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The influences of various parameters on the numerical solution of nonisothermal DAEM equation

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Abstract

This paper describes the effect of some parameters on the numerical solution of nonisothermal distributed activation energy model equation. Investigated parameters are integral upper limits, integral interval number, heating rate, frequency factor, mean of activation energy distribution and standard deviation of activation energy distribution. In the numerical solution of DAEM equation, 500 kJ mol^{-1} value can be used for the upper limit of dE integral. The interval number of dE integral is better to be chosen as 50 both to have no oscillations in the results and to keep the solution time short. Integration step size of dt integral must be automatically adjusted by the program as numerical integration progressed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: DAEM; TGA

1. Introduction

The models which are used to explain the thermal decomposition processes can be investigated under two main headings: (i) single-reaction and (ii) multi-reaction models. Detailed information on these models is available in literature [1–3].

The numerical solutions of model equations are used to determine the kinetic parameters. To obtain realistic results, parameters affecting the numerical solution of model equations must be known. A detailed review the influences of various parameters on the single-reaction models can be found in the literature [4]. In this study, the influences of various parameters on the numerical solution of nonisothermal distributed activation energy model (DAEM) equation have been studied.

2. Nonisothermal DAEM equation and its numerical solution

DAEM is one of the multi-reaction models used widely to clarify the thermal decomposition processes. Assumptions and restrictions of DAEM, and the derivation of its equations can be found in the literature [1,5]. DAEM equation for the nonisothermal processes is given below [1]:

$$1-x=\int_0^\infty \exp\left(-\int_0^t k_0\exp\left(\frac{-E}{RT}\right)\mathrm{d}t\right)\frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(E-E_0)^2}{(2\sigma^2)}\right)\mathrm{d}E. \tag{1}$$

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In the above equation, E is the activation energy, E_0 the mean of activation energy distribution, k_0 the frequency factor, R the universal gas constant, T the absolute temperature, t the time, σ the standard deviation of the activation energy distribution and x is the mass fraction of releasing volatiles.

The numerical value of the frequency factor is assumed to be constant at $1.67 \times 10^{13}\ \mathrm{s}^{-1}$ [1]. The thermogravimetric analysis (TGA) technique is extensively used to determine the relation between temperature and time in Eq. (1). Detailed information about TGA can be found in the literature [4,6]. In the numerical studies, $T = 293 + 20t$ equation is used. In addition to that, effect of heating rate on numerical results is also illustrated.

DAEM equation can be solved by using numerical techniques for certain E_0 and σ values. For this purpose, either general purposed mathematical software or a computer program developed in any programming language is used. In this study, a computer program which employs Simpson's 1/3 rule for integration has been used for the numerical solution of Eq. (1). Detailed information about this computer program can be found in the literature [7,8].

3. Results and discussion

For numerical integration of the Eq. (1), integration upper limits and integral interval numbers must be determined. For the values $E_0 = 230\ \mathrm{kJ\ mol^{-1}}$ and $\sigma = 50\ \mathrm{kJ\ mol^{-1}}$ as the characteristic thermal decomposition kinetics, the effect of upper limit (E_∞) of dE integral on numerical results is shown in Fig. 1. At the beginning of thermal decomposition, the remaining mass proportion $(1-x)$ must be close to 1. Whereas in Fig. 1, it is observed that the remaining mass proportion is less than 1 for $E_\infty < 400\ \mathrm{kJ\ mol^{-1}}$ values. When 400, 500 and $900\ \mathrm{kJ\ mol^{-1}}$ values are used for E_∞, the results are more accurate and closely proximate to each other. Therefore, $500\ \mathrm{kJ\ mol^{-1}}$ value can be used for the upper limit of dE integral. This value is so close to $E_0 + 3\sigma$ value where confidence interval of Gauss distribution is 99% [9].

