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Kinetic modelling of pressure influences on reactions in solids

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Pressure-dependent reactions

1. Gaseous Reactant ,
   Reduction of Metal Oxide under partial pressure of H_2
   total pressure of gas mixture is 1 bar

   $A(s) + B(g) \rightarrow P(s)$

2. Gaseous Reactant in Reversible Reactions
   Decomposition of $CaCO_3$ under partial pressure of CO_2
   total pressure of gas mixture is 1 bar

   $A(s) \rightleftarrows P1(s) + P2(g)$

3. Pressure-Dependent Reactions in Inert Gas
   Decomposition of $CaOx*H_2O$ in N_2
   total pressure of N2 is from 1 to 50 bar

   $A(s) \rightleftarrows P1(s) + P2(g)$

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1 Gaseous Reactant

Reduction of Metal Oxide in presence of H_2

2.1 Partial Pressure of Gaseous Reactant

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

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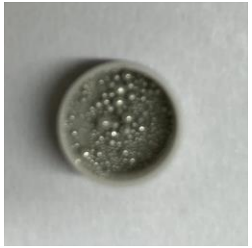
STA 509 with Hydrogen Generator

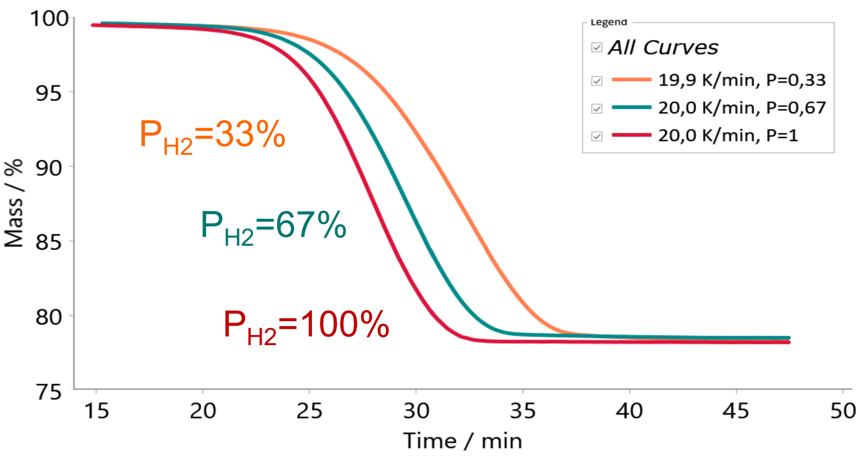
Metal Oxide with Hydrogen

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

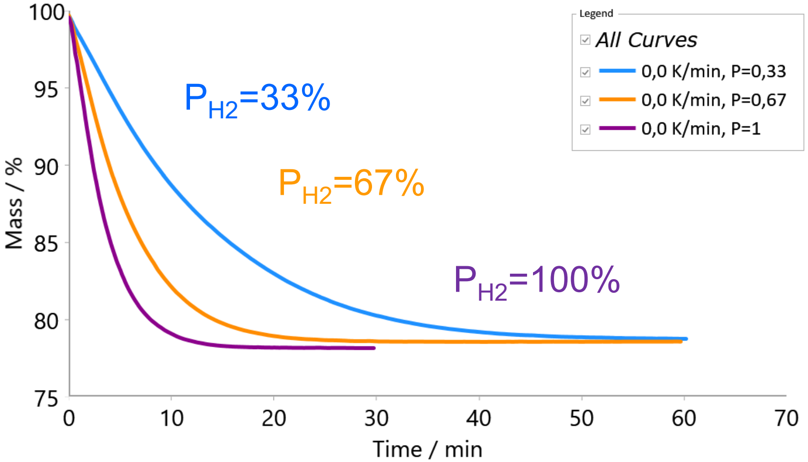
Atmosphere: Nitrogen and Hydrogen



20K/min, different partial pressure of H_2



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



Reduction of metal from metal oxide in Nitrogen with partial pressure of H2

Nitrogen with Hydrogen

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

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

Hydrogen is the reactive gas.

