




# Exact solution of Arrhenius equation for non-isothermal kinetics at constant heating rate and $n$ -th order of reaction

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Received: 5 March 2019 / Accepted: 12 August 2019 / Published online: 16 August 2019  
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## Abstract

This paper provides exact solution of Arrhenius equation for non-isothermal kinetics at constant heating rate and  $n$ th-order of reaction instead of using numerical methods. This model is built to be capable of solving one and multi-order of reaction which is based on natural chemical components and other additives. We note that the presented solution can be useful to give more significant physical description than the previous approximation methods under the same values of the activation energy and pre-exponential factor parameters, and more generally the method may enable us to control parameters which is deterministic but unknown.

**Keywords** Arrhenius-equation · Non-isothermal-process ·  $n$ th-order-of-reaction · Activation-energy · Pre-exponential-factor

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## 1 Introduction

In respect of non-isothermal chemical processes, these processes were designed by developing empirical functional relationships according to the kinetic variables and parameters such as time, temperature, sample size, heating rate, pre-exponential factor, activation energy, etc [1,2].

During last decades, the thermal methods of non-isothermal procedures have been extensively investigated to discuss several types processes. These thermal techniques have been successfully developed to study physical or/and chemical changes in investigated ensembles over a temperature scale at an arbitrary heating rate. Hence, the empirical or mathematical functional relationships were formulated based on the thermal techniques in mathematical, statistical and numerical tools in order to find adequate interpretations for various physical and chemical states in gases, liquids and solids [4,5]. Moreover, the knowledge of exact values of kinetic variables are important for the progression of the realistic thermal chemical models [6,7].

Some of the governing thermal relations have been described in the differential equations over time and temperature domains for non-isothermal kinetics as Arrhenius equation.

More than a century ago, the thermal chemical reaction has been an example for one of the chemical reactions which has been taken into account to be studied by Van't Hoff in 1884. He suggested notes about the thermal chemical reaction [8]. In 1889, Arrhenius formulated an equation about the thermal decomposition by the heat according to Van't Hoff's notes, namely, Arrhenius equation [9,10]. Arrhenius equation was introduced as a functional relationship for the dependence of temperature-chemical reaction rate of the mass conversion fraction [8–10]. In the non-isothermal process, if an arbitrary material ensemble dissolved thermally, then the mass conversion fraction of degradable ensemble  $\chi$  would be described in what follows:

$$\chi = \frac{m_0 - m(t)}{m_0 - m_\infty}, \quad (1)$$

where  $m_0$ ,  $m(t)$  and  $m_\infty$  are the initial mass, degradable mass at a time  $t$ , and terminal mass of a degradable ensemble respectively. The residual mass fraction of degradable ensemble  $1 - \chi$  was expressed as:

$$1 - \chi = \frac{m(t) - m_\infty}{m_0 - m_\infty}, \quad (2)$$

Hence, the Arrhenius equation (AE), the rate of mass conversion fraction of degradable ensemble  $\chi$  with respect to time, in the kinetic analysis of data for ensemble decomposition, is described by [9,10]:

$$\frac{d\chi}{dt} = A \exp\left(-\frac{E}{RT}\right) (1 - \chi)^n. \quad (3)$$

where  $A$  is pre-exponential factor (unit  $\text{time}^{-1}$ ) which refers to the process of breaking chemical bonds in molecules per minutes,  $E$  is the least amount energy required to activate atoms or molecules to begin in a chemical reaction namely activation energy (kJ/mol) for ensemble,  $R$  is a gas constant (kJ/mol.K.),  $T$  is an absolute temperature (K) and  $n$  is the reaction order. AE is linear if  $n = 1$  and otherwise, is nonlinear. Many researches have attempted to solve Arrhenius equation but it has not been yet solved. Therefore, they have focused to evaluate the activation energy, pre-exponential factor and order of reaction parameters with different numerical methods.

These kinetic parameters were computed from rate-conversion data by the thermogravimetric in order to be useful in the explanation of degradation mechanisms. In what follows, these variables and parameters were estimated from experimental data by some different methods which are presented in brief forms. In 1949, and 1955, Murray and White worked to derive a relationship from AE to determine the kinetic parameters for a linear order of reaction,  $n = 1$ . According to Murray–White the govern equation was expressed as [11–13]:

$$\frac{d\left(\ln\left(\frac{1}{T_m^2} \frac{dT}{dt}\right)\right)}{d\left(\frac{1}{T_m}\right)} = -\frac{E}{R}. \quad (4)$$

where the maximum deflection value  $\frac{d\chi}{dt}$  occurred at the maximum temperature  $T_m$  and  $\frac{dT}{dt}$  is heating rate. In 1956, Kissinger performed the series of experiments to verify Murray–White equation experimentally at the peak temperatures for different heating rate values to measure kinetic constants [14]. In 1957, Kissinger deduced a new equation for the linear order of reaction  $n = 1$ , at constant heating rate  $\beta = \frac{dT}{dt}$  and maximum peak temperature  $T_m$  to describe exothermic reaction. Kissinger equation was described by [15]:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m}. \quad (5)$$

