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非线性等转化率的微、积分法及其在含能材料物理化学研究中的应用 V. 基于 Kooij 公式的理论和数值方法

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摘要: 推导了从等温和非等温数据计算表观活化能(E_α)的基于 Kooij 公式的 8 个典型非线性等转化率微、积分方程。提出了通过这 8 个方程计算含能材料分解反应 E_α 值的数值方法。

关键词: 物理化学; 含能材料; 非线性等转化率微分法; 非线性等转化率积分法; 分解反应; 表观活化能

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1 引 言

在文献[1]中,我们提出了基于 Arrhenius 公式[活化能(E)和指前因子(A)与温度(T)无关] 求活化能(E_α)的非线性等转化率的微、积分法,并用该法所得的 E_α 值成功地核实了其它方法所得的表观活化能(E_α)值[2-7]。本工作作为文献[1]的拓展,报道基于 Kooij 公式(E 和 A 与 T 有关)的非线性等转化率法求 E_α 的数学表达式的导出途径和数值方法。

2 理论和方法

2.1 非线性等转化率的微分法

由速率常数用 Kooij 公式描述的非等温动力学方程的微分式

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} f(\alpha) T^b \exp(-E/RT) \tag{1}$$

及等 α,得

$$\frac{\beta_1}{A}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_1 T^b \exp(E_\alpha/RT_{\alpha,1}) = \frac{\beta_2}{A}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_2 T^b \exp(E_\alpha/RT_{\alpha,2}) = \cdots = \frac{\beta_n}{A}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_n T^b \exp(E_\alpha/RT_{\alpha,n}) \tag{2}$$

于是有

$$\frac{\beta_1\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_1 T^b_{\alpha,1}\exp(E_\alpha/RT_{\alpha,1})}{\beta_2\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_2 T^b_{\alpha,2}\exp(E_\alpha/RT_{\alpha,2})} + \frac{\beta_1\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_1 T^b_{\alpha,1}\exp(E_\alpha/RT_{\alpha,1})}{\beta_3\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_3 T^b_{\alpha,3}\exp(E_\alpha/RT_{\alpha,3})} + \cdots + \frac{\beta_1\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_1 T^b_{\alpha,1}\exp(E_\alpha/RT_{\alpha,1})}{\beta_n\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_n T^b_{\alpha,n}\exp(E_\alpha/RT_{\alpha,n})} +$$

$$\frac{\beta_2\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_2 T^b_{\alpha,2}\exp(E_\alpha/RT_{\alpha,2})}{\beta_1\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_1 T^b_{\alpha,1}\exp(E_\alpha/RT_{\alpha,1})} + \frac{\beta_2\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_2 T^b_{\alpha,2}\exp(E_\alpha/RT_{\alpha,2})}{\beta_3\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_3 T^b_{\alpha,3}\exp(E_\alpha/RT_{\alpha,3})} + \cdots + \frac{\beta_2\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_2 T^b_{\alpha,2}\exp(E_\alpha/RT_{\alpha,2})}{\beta_n\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_n T^b_{\alpha,n}\exp(E_\alpha/RT_{\alpha,n})} + \cdots +$$

$$\frac{\beta_m\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_m T^b_{\alpha,m}\exp(E_\alpha/RT_{\alpha,m})}{\beta_1\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_1 T^b_{\alpha,1}\exp(E_\alpha/RT_{\alpha,1})} + \frac{\beta_m\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_m T^b_{\alpha,m}\exp(E_\alpha/RT_{\alpha,m})}{\beta_2\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_2 T^b_{\alpha,2}\exp(E_\alpha/RT_{\alpha,2})} + \cdots + \frac{\beta_m\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_m T^b_{\alpha,m}\exp(E_\alpha/RT_{\alpha,m})}{\beta_{m-1}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{m+1} T^b_{\alpha,m-1}\exp(E_\alpha/RT_{\alpha,m-1})} +$$

