Analyzing & Testing

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Selection of the Suitable Kinetic Method and Models by means of Kinetics Neo

Webinar

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11/15/2022

Agenda

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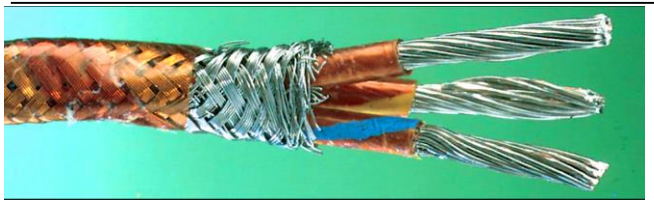
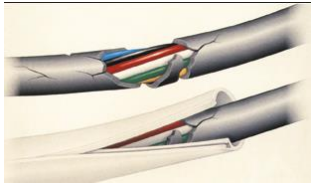
1. Data and degree of conversion for kinetic analysis
2. Methods of kinetic analysis: model-free or model based?
   - 2.1. Model-free methods: single-point and multi-point methods
   - 2.2. Model based methods
     - 2.2.1. Selection number of steps
     - 2.2.2. Construction of the multi-step kinetic model
     - 2.2.2. Selection of reaction type for individual steps
3. Examples
   - 3.1 Decomposition
   - 3.2 Curing & cross-linking
   - 3.3 Crystallization
   - 3.3 Sintering

1. Data and degree of conversion for kinetic analysis

Problems Solving by Polymer Kinetics: Chemical or Physical Processes





Life time predictions
Recycling, pyrolysis
Thermal stability

Curing, cross-linking

Problem: Find reaction mechanism and predict material behavior at the conditions where it is impossible /very hard /expensive to measure

Data for analysis

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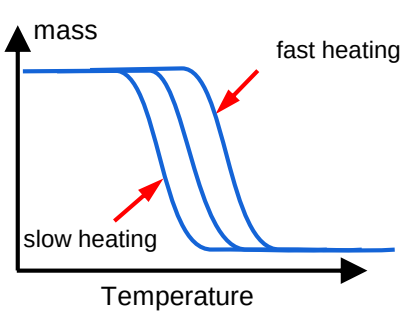
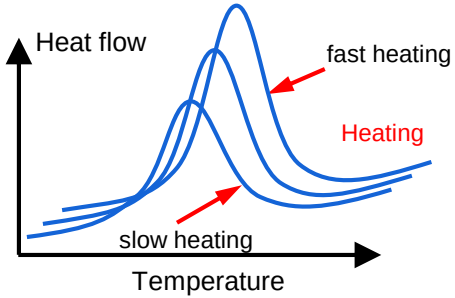
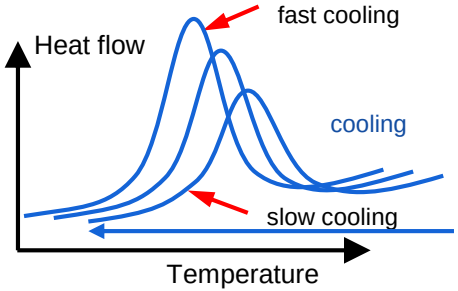
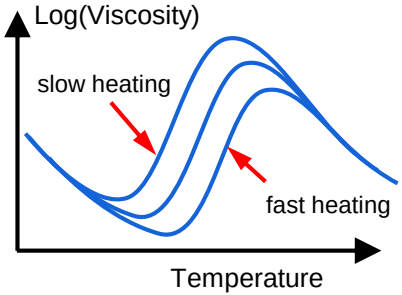


DSC

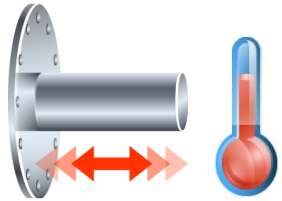


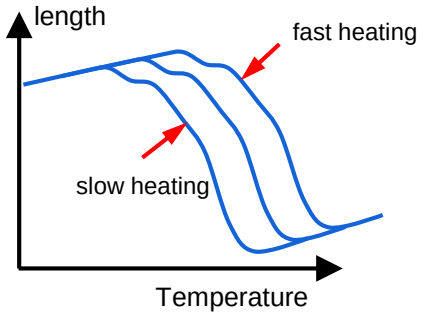


Rheometry



DIL





Degree of conversion α(t)
(extent of conversion, conversion, extent of reaction)

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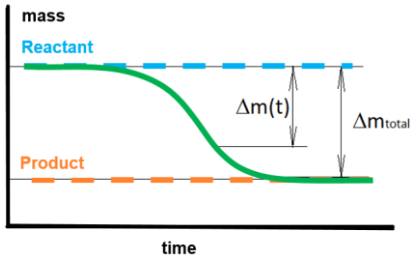

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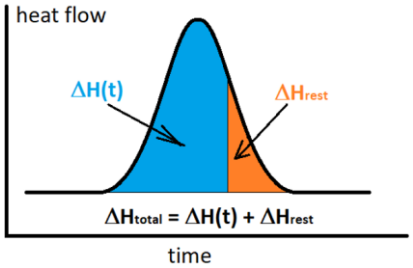
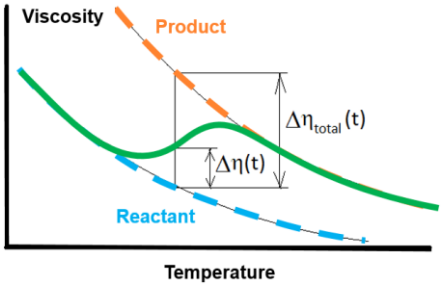


Rheometry



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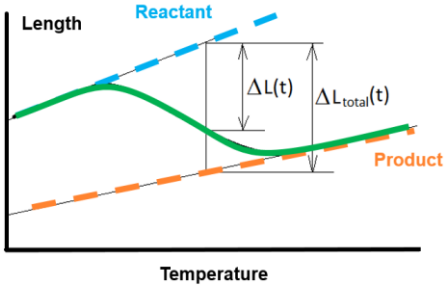
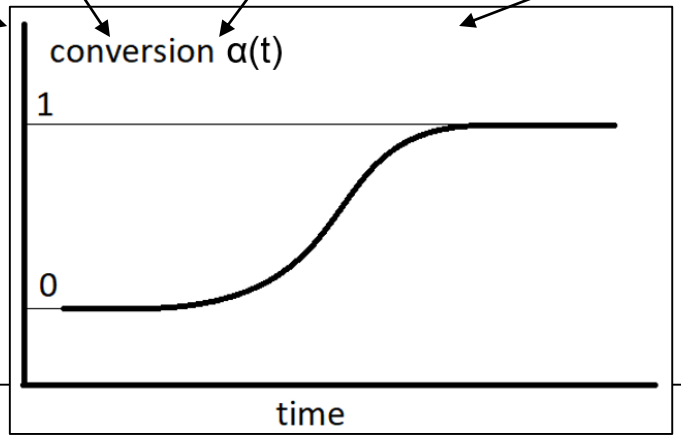


$$\alpha(t) = \frac{\Delta m(t)}{\Delta m_{total}}$$

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{total}}$$

$$\alpha(t) = \frac{\Delta \eta(t)}{\Delta \eta_{total}(t)}$$

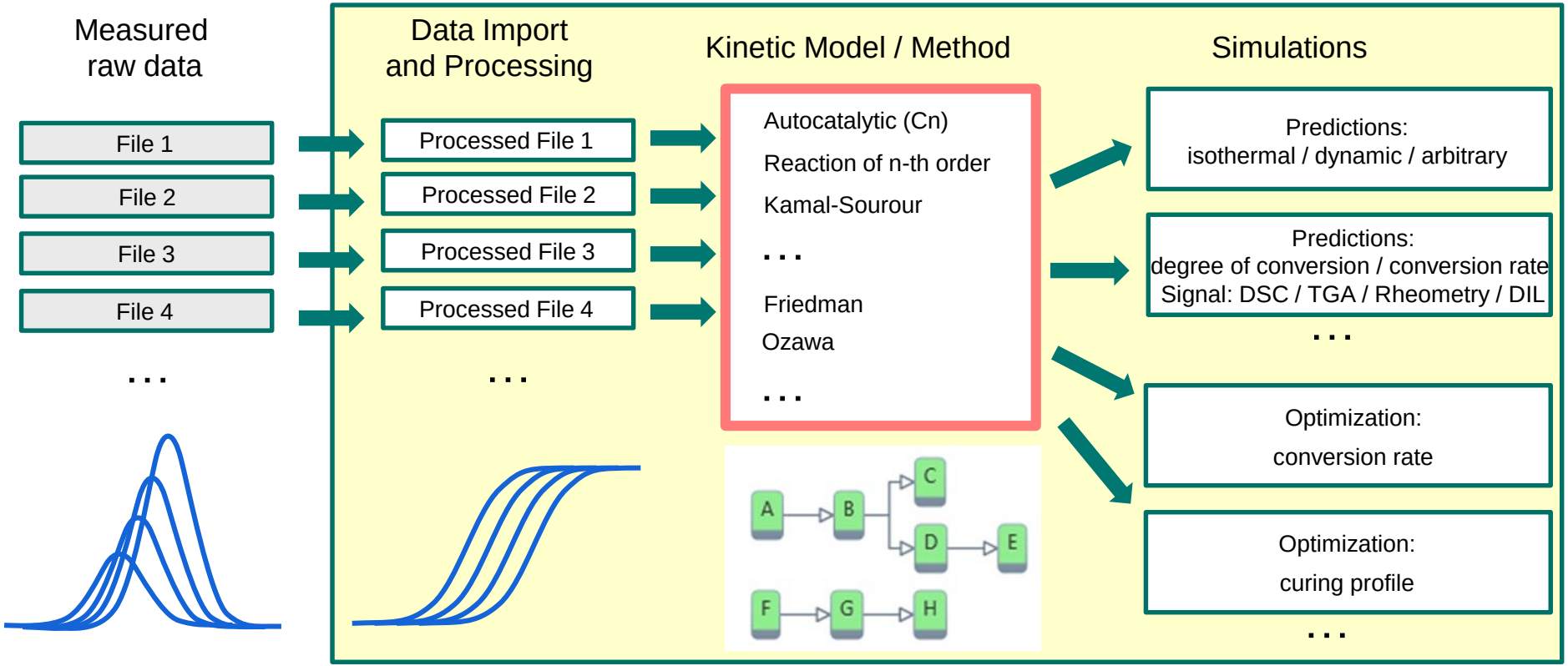
$$\alpha(t) = \frac{\Delta L(t)}{\Delta L_{total}(t)}$$



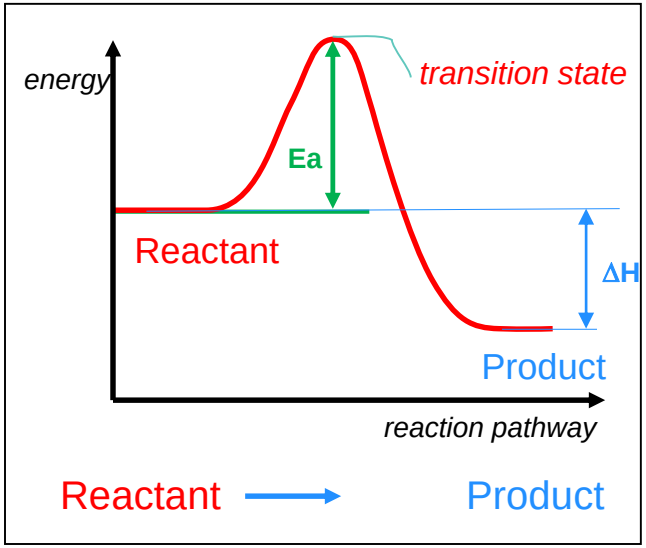
Conversion is commonly denoted by **α** and defined as the ratio of the partial to total change of a physical property.

α=0 before reaction start
α=1 after reaction end

Steps to Solve Kinetic Tasks in Kinetics Neo



Arrhenius Equation. Activation Energy. Kinetic Triplet



$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$$

Arrhenius equation (1889) for reaction rate:

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

Conversion α: degree of conversion, changing from 0 to 1

Pre-exponent A: collision frequency [1/s]

Activation energy Ea [kJ/mol]

$f(\alpha)$ Reaction type (nth order, autocatalysis, nucleation …)

R: gas constant 8.31 [J/(mol K)] T: absolute temperature [K] T[K]=T[°C]+273.15

2. Kinetic Methods: Model free or model based?

Kinetic Analysis Methods in Kinetics Neo

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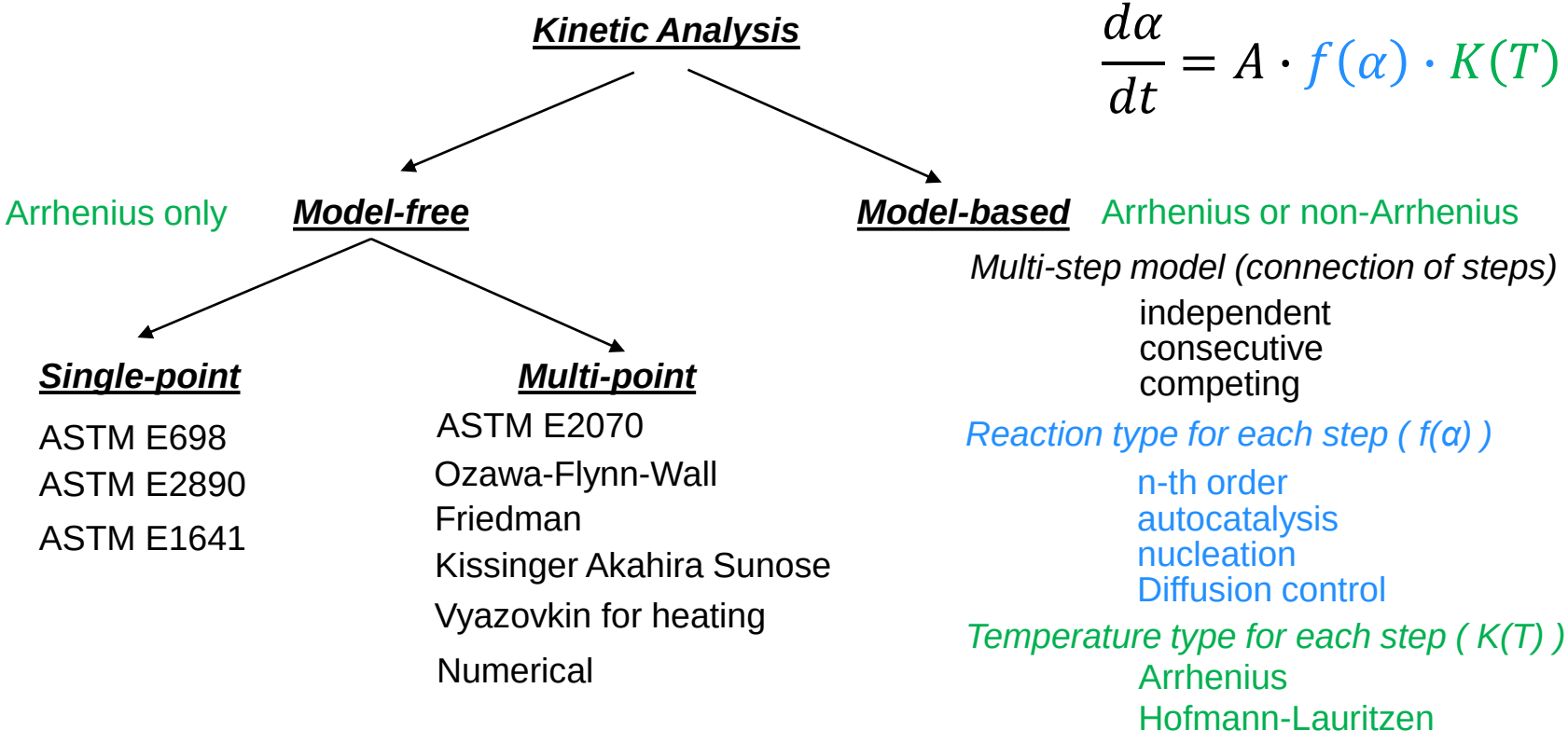

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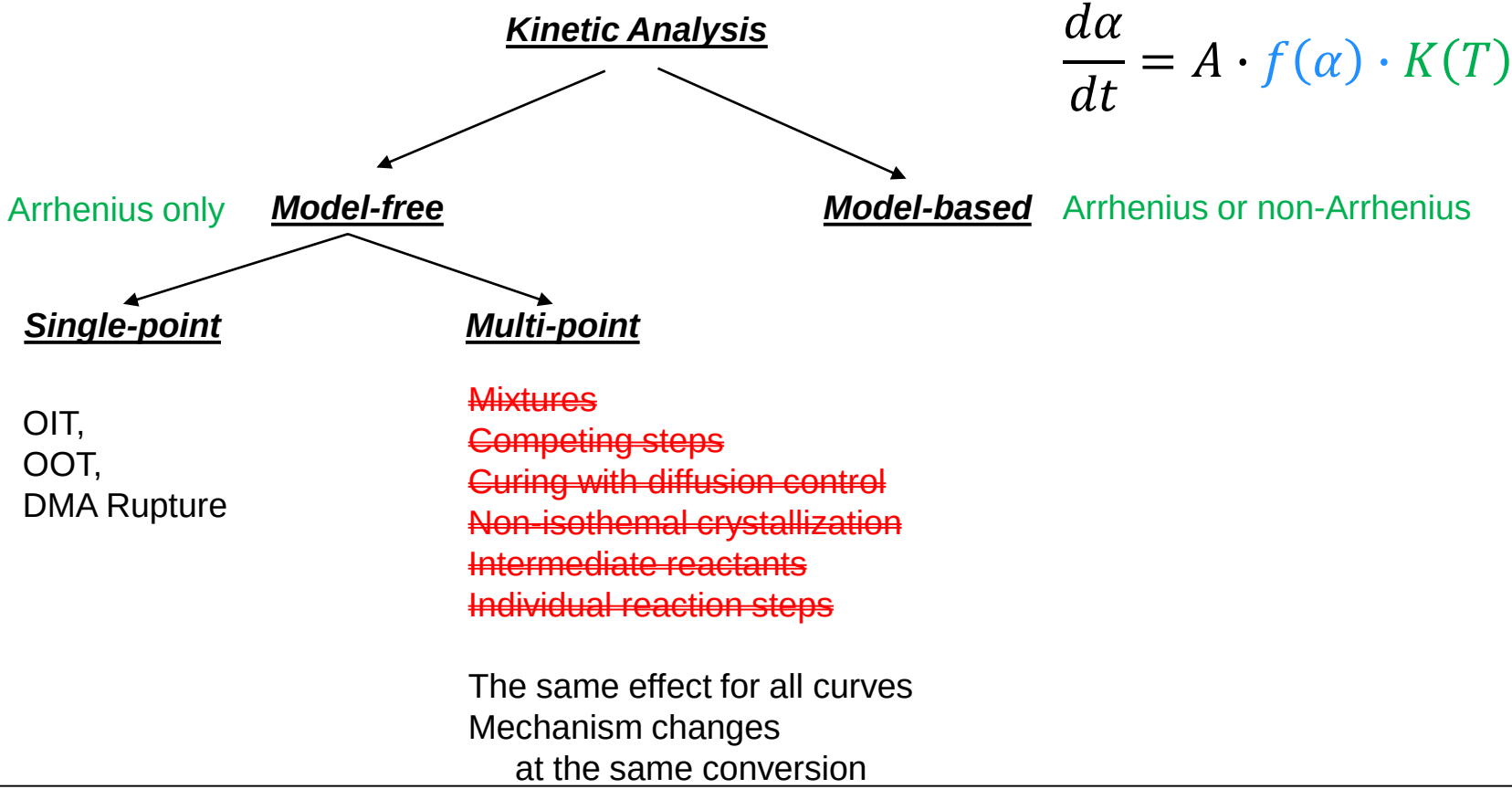

Kinetic Analysis
$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$
Arrhenius only
Model-free
Model-based
Arrhenius or non-Arrhenius
Single-point
Multi-point
OIT,
OOT,
DMA Rupture
~~Mixtures~~
~~Competing steps~~
~~Curing with diffusion control~~
~~Non-isothemal crystallization~~
~~Intermediate reactants~~
~~Individual reaction steps~~
The same effect for all curves
Mechanism changes
at the same conversion

2.1. Model-free Kinetic Methods

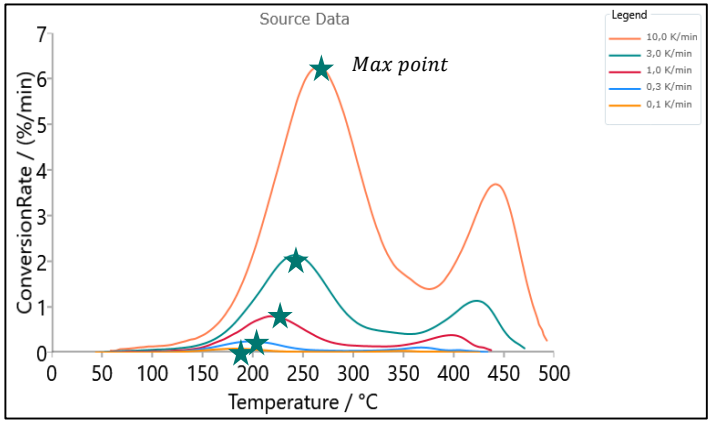
Model-Free Methods (Arrhenius approach only)

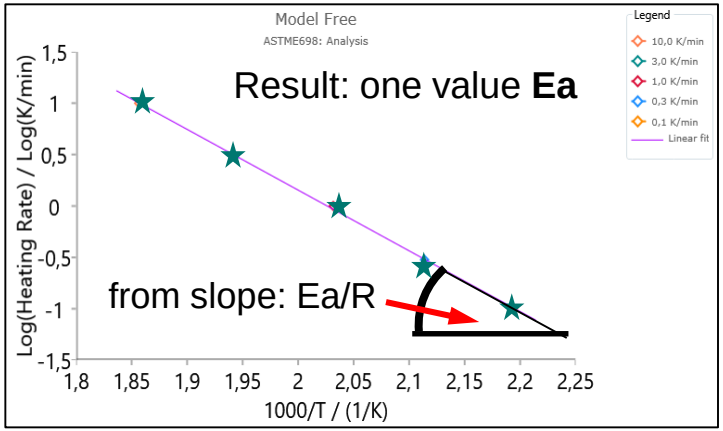
Created in last century before the modern possibilities of personal computers

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

Single-point model free methods

- ASTM E698
- ASTM E2890
- ASTM E1641





Only one point is analyzed,
All information about other data are lost.
May be used correct **for single-step reactions** where activation energy is constant
May be used **for single-point analysis** like OIT(oxidation induction time) or OOT(oxidation onset temperature)

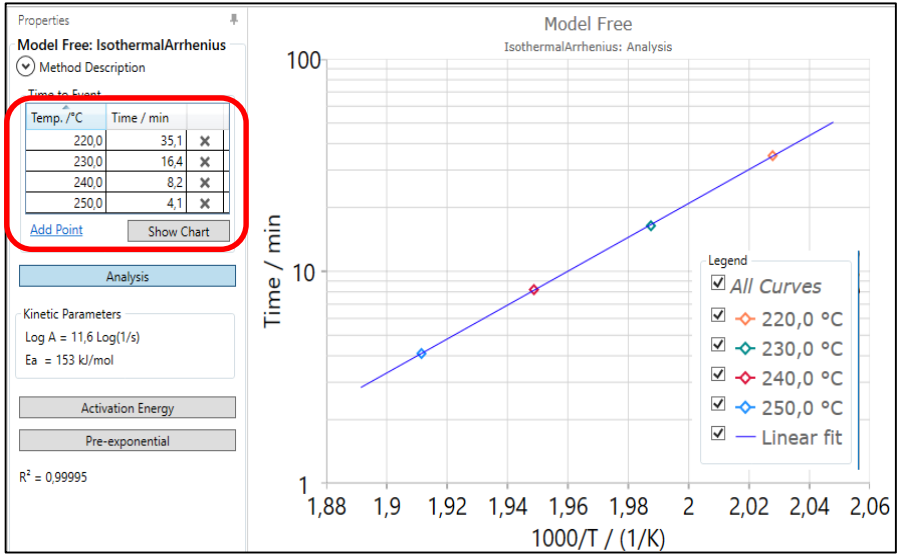
For multi-step reactions result is enable only at one point.
Result may used for single-point predictions

Time to Event: Analysis and Predictions (DSC, DMA etc.)

