



Influence of mass-transfer effect on isoconversional calculations

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ABSTRACT

A theoretical simulation of the influence of mass-transfer effect on the kinetics of solid–gas reactions has been carried out. The influence of mass-transfer phenomena on the shape of the thermoanalytical curves and on the apparent activation energy, calculated by advanced isoconversional methods (Vyazovkin method) is discussed. The Vyazovkin equation has been adapted to CRTA data and, a modification of this equation, to account for pressure correction term in the reaction rate was achieved. To check the equations developed in this paper, the standard isoconversional procedure has been modified, instead of a set of experiments performed under different heating rates (or reaction rates C in the case of CRTA) for a given conversion we use a set of experiments under different pressure of the gas self-generated in the reaction at one heating rate β (or reaction rate C), respectively.

The results obtained allow for trustworthy estimates of the activation energy from advanced isoconversional method in reaction systems whose kinetics are affected by the pressure of the gases self-generated by the reaction. Theoretical considerations are verified on simulated non-isothermal TG, and non-isothermal non-linear controlled rate thermal analysis (CRTA) data. Experimental data of calcite have been used.

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1. Introduction

It is well known that the major failures of dynamic methods of TA arise from the influence of the experimental factors. The source, nature and magnitude of random and systematic errors in experimentally determined values of $\alpha-t$ have been the subject of detailed discussion in the literature. The weak control of the external parameters (gas atmosphere, sample size, heating rate...) on thermal analysis may be expected to be the cause of uncertainties and discrepancies concerning the kinetic results. A pronounced influence of such factors on the course of the reaction has been reported in a great numbers of papers [1–8]. A serious drawback of the thermal analysis techniques is the lack of reproducibility because of the influence of these external factors. Among these factors the pressure of the gases generated by the reaction play a prominent role, and the kinetics of reversible solid-state reactions are often highly sensitive to the mass-transfer phenomena provoked by the increase of pressure. If the gaseous product of a reversible reaction is not being effectively and completely removed from the sample environment the activation energy may be strongly influenced. For example the decomposition of calcite shows wide variations of the kinetic parameters [9–14] owing to the sensitivity of reaction rate to the availability of CO_2 . It is worth noting that the reported

kinetic results were distorted by the effect of the partial pressure of evolved CO_2 which is usually neglected in the conventional kinetic calculation. Accordingly, the kinetic measurements at a slow decomposition rate under high vacuum are strongly recommended. The mass-transfer effects on the activation energy are strongly dependent on the experimental conditions, the influence of pressures of CO_2 on the rates of calcite decomposition is important above $10^{-2} \times P_{\text{eq}}$ [15] at lower pressure, the rates are independent of $P(\text{CO}_2)$, in atmosphere of CO_2 very large apparent values of the activation energy are found [11]. Criado et al. [16] have demonstrated that the removal of the gases generated during the thermal decomposition of solids is not attained even by using a very large flow of an inert gas. In the literature there are a few theoretical concepts describing the relation between the pressure in the system and the rate of the reaction.

The purpose of this study is to investigate the relation between pressure and the reaction rate and to analyze the mass-transfer effect on the activation energy, obtained from isoconversional methods, of reversible solid–gas reactions of the type: $A(\text{solid}) \rightleftharpoons B(\text{solid}) + C(\text{gas})$. The equilibrium constant of this kind of reaction has been frequently determined from direct measurements in which the solids A and B are allowed to equilibrate with the gas C at different temperatures. A theoretical simulation of the mass-transfer phenomena has been used to investigate the influence of the above phenomena on the shape of non-isothermal TG and CRTA (controlled rate thermal analysis) curves in order to make a comparison with the experimental behaviour.

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Table 1
Set of reaction models to describe the reaction kinetics in solid-state reactions

Symbol	Model	Differential $f(\alpha)$ function	Integral $g(\alpha)$ function
JMA (A_n)	Nucleation and growth ($n=0.5, 1, 1.5, 2, 2.5, 3, 4$)	$n(1-\alpha)[- \ln(1-\alpha)]^{1-1/n}$	$[- \ln(1-\alpha)]^{1/n}$
R_n	Phase-boundary controlled reaction $n=0, 1/2$ and $2/3$	$(1-\alpha)^n$	$(1-(1-\alpha)^{1-n})/1-n$
D1	1D-diffusion	$1/2\alpha$	α^2
D2	2D-diffusion	$-1/\ln(1-\alpha)$	$\alpha + (1-\alpha)\ln(1-\alpha)$
D3	3D-diffusion (Jander Eq.)	$[3(1-\alpha)^{2/3}]/[2[1-(1-\alpha)^{1/3}]]$	$[1-(1-\alpha)^{1/3}]^2$
D4	3D-diffusion (Ginstling–Brounshtein Eq.)	$3/2[(1-\alpha)^{-1/3} - 1]$	$1 - 2\alpha/3 - (1-\alpha)^{2/3}$
P_n	Power law ($n=1, 2, 3, 4$)	$n\alpha^{(n-1)/(n)}$	$\alpha^{1/n}$

