E

KINETICS SOFTWARE

NETZSCH

Thermokinetic Analysis

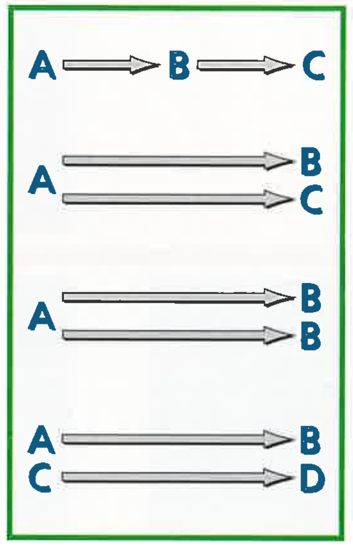
NETZSCH reaction kinetics software permits the simultaneous evaluation of up to five dynamic test data sets. For the first time a reliable estimation of kinetic parameters and of complex reaction models (multiple-step reaction) is possible.

Incorporating advanced analytical techniques and statistical criteria, it represents the state-of-art in kinetic analysis.

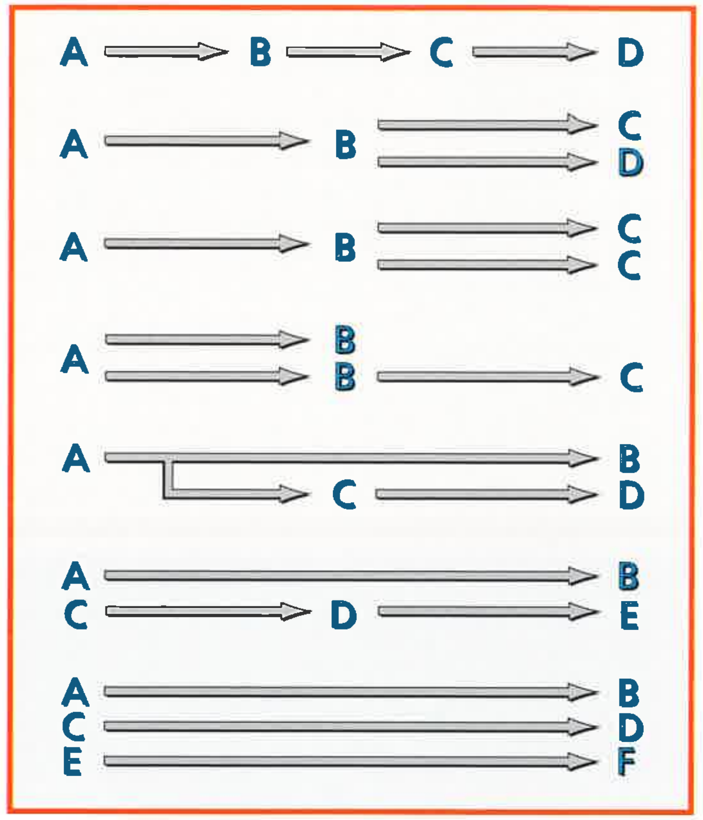
NETZSCH reaction kinetics software permits the analysis of complex reactions such as competitive, parallel, independent and single step type reactions.

single-step reactions

double-step reactions



triple-step reactions



NETZSCH reaction kinetics software is:

versatile evaluates
thermogravimetric
differential calorimetric
dilatometric
evolved gas data

discerning determines
kinetic parameters of complex reactions
- single step
- double step
- triple step

with following, competitive, parallel and independent reactions
reaction types
- n-th order
- phase boundary
- nucleation
- diffusion
- autocatalytic

precise utilizes
non-linear regression
time-based 4-th order integration
correlation analysis
f-test for selection of the most probable kinetic model

fast offers
pull-down menu driven format
direct access to all NETZSCH data sources by means of ASCII-files

encompassing provides
complete graphical presentation
- graphic of multiple-step reactions
- graphic of FRIEDMAN- or OFW-Analysis
- simulated engineering graphics

Procedures

TA-Method-Selection

Reading of NETZSCH ASCII-data-files

Model-free Estimation of Activation Energies
- FRIEDMAN-Analysis
- OZAWA-FLYNN-WALL-Analysis

Analysis of single-step reactions by modified DANIELS/BORCHARDT-method
(multiple linear regression) transformation of the data into degree of conversion, logarithmation.
Applying well-aimed weighting factors improve the approximation.

