文章编号：1006-9941(2015)09-0818-013

自催化反应速率方程的导出途径及其在含能材料热行为研究中的应用

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摘 要：提出了经验级数自催化反应速率方程和13个派生式的导出途径。导出了描述自催化反应速率曲线特性[α_{max}和$(d\alpha/dt)_{max}$]的方程和反应进度(α)随时间(t)和温度(T)变化的方程。编制了计算自催化反应动力学参数(E、A或E_1、A_1、E_2、A_2)、经验级数(m、n、p)和α_{max}、$(d\alpha/dt)_{max}$值的计算机程序。提出了描述六硝基六氮杂异伍兹烷(HNIW)自催化分解反应的速率方程和硝化棉(NC)(12.82%、12.97%、13.54%、13.61%、13.86%、13.88%、14.14% N)自催化分解反应的动力学参数——催化系数K_{cat}、速率曲线特性参数和α随t变化的方程。

关键词：自催化反应；动力学参数；曲线特性参数；反应进度；六硝基六氮杂异伍兹烷(HNIW)；硝化棉(NC)

中图分类号：TJ55；O643 **文献标志码**：A **DOI**：10.11943/j.issn.1006-9941.2015.09.001

1 引 言

含能材料(EM)体系自(动)催化反应的动力学行为和动力学三因子,在EM对热抵抗能力的评估,热爆炸临界温度、热爆炸临界温升速率、撞击感度(特性落高)、放热系统热感度、绝热至爆时间、燃烧速度的估算和放热分解反应诱导温度与诱导时间关系的定量描述方面扮演重要角色[1-6]。导出该类反应的速率方程、速率曲线方程和反应进度(α)随时间(t)和温度(T)变化的方程,对描述、定量评估自催化反应的动力学行为,有一定学术意义。本文依据EM体系自催化反应的特性：(1)自催化反应由催化剂生成反应和催化剂催化EM的催化反应组成,体系自催化反应速率则是催化剂生成反应速率和催化反应速率的加和；(2)引导起始催化反应不能从反应进度$\alpha=0$开始,需要有催化产物；(3)具有催化功能的反应产物使反应经过一段诱导期后才能出现反应加速；(4)反应速率随某一催化反应产物浓度而增长；(5)自催化反应速率有最大值,从α与反应能量变化的关系,导出了经验级数自催化反应的速率方程。由经验级数自催化反应速率方程,导出了13个自催化反应速率的派生式。由自催化反应特性(5)导出了描述自催化反应速率曲线特性[α_{max}和$(d\alpha/dt)_{max}$]的方程。通过速率方程的积分处理,导出了α随t和T变化的方程。报道了描述六硝基六氮杂异伍兹烷(HNIW)自催化分解反应的速率方程和硝化棉(NC)(12.82%、12.97%、13.54%、13.61%、13.86%、13.88%、14.14% N)自催化分解反应的动力学参数—催化系数K_{cat}、速率曲线特性参数和α随t变化的方程。

2 理论和方法

2.1 经验级数自催化反应速率方程的导出途径

EM体系的自(动)催化反应由催化剂(B)的生成反应和催化剂催化EM的催化反应组成,体系自催化反应速率则是催化剂生成反应速率和催化反应速率的加和。

由催化剂生成反应

$$m\mathrm{EM} \xrightarrow{k_{\mathrm{CFR}}} n\,\mathrm{EM_p} + \mathrm{B} \quad (1)$$

和边界条件

$$\left.\begin{array}{lllll} t=0 & c_0 & \alpha_0=0 & 0 & Q_0=0 \\ t=t & c & \alpha & c_0-c & Q \\ t=\infty & c_\infty=0 & \alpha_\infty=1 & & Q_\infty \end{array}\right\} \quad (2)$$

式(1)中,下角标"p"代表产物；"CFR"代表催化剂生成反应。

知反应进度(α或c)与反应能量变化的关系[7]：

$$\frac{c_0-c}{c_0-c_\infty}=\frac{\alpha_0-\alpha}{\alpha_0-\alpha_\infty}=\frac{Q_0-Q}{Q_0-Q_\infty} \quad (3)$$

收稿日期：2015-02-10；**修回日期**：2015-03-16

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$$\frac{c_0-c}{c_0}=\alpha=\frac{Q}{Q_\infty} \tag{4}$$

$$c=c_0(1-\alpha) \tag{5}$$

$$c_0-c=c_0\alpha \tag{6}$$

和催化剂生成速率方程的微分式

$$\frac{\mathrm{d}(c_0-c)}{\mathrm{d}t}=k_{\mathrm{CFR}}c^m \tag{7}$$

$$c_0\frac{\mathrm{d}\left(\frac{c_0-c}{c_0}\right)}{\mathrm{d}t}=k_{\mathrm{CFR}}[c_0(1-\alpha)]^m \tag{8}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_{\mathrm{CFR}}c_0^{m-1}(1-\alpha)^m \tag{9}$$

令

$$k_1=k_{\mathrm{CFR}}c_0^{m-1} \tag{10}$$

则

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_1(1-\alpha)^m \tag{11}$$

式中，c、α、Q 和 k 有通常的含义。

由催化反应

$$\begin{array}{l} n\mathrm{EM}+\mathrm{B}\rightarrow n\mathrm{EMB} \\ \underline{+n\mathrm{EMB}+p\mathrm{EM}\rightarrow(n+p)\mathrm{EM_p}+\mathrm{B}} \\ n\mathrm{EM}+p\mathrm{EM}\xrightarrow{k_{\mathrm{CR}}}(n+p)\mathrm{EM_p} \end{array} \tag{12}$$

和边界条件

$$\left.\begin{array}{llllll} t=0 & & c_0 & 0 & \alpha_0=0 & Q_0=0 \\ t=t & c_0-c & c & c_0-c & \alpha & Q \\ t=\infty & & c_\infty=0 & & \alpha_\infty=1 & Q_\infty \end{array}\right\} \tag{13}$$

知方程(3)～(6)和催化反应速率方程的微分式

$$\frac{\mathrm{d}(c_0-c)}{\mathrm{d}t}=k_{\mathrm{CR}}(c_0-c)^n c^p \tag{14}$$

$$\frac{c_0}{c_0}\frac{\mathrm{d}(c_0-c)}{\mathrm{d}t}=k_{\mathrm{CR}}(c_0\alpha)^n[c_0(1-\alpha)]^p \tag{15}$$

$$c_0\frac{\mathrm{d}\left(\frac{c_0-c}{c_0}\right)}{\mathrm{d}t}=k_{\mathrm{CR}}c_0^{n+p}\alpha^n(1-\alpha)^p \tag{16}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_{\mathrm{CR}}c_0^{n+p-1}\alpha^n(1-\alpha)^p \tag{17}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_2\alpha^n(1-\alpha)^p \tag{18}$$

式中

$$k_2=k_{\mathrm{CR}}c_0^{n+p-1} \tag{19}$$

反应初期，$\alpha\ll1$，式(18)可变为

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_2\alpha^n \tag{20}$$

$$\alpha^{-n}\mathrm{d}\alpha=k_2\mathrm{d}t \tag{21}$$

方程两边积分

$$\int\alpha^{-n}\mathrm{d}\alpha=\int k_2\mathrm{d}t \tag{22}$$

得

$$\frac{\alpha^{1-n}}{1-n}=k_2+\mathrm{const} \tag{23}$$

据此不难看出，引导起始反应不能从 $\alpha=0$ 开始，需要有催化产物，催化方程(18)应写为

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_2(\alpha+\alpha_0)^n(1-\alpha)^p \tag{24}$$

考虑体系中还独立地进行着从 $k_1(1-\alpha)^m$ 速率给出催化产物的反应，因此，自催化方程应写为

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_1(1-\alpha)^m+k_2(\alpha+\alpha_0)^n(1-\alpha)^p \tag{25}$$

我们称式(25)为经验级数自催化反应速率方程。

2.2 经验级数自催化速率方程派生式的导出途径

由经验级数(m、n、p)速率方程(25)导出的 13 个派生式见图 1。其中，式(25-7)～(25-13)为自催化速率方程；式(25-1)、(25-2)、(25-3)和(25-4)为催化速率方程；式(25-2)、(25-3)和(25-4)分别称为第三类微分方程式、第二类微分方程式和第一类微分方程式。

式(25-10)和(25-11)中的 K_{cat} 称催化系数，特指自催化方程 $\mathrm{d}\alpha/\mathrm{d}t=k_1(1-\alpha)^m+k_2\alpha^n(1-\alpha)^p$ 中 k_2 与 k_1 的比值：

$$K_{\mathrm{cat}}=\frac{k_2}{k_1}=\frac{\text{催化反应速率常数}}{\text{催化剂生成反应速率常数}}$$

对框图 1 中各方程的参数：方程(25-2)、(25-3)、(25-4)和(25-6)中的 2 参数(A_2、E_{a2}；A_2、E_{a2}；A_2、E_{a2}；A_2、E_{a2})，方程(25-5)和(25-11)中的 3 参数(A_2、E_{a2}、p；A_1、E_{a1}、K_{cat})，方程(25-1)、(25-7)、(25-8)、(25-10)、(25-12)和(25-13)中的 4 参数(分别为 A_2、E_{a2}、n，p；A_1、A_2、E_{a1}、E_{a2}；A_1、A_2、E_{a1}、E_{a2}；A_1、E_{a1}、m、K_{cat}；A_1、A_2、E_{a1}、E_{a2}；A_1、A_2、E_{a1}、E_{a2})，方程(25-9)中的 5 参数(A_1、A_2、E_{a1}、E_{a2}、m)和方程(25)中的 7 参数(A_1、A_2、E_{a1}、E_{a2}、m、n、p)可用线性最小二乘法和信赖域方法求解[4-6,8]，也可将方程(25-13)改写为

$$\frac{\mathrm{d}y}{\mathrm{d}t}=-k_1(T)y-k_2(T)y(1-y)$$

和

$$\beta\frac{\mathrm{d}y}{\mathrm{d}T}=-[k_1(T)+k_2(T)]y+k_2(T)y^2$$

的形式，通过解伯努利方程(Bernoulli 方程)，得 4 参数(A_1、A_2、E_{a1}、E_{a2})[9]。

这里，y 是未反应物质的分数；$1-y$ 是已发生反应物质

的分数；T为温度；t为时间；$k_1(T)$和$k_2(T)$是一阶自催化方程在温度T的速率常数；$k_1(T)=A_1\exp(-E_1/RT)$，$k_2(T)=A_2\exp(-E_2/RT)$；为指前因子；E为活化能；$\mathrm{d}t=\mathrm{d}T/\beta$，$\beta$是线性升温速率。

