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Proven Excellence.

How fast are chemical reactions?

kinetics.netzsch.com



Kinetics Neo

Kinetic Analysis Software for Thermal Measurements of Chemical Reactions.
Model-Free and Model-Based Methods

Analyzing & Testing

Substances with well-defined properties can be converted into other substances with different properties by the chemical reactions of a set of reactants. Reactions can run their course within a fraction of a second, as with explosions, or can take thousands or even million of years, as with the formation of minerals.

Kinetics, also called reaction kinetics or chemical kinetics, investigates the rates of chemical processes and allows for the determination of reaction rates. It also takes the factors that control these rates into consideration. Knowledge about points such as these can give deep insight into the detailed molecular mechanisms behind elementary reactions.

Applications

- Prediction of degree of cure during curing process including determination of the curing time in case the material changes its properties. The simulation accounts for autocatalytic reactions, reactions with diffusion control and changing of the glass transition temperature during the curing process.
→ Automotive and aerospace industry, paints, epoxy coatings, composites, adhesives, etc.
- Research of the reaction mechanism for complex process, including information about each reaction step and all its parameters from activation energy and reaction order to the number of reaction steps and their contribution to the total process.
- Crystallization of polymers during fast cooling → Injection molding
- Optimization of the polymer debinding process for highest quality in shortest time.
→ Sintering during powder metallurgy processes
- Relatively fast and cost-effective optimization of the firing profile for optimum binder burnout and shrinkage behavior to prevent cracking and caves
→ Production of ceramics, sintering behavior
- How long can a pharmaceutical be stored until it loses its activity?
→ Pharmaceutical research and industry
- How long can epoxy coatings or polymer insulations withstand gases, liquids and electrical lines at a certain temperature?
→ Packaging industry
- How long can a high-energy material or hazardous substance be stored under certain climatic conditions and when can a thermal runaway reaction be expected?
→ Chemical and military industry

Data Type

TGA, DSC, DTA, DIL, DEA



FOR ANY REACTING MATERIAL...

Kinetics Neo

*can analyze any process
for which the rate
depends on temperature*

NETZSCH Kinetics Neo software is used to analyze kinetics of temperature-dependent chemical processes. The result of such analysis is a kinetics model or method correctly describing experimental data under different temperature conditions. Use of the method/model allows for predictions of a chemical system's behavior under user-defined temperature conditions. Alternatively, such models can be used for process optimization.

The software can analyze different types of thermal curves that depict the changes in a given material property measured during a process. Potential data sources include studies using thermogravimetry, dilatometry, differential scanning calorimetry, Fourier-Transform infrared spectroscopy, mass spectrometry and rheometry, as well as temperature analysis during adiabatic measurements.

The unique model-based kinetic analysis is capable of determining **the number of reaction steps**, and for each step the following values:

- Enthalpy (exo/endothermal DSC effects) or mass loss (TGA)
- Reaction type
- Activation energy
- Pre-exponential factor
- Order of reaction
- Order of autocatalysis
- Additional kinetic parameters
- Crystallization parameters

All Kinds of Advantages

The primary advantage of Kinetics Neo is its ability to analyze both heterogeneous and phase-boundary reactions – and to analyze such reactions with diffusion and nucleation. Furthermore, reactions with partial diffusion control can be studied; for example, processes which change the state of a substance from the glassy to the non-glassy state.

Kinetic Analysis

Model-based or
model-free



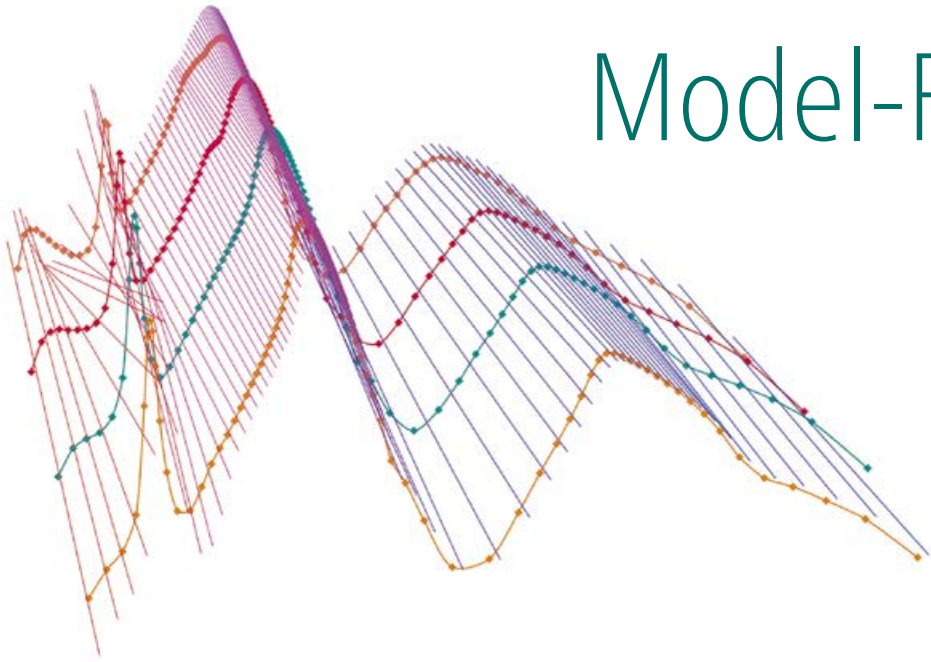
Prediction

of user-defined
temperature profile



Process Optimization

Model-Free Analysis



Kinetics Neo allows for the use of both model-free and model-based methods.

Starting Points for a Kinetic Analysis

Each kinetic analysis requires a set of analytical measurements carried out under different temperature conditions. These can include dynamic test runs using different heating rates or isothermal measurements monitored at different temperatures. Even a combination of dynamic and isothermal measurements is suitable for kinetic studies.

