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A NUMERICAL METHOD OF COMPUTING KINETIC PARAMETERS OF DECOMPOSITION REACTION OF INITIATING EXPLOSIVE USING THE RATE EQUATION

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ABSTRACT A numerical method of computing kinetic parameters of exothermic decomposition reaction of initiating explosive by means of exothermic rate equation is presented.

KEY WORDS initiating explosive 792, decomposition reaction, exothermic rate equation, kinetic parameter.

According to our previous papers[1,2], the exothermic rate equation used to determine non-isothermal kinetic paramerters by a single non-isothermal DSC curve is

$$\ln\frac{dH_t}{dt}=\ln\left\{AH_0f(\alpha)\left[1+\frac{E}{RT}\left(1-\frac{T_0}{T}\right)\right]\right\}-\frac{E}{RT} \tag{1}$$

Where H_t, H_0, α, T, $f(\alpha)$, T_0, t, R, A and E have the usual meanings[1,2].

In order to obtain the kinetic parameters, we took the minimal values of evaluation functions $\Omega\ (E,A\cdots)$

$$\Omega=\sum_{i=1}^{l}\left\{\ln\left(\frac{dH_t}{dt}\right)_i-\ln\left\{AH_0f(\alpha_i)\left[1+\frac{E}{RT_i}\left(1-\frac{T_0}{T_i}\right)\right]\right\}+\frac{E}{RT_i}\right\}^2 \tag{2}$$

The kinetic parameters and the condition of taking minimal values of function $\Omega(E, A,\cdots)$, and fifteen normal equations of computing the kinetic parameters obtained from eqn. (2) and all the forms of $f(\alpha)$ listed in Table 1 are presented in Table 2.

Table 1 Several kinetic functions used for the present analysis

Function No.	$f(\alpha)$[1)]	Function No.	$f(\alpha)$[1)]
1	$(1-\alpha)^n$	9	$\alpha^m[-\ln(1-\alpha)]^k$
2	α^m	10	$(1-\alpha)^n[-\ln(1-\alpha)]^k$
3	$[1-\ln(1-\alpha)]^k$	11	$\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^k$
4	$\alpha^m(1-\alpha)^n$	12	$(1-\alpha)^n[1-(1-\alpha)^{1/3}]^k$
5	$\alpha^m[1-\ln(1-\alpha)]^k$	13	$(1-\alpha)^n[1-(1-\alpha)^{1/2}]^k$
6	$(1-\alpha)^n[1-\ln(1-\alpha)]^k$	14	$(1-\alpha)^n[(1-\alpha)^{-1/3}-1]^k$
7	$\alpha^m(1-\alpha)^n[1-\ln(1-\alpha)]^k$	15	$(1+\alpha)^n[(1+\alpha)^{1/3}-1]^k$
8	$[-\ln(1-\alpha)]^k$		

1) Function form (differential form).

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Table 2 Normal equations corresponding to fifteen differential mechanism functions in Table 1

