CHARACTERISATION OF AN EXOTHERMIC REACTION USING ADIABATIC AND ISOTHERMAL CALORIMETRY

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A simple esterification reaction is used to demonstrate standard procedures for determining the thermokinetic parameters of an exothermic reaction from adiabatic calorimetric data. The influence of variations in the heat capacity of the sample due to changes in temperature and concentration is explored. Shortcomings in the simple interpretation of adiabatic data are identified and isothermal heatflow calorimetry is used to reveal autocatalytic effects which were not apparent from the adiabatic experiments. A more rigorous interpretation of the adiabatic and isothermal data is outlined and used to predict the conditions which can lead to exothermic runaway in a batch reactor. Mathematical simulation of the conditions in a jacketed reactor is used to demonstrate the importance of developing reliable kinetic expressions before assessing the safety of a batch process.

Keywords: adiabatic and isothermal calorimetry, batch reactor, esterification kinetics, mathematical simulation

1. Introduction

In order to evaluate the hazards associated with exothermic reaction or decomposition, it is necessary to determine the temperature and concentration dependence of the rate of heat generation. Adiabatic techniques such as accelerating rate calorimetry [1], adiabatic dewar calorimetry [2] and, more recently, adiabatic calorimetry for the design of emergency pressure relief systems [3, 4], are used extensively to determine the thermokinetic properties of an exothermic reaction. The broad objective of these techniques is to determine the rate of temperature (and pressure) rise as a function of temperature for an exothermic reaction under conditions where heat losses to the surroundings are eliminated. A number of important assumptions are made in order to derive the thermokinetic parameters of an exothermic reaction from experimental data on the rate of self-heating under adiabatic conditions:
- the reaction mechanism is assumed to be independent of temperature so that the temperature and concentration dependencies can be treated separately.
- the total heat generated is evaluated directly from the adiabatic temperature rise assuming constant heat capacity.
- at any stage in the reaction, the heat generated is assumed to correspond to changes in concentration such that the rate of change of concentration and the rate of heat generation are directly proportional to the rate of temperature rise under adiabatic conditions, with the extent of reaction equal to the temperature increase expressed as a fraction of the total adiabatic temperature rise.
- the temperature dependence of the reaction rate constant is assumed to follow the Arrhenius equation.
- the dependence of reaction rate on concentration is represented by a single order of reaction with fractional values used so that complex mechanisms can be represented by simple overall kinetic expressions.

These assumptions are necessary particularly where only limited data are available on physical and chemical properties of the reaction system. However, simple interpretations based on these assumptions can lead to major inaccuracies in determining safe process conditions, and temperature evolutions during industrial production.

The form of the experimental record of self-heat rate against time for an exothermic reaction proceeding under adiabatic conditions tends to be dominated by the temperature, rather than the concentration, dependence of reaction rate. Adiabatic experiments can fail to detect concentration effects such as autocatalysis which become important when the reaction is performed under industrial conditions.

The present study was designed to illustrate the problems which can arise if hazard evaluation is based on a single adiabatic technique without proper reference to the process chemistry and without investigating the reaction under isothermal conditions.

Adiabatic calorimetry has been applied to an exothermic reaction, and the results are interpreted, initially, on the assumption that no other information is available on the reaction mechanism or the variation of the rate of heat generation with time under isothermal conditions. Thermokinetic parameters are derived assuming a constant heat capacity for the reaction system. The known chemistry and stoichiometry of the reaction system are then used to determine the changes in heat capacity during the course of reaction and the effect of these variations on the evaluated thermokinetic parameters is explored.

The results of isothermal heat flow calorimetry are used to identify the shortcomings of the simple interpretation. A revised rate equation is proposed to take account of both the adiabatic and isothermal data and corresponding values for the thermokinetic constants are evaluated.

The simple interpretation of adiabatic data, including the variations in heat capacity, is used to predict temperature-time histories when the reaction is per-