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$$\frac{\beta_m(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_m T^b_{\alpha,m}\exp(E_\alpha/RT_{\alpha,m})}{\beta_{m+1}(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_1 T^b_{\alpha,m+1}\exp(E_\alpha/RT_{\alpha,m+1})} + \cdots + \frac{\beta_m(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_m T^b_{\alpha,m}\exp(E_\alpha/RT_{\alpha,m})}{\beta_n(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_n T^b_{\alpha,n}\exp(E_\alpha/RT_{\alpha,n})} + \cdots +$$

$$\frac{\beta_n(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_n T^b_{\alpha,n}\exp(E_\alpha/RT_{\alpha,n})}{\beta_1(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_1 T^b_{\alpha,1}\exp(E_\alpha/RT_{\alpha,1})} + \frac{\beta_n(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_n T^b_{\alpha,n}\exp(E_\alpha/RT_{\alpha,n})}{\beta_2(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_2 T^b_{\alpha,2}\exp(E_\alpha/RT_{\alpha,2})} + \cdots + \frac{\beta_n(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_n T^b_{\alpha,n}\exp(E_\alpha/RT_{\alpha,n})}{\beta_{n-1}(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_{n-1} T^b_{\alpha,n-1}\exp(E_\alpha/RT_{\alpha,n-1})}$$

$$= \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{\beta_i(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_i T^b_{\alpha,i}\exp(E_\alpha/RT_{\alpha,i})}{\beta_j(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_j T^b_{\alpha,j}\exp(E_\alpha/RT_{\alpha,j})} = n(n-1) \tag{3}$$

式中，α，T，A，$f(\alpha)$，E，R，和 β 有通常的含义[8]；b 为常数。

对方程(3)取评价函数的最小值，得

$$\Omega_{\mathrm{KDb}}(E_\alpha) = \min\left|\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{\beta_i(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_i T^b_{\alpha,i}\cdot\exp(E_\alpha/RT_{\alpha,i})}{\beta_j(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_j T^b_{\alpha,j}\cdot\exp(E_\alpha/RT_{\alpha,j})} - n(n-1)\right| \tag{4}$$

代一系列非等温 TG-DTG 或 DSC 曲线上测得的同一 α 处的原始数据：β_i，$(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_i$，$T_{\alpha,i}$ $(i=1,2,\cdots,n)$ 和常数 b，入方程(4)，得满足该方程最小值的 E_α 值。

该 E_α 值视作最可几的活化能值，用于核实其它方法所得的动力学参数。

我们称这种求 E_α 的方法为 Kooij 型非线性等转化率微分法[differential isoconversional non-linear (NL-DIF) method]，$b=0$ 的 NL-DIF 法为 Arrhenius 型 NL-DIF 法(简称 NL-DIF 法)。

如果对非等温动力学方程的微分式

$$f(\alpha) = \frac{\frac{\mathrm{d}H}{\mathrm{d}t}\exp(E/RT)}{AT^bH_0\left[1+(\frac{b}{T}+\frac{E}{RT^2})(T-T_0)\right]} = \frac{\beta(\frac{\mathrm{d}\alpha}{\mathrm{d}T})\exp(E/RT)}{AT^b\left[1+(\frac{b}{T}+\frac{E}{RT^2})(T-T_0)\right]} \tag{5}$$

作类似处理，则有

$$\Omega_{\mathrm{2KDb1}}(E_\alpha) = \min\left|\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{(\frac{\mathrm{d}H}{\mathrm{d}t})_i e^{E_\alpha/RT_{\alpha,i}}\Big/\left\{\left[1+(\frac{b}{T_{\alpha,i}}+\frac{E_\alpha}{RT^2_{\alpha,i}})(T_{\alpha,i}-T_{0,i})\right]H_{0,i}\right\}}{(\frac{\mathrm{d}H}{\mathrm{d}t})_j e^{E_\alpha/RT_{\alpha,j}}\Big/\left\{\left[1+(\frac{b}{T_{\alpha,j}}+\frac{E_\alpha}{RT^2_{\alpha,j}})(T_{\alpha,j}-T_{0,j})\right]H_{0,j}\right\}} - n(n-1)\right| \tag{6}$$

