

NC-based energetic materials - stability, decomposition, and ageing

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Nitrocellulose - Supply, Ageing and Characterization

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Content

Abstract

Stability 'versus' ageing

Stability tests for NC and NC-based materials

Bergmann-Junk, Abel, Vacuum Stability, Mass Loss, Dutch Mass Loss Test

Aspects of NC decomposition

Thermolysis, hydrolysis, chain splitting, bond dissociation enthalpies

Accelerated ageing - objectives

Measurements on NC alone – Comparison of results of four stability tests

Modelling - benefits

Modelling of primary (added at production) stabilizer consumption

models 'S: exponential + linear', 'S: nth order', 'S: extended'

Applications

Prediction of a real ageing over 16 years of a singlebase propellant used in automotive seat belt restraint systems

Combined modelling of stabilizer consumption and the course of consecutive products

Forming reactivities of consecutive products of DPA

Modelling of molar mass decrease of NC

model 1: chain splitting by decomposition of chain element (= monomer unit)

model 2: chain splitting by bond breaking, number of chain elements is constant

Application, examples and meaning

molar mass decrease and shift of ductile-brittle transition temperature

molar mass decrease and decrease of mechanical strength

Ageing of New Type gun propellants

Literature



Abstract

Nitrocellulose (NC) has itself re-established as an essential ingredient in recent gun propellant formulations containing RDX and newer type of plasticizers. All the efforts to replace NC by other polymeric binders have been successful in a rather small part only. Surely NC decomposition is present also in the modern formulations and the ageing of such propellants has to be considered carefully. To master the ageing of NC based energetic materials knowledge of the basic decomposition behaviour of NC is necessary. Data of bond dissociation energies and activation energies of NC decomposition will be compiled and discussed. Experimental results and quantum mechanically obtained data are used for this. The way or the severity of NC decomposition will be discussed and formulated in a scheme. Kinetic models to describe NC decomposition are presented for mass loss and molar mass degradation.

Stabilization is a main issue with NC-based materials. Stabilizer reactions and their modelling are presented. With examples of ageing of gun propellants and rocket propellants including new type of gun propellants containing RDX, the way of prediction of the use time (life time) is shown. Several experimental methods as mass loss, stabilizer consumption, molar mass degradation, heat generation can be used and their suitability and the special demands for prediction purposes are demonstrated.



Stability 'versus' Ageing

Stability tests use reduced time-temperature loads compared to ageing investigations, typically only one temperature and one time period.

Stability tests determine the momentary state of the material.

In contrast the determination of ageing behaviour gives a prediction possibility based on information obtained from an extended time-temperature behaviour of the material.

For both aspects molecular decomposition is the base, especially with chemical stability.

With ageing also physical phenomena are included as migration of surface treatment agents (burning phlegmatizer for gun propellant grains)

Stability tests

The NC-decomposition causes

- formation of permanent gases
- formation of NO_x
- generation of reaction heat
- polymer chain degradation

The older tests are based mainly on the generation of NO_x caused by a time – temperature load

Using the effects of NO₂ – namely oxidizing and forming of HNO₃ , many tests have been developed and most of these are connected with famous names:

Abel, Bergmann-Junk, Hanson-Metz, Vieille, Methyl-Violet-Test

time to visible NO_x (the well-known 65.5°C (=150 °F) surveillance test, introduced by the US Navy, about 1905)

Self ignition temperature, Silvered Vessel-Test (Dewar-Test)

Then somewhat later mass loss and gas generation (vacuum stability test) were used

Newer methods use the same basic effects but the detection is much improved

- NO_x-Chemiluminescence
- GPC (SEC)
- microcalorimeter (heat generation rate), ARC (adiabatic self heating)
- gas analysis by FTIR-EGA, GC, GC-MS

Bergmann-Junk-Test (Bergmann-Junk-Siebert-Test)