Reaction rate depends on the hydrogen concentration

the higher partial pressure of hydrogen - the higher reaction rate

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

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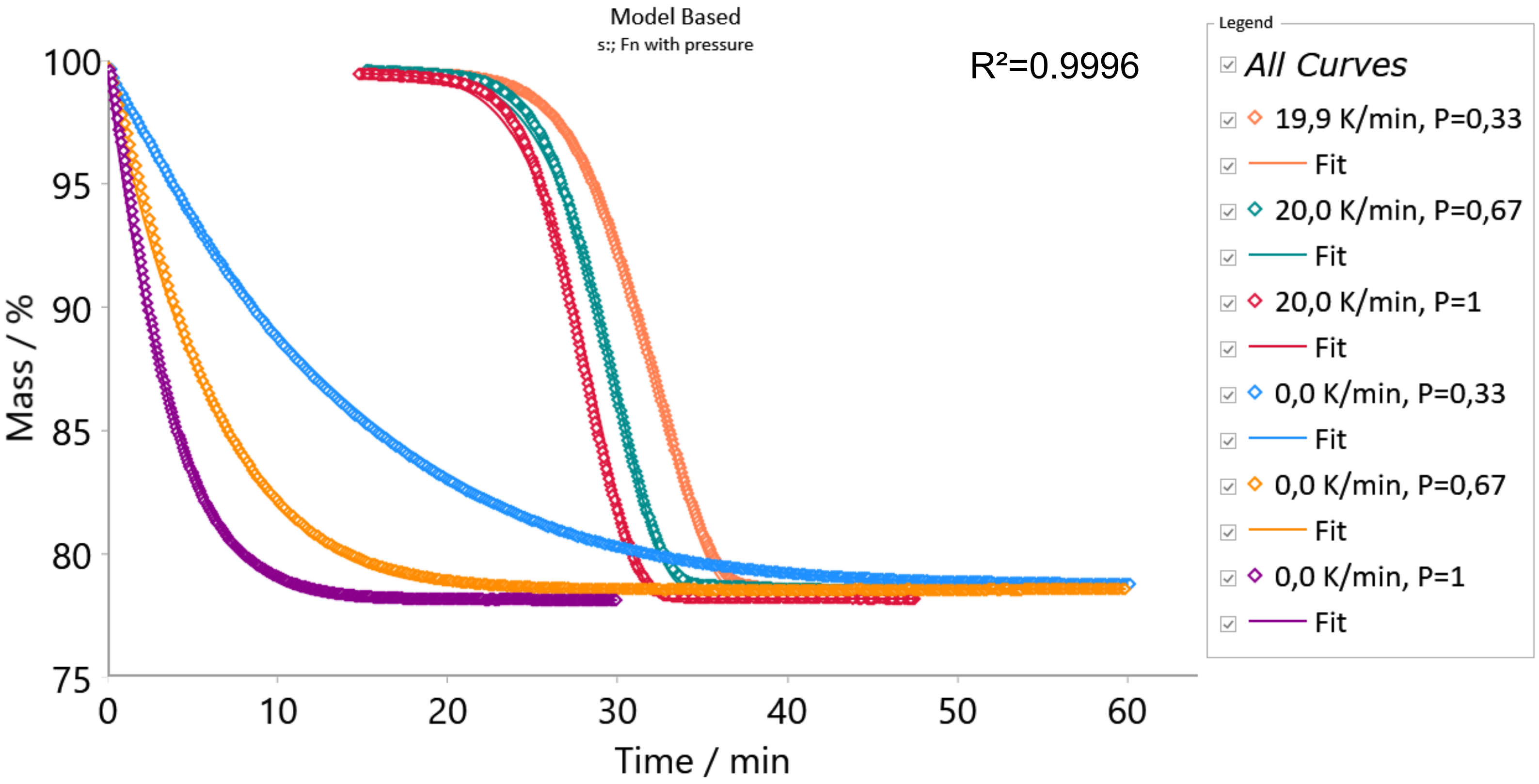

Optimal parameter for pressure: n_{H2}= 1.2

Measurements: Jan Hanss, NGB Laboratory

Optimal parameters and equations

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

$$\frac{d\alpha}{dt} = P^{n_p} A\,(1-\alpha)^n \exp\left(\frac{-E_A}{RT}\right)$$

P is partial pressure of H_2

Reaction Type: Fn
Equation: d(a->b)/dt=PreExp*(Pressure)^(nPressure)*a^n*Exp[-ActivationEnergy/(RT)]
ActivationEnergy: 106,4 kJ/mol
Log(PreExp): 3,9 Log(1/s)
ReactOrder n: 0,76
nPressure: 1,2
Contribution: 1,000

