



Component Kinetics

The Program is the software module for the kinetic evaluation of measurements with reactions in homogeneous mixtures, but reactions on the phase interfaces are not included. Different data types can be evaluated; as long as they show distinct correlations to concentrations changes of the reactants. The kinetic analysis allows the determination of the most probable reaction model as the sum of elementary reactions, the determination of the pre-exponential factor and activation energy for elementary reactions and then the prediction and optimization of the reaction behaviour for any temperature conditions.

The predictions using the most probable kinetic model are assured only inside the tested ranges of time, temperature and concentrations, extrapolation can bring deviation from the real behaviour. Therefore the collective evaluation of isothermal and dynamic measurement data with the greatest possible range of heating rates and initial concentrations of reagents is not only wishful, but strong recommended. This is considered by Component Kinetics.

Special features

Advantages in comparison with „NETZSCH Thermokinetics“

- Free formulation of the proposed reaction model by user as the set of elementary reactions
- Data input as chemical equation
- Direct input as concentrations of the reactants or calculation of its concentrations by the software after input of the corresponding masses
- Considerably enhanced possibility to find the correct reaction model by the input of concentration curves for intermediate products, see example 4
- Possibility to formulate reversible reaction steps as permanent equilibrium (preequilibria), if these steps are very fast in comparison with the remaining elementary reactions.
- Simultaneous evaluation for reacting system
 - With variation of composition
 - Without solvent and/or with variation of kind and quantity of solvent
 - With variation of kind and quantity of catalysts and inhibitors
- Taking into account volume changes during the reaction, if the densities of all reactants are known.
- Taking into account the probable different functions of reagents
- Simultaneous evaluation of up to 32 measurements, the reaction models can consist of up to 20 elementary steps

The common features with „NETZSCH Thermokinetics“

- Determination of the optimal kinetic parameters for all elementary reactions by using of non-linear regression
- Predictions of the reaction behaviour for any combination of isothermal and dynamic temperature segments
 - Signal (DSC, TG)
 - Degree of conversion
 - Concentrations
- User interface corresponds to the software „NETZSCH Thermokinetics“

Application fields

- **All fields of chemistry, biochemistry, material sciences**
- **Fundamental research, applied research, process optimization and process control**

Verification of the program

For the following simple and complex mechanisms, important in chemistry, the results for heat flow and concentration were simulated by independent software:

- Consecutive reactions
- Competitive and independent parallel reactions
- Equilibrium reactions
- Combination of these basic types

In all cases the calculation was started with initial values of kinetic parameters having very big deviation from known results (and with big deviations of reaction enthalpy in case of heat flow curves). Nevertheless, after calculation the expected values have been obtained and the observed deviation have been in the range of some tenth of a percent.

Thus here is the proof, that component kinetics is a valuable and reliable tool with the determination of the model parameters and forecasts based on it. If the mechanism is unknown component kinetics can help to find the most probable reaction mechanism.