Analysis of multiple-step reactions by NON-LINEAR REGRESSION
statistically optimal approximation as the approximation will be made to the original data without transformation or logarithmation. Multiple step reactions are only in this way to be analyzed.

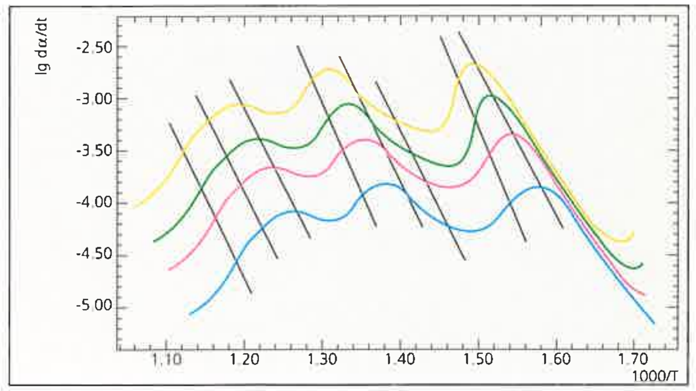
Results
kinetic parameters, statistics, F-test for selection of the most probable model, complete graphical presentation

Engineering Graphics
- stability
- durability
- process optimization

Model-free Estimation of Activation Energies:

FRIEDMAN-Analysis

The FRIEDMAN-analysis indicates that the pyrolysis of poly (1.4-phenylene-di(methoxy-phenyl) vinylene) in Ar flow proceeds as three-step process with activation energies of approx. 200, 263, and 258 kJ/mol for the 1st, 2nd and 3rd step, respectively.
Heating rates: 1.0, 2.5, 5.0 and 10 K/min



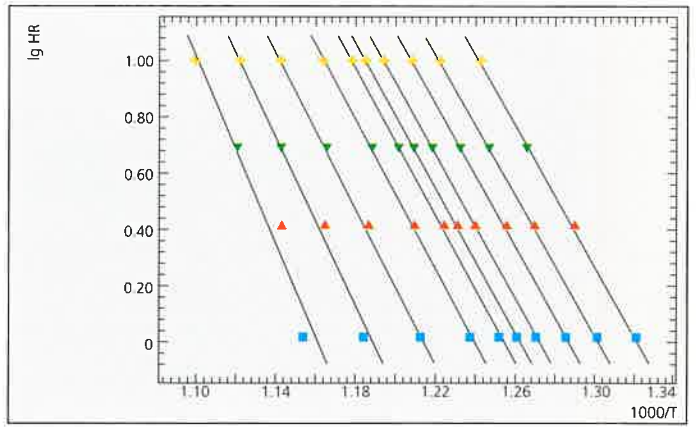
For α = const the plot of $\lg d\alpha/dt = \lg A - 0.434 \cdot E/RT + \lg f(\alpha)$ versus 1/T yields lines with the slope $m = -0.434 \cdot E/RT$. The values of lg (A·s) are estimated assuming $f(\alpha) = 1-\alpha$.

Activation Energies

Alpha	E kJ/mol			lg (A·s)
0.95	272.79	+−	22.62	13.77
0.90	257.67	+−	7.39	13.28
0.80	266.40	+−	7.16	14.31
0.60	295.91	+−	16.66	17.56
0.40	265.35	+−	4.97	16.01
0.30	261.46	+−	4.86	16.14
0.20	318.03	+−	23.21	22.06
0.10	246.19	+−	5.46	16.80
0.05	201.98	+−	4.65	13.13
0.02	187.04	+−	7.08	11.80

OZAWA-FLYNN-WALL-Analysis

OZAWA-FLYNN-WALL-analysis of the pyrolysis of poly (1.4-phenylene-di(phenoxy-phenyl)vinylene) in Ar
Heating rates: 1.0, 2.5, 5.0 and 10 K/min