Verification

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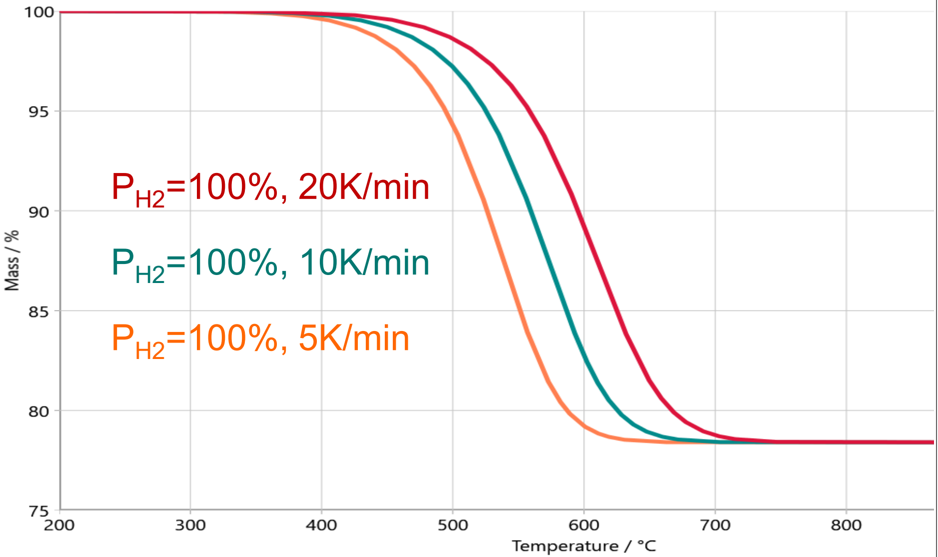
Partial pressure of Hydrogen

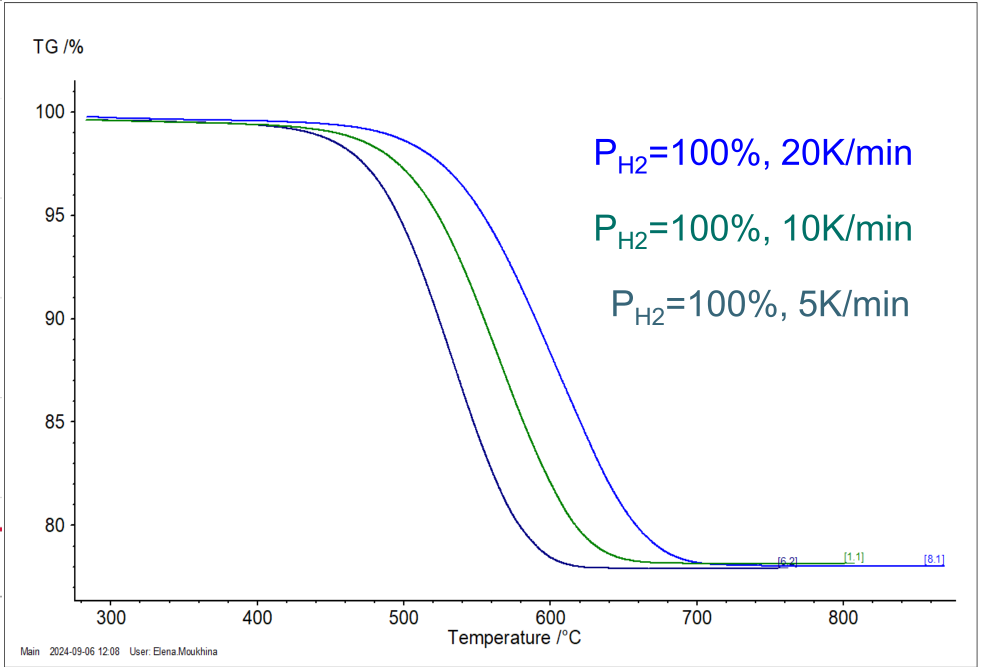
Heating Rate	33%	67%	100%
0 K/min	K	K	K
5 K/min			V
10 K/min			V
20 K/min	K	K	K

