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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.

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 α–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 $10^{-2} \times P_{eq}$ [15] at lower pressure, the rates are independent of $P(CO_2)$, 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(solid) ↔ B(solid) + C(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–Brounshteinn 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:

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

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 produces 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:

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

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

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

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

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

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 $\Delta\alpha$:

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

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:

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

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:

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

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:

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

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.

2.1.2. *Case (ii)*

The theoretical bases of both Evolved Gas Analysis (EGA) and Temperature Programmed Desorption (TDP) techniques [26] indicates that the partial pressure of the gas in the close vicinity of the sample at the reaction temperature is proportional to the reaction rate. Altorfer [27] found that the partial pressure P can be written in terms of flow gas parameters:

$$P = P_\text{f}\frac{V_\text{M}}{Q_\text{f}}\frac{m_0}{m_\text{M}}\beta\frac{\text{d}\alpha}{\text{d}T} \tag{9}$$

Where:

P_f = Pressure of flow gas.
V_M = Molar volume of flow gas at normal conditions.
Q_f = Volume flow of flow gas.
m_0 = initial mass of sample.
m_M = molar mass of sample.

Eq. (9) can be conveniently expressed as:

$$P = a\frac{\text{d}\alpha}{\text{d}T}\,(\text{or}\,aC) \tag{10}$$

Where a is a temperature independent constant given by:

$$a = P_\text{f}\frac{V_\text{M}}{Q_\text{f}}\frac{m_0}{m_\text{M}}\beta$$

From Eqs. (7), (8) and (10) the reaction rate takes the form:

$$\frac{\text{d}\alpha}{\text{d}t}\,(\text{or}\,C) = \frac{A\exp(-E/RT)f(\alpha)}{1+(aA/Z)\exp[(\Delta H-E)/RT]f(\alpha)} \tag{11}$$

2.2. *Simulations*

In a previous paper [23] it has been concluded that the thermal decomposition of calcium carbonate under high vacuum (5×10^{-3} mbar) and very small sample mass obeys the R3 (contracting sphere) kinetic model yielding the following kinetic parameters: E = 167 kJ/mol and $A = 2\times10^8\,\text{min}^{-1}$. Vyazovkin [18] has shown that in this reaction there is a dependence of the activation energy on extent of reaction under a pressure of 0.5 mbar. In this paper we use the calcite as a model compound and we simulate a process that involves a linear variation of the effective activation energy with α, such as:

$$E = \text{Eo} + b\alpha \quad (\text{with}\,b = 30\,\text{and}\,\text{Eo} = 167\,\text{kJ mol}^{-1}) \tag{12}$$

This was explained in reference [28]. On the other hand when E depends on the degree of conversion, the apparent kinetic parameters (E and A) are correlated through the compensation effect relationship which is the consequence of the application of the Arrhenius equation. In accordance with this, only one value of A, corresponds to each E value. Thus, in this paper the compensation effect has the following functional form:

$$\log_{10}A = mE + n = m(\text{Eo}+b\alpha)+n \quad (\text{with}\,m = 0.07\,\text{and}\,n = -3.3) \tag{13}$$

These parameters have been used because they are in accordance with the initial activation energy Eo = 167 kJ/mol and the initial value of the preexponential factor $A = 2\times10^8\,\text{min}^{-1}$ in high vacuum [23]. Eqs. (7), (8), (12) and (13) give for case (i):

$$\frac{\text{d}\alpha}{\text{d}t}\,(\text{or}\,C) = 10^{m(\text{Eo}+b\alpha)+n}f(\alpha)\left[1-\frac{P}{Z\exp(-\Delta H/RT)}\right]\exp\left(\frac{-(\text{Eo}+b\alpha)}{RT}\right), \quad \text{with}\,f(\alpha) = (1-\alpha)^{2/3} \tag{14}$$