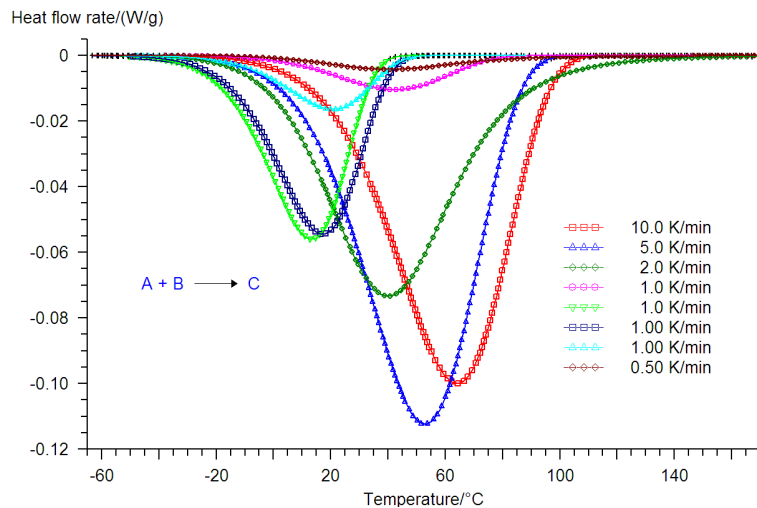
Applications

Example 1: simulated reaction of 2nd order of the type $A + B \rightarrow C$

Parameter	$\log A / (\text{s}^{-1} \text{ l mol}^{-1}) = 5$, $E_A = 50 \text{ kJ mol}^{-1}$, $Q_r = -37 \text{ kJ mol}^{-1}$
Molar masses / g mol^{-1}	A = 100, B = 50, C = 150
Densities / g ml^{-1}	A = 1, B = 1.5, C = 2, Solvent = 1.25
Heating rates / K min^{-1}	0.5, 1, 2, 5, 10
Concentration relationship A : B	1:5, 1:4, 1:3, 1:2, 1:1, 5:32, 9:1

Characteristics:

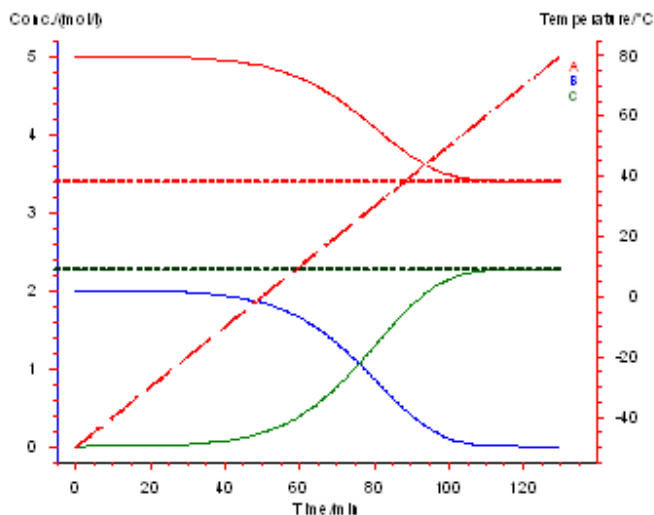
- extreme variation of the relationship of the starting concentrations of A and B
- presence of strongly different solvent quantities,
- strongly different densities



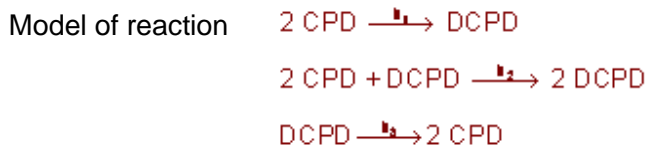
- perfect adjustment to the simulated curves
- model parameters are practically identical to the defaults:
 $\lg A = 5.001 \text{ s}^{-1}(\text{l/mol})$,
 $E_A = 50 \text{ kJ mol}^{-1}$,
 $Q_r = -36.97 \text{ kJ mol}^{-1}$

Examination of the calculated concentration profile for curve ($\beta = 1 \text{ K mi}^{-1}$); based on the initial values (first column) the final concentrations should correspond to those from the last column

Initial amount of substance	Final amount of substance	Final mass	Final Volume	Final Concentration
$n_{A,0}$: 5 mol	$n_{A,f}$: 3 mol	$m_{A,f}$: 300 g	V_A : 300 ml	$c_{A,f}$: $3.3962 \text{ mol l}^{-1}$
$n_{B,0}$: 2 mol	$n_{B,f}$: 0 mol	$m_{B,f}$: 0 g	V_B : 0 ml	$c_{B,f}$: 0 mol l^{-1}
$n_{C,0}$: 0 mol	$n_{C,f}$: 2 mol	$m_{C,f}$: 300 g	V_C : 150 ml	$c_{C,f}$: $2.2642 \text{ mol l}^{-1}$
			V_{solvent} : 433.33 ml	
			V_{total} : 883.33 ml	



