

КАЗАНСКИЙ (ПРИВОЛЖСКИЙ) ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Evolution of Isoconversional Methods

Early Methods

$$\log t = \frac{Q}{T} - F(w),$$

$$g(\alpha) \equiv \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = A \exp\left(\frac{-E}{RT}\right) t,$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(\frac{-E}{RT}\right) f(\alpha).$$

$$\log t = \frac{E}{2.303RT} - \log\left[\frac{g(\alpha)}{A}\right].$$



Friedman methods

$$\log t = \frac{Q}{T} - F(w),$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(\frac{-E}{RT}\right) f(\alpha), \qquad \ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha,i} = \ln[f(\alpha) \ A_{\alpha}] - \frac{E_{\alpha}}{RT_{\alpha,i}},$$

$$S(T) \approx \int_{0}^{T} \exp\left(\frac{-E}{RT}\right) dT.$$
$$g(\alpha) = A \int_{0}^{T} \exp\left(\frac{-E}{RT}\right) dt.$$
$$T = T_{0} + \beta t,$$
$$g(\alpha) = \frac{A}{T} \int_{0}^{T} \exp\left(\frac{-E}{RT}\right) dT \equiv \frac{A}{T} I(0)$$

$$g(\alpha) = \frac{A}{B} \int_{a}^{T} \exp\left(\frac{-E}{RT}\right) dT \equiv \frac{A}{B}I(E,T),$$
$$S(T) \approx \int_{0}^{T} \exp\left(\frac{-E}{RT}\right) dT.$$

$$I(E,T) \approx S(T) - S(T_0).$$

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^B}\right) = \operatorname{Const} - C\left(\frac{E_\alpha}{RT_{\alpha,i}}\right),$$



Fig.1.2.

The relative error in the activation energy as a function of the activation energy and the distance between the initial temperature (T0) and temperature of a given conversion (Tf1) at the slowest heating rate $\beta 1$. (Reproduced from Starink [18] with permission of Springer)

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^B}\right) = \operatorname{Const} - C\left(\frac{E_\alpha}{RT_{\alpha,i}}\right),$$

Ozawa, and Flynn and Wall

$$\ln(\beta_i) = \text{Const} - 1.052 \left(\frac{E_{\alpha}}{RT_{\alpha,i}}\right),$$

Kissinger–Akahira–Sunose

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \operatorname{Const} - \frac{E_\alpha}{RT_{\alpha,i}}.$$

Starink

$$\ln\!\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = \text{Const} - 1.0008 \left(\frac{E_\alpha}{RT_{\alpha,i}}\right).$$



Fig. 1.3. The activation energies determined by Friedman for the thermal degradation of phenolic plastic. (Reproduced from Friedman [13] with permission of Wiley)

Modern Methods (Vyazovkin)

$$g(\alpha) = A \int_{0}^{t} \exp\left(\frac{-E}{RT}\right) dt.$$

$$g(\alpha) = \frac{A_{\alpha}}{\beta_1} I(E_{\alpha}, T_{\alpha,1}) = \frac{A_{\alpha}}{\beta_2} I(E_{\alpha}, T_{\alpha,2}) = \dots = \frac{A_{\alpha}}{\beta_n} I(E_{\alpha}, T_{\alpha,n}).$$

$$\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{I(E_{\alpha},T_{\alpha,i})\beta_{j}}{I(E_{\alpha},T_{\alpha,j})\beta_{i}}=n(n-1).$$

$$\Phi(E_{\alpha}) = \sum_{i=1}^{n} \sum_{j\neq i}^{n} \frac{J[E_{\alpha}, T_{i}(t_{\alpha})]}{J[E_{\alpha}, T_{j}(t_{\alpha})]},$$
$$J[E_{\alpha}, T(t_{\alpha})] = \int_{0}^{t_{\alpha}} \exp\left[\frac{-E_{\alpha}}{RT(t)}\right] dt$$



Fig 1.4

Relative error in the activation energy as a function of x= E RT ; nonlinear method,(circles), linear Kissinger–Akahira– Sunose equation, Eq. 2.13 (squares). (Reproduced from Vyazovkin and Dollimore [34] with permission of ACS

$$\sum_{i=1}^{n} \sum_{j\neq i}^{n} \frac{I(E_{\alpha}, T_{\alpha,j})\beta_{j}}{I(E_{\alpha}, T_{\alpha,j})\beta_{i}} = n(n-1).$$
$$\Phi(E_{\alpha}) = \sum_{i=1}^{n} \sum_{j\neq i}^{n} \frac{J[E_{\alpha}, T_{i}(t_{\alpha})]}{J[E_{\alpha}, T_{j}(t_{\alpha})]},$$
$$J[E_{\alpha}, T(t_{\alpha})] = \int_{0}^{t_{\alpha}} \exp\left[\frac{-E_{\alpha}}{RT(t)}\right] dt$$

$$J[E_{\alpha}, T(t_{\alpha})] = \int_{t_{\alpha-A\alpha}}^{t_{\alpha}} \exp\left[\frac{-E_{\alpha}}{RT(t)}\right] dt.$$

$$I(E_{\alpha}, T_{\alpha}) = \int_{T_{\alpha-A\alpha}}^{T_{\alpha}} \exp\left(\frac{-E_{\alpha}}{RT}\right) dT$$



Fig 1.5

For a process that takes place on cooling from T0 to T, the flexible methods estimate $E\alpha$ from the area S(TO)-S(T) that corresponds to the actually accomplished extent of conversion. The rigid methods estimate $E\alpha$ from S(T) that represents the conversion, which is yet to be accomplished