和

$$\Omega_{\mathrm{2KDb2}}(E_\alpha) = \min\left|\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{\beta_i(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_i e^{E_\alpha/RT_{\alpha,i}}\Big/\left[1+(\frac{b}{T_{\alpha,i}}+\frac{E_\alpha}{RT^2_{\alpha,i}})(T_{\alpha,i}-T_{0,i})\right]}{\beta_j(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_j e^{E_\alpha/RT_{\alpha,j}}\Big/\left[1+(\frac{b}{T_{\alpha,j}}+\frac{E_\alpha}{RT^2_{\alpha,j}})(T_{\alpha,j}-T_{0,j})\right]} - n(n-1)\right| \tag{7}$$

式中，t 为时间；T_0 为 DTG 或 DSC 曲线偏离基线的始点温度；H 为物质在某时刻的反应热，相当于 DSC 曲线下的部分面积；H_0 为反应完成后物质的总放热量，相当于 DSC 曲线的总面积。

代一系列 DSC 曲线的原始数据：$H_{0,i}$，$T_{0,i}$，$T_{\alpha,i}$，$(\frac{\mathrm{d}H}{\mathrm{d}t})_i$ $(i=1,2,...,n)$ 和常数 b，入方程(6)，代一系列 DTG 或 DSC 曲线的原始数据：β_i，$(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_i$，$T_{0,i}$，$T_{\alpha,i}$，$(i=1,2,...,n)$ 和常数 b，入方程(7)，可得相应 E_α 值。

对等温动力学方程的微分式

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=kf(\alpha) \tag{8}$$

由

$$f(\alpha)=\frac{\mathrm{d}\alpha}{\mathrm{d}t}\frac{1}{k}=\frac{\mathrm{d}\alpha}{\mathrm{d}t}\frac{1}{AT^{b}}\mathrm{e}^{E/RT} \tag{9}$$

及等 α,知

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_1\frac{\mathrm{e}^{E_\alpha/RT_{\alpha,1}}}{AT^b_{\alpha,1}}=\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_2\frac{\mathrm{e}^{E_\alpha/RT_{\alpha,2}}}{AT^b_{\alpha,2}}=\cdots=\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_n\frac{\mathrm{e}^{E_\alpha/RT_{\alpha,n}}}{AT^b_{\alpha,n}} \tag{10}$$

得

$$\Omega_{\mathrm{isoKD}}(E_\alpha)=\min\left|\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_i T^b_{\alpha,j}\cdot\exp(E_\alpha/RT_{\alpha,i})}{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_j T^b_{\alpha,i}\cdot\exp(E_\alpha/RT_{\alpha,j})}-n(n-1)\right| \tag{11}$$

代一系列等温 TG-DTG 或 DSC 曲线上测得的同一 α 处的数据,$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_i$, $T_{\alpha,i}$ $(i=1,2,\ldots,n)$ 和常数 b,入方程(11),得满足该方程最小值的 E_α 值。

2.2 非线性等转化率的积分法

由 Kooij 型速率常数描述的非等温动力学方程的积分式

$$G(\alpha)=\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}T^b(T-T_0)\exp(-E/RT) \tag{12}$$

及等 α,得

$$\frac{A}{\beta_1}T^b_{\alpha,1}(T_{\alpha,1}-T_{0,1})\exp(-E_\alpha/RT_{\alpha,1})=\frac{A}{\beta_2}T^b_{\alpha,2}(T_{\alpha,2}-T_{0,2})\exp(-E_\alpha/RT_{\alpha,2})=\cdots$$
$$=\frac{A}{\beta_n}T^b_{\alpha,n}(T_{\alpha,n}-T_{0,n})\exp(-E_\alpha/RT_{\alpha,n}) \tag{13}$$