K: experiment for kinetics analysis

V: experiment for verification of model

Verification: Predictions for 100% H_2, different heating rates





Predictions

Verification

Verification: comparison of simulated and measured data

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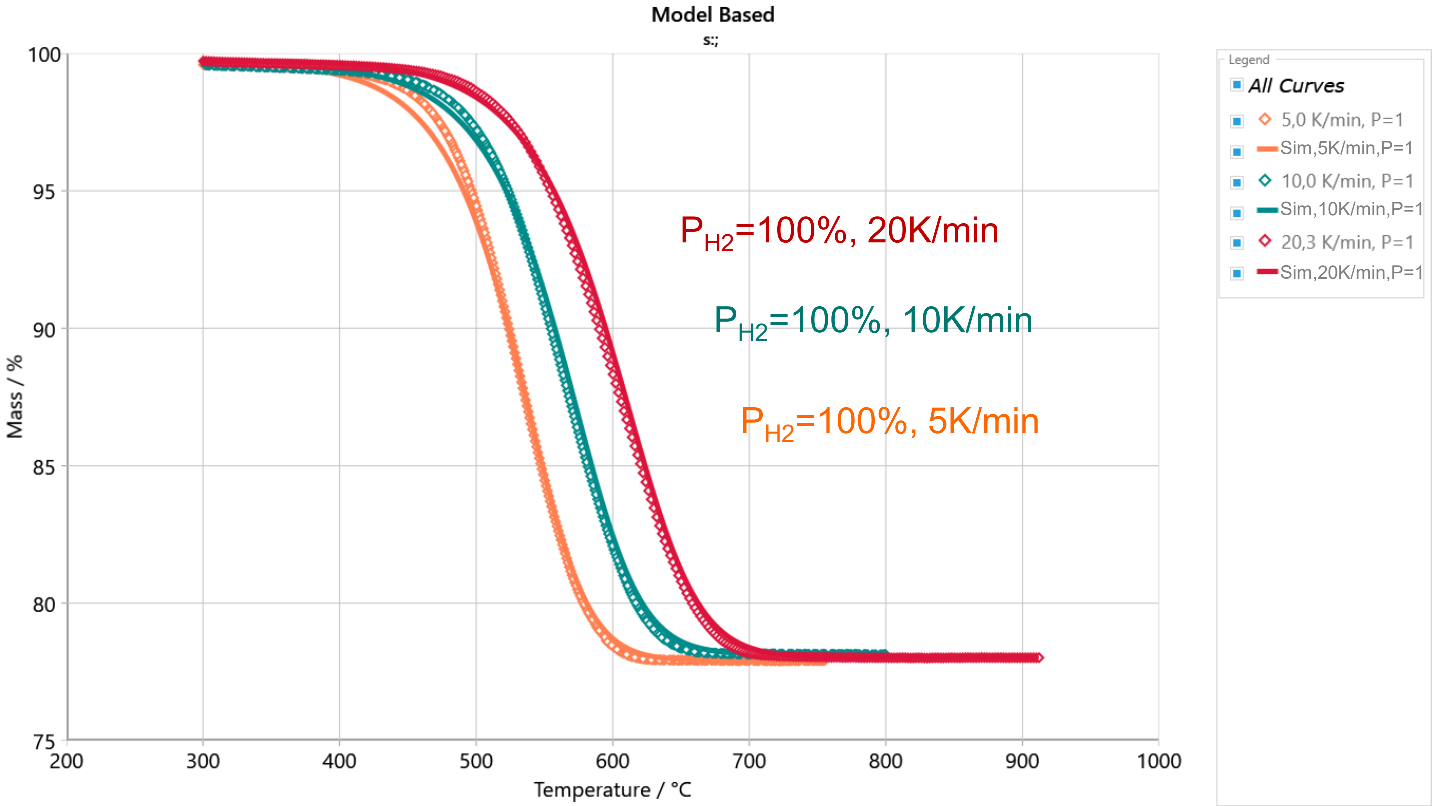

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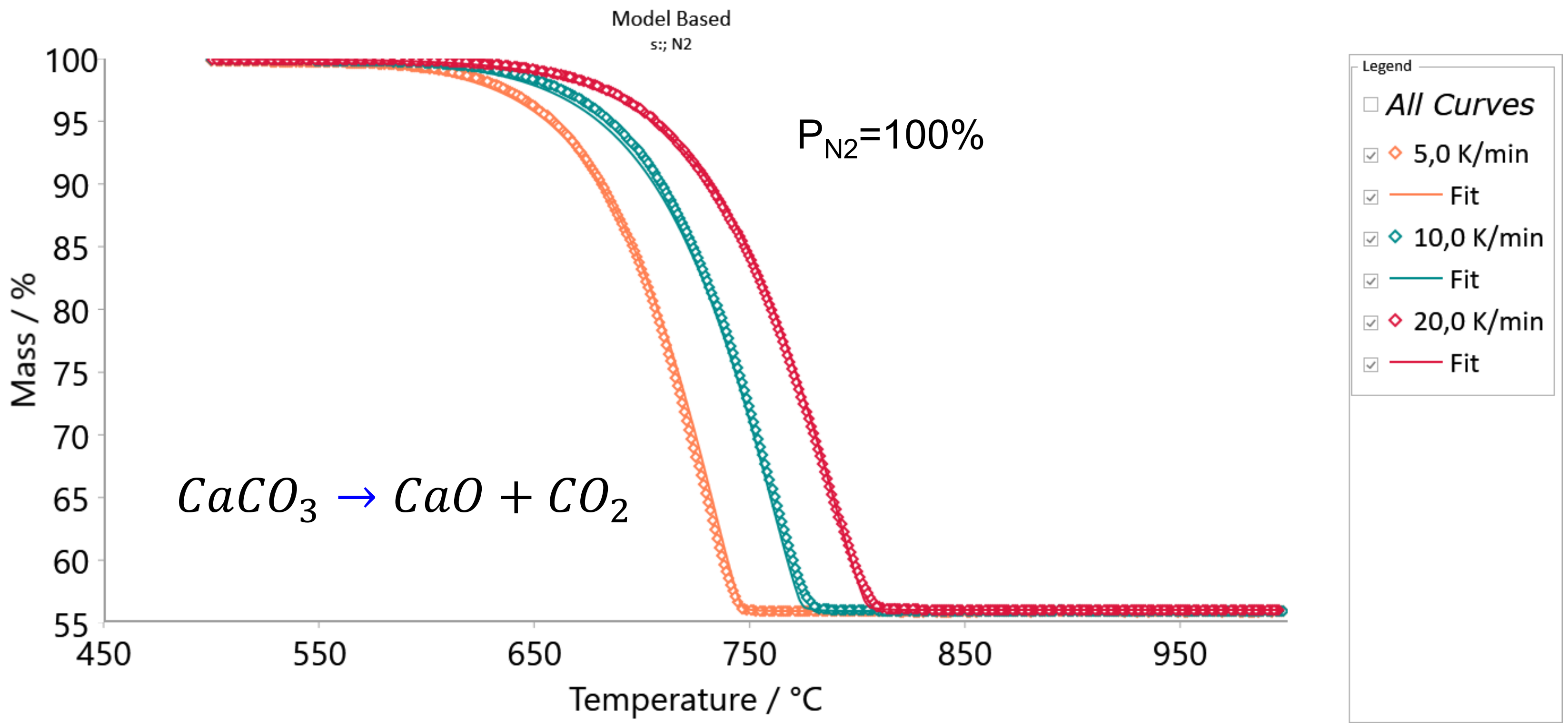
2 Gaseous Reactant in Reversible Reactions

