Analyzing & Testing

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Proven Excellence.

NETZSCH Kinetics Neo
Major Release 3.0 with Unique New Features

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2024

Agenda

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1. Reactions depending on additional parameter
2. Pressure-dependent reactions
    1. Partial Pressure of Gaseous Reactant like Hydrogen for Metal Oxides.
    2. Reversible Reactions with Gaseous Reactant in Reverse Reaction
    3. Pressure-Dependent Reactions in Inert Gas
3. Thermosets, composites, photopolymers:
    1. Curing kinetics depending on intensity of UV light
    2. Curing reactions with diffusion control (DEA, Rheology)
4. Flexible Data Evaluation
    1. Evaluation of Arbitrary Data
    2. Kinetics for Incomplete Data
    3. New Reaction Types
5. User Interface (UI) is reworked for native look in Windows 11

1. Dependence on the additional parameter

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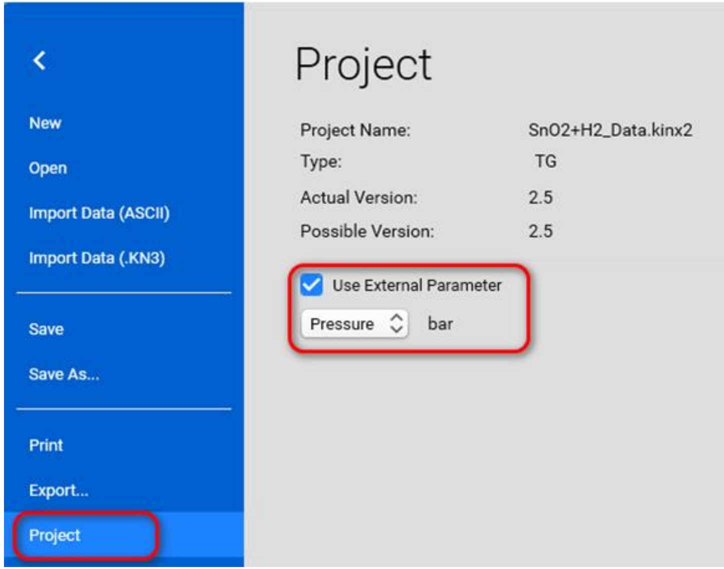


Examples of the additional external parameter:

- Partial Pressure of Gaseous Reactant
- Reversible Reactions with Gaseous Reactant in Reverse Reaction
- Pressure-Dependent Reactions in Inert Gas
- Intensity of UV light for curing of photopolymers
- Other parameters

The rate of chemical reactions and crystallization depends on different parameters, the first of them is temperature.

Now we have the possibility to use the second parameter in the common kinetic model, where reaction rate depends on two parameters.

2

Pressure-Dependent Reactions

2.1 Partial Pressure of Gaseous Reactant

2.2 Reversible Reactions with Gaseous Reactant

2.3 Pressure-Dependent Reactions in Inert Gas

2.1 Partial Pressure of Gaseous Reactant

Reduction of Metal Oxide in H_2

total pressure of gas mixture is 1 bar

Reduction of metal from metal oxide in Nitrogen with partial pressure of Hydrogen

Nitrogen with Hydrogen

$$MeO_2 + H_2 \rightarrow Me + H_2O$$

$$\frac{d\alpha}{dt} = P_{H2}^{n_p} \, A \, exp\left(\frac{-E_A}{RT}\right) f(\alpha)$$


STA 509 with Hydrogen Generator

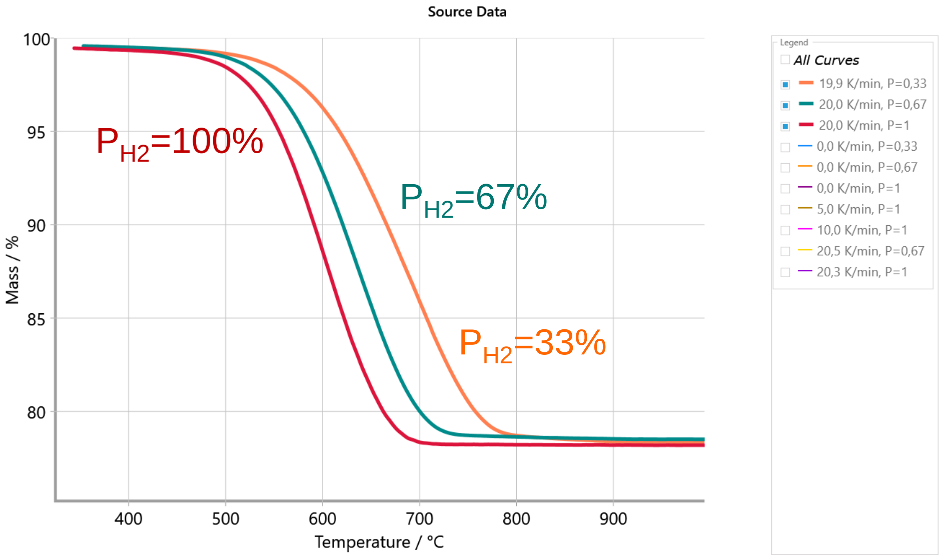
Hydrogen is the reactive gas.

Reaction rate depends on the hydrogen concentration

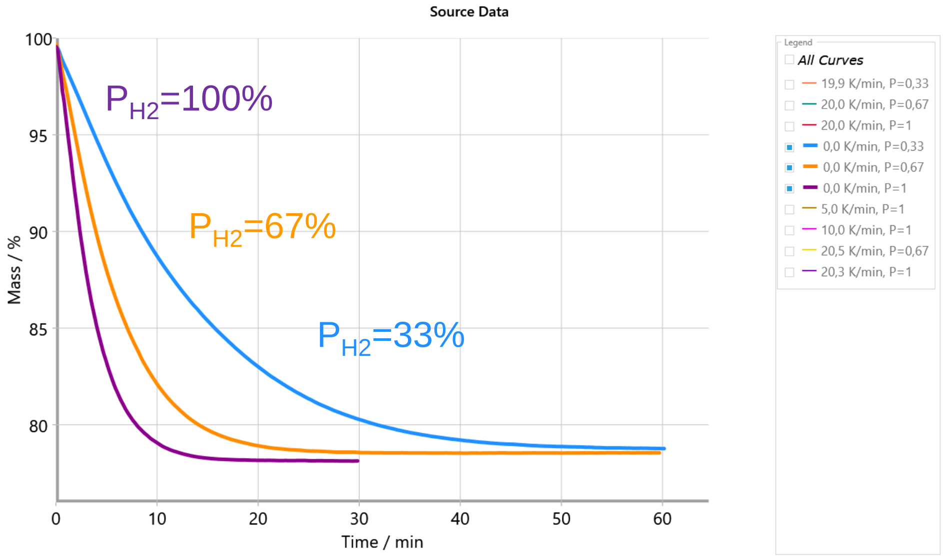
the higher partial pressure of hydrogen - the higher reaction rate

Data series for analysis

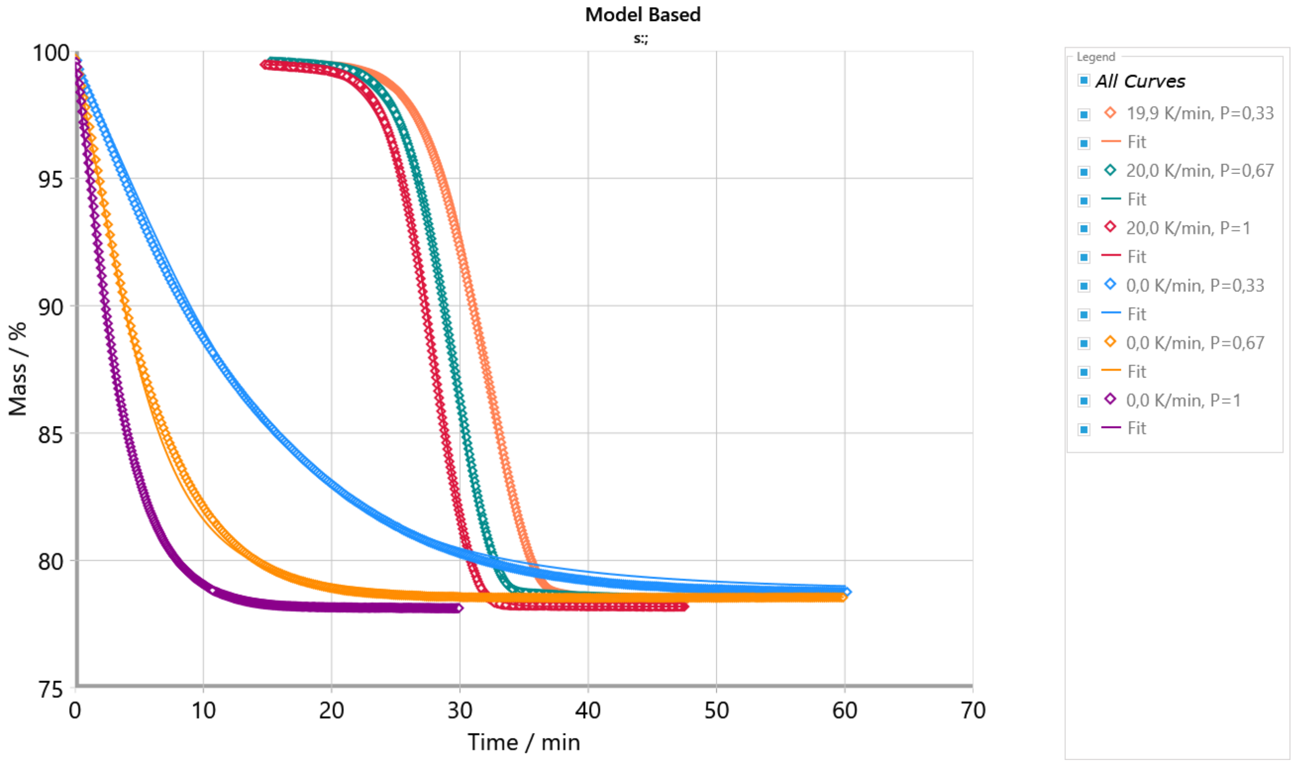
20K/min, different partial pressure of H_2



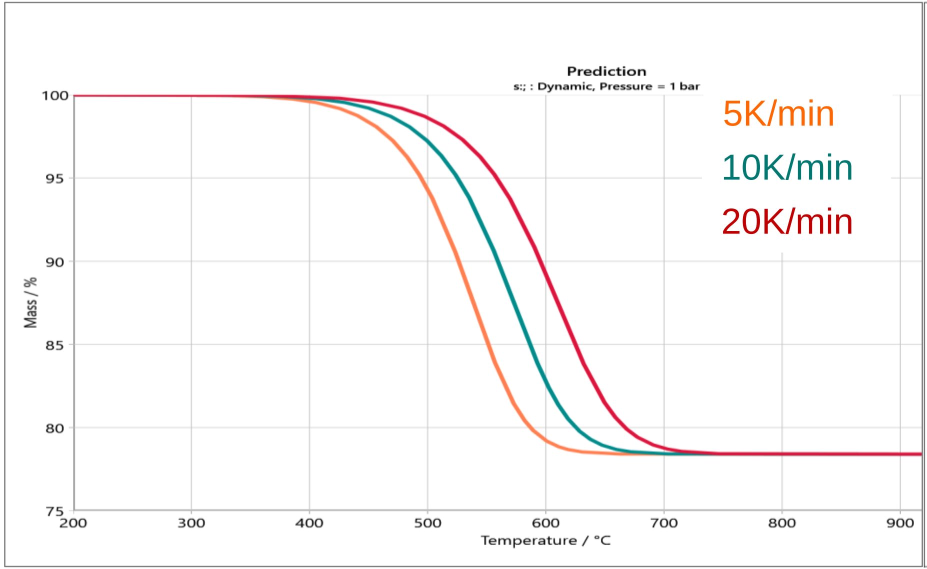
Isothermal T=600°C, different partial pressure of H_2