In 2002, Vyazovkin indicated that the Kissinger equation is only applicable for positive heating rate (heating process) while for negative heating rate (cooling process) it is not valid [16]. In 2009, Pere-Jordi solved Kissinger equation analytically [17]. Šesták, Holba and Živković deduced that the derivation of Kissinger equation was based on the false assumption because the heat inertia term was omitted from the true balance of heat flux. Consequently, this decisive mistake deformed Kissinger equation and the values of activation energies were shifted from the accurate values [18]. In 1958, Freeman-carroll [19] formed a relation by taking the natural logarithm for AE at different values of  $\frac{d\chi}{dT}$  which occurred at arbitrary temperatures  $T$  as follows:

$$\ln\left(\frac{d\chi}{dT}\right) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} + n \ln(1 - \chi). \quad (6)$$

It is noted that there are critical considerations about Freeman–Carroll method which are taken into account for its application on experimental data to obtain accurate results. These critical considerations were discussed in details for many manuscripts like [20,21]. From 1961 to 1965, Doyle promoted several works about the kinetic analysis of thermogravimetric data [22–25]. Coats and Redfern [26] formulated a relation for evaluating the kinetic parameters which was expressed as:

$$\ln\left(\frac{1 - (1 - \chi)^{1-n}}{(1-n)T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) \left(1 - \frac{2RT}{\beta E}\right) - \frac{E}{2.303RT} \quad \text{for } n \neq 1. \quad (7)$$

$$\ln\left(\frac{-\ln(1 - \chi)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) \left(1 - \frac{2RT}{\beta E}\right) - \frac{E}{2.303RT} \quad \text{for } n = 1. \quad (8)$$

In 1964, Friedmann [27] suggested a method to determine the activation energy based on distinguishability of different loss rates  $\frac{d\chi}{dt}$  for the values mass conversion fraction  $\chi$  at different heating rates which was described by

$$\ln\left(\frac{d\chi}{dt}\right) = \ln(A(1 - \chi)^n) - \frac{E}{RT}. \quad (9)$$

This is a linear relation between  $\ln\left(\frac{d\chi}{dt}\right)$  against  $-\frac{1}{T}$  where  $-\frac{E}{R}$  is the slope which is determined according to experimental data. In 1965 and 1970, Ozawa discussed the idea of how to determine the kinetic parameters [28,29]. He presented a simple method to analyze thermogravimetric data in order that the activation energy is measured directly from  $(1 - \chi)^n$  versus temperature  $T$  as follows:

$$\ln(1 - \chi)^n = \ln\left(\frac{AE}{R}\right) - \ln\beta - 2.315 - \frac{0.4567E}{RT}. \quad (10)$$

where  $\frac{E}{RT} > 20$  according to Doyle's approximation [22]. In 1966 and 1980 Flynn–Wall developed a method to determine the kinetic parameters especially activation energy [30–32]. They proposed a relation based on two peak temperatures  $T_{m1}$  and  $T_{m2}$  at two different heating rates  $\beta_1$  and  $\beta_2$  for mass conversion fraction  $\chi_{m1}$  and  $\chi_{m2}$  respectively to calculate the activation energy in what follows:

$$E = R \left(\frac{T_{m1}T_{m2}}{T_{m1} - T_{m2}}\right) \ln \left[ \left(\frac{\beta_1}{\beta_2}\right) \left(\frac{1 - \chi_{2m}}{1 - \chi_{1m}}\right)^{n-1} \left(\frac{T_{2m}}{T_{1m}}\right)^2 \right]. \quad (11)$$

Thus, several famous methods were proposed to treat Arrhenius equation in order to determine the kinetic parameters [11–33]. Arrhenius equation plays an important role in many applications in various fields of life as in pyrolysis process [34–44]. pyrolysis

process is used to recycle wastes, as rubber tires, to reproduce new useful products [45–51], as well as wood treatment [52] and also for designing battery packs (Nickel Metal Hydride (NiMH) cells) [53].

In this study, we introduce significant theoretical work which is applicable for different kinetic analysis of non-isothermal decomposition experiments. The solution of Arrhenius equation is posed as the problem which has not been yet solved mathematically since 1889, because of the integral  $\int y^{-2}e^{-y}dy$  has not yet been evaluated in closed form. Consequently, the results are always approximated. The main aim of this work is devoted to determine the exact solution of Arrhenius equation at a constant heating rate. In fact, the manuscript focuses on the mathematical treatment which supports physical and chemical meaning. Hence, the exact solution of the Arrhenius equation completes the missing mathematical part and adds new values to previous physical and chemical approaches. The exact solution may be confirmed via different decomposition experiments for fixed values of kinetic physical parameters like temperature. Here, the values of the kinetic parameters do not represent a certain material rather they represent a generalized description which may help us to study the relations of residual mass with temperature. In section one, we consider an arbitrary ensemble of material which is thermally dissolved in the non-isothermal process at a constant heating rate where the temperature depends linearly on time. The activation energy is redefined in terms of an activation temperature. Also, the pre-exponential factor and the constant heat rate are also redefined together in terms of an expansion temperature. The integral  $\int y^{-2}e^{-y}dy$  is expressed in two equivalent closed forms and have the same equivalent solution. In what follows, the residual mass fraction is studied for different values of activation and expansion temperatures and higher orders of chemical reaction respectively by various two-dimension graphs which are done by Mathematica. Beside each graph there is a table which includes the temperatures corresponding to values of the residual mass fraction at less than 0.5, 0.25, 0.1 and 0.01 respectively. Section 3 presents the results and discussion.