Function No.	Kinetic parameters	Condition of taking minimal values of function $\Omega(E, A, \cdots)$	The corresponding normal eqns.
1	A n E	$\partial\Omega/\partial A=0$ $\partial\Omega/\partial n=0$ $\partial\Omega/\partial E=0$	$\begin{bmatrix} l & a_1 \\ a_1 & \theta_1 \\ q & r_1 \end{bmatrix}\begin{bmatrix} Z \\ n \end{bmatrix}=\begin{bmatrix} B \\ F_1 \\ G \end{bmatrix}$
2	A m E	$\partial\Omega/\partial A=0$ $\partial\Omega/\partial m=0$ $\partial\Omega/\partial E=0$	$\begin{bmatrix} l & a_2 \\ a_2 & \theta_2 \\ q & r_2 \end{bmatrix}\begin{bmatrix} Z \\ m \end{bmatrix}=\begin{bmatrix} B \\ F_2 \\ G \end{bmatrix}$
3	A k E	$\partial\Omega/\partial A=0$ $\partial\Omega/\partial k=0$ $\partial\Omega/\partial E=0$	$\begin{bmatrix} l & a_3 \\ a_3 & \theta_3 \\ q & r_3 \end{bmatrix}\begin{bmatrix} Z \\ k \end{bmatrix}=\begin{bmatrix} B \\ F_3 \\ G \end{bmatrix}$
4	A n m E	$\partial\Omega/\partial A=0$ $\partial\Omega/\partial n=0$ $\partial\Omega/\partial m=0$ $\partial\Omega/\partial E=0$	$\begin{bmatrix} l & a_1 & a_2 \\ a_1 & \theta_1 & \theta_4 \\ a_2 & \theta_4 & \theta_2 \\ q & r_1 & r_2 \end{bmatrix}\begin{bmatrix} Z \\ n \\ m \end{bmatrix}=\begin{bmatrix} B \\ F_1 \\ F_2 \\ G \end{bmatrix}$
5	A m k E	$\partial\Omega/\partial A=0$ $\partial\Omega/\partial m=0$ $\partial\Omega/\partial k=0$ $\partial\Omega/\partial E=0$	$\begin{bmatrix} l & a_2 & a_3 \\ a_2 & \theta_2 & \theta_6 \\ a_3 & \theta_6 & \theta_3 \\ q & r_2 & r_3 \end{bmatrix}\begin{bmatrix} Z \\ m \\ k \end{bmatrix}=\begin{bmatrix} B \\ F_2 \\ F_3 \\ G \end{bmatrix}$
6	A n k E	$\partial\Omega/\partial A=0$ $\partial\Omega/\partial n=0$ $\partial\Omega/\partial k=0$ $\partial\Omega/\partial E=0$	$\begin{bmatrix} l & a_1 & a_3 \\ a_1 & \theta_1 & \theta_5 \\ a_3 & \theta_5 & \theta_3 \\ q & r_1 & r_3 \end{bmatrix}\begin{bmatrix} Z \\ n \\ k \end{bmatrix}=\begin{bmatrix} B \\ F_1 \\ F_3 \\ G \end{bmatrix}$
7	A n m k E	$\partial\Omega/\partial A=0$ $\partial\Omega/\partial n=0$ $\partial\Omega/\partial m=0$ $\partial\Omega/\partial k=0$ $\partial\Omega/\partial E=0$	$\begin{bmatrix} l & a_1 & a_2 & a_3 \\ a_1 & \theta_1 & \theta_4 & \theta_5 \\ a_2 & \theta_4 & \theta_2 & \theta_6 \\ a_3 & \theta_5 & \theta_6 & \theta_3 \\ q & r_1 & r_2 & r_3 \end{bmatrix}\begin{bmatrix} Z \\ n \\ m \\ k \end{bmatrix}=\begin{bmatrix} B \\ F_1 \\ F_2 \\ F_3 \\ G \end{bmatrix}$
8	A k E	$\partial\Omega/\partial A=0$ $\partial\Omega/\partial k=0$ $\partial\Omega/\partial E=0$	$\begin{bmatrix} l & a_4 \\ a_4 & \theta_7 \\ q & r_4 \end{bmatrix}\begin{bmatrix} Z \\ k \end{bmatrix}=\begin{bmatrix} B \\ F_4 \\ G \end{bmatrix}$

Table 2 (continued)