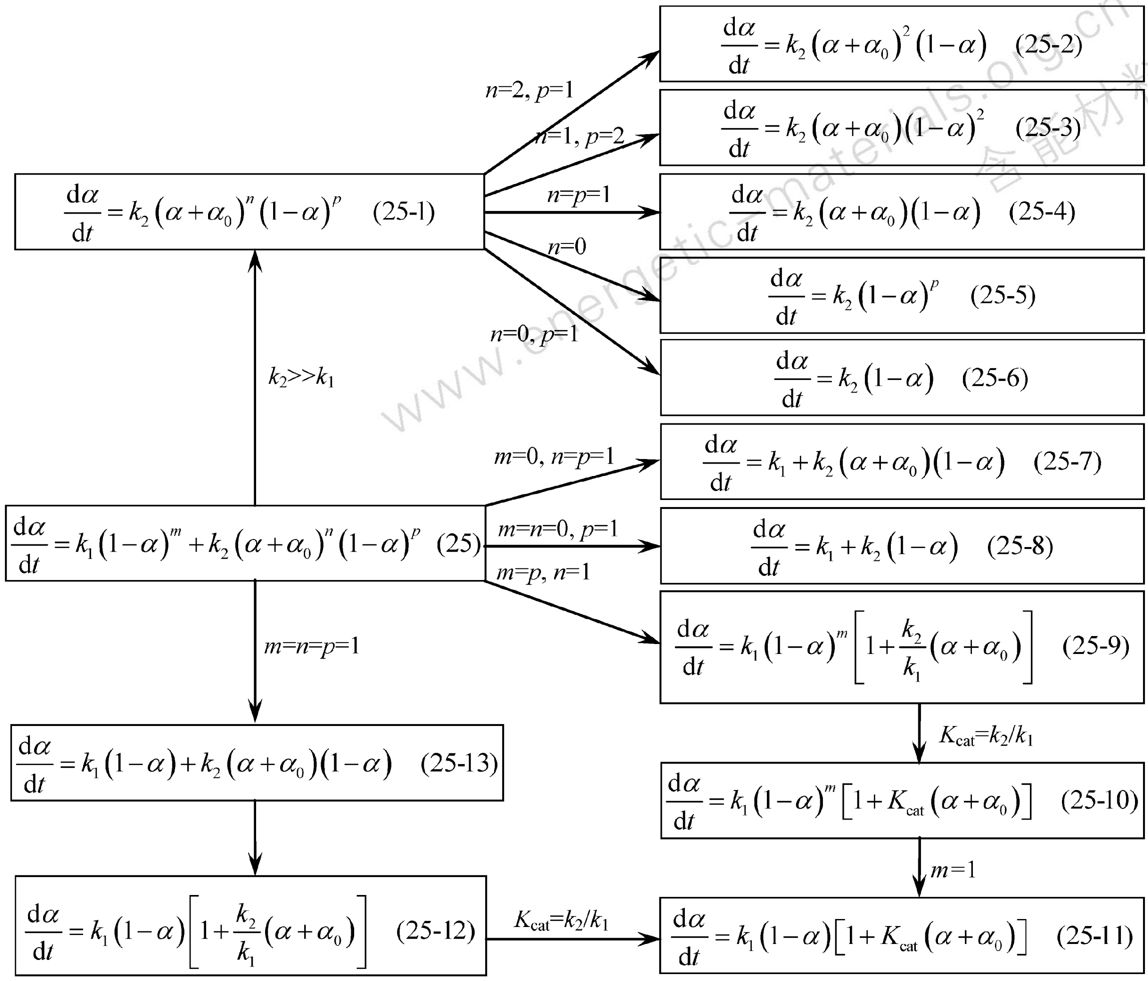

图1 经验级数自催化反应速率方程和派生式的导出过程框图

Fig.1 Block diagram of the derivation process of empiric-order autocatalytic reaction rate equation and its thirteen-derived formulate

2.3 自催化反应速率曲线特性—α_{max}和$(\mathrm{d}\alpha/\mathrm{d}t)_{max}$—表达式的导出途径

由方程(25)两边对t求导

$$\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}=k_1m(1-\alpha)^{m-1}(-1)\frac{\mathrm{d}\alpha}{\mathrm{d}t}+k_2n(\alpha+\alpha_0)^{n-1}\frac{\mathrm{d}\alpha}{\mathrm{d}t}(1-\alpha)^p+k_2(\alpha+\alpha_0)^np(1-\alpha)^{p-1}(-1)\frac{\mathrm{d}\alpha}{\mathrm{d}t}$$

$$=\frac{\mathrm{d}\alpha}{\mathrm{d}t}[-k_1m(1-\alpha)^{m-1}+k_2n(\alpha+\alpha_0)^{n-1}(1-\alpha)^p-k_2p(\alpha+\alpha_0)^n(1-\alpha)^{p-1}] \quad (26)$$

和$\mathrm{d}^2\alpha/\mathrm{d}t^2=0$，速率达最大值，得

$$k_2n(\alpha_{max}+\alpha_0)^{n-1}(1-\alpha_{max})^p=k_1m(1-\alpha_{max})^{m-1}+k_2p(\alpha_{max}+\alpha_0)^n(1-\alpha_{max})^{p-1} \quad (27)$$

由$m=0$，得

$$k_2n(\alpha_{max}+\alpha_0)^{n-1}(1-\alpha_{max})^p=k_2p(\alpha_{max}+\alpha_0)^n(1-\alpha_{max})^{p-1} \quad (28)$$

$$n(1-\alpha_{max})=p(\alpha_{max}+\alpha_0) \quad (29)$$

$$n-n\alpha_{max}=p\alpha_{max}+p\alpha_0 \quad (30)$$

$$(n+p)\alpha_{max}=n-p\alpha_0 \quad (31)$$

$$\alpha_{max}=\frac{n-p\alpha_0}{n+p} \quad (32)$$

将α_{max}表达式(32)代入方程(25-1)，得

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{max}=k_2(\alpha_{max}+\alpha_0)^n(1-\alpha_{max})^p$$

$$=k_2\left(\frac{n-p\alpha_0}{n+p}+\alpha_0\right)^n\left(1-\frac{n-p\alpha_0}{n+p}\right)^p$$

$$=k_2\left(\frac{n-p\alpha_0+n\alpha_0+p\alpha_0}{n+p}\right)^n\left(\frac{n+p-n+p\alpha_0}{n+p}\right)^p$$

$$=k_2\left[\frac{n(1+\alpha_0)}{n+p}\right]^n\left[\frac{p(1+\alpha_0)}{n+p}\right]^p$$

$$=k_2n^np^p\left(\frac{1+\alpha_0}{n+p}\right)^{n+p} \quad (33)$$

当 $\alpha_0 \ll 1$ 时

$$\alpha_{max}=\frac{n}{n+p} \tag{34}$$

$$\left(\frac{d\alpha}{dt}\right)_{max}=k_2 n^n p^p\left(\frac{1}{n+p}\right)^{n+p} \tag{35}$$

对 $n=2$，$p=1$ 的派生式(25-2)，由式(32)和(33)知

$$\alpha_{max}=\frac{n-p\alpha_0}{n+p}=\frac{2-\alpha_0}{3} \tag{36}$$

$$\left(\frac{d\alpha}{dt}\right)_{max}=k_2 n^n p^p\left(\frac{1+\alpha_0}{n+p}\right)^{n+p}=\frac{4}{27}k_2\ (1+\alpha_0)^3 \tag{37}$$

当 $\alpha_0 \ll 1$ 时

$$\alpha_{max}\approx\frac{2}{3} \tag{38}$$

$$\left(\frac{d\alpha}{dt}\right)_{max}\approx\frac{4}{27}k_2 \tag{39}$$

对 $n=1$，$p=2$ 的派生式(25-3)，由式(32)和(33)知

$$\alpha_{max}=\frac{n-p\alpha_0}{n+p}=\frac{1-2\alpha_0}{3} \tag{40}$$

$$\left(\frac{d\alpha}{dt}\right)_{max}=k_2 n^n p^p\left(\frac{1+\alpha_0}{n+p}\right)^{n+p}=\frac{4}{27}k_2\ (1+\alpha_0)^3 \tag{41}$$

当 $\alpha_0 \ll 1$ 时

$$\alpha_{max}\approx\frac{1}{3} \tag{42}$$

$$\left(\frac{d\alpha}{dt}\right)_{max}\approx\frac{4}{27}k_2 \tag{43}$$

对 $n=p=1$ 的派生式(25-4)

$$\alpha_{max}=\frac{n-p\alpha_0}{n+p}=\frac{1-\alpha_0}{2} \tag{44}$$

$$\left(\frac{d\alpha}{dt}\right)_{max}=k_2 n^n p^p\left(\frac{1+\alpha_0}{n+p}\right)^{n+p}=\frac{1}{4}k_2\ (1+\alpha_0)^2 \tag{45}$$