Decomposition of $CaCO_3$ under presence of CO_2

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



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

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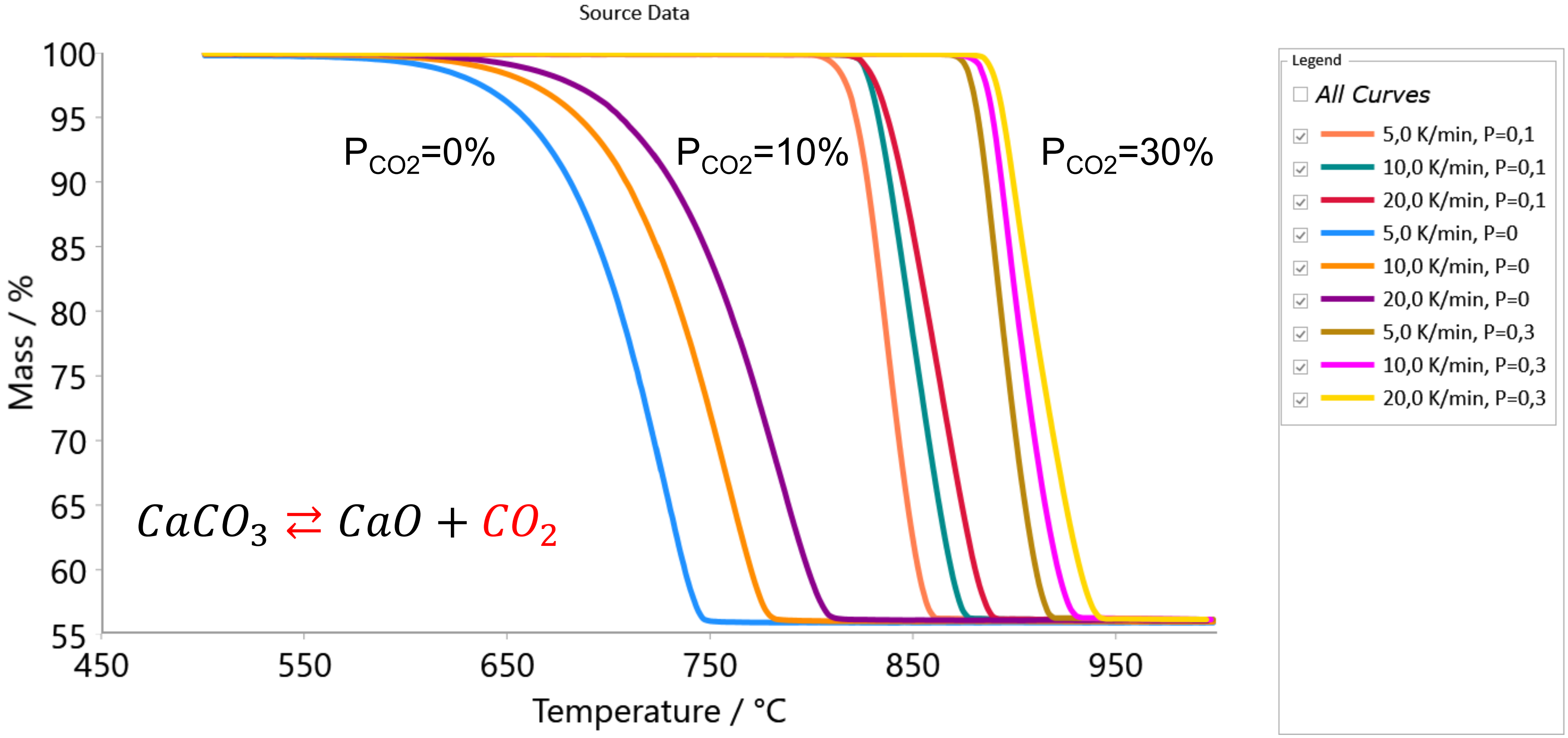