Function No.	Kinetic parameters	Condition of taking minimal values of function $\Omega(E, A, \cdots)$	The corresponding normal eqns.
9	A	$\partial\Omega/\partial A=0$	$\begin{bmatrix} l & a_2 & a_4 \\ a_2 & \theta_2 & \theta_9 \\ a_4 & \theta_9 & \theta_7 \\ q & r_2 & r_4 \end{bmatrix} \begin{bmatrix} Z \\ m \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_2 \\ F_4 \\ G \end{bmatrix}$
	m	$\partial\Omega/\partial m=0$	
	k	$\partial\Omega/\partial k=0$	
	E	$\partial\Omega/\partial E=0$	
10	A	$\partial\Omega/\partial A=0$	$\begin{bmatrix} l & a_1 & a_4 \\ a_1 & \theta_1 & \theta_8 \\ a_4 & \theta_8 & \theta_7 \\ q & r_1 & r_4 \end{bmatrix} \begin{bmatrix} Z \\ n \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_4 \\ G \end{bmatrix}$
	n	$\partial\Omega/\partial n=0$	
	k	$\partial\Omega/\partial k=0$	
	E	$\partial\Omega/\partial E=0$	
11	A	$\partial\Omega/\partial A=0$	$\begin{bmatrix} l & a_1 & a_2 & a_4 \\ a_1 & \theta_1 & \theta_4 & \theta_8 \\ a_2 & \theta_4 & \theta_2 & \theta_9 \\ a_4 & \theta_8 & \theta_9 & \theta_7 \\ q & r_1 & r_2 & r_4 \end{bmatrix} \begin{bmatrix} Z \\ n \\ m \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_2 \\ F_4 \\ G \end{bmatrix}$
	n	$\partial\Omega/\partial n=0$	
	m	$\partial\Omega/\partial m=0$	
	k	$\partial\Omega/\partial k=0$	
	E	$\partial\Omega/\partial E=0$	
12	A	$\partial\Omega/\partial A=0$	$\begin{bmatrix} l & a_1 & a_5 \\ a_1 & \theta_1 & \theta_{11} \\ a_5 & \theta_{11} & \theta_{10} \\ q & r_1 & r_5 \end{bmatrix} \begin{bmatrix} Z \\ n \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_5 \\ G \end{bmatrix}$
	n	$\partial\Omega/\partial n=0$	
	k	$\partial\Omega/\partial k=0$	
	E	$\partial\Omega/\partial E=0$	
13	A	$\partial\Omega/\partial A=0$	$\begin{bmatrix} l & a_1 & a_6 \\ a_1 & \theta_1 & \theta_{13} \\ a_6 & \theta_{13} & \theta_{12} \\ q & r_1 & r_6 \end{bmatrix} \begin{bmatrix} Z \\ n \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_6 \\ G \end{bmatrix}$
	n	$\partial\Omega/\partial n=0$	
	k	$\partial\Omega/\partial k=0$	
	E	$\partial\Omega/\partial E=0$	
14	A	$\partial\Omega/\partial A=0$	$\begin{bmatrix} l & a_1 & a_7 \\ a_1 & \theta_1 & \theta_{15} \\ a_7 & \theta_{15} & \theta_{14} \\ q & r_1 & r_7 \end{bmatrix} \begin{bmatrix} Z \\ n \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_1 \\ F_7 \\ G \end{bmatrix}$
	n	$\partial\Omega/\partial n=0$	
	k	$\partial\Omega/\partial k=0$	
	E	$\partial\Omega/\partial E=0$	
15	A	$\partial\Omega/\partial A=0$	$\begin{bmatrix} l & a_8 & a_9 \\ a_8 & \theta_{16} & \theta_{18} \\ a_9 & \theta_{18} & \theta_{17} \\ q & r_8 & r_9 \end{bmatrix} \begin{bmatrix} Z \\ n \\ k \end{bmatrix} = \begin{bmatrix} B \\ F_8 \\ F_9 \\ G \end{bmatrix}$
	n	$\partial\Omega/\partial n=0$	
	k	$\partial\Omega/\partial k=0$	
	E	$\partial\Omega/\partial E=0$	

Notation:

$y_i = \ln(\mathrm{d}H_i/\mathrm{d}t)_i$;

$a_1 = \sum_{i=1}^{l} \ln(1-\alpha_i)$;

$a_2 = \sum_{i=1}^{l} \ln\alpha_i$;

$a_3 = \sum_{i=1}^{l} \ln[1-\ln(1-\alpha_i)]$;

