

RECENT ADVANCES IN KINETICS AND MECHANISMS OF CONDENSED PHASE PROCESSES: A MINI-REVIEW

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Abstract. This mini-review deals with the state of the art research in the field of condensed phase kinetics in particular regard to prediction of reaction mechanisms. Determination of condensed phase reaction models, which provide plausible description of the reaction mechanisms of condensed phase processes, has been confronting with serious issues for a long while. The roots of the stated problem lied in the use of oversimplified methods to cope with the complex multi-step kinetics. In the said regard, this paper initially reviews in a concise way the pre-existing reaction model determination approaches along with their merits and demerits. Afterwards, special emphasis is put on the advanced kinetic approach to reaction mechanisms, which takes into consideration the dependence of activation energy of system on degree of reaction advancement and/or temperature. Certain important applications of the advanced kinetic approach on various emerging research domains including, polymers/polymer composites, fuel, management and valorization of waste, and crystallization in amorphous materials are brought to light and its future perspectives are discussed.

1. INTRODUCTION

Thermally stimulated condensed phase process belong to that class of condensed phase processes in which the system needs to cross a potential energy barrier in order to shift itself from reactants to products. The energy distribution along the relevant coordinates in such a system is known to be governed by Boltzmann statistics. If the processes occurring in condensed phase are taken into consideration, several prominent physical phenomena and chemical reactions fall in this category [1]. Physical phenomena include; vaporization and sublimation, glass transition and glass aging, nucleation, melting and crystallization of polymers, solid-solid transition (for instance, ferromagnetic to paramagnetic transitions), etc. On the other hand, chemical reactions comprise; thermal decomposition of organic/inorganic materials, polymerization

and cross linking reactions in polymers and thermal/thermo-oxidative degradation of polymeric materials [2]. Kinetic modeling of thermally activated processes is capable of simulating their reaction rates by parameterizing generally the two variables i.e. degree of conversion ' α ' and temperature ' T ', in order to probe those processes. Nevertheless, this task is considerably complicated as even an apparently simple process, which is usually dealt macroscopically, may consist of a number of complex processes occurring simultaneously (parallel/consecutive or both). It is worth mentioning that in order to kinetically interpret these kinds of complicated processes, some facile methods have been available in thermal analysis which could just partially fulfill the challenges of this field in respect of the notable complexity of these processes [2]. These issues were highlighted in International confederation for Thermal Analysis and Calorimetry

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(ICTAC) kinetic project [3-7] and in ICTAC kinetic committee recommendations [8]. Indeed, the complexity of a condensed phase process may be implicitly visualized by isoconversional kinetic analysis [9,10], yet the prediction of reaction mechanisms inevitably demands the determination of explicit reaction model for the process. Unluckily, the well known reaction model determination methods, which were envisaged reliable in the thermal analysis field, employ either single choice of activation energy (effective energy), the use of approximations, or worth questioning compensation principle [11-15].

In the above mentioned frame of reference, this review reports the attempts made to solve the reaction mechanism prediction problem in the case of complex multi-step condensed phase processes. This review encompasses the most recent kinetic approaches to mechanisms of condensed phase processes. These approaches are not only helpful in predicting the reaction mechanisms of complex processes but also they might provide basis to derive new reaction models to deal with intricate mechanisms. A brief account of the important results obtained by applying the proposed approaches on the thermally activated processes occurring in various materials will be reported and discussed.

2. THEORETICAL BASIS OF CONDENSED PHASE KINETICS

The progress of a thermally stimulated condensed phase process is denoted by a term degree of conversion 'α' which is defined as following:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty}, \tag{1}$$

where, 'm₀' is the initial mass of reactant, 'm_t' is its mass at certain temperature (non-isothermal analysis) or time (isothermal analysis) during the reaction and 'm_∞' is its mass at end of reaction. If differential scanning calorimetry (DSC) is employed to carry out the kinetic analysis, the degree of conversion can be determined by the following expressions:

In non-isothermal DSC,

$$\alpha_T = \frac{\Delta H_T}{\Delta H_{Total}} = \frac{\int_{T_0}^T \left(\frac{dH}{dT}\right) dT}{\int_{T_0}^{T_\infty} \left(\frac{dH}{dT}\right) dT}. \tag{2}$$

In isothermal DSC,

$$\alpha_t = \frac{\Delta H_t}{\Delta H_{Total}} = \frac{\int_{t_0}^t \left(\frac{dH}{dt}\right) dt}{\int_{t_0}^{t_\infty} \left(\frac{dH}{dt}\right) dt}, \tag{3}$$

where, T₀, T & T_∞ and t₀, t & t_∞ are the onset, arbitrary, and end crystallization temperatures/times respectively; dH is the heat released in an infinitesimally small temperature or time interval dT or dt respectively.