Decomposition of $CaCO_3$ in Nitrogen with CO_2

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1. Nitrogen only
only forward reaction

$$CaCO_3 \rightleftarrows CaO + CO_2$$

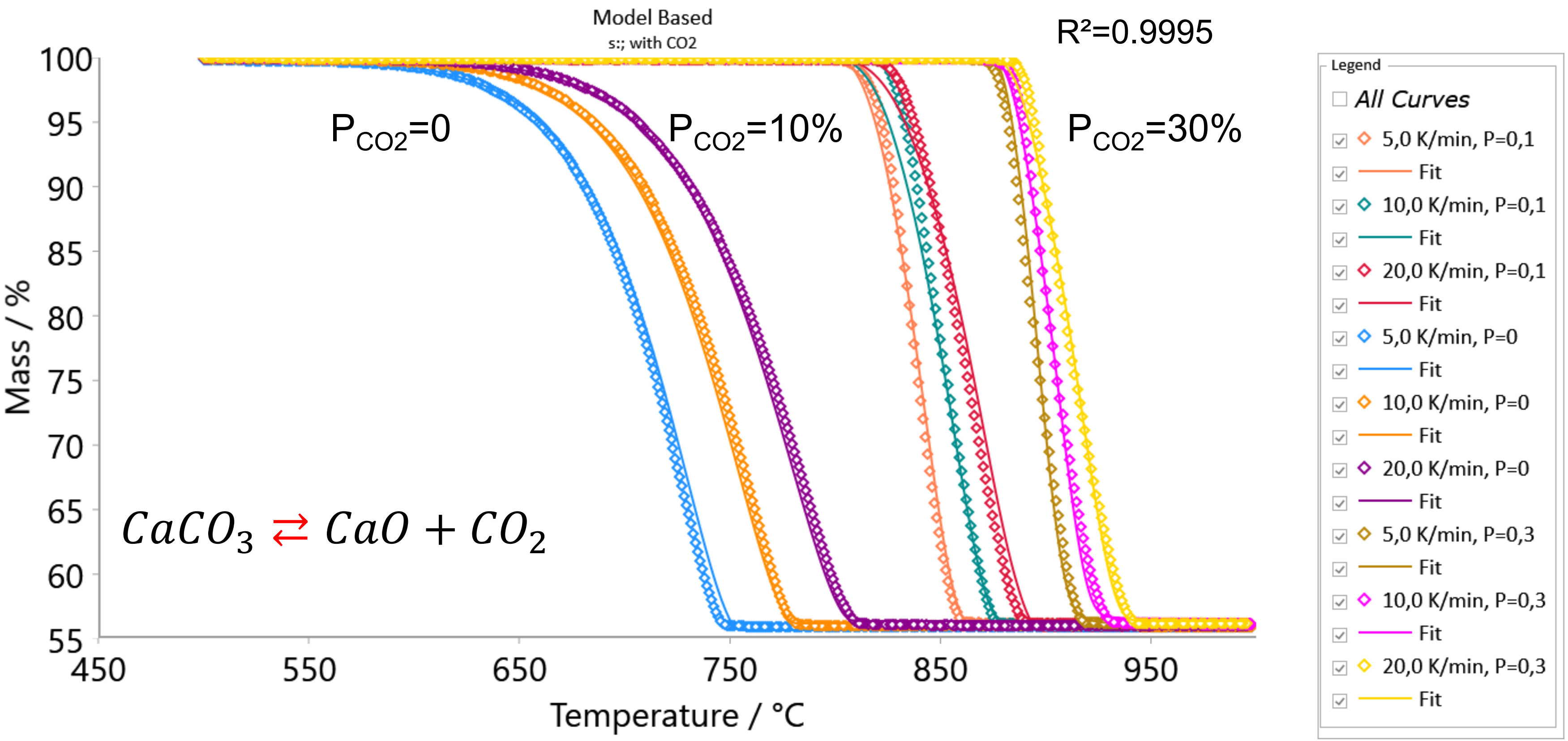
$$\frac{d\alpha}{dt} = A\,exp\left(\frac{-Ea}{RT}\right) f(\alpha) - P_{CO_2}^{n} A_2 exp\left(\frac{-E_2}{RT}\right) f_2(\alpha)$$