于是有

$$\frac{\beta_2\cdot T^b_{\alpha,1}(T_{\alpha,1}-T_{0,1})\exp(-E_\alpha/RT_{\alpha,1})}{\beta_1\cdot T^b_{\alpha,2}(T_{\alpha,2}-T_{0,2})\exp(-E_\alpha/RT_{\alpha,2})}+\frac{\beta_3\cdot T^b_{\alpha,1}(T_{\alpha,1}-T_{0,1})\exp(-E_\alpha/RT_{\alpha,1})}{\beta_1\cdot T^b_{\alpha,3}(T_{\alpha,3}-T_{0,3})\exp(-E_\alpha/RT_{\alpha,3})}+\cdots+$$
$$\frac{\beta_n\cdot T^b_{\alpha,1}(T_{\alpha,1}-T_{0,1})\exp(-E_\alpha/RT_{\alpha,1})}{\beta_1\cdot T^b_{\alpha,n}(T_{\alpha,n}-T_{0,n})\exp(-E_\alpha/RT_{\alpha,n})}+\frac{\beta_1\cdot T^b_{\alpha,2}(T_{\alpha,2}-T_{0,2})\exp(-E_\alpha/RT_{\alpha,2})}{\beta_2\cdot T^b_{\alpha,1}(T_{\alpha,1}-T_{0,1})\exp(-E_\alpha/RT_{\alpha,1})}+$$
$$\frac{\beta_3\cdot T^b_{\alpha,2}(T_{\alpha,2}-T_{0,2})\exp(-E_\alpha/RT_{\alpha,2})}{\beta_2\cdot T^b_{\alpha,3}(T_{\alpha,3}-T_{0,3})\exp(-E_\alpha/RT_{\alpha,3})}+\cdots+\frac{\beta_n\cdot T^b_{\alpha,2}(T_{\alpha,2}-T_{0,2})\exp(-E_\alpha/RT_{\alpha,2})}{\beta_2\cdot T^b_{\alpha,n}(T_{\alpha,n}-T_{0,n})\exp(-E_\alpha/RT_{\alpha,n})}+\cdots+$$
$$\frac{\beta_1\cdot T^b_{\alpha,m}(T_{\alpha,m}-T_{0,m})\exp(-E_\alpha/RT_{\alpha,m})}{\beta_m\cdot T^b_{\alpha,1}(T_{\alpha,1}-T_{0,1})\exp(-E_\alpha/RT_{\alpha,1})}+\frac{\beta_2\cdot T^b_{\alpha,m}(T_{\alpha,m}-T_{0,m})\exp(-E_\alpha/RT_{\alpha,m})}{\beta_m\cdot T^b_{\alpha,2}(T_{\alpha,n}-T_{0,2})\exp(-E_\alpha/RT_{\alpha,2})}+\cdots+$$
$$\frac{\beta_{m-1}\cdot T^b_{\alpha,m}(T_{\alpha,m}-T_{0,m})\exp(-E_\alpha/RT_{\alpha,m})}{\beta_m\cdot T^b_{\alpha,m-1}(T_{\alpha,m-1}-T_{0,m-1})\exp(-E_\alpha/RT_{\alpha,m-1})}+\frac{\beta_{m+1}\cdot T^b_{\alpha,m}(T_{\alpha,m}-T_{0,m})\exp(-E_\alpha/RT_{\alpha,m})}{\beta_m\cdot T^b_{\alpha,m+1}(T_{\alpha,m+1}-T_{0,m+1})\exp(-E_\alpha/RT_{\alpha,m+1})}+\cdots+$$
$$\frac{\beta_n\cdot T^b_{\alpha,m}(T_{\alpha,m}-T_{0,m})\exp(-E_\alpha/RT_{\alpha,m})}{\beta_m\cdot T^b_{\alpha,n}(T_{\alpha,n}-T_{0,n})\exp(-E_\alpha/RT_{\alpha,n})}+\cdots+$$
$$\frac{\beta_1\cdot T^b_{\alpha,n}(T_{\alpha,n}-T_{0,n})\exp(-E_\alpha/RT_{\alpha,n})}{\beta_n\cdot T^b_{\alpha,1}(T_{\alpha,1}-T_{0,1})\exp(-E_\alpha/RT_{\alpha,1})}+\frac{\beta_2\cdot T^b_{\alpha,n}(T_{\alpha,n}-T_{0,n})\exp(-E_\alpha/RT_{\alpha,n})}{\beta_n\cdot T^b_{\alpha,2}(T_{\alpha,2}-T_{0,2})\exp(-E_\alpha/RT_{\alpha,2})}+\cdots+$$
$$\frac{\beta_{n-1}\cdot T^b_{\alpha,n}(T_{\alpha,n}-T_{0,n})\exp(-E_\alpha/RT_{\alpha,n})}{\beta_n\cdot T^b_{\alpha,n-1}(T_{\alpha,n-1}-T_{0,n-1})\exp(-E_\alpha/RT_{\alpha,n-1})} \tag{14}$$