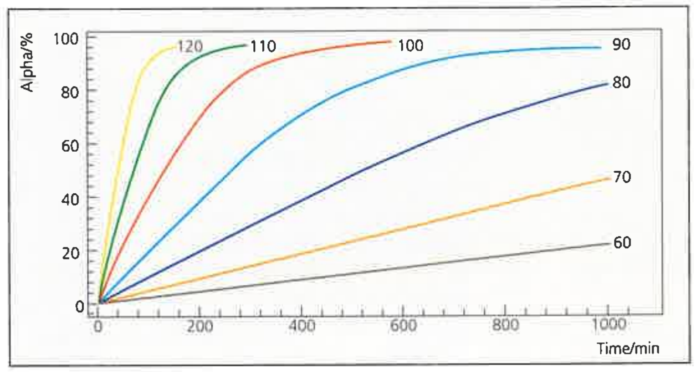


In experiments with constant but different heating rates, $\beta = dT/dt$, the plot of $\lg \beta$ vs. 1/T of points with the same degree of conversion $\alpha = \alpha_j$ yields lines with the slope $m = -b \cdot E/RT$. The value of b = 0.457, given by DOYLE, is correct for $E/RT \approx 37$. Hence, for a more precise estimation of activation energies the NETZSCH kinetics software considers the dependence of b from E/RT by a new straightforward strategy.

Engineering Graphics

The engineering graphics allow predictions on the isothermal behaviour of the sample investigated by non-isothermal methods. In this way advantageous conditions for the curing of a phenolic resin can be found, for example.

Isothermal plot of degree of conversion vs. time for the curing reaction of a phenolic resin. For this example a 1st order reaction with autocatalysis is obtained in the kinetic analysis.

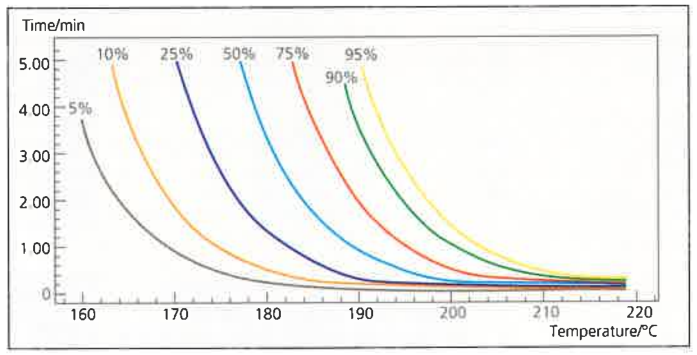


model: A —C 1→ B

parameters:

lg 10 A1·s:	6.70
E/kJmol⁻¹:	77.86
lg k-cat:	0.27

Isoconversion plot for different degrees of conversion vs. time and temperature shows the conditions to achieve a certain progress of the reaction beside 100% conversion. Here the conditions for the vulcanization of an EPDM rubber are given according to an n-th order reaction model.



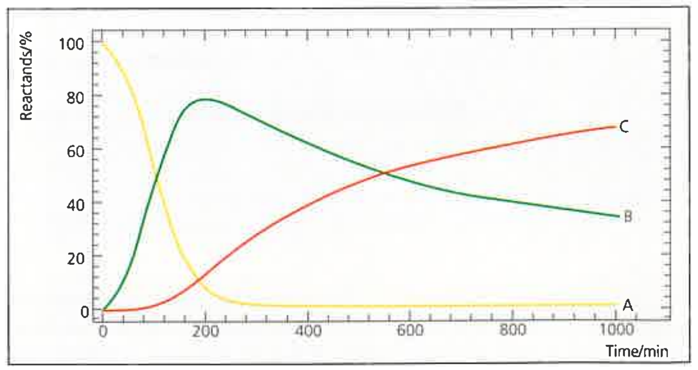
model: A —Fn→ B

parameters:

lg 10 (A1·s):	23.00614
E1 / kJmol⁻¹:	220.96712
React. ord.1:	1.19089

Isothermal plot of reactands vs. time, using kinetic parameters and a model obtained by non-linear regression of the pyrolitic decomposition of poly(1.4-phenylene-di(phenoxy-phenyl) vinylene).

Temperature: 480°C

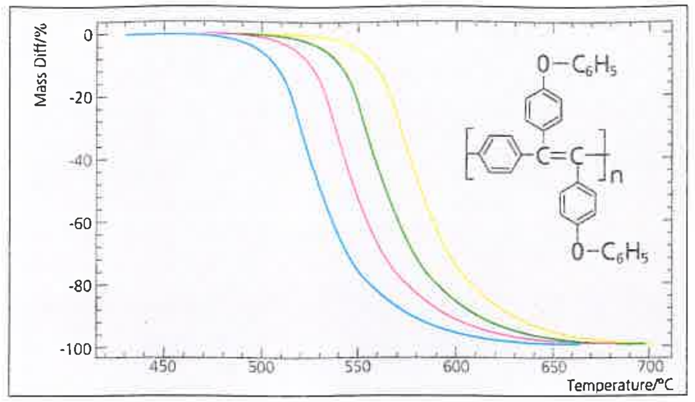


model: A —C 1→ B —Fn→ C

Analysis of multiple-step reactions by non-linear regression (NLR)

The precise curve fitting of data obtained under different conditions is the reliable base for each prediction. The advantages of the multiple-scan analysis in combination with NLR are both high flexibility of model selection and relevance of the estimated results.