The Basics of Model-Free Analysis

Model-free analysis allows for the determination of the activation energy of a reaction process without assuming a kinetic model for the process. Also, the reaction type is usually not required to calculate the activation energy.

However, it is not possible to determine the number of reaction steps, their contribution to the total effect or the order in which they occur.

Model-free analysis is based on two assumptions:

- 1 The reaction rate is described by a kinetic equation for the degree of reaction α :

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

where $E(\alpha)$ is the activation energy depending on the conversion α , and $A(\alpha)$ is the pre-exponential factor.

- 2 The reaction rate at a constant value of conversion is only a function of temperature.

In addition to having its own specific advantageous features, Kinetics Neo is also in accordance with the following standards, common and special methods:

Analysis

Model-Free

- ASTM E698
- ASTM E2890
- ASTM E1641
- ASTM E2070
- Friedman
- Ozawa-Flynn-Wall (OFW)
- Kissinger-Akahira-Sunose (KAS)
- Numeric Optimization

There is No Assumption of the Reaction Type

The Model-Free Analysis Methods – Advantages and Disadvantages

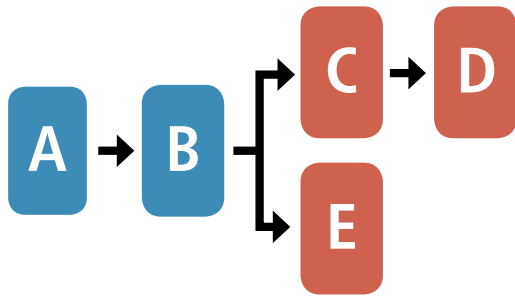
The **Friedman** analysis is an isoconversional method whereas the **Ozawa-Flynn-Wall (OFW)** and **Kissinger-Akahira-Sunose (KAS)** analyses are integral isoconversional methods. In all methods, the measurements are analyzed for multiple conversion levels. Friedman requires at least two measurements. In addition to two dynamic measurements, OFW and KAS require positive heating rates.

The **Numerical Optimization** uses digital simulation in determining the activation energy and pre-exponential factor to achieve the best agreement between simulated and experimental curves. At least two measurements are required.

In all of the methods, the activation energy is determined using the points at the same conversion (0.01, 0.02, ..., 0.99) from the measurements at different heating rates or under different isothermal conditions (for Friedman and Numerical Optimization).

Methods Included in Kinetics Neo		Advantage	Disadvantage
Conversion-dependent methods	Friedman	<ul style="list-style-type: none"> For multiple-step reactions without parallel reaction steps Evaluation of each reaction point Suitable for dynamic and isothermal measurements 	For parallel and independent reactions, the mean values of E_a are given
	Ozawa-Flynn-Wall (OFW)	<ul style="list-style-type: none"> For multiple-step reactions without parallel reaction steps Evaluation of each reaction point 	<ul style="list-style-type: none"> Suitable only for dynamic runs For parallel and independent reactions, the mean values of E_a are given
	Kissinger-Akahira-Sunose (KAS)	<ul style="list-style-type: none"> For multiple-step reactions without parallel reaction steps Evaluation of each reaction point 	<ul style="list-style-type: none"> Suitable only for dynamic runs For parallel and independent reactions, the mean values of E_a are given
	Numerical Optimization	<ul style="list-style-type: none"> For multiple-step reactions without parallel reaction steps Evaluation of each reaction point Suitable for dynamic and isothermal measurements 	For parallel and independent reactions, the mean values of E_a are given
	ASTM E2070	Evaluation of each reaction point	Suitable for isothermal runs only
Methods based on a single conversion	ASTM E698 ASTM E1641 ASTM E2890		<ul style="list-style-type: none"> Only for one-step reactions; for complex reactions, the points are not on a straight line Only for dynamic measurements Only one point is evaluated; all other information is not used

The difference between Ozawa-Flynn-Wall and Kissinger-Akahira-Sunose are in the calculation formula and results. The same is true for the Friedman analysis method and Numerical Optimization.



Model-Based Kinetics –
Eliminates All the Disadvantages
of Model-Free Analysis Methods

Model-Based Kinetics for Comprehensive Analysis of Chemical Reactions

The extraordinary model-based analysis was developed by NETZSCH. It uses powerful cutting-edge mathematical calculations to create the best kinetic model; the different kinetic models can then also be compared statistically. Therefore, this approach has none of the disadvantages which can be observed when using model-free methods.

The Unique Model-Based Analysis

The Model-Based Kinetic Analysis Is Based on Three Assumptions

- 1 The reaction consists of several elementary reaction steps, and the reaction rate of each step can be described by a kinetic equation of its own for the given step, depending on the concentration of the initial reactant e_j , the concentration of product p_j , the pre-exponential factor A_j and the activation energy E_j , specific only for this step with number j , as follows:

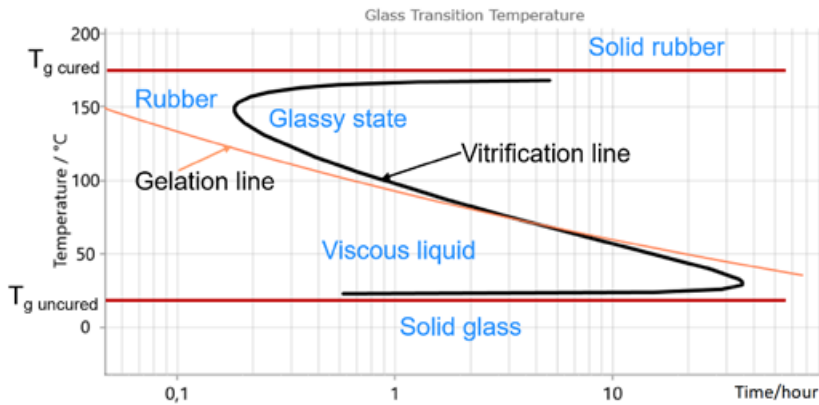
$$\text{Reaction Rate}_j = A_j \cdot f_j(e_j, p_j) \cdot \exp\left(\frac{-E_j}{RT}\right)$$

Each step has its own reaction type described by the function $f_j(e_j, p_j)$.

