Journal of Thermal Analysis and Calorimetry, Vol. 72 (2003) 831–837

PREDICTION OF THE ISOTHERMAL BEHAVIOUR OF SOLID–GAS SYSTEMS FROM NON-ISOTHERMAL DATA

Differential isoconversional procedure

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Abstract

A new procedure for the prediction of the isothermal behaviour of the solid–gas system from non-isothermal data is suggested. It bypasses the use of various approximations of the temperature integral that ground the integral methods of prediction. The procedure was checked for: (1) simulated data corresponding to a first order reaction; (2) experimental data obtained in the isothermal and non-isothermal decompositions of ammonium perchlorate. For the simulated data, a very good agreement between calculated isotherms and those evaluated by means of the suggested procedure was obtained. A satisfactory agreement (errors in time evaluation corresponding to a given degradation lower than 18%, for $0.10\leq\alpha\leq0.37$ and lower than 10% for $0.37\leq\alpha\leq0.70$) was obtained for the experimental data corresponding to the decomposition of ammonium perchlorate. In this last case, the mentioned differences between experimental and calculated data can be due both to the inherent errors in the evaluation of the decomposition isotherms and to the dependence of the activation energy on the conversion degree.

Keywords: isothermal kinetics, non-isothermal kinetics, solid–gas systems

Introduction

One of the applications of the chemical kinetics is the prediction of the behaviour of the investigated system in different conditions with respect to those used to evaluate the kinetic parameters. As an example, the evaluation of the thermal lifetime of electroinsulating polymeric materials from isothermal accelerated aging data according to procedure recommended by IEC-216 Standard [1] have to be mentioned.

The methods of extrapolation of the results obtained from non-isothermal data to isothermal conditions [2–7] are based on the assumption of agreement between isothermal and non-isothermal kinetic parameters. The cases when in the investigated system only one main decomposition reaction occurs, the rate of which is given by the relations [8]:

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1388–6150/2003/ $ 20.00
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Kluwer Academic Publishers, Dordrecht

- in isothermal conditions:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{1}$$

- in non-isothermal conditions:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where α is the conversion degree, t – the time, A – the pre-exponential factor, E – the activation energy, T – the temperature, $f(\alpha)$ is the differential function of conversion and $\beta=\mathrm{d}T/\mathrm{d}t$ is the linear heating rate, are going to be analyzed.

The methods of obtaining the isotherms from non-isothermal data [2–7] use the integral forms of Eqs (1) and (2):

- in isothermal conditions, at the temperature T_0:

$$g(\alpha)=At_{\mathrm{iso}}\exp\left(-\frac{E}{RT_0}\right) \tag{3}$$

- in non-isothermal conditions, at the heating rate β:

$$g(\alpha)=\frac{A}{\beta}\int_0^{T_\alpha}\left[\exp\left(-\frac{E}{RT}\right)\right]\mathrm{d}T\equiv\frac{AE}{\beta R}p\left(\frac{E}{RT_\alpha}\right) \tag{4}$$

where $g(\alpha)=\int_0^{\alpha}[1/f(\alpha)]\mathrm{d}\alpha$ is the integral function of conversion and $p(E/RT_\alpha)$ is the integral temperature.

Through introduction of the A, E and $g(\alpha)$ values as determined from non-isothermal data in Eq. (3), the isotherms $\alpha=\alpha(t)$ could be obtained. This procedure supposes the knowledge of the analytical form of $f(\alpha)$ or $g(\alpha)$, which, in some cases, could be a relatively difficult problem. In order to bypass this problem, Toop [3–5] used the right members of Eqs (3) and (4) for a given conversion and obtained:

$$t_{\mathrm{iso}}=\frac{E}{\beta R}p\left(\frac{E}{RT_\alpha}\right)\exp\left(\frac{E}{RT_0}\right) \tag{5}$$

The logarithmic variant of Eq. (5):

$$\log t_{\mathrm{iso}}=\frac{E}{2.303RT_0}+\log\frac{E}{\beta R}+\log p\left(\frac{E}{RT_\alpha}\right) \tag{6}$$

was used by Toop [3] for the fast evaluation of the temperature index (temperature corresponding to a thermal lifetime of 20000 h [1]) of some wire enamels.

From relations (3) and (4) it turns out that:

$$t_{\mathrm{iso}} \equiv t_\alpha = \frac{\int\limits_0^{T_\alpha}\left[\exp\left(-\frac{E}{RT}\right)\right]\mathrm{d}T}{\beta\exp\left(-\frac{E}{RT_0}\right)} \tag{7}$$

derived by Vyazovkin and Lesnikovich [6, 7]. This is another way of writing the Eq. (5) previously derived by Toop.

In order to apply the method based on Eq. (5), the activation energy is evaluated using an isoconversional method (a critical discussion of such methods is given in [9]). Obviously the results obtained using such a method are influenced by the adopted approximation for the temperature integral.