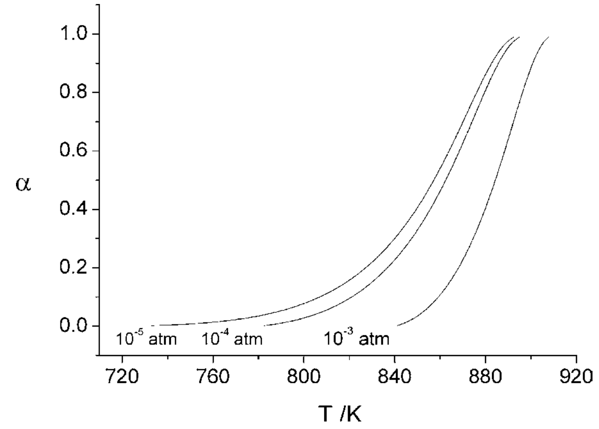

Fig. 1. Effect of pressure on theoretical non-isothermal TG curves constructed from Eq. (14) with $\beta = 1\,\text{K min}^{-1}$.

Eq. (14), was used in the present paper to simulate the mass-transfer effect on the non-isothermal and CRTA thermoanalytical curves when there is a dependence of E and A on the conversion degree α, the experiments are carried out with a conventional open system under a controlled flow of the sweep gas and the pressure of the gases generated by the reaction is assumed to be nearly constant. When the pressure is proportional to the reaction rate Eqs. (11), (12) and (13) give for case (ii):

$$\frac{\text{d}\alpha}{\text{d}t}\,(\text{or}\,C) = \frac{10^{m(\text{Eo}+b\alpha)+n}\exp(-(\text{Eo}+b\alpha)/RT)f(\alpha)}{1+(a10^{m(\text{Eo}+b\alpha)+n}/Z)\exp[(\Delta H-(\text{Eo}+b\alpha))/RT]f(\alpha)} \tag{15}$$

3. Results

3.1. *Case (i): use of Eq. (14)*

Taking the decomposition of calcium carbonate as a model example, between 500 and 1000 °C, Eq. (8) is very closely fitted with $Z = 4\times10^7$ and ΔH = 169 kJ/mole. Eq. (14) can be numerically integrated in order to determine the influence of mass transfer on the effective activation energy calculated by means of isoconversional methods. The equilibrium pressure was calculated from Eq. (8). It must be taken into account that the direct measurements of the equilibrium constant of this kind of solid–gas reaction are frequently unreliable since in some cases "pseudo-equilibria" appear, i.e., different constant pressure are obtained depending on whether the equilibrium is approached from above or below. This behaviour can be understood by considering that when the forward and reverse reactions are proceeding, a progressive decrease of their rate take place; thus equilibrium is not reached and the reaction merely becomes very slow.

3.1.1. *Effect of pressure on the shape of curves*

If there is no significant change in the partial pressure P of the gas generated in the reaction, we use Eq. (14), in order to check the validity of the above arguments and to show that the pressure in the close vicinity of the sample plays an important part in determining the shape of thermoanalytical curves, we have constructed in Figs. 1 and 2 the non-isothermal TG and CRTA diagrams calculated by assuming a constant heating rate β and a constant reaction rate C, respectively, and the kinetic parameters given by Eqs. (12) and (13). The non-isothermal TG curves in Fig. 1 are almost insensitive to the variation of pressure within the range considered (10^{-5}–10^{-3} atm).

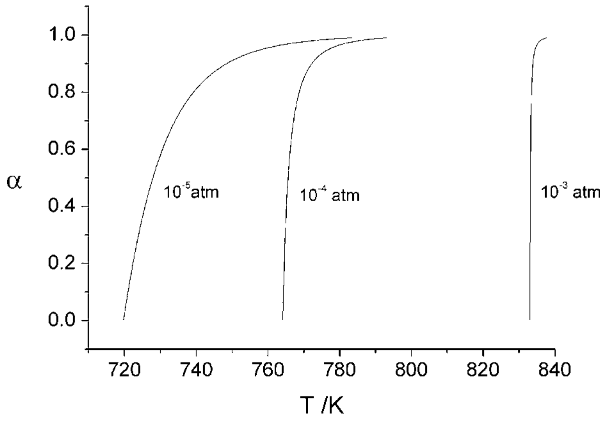

Fig. 2. Effect of pressure on theoretical CRTA curves constructed from Eq. (14) with $C = 10^{-4}\ \mathrm{min}^{-1}$.