Some examples of these functions include a second-order reaction which has $f = e^2$, a Prout–Thompkins reaction with acceleration which has $f = e^m p^n$ and a reaction with a one-dimensional diffusion which has $f = 0.5/p$. The number of kinetic equations is equal to the number of reaction steps; the concentration for each reactant increases for the reaction steps where this reactant is a product, and decreases for the reaction steps where this reactant is a starting substance.

- 2 All kinetic parameters including the activation energy, pre-exponential factor, order of reaction, and reaction type are assumed to be constant during the reaction progress for every individual reaction step.
- 3 The total thermoanalytical signal is the sum of the signals of the individual reaction steps. The signal of each step is calculated as the reaction rate multiplied by the total effect of the given step; e.g., total enthalpy change or total mass loss.
- 4 Kinetic parameters are determined by the software to obtain the best fit either for signal (default) or for conversion curves.

TTT: Time Temperature Transition diagram



Kinetics Neo
Includes a
Variety of
Reaction Types

Code	Function in Kinetics Neo	Type of Reaction
F1	$f = e$	Reaction of 1 st order
F2	$f = e^2$	Reaction of 2 nd order
Fn	$f = e^n$	Reaction of n th order
R2	$f = 2e^{1/2}$	Two-dimensional phase boundary
R3	$f = 3e^{2/3}$	Three-dimensional phase boundary
D1	$f = 0.5/p$	One-dimensional diffusion
D2	$f = -1/\ln(e)$	Two-dimensional diffusion
D3	$f = 1.5e^{2/3} / (1 - e^{1/3})$	Three-dimensional diffusion – Jander's type
D4	$f = 1.5 / (e^{-1/3} - 1)$	Three-dimensional diffusion – Ginstling-Brounstein
B1	$f = e \cdot p$	Prout-Tompkins equation
Bna	$f = e^n \cdot p^a$	Expanded Prout-Tompkins equation
C1	$f = e \cdot (1 + \text{AutocatOrder} \cdot p)$	Reaction of 1 st order with autocatalysis by product
Cn	$f = e^n \cdot (1 + \text{AutocatOrder} \cdot p)$	Reaction of n th order with autocatalysis by product
Cmn	$f = e^n \cdot (1 + \text{AutocatOrder} \cdot p^m)$	Reaction of n th order with autocatalysis of m th order by product
Kamal-Sourour	Two parallel reactions with the same reactant and the same product. One is the reaction of the n th order, the second is the autocatalytic reaction with its own activation energy	
A2	$f = 2e \cdot [-\ln(e)]^{1/2}$	Two-dimensional nucleation according to Avrami
A3	$f = 3e \cdot [-\ln(e)]^{2/3}$	Three-dimensional nucleation according to Avrami
An	$f = n \cdot e \cdot [-\ln(e)]^{(n-1)/n}$	n-dimensional nucleation according to Avrami-Erofeev
Nk	$n \cdot e \cdot [-\ln(e)]^{(n-1)/n} \text{HL}(T)$	Nakamura crystallization with Hoffman-Lauritzen temperature dependence HL(T)

Each reaction step j is of a certain reaction type which is mathematically included via the function $f_j(e, p)$. Kinetics Neo includes all listed types of reaction.

Predictions



Based on the created kinetic model (model-free or model-based), the software simulates the signal, conversion rate and conversion for user-defined temperature programs. This allows for the prediction of sample properties for temperature conditions which differ from the conditions originally used during the measurement(s).

A careful model-free or model-based analysis of the experimental data is recommended prior to the calculation of predictions. For predictions, a variety of temperature programs are available within NETZSCH Kinetics Neo (see column at right).

A long-term prediction of material aging, including the prediction of time to failure at a given temperature, can be made using the Arrhenius approach where no complete measurement is available. First data is the failure temperature during heating (e.g., OIT or specimen fracture during DMA tests) and the experimental time to failure under isothermal conditions.

Process Optimization

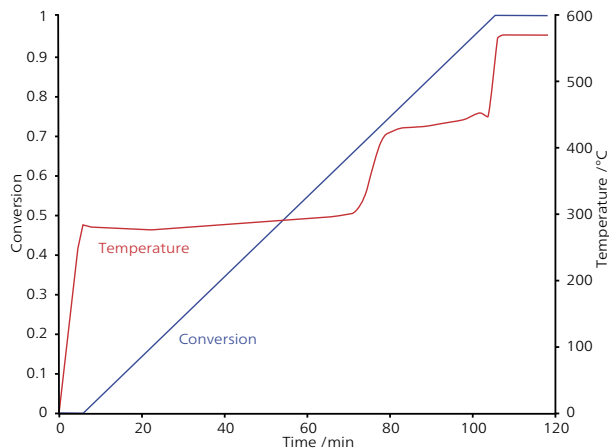
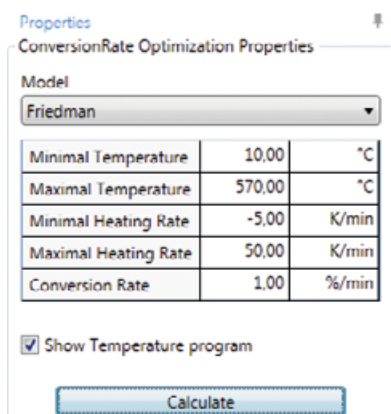
This feature allows for the simulation of data once the experimental data is described by model-free or model-based kinetics. The temperature profile can be calculated and optimized taking into account defined boundary conditions; e.g., constant or user-defined conversion rate, constant signal rate, temperature range and range of heating rates. The results depend on the chosen model-free or model-based method and its parameters. Careful kinetic analysis of the experimental data is required prior to calculating the optimization (see column at right).

