Molar mass degradation of NC and cellulose; Modelling by random chain scission and chain recombination including non-isothermal data

Dr. Manfred A. Bohn
Fraunhofer-Institut fuer Chemische Technologie, ICT
Pfinztal, Germany

Presentation on the 6th International Nitrocellulose Symposium
April 23 - 24, 2014
TNO, Rijswijk, The Netherlands

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Motivations and Objectives

- Nitrocellulose (NC) will be used further on in gun propellants and other types of propellants, also such of LOVA (low vulnerability) type.
- NC needs to be stabilized to prevent against accelerated decomposition.
- The intrinsic decomposition cannot be prevented, therefore stabilizer is always consumed.
- Together with stabilizer consumption chain splitting happens, and this by a mechanism causing mass loss.
- Chain splitting occurs randomly and by chain element decomposition.
- Kinetic models for stabilizer consumption and for chain splitting or molar mass decrease are in use already.
- But recently new aspects arose which caused reconsideration of both processes.

- Molar mass degradation of NC was found to proceed slower than predicted by already existing models – New models have been developed, which include chain recombination. This causes a slower decrease of molar mass degradation.
- Non-isothermal data description is a challenge – Besides necessary data at several heating rates, the way of applying the model is important, which can be:
  (1) incremental method, (2) solution of integrated rate equation, (3) rate equation.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Models for molar mass degradation of polymers

(not only for NC)

Usable for all polymers degrading by *random chain scission* processes.
The cause can be any, as thermal, hydrolysis, radiation, tribological, shearing,….

Two main splitting processes are considered:

1. Polymer chain splitting by decomposition of chain elements (monomers).

   > this causes mass loss
   > finally all the material is decomposed, nothing is left.

2. Polymer chain splitting by scission of bonds between chain elements.

   > no mass loss
   > finally all the material is decomposed into monomers (chain elements).

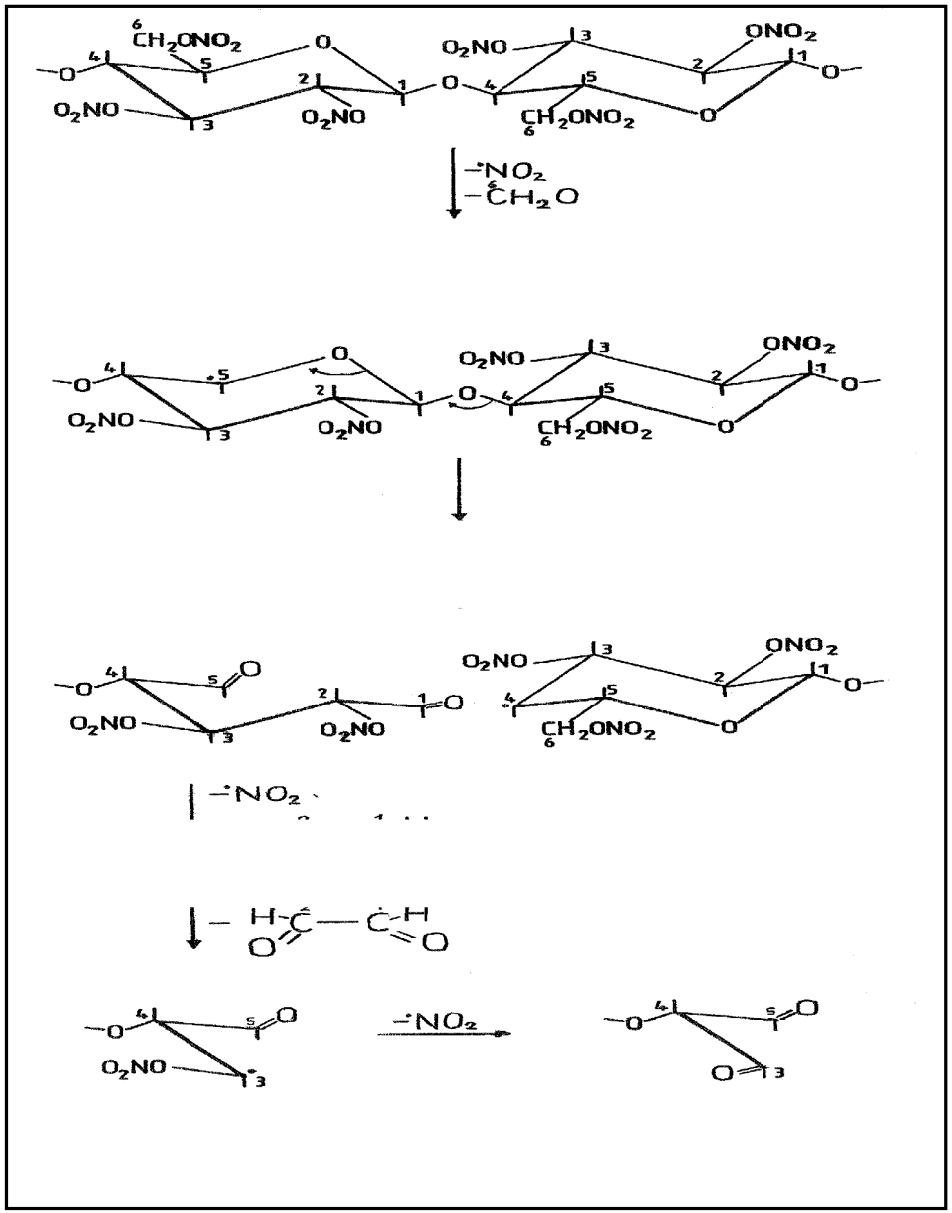
Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Decomposition of NC

By splitting-off of one NO_2 group from any ester group the corresponding glucose ring will be destroyed.
See as example the decomposition pathway on the right.

This means the mean molar masses of NC decrease all the time caused by the slow intrinsic decomposition of NC, which cannot be stopped by stabilizers.



Pathway taken from
NC-based energetic materials - stability, decomposition, and ageing.
Manfred A. Bohn
Presentation on the Meeting
'Nitrocellulose - Supply, Ageing and Characterization'
April 24 to 25, 2007,
AWE, Aldermaston, England.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Meaning of symbols

nc(t)	number of polymer chains at time t
Nm(t)	total number of chain elements (monomers) at time t
Mn(t)	number averaged mean molar mass at time t, in mass/mol
m	molar mass of one chain element (monomer), in mass /mol
Pn(t)	number averaged degree of polymerisation at time t, Pn(t) = Mn(t)/m
B(t)	number of bonds between chain elements (monomers) at time t
k_{M1}	reaction rate constant of first order reaction of chain element decomposition, in 1/time
k_{B1}	reaction rate constant of first order reaction of bond decomposition, in 1/time
k_{M2}	reaction rate constant for chain recombination, in 1/time
k_{B2}	reaction rate constant for chain recombination, in 1/time

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Basic setup to achieve the expression for Mn(t,T)

The essential final target is to get an expression for the number averaged mean molar mass Mn as function of start condition Mn(0) and time and temperature in the model expression Exm.

$$Mn(t,T(t)) = f\big(Mn(0), Exm(t,T(t))\big)$$

The first target is always to obtain the corresponding rate equation.

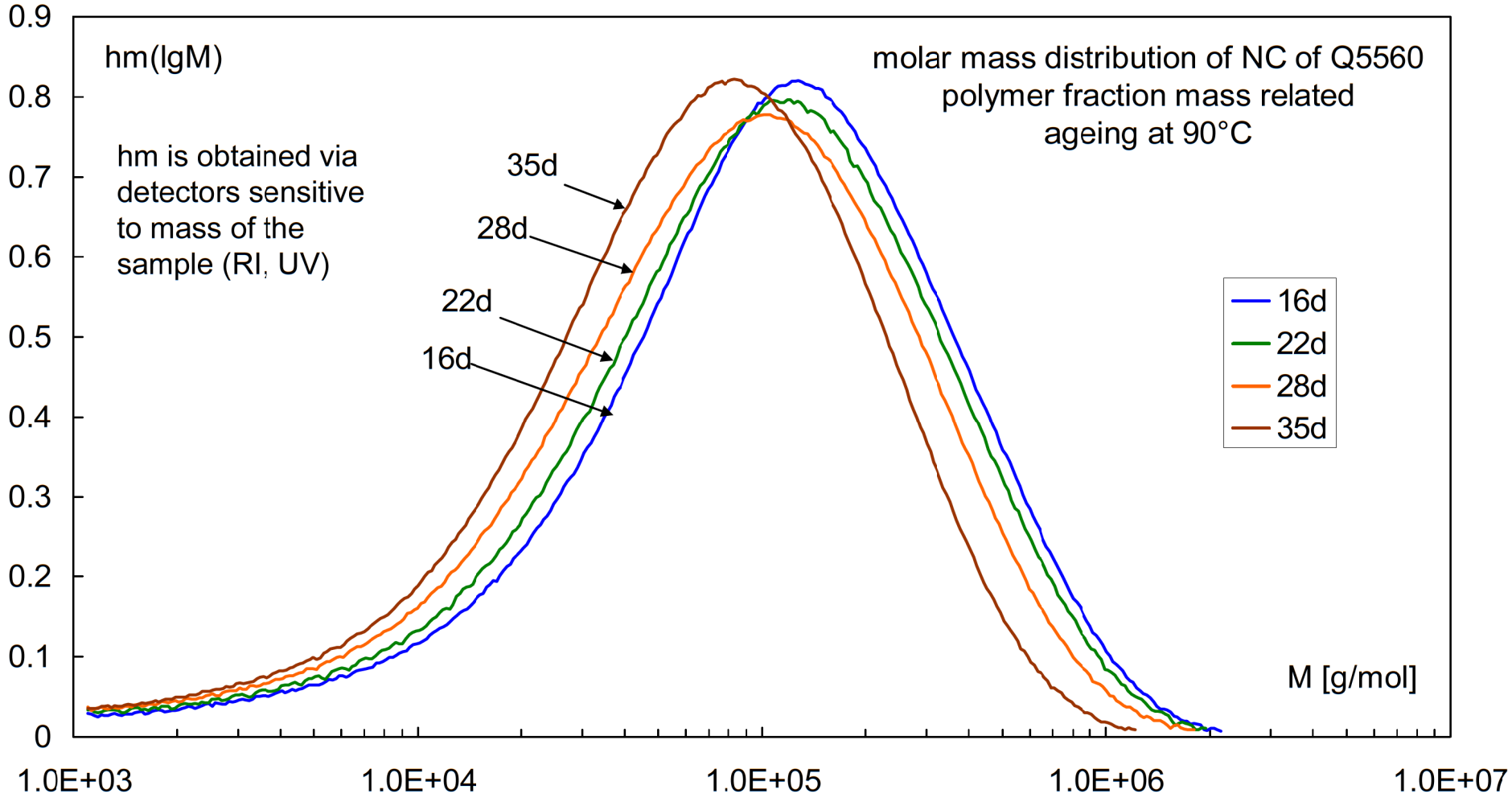
$$\frac{dMn(t,T(t))}{dt} = f_{rate}\left(Mn(0), \frac{dExm(t,T(t))}{dt}\right)$$

Note:
reaction kinetically the number averaged mean molar mass Mn is the correct quantity, because molecules react with each other and not their mass, which would be the implication by using Mw, the mass averaged mean molar mass.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

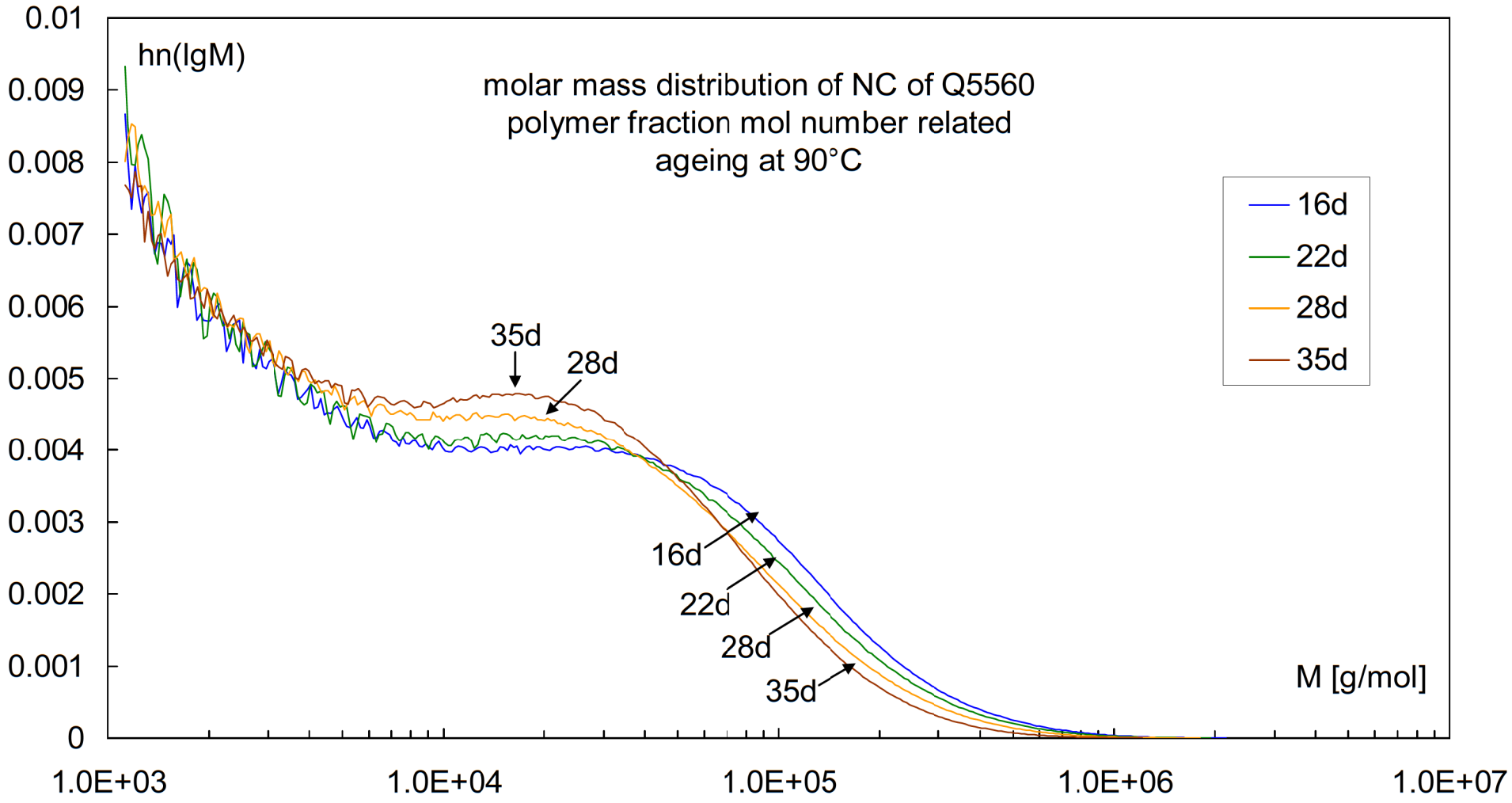
Types of MMD: hm – related to the masses of the polymer in the GPC fractions



Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

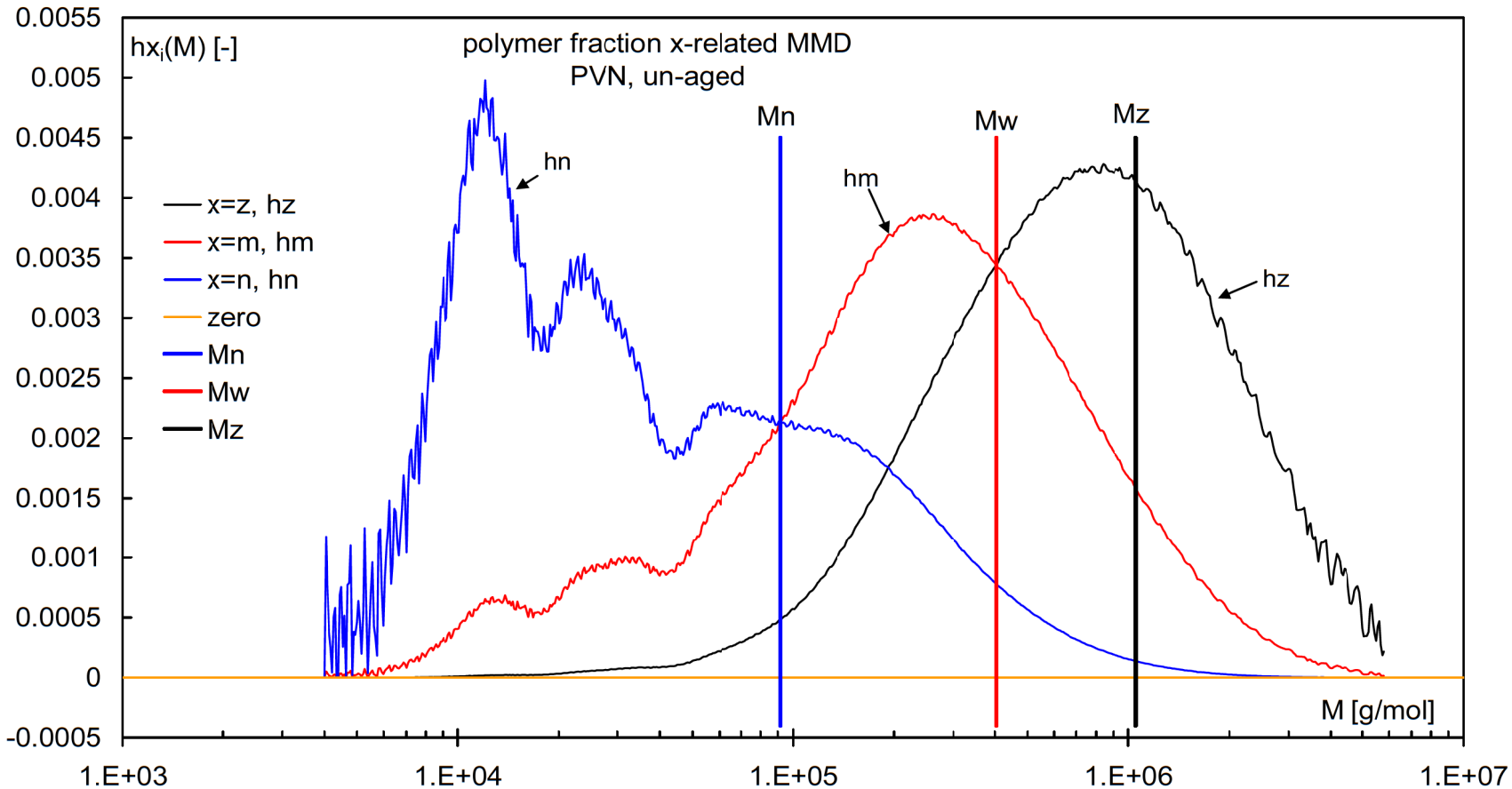
Types of MMD: hn – related to the mol numbers of the polymer in the GPC-fractions



Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Example of MMDs according to the main three types of weighting: number, mass, z



Note: here the normalisation of the MMDs is with regard to M, not lg(M).

The three types of weighting show the distinct emphases of the molar mass regions by the type of MMD and therefore of their mean values, which are arithmetic means or 'center of gravity' values of the corresponding MMD:

low M by hn, medium M by hm, high M by hz

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

General scheme, shown with the two types of random chain splitting

Chain element decomposition

$$\frac{dnc(t)}{dt} = k_{M1} \cdot Nm(t) = -\frac{dNm(t)}{dt}$$

$$Nm(t) = Nm(0) \cdot \exp(-k_{M1} \cdot t)$$

$$nc(t) = Nm(t) \cdot \frac{m}{Mn(t)} = \frac{Nm(t)}{Pn(t)}$$

$$\frac{dnc(t)}{dt} = \frac{dNm(t)}{dt} \cdot \frac{m}{Mn(t)} - Nm(t) \cdot \frac{m}{Mn(t)^2} \frac{dMn(t)}{dt}$$

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -k_{M1} \cdot \left(\left(\frac{Mn(t)}{m}\right)^2 + \left(\frac{Mn(t)}{m}\right)\right)$$

$$\frac{Mn(t)}{m} = \frac{\exp(-k_{M1} \cdot t)}{\frac{m}{Mn(0)} + 1 - \exp(-k_{M1} \cdot t)}$$

first order decomposition

bond scission between elements

$$\frac{dnc(t)}{dt} = k_{B1} \cdot B(t) = -\frac{dB(t)}{dt}$$

$$B(t) = B(0) \cdot \exp(-k_{B1} \cdot t)$$

$$nc(t) = Nm(0) \cdot \frac{m}{Mn(t)}$$

$$\frac{dnc(t)}{dt} = -Nm(0) \cdot \frac{m}{Mn(t)^2} \frac{dMn(t)}{dt}$$

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -k_{B1}\left(\left(\frac{Mn(t)}{m}\right)^2 - \left(\frac{Mn(t)}{m}\right)\right)$$

$$\frac{Mn(t)}{m} = \frac{\exp(+k_{B1} \cdot t)}{\frac{m}{Mn(0)} - 1 + \exp(+k_{B1} \cdot t)}$$

these two ways provide equations, which are morphologically similar. There is a systematic change in the signs + and – in the solutions

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Calculation and prediction of in-service times $ty_{Mn}(T)$ with $y_{Mn} = Mn(t)/Mn(0)$

Model CS by BS (chain scission by bond splitting)

$$\frac{Mn(t)}{m} = \frac{\exp(+k_{B1} \cdot t)}{\frac{m}{Mn(0)} - 1 + \exp(+k_{B1} \cdot t)}$$

$$ty_{Mn}(T) = -\frac{1}{k_{B1}(T)} \cdot \ln\left(\frac{\frac{Mn(0)}{m} - \frac{1}{y_{Mn}}}{\frac{Mn(0)}{m} - 1}\right)$$

Model CS by ED (chain scission by chain element decomposition)

$$\frac{Mn(t)}{m} = \frac{\exp(-k_{M1} \cdot t)}{\frac{m}{Mn(0)} + 1 - \exp(-k_{M1} \cdot t)}$$

$$ty_{Mn}(T) = \frac{1}{k_{M1}(T)} \cdot \ln\left(\frac{\frac{1}{y_{Mn}} + \frac{Mn(0)}{m}}{1 + \frac{Mn(0)}{m}}\right)$$

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Chain element decomposition according to zero order and second order

zero order decomposition ← **of chain elements** → **second order decomposition**

$$\frac{dnc(t)}{dt} = k'_{M0} = -\frac{dNm(t)}{dt}$$

$$k_{M0} = \frac{k'_{M0}}{Nm(0)}$$

$$Nm(t) = Nm(0) \cdot (1 - k_{M0} \cdot t)$$ zero order

$$\frac{dnc(t)}{dt} = k'_{M,2} \cdot Nm(t)^2 = -\frac{dNm(t)}{dt}$$

$$k_{M,2} = Nm(0) \cdot k'_{M,2}$$

$$Nm(t) = Nm(0) \cdot \frac{1}{1 + k_{M,2} \cdot t}$$ second order

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -\frac{k_{M0}}{(1 - k_{M0} \cdot t)} \cdot \left(\left(\frac{Mn(t)}{m}\right)^2 + \left(\frac{Mn(t)}{m}\right)\right)$$

$$\frac{Mn(t)}{m} = \frac{1 - k_{M0} \cdot t}{\frac{m}{Mn(0)} + k_{M0} \cdot t}$$

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -\frac{k_{M,2}}{(1 + k_{M,2} \cdot t)} \cdot \left(\left(\frac{Mn(t)}{m}\right)^2 + \left(\frac{Mn(t)}{m}\right)\right)$$

$$\frac{Mn(t)}{m} = \frac{1}{\frac{m}{Mn(0)} + k_{M,2} \cdot t \cdot \left(\frac{m}{Mn(0)} + 1\right)}$$

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Random chain scission by first order reactions and with decaying reactivity

chain element decomposition

$$\frac{dnc(t)}{dt} = k_{M1}(t) \cdot Nm(t) = -\frac{dNm(t)}{dt}$$

$$k_{M1}(t,T) = k_{M1o}(T) \cdot \exp(-k(T) \cdot t)$$

$$Nm(t,T) = Nm(0) \cdot \exp\left(-\frac{k_{M1o}(T)}{k(T)} \cdot \exp(-k(T) \cdot t)\right)$$

$$\frac{d\left(\frac{Mn(t,T)}{m}\right)}{dt} = -k_{M1o}(T) \cdot \exp(-k(T) \cdot t) \cdot \left(\left(\frac{Mn(t,T)}{m}\right)^2 + \left(\frac{Mn(t,T)}{m}\right)\right)$$

$$\frac{Mn(t,T)}{m} = \frac{\exp\left(-\frac{k_{M1o}(T)}{k(T)} \cdot (1 - \exp(-k(T) \cdot t))\right)}{\left(\frac{m}{Mn(0)} + 1\right) - \exp\left(-\frac{k_{M1o}(T)}{k(T)} \cdot (1 - \exp(-k(T) \cdot t))\right)}$$

Decay of reactivity finally to zero in $k_{Xi}(t)$

bond scission between elements

$$\frac{dnc(t)}{dt} = k_{B1}(t) \cdot B(t) = -\frac{dB(t)}{dt}$$

$$k_{B1}(t,T) = k_{B1o}(T) \cdot \exp(-k(T) \cdot t)$$

$$B(t,T) = B(0) \cdot \exp\left(-\frac{k_{B1o}(T)}{k(T)} \cdot \exp(-k(T) \cdot t)\right)$$

$$\frac{d\left(\frac{Mn(t,T)}{m}\right)}{dt} = -k_{B1o}(T) \cdot \exp(-k(T) \cdot t) \cdot \left(\left(\frac{Mn(t,T)}{m}\right)^2 - \left(\frac{Mn(t,T)}{m}\right)\right)$$

$$\frac{Mn(t,T)}{m} = \frac{\exp\left(+\frac{k_{B1o}(T)}{k(T)} \cdot (1 - \exp(-k(T) \cdot t))\right)}{\left(\frac{m}{Mn(0)} - 1\right) + \exp\left(+\frac{k_{B1o}(T)}{k(T)} \cdot (1 - \exp(-k(T) \cdot t))\right)}$$

This model was formulated by Emsley a.o. in 1997 but only in the approximated form.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Random chain scission by first order reactions - with decaying reactivity- but not to zero

chain element decomposition

$$\frac{dnc(t)}{dt} = k_{M1}(t)\cdot Nm(t) = -\frac{dNm(t)}{dt}$$

$$k_{M1}(t,T) = k_{M1\infty}(T) + \left(k_{M1o}(T) - k_{M1\infty}(T)\right)\cdot \exp\left(-k(T)\cdot t\right)$$

$$\frac{Nm(t,T)}{Nm(0)} = \exp\left(-k_{M1\infty}(T)\cdot t\right)\cdot \exp\left(-\frac{k_{M1o}(T) - k_{M1\infty}(T)}{k(T)}\cdot\left(1-\exp(k(T)\cdot t)\right)\right)$$

$$\frac{d\left(\frac{Mn(t,T)}{m}\right)}{dt} = -\left(k_{M1\infty}(T) + \left(k_{M1o}(T) - k_{M1\infty}(T)\right)\cdot \exp\left(-k(T)\cdot t\right)\right)$$

$$\cdot\left(\left(\frac{Mn(t,T)}{m}\right)^2 + \left(\frac{Mn(t,T)}{m}\right)\right)$$

$$\frac{Mn(t)}{m} = \frac{\exp\left(-k_{M1\infty}\cdot t\right)\cdot \exp\left(-\frac{k_{M1o} - k_{M1\infty}}{k}\cdot\left(1-\exp(-k\cdot t)\right)\right)}{\left(\frac{m}{Mn(0)}+1\right) - \exp\left(-k_{M1\infty}\cdot t\right)\cdot \exp\left(-\frac{k_{M1o} - k_{M1\infty}}{k}\cdot\left(1-\exp(-k\cdot t)\right)\right)}$$

bond scission between elements

$$\frac{dnc(t)}{dt} = k_{B1}(t)\cdot B(t) = -\frac{dB(t)}{dt}$$

$$k_{B1}(t,T) = k_{B1\infty}(T) + \left(k_{B1o}(T) - k_{B1\infty}(T)\right)\cdot \exp\left(-k(T)\cdot t\right)$$

$$\frac{B(t,T)}{B(0)} = \exp\left(-k_{B1\infty}(T)\cdot t\right)\cdot \exp\left(-\frac{k_{B1o}(T) - k_{B1\infty}(T)}{k(T)}\cdot\left(1-\exp(k(T)\cdot t)\right)\right)$$

$$\frac{d\left(\frac{Mn(t,T)}{m}\right)}{dt} = -\left(k_{B1\infty}(T) + \left(k_{B1o}(T) - k_{B1\infty}(T)\right)\cdot \exp\left(-k(T)\cdot t\right)\right)$$

$$\cdot\left(\left(\frac{Mn(t,T)}{m}\right)^2 - \left(\frac{Mn(t,T)}{m}\right)\right)$$

$$\frac{Mn(t)}{m} = \frac{\exp\left(+k_{B1\infty}\cdot t\right)\cdot \exp\left(+\frac{k_{B1o} - k_{B1\infty}}{k}\cdot\left(1-\exp(-k\cdot t)\right)\right)}{\left(\frac{m}{Mn(0)}-1\right) + \exp\left(+k_{M1\infty}\cdot t\right)\cdot \exp\left(+\frac{k_{B1o} - k_{B1\infty}}{k}\cdot\left(1-\exp(-k\cdot t)\right)\right)}$$