## 2 The model

In order to solve Arrhenius equation, one has to take into account the temperature which is a function of time and how to evaluate the integral analytically. A simple but sufficient condition is to consider the heating rate of reaction to be constant. Therefore, we consider the heating rate is  $\frac{dT}{dt} = \beta$ . It is clear that the temperature varies linearly with time for different orders of reaction which is consistent with the experiments. Hence, the parameter  $\beta$  is determined by:

$$\beta = \frac{T_f - T_0}{\tau}, \quad (12)$$

where  $T_0$  is the initial absolute reaction temperature,  $T_f$  is the final absolute reaction temperature for non-isothermal process and  $\tau$  is the non-isothermal process time from  $T_0$  to  $T_f$ . Hence, temperature is going linearly time dependent with the slope  $\beta$  i.e.

$$T = \beta t + T_0. \quad (13)$$

where  $0 \leq t \leq \tau$ . Thus, Eq. (3) is rewritten as the temperature rate of mass conversion fraction in the form:

$$\frac{d\chi}{dT} = \frac{1}{\alpha} e^{-\delta/T} (1 - \chi)^n, \quad (14)$$

where  $\alpha = \beta/A$  and  $\delta = E/R$  are scalar parameters and have the same unit of an absolute temperature (Kelvin). The two parameters  $\alpha$  and  $\delta$  are interpreted physically as absolute temperatures. Firstly, a temperature parameter  $\alpha$  depends on two parameters  $\beta$  and  $A$  and can be so-called the expansion temperature. It is clear that the pre-exponential parameter  $A$  is constant for each material but the constant heating rate  $\beta$  must vary depending on the value of  $\alpha$ . The expansion temperature  $\alpha$  depends on  $\beta$  and  $A$ . Secondly  $\delta$  is proportional to an activation energy  $E$  and can be called the activation temperature. In other words, the minimal value of activation energy  $E_{\min}$  is the required lowest energy in order to start a non-isothermal process that corresponds to the minimal activation temperature  $T_{\min}$ . Similarly, the maximal activation energy requires the greatest energy  $E_{\infty}$  which corresponds to  $T_{\infty}$  and occurs when the non-isothermal process has finished completely. In the end, the constant heating rate and the activation energy are expressed in terms of the expansion and activation temperatures respectively. Equation (14) is treated by the method of separation of variables as:

$$\frac{1}{\alpha} \int_{T_0}^T e^{-\delta/T} dT = \int_0^\chi \frac{d\chi}{(1 - \chi)^n} \quad (15)$$

In order to solve Eq. (15) analytically, the substitution  $y = \frac{\delta}{T}$  is used. Consequently, Eq. (15) is formulated in terms of  $1 - \chi$  and  $y$  as:

$$\frac{\delta}{\alpha} \int_{y_0}^y \frac{e^{-y}}{y^2} dy = \begin{cases} \ln(1 - \chi) & \text{if } n = 1, \\ \frac{1}{n-1} \left\{ \frac{1}{(1-\chi)^{n-1}} - 1 \right\} & \text{if } n \neq 1, \end{cases}, \quad (16)$$

A simple technique is applied to manipulate the second problem which is evaluating the integral analytically in two closed forms. Generally, the idea of the integral is based on the expansion of the integrand about zero in terms of Maclurin series to separate singular terms for non-singular terms. Thus, the non-singular terms are rewritten in terms of a confluent hypergeometric function  ${}_1F_1$ . Hence, the integral of singular terms is simply evaluated and the integral of a confluent hypergeometric function is evaluated in terms of generalized hypergeometric function  ${}_2F_2$  in Appendix A. Hence, the differential Eq. (6) is solved analytically and the exact solution is expressed as:

$$1 - \chi = \begin{cases} \exp [P_j(T)], & \text{if } n = 1, j = 1, 2 \text{ and } T_0 \leq T, \\ \frac{1}{\sqrt[n-1]{1 - (n-1) P_j(T)}}, & \text{if } n \neq 1, j = 1, 2 \text{ and } T_0 \leq T, \end{cases}, \quad (17)$$

where the definite integral of the right hand side of Eq. (15),  $P_j(T)$ 's are functions in temperature  $T$  and are described by:

$$P_1(T) = \frac{T_0 - T}{\alpha} + \frac{\delta}{\alpha} \ln\left(\frac{T}{T_0}\right) + \frac{\delta^2}{2\alpha T} {}_2F_2\left(1, 1; 3, 2; -\frac{\delta}{T}\right) - \frac{\delta^2}{2\alpha T_0} {}_2F_2\left(1, 1; 3, 2; -\frac{\delta}{T_0}\right). \quad (18)$$