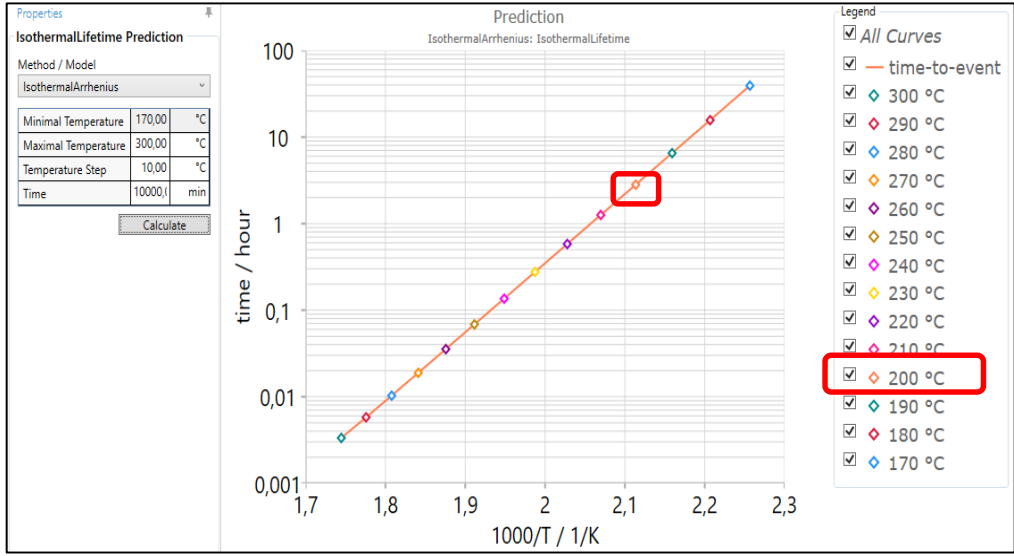
OIT (Oxidation induction time)

What is OIT at 200°C?

Analysis



Predictions



OIT at 200°C is 3 hours

Model-Free

A → B

α – degree of conversion

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

Unknown: Ea(α) and A(α)
A(α) can be found only with assumption of f(α)

Assumptions:
f(α) = 1
f(α) = 1 - α

Assumptions of this method (all must be fulfilled)

1. Only **one** kinetic equation
2. Ea and A **depend on α**
3. Reaction rate at the same conversion is only a function of temperature
4. Total effect (total mass loss or total peak area) must be the **same for all curves**
5. **Changes** of mechanism should be at the **same conversion** value

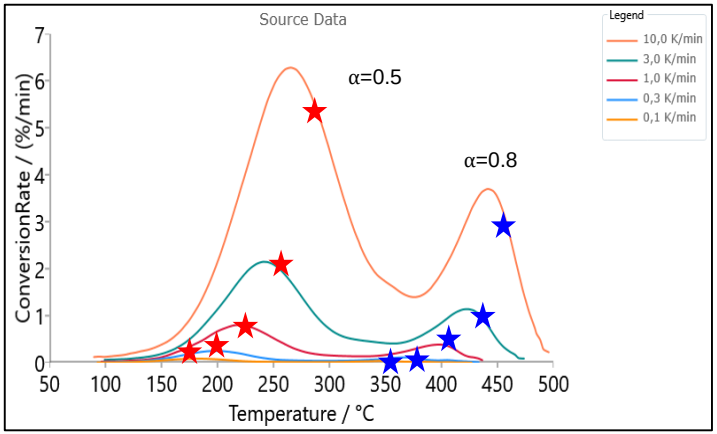
Model-Free Methods (Arrhenius Approach Only)

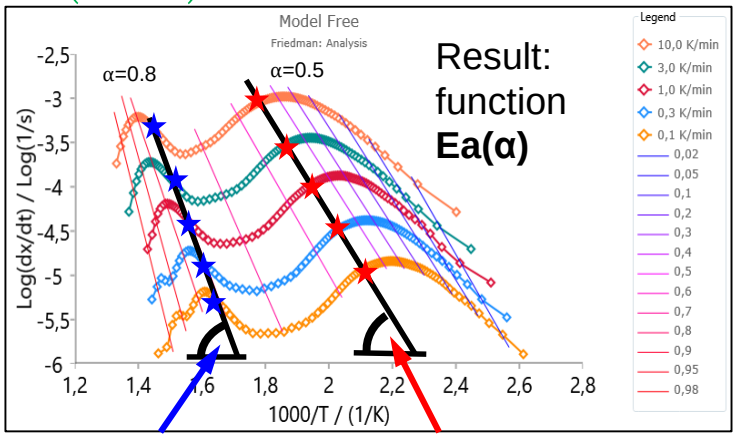
**Created in last century before the modern possibilities of personal computers*

Multi-points model free methods

- Ozawa-Flynn-Wall (1965)*
- Kissinger-Akahira-Sunose (1956)*
- Friedman method (1966)*
- Vyazovkin for heating (1996)*
- Numerical optimization

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





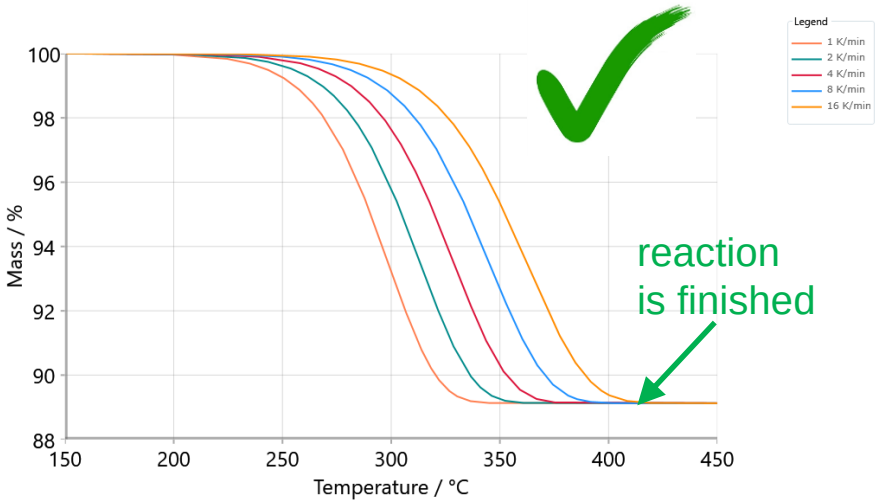
Ea (0.8) Ea (0.5)

All data are analyzed,
May be used correctly **for single-step reactions** where activation energy is constant
May be used correctly **for multi-reactions** where activation energy changes very slow

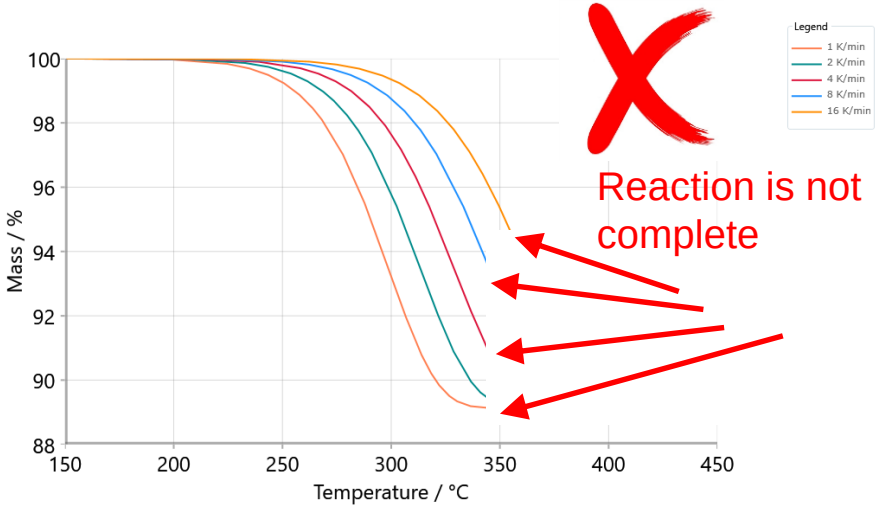
For multi-step reactions result is enable only under some conditions
Result may be used for predictions inside of the ranges of temperature and heating rates using for experimental data

When Model-Free Method is Applicable?

Reaction must be measured completely until its end



Model-free is applicable

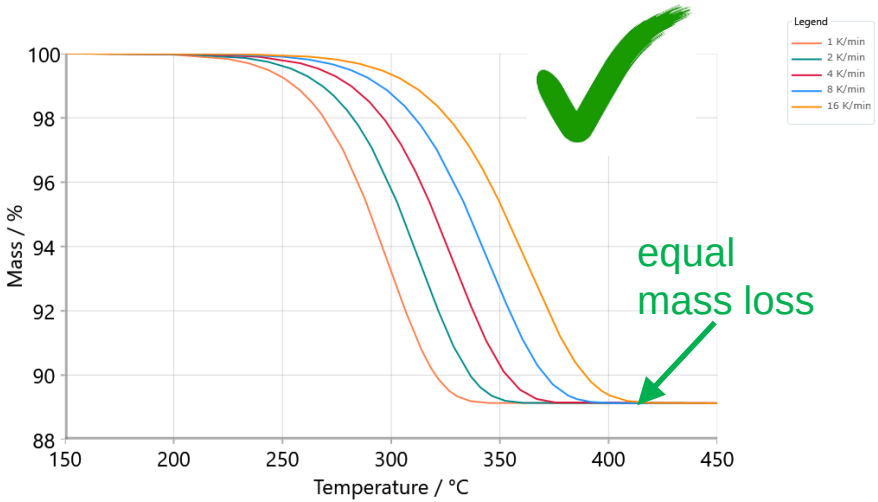


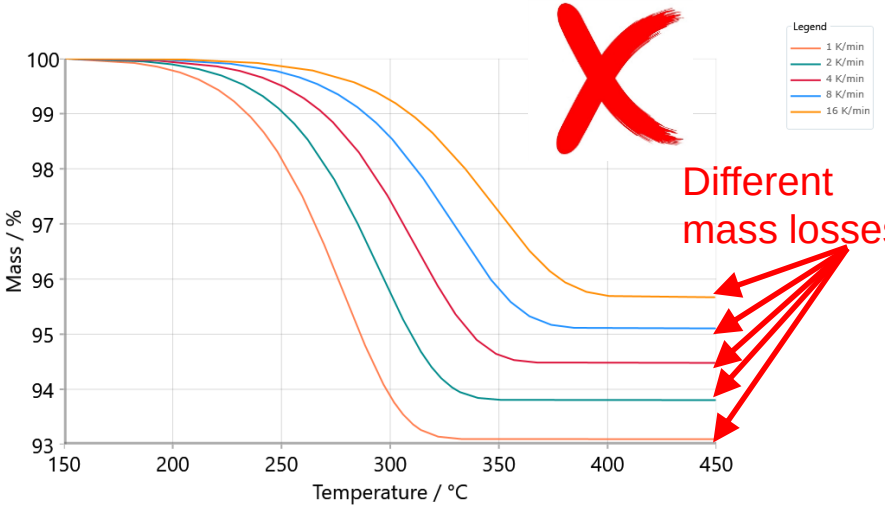
Model-free is **not** applicable

Solution: Model-based method
where total effect is unknown

When Model-Free Method is Applicable?

Total effect (total mass loss or total peak area) must be **the same** for all curves

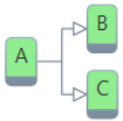




Model-free is applicable

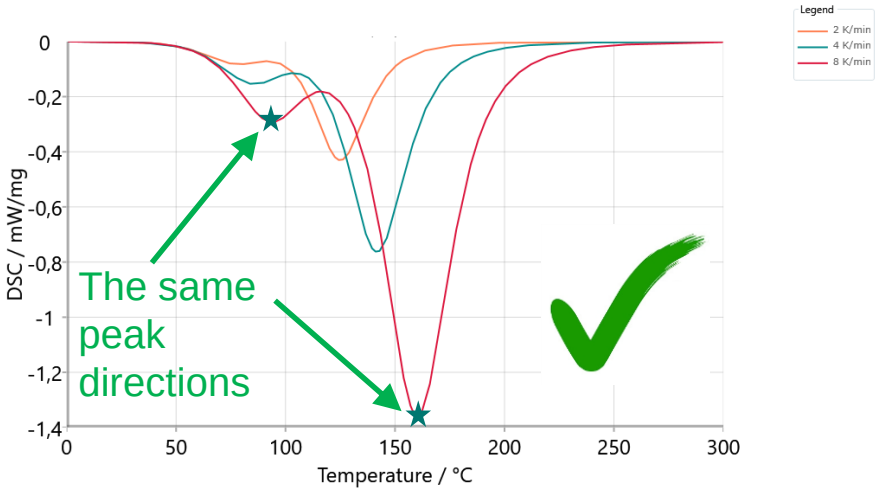
Model-free is **not** applicable

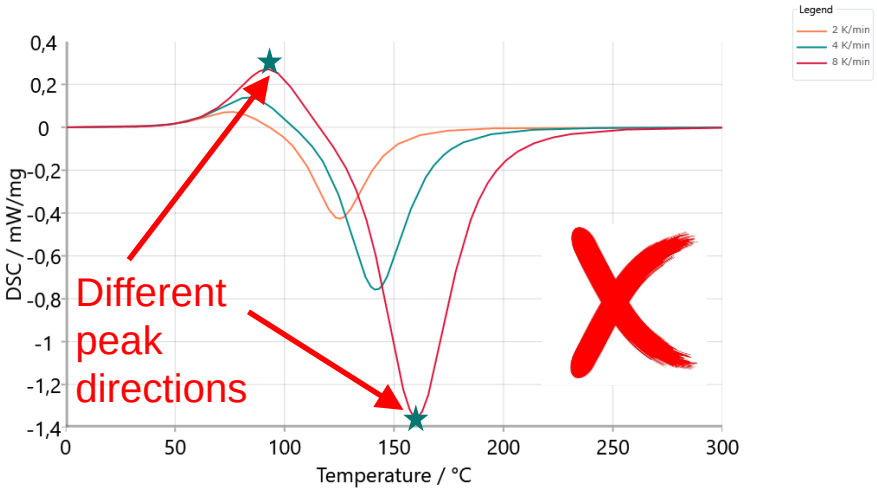
Solution: Model-based method
with competitive steps



When Model-Free Method is Applicable?

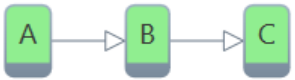
There is no reaction steps of **different directions**
(e.g. exothermal and endothermal, mass loss and mass gain)





Model-free is applicable

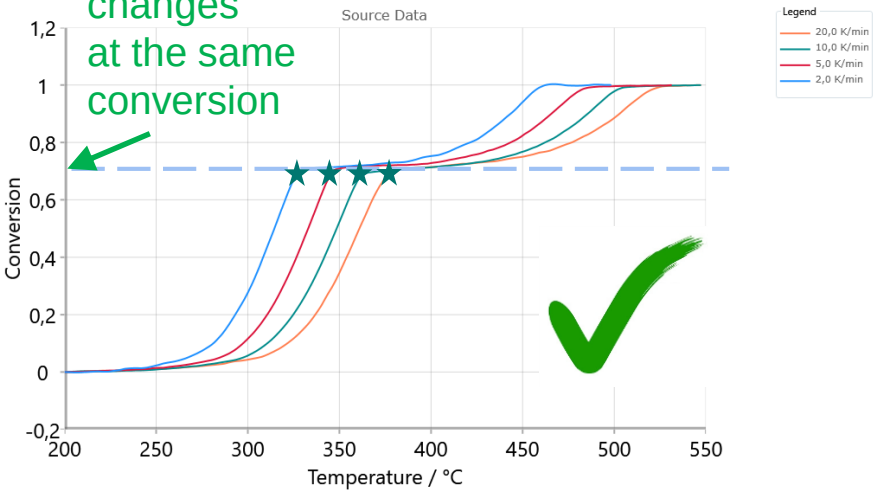
Model-free is **not** applicable
Solution: Model based method
with steps contributions of different signs



When Model-Free Method is Applicable?

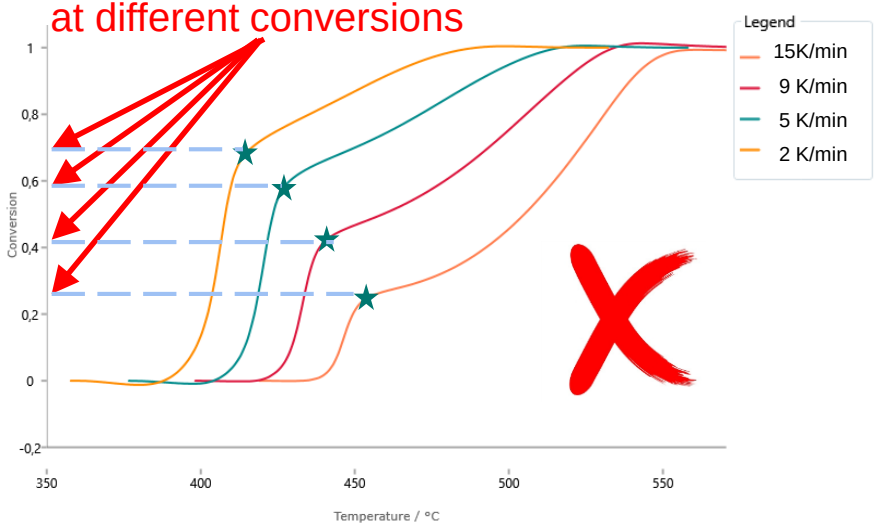
Changes of mechanism should be at **the same conversion** value

Mechanism changes at the same conversion



Model-free is applicable

Mechanism changes at different conversions



Model-free is **not** applicable

Solution: Model-based method with competitive steps

When model-free method is applicable

Total effect (total mass loss or total peak area) must be the same for all curves

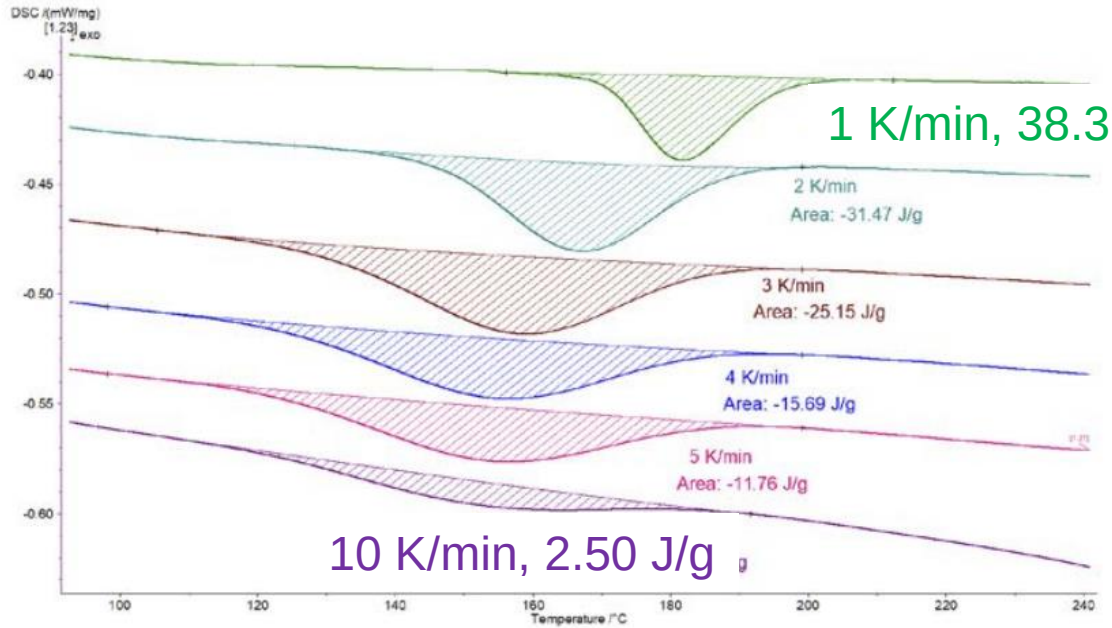


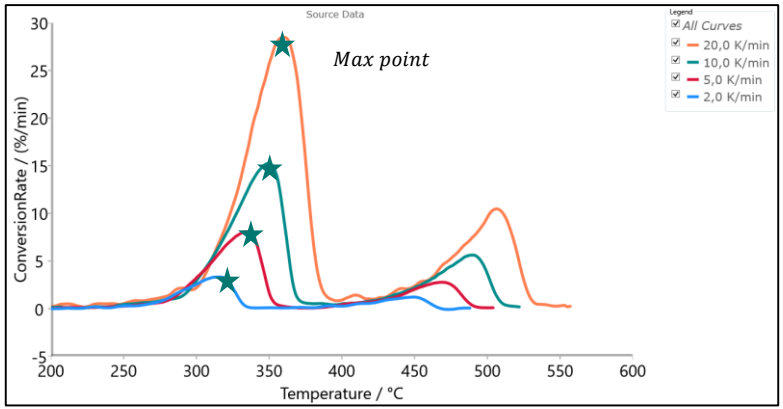
Fig. 1. Crystallization curves for polyethylene terephthalate (PET) measured at cooling rates from 1 to 10 K/min

Model free is **not** applicable

Solution: Model based method with non-Arrhenius approach

Crystallizatin of PET during cooling

ASTM E698 (refined Ozawa method for Maximum points)



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

$$G(x) = \int_0^x \frac{dx}{f(x)} = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E}{RT}\right) dT$$