Decay of reactivity
not to zero in $k_{Xi}(t)$

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Random chain scission by first order reactions - with decreasing molar mass m

chain element decomposition | **bond scission between elements**

$$\boxed{m(t) = m(0)\cdot\exp(-km\cdot t)}$$

$$Mn(t) = m(t)\cdot Pn(t)$$

$$\frac{dMn(t)}{dt} = \frac{dm(t)}{dt}\cdot Pn(t) + m(t)\cdot\frac{dPn(t)}{dt}$$

$$Pn(t) \neq f(m(t))$$

$$\frac{d\left(\frac{Mn(t)}{m(0)}\right)}{dt} = \frac{d\left(\frac{m(t)}{m(0)}\right)}{dt}\cdot Pn(t) + \frac{m(t)}{m(0)}\cdot\frac{dPn(t)}{dt}$$

$$\frac{dPn(t)}{dt} = -k_{M1}\cdot\left((Pn(t))^2 + Pn(t)\right)$$

$$\frac{dPn(t)}{dt} = -k_{B1}\cdot\left((Pn(t))^2 - Pn(t)\right)$$

$$\frac{d\left(\frac{Mn(t)}{m(0)}\right)}{dt} = -km\cdot\exp(-km\cdot t)\cdot Pn(t) + \exp(-km\cdot t)\cdot\left(-k_{M1}\cdot(Pn(t))^2 - k_{M1}\cdot Pn(t)\right)$$

$$\frac{d\left(\frac{Mn(t)}{m(0)}\right)}{dt} = -km\cdot\exp(-km\cdot t)\cdot Pn(t) + \exp(-km\cdot t)\cdot\left(-k_{B1}\cdot(Pn(t))^2 + k_{B1}\cdot Pn(t)\right)$$

$$\frac{Mn(t)}{m(0)} = \exp(-km\cdot t)\cdot\frac{\exp(-k_{M1}\cdot t)}{\frac{m(0)}{Mn(0)} + 1 - \exp(-k_{M1}\cdot t)}$$

$$\frac{Mn(t)}{m(0)} = \exp(-km\cdot t)\cdot\frac{\exp(+k_{B1}\cdot t)}{\frac{m(0)}{Mn(0)} - 1 + \exp(+k_{B1}\cdot t)}$$

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Random chain scission by first order reactions - with decreasing molar mass m

chain element decomposition | **bond scission between elements**

Second order decrease of m(t)

$$m(t) = \frac{m(0)}{1 + km \cdot t}$$

$$\frac{d\left(\frac{Mn(t)}{m(0)}\right)}{dt} = -km \cdot \left(\frac{1}{1 + km \cdot t}\right)^2 \cdot Pn(t) + \frac{1}{1 + km \cdot t} \cdot \left(-k_{M1} \cdot Pn(t)^2 - k_{M1} \cdot Pn(t)\right)$$

$$\frac{Mn(t)}{m(0)} = \frac{1}{1 + km \cdot t} \cdot \frac{\exp(-k_{M1} \cdot t)}{\frac{m(0)}{Mn(0)} + 1 - \exp(-k_{M1} \cdot t)}$$

$$\frac{d\left(\frac{Mn(t)}{m(0)}\right)}{dt} = -km \cdot \left(\frac{1}{1 + km \cdot t}\right)^2 \cdot Pn(t) + \frac{1}{1 + km \cdot t} \cdot \left(-k_{B1} \cdot Pn(t)^2 + k_{B1} \cdot Pn(t)\right)$$

$$\frac{Mn(t)}{m(0)} = \frac{1}{1 + km \cdot t} \cdot \frac{\exp(+k_{B1} \cdot t)}{\frac{m(0)}{Mn(0)} - 1 + \exp(+k_{B1} \cdot t)}$$

zero order decrease of m(t)

$$m(t) = m(0) \cdot (1 - km \cdot t)$$

$$\frac{d\left(\frac{Mn(t)}{m(0)}\right)}{dt} = -km \cdot Pn(t) + (1 - km \cdot t) \cdot \left(-k_{M1} \cdot Pn(t)^2 - k_{M1} \cdot Pn(t)\right)$$

$$\frac{Mn(t)}{m(0)} = (1 - km \cdot t) \cdot \frac{\exp(-k_{M1} \cdot t)}{\frac{m(0)}{Mn(0)} + 1 - \exp(-k_{M1} \cdot t)}$$

$$\frac{d\left(\frac{Mn(t)}{m(0)}\right)}{dt} = -km \cdot Pn(t) + (1 - km \cdot t) \cdot \left(-k_{B1} \cdot Pn(t)^2 + k_{B1} \cdot Pn(t)\right)$$

$$\frac{Mn(t)}{m(0)} = (1 - km \cdot t) \cdot \frac{\exp(+k_{B1} \cdot t)}{\frac{m(0)}{Mn(0)} - 1 + \exp(+k_{B1} \cdot t)}$$

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Models with chain scission and chain recombination by approximated 2nd order

chain element decomposition

$$\frac{dnc(t)}{dt} = k_{M1} \cdot Nm(t) - k_{M2} \cdot (nc(t) - nc(0))$$

$$k_{M2} = k'_{M2} \cdot nc_0$$

$$Nm(t) = Nm(0) \cdot \exp(-k_{M1} \cdot t)$$

$$\frac{dnc(t)}{dt} = \frac{Nm(t)}{dt} \cdot \frac{m}{Mn(t)} - Nm(t) \cdot \frac{m}{Mn(t)^2} \frac{dMn(t)}{dt}$$

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -\left(k_{M1} + k_{M2} \cdot \exp(+k_{M1} \cdot t) \cdot \frac{m}{Mn(0)}\right) \cdot \left(\frac{Mn(t)}{m}\right)^2 - (k_{M1} - k_{M2}) \cdot \left(\frac{Mn(t)}{m}\right)$$

$$\frac{Mn(t)}{m} = \frac{\exp(-k_{M1} \cdot t)}{\frac{m}{Mn(0)} + \frac{k_{M1}}{k_{M1} - k_{M2}} \cdot (\exp(-k_{M2} \cdot t) - \exp(-k_{M1} \cdot t))}$$

Approximation used

bond scission between elements

$$\frac{dnc(t)}{dt} = k_{B1} \cdot B(t) - k_{B2} \cdot (nc(t) - nc(0))$$

$$k_{B2} = k'_{B2} \cdot nc_0$$

$$B(t) = Nm(0) \cdot \left(1 - \frac{m}{Mn(t)}\right)$$

$$\frac{dnc(t)}{dt} = -Nm(0) \cdot \frac{m}{Mn(t)^2} \frac{dMn(t)}{dt}$$

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -\left(k_{B1} + k_{B2} \cdot \frac{m}{Mn(0)}\right) \cdot \left(\frac{Mn(t)}{m}\right)^2 + (k_{B1} + k_{B2}) \cdot \left(\frac{Mn(t)}{m}\right)$$

$$\frac{Mn(t)}{m} = \frac{\exp(+(k_{B1} + k_{B2}) \cdot t)}{\frac{m}{Mn(0)} + \frac{k_{B1} + k_{B2} \cdot \frac{m}{Mn(0)}}{k_{B1} + k_{B2}} \cdot (\exp(+(k_{B1} + k_{B2}) \cdot t) - 1)}$$

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Random chain scission by first order reactions and CR - with decreasing molar mass m

chain element decomposition ← | → **bond scission between elements**

$$\boxed{m(t) = m(0)\cdot\exp(-km\cdot t)}$$

$$Mn(t) = m(t)\cdot Pn(t)$$

$$\frac{dMn(t)}{dt} = \frac{dm(t)}{dt}\cdot Pn(t) + m(t)\cdot\frac{dPn(t)}{dt}$$

$$Pn(t) \neq f(m(t))$$

$$\frac{d\left(\frac{Mn(t)}{m(0)}\right)}{dt} = \frac{d\left(\frac{m(t)}{m(0)}\right)}{dt}\cdot Pn(t) + \frac{m(t)}{m(0)}\cdot\frac{dPn(t)}{dt}$$

$$\frac{d\left(\frac{Mn(t)}{m(0)}\right)}{dt} = -km\cdot\exp(-km\cdot t)\cdot Pn(t) + \exp(-km\cdot t)\cdot\left(-\left(k_{M1} + k_{M2}\cdot\exp(+k_{M1}\cdot t)\cdot\frac{1}{Pn(0)}\right)\cdot(Pn(t))^2 - (k_{M1} - k_{M2})\cdot Pn(t)\right)$$

$$\frac{Mn(t)}{m(0)} = \exp(-km\cdot t)\cdot\frac{\exp(-k_{M1}\cdot t)}{\frac{m(0)}{Mn(0)} + \frac{k_{M1}}{k_{M1} - k_{M2}}\cdot\left(\exp(-k_{M2}\cdot t) - \exp(-k_{M1}\cdot t)\right)}$$

$$\frac{d\left(\frac{Mn(t)}{m(0)}\right)}{dt} = -km\cdot\exp(-km\cdot t)\cdot Pn(t) + \exp(-km\cdot t)\cdot\left(-\left(k_{B1} + k_{B2}\cdot\frac{1}{Pn(0)}\right)\cdot(Pn(t))^2 + (k_{B1} + k_{B2})\cdot Pn(t)\right)$$

$$\frac{Mn(t)}{m(0)} = \exp(-km\cdot t)\cdot\frac{\exp\left(+(k_{B1} + k_{B2})\cdot t\right)}{\frac{m(0)}{Mn(0)} + \frac{(k_{B1} + k_{B2})\cdot\frac{m(0)}{Mn(0)}}{(k_{B1} + k_{B2})}\cdot\left(\exp\left(+(k_{B1} + k_{B2})\cdot t\right) - 1\right)}$$

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Calculation and prediction of in-service times for models with CR

Model CS by BS and CR

$$\frac{Mn(t)}{m} = \frac{\exp\left(+(k_{B1}+k_{B2})\cdot t\right)}{\frac{m}{Mn(0)} + \frac{k_{B1}+k_{B2}\cdot\frac{m}{Mn(0)}}{k_{B1}+k_{B2}}\cdot\left(\exp\left(+(k_{B1}+k_{B2})\cdot t\right)-1\right)}$$

$$t = \frac{1}{k_{B1}+k_{B2}}\cdot\ln\left(\frac{\frac{m}{Mn(0)}-k_{Be}}{\frac{m}{Mn(t)}-k_{Be}}\right)$$

$$k_{Be} = \frac{k_{B1}+k_{B2}\cdot\frac{m}{Mn(0)}}{k_{B1}+k_{B2}}$$

Model CS by ED and CR

$$\frac{Mn(t)}{m} = \frac{\exp\left(-k_{M1}\cdot t\right)}{\frac{m}{Mn(0)} + \frac{k_{M1}}{k_{M1}-k_{M2}}\cdot\left(\exp(-k_{M2}\cdot t)-\exp\left(-k_{M1}\cdot t\right)\right)}$$

$$\exp\left(+k_{M1}\cdot t\right) = \frac{\frac{m}{Mn(t)}+k_{Me}}{\frac{m}{Mn(0)}+k_{Me}\exp\left(-k_{M2}\cdot t\right)}$$

$$k_{Me} = \frac{k_{M1}}{k_{M1}-k_{M2}}$$

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Model with chain scission by chain element decomposition and chain recombination by not approximated second order reaction

$$\frac{dnc(t)}{dt} = k_{M1} \cdot Nm(t) - k'_{M2} \cdot nc(t) \cdot \left(nc(t) - nc(0)\right)$$

$$Nm(t) = Nm(0) \cdot \exp(-k_{M1} \cdot t)$$

$$k_{M2} = k'_{M2} \cdot Nm(0)$$

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -k_{M1}\left(\frac{Mn(t)}{m}\right)^2 - \left(k_{M1} + k_{M2} \cdot \frac{m}{Mn(0)}\right) \cdot \left(\frac{Mn(t)}{m}\right) + k_{M2} \cdot \exp(-k_{M1} \cdot t)$$

Riccati type differential equation

$$\left\{\left\{M[x] \to \left(\left(\frac{\sqrt{k2}}{\sqrt{k1}}\right)^{\frac{2\,k2}{k1\,Mo}} k2\,\text{Hypergeometric0F1Regularized}\left[1 - \frac{k2}{k1\,Mo}, \frac{e^{-k1\,x}\,k2}{k1}\right] \left(\text{Hypergeometric0F1Regularized}\left[1 + \frac{k2}{k1\,Mo}, \frac{k2}{k1}\right] + Mo\,\text{Hypergeometric0F1Regularized}\left[2 + \frac{k2}{k1\,Mo}, \frac{k2}{k1}\right]\right) - \left(\frac{\sqrt{e^{-k1\,x}}\,\sqrt{k2}}{\sqrt{k1}}\right)^{\frac{2\,k2}{k1\,Mo}} \text{Hypergeometric0F1Regularized}\left[1 + \frac{k2}{k1\,Mo}, \frac{e^{-k1\,x}\,k2}{k1}\right] \left(k2\,\text{Hypergeometric0F1Regularized}\left[1 - \frac{k2}{k1\,Mo}, \frac{k2}{k1}\right] + k1\,Mo\,\text{Hypergeometric0F1Regularized}\left[-\frac{k2}{k1\,Mo}, \frac{k2}{k1}\right]\right)\right) \Big/ \left(\left(\frac{\sqrt{e^{-k1\,x}}\,\sqrt{k2}}{\sqrt{k1}}\right)^{\frac{2\,k2}{k1\,Mo}} k2\,Mo\,\text{Hypergeometric0F1Regularized}\left[2 - \frac{k2}{k1\,Mo}, \frac{k2}{k1}\right] \text{Hypergeometric0F1Regularized}\left[2 + \frac{k2}{k1\,Mo}, \frac{e^{-k1\,x}\,k2}{k1}\right] - e^{k1\,x}\,k1 \left(\frac{\sqrt{k2}}{\sqrt{k1}}\right)^{\frac{2\,k2}{k1\,Mo}} \left(\text{Hypergeometric0F1Regularized}\left[1 + \frac{k2}{k1\,Mo}, \frac{k2}{k1}\right] + Mo\,\text{Hypergeometric0F1Regularized}\left[2 + \frac{k2}{k1\,Mo}, \frac{k2}{k1}\right]\right) \text{Hypergeometric0F1Regularized}\left[-\frac{k2}{k1\,Mo}, \frac{e^{-k1\,x}\,k2}{k1}\right]\right)\right\}\right\}$$

The solution of this rate equation was obtained with the program package Mathematica™ and contains a lot of difficult to handle series.

© Fraunhofer ICT, Pfinztal, Germany

Approximation for cases with m/Mn(t) << 1

chain element decomposition

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -k_{M1}\cdot\left(\left(\frac{Mn(t)}{m}\right)^2 + \left(\frac{Mn(t)}{m}\right)\right)$$

$$\frac{Mn(t)}{m} = \frac{\exp(-k_{M1}\cdot t)}{\frac{m}{Mn(0)} + 1 - \exp(-k_{M1}\cdot t)}$$

This is equal to

$$\ln\left(1+\frac{m}{Mn(t,T)}\right) = \ln\left(1+\frac{m}{Mn(0)}\right) + k_{M1}(T)\cdot t$$

Apply $\ln(1+X) \approx= +X$ for $X \ll 1$

$$\frac{m}{Mn(t,T)} = \frac{m}{Mn(0)} + k_{M1}(T)\cdot t$$

$$\left.\left(\frac{d\left(\frac{Mn(t,T)}{m}\right)}{dt}\right)\right|_T = -k_{M1}(T)\cdot\left(\frac{Mn(t,T)}{m}\right)^2$$

first order decomp.

The two models are no longer distinguishable!