- The final concentrations for A and C (dashed lines) correspond exactly to the calculate values
- The volume change during reaction is taken into account correctly

Example 2: Dimerization of cyclopentadien,

CPD: Cyclopentadien, DCPD: Dicyclopentadien

(Combination of a 2nd order reaction, a 2nd order autocatalyzed reaction and a reversible reaction of 1st order)

Formulation of the model in the software:

Model name: Dimerisierung von Cyclopentadien

Elementary reactions | Equilibrium reactions | Molar mass

$n1 \cdot \text{Educt 1} + n2 \cdot \text{Educt 2} \rightarrow p1 \cdot \text{Product 1} + p2 \cdot \text{Product 2} + p3 \cdot \text{Product 3}$

#	n1	Educt 1	n2	Educt 2	p1	Product 1	p2	Product 2	p3	Product 3	dc
1	2	CPD			1	DCPD					N
2	2	CPD	1	DCPD	2	DCPD					N
3	1	DCPD			2	CPD					N
4											
5											

No. element.: 3
No. equilibs.: 0
Clear Reactions

Input of the molar masses and densities (global characteristics of all measurements)

Model name: Dimerisierung von Cyclopentadien

Elementary reactions | Equilibrium reactions | Molar mass

#	Reactant	Mol.mass/(g/mol)	Density/(g/ccm)	Catalyst	Optim.	Dest.	Func.
0	Solvent/Filler		1.000	N		0	
1	CPD	66.05	0.7970	N		0	1
2	DCPD	132.11	0.9770	N		0	1
3							

Densities = 1

No. element.: 3
No. equilibs.: 0
Clear list
No catalyst

Input of the initial masses and/or - concentrations (local characteristic of each measurement)

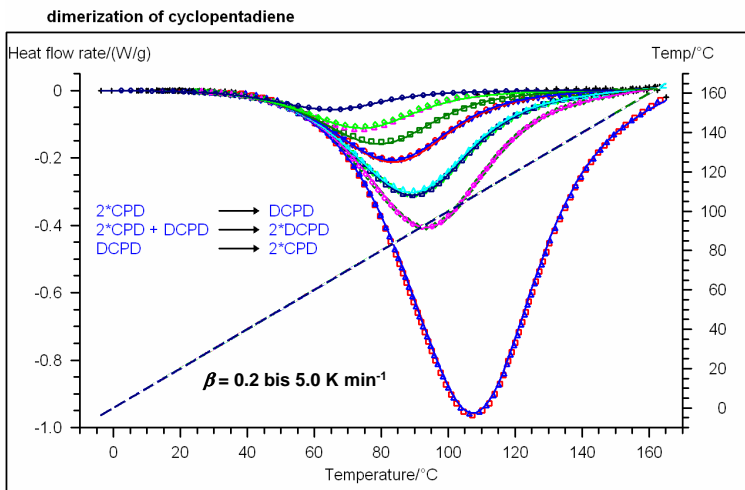
Scan [1 ...32]: 1 Heating rate/(K/min): 5.00044 CP14MOD.D7 Cyclopentadien-Dimerisieru

Settings | Variables | Start mass/conc. | Data Identity

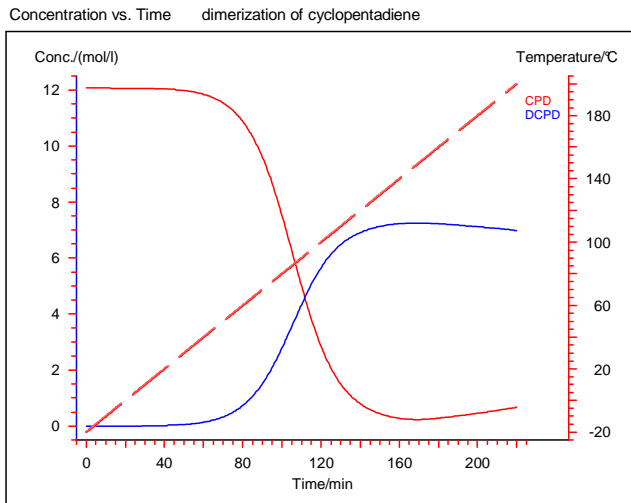
#	Reactant	Molar mass	Start conc./(mol/l)	Start mass/g
1	CPD	66.05	12.066616	797.000310
2	DCPD	132.11	0.0	0.0
3				
4				
5				
6				
7				
8				
9				
10				
11				
11				