$a_4 = \sum_{i=1}^{l} \ln[-\ln(1-\alpha_i)]$;

$a_5 = \sum_{i=1}^{l} \ln[1-(1-\alpha_i)^{1/3}]$;

$$a_6 = \sum_{i=1}^{l} \ln[1-(1-\alpha_i)^{1/2}];$$

$$a_7 = \sum_{i=1}^{l} \ln[(1-\alpha_i)^{-1/3}-1];$$

$$a_8 = \sum_{i=1}^{l} \ln(1+\alpha_i);$$

$$a_9 = \sum_{i=1}^{l} \ln[(1+\alpha_i)^{1/3}-1];$$

$$b = \sum_{i=1}^{l} y_i;$$

$$C = \sum_{i=1}^{l} \frac{1}{T_i};$$

$$D_i = \ln[1+(1-T_0 \cdot T_i^{-1})E/RT_i];$$

$$d = \sum_{i=1}^{l} D_i;$$

$$\theta_1 = \sum_{i=1}^{l} \ln^2(1-\alpha_i);$$

$$\theta_2 = \sum_{i=1}^{l} \ln^2\alpha_i;$$

$$\theta_3 = \sum_{i=1}^{l} \ln^2[1-\ln(1-\alpha_i)];$$

$$\theta_4 = \sum_{i=1}^{l} \ln\alpha_i \cdot \ln(1-\alpha_i);$$

$$\theta_5 = \sum_{i=1}^{l} \ln[1-\ln(1-\alpha_i)] \cdot \ln(1-\alpha_i);$$

$$\theta_6 = \sum_{i=1}^{l} \ln[1-\ln(1-\alpha_i)] \cdot \ln\alpha_i;$$

$$\theta_7 = \sum_{i=1}^{l} \ln^2[-\ln(1-\alpha_i)];$$

$$\theta_8 = \sum_{i=1}^{l} \ln(1-\alpha_i) \cdot \ln[-\ln(1-\alpha_i)];$$

$$\theta_9 = \sum_{i=1}^{l} \ln\alpha_i \cdot \ln[-\ln(1-\alpha_i)];$$

$$\theta_{10} = \sum_{i=1}^{l} \ln^2[1-(1-\alpha_i)^{1/3}];$$

$$\theta_{11} = \sum_{i=1}^{l} \ln(1-\alpha_i) \cdot \ln[1-(1-\alpha_i)^{1/3}];$$

$$\theta_{12} = \sum_{i=1}^{l} \ln^2[1-(1-\alpha_i)^{1/2}];$$

$$\theta_{13} = \sum_{i=1}^{l} \ln(1-\alpha_i) \cdot \ln[1-(1-\alpha_i)^{1/2}];$$

$$\theta_{14} = \sum_{i=1}^{l} \ln^2[(1-\alpha_i)^{-1/3}-1];$$

$$\theta_{15} = \sum_{i=1}^{l} \ln(1-\alpha_i) \cdot \ln[(1-\alpha_i)^{-1/3}-1];$$

$$\theta_{16} = \sum_{i=1}^{l} \ln^2(1+\alpha_i);$$

$$\theta_{17} = \sum_{i=1}^{l} \ln^2[(1+\alpha_i)^{1/3}-1];$$

$$\theta_{18} = \sum_{i=1}^{l} \ln(1+\alpha_i) \cdot \ln[(1+\alpha_i)^{1/3}-1];$$

