ESTIMATION OF THE PARAMETERS DESCRIBING THE CHANGES OF CONVERSION DEGREE UNDER POLYISOTHERMAL CONDITIONS

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Abstract

The possibility of estimation of a slope of the independent variable $1/T$, for the observed conversion degree in the form of a [time* temperature] matrix, has been analyzed. It has been shown that for such a case the covariance of time and temperature does not amount of zero; the procedure of estimation of the slope can be simplified by making one of the variables (time) latent.

Keywords: conversion degree, estimation of slope, kinetic investigations

Introduction

Investigations of the characteristics of chemical or physical reactions processes described by the relationship of one variable, temperature or time, are often limited to estimation of the slope of a function transformed to a linear form.

The most important examples can be illustrated by the following laws:

I. The van't Hoff isobar:

$$\left[\frac{\partial \ln K_a}{\partial \left(\frac{1}{T}\right)}\right]_{p^\circ} = -\frac{\Delta H}{R} \tag{1}$$

II. The Arrhenius equation:

$$\frac{\mathrm{d}\ln k}{\mathrm{d}\left(\frac{1}{T}\right)} = -\frac{E}{R} \tag{2}$$

III. The Kissinger equation:

$$\frac{\mathrm{d}\ln\left(\frac{q}{T_m^2}\right)}{\mathrm{d}\left(\frac{1}{T_m}\right)} = -\frac{E}{R} \tag{3}$$

IV. The kinetic equation:

$$\left[\frac{\mathrm{d}g(\alpha)}{\mathrm{d}\tau}\right]_T = k \tag{4}$$

V. A temperature criterion [1–4] which can be brought into the following form for isothermal conditions:

$$\left[\frac{\mathrm{d}\ln\alpha}{\mathrm{d}\left(\frac{1}{T}\right)}\right]_\tau = -\left(\frac{E}{R}\right) \text{for } 0<\alpha<\approx 0.2, \quad T=\text{idem} \tag{5}$$

Equations (1) to (5) are presented in a form indicating only one constant, while the free term is intentionally omitted.

The aim of the work

The aim of the current work is to analyze the possibility of the interpretation of the results of kinetic investigations under polyisothermal conditions by examining the time–temperature function of the conversion degree.

Our analysis can concern not only the most simple cases, described by T-const, i.e.
– the temperature criterion:

$$\ln\alpha \ \textit{vs. } 1/T \tag{6}$$

– kinetics of the 0th order:

$$\alpha = k\tau \tag{7}$$

or corrected forms:

$$\alpha^{1/p} = k\tau, \ p=1/2; \ 1; \ 2; \ 3 \tag{8}$$

but also all kinds of other categories that can be obtained by substitution of the integral mass $g(\alpha)$ for α in Eqs (6) to (8).

After the introduction of the classical Arrhenius equation, Eqs (7) and (8) can be brought into a form depending upon the correction parameter p. This parameter plays an important role during analysis of the complicated chemical reactions [5].

A time–temperature function was reduced to a relation including the single variable term, temperature $1/T$:

$$\ln\frac{\alpha^{1/p}}{\tau} = \ln A - \frac{E}{RT}, \ p=1/2; \ 1; \ 2; \ 3 \tag{9}$$

The examples analyzed in the current work are only of the type of (6) and (9) for $p=1$.

Analysis of the problem

Case I

In kinetic experiments performed under polyisothermal conditions, we can make use of the conversion degree. In such procedures, we determine the experimental matrix of the [time* temperature] type. Such a matrix can be

1. rectangular:

$$\alpha = [\alpha_{ij}], \; i \neq j, \; 0 < \alpha_{ij} \leq 1 \tag{10}$$

2. square:

$$\alpha = |\alpha_{ij}|, \; i = j, \; 0 < \alpha_{ij} \leq 1 \tag{11}$$

$$\mathrm{cov}(\tau, T) = 0 \tag{12}$$

where index i describes the time-dependent columns $\tau_{1\ldots i}$, while index j describes the temperature-dependent rows $T_{1\ldots j}$.

Condition (12) significantly changes the nature of the time variable in a function, because it can be hidden (by means of the formation of the new matrices $[\alpha/\tau], [g(\alpha)/\tau]$ if $\tau \neq 0$ or it can be omitted. The time variable therefore changes to a parameter indexing series m of the temperature variable. As a result, a slope is generated from series m of τ=const in relation to the independent variable (in this case $1/T$). It appeared from an earlier analysis [6] that the coefficient of the linear determination r^2 decreases, even if in each series r_m^2 amounts to 1, but the number of data increases. Therefore, one should not bother with the distance from the upper limit 1. It is the sig-
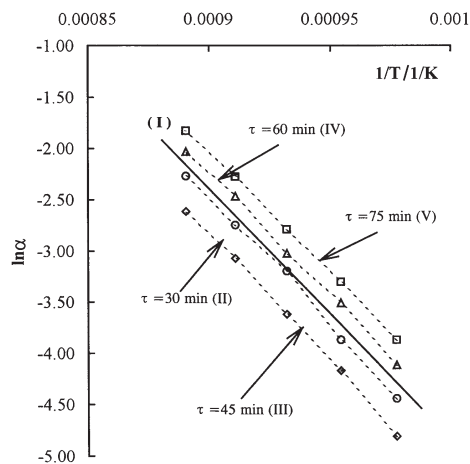
Fig. 1 Graphical example of generation of slope I ($-E/R$) from the m=4 series (II–V) for data consisting of N=20 observables; if τ=idem (ln α=19.59–24432.7/T; r^2=84.86%, s.l.=0.0$^{(5)}$), activation energy E amounts to 203.1 kJ mol^{-1} data according to Kubas [7]

nificance level of the slope estimated, i.e. the F test, that is much more important in this case. Figure 1 gives an example of temperature criterion (6) for a low conversion degree ($0<\alpha\leq0.16$) describing the thermal dissociation of calcium carbonate.