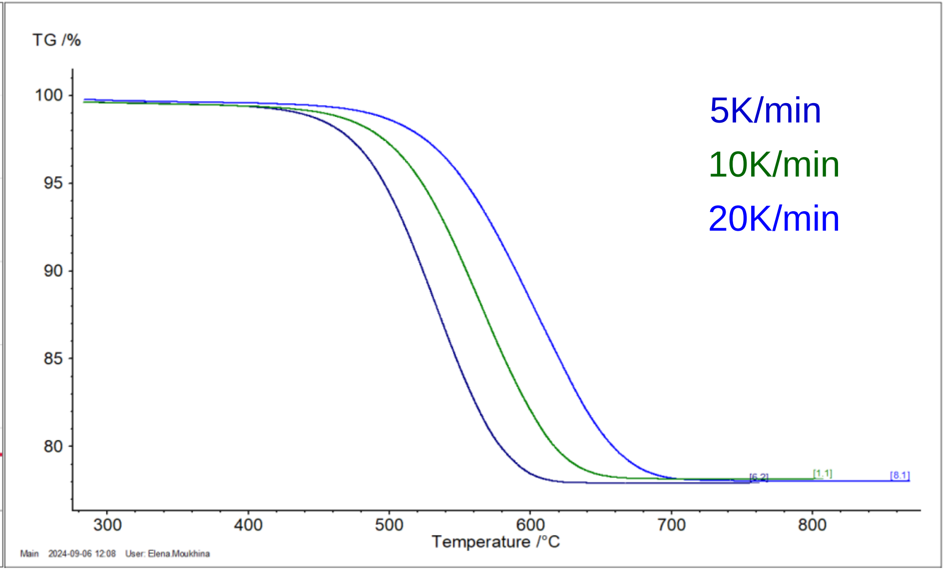


Common model in Kinetics Neo depending on the partial pressure of gaseous reactant



Verification: Predictions for 100% H_2, different heating rates





Simulations for 100% of H_2

Experiment

Verification of kinetic model: comparison of simulated and measured data

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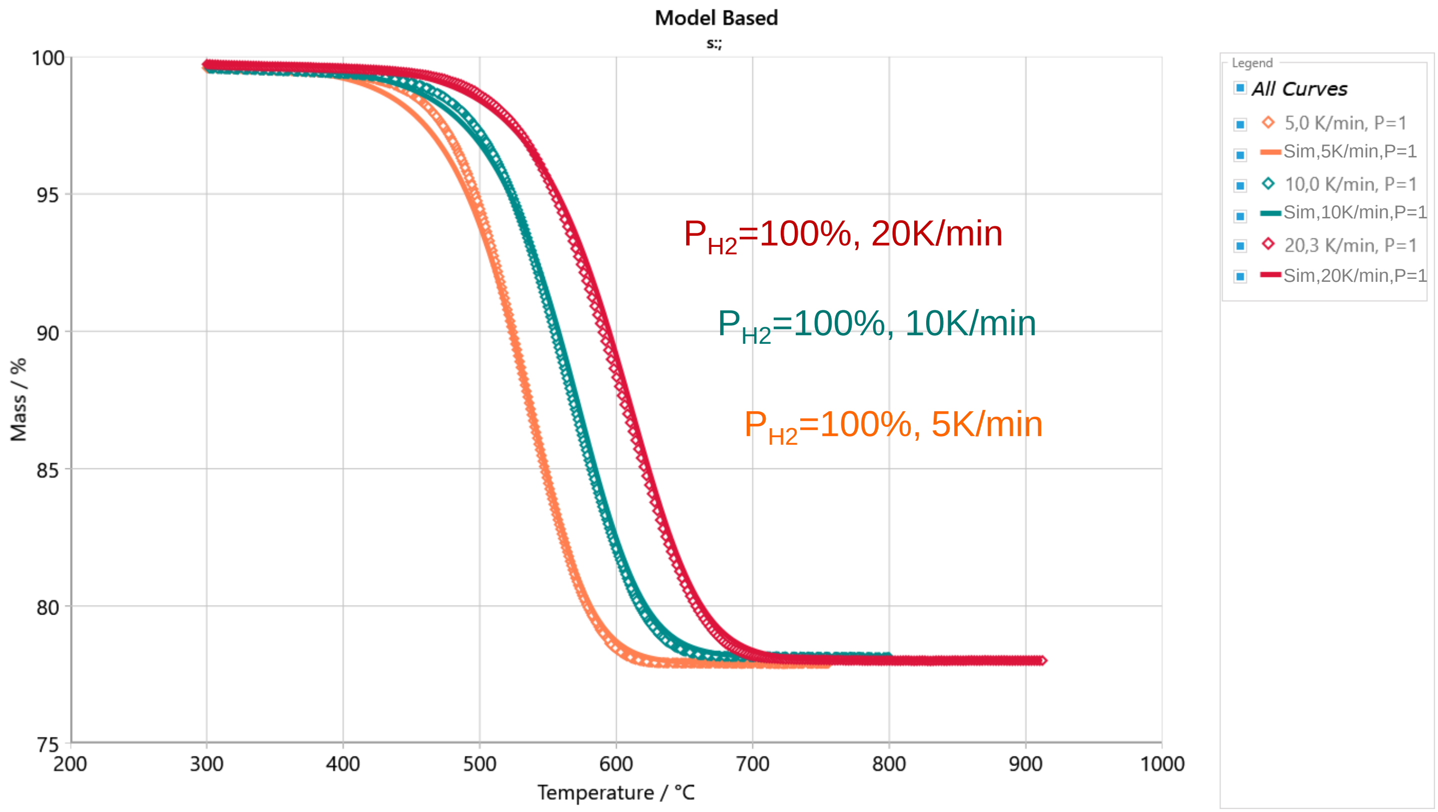

2.2 Reversible reactions with Gaseous Reactant

Decomposition of $CaCO_3$ under partial pressure of CO_2

total pressure of gas mixture is 1 bar

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Reversible reactions

$$A \rightleftarrows B$$

Forward: $A \rightarrow B$ $A_1\, exp\left(\frac{-E_1}{RT}\right)\, f_1(\alpha)$

Reverse: $A \leftarrow B$ $A_2\, exp\left(\frac{-E_2}{RT}\right)\, f_2(\alpha)$

Rection rate $_{total}$ = *Reaction rate* $_{forward}$ − *Reaction rate* $_{reverse}$

$$\frac{d\alpha}{dt} = A_1\, exp\left(\frac{-E_1}{RT}\right)\, f_1(\alpha) - A_2 exp\left(\frac{-E_2}{RT}\right) f_2(\alpha)$$

Decomposition of $CaCO_3$ in Nitrogen

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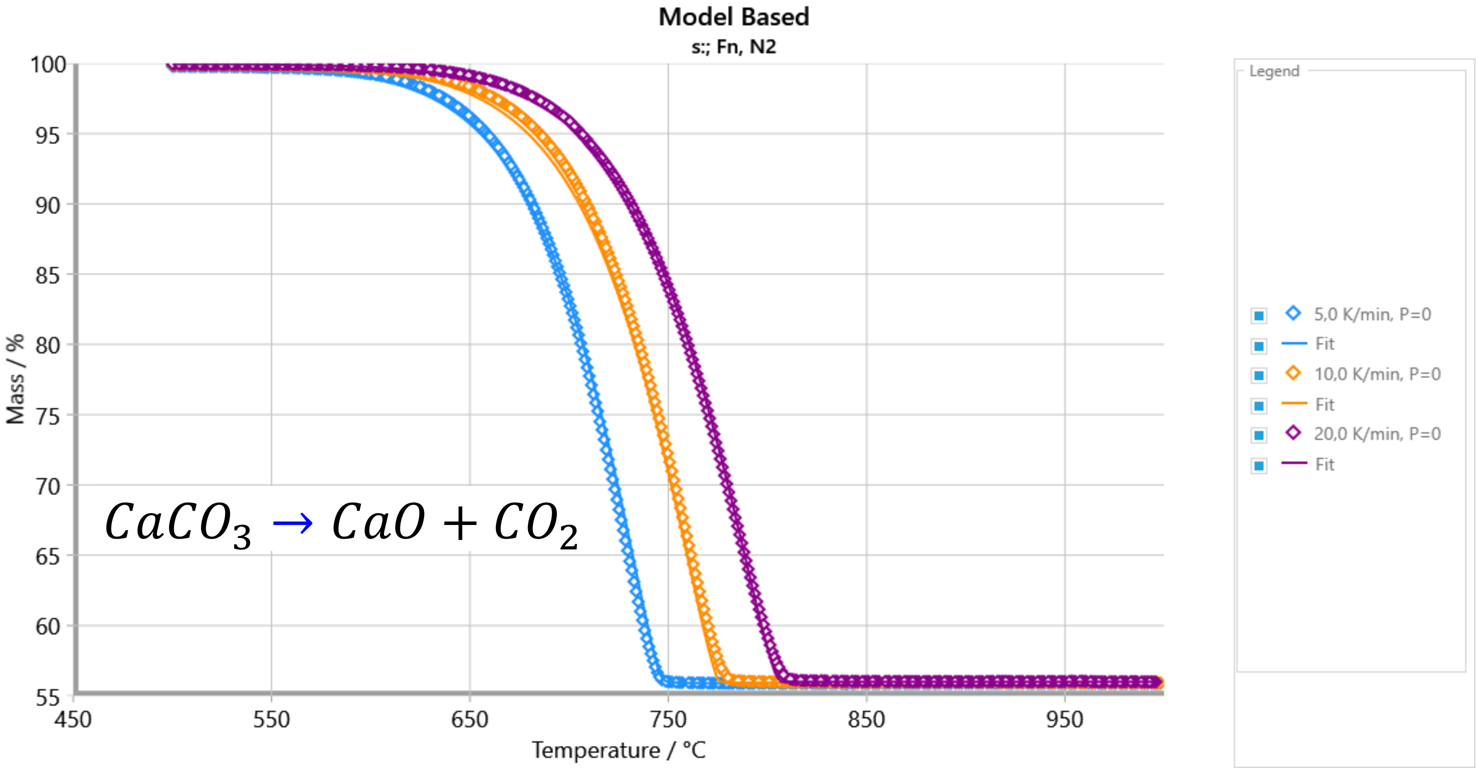
1. Nitrogen only

$$CaCO_3 \rightarrow CaO + CO_2$$

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

Decomposition of $CaCO_3$ in Nitrogen, Pressure=1bar



$$CaCO_3 \rightarrow CaO + CO_2$$

Decomposition of $CaCO_3$ in Nitrogen with CO_2

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1. Nitrogen only (only forward reaction)