当 $\alpha_0 \ll 1$ 时

$$\alpha_{max}\approx\frac{1}{2} \tag{46}$$

$$\left(\frac{d\alpha}{dt}\right)_{max}\approx\frac{1}{4}k_2 \tag{47}$$

对 $m=0$，$n=p=1$ 的派生式(25-7)，由式(27)知

$$k_2(1-\alpha_{max})=k_2(\alpha_{max}+\alpha_0) \tag{48}$$

$$1-\alpha_{max}=\alpha_{max}+\alpha_0$$

$$1-\alpha_0=2\alpha_{max}$$

$$\alpha_{max}=\frac{1-\alpha_0}{2} \tag{49}$$

$$\left(\frac{d\alpha}{dt}\right)_{max}=k_1+k_2(\alpha_{max}+\alpha_0)(1-\alpha_{max})$$

$$=k_1+k_2\left(\frac{1-\alpha_0}{2}+\alpha_0\right)\left(1-\frac{1-\alpha_0}{2}\right)$$

$$=k_1+k_2\left(\frac{1-\alpha_0+2\alpha_0}{2}\right)\left(\frac{1+\alpha_0}{2}\right)$$

$$=k_1+k_2\left(\frac{1+\alpha_0}{2}\right)^2 \tag{50}$$

当 $\alpha_0 \ll 1$ 时

$$\alpha_{max}\approx\frac{1}{2} \tag{51}$$

$$\left(\frac{d\alpha}{dt}\right)_{max}\approx k_1+\frac{1}{4}k_2 \tag{52}$$

对 $m=n=0$，$p=1$ 的派生式(25-8)，由式(27)知

$$k_2=0 \tag{53}$$

$$\left(\frac{d\alpha}{dt}\right)_{max}=k_1+k_2(1-\alpha_{max})=k_1 \tag{54}$$

对 $m=n=p=1$ 的派生式(25-13)，由式(27)知

$$k_2(1-\alpha_{max})=k_1+k_2(\alpha_{max}+\alpha_0) \tag{55}$$

$$k_2-k_2\alpha_{max}=k_1+k_2\alpha_{max}+k_2\alpha_0$$

$$2k_2\alpha_{max}=k_2-k_1-k_2\alpha_0$$

$$\alpha_{max}=\frac{k_2(1-\alpha_0)-k_1}{2k_2} \tag{56}$$

$$\left(\frac{d\alpha}{dt}\right)_{max}=k_1(1-\alpha_{max})+k_2(\alpha_{max}+\alpha_0)(1-\alpha_{max})$$

$$=(1-\alpha_{max})[k_1+k_2(\alpha_{max}+\alpha_0)] \tag{57}$$

令 $K_{cat}=k_2/k_1$，则

$$\left(\frac{d\alpha}{dt}\right)_{max}=k_1(1-\alpha_{max})[1+K_{cat}(\alpha_{max}+\alpha_0)]$$

$$=k_1\left[1-\frac{k_2(1-\alpha_0)-k_1}{2k_2}\right]\left\{1+K_{cat}\left[\frac{k_2(1-\alpha_0)-k_1}{2k_2}+\alpha_0\right]\right\}$$

$$=k_1\left(1-\frac{k_2-k_2\alpha_0-k_1}{2k_2}\right)\left[1+K_{cat}\left(\frac{k_2-k_2\alpha_0-k_1}{2k_2}+\alpha_0\right)\right]$$

$$=k_1\left[\frac{k_2(1+\alpha_0)+k_1}{2k_2}\right]\left\{1+K_{cat}\left[\frac{k_2(1+\alpha_0)-k_1}{2k_2}\right]\right\} \tag{58}$$

当 $\alpha_0 \ll 1$ 时

$$\alpha_{max}\approx\frac{k_2-k_1}{2k_2} \tag{59}$$

$$\left(\frac{d\alpha}{dt}\right)_{max}=k_1\left(\frac{k_2+k_1}{2k_2}\right)\left[1+K_{cat}\left(\frac{k_2-k_1}{2k_2}\right)\right] \tag{60}$$

2.4 自催化反应的 α 随 t 变化方程的导出途径

对方程(25-13)，由

$$\int_0^{\alpha}\frac{1}{k_1(1-\alpha)+k_2(\alpha+\alpha_0)(1-\alpha)}d\alpha=\int_0^t dt \tag{61}$$

知

$$\int_0^\alpha \frac{1}{k_1(1-\alpha)+k_2(\alpha+\alpha_0)(1-\alpha)}\mathrm{d}\alpha$$

$$=\int_0^\alpha\left\{\frac{1}{[k_1+k_2(1+\alpha_0)](1-\alpha)}+\frac{k_2}{[k_1+k_2(1+\alpha_0)][k_1+k_2(\alpha+\alpha_0)]}\right\}\mathrm{d}\alpha$$

$$=\frac{1}{k_1+k_2(1+\alpha_0)}\int_0^\alpha\left\{\frac{1}{1-\alpha}+\frac{k_2}{k_1+k_2(\alpha+\alpha_0)}\right\}\mathrm{d}\alpha$$

$$=\frac{1}{k_1+k_2(1+\alpha_0)}\{-\ln(1-\alpha)+\ln[k_1+k_2(\alpha+\alpha_0)]\}\Big|_0^\alpha$$

$$=\frac{1}{k_1+k_2(1+\alpha_0)}\{-\ln(1-\alpha)+\ln[k_1+k_2(\alpha+\alpha_0)]-\ln(k_1+k_2\alpha_0)\}$$

$$=\frac{1}{k_1+k_2(1+\alpha_0)}\ln\frac{k_1+k_2(\alpha+\alpha_0)}{(1-\alpha)(k_1+k_2\alpha_0)} \quad (62)$$

得

$$\frac{1}{k_1+k_2(1+\alpha_0)}\ln\frac{k_1+k_2(\alpha+\alpha_0)}{(1-\alpha)(k_1+k_2\alpha_0)}=t \quad (63)$$

$$\frac{k_1+k_2(\alpha+\alpha_0)}{(1-\alpha)(k_1+k_2\alpha_0)}=\mathrm{e}^{[k_1+k_2(1+\alpha_0)]t} \quad (64)$$

$$k_1+k_2(\alpha+\alpha_0)=(1-\alpha)(k_1+k_2\alpha_0)\mathrm{e}^{[k_1+k_2(1+\alpha_0)]t} \quad (65)$$

$$k_1+k_2\alpha_0+k_2\alpha=(k_1+k_2\alpha_0)\mathrm{e}^{[k_1+k_2(1+\alpha_0)]t}-(k_1+k_2\alpha_0)\alpha\mathrm{e}^{[k_1+k_2(1+\alpha_0)]t} \quad (66)$$

$$k_2\alpha+(k_1+k_2\alpha_0)\alpha\mathrm{e}^{[k_1+k_2(1+\alpha_0)]t}=(k_1+k_2\alpha_0)\mathrm{e}^{[k_1+k_2(1+\alpha_0)]t}-(k_1+k_2\alpha_0) \quad (67)$$

$$\alpha=(k_1+k_2\alpha_0)\frac{\mathrm{e}^{[k_1+k_2(1+\alpha_0)]t}-1}{k_2+(k_1+k_2\alpha_0)\mathrm{e}^{[k_1+k_2(1+\alpha_0)]t}} \quad (68)$$

$$\alpha=\frac{(k_1+k_2\alpha_0)[\mathrm{e}^{[k_1+k_2(1+\alpha_0)]t}-1]+(k_2-k_2)}{k_2+(k_1+k_2\alpha_0)\mathrm{e}^{[k_1+k_2(1+\alpha_0)]t}} \quad (69)$$

$$\alpha=1-\frac{k_1+k_2(1+\alpha_0)}{(k_1+k_2\alpha_0)\mathrm{e}^{[k_1+k_2(1+\alpha_0)]t}+k_2} \quad (70)$$

对 $\alpha_0=0.0001\approx0$ 的方程(25-13)，由

$$\int_0^\alpha\frac{1}{k_1(1-\alpha)+k_2\alpha(1-\alpha)}\mathrm{d}\alpha=\int_0^t\mathrm{d}t \quad (71)$$

知

$$\int_0^\alpha\frac{1}{k_1(1-\alpha)+k_2\alpha(1-\alpha)}\mathrm{d}\alpha$$

$$=\int_0^\alpha\left[\frac{1}{(k_1+k_2)(1-\alpha)}+\frac{k_2}{(k_1+k_2)(k_1+k_2\alpha)}\right]\mathrm{d}\alpha$$

$$=\frac{1}{k_1+k_2}\int_0^\alpha\left(\frac{1}{1-\alpha}+\frac{k_2}{k_1+k_2\alpha}\right)\mathrm{d}\alpha$$

$$=\frac{1}{k_1+k_2}[-\ln(1-\alpha)+\ln(k_1+k_2\alpha)]\Big|_0^\alpha$$

$$=\frac{1}{k_1+k_2}[-\ln(1-\alpha)+\ln(k_1+k_2\alpha)-\ln k_1]$$

$$=\frac{1}{k_1+k_2}\ln\frac{k_1+k_2\alpha}{k_1(1-\alpha)} \quad (72)$$

得

$$\frac{1}{k_1+k_2}\ln\frac{k_1+k_2\alpha}{k_1(1-\alpha)}=t \quad (73)$$

$$\frac{k_1+k_2\alpha}{k_1(1-\alpha)}=\mathrm{e}^{(k_1+k_2)t} \quad (74)$$

$$k_1+k_2\alpha=k_1(1-\alpha)\mathrm{e}^{(k_1+k_2)t} \quad (75)$$

$$k_2\alpha+k_1\alpha\mathrm{e}^{(k_1+k_2)t}=k_1\mathrm{e}^{(k_1+k_2)t}-k_1 \quad (76)$$

$$\alpha=\frac{k_1\mathrm{e}^{(k_1+k_2)t}-k_1}{k_1\mathrm{e}^{(k_1+k_2)t}+k_2} \quad (77)$$

$$\alpha=1-\frac{k_1+k_2}{k_1\mathrm{e}^{(k_1+k_2)t}+k_2} \quad (78)$$

对方程(25-8)，由

$$\int_0^\alpha\frac{1}{k_1+k_2(1-\alpha)}\mathrm{d}\alpha=\int_0^t\mathrm{d}t \quad (79)$$