Case II

The experimental data are registered while changing time and temperature in the range that is convenient for the experimenter, provided that

$$cov(\tau,T)\neq0 \qquad (13)$$

Use of the procedures discussed previously does not always give satisfactory results. An example is given in Fig. 2. In such a case, one uses consecutively following equations:

$$g(\alpha)=k\tau, \; T=\text{idem} \qquad (14)$$

and the Arrhenius law:

$$\ln k=\ln A-\frac{E}{RT} \qquad (15)$$

Two versions of the use of Eqs (14) and (15) will be presented below.

Version I (complicated)

The procedure is based on defining the latent (unified) time variable for all the data narrowed to a range consistent with the changes in conversion degree at the maximal temperature used in the experiment. Therefore, the range of the time changes is reduced and condition (12) is obeyed.
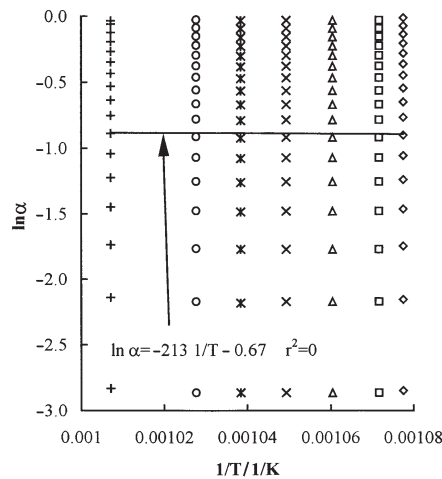
Fig. 2 Relationship (6) for N=119 observables, if $cov(\tau, T)\neq0$, data according to Maciejewski [8]

The data presented in Fig. 2 give

$$\ln\left(\frac{\alpha}{\tau_z}\right)=17.56-\frac{19535.9}{T}, \quad r^2=98.73\%, \quad s.l.=0.0^{(5)} \tag{16}$$

i.e. $E=162.4$ kJ mol^{-1} (according to [8], $E=161.6$–173.3 kJ mol^{-1}). In this particular case, the slope is generated from the $m=7$ series, each having $N=17$ data.

Version II (easier)

The combination of Eqs (14) and (15) is used directly [5, 9]:

$$\ln\left(\frac{g(\alpha)}{\tau}\right)=\ln A-\frac{E}{RT}, \quad T=\text{idem} \tag{17}$$

If $g(\alpha)=\alpha$, one obtains for the data presented in Fig. 2

$$\ln\left(\frac{\alpha}{\tau}\right)=18.44-\frac{203503}{T}, \quad r^2=97.46\%, \quad s.l.=0.0^{(5)} \tag{18}$$

i.e. $E=169.2$ kJ mol^{-1} (according to [8], $E=161.6$–173.3 kJ mol^{-1}). Figure 3 illustrates this equation.
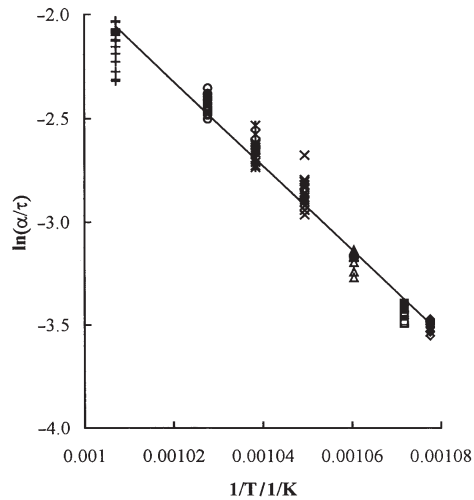

Fig. 3 Graphical analysis of Eq. (18)

Conclusions

Comparison of the parameters of Eqs (16) and (18) leads to the conclusion that for the cases of cov(τ, T)$\neq$0 the problem is reduced to hiding the independent variable of

time. The results obtained by using the procedure of version II are not worse than those given by version I, which is much more complicated than the latter.

Symbols unexplained in the text

A	frequency constant in the Arrhenius equation, min^{-1},
E	activation energy, $\mathrm{J\ mol}^{-1}$,
$g(\alpha)$	weight integrals,
ΔH	enthalpy, $\mathrm{J\ mol}^{-1}$,
k	reaction rate, min^{-1},
K_a	thermodynamic equilibrium constant,
p^o	standard pressure, kPa,
q	rate of heating, $\mathrm{K\ min}^{-1}$
r_m^2	coefficient of the linear determination for the m th series, %,
$s.l.$	significance level,
T	temperature, K,
T_m	temperature at maximal reaction rate, K,
α	conversion degree,
τ	time, min,
τ_z	latent time variable, min.

References

1 J. Szarawara and Cz. Kozik, Chemia Stosowana, 17 (1973) 279.
2 J. Szarawara and Cz. Kozik, ibid, 17 (1973) 295.
3 J. Szarawara and Cz. Kozik, ibid, 20 (1976) 45.
4 J. Szarawara, Termodynamika chemiczna, WNT Warszawa 1985.
5 J. Surygała and A. Mianowski, Pr. N. Instytutu Chemii i Technologii Nafty i Węgla, 55 (1996) 251.
6 A. Mianowski, BW-465/RCh-6/96, unpublished work, Politechnika Śląska, 1996.
7 Z. Kubas, Archiwum Hutnictwa, 9 (1964) 269.
8 M. Maciejewski, Pr. N. Politechniki Warszawskiej (Chemia 44), Warszawa 1988.
9 A. Mianowski, Thermochim. Acta, 241 (1994) 213.