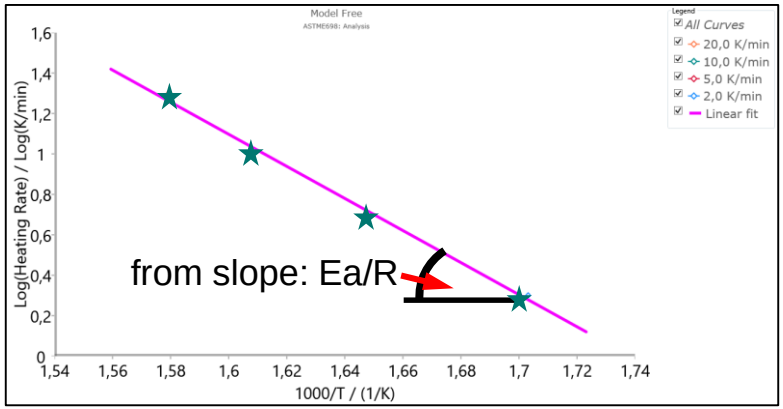
Take Integral, logarithm and approximate

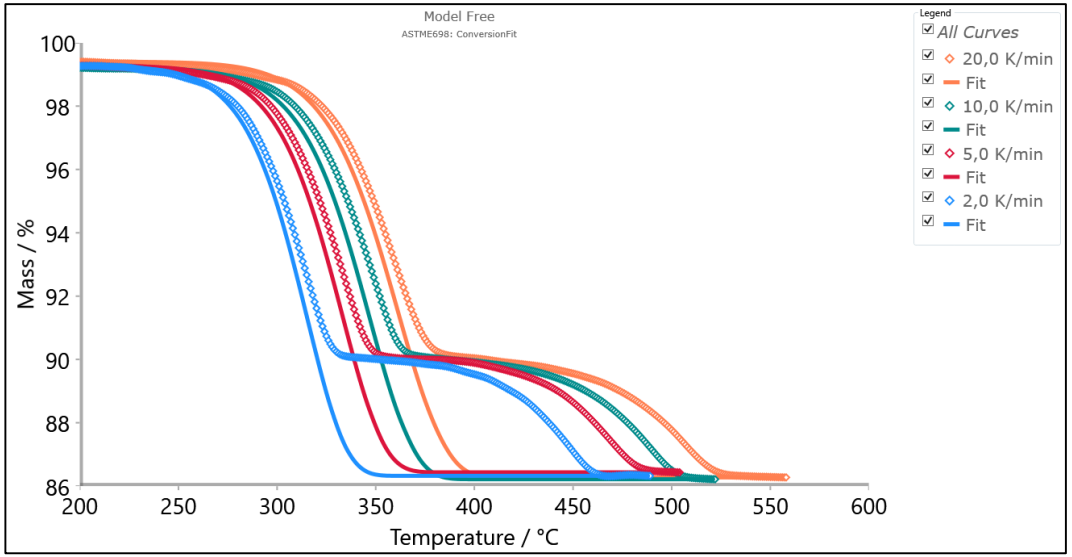
intersect

slope

$$\ln \beta = \ln\left(\frac{AE}{R}\right) - \ln G(x) - 5.3305 + 1.052\frac{E}{RT}$$

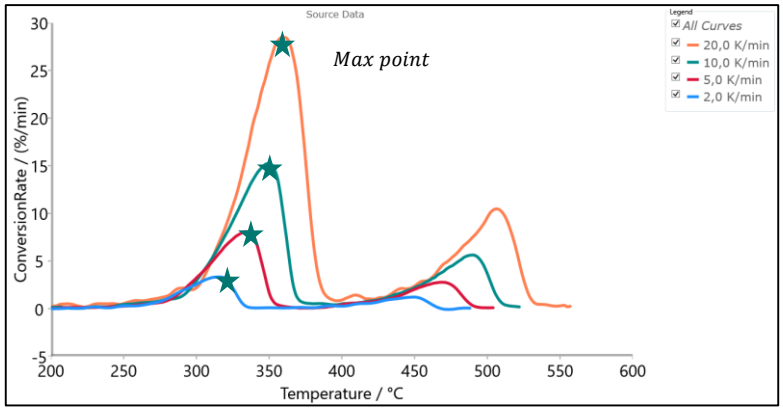
refine $E(\alpha) = -a \cdot R \Big/ \left(1 - \frac{1}{z} - \frac{1}{z+2}\right)$ where $z = \frac{-E(\alpha)}{RT}$





β is the heating rate, Data: decomposition of $La(OH)_3$

ASTM E2890 (Kissinger method)

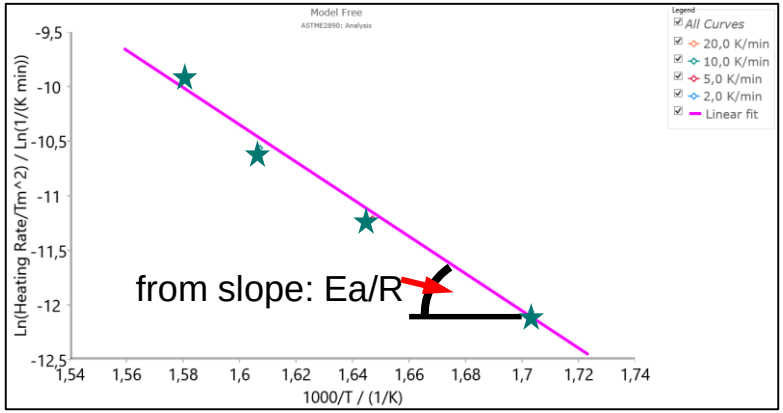


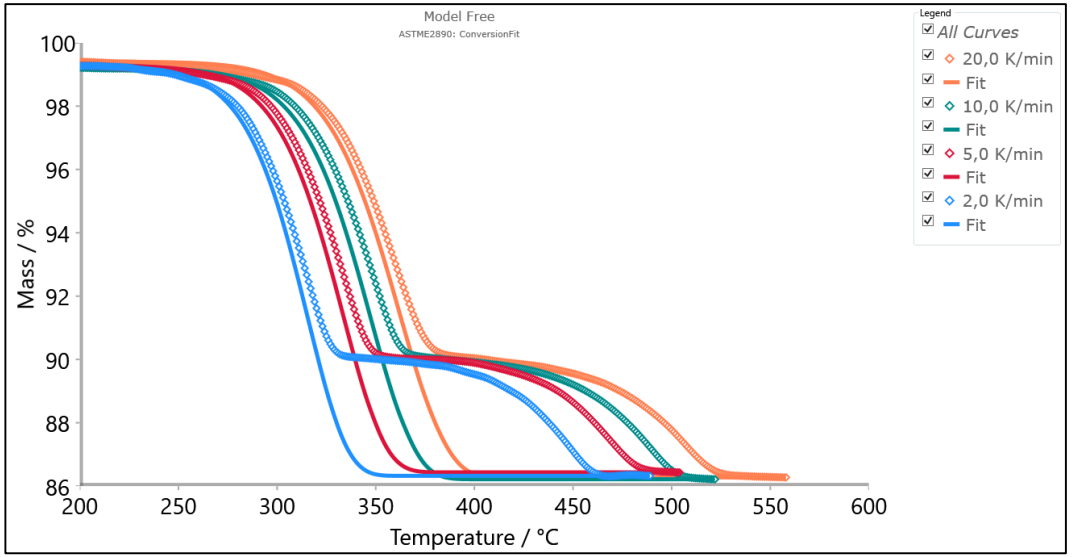
$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot exp\left(\frac{-Ea}{RT}\right)$$

Derivative at maximum point=0

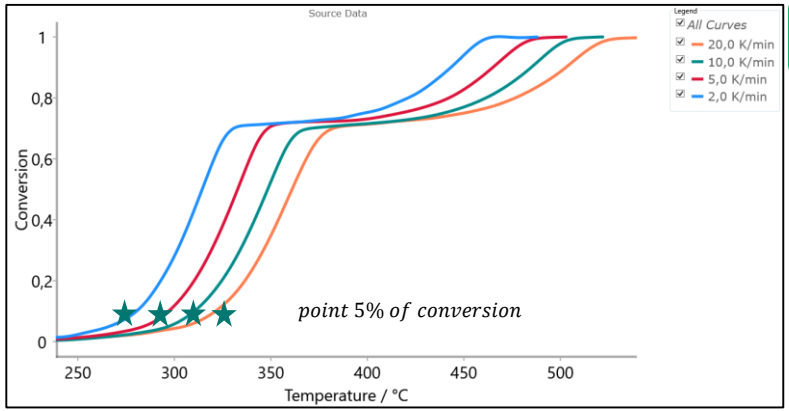
intersect slope

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{E}\frac{df(\alpha)}{d\alpha} - \frac{E(\alpha)}{RT}$$





ASTM E1641 (Ozawa method for 5% of conversion)



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

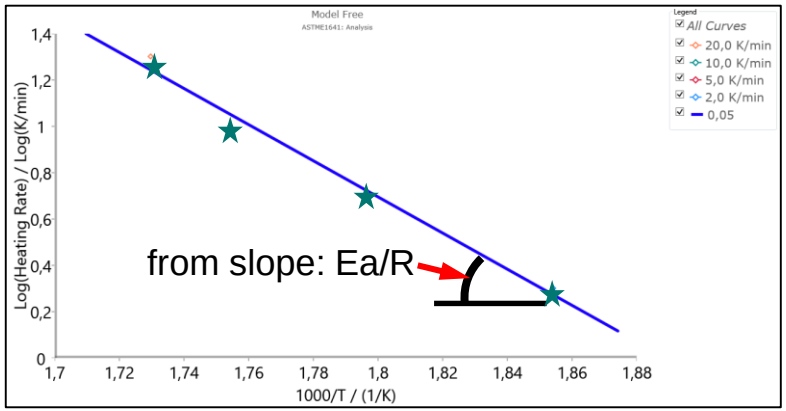
$$G(x) = \int_0^x \frac{dx}{f(x)} = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E}{RT}\right)dT$$

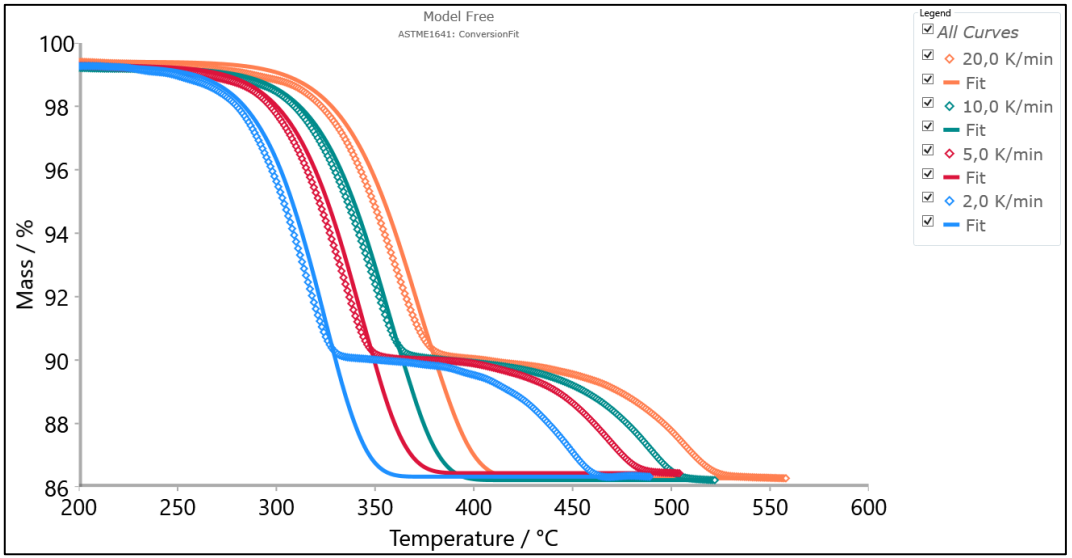
Take Integral and approximate

intersect

slope

$$\ln \beta = \ln\left(\frac{AE}{R}\right) - \ln G(x) - 5.3305 + 1.052\frac{E}{R}\frac{1}{T}$$





Ozawa-Flynn-Wall (1965, 1966) with Doyle Approximation (1962)

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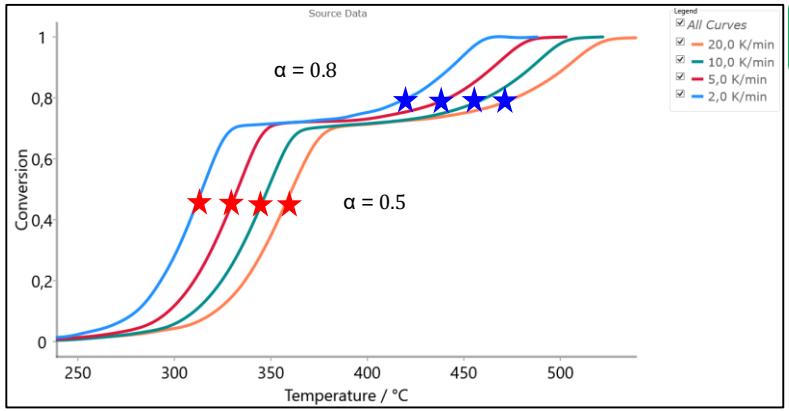


$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot exp\left(\frac{-Ea}{RT}\right)$$

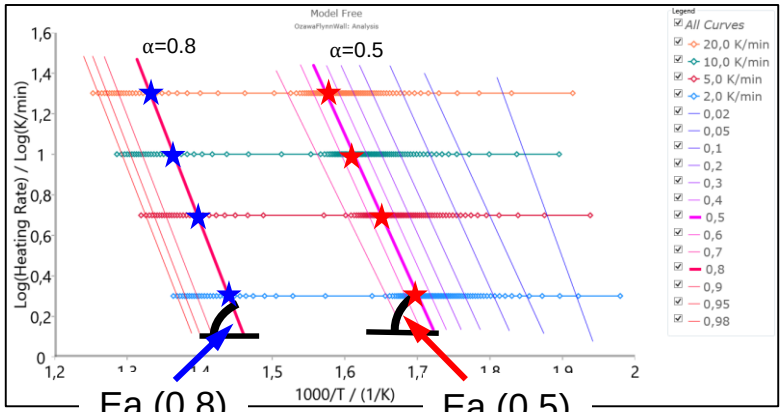
$$G(x) = \int_0^x \frac{dx}{f(x)} = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E}{RT}\right)dT$$

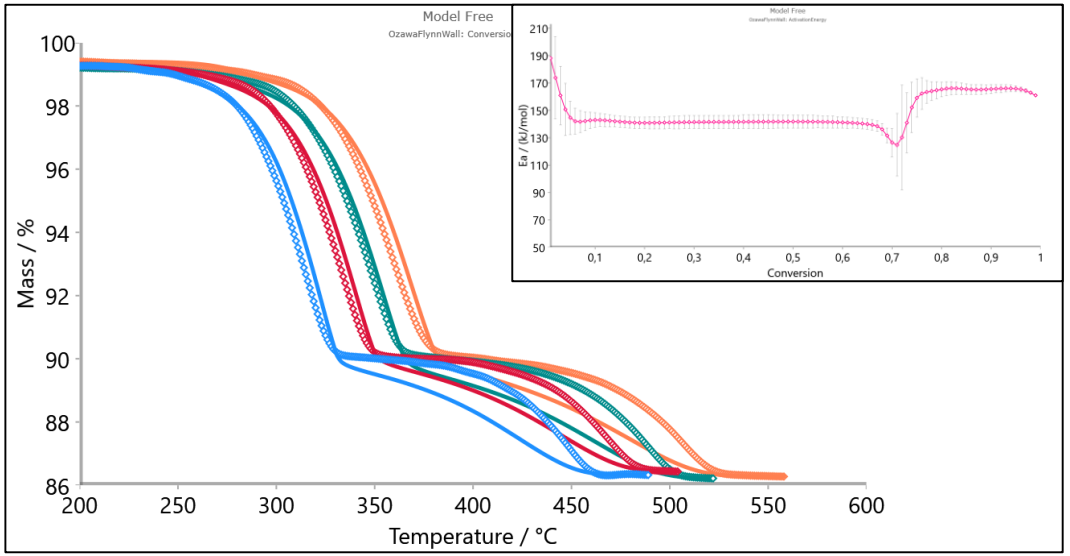
Take Integral and approximate

intersect

slope

$$\ln \beta = \ln\left(\frac{AE}{R}\right) - \ln G(x) - 5.3305 + 1.052\frac{E}{R}\frac{1}{T}$$





Kissinger-Arahira-Sunose (1956)

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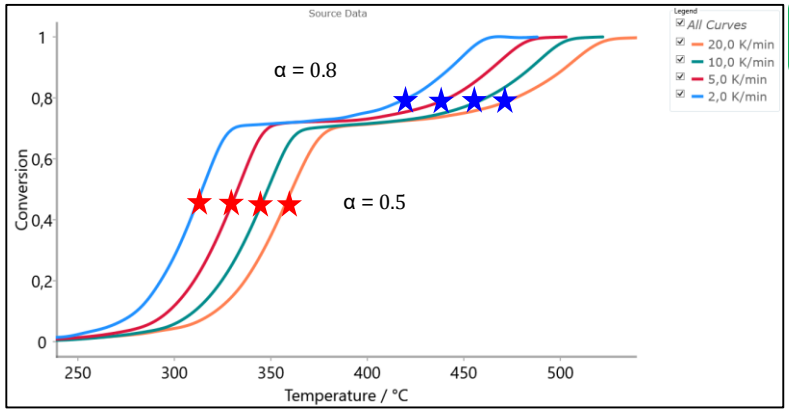


$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot exp\left(\frac{-Ea}{RT}\right)$$

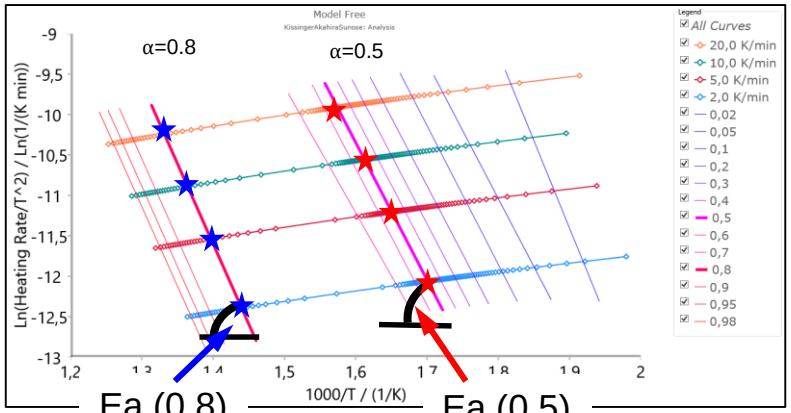
$$G(x) = \int_0^x \frac{dx}{f(x)} = \frac{A}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E}{RT}\right)dT$$

Take Integral, create series, take logarithm

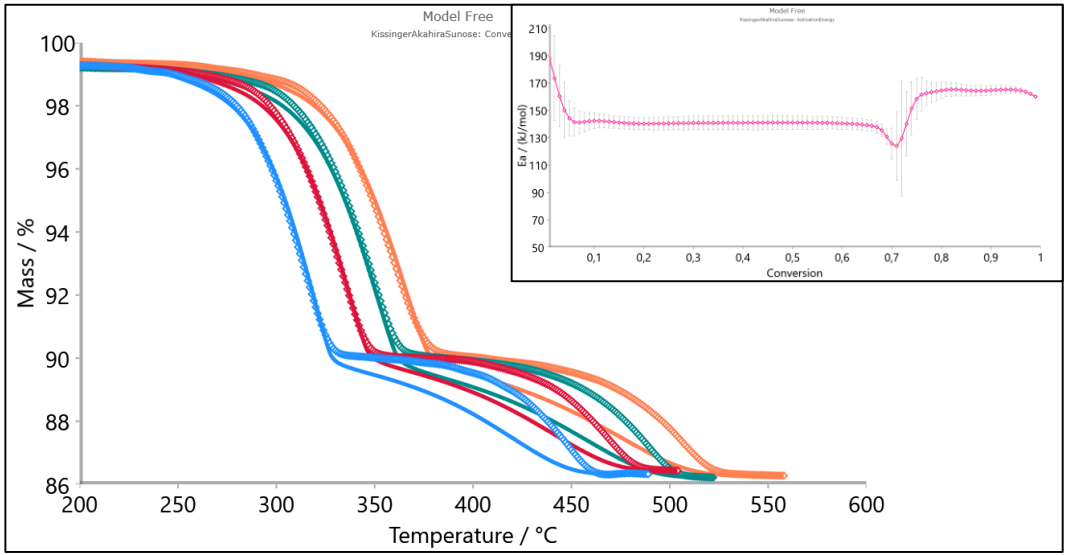
intersect

slope

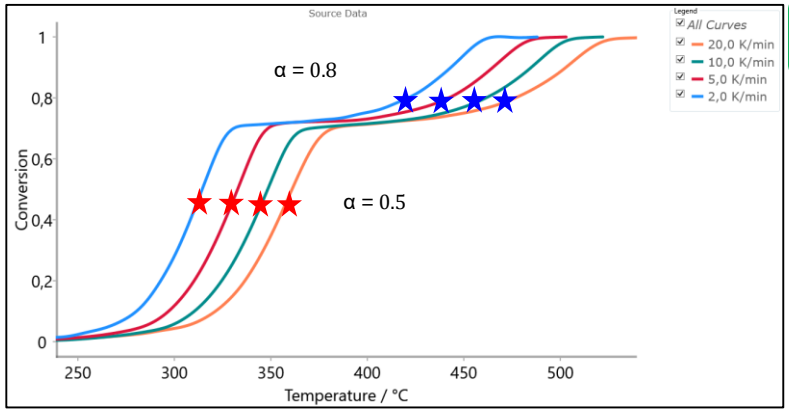
$$ln\left(\frac{\beta}{T^2}\right) = \boxed{ln[A(\alpha)] - ln\int_0^{\alpha}\frac{d\alpha}{f(\alpha)} + ln\left(\frac{R}{E}\right)} - \boxed{\frac{E}{RT}}$$



Ea (0.8) Ea (0.5)



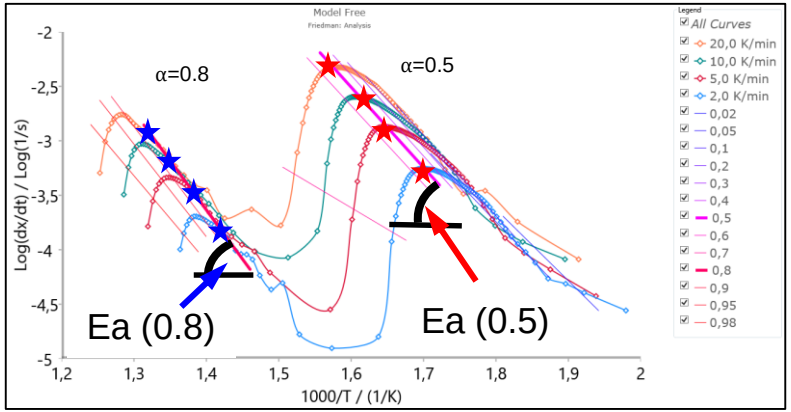
Friedman (1966)

