第 11 卷　第 1 期
2003 年 3 月

含 能 材 料
ENERGETIC MATERIALS

Vol. 11, No. 1
March, 2003

**Article ID**: 1006-9941(2003)00-0018-06

# Estimation of the Critical Temperature of Thermal Explosion for Energetic Materials Using Non-isothermal Analysis Method

HU Rong-zu[1], NING Bin-ke[2,3], YU Qing-sen[3], ZHANG Tong-lai[4], LIU Rong[5],
YANG Zheng-quan[2], GAO Sheng-li[1], ZHAO Hong-an[1], SHI Qi-zhen[1]

(1. *Department of Chemistry*, *Northwest University/Shaanxi Key Laboratory of Physico-Inorganic Chemistry*, *Xi'an* 710069, *China*;
2. *Xi'an Modern Chemistry Research Istitute*, *Xi'an* 710065, *China*;
3. *Department of Chemistry*, *Zhejiang University*, *Hangzhou* 310027, *China*;
4. *Department of Mechano-electric Engineering*, *BIT*, *Beijing* 100081, *China*;
5. *Department of Food Engineering*, *Nanchang University*, *Nanchang* 330047, *China*)

**Abstract**: Two methods for estimating the critical temperature ($T_b$) of thermal explosion for energetic materials (EMs) are derived from the Semenov's thermal explosion theory and two non-isothermal kinetic equations, $d\alpha/dt = A(1-\alpha)e^{-E_a/RT}$ and $d\alpha/dt = A(1-\alpha)[1+E_a/(RT)(1-T_0/T)]e^{-E_a/RT}$, using reasonable hypotheses. We can easily obtain the values of the autocatalytic reaction activation energies ($E_a$), the onset temperature ($T_e$) and the initial temperature ($T_0$) at which DSC curve deviates from the baseline of the non-isothermal DSC curve of EMs, and then calculate the critical temperature ($T_b$) of thermal explosion by the two derived formulae. The results obtained with the two methods for nitrocellulose (NC) are in agreement to each other.

**Key words**: critical temperature; DSC; energitic materials; NC; non-isothermal
**CLC number**: O643.11; TQ564.2　　**Document code**: A

## 1 Introduction

The critical temperature ($T_b$) of thermal explosion is a very important parameter for energetic materials (EMs). Much research has been done in this area[1~7]. However, the estimation of the critical temperature ($T_b$) of thermal explosion of the first order autocatalytic reaction system using non-isothermal analysis method has never been reported so far. The aim of this work is to present two methods for estimating the value of $T_b$ of this system. The data needed for the two methods can be obtained by the non-isothermal DSC measurement alone.

## 2 Theoretical

The thermal decomposition, as an autocatalytic reaction, can be described by Eqs. (1) and (2):

$$A \xrightarrow{k_1} B \qquad (1)$$

$$A + B \xrightarrow{k_2} 2B \qquad (2)$$

where A represents the initial reactant and B represents the thermal decomposition products. The rate expression that corresponds to this scheme is

$$\frac{d\alpha}{dt} = k_1(1-\alpha) + k_2\alpha(1-\alpha) \qquad (3)$$

The experimental results relating to the thermal decomposition of nitrocellulose[8~12] reveal that the catalyst concentration achieves a stationary state:

$$\alpha_{cat.} \approx \text{const.} \qquad (4)$$

Substitution of Eq. (4) into Eq. (3) gives

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha)(1-\alpha) \equiv k(1-\alpha) \qquad (5)$$

Equations (3) ~ (5) explain why such a catalytic thermal decomposition can be described by a first-order reaction. The reaction rate $k$ depends on the temperature

---

**Received date**: 2001-10-17

**Biography**: HU Rong-zu (1938 – ), male, professor, research fields: thermochemistry and thermal analysis; published over 230 papers.