$$f_1 = \sum_{i=1}^{l} y_i \cdot \ln(1-\alpha_i);$$

$$f_2 = \sum_{i=1}^{l} y_i \cdot \ln\alpha_i;$$

$$f_3 = \sum_{i=1}^{l} y_i \cdot \ln[1-\ln(1-\alpha_i)];$$

$$f_4 = \sum_{i=1}^{l} y_i \cdot \ln[-\ln(1-\alpha_i)];$$

$$f_5 = \sum_{i=1}^{l} y_i \cdot \ln[1-(1-\alpha_i)^{1/3}];$$

$$f_6 = \sum_{i=1}^{l} y_i \cdot \ln[1-(1-\alpha_i)^{1/2}];$$

$$f_7 = \sum_{i=1}^{l} y_i \cdot \ln[(1-\alpha_i)^{-1/3}-1];$$

$$f_8 = \sum_{i=1}^{l} y_i \cdot \ln(1+\alpha_i);$$

$$f_9 = \sum_{i=1}^{l} y_i \cdot \ln[(1+\alpha_i)^{-1/3}-1];$$

$$g_1 = \sum_{i=1}^{l} [\ln(1-\alpha_i)/T_i];$$

$$g_2 = \sum_{i=1}^{l} [\ln\alpha_i/T_i];$$

$$g_3 = \sum_{i=1}^{l} \{\ln[1-\ln(1-\alpha_i)]/T_i\};$$

$$g_4 = \sum_{i=1}^{l} \{\ln[-\ln(1-\alpha_i)]/T_i\};$$

$$g_5 = \sum_{i=1}^{l} \{\ln[1-(1-\alpha_i)^{1/3}]/T_i\};$$

$$g_6 = \sum_{i=1}^{l} \{\ln[1-(1-\alpha_i)^{1/2}]/T_i\};$$

$$g_7 = \sum_{i=1}^{l} \{\ln[(1-\alpha_i)^{-1/3}-1]/T_i\};$$

$$g_8 = \sum_{i=1}^{l} [\ln(1+\alpha_i)/T_i];$$

$$g_9 = \sum_{i=1}^{l} \{\ln[(1+\alpha_i)^{1/3}-1]/T_i\};$$

$$h_1 = \sum_{i=1}^{l} D_i \cdot \ln(1-\alpha_i);$$

$$h_2 = \sum_{i=1}^{l} D_i \cdot \ln\alpha_i;$$

$$h_3 = \sum_{i=1}^{l} D_i \cdot \ln[1 - \ln(1 - \alpha_i)];$$

$$h_4 = \sum_{i=1}^{l} D_i \cdot \ln[-\ln(1 - \alpha_i)];$$

$$h_5 = \sum_{i=1}^{l} D_i \cdot \ln[1 - (1 - \alpha_i)^{1/3}];$$

$$h_6 = \sum_{i=1}^{l} D_i \cdot \ln[1 - (1 - \alpha_i)^{1/2}];$$

$$h_7 = \sum_{i=1}^{l} D_i \cdot \ln[(1 - \alpha_i)^{-1/3} - 1];$$

$$h_8 = \sum_{i=1}^{l} D_i \cdot \ln(1 + \alpha_i);$$

$$h_9 = \sum_{i=1}^{l} D_i \cdot \ln[(1 + \alpha_i)^{1/3} - 1];$$

$$Q_i = \frac{1}{RT_i}\left[1 - \frac{1 - \frac{T_0}{T_i}}{1 + \frac{E}{RT_i}\left(1 - \frac{T_0}{T_i}\right)}\right],$$

