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ADIABATIC CALORIMETRY USING DIRECTLY AGITATED TEST CELLS

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Abstract

This paper explains why directly agitated test cells are sometimes required in order to obtain good adiabatic calorimetry data that can be used with confidence to predict large scale plant behaviour. Experiments for methyl methacrylate polymerisation are reported. Simple procedures are presented for calculating genuine thermo-kinetic parameters from data which includes energy dissipation from the stirrer drive system.

Keywords: adiabatic, calorimetry, mixing, runaway, self-heating, stirring

Introduction

Mixing and chemical reaction

In this paper we focus on batch and semi-batch liquid phase, exothermic chemical reactions. For most reactions the intrinsic batch reaction rate is a function of temperature and composition (concentration) alone: scale up from laboratory to industrial production may therefore appear to be a straightforward matter. The gross mixing in any reactor (as encapsulated in the eddies, swirls and re-circulation) is described as the macroscale mixing pattern and this is usually thought of as occurring on a scale greater than ~1000 microns. The form of this is strongly dependent on the pumping capacity of the impeller used for mixing. Reactions, of course, occur on the molecular level and it is on the microscale that the mixing energy is dissipated and pockets or 'clumps' of fluid are finally reduced to uniform composition. This typically occurs on a scale below 100 microns. The concentration-temperature-time history of any molecules in, or entering, a reactor will as a consequence be dependent on the choice of agitator, stirring speed and baffling system. Even for single phase liquid systems, the effective kinetics, fractional conversion of feed, and yield and selectivity to a desired product, may therefore all depend on the performance of the mixing system.

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Adiabatic calorimetry

The use of low phi factor adiabatic calorimeters to simulate the thermal runaway in large vessels on loss of cooling is well documented, for example [1] and [2]. The progress of the reaction is monitored using a fast responding thermocouple immersed in the reactants. (In some older designs of calorimeter the thermocouple is mounted on a clip on the external surface of the test cell: under severe runaway conditions this can introduce significant dynamic lag into the temperature readings.) The assumption is made that the single temperature reading is representative of the whole body of reacting fluid. If this is not the case then complex flow mixing models are required to describe the non-idealities. The fractional change in temperature is also assumed to be proportional to the fractional change in reactant concentration. This is strictly only true if a single reaction is taking place with a reaction enthalpy that is independent of temperature. A relatively simple procedure then allows the adiabatic runaway data to be modelled using n^{th} order kinetics [3]. Provision of a magnetically driven agitation bar within the sample test cell ensures that for low viscosity systems the ‘well mixed’ assumption is valid for all but the most extreme self-heat rates.

For reactions with very fast intrinsic kinetics, high viscosity reactants or multiphase systems (involving immiscible liquids or mixtures of liquids and solids) a magnetically driven mixing bar may be inadequate to maintain uniformity of temperature and composition within the test cell at any time. In this case poor quality data which is very noisy will result, kinetic analysis will be impossible and the small scale results are specific to the test conditions and cannot be used to predict large scale behaviour, [4]. It is in these circumstances that the use of directly agitated test cells is vital, but the benefits associated with their use may have an associated disadvantage which must be clearly appreciated. This arises from the power required to drive the stirring system which can give rise to significant self-heating. It is easy to confuse this with the genuine self-heating associated with exothermic chemical activity and this must be avoided [5].

Experimental tests using directly agitated cells

All the experimental studies were made in the PHI-TEC II adiabatic calorimeter. This is illustrated in Fig. 1. Sample material (A) is contained in a test cell (B). In all the experiments described in this paper 316 stainless steel test cells with a volume of 114 ml and a thermal mass of 23.9 J K^{-1} were used. These cells have a wall thickness of only 0.15 mm. As the pressure in the test cell rises during a runaway reaction, nitrogen is admitted into the main pressure containment vessel (C) so as to keep the pressure differential across the test cell wall small and hence prevent it from rupturing. Three guard heaters around the test cell (D) track the measured temperature within the cell and thus minimise heat losses. These cells have an anchor type stirrer mounted on a ground stainless steel shaft. This shaft runs on bearings mounted in a housing on the top face of the cell. O rings above and below the bearing provide the pressure seal: materials of the latter can be Viton, Nitrile, EP, Perlast or PTFE and