2. Nitrogen with CO_2

reaction is reversible,
P is partial pressure of CO_2

CO2 is the reactive gas for reverse reaction. The rate of reverse reaction depends on the CO2 concentration.
The higher partial pressure of CO2 - 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)



Optimal parameters for pressure: n_{CO2}= 0.2

Measurements: Jan Hanss, NGB Laboratory

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Pressure-Dependent Reactions in Inert Gas

Decomposition of $CaC_2O_4 * H_2O$
under high pressure of N_2 *(1 to 50 bar)*

Decomposition of $CaC_2O_4*H_2O$ in Nitrogen

1. Nitrogen, normal pressure

$$CaC_2O_4 * H_2O \rightarrow CaC_2O_4 + H_2O$$

$$CaC_2O_4 \rightarrow CaCO_3 + CO$$

$$CaCO_3 \rightarrow CaO + CO_2$$

2.3 Pressure-Dependent Reactions in Inert Gas

CaOx*H_2O at different heating rates and different pressure of N_2

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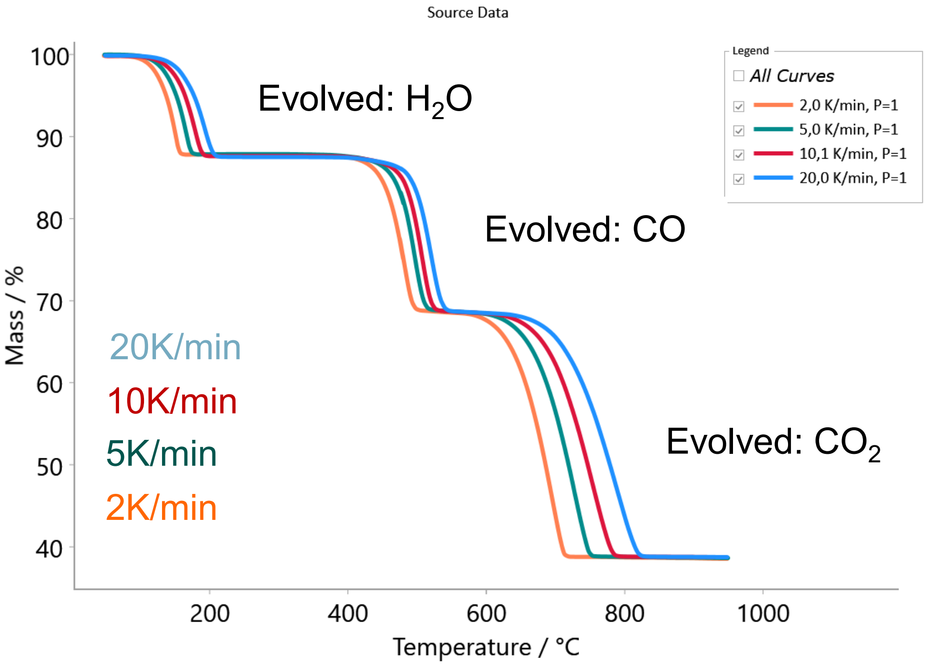