The effect of integral interval number used in dE integral on the results is given in Fig. 2. When the results obtained for the values 10, 25, 50 and 200 are investigated, it is seen that the use of small interval

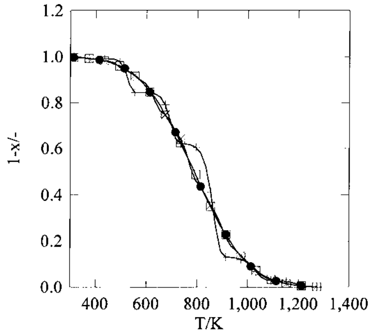

Fig. 1. The effect of upper limit of dE integral on the numerical results ($E_0 = 230\ \mathrm{kJ\ mol^{-1}}$, $\sigma = 50\ \mathrm{kJ\ mol^{-1}}$, $k_0 = 1.67 \times 10^{13}\ \mathrm{s}^{-1}$, $T = 293 + 20t$). $E_\infty(\mathrm{kJ\ mol^{-1}})$: + = 250; x = 300; o = 400; ● = 500; □ = 900.

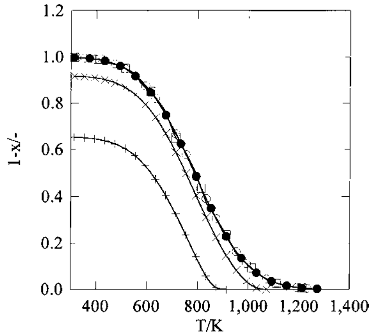

Fig. 2. The effect of integral interval number used in dE integral on the numerical results ($E_0 = 230\ \mathrm{kJ\ mol^{-1}}$, $\sigma = 50\ \mathrm{kJ\ mol^{-1}}$, $k_0 = 1.67 \times 10^{13}\ \mathrm{s}^{-1}$, $T = 293 + 20t$). Integral interval number: + = 10; x = 25; ● = 50; □ = 200.

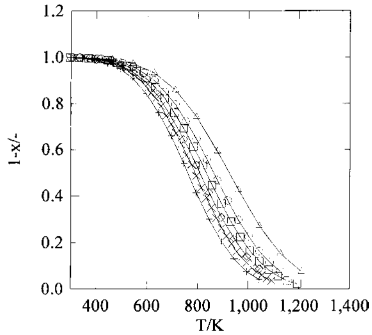

Fig. 3. The effect of heating rate (b) on the numerical solution of DAEM equation ($E_0 = 230\ \mathrm{kJ\ mol^{-1}}$, $\sigma = 50\ \mathrm{kJ\ mol^{-1}}$, $k_0 = 1.67 \times 10^{13}\ \mathrm{s}^{-1}$). b (Kmin^{-1}): + = 5; x = 20; ● = 50; □ = 150; o = 500; Δ = 5000.