In condensed phase processes, the reaction rate dα/dt being the function of 'α' can be represented as:

$$\frac{d\alpha}{dt} = kf(\alpha). \tag{4}$$

Eq. (4) is the basic kinetic equation of condensed phase processes. In the case of thermally stimulated processes, the value of rate constant 'k' is often substituted in Eq. (4) by Arrhenius equation which then takes the following form:

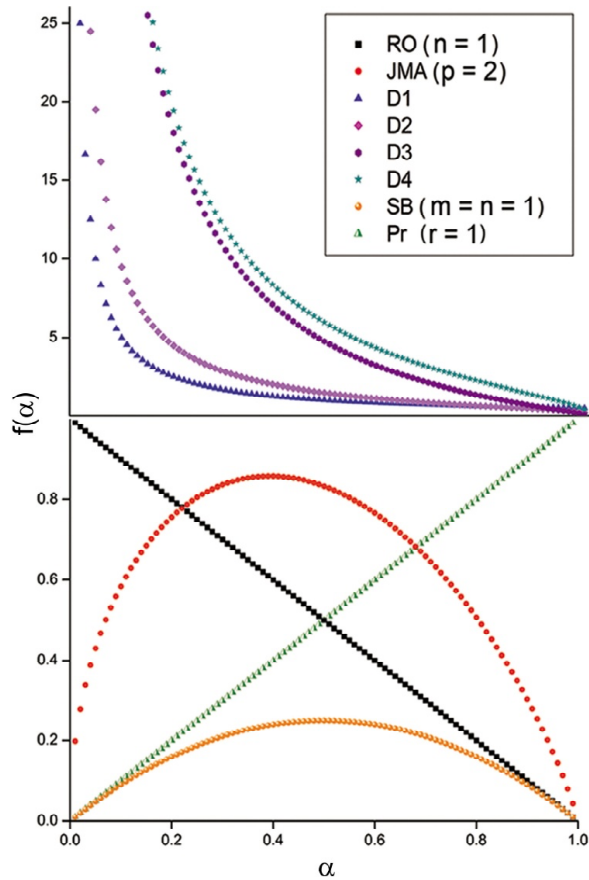


Fig. 1. Graphical representation of different cases of well known condensed phase reaction models.

Table 1. Well known reaction models and integrated reaction models with their physical meanings [16-23].

Reaction model	Symbol	$f(\alpha)$	$g(\alpha)$
Reaction n th order model	F_n/RO	$(1-\alpha)^n$	$\frac{1}{n-1} \left[\frac{1}{(1-\alpha)^{n-1}} - 1 \right]$
Johnson Mehl Avrami general equation (growth of nuclei)	JMA	$m(1-\alpha) \times \{-\ln(1-\alpha)\}^{1-1/m}$	$[-\ln(1-\alpha)]^{1/m}$ a similar relation is derived for n -dimensional nucleation (Avrami-Erofeev equation)
One-dimensional diffusion	D_1	$1/2 \alpha$	α^2
Two-dimensional diffusion	D_2	$-1/\ln(1-\alpha)$	$\ln\{(1-\alpha)^\alpha(1-\alpha)e^{\alpha^2}\}$
Jander's equation (three-dimensional diffusion)	D_3	$\frac{3(1-\alpha)^{2/3}}{2\{1-(1-\alpha)^{1/2}\}}$	$2\{1-(1-\alpha)^{1/3}\} + \{(1-\alpha)^{2/3}-1\}$
Ginstling equation (three-dimensional diffusion)	D_4	$\frac{3}{2\{(1-\alpha)^{-1/3}-1\}}$	$1-(1-\alpha)^{2/3}-2\alpha/3$
Sestak Berggren (autocatalytic model)	SB (m,n)	$\alpha^m(1-\alpha)^n$	Dependent upon the values of m and n (a generalized case of Prout-Tompkin (P-T) model)
Power law (nucleation)	Pr	$(\alpha)^r$	$-\frac{1}{(r-1)(\alpha)^{r-1}}$ when $r \neq 1$ $\ln(\alpha)$ when $r=1$

$$\frac{d\alpha}{dt} = A \exp(-E_\alpha / RT) f(\alpha), \quad (5)$$

where, 'A' is the pre-exponential factor, E_α is the energy of activation, $f(\alpha)$ is the function of degree of conversion, called reaction model, and R is the gas constant. Physically, 'A' describes the collision frequency of the particles involved in the formation of activated complex, E_α is the activation energy barrier(s) of reaction, and $f(\alpha)$ is an expression for the mechanism of reaction [1]. Some well known condensed phase reaction models are given in Table 1 and Fig. 1.

2.1. Determination of activation energy

Isoconversional methods are employed to examine the variation in activation energy with the degree of conversion, and therefore the nature and complexity of process. A condensed phase process is fairly approximated as single step if the variation in its activation energy with the degree of conversion is insubstantial, otherwise, the reaction is deemed as following a complex reaction pathway. Isoconversional methods can be isothermal/non-isothermal, differential/integral and linear/nonlinear [8].

2.1.1. Differential isoconversional method

Taking logarithm of Eq. (5) gives the following linear differential isoconversional method, known as the Friedman's method [24].

$$\ln(d\alpha / dt)_{\alpha,\beta} = -E_\alpha / RT_{\alpha,\beta} + \ln Af(\alpha). \quad (6)$$

The E_α values can be determined by plotting $\ln(d\alpha/dt)$ versus $1/T_\alpha$ at constant values of α which demands numerical differentiation. The resulting E_α values might therefore be irregular.

2.1.2. Integral isoconversional methods

Numerical differentiation can be avoided by using integral methods. Therefore, integration of Eq. (5) results in:

$$g(\alpha) = \int_0^\alpha d\alpha / f(\alpha) = \int_0^T \exp(-E / RT) dT = (A/\beta) I(E, T), \quad (7)$$

where, $g(\alpha)$ is called the integrated reaction model in Eq. (7) and $\beta = dT/dt$ is the heating rate. A list of

various condensed phase integrated reaction models has already been given in Table 1. Eq. (7) contains temperature integral $I(E, T)$ which has no analytical solution [25]. A number of approximations applied to numerically solve the temperature integral give the following linear integral isoconversional method [8]:

$$\ln\left(\frac{\beta}{T_\alpha^b}\right) = \text{Const.} - \left(\frac{\alpha E_\alpha}{RT_\alpha}\right). \quad (8)$$

In Eq. (6), 'a' and 'b' are the constants which depend on temperature integral approximation [25]. For instance, (a,b) = (1.052, 0) for Ozawa-Flynn-Wall (OFW) method [26]; (a,b) = (1, 2) in the case of Kissinger-Akahira-Sunose (KAS) method [27] and (a,b) = (1.0008, 1.92) in the case of Starink's method [28], etc.