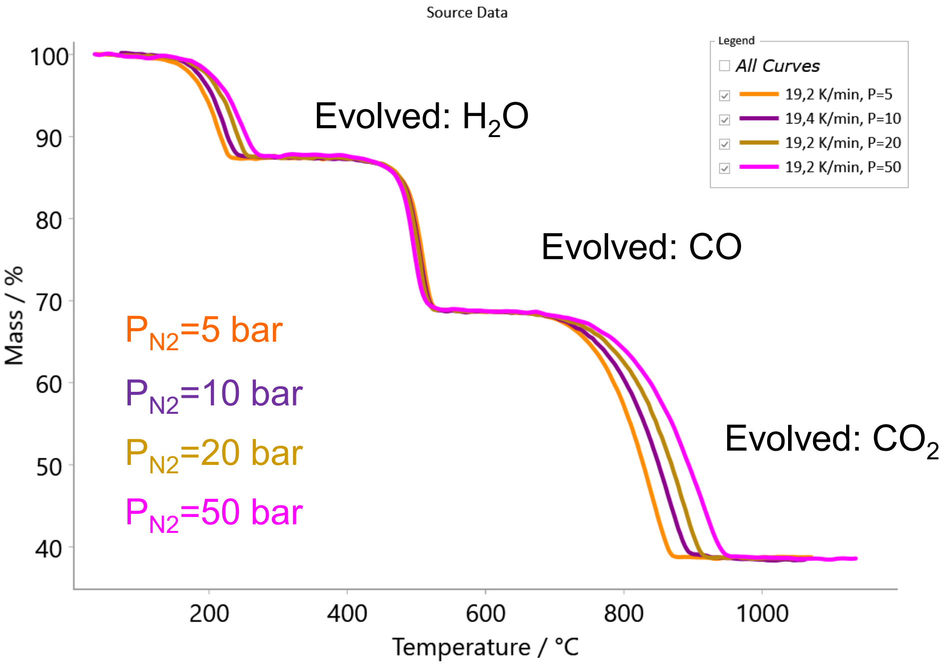

normal pressure 1 bar,
different heating rates

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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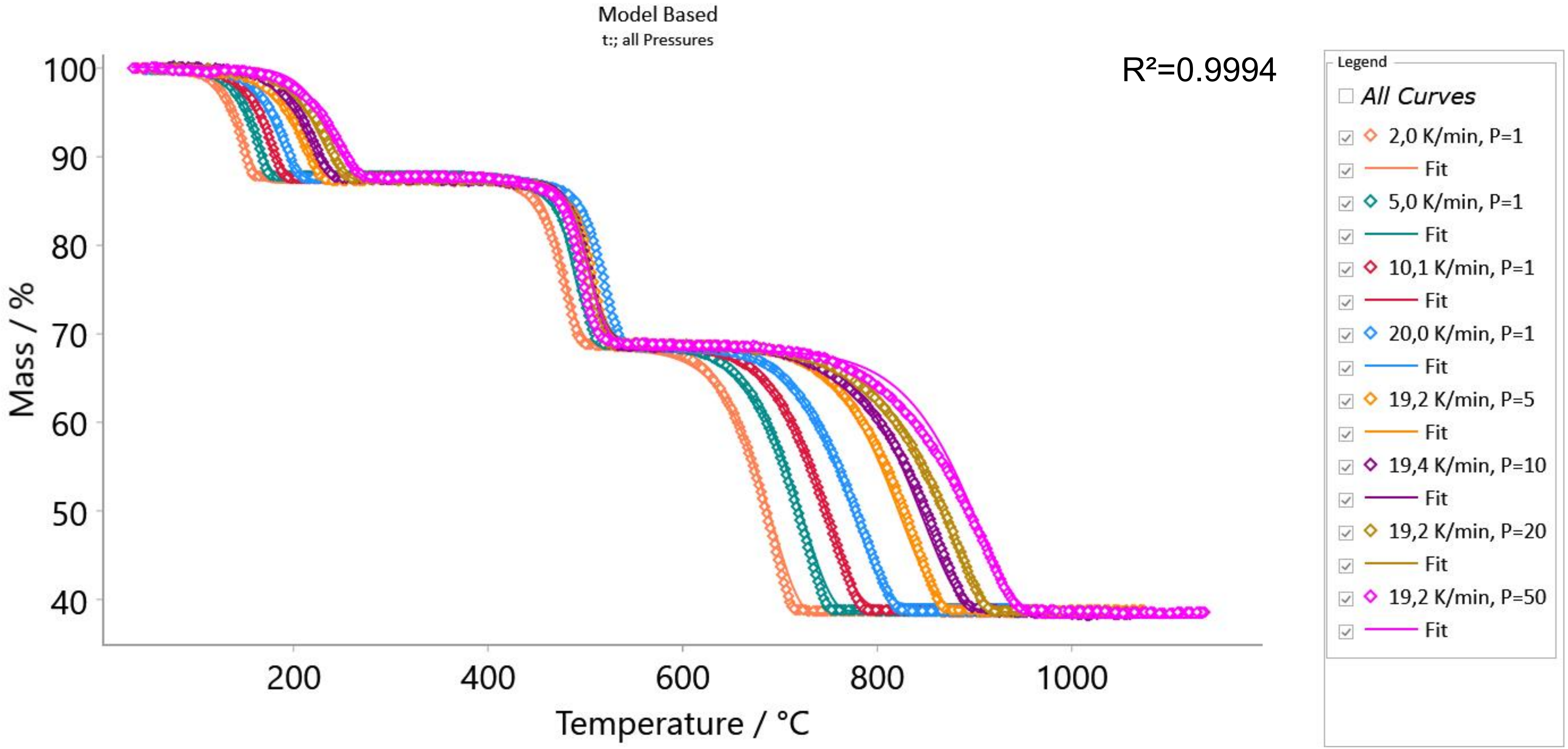

Optimal parameters for pressure: n_1= - 0.75, n_3= - 0.73

Conclusion

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Kinetics Neo Software is able to create two-dimensional model, depending on two parameters:

1. Temperature
2. Pressure of gaseous reactant
    1. Partial pressure of active reactant (hydrogen, oxygen)
    2. Partial pressure of active reactant for reverse reaction (CO2 for Carbonates, H2O for dehydratation)
    3. Total pressure of inert gas for reversible reactions

Verification confirmes the created kinetic models

You can rely on NETZSCH.

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