$$CaCO_3 \rightarrow CaO + CO_2$$

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

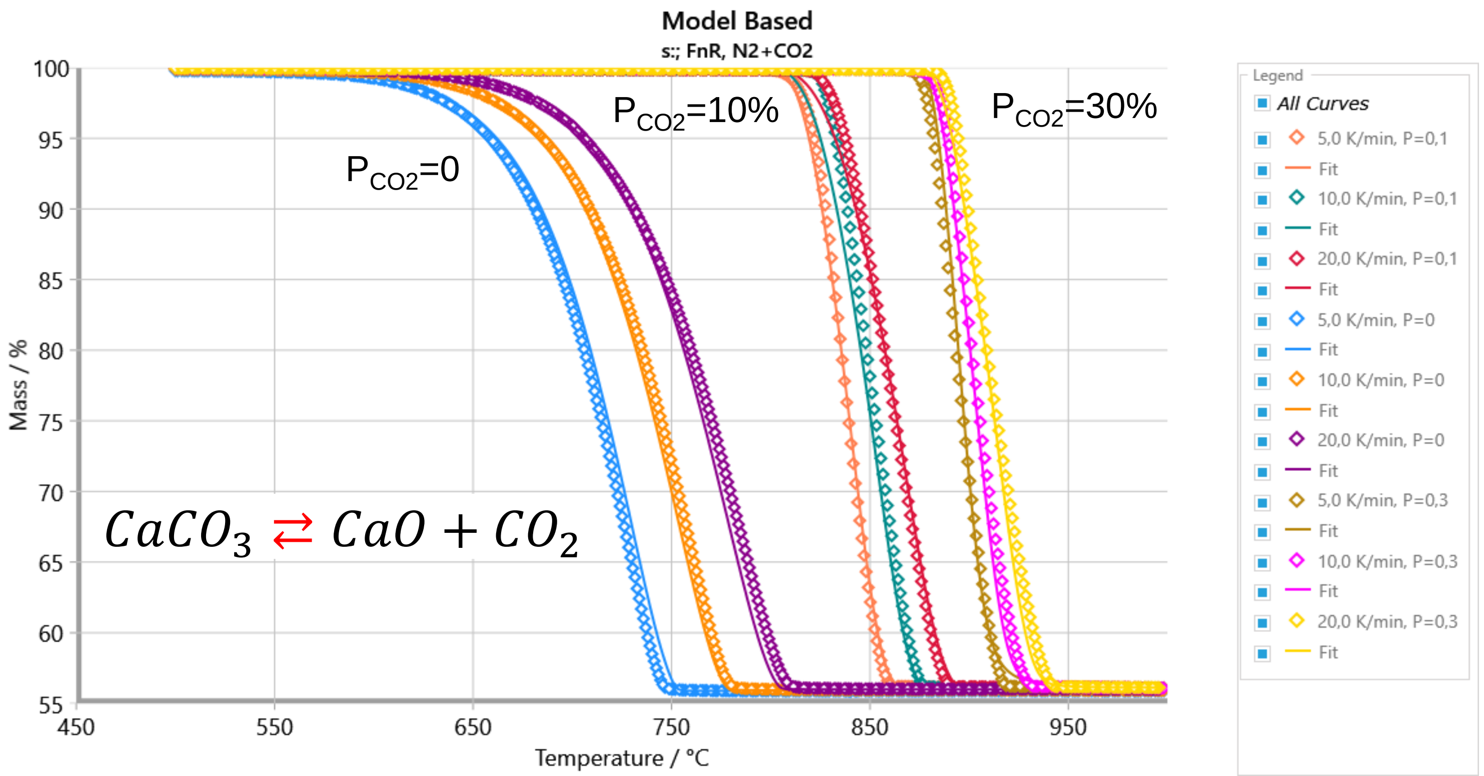
2. Nitrogen with CO_2 (reaction is reversible, P is partial pressure of CO_2)

$$CaCO_3 \rightleftarrows CaO + CO_2$$

$$\frac{d\alpha}{dt} = A_1\, exp\left(\frac{-E_1}{RT}\right) f_1(\alpha) - P^n A_2 exp\left(\frac{-E_2}{RT}\right) f_2(\alpha)$$

CO_2 is the reactive gas for reverse reaction
The rate of reverse reaction depends on the CO_2 concentration
The higher partial pressure of CO_2 - the higher rate of reverse reaction and therefore, the total decomposition is later

Common kinetic model for decomposition of $CaCO_3$ in Nitrogen with partial pressure CO_2 (total Pressure=1 bar)



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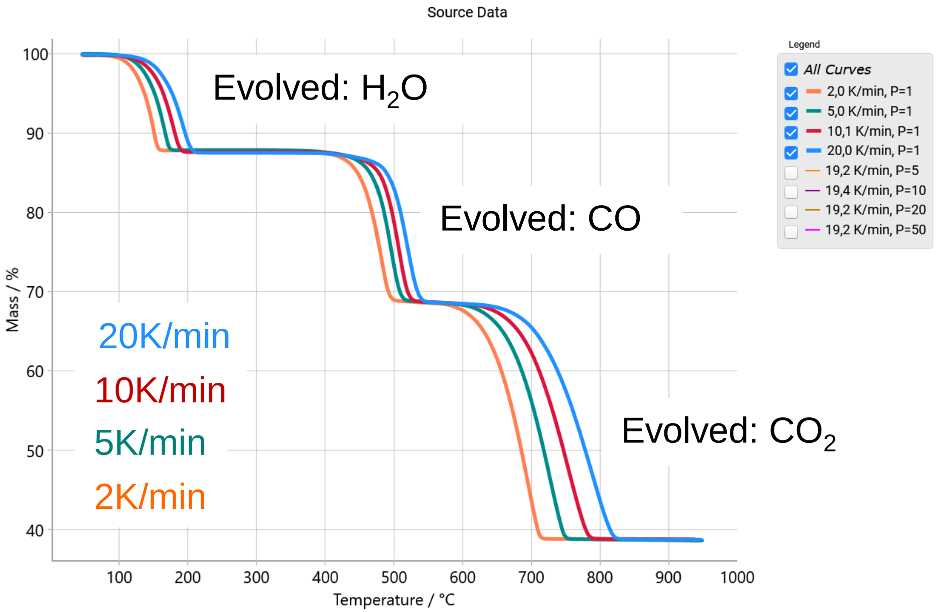
2.3 Pressure-Dependent Reactions in Inert Gas

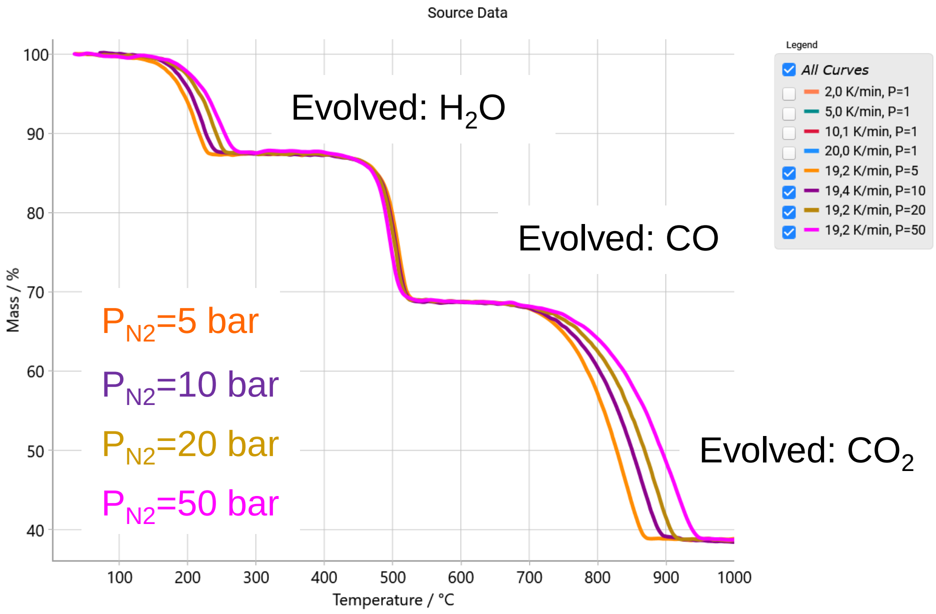
Decomposition of $CaOx*H_2O$ under high pressure of N_2

total pressure of N2 is from 1 to 50 bar

CaOx*H2O at different heating rates and different pressure of N2



normal pressure 1 bar,
different heating rates



Heating rate 20K/min,
different pressures of N2

Decomposition of $CaC_2O_4*H_2O$ in Nitrogen under high pressure

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Nitrogen, High Pressure

$$CaC_2O_4 * H_2O \rightleftarrows CaC_2O_4 + H_2O$$

$$CaC_2O_4 \rightarrow CaCO_3 + CO$$

$$CaCO_3 \rightleftarrows CaO + CO_2$$

N_2 is the inert gas. It has no influence on the forward reactions for all steps.
It has no influence on the second step, because the second step is non-reversible reaction.
For high pressure of N_2 the diffusion coefficient is lower and the products (H_2O for the first step and CO_2 for the third step) can not be removed fast from reaction zone.
Then for high pressure the reverse reaction is faster, and the total decomposition is later.

Decomposition of $CaCO_3$ in Nitrogen with CO_2

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Step 1: reaction is reversible, prefix F: forward reaction, B: reverse reaction, P is pressure of N_2

$$CaC_2O_4 * H_2O \rightleftarrows CaC_2O_4 + H_2O$$

$$\frac{d\alpha}{dt} = A_{1F}\, exp\left(\frac{-E_{1F}}{RT}\right) f_{1F}(\alpha) - A_{1B} exp\left(\frac{-E_{1B}}{RT}\right) f_{1B}(\alpha) \qquad = P^{n1} A_1 exp\left(\frac{-E_1}{RT}\right) f_1(\alpha)$$

Step 2: only forward reaction

$$CaC_2O_4 \rightarrow\ CaCO_3\ + CO$$

$$\frac{d\alpha}{dt} = A_2\, exp\left(\frac{-E_2}{RT}\right) f_2(\alpha)$$

Step 3: reaction is reversible, prefix F: forward reaction, B: reverse reaction, P is pressure of N_2

$$CaCO_3 \rightleftarrows CaO + CO_2$$

$$\frac{d\alpha}{dt} = A_{3F}\, exp\left(\frac{-E_{3F}}{RT}\right) f_{3F}(\alpha) - A_{3B} exp\left(\frac{-E_{3B}}{RT}\right) f_{3B}(\alpha) \qquad = P^{n3} A_3 exp\left(\frac{-E_3}{RT}\right) f_3(\alpha)$$

Common kinetic model for decomposition of $CaC_2O_4*H_2O$ in Nitrogen, different pressures from 1 bar to 50 bar, different heating rates: see legend