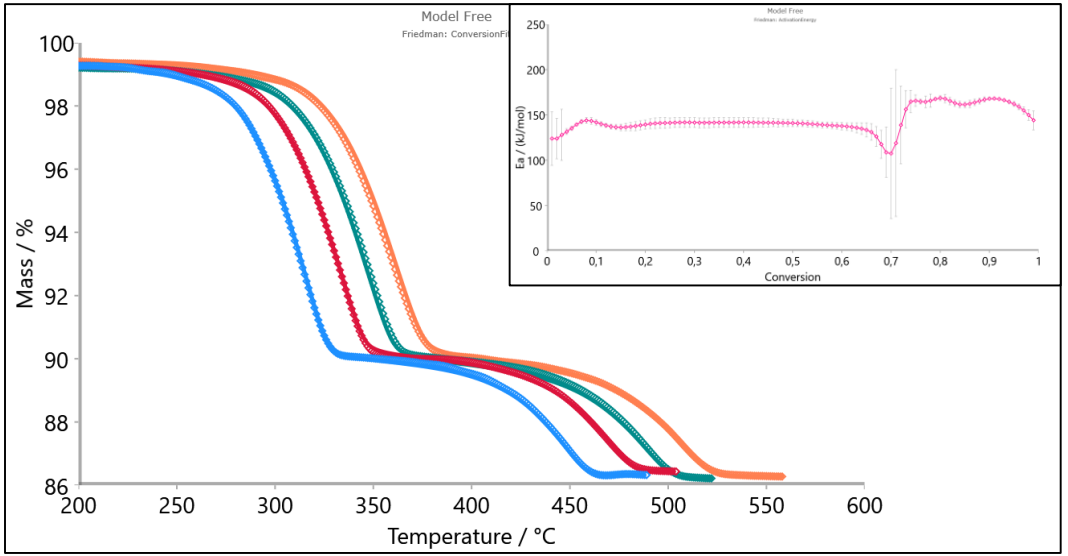


$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot exp\left(\frac{-Ea}{RT}\right)$$

intersect slope

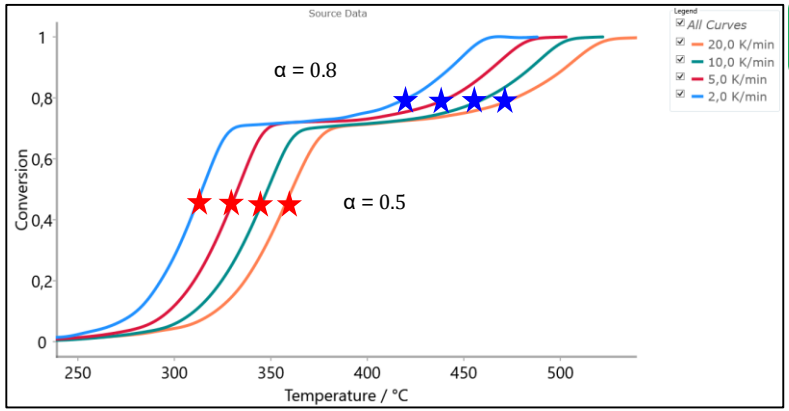
Take logarithm $\ln\left(\frac{dx}{dt}\right)_{x=\alpha_i} = \ln\left(A \cdot f(x)\right) - \frac{E}{R} \cdot \frac{1}{T}$





x is degree of conversion (the same as α)

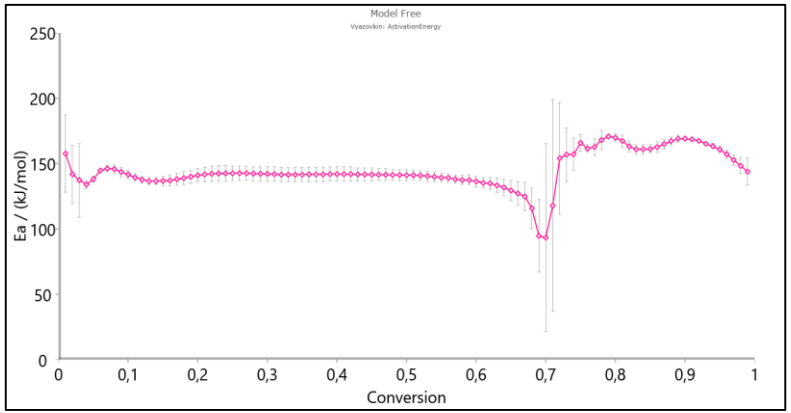
Vyazovkin (1996)

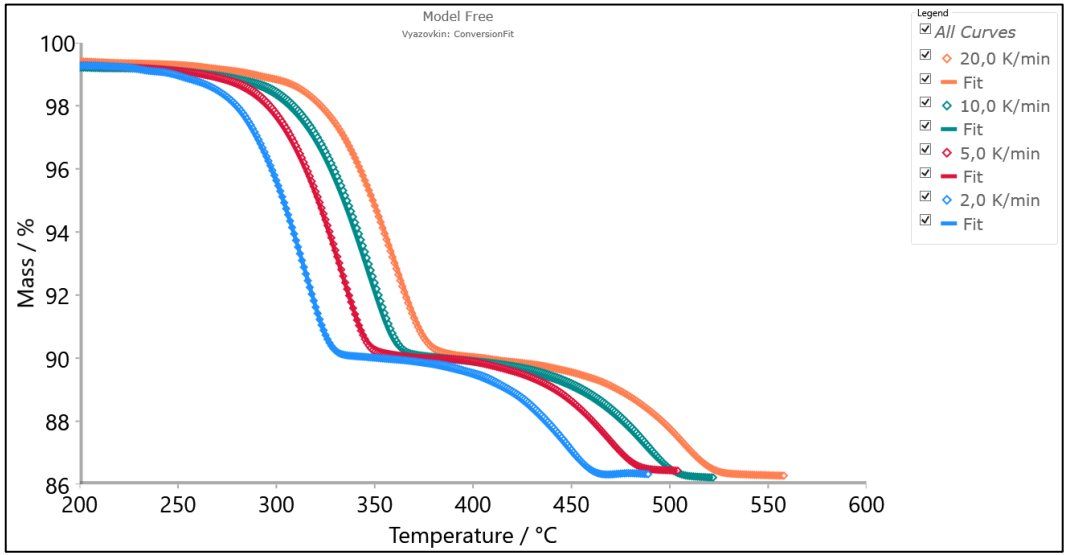


$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot exp\left(\frac{-Ea}{RT}\right)$$

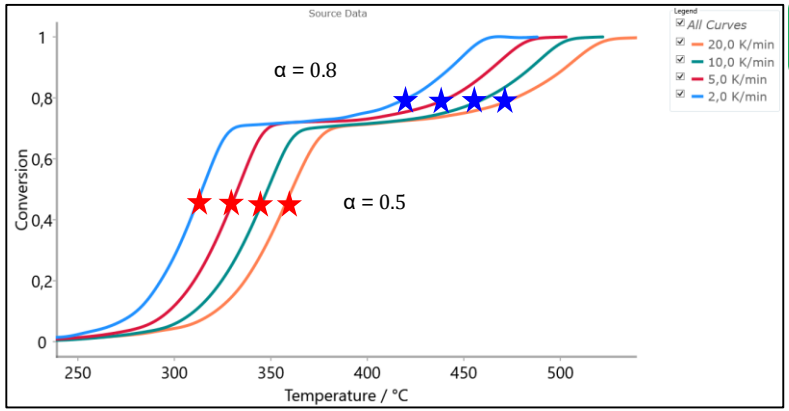
Find minimum of function

$$\psi(\alpha_k) = \sum_i \sum_{j \neq i} \frac{\frac{1}{\beta_i} \cdot \int_{T_0}^{T_{ki}} exp\left(\frac{-E(\alpha)}{RT}\right) dT}{\frac{1}{\beta_j} \cdot \int_{T_0}^{T_{kj}} exp\left(\frac{-E(\alpha)}{RT}\right) dT}$$





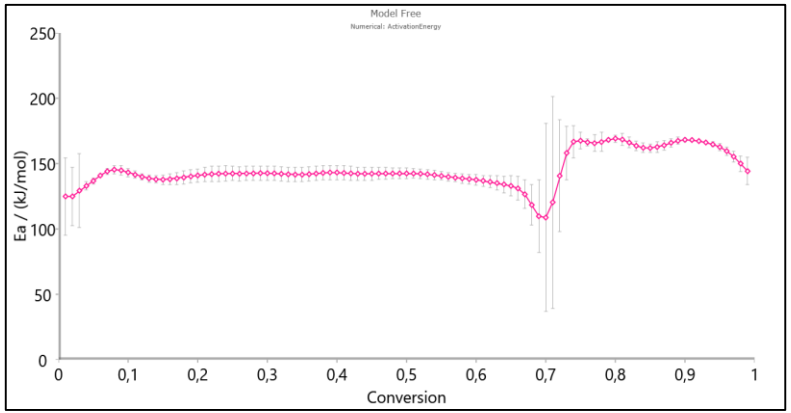
Numerical

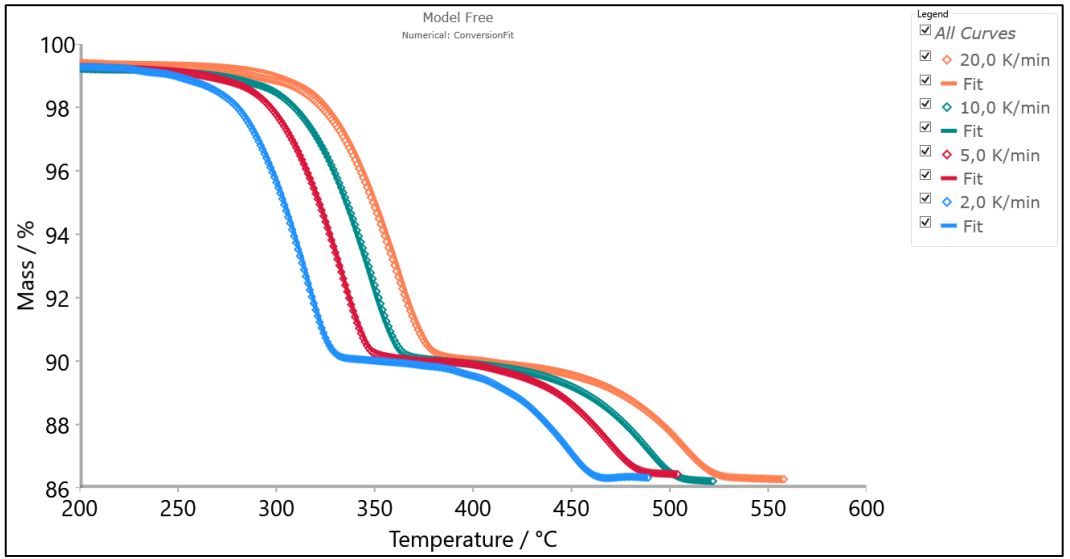


$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot exp\left(\frac{-Ea}{RT}\right)$$

Find minimum of function

$$\psi = \sum_{curves} \sum_{points} \left(\alpha_i^{calc} - \alpha_i^{exp}\right)^2$$

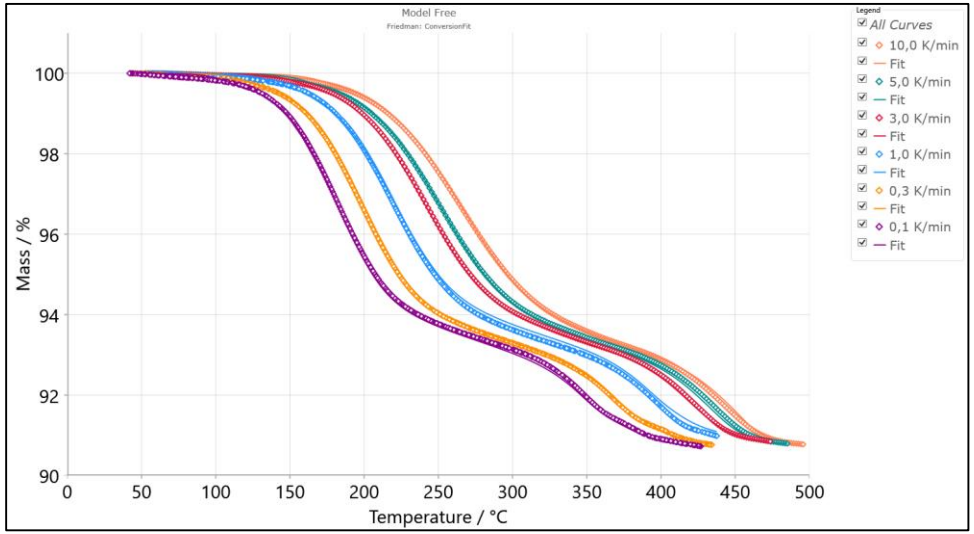




Comprison of results

Method/Model	Fit To	R^2	Sum of dev. squares	Mean Residual	Students coef. 95%	F-Test	Degree of Freedom	
Numerical	Signal	0,99984	9,782	0,063	1,962	1,000	1075	✕
Vyazovkin	Signal	0,99980	11,957	0,073	1,962	1,222	1075	✕
Friedman	Signal	0,99977	14,122	0,083	1,962	1,444	1075	✕
OzawaFlynnWall	Signal	0,99081	552,587	0,471	1,962	56,488	1075	✕
KissingerAkahiraSunose	Signal	0,99006	596,912	0,467	1,962	61,019	1075	✕
ASTME1641	Signal	0,92794	4194,172	1,219	1,962	362,628	1271	✕
ASTME2890	Signal	0,91803	4746,057	1,294	1,962	410,344	1271	✕
ASTME698	Signal	0,91783	4757,105	1,297	1,962	411,300	1271	✕
ASTME2070	Signal	0,78944	11374,434	1,934	1,962	1162,740	1075	✕

Model-free method (Friedman analysis) is applicable *if conditions are met*



1. Measurements are done for the whole reaction until its end
2. Total effect (total mass loss or total peak area) is the same for all curves
3. There is no reaction steps of different directions
4. Changes of mechanism should be at the same conversion value

~~Mixtures~~
~~Competing steps~~
~~Curing with diffusion control~~
~~Non-isothemal crystallization~~

~~Information about intermediate reactants~~
~~Information about individual reaction steps~~

The same effect for all curves
Mechanism changes at the same conversion

We recommend to use model-free methods:

1. Friedman
2. Vyazovkin
3. Numerical

2.2. Model-based Kinetic Methods

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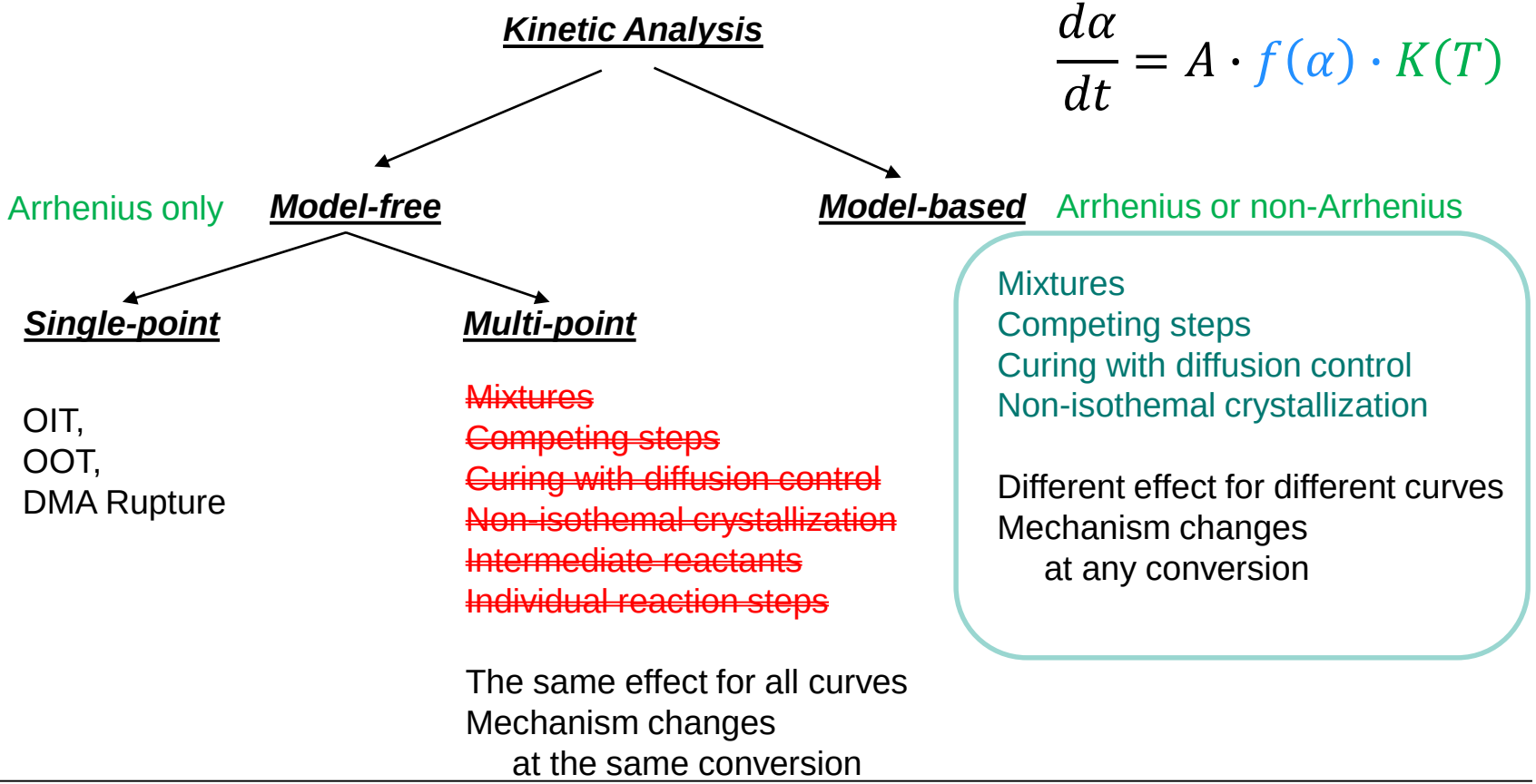

Kinetic Analysis
$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$
Arrhenius only
Model-free
Model-based
Arrhenius or non-Arrhenius
Single-point
Multi-point
OIT,
OOT,
DMA Rupture
~~Mixtures~~
~~Competing steps~~
~~Curing with diffusion control~~
~~Non-isothemal crystallization~~
~~Intermediate reactants~~
~~Individual reaction steps~~
The same effect for all curves
Mechanism changes
at the same conversion
Mixtures
Competing steps
Curing with diffusion control
Non-isothemal crystallization
Different effect for different curves
Mechanism changes
at any conversion

NETZSCH

Model based

A → B → C → …

a – concentration of A
b – concentration of B
c – concentration of C

$$\frac{d(a \rightarrow b)}{dt} = A_1 \cdot f_1(a.b) \cdot exp\left(\frac{-E_{A1}}{RT}\right)$$

$$\frac{d(b \rightarrow c)}{dt} = A_2 \cdot f_2(b.c) \cdot exp\left(\frac{-E_{A2}}{RT}\right)$$

The number of unknown kinetic triplets equals the number of the steps

Assumptions:

1. Reaction consists of **several individual reaction steps** with own equations.
2. All kinetic parameters which are the **constant values**
3. The **total signal** is the **sum** of the signals of the single reaction steps having **own weight**

Model-based approach requires selection

Multi-step model (connection of steps)

independent
consecutive
competing

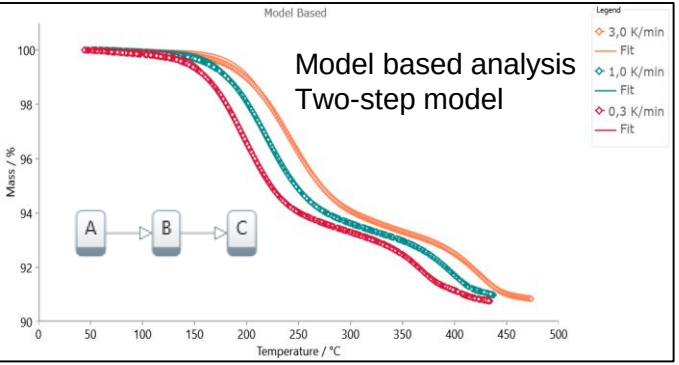
Reaction type for each step (f(α))

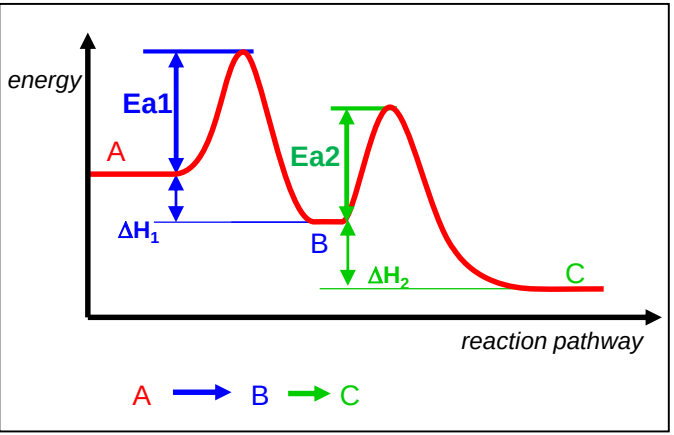
n-th order
autocatalysis
nucleation
Diffusion control

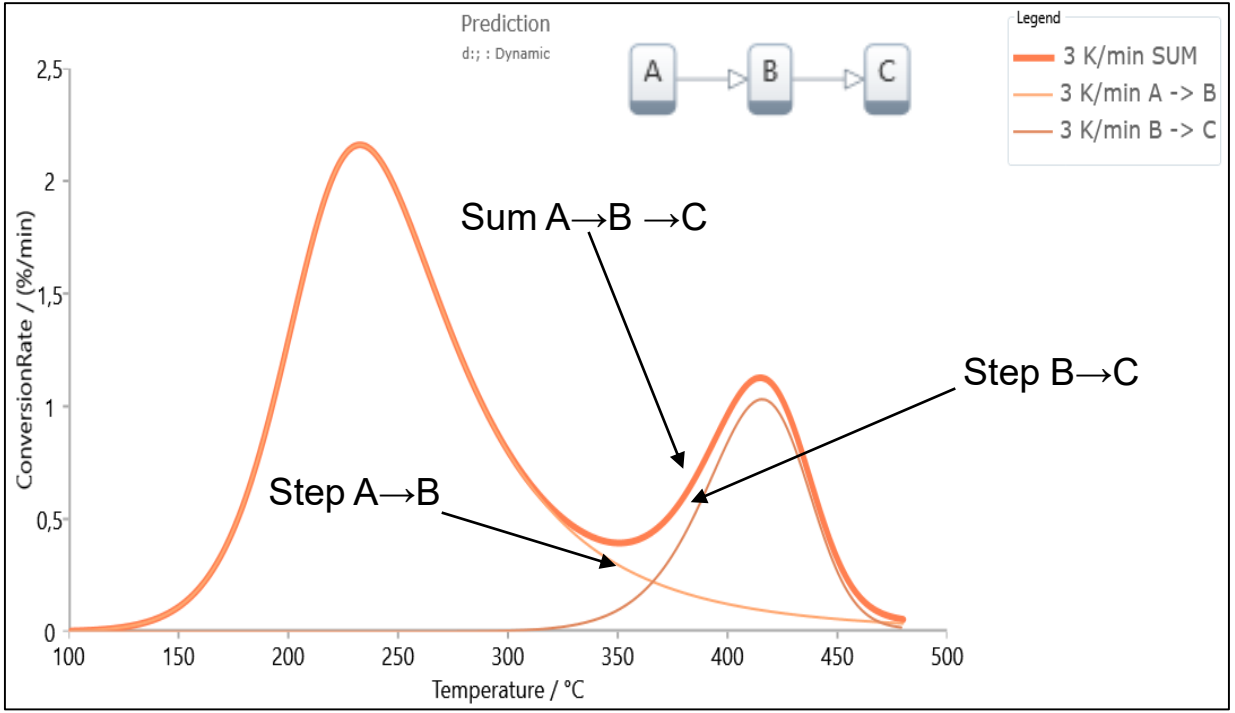
Temperature type for each step (K(T))