In the CRTA experiments the temperature profiles required to maintain the partial pressure of the evolved gases constant during the course of the reaction are recorded as a function of time. Because the partial pressure is proportional to the rate of overall mass-change, in a constant volume vacuum apparatus with a constant pumping rate, the reaction proceeds at a constant overall decomposition rate under a constant partial pressure of evolved gas. In this study we assumed that the gas self-generated in the reaction is not chemisorbed on the surface of the corresponding oxide because in this case the active phase boundary would be expressed by introducing in the rate equation the adsorption coefficient.

2. Theoretical equations

Most of the kinetic data are collected under non-isothermal conditions for which the basic kinetic equation takes the form:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) \exp\left(\frac{-E}{RT}\right) \quad (1)$$

Where β is the heating rate and the functions $f(\alpha)$ most frequently used in solid-state reactions are included in Table 1. It is well known that almost any $f(\alpha)$ can satisfactorily fit data at the cost of drastic variations in the activation energy [17]. For this reason the analysis of a single thermoanalytical curve tends to produce highly uncertain values of activation energies.

The ambiguity can be overcome when using multi-heating rate methods (isoconversional methods) that are known to allow for model-independent estimates of the activation energy. In many heterogeneous reactions there is a dependence of the effective activation energy on the extent of conversion α [18] and usually involves multiple steps that contribute to the overall reaction rate, thus the detection of multi-step processes allows drawing certain mechanistic conclusions. Integration of Eq. (1) leads for a linear heating rate, $\beta = dT/dt$, to:

$$g(\alpha) = A \int_0^t \exp\left(\frac{-E}{RT(t)}\right) dt \quad (2)$$

the integral form of Eq. (2) is represented as:

$$g(\alpha) = \frac{AE}{\beta R} p(x) \quad (3)$$

$p(x)$ is the temperature integral and is given by:

$$p(x) = \int_x^\infty \frac{\exp(-x)}{x^2} dx \quad (4)$$

where $x = E/RT$. This function does not have an exact analytical solution and a large number of approximate equations have been proposed in the literature for performing the kinetic analysis of solid-state reactions. In the theoretical simulations of this paper the Senum–Yang [19] approximation was used which even at $x = 5$ gives only 0.02% deviation from the exact value of the temperature integral and such deviations do not practically affect the values of the activation energy. Vyazovkin [20] has developed an advanced non-linear integral procedure which uses integration over small

time segments as follows, as a result the constancy of E is assumed for only a small segment $\Delta\alpha$:

$$\Delta g(\alpha) = g(\alpha - \Delta\alpha, \alpha) = A_\alpha J[E_\alpha, T(t_\alpha)] \quad (5)$$

Where:

$$J[E_\alpha, T(t_\alpha)] = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left(\frac{-E_\alpha}{RT(t)}\right) dt$$

Using a general assumption [21,22] that the reaction model is independent of the heating rate, for a set of experiments performed at different heating rates the $g(\alpha)$ is canceled. According to this procedure [20] the value of E_α is determined as the value that minimizes the function:

$$\sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (6)$$

2.1. Mass-transfer equations

It is worth noting that the reported kinetic results are distorted by the effect of the partial pressure of evolved gases which are usually neglected in the conventional kinetic calculation. In this work two situations are considered: (i) The pressure of gases generated by the reaction is assumed nearly constant and (ii) The pressure change and is proportional to the reaction rate.

2.1.1. Case (i)

It was indicated experimentally [23] that the kinetics can be described by taking account of the partial pressure, P , with respect to the equilibrium pressure, P_{eq} . Assuming the experimentally verified linear dependence of the reaction rate on partial pressure [24,25] one obtains the influence of the residual pressure, P , self-generated in the reaction at temperature T and, Eq. (1) can be conveniently expressed as:

$$\frac{d\alpha}{dt} (\text{or } C) = Af(\alpha) \left[1 - \frac{P}{P_{eq}}\right] \exp\left(\frac{-E}{RT}\right) \quad (7)$$

Where C is the constant reaction rate for CRTA experiments. The pressure term in Eq. (7) can be estimated by monitoring the partial pressure of the evolved gas. The temperature dependence of the equilibrium pressure P_{eq} is given by the Van't Hoff relationship:

$$P_{eq} = Z \exp\left(\frac{-\Delta H}{RT}\right) \quad (8)$$

One can deduce from Eq. (7) that the reaction rate decreases with increasing partial pressure P and, therefore, the corresponding curves move to higher temperatures. The pressure term in the right hand of Eq. (7) is neglected for a negligible P value with respect to P_{eq} , this is required for reducing the influences of the mass-transfer phenomena on the kinetics.

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