Input
 Mass
 Concentration

Mass solvent,filler/g: 0.0
 Volume solvent/ccm: 0.0
 Total volume/ccm: 1000.0004
 1000.0004

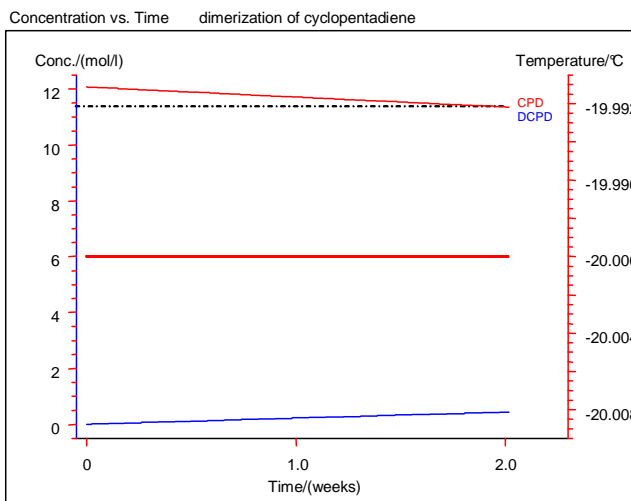


- Comparison of the measured data (symbols) and the calculated curves
- perfect adjustment of the model to all curves



Temperature Program for Prediction			
Name:		not defined	Project name:
#	Mode	Final temp/°C	Scan rate/(K/min)
0	initial	-20.00	
1	dynamic	200.00	1.000

- clearly visible revers reaction at higher temperatures

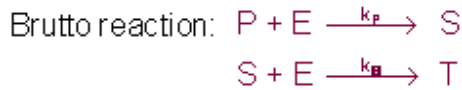


Temperature Program for Prediction				
Name:		not defined	Project name:	
#	Mode	Final temp/°C	Scan rate/(K/min)	Time/min
0	initial	-20.00		0.00
1	isothermal	-20.00	0.000	20160.00

- Stability prediction for storage at 20°C
- Loss of monomers during storage 0.42 % per day

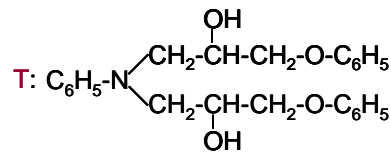
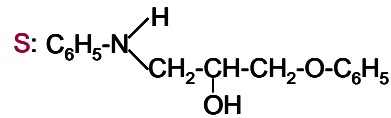
Example 3: Reaction of a mono-functional epoxy (phenylglycid ether) with a primary, bi-functional amine (aniline)

DSC measurements with epoxy/amine ratios of 1:2, 1:1 and 2:1



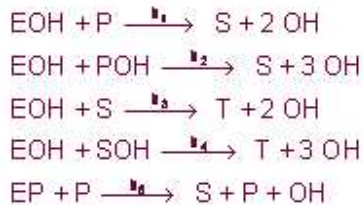
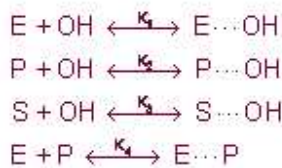
P: Anilin, $C_6H_5NH_2$