Arrhenius
Hofmann-Lauritzen

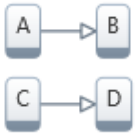
Model based: sum of individual reactions







Multi-step model-fitting: connection between steps

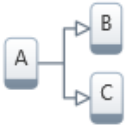


Independent

Mixture of non-interacting components

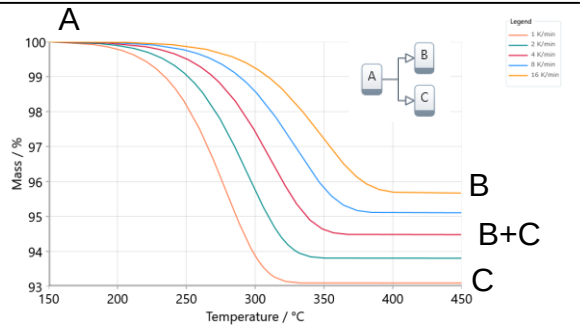
Consecutive

Reaction in the single component



Competing

Product depends on heating rate



Competing

Independent: reactant and product are not involved in other steps

Consecutive: product of one step is a reactant of another step

Competing: involve the same reactant

2.2. Model-based Kinetic Methods

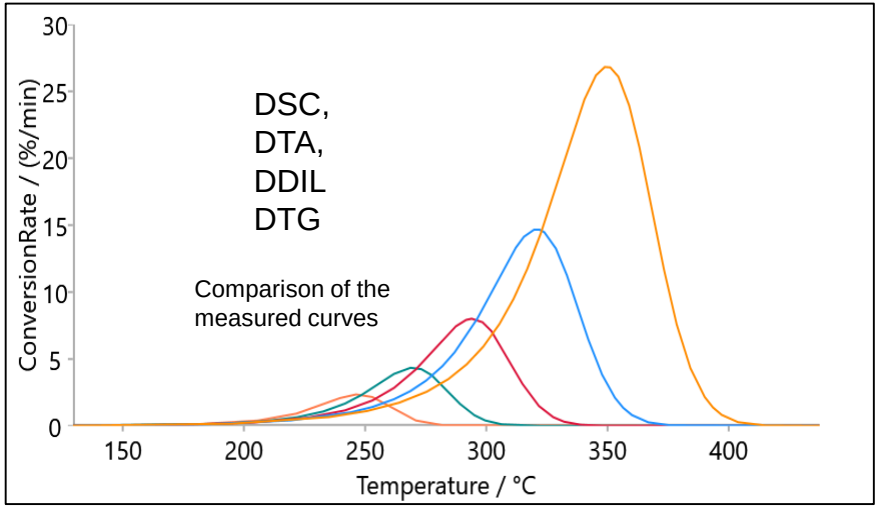
2.2.1 Selection number of steps

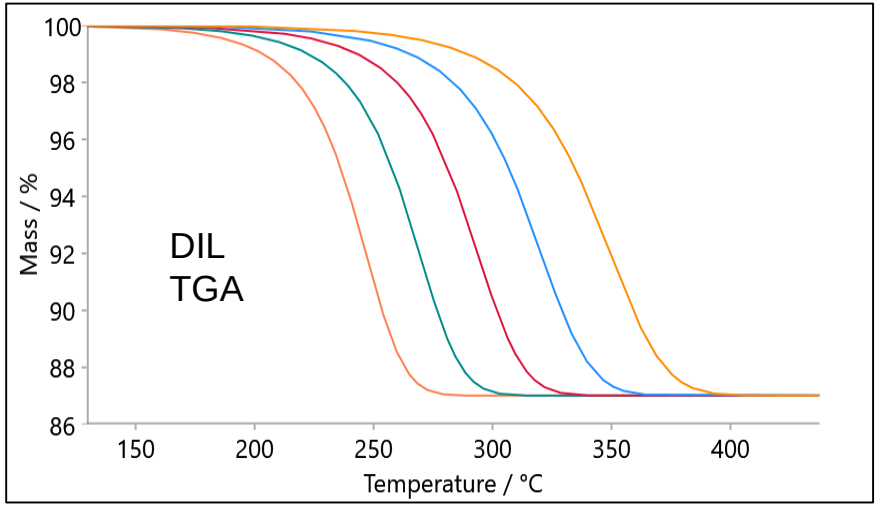
2.2.2 Are there competing steps?

2.2.3 Reaction type for individual steps

Single-step or multi-step Reaction?

Characteristic for single-step reactions:

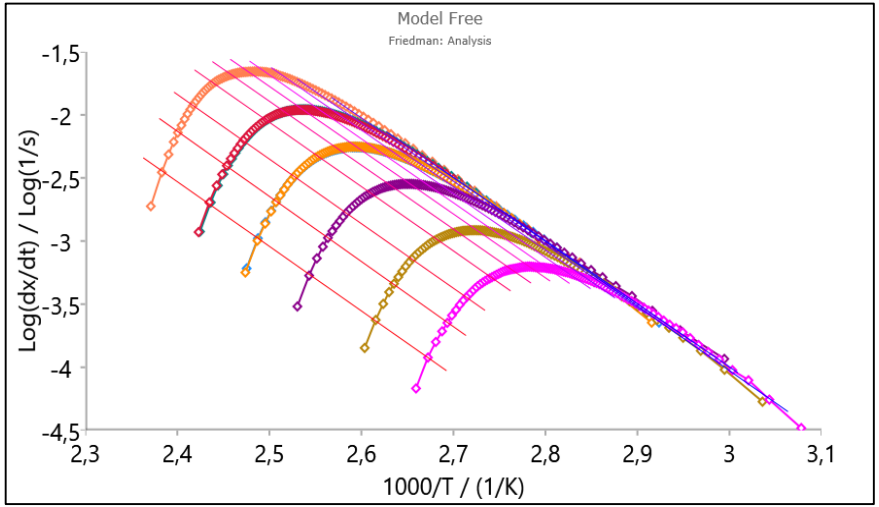


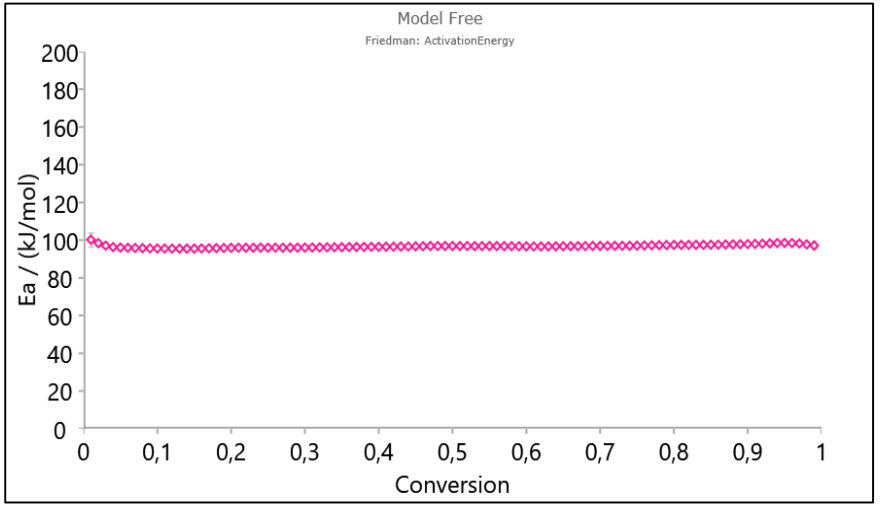


One effect (peak, step, etc.) per measurement and/or the peak area, the mass loss or the length change (DIL) is independent from the heating rate.

Single-step or multi-step Reaction?

Characteristic for single-step reactions:



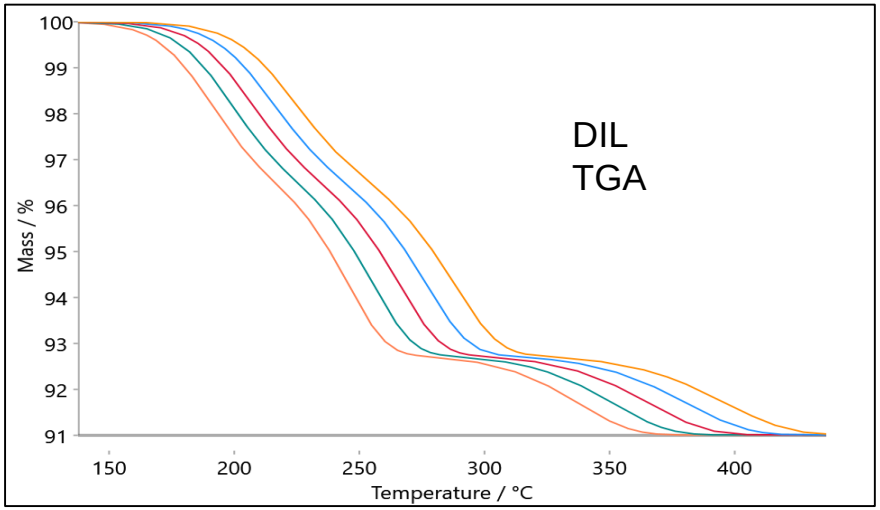


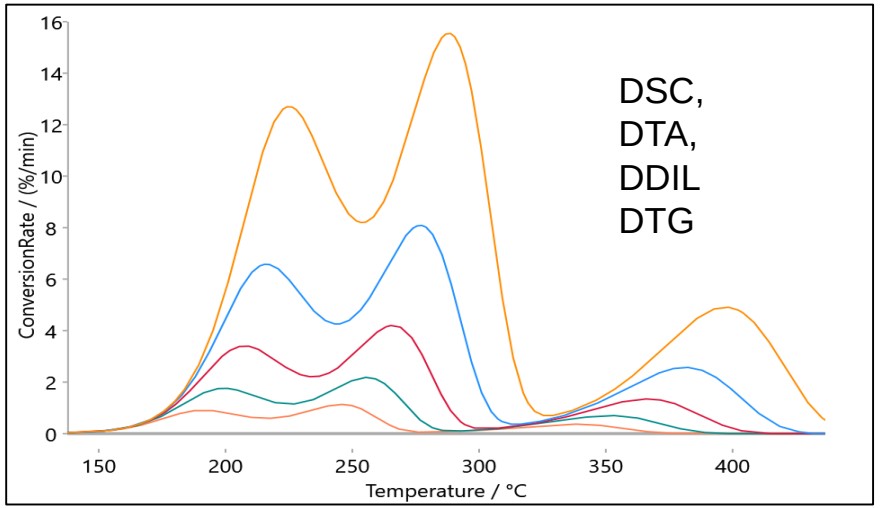
In the Friedman-Energy plot, the activation energy is constant

Pre-installed Example:Azobenc_Analysis.kinx2

Single-step or multi-step Reaction?

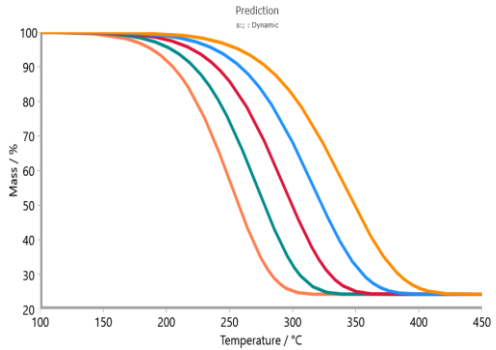
Characteristic for multi-step reactions (1):



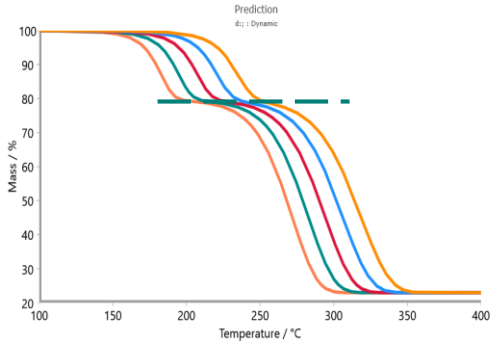


Several effects per measurement

Model choice: consecutive steps

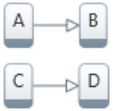


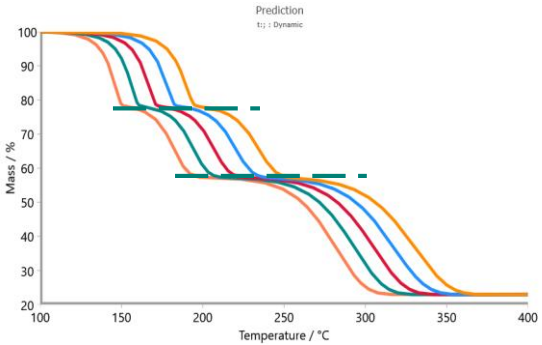
Single-step reaction



Decomposition of one component

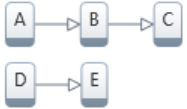
Decomposition of mixture
of two independent components



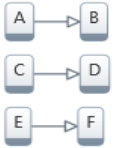


One component

Mixture of two independent components

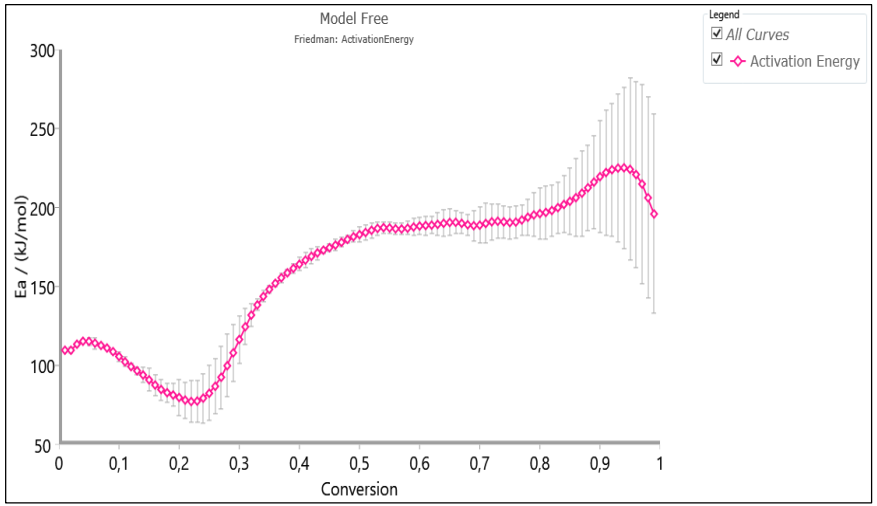


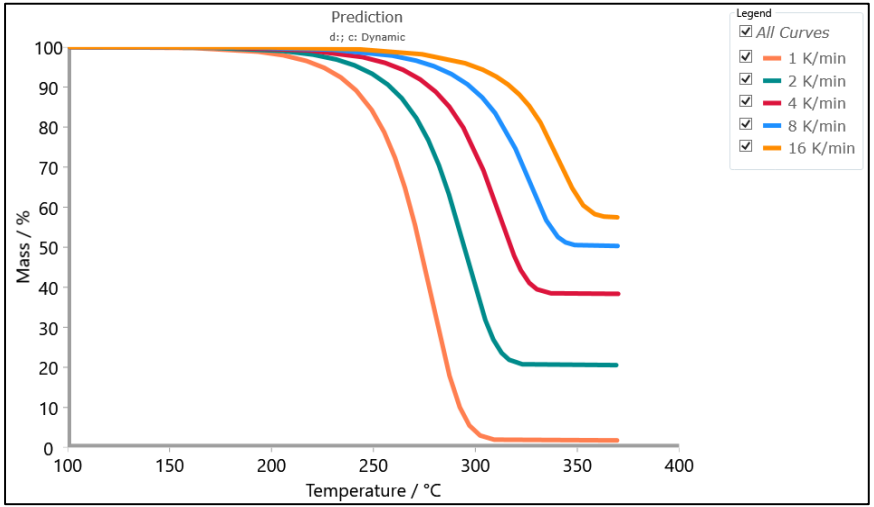
Mixture of three components



Single-step or multi-step Reaction?

Characteristic for multi-step reactions (2):

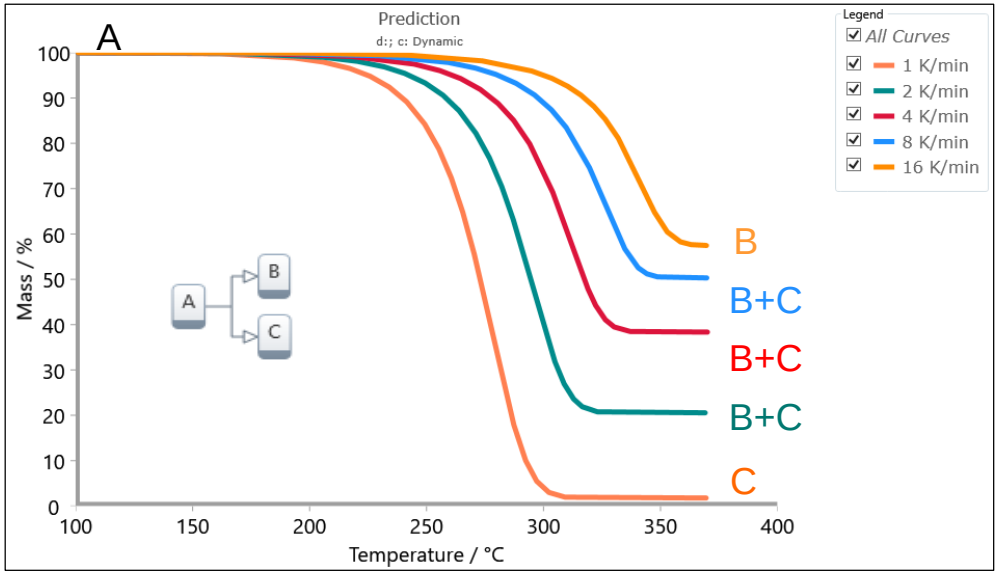




The activation energy in the Friedman-Energy plot is not constant (difference more than 20%)

The peak area, mass loss or length change are dependent on the heating rate

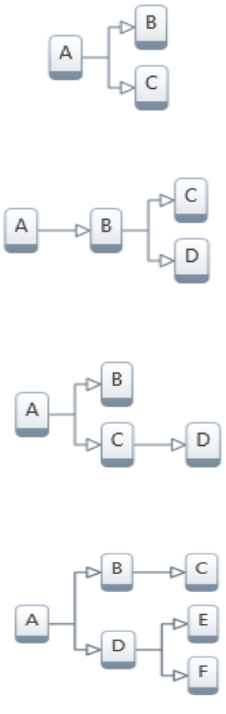
Are Competing Reactions Involved?



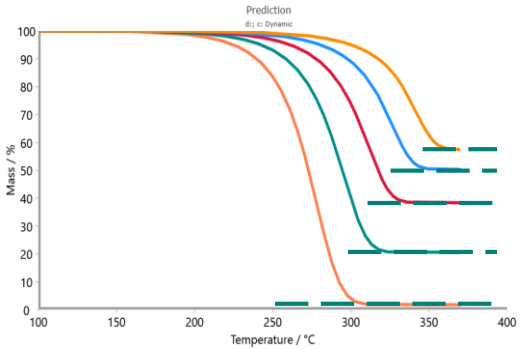
If the peak area, the mass loss or the length change are dependent on the heating rate, a reaction branching occurs.

Each branching shows only one peak in the corresponding DSC (DTA, DDIL, DTGA) curve.

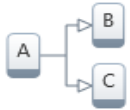
Competing reactions

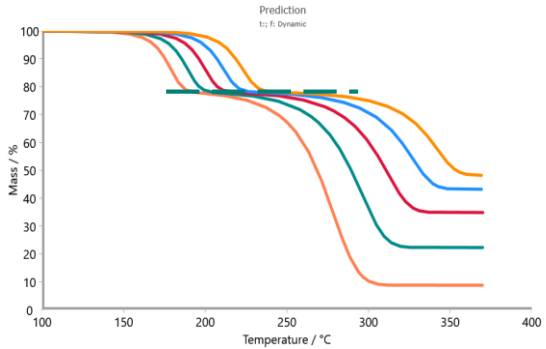


Model choice: competitive steps

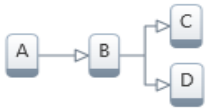


Final material is
the mixture of two products

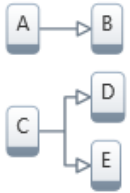


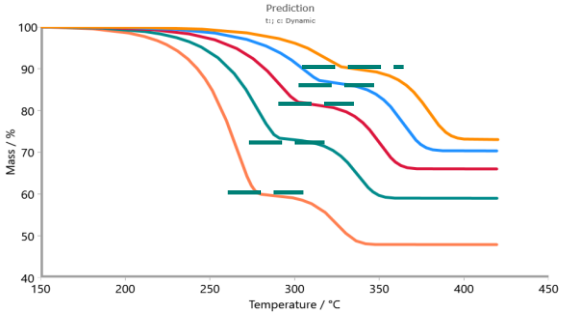


Decomposition of one component



Decomposition of mixture
of two independent components

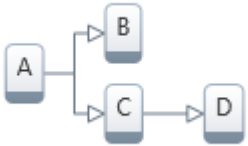




Decomposition of one component

The first step is competing
with two products

Then one of products decomposes again



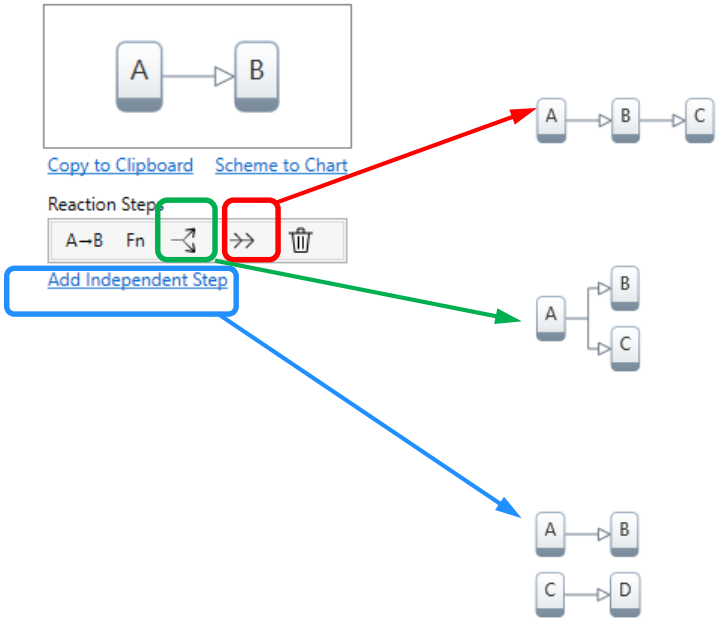
How many steps do we really need in the model?