Aiming to determine the reliable activation energies of condensed phase processes, a generalized linear integral isoconversional method (GLIM) has been suggested by Arshad and Maaroufi by mathematically treating Eq. (8), with the following expression [29]:

$$E_\alpha = \frac{R}{a} \left[b \frac{d \ln T_\alpha}{d(1/T_\alpha)} - \frac{d \ln \beta}{d(1/T_\alpha)} \right]. \quad (9)$$

The activation energy of a condensed phase process at any value of ' α ' can be directly determined by employing Eq. (9), provided that the values of $d \ln \beta / d(1/T_\alpha)$ and $d \ln T_\alpha / d(1/T_\alpha)$ at the respective value of ' α ' are known.

A numerically accurate non-linear integral isoconversional method, called advanced isoconversional method, was suggested by Vyazovkin by solving Eq. (7) using numerical integration within the infinitesimally small intervals of extent of conversion [30]. The general expression for the advanced isoconversional method is given in the following Eq. (10):

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]}, \quad (10)$$

where, $J[E_\alpha, T(t_\alpha)]$ is the notation in Eq. (10) for integration with respect to time over an infinitesimally small interval $[\alpha, \alpha + \Delta\alpha]_{\Delta\alpha \rightarrow 0}$, and is defined as following:

$$J[E_\alpha, T(t_\alpha)] = \int_{\alpha}^{\alpha + \Delta\alpha} \exp(-E_\alpha / RT(t)) dt. \quad (11)$$

According to this method, the activation energy at each value of α is the value that minimizes $\Phi(E_\alpha)$ function.

2.2. Determination of reaction model

As discussed in the previous section, a reaction model is capable of giving information regarding the nature and mechanism of a condensed phase process [1]. It can either be a simple or a complicated mathematical function of the degree of conversion, constituting one or more. A list of some most common reaction models with their probable physical meanings is shown in Table 1.

2.2.1. Pre-existing reaction model determination approaches

The reaction model for condensed phase processes can be determined by either model fitting or model free methods. The former deals with fitting data-sets by the available reaction models. The most common in model fitting approaches is the Coats and Redfern's method [31] as mathematically expressed below:

$$\ln\{g(\alpha) / T^2\} = \ln(AR / \beta E) - E / RT. \quad (12)$$

As a matter of fact, this approach may give appropriate fits to the experimental data-sets even with widely diverged kinetic triplets, and therefore its credibility is indeed questionable [8].

In model free case, one of the useful methodologies was suggested by Malèk [11,32]. An average value of activation energy from isoconversional methods should already be known and then a pair of functions $y(\alpha)$ and $z(\alpha)$ can be utilized to determine the reaction model and its associated parameters as described in Eqs. (13) and (14) respectively:

$$y(\alpha) \approx (d\alpha / dt) \exp(x), \quad (13)$$

$$z(\alpha) \approx \pi(x) (d\alpha / dt) T / \beta. \quad (14)$$

In Eqs. (13) and (14) $x = E/RT$ and $\pi(x)$ is a temperature integral function. A more precise numerical approximation of $\pi(x)$ was initially proposed by Senum and Yang [33] and then modified by Flynn [25] as following:

$$\pi(x) = \frac{x^4 + 18x^3 + 86x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \times \left(\frac{\exp(-x)}{x}\right). \quad (15)$$

The maxima (α_{M_p} , α_p^∞) of $y(\alpha)$ and $z(\alpha)$ functions respectively and ' α_p ' as the degree of conversion at maximum reaction rate guide to the most appropriate reaction models according to the proposed criterion [11,32].

Another efficacious reaction model determination methodology is called the generalized master plots method [12,34]. Similar to the previous case, an average value of activation energy from isoconversional methods should be known and then the following equation is used to determine the suitable reaction models for the processes under consideration:

$$\frac{f(\alpha)}{f(0.5)} = \frac{d\alpha/dt}{(d\alpha/dt)_{0.5}} \frac{\exp(E/RT)}{\exp(E/RT_{0.5})}, \quad (16)$$

where, $T_{0.5}$ is attributed to $\alpha = 0.5$.

It should be taken into account that the above discussed reaction model determination methodologies give fairly reliable results if the change in activation energy of the reaction with degree of conversion is insignificant. If the activation energy of the system shows dependence on degree of conversion or temperature, those reaction model determination methodologies are not recommended.

2.3. An advanced kinetic approach to reaction mechanisms in condensed phase processes

As demonstrated in the previous section, the pre-existing reaction model determination approaches are not considered appropriate in the case of complicated multi-step processes. In order to solve this matter, Arshad and Maaroufi have put forward an innovative reaction model determination methodology taking into account the variable activation energy concept in order to kinetically interpret the mechanisms of thermally activated condensed phase processes [35]. They have developed various functions of degree of conversion for isothermal/non-isothermal and single-step/multi-step kinetics so as to predict the reaction mechanisms. The details of various mechanistic functions along with their derivations are given in the following sections.