However, the CRTA curves in Fig. 2 become narrower with the increase of pressure, and at $P \approx 10^{-3}$ atm the reaction takes place without any change in temperature, i.e., isothermally. The above conclusions are supported by the experimental data of the thermal decomposition of calcite using the derivatograph developed by Paulik and Paulik [29]. The CRTA curves under high vacuum and the Q-TG (Quasi-isothermal and Quasi-isobaric techniques by using the so-called labyrinth crucible) are shown in Fig. 3. We can see that in the case of Q-TG curve, the transformation takes place at a defined temperature in a quasi-isothermal manner. This is in agreement with the forecast from Eq. (14).

3.1.2. *Influence on the activation energy*

Thus, now we examine the influence of the pressure term on the calculated value of the activation energy, from non-isothermal TG data, using the advanced isoconversional method of Vyazovkin [20]. Fig. 4 shows the non-isothermal TG curves constructed by means of Eq. (14) and the kinetic parameters given by Eqs. (12) and (13). The activation energies of kinetic data of Fig. 4 are determined at any particular value of α by finding E_α which minimizes the function given by Eq. (6) for a linear heating program ($\mathrm{d}T = \beta\,\mathrm{d}t$). Fig. 5 shows the relative error obtained in this activation energy if the pressure correction term $(1 - P/P_{\mathrm{eq}})$ in Eq. (7) is neglected. We can see in Fig. 5 that the error is very large (the same error is obtained from the differential Friedman method [30] but for the sake of brevity is not included here). The error decreases when α increase to an asymptotic value. If the effect of pressure is taken into account, it is possible to obtain correct kinetic parameters. To achieve this goal, the Vyazovkin equation (6) must be modified to account for pressure correction term in case (i). The following relationship is obtained from Eq. (6) for a linear heating program:

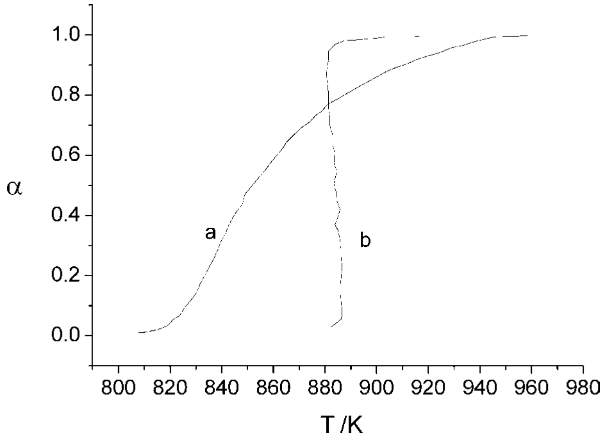

Fig. 3. (a) CRTA curve under high vacuum and (b) CRTA (Q-TG) curve using a labyrinth open crucible for the thermal decomposition of calcite. Ref [13].

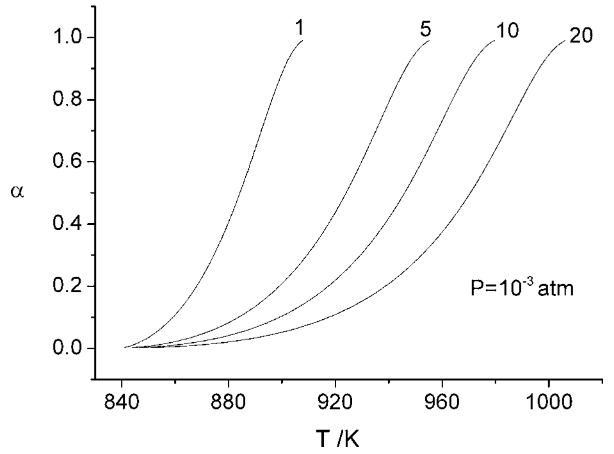

Fig. 4. Non-isothermal TG curves obtained from Eq. (14) at 10^{-3} atm. The heating rate is indicated by each curve.