Predictions

- Isothermal
- Isothermal lifetime
- Dynamic
- Multiple step
- Step iso
- Modulated isothermal
- Modulated dynamic
- Adiabatic
- Time-Temperature-Transition (TTT)

Optimization

- Conversion rate
- Signal rate (RCM for thermogravimetry and RCS for dilatometry)



Optimization of the conversion rate at 1 %/min



What Makes Kinetics Neo So Valuable ...

- Completely rewritten from scratch, this innovative software is based on the latest technologies.
- The improved user interface is fast and easy to operate.
- All model-free and model-based methods are included. The results from all of these methods can be statistically compared with one another.
- The powerful new numerical model-free method ensures fast determination of the best model-free solution.
- Predictions and optimizations can be achieved by means of both model-free and model-based methods.
- A visual kinetic model can be created quickly and easily using the model-based method.
- Unlimited number of kinetic models.
- The kinetic model can contain any number of individual reaction steps in any combination. Reaction steps can be easily added, removed or changed by the user.
- The position of individual reaction steps can be visually adjusted at any time.
- An individual step or the entire kinetic model can be optimized with just a click of the mouse.
- The software provides the formal concentration of each reactant and reaction rate for each reaction step as a function of time or temperature.
- Crystallization processes for isothermal and cooling conditions can be analyzed and predicted.

MODEL-BASED
PREDICTIONS
OPTIMIZATION
VISUAL ADJUSTMENT
ANY NUMBER OF
REACTION STEPS
**ISOTHERMAL
AND DYNAMIC
CRYSTALLIZATION**
NEW MODELS
**COMBINATION OF
REACTION STEPS**
FAST AND EASY-
TO-USE INTERFACE
TTT DIAGRAM
IN ACCORDANCE
WITH STANDARDS
MODEL-FREE

Simulation for Reliable Predictions and Process

Analyzing the Curing Behavior of an Epoxy-Based Adhesive

- What is the minimum temperature needed for a specified cure over a given duration of time?
- What is the degree of curing for a given temperature program?

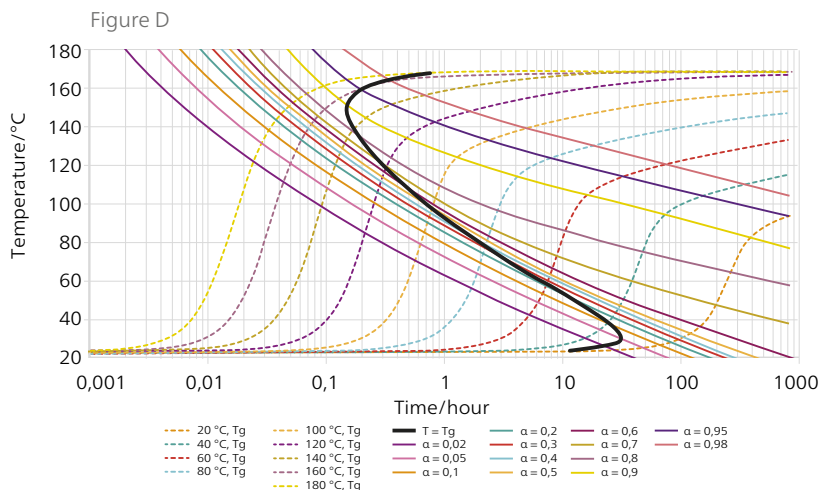
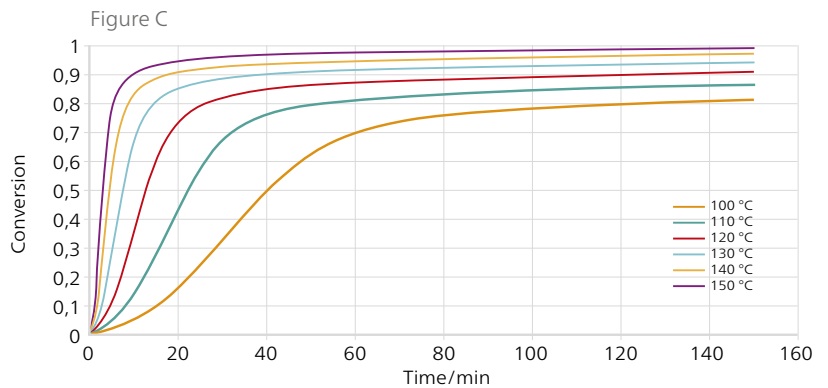
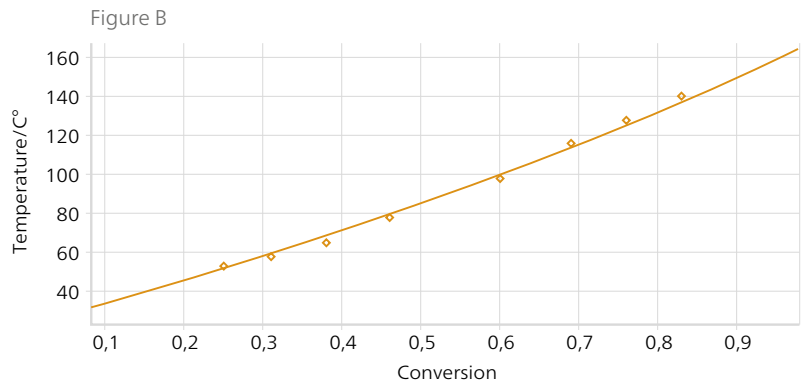
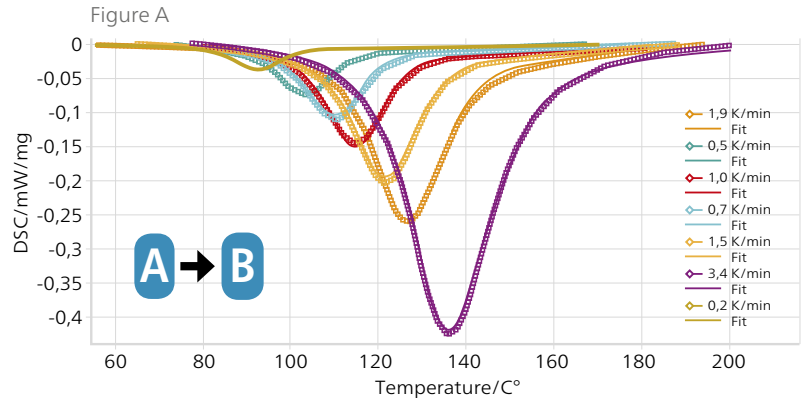
If the glass transition occurs during the cross-linking of a thermoset, the reaction is divided into two areas which are dominated by different mechanisms: The part above the glass transition depends on the chemical reaction and can be described by the Arrhenius relation. In the vicinity of the glass transition, the diffusion-controlled mechanisms dominate the reaction behavior. Therefore, the reaction rate around the glass transition is influenced by both processes, requiring the kinetic model to be extended by the special diffusion control algorithms to take into account the change in material behavior.