and on the thermodynamic properties of the reaction phase determining the solubility of the volatile catalytic products ($\alpha^*$):

$$k = k_1 + k_2\alpha \qquad (6)$$

The classical Arrhenius equation with two adjustable parameters ($E_a$ and $A$) is widely accepted as describing the relationship between rate constant and temperature. Equation (6) may be written in the following form:

$$k \equiv k_1 + k_2\alpha = A_1 e^{-E_{a1}/RT} + a^* A_2 e^{-E_{a2}/RT} \equiv A e^{-E_a/RT} \qquad (7)$$

where $A_1$, $A_2$ and $A$ are pre-exponential factors, and $E_{a_1}$, $E_{a_2}$ and $E_a$ are the activation energies for the first-order, autocatalytic and overall reactions, respetively. The value of $E_a$ depends not only on the kinetics, but also on thermodynamic factors such as the relation between the stability of volatile catalyst ($\alpha^*$) and temperature.

Combining Eqs. (5) and (7), we obtain

$$\frac{d\alpha}{dt} = A(1-\alpha)e^{-E_a/RT} \qquad (8)$$

The other rate expression commomly adopted is equation (9)

$$\frac{d\alpha}{dt} = A(1-\alpha)\left[1 + \frac{E_a}{RT}\left(1 - \frac{T_0}{T}\right)\right]e^{-E_a/RT} \qquad (9)$$

Equations (8) and (9) are two rate expressions for an autocatalytic overall reaction.

### 2.1 Method Ⅰ

The enthalpy ($q_1$) of thermal decomposition reaction per unit time for EMs can be expressed by the equation

$$q_1 = Q\frac{VD\,d\alpha}{M\,dt} \qquad (10)$$

where $Q$ is the enthalpy of the thermal decomposition reaction in J · mol$^{-1}$, $V$ is the volume of EMs loaded in cm$^3$, $d$ is the loading density in g · cm$^{-3}$, $M$ is the mole mass of EMs in g · mol$^{-1}$ and $d\alpha/dt$ is the reaction rate. According to previous papers [2,3], the reaction rate may be expressed as

$$\frac{d\alpha}{dt} = A(1-\alpha)\left[1 + \frac{E_a}{RT}\left(1 - \frac{T_\infty}{T}\right)\right]e^{-E_a/RT} \qquad (11)$$

where $\alpha$ stands for the conversion degree, $T$ for the temperature (K), $(1-\alpha)$ for the differential mechanism functions, $t$ for the time, $R$ for the gas constant, $A$ for the preexponential factor, and $E_a$ for the activation energy. $T_\infty$ is the initial temperature at which the DSC curve deviates from the baseline when the heating rate tends to zero in K.

Since the transition from thermal decomposition to combustion starts in the range of low conversion degree, i. e., $f(\alpha) \approx 1$, the enthalpy of decomposition reaction in unit time for one mole EMs may be expressed as

$$q_1 = QA\left[1 + \frac{E_a}{RT}\left(1 - \frac{T_\infty}{T}\right)\right]e^{-E_a/RT} \qquad (12)$$

At the same time, the amount of heat ($q_2$) transferred by the wall of the reactor to surrounding medium in unit time is

$$q_2 = k'(T - T_c)S \qquad (13)$$

where $S$ is the external surface of the loaded sample in cm$^2$, $k'$ is an overall heat transfer coefficient in J · cm$^{-2}$ · K$^{-1}$ · s$^{-1}$, $T_c$ is the temperature of the reaction wall and surroundings according to the linear relationship $T_c = T_0 + \beta t$, where $\beta$ is the heating rate in K · min$^{-1}$. When the thermal explosion starts, Eq. (13) becomes

$$q_2 = k'(T_b - T_{eo})S \qquad (14)$$

where $T_b$ is the thermal explosion temperature of EMs in K (Fig. 1); $T_{eo}$ is the onset temperature in the DSC curve under linear temperature increase condition when $\beta$ tends to zero (Fig. 2).