$$\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{\beta_j[J(E_\alpha, T_{\alpha,i}) - (P/Z)H(E_\alpha, T_{\alpha,i})]}{\beta_i[J(E_\alpha, T_{\alpha,j}) - (P/Z)H(E_\alpha, T_{\alpha,j})]} \tag{16}$$

Where:

$$H[E_\alpha, T_{\alpha,i})] = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left(\frac{\Delta H - E_\alpha}{RT_{\alpha,i}}\right)\mathrm{d}T$$

If the pressure correction term $(1 - P/P_{\mathrm{eq}})$ in Eq. (7) is neglected, the calculated value of the activation energy is overestimated particularly at low temperature and high pressure. When the pressure correction term is included into Vyazovkin equation, Eq. (16), the error is eliminated and a true value of the activation energy is obtained. This explains the well known fact that the decomposition of calcite in vacuum leads to reasonable values of E [31,32] and decomposition under an uncontrolled atmosphere of $\mathrm{CO_2}$ gives completely misleading values [33].

The same results were obtained from CRTA curves (Fig. 6), at the same pressure value (10^{-3} atm) in a similar range of tempera-

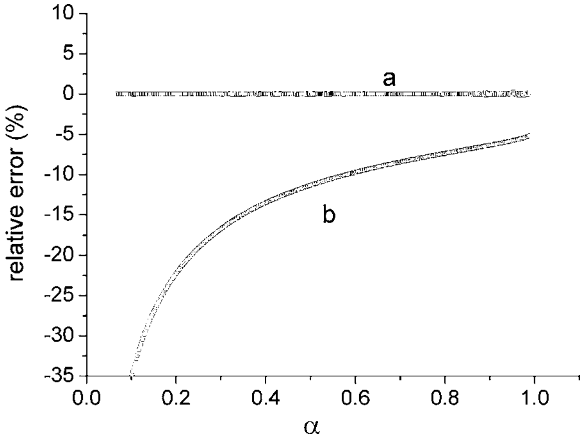

Fig. 5. Dependence of the relative error in E on the extent of reaction for non-isothermal TGA data of Fig. 4 evaluated by isoconversional method (a) Vyazovkin modified equation (Eq. (16)) and (b) Vyazovkin equation (Eq. (6)).

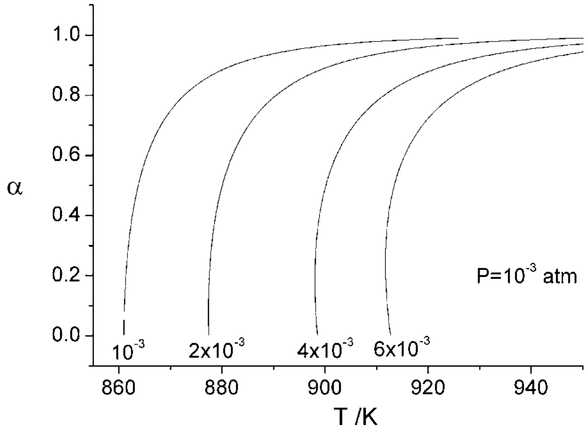

Fig. 6. Non-isothermal CRTA curves obtained from Eq. (14) at 10^{-3} atm. The reaction rate C is indicated by each curve.

tures. In this special case of non-linear non-isothermal data, such as CRTA experiments, where the reaction rate C is constant and the time dependence of the temperature $T(t)$ is not simple (or not known), it is not possible to use Eq. (6) and consequently the Vyazovkin equation must be adapted to CRTA data because the integral form cannot be used. For CRTA experiments we can write this equation, when pressure correction term is neglected, in the form:

$$\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{C_j\,\exp(-E_\alpha/RT_{\alpha,i})}{C_i\,\exp(-E_\alpha/RT_{\alpha,j})} \tag{17}$$

The activation energies of CRTA data of Fig. 6 are determined at any particular value of α by finding E_α which minimizes the function given by Eq. (17). Fig. 7 shows the relative error obtained in the activation energy if the pressure correction term in Eq. (7) is neglected. We can see in Fig. 7 that the error is, as in the case of non-isothermal TG data, very large. Following the same procedure as above a modification was introduced in Eq. (17) to account for pressure correction term:

$$\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{C_j(1-(P/Z\,\exp(-\Delta H/RT_{\alpha,i})))\,\exp(-E/RT_{\alpha,i})}{C_i(1-(P/Z\,\exp(-\Delta H/RT_{\alpha,j})))\exp(-E/RT_{\alpha,j})} \tag{18}$$

The same trend (Fig. 7) as above was observed in the relative error. Thus, a good value of the effective activation energy is obtained from CRTA data when the pressure correction term is not neglected.