Figure A shows the DSC data (points) of a curing process at seven different heating rates and the simulation based on a model with diffusion control in solid lines. This kinetic model is used to calculate the prediction of the reaction rate at different temperature conditions.

Figure B exhibits the experimental glass transition temperatures at different degrees of curing. The solid line is the fit according to the Di Benedetto equation.

Figure C depicts curing behavior for many isothermal conditions. The curing reaction slows down at higher conversion values due to diffusion control, e.g., 90% conversion is achieved at 110°C after 52 min, at 120°C after 26 min, and at 140°C after 8.7 min.

Figure D shows Time-Temperature-Transition diagram (TTT diagram) for a longer time period.



Optimization

Optimization of the Burnout Process of a Polymer Binder for Improved Product Quality

In sinter metallurgy, the added polymeric binder provides improved adhesion to the metal powder. However, if the 1st heating phase is too quick, outgassing of the binder may cause micro-cracking. For the production process, this means finding a good balance between the following two problems:

- Slow heating results in an increased process time.
- Fast heating leads to quality defects due to intensive gas evolution during polymer decomposition.

Therefore, the optimum temperature profile over all zones of the tunnel kiln has to be determined to ensure a favorable relationship between process duration and product quality.

Figure A shows thermogravimetric measurements carried out at different heating rates. The three-step model used here allows for a high-quality approximation of all measurements. The higher the fit quality, the more confident the predictions.

Figure B shows the optimum temperature profile for the polymer burnout under laboratory conditions. For the best material quality, a constant mass-loss rate of 0.05%/min should be maintained over the entire process.

Figure C depicts the mass-loss prediction in a 5-zone tunnel kiln for a temperature program corresponding to the optimum zone temperatures for the polymer burnout during the production process.

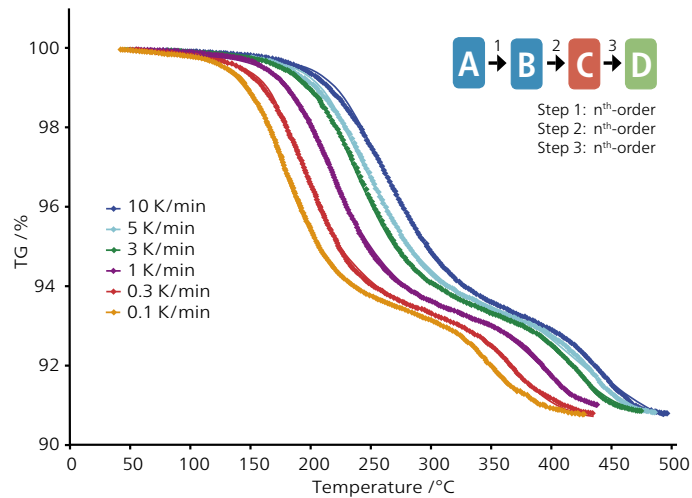


Figure A: Model-Based; TG 209 *F1* *Libra* measurements on polymer binder with sample masses between 40 mg and 50 mg

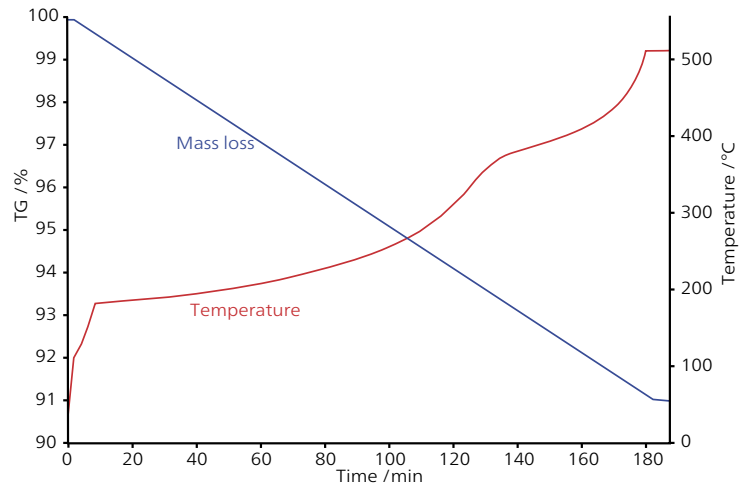


Figure B: Optimization; Temperature profile for constant mass-loss rate 0.05%/min