2.3.1. Non-isothermal kinetics

Under non-isothermal conditions, degree of conversion, energy of activation and pre-exponential factor vary in the following way [35]:

$$\alpha = \Phi_1(T, t), \quad E = \Phi_2(\alpha, T), \quad A = \Phi_3(\alpha, T).$$

The pre-exponential factor is known to vary with temperature by following the relationship as given below [36]:

$$\frac{A}{A_0} = \left(\frac{T}{T_0} \right)^n, \quad (17)$$

where, ' A_0 ' is the value of pre-exponential factor at initial temperature ' T_0 ' and ' n ' is a numerical constant. Usually, $n \in [0, 1]$ but it may have positive values other than mentioned in the interval and it can even be a negative number [36]. The parameter ' n ' is in fact helpful in extracting rather detailed mechanistic information of reaction complementary to $f(\alpha)$ [29].

Putting the value of ' A ' from Eq. (17) into Eq. (5) yields the following equation:

$$\frac{d\alpha}{dt} = A_0 (T/T_0)^n \exp(-E_\alpha/RT) f(\alpha). \quad (18)$$

The overall change in the reaction rate as reaction advances can be described by differentiating Eq. (18) with respect to degree of conversion which, on series of mathematical operations [35], generates the following expressions:

$$\frac{f'(\alpha)}{f(\alpha)} = \frac{dE/d\alpha}{RT} - \frac{\beta}{T(d\alpha/dt)} \left\{ n + \frac{E_\alpha}{RT} \right\} + \frac{d^2\alpha/dt^2}{(d\alpha/dt)^2}, \quad (19)$$

$$\frac{f'(\alpha)}{f(\alpha)} = \frac{1}{(d\alpha/dt)} \left[\frac{\beta(dE/dT)}{RT} - \frac{\beta}{T} \left\{ n + \frac{E_\alpha}{RT} \right\} + \frac{d^2\alpha/dt^2}{(d\alpha/dt)^2} \right]. \quad (20)$$

In order to determine the parameter ' n ' present in Eqs. (19)-(20), Eq. (18) can be transformed into the following non-linear differential form:

$$y = a(x)^b \exp(-c/x), \quad (21)$$

where, $x = T$, $y = d\alpha/dt$, $a = \varphi(\alpha) = \{A_0/(T_0)^n\} f(\alpha)$, $b = n$, $c = E_\alpha/R$.

As the reaction rate varies exponentially with temperature at constant values of ' α ', the variation in reaction rate with temperature at constant values of ' α ' can be fitted by an exponential type user defined fitting function (UDF) based on Eq. (21) employing Levenberg-Marquardt algorithm (LMA) for 2D curves which results in the generation of parameters a , b , and c [29]. It is however worth pointing out here that the accuracy of reaction model of a condensed phase process becomes sensitive to parameter ' n ' when its activation energy acquires relatively lower value. However, when E_α/RT factor in Eq. (18) attains a value equal to or greater than 30 [37], the influence of parameter ' n ' on the reaction

Table 2. $f(\alpha)$ and $h(\alpha)$ expressions of well known reaction models; maxima of $h(\alpha)$ function ($\alpha_{max.}$), where applicable.

Reaction model	Notation	$f(\alpha)$	$h(\alpha)$	maxima of $h(\alpha)$ ($\alpha_{max.}$)
Reaction order	RO(n)	$(1-\alpha)^n$	$-n/(1-\alpha)$	-
Johnson Mehl Avrami General Equation	JMA ($m>1$)	$m(1-\alpha)\{-\ln(1-\alpha)\}^{1-1/m}$	$\left(\frac{1-1/m}{\ln(1/1-\alpha)} - 1 \right) (1-\alpha)$	-
1D-Diffusion	D_1	$1/2\alpha$	$-1/\alpha$	-
2D- Diffusion	D_2	$-1/\ln(1-\alpha)^{1-\alpha}$	$\ln(1-\alpha)^{1-\alpha}$	0.632
3D-Diffusion (Jander's equation)	D_3	$\frac{3(1-\alpha)^{2/3}}{2\{1-(1-\alpha)^{1/3}\}}$	$-\frac{2}{3}\left[\frac{1}{1-\alpha} + \frac{1}{2(1-\alpha)^{2/3}\{1-(1-\alpha)^{1/3}\}}\right]$	0.522
3D-Diffusion (Ginstling equation)	D_4	$\frac{3}{2\{(1-\alpha)^{-1/3} - 1\}}$	$-\frac{1}{3}\left[\frac{1}{\{(1-\alpha)^{1/3} - 1\}(1-\alpha)^{4/3}}\right]$	0.581
Sestak Berggren Power law (nucleation)	SB (m, n) Pr	$\alpha^m(1-\alpha)^n$ $(\alpha)^r$	$(m/\alpha)-(n/(1-\alpha))$ r/α	- -

model is generally insignificant, and Eqs. (19)-(20) take the following forms:

$$h(\alpha) = \frac{dE/d\alpha}{RT} + \frac{1}{d\alpha/dt} \left[\frac{d^2\alpha/dt^2}{d\alpha/dt} - \frac{\beta E_\alpha}{RT^2} \right], \quad (22)$$

$$h(\alpha) = \frac{1}{d\alpha/dt} \times \left[\frac{\beta(dE/dT)}{RT} - \frac{\beta E_\alpha}{RT^2} + \frac{d^2\alpha/dt^2}{d\alpha/dt} \right]. \quad (23)$$

where, $h(\alpha)$ is an expression to describe the ratio between differentiated and actual reaction model. Mathematical expressions and graphical representations of $h(\alpha)$ functions of well known reaction models are respectively given in Table 2 and Fig. 2.