和

$$\Omega_{\mathrm{KI}}(E_\alpha) = \min\left|\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{\beta_j\cdot T_{\alpha,i}^{b}(T_{\alpha,i}-T_{0,i})\exp(-E_\alpha/RT_{\alpha,i})}{\beta_i\cdot T_{\alpha,j}^{b}(T_{\alpha,j}-T_{0,j})\exp(-E_\alpha/RT_{\alpha,j})}-n(n-1)\right| \tag{15}$$

代一系列非等温 TG 或 DSC 曲线上测得的同一 α 处的原始数据：β_i、$T_{\alpha,i}$，$T_{0,i}$（$i=1,2,...,n$）和常数 b，入方程(15)，得满足该方程最小值的 E_α 值。

我们称这种求 E_α 的方法为 Kooij 型非线性等转化率积分法[integral isoconversional non-linear (NL-INT) method]，$b=0$ 的 NL-INT 法为 Arrhenius 型 NL-INT$_0$ 法（简称 NL-INT$_0$ 法）。

对等温热分析动力学方程的积分式

$$G(\alpha) = kt = tAT^{b}\mathrm{e}^{-E/RT} \tag{16}$$

我们有

$$t_1AT_{\alpha,1}^{b}\mathrm{e}^{-E/RT_{\alpha,1}} = t_2AT_{\alpha,2}^{b}\mathrm{e}^{-E/RT_{\alpha,2}} = \cdots = t_nAT_{\alpha,n}^{b}\mathrm{e}^{-E/RT_{\alpha,n}} \tag{17}$$

和

$$\Omega_{\mathrm{isoI}}(E_\alpha) = \min\left|\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{t_i\cdot T_{\alpha,i}^{b}\mathrm{e}^{-E_\alpha/RT_{\alpha,i}}}{t_j\cdot T_{\alpha,j}^{b}\mathrm{e}^{-E_\alpha/RT_{\alpha,j}}}-n(n-1)\right| \tag{18}$$

代一系列等温 TG 或 DSC 曲线上测得的同一 α 处的数据：t_i，$T_{\alpha,i}$（$i=1,2,...,n$）和常数 b 入方程(18)，得满足该方程最小值的 E_α 值。

2.3 改进的非线性等转化率积分法

设 α 以步长 $\Delta\alpha=(m+1)^{-1}$ 和间距数 m 在 $2\Delta\alpha$ 到 $1-\Delta\alpha$ 区间内变化，如图 1 所示。