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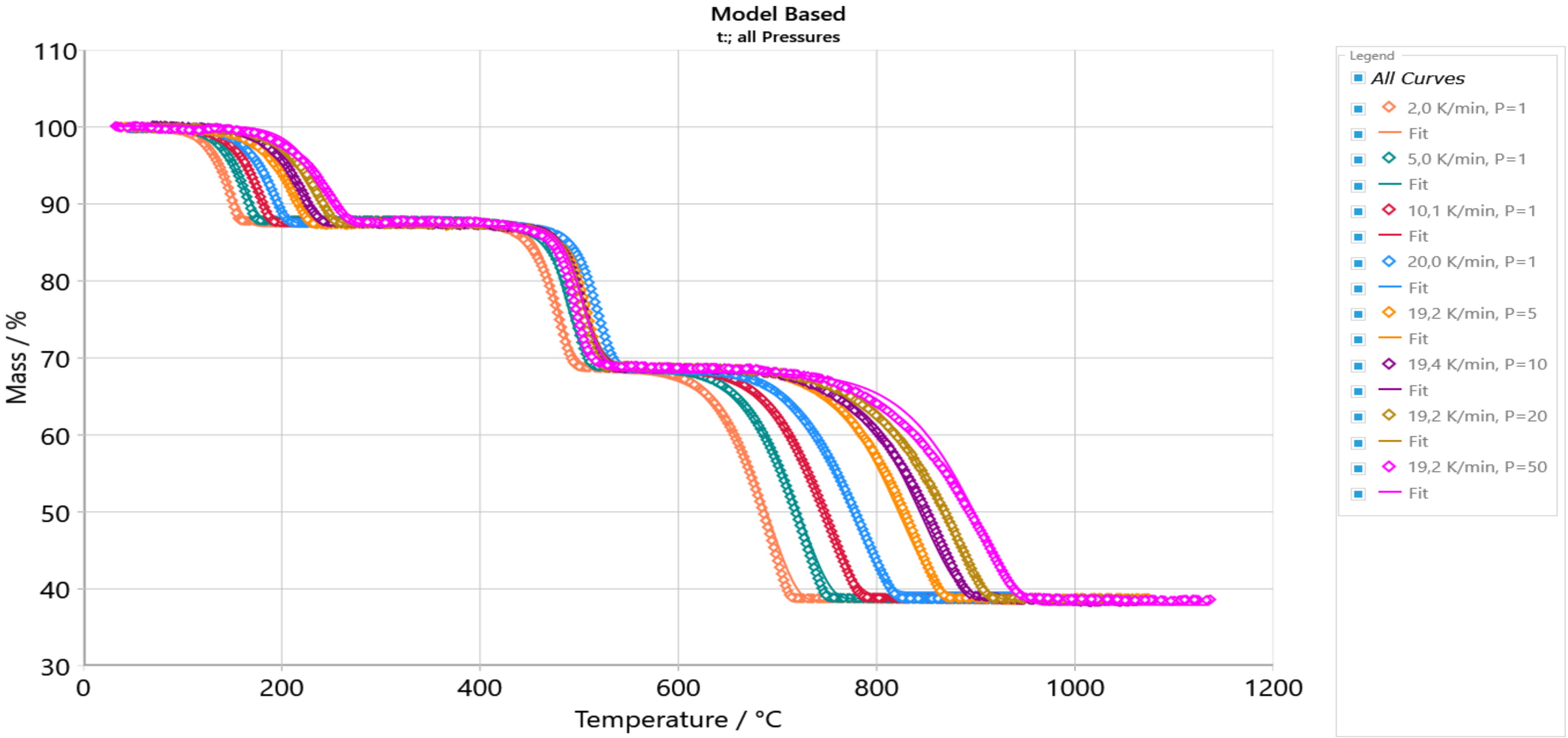

Optimal parameters for pressure: n_1= - 0.75, n_3= - 0.73

3

Thermosets, composites, photopolymers

3.1 UV intensity for DSC, DEA

3.2 Diffusion control for DEA, Rheology

3.1 Curing depending on intensity of UV light

UV curing at different temperatures and different intensities (10kHz)

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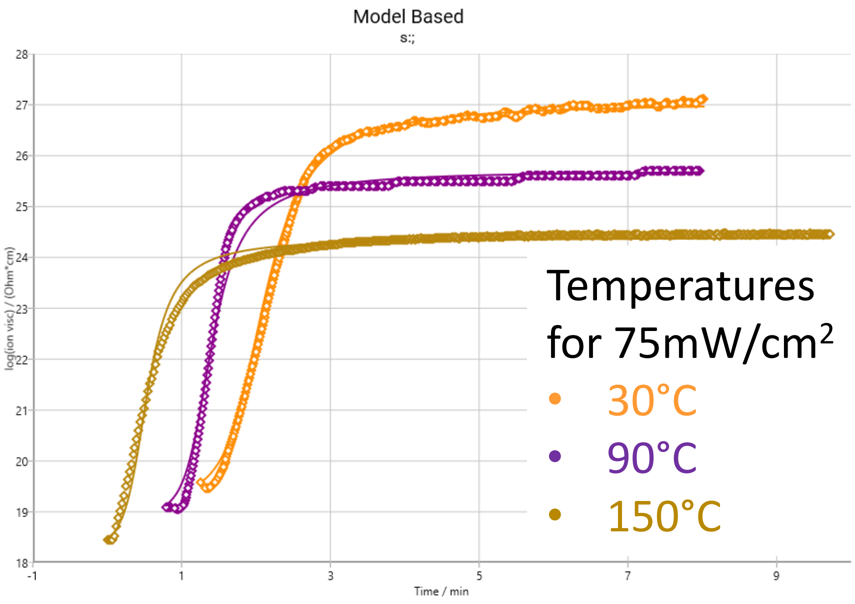

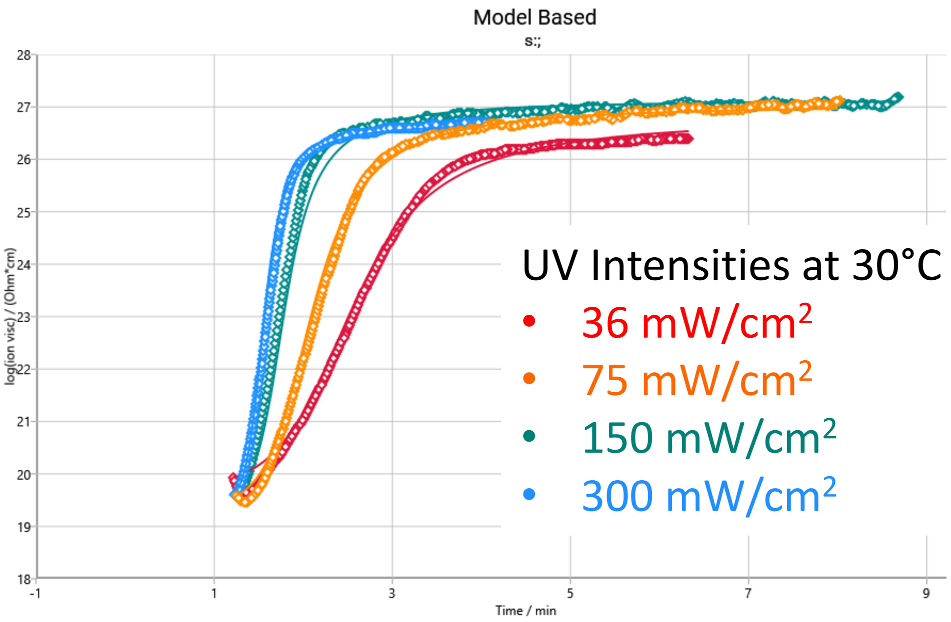

Isothermal DEA measurements at 30°C, 90°C, 150°C for light exposure at 75mW/cm^2

Isothermal DEA measurements at 30°C for light exposure at different intensities from 75mW/cm^2 to 150mW/cm^2

Data: https://4spepublications.onlinelibrary.wiley.com/doi/10.1002/pen.26353

Common model in Kinetics Neo depending on both temperature and the intensity of UV light

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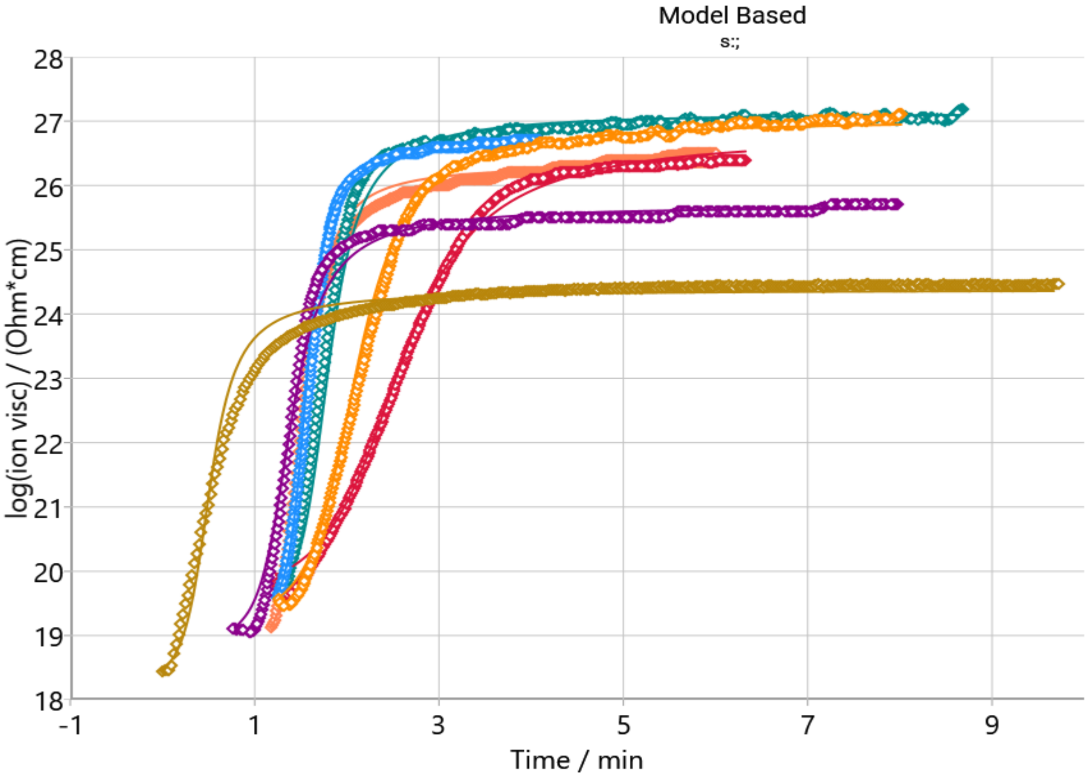