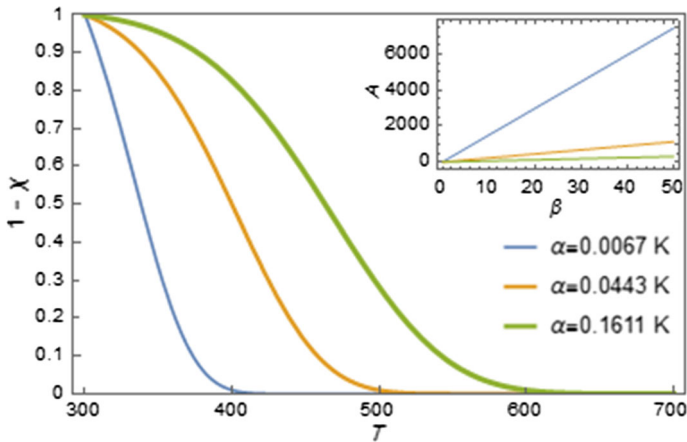
$$P_2(T) = \frac{T_0}{\alpha} e^{-\delta/T_0} - \frac{T}{\alpha} e^{-\delta/T} + \frac{\delta}{\alpha} \ln\left(\frac{T}{T_0}\right) + \frac{\delta^2}{\alpha T} {}_2F_2\left(1, 1; 2, 2; -\frac{\delta}{T}\right) - \frac{\delta^2}{\alpha T_0} {}_2F_2\left(1, 1; 2, 2; -\frac{\delta}{T_0}\right). \quad (19)$$

where  $P_j(T)$  is dimensionless because all terms are dimensionless. Thus, the exact analytical solution is obtained for Arrhenius equation at constant heating rate and for different order of reaction. The solution shows the effects of the activation energy and pre-exponential factor for non-isothermal kinetics. According to Eq. (1), the residual mass fraction of degradable ensemble represents the ratio between two changes in the mass. The first mass-change (in numerator) is from the initial mass to the arbitrary mass at time  $t$ , during the non-isothermal process. The second mass-change (in denominator) is also from the initial mass to the terminal mass. Thus, in the numerator, the mass difference is always less than or equal to the mass difference in the denominator. The residual mass fraction  $1 - \chi$  of the ensemble has a range between zero and one starting from initial absolute reaction temperature  $T_0$  to the maximal absolute reaction temperature  $T_f$ . Also, the residual mass ratio is a monotonic decreasing function in the same domain of the absolute temperature, which is always positive. Consequently, for an arbitrary temperature over a temperature scale from  $T_0$  to  $T_f$ , the residual mass of ensemble  $m(T)$  in Eq. (2) is determined by:

$$m = \begin{cases} m_0 (r + (1 - r) \exp[P_j(T)]), & \text{if } n = 1, T_0 \leq T, \text{ and } j = 1, 2 \\ m_0 \left( r + \frac{(1 - r)}{{}^{n-1}\sqrt{1 - (n - 1) P_j(T)}} \right), & \text{if } n \neq 1, T_0 \leq T, \text{ and } j = 1, 2 \end{cases} \quad (20)$$

where  $r = m_\infty/m_0$ , is the ratio between the terminal mass to the initial mass and is always enclosed between zero and one. Especially, at the end of the non-isothermal process, the initial mass is converted into new products while the degradable mass is expressed as:

$$m = \begin{cases} m_0 \exp[P_j(T)], & \text{if } n = 1, T_0 \leq T, \text{ and } j = 1, 2 \\ \frac{m_0}{{}^{n-1}\sqrt{1 - (n - 1) P_j(T)}}, & \text{if } n \neq 1, T_0 \leq T, \text{ and } j = 1, 2 \end{cases} \quad (21)$$



**Fig. 1** Temperature  $T$  versus residual mass fraction  $1 - \chi$  and constant heating rate  $\beta$  against pre-exponential factor  $A$  for  $\delta = 2686.7$  K,  $E = 24$  kJ/mol,  $n = 1$  and  $\alpha = 0.0067$  K,  $0.0443$  K,  $0.1611$  K

### 3 Results and discussion

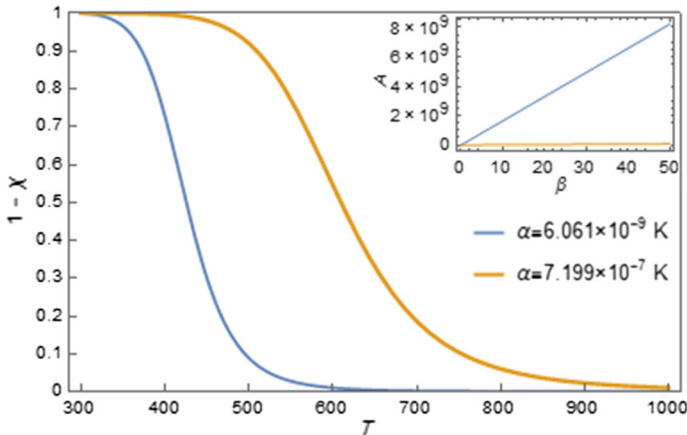
In this section, a behavior of the non-isothermal process is discussed in details by the residual mass fraction of the degradable ensemble  $1 - \chi$ . Arrhenius Eq. (14), treated mathematically at a constant heating rate to find the exact analytical solution of Arrhenius Eqs. (17–19). The behavior of non-isothermal process is studied at different values of expansion and activation temperatures  $\alpha$ 's and  $\delta$ 's and orders of reaction  $n$  respectively. In two following figures, the residual mass fraction  $1 - \chi$  is plotted versus absolute temperature  $T$  and the pre-exponential factor  $A = \beta/\alpha$  is plotted against the constant heating rate  $\beta$  which varies from zero to 50 K/min in a linear relationship where its slope is equal to the reciprocal of the expansion temperature  $\alpha$ . All figures are plotted in two dimensions and are done by Mathematica. Also two functions  $P_1(T)$  and  $P_2(T)$  are used to evaluate the same figures and tables in order to confirm their validity. The initial temperature  $T_0$  of the system is 300 K. All residual mass fraction curves have the maximum value at  $T_0 = 300$  K which is one and the minimum value which is zero if temperature approaches infinity. They are monotonic decreasing functions with inflection points.

