



КАЗАНСКИЙ (ПРИВОЛЖСКИЙ) ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Evolution of Isoconversional Methods



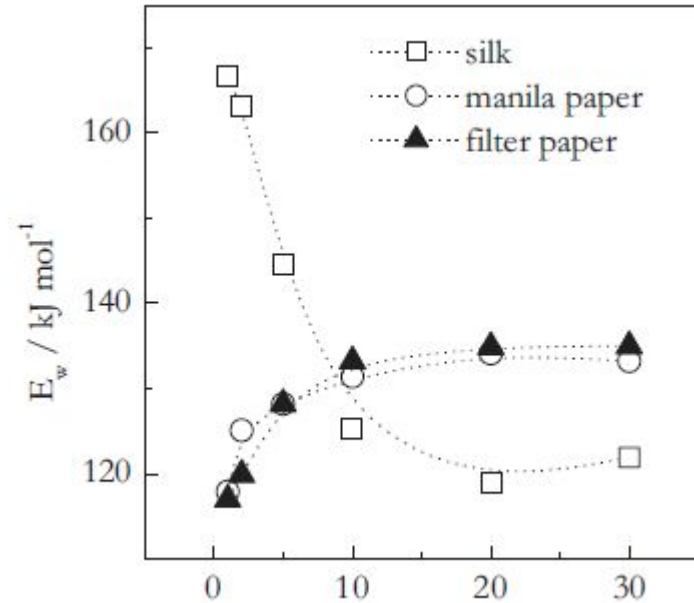
Early Methods

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

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

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

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



Friedman methods

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

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

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

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

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

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

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

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

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

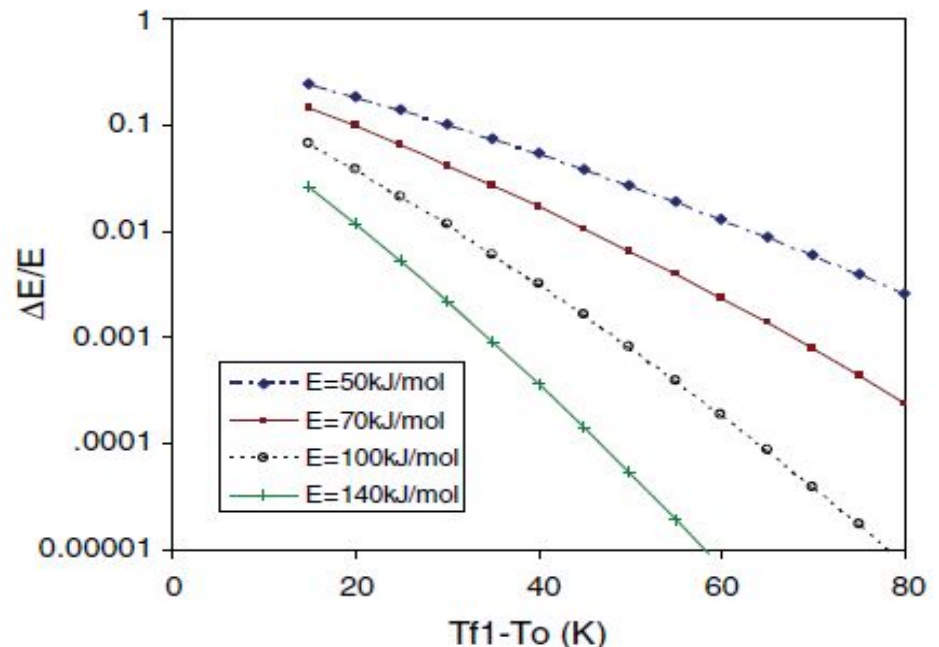


Fig.1.2.

The relative error in the activation energy as a function of the activation energy and the distance between the initial temperature (T_0) and temperature of a given conversion (T_{f1}) at the slowest heating rate β_1 . (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