知

$$\int_0^\alpha\frac{1}{k_1+k_2(1-\alpha)}\mathrm{d}\alpha$$

$$=\int_0^\alpha\frac{1}{k_1+k_2(1-\alpha)}\frac{-1}{k_2}\mathrm{d}[k_1+k_2(1-\alpha)]$$

$$=-\frac{1}{k_2}\ln[k_1+k_2(1-\alpha)]\Big|_0^\alpha$$

$$=-\frac{1}{k_2}\{\ln[k_1+k_2(1-\alpha)]-\ln(k_1+k_2)\}$$

$$=-\frac{1}{k_2}\ln\frac{k_1+k_2(1-\alpha)}{k_1+k_2} \quad (80)$$

$$\int_0^t\mathrm{d}t=t \quad (81)$$

得

$$-\frac{1}{k_2}\ln\frac{k_1+k_2(1-\alpha)}{k_1+k_2}=t \quad (82)$$

$$\ln\frac{k_1+k_2(1-\alpha)}{k_1+k_2}=-k_2t \quad (83)$$

$$\frac{k_1+k_2(1-\alpha)}{k_1+k_2}=\mathrm{e}^{-k_2t} \quad (84)$$

$$k_1+k_2(1-\alpha)=(k_1+k_2)\mathrm{e}^{-k_2t} \quad (85)$$

$$\alpha=\frac{k_1+k_2}{k_2}(1-\mathrm{e}^{-k_2t}) \quad (86)$$

对方程(25-11)，由

$$\int_0^\alpha\frac{1}{k_1(1-\alpha)[1+K_{\mathrm{cat}}(\alpha+\alpha_0)]}\mathrm{d}\alpha=\int_0^t\mathrm{d}t \quad (87)$$

知

$$\int_0^\alpha \frac{1}{k_1(1-\alpha)[1+K_{cat}(\alpha+\alpha_0)]}d\alpha$$
$$=\frac{1}{k_1}\int_0^\alpha\left[\frac{1}{(1+K_{cat}+K_{cat}\alpha_0)(1-\alpha)}+\frac{K_{cat}}{(1+K_{cat}+K_{cat}\alpha_0)(1+K_{cat}\alpha+K_{cat}\alpha_0)}\right]d\alpha$$
$$=\frac{1}{k_1(1+K_{cat}+K_{cat}\alpha_0)}\int_0^\alpha\left(\frac{1}{1-\alpha}+\frac{K_{cat}}{1+K_{cat}\alpha+K_{cat}\alpha_0}\right)d\alpha$$
$$=\frac{1}{k_1(1+K_{cat}+K_{cat}\alpha_0)}[-\ln(1-\alpha)+\ln(1+K_{cat}\alpha+K_{cat}\alpha_0)]\Big|_0^\alpha$$
$$=\frac{1}{k_1(1+K_{cat}+K_{cat}\alpha_0)}[-\ln(1-\alpha)+\ln(1+K_{cat}\alpha+K_{cat}\alpha_0)-\ln(1+K_{cat}\alpha_0)]$$
$$=\frac{1}{k_1(1+K_{cat}+K_{cat}\alpha_0)}\ln\frac{1+K_{cat}\alpha+K_{cat}\alpha_0}{(1-\alpha)(1+K_{cat}\alpha_0)} \tag{88}$$

得

$$\frac{1}{k_1(1+K_{cat}+K_{cat}\alpha_0)}\ln\frac{1+K_{cat}\alpha+K_{cat}\alpha_0}{(1-\alpha)(1+K_{cat}\alpha_0)}=t \tag{89}$$

$$\ln\frac{1+K_{cat}\alpha+K_{cat}\alpha_0}{(1-\alpha)(1+K_{cat}\alpha_0)}=k_1(1+K_{cat}+K_{cat}\alpha_0)t \tag{90}$$

$$1+K_{cat}\alpha+K_{cat}\alpha_0=(1-\alpha)(1+K_{cat}\alpha_0)e^{k_1(1+K_{cat}+K_{cat}\alpha_0)t} \tag{91}$$

$$1+K_{cat}\alpha+K_{cat}\alpha_0=(1+K_{cat}\alpha_0)e^{k_1(1+K_{cat}+K_{cat}\alpha_0)t}-(1+K_{cat}\alpha_0)e^{k_1(1+K_{cat}+K_{cat}\alpha_0)t}\alpha \tag{92}$$

$$K_{cat}\alpha+(1+K_{cat}\alpha_0)e^{k_1(1+K_{cat}+K_{cat}\alpha_0)t}\alpha=(1+K_{cat}\alpha_0)e^{k_1(1+K_{cat}+K_{cat}\alpha_0)t}-(1+K_{cat}\alpha_0) \tag{93}$$

$$\alpha=\frac{(1+K_{cat}\alpha_0)[e^{k_1(1+K_{cat}+K_{cat}\alpha_0)t}-1]}{K_{cat}+(1+K_{cat}\alpha_0)e^{k_1(1+K_{cat}+K_{cat}\alpha_0)t}}=1-\frac{K_{cat}+(1+K_{cat}\alpha_0)}{K_{cat}+(1+K_{cat}\alpha_0)e^{k_1(1+K_{cat}+K_{cat}\alpha_0)t}} \tag{94}$$

对 $\alpha_0=0.0001\approx0$ 的方程(25-11),由

$$\int_0^\alpha\frac{1}{k_1(1-\alpha)(1+K_{cat}\alpha)}d\alpha=\int_0^t dt \tag{95}$$

知

$$\int_0^\alpha\frac{1}{k_1(1-\alpha)(1+K_{cat}\alpha)}d\alpha$$
$$=\frac{1}{k_1}\int_0^\alpha\left[\frac{1}{(1+K_{cat})(1-\alpha)}+\frac{K_{cat}}{(1+K_{cat})(1+K_{cat}\alpha)}\right]d\alpha$$
$$=\frac{1}{k_1(1+K_{cat})}\int_0^\alpha\left(\frac{1}{1-\alpha}+\frac{K_{cat}}{1+K_{cat}\alpha}\right)d\alpha$$
$$=\frac{1}{k_1(1+K_{cat})}[-\ln(1-\alpha)+\ln(1+K_{cat}\alpha)]\Big|_0^\alpha$$
$$=\frac{1}{k_1(1+K_{cat})}[-\ln(1-\alpha)+\ln(1+K_{cat}\alpha)]$$
$$=\frac{1}{k_1(1+K_{cat})}\ln\frac{1+K_{cat}\alpha}{1-\alpha} \tag{96}$$

得

$$\frac{1}{k_1(1+K_{cat})}\ln\frac{1+K_{cat}\alpha}{1-\alpha}=t \tag{97}$$

$$\ln\frac{1+K_{cat}\alpha}{1-\alpha}=k_1(1+K_{cat})t \tag{98}$$

$$1+K_{cat}\alpha=(1-\alpha)e^{k_1(1+K_{cat})t} \tag{99}$$

$$1+K_{cat}\alpha=e^{k_1(1+K_{cat})t}-e^{k_1(1+K_{cat})t}\alpha \tag{100}$$

$$K_{cat}\alpha+e^{k_1(1+K_{cat})t}\alpha=e^{k_1(1+K_{cat})t}-1 \tag{101}$$

$$\alpha=\frac{e^{k_1(1+K_{cat})t}-1}{K_{cat}+e^{k_1(1+K_{cat})t}}=1-\frac{K_{cat}+1}{K_{cat}+e^{k_1(1+K_{cat})t}} \tag{102}$$

对方程(25-4),由

$$\int_0^\alpha\frac{1}{k_2(\alpha+\alpha_0)(1-\alpha)}d\alpha=\int_0^t dt \tag{103}$$

知

$$\int_0^\alpha\frac{1}{k_2(\alpha+\alpha_0)(1-\alpha)}d\alpha$$
$$=\frac{1}{k_2(\alpha_0+1)}\int_0^\alpha\left(\frac{1}{\alpha+\alpha_0}+\frac{1}{1-\alpha}\right)d\alpha$$
$$=\frac{1}{k_2(\alpha_0+1)}[\ln(\alpha+\alpha_0)-\ln(1-\alpha)]\Big|_0^\alpha$$
$$=\frac{1}{k_2(\alpha_0+1)}[\ln(\alpha+\alpha_0)-\ln(1-\alpha)-\ln\alpha_0]$$
$$=\frac{1}{k_2(\alpha_0+1)}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)} \tag{104}$$

得

$$\frac{1}{k_2(\alpha_0+1)}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=t \tag{105}$$

$$\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=k_2(\alpha_0+1)t \tag{106}$$

$$\alpha+\alpha_0=\alpha_0(1-\alpha)e^{k_2(\alpha_0+1)t} \tag{107}$$

$$[1+\alpha_0e^{k_2(\alpha_0+1)t}]\alpha=\alpha_0[e^{k_2(\alpha_0+1)t}-1] \tag{108}$$

$$\alpha=\frac{\alpha_0[e^{k_2(\alpha_0+1)t}-1]}{1+\alpha_0e^{k_2(\alpha_0+1)t}}=1-\frac{1+\alpha_0}{1+\alpha_0e^{k_2(\alpha_0+1)t}} \tag{109}$$

反应初期,$\alpha_0\ll1$

$$\alpha=\alpha_0[e^{k_2(\alpha_0+1)t}-1]\approx\alpha_0e^{k_2(\alpha_0+1)t} \tag{110}$$

显示反应随时间呈指数变化的规律。

对 $\alpha_0\ll1$,$\alpha_0=0.0001\approx0$ 的方程(25-4),由

$$\int_{0.0001}^\alpha\frac{1}{k_2\alpha(1-\alpha)}d\alpha=\int_0^t dt \tag{111}$$