1. The number of steps must correspond to the number of visible peaks/shoulders
2. The additional competing steps may be inserted if the total effect depends on heating rate
3. The model with n+1 steps must be compared with the model with n steps according to F-Test

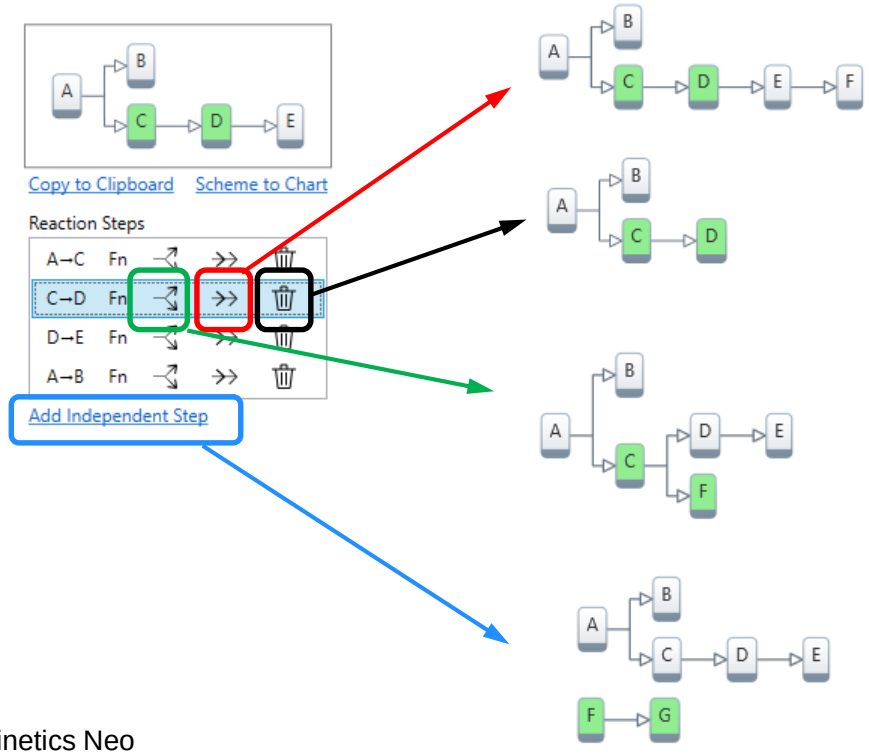
Method/Model	Fit To	R^2	Sum of dev. squares	Mean Residual	Students coef. 95%	F-Test	Degree of Freedom	
Numerical	Signal	0,99960	2,035	0,035	1,964	1,000	541	✕
s;;	Signal	0,99955	2,325	0,044	1,963	0,842	734	✕
Friedman	Signal	0,99923	3,921	0,052	1,964	1,927	541	✕
KissingerAkahiraSunose	Signal	0,98024	100,227	0,217	1,964	49,259	541	✕
OzawaFlynnWall	Signal	0,97675	117,695	0,242	1,964	57,844	541	✕
ASTME1641	Signal	0,97151	143,843	0,263	1,963	51,895	737	✕
ASTME2890	Signal	0,95555	222,630	0,443	1,963	80,319	737	✕
ASTME698	Signal	0,94781	260,361	0,453	1,963	93,931	737	✕

Add/Delete steps in the model in Kinetics Neo

1. Current single step model:



2. Current multi-step model with selected step C-D



There is no limitations in number of steps or their connections in Kinetics Neo

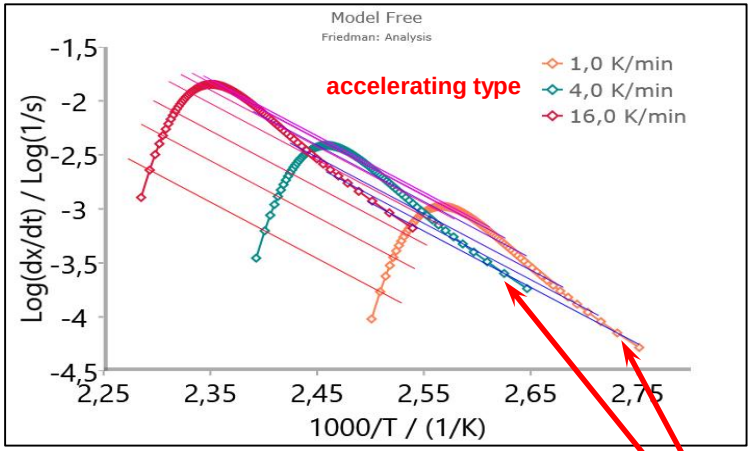
2.2. Model-based Kinetic Methods

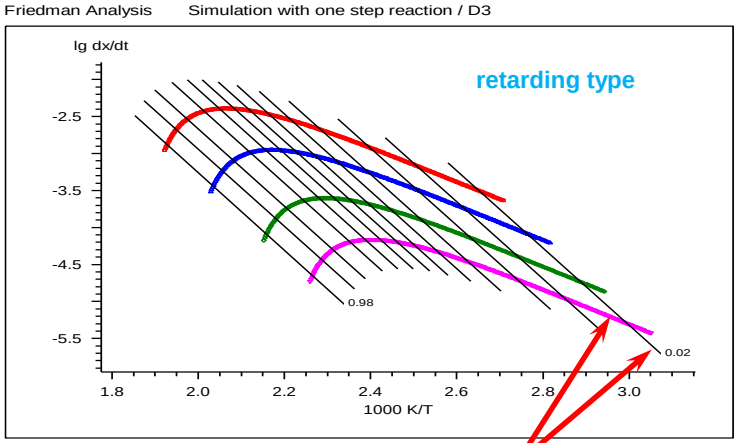
2.2.1 Selection number of steps

2.2.2 Are there competing steps?

2.2.3 Reaction type for individual steps

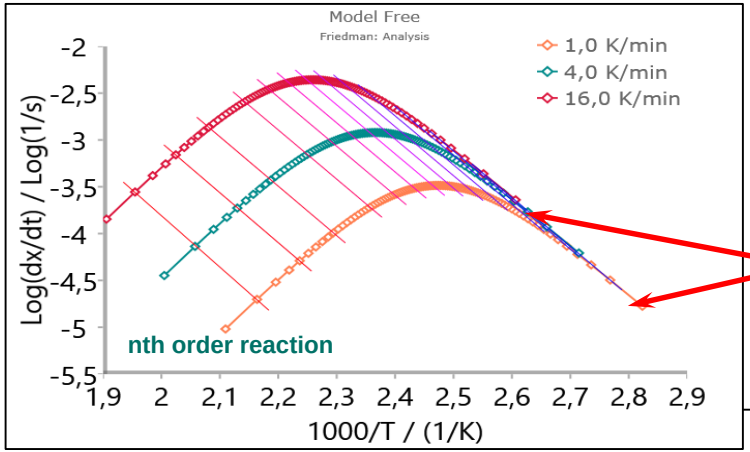
Beginning of reaction from Friedman analysis





The slope of measured values at the start of the reaction is less than the iso conversion lines

The slope of measured values at the start of the reaction is steeper than the iso conversion lines



The slope of the measured values is the same as the slope of iso conversion lines

$$\ln\left(\frac{dx}{dt}\right)_{x=\alpha_i} = \ln A + \ln f(x) - \frac{E}{R}\cdot\frac{1}{T}$$

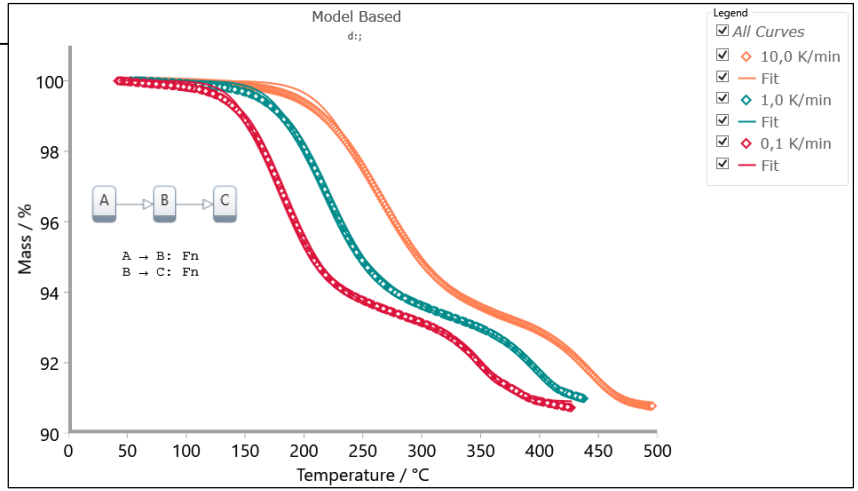
Reaction types: Decomposition

Arrhenius equation

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

Reaction of n-th order is typical for decomposition

Fn $$\frac{d\alpha}{dt} = A \cdot (1-\alpha)^n \cdot \exp\left(\frac{-E_{a1}}{RT}\right)$$



Example: decomposition of polymer binder: Two consecutive steps of n-th order reactions

Phase-boundary reactions are the partial case of n-th order reaction

2-dimensional phase-boundary reaction R2: n=1/2

3-Dimensional phase boundary reaction R3: n=2/3

Recommended reaction types:
- Fn: n-th order reaction
- F1: first order
- F2: Second order
- R2: 2-dimensional phase-boundary
- R3: 3-dimensional phase-boundary

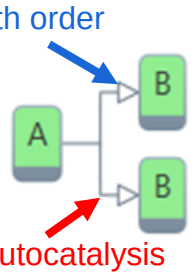
Reaction types: Kinetic Modelling for Curing

Chemical process is **generally** described by Arrhenius equation:

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

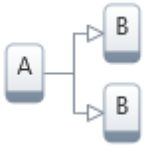
Curing can be described by the equation **Kamal-Sourour** for autocatalytic reaction:

$$\frac{d\alpha}{dt} = \underbrace{A \cdot (1-\alpha)^n \cdot \exp\left(\frac{-E_{a1}}{RT}\right)}_{\text{n-th order}} + \underbrace{A \cdot K \cdot (1-\alpha)^n \cdot \alpha^m \cdot \exp\left(\frac{-E_{a2}}{RT}\right)}_{\text{autocatalysis}}$$



Cmn – reaction of the n[th] order with autocatalysis of m[th] order by product

$$\frac{d\alpha}{dt} = A \cdot (1-\alpha)^n \cdot \exp\left(\frac{-E_{a1}}{RT}\right) (1 + K \cdot \alpha^m)$$



Cn – reaction of the n[th] order with autocatalysis of 1[st] order by product

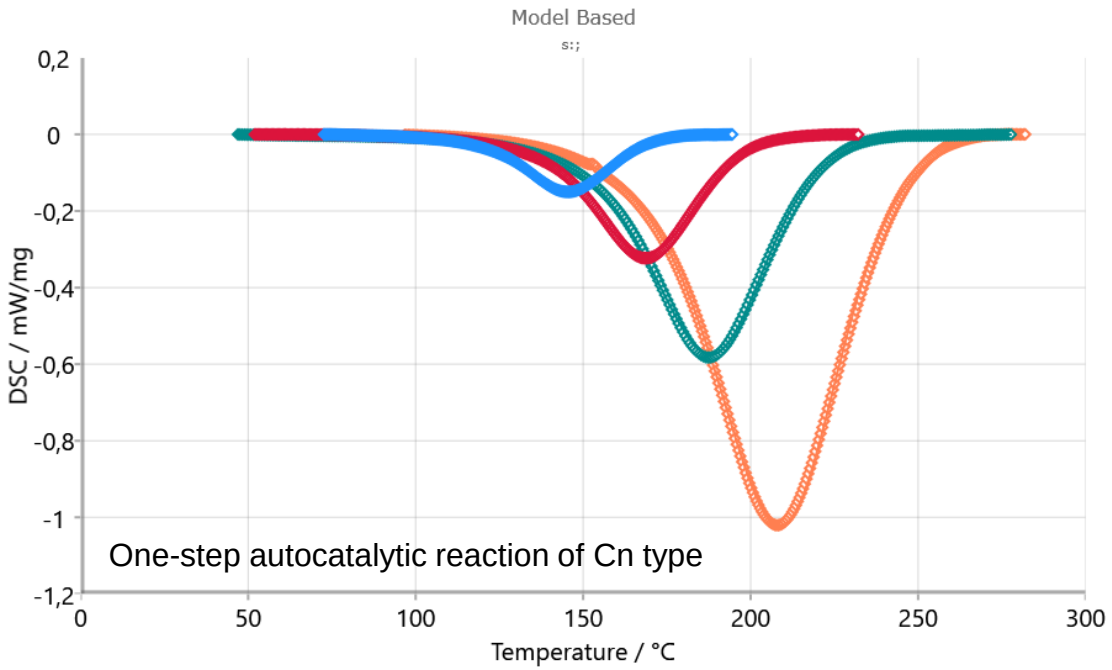
$$\frac{d\alpha}{dt} = A \cdot (1-\alpha)^n \cdot \exp\left(\frac{-E_{a1}}{RT}\right) (1 + K \cdot \alpha)$$

Bna – autocatalytical reacton of Prout-Tompkins

$$\frac{d\alpha}{dt} = A \cdot (1-\alpha)^n \cdot \exp\left(\frac{-E_{a1}}{RT}\right) \cdot \alpha^m$$

This **equation** with its parameters A, E_{a1}, n, E_{a2} , K, m, is the **kinetic model**.

Autocatalytic model for mono-functional epoxy (phenyl glycidyl ether with aniline)

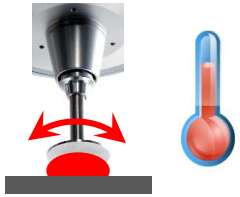


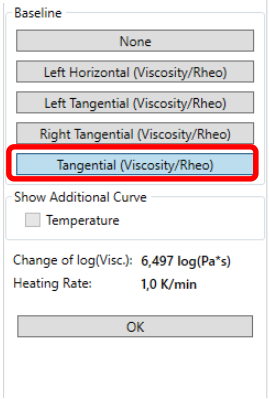
Recommended autocatalytic reaction types for curing:

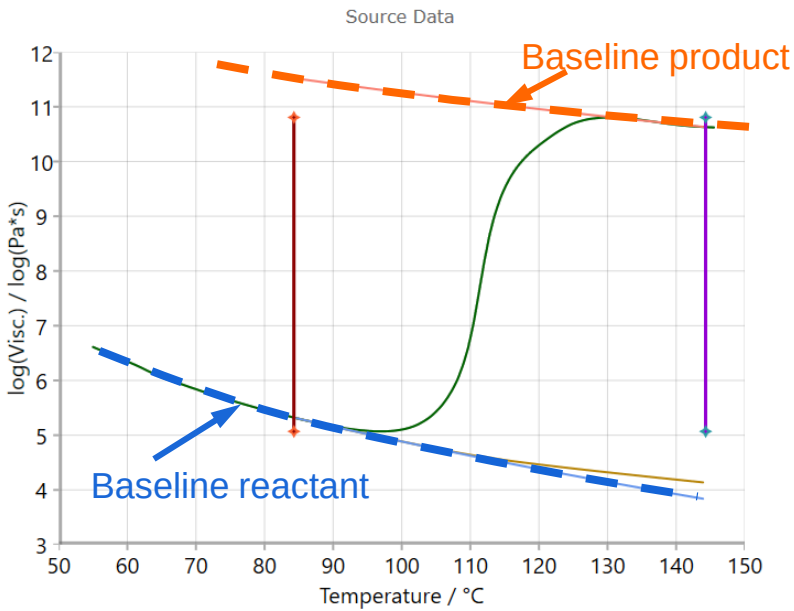
C1: 1st order reaction
with 1st order Autocatalysis
Cn: nth order reaction
with 1st order Autocatalysis
Cmn: nth order reaction
with mth order Autocatalysis
KS: Kamal-Sourour

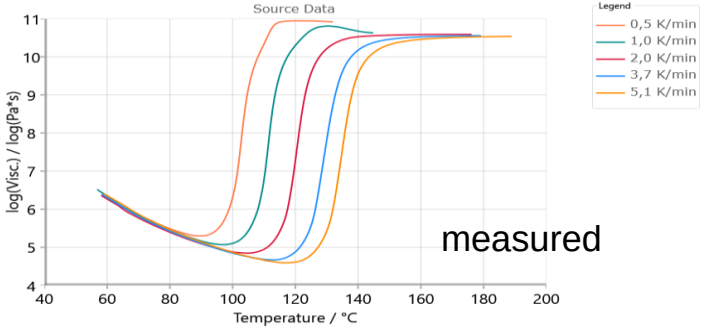
Hans-Jürgen Flammersheim, Johannes R.Opfermann, Macrmol.Mater.Eng.,2001, 286, 143-150

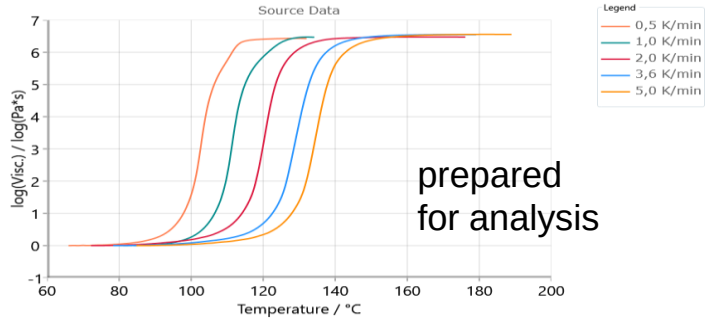
Rheology data: curing of epoxy system

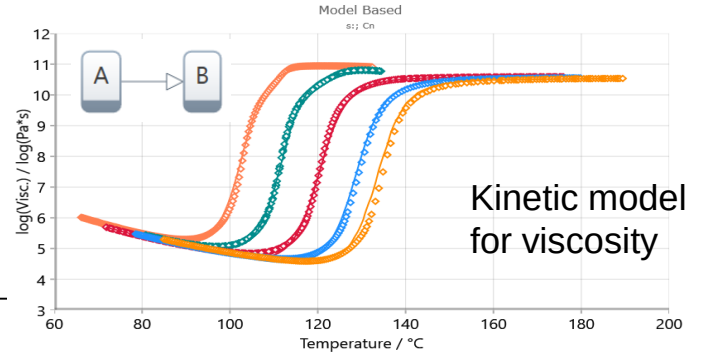






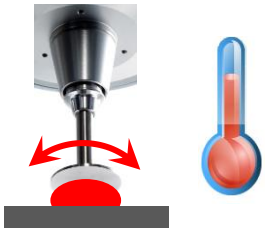


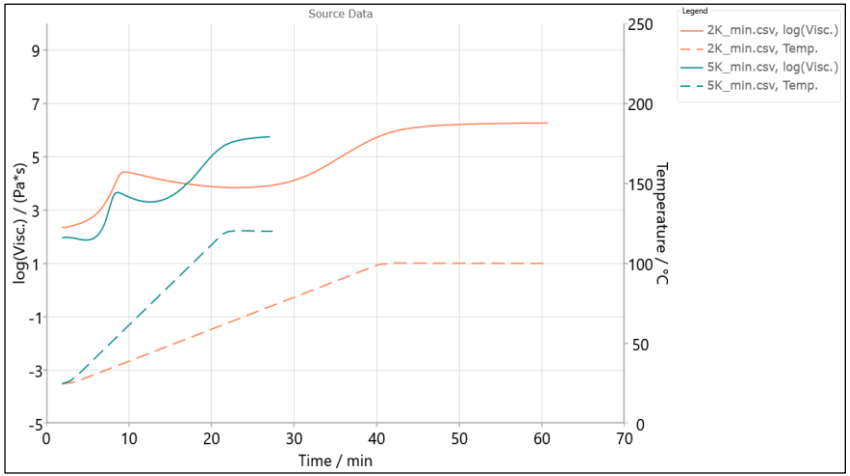


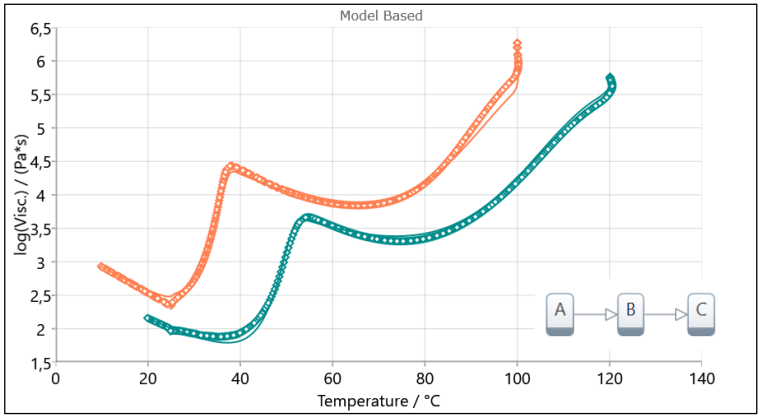


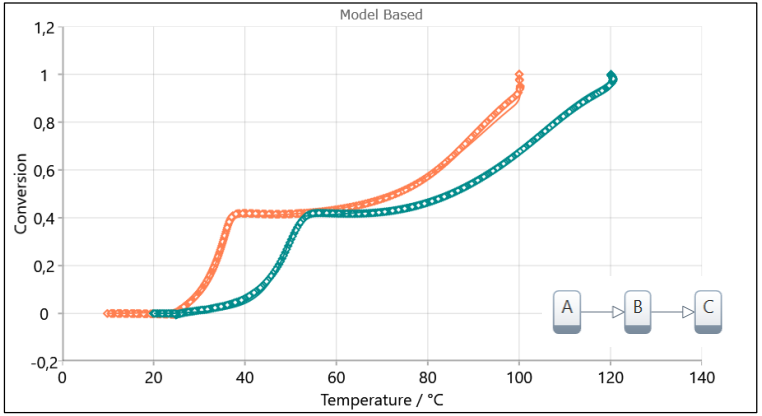
Tangential baseline for heating

ARALDITE, Rheometry measurements and kinetic model









Reaction finished

Cold

Glassy state

Warm

Rubbery or liquid state

Tg

Slow curing
T<Tg

Fast curing
T>Tg

Glass transition

Glass Transition Temperature vs Conversion

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Properties

Glass Transition Temperature

Conversion	Tg / °C	
0,000	25,0	✕
0,250	53,0	✕
0,310	58,0	✕
0,380	65,0	✕
0,460	78,0	✕
0,600	98,0	✕
0,690	116,0	✕
0,760	128,0	✕
0,830	140,0	✕
1,000	165,0	✕