This work is dedicated to a differential isoconversional method for obtaining the isotherms of the thermal decomposition or degradation in solid–gas systems from non-isothermal data.

Theoretical part

Considering *a*) the equality between isothermal and non-isothermal kinetic parameters, and *b*) the validity of Eqs (1) and (2) for the reaction rate in isothermal and non-isothermal conditions respectively, through elimination of $Af(\alpha)$ from Eqs (1) and (2), for a given value of α we get:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha,\mathrm{T}_0} = \beta\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_\alpha \exp\left[-\frac{E}{R}\left(\frac{1}{T_0}-\frac{1}{T_\alpha}\right)\right] \tag{8}$$

In relation (8) T_α is the temperature corresponding to the degree of conversion α, T_0 – temperature of the calculated isotherm and the rate $(\mathrm{d}\alpha/\mathrm{d}T)_\alpha$ is determined at a heating rate which equals to β.

If the value of the activation energy is known, using an $\alpha(T)$ curve recorded at a given heating rate, the values of $(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{T}_0}$ corresponding to a given temperature T_0 and a set of conversion degree can be calculated. According to the theorem of the inverse function $(\mathrm{d}t/\mathrm{d}\alpha)_{\mathrm{T}_0}$, has the reciprocal value of $(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{T}_0}$. In such a way the curve $(\mathrm{d}t/\mathrm{d}\alpha)_{\mathrm{T}_0}$ *vs*. α can be recorded, and:

$$t_{\alpha,\mathrm{T}_0} = \int\limits_0^\alpha \left(\frac{\mathrm{d}t}{\mathrm{d}\alpha}\right)_{\mathrm{T}_0}\mathrm{d}\alpha \tag{9}$$

The use of this procedure supposes the knowledge of the dependence *E vs*. α. This could be done by help of an isoconversional method applied to a set of non-isothermal data recorded at several heating rates. The procedure does not require the knowledge of the analytical form of the conversion function.

Relation (8) could be eventually used even when *E* depends on α, considering for each α value the corresponding *E* value. Under such conditions one has to mention two problems, namely: *a*) the choice of the method to establish the dependence *E vs*. α, and *b*) the possibility of the dependence of E on the temperature range used for applying the isoconversional method. Concerning the first problem, it was shown [9, 11–13] that if E depends on α a differential isoconversional method like Friedman's one [14] or a nonlinear differential method [15] based on Eq. (2) are recommended. The differences between the results obtained by means of such methods and those obtained using integral isoconversional methods are due to the way of deriving relation (4) which grounds these methods. This relation was derived considering that E and A do not depend on α. Concerning problem *b*), it was noticed [13, 16, 17] if E depends on α, the dependencies which ground the isoconversional linear methods are actually not linear but exhibit convex or concave forms which show a dependence of the activation energy on the temperature. The quantitative coherence of $E(\alpha)$ dependencies of isoconversional methods can be improved by bringing the temperature regions of isothermal and non-isothermal experiments closer to each other [17, 18].

Simulations

Firstly, the suggested procedure will be checked for isothermal and non-isothermal data corresponding to a single first order reaction. Obviously, unlike the experimental data, these data are not affected by noises and therefore are suitable for the verification of the suggested procedure.

The simulation was performed for $f(\alpha)=1-\alpha$; $E=58.5$ kJ mol^{-1}, $A=900$ s^{-1} and: *a*) non-isothermal conditions and heating rates of 0.5; 0.9; 3; 5; 10 and 15 K min^{-1}; *b*) isothermal conditions for temperatures of 50 and 100°C.

In order to evaluate E, Friedman's isoconversional differential method was used. The $(d\alpha/dT)_\alpha$ values were obtained through numeric differentiation of the curves α *vs.* T. Using relation (8), the values $(d\alpha/dt)_{\alpha,T_0}$ corresponding to various pairs (β, T_0) were calculated. The so calculated values $(d\alpha/dt)_{\alpha,T_0}$ coincided with those directly resulted from isothermal data. The values $(d\alpha/dt)_{\alpha,T_0}$ calculated from non-isothermal data were used for the evaluation of the corresponding isotherms. A comparison between an isotherm so

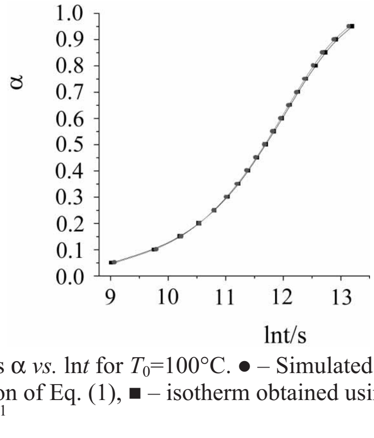

Fig. 1 The dependencies α *vs.* ln$t$ for T_0=100°C. ● – Simulated isotherm obtained through integration of Eq. (1), ■ – isotherm obtained using the non-isothermal data for 5 K min^{-1}

calculated from non-isothermal data for β=5 K min^{-1} and another one obtained directly through integration of relation (1) is shown in Fig. 1. The standard deviation of the t values calculated from non-isothermal data with respect to those calculated from relation (1) through integration is comprised in the range –3.7 – +4.9%.