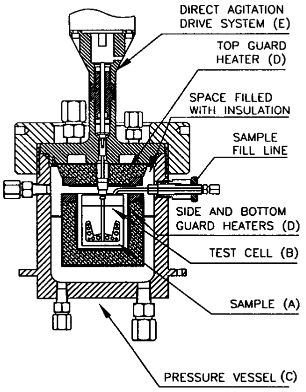

Fig. 1 The PHI-TEC II adiabatic calorimeter

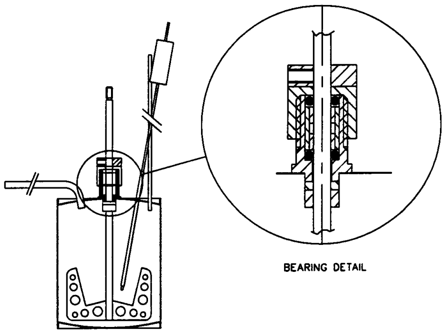

Fig. 2 Details of the directly agitated test cell, bearings and seals

are chosen to remain unaffected by the sample under test. Details of the test cell bearings and seals are illustrated in Fig. 2. The direct drive agitation system (E in Fig. 1) locates into a fitting on the end of the test cell stirrer shaft.

Each set of bearings, seals and shaft are unique so that initial frictional losses, and the extent to which individual sets of bearings and seals 'bed in' after a defined period of use, are not fully reproducible. However, all data presented in the remainder of this paper show typical behaviour.

Experiments with empty test cells

The first set of experiments was to measure the temperature within an empty test cell when the stirring drive system was run at a range of constant speeds over an extended period of time. Results are shown in Fig. 3. In this case the observed rate of self-heating is the result of power dissipation in the bearing and seals alone. For a typical stirrer drive speed of 200 to 300 rpm the self-heat rate falls between ~1.2 and 1.5°C min^{-1}.

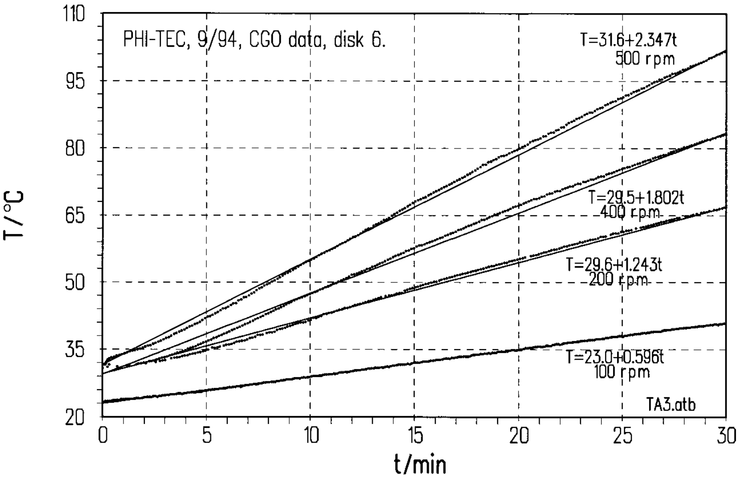

Fig. 3 Temperature *vs.* time in an empty test cell for a range of stirring speeds

Experiments with test cells containing water

Several sets of experiments then followed in which the same measurements were made but with the test cell containing 30, 60 and finally 90 g water. Results for the last case are shown in Fig. 4. The presence of the water in the cell greatly increases the thermal mass so that, at the 200 to 300 rpm range of speeds, self-heating at rates of 0.02 to 0.04°C $\min^{-1}$ is normal.

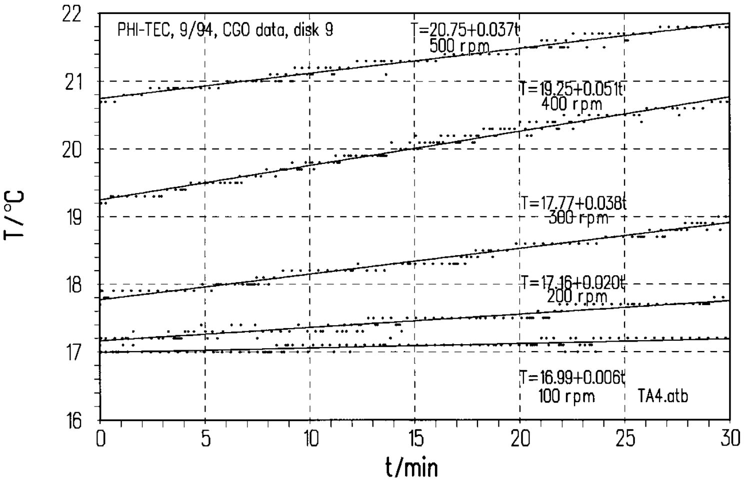

Fig. 4 Temperature *vs.* time in a test cell containing 90 g of water for a range of stirrer speeds