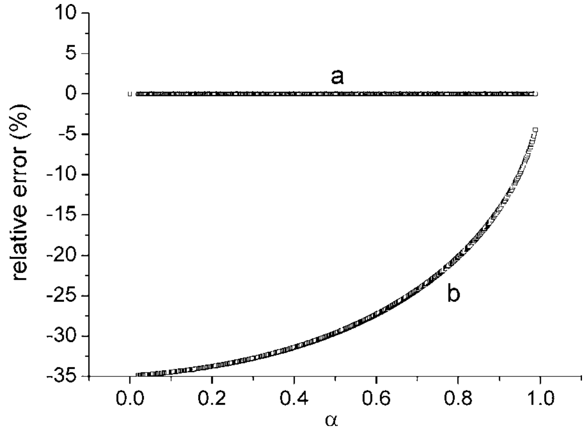

Fig. 7. Dependence of the relative error in E on the extent of reaction calculated for non-isothermal CRTA data of Fig. 6 by (a) Vyazovkin CRTA modified equation (Eq. (18)) and (b) Vyazovkin CRTA equation (Eq. (17)).

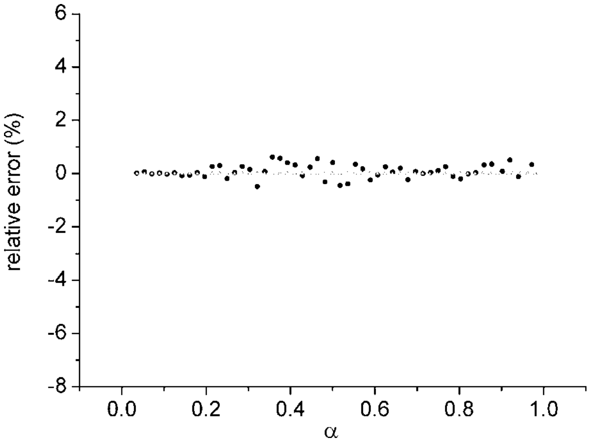

Fig. 8. Relative error in the activation energy for isoconversional TG data of Fig. 1 (circles) computed by Eq. (16) and CRTA data of Fig. 2 (triangles) evaluated by Eq. (18).

Finally, we take advantage of the above equations, to check if the true effective activation energy can be calculated from a series of thermoanalytical curves under different pressures of the gas generated by the reaction by using the pressure correction term. In this calculation the advanced isoconversional method has also been applied but, in this case, the procedure of the standard isoconversional method has been modified, instead of a set of experiments performed under different heating rates (or reaction rates C), for a given conversion α, we use a set of experiments under different pressures (data from Fig. 1 or Fig. 2) of the gas generated in the reaction at one heating rate β (or reaction rate C), respectively. Fig. 8 shows the relative error in the activation energy computed by Eq. (16) (non-isothermal TG data) and 18 (CRTA data) with this new procedure.

We can see that when the correction of pressure $(1-P/P_{\text{eq}})$ is taken into account, the effective activation energy of thermoanalytical data, when the effect of the pressure self-generated in the reaction is important, can be properly calculated.

3.2. *Case (ii): use of Eq. (15)*

When the pressure is proportional to the reaction rate, Eq. (15) instead of Eq. (14) was used. The same procedure as above was followed to assess the effect of the pressure on the shape of curves and on the activation energy.