Both Eqs. (22)-(23) deal with the determination of reaction models under variable conditions of activation energy. The right hand sides of Eqs. (22)-(23) can be obtained by the experimental thermo-analytical data while their left hand sides can be simulated by the $h(\alpha)$ functions. A fair agreement between curves generated from thermo-analytical data and theoretical models can guide to the appropriate

reaction models. Both Eqs. (22)-(23) take the following form when the reaction follows single step kinetics:

$$h(\alpha) = \frac{1}{d\alpha/dt} \left[\frac{d^2\alpha/dt^2}{d\alpha/dt} - \frac{\beta E}{RT^2} \right]. \quad (24)$$

2.3.2. Isothermal kinetics

Putting $\beta = dT/dt = 0$ in Eq. (22) and rearranging it, gives the following expression:

$$h(\alpha) = \frac{dE/d\alpha}{RT} + \frac{d^2\alpha/dt^2}{(d\alpha/dt)^2}. \quad (25)$$

In isothermal kinetics, the evaluation of reaction model follows the similar route as discussed in the previous section. Eq. (25) takes the following form if the reaction consists of only one step:

$$h(\alpha) = \frac{d^2\alpha/dt^2}{(d\alpha/dt)^2}. \quad (26)$$

An interesting fact noticed in Eq. (26) is that, if reaction follows single step isothermal kinetics then its mechanistic information can be directly obtained by thermo-analytical data, independent of its activation energy and pre-exponential factor. Although

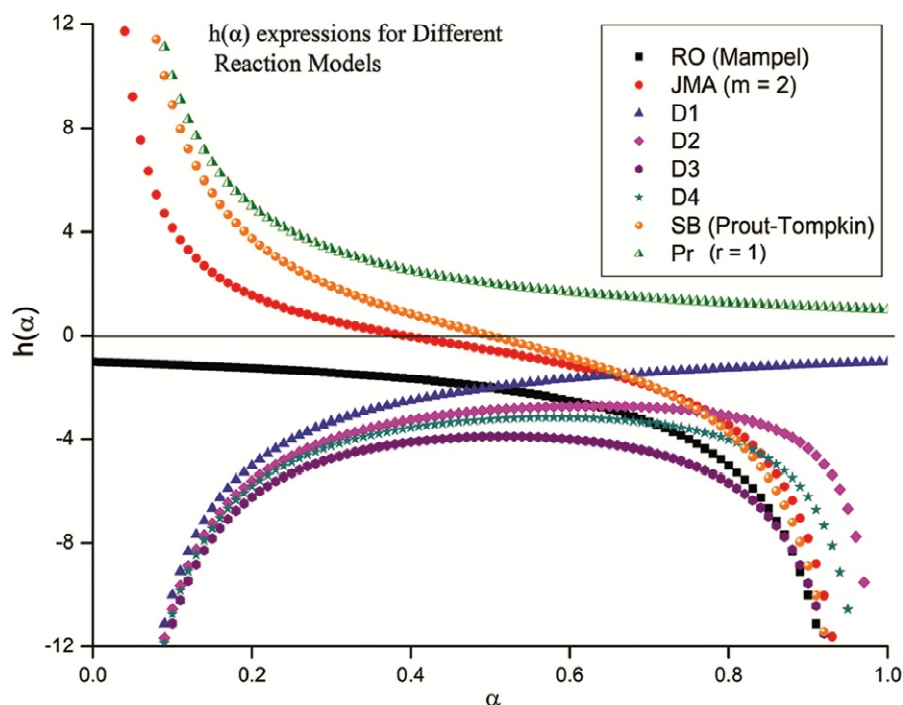


Fig. 2. $h(\alpha)$ expressions of some well known reaction models as shown in Fig. 1.

the $h(\alpha)$ functions as shown in Table 2 and graphically in Fig. 2 can fairly lead to the most probable reaction models in the case of single-step processes, yet such processes are not very common in condensed phase kinetics. An accurate picture of reaction model over the whole range of degree of conversion for complicated multi-step reactions can however be visualized by the proposed approach. By definition, $h(\alpha)$ function is expressed as following:

$$\frac{f'(\alpha)}{f(\alpha)} = h(\alpha). \quad (27)$$

Integration of Eq. (27) gives the following relation:

$$f(\alpha) = \exp\left(\int_{\alpha_0}^{\alpha} h(\alpha) d\alpha\right), \quad (28)$$

where, α_0 is a value greater than zero, obtained by adding an infinitesimally small positive digit to zero. Reaction models of complex condensed phase processes can be calculated by performing numerical integration of the curve obtained from Eqs. (19)-(20)/(22)-(23) in non-isothermal kinetics and/or Eq. (25) in isothermal kinetics over (0,1] and taking natural exponent of the resulting definite integral.