The corresponding rate equations

bond scission between elements

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -k_{B1}\left(\left(\frac{Mn(t)}{m}\right)^2 - \left(\frac{Mn(t)}{m}\right)\right)$$

$$\frac{Mn(t)}{m} = \frac{\exp(+k_{B1}\cdot t)}{\frac{m}{Mn(0)} - 1 + \exp(+k_{B1}\cdot t)}$$

This is equal to

$$\ln\left(1-\frac{m}{Mn(t,T)}\right) = \ln\left(1-\frac{m}{Mn(0)}\right) - k_{B1}(T)\cdot t$$

Apply $\ln(1-X) \approx= -X$ for $X \ll 1$

$$\frac{m}{Mn(t,T)} = \frac{m}{Mn(0)} + k_{B1}(T)\cdot t$$

$$\left.\left(\frac{d\left(\frac{Mn(t,T)}{m}\right)}{dt}\right)\right|_T = -k_{B1}(T)\cdot\left(\frac{Mn(t,T)}{m}\right)^2$$

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

The Ekenstam equation (Alf af Ekenstam, in Berichte 69(1936) 553-559, in German)

104. Alf af Ekenstam: Über das Verhalten der Cellulose in Mineralsäure-Lösungen, II. Mitteil.: Kinetisches Studium des Abbaus der Cellulose in Säure-Lösungen.

Aus d. Institut für Organ. Chemie d. Universität Lund.

(Eingegangen am 22. Januar 1936.)

In der vorhergehenden I. Mitteilung wurde beschrieben, daß Molekulargewichts-Bestimmungen an Cellulose in Säure-Lösungen nach der bekannten viscosimetrischen Methode von Staudinger ausgeführt werden können. Der Abbau der Cellulose kann auch nach der viscosimetrischen Methode kinetisch verfolgt werden. Ich habe die abfallende Viscosität von Cellulose-Lösungen gemessen und daraus das mittlere Molekulargewicht der Cellulose zum jeweiligen Zeitpunkt der Messung berechnet. Die Geschwindigkeit des Cellulose-Abbaus kann durch Einsetzen der gefundenen Molekulargewichte in die unten abgeleitete Formel berechnet werden.

M = mittleres Mol.-Gew. der Cellulose zu Beginn des Versuches.
x = mittleres Mol.-Gew. der Cellulose nach der Zeit t.
m = mittleres Mol.-Gew. der Cellulose am Ende des Abbaus.
P = Anzahl aufspaltbare Bindungen zu Beginn des Versuches.
y = Anzahl aufgespaltene Bindungen pro mittlere Molekül-Kettenlänge nach der Zeit t.
$\frac{dy}{dt}$ = Aufgespaltene Bindungen im Molekül mittleren Molekulargewichts pro Zeiteinheit.
K = Konstante.

Nach der Zeit t sind $(P-y-1)$ Bindungen von mittlerer Ketten-Länge noch vorhanden.

$$\frac{dy}{dt} = K(P-y-1) \quad \ldots\ldots \quad (1)$$

$$P = \frac{M}{m} \quad \ldots\ldots \quad (2) \qquad y = \frac{M}{x} - 1 \quad \ldots\ldots \quad (3)$$

Werden (2) und (3) in (1) eingesetzt:

$$\frac{dy}{dt} = K\left(\frac{M}{m} - \frac{M}{x}\right) \quad \ldots\ldots \quad (4)$$

Aus (3) wird erhalten:

$$\frac{dy}{dt} = -\frac{M}{x^2}\frac{dx}{dt} \quad \ldots\ldots \quad (5)$$

Aus (4) und (5):

$$-\frac{M}{x^2}\frac{dx}{dt} = K\left(\frac{M}{m} - \frac{M}{x}\right) \qquad \frac{dx}{dt} = -\frac{K}{m}(x^2 - mx)$$

$$t = \int -\frac{m}{K}\frac{dx}{x^2 - mx} + \text{Konstant.}$$

Hieraus (wir führen M_t statt x ein):

$$K = \frac{1}{t}\ln\frac{1 - \frac{m}{M}}{1 - \frac{m}{M_t}} \quad \ldots\ldots \quad (6)$$

This is the Ekenstam equation

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

The Ekenstam equation (Alf af Ekenstam, in Berichte 69(1936) 553-559, in German)

On the behaviour of cellulose in mineral acid solutions, 2nd communication:
Kinetic study of the degradation of cellulose in acidic solution.

(1936) *Ekenstam.* **Berichte 69 (1936) 553-559**

104. Alf af Ekenstam: Über das Verhalten der Cellulose in Mineralsäure-Lösungen, II. Mitteil.: Kinetisches Studium des Abbaus der Cellulose in Säure-Lösungen.

Aus d. Institut für Organ. Chemie d. Universität Lund.
(Eingegangen am 22. Januar 1936.)

In der vorhergehenden I. Mitteilung wurde beschrieben, daß Molekulargewichts-Bestimmungen an Cellulose in Säure-Lösungen nach der bekannten viscosimetrischen Methode von Staudinger ausgeführt werden können. Der Abbau der Cellulose kann auch nach der viscosimetrischen Methode kinetisch verfolgt werden. Ich habe die abfallende Viscosität von Cellulose-Lösungen gemessen und daraus das mittlere Molekulargewicht der Cellulose zum jeweiligen Zeitpunkt der Messung berechnet. Die Geschwindigkeit des Cellulose-Abbaus kann durch Einsetzen der gefundenen Molekulargewichte in die unten abgeleitete Formel berechnet werden.

M = mittleres Mol.-Gew. der Cellulose zu Beginn des Versuches.
x = mittleres Mol.-Gew. der Cellulose nach der Zeit t.
m = mittleres Mol.-Gew. der Cellulose am Ende des Abbaus.
P = Anzahl aufspaltbare Bindungen zu Beginn des Versuches.
y = Anzahl aufgespaltene Bindungen pro mittlere Molekül-Kettenlänge nach der Zeit t.
$\frac{dy}{dt}$ = Aufgespaltene Bindungen im Molekül mittleren Molekulargewichts pro Zeiteinheit.
K = Konstante.

Nach der Zeit t sind (P—y—l) Bindungen von mittlerer Ketten-Länge noch vorhanden.

$$\frac{dy}{dt} = K(P - y - 1) \quad \ldots\ldots \quad (1)$$

$$P = \frac{M}{m} \quad \ldots\ldots \quad (2) \qquad y = \frac{M}{x} - 1 \quad \ldots\ldots \quad (3)$$

Werden (2) und (3) in (1) eingesetzt:

$$\frac{dy}{dt} = K\left(\frac{M}{m} - \frac{M}{x}\right) \quad \ldots\ldots \quad (4)$$

Aus (3) wird erhalten:

$$\frac{dy}{dt} = -\frac{M}{x^2}\frac{dx}{dt} \quad \ldots\ldots \quad (5)$$

Aus (4) und (5):

$$-\frac{M\,dx}{x^2\,dt} = K\left(\frac{M}{m} - \frac{M}{x}\right) \qquad \frac{dx}{dt} = -\frac{K}{m}(x^2 - mx)$$

$$t = \int -\frac{m}{K}\frac{dx}{x^2 - mx} + \text{Konstant.}$$

Hieraus (wir führen M_t statt x ein):

$$K = \frac{1}{t}\ln\frac{1 - \frac{m}{M}}{1 - \frac{m}{M_t}} \quad \ldots\ldots \quad (6)$$

This is the Ekenstam equation

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

The Ekenstam equation – true and simplified version (the last is not from Ekenstam)

True Ekenstam eq.

$$K = \frac{1}{t} \cdot \ln\left(\frac{1 - \frac{m}{M}}{1 - \frac{m}{M_t}} \right)$$

Ekenstam eq. in form with nowadays symbols

$$K(T) = \frac{1}{t} \cdot \ln\left(\frac{1 - \frac{m}{M(0)}}{1 - \frac{m}{M(t,T)}} \right)$$

$$k(T) \cdot t = \ln\left(\frac{1 - \frac{m}{Mn(0)}}{1 - \frac{m}{Mn(t,T)}} \right)$$

True Ekenstam equation is in full identical to this equation

$$\frac{Mn(t)}{m} = \frac{\exp(+k_{B1} \cdot t)}{\frac{m}{Mn(0)} - 1 + \exp(+k_{B1} \cdot t)}$$

or $$\ln\left(1 - \frac{m}{Mn(t,T)}\right) = \ln\left(1 - \frac{m}{Mn(0)}\right) - k_{B1}(T) \cdot t$$

Simplification of true Ekenstam equation, it is valid only as long as Mn(t) >> m

$$k(T) \cdot t = \ln\left(1 - \frac{m}{Mn(0)}\right) - \ln\left(1 - \frac{m}{Mn(t,T)}\right) = -\frac{m}{Mn(0)} + \frac{m}{Mn(t,T)}$$

Approximation in using: ln(1-x) = -x with x<< 1
Note: this is **not** a zero order approximation as sometimes said in literature

$$\frac{m}{Mn(t,T)} = \frac{m}{Mn(0)} + k(T) \cdot t$$

Very often this is referred as Ekenstam equation, but it was never offered by him and not used by him!

Often this version is used in cases where the approximation is not valid!

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Application of the models to non-isothermal data

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Methods to apply the models to non-isothermal data - 1

Method 0

$$h = dT/dt \qquad t = (T(t) - T(0))/h$$

$$Mn((T(t)) = m \cdot \frac{\exp\left(-k_{M1}(T(t)) \cdot (T(t) - T(0))/h\right)}{\frac{m}{Mn(T(0))} + \left(1 - \exp\left(-k_{M1}(T(t)) \cdot (T(t) - T(0))/h\right)\right)}$$

This is severely wrong !!

For all the data points at time t and temperature T, which is reached experimentally after time t during the heating, the procedure simulates a stepwise isothermal behaviour for each data point in going from time zero to time t(T), means to the time where temperature T was reached in the experiment.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Methods to apply the models to non-isothermal data - 2

Method 1 – incremental evolution using the isothermal equation

Stepwise calculation of the reaction conversion with time and temperature increments dt and dT. In the present step i+1 the achieved $Mn(t_i)/m$ from the just previous step i is the start value Mn(0)/m in the calculation of $Mn(t_{i+1})$.

Start with Ta and Mn(Ta)

$$dT = h \cdot dt \qquad T_{i+1} = T_i + dT$$

$$\frac{Mn(Ta+dT)}{m} = \frac{Mn(T_1)}{m} = \frac{\exp(+k(Ta)\cdot dt)}{\frac{m}{Mn(Ta)} - 1 + \exp(+k(Ta)\cdot dt)}$$

$$\frac{Mn(T_1+dT)}{m} = \frac{Mn(T_2)}{m} = \frac{\exp(+k(T_1)\cdot dt)}{\frac{m}{Mn(T_1)} - 1 + \exp(+k(T_1)\cdot dt)}$$

$$\frac{Mn(T_2+dT)}{m} = \frac{Mn(T_3)}{m} = \frac{\exp(+k(T_2)\cdot dt)}{\frac{m}{Mn(T_2)} - 1 + \exp(+k(T_2)\cdot dt)}$$

$$\frac{Mn(T_{i+1})}{m} = \frac{Mn(Te)}{m} = \frac{\exp(+k(T_i)\cdot dt)}{\frac{m}{Mn(T_i)} - 1 + \exp(+k(T_i)\cdot dt)}$$

This method works then correct, if a 'linear' relation between isothermal and non-isothermal solution exits, see below.

$$k(Ta+dT) = k(T_1) = Z * \exp\left(-\frac{Ea}{R\cdot(Ta+273.15+dT)}\right)$$

Increment dt is always constant,
dt determines dT via the relation dT = h·dt

Parameter determination with non-linear algorithms as of Levenberg-Marquardt type

loop until T_{i+1} = Te (the end temperature)

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Methods to apply the models to non-isothermal data - 3

Method 2 – use the integrated solution of the non-isothermal rate equation

This method works, when the non-isothermal solution exits in handsome manner.

Parameter determination with non-linear algorithms as of Levenberg-Marquardt type

Method 3 – use the non-isothermal rate equation

(1) numerical integration of the rate equation with preset parameters (Runge-Kutta type)
(2) transfer to the non-linear parameter fitting
(3) find the correction to the parameters
(4) back to numerical integration with the new parameters
(5) transfer to non-linear parameter fitting, correction of the parameters
(6) numerical integration….
(7) non-linear parameter fitting….

…until convergence is reached.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Model CS-ED: Application to non-isothermal data

$$h = dT/dt \qquad dt = dT/h \qquad t - t_0 = \frac{1}{h}\cdot(T - Ta) \qquad k_{M1} = Z_{M1}\cdot\exp(-Ea_{M1}/RT)$$

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -k_{M1}\cdot\left(\left(\frac{Mn(t)}{m}\right)^2 + \left(\frac{Mn(t)}{m}\right)\right)$$

Rate equation in isothermal case

$$\frac{d\left(\frac{Mn(T)}{m}\right)}{dT} = -\frac{k_{M1}(T)}{h}\cdot\left(\left(\frac{Mn(T)}{m}\right)^2 + \left(\frac{Mn(T)}{m}\right)\right)$$

Reformulation to non-isothermal case, the non-isothermal rate equation results

There is a 'linear' relation between the non-isothermal and isothermal solution, means the morphological structures of both equations are equal. The incremental method is applicable.

$$\frac{Mn(T)}{m} = \frac{\exp\left(-\frac{Z_{M1}}{h}\cdot\int_{Ta}^{T}\exp\left(-\frac{Ea_{M1}}{RT}\right)\cdot dT\right)}{1 + \frac{m}{Mn(Ta)} - \exp\left(-\frac{Z_{M1}}{h}\cdot\int_{Ta}^{T}\exp\left(-\frac{Ea_{M1}}{RT}\right)\cdot dT\right)}$$

$$\longleftrightarrow \quad \frac{Mn(t)}{m} = \frac{\exp(-k_{M1}\cdot t)}{1 + \frac{m}{Mn(0)} - \exp(-k_{M1}\cdot t)}$$

or

$$\frac{Mn(T)}{m} = \frac{\exp\left(-\frac{1}{h}\cdot\int_{Ta}^{T}k_{M1}(T)\cdot dT\right)}{1 + \frac{m}{Mn(Ta)} - \exp\left(-\frac{1}{h}\cdot\int_{Ta}^{T}k_{M1}(T)\cdot dT\right)}$$

The morphological structures of both non-isothermal and isothermal equations are equal.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Approximated model CS-ED: Application to non-isothermal data

$$h = dT/dt \qquad dt = dT/h \qquad t - t_0 = \frac{1}{h}\cdot(T - Ta) \qquad k_{M1} = Z_{M1}\cdot\exp(-Ea_{M1}/RT)$$

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -k_{M1}\cdot\left(\left(\frac{Mn(t)}{m}\right)^2\right)$$

Rate equation in isothermal case

$$\frac{d\left(\frac{Mn(T)}{m}\right)}{dT} = -\frac{k_{M1}(T)}{h}\cdot\left(\left(\frac{Mn(T)}{m}\right)^2\right)$$

Reformulation to non-isothermal case, the non-isothermal rate equation results

There is a 'linear' relation between the non-isothermal and isothermal solution, means the morphological structures of both equations are equal. The incremental method is applicable.

$$\frac{m}{Mn(T)} = \frac{m}{Mn(Ta)} + \frac{Z_{M1}}{h}\cdot\int_{Ta}^{T}\exp\left(-\frac{Ea_{M1}}{RT}\right)\cdot dT$$

$$\frac{m}{Mn(T)} = \frac{m}{Mn(Ta)} + \frac{1}{h}\cdot\int_{Ta}^{T}k_{M1}(T)\cdot dT$$

$$\longleftrightarrow \qquad \frac{m}{Mn(t,T)} = \frac{m}{Mn(0)} + k_{M1}(T)\cdot t$$

