Kinetic Analysis of Single Processes in Mathematica

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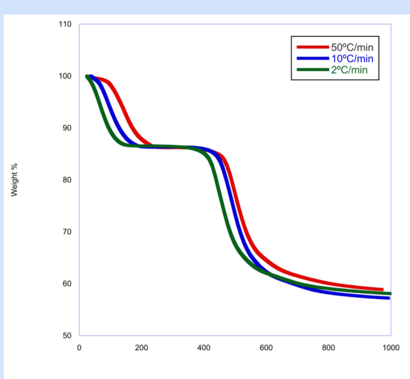
Introduction

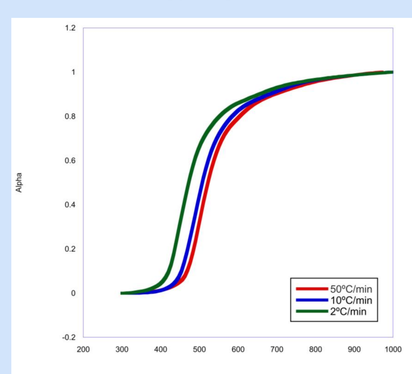
- Thermogravimetric Analysis (TGA) characterizes mass loss of solid-state reactions
- The conversion factor α of the reaction is given by

$$\alpha = \frac{m_0 - m(t)}{m_0 - m_f}$$

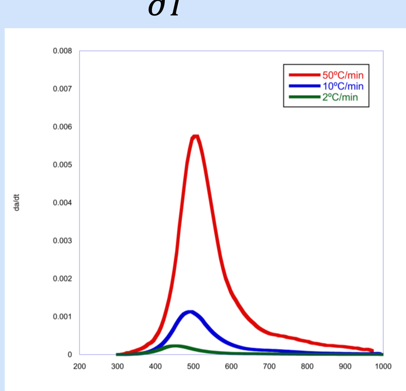
TGA – Mass vs T



α vs T



$\frac{\partial \alpha}{\partial T}$ vs T



Modeling

$$\frac{\partial \alpha}{\partial T} = \frac{1}{\beta} \cdot A e^{-\frac{E_a}{RT}} \cdot f(\alpha)$$

β = Heating Rate A = Pre-Exponential Factor

Common Model Functions include

First Order (F1)
F(α) = (1-α)

Second Order (F2)
F(α) = $(1-\alpha)^2$

Third Order (F3)
F(α) = $(1-\alpha)^3$

A(m) Model Form
F(α) = m (1-α) $[-\ln(1-\alpha)]^{(1-(1/m))}$

Simplified Sestak-Berggren Form
F(α) = $\alpha^m (1-\alpha)^n$

Modeling dα/dT Data

Different activation energies were assigned to different model functions in order to get a process with a maximum around 800° C

F1,F2,F3 Processes
E_a ~ 170 kJ/mol

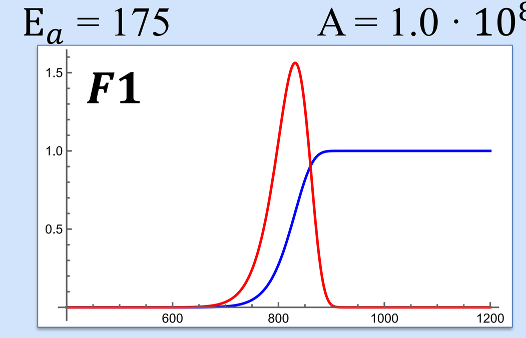
D1,D2,D3,D4 Processes
E_a ~ 185 kJ/mol

A1,A2,A3,A4 Processes
E_a ~ 170 kJ/mol

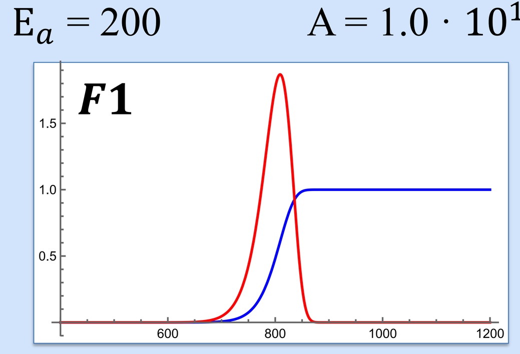
AC Process
E_a ~ 150 kJ/mol

You can get the same Process with different activation energies and Arrhenius constants