A serious issue in the case of multi-step processes is associated with identifying the mechanisms of the individual reactions within them. This trouble originates from the fact that only nucleation/growth

models show peak functions, and the rest of reaction models (if available in the reaction model curve) might not be visible in the plots of $f(\alpha)$ by using Eq. (28) as evident in Fig. 1. In order to solve this matter, a new kinetic function $F(\alpha, T)$, taking into consideration the variation of reaction mechanism with temperature, is introduced in non-isothermal kinetics which is defined as:

$$F(\alpha, T) = \frac{df(\alpha)}{dT} = f'(\alpha) \frac{d\alpha}{dT} = \frac{1}{\beta} f'(\alpha) \frac{d\alpha}{dt}. \quad (29)$$

The obtained characteristic shapes of $F(\alpha, T)$ functions by applying Eq. (29) on the reaction models shown in Fig. 1, using an arbitrary single step reaction simulated by Runge-Kutta (RK4) method at $10^\circ\text{C}\cdot\text{min}^{-1}$, are represented in Fig. 3. It has been demonstrated that $F(\alpha, T)$ function might be highly useful in identifying and distinguishing between various individual reaction mechanisms in a multi-step process [38].

3. MAJOR APPLICATIONS

3.1. Thermal degradation mechanisms in polymer composites filled with metal particles

Polymer composites containing metal particles define a fascinating class of materials in regard particularly to their valuable worldwide applications. They may either be electrically/thermally insulating

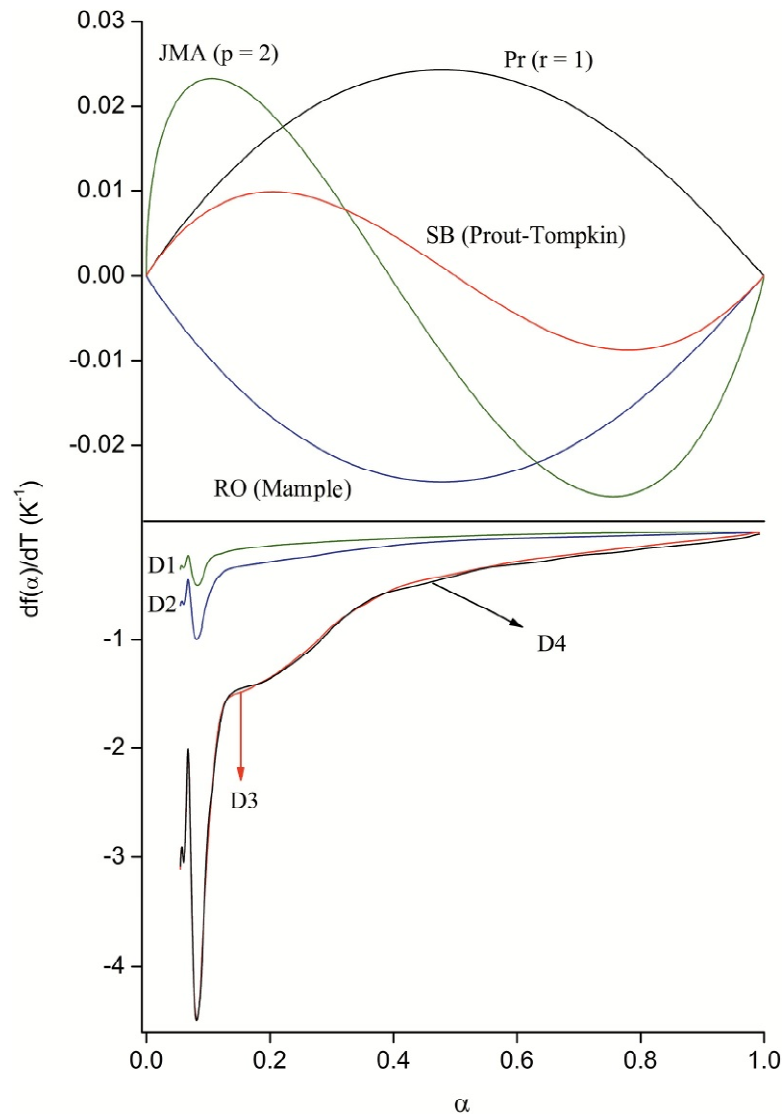


Fig. 3. Graphical representation of the application of new kinetic function $F(\alpha, T) = df(\alpha)/dT$ on reaction models described in Fig. 1 at $10^\circ Cmin^{-1}$.

or conducting, though both of them are equally useful. For example, insulating composites are applicable as thermal greases, thermal interface materials, and electric cable insulations, while conductive composites are employable in thermoelectrical and thermomechanical applications and solar devices [39]. However, one of the crucial tasks related to these materials is the process control for their eventual efficiency optimization. This task requires profound insights into the said materials; not only their structures, but also and especially the temperature dependent processes taking place in them need consideration. The suggested kinetic approach plays a vital role in the mentioned concern. Application of the proposed kinetic approach on insulating and conducting epoxy/Sn composites reveals new and interesting mechanistic information about the thermal degradation processes of epoxy/Sn compos-

ites [40]. It has been pointed out that thermal degradation of epoxy resin fairly follows single-step reaction pathway. Tin does not alter the reaction mechanism of epoxy, though it accelerates the thermal degradation rate of epoxy by lowering the activation energy barrier of reaction. In addition, the increase in reaction rate of epoxy depends on tin contents in epoxy.