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

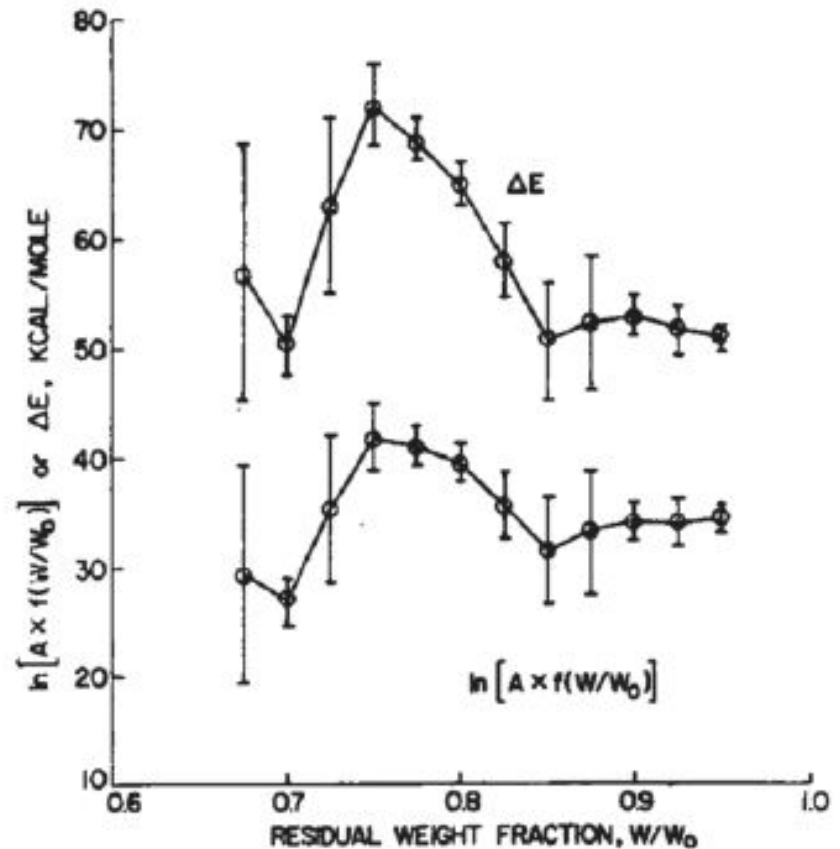


Fig. 1.3. The activation energies determined by Friedman for the thermal degradation of phenolic plastic. (Reproduced from Friedman [13] with permission of Wiley)

Modern Methods (Vyazovkin)

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

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

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

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

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

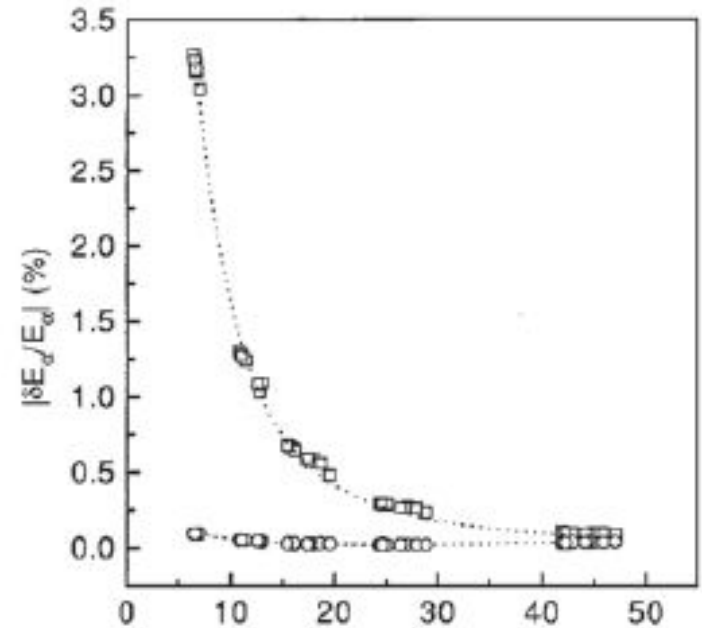


Fig 1.4

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)

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

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

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

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

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

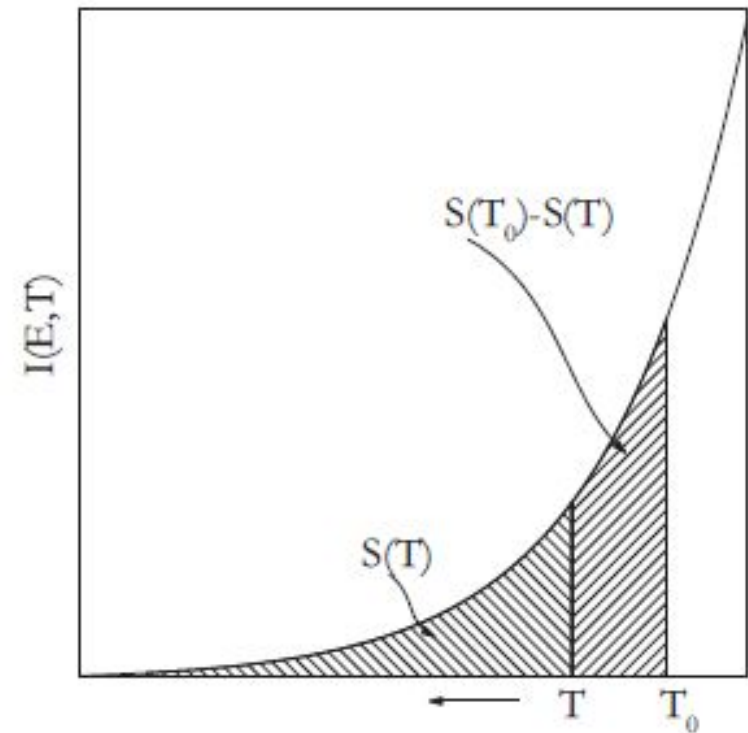


Fig 1.5

For a process that takes place on cooling from T_0 to T , the flexible methods estimate E_α from the area $S(T_0) - S(T)$ that corresponds to the actually accomplished extent of conversion. The rigid methods estimate E_α from $S(T)$ that represents the conversion, which is yet to be accomplished