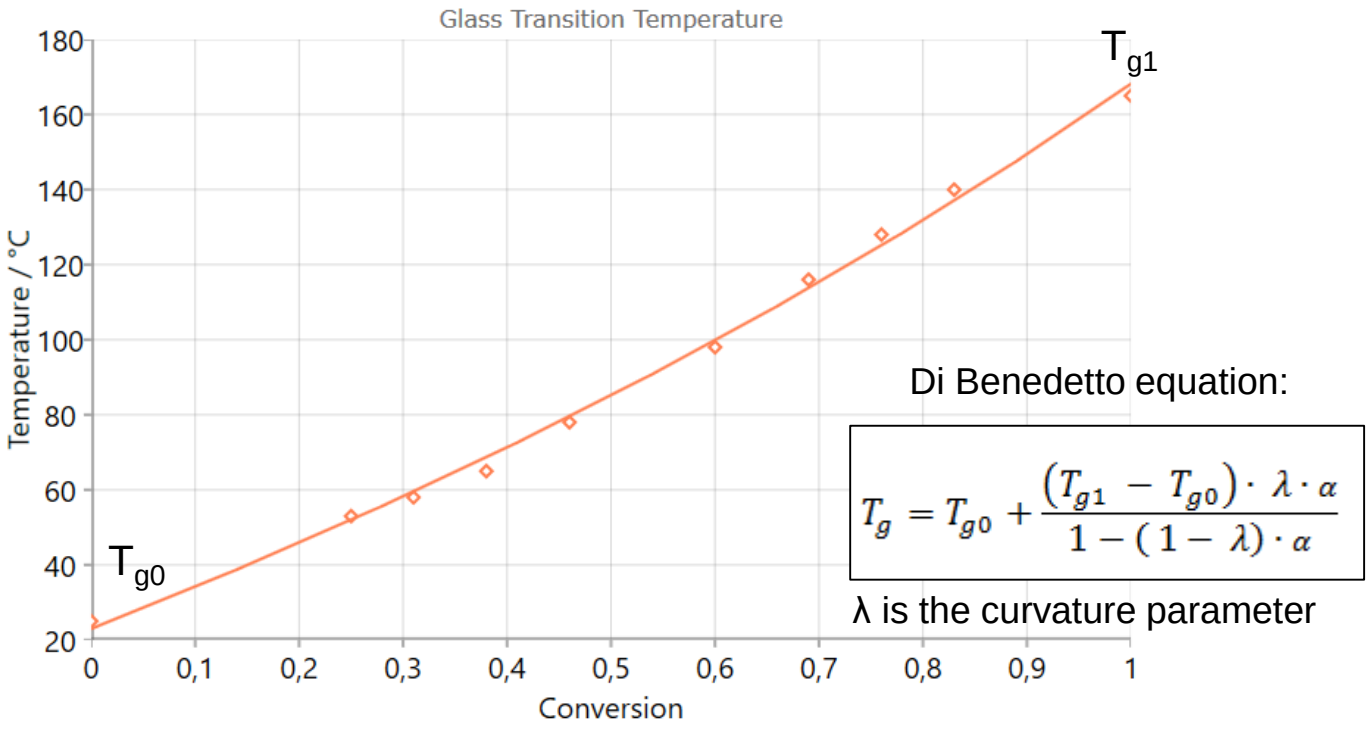
Add Point | Calculate

Interpolation

Spline | Di Benedetto

Parameters:

Tg0	22,97
Tg1	168,16
Lambda	0,75



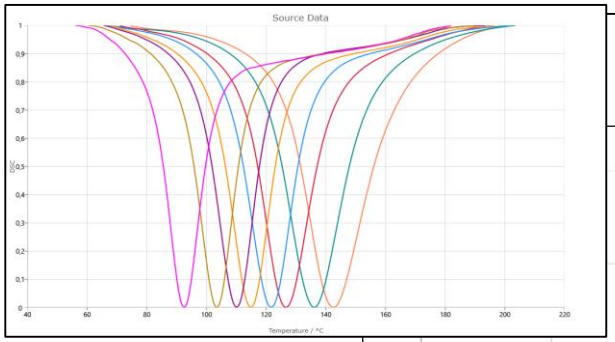
Di Benedetto equation:

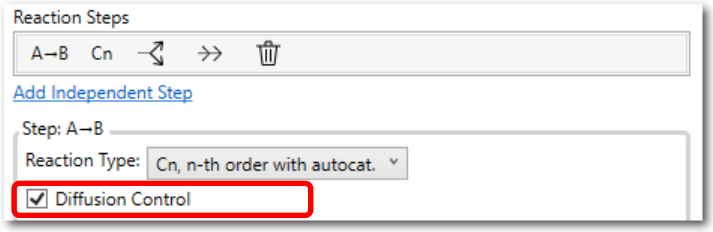
$$T_g = T_{g0} + \frac{(T_{g1} - T_{g0}) \cdot \lambda \cdot \alpha}{1 - (1 - \lambda) \cdot \alpha}$$

λ is the curvature parameter

epoxid/5 % Zn(OCN)2(MeImid)2

Experiment and Model Fit for diffusion control



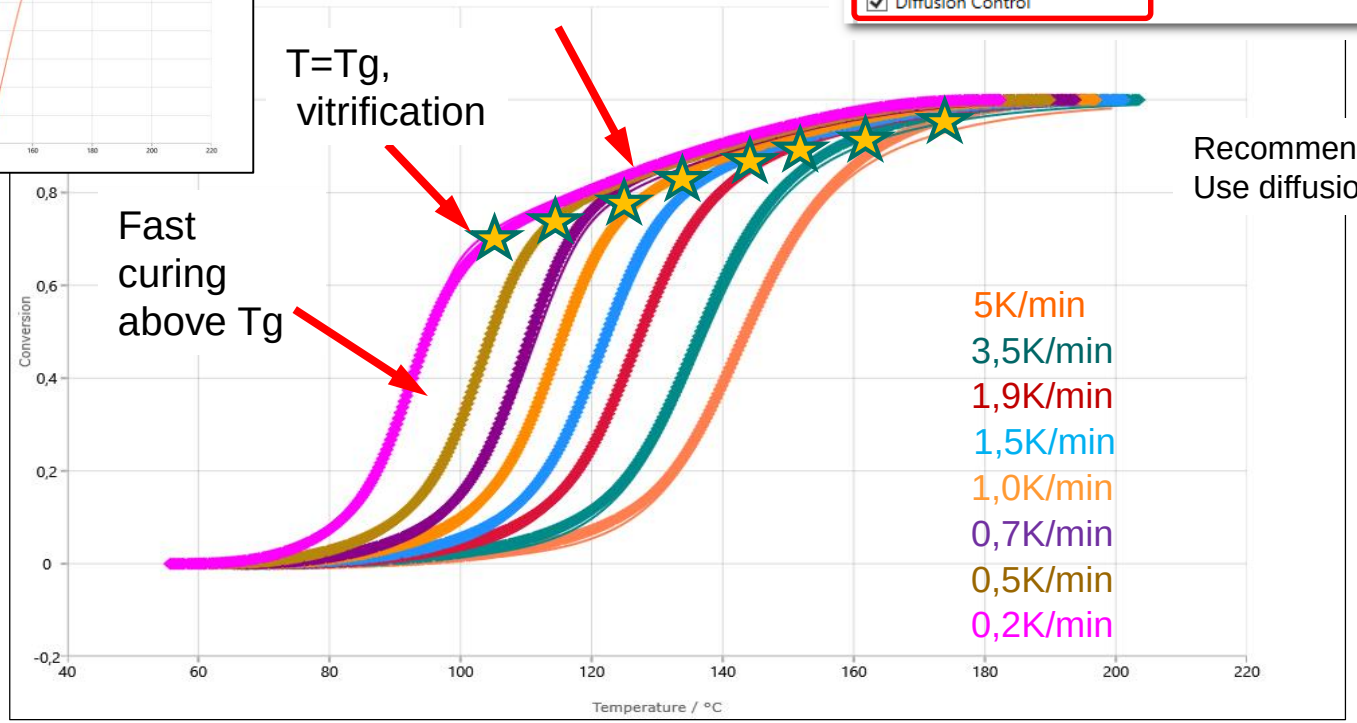


Slow curing below Tg

T=Tg, vitrification

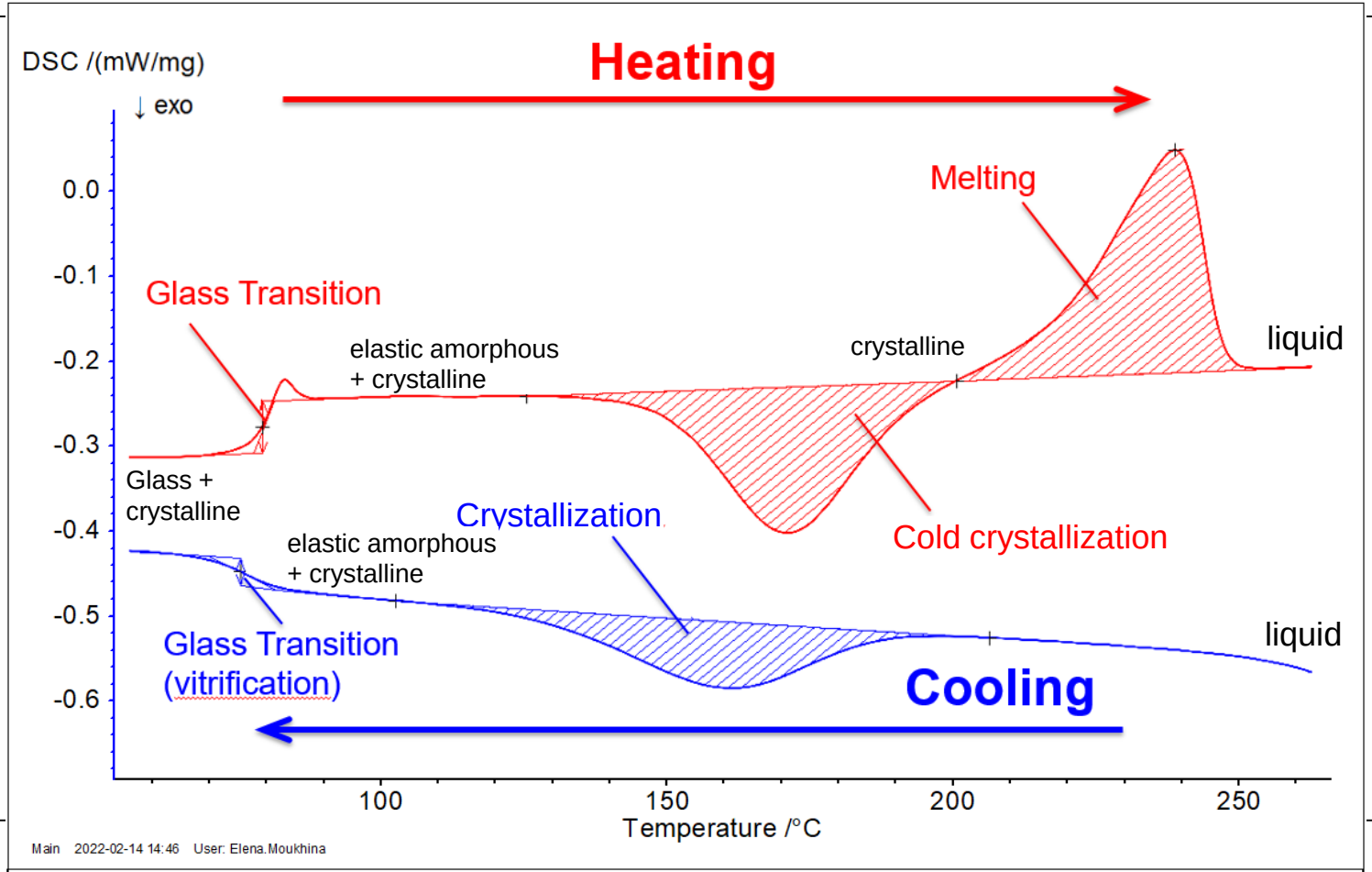
Fast curing above Tg

Recommended: Use diffusion control

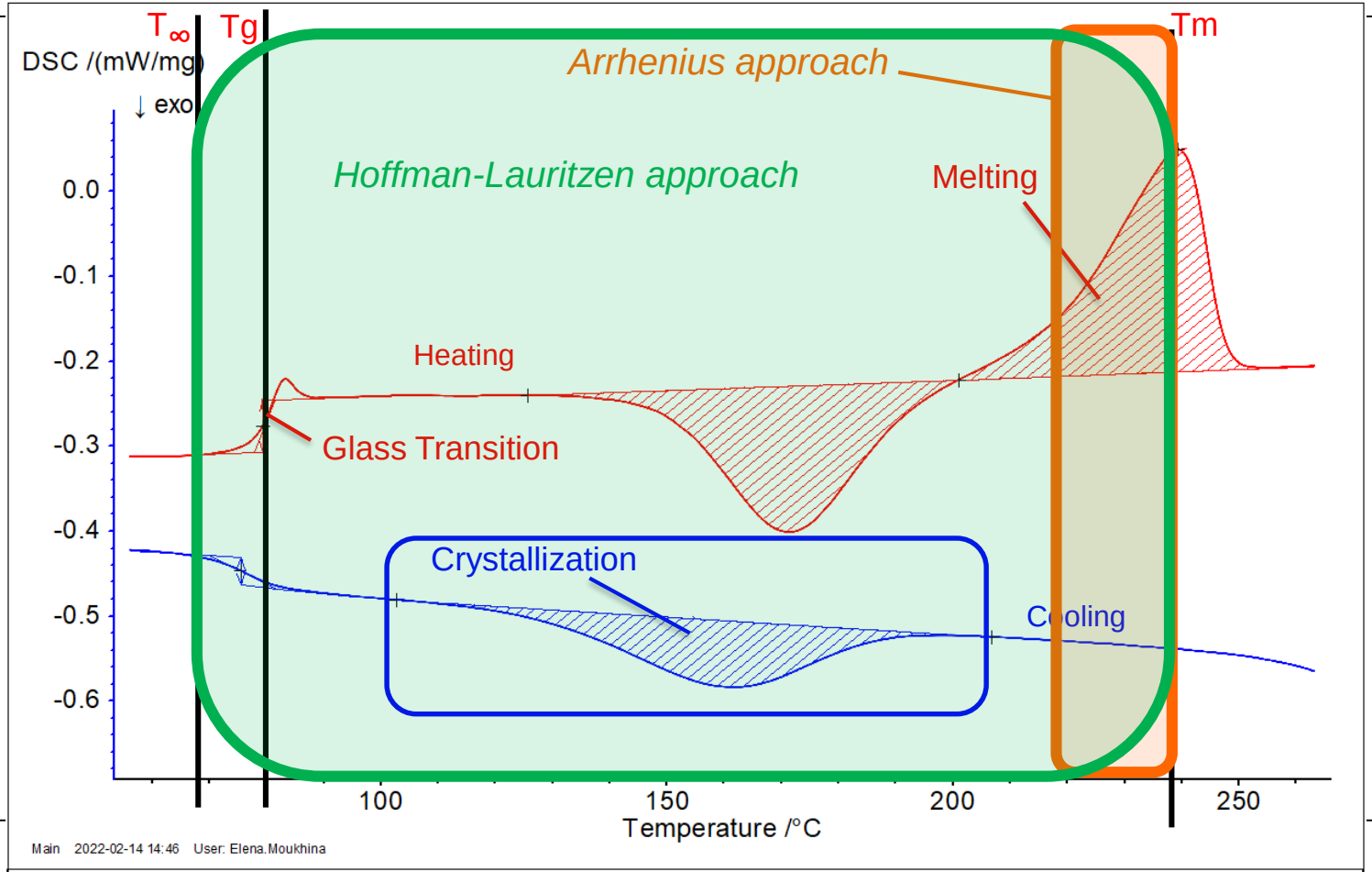


H.J. Flammersheim and J. Opfermann, Thermochimica Acta 337 (1999) 141 - 148

Crystallization kinetics: Polymer for Heating and Cooling



Polymer: Heating and Cooling



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Crystallization rate

Model based

Avrami nucleation

Sestak-Berggren

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$$

Arrhenius

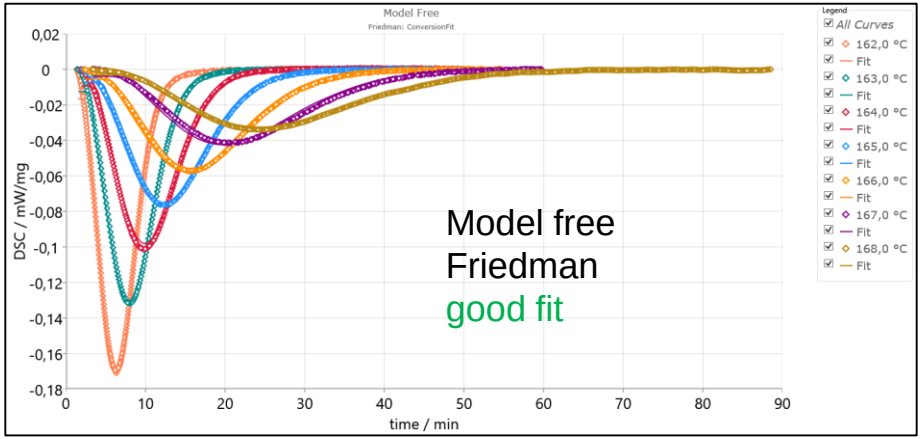
Non-Arrhenius
Hoffman-Lauritzen Theory

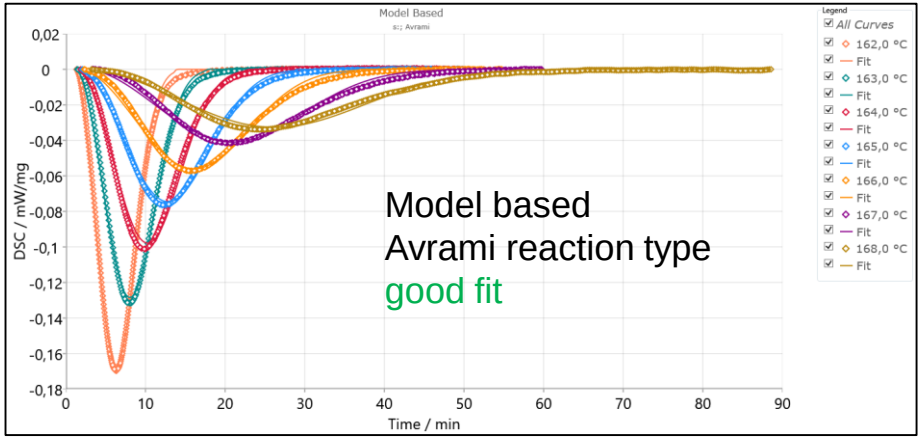
Model free

$$\frac{d\alpha}{dt} = A(\alpha) \cdot exp\left[\frac{-E(\alpha)}{RT}\right]$$

Isothermal crystallization: Arrhenius approach

Isothermal crystallization of PA12





Arrhenius approach works well for isothermal crystallization
by using of model free (Friedman and Numerical) and for model based (Avrami and Sestak-Berggren)

Apparent activation energy is negative. Here E ≈ -400kJ/mol

Recommended reaction types
for isothermal crystallization:

An: Avrami crystallization
SB: Sestak-Berggren reaction
Nk: Nakamura crystallization
SbC: Sbirrazzuolli crystallization

When model-free method is applicable?

Total effect (total mass loss or total peak area) must be the same for all curves

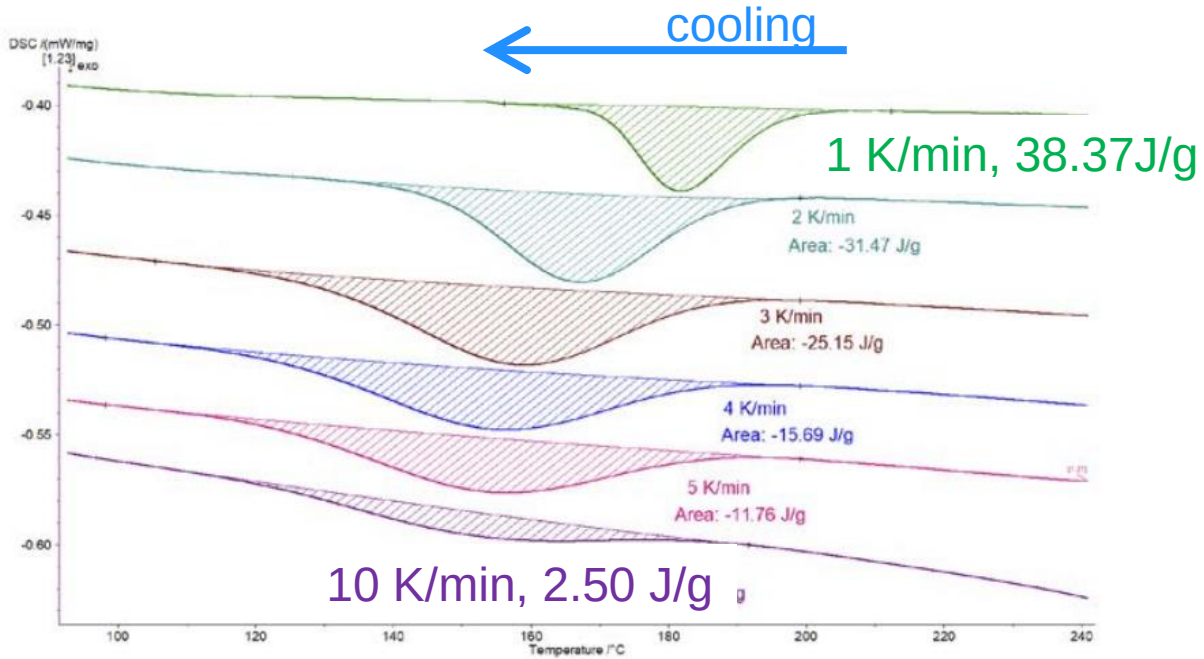


Fig. 1. Crystallization curves for polyethylene terephthalate (PET) measured at cooling rates from 1 to 10 K/min

PET

Crystallizatin of PET during cooling

Crystallization kinetics:
non-Arrhenius approach: Nakamura und Hoffman-Lauritzen

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Avrami nucleation

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$$

Diffusion term

Nucleation term

$$K(T) = exp\left(\frac{-U^*}{R(T - T_\infty)}\right) \cdot exp\left(\frac{-K_G}{T \cdot \Delta T \cdot f}\right)$$

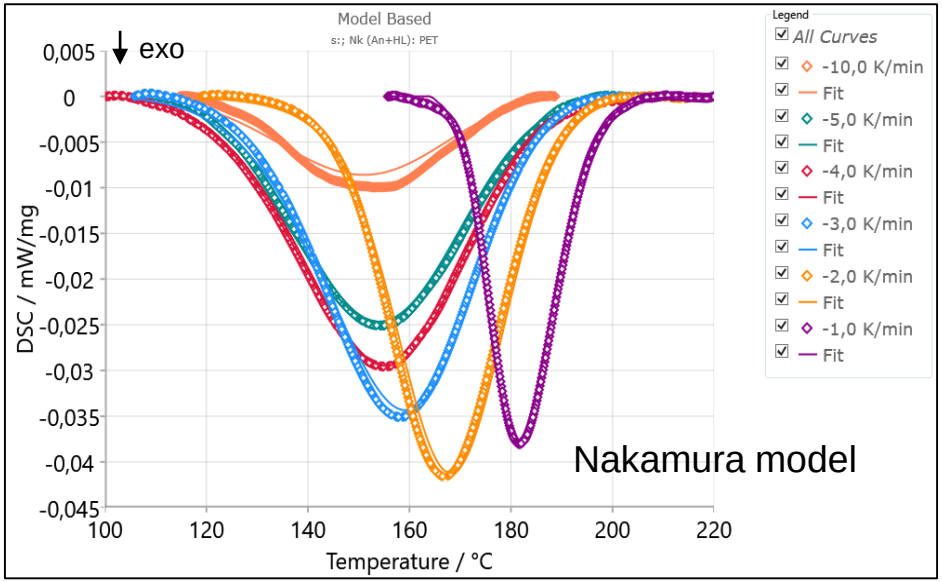
No viscose flow below Tg

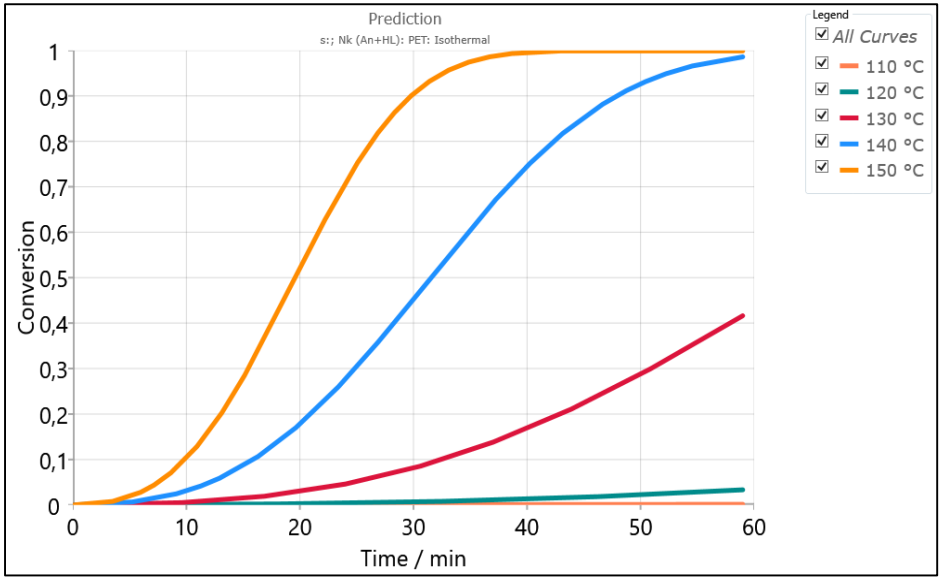
Supercooling

U*	activation energy of segmental jump in polymers, this parameter has universal value 6.3kJ/mol
K_G	kinetic parameter for nucleation
ΔT=Tm-T	undercooling from the equilibrium ***melting point Tm***
T_∞=Tg-30	temperature at which crystallization transport is finished, this temperature is 30K below the ***glass transition temperature Tg***.
f=2T/(T+Tm)	correction factor

This method defined for total temperature range between T_∞ and $T_{melting}$

Model-base analysis:
Non-isothermal Crystallization Prediction for Polyethylene Terephthalate (PET)





One can observe that at temperatures of 110°C to 120°C, no crystallization occurs and the bottles remain in the glassy state and transparent. If the production temperature is too high – e.g., 140°C – then crystallization starts earlier, and the bottles get turbid.

