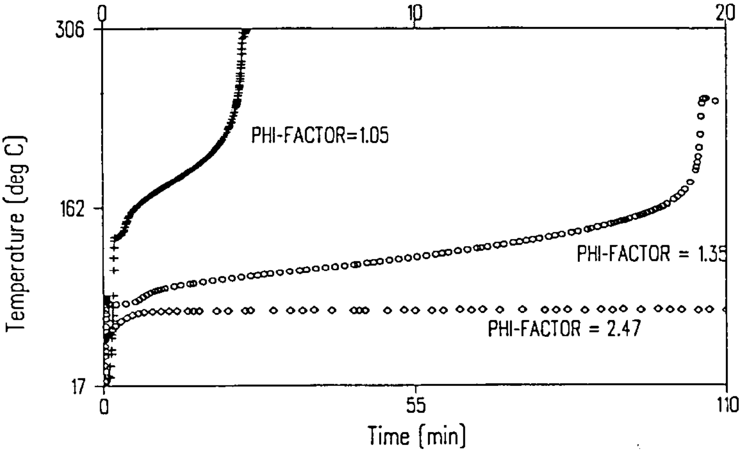

Fig. 7. Amine-initiated cyanide reaction.

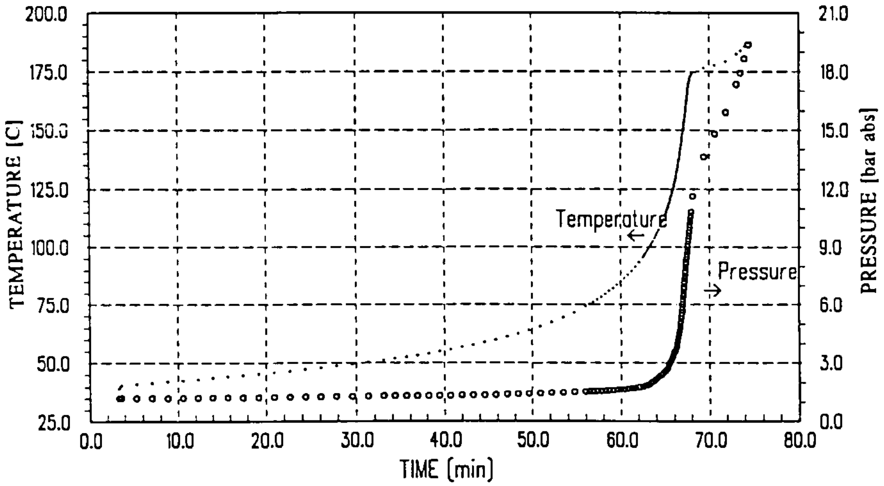

Fig. 8. NaOH-catalysed phenolic reaction: pressure and temperature vs time.

very high pressures without any additional heating, starting from ambient temperature).

Therefore, $\phi = 2.47$ data would indicate that the system is quite safe and even $\phi = 1.35$ gives little clue as to the real extent of the problem. Equally important, there is no way to go from one set of data to another by extrapolation—no activation energy can be assigned to the exothermic reactions.

Another example that illustrates the value of low ϕ-factor data is the production of phenolic resin by the reaction of phenol with formaldehyde. The case of a caustic-initiated reaction at 40°C is shown in Fig. 8 (for $\phi = 1.07$). The important thing to note is the pressure trace towards the end of the exotherm: the pressure rises by about 9 bar (almost doubles) with very little temperature increase. Clearly decomposition of the product occurs at the elevated temperature reached by the exotherm and leads to rapid gas production. Use of a high ϕ-factor test cell would not have indicated the presence of this reaction (unless the reactants were externally heated to the higher temperature). Extrapolation of data to predict the maximum pressure would grossly underpredict the rise and, hence, lead to a dangerous conclusion.

CONCLUSIONS

Conventional adiabatic calorimeters requiring a few grammes of sample in a heavy sample cell, which are used to predict exothermic reaction hazards, are extremely limited in the types of reactions that can be examined and the test conditions that can be set up. Moreover, the relevance of the data to large-scale plant is questionable and very difficult to interpret. The

PHI-TEC II device offers a range of novel design features that allow realistic data to be generated without the need for extensive modelling or extrapolation. This is achieved without loss of sensitivity and therefore PHI TEC II constitutes a single instrument that can be used for virtually all applications.

REFERENCES

1 D. I. Townsend, and J. C. Tou, Thermal hazard evaluation by an accelerating rate calorimeter, Thermochim. Acta, 37 (1980) 1–30.
2 J. Singh, Understanding chemical reaction hazards by adiabatic calorimetry, Polym. Paint Colour J. 20 Sept (1989) 127.
3 J. Singh, PHI-TEC: enhanced vent sizing calorimeter—application and comparison with existing devices, Int. Symp. on Runaway Reactions, Cambridge, MA, AIChE, New York, 1989, p. 313.
4 H. G. Fisher, DIERS—An overview of the AIChE Program, AIChE Spring National Meeting 1985, Houston, Texas, AIChE, New York, Paper 55a.
5 J. Singh and D. Boey, Design of quench system for runaway reactions using bench-scale equipment, Plant/Operations Progress, (1) (1991).
6 J.E. Huff, Emergency venting requirements, Plant/Operations Progress, (4) (1982) 211–229.
7 T Kikuchi, Sumitomo Chemicals, Japan, private communication, 1991.