Temperatures

- 30°C
- 90°C
- 150°C

UV Intensities

- 36mW/cm^2
- 75mW/cm^2
- 150mW/cm^2
- 300mW/cm^2

Data: https://4spepublications.onlinelibrary.wiley.com/doi/10.1002/pen.26353

3.2 Diffusion control for DEA, Rheology

Diffusion control for new data: DEA, Rheology

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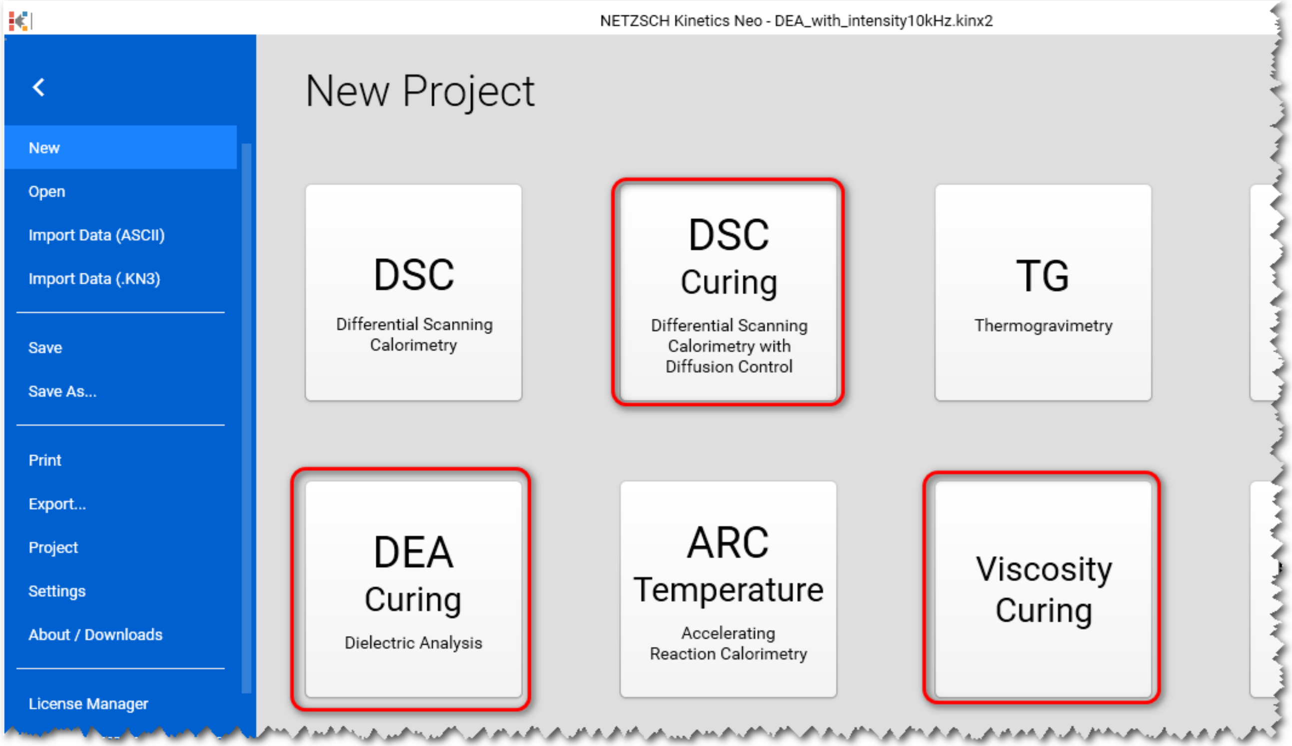


Reactions of curing and cross-linking near glass transition temperature are diffusion controlled

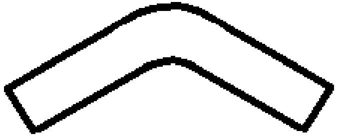
Amorphous material (Polymer)