E_a = 175 A = $1.0 \cdot 10^8$



E_a = 200 A = $1.0 \cdot 10^{10}$



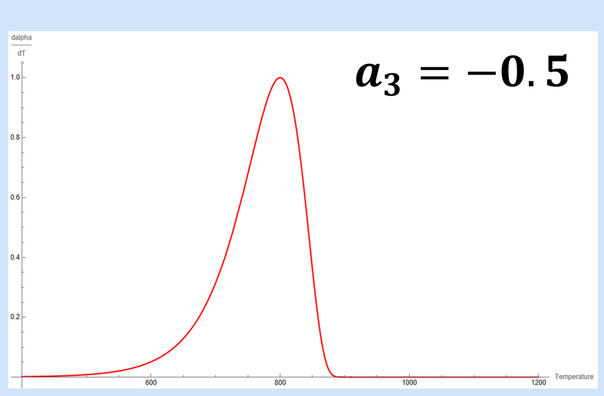
red = α -T Plot blue = $\frac{\partial \alpha}{\partial T}$ Plot

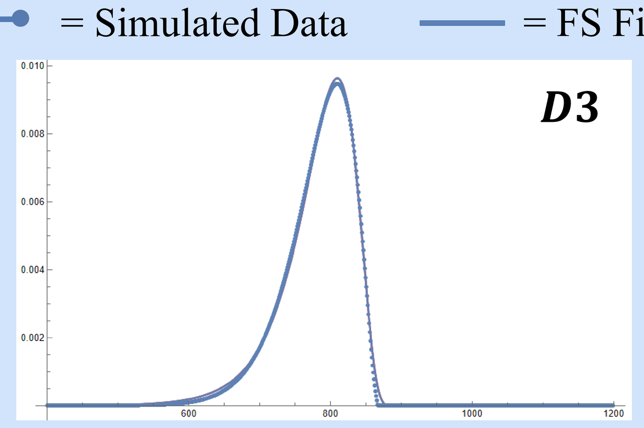
Frazier-Suzuki Fitting

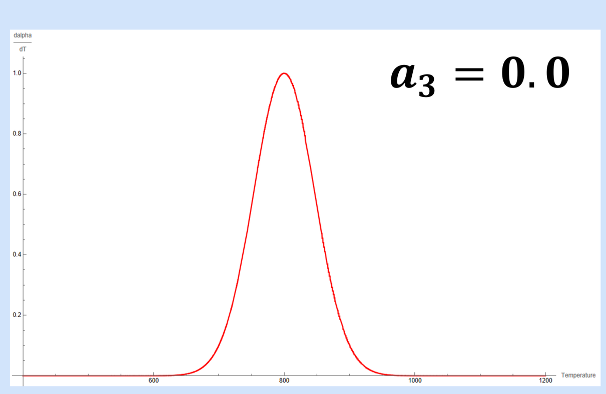
$$y = a_0 \exp\left[-\ln 2 \left[\frac{\ln\left(1 + \frac{2a_3(x-a_1)}{a_2}\right)}{a_3}\right]^2\right]$$

FS Function in which
a_0 = Height
a_1 = Position of Max
a_2 = Width
a_3 = Asymmetry