Energy dissipation rates

Some average energy dissipation rates from the stirrer system are now calculated from the results of many experiments such as those described above. As an example the case of stirring at the very extreme speed of 500 rpm is used. In the empty test cell linear regression of several sets of data gives an average value of the self-heat rate of 2.315°C min^{-1}. This corresponds to an energy dissipation rate of 0.92 W. For the test cells with 30 g of water the analogous average heating rate was 0.390°C min^{-1} with a corresponding power of 0.98 W and for the cell with 60 g of water these figures were 0.178°C min^{-1} and 0.82 W. Within the limits of experimental accuracy the energy dissipation rates within the test cell are seen to be independent of the presence of the variable charge of water. The following investigations were then made to see whether these observations could be explained rationally.

Each geometry of mixing system has a unique relationship between the Power number, $P/(\rho N^3D^5)$ and the Reynolds number $(D^2N\rho)/\mu$, where P is the power required for mixing, ρ is the liquid specific density, N is the stirring speed, D is the impeller diameter and μ the viscosity of the liquid being stirred. This relationship was determined for the test cell and agitator. The impeller was mounted in a variable speed drive with an associated torque transducer. The results thus pertain to the mixing system alone and do not include the test cell bearing. In order to cover Reynolds numbers from 0.01 to 10^5 a number of different Newtonian fluids were used. These included 100, 92 and 68% glycerol and water at various temperatures. With the anchor mixer running at 500 rpm the Reynolds number was ~14,000 and the corresponding Power number had levelled out to an approximately constant value of 0.4. For water at ambient temperature being mixed at 500 rpm with a 4.1 mm diameter impeller this corresponds to a fluid power requirement for mixing of ~0.027 W. Obviously this is only a tiny fraction (~3%) of the typical power required to overcome friction in the bearings. Thus virtually all of the test cell heating from the mixer drive system is attributable to frictional losses in the bearings and seals rather than the fluid mixing duty. This conclusion is widely applicable. Note that because the power for fluid mixing varies directly with liquid density, with the cube of the stirring speed and the fifth power of the impeller diameter, occasional exceptions to this conclusion should be anticipated.

Experiments with methyl methacrylate

Many experiments on the polymerisation of methyl methacrylate were made. Most of these were with 1000 ppm of an initiator, the exact detail of which is not revealed because of commercial sensitivity. Data from a typical closed cell experiment at a stirring speed of 300 rpm are shown in Fig. 5. The experiment starts at 40°C and heating at an essentially constant rate continues for almost 4 h. A fairly rapid runaway then takes place and is complete in some 15 min. At the end of it the stirrer is still running at 300 rpm and a return to self-heating at an essentially constant background rate is again observed. These data are shown in Fig. 5.

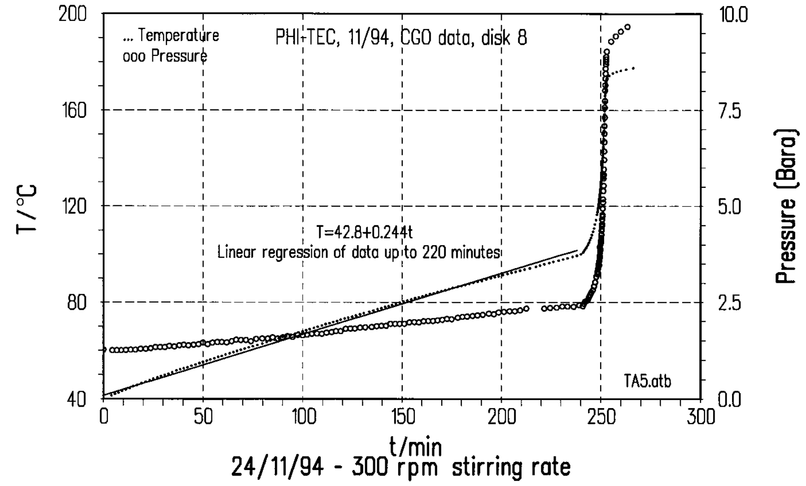

Fig. 5 Temperature and pressure *vs*. time. MMA and 1000 ppm of initiator

Discussion

Processing the adiabatic data to give thermokinetic information

The extraction of kinetic parameters from the experimental data is carried out following the procedure outlined in [3]. The fractional change in temperature is taken as being directly equivalent to the fractional change in composition. This enables the ideal design equation for an *n*th order reaction in a batch reactor to be rewritten in terms of temperature. Re-arrangement then leads to Eq. (1):