According to Semenov's thermal explosion theory[13], the sufficient and essential conditions from thermal decomposition to thermal explosion are as follows:

$$(q_1)_{T_b} = (q_2)_{T_b} \qquad (15)$$

$$\left(\frac{dq_1}{dT}\right)_{T_b} = \left(\frac{dq_2}{dT}\right)_{T_b} \qquad (16)$$

When the thermal explosion starts, Eq. (12) becomes

$$q_1 = QA\left[1 + \frac{E_a}{RT_b}\left(1 - \frac{T_\infty}{T_b}\right)\right]e^{-E_a/RT_b} \qquad (17)$$

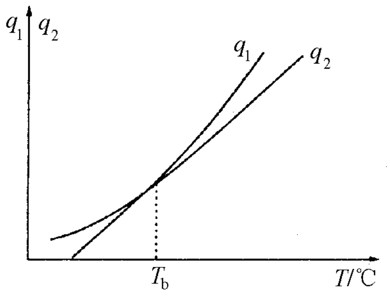

Fig. 1 $q_1$-$q_2$ relation

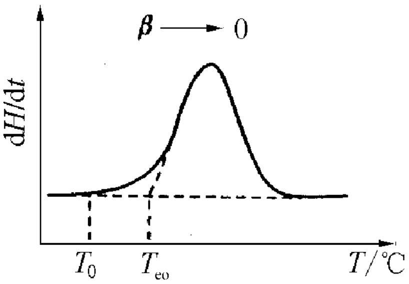

Fig. 2 Schematic diagrams of typical DSC curves of thermal decomposition for EMs

Differentiation of Eq. (12) with respect to $t$ gives

$$\left.\frac{\mathrm{d}q_1}{\mathrm{d}t}\right|_{T=T_b} = QA\mathrm{e}^{-E_a/RT_b}\frac{E_a}{RT_b^2}\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_b\left[\frac{2T_\infty}{T_b}+\frac{E_a}{RT_b}\left(1-\frac{T_\infty}{T_b}\right)\right] \quad (18)$$

Differentiation of Eq. (13) with respect to $t$ gives

$$\left.\frac{\mathrm{d}q_2}{\mathrm{d}t}\right|_{T=T_b} = k'S\left[\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_b-\beta\right] \quad (19)$$

Combining Eqs. (14), (15) and (17), we have

$$QA\left[1+\frac{E_a}{RT_b}\left(1-\frac{T_\infty}{T_b}\right)\right]\mathrm{e}^{-E_a/RT_b} = k'S(T_b-T_{eo}) \quad (20)$$

Combining Eqs. (16), (18) and (19), we have

$$k'S\left[\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_b-\beta\right] = QA\mathrm{e}^{-E_a/RT_b}\frac{E_a}{RT_b^2}\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_b\left[\frac{2T_\infty}{T_b}+\frac{E_a}{RT_b}\left(1-\frac{T_\infty}{T_b}\right)\right] \quad (21)$$

Mutiplying both sides of Eq. (21) by ( $T_b - T_{eo}$ ), we obtain

$$k'S\left[\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_b-\beta\right](T_b-T_{eo}) = QA\mathrm{e}^{-E_a/RT_b}\frac{E_a}{RT_b^2}\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_b\left[\frac{2T_\infty}{T_b}+\frac{E_a}{RT_b}\left(1-\frac{T_\infty}{T_b}\right)\right](T_b-T_{eo}) \quad (22)$$

Substituting Eq. (20) into Eq. (22), we obtain

$$\frac{\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_b-\beta}{\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_b} = \frac{\frac{E_a}{RT_b^2}\left[\frac{2T_\infty}{T_b}+\frac{E_a}{RT_b}\left(1-\frac{T_\infty}{T_b}\right)\right](T_b-T_{eo})}{1+\frac{E_a}{RT_b}\left(1-\frac{T_\infty}{T_b}\right)} \quad (23)$$