Reaction

finished

Glassy

state



Rubbery or liquid

state

Tg

Slow curing

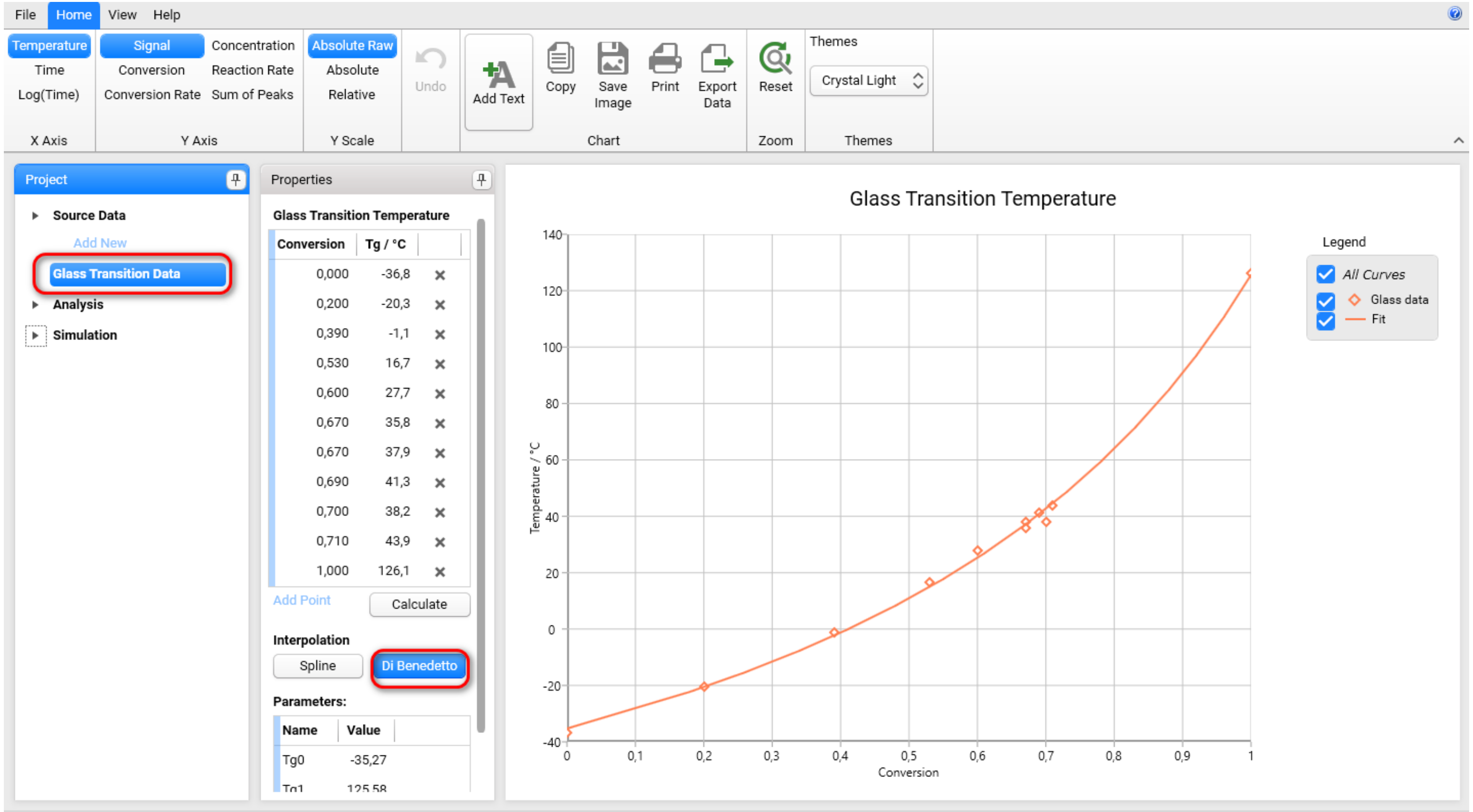
T<Tg

Fast curing

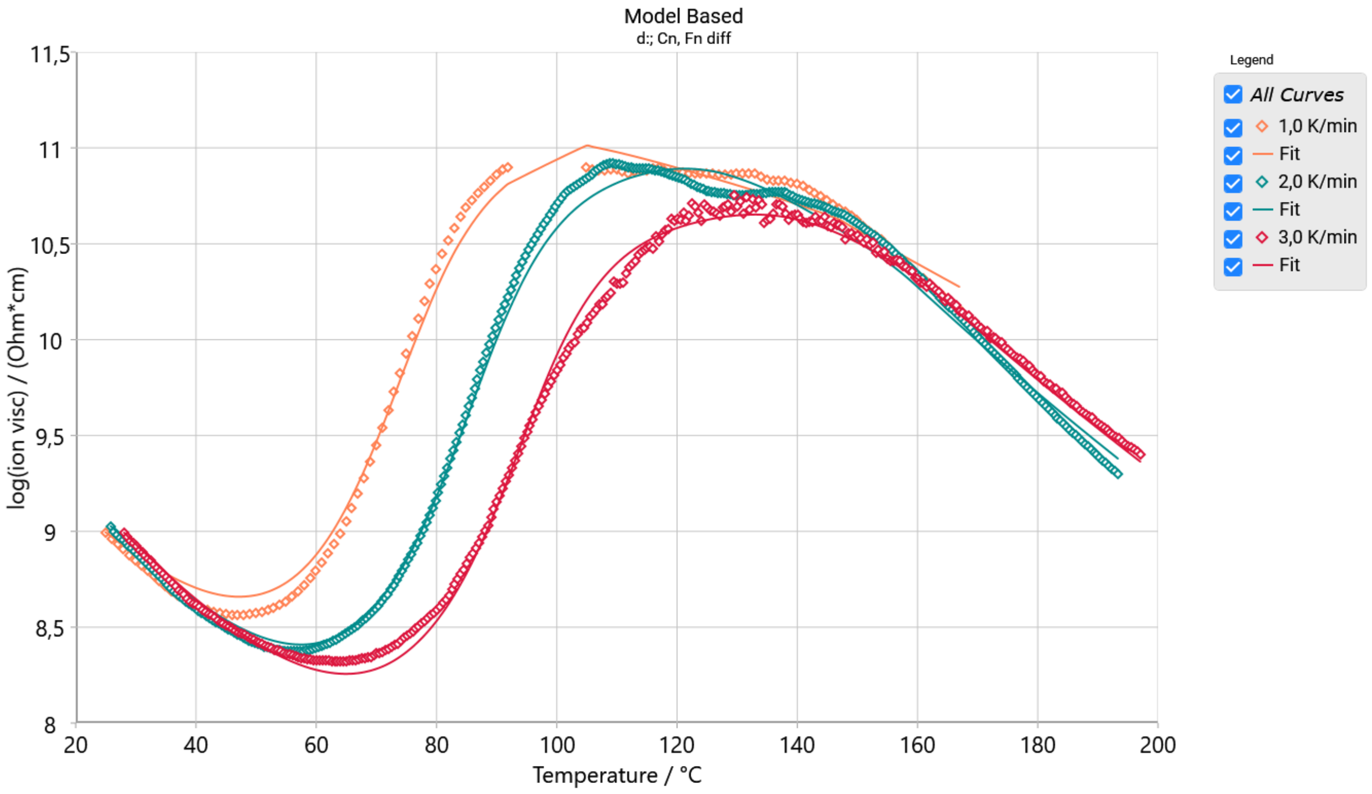
T>Tg

Glass transition

Kinetic analysis of DEA data for curing with diffusion control



Kinetics on DEA Data for epoxy curing with diffusion control



4

Flexible Data Evaluation

4.1 Evaluation of arbitrary data

4.2 Kinetics for incomplete data

4.3 New reaction types

4.1 Evaluation of Arbitrary Data

- Differential data
- Integral data

Arbitrary data

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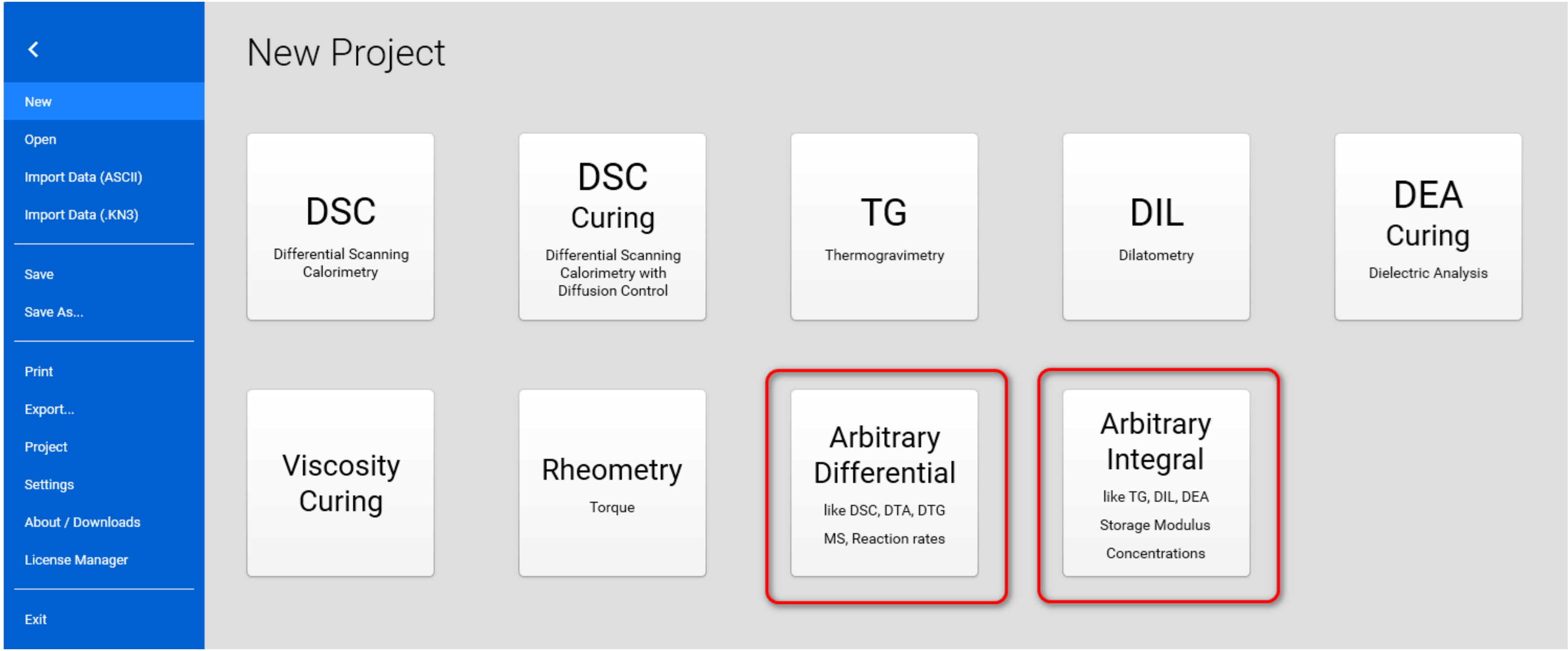
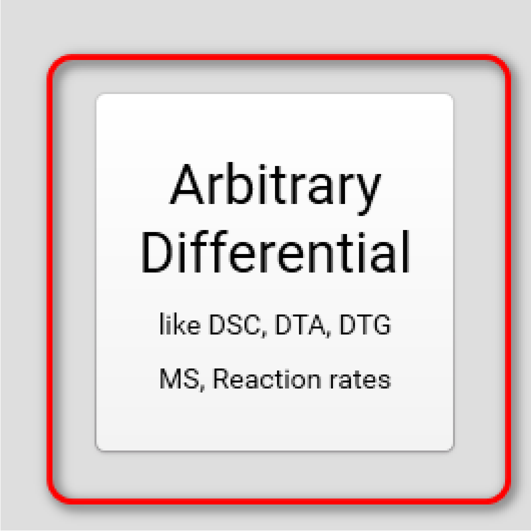


Arbitrary differential data

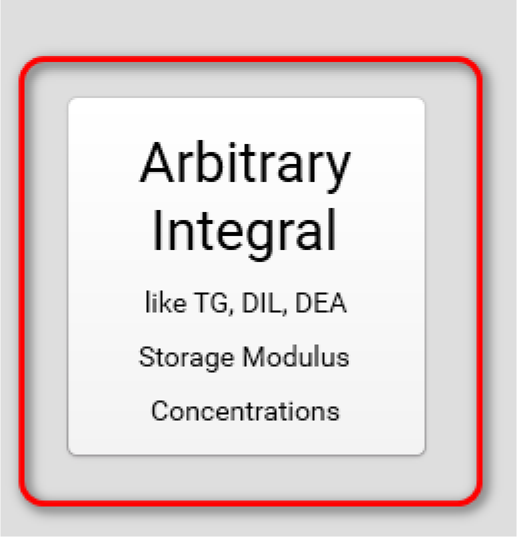
Usage:



- DTA (differential thermal analysis)
- MS (mass-spectrometry)
- Other differential data,
  containing the reaction peak like **DSC**

Arbitrary Integral Data

Usage:



- Measured concentrations
- Conversion
- Storage modulus
- Absorbance
- Other integral data
  containing reaction step like **TG**

4.2 Kinetics for Incomplete Data

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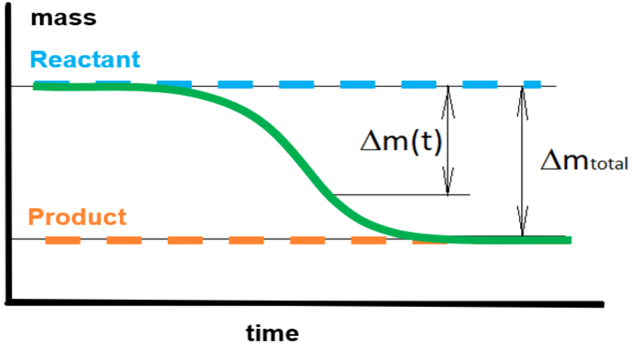
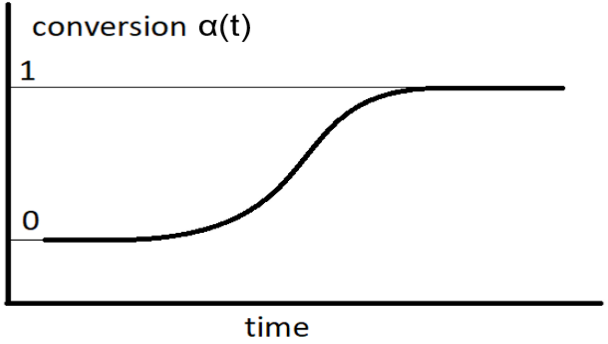
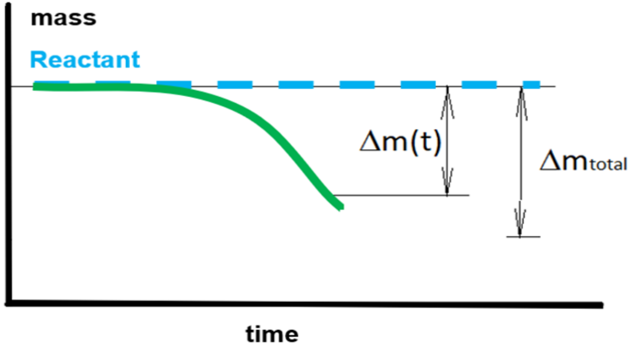
Complete

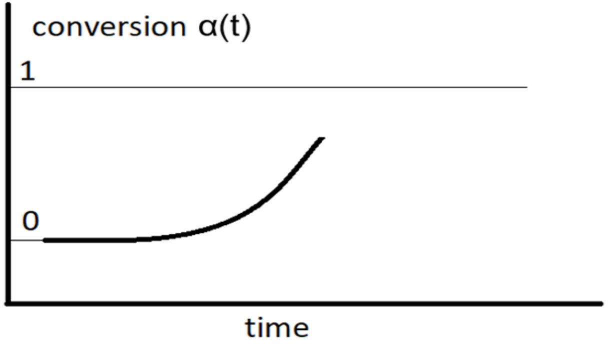




$$\alpha(t) = \frac{\Delta m(t)}{\Delta m_{total}}$$

Incomplete





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

Incomplete Measured Data

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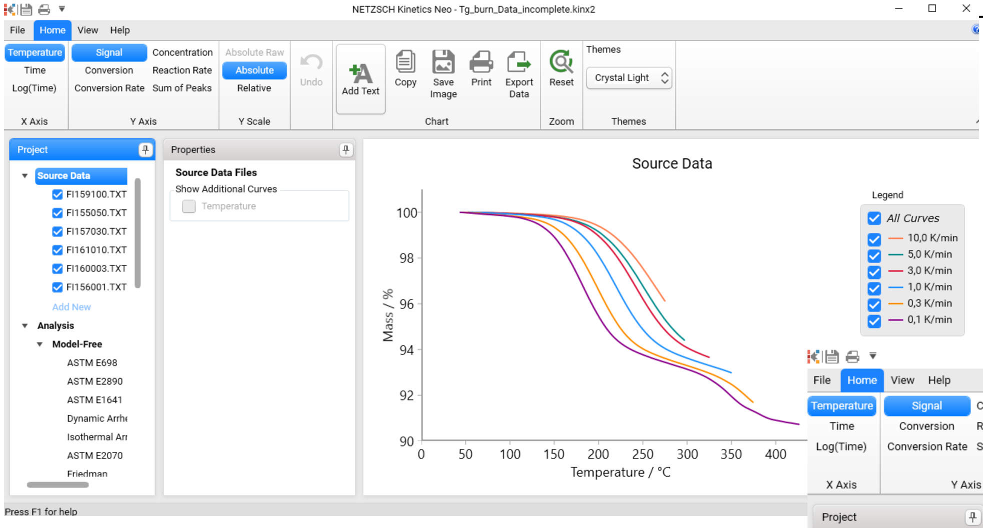
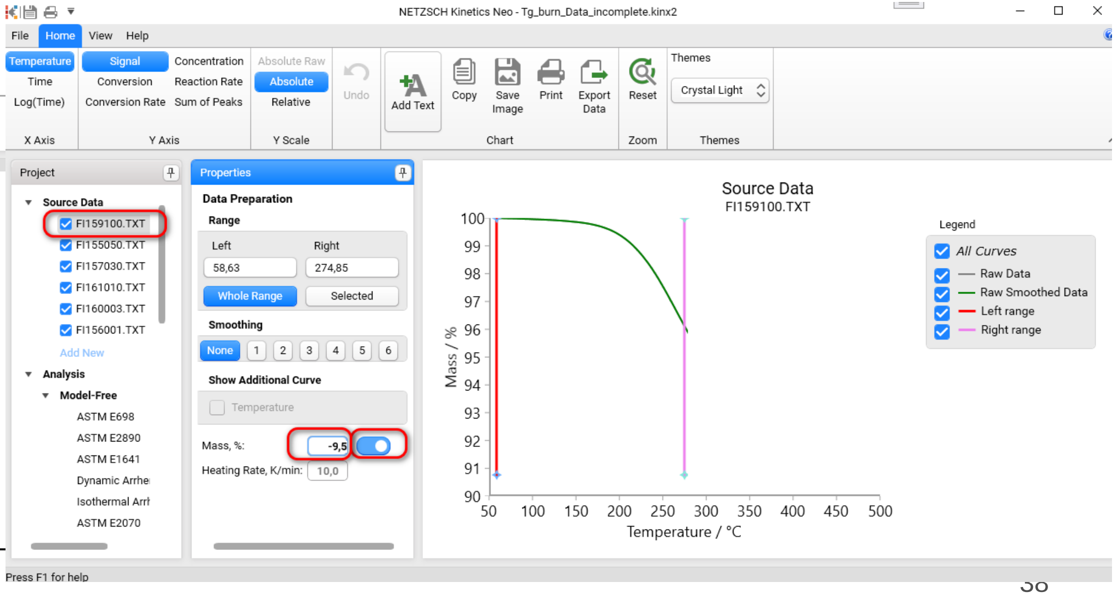


