КАЗАНСКИЙ (ПРИВОЛЖСКИЙ) ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Evolution of Isoconversional Methods

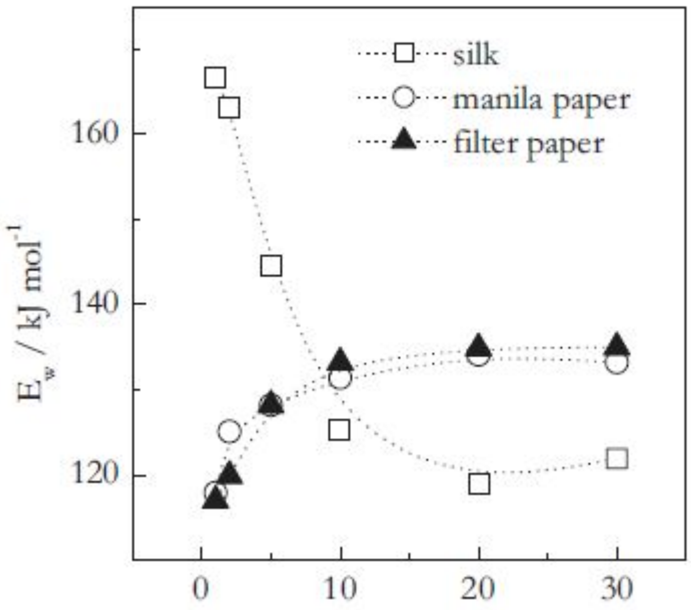
Early Methods

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

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

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

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



Friedman methods

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

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

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[f(\alpha)\, A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}},$$

$$S(T) \approx \int_0^T \exp\left(\frac{-E}{RT}\right) dT.$$

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

$$T = T_0 + \beta t,$$

$$g(\alpha) = \frac{A}{\beta} \int^T \exp\left(\frac{-E}{RT}\right) dT \equiv \frac{A}{\beta} I(E,T),$$

$$S(T) \approx \int_0^T \exp\left(\frac{-E}{RT}\right) dT.$$

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

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

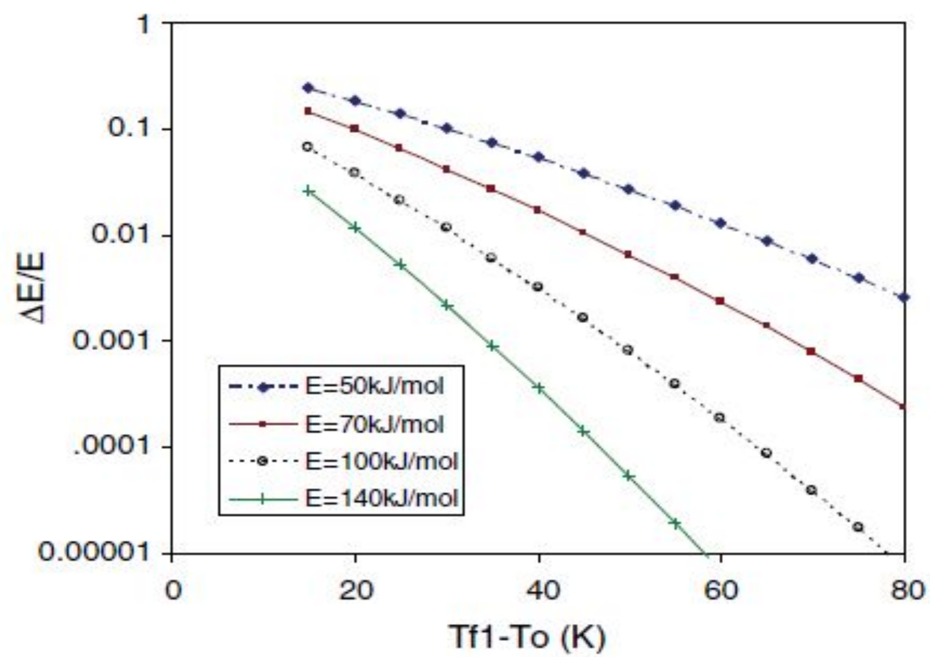


Fig.1.2.
The relative error in the activation energy as a function of the activation energy and the distance between the initial temperature (T0) and temperature of a given conversion (Tf1) at the slowest heating rate β1 . (Reproduced from Starink [18] with permission of Springer)