As the thermal explosion starts, $(\mathrm{d}T/\mathrm{d}t)_b \gg \beta$, and Eq. (23) may be simplified to the form

$$\frac{E_a(T_b-T_\infty)+2RT_bT_\infty}{RT_b^2+E_a(T_b-T_\infty)}\frac{E_a}{RT_b^2}(T_b-T_{eo}) = 1 \quad (24)$$

or

$$R^2T_b^4+RE_aT_b^3-(3RE_aT_\infty+E_a^2)T_b^2+(E_a^2T_{eo}+E_a^2T_\infty+2RE_aT_{eo}T_\infty)T_b-E_a^2T_{eo}T_\infty = 0 \quad (25)$$

Equation (25) is the relation formula for estimating the critical temperature of thermal explosion of EMs under linear temperature increase conditions.

Substituting the measured values of $T_\infty$, $T_{eo}$ and $E_a$ into Eq. (25), the value of $T_b$ is obtained.

### 2.2 Method Ⅱ

If the reaction rate of thermal decomposition of EMs is expressed as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Af(\alpha)\mathrm{e}^{-E_a/RT} \quad (26)$$

Substituting $\mathrm{d}\alpha/\mathrm{d}t$ in Eq. (10) with Eq. (26), the expression for $q_1$ becomes

$$q_1 = Q\frac{Vd}{M}Af(\alpha)\mathrm{e}^{-E_a/RT} \quad (27)$$

with linear increase in temperature

$$T = T_0+\beta t \quad (28)$$

where $\beta$ is the heating rate in K · min$^{-1}$, $T_0$ is the initial temperature of the reaction system in K, $t$ is the heating time in s$^{-1}$, $T$ is the temperature of the reaction system at time $t$ in K.

Therefore, it is apparent that the enthalpy of thermal decomposition $q_1$ is proportional to the exponent of the reciprocal of reaction temperature $T$. At the same time, the heat ( $q_2$ ) lost from the reaction system in unit time may be expressed

$$q_2 = k'S(T-T_s) \quad (29)$$

where $k'$ is an overall heat transfer coefficient in J · cm$^{-2}$ · K$^{-1}$ · s$^{-1}$, $S$ is the external surface area of the loaded sample in cm$^2$, $T$ is the temperature of the reaction system in K, $T_s$ is the surrounding temperature in K, which is determined by the linear temperature increase in DSC analysis.

With the boundary conditions of thermal explosion, Eq. (27) becomes

$$q_1|_{T_b} = Q\frac{Vd}{M}Af(\alpha_b)e^{-E_a/RT_b} \quad (30)$$

and Eq. (29) becomes

$$q_2|_{T_b} = k'S(T_b-T_{sb}) \quad (31)$$

where $T_{sb}$ is the surrounding temperature at the beginning of the thermal explosion in K.

According to Semenov's thermal explosion theory [13], the sufficient and essential conditions from thermal decomposition to thermal explosion might be expressed as

$$\begin{cases} q_1 \big|_{T_b} = q_2 \big|_{T_b} & (32) \\ \left.\dfrac{dq_1}{dT}\right|_{T_b} = \left.\dfrac{dq_2}{dT}\right|_{T_b} & (33) \end{cases}$$

Differentiating Eq. (27) with respect to $T$, and considering Eq. (28), we obtain

$$\left.\frac{dq_2}{dT}\right|_{T=T_b,\alpha=\alpha_b} = \frac{1}{(dT/dt)_{T_b}} \frac{QVd}{M} Af(\alpha_b) e^{-E_a/RT_b} \left[Af'(\alpha_b) e^{-E_a/RT_b} + \frac{E_a}{RT_b^2}\left(\frac{dT}{dt}\right)_{T_b}\right] \qquad (34)$$

Differentiation Eq. (29) with respect to $T$, and considering Eq. (28), we obtain

$$\left.\frac{dq_2}{dT}\right|_{T=T_b} = \frac{1}{(dT/dt)} k'S\left[\left(\frac{dT}{dt}\right)_{T_b} - \beta\right] \qquad (35)$$