E: Phenylglycidether, $C_6H_5-O-CH_2-CH-CH_2$



typical characteristics

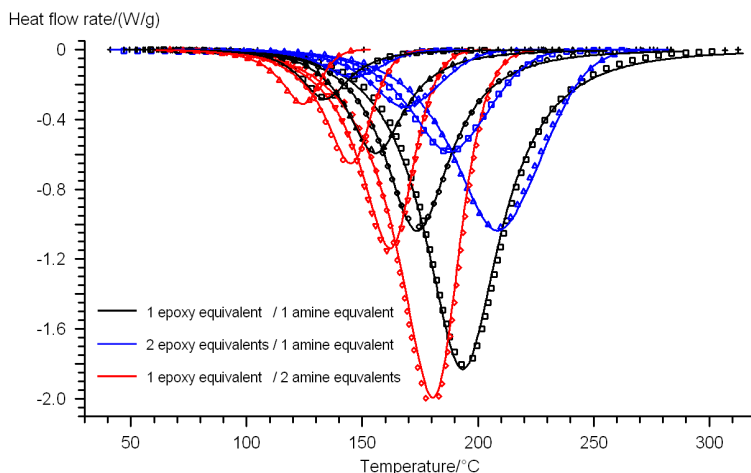
- equilibria reactions
- at least 2 parallel reactions
- autocatalysis by OH-groups



#	Exp	No.Elem.	No.Equil.	Model name
0	1.000	5	4	curing of phenylglycidylether / aniline

Elementary reactions		Equilibrium reactions		Molar mass	
n1	Educt 1	n2	Educt 2	n3	Product
1	E	1	OH	1	EOH
2	P	1	OH	1	POH
3	S	1	OH	1	SOH
4	E	1	P	1	EP

Elementary reactions		Equilibrium reactions		Molar mass					
n1	Educt 1	n2	Educt 2	p1	Product 1	p2	Product 2	p3	Product
1	EOH	1	P	1	S	2	OH		
2	EOH	1	POH	1	S	3	OH		
3	EOH	1	S	1	T	2	OH		
4	EOH	1	SOH	1	T	3	OH		
5	EP	1	P	1	S	1	OH	1	P

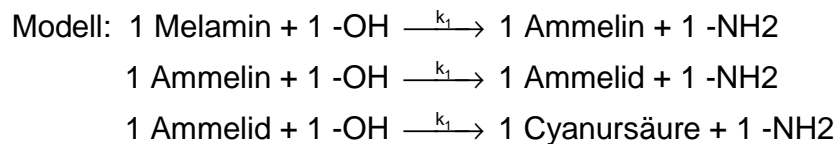


- successful description of the complete data set by the used model, independent from the starting composition!
- Heating rates in each case 1, 2, 5 und 10 K min⁻¹

Example 4: Hydrolyse of Melamin with NaOH at three temperatures (125, 150 and 175°C)

Data: HPLC

Origin: M. Leidl, Institut for chemical technology of organic materials,
Johannes Kepler University of Linz



Cut-out from the project initialization: 3 measurements at 3 corresponding temperatures and in each case 3 concentrations (Melamin, Ammelin und Ammelid) for each measurement

Project Initialization

Project name: Melamin/1n NaOH

Material: Melamin

Type of measurement: HPLC/GC

No of Scans[1...32]: 3

Concentrations for each scan [1...16]: 3

Direction of exotherm: not used

OK Cancel

Model input:

Definition of Reaction Steps

Tested Models

#	Fexp	No.Elemt.	No.Equil.	Model name
0	1.000	3	0	Melamin_NaOH

Model name: Melamin_NaOH

Elementary reactions | Equilibrium reactions | Molar mass

$n1 * \text{Educt 1} + n2 * \text{Educt2} \rightarrow p1 * \text{Product1} + p2 * \text{Product 2} + p3 * \text{Product 3}$