The morphological structures of both non-isothermal and isothermal equations are equal.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Model CS-ED: Application to non-isothermal data in the time domain

$$h = dT/dt \qquad dt = dT/h \qquad t - t_0 = \frac{1}{h}\cdot(T - Ta) \qquad k_{M1} = Z_{M1}\cdot\exp(-Ea_{M1}/RT)$$

$$T - Ta = (t - t_0)\cdot h \qquad T = Ta + t\cdot h$$

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -Z_{M1}\cdot\exp\left(-\frac{Ea_{M1}}{R\cdot(Ta+h\cdot t)}\right)\cdot\left(\frac{Mn(t)}{m}\right)^2 - Z_{M1}\cdot\exp\left(-\frac{Ea_{M1}}{R\cdot(Ta+h\cdot t)}\right)\cdot\left(\frac{Mn(t)}{m}\right)$$

Integrated solution is $\frac{Mn(t)}{m} = \frac{EX}{\left(1+\frac{m}{Mn(0)}\right) - EX}$

$$EX = \exp\left(-\frac{Z_{M1}}{h}\cdot\left(\begin{array}{l}(Ta+h\cdot t)\cdot\exp(-Ea_{M1}/R/(Ta+h\cdot t)) + \frac{Ea_{M1}}{R}\cdot ExpInt(-Ea_{M1}/R/(Ta+h\cdot t)) \\ -Ta\cdot\exp(-Ea_{M1}/R/Ta) - \frac{Ea_{M1}}{R}\cdot ExpInt(-Ea_{M1}/R/Ta)\end{array}\right)\right)$$

ExpInt = EI = Exponential Integral (Caution: EI is only semi-convergent)

$$\int_{xa}^{x}\exp\left(-\frac{Ea}{R\cdot x}\right)\cdot dx = x\cdot\exp\left(-\frac{Ea}{R\cdot x}\right) + \frac{Ea}{R}\cdot EI\left(-\frac{Ea}{R\cdot x}\right) - xa\cdot\exp\left(-\frac{Ea}{R\cdot xa}\right) - \frac{Ea}{R}\cdot EI\left(-\frac{Ea}{R\cdot xa}\right) \cong$$

$$x\cdot\exp\left(-\frac{Ea}{Rx}\right)\cdot\left(\frac{Rx}{Ea} - 2\left(\frac{Rx}{Ea}\right)^2 + 6\left(\frac{Rx}{Ea}\right)^3 - 24\left(\frac{Rx}{Ea}\right)^4 + 120\left(\frac{Rx}{Ea}\right)^5 - 720\left(\frac{Rx}{Ea}\right)^6 + 5040\left(\frac{Rx}{Ea}\right)^7 - +\right)$$

$$-xa\cdot\exp\left(-\frac{Ea}{Rxa}\right)\cdot\left(\frac{Rxa}{Ea} - 2\left(\frac{Rxa}{Ea}\right)^2 + 6\left(\frac{Rxa}{Ea}\right)^3 - 24\left(\frac{Rxa}{Ea}\right)^4 + 120\left(\frac{Rxa}{Ea}\right)^5 - 720\left(\frac{Rxa}{Ea}\right)^6 + 5040\left(\frac{Rxa}{Ea}\right)^7 - +\right)$$

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -k_{M1}(t)\cdot\left(\frac{Mn(t)}{m}\right)^2 - k_{M1}(t)\cdot\left(\frac{Mn(t)}{m}\right)$$

$$\frac{Mn(t)}{m} = \frac{\exp\left(-\int_{ta=0}^{t} k_{M1}(t)\cdot dt\right)}{\frac{m}{Mn(0)} + 1 - \exp\left(-\int_{ta=0}^{t} k_{M1}(t)\cdot dt\right)}$$

$$\frac{Mn(t)}{m} = \frac{\exp\left(-Z_{M1}\cdot\int_0^t \exp\left(-\frac{Ea_{M1}}{R\cdot(Ta+h\cdot t)}\right)\cdot dt\right)}{1 + \frac{m}{Mn(0)} - \exp\left(-Z_{M1}\cdot\int_0^t \exp\left(-\frac{Ea_{M1}}{R\cdot(Ta+h\cdot t)}\right)\cdot dt\right)}$$

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Approximated model CS-ED: Application to non-isothermal data in time domain

$$h = dT / dt \qquad dt = dT / h \qquad t - t_0 = \frac{1}{h} \cdot (T - Ta) \qquad k_{M1} = Z_{M1} \cdot \exp(-Ea_{M1} / RT)$$

$$\frac{d\left(\frac{Mn(t)}{m}\right)}{dt} = -k_{M1}(t) \cdot \left(\left(\frac{Mn(t)}{m}\right)^2\right)$$

Rate equation in non-isothermal case in time domain

$$\frac{m}{Mn(t)} = \frac{m}{Mn(0)} + Z_{M1} \cdot \int_{ta=0}^{t} \exp\left(-\frac{Ea_{M1}}{R \cdot (Ta + h \cdot t)}\right) \cdot dt \qquad T - Ta = (t - t_0) \cdot h$$

$$\frac{m}{Mn(t)} = \frac{m}{Mn(0)} + \int_{ta=0}^{t} k_{M1}(t) \cdot dt \quad \longleftrightarrow \quad \frac{m}{Mn(t,T)} = \frac{m}{Mn(0)} + k_{M1}(T) \cdot t$$

The morphological structures of both non-isothermal and isothermal equations are equal.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Model CS-ED with chain recombination

$$\frac{d\left(\frac{Mn(T)}{m}\right)}{dT} = -\frac{1}{h}\left(k_{M1}(T) + k_{M2}(T)\exp(+k_{M1}(T)\cdot\frac{1}{h}\cdot(T-Ta))\cdot\frac{m}{Mn(0)}\right)\cdot\left(\frac{Mn(T)}{m}\right)^2 - \frac{1}{h}(k_{M1}(T) - k_{M2}(T))\cdot\left(\frac{Mn(T)}{m}\right)$$

$$\frac{Mn(T)}{m} = \frac{EXI(T)}{\frac{m}{Mn(Ta)} + \int_{Ta}^{T} EXI(T'')k_{M1}(T'')\cdot dT'' + \frac{m}{Mn(Ta)}\int_{Ta}^{T} EXI(T'')k_{M2}(T'')\cdot\exp((T''-Ta)\cdot k_{M1}(T''))\cdot dT''}$$

$$EXI(T) = \exp\left(-\frac{Z_{M1}}{h}\cdot\int_{Ta}^{T}\exp\left(-\frac{Ea_{M1}}{RT'}\right)\cdot dT' + \frac{Z_{M2}}{h}\cdot\int_{Ta}^{T}\exp\left(-\frac{Ea_{M2}}{RT'}\right)\cdot dT'\right)$$

The nominator has still 'linear' relation to isothermal case.

$$EXI(T'') = \exp\left(-\frac{Z_{M1}}{h}\cdot\int_{Ta}^{T''}\exp\left(-\frac{Ea_{M1}}{RT'}\right)\cdot dT' + \frac{Z_{M2}}{h}\cdot\int_{Ta}^{T''}\exp\left(-\frac{Ea_{M2}}{RT'}\right)\cdot dT'\right)$$

No 'linear' relation, nested integrations in the denominator are necessary

---

No 'linear' relation between the non-isothermal and isothermal solution.
The incremental method fails!

$$\frac{Mn(t)}{m} = \frac{\exp(-(k_{M1}-k_{M2})\cdot t)}{\frac{m}{Mn(0)} + \frac{k_{M1}}{k_{M1}-k_{M2}}\cdot(1-\exp(-(k_{M1}-k_{M2})\cdot t)) + \frac{m}{Mn(0)}\cdot(\exp(+k_{M2}\cdot t)-1)}$$

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Example – isothermal case

© Fraunhofer ICT, Pfinztal, Germany

Abbreviations used to identify the models

CS-ED with CR chain splitting by chain element decomposition and chain recombination
also CS by ED and CR

CS-BS with CR chain splitting by bond scission betw. chain elements and chain recombination
also CS by BS and CR

CS-ED chain splitting by chain element decomposition
also CS by ED

CS-BS chain splitting by bond scission between chain elements
also CS by BS

Fraunhofer ICT

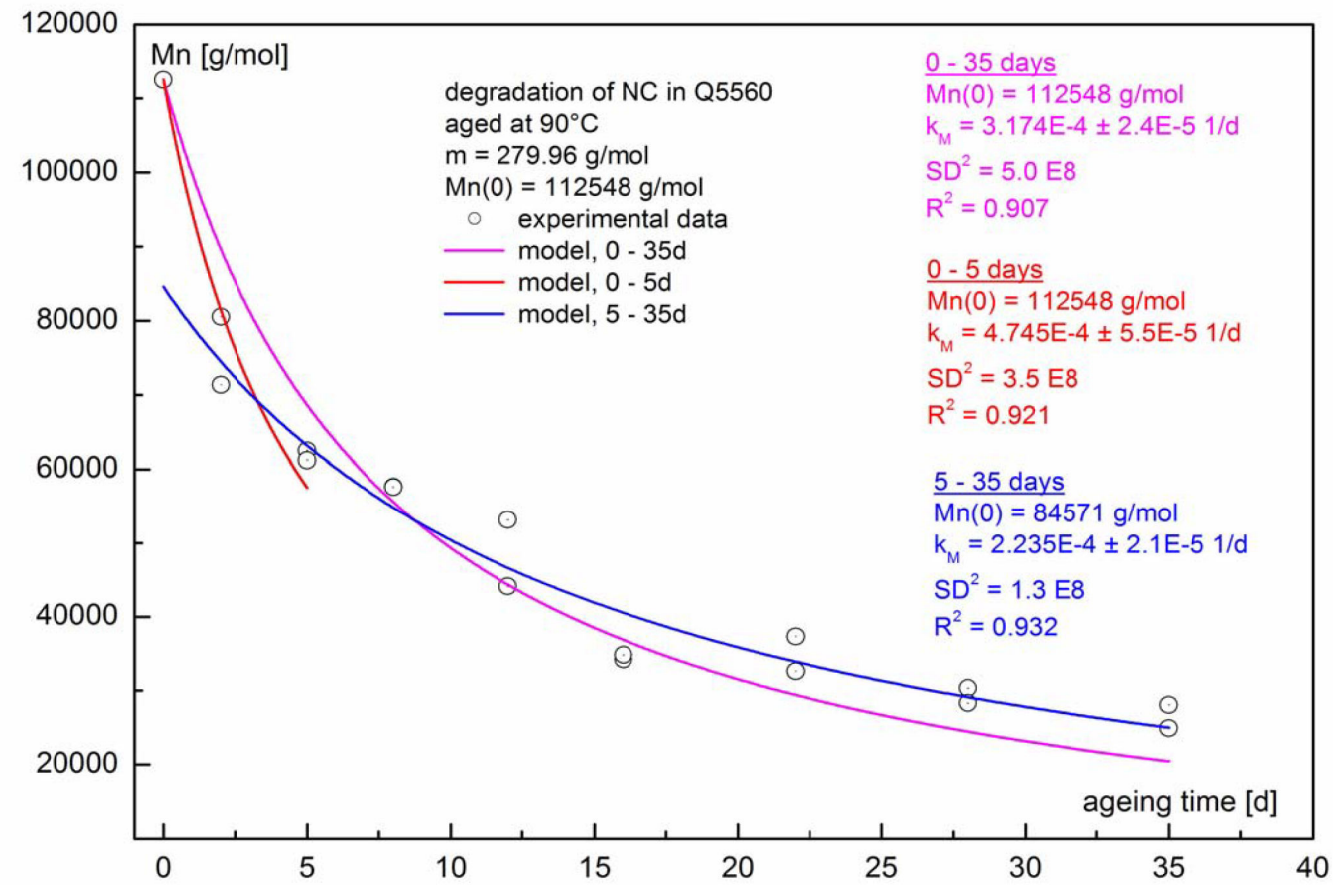
© Fraunhofer ICT, Pfinztal, Germany

Description of molar mass decrease of NC in a gun propellant - Model CS by ED

The description with model CS-ED is not satisfying.

The description must be done in two steps, to get adequate modelling.

An artificial splitting of the experimental data is necessary to achieve a formally good description. But this splitting has aspects of arbitrariness therefore.



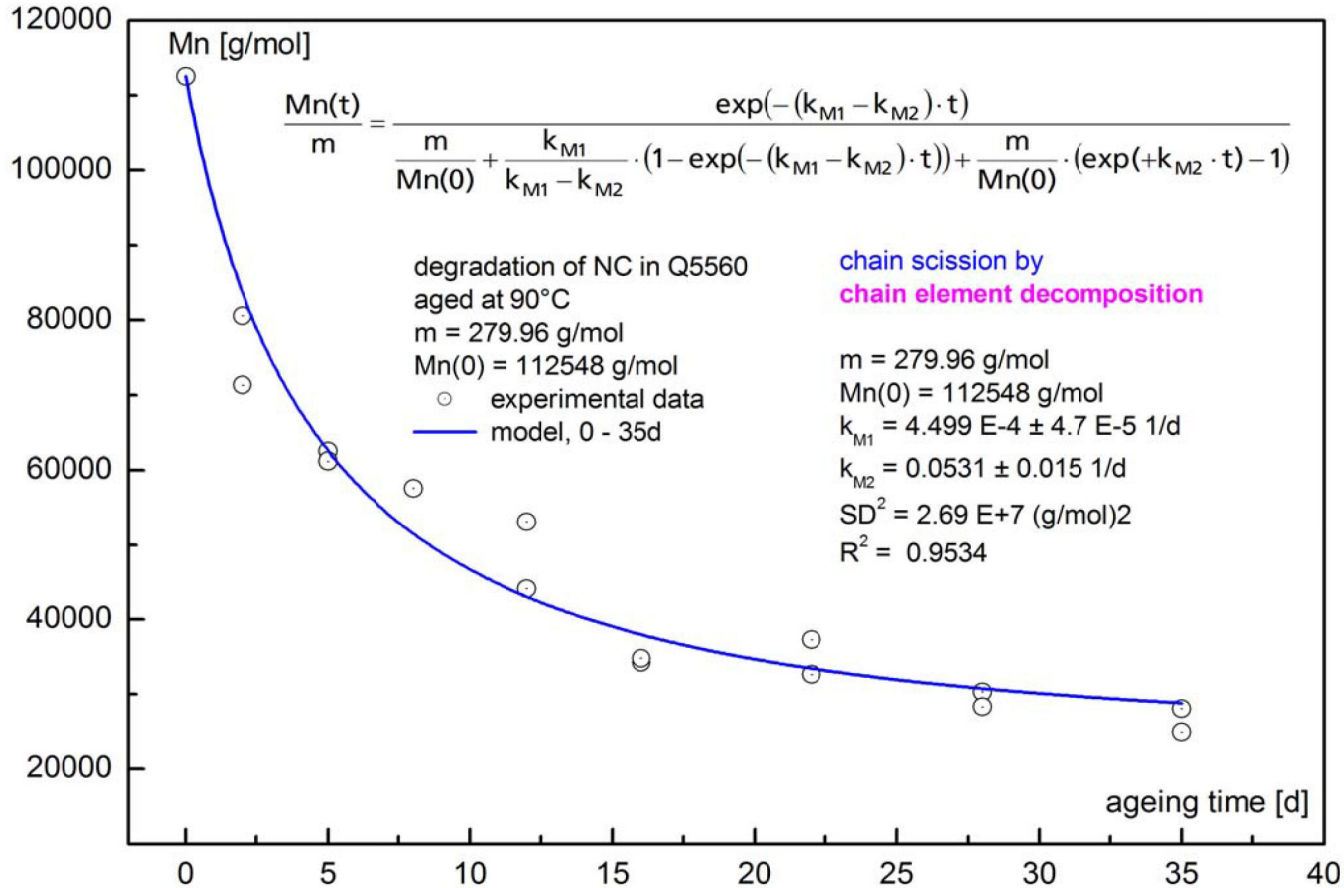
Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Description molar mass decrease with model CS by ED and CR

The description with model CS-ED with CR is now satisfying.