Combining Eqs. (30), (31), and (32)

$$\frac{QVd}{M} Af(\alpha_b) e^{-E_a/RT_b} = k'S(T_b - T_{sb}) \qquad (36)$$

Combining Eqs. (33), (34) and (35)

$$\frac{QVd}{M} Af(\alpha_b) e^{-E_a/RT_b}\left[Af'(\alpha_b) e^{-E_a/RT_b} + \frac{E_a}{RT_b^2}\left(\frac{dT}{dt}\right)_{T_b}\right] = k'S\left[\left(\frac{dT}{dt}\right)_{T_b} - \beta\right] \qquad (37)$$

Combining Eqs. (36) and (37)

$$\left[Af'(\alpha_b) e^{-E_b/RT_b} + \frac{E_a}{RT_b^2}\left(\frac{dT}{dt}\right)_{T_b}\right](T_b - T_{sb}) = \left(\frac{dT}{dt}\right)_{T_b} - \beta \qquad (38)$$

When the transition from thermal decomposition to thermal explosion is triggered, the fraction of the material reacted $\alpha$ is very small, i. e. $f(\alpha) = 1 - \alpha \approx 1$ and $f'(\alpha) = 0$. Equation (38) may therefore be expressed as

$$\frac{E_a}{RT_b^2}(T_b - T_{sb}) = \frac{(dT/dt)_{T_b} - \beta}{(dT/dt)_{T_b}} \qquad (39)$$

where $(dT/dt)_{T_b}$ is the increasing rate of temperature in the sample when its thermal decomposition converts into thermal explosion. This is difficult to solve directly from conventional experiments.

When the transition from thermal decomposition to thermal explosion begins, the surrounding temperature is near to the onset temperature $T_e$ of the DSC curve. Substitution $T_e$ of the DSC curves with heating rate $\beta_i$ for $T_{sb}$, when $\beta_i$ tends to zero, we take the limitation of both sides of Eq. (39)

$$\lim_{\beta\to 0}\frac{E_a}{RT_b^2}(T_b - T_{sb}) = \lim_{\beta\to 0}\frac{E_a}{RT_b^2}(T_b - T_e) = \frac{E_a}{RT_b^2}(T_b - T_{eo}) \qquad (40)$$

$$\lim_{\beta\to 0}\frac{(dT/dt)_{T_b} - \beta}{(dT/dt)_{T_b}} = 1 \qquad (41)$$

Therefore, Eq. (39) can be simplified into the form

$$\frac{E_a}{RT_b^2}(T_b - T_{eo}) = 1 \qquad (42)$$

It may also be expressed as

$$T_b = \frac{E_a - \sqrt{E^2 - 4E_a RT_{eo}}}{2R} \qquad (43)$$

Because the root of Eq. (42) is unreasonable, it is omitted. The value of $T_{eo}$ corresponding to $\beta = 0$ may be obtained by using linear by using linear regression of $T_{ei}$ and $\beta_i$ as described in Eq. (44)

$$T_{ei} = a + b\beta_i + c\beta_i^2 + d\beta_i^3 \qquad (44)$$

The value of $T_{ei}$ is easily obtained from the DSC cruve with the heating rate $\beta_i$, and a unique equation set can be defined using four groups of $T_{ei}$ and $\beta_i$. When $\beta_i$ tends to zero, the value of $T_{ei}$ equals the value of $a$, and it is designated $T_{eo}$. The value of the activation energy $E_a$ may be obtained using the same DSC analyses with Kissnger's method [14] or Ozawa's method [15].

## 3 Experimental

### 3.1 Materials

The nitrocellulose (NC) containing 13.54%, 12.97% and 11.92% of nitrogen used in this work was prepared and purified at Xi'an Modern Chemistry Research Institute.