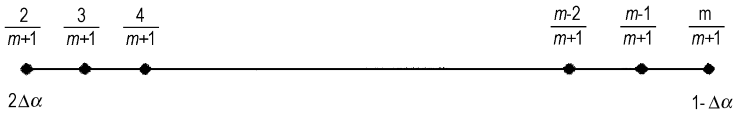

图 1 α 在 $2\Delta\alpha$ 到 $1\text{-}\Delta\alpha$ 区间的变化

Fig. 1 α varies from $2\Delta\alpha$ to $1-\Delta\alpha$

则有

$$2\Delta\alpha-\Delta\alpha = \Delta\alpha = \frac{1}{m+1},\ 1-\Delta\alpha = 1-\frac{1}{m+1} = \frac{m}{m+1},\ \text{和}\ \lim_{\substack{\Delta\alpha\to0\\ \Delta T\to0}}\frac{\Delta\alpha}{\Delta T} = \frac{\mathrm{d}\alpha}{\mathrm{d}T}\approx 1$$

知

$$T_{\alpha-\Delta\alpha} = T_\alpha-\Delta T = T_\alpha-\frac{\Delta\alpha}{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)}\approx T_\alpha-\Delta\alpha = T_\alpha-\frac{1}{m+1} \tag{19}$$

由

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) = AT^{b}\mathrm{e}^{-E/RT}f(\alpha)$$

知

$$\begin{aligned}G(\alpha) &\equiv \int_{\alpha-\Delta\alpha}^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)} = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha}AT_i^{b}(t)\,\mathrm{e}^{-E_\alpha/RT_i(t)}\,\mathrm{d}t^{T=T_0+\beta t} = \frac{A}{\beta_i}\int_{T_{\alpha-\Delta\alpha}}^{T_\alpha}T_i^{b}\exp(-E_\alpha/RT_i)\,\mathrm{d}T\\ &= \frac{A}{\beta_i}\left[T_{\alpha,i}^{b}(T_{\alpha,i}-T_{0,i})\exp(-E_\alpha/RT_{\alpha,i})-T_{\alpha-\Delta\alpha,i}^{b}(T_{\alpha-\Delta\alpha,i}-T_{0,i})\exp(-E_\alpha/RT_{\alpha-\Delta\alpha,i})\right]\end{aligned} \tag{20}$$

由等 α，得

$$G(\alpha) = \frac{A}{\beta_i}\left[T_{\alpha,1}^{b}(T_{\alpha,1}-T_{0,1})\exp(-E_\alpha/RT_{\alpha,1})-T_{\alpha-\Delta\alpha,1}^{b}(T_{\alpha-\Delta\alpha,1}-T_{0,1})\exp(-E_\alpha/RT_{\alpha-\Delta\alpha,1})\right]$$

$$= \frac{A}{\beta_2}[T^b_{\alpha,2}(T_{\alpha,2} - T_{0,2})\exp(-E_\alpha/RT_{\alpha,2}) - T^b_{\alpha-\Delta\alpha,2}(T_{\alpha-\Delta\alpha,2} - T_{0,2})\exp(-E_\alpha/RT_{\alpha-\Delta\alpha,2})] = \cdots$$

$$= \frac{A}{\beta_n}[T^b_{\alpha,n}(T_{\alpha,n} - T_{0,n})\exp(-E_\alpha/RT_{\alpha,n}) - T^b_{\alpha-\Delta\alpha,n}(T_{\alpha-\Delta\alpha,n} - T_{0,n})\exp(-E_\alpha/RT_{\alpha-\Delta\alpha,n})] \quad (21)$$

于是有

$$\Omega_{\mathrm{KM1}}(E_\alpha) = \min\left|\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{\beta_j[T^b_{\alpha,i}(T_{\alpha,i} - T_{0,i})\exp(-E_\alpha/RT_{\alpha,i}) - T^b_{\alpha-\Delta\alpha,i}(T_{\alpha-\Delta\alpha,i} - T_{0,i})\exp(-E_\alpha/RT_{\alpha-\Delta\alpha,i})]}{\beta_i[T^b_{\alpha,j}(T_{\alpha,j} - T_{0,j})\exp(-E_\alpha/RT_{\alpha,j}) - T^b_{\alpha-\Delta\alpha,j}(T_{\alpha-\Delta\alpha,j} - T_{0,j})\exp(-E_\alpha/RT_{\alpha-\Delta\alpha,j})]} - n(n-1)\right| \quad (22)$$