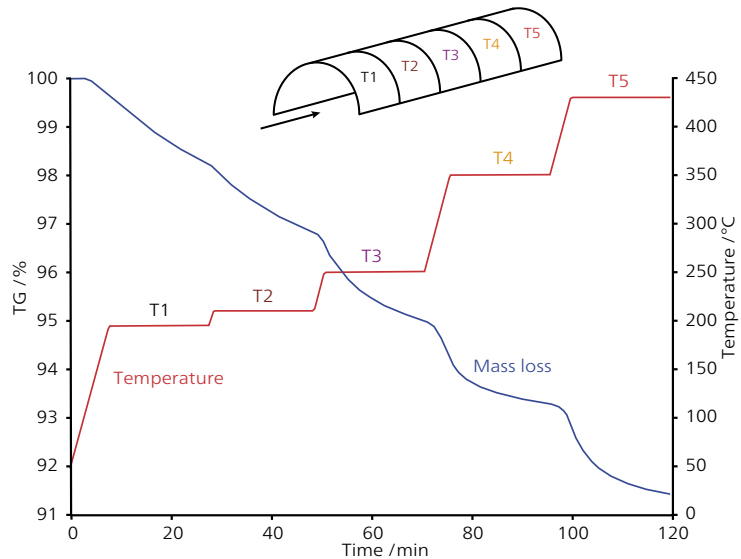


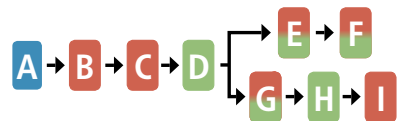
Figure C: Prediction; Mass-loss behavior for a given temperature profile

What Exactly Happens During Thermal Decomposition?

Understanding Complex Chemical Reactions – Tracking Decomposition Pathways

The decomposition of ammonium paratungstate tetrahydrate (APT) as studied under an oxidizing atmosphere using four heating rates with the NETZSCH STA simultaneous (TGA-DTA/DSC) thermal analyzer (figure A). In order to better understand the various endo- and exothermal effects of this complex decomposition process, the STA 449 **F1 Jupiter**® system was coupled to the QMS for simultaneous evolved gas analysis (EGA).

From the kinetic analysis of the MS data for water (figure B; measured points and calculated solid lines) and ammonia (figure C; measured points and calculated solid lines), it was possible to determine the decomposition path as a system of consecutive and competing reactions. On the basis of the kinetic model and the quantified MS data according to the known initial amount of N and O in APT, it was possible to determine the entire path, as follows:



Kinetic model of the decomposition of APT·2.9H₂O (blue): partial steps for water (red) and ammonia (green).

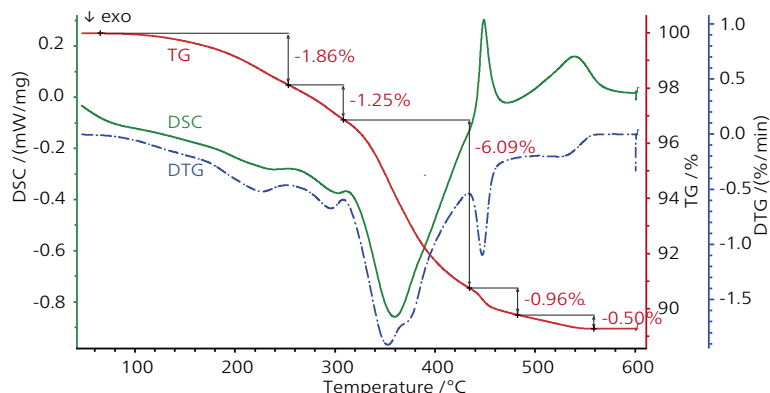


Figure A: STA measurement of the decomposition of APT

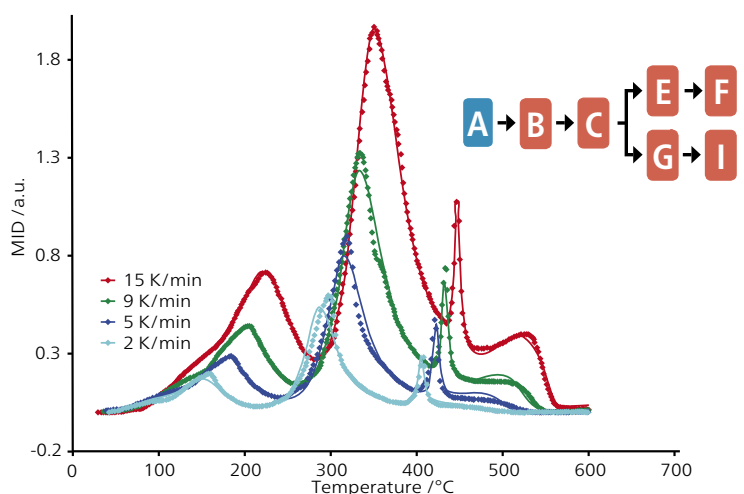


Figure B: Model-Based; MS spectra of the water release at different heating rates

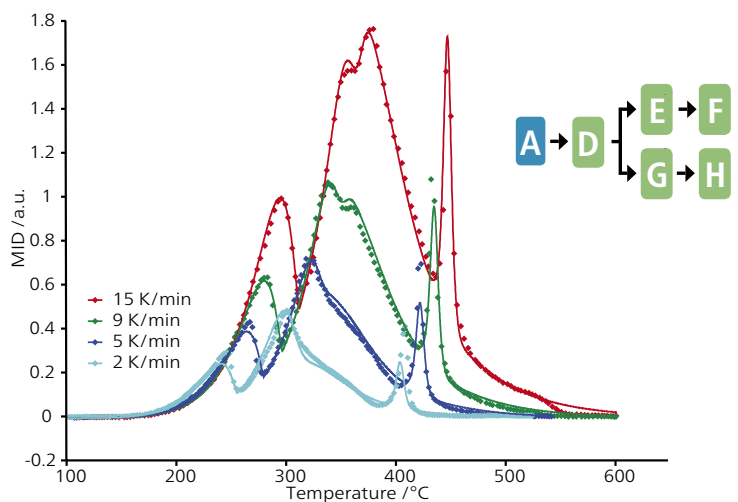


Figure C: Model-Based; MS spectra of the ammonia release at different heating rates

Optimization of Sintering Processes

Tuning the Product Quality of High-Tech Ceramics – Si_3N_4 Green Body

The temperature program during the firing process of a ceramic green body, most of all during the binder burnout and sintering phase, has paramount influence on the later product quality. By modifying the temperature program of a dilatometer measurement, it is possible to optimize the properties of sintering products; e.g., densification and grain size distribution.