$$k = \frac{\mathrm{d}T/\mathrm{d}t}{[T_\mathrm{f} - T_\mathrm{s}]\,[(T_\mathrm{f} - T)/(T_\mathrm{f} - T_\mathrm{s})]^\mathrm{n}} = k_1 C_{\mathrm{Ao}}^{\mathrm{n}-1}, \qquad (1)$$

where $k_1 = k_0 \exp(-E/RT)$,
or

$$\ln k = \ln(k_0 C_{\mathrm{Ao}}^{\mathrm{n}-1}) - E/RT, \qquad (2)$$

where T denotes the temperature at any time t. Subscripts s and f denote start and final values, n is the reaction order, k_1 the Arrhenius rate coefficient (with pre-exponential factor k_0) and C_{Ao} the initial concentration of the species on which the reaction rate depends. It is important to note that the 'pseudo' rate coefficient k can be determined from a single experiment. If the runaway reaction, or a certain stage of it, can be described by global n^{th} order kinetics then plotting $\ln k$ as a function of reciprocal absolute temperature will give a straight line for the correct choice of reaction order n. Analogous derivations for more complex forms of kinetics can be made (e.g. series reactions or autocatalytic processes) but the mathematics is not amenable to simple graphical interpretation. The slope of the plot of ln*k* *vs*. reciprocal absolute temperature equals the activation energy, *E*, divided by the ideal gas constant *R*. A plot of this form for the data in Fig. 5 is presented for first order kinetics in Fig. 6. The start temperature for the exotherm has been taken as 40°C and the final temperature as 177°C. For clarity only data at the start of the exotherm are shown.

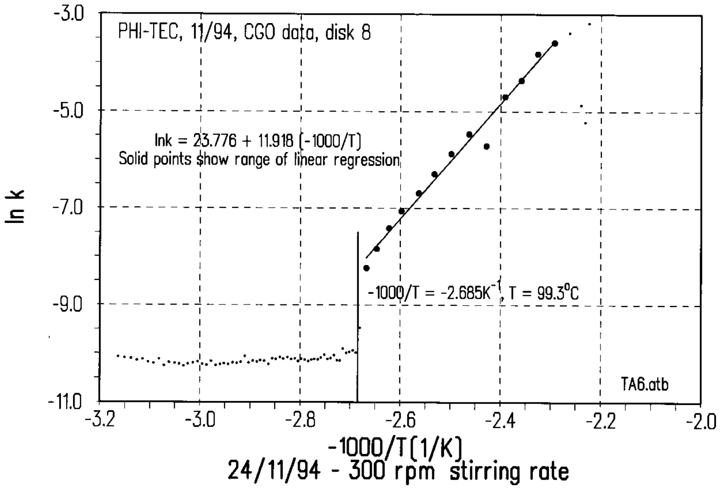

Fig. 6 ln*k* *vs*. –1000/temperature. MMA and 1000 ppm of initiator. First order kinetics

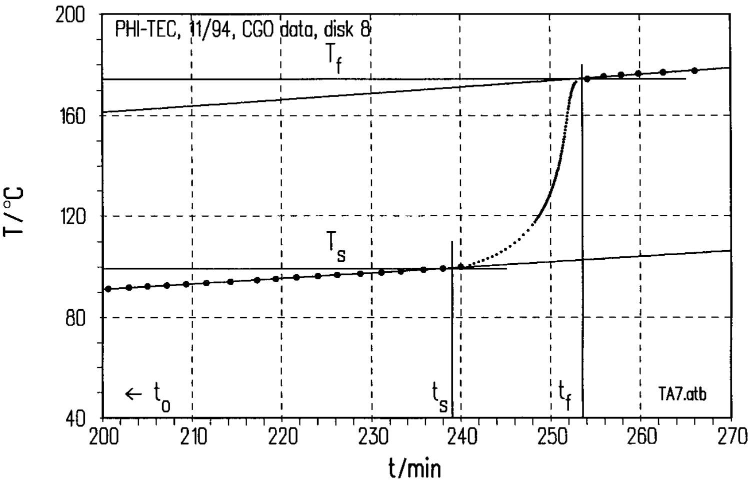

Fig. 7 Idealised form of temperature *vs*. time data

It is immediately apparent that a sharp discontinuity in the data is present at –1000/*T* equals –2.685 K^{-1}, i.e. 99.3°C. Up to this value the kinetic analysis shows that the self-heat rate is independent of temperature (the slope of the plot is essentially zero).