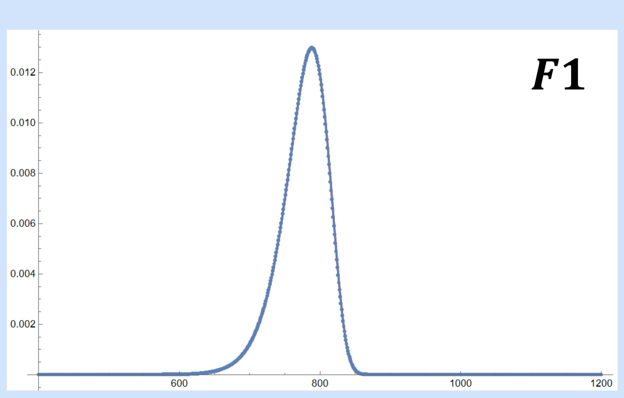
= Simulated Data = FS Fit

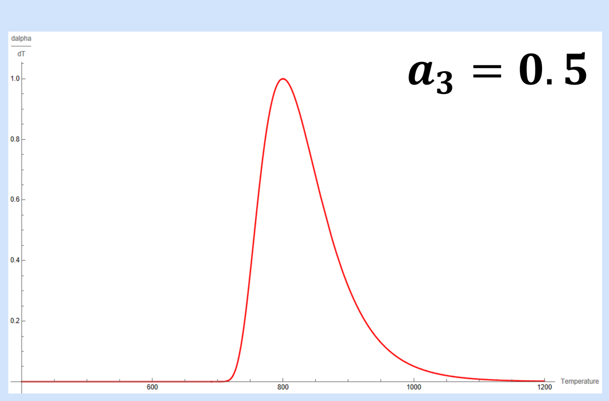


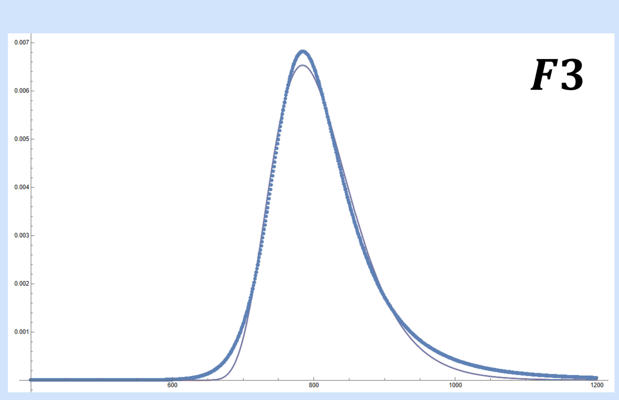




When a_3 is zero, the curve is the same as a Gauss curve







Asymmetry Parameters

Model Functions	β=5°C/min	β=125°C/min
F1	-0.326	-0.319
F2	0.089	0.098
F3	0.335	0.343
A1	-0.326	-0.319
A2	-0.362	-0.359
A3	-0.375	-0.373
D2	-0.979	-0.966
D3	-0.512	-0.500
AC	-0.083	-0.076

Summary

Peak fitting using Frazier-Suzuki (FS) functions is a standard approach to analyzing TGA data. The FS fitting addresses four (4) parameters simultaneously. It is known that a_0, a_1, and a_2 change significantly with changing heating rates β. Our goal was to test the dependency of the asymmetry parameter a_3 on the heating rate β.
We pursue the target using Mathematica to model TGA data and subsequently fit the data using Frazier-Suzuki functions. We find that a_3 reflects the choice of conversion model: each model relates to a characteristic value of a_3. Furthermore, a_3's dependency on the heating rate β is small, even if β varies by two orders of magnitude. Hence, the asymmetry parameter a_3 is a valuable tool for determining the conversion model and reaction order based on TGA data. In the future, we will use the knowledge to characterize multi-process conversions.

References

- Criado J.M; Ortega A; Gotor F. Correlation Between The Shape Of Controlled-Rate Thermal Analysis Curves And The Kinetics Of Solid-State Reactions; Thermochimica Acta, 157; Elsevier Science Publishers. 1990; 171-179.
- Svoboda R. Fraser-Suzuki Function as an Essential Tool for Mathematical Modeling of Crystallization in Glasses. Journal of the European Ceramic Society. 2024; Volume 44, Issue 1: 401-407
- R.D.B Frazer, E. Suzuki; Resolution of Overlapping Absorption Bands by Least Squares Procedures; Anal. Chem., 38(1966), 1770-1773

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