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

Ozawa, and Flynn and Wall

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

Kissinger–Akahira–Sunose

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

Starink

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

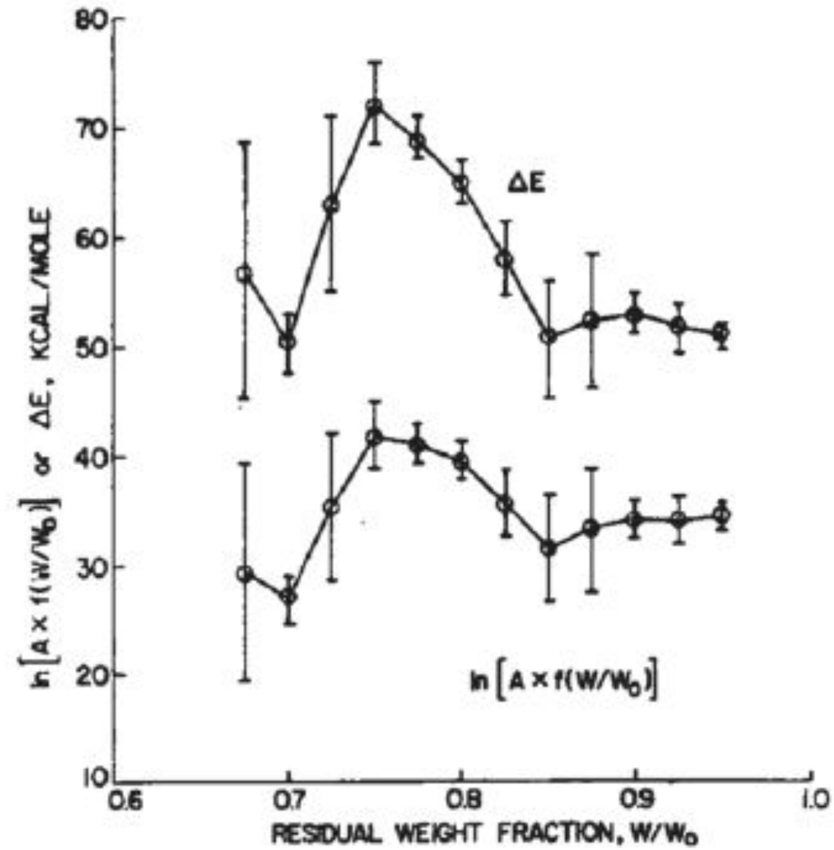


Fig. 1.3. The activation energies determined by Friedman for the thermal degradation of phenolic plastic. (Reproduced from Friedman [13] with permission of Wiley)

Modern Methods (Vyazovkin)

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

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

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

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n} \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]},$$

$$J[E_\alpha, T(t_\alpha)] = \int_0^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT(t)}\right]\mathrm{d}t$$