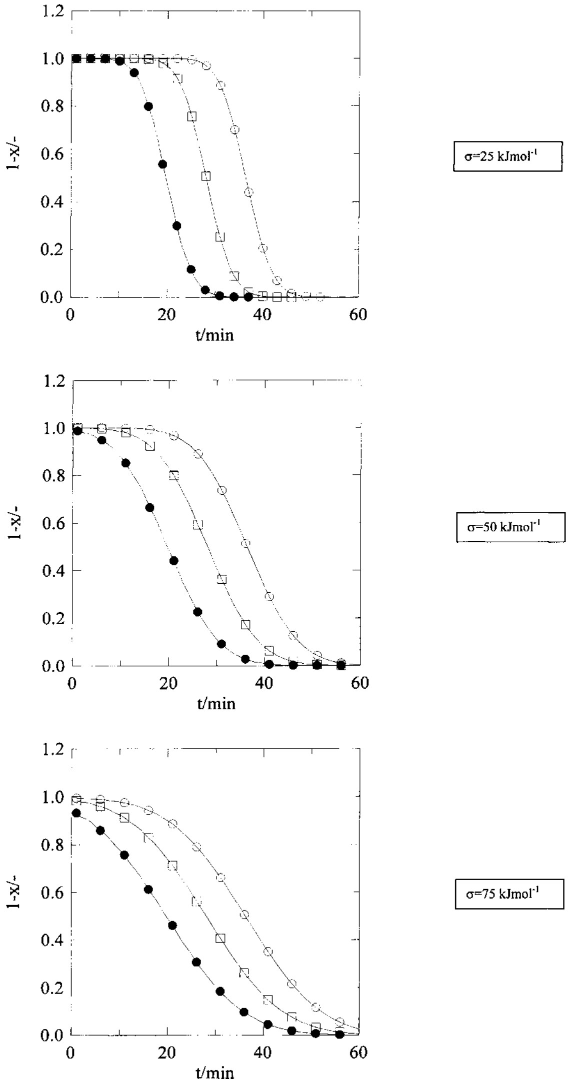

Fig. 4. The effect of mean activation energy (E_0) and standard deviation (σ) on the numerical solution of DAEM equation ($k_0 = 1.67 \times 10^{13}\ \mathrm{s}^{-1}$, $T = 293 + 20t$). E_0 (kJ mol^{-1}): ● = 200; □ = 250; o = 300.

number ($n = 10$) causes oscillations in the solution. When interval number is 25, these oscillations still continue by getting less. When interval number is 50 and over 50, the results are closely approximate to each other. So, it means that interval number is better to be chosen as 50 both to have no oscillations in the results and to keep the solution time short.

As the upper limit in the inner dt integral, the t value the solution of which made at that moment is used. Integration step size has been automatically adjusted by the program as numerical integration progressed.

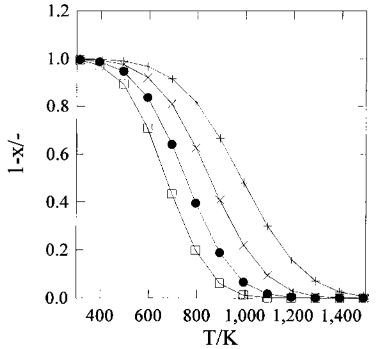

Fig. 5. The effect of frequency factor (k_0) on the numerical solution of DAEM equation ($E_0 = 230$ kJ mol^{-1}, $\sigma = 50$ kJ mol^{-1}, $T = 293 + 20t$). k_0(s^{-1}): + = $E10$; $x = E12$; ● = $E14$; □ = $E16$.

The effect of heating rate on DAEM results is illustrated in Fig. 3, where it is seen that remaining mass fraction curves is shifted up the temperature scale by an increase in the rate.

The effect of mean activation energy (E_0) and standard deviation (σ) on numerical results are given in Fig. 4. Increase in E_0 values causes $(1-x)$ curves to lead towards right direction as parallel to each other. Increase in σ values causes slopes of $(1-x)$ curves to get less.

In DAEM equation, for k_0, $1.67 \times 10^{13}\ \mathrm{s}^{-1}$ is usually taken. In some studies summarized by Solomon et al. [3], k_0 value is also taken as independent variable. The effect of k_0 values on the numerical results is illustrated in Fig. 5. According to these curves, the increase in k_0 value causes $(1-x)$ curves to lead toward left direction.

4. Conclusion

In the numerical solution of DAEM equation, 500 kJ mol^{-1} value can be used for the upper limit of dE integral. This value is so close to $E_0 + 3\sigma$ value where confidence interval of Gauss distribution is 99%. The interval number of dE integral is better to be chosen as 50 both to have no oscillations in the results and to keep the solution time short. As the upper limit in the inner dt integral, the t value the solution of which made at that moment must be used. Integration step size of dt integral must be automatically adjusted by the program as numerical integration progressed.

The changing of heating rate, the mean of activation energy distribution, standard deviation of activation energy distribution and frequency factor effects the form of remaining mass fraction curves. This effect can be used to determine the kinetic parameters of DAEM equation from TGA data.

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