$$r_1 = \sum_{i=1}^{l} Q_i \cdot \ln(1 - \alpha_i);$$

$$r_2 = \sum_{i=1}^{l} Q_i \cdot \ln\alpha_i;$$

$$r_3 = \sum_{i=1}^{l} Q_i \cdot \ln[1 - \ln(1 - \alpha_i)];$$

$$r_4 = \sum_{i=1}^{l} Q_i \cdot \ln[-\ln(1 - \alpha_i)];$$

$$r_5 = \sum_{i=1}^{l} Q_i \cdot \ln[1 - (1 - \alpha_i)^{1/3}];$$

$$r_6 = \sum_{i=1}^{l} Q_i \cdot \ln[1 - (1 - \alpha_i)^{1/2}];$$

$$r_7 = \sum_{i=1}^{l} Q_i \cdot \ln[(1 - \alpha_i)^{-1/3} - 1];$$

$$r_8 = \sum_{i=1}^{l} Q_i \cdot \ln(1 + \alpha_i);$$

$$r_9 = \sum_{i=1}^{l} Q_i \cdot \ln[(1 + \alpha_i)^{1/3} - 1];$$

$$P = \sum_{i=1}^{l} Q_i \cdot y_i;$$

$$q = \sum_{i=1}^{l} Q_i;$$

$$S = \sum_{i=1}^{l} D_i \cdot Q_i;$$

$$W = \sum_{i=1}^{l} (Q_i/T_i);$$

$$B = b + \frac{E}{R}C - d;$$

$$F_j = f_j + \frac{E}{R}g_i - h_j (j = 1, 2, 3, \cdots, 9);$$

$$Z = \ln(AH_0) = \ln A + \ln H_0;$$

$$G = P + \frac{E}{R}W - S;$$

The method of solving the nonlinear normal equations in Table 2 for the kinetic parameters is to solve the equation $\partial\Omega/\partial E = 0$ for the value of E, and then normal equation consisting of the equation else for the kinetic parameters else. In the iterative computation process of combined dichotomous and least-squares methods, we take $AA = 10^{-1}$, $BB = 10^{10}$, $H = 50.0$, $E_1 = 10^{-10}$ and $E_2 = 10^{-5}$, where E is the root of the eqn. $\partial\Omega/\partial E = 0$. $[AA, BB]$ is the root interval of the eqn. $\partial\Omega/\partial E = 0$. H is the step size and E_1 and E_2 are two constants of the control precision. When the value of a certain point on the left side of the eqn. $\partial\Omega/\partial E = 0$ is less than E_1 or a half of the little interval length is less than E_2, this point or the intermediate point of the little interval is the solution of the eqn. $\partial\Omega/\partial E = 0$.

For example, by substituting the original data of initiating explosive 792, listed in Table 3, and all the forms of $f(\alpha)$ in Table 1 into all the normal equations in Table 2, the corresponding values of E and A and the probable mechanism functions are obtained by the method of logical choices[1]. These values of E and A are in agreement with the calculated values obtained by Kissinger's method and by means of the integral and differential methods[1] (data see Table 4). This fact shows that the numerical method presented by us is suitable for computing the values of E, A and n of exothermic decomposition reaction of initiating explosive.

Table 3 Data of initiating explosive 792 determined by DSC

Data point	Temperature T/(K)	Reaction Deep (H_t/H_0)	Exothermic Rate (dH_t/dt)/(mJ/s)	$d(H_t/H_0)/dT\times10^3$ (1/℃)
1	451.2	0.0294	0.9439	3.451
2	456.2	0.0475	1.305	4.773
3	460.2	0.0701	2.042	7.466
4	464.2	0.0996	2.818	10.31
5	467.2	0.1357	3.635	13.29
6	469.2	0.1787	4.539	16.60
7	472.2	0.2262	5.838	21.35
8	475.2	0.2851	7.029	25.70
9	478.2	0.3665	8.335	30.48
10	480.7	0.4615	9.586	35.05
11	483.2	0.5701	10.04	36.72
	T_0=433.2K	H_0=2958mJ	φ=9.243×10^{-2}℃/s	

Table 4 Calculated values of kinetic parameters of exothermic decomposition reaction for initiating explosive 792

Kissinger method					Integral method		Differential method		This work		
φ	T_m	E_k	$\log A_k$	r_k	E	$\log A$	E	$\log A$	E	$\log A$	n
1.052	185.8	238.1	24.53	0.9966	224.9	22.73	228.9	23.18	226.3	23.18	0.4732
2.159	189.5										
5.333	196.8										
10.75	201.5										
20.91	207.8										

Notation:

φ, heating rate, ℃ · min^{-1}; T_m, maximum peak temperature, ℃; E, apparent activation energy, kJ · mol^{-1}; A, pre-exponential constant, s^{-1}; r, linear correlation coefficient; n, reaction order. Subscript k, data obtained by Kissinger's method[3].

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