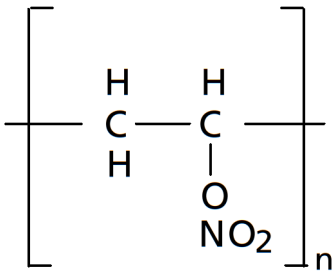
No data splitting necessary, all data are described at once



Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

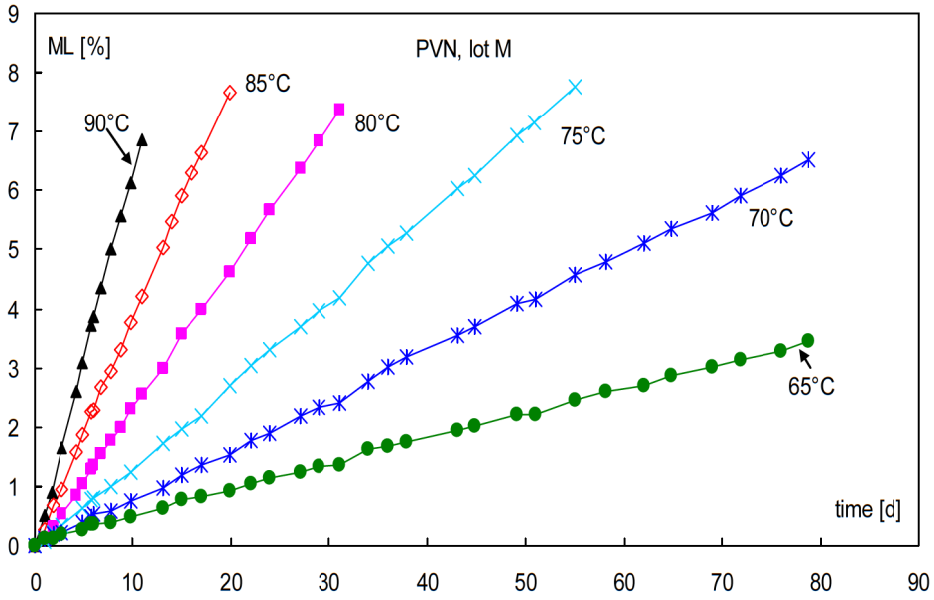
Polyvinylnitrate (PVN) – a speciality polymer

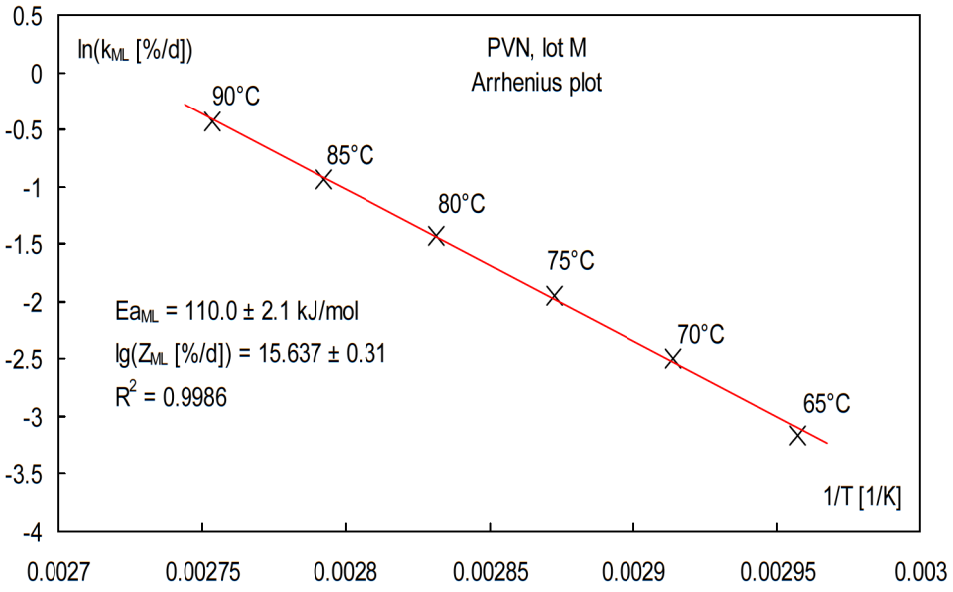


PVN is used as thickener for MNT (mononitro toluene), which is used as flowing aid in casting TNT containing high explosives.

PVN shows mass loss during ageing and during decomposition.
The lot PVN-M was manufactured at Fraunhofer ICT.

M.A. Bohn, J. Aniol, M. Dörich, K. Hartlieb, H. Pontius
Stability, Ageing and Usetime Prediction of Polyvinylnitrate (PVN).
Paper 73, pages 73-1 to 73-18, in Proceedings of the 37th International Annual Conference of ICT, June 27 to 30, 2006, Karlsruhe, Germany. Fraunhofer-Institut für Chemische Technologie (Fraunhofer ICT), D76318 Pfinztal, Germany.

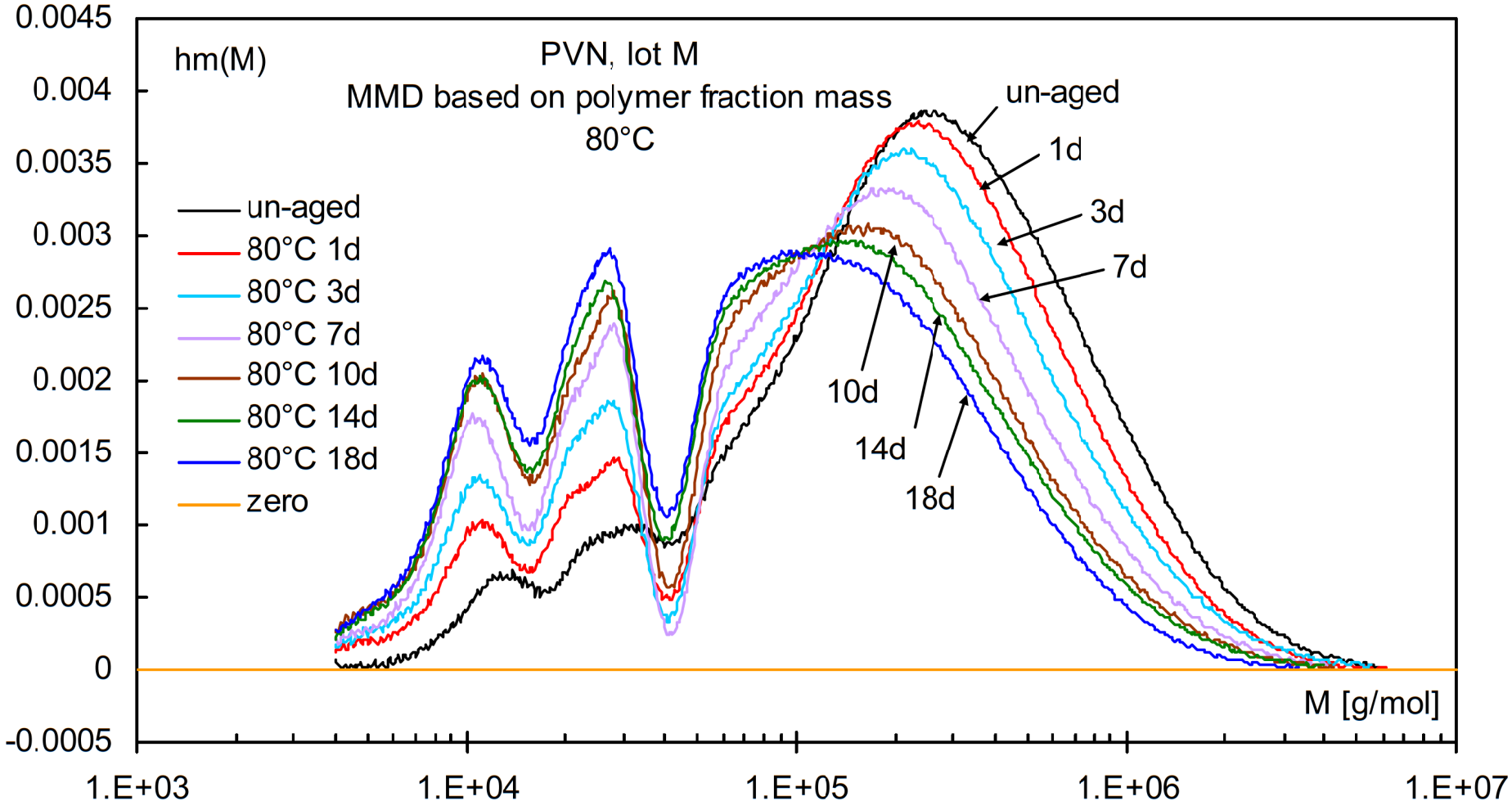




Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

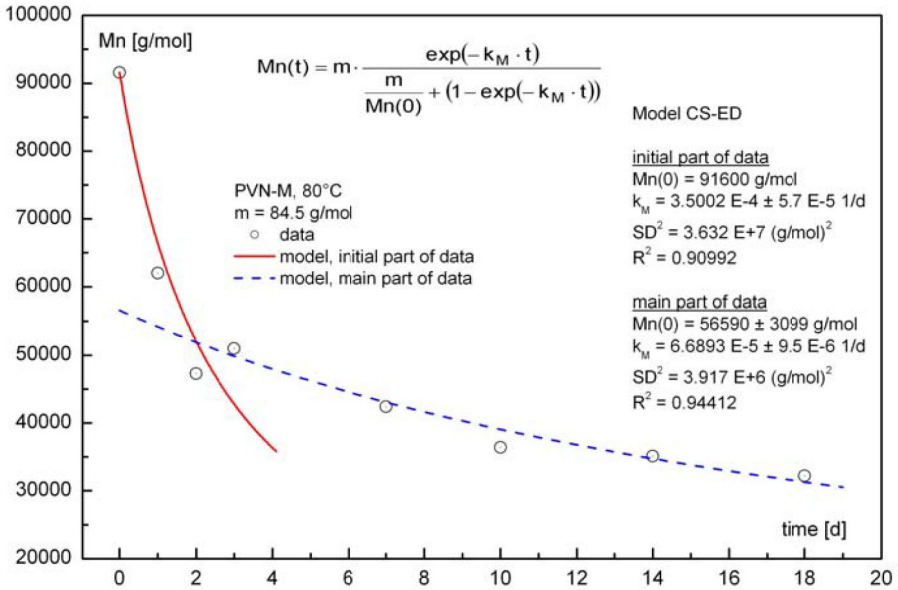
Molar mass distribution functions of ageing series at 80°C of PVN, lot M

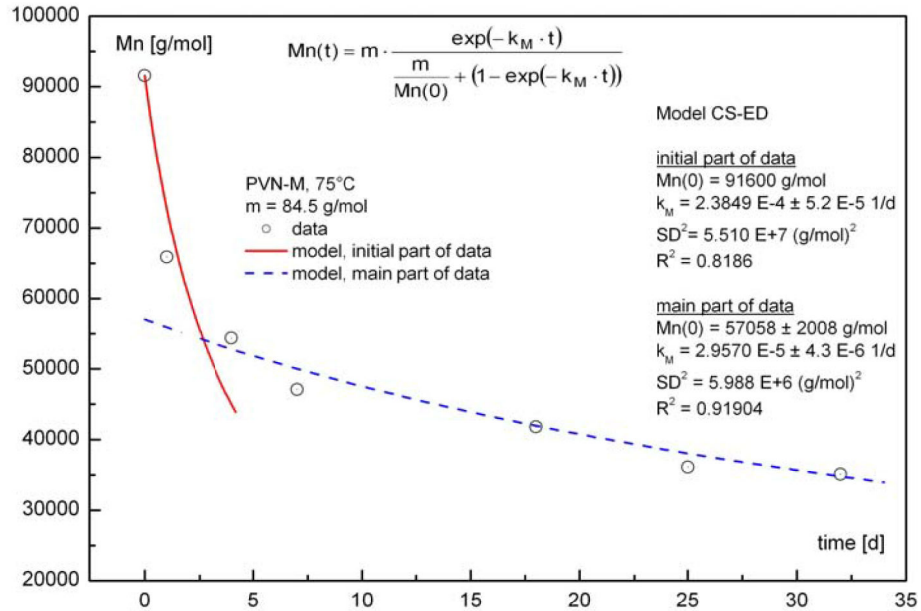


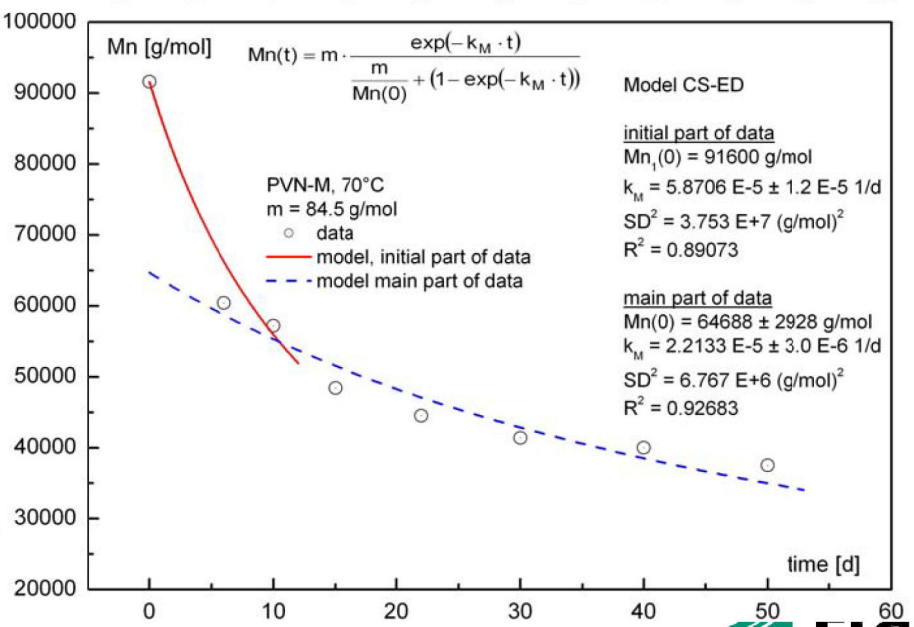
Fraunhofer ICT

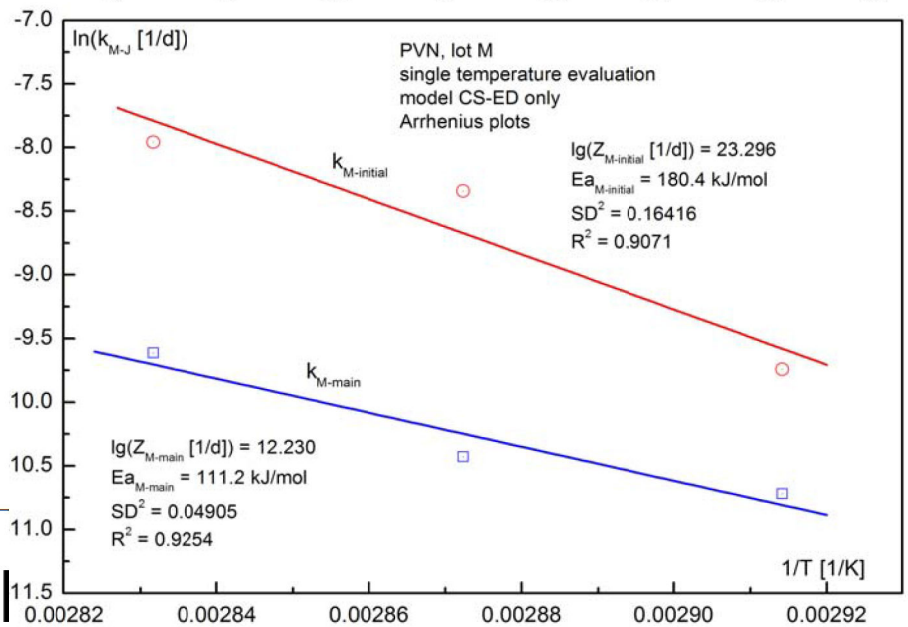
© Fraunhofer ICT, Pfinztal, Germany

Molar mass decrease of PVN, lot M – model CS-ED (without CR)