3.2.1. *Effect of pressure on the shape of curves*

We have presented in Figs. 9 and 10 the non-isothermal TG and CRTA diagrams calculated by assuming a constant heating rate β and a constant reaction rate C, respectively, with kinetic parameters given by Eqs. (12) and (13) and different values of the parameter a in Eq. (10) conveniently choose to limit the pressure to the same range as that in Figs. 1 and 2. We can see that the shape of curves follows the same trend as that in Figs. 1 and 2. The non-isothermal TG curves in Fig. 9 are almost insensitive to the variation of pressure within the range considered (10^{-5}–10^{-3} atm). However, the CRTA curves in Fig. 10 become narrower with the increase of a, and for $a = 1.0$ (10^{-3} atm) the curve becomes isothermal.

3.2.2. *Effect of pressure on the activation energy*

The advanced isoconversional method [20] can be used to calculate the error in the activation energy when the pressure varies

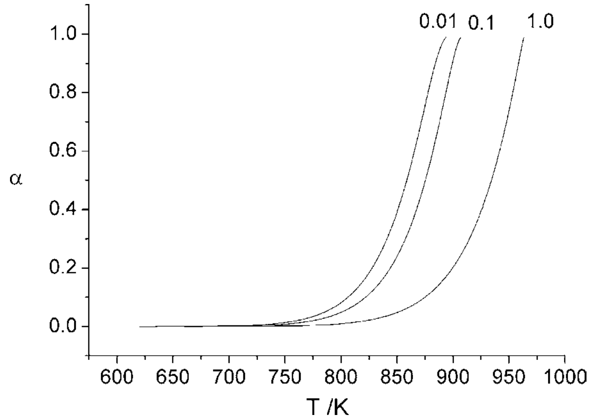

Fig. 9. Effect of pressure on theoretical non-isothermal TG curves constructed from Eq. (15) with $\beta = 1\,\mathrm{K\,min^{-1}}$, and different values of a which are indicated by each curve. The pressure ranges from 10^{-5} to 10^{-3} atm.

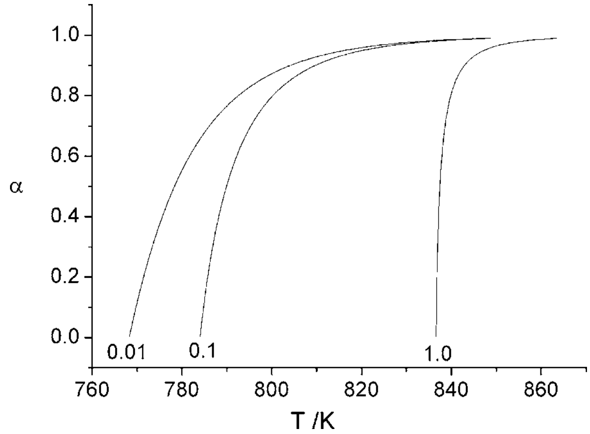

Fig. 10. Effect of pressure on theoretical CRTA curves constructed from Eq. (15) with $C = 10^{-3}\,\mathrm{min^{-1}}$, and different values of a which are indicated by each curve. The pressure ranges from 10^{-5} to 10^{-3} atm.

with the reaction rate. Figs. 11 and 12 show the dependence of the relative error on the conversion α for non-isothermal TG and CRTA data obtained at different values of the parameter **a** in Eq. (15). The error increases with the parameter **a** (i.e., by increasing the partial pressure of the gases generated in the reaction) and follows a similar trend to that of the reaction rate, the maximum error is obtained at $\alpha \approx 0.9$. On the other hand, by increasing the constant **a** (i.e., by decreasing the efficiency of the experimental system for removing the gases yielded in the reaction), the curves are shifted to higher temperature. Similar trend is obtained from TG and CRTA data. In a theoretical strict sense, using CRTA technique instead of conventional TG, a much greater sensitivity could be achieved, thus it is expected that the influence of the mass-transfer effect on the error in the activation energy should decrease in CRTA experiments because in CRTA the partial pressure of the gas self-generated in the reaction is kept constant, since the reaction rate C is constant over the whole range of conversion. This result has been confirmed experimentally in numerous papers [13,34–37], where it has been shown that CRTA permit to lower to a negligible extent the pressure and temperature gradients within the sample, and consequently this technique allows to carry out more meaningful experiments. But the result obtained in this simulation is not in agreement with this statement, where the relative error in the activation energy is similar in both techniques. Consequently the advantage of CRTA technique can be explained by considering that CRTA traces are most sensitive than conventional non-isothermal TG to the effect of pressure of the gases self-generated in the reaction such as Figs. 2, 3 and 10 show.