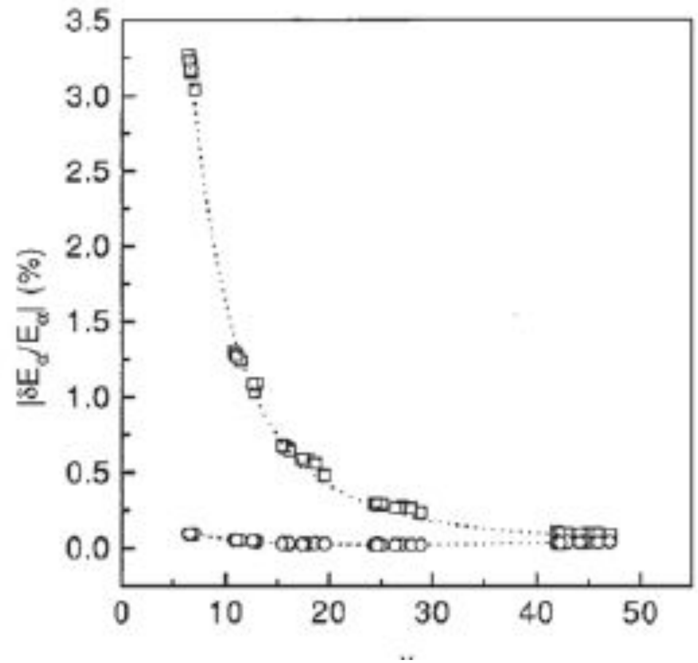


Fig 1.4
Relative error in the activation energy as a function of x= E RT ; nonlinear method,(circles), linear Kissinger–Akahira– Sunose equation, Eq. 2.13 (squares). (Reproduced from Vyazovkin and Dollimore [34] with permission of ACS

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

$$\Phi(E_{\alpha})=\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{J[E_{\alpha},T_{i}(t_{\alpha})]}{J[E_{\alpha},T_{j}(t_{\alpha})]},$$

$$J[E_{\alpha},T(t_{\alpha})]=\int_{0}^{t_{\alpha}}\exp\left[\frac{-E_{\alpha}}{RT(t)}\right]\mathrm{d}t$$

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

$$I(E_{\alpha},T_{\alpha})=\int_{T_{\alpha-\Delta\alpha}}^{T_{\alpha}}\exp\left(\frac{-E_{\alpha}}{RT}\right)\mathrm{d}T$$

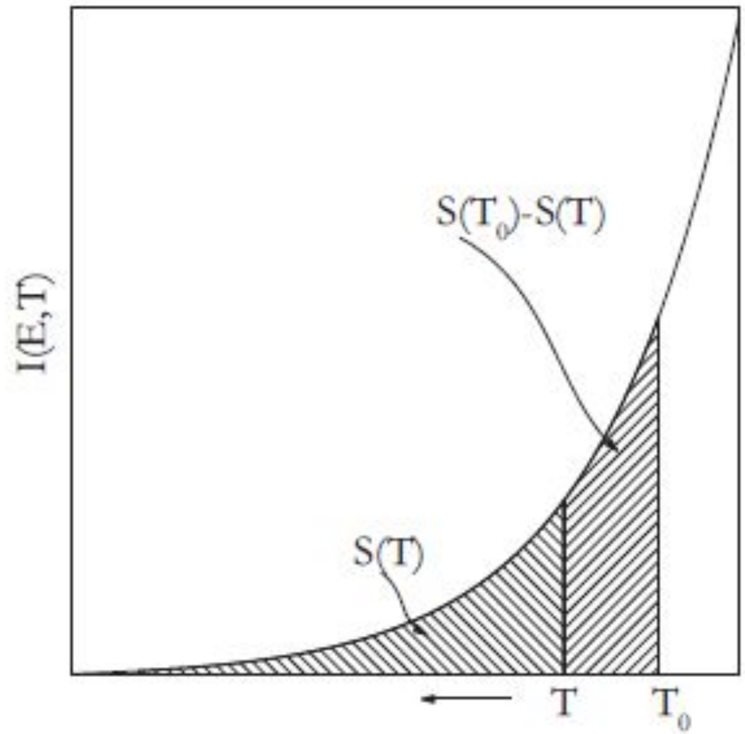


Fig 1.5
For a process that takes place on cooling from T0 to T, the flexible methods estimate Eα from the area S(T0)−S(T) that corresponds to the actually accomplished extent of conversion. The rigid methods estimate Eα from S(T) that represents the conversion, which is yet to be accomplished