Thermochimica Acta, 134 (1988) 441–444
Elsevier Science Publishers B.V., Amsterdam

MATHEMATICAL MODELLING OF INDUSTRIAL REACTIONS USING THERMOANALYTICAL METHODS

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ABSTRACT

Non-isothermal methods of kinetic analysis have been usually neglected in the development of mathematical models for industrial reactions. Some interest has been paid to heterogeneous gas-solid decomposition reactions due to the development of experimental and analytical tools such as thermogravimetry, but only few attempts have been reported on the application of thermoanalytical methods to the modelling of industrial reactions. A general explanation of the main procedures allowing the determination of the influence of temperature and concentration in the kinetic model will be given.

INTRODUCTION

The design of a reactor and its operating regime, optimization and control require knowledge of the behaviour of the process or, more specifically of the quantitative aspects of its behaviour. The process is usually described in the form of equations and relationships containing its properties. The set of computational relationships describing the behaviour of the process is termed a mathematical model.

The kinetic behaviour of the reaction taking place in the system may depend on the equipment if macrokinetic parameters are specific of the technical element, but any system of data transfer should be based on subdivision into micro and macrokinetic parameters.

For the formulation of a mathematical model of the process it is essential the knowledge of the concentration changes of the species

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

due to the reaction microkinetics. At the present time there is no way of determining the values of the reaction rate other than by experimental methods, which are thus indispensable for determining the reaction rate equation..

From the temperature point of view two different methods have been followed in the kinetic evaluation of chemical reactions: isothermal and non-isothermal; according to heat balance considerations adiabatic methods have been developed by Root and Schmitz (1) and Hugo and Schaper (2) but uncertainties in the concentration are difficult to be avoided due to the indirect evaluation through the temperature.

A programmed temperature method, which can be understood as a thermoanalytical method has been previously reported for liquid phase reactions and potential kinetic laws (3,4). A multi-step method will be developed in this work in order to set the kinetic model and parameters from one experiment taking into account reversible reactions.

DEVELOPMENT OF THE METHOD

Many papers have reported isothermal kinetic studies of different reactions, where an initial function of the temperature (T) and concentration (C) is taken for the reaction rate (r):

$$r=F(T,C) \qquad (1)$$

Many reactions are described by separable-variables models, where the function of temperature and concentration can be separated, this case has been previously developed and applied to a non-isothermal kinetic analysis (5,6). Three different hypotheses can be considered in the case of non separable-variables models: (i) Reversible reaction (ii) Complex kinetic model (usually hyperbolic equations have been suggested) and (iii) Complex reaction systems, where several reactions may take place in the reaction system.

The third case depends very much on the reaction network and non-isothermal methods could be applied for optimization purposes.

Reversible reactions

In this case equation (1) can be simplified to:

$$r=f_T(T)\ [f_+(C_i)-f_-(T)f_-(C_i)] \qquad (2)$$

Assuming the Arrhenius equation for $f_T(T)$ and the van't Hoff equation for $1/f_-(T)$:

$$r=K_o\exp(-\frac{E}{RT})\ [f_+(C_i)-1/K_o\exp(-\frac{\Delta H}{RT})\ f_-(C_i)] \qquad (3)$$

A multistep procedure can be developed for the modelling of reversible reactions. The method is based on a temperature-time profile as it is shown in figure 1.

An experimental evaluation of the conversion-time curves should be performed as it is shown in figure 2.

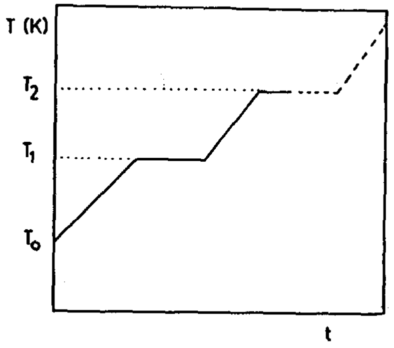

Figure 1. Temperature-time profile

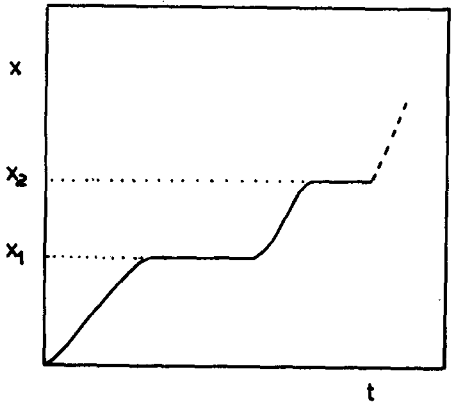

Figure 2. Conversió-time profile

The main problem for the evaluation of the kinetic model lies in the coupling between $F(C_i)=f_-(C_i)/f_+(C_i)$ and $ko = \exp(-\Delta H/RT)$.

The evaluation of the system depends in the previously suggested kinetic models, a sequential procedure can be followed, where:

a) Testing of the influence of C_{io} on $x_1 \ldots x_2$

b) Expression for $F(C_i)$

c) Testing of the equilibrium model, ln $F(C_i)$ vs $\frac{1}{T}$

d) Evaluation of equilibrium parameters, ko and $-\Delta H/R$

e) Evaluation of the kinetic parameters by the integral method using results of the different steps, where

$$I = \int_{C_{io}}^{C_i} \frac{dC_i}{f_+(C_i) - 1/k_o \exp(-\frac{\Delta H}{RT}) f_-(C_i)} = \int_{T_o}^{T} K_o \exp(-E/RT) dt \qquad (4)$$

This method, which will be described using a simple test reaction, the ethyl acetate saponification with sodium hydroxide allows a systematic approach to the kinetic behaviour of a reaction in a wide range of variables temperature and/or initial concentration leading to a maximum knowledge of the reaction through a minimum experimental effort, in this case one thermoanalytical experiment leads to the kinetic model and parameters for a reversible reaction.

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