### 3.2 Instrument and conditions

In the present experiments, the initial data needed for calculating all the kinetic parameters were obtained from using a CDR-1 differential scanning calorimeter (Shanghai Tianping Instrument Factory, China) with an aluminium cell. The conditions of the DSC analyses were: sample mass, about 0.7 mg; heating rates, 1, 2, 5, 10 and 20 K · min$^{-1}$, respectively; calorimetric sensitivities, ± 20.92 and ± 41.84 mJ · s$^{-1}$; atmosphere, static air; reference sample, $\alpha$-$Al_2O_3$; the precision of temperature was 0.25 K; the temperature and heat were calibrated using pure indium and tin powders.

**Table 1 Calculated values of the critical temperature of thermal explosion for NC**

| $\beta$/K·min$^{-1}$ | $T_0$/K | $T_e$/K | $E_{aoe}$/kJ·mol$^{-1}$ | $T_\infty$/K | $T_{eo}$/K | $T_b$/K | |
|---|---|---|---|---|---|---|---|
| | | | | | | Eq.(25) | Eq.(43) |
| NC(13.54% N) | | | | | | | |
| 1.015 | 441.65 | 451.95 | 180.2 | 438.38 | 441.74 | 448.05 | 451.13 |
| 2.044 | 443.65 | 458.90 | | | | | |
| 5.182 | 444.40 | 465.45 | | | | | |
| 11.68 | 448.15 | 472.65 | | | | | |
| 18.02 | 455.15 | 480.95 | | | | | |
| NC(12.97% N) | | | | | | | |
| 1.031 | 440.65 | 451.95 | 176.7 | 440.27 | 446.45 | 453.36 | 456.24 |
| 2.146 | 443.65 | 458.90 | | | | | |
| 5.131 | 444.25 | 465.45 | | | | | |
| 10.59 | 448.15 | 472.65 | | | | | |
| 21.59 | 455.65 | 481.45 | | | | | |
| NC(11.92% N) | | | | | | | |
| 1.047 | 440.15 | 450.45 | 166.5 | 440.40 | 446.42 | 453.71 | 456.84 |
| 2.075 | 443.15 | 457.65 | | | | | |
| 5.378 | 443.70 | 465.20 | | | | | |
| 10.53 | 449.15 | 473.65 | | | | | |
| 19.70 | 455.40 | 481.20 | | | | | |

Note: $\beta$ – heating rate; $T_0$ – initial temperature at which the DSC curve deviates from the baseline; $T_e$ – onset temperature in the DSC curve; $E_{aoe}$ – apparent activation energy obtained by Ozawa's method[14].

## 4 Results and discussion

The measured values of $\beta_i$, $T_{oi}$ and $T_{ei}$ ($i = 1, 2, \cdots 5$), the calculated value of $E_{aoe}$ by Ozawa's method and the obtained values of $T_\infty$ and $T_{eo}$ when $\beta$ tends to zero, together with the reasonable values of $T_b$ obtained by substituting the above-mentioned values into Eqs. (25) and (43), are shown in Table 1. It can be seen that the calculated values of $T_b$ obtained by the two different methods agree well to each other, clearly demonstrating that Eqs. (25) and (43) are suitable for estimating the values of $T_b$ for NC.

## REFERENCES:

[1] HU Rong-zu, YANG Zheng-quan, LIANG Yan-jun, et al. Numerical solution of the critieal temperature of thermal explosion of explosive under linearly increasing temperature conditions[J]. Baozha Yu Chongji, 1987, 7(4): 348 – 351.

[2] HU Rong-zu, YANG Zheng-quan, LIANG Yan-jun. A study of reaction between RDX and urea by a single non-isothermal DSC curve[J]. Thermochim. Acta, 1988, 134: 429 – 434.

[3] XIE Yi, HU Rong-zu, YANG Zheng-quan, et al. Studies on the critical temperature of thermal explosion for 3-nitro-1,2,4-triazol-5-one (NTO) and its salts[J]. Propellants, Explosives, Pyrotechnics, 1992, 17(6): 298 – 302.