In Fig. 1, the temperature varies from 300 to 700 K for the values  $n = 1$ ,  $E = 24$  kJ/mol,  $\delta = 2686.7$  K, and  $\alpha = 0.0067$  K,  $0.0443$  K and  $0.1611$  K. In Table 1, the residual mass fraction is equal to half if the temperatures are raised by 338.05655 K, 399.8878 K and 463.185 K for  $\alpha = 0.0067$  K,  $0.0443$  K and  $0.1611$  K respectively. The residual mass fraction is equal to 0.25 with increasing the temperature to 356.7911 K, 431.4807 K and 506.0065 K respectively. Temperatures is raised by 373.39522 K, 458.0967 K and 542.261 K for the same values of  $\alpha$ -parameter, the residual mass fraction decreases to 0.1. The residual mass fraction becomes equal to 0.01 at higher temperatures 400.0897 K, 500.00312 K and 600.0081 K respectively. It is clear that the curve at ( $\alpha = 0.0067$  K) thermally decomposes up to half the original mass while the curve ( $\alpha = 0.1611$  K) requires a temperature about 125.13 °C extra



**Table 1** Residual mass fraction at different values and corresponding temperatures for  $n = 1$  and  $E = 24$  kJ/mol

$n = 1, E = 24$ kJ/mol,					
$\alpha = 0.0067$ K		$\alpha = 0.0443$ K		$\alpha = 0.161$ K	
T (K)	$1 - \chi$	T (K)	$1 - \chi$	T (K)	$1 - \chi$
338	0.5	400	0.5	363	0.5
357	0.25	431	0.25	506	0.25
373	0.1	458	0.1	542	0.1
400	0.01	500	0.01	600	0.01



**Fig. 2** Temperature  $T$  versus residual mass fraction  $1 - \chi$  and constant heating rate  $\beta$  against pre-exponential factor  $A$  for  $\delta = 5773.39$  K,  $E = 48$  kJ/mol,  $n = 2$  and  $\alpha = 6.061 \times 10^{-9}$  K,  $7.199 \times 10^{-7}$  K

above to have the same decomposition. The  $\alpha$ -parameter is represented by the linear slope between the pre-exponential factor  $A$ , and the constant heating rate. The value of  $\alpha$ -parameter varies depending on the ratio  $A/\beta$ .

In Fig. 2, the temperature changes from 300 to 1000 K for the values  $n = 2$ ,  $E = 48$  kJ/mol,  $\delta = 5773.39$  K, and  $\alpha = 6.061 \times 10^{-9}$  K and  $7.199 \times 10^{-7}$  K. In Table 2, the residual mass fraction is equal to 0.5 for temperatures 425.346 K and 609.6663 K and  $\alpha = 6.061 \times 10^{-9}$  K and  $7.199 \times 10^{-7}$  K respectively. For raised temperatures 457.7023 K and 674.6496 K and  $\alpha = 6.061 \times 10^{-9}$  K and  $7.199 \times 10^{-7}$  K respectively, the material is thermally decomposed to 0.25. It is obvious that the material is degraded to be equal to 0.1 at higher temperatures 495.0375 K and 753.58 K and  $\alpha = 6.061 \times 10^{-9}$  K and  $7.199 \times 10^{-7}$  K respectively. The residual mass fraction reaches 0.01 for raised temperatures 599.999 K and 1000.0019 K and  $\alpha = 6.061 \times 10^{-9}$  K and  $7.199 \times 10^{-7}$  K respectively. Clearly, the material is degraded from 0.1 to 0.01 over the temperature differences 104.96 °C and 246.42 °C and  $\alpha = 6.061 \times 10^{-9}$  K and  $7.199 \times 10^{-7}$  K respectively. Thus, the material is degraded with 0.9 over the temperature difference 27.35 K and 63.59 K for  $\alpha = 6.061 \times 10^{-9}$  K and 14.13 K respectively. It is obvious that the material is degraded from 0.90026 to 0.99 over the temperature difference 272.65 K and 636.41 K for  $\alpha = 6.061 \times 10^{-9}$  K

**Table 2** Residual mass fraction at different values and corresponding temperatures for  $n = 2$  and  $E = 48$  kJ/mol

$n = 2, E = 48$ kJ/mol,			
$\alpha = 6.061 \times 10^{-9}$ K		$\alpha = 7.199 \times 10^{-7}$ K	
T (K)	$1 - \chi$	T (K)	$1 - \chi$
425	0.5	610	0.5
457	0.25	675	0.25
495	0.01	754	0.01
600	0.01	1000	0.01

and  $7.199 \times 10^{-7}$  K respectively. In contrast by comparing Figs. 1 and 2, the residual mass fraction curves are geometrically similar but the temperature domains are very far as shown in Tables 1 and 2.