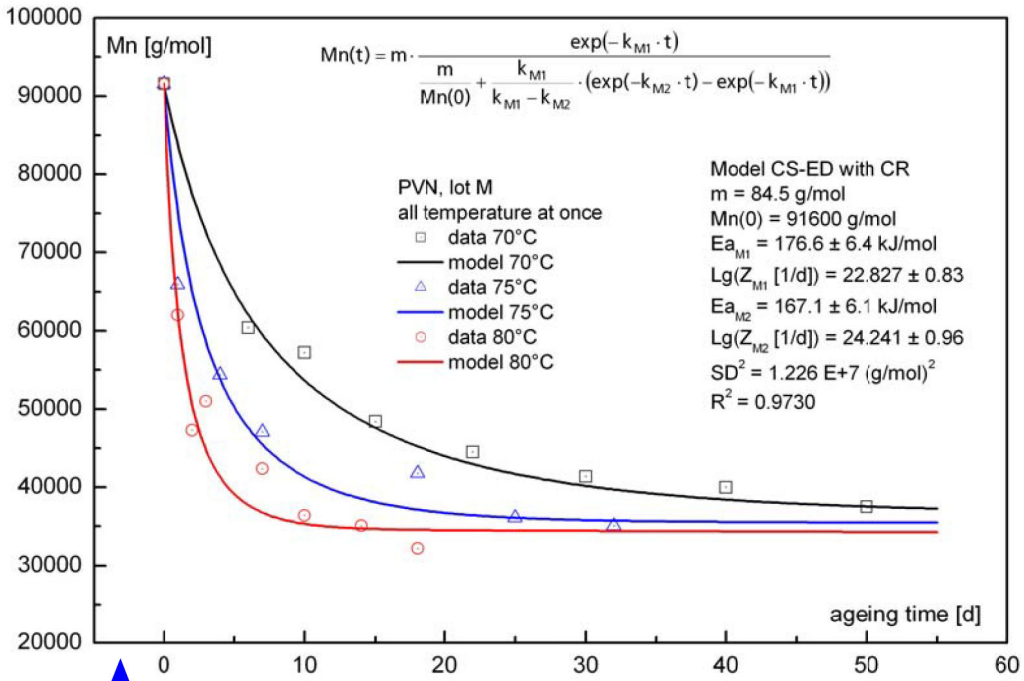


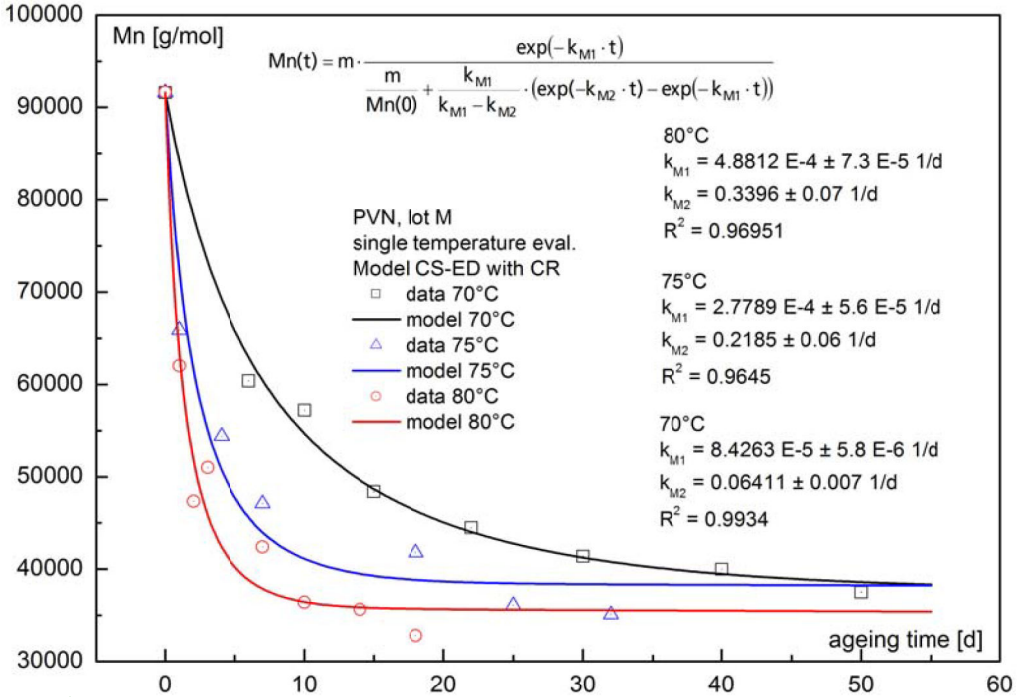




© Fraunhofer ICT, Pfinztal, Germany

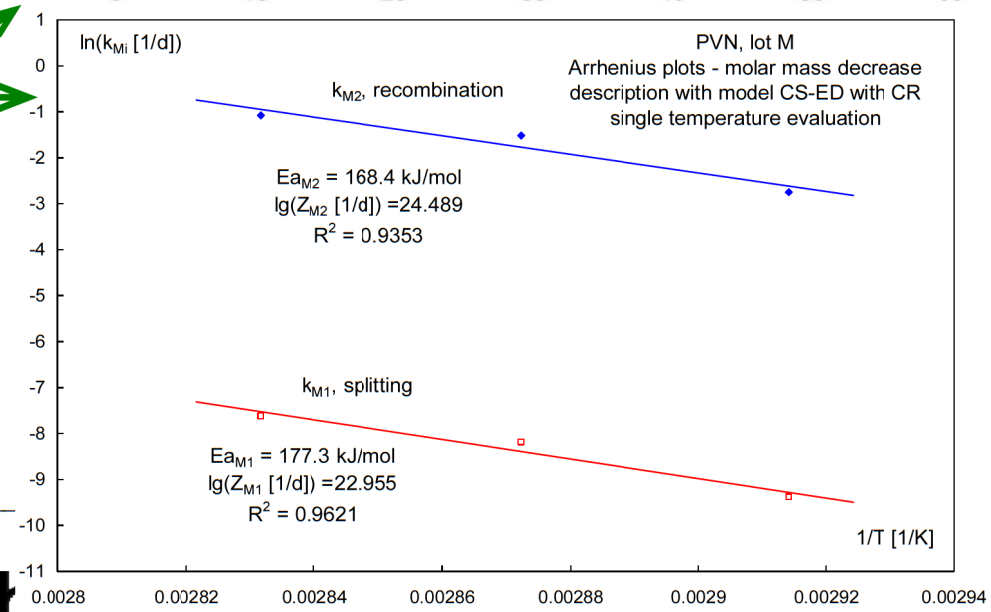
Comparison of type of evaluation





The equation has been **fitted at once to all data (all temperatures) using the Arrhenius parameters** of the two rate constant as fitting parameters

The equation has been **fitted to each temperature data** and the rate constants have been determined via Arrhenius plots

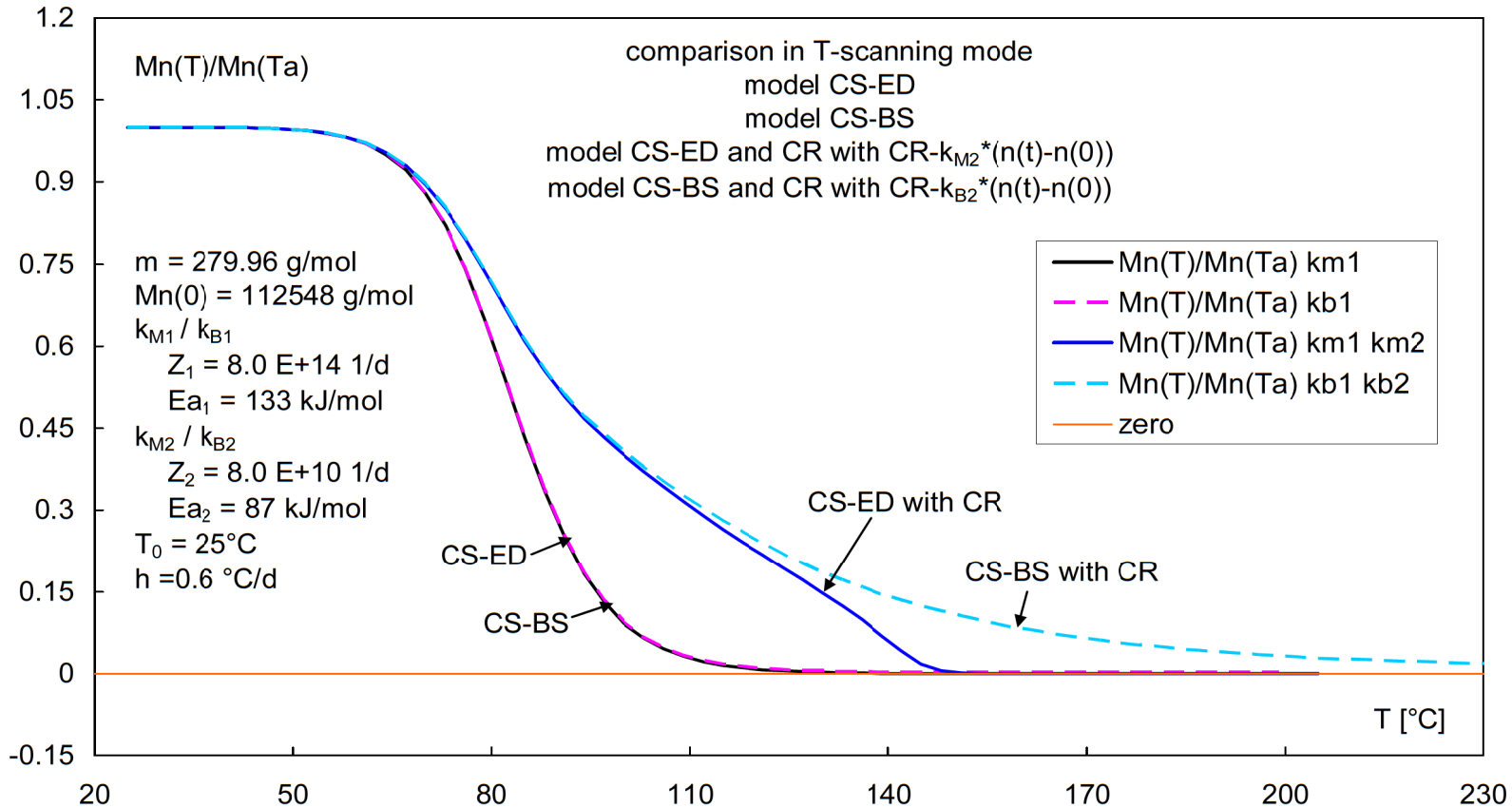


© Fraunhofer ICT, Pfinztal, Germany

Non-isothermal example

© Fraunhofer ICT, Pfinztal, Germany

Principal courses of the Mn decrease in non-isothermal case



Model CS-BS and CR shows always a monotonic tailing towards the very final value Mn = m.

Model CS-ED and CR reaches Mn equal to zero in the very final end.

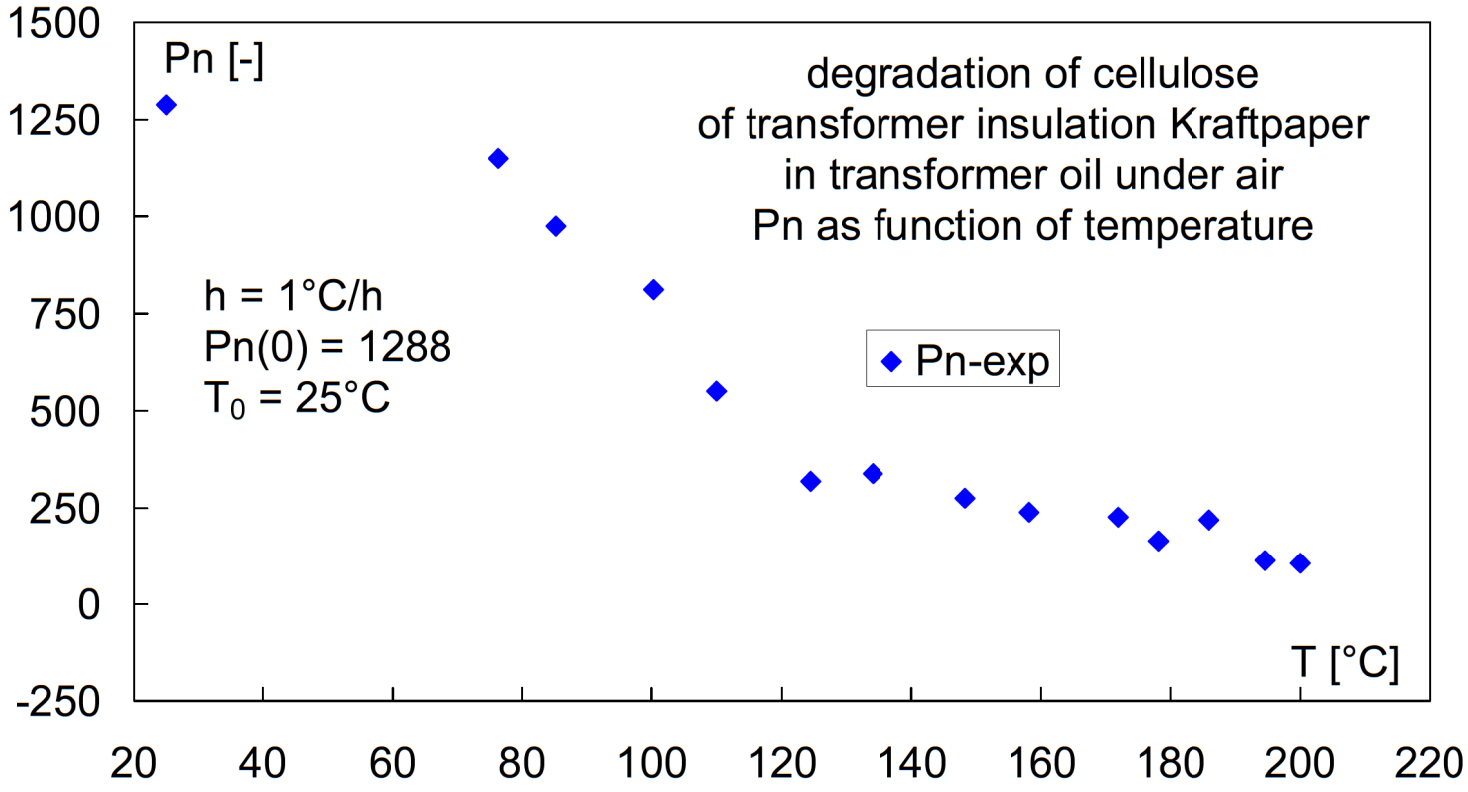
The two models are therefore distinguishable in non-isothermal experiments.