Developed from E. Bergmann and A. Junk in Germany, improved by Siebert

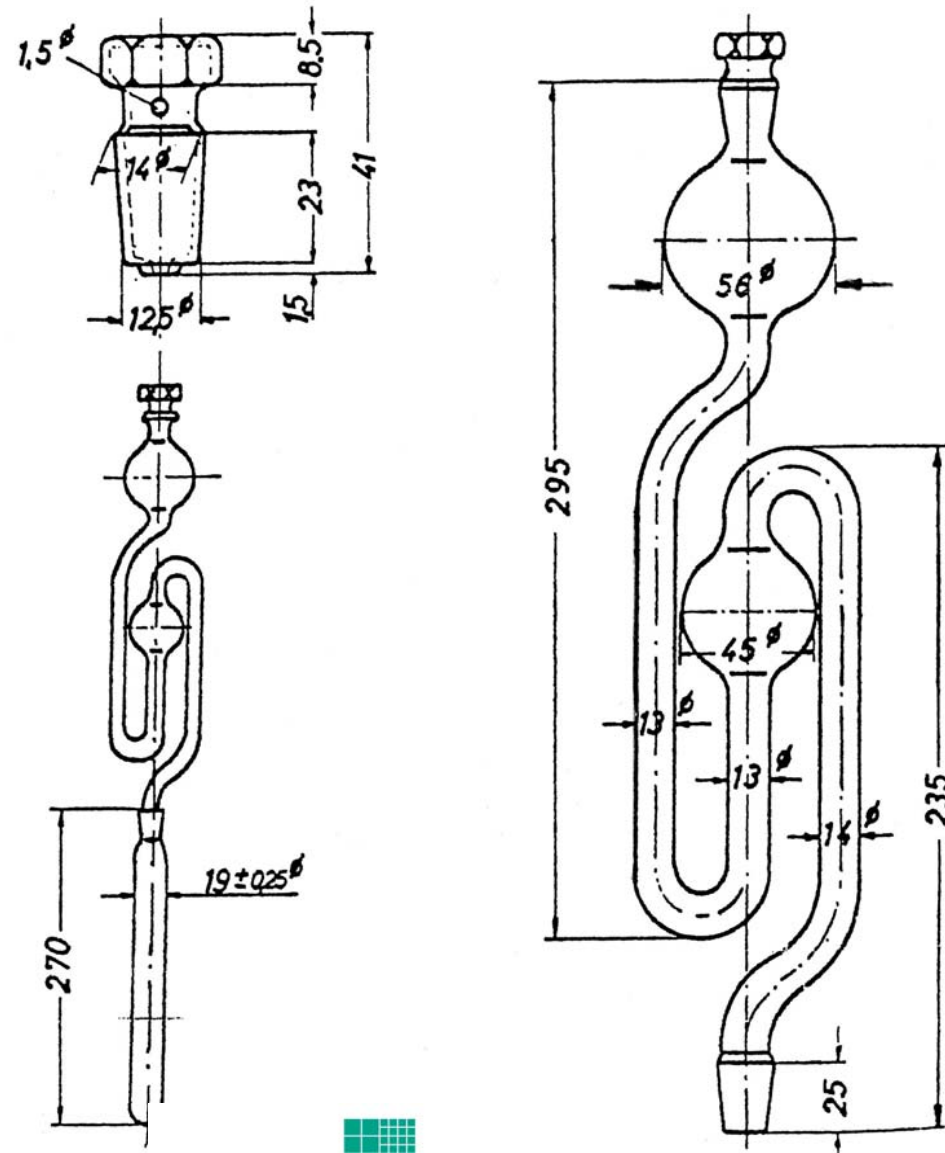
substance	Substance amount [g]	Test temp. [°C]	Test time [h]	Criterion: consumption of 0.01n NaOH to neutralize HNO ₃ formed by absorbed and oxidized NO ₂
Nitrocellulose	2	132	2	≤ 12.5 ml/g
Sb gun propellant (propellant not containing blasting oils)	5	132	5	≤ 10 to 12 ml/g *)
Db gun propellant with blasting oil content up to 10 mass-%	5	115	16	≤ 10 to 12 ml/g *)
Db gun propellant with blasting oil content greater than 10 mass-%	5	115	8	≤ 10 to 12 ml/g *)
Db rocket propellant	5	115	16	≤ 10 to 12 ml/g *)

*) limit value is often fixed for the individual propellant in the range 10 to 12ml per g of propellant