假设 $G(\alpha)$ 与 β 无关,则有

$$\Omega_{\mathrm{KM2}}(E_\alpha) = \min\left|\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{[T^b_{\alpha,i}(T_{\alpha,i} - T_{0,i})\exp(-E_\alpha/RT_{\alpha,i}) - T^b_{\alpha-\Delta\alpha,i}(T_{\alpha-\Delta\alpha,i} - T_{0,i})\exp(-E_\alpha/RT_{\alpha-\Delta\alpha,i})]}{[T^b_{\alpha,j}(T_{\alpha,j} - T_{0,j})\exp(-E_\alpha/RT_{\alpha,j}) - T^b_{\alpha-\Delta\alpha,j}(T_{\alpha-\Delta\alpha,j} - T_{0,j})\exp(-E_\alpha/RT_{\alpha-\Delta\alpha,j})]} - n(n-1)\right| \quad (23)$$

$$\Omega_{\mathrm{KM3}}(E_\alpha) = \min\left|\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{[T^b_{\alpha,i}(T_{\alpha,i} - T_{0,i})\exp(-E_\alpha/RT_{\alpha,i}) - T^b_{\alpha-\Delta\alpha,i}(T_{\alpha-\Delta\alpha,i} - T_{0,i})\exp(-E_\alpha/RT_{\alpha-\Delta\alpha,i})]}{[T^b_{\alpha,j}(T_{\alpha,j} - T_{0,j})\exp(-E_\alpha/RT_{\alpha,j}) - T^b_{\alpha-\Delta\alpha,j}(T_{\alpha-\Delta\alpha,j} - T_{0,j})\exp(-E_\alpha/RT_{\alpha-\Delta\alpha,j})]}\right| \quad (24)$$

于是,代一系列非等温 TG 或 DSC 曲线上测得的同一 α 处的原始数据: $\beta_i, T_{\alpha,i}, T_{\alpha-\Delta\alpha,i}, T_{0,i}(i=1,2,\cdots,n)$ 和常数 b,入方程(22)或(23)和(24),可得满足相应方程最小值的 E_α 值。

我们称这种求 E_α 的方法为改进的 Kooij 型非线性等转化率积分法[modified integral isoconversional non-linear (MNL-INT) method]。

3 结束语

从速率常数用 Kooij 公式表示的等温和非等温第Ⅰ类和第Ⅱ类动力学方程的微、积分式,可方便地导出非线性等转化率微、积分法求 E_α 的数学表达式。

上述求 E_α 的计算机软件已编制,有关应用实例,将在以后各报中陆续报道。

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Non-isothermal Crystallization Kinetics of Polyethylene Glycol

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Abstract: The non-isothermal crystallization kinetics of polyethylene glycol (PEG) was studied with differential scanning calorimetry. The non-isothermal crystallization data of PEG was analyzed by the methods of Ozawa, Jeziorny, and MO Zhi-shen. Results show that the non-isothermal crystallization process of PEG may be described with Ozawa kinetic equation, but does not agree with Avrami equation processed in the Jeziorny method. The linearity of treating non-isothermal crystallization kinetic curves with Ozawa method and MO Zhi-shen method is better. Parameter of crystallization velocity for PEG is 0.098.

Key Words: physical chemistry; polyethylene glycol (PEG); non-isothermal crystallization; kinetics; differential scanning calorimetry (DSC)

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Differential and Integral Isoconversional Non-linear Methods and their Application in Physical Chemistry Study of Energetic Materials V. Theory and Numerical Method Based on Kooij's Formula

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Abstract: Eight typical differential and integral isoconversional non-linear equations based on Kooij's formula for computing the apparent activation energy (E_α) from isothermal and non-isothermal data were derived. The numerical methods of computing the value of E_α of decomposition reaction of energetic materials via the equations were presented.

Key words: physical chemistry; energetic materials; differential isoconversional non-linear method; integral isoconversional non-linear method; decomposition reaction; apparent activation energy