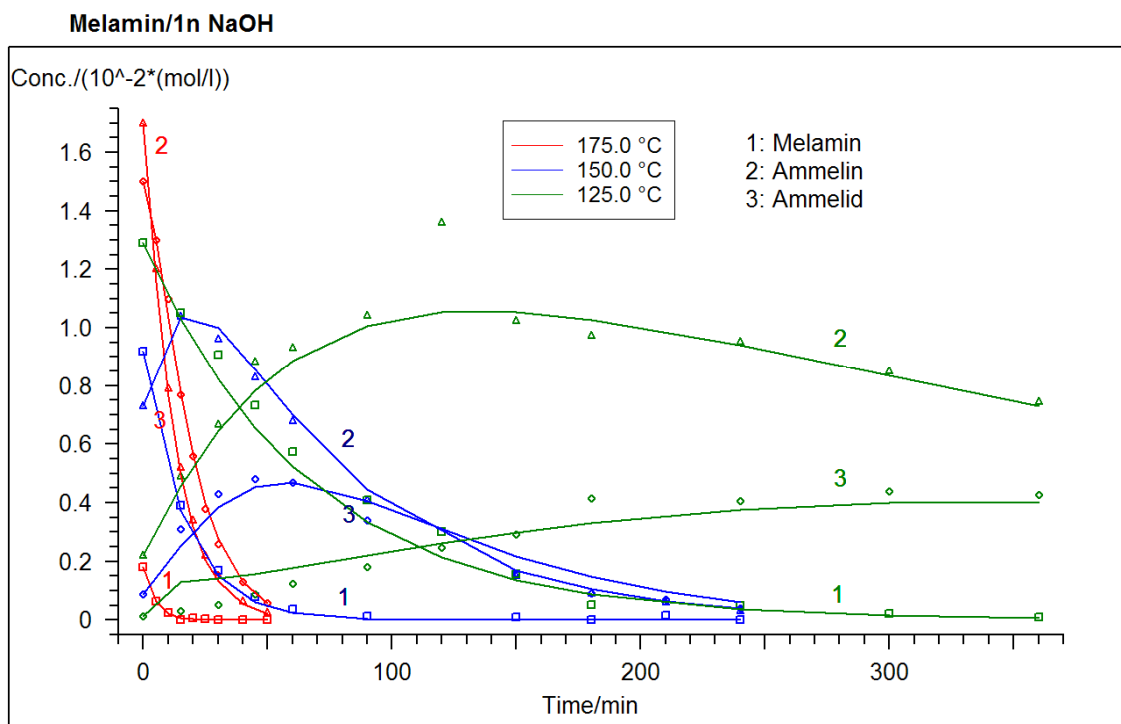
#	n1	Educt 1	n2	Educt 2	p1	Product1	p2	Product2	p3	Product3	dc
1	1	Melamin	1	OH-	1	Ammelin	1	NH2-			N
2	1	Ammelin	1	OH-	1	Ammelid	1	NH2-			N
3	1	Ammelid	1	OH-	1	Cyanursäure	1	NH2-			N
4											

No. element.: 3

No. equilibs.: 0

Clear Reactions

Adjustment of the model to the data:



kinetic parameters:

Results using Melamin_NaOH

Parameters | Statistics | Termination Criteria | Regression Values | F-test: Fit Quality | F-test: Step Significance

#	Parameter Name	Initial Value	Optimum Value	Sign.	t*S(Par)
0	lg {A 1/(s ⁻¹ [l/mol])}	6.8460	6.6374		0.7587
1	Ea 1/(kJ/mol)	79.6597	78.0315	+	9.5985
2	lg {A 2/(s ⁻¹ [l/mol])}	9.7094	9.8217		-0.2089
3	Ea 2/(kJ/mol)	107.1830	108.3399	+	4.3105
4	lg {A 3/(s ⁻¹ [l/mol])}	8.6704	8.6966		-0.4516
5	Ea 3/(kJ/mol)	97.2938	97.6813	+	6.1617

Statistics:

Weighted Least Squares: 2.1382E-05

Correlation coefficient: 0.9996426

Mean residual: 2.8044E-04

t-Val(alpha=0.95,87): 1.97989

Durbin-Watson value: 1.08827

Additional information about NETZSCH Component Kinetics can be found on www.therm-soft.com