Note: the two models without CR are very similar in data description, they are not able to describe the retarded decrease of Mn.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Non-isothermal data of cellulose degradation in transformer oil under air

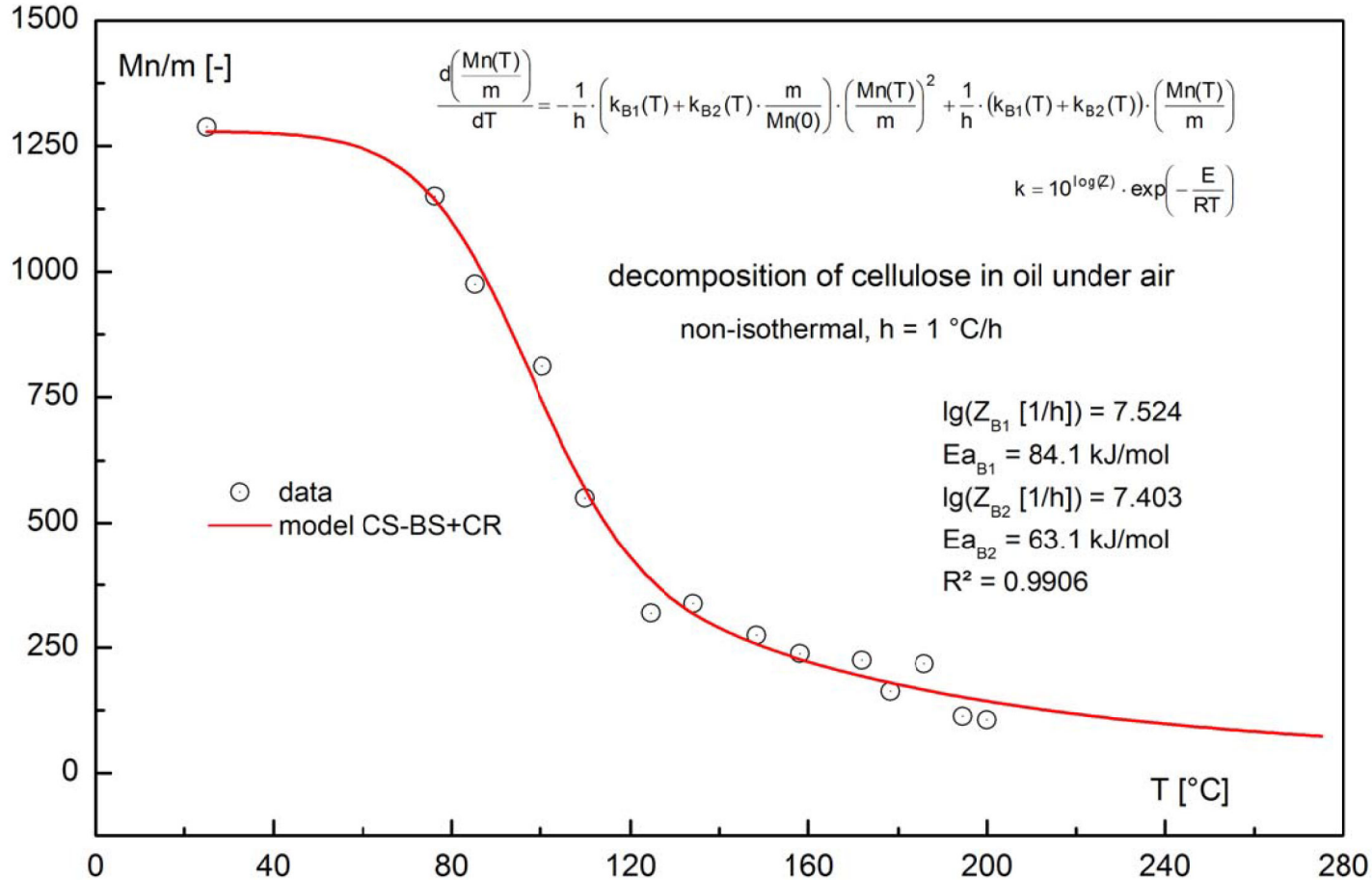


Non-isothermal data of the cellulose degradation in so-named Kraft-paper used in electrical transformers as insulation. Degradation performed in laboratory in hot transformer oil, under air atmosphere. Data obtained from S.W. Bigger University of Victoria, Melbourne, Australia.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Description with model CS by BS and CR

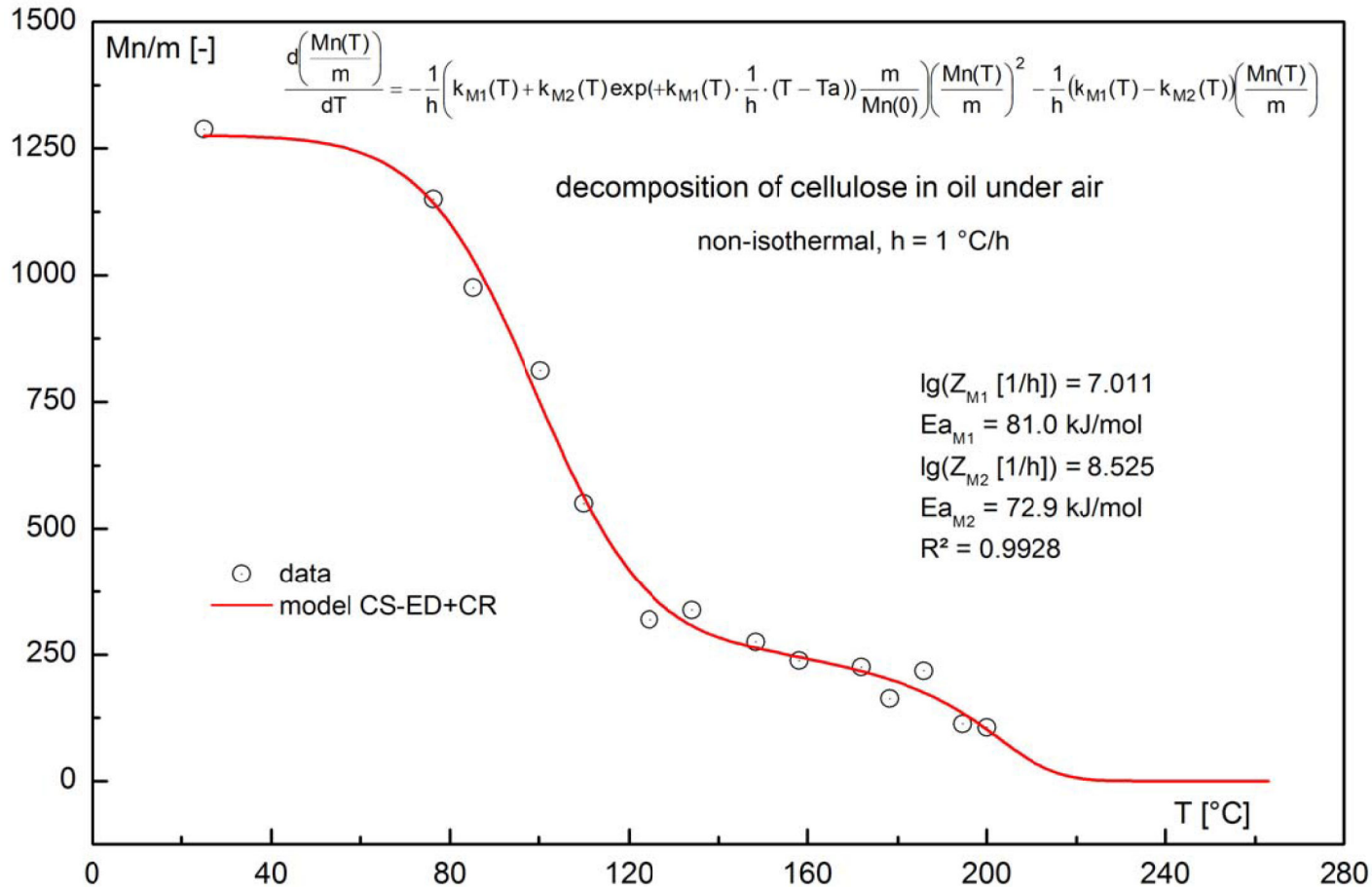


Non-isothermal data on cellulose degradation described with model CS-BS with CR (chain scission by bond splitting between chain elements with chain recombination). The typical monotonic tailing of this model can be seen. Coupled procedure of numerical integration of the rate equation and non-linear parameter fitting

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Description with model CS by ED and CR

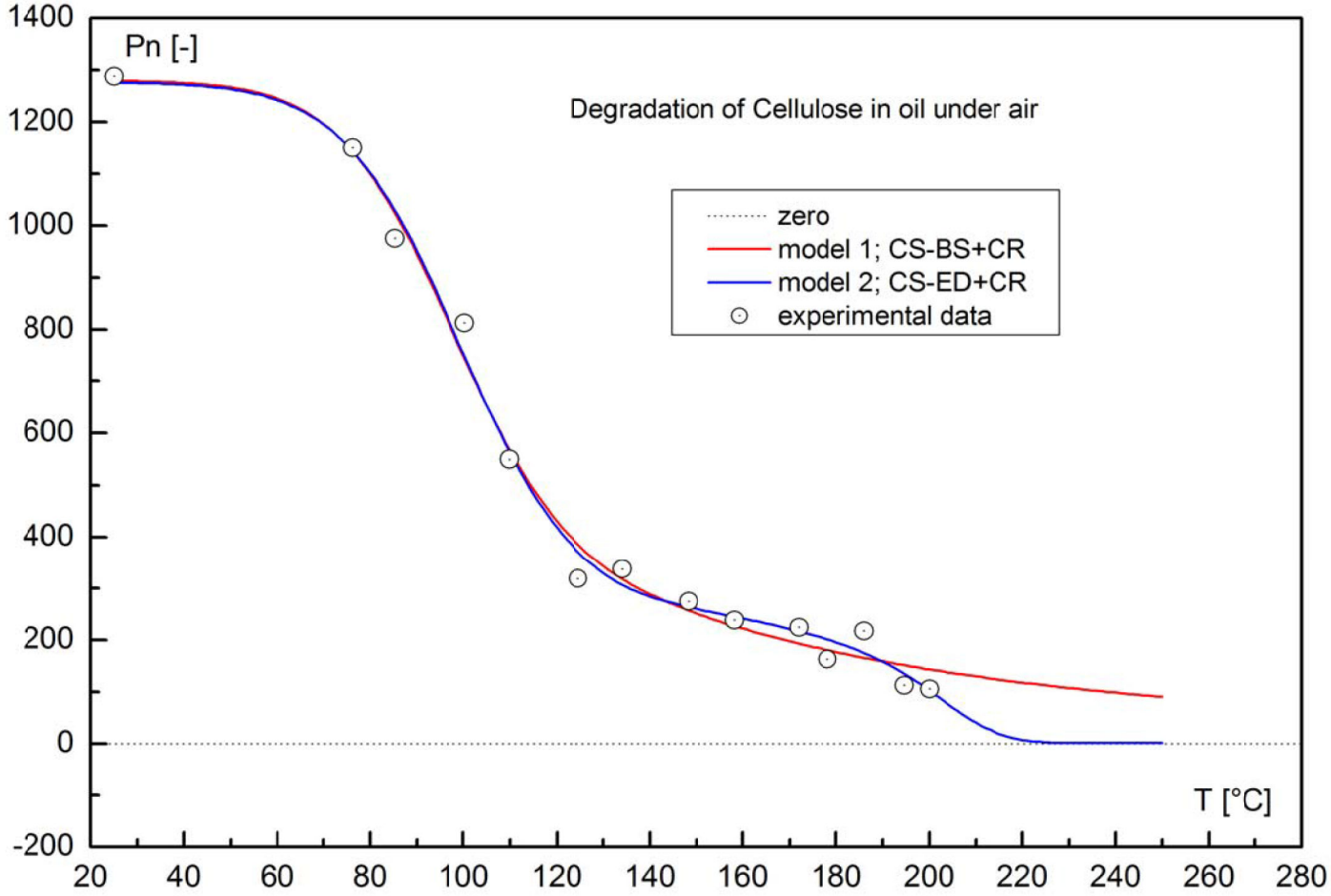


Non-isothermal data on cellulose degradation described with model CS-ED with CR (chain scission by chain element decomposition with chain recombination). Cellulose decomposes with mass loss and therefore with chain element decomposition. Coupled procedure of numerical integration and non-linear parameter fitting.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Comparison of descriptions with CS by ED + CR and CS by BS + CR



Comparison of the two non-isothermal descriptions with the models CS-BS with CR and CS-ED with CR. It seems the model with chain element decomposition describes the data better.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Conclusions – molar mass degradation

Models based on random chain scission seem appropriate for NC, cellulose, PVN.

Two principle possibilities of chain scission
(1) splitting by bond scission between chain elements (CS-BS)
(2) splitting by chain element decomposition (CS-ED),

The models using chain element decomposition are the right ones for NC, cellulose, PVN.

Avoid to use the simplified form of the equation CS-ED or CS-BS, often referred as Ekenstam equation.

$$\frac{m}{Mn(t,T)} = \frac{m}{Mn(0)} + k(T) \cdot t$$

But this is not the true Ekenstam equation!
It is the approximated Ekenstam equation, but this form was never used by Ekenstam.

It seems that molar mass of NC decreases slower than assumed by the model with mere chain scissioning. – Models considering chain recombination besides chain scissioning give a much better description in such cases.

To use the models with non-isothermal data, the best is to use them in the form of their differential rate equations and determining the reaction rate constants by numerical integration and non-linear fitting of the rate equation to the (integral) data.

The degradation of cellulose itself can be described with the presented models.

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany

Thank you for your Attention

Fraunhofer ICT

© Fraunhofer ICT, Pfinztal, Germany