知

$$\int_{0.0001}^{\alpha}\frac{1}{k_2\alpha(1-\alpha)}d\alpha$$
$$=\frac{1}{k_2}\int_{0.0001}^{\alpha}\left(\frac{1}{\alpha}+\frac{1}{1-\alpha}\right)d\alpha$$
$$=\frac{1}{k_2}[\ln\alpha-\ln(1-\alpha)]\Big|_{0.0001}^{\alpha}$$
$$=\frac{1}{k_2}[\ln\alpha-\ln(1-\alpha)-\ln0.0001+\ln(1-0.0001)]$$
$$=\frac{1}{k_2}\ln\frac{9999\alpha}{1-\alpha}\tag{112}$$

得

$$\frac{1}{k_2}\ln\frac{9999\alpha}{1-\alpha}=t\tag{113}$$
$$\ln\frac{9999\alpha}{1-\alpha}=k_2t\tag{114}$$
$$9999\alpha=(1-\alpha)e^{k_2t}\tag{115}$$
$$(9999+e^{k_2t})\alpha=e^{k_2t}\tag{116}$$
$$\alpha=\frac{e^{k_2t}}{9999+e^{k_2t}}=1-\frac{9999}{e^{k_2t}}\tag{117}$$

对方程(25-2)，由

$$\int_0^{\alpha}\frac{1}{k_2(\alpha+\alpha_0)^2(1-\alpha)}d\alpha=\int_0^t dt\tag{118}$$

知

$$\int_0^{\alpha}\frac{1}{k_2(\alpha+\alpha_0)^2(1-\alpha)}d\alpha$$
$$=\frac{1}{k_2}\int_0^{\alpha}\frac{(1+\alpha_0)^2}{(1+\alpha_0)^2(\alpha+\alpha_0)^2(1-\alpha)}d\alpha$$
$$=\frac{1}{k_2}\int_0^{\alpha}\left[\frac{1}{(1+\alpha_0)(\alpha+\alpha_0)^2}+\frac{1}{(1+\alpha_0)^2(1-\alpha)}+\frac{1}{(1+\alpha_0)^2(\alpha+\alpha_0)}\right]d\alpha$$
$$=\frac{1}{k_2}\left[-\frac{1}{(1+\alpha_0)(\alpha+\alpha_0)}-\frac{\ln(1-\alpha)}{(1+\alpha_0)^2}+\frac{\ln(\alpha+\alpha_0)}{(1+\alpha_0)^2}\right]\Bigg|_0^{\alpha}$$
$$=\frac{1}{k_2}\left[-\frac{1}{(1+\alpha_0)(\alpha+\alpha_0)}-\frac{\ln(1-\alpha)}{(1+\alpha_0)^2}+\frac{\ln(\alpha+\alpha_0)}{(1+\alpha_0)^2}+\frac{1}{(1+\alpha_0)\alpha_0}-\frac{\ln\alpha_0}{(1+\alpha_0)^2}\right]$$
$$=\frac{1}{k_2}\left[\frac{1}{(1+\alpha_0)^2}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}+\frac{1}{(1+\alpha_0)\alpha_0}-\frac{1}{(1+\alpha_0)(\alpha+\alpha_0)}\right]$$
$$=\frac{1}{k_2(1+\alpha_0)}\left[\frac{1}{1+\alpha_0}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}+\frac{1}{\alpha_0}-\frac{1}{\alpha+\alpha_0}\right]\tag{119}$$

得

$$\frac{1}{k_2(1+\alpha_0)}\left[\frac{1}{1+\alpha_0}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}+\frac{1}{\alpha_0}-\frac{1}{\alpha+\alpha_0}\right]=t\tag{120}$$

对 $\alpha_0\ll1$，$\alpha_0=0.0001\approx0$ 的方程(25-2)，由

$$\int_{0.0001}^{\alpha}\frac{1}{k_2\alpha^2(1-\alpha)}d\alpha=\int_0^t dt\tag{121}$$

知

$$\int_{0.0001}^{\alpha}\frac{1}{k_2\alpha^2(1-\alpha)}d\alpha$$
$$=\frac{1}{k_2}\int_{0.0001}^{\alpha}\left(\frac{1}{\alpha^2}+\frac{1}{\alpha}+\frac{1}{1-\alpha}\right)d\alpha$$
$$=\frac{1}{k_2}\left[-\frac{1}{\alpha}+\ln\alpha-\ln(1-\alpha)\right]\Bigg|_{0.0001}^{\alpha}$$
$$=\frac{1}{k_2}\left[-\frac{1}{\alpha}+\ln\alpha-\ln(1-\alpha)+10000-\ln0.0001+\ln(1-0.0001)\right]$$
$$=\frac{1}{k_2}\left(-\frac{1}{\alpha}+\ln\frac{9999\alpha}{1-\alpha}+10000\right)\tag{122}$$

得

$$\frac{1}{k_2}\left(-\frac{1}{\alpha}+\ln\frac{9999\alpha}{1-\alpha}+10000\right)=t\tag{123}$$
$$\frac{1}{k_2}\left(-\frac{1}{\alpha}+\ln\frac{9999\alpha}{1-\alpha}+10000\right)=t\tag{124}$$
$$-\frac{1}{\alpha}+\ln\frac{9999\alpha}{1-\alpha}+10000=k_2t\tag{125}$$

对方程(25-3)，由

$$\int_0^{\alpha}\frac{1}{k_2(\alpha+\alpha_0)(1-\alpha)^2}d\alpha=\int_0^t dt\tag{126}$$

知

$$\int_0^{\alpha}\frac{1}{k_2(\alpha+\alpha_0)(1-\alpha)^2}d\alpha$$
$$=\frac{1}{k_2}\int_0^{\alpha}\left[\frac{1}{(1+\alpha_0)^2(1-\alpha)}+\frac{1}{(1+\alpha_0)(1-\alpha)^2}+\frac{1}{(1+\alpha_0)^2(\alpha+\alpha_0)}\right]d\alpha$$
$$=\frac{1}{k_2(1+\alpha_0)^2}\int_0^{\alpha}\left[\frac{1}{1-\alpha}+\frac{1+\alpha_0}{(1-\alpha)^2}+\frac{1}{\alpha+\alpha_0}\right]d\alpha$$
$$=\frac{1}{k_2(1+\alpha_0)^2}\left[-\ln(1-\alpha)+\frac{1+\alpha_0}{1-\alpha}+\ln(\alpha+\alpha_0)\right]\Bigg|_0^{\alpha}$$
$$=\frac{1}{k_2(1+\alpha_0)^2}\left[-\ln(1-\alpha)+\frac{1+\alpha_0}{1-\alpha}+\ln(\alpha+\alpha_0)-(1+\alpha_0)-\ln\alpha_0\right]$$
$$=\frac{1}{k_2(1+\alpha_0)^2}\left[\frac{\alpha(1+\alpha_0)}{1-\alpha}+\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}\right]\tag{127}$$

得

$$\frac{1}{k_2(1+\alpha_0)^2}\left[\frac{\alpha(1+\alpha_0)}{1-\alpha}+\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}\right]=t\tag{128}$$
$$\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=k_2(1+\alpha_0)^2t-\frac{\alpha(1+\alpha_0)}{1-\alpha}\tag{129}$$

对 $\alpha_0\ll1$，$\alpha_0=0.0001\approx0$ 的方程(25-3)，由

$$\int_{0.0001}^{\alpha}\frac{1}{k_2\alpha(1-\alpha)^2}d\alpha=\int_0^t dt\tag{130}$$

知

$$\int_{0.0001}^{\alpha}\frac{1}{k_2\alpha(1-\alpha)^2}d\alpha$$

$$=\frac{1}{k_2}\int_{0.0001}^{\alpha}\frac{1}{\alpha(1-\alpha)^2}d\alpha$$

$$=\frac{1}{k_2}\int_{0.0001}^{\alpha}\left[\frac{1}{\alpha}+\frac{1}{1-\alpha}+\frac{1}{(1-\alpha)^2}\right]d\alpha$$

$$=\frac{1}{k_2}\left[\ln\alpha-\ln(1-\alpha)+\frac{1}{1-\alpha}\right]\Bigg|_{0.0001}^{\alpha}$$

$$=\frac{1}{k_2}\left[\ln\alpha-\ln(1-\alpha)+\frac{1}{1-\alpha}-\ln0.0001+\ln(1-0.0001)-\frac{1}{1-0.0001}\right]$$

$$=\frac{1}{k_2}\left(\frac{1}{1-\alpha}+\ln\frac{9999\alpha}{1-\alpha}-\frac{10000}{9999}\right) \tag{131}$$

得

$$\frac{1}{k_2}\left(\frac{1}{1-\alpha}+\ln\frac{9999\alpha}{1-\alpha}-\frac{10000}{9999}\right)=t \tag{132}$$

$$\frac{1}{1-\alpha}+\ln\frac{9999\alpha}{1-\alpha}-\frac{10000}{9999}=k_2t \tag{133}$$

$$\ln\frac{9999\alpha}{1-\alpha}=k_2t-\frac{1}{1-\alpha}+\frac{10000}{9999} \tag{134}$$

对方程(25-5),由

$$\int_0^{\alpha}\frac{1}{k_2(1-\alpha)^p}d\alpha=\int_0^t dt \tag{135}$$

知

$$\int_0^{\alpha}\frac{1}{k_2(1-\alpha)^p}d\alpha=\frac{1}{k_2}\int_0^{\alpha}\frac{1}{(1-\alpha)^p}d\alpha$$

$$=\frac{1}{k_2}\frac{(1-\alpha)^{1-p}-1}{p-1} \tag{136}$$

得

$$\frac{1}{k_2}\frac{(1-\alpha)^{1-p}-1}{p-1}=t \tag{137}$$

$$(1-\alpha)^{1-p}=(p-1)k_2t+1 \tag{138}$$

$$\alpha=1-[(p-1)k_2t+1]^{\frac{1}{1-p}} \tag{139}$$

对方程(25-6),由

$$\int_0^{\alpha}\frac{1}{k_2(1-\alpha)}d\alpha=\int_0^t dt \tag{140}$$

知

$$\int_0^{\alpha}\frac{1}{k_2(1-\alpha)}d\alpha=\frac{1}{k_2}\int_0^{\alpha}\frac{1}{1-\alpha}d\alpha=\frac{1}{k_2}[-\ln(1-\alpha)]\Big|_0^{\alpha}$$

$$=-\frac{1}{k_2}\ln(1-\alpha) \tag{141}$$

得

$$-\frac{1}{k_2}\ln(1-\alpha)=t \tag{142}$$

$$\ln(1-\alpha)=-k_2t \tag{143}$$

$$\alpha=1-e^{-k_2t} \tag{144}$$

2.5 自催化反应的 α 随 T 变化方程的导出途径

对第Ⅰ类动力学方程[11]

$$\int_0^{\alpha}\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^T\exp\left(-\frac{E}{RT}\right)dT \tag{145}$$