The pyrolytic decomposition of a poly (1.4-phenylene-di(phenoxy-phenyl)vinylene) sample in Ar-flow is identified as a follow-up reaction when evaluating TG mass loss curves. Heating rates: 1.0, 2.5, 5.0 and 10 K/min

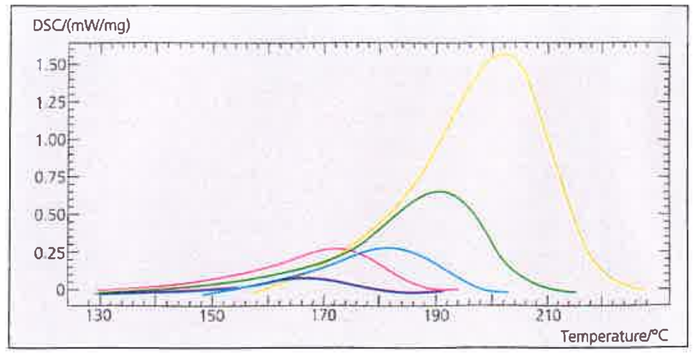


model: A —C 1 (1)→ B —Fn (2)→ C

Parameters and deviations

Parameter		Optimum value	t-Stand. Dev.
lg10	(A1·s)	11.38398	0.05819
E1	kJ/mol	228.62285	0.95264
lg k-cat 1		1.08848	0.01865
lg10	(A2·s)	15.28171	0.50598
E2	kJ/mol	282.99333	4.17640
React. ord. 2		2.20523	0.04647
Foll. React. 1		0.51529	0.04774
Mass Diff. 1/%		-100.00000	const.
Mass Diff. 2/%		-100.00000	const.
Mass Diff. 3/%		-100.00000	const.
Mass Diff. 4/%		-100.00000	const.

The vulcanization of an EPDM rubber was measured by DSC at five different heating rates (1 to 20 K/min). The exothermal DSC peaks are recorded from 130°C to 220°C. The curve fitting in the multiple scan analysis by the non-linear regression method (NLR) is excellent. The kinetic parameters show an overlapping endothermal effect (negative following reaction) upon the main curing reaction.



model: A —Fn (1)→ B —Fn (2)→ C

Parameters and deviations

Parameter		Optimum value	t-Stand. Dev.
lg10	(A1·s)	18.57249	0.03046
E1	kJ/mol	178.18989	0.41617
React. ord. 1		0.98844	0.05809
lg10	(A2·s)	0.75647	0.25688
E2	kJ/mol	19.76593	2.36022
React. ord. 2		0.77228	0.02542
Foll React 1		–0.32654	0.03605
Area1/(J/g)		15.05956	const.
Area2/(J/g)		16.59976	const.
Area3/(J/g)		15.45947	const.
Area4/(J/g)		19.46043	const.
Area5/(J/g)		15.11410	const.

Fields of Application

Thermogravimetry (TG)

decomposition
oxidation
adsorption
desorption

Differential Scanning Calorimetry (DSC)

decomposition
oxidation
polymerization
curing/cross linking
vulcanization
crystallization

Thermomechanical Analysis/ Dilatometry (TMA/DIL)

sintering

subject to technical change

Service of the Software

- prediction of technical processes (process optimization by fixing of time-temperature correlations and temperature cycling)
- test modelling
- stability and durability prediction
- information about intermediate-products of multiple-step reactions

Hardware-Requirements

Minimum system: IBM® AT-compatible with co-processor; 640 KB RAM; 2 MB harddisk space; MS DOS version 3.1 or newer; CGA, EGA, Hercules or VGA graphics adapter.

Recommended system: 386 SX/ 386 with co-processor or 486; Epson graphics compatible 8/9 or 24 pin oder ink jet printer.

Further Software Solutions

Thermal analysis software for the acquisition and analysis of TG, DSC, TMA/DIL data. Thermal analysis mass spectrometer software for the programmation, data controlling and evaluation of simultaneous TA-mass spectrometer data.

NETZSCH – The Exact Solution

NETZSCH
Thermal Analysis

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