Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 79–83

THE COINCIDENCE OF MASS INTEGRALS $g(\alpha)$

A. Mianowski

Department of Chemistry, Silesian Technical University in Gliwice, Gliwice, Poland

Abstract

The idea of the generation of thermokinetic models on the basis of the analysis of kinetic equations (isothermal conditions) and thermokinetic equations (dynamic conditions) is presented. The method resembles that used in polisothermal conditions, which consists in analysis of the relation of the equilibrium conversion degree *vs*. temperature. The interpretation of the coincidence of mass integrals $g(\alpha)$ in the relation α *vs*. temperature has been attempted.

Keywords: conversion degree, corrected models, mass integral, thermokinetic models

Introduction

It is well known that the results of experimental investigations of the kinetics of chemical reactions can be described by using many mathematical forms, called mass integrals $g(\alpha)$. The literature relating to this problem includes many records, covering not only dynamic conditions [1–11], but also isothermal ones [1, 5, 6, 8, 10, 12–14], and especially experiments performed polyisothermally by using the experimental matrix of the [time * temperature] type [13, 14]. Generally, the estimated constants of the Arrhenius equation form an isokinetic effect [9] in a linear forms: ln$A$ *vs*. E. This fact, together with the analysis [15] with the correction coefficient, changes our opinion on the spread observed in the estimated activation energy values.

The aim of the current work is to present the idea of relating a certain set of experimental data with many forms of the mass integrals $g(\alpha)$.

Kinetic and thermokinetic equations

The most simple kinetic model for isothermal processes, in which the Arrhenius constants do not depend upon temperature, will be assumed for the needs of our analysis:

$$g(\alpha)-g(\alpha_i)=A_o e^{-E/RT}\tau, \qquad T=\text{idem} \tag{1}$$

where α_i is the initial conversion degree.

Let us assume for simplification that $g(\alpha_i)=0$. The time variable in Eq. (1) can include an exponent, a correction parameter, taking values $p=2$, 3 or even 4 [16] and in a special case $p=1/2$. This parameter can also assume other values [14].

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

In general, Eq. (1) should take a form:

$$[g(\alpha)]^{1/p}=Ae^{-E/RT}\tau,\quad T=\text{idem},\ 0<p<4 \tag{2}$$

If $p\neq 1$, the Arrhenius constants would take other values than these constants for other kinetic models given by (1), i.e. $E_o\to E$, $A_o\to A$.

For processes occurring under dynamic conditions at a heating rate $q=dT/d\tau$, we obtain the thermokinetic equation

$$g(\alpha)=\frac{A}{q}I(T),\ \text{where}\ I(T)=\int_o^T e^{-E/RT}dT \tag{3}$$

Most often, the non-elementary temperature integral $I(T)$ is approximated by

$$I(T)=\frac{RT^2}{E}e^{-E/RT} \tag{4}$$

or

$$I(T)=(T-T_i)e^{-E/RT} \tag{5}$$

where T_i refers to the maximal temperature for which $\alpha=0$.

It is often assumed that $T_i=0$ K [10, 17, 18]. Combining Eqs (3) and (5) and assuming $T_i=298$ K results in

$$g(\alpha)=Ae^{-E/RT}\frac{T-298}{q} \tag{6}$$

which corresponds directly to Eq. (1) for $p=1$, because

$$\frac{T-298}{q}=\tau \tag{7}$$

Thus, it is proven that the thermokinetic equation can be treated as a special case of Eq. (1), which means that it is identical to that describing isothermal processes, or more precisely polyisothermal ones.

The coincidence of mass integrals $g(\alpha)$

To make the analysis simpler, we assume that the reversible reaction takes place under isothermal conditions (T=idem). The reaction proceeds at low-temperature, which results in a low reaction rate.

This example is shown in Fig. 1. After a very long time, the conversion degree will assume a value near the equilibrium $\dot{\alpha}$ at this temperature. Curve A is given by the equation in which the reaction force $(\dot{\alpha}-\alpha)$ is given relative to $\dot{\alpha}$:

$$\frac{d\alpha}{d\tau}=k\left(1-\frac{\alpha}{\dot{\alpha}}\right)^n,\qquad T=\text{idem},\ n>0 \tag{8}$$

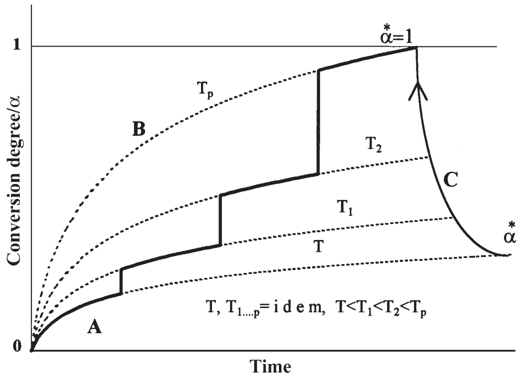

Fig. 1 The idea of the generation of a function α *vs*. *T* on the basis of kinetic analysis α *vs*. time starting from isothermal conditions

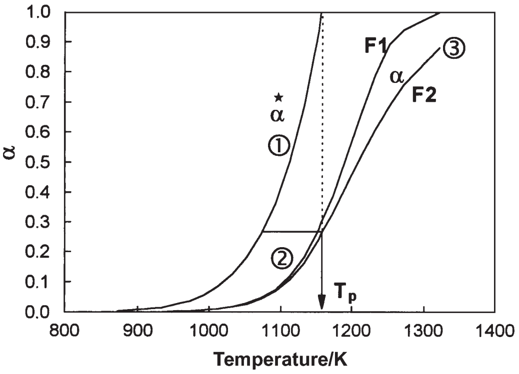

Fig. 2 The relationship between the conversion degree and temperature for 1 – $\dot{\alpha}$; 2 – α and the F1 model; 3 – α and the F2 model

The ratio $\alpha/\dot{\alpha}=K/K_a$ forms an analogy to the thermodynamic threshold described by Błażejowski [11, 17–19].