由 Frank-Kameneskii 近似式[10]

$$\int_0^T\exp\left(-\frac{E}{RT}\right)dT=\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right) \tag{146}$$

知

$$\int_0^{\alpha}\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right) \tag{147}$$

由第三类微分方程式(25-2),知

$$f(\alpha)=(\alpha+\alpha_0)^2(1-\alpha) \tag{148}$$

$$\int_0^{\alpha}\frac{d\alpha}{f(\alpha)}$$

$$=\int_0^{\alpha}\frac{1}{(\alpha+\alpha_0)^2(1-\alpha)}d\alpha$$

$$=\int_0^{\alpha}\frac{(1+\alpha_0)^2}{(1+\alpha_0)^2(\alpha+\alpha_0)^2(1-\alpha)}d\alpha$$

$$=\int_0^{\alpha}\left[\frac{1}{(1+\alpha_0)(\alpha+\alpha_0)^2}+\frac{1}{(1+\alpha_0)^2(1-\alpha)}+\frac{1}{(1+\alpha_0)^2(\alpha+\alpha_0)}\right]d\alpha$$

$$=\left[-\frac{1}{(1+\alpha_0)(\alpha+\alpha_0)}-\frac{\ln(1-\alpha)}{(1+\alpha_0)^2}+\frac{\ln(\alpha+\alpha_0)}{(1+\alpha_0)^2}\right]\Bigg|_0^{\alpha}$$

$$=-\frac{1}{(1+\alpha_0)(\alpha+\alpha_0)}-\frac{\ln(1-\alpha)}{(1+\alpha_0)^2}+\frac{\ln(\alpha+\alpha_0)}{(1+\alpha_0)^2}+$$

$$\frac{1}{(1+\alpha_0)\alpha_0}-\frac{\ln\alpha_0}{(1+\alpha_0)^2}$$

$$=\frac{1}{(1+\alpha_0)^2}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}+\frac{1}{(1+\alpha_0)\alpha_0}-\frac{1}{(1+\alpha_0)(\alpha+\alpha_0)}$$

$$=\frac{1}{1+\alpha_0}\left[\frac{1}{1+\alpha_0}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}+\frac{1}{\alpha_0}-\frac{1}{\alpha+\alpha_0}\right] \tag{149}$$

由式(147)和式(149)联立,得

$$\frac{1}{1+\alpha_0}\left[\frac{1}{1+\alpha_0}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}+\frac{1}{\alpha_0}-\frac{1}{\alpha+\alpha_0}\right]=\frac{A}{\beta}\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right) \tag{150}$$

由第二类微分方程式方程(25-3),知

$$f(\alpha)=(\alpha+\alpha_0)(1-\alpha)^2 \tag{151}$$

$$\int_0^{\alpha}\frac{d\alpha}{f(\alpha)}$$

$$=\int_0^{\alpha}\frac{1}{(\alpha+\alpha_0)(1-\alpha)^2}d\alpha$$

$$=\int_0^\alpha\left[\frac{1}{(1+\alpha_0)^2(1-\alpha)}+\frac{1}{(1+\alpha_0)(1-\alpha)^2}+\frac{1}{(1+\alpha_0)^2(\alpha+\alpha_0)}\right]\mathrm{d}\alpha$$

$$=\frac{1}{(1+\alpha_0)^2}\int_0^\alpha\left[\frac{1}{1-\alpha}+\frac{1+\alpha_0}{(1-\alpha)^2}+\frac{1}{\alpha+\alpha_0}\right]\mathrm{d}\alpha$$

$$=\frac{1}{(1+\alpha_0)^2}\left[-\ln(1-\alpha)+\frac{1+\alpha_0}{1-\alpha}+\ln(\alpha+\alpha_0)\right]\Big|_0^\alpha$$

$$=\frac{1}{(1+\alpha_0)^2}\left[-\ln(1-\alpha)+\frac{1+\alpha_0}{1-\alpha}+\ln(\alpha+\alpha_0)-(1+\alpha_0)-\ln\alpha_0\right]$$

$$=\frac{1}{(1+\alpha_0)^2}\left[\frac{\alpha(1+\alpha_0)}{1-\alpha}+\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}\right] \tag{152}$$

由式(147)和式(152)联立，得

$$\frac{1}{(1+\alpha_0)^2}\left[\frac{\alpha(1+\alpha_0)}{1-\alpha}+\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}\right]=\frac{A}{\beta}\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right) \tag{153}$$

由第一类微分方程式方程(25-4)，知

$$f(\alpha)=(\alpha+\alpha_0)(1-\alpha) \tag{154}$$

$$\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}$$

$$=\int_0^\alpha\frac{1}{(\alpha+\alpha_0)(1-\alpha)}\mathrm{d}\alpha$$

$$=\frac{1}{\alpha_0+1}\int_0^\alpha\left(\frac{1}{\alpha+\alpha_0}+\frac{1}{1-\alpha}\right)\mathrm{d}\alpha$$

$$=\frac{1}{\alpha_0+1}\left[\ln(\alpha+\alpha_0)-\ln(1-\alpha)\right]\Big|_0^\alpha$$

$$=\frac{1}{\alpha_0+1}\left[\ln(\alpha+\alpha_0)-\ln(1-\alpha)-\ln\alpha_0\right]$$

$$=\frac{1}{\alpha_0+1}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)} \tag{155}$$

由式(147)和式(155)联立，得

$$\frac{1}{\alpha_0+1}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=\frac{A}{\beta}\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right) \tag{156}$$

$$\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=\frac{A}{\beta}\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right)(\alpha_0+1) \tag{157}$$

$$\alpha+\alpha_0=\alpha_0(1-\alpha)\exp\left[\frac{A}{\beta}\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right)(\alpha_0+1)\right] \tag{158}$$

$$\left\{1+\alpha_0\exp\left[\frac{A}{\beta}\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right)(\alpha_0+1)\right]\right\}\alpha$$

$$=\alpha_0\left\{\exp\left[\frac{A}{\beta}\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right)(\alpha_0+1)\right]-1\right\} \tag{159}$$

$$\alpha=\frac{\alpha_0\left\{\exp\left[\frac{A}{\beta}\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right)(\alpha_0+1)\right]-1\right\}}{1+\alpha_0\exp\left[\frac{A}{\beta}\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right)(\alpha_0+1)\right]}$$

$$=1-\frac{1+\alpha_0}{1+\alpha_0\exp\left[\frac{A}{\beta}\frac{RT^2}{E}\exp\left(-\frac{E}{RT}\right)(\alpha_0+1)\right]} \tag{160}$$

对第Ⅱ类动力学方程[11]

$$\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{T_0}^T\left[1+\frac{E}{RT}\left(1-\frac{T_0}{T}\right)\right]\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{161}$$

由

$$\int_{T_0}^T\left[1+\frac{E}{RT}\left(1-\frac{T_0}{T}\right)\right]\exp\left(-\frac{E}{RT}\right)\mathrm{d}T=(T-T_0)\exp\left(-\frac{E}{RT}\right) \tag{162}$$

知

$$\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}(T-T_0)\exp\left(-\frac{E}{RT}\right) \tag{163}$$

由式(149)和(163)式联立，得

$$\frac{1}{1+\alpha_0}\left[\frac{1}{1+\alpha_0}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}+\frac{1}{\alpha_0}-\frac{1}{\alpha+\alpha_0}\right]=\frac{A}{\beta}(T-T_0)\exp\left(-\frac{E}{RT}\right) \tag{164}$$

由式(152)和式(163)联立，得

$$\frac{1}{(1+\alpha_0)^2}\left[\frac{\alpha(1+\alpha_0)}{1-\alpha}+\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}\right]=\frac{A}{\beta}(T-T_0)\exp\left(-\frac{E}{RT}\right) \tag{165}$$

由式(155)和式(163)联立，得

$$\frac{1}{\alpha_0+1}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=\frac{A}{\beta}(T-T_0)\exp\left(-\frac{E}{RT}\right) \tag{166}$$

$$\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=\frac{A}{\beta}(T-T_0)\exp\left(-\frac{E}{RT}\right)(\alpha_0+1) \tag{167}$$

$$\alpha+\alpha_0=\alpha_0(1-\alpha)\exp\left[\frac{A}{\beta}(T-T_0)\exp\left(-\frac{E}{RT}\right)(\alpha_0+1)\right] \tag{168}$$

$$\left\{1+\alpha_0\exp\left[\frac{A}{\beta}(T-T_0)\exp\left(-\frac{E}{RT}\right)(\alpha_0+1)\right]\right\}\alpha$$

$$=\alpha_0\left\{\exp\left[\frac{A}{\beta}(T-T_0)\exp\left(-\frac{E}{RT}\right)(\alpha_0+1)\right]-1\right\} \tag{169}$$

$$\alpha=\frac{\alpha_0\left\{\exp\left[\frac{A}{\beta}(T-T_0)\exp\left(-\frac{E}{RT}\right)(\alpha_0+1)\right]-1\right\}}{1+\alpha_0\exp\left[\frac{A}{\beta}(T-T_0)\exp\left(-\frac{E}{RT}\right)(\alpha_0+1)\right]}$$

$$=1-\frac{1+\alpha_0}{1+\alpha_0\exp\left[\frac{A}{\beta}(T-T_0)\exp\left(-\frac{E}{RT}\right)(\alpha_0+1)\right]} \tag{170}$$