## 4 Conclusion

An ensemble of material is dissolved thermally at constant heating rate of  $n$ th-order of reaction in a non-isothermal process according to Arrhenius equation where the temperature is linearly dependent on time. Arrhenius equation is solved analytically to find the exact solution of the residual mass fraction as a function of temperature at constant heating rate and different orders of reaction Eqs. (17–19). The exact solution is described by two equivalent closed forms of the integral  $\int y^{-2} e^{-y} dy$ . This exact solution is more reliable than numerical methods for a non-isothermal process. It is noted that the residual mass fraction is monotonically decreasing from one to zero as shown in Figs. 1 and 2. The solution describes the relationship between these parameters which control the non-isothermal process; activation energy, pre-exponential factor, the order of reaction and a constant heating rate. Therefore, these parameters were investigated. The activation energy is expressed in terms of an activation temperature. Also, the pre-exponential factor and constant heating rate were expressed together in terms of an expansion temperature. Also, the residual mass is obtained by Eqs. (20–21). The activation energy, order of reaction and expansion temperature are investigated in different graph. The residual mass fraction needs higher temperatures to descend through the ratios of 0.5, 0.25, 0.1, 0.01 and 0.001 as the values of  $\alpha$  increases as shown in Tables 1 and 2. Finally, Arrhenius equation used in the analysis of thermal decomposition has been considered a dark chapter in chemical reaction because they are developed empirically, without an understanding of the underlying physics. In order to make better use of the non-thermal process in industries in the future, the discussing mathematical model of the exact solution would assist a better understanding of the physical principles behind the experiments. The exact solution of the Arrhenius equation may be taken into account by others to deduce new computational methods which determine the activation energy, pre-exponential factor, and order of reaction.

**Acknowledgements** The authors thank gratefully Prof. Mostafa Ismael at Faculty of Engineering-Helwan University, Prof. Nashat Fareed, Prof. Ismael Kaoud and Mohammed Nabawy, at Faculty of Science, Ain Shams University for their significant comments.

## Appendix A

In this Appendix, the integral  $\int y^{-2}e^{-y}dy$  is evaluated in two closed forms with two different techniques. Two closed forms are mainly expressed in terms of the generalized hypergeometric functions  ${}_2F_2$  with different arguments and other functions like a natural logarithm and rational functions. Two techniques depend essentially on the expansion of the integrable function in terms of Maclaurin's series in order to separate between the singular terms and non-singular terms. Singular terms are integrated to evaluate a natural logarithm and rational functions. Non-singular terms are integrated to evaluate the generalized hypergeometric function  ${}_2F_2$ . In the beginning, the generalized hypergeometric function  ${}_mF_n$  are defined. In Proposition 1, the indefinite integral of generalized hypergeometric function  ${}_mF_n$  is evaluated in terms of  $y {}_{m+1}F_{n+1}$ . In Proposition 2, the integrable function  $y^{-1}e^{-y}$  is expanded in terms of Maclaurin's series to be formulated in terms of the a rational function  $y^{-1}$  and the confluent hypergeometric function  ${}_1F_1$ . In Proposition 3, the first technique includes the integrating by parts as the first step for the integral  $\int y^{-2}e^{-y}dy$  to evaluate a function  $y^{-1}e^{-y}$  and the new integral  $\int y^{-1}e^{-y}dy$ . The integral  $\int y^{-1}e^{-y}dy$  is evaluated according to Proposition 2 and Proposition 1 respectively in terms of the natural logarithm  $\ln y$  and the generalized hypergeometric function  ${}_2F_2$ . In Proposition 4, the integrable function  $y^{-2}e^{-y}$  is directly expanded by Maclaurin's series to find the singular terms  $y^{-1}$  and  $y^{-2}$  and non-singular terms which is described by the confluent hypergeometric function  ${}_1F_1$ . In Proposition 5, the second technique of the integral  $\int y^{-2}e^{-y}dy$  is evaluated in terms of the rational function  $y^{-1}$ , the natural logarithm  $\ln y$  and the generalized hypergeometric function  ${}_2F_2$ . In Proposition 6, two closed forms are proved to be equivalent. Hence, the integral  $\int y^{-2}e^{-y}dy$  is evaluated in two closed forms as shown in the following Eq. (22).

$$\int \frac{e^{-y}}{y^2} dy = \begin{cases} -\frac{e^{-y}}{y} - \ln y + y {}_2F_2(1, 1; 2, 2; -y) + c. \\ -\frac{1}{y} - \ln y + \frac{y}{2} {}_2F_2(1, 1; 3, 2; -y) + c. \end{cases} \quad (22)$$

### Definition 1

Consider the generalized hypergeometric function  ${}_mF_n$  which is defined by [54]:

$${}_mF_n \left( \begin{matrix} \alpha_1, \alpha_2, \dots, \alpha_m; x \\ \beta_1, \beta_2, \dots, \beta_n \end{matrix} \right) = \sum_{k=0}^{\infty} \frac{(\alpha_1)_k (\alpha_2)_k \dots (\alpha_m)_k}{(\beta_1)_k (\beta_2)_k \dots (\beta_n)_k} \frac{x^k}{k!}. \quad (A1)$$

where  $(\xi)_k = \Gamma(\xi + k) / \Gamma(\xi)$  is Pochhammer symbol and  $\Gamma(z)$  is a gamma function. If  $\xi = r + 1$  is an integer, then  $(r + 1)_k = (k + r)!$ .