In special case for n=1, Eq. (8) could describe irreversible reaction of type X↔Y, when initial concentration of compound Y is equal 0.

However, before the conversion degree reaches equilibrium, the temperature is increased to shift the process into curve B. In fact, the process is realized by manifold shifts to the consecutive curves, at last reaching curve B, which is described by a similar equation:

$$\frac{d\alpha}{d\tau}=k_p(1-\alpha)^n, \qquad T_p=\text{idem}, \dot{\alpha}=1 \qquad (9)$$

Curve B, however, relates to an irreversible reaction. Kinetic constants k and k_p can be given by a classical Arrhenius law ($k=A\exp[-E/(RT)]$), while the increase in the equilibrium conversion degree with the temperature $T \rightarrow T_p$ (curve C in Fig. 1) can be defined by the following equation [15]:

$$\ln\dot{\alpha}=-\frac{\Delta H_{\mathrm{d}}}{\nu R}\left(\frac{1}{T}-\frac{1}{T_{\mathrm{p}}}\right)-\ln\frac{T}{T_{\mathrm{p}}},\ T=T_{\mathrm{p}},\ \dot{\alpha}=1 \tag{10}$$

The term ($-\ln T/T_{\mathrm{p}}$) can be omitted in Eq. (10).

The generation of the function α *vs*. T consists in the integration of Eq. (8). Therefore, we obtain

$$\begin{aligned} &\text{for } n=1:\ -\dot{\alpha}\ln\left(1-\frac{\alpha}{\dot{\alpha}}\right)=k\tau \\ &\text{for } n\neq1:\ \frac{\dot{\alpha}}{1-n}\left[1-\left(1-\frac{\alpha}{\dot{\alpha}}\right)^{1-n}\right]=k\tau \end{aligned} \tag{11}$$

where

$$k\tau=A\mathrm{e}^{-E/RT}\frac{T-298}{q} \tag{12}$$

Table 1 A list of the best fitted thermokinetic models significance level=0.0$^{(5)}$, N=number of observables

Mechanism assumed and activation energy	Symbol of mechanism	E/kJ mol^{-1}	Correction factor acc. to [15]	Corrected value of E/kJ mol^{-1}	r^2/%	F test
F1 E=220 kJ mol^{-1}	A2	99.0	1/2	198.0	100.0	508729
	F1	215.6	1	215.6	99.99	395603
	A3	60.1	1/3	180.3	99.99	253153
	2F1-R1	227.2	1	227.2	99.84	13017
	D3	427.3	2	213.7	99.67	6435
	(N=23)					
	lnα *vs*. 1/T	227.5	1	227.5	100.0	701673
	(N=16)					
F2 E=220 kJ mol^{-1}	F2/2	99.4	1/2	198.8	99.98	117583
	F2	216.4	1	216.4	99.98	97676
	2F1-R1	228.2	1	228.2	99.88	18009
	F1	199.1	1	199.1	99.45	3832
	A2	90.7	1/2	181.4	99.27	2851
	(N=23)					
	lnα *vs*. 1/T	224.1	1	224.1	99.99	227279
	(N=16)					

The interchangeability of the time and temperature variables (7) enables one to bring Eq. (6) into a form convenient for further calculations.

The structure of Eqs (11) and (12) results in the coincidence of the mass integrals $g(\alpha)$.

Conclusions

The process of thermal dissociation of $CaCO_3$ was analyzed, with assumption of the data given in [13] and [15]: A=34.7 10^6 min^{-1}, E=220 kJ mol^{-1}, ΔH_d=176 kJ mol^{-1}, T_p=1157.4 K, ν=1 and q=10 K min^{-1}. Equations (11), (12) and (10) (for n=1 and n=2) were used to form the model illustrated in Fig. 2. The generated curves of α *vs.* T were correlated by using the generally known methods (Eqs (3) and (4)) to obtain a series of significant relation in the function scales of $\ln[g(\alpha)/T^2]$ *vs.* $1/T$. Table 1 gives each five best fitted thermokinetic models. The relationships obtained are closely related to the assumed order of the reaction F1 and F2. The best A2 model comes from the F1 model (p=2). In the second case, the assumed formula for n=2 was corrected by F2/2, i.e. $g(\alpha)=[\alpha/(1-\alpha)]^{1/2}$ (also p=2). Initially, for low conversion degree all the models are linearly convergent in relation to α (Fig. 2). Further if $T \geq T_p$, there are several possible routes to reach α=1; therefore, there is a small spread among the experimental data describing the final phase of dissociation that gives a possibility for many approximations with different mass integrals $g(\alpha)$. The symbols are labeled according to [15].

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