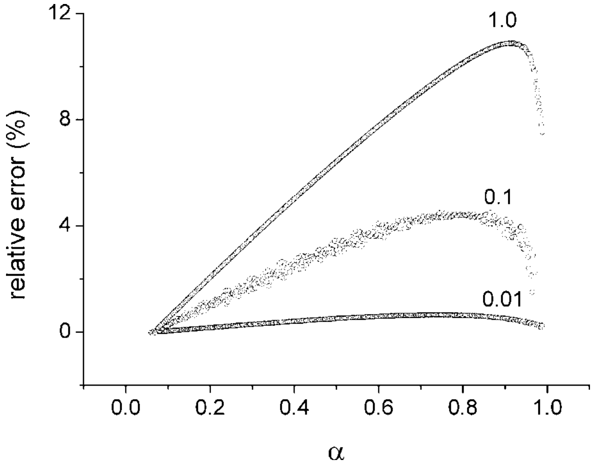

Fig. 11. Relative error in the activation energy as a function of α evaluated by isoconversional method (Eq. (6)), from conventional TG data simulated for different values of the constant a in Eq. (15) (indicated by each curve). Range of pressure = 10^{-1}–10^{-4} atm.

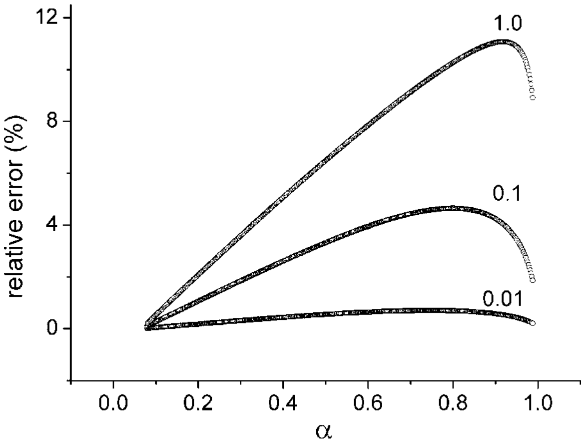

Fig. 12. Relative error in the activation energy as a function of α, evaluated by isoconversional method (Eq. (17)), from CRTA data simulated for different values of the constant a in Eq. (15) (indicated by each curve). Range of pressure = 10^{-1}–10^{-4} atm.

As above, a reliable determination of the activation energy can be expected by using the Vyazovkin equation modified to account for the effect of pressure in case (ii). This modification is not possible for non-isothermal TG experiments since an analytical form of the $g(\alpha)$ function cannot be achieved from Eq. (15). For CRTA it is possible this modification and can be expressed by the following relationship:

$$\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{C_j(1-(aC_i/Z\exp(-\Delta H/RT_{\alpha,i})))\exp(-E/RT_{\alpha,i})}{C_i(1-(aC_j/Z\exp(-\Delta H/RT_{\alpha,j})))\exp(-E/RT_{\alpha,j})} \qquad (19)$$

As above, when this modification is used, a proper value of the effective activation energy is obtained, for CRTA data, computed from Eq. (19) This may be considered as an interesting argument to explain the advantage of CRTA technique for calculating the activation energy of solid–gas reaction when the pressure of the gases self-generated in the reaction is variable and proportional to the reaction rate such as in case (ii).

4. Conclusions

The lack of agreement and reproducibility in many solid-state reactions and the large deviations in the value of the activation energy for the thermal decomposition of many solids (these deviations are exemplified by the reported values of calcite) are probably due to the weak control of experimental parameters. Thus, the use of the pressure correction term in the reaction rate could resolve the problem of disagreement between non-isothermal results. The advanced isoconversional method provides a sound way of estimating the effective activation energy for thermoanalytical data when this correction term is included in the computation. Accordingly, the kinetic measurements at a slow reaction rate under a high vacuum are recommended for simplifying the kinetic calculations by neglecting the pressure term.

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