**Proposition 1** The indefinite integral of generalized hypergeometric function  ${}_mF_n(\alpha_1, \alpha_2, \dots, \alpha_m; \beta_1, \beta_2, \dots, \beta_n; \lambda y)$  is evaluated as follows:

$$\int {}_mF_n(\alpha_1, \alpha_2, \dots, \alpha_m; \beta_1, \beta_2, \dots, \beta_n; \lambda y) dy = y {}_{m+1}F_{n+1}(\alpha_1, \alpha_2, \dots, \alpha_m, 1; \beta_1, \beta_2, \dots, \beta_n, 2; \lambda y) + c. \quad (\text{A2})$$

**Proof**

$$\begin{aligned} \int {}_mF_n(\alpha_1, \alpha_2, \dots, \alpha_m; \beta_1, \beta_2, \dots, \beta_n; \lambda y) dy &= \int \left( \sum_{k=0}^{\infty} \frac{(\alpha_1)_k (\alpha_2)_k \dots (\alpha_m)_k (\lambda y)^k}{(\beta_1)_k (\beta_2)_k \dots (\beta_n)_k k!} \right) dy \\ &= \sum_{k=0}^{\infty} \frac{(\alpha_1)_k (\alpha_2)_k \dots (\alpha_m)_k \lambda^k y^{k+1}}{(\beta_1)_k (\beta_2)_k \dots (\beta_n)_k k! (k+1)} + c \\ &= y \sum_{k=0}^{\infty} \frac{(\alpha_1)_k (\alpha_2)_k \dots (\alpha_m)_k k! (\lambda y)^k}{(\beta_1)_k (\beta_2)_k \dots (\beta_n)_k (k+1)! k!} + c \\ &= y \sum_{k=0}^{\infty} \frac{(\alpha_1)_k (\alpha_2)_k \dots (\alpha_m)_k \Gamma(k+1) (\lambda y)^k}{(\beta_1)_k (\beta_2)_k \dots (\beta_n)_k \Gamma(k+2) k!} + c \\ &= y \sum_{k=0}^{\infty} \frac{(\alpha_1)_k (\alpha_2)_k \dots (\alpha_m)_k (1)_k (\lambda y)^k}{(\beta_1)_k (\beta_2)_k \dots (\beta_n)_k (2)_k k!} + c \\ &= y {}_{m+1}F_{n+1}(\alpha_1, \alpha_2, \dots, \alpha_m, 1; \beta_1, \beta_2, \dots, \beta_n, 2; \lambda y) + c. \end{aligned}$$

□

**Proposition 2** A function  $\frac{e^{-y}}{y}$  is expanded as follows:

$$\frac{e^{-y}}{y} = \frac{1}{y} - {}_1F_1(1; 2; -y). \quad (\text{A3})$$

**Proof**

$$\begin{aligned} \frac{e^{-y}}{y} &= \frac{1}{y} \left( \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} y^k \right) \\ &= \frac{1}{y} + \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} y^{k-1} \\ &= \frac{1}{y} - \sum_{k=0}^{\infty} \frac{(-1)^k}{(k+1)!} y^k \\ &= \frac{1}{y} - \sum_{k=0}^{\infty} \frac{\Gamma(k+1) (-y)^k}{\Gamma(k+2) k!} \end{aligned}$$

$$\begin{aligned}\frac{e^{-y}}{y} &= \frac{1}{y} - \sum_{k=0}^{\infty} \frac{(1)_k}{(2)_k} \frac{(-y)^k}{k!} \\ &= \frac{1}{y} - {}_1F_1(1; 2; -y).\end{aligned}\quad \square$$

**Proposition 3**

The first closed form of the integrand  $\frac{e^{-y}}{y^2}$  is evaluated by [55]:

$$\int \frac{e^{-y}}{y^2} dy = -\frac{e^{-y}}{y} - \ln y + y {}_2F_2(1, 1; 2, 2; -y) + c. \quad (\text{A4})$$

**Proof**

$$\begin{aligned}\int \frac{e^{-y}}{y^2} dy &= -\frac{e^{-y}}{y} - \int \frac{e^{-y}}{y} dy \\ &= -\frac{e^{-y}}{y} - \int \left( \frac{1}{y} - {}_1F_1(1; 2; -y) \right) dy \\ \int \frac{e^{-y}}{y^2} dy &= -\frac{e^{-y}}{y} - \ln y + y {}_2F_2(1, 1; 2, 2; -y) + c_1.\end{aligned}\quad \square$$

**Proposition 4**

A function  $\frac{e^{-y}}{y^2}$  is expanded as follows:

$$\frac{e^{-y}}{y^2} = \frac{1}{y^2} - \frac{1}{y} + \frac{1}{2} {}_1F_1(1; 3; -y). \quad (\text{A5})$$