Figure A shows the length change (sintering) between 1050°C and 1850°C under the influence of different heating rates. As the heating rate increases, sintering is shifted to higher temperatures. For the kinetic analysis, a 4-step model was employed. Based on this model, a non-linear regression was carried out adjusting the different reaction parameters, such as pre-exponential factors and activation energies (solid lines; measurement data is depicted in points).

It becomes possible to calculate the sintering process for different temperature profiles or for constant shrinkage rates. Figure B depicts the temperature profile for rate controlled sintering (RCS) at a constant length change rate of 0.087%/min.

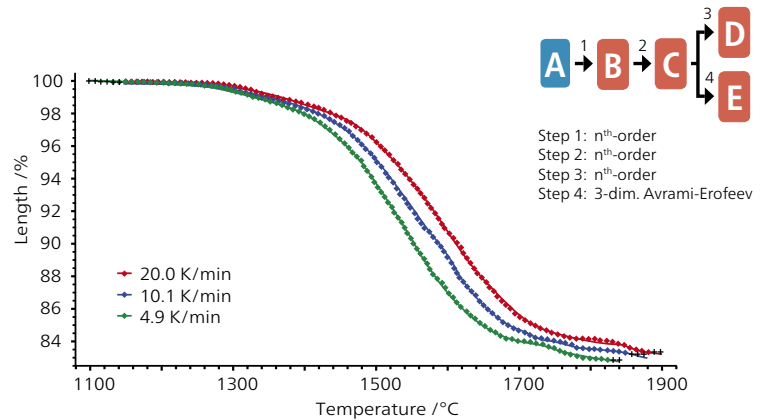


Figure A: Dilatometer measurements on Si_3N_4 powder containing 5 m% of Y_2O_3 and 5 m% of Al_2O_3 as sintering additives. The tests were carried out with the NETZSCH DIL 402 *Expedis*.

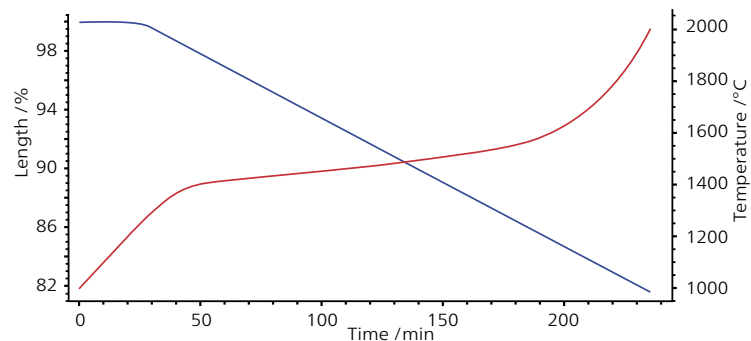
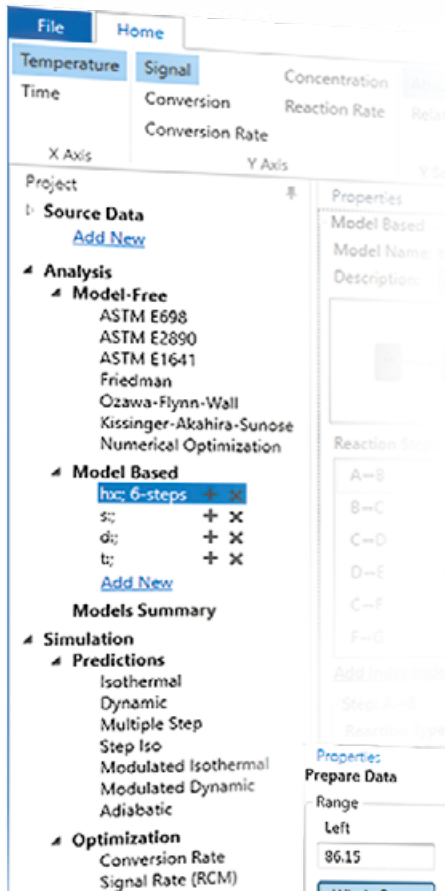


Figure B: Predicted temperature profile for RCS at a constant length change of 0.087%/min

Kinetics Neo finds the temperature program for a given reaction rate or a given rate of final product production.

Optimization of the Sintering Process via Kinetic Analysis on the Basis of Dilatometer Measurements

SOFTWARE DETAILS



The screenshot shows the 'Analysis' menu in Kinetics Neo. It is divided into several sections:

- Model-Free:** Includes ASTM E698, ASTM E2890, ASTM E1641, Friedman, Ozawa-Flynn-Wall, Kissinger-Akahira-Sunose, and Numerical Optimization.
- Model Based:** Includes 'hx: 6-steps' (highlighted) and other models with '+' and 'x' icons.
- Models Summary:** A section for summarizing models.
- Simulation:** Includes Predictions (Isothermal, Dynamic, Multiple Step, Step Iso, Modulated Isothermal, Modulated Dynamic, Adiabatic) and Optimization (Conversion Rate, Signal Rate (RCM)).