[4] ZHANG Tong-lai, HU Rong-zu, XIE Yi, et al. The estimation of critical temperature of thermal explosion for energetic materials using non-isothermal DSC[J]. Thermochim. Acta, 1994, 244: 171 – 176.

[5] Frank-Kamenetskii D A, Frank-Kamenetskii O A. Temperature distribution in reaction vessel and stationary theory of thermal explosion[J]. J. Phys. Chem., (USSR). 1939, 13(6): 738 – 755.

[6] Zinn J, Mader C L. Thermal initiation of explosives[J]. J. Appl. Phys., 1960, 31(2): 323 – 328.

[7] Zinn J, Rogers R N. Thermal initiation of explosivers[J]. J. Phys. Chem., 1962, 66(12): 2646 – 2653.

[8] Eisenreich N, Pfeil A. Non-linear least – squares fit of non-isothermal thermoanalytical curves. Reinvestigation of the kinetics of the autocatalytic decomposition of nitrated cellulose [J]. Thermochim. Acta, 1983, 61: 13 – 21.

[9] Eisenreich N. Doctorate dissertation. Beitrag zur kinetik thermischer zersetzungseaktionen (Thermoanalytische auswertung der zersetzung von nitrocellulose) [D]. Technical University of Munich. 1978.

[10] NING Bin-ke, LIU Rong, YANG Zheng-quan, et al. Studies on the kinetics of the first – order autocalalytic decomposition reaction of highly nitrated nitrocellulose [J]. J. Therm. Anal. Cal., 1999, 58(2): 403 – 411.

[11] NING Bin-ke, LIU Rong, YANG Zheng-quan, et al. Numerical simulation of kinetie parameters of the first - order autocatalytic decomposition of NC[J]. Hanneng Cailiao, 1999, 7(4): 162 - 165.

[12] HU Rong-zu, SHI Qi-zhen. Thermal Analysis Kinetics [M]. Beijing: Science Press, 2001, Chapter Ⅸ.

[13] Semenov N N. On Some Problesms of Chemical Kinetics and Reactivity[M]. Moscow: Ind AN SSSR, 1958, P. 421.

[14] Kissinger H E. Reaction kinetics on differential thermal analysis[J]. Anal. Chem., 1957, 29(11): 1702 - 1706.

[15] Ozawa T. A new method of analyzing thermogravimatric data[J]. Bull. Chem. Soc. Jpn., 1965, 38(1): 1881 - 1886.

# 用非等温分析法估算含能材料的热爆炸临界温度

胡荣祖[1]，宁斌科[2,3]，俞庆森[3]，张同来[4]，刘　蓉[5]，
杨正权[2]，高胜利[1]，赵宏安[1]，史启祯[1]
（1. 西北大学化学系/陕西省物理无机化学重点实验室，陕西 西安 710069；
2. 西安近代化学研究所，陕西 西安 710065；3. 浙江大学化学系，浙江 杭州 310027；
4. 北京理工大学机电工程学院，北京 100081；5. 南昌大学食品工程系，江西 南昌 330047）

**摘要：**通过合理的假设，从谢苗诺夫(Semenov)的热爆炸理论和两种非等温动力学方程：$\mathrm{d}\alpha/\mathrm{d}t = A(1-\alpha)\mathrm{e}^{-E_a/RT}$ 和 $\mathrm{d}\alpha/\mathrm{d}t = A(1-\alpha)[1+E_a/(RT)(1-T_0/T)]\mathrm{e}^{-E_a/RT}$，导出了估算含能材料(EMs)热爆炸临界温度($T_b$)的两种方法。从 EMs 的非等温 DSC 曲线，我们很容易得到计算 $T_b$ 值所用的自催化反应活化能($E_a$)、onset 温度($T_e$)和偏离基线的初始点温度($T_0$)。对硝化棉而言，两种方法所得的 $T_b$ 值彼此吻合。

**关键词：**临界温度；DSC；含能材料；非等温

**中图分类号：**O643.11；TQ 564.2　　**文献标识码：**A