由 Harcourt-Esson 方程的积分式(171)[12]

$$G(\alpha)=\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^T T^a\mathrm{d}T$$

$$=\frac{A_0}{\beta}\frac{1}{a+1}T^{a+1}\Big|_0^T=\frac{A}{\beta(a+1)}T^{a+1} \tag{171}$$

与式(149)联立，得

$$\frac{1}{1+\alpha_0}\left[\frac{1}{1+\alpha_0}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}+\frac{1}{\alpha_0}-\frac{1}{\alpha+\alpha_0}\right]=\frac{A}{\beta(a+1)}T^{a+1} \tag{172}$$

由式(152)和式(171)联立，得

$$\frac{1}{(1+\alpha_0)^2}\left[\frac{\alpha(1+\alpha_0)}{1-\alpha}+\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}\right]=\frac{A}{\beta(a+1)}T^{a+1} \tag{173}$$

由式(155)和式(171)联立,得

$$\frac{1}{\alpha_0+1}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=\frac{A}{\beta(a+1)}T^{a+1} \tag{174}$$

$$\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=\frac{A}{\beta(a+1)}T^{a+1}(\alpha_0+1) \tag{175}$$

$$\alpha+\alpha_0=\alpha_0(1-\alpha)\exp\left[\frac{A}{\beta(a+1)}T^{a+1}(\alpha_0+1)\right] \tag{176}$$

$$\left\{1+\alpha_0\exp\left[\frac{A}{\beta(a+1)}T^{a+1}(\alpha_0+1)\right]\right\}\alpha$$
$$=\alpha_0\left\{\exp\left[\frac{A}{\beta(a+1)}T^{a+1}(\alpha_0+1)\right]-1\right\} \tag{177}$$

$$\alpha=\frac{\alpha_0\left\{\exp\left[\frac{A}{\beta(a+1)}T^{a+1}(\alpha_0+1)\right]-1\right\}}{1+\alpha_0\exp\left[\frac{A}{\beta(a+1)}T^{a+1}(\alpha_0+1)\right]}$$
$$=1-\frac{1+\alpha_0}{1+\alpha_0\exp\left[\frac{A}{\beta(a+1)}T^{a+1}(\alpha_0+1)\right]} \tag{178}$$

由 Berthelot 方程的积分式(179)[12]

$$\int_0^\alpha\frac{d\alpha}{f(\alpha)}\approx\frac{A}{b\beta}\exp(bT) \tag{179}$$

与式(149)式联立,得

$$\frac{1}{1+\alpha_0}\left[\frac{1}{1+\alpha_0}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}+\frac{1}{\alpha_0}-\frac{1}{\alpha+\alpha_0}\right]=\frac{A}{b\beta}\exp(bT) \tag{180}$$

由式(152)和式(179)联立,得

$$\frac{1}{(1+\alpha_0)^2}\left[\frac{\alpha(1+\alpha_0)}{1-\alpha}+\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}\right]=\frac{A}{b\beta}\exp(bT) \tag{181}$$

由式(155)和式(179)联立,得

$$\frac{1}{\alpha_0+1}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=\frac{A}{b\beta}\exp(bT) \tag{182}$$

$$\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=\frac{A}{b\beta}\exp(bT)(\alpha_0+1) \tag{183}$$

$$\alpha+\alpha_0=\alpha_0(1-\alpha)\exp\left[\frac{A}{b\beta}\exp(bT)(\alpha_0+1)\right] \tag{184}$$

$$\left\{1+\alpha_0\exp\left[\frac{A}{b\beta}\exp(bT)(\alpha_0+1)\right]\right\}\alpha$$
$$=\alpha_0\left\{\exp\left[\frac{A}{b\beta}\exp(bT)(\alpha_0+1)\right]-1\right\} \tag{185}$$

$$\alpha=\frac{\alpha_0\left\{\exp\left[\frac{A}{b\beta}\exp(bT)(\alpha_0+1)\right]-1\right\}}{1+\alpha_0\exp\left[\frac{A}{b\beta}\exp(bT)(\alpha_0+1)\right]}$$
$$=1-\frac{1+\alpha_0}{1+\alpha_0\exp\left[\frac{A}{b\beta}\exp(bT)(\alpha_0+1)\right]} \tag{186}$$

由积分式(187)[11]

$$\int_0^\alpha\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^T\exp(bT)\,[1+(T-T_0)\,b]\,dT$$
$$=\frac{A}{\beta}(T-T_0)\exp(bT) \tag{187}$$

与式(149)联立,得

$$\frac{1}{1+\alpha_0}\left[\frac{1}{1+\alpha_0}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}+\frac{1}{\alpha_0}-\frac{1}{\alpha+\alpha_0}\right]=\frac{A}{\beta}(T-T_0)\exp(bT) \tag{188}$$

由式(152)和式(187)联立,得

$$\frac{1}{(1+\alpha_0)^2}\left[\frac{\alpha(1+\alpha_0)}{1-\alpha}+\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}\right]=\frac{A}{\beta}(T-T_0)\exp(bT) \tag{189}$$

由式(155)和式(187)联立,得

$$\frac{1}{\alpha_0+1}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=\frac{A}{\beta}(T-T_0)\exp(bT) \tag{190}$$

$$\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=\frac{A}{\beta}(T-T_0)\exp(bT)(\alpha_0+1) \tag{191}$$

$$\alpha+\alpha_0=\alpha_0(1-\alpha)\exp\left[\frac{A}{\beta}(T-T_0)\exp(bT)(\alpha_0+1)\right] \tag{192}$$

$$\left\{1+\alpha_0\exp\left[\frac{A}{\beta}(T-T_0)\exp(bT)(\alpha_0+1)\right]\right\}\alpha$$
$$=\alpha_0\left\{\exp\left[\frac{A}{\beta}(T-T_0)\exp(bT)(\alpha_0+1)\right]-1\right\} \tag{193}$$

$$\alpha=\frac{\alpha_0\left\{\exp\left[\frac{A}{\beta}(T-T_0)\exp(bT)(\alpha_0+1)\right]-1\right\}}{1+\alpha_0\exp\left[\frac{A}{\beta}(T-T_0)\exp(bT)(\alpha_0+1)\right]}$$
$$=1-\frac{1+\alpha_0}{1+\alpha_0\exp\left[\frac{A}{\beta}(T-T_0)\exp(bT)(\alpha_0+1)\right]} \tag{194}$$

由积分式(195)

$$\int_0^\alpha\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\int_0^T T^a\left[1+(T-T_0)\frac{a}{T}\right]dT=\frac{A}{\beta}T^a(T-T_0) \tag{195}$$

与式(149)联立,得

$$\frac{1}{1+\alpha_0}\left[\frac{1}{1+\alpha_0}\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}+\frac{1}{\alpha_0}-\frac{1}{\alpha+\alpha_0}\right]=\frac{A}{\beta}T^a(T-T_0) \tag{196}$$

由式(152)和式(195)联立,得

$$\frac{1}{(1+\alpha_0)^2}\left[\frac{\alpha(1+\alpha_0)}{1-\alpha}+\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}\right]=\frac{A}{\beta}T^a(T-T_0) \tag{197}$$

由式(155)和式(195)联立,得

$$\ln\frac{\alpha+\alpha_0}{\alpha_0(1-\alpha)}=\frac{A}{\beta}T^a(T-T_0)(\alpha_0+1) \tag{198}$$

$$\alpha+\alpha_0=\alpha_0(1-\alpha)\exp\left[\frac{A}{\beta}T^a(T-T_0)(\alpha_0+1)\right] \tag{199}$$

$$\left\{1+\alpha_0\exp\left[\frac{A}{\beta}T^a(T-T_0)(\alpha_0+1)\right]\right\}\alpha$$

$$=\alpha_0\left\{\exp\left[\frac{A}{\beta}T^a(T-T_0)(\alpha_0+1)\right]-1\right\} \quad (200)$$

$$\alpha=\frac{\alpha_0\left\{\exp\left[\frac{A}{\beta}T^a(T-T_0)(\alpha_0+1)\right]-1\right\}}{1+\alpha_0\exp\left[\frac{A}{\beta}T^a(T-T_0)(\alpha_0+1)\right]}$$

$$=1-\frac{1+\alpha_0}{1+\alpha_0\exp\left[\frac{A}{\beta}T^a(T-T_0)(\alpha_0+1)\right]} \quad (201)$$

3 计算实例

由不同升温速率的 DSC 获得 HNIW 的试验数据见表 1。根据表 1 中 $\{(\alpha_i, T_i)\}_{i=1}^{N}$，得 $t_i=(T_i-T_0)/\beta$，$i=1, 2, \cdots, N$ 及 $(\mathrm{d}\alpha/\mathrm{d}t)_i\approx(\alpha_i-\alpha_{i-1})/(t_i-t_{i-1})$，$i=1, 2, \cdots, N$。代数据：$(\mathrm{d}\alpha/\mathrm{d}t)_i$、$\alpha_i$，$i=1, 2, \cdots L_i$，入自催化的 n 级反应（C_nB）速率方程

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n(1+K_{\mathrm{cat}}\alpha) \quad (202)$$

的非线性优化模型

$$\min_{A,E,n,K_{\mathrm{cat}}}\sum_{i=2}^{N}\left[\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_i-A\exp\left(-\frac{E}{RT_i}\right)(1-\alpha_i)^n(1+K_{\mathrm{cat}}\alpha_i)\right]^2 \quad (203)$$

s.t. $10^{12.5}\ \mathrm{s^{-1}}\leqslant A\leqslant 10^{13.5}\ \mathrm{s^{-1}}$，$150000\ \mathrm{J\cdot mol^{-1}}\leqslant E\leqslant 165000\ \mathrm{J\cdot mol^{-1}}$，$0.9\leqslant n\leqslant 1.1$，$10\leqslant K_{\mathrm{cat}}\leqslant 15$