The innovative kinetic approach has also been applied to predict the thermal degradation mechanisms in urea-formaldehyde cellulose composites filled with metal particles (UFC/metal composites; while, metal = Al, Zn, Sn) [38,41,42]. The isoconversional kinetic analysis of UFC/metal composites reveals that their thermal degradation might follow intricate reaction pathways. Since the activation energies of UFC/metal composites show substantial variations with the degree of reaction ad-

vancement, kinetic approaches capable of dealing with single-step processes become inapplicable in the case of UFC/metal composites. For that reason, advanced reaction determination methodology is employed on the thermoanalytical data of UFC/metal composites in order to probe their reaction mechanisms. Advanced reaction determination methodology not only confirms the findings of the isoconversional kinetic analysis but also provides interesting and important insights into the reactions mechanisms of UFC/metal composites. The obtained set of mechanistic information shows that the thermal degradation of UFC resin follows multi-step reaction mechanisms pursuing several parallel/consecutive reactions with predominantly nucleation/growth pathways. A detailed account of the dependence of reaction mechanism of UFC resin on the nature and contents of metal (particularly zinc and aluminum) particles has also been given and discussed [38,41,42].

3.2. Thermal decomposition mechanism of calcium hydroxyzincate dihydrate $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$

Recently, Ouanji et al. have reported an interesting application of suggested kinetic approach on the thermal decomposition process of *calcium hydroxyzincate dihydrate* (CZO) with an aim of synthesizing biodiesel catalyst CaO-ZnO . CZO is familiar in literature as a retardant for cement hydration, as a novel antifungal precursor of protective coatings for marble and limestone, and a promising material in photocatalytic degradation of textile dyes under sunlight. In their study, authors have pointed out that the thermal decomposition process consists of five complicated limited nucleation/growth steps as revealed by the advanced kinetic approach. On the basis of conforming information obtained by kinetic study and characterization of thermally activated structural transformation of CZO, authors have suggested a plausible thermal decomposition mechanism of CZO [43].

3.3. Waste management and valorization

Waste management is one of the hottest issues in the modern era. One of its sub-domains is research, treatment and eventual valorization of solid sludge produced by drinking and wastewater treatment plants. Analysis of the nature of constituents present in sludge as well as thermally activated processes

taking place in it over long temperature ranges might be helpful in the effective valorization of sludge. In this context, Dahhou et al. [44] carry out a combined study on thermally stimulated structural transformation and isoconversional kinetic analysis of the drinking water sludge by employing Eq. (9). The obtained results along with mechanistic information enable the authors to exploit the studied drinking water sludge into the materials of construction [45].

3.4. Kinetics of crystallization processes in amorphous materials

An important application of the innovative kinetic approach can be found on the kinetics of crystallization processes in amorphous materials. The set of theoretical models suggested in the theoretical section can be exploited to model the crystallization processes taking place in amorphous materials, say, crystallization in polymers, glasses, alloys, etc. In general, JMA and SB (m, n) models as shown in Table 1, can satisfactorily describe the crystallization processes in amorphous materials. As a matter of fact, SB (m, n) model is an empirical model which suffered from physical meaninglessness of its parameters (m, n) [46]. Arshad and Maaroufi have developed a relationship between JMA and SB (m, n) models [47-50] as given below, by employing the approach reported in the present paper:

$$\frac{1}{p} + \ln(1-\alpha)n - \left(\frac{1-\alpha}{\alpha}\right) \ln(1-\alpha)m - \ln(1-\alpha) = 0. \quad (30)$$

Which, on simplification, yields the following expression [47]:

$$\frac{1}{p} + \frac{3}{4}m - n = 0, \quad (31)$$

where, ' p ' is the parameter in JMA model.

Eq. (21) not only defines an explicit relationship between JMA and SB (m, n) reaction models but also it attributes parameters of empirical model to nucleation/growth phenomena of crystal formation in amorphous phases within the phenomenological limits [47].

Another fact is encountered while analyzing JMA model using the advanced kinetic approach that JMA model is not merely restricted to phase transformations following nucleation/growth mechanism but also the relatively higher values of JMA exponents

in the interval (0,1) of degree of conversion might also explain the condensed phase processes analogous to diffusion [47].

4. CONCLUSION AND FUTURE PERSPECTIVES

This review has reported the history of the problem of reaction mechanisms of condensed phase processes by kinetic approaches along with the most recent progress in the field. It can be stated that the recently suggested kinetic approach is quite efficacious in predicting the thermal degradation mechanisms of condensed phase processes. Its main advantage is that, it is applicable to both simple and complex reactions taking place under isothermal/non-isothermal conditions. Care must however be done in computing the precise values of reaction models as the suggested methodology is purely a differential approach, and a data smoothening filter is necessary to reduce the noise in data. Although initially proposed for thermally stimulated condensed phase processes, the suggested kinetic approach may be generalized on the processes following Arrhenius temperature dependence of reaction rates; for instance, thermally accelerated photoreactions in energy materials. Likewise, it might be capable of contributing in renewable and sustainable energy research.