Model based analysis with Hofmann-Lauritzen dependence on temperature

Crystallization model SBC with Sestak-Berggren reaction type

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Crystallization rate $\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$

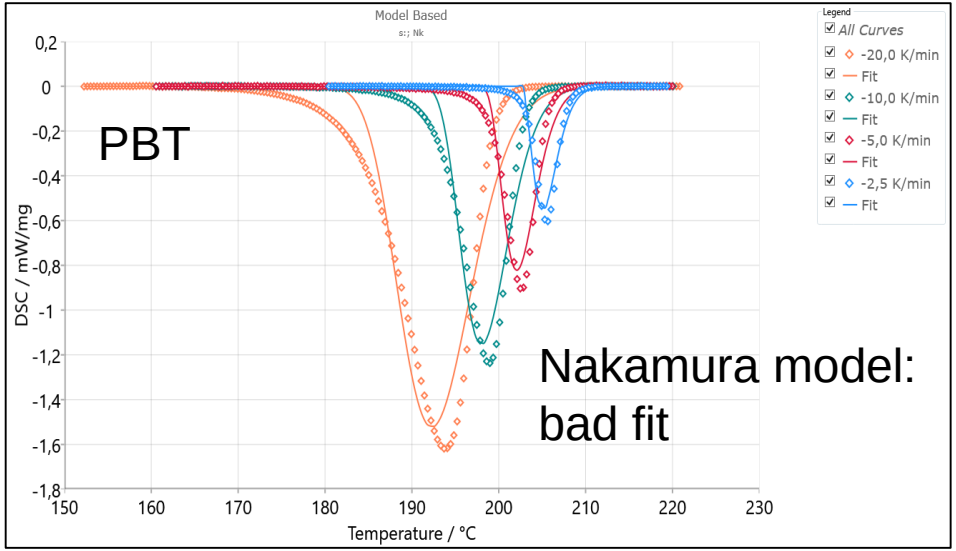
Hoffman-Lauritzen Theory

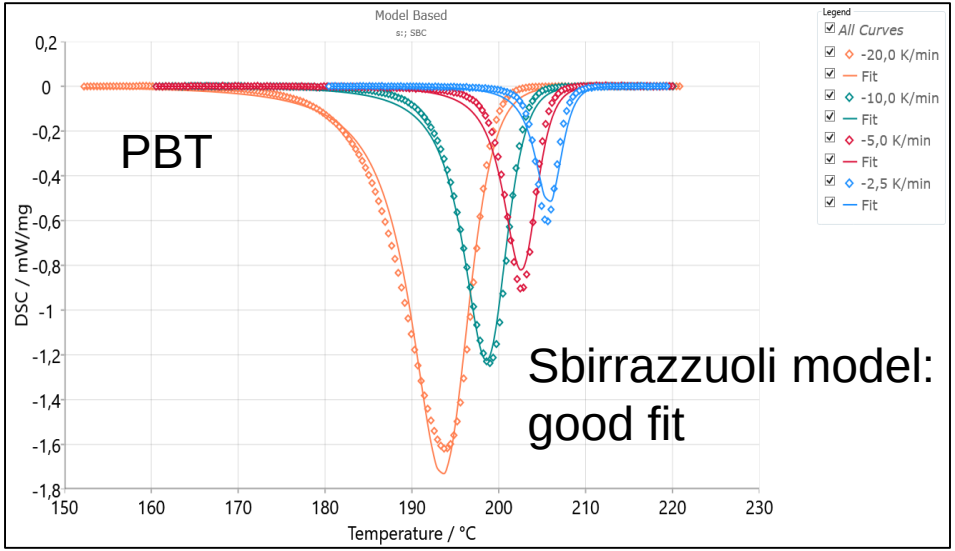
Avrami nucleation

$f(\alpha)=n\cdot (1-\alpha) \cdot[-\ln((1-\alpha))]^{(n-1)/n}$

Sestak-Berggren Crystallization

$f(\alpha)=(1-\alpha)^n \cdot \alpha^m \cdot [-\ln((1-\alpha))]^q$





Nathanael Guigo, Jesper van Berkel, Ed de Jong , Nicolas Sbirrazzuoli, Thermochimica Acta 650 (2017) 66-75

Models for Crystallization kinetics

Avrami nucleation

Sestak-Berggren

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$$

Arrhenius

Non-Arrhenius
Hoffman-Lauritzen Theory

Model based reaction type:

An: Avrami+ Arrhenius

SB: Sestak Berggren + Arrhenius

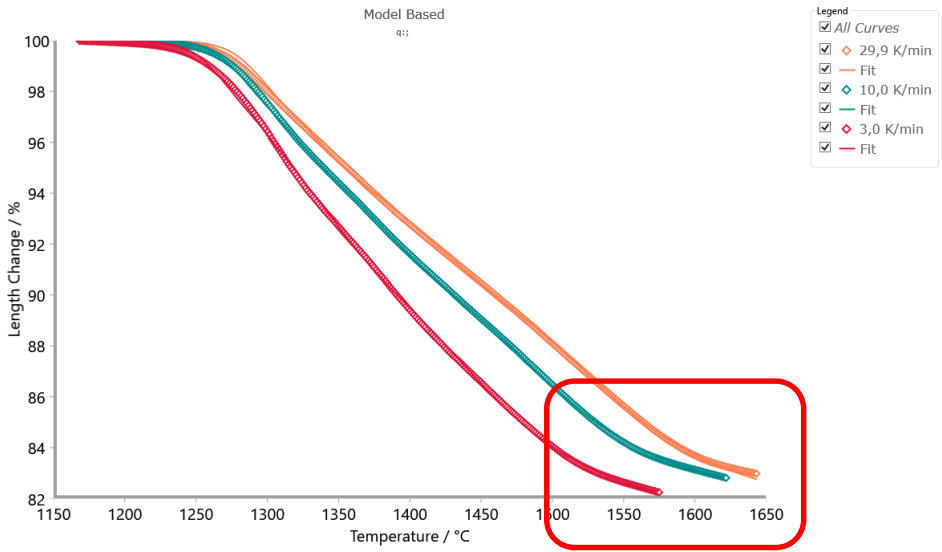
Valid: isothermal crystallization,
small temperature range

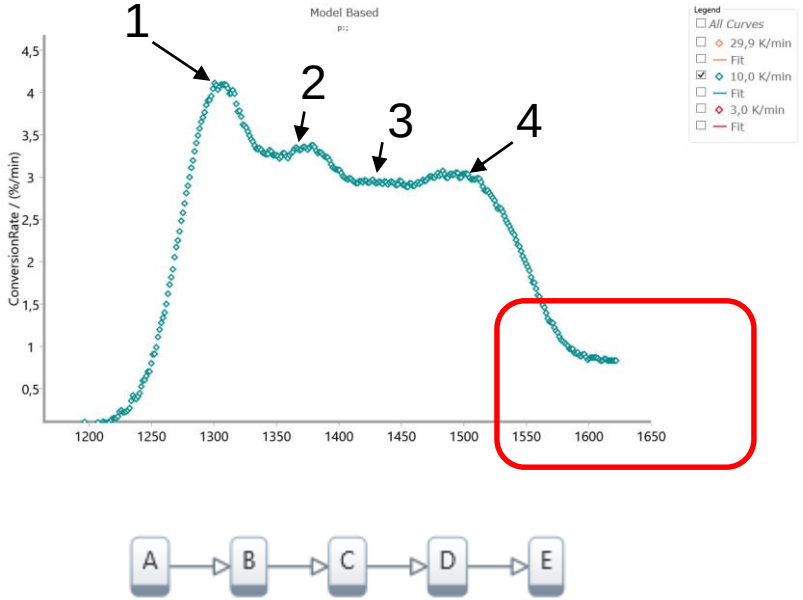
Nakamura: Avrami+ Hoffman-Lauritzen

SBC: Sestak-Berggren+ Hoffman-Lauritzen

Valid: both isothermal and cooling crystallization
complete temperature range between T_∞ and Tm

Sintering: Al2O3

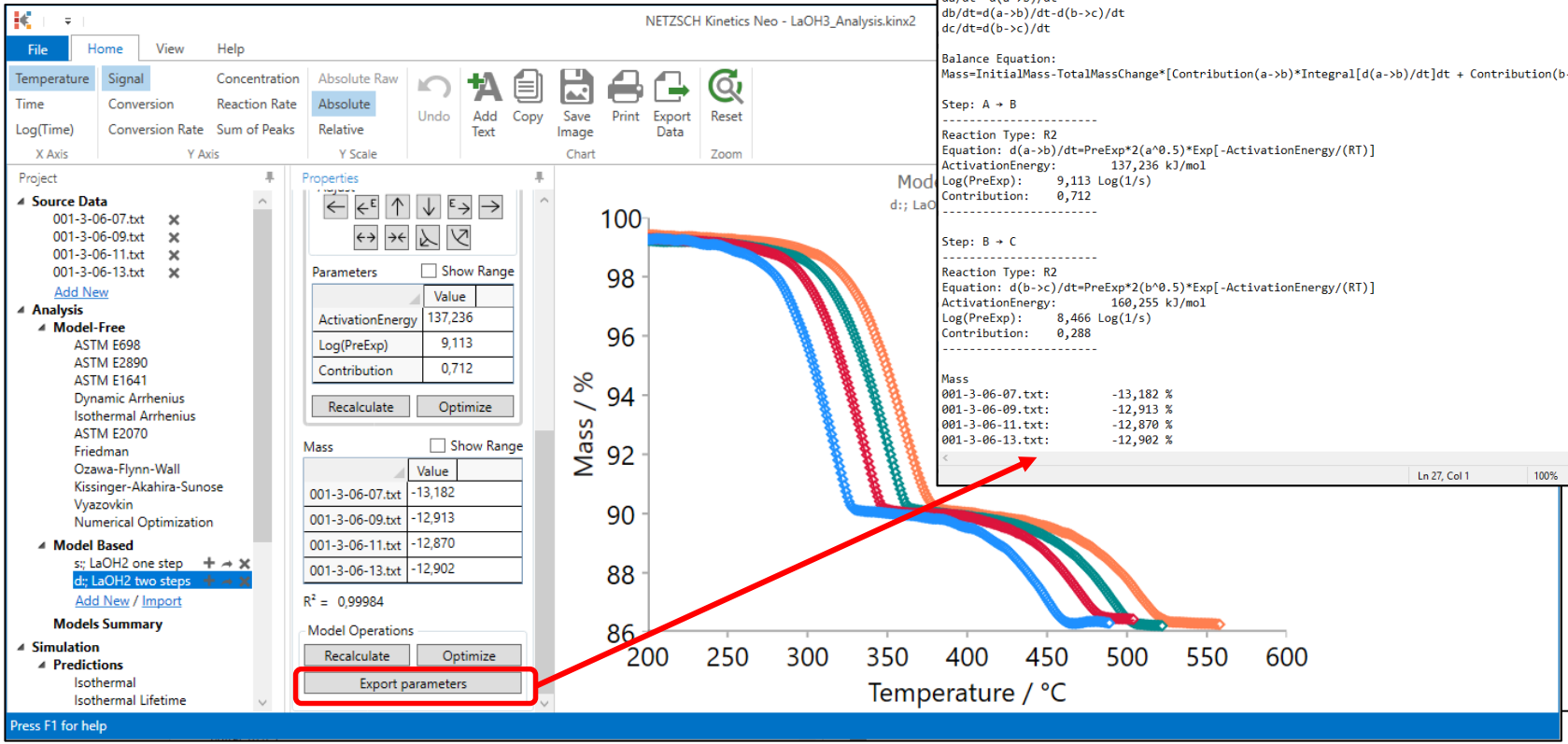




Reason for model-based analysis:

Final part of sintering is not measured

Export equations and parameters



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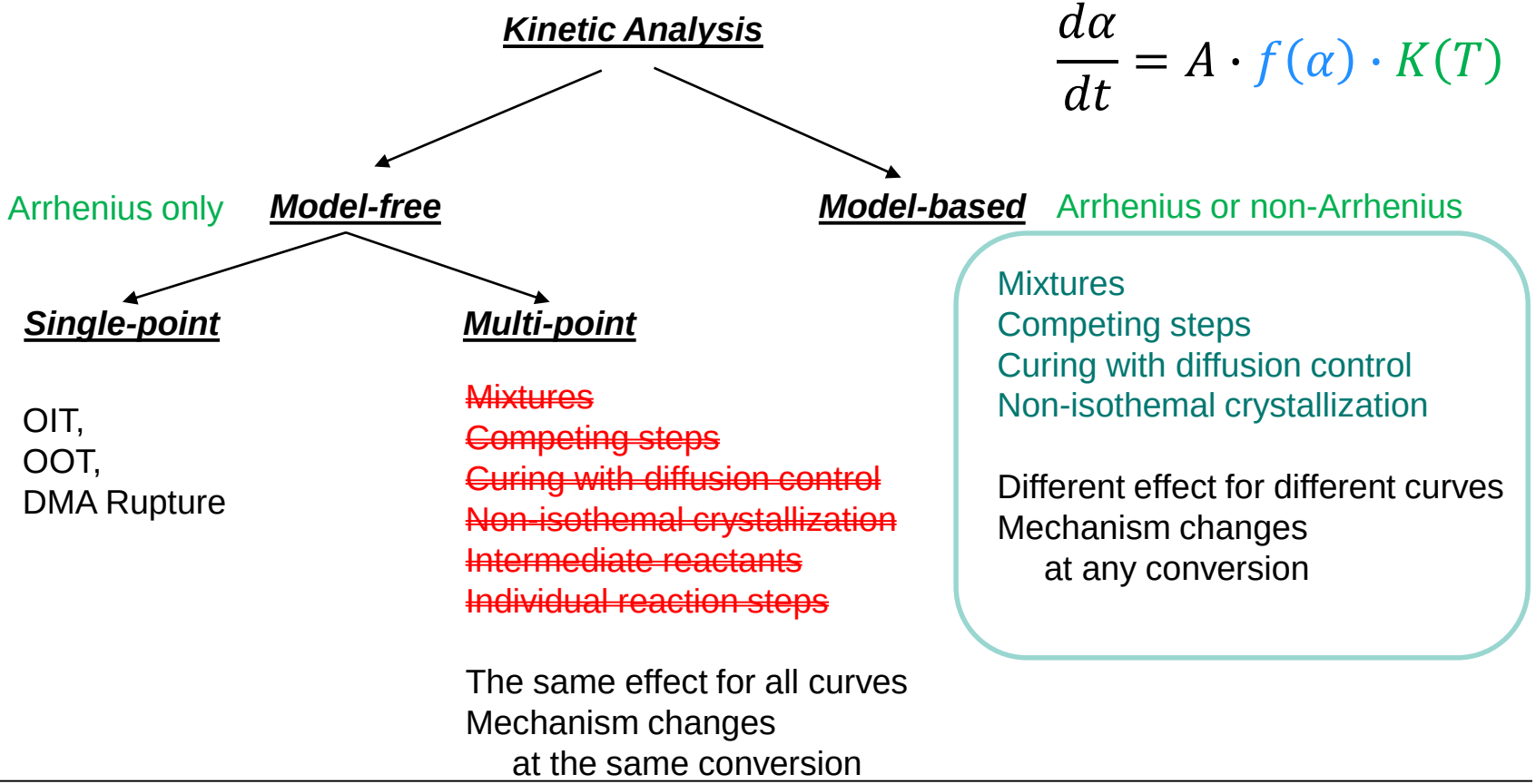
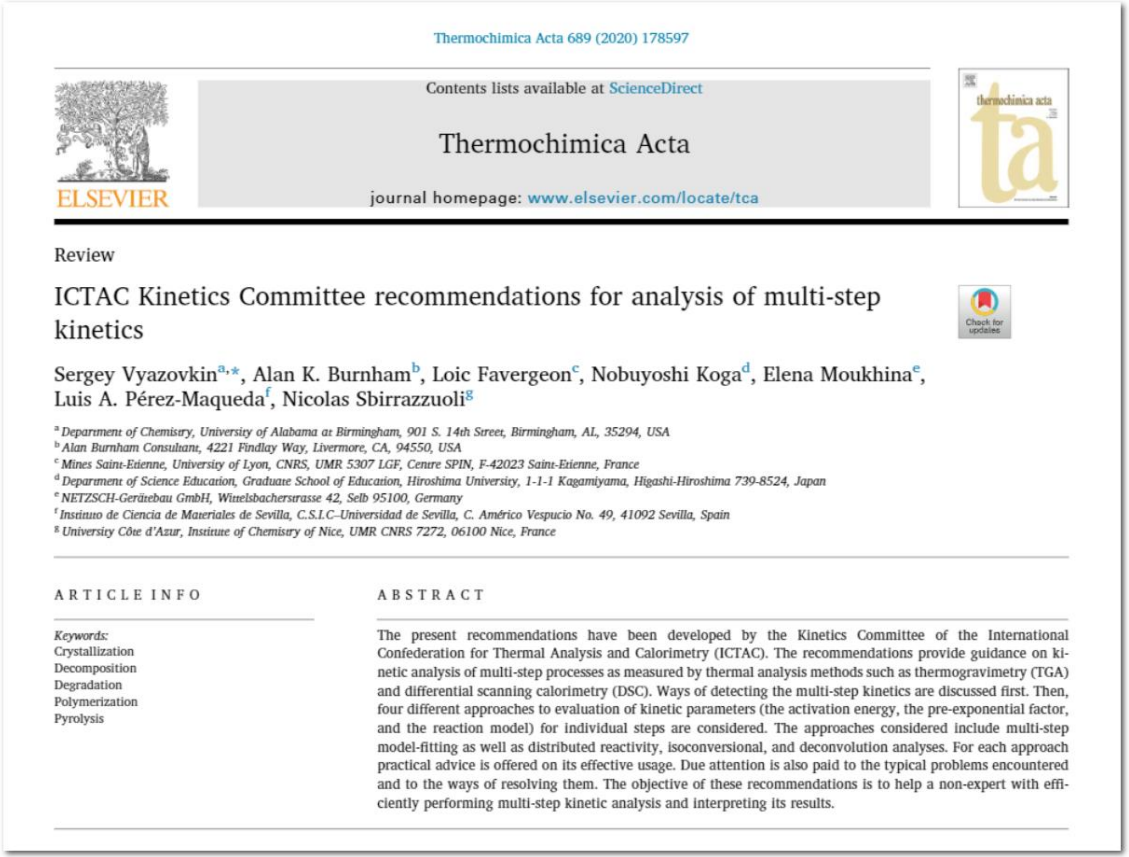

Kinetic Analysis
$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$
Arrhenius only
Model-free
Model-based
Arrhenius or non-Arrhenius
Single-point
Multi-point
OIT,
OOT,
DMA Rupture
~~Mixtures~~
~~Competing steps~~
~~Curing with diffusion control~~
~~Non-isothemal crystallization~~
~~Intermediate reactants~~
~~Individual reaction steps~~
The same effect for all curves
Mechanism changes
at the same conversion
Mixtures
Competing steps
Curing with diffusion control
Non-isothemal crystallization
Different effect for different curves
Mechanism changes
at any conversion

Kinetics Analysis Must Fulfil ICTAC Kinetics Recommendations

NETZSCH

International Confederation for Thermal Analysis and Calorimetry



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Review

ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics

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ABSTRACT

The present recommendations have been developed by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC). The recommendations provide guidance on kinetic analysis of multi-step processes as measured by thermal analysis methods such as thermogravimetry (TGA) and differential scanning calorimetry (DSC). Ways of detecting the multi-step kinetics are discussed first. Then, four different approaches to evaluation of kinetic parameters (the activation energy, the pre-exponential factor, and the reaction model) for individual steps are considered. The approaches considered include multi-step model-fitting as well as distributed reactivity, isoconversional, and deconvolution analyses. For each approach practical advice is offered on its effective usage. Due attention is also paid to the typical problems encountered and to the ways of resolving them. The objective of these recommendations is to help a non-expert with efficiently performing multi-step kinetic analysis and interpreting its results.

KINETICS NEO

- Model free analysis
- Multi-step model-fitting (model based)
- Diffusion control for curing
- Crystallization kinetics
- Kamal model for curing
- Deconvolution analysis (sum of peaks)

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