**Proof**

$$\begin{aligned}\frac{e^{-y}}{y^2} &= \frac{1}{y^2} \left( \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} y^k \right) \\ &= \frac{1}{y^2} - \frac{1}{y} + \sum_{k=0}^{\infty} \frac{(-1)^k}{(k+2)!} y^k \\ &= \frac{1}{y^2} - \frac{1}{y} + \sum_{k=0}^{\infty} \frac{\Gamma(k+1)}{\Gamma(k+3)} \frac{(-y)^k}{k!} \\ &= \frac{1}{y^2} - \frac{1}{y} + \frac{1}{2} \sum_{m=0}^{\infty} \frac{(1)_m}{(3)_m} \frac{(-y)^m}{m!} \\ &= \frac{1}{y^2} - \frac{1}{y} + \frac{1}{2} {}_1F_1(1; 3; -y).\end{aligned}\quad \square$$

**Proposition 5**

The second closed form of the integrand  $\frac{e^{-y}}{y^2}$  is evaluated by:

$$\int \frac{e^{-y}}{y^2} dy = -\frac{1}{y} - \ln y + \frac{y}{2} {}_2F_2(1, 1; 3, 2; -y) + c. \quad (\text{A6})$$

**Proof**

$$\begin{aligned} \int \frac{e^{-y}}{y^2} dy &= \int \left( \frac{1}{y^2} - \frac{1}{y} + \frac{1}{2} {}_1F_1(1; 3; -y) \right) dy \\ &= -\frac{1}{y} - \ln y + \frac{y}{2} {}_2F_2(1, 1; 3, 2; -y) + c_2. \quad \square \end{aligned}$$

**Proposition 6**

Two closed forms are equivalent.

**Proof**

$$\begin{aligned} l.h.s &= -\frac{e^{-y}}{y} - \ln y + y {}_2F_2(1, 1; 2, 2; -y) + c_1 \\ &= -\frac{1}{y} - \ln y + {}_1F_1(1; 2; -y) + y {}_2F_2(1, 1; 2, 2; -y) + c_1 \end{aligned}$$

It is clear that first two terms of the right hand side exist into the second closed form. We have to prove that  ${}_1F_1(1; 2; -y) + y {}_2F_2(1, 1; 2, 2; -y)$  is equivalent to  $\frac{y}{2} {}_2F_2(1, 1; 3, 2; -y)$  in what follows:

$$\begin{aligned} S &= {}_1F_1(1; 2; -y) + y {}_2F_2(1, 1; 2, 2; -y) \\ &= \sum_{k=0}^{\infty} \frac{(1)_k}{(2)_k} \frac{(-y)^k}{k!} + y \sum_{k=0}^{\infty} \frac{(1)_k (1)_k}{(2)_k (2)_k} \frac{(-y)^k}{k!} \\ &= \sum_{k=0}^{\infty} \frac{(-1)^k (1)_k}{(2)_k} \frac{y^k}{k!} + \sum_{k=0}^{\infty} \frac{(-1)^k (1)_k (1)_k}{(2)_k (2)_k} \frac{y^{k+1}}{k!} \\ &= 1 + \sum_{k=1}^{\infty} \frac{(-1)^k k!}{(k+1)!} \frac{y^k}{k!} + \sum_{k=0}^{\infty} \frac{(-1)^k (k!) (k!)}{(k+1)! (k+1)!} \frac{y^{k+1}}{k!} \\ &= 1 + \sum_{k=1}^{\infty} \frac{(-1)^k}{(k+1)!} y^k - \sum_{k=1}^{\infty} \frac{(-1)^k (k-1)!}{k! k!} y^k \\ &= 1 + \sum_{k=1}^{\infty} \left( \frac{1}{(k+1)!} - \frac{(k-1)!}{k! k!} \right) (-y)^k \end{aligned}$$

$$\begin{aligned}
&= 1 + \sum_{k=1}^{\infty} \left( \frac{k!k! - (k-1)!(k+1)!}{(k+1)!k!k!} \right) (-y)^k \\
&= 1 + \sum_{k=1}^{\infty} \left( \frac{(k^2 - k(k+1))(k-1)!(k-1)!}{(k+1)!k!k!} \right) (-y)^k \\
&= 1 - \sum_{k=1}^{\infty} \left( \frac{k!(k-1)!}{(k+1)!k!k!} \right) (-y)^k \\
&= 1 - \sum_{k=1}^{\infty} \left( \frac{(k-1)!}{(k+1)!k!} \right) (-y)^k \\
&= 1 - \sum_{k=0}^{\infty} \left( \frac{k!}{(k+2)!(k+1)!} \right) (-y)^{k+1} \\
&= 1 + y \sum_{k=0}^{\infty} \frac{k!k!}{(k+2)!(k+1)!} \frac{(-y)^k}{k!} \\
&= 1 + \frac{y}{2} \sum_{k=0}^{\infty} \frac{(1)_k (1)_k}{(3)_k (2)_k} \frac{(-y)^k}{k!} = 1 + \frac{y}{2} {}_2F_2(1, 1; 3, 2; -y) \\
l.h.s &= -\frac{1}{y} - \ln y + \frac{y}{2} {}_2F_2(1, 1; 3, 2; -y) + 1 + c_1 \\
&= -\frac{1}{y} - \ln y + \frac{y}{2} {}_2F_2(1, 1; 3, 2; -y) + c_2.
\end{aligned}$$

□

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