REFERENCES

- [1] M.E. Brown and P.K. Gallagher, *Handbook of Thermal Analysis and Calorimetry: Recent Advances, Techniques and Applications* (Elsevier, Amsterdam, 2008).
- [2] S. Vyazovkin, *Isoconversional Kinetics of Thermally Stimulated Processes* (Springer, New York, 2015).
- [3] M.E. Brown, M. Maciejewski and S. Vyazovkin // *Thermochim. Acta* **355** (2000) 125.
- [4] M. Maciejewski // *Thermochim. Acta* **355** (2000) 145.
- [5] S. Vyazovkin // *Thermochim. Acta* **355** (2000) 155.
- [6] A.K. Burnham // *Thermochim. Acta* **355** (2000) 165.
- [7] B. Roduit // *Thermochim. Acta* **355** (2000) 171.
- [8] S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Perez-Maqueda, C. Popescu and N. Sbirrazzuoli // *Thermochim. Acta* **520** (2011) 1.
- [9] S. Vyazovkin and N. Sbirrazzuoli // *Macromolecules* **29** (1996) 1867.
- [10] S. Vyazovkin and N. Sbirrazzuoli // *Macromol. Rapid Commun.* **27** (2006) 1515.
- [11] J. Malek // *Thermochim. Acta* **200** (1992) 257.
- [12] P.E. Sanchez-Jimenez, L.A. Perez-Maqueda, A. Perejon and J.M. Criado // *Thermochim. Acta* **552** (2013) 54–59.
- [13] S. Vyazovkin and W. Linert // *Chem. Phys.* **193** (1995) 109.
- [14] P.J. Barrie // *Phys. Chem. Chem. Phys.* **14** (2012) 318.
- [15] P.J. Barrie // *Phys. Chem. Chem. Phys.* **14** (2012) 327.
- [16] M.E. Brown, D. Dollimore and A.K. Galwey, *Comprehensive Chemical Kinetics* (Elsevier, Amsterdam, 1980).
- [17] M. Fanfoni and M. Tomellini // *Il Nuovo Cimento* **20** (1998) 1171.
- [18] F.A. Booth // *Trans. Faraday Soc.* **44** (1948) 796.
- [19] A. Khawam and D.R. Flanagan // *J. Phys. Chem. B* **110** (2006) 17315.
- [20] A.M. Ginstling and B.I. Brounshtein // *J. Appl. Chem. USSR* **23** (1950) 1327.
- [21] W. Jander // *Z. Anorg. Allg. Chem.* **163** (1927) 1.
- [22] J. Sestak J and G. Berggren // *Thermochim. Acta* **3** (1971) 1.
- [23] P.W.M. Jacobs and F.C. Tompkins, *Chemistry of the Solid State* (Academic Press, New York, 1955).
- [24] H.L. Friedman // *J. Polym. Sci.* **6(C)** (1965) 183.
- [25] J.H. Flynn // *Thermochim. Acta* **300** (1997) 83.
- [26] J.H. Flynn and L.A. Wall // *J. Res. Nat. Bur. Standards-A Phys. & Chem.* **70** (1966) 487.
- [27] T. Akahira and T. Sunose // *Res. Rep. Chiba Inst. Technol. (Sci. Technol.)* **16** (1971) 22.
- [28] M.J. Starink // *Thermochim. Acta* **404** (2003) 163.
- [29] M.A. Arshad, A. Maaroufi, G. Pinto, S. El-Barkany and A. Elidrissi // *Bull. Mater. Sci.* **39** (2016) 1609.
- [30] S. Vyazovkin // *J. Comput. Chem.* **22** (2001) 178.
- [31] A.W. Coats and J.P. Redfern // *Nature* **201** (1964) 68.
- [32] J. Malek, T. Mitsuhashi and J.M. Criado // *J. Mat. Res.* **16** (2001) 1862.

- [33] G.I. Senum and R.T. Yang // *J. Therm. Anal.* **11** (1977) 445.
- [34] P.E. Sánchez-Jiménez, L.A. Pérez-Maqueda, A. Perejón and J.M. Criado // *J. Phys. Chem. A* **2010** (114) 7868.
- [35] M.A. Arshad and A. Maaroufi // *Thermochim. Acta* **585** (2014) 25.
- [36] R.W. Carr, Modeling of Chemical Reactions (Elsevier, Amsterdam, 2007).
- [37] J.M. Criado, L.A. Perez-Maqueda and P.E. Sanchez-Jimenez // *J. Therm. Anal. Calorim.* **82** (2005) 671.
- [38] M.A. Arshad, A. Maaroufi, R. Benavente and G. Pinto // *J. Appl. Polym. Sci.* **134** (2017) 1.
- [39] M.A. Arshad and A. Maaroufi // *Soc. Plast. Eng.* 2015. DOI: 10.2417/spepro.006183.
- [40] M.A. Arshad, A. Maaroufi, R. Benavente and G. Pinto // *Polym. Compos.* **38** (2017) 1529.
- [41] M.A. Arshad, A. Maaroufi, R. Benavente and G. Pinto // *J. Mat. Sci.: Mat. Electron.* **28** (2017) 11832
- [42] M.A. Arshad, A. Maaroufi, R. Benavente and G. Pinto // *Polym. Compos.* 2017; accepted manuscript. DOI: 10.1002/pc.24516.
- [43] F. Ouanji, M. Khachani, S. Arsalane, M. Kacimi, M. Halim and E.H. Adnane // *Monatsh. Chem.* **147** (2016) 1693.
- [44] M. Dahhou, M. El Moussaouiti, A. Benlalla, A. El Hamidi, M. Taibi and M.A. Arshad // *Waste Biomass Valor.* **7** (2016) 1177.
- [45] A. Benlalla, M. Elmoussaouiti, M. Dahhou and M. Assafi // *Appl. Clay Sci.* **118** (2015) 171.
- [46] J. Malek // *Thermochim. Acta* **355** (2000) 239.
- [47] M.A. Arshad and A. Maaroufi // *J. Non-Cryst. Solids* **413** (2015) 53.
- [48] A.H. Ammar, A.M. Farid and A.A.M. Farag // *J. Non-Cryst. Solids* **434** (2016) 85.
- [49] J. Militky and J. Sestak J // *J. Therm. Anal. Calorim.* **127** (2016) 1131.
- [50] A.K. Burnham, *Introduction to Chemical Kinetics: Global Chemical Kinetics of Fossil Fuels* (Springer, New York, 2017).