由线性最小二乘法和信赖域方法[4-6,8]得模型中的 4 参数（A、E、n、K_{cat}）。

$\beta=2\ \mathrm{K\cdot min^{-1}}$时，自催化分解反应的动力学参数为：$E=160.46\ \mathrm{kJ\cdot mol^{-1}}$，$A=10^{13.52}$，$K_{\mathrm{cat}}=15.0$，$n=0.90$；计算值与实验值的相对误差 $\Delta\delta=\sqrt{\sum_{i=1}^{n}[(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{cald},i}-(\mathrm{d}\alpha/\mathrm{d}t)_{\mathrm{exp},i}]^2/\sum_{i=1}^{n}(\mathrm{d}\alpha/\mathrm{d}t)^2_{\mathrm{exp},i}}=0.08814$；$\beta=5\ \mathrm{K\cdot min^{-1}}$时，自催化分解反应动力学参数为：$E=161.00\ \mathrm{kJ\cdot mol^{-1}}$，$A=10^{13.50}$，$K_{\mathrm{cat}}=15.0$，$n=0.90$，$\Delta\delta=0.07289$；$\beta=10\ \mathrm{K\cdot min^{-1}}$时，自催化分解反应动力学参数为：$E=158.77\ \mathrm{kJ\cdot mol^{-1}}$，$A=10^{13.30}$，$K_{\mathrm{cat}}=15.0$，$n=0.90$，$\Delta\delta=0.07466$；$\beta=20\ \mathrm{K\cdot min^{-1}}$时，自催化分解反应动力学参数为：$E=160.69\ \mathrm{kJ\cdot mol^{-1}}$，$A=10^{13.50}$，$K_{\mathrm{cat}}=15.0$，$n=0.90$，$\Delta\delta=0.09100$。

从计算结果可知，$\Delta\delta$ 很小，表明非等温条件下，用 C_nB 速率方程

$$\mathrm{d}\alpha/\mathrm{d}t=10^{13.46}\exp(-160230/RT)(1-\alpha)^{0.90}(1+15\alpha)$$

描述 HNIW 的热分解过程是可取的。若视 $n=0.90\approx1$，

表 1 由 DSC 测得 HNIW 的数据[13]

Table 1 Data of HNIW determined by DSC[13]

data point	α_i	T_i/K			
		2 K·min^{-1}	5 K·min^{-1}	10 K·min^{-1}	20 K·min^{-1}
1	0	473.20	483.05	491.58	498.56
2	0.025	488.29	499.59	508.08	516.02
3	0.050	490.63	502.22	510.46	518.78
4	0.075	491.96	503.83	512.03	520.49
5	0.100	492.97	504.98	513.19	521.77
6	0.125	493.75	505.88	514.13	522.82
7	0.150	494.45	506.67	514.93	523.69
8	0.175	495.06	507.35	515.63	524.47
9	0.200	495.61	507.96	516.26	525.16
10	0.225	496.13	508.52	516.84	525.79
11	0.250	496.66	509.04	517.37	526.38
12	0.275	497.09	509.54	517.86	526.93
13	0.300	497.49	510.02	518.34	527.45
14	0.325	497.84	510.48	518.79	527.94
15	0.350	498.19	510.91	519.23	528.42
16	0.375	498.51	511.32	519.65	528.87
17	0.400	498.85	511.71	520.06	529.29
18	0.425	499.17	512.09	520.45	529.70
19	0.450	499.50	512.46	520.84	530.10
20	0.475	499.82	512.83	521.22	530.48
21	0.500	500.14	513.19	521.59	530.85
22	0.525	500.43	513.53	521.95	531.20
23	0.550	500.71	513.88	522.31	531.56
24	0.575	501.00	514.20	522.65	531.89
25	0.600	501.29	514.53	522.99	532.23
26	0.625	501.59	514.86	523.31	532.55
27	0.650	501.88	515.17	523.64	532.87
28	0.675	502.14	515.48	523.94	533.17
29	0.700	502.42	515.78	524.25	533.47

则可用方程（94）和（102）描述 α 随 t 的变化。

类似地，由描述 NC（12.82% N）自催化分解反应的速率方程[3]

$$\mathrm{d}\alpha/\mathrm{d}t=10^{16.4}\exp(-178000/RT)(1-\alpha)+10^{17.0}\exp(-174000/RT)\alpha(1-\alpha)$$

可得：$T_{\max}=479.55\ \mathrm{K}$，$\alpha_{\max}=0.4539$，$K_{\mathrm{cat}}=10.86$。

由描述 NC（12.97% N）自催化分解反应的速率方程[5]

$$\mathrm{d}\alpha/\mathrm{d}t=10^{16.00}\exp(-174520/RT)(1-\alpha)+10^{16.00}\exp(-163510/RT)\alpha(1-\alpha)$$

可得：$T_{\max}=481.19\ \mathrm{K}$，$\alpha_{\max}=0.4680$，$K_{\mathrm{cat}}=15.68$。

由描述 NC（13.54% N）自催化分解反应的速率方程[4]

$$\mathrm{d}\alpha/\mathrm{d}t=10^{15.82}\exp(-170020/RT)(1-\alpha)^{1.11}+10^{15.82}\exp(-157140/RT)\alpha^{1.51}(1-\alpha)^{2.51}$$

可得：$T_{\max}=482.25\ \mathrm{K}$，$\alpha_{\max}=0.3411$，$K_{\mathrm{cat}}=24.84$。

由描述 NC(13.61% N)自催化分解反应的速率方程[3]

$$d\alpha/dt=10^{16.5}\exp(-184700/RT)(1-\alpha)+10^{16.9}\exp(-174700/RT)\alpha(1-\alpha)$$

可得：$T_{max}=478.75$ K，$\alpha_{max}=0.4838$，$K_{cat}=30.98$。

由描述 NC(13.86% N)自催化分解反应的速率方程[14]

$$d\alpha/dt=10^{16.30}\exp(-181860/RT)(1-\alpha)+10^{16.70}\exp(-173050/RT)\alpha(1-\alpha)$$

可得：$T_{max}=477.00$ K，$\alpha_{max}=0.4783$，$K_{cat}=23.16$。

由描述 NC(13.88% N)自催化分解反应的速率方程[3]

$$d\alpha/dt=10^{16.40}\exp(-181860/RT)(1-\alpha)+10^{16.70}\exp(-171730/RT)\alpha(1-\alpha)$$

可得：$T_{max}=476.95$ K，$\alpha_{max}=0.4805$，$K_{cat}=25.67$。

由描述 NC(14.14% N)自催化分解反应的速率方程[6]

$$d\alpha/dt=10^{15.76}\exp(-170800/RT)(1-\alpha)^{0.95}+10^{15.76}\exp(-159100/RT)\alpha^{1.81}(1-\alpha)^{1.16}$$

可得：$T_{max}=489.61$ K，$\alpha_{max}=0.5756$，$K_{cat}=17.71$。

上述计算结果表明，非等温条件下，NC(13.54%、14.14% N)的热分解过程可用经验级数自催化反应速率方程(25)描述。NC(12.82%、12.97%、13.61%、13.86%、13.88% N)的热分解过程可用一级($m=1$、$n=1$、$p=1$)自催化分解反应速率方程(25-13)描述。对一级自催化分解反应，可用方程(56)和(59)描述 α_{max} 和 K_{cat} 的关系，可用方程(57)和(58)描述 $(d\alpha/dt)_{max}$ 和 α_{max}、K_{cat}、E_1/RT_{max} 的关系，可用方程(70)和(77)描述 α 随的 t 变化。E_2 大于 E_1，表明：催化分解反应速率大于催化剂生成反应速率，催化产物存在下的催化分解反应易于发生。

4 结 论

(1) 导出了经验级数自催化反应速率方程和 13 个派生式。提出了描述自催化分解反应速率曲线特性的方程，以及反应进度随时间和温度变化的方程。

(2) 描述 HNIW 分解过程的速率方程为自催化的 n 级反应(C_nB)速率方程：

$$\frac{d\alpha}{dt}=1013.46\exp\left(-\frac{160230}{RT}\right)(1-\alpha)^{0.90}(1+15\alpha)$$

(3) 提出了正文中描述 NC(12.82%、12.97%、13.54%、13.61%、13.86%、13.88%、14.14% N)自催化分解过程的反应动力学参数—催化系数 K_{cat}、速率曲线特性参数和 α 随 t 变化的方程。

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Derived Ways of the Rate Equations of Autocatalytic Reaction and Their Application in Thermal Behavior Study of Energetic Materials

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Abstract: The derived ways of empiric-order autocatalytic reaction rate equation and its thirteen derived formulae were presented The equation of rate curve characteristics [α_{max} and $(d\alpha/dt)_{max}$] and the equation of change in reaction extent (α) with time (t) and temperature (T) describing the autocatalytic reaction were derived. The computer program of calculating the kinetic parameters (E, A or E_1, A_1, E_2, A_2) and empiric-order (m, n, p) of autocatalytic reaction and the values of α_{max} and $(d\alpha/dt)_{max}$ was written. The rate equation describing the autocatalytic decomposition reaction of hexanitrohexaazaisowurtzitane (HNIW) and the kinetic parameters, catalytic coefficient K_{cat}, rate curve characteristic parameters and the equation of change in α with t describing the autocatalytic decomposition reaction of nitrocellulose (NC) (12.82%, 12.97%, 13.54%, 13.61%, 13.88%, 14.14% N) were presented.

Key words: autocatalytic reaction; kinetic parameters; curve characteristic parameters; reaction extent; hexanitrohexaazaisowurtzitane(HNIW); nitrocellulose(NC)

CLC number: TJ55; O643 **Document code**: A **DOI**: 10.11943/j.issn.1006-9941.2015.09.001