Experimental example

Thermal decomposition of ammonium perchlorate

The isothermal (T_0=538.2; 543.2; 548.2; 553.2; 558.2 K) and non-isothermal (β=2.52; 5.16; 7.58; 10.49; 12.79; 15.45 K min^{-1}) data from the ICTAC Kinetic Project [10] were used. For $0.05\le\alpha\le0.82$ the Friedman's differential isoconversional method [14] was used to obtain the dependence E *vs*. α. A similar procedure was used to obtain the dependence E *vs*. α from isothermal data. The isothermal as well as the non-isothermal data showed that E depends on α. A decrease of E with α was recorded in the range $0.05\le\alpha\le0.15$ (E decreases from 100–110 kJ mol^{-1} to 80–90 kJ mol^{-1}). An increase of E with α for $0.15\le\alpha\le0.40$ (from 80–90 kJ mol^{-1} to 115–120 kJ mol^{-1}) was obtained. Finally, in the range $0.40\le\alpha\le0.82$, the activation energy keeps practically a constant value (116±6 kJ mol^{-1}). These results are in agreement with those obtained by means of the differential methods by Burnham [19] and Roduit [18] and presented graphically by Vyazovkin [20]. The values of E resulted from isothermal data for $0.05\le\alpha\le0.30$ exhibit relative high standard deviations (until ±17%). These deviations might result from the temperature jump at the start of each isothermal experiment. For $0.40\le\alpha\le0.82$ the standard deviations of the activation energy are relatively low (until ±7.6%) and the isothermal as well as the non-isothermal data lead practically to the same value of E (116±6 kJ mol^{-1}).

The dependence E_{FR} *vs*. α (E_{FR} is the activation energy obtained by means of Friedman method) as well as the dependence $(d\alpha/dT)$ *vs*. α obtained for each TG curve, were used to work the curves $(d\alpha/dt)_{T_0}$ *vs*. α for each value of T_0. From these curves, through the procedure suggested in this work, the isotherms of ammonium perchlorate decomposition were obtained. For each isotherm, the value of t for a given value of α was considered as the average value of t obtained for each heating rate. For the same T_0 and t, the absolute value of the standard deviation of t with respect to the average value is lower than 8%.

Figure 2 shows the calculated and experimental isotherms for T_0=538.2 K and T_0=558.2 K. A satisfactory agreement between them can be noticed. Nevertheless for all values of T_0, the absolute deviation (e) of t_{calc} with respect of t_{exp} exhibit values comprised between 10 and 18% in the ranges of α: $0.10\le\alpha\le0.37$ and $0.70\le\alpha\le0.82$. For $0.37\le\alpha\le0.70$, $|e|<10\%$. The relatively high deviation of t_{calc} with respect of t_{exp} might be due to one of the following reasons: *a*) some errors in t evaluation through isotherm experiments due to the heating of the sample from room temperature to the working temperature; *b*) complexity of the ammonium perchlorate decomposition that determines dependencies of the activation energy on the degree of conversion and temperature.

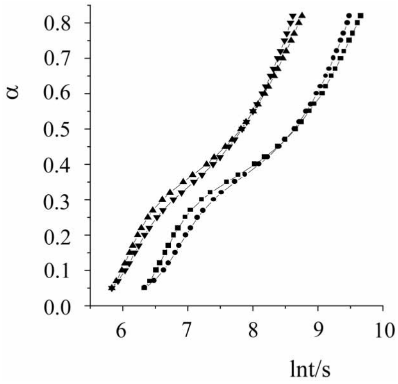

Fig. 2 The isotherms α *vs.* ln*t* for: 538.2 K: ■ – *t* calculated; ● – *t* experimental; 558.2 K: ▲ – *t* calculated; ▼ – *t* experimental

Conclusions

An isoconversional differential method to evaluate the isotherms of solid–gas decomposition from non-isothermal data was suggested. The method does not require the use of an approximation for the temperature integral.

The suggested procedure was applied to: *a*) simulated data corresponding to a first order reaction, and *b*) thermal decomposition of ammonium perchlorate. For the simulated data, a very good agreement between calculated isotherms and those evaluated by means of the suggested procedure was obtained. For the decomposition of ammonium perchlorate that exhibits a dependence of the activation energy on the conversion degree, a satisfactory agreement between the experimental and calculated isotherms was obtained.

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