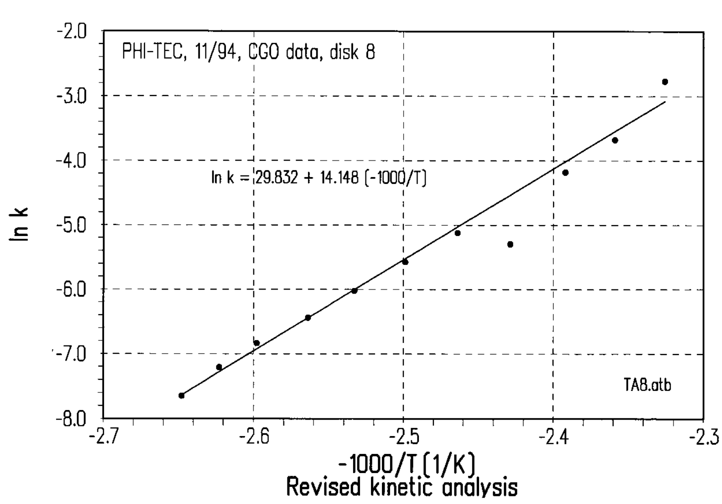

Fig. 8 ln*k* *vs*. –1000/temperature. MMA and 1000 ppm of initiator. First order kinetics

This is exactly as observed in Figs 3, 4 and the early portion of Fig. 5. At 99.3°C, temperature sensitive self-heating is first detected and the slope of the kinetic analysis in Fig. 6 jumps to a value of 11.92 K. This corresponds to an activation energy of 99 kJ mol^{-1}: first order kinetics adequately describe the early stages of reaction up to ~160°C, $-1000/T = -2.3\ K^{-1}$. It is now very easy to de-couple the slow, constant self-heating resulting from friction in the test cell bearings and seals from the self-heating due to the thermal runaway. This is done by assuming that the experimental data has the idealised form shown in Fig. 7. This is in fact the identical temperature data to that shown in Fig. 5. Background self-heating at a rate of 0.244°C min^{-1} (Fig. 5) is subtracted from all of the self-heat rate data for the experiment. The 'onset' temperature (T_s) for exothermic runaway is 99.3°C and the final temperature (T_f) is the first data point at which the corrected self-heat rate falls to zero. For this data set T_f is 173.2°C. The corresponding values of time are 239.0 min and 253.5 min giving a duration of 14.5 min for the true chemical exotherm.

The enthalpy of reaction can now be estimated from the adiabatic temperature rise as follows:

$$-\Delta H_r = [(T_f - T_s) - (14.5)(0.244)]C_p\Phi =$$

$$= [(173.2 - 99.3) - 3.538]\,(2.26)\,(1.28) = 203.5\ \text{J (g reaction mixture)}^{-1},$$

where C_p is the mean specific heat of methyl methacrylate over the temperature range involved and Φ is the phi factor for the test cell and contents, see [6] for example. In an analogous manner Eq. (1) can be re-derived to take account of the mechanical energy input from the test cell shaft drive system [4]. For first order kinetics this gives:

$$k = \frac{(\mathrm{d}T/\mathrm{d}t - (\mathrm{d}T/\mathrm{d}t)_{Ts})}{[(T_f - T) - (t_f - t_s)\,(\mathrm{d}T/\mathrm{d}t)_{Ts}]} = k_1 C_{Ao}^{n-1} \qquad (3)$$

The data from Fig. 6 are re-plotted in this form in Fig. 8. A good straight line fit to the runaway data exists from 99.3 to ~153°C with a slope that is some 19% higher than in Fig. 6: the latter corresponds to an activation energy of 117.6 kJ mol^{-1}.

Conclusions

The background self-heating arising from a directly driven agitation system in an adiabatic test cell can be accounted for in a simple manner. This is particularly so when the chemical self-heat rate accelerates to values greatly in excess of the background rates: this is the case in this example with the chemical exotherm eventually running away at self-heat rates rising to over 7°C min^{-1}. Enthalpy release, reaction order and activation energy can all be evaluated. With stirring speeds of 200 to 300 rpm and PHI-TEC II stainless steel, test cells which are used with a void fraction of ~ 20%, background self-heat rates of the order of 0.04 to 0.4°C min^{-1} may be present.

The characteristics of many different chemical systems of a thick, viscous or multiphase nature confirm that the form of results reported in this paper is quite general and that the experimental results are reproducible.

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