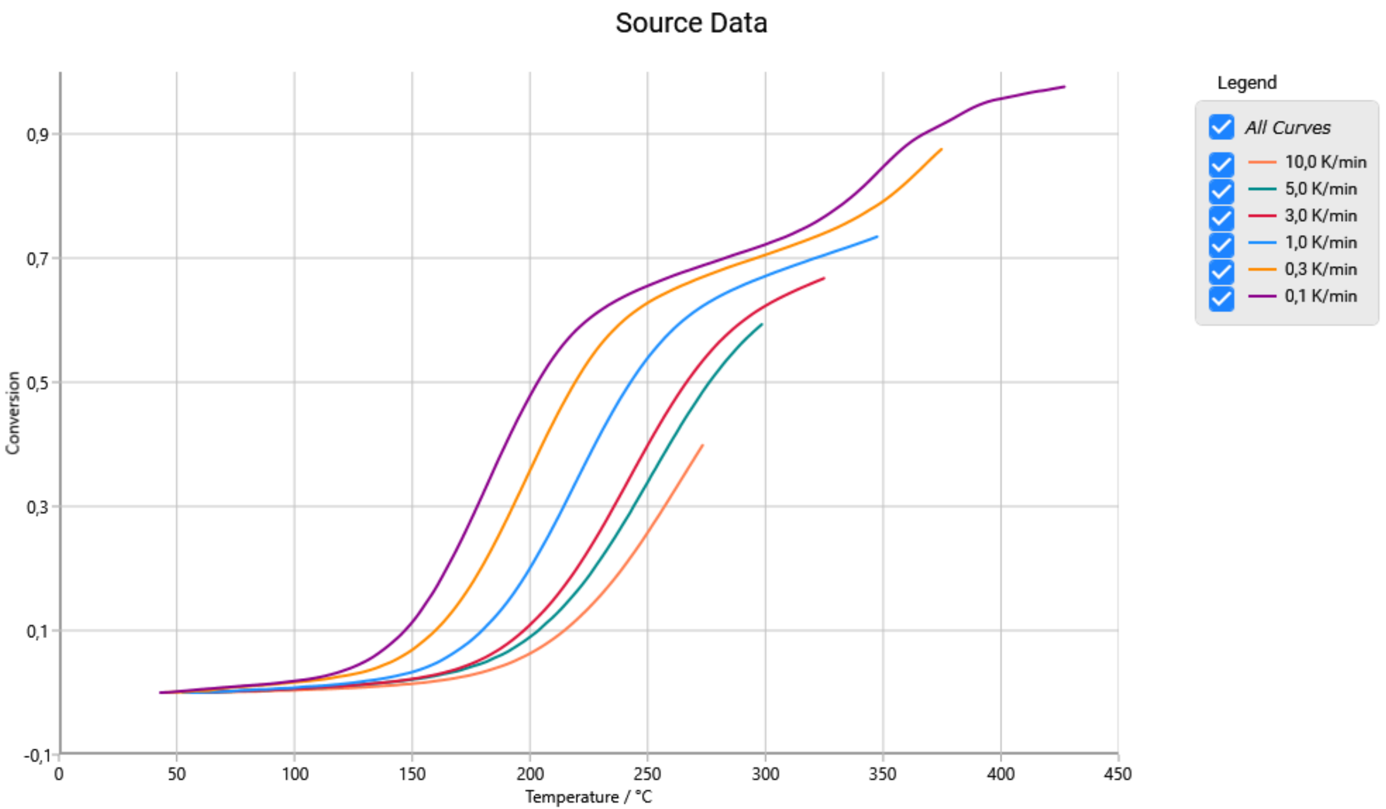
Set total thermal effect
for each measured curve



Total thermal effect:

- Mass loss (TG)
- Peak area (DSC)
- Length change (DIL)
- Signal change (DEA, Rheometry)

Incomplete Measured Data: Final Part of Reaction Is not Present



Model Based Analysis for Incomplete Data

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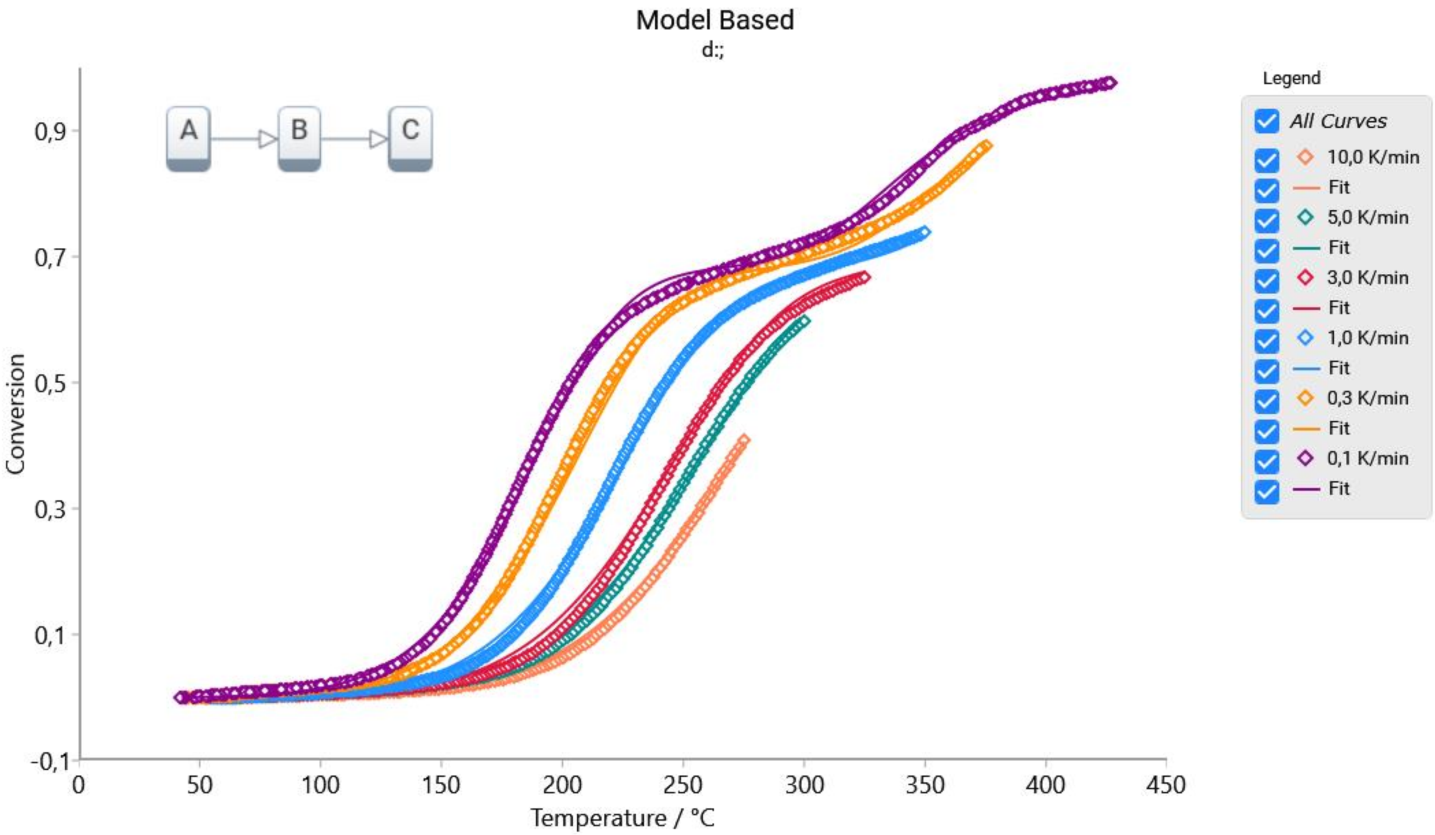
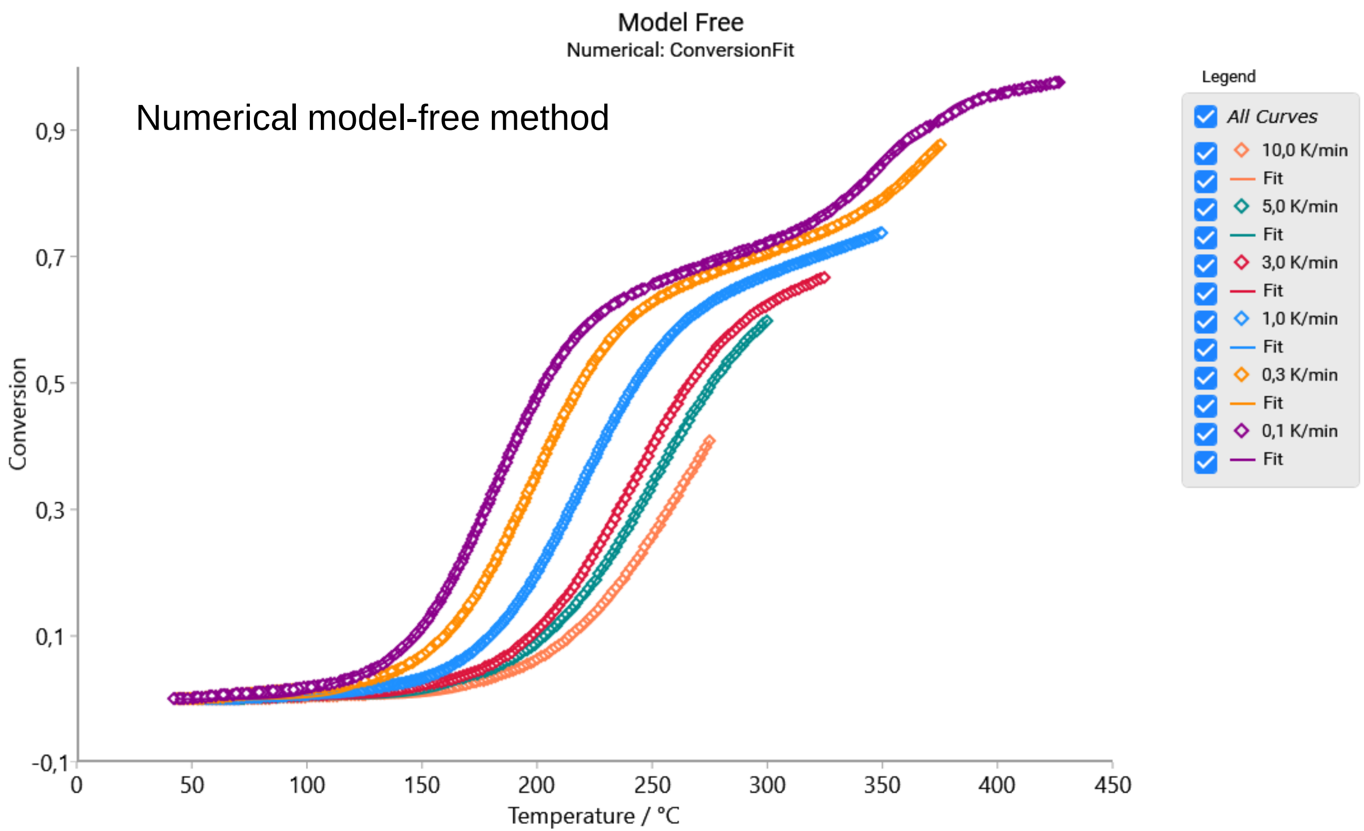