General Information

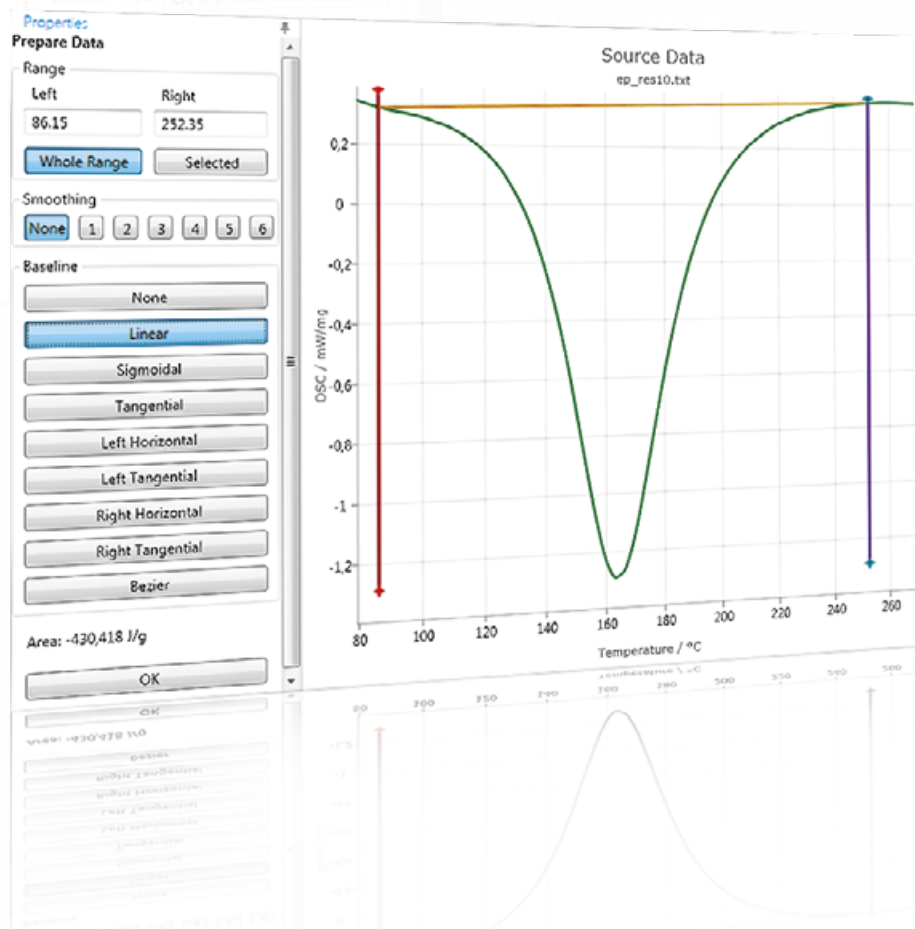
Kinetics Neo runs under Microsoft Windows 10, Windows 8.x, or Windows 7 (either the 32-bit or the 64-bit version). The latest Microsoft .NET Framework is required.

Minimal hardware requirements are: 4 GB RAM and 20 GB hard disk space. Better processor and bigger RAM increase calculation speed.

Data for Analysis

Source data for kinetic analysis may be of different types: TGA, DTA, DSC, DIL, EGA, rheometry, viscosity, DEA, DMA-E', pressure, and temperature increase.

An unlimited number of measurements per analysis can be used. Data stemming from any manufacturer can be imported; the data import function uses ASCII or CVS format. The software offers various baseline types.



Is the model ready? You're just a click away from predicting and optimizing your process for many different conditions!

Model-Free Methods – Results

- Analysis graph with Y-axis:
 - log (heating rate),
 - log (heating rate/T²)
 - log dx/dt versus 1000/T
- Plots of activation energy and pre-exponential factor vs. conversion
- Master plot for f(α)
- Conversion fit

Unique Flexible Model Designer

Model-based kinetic analysis offers the possibility of visual design for kinetic models with an unlimited number of steps connecting in any combinations.

The models can be flexibly designed by adding new reactions as independent, consecutive or competitive steps to any place in the model.

A simulated reaction step can be visually moved to the corresponding step on the experimental curve. Then the parameters of this step can be optimized.

Model-Based Methods' Results

Approximately 95% of all chemical reactions are multi-step reactions. This requires a multi-step analytical engine as offered by the Kinetics Neo software. The engine uses non-linear regression methods and allows for the optimization of parameters for individual steps or for the complete model. The fit results present the agreement between the experimental and simulated curves for:

- Signal
- Conversion
- Conversion rate
- Concentration of all reactants
- Reaction rates for all steps
- Equations for reaction rate, concentrations, balance equation for signal

Model-Based Methods – Statistical Results

The statistical results incorporate:

- Correlation coefficient
- Sum of the squares of deviations
- Mean residual
- t-value
- F-test for fit quality
- F-test for a number of steps
- Durbin-Watson value
- Durbin-Watson test

Predictions




Predictions can be calculated under various conditions (see also page 8). Depending on the condition, the results can be demonstrated in various ways including:

- Conversion curve as a function of time with temperature as a parameter
- Concentration over time of the formal reactants with temperature as a parameter
- Partial reaction, mass loss and area
- Reaction rate for individual reaction steps
- ... and many more.

Process Optimization

The goal is to develop a suitable temperature program for optimum product quality without trial and error. The results of the optimization can be achieved for:

- A constant rate of output signal like RCM or RCS
- A constant conversion rate



The NETZSCH Group is a mid-sized, family-owned German company engaging in the manufacture of machinery and instrumentation with worldwide production, sales, and service branches.

The three Business Units – Analyzing & Testing, Grinding & Dispersing and Pumps & Systems – provide tailored solutions for highest-level needs. Over 3,500 employees at 210 sales and production centers in 35 countries across the globe guarantee that expert service is never far from our customers.

When it comes to Thermal Analysis, Calorimetry (adiabatic & reaction) and the determination of Thermophysical Properties, NETZSCH has it covered. Our 50 years of applications experience, broad state-of-the-art product line and comprehensive service offerings ensure that our solutions will not only meet your every requirement but also exceed your every expectation.

Proven Excellence. ■

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