NEW: Model-Free Analysis for Incomplete Measured Data



4.3 New Reaction Types

- Reversible reactions
- Reaction of n-th order with diffusion

Reversible Reactions of n-th order

NEW: FnR

$$A \rightleftarrows B$$

Forward:	$A \rightarrow B$	$A_1\, exp\left(\frac{-E_1}{RT}\right) f_1(\alpha)$
Reverse:	$A \leftarrow B$	$A_2\, exp\left(\frac{-E_2}{RT}\right) f_2(\alpha)$

$$\frac{d\alpha}{dt} = A_1\, exp\left(\frac{-E_1}{RT}\right) f_1(\alpha) - A_2\, exp\left(\frac{-E_2}{RT}\right) f_2(\alpha)$$

Rection rate $_{total}$ *= Reaction rate* $_{forward}$ *– Reaction rate* $_{reverse}$

Reaction of n-th order with diffusion

3-dimensional diffusion in the literature

D3:Jander $1.5 * (1-\alpha)^{2/3} / (1-(1-\alpha)^{1/3})$

D4:Ginstling-Brounstein $1.5 * (1-\alpha)^{1/3} / (1-(1-\alpha)^{1/3})$

Zhuravlev-Lasokin-Tempelman $1.5 * (1-\alpha)^{5/3} / (1-(1-\alpha)^{1/3})$

General equation: $\boldsymbol{1.5 * (1-\alpha)^{n} / (1-(1-\alpha)^{1/3})}$

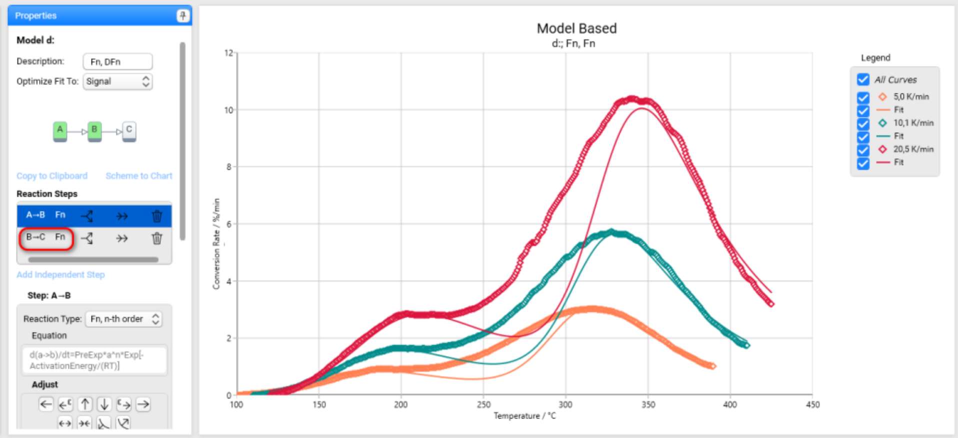
https://doi.org/10.1016/S0040-6031(03)00222-3

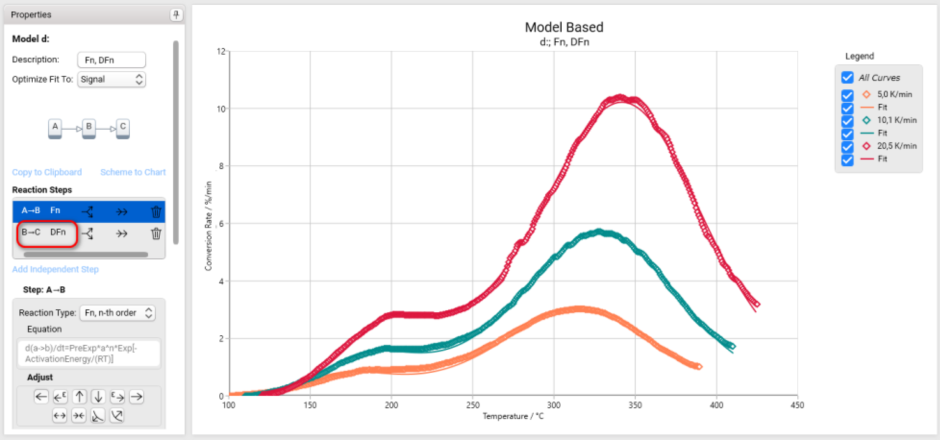
1-dimensional diffusion

D1: $0.5 / \alpha$

NEW DFn: $0.5 / \alpha * (1-\alpha)^{n}$

Reaction of n-th order with one-dimensional diffusion for decomposition





Fn

NEW: DFn

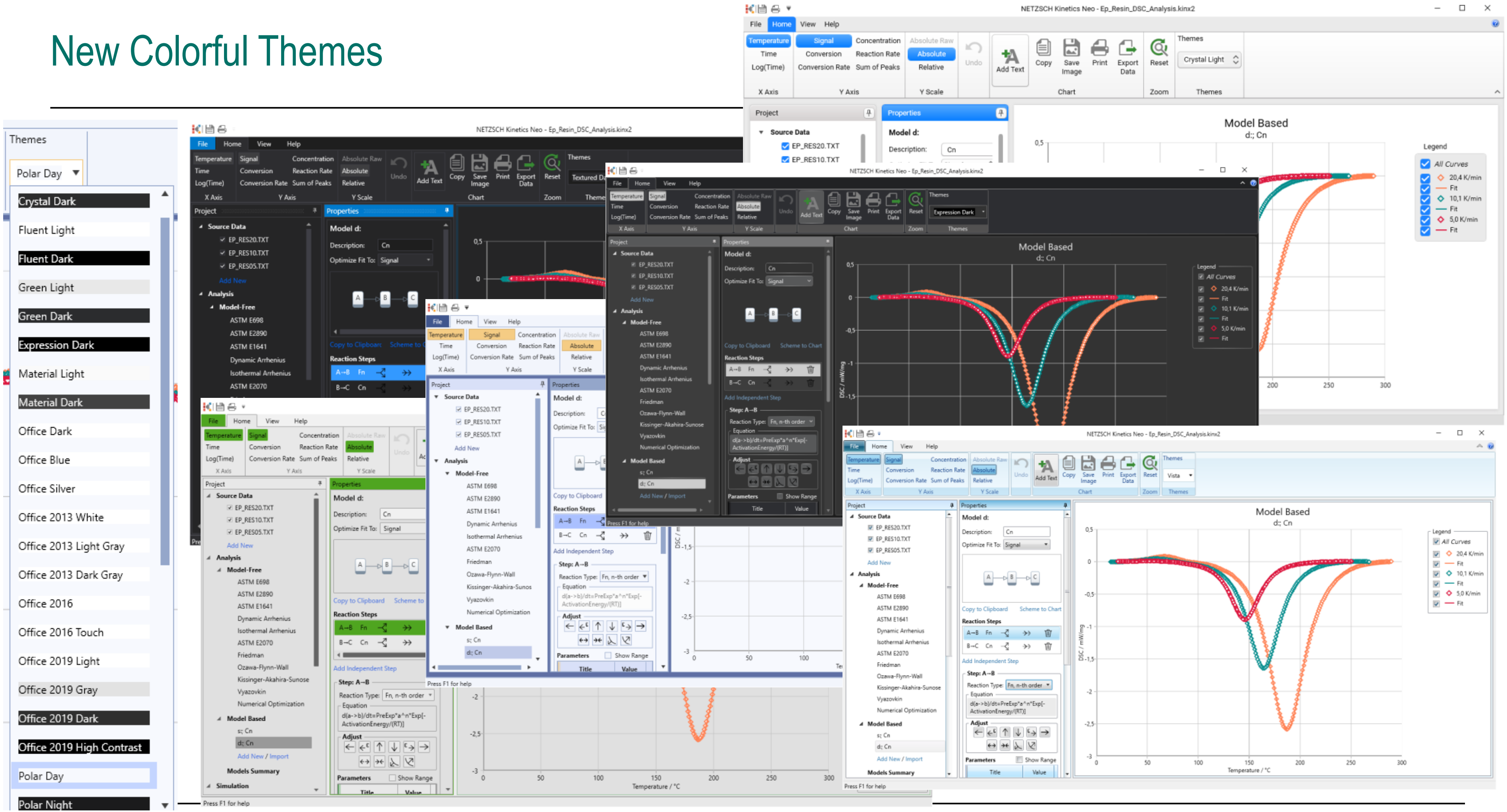
New reaction type ***DFn*** for the *first-dimensional diffusion with n-th order*.
DFn reaction type considers diffusion process in the material during decomposition.
It adds the diffusion mechanism to the classical reaction of n-th order (Fn).

5

User Interface (UI) is reworked for native look in Windows 11

New colorful themes

New Colorful Themes



Subscription Support Provides Updates for Free

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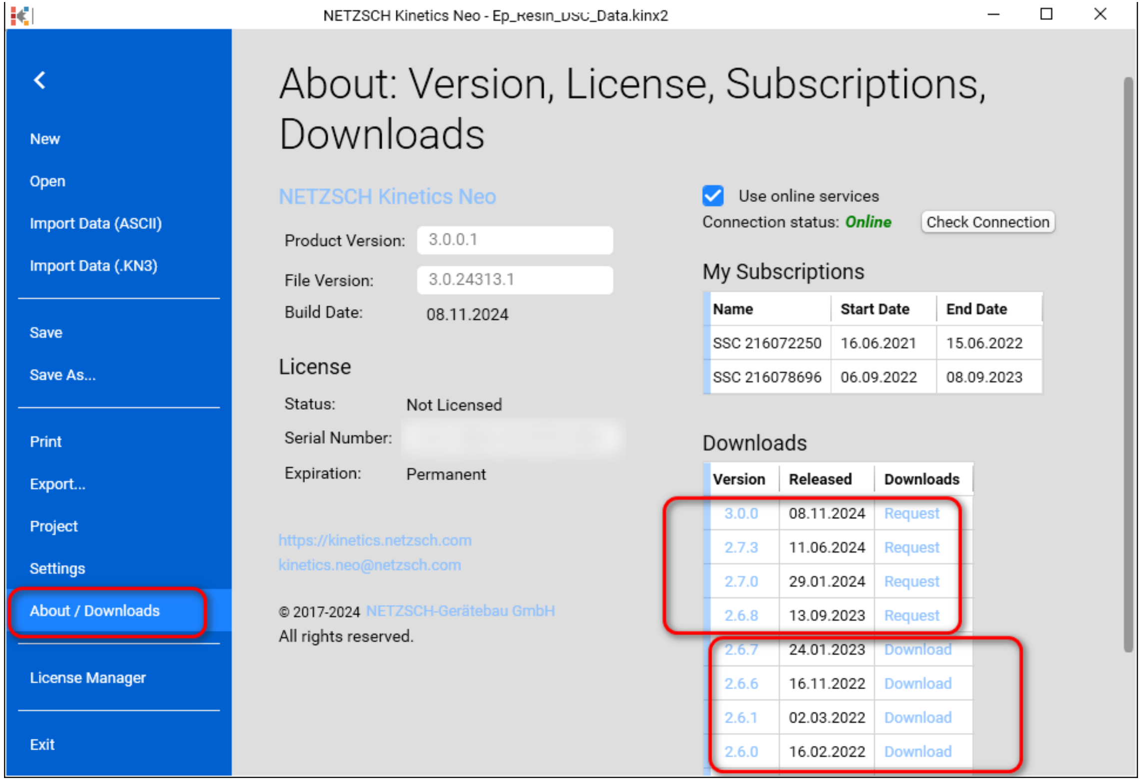

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