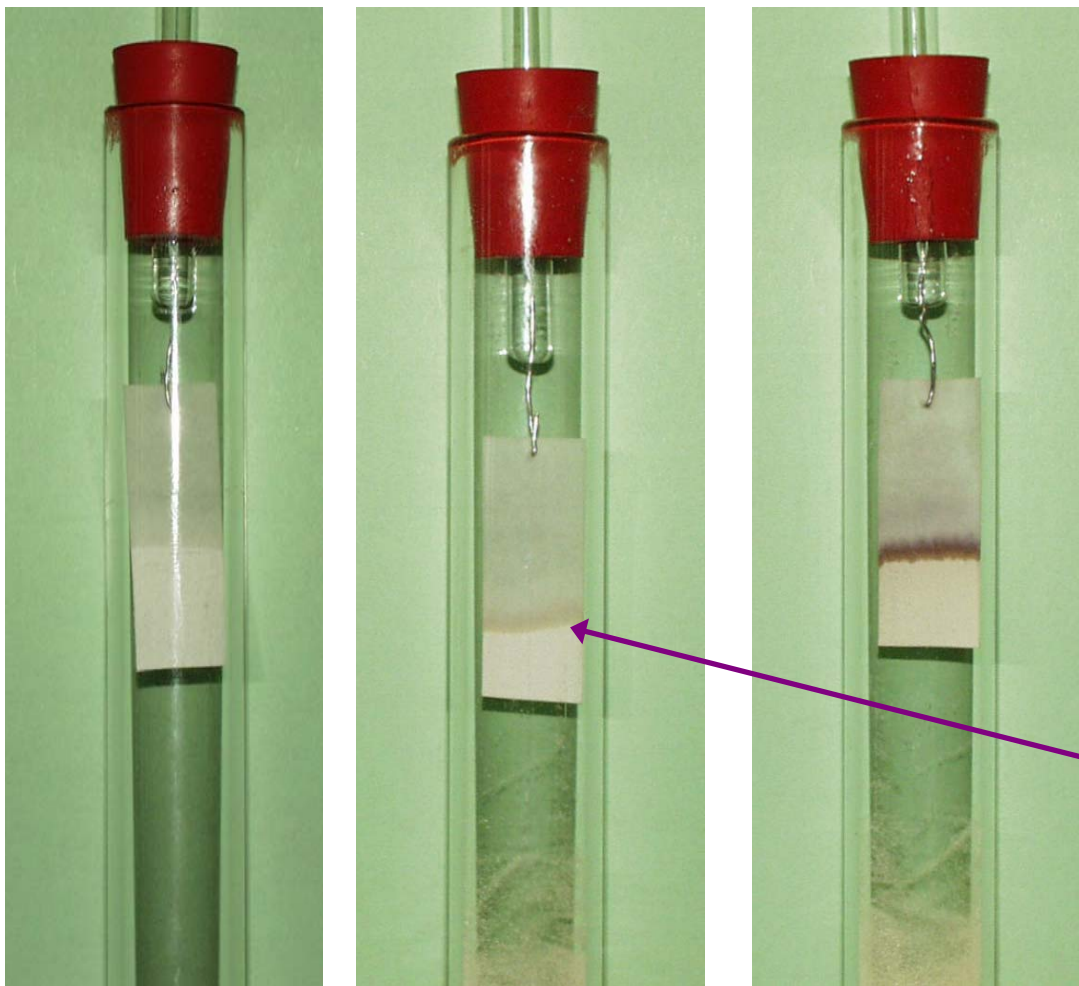
This test is not used with triple base propellants

Bergmann-Junk-Test (Bergmann-Junk-Siebert-Test)

Dimensions in mm



Abel-Test - German conditions and typical results



Substance	test temp. [°C]	Sample amount [g]	test limit [min]
Nitroglycerine, BTTN, TMETN, DEGN	80	2	≥ 15
Nitrocellulose	80	1.3	≥ 10
TNT	80	1	≥ 30

KJ starch paper, wetted by water - glycerine (1:1) to half length. At the interface colour change occurs caused by NO_2 in oxidizing iodide to iodine and this forms a coloured product with starch.

Time taken at this point of colour change

Vacuum stability test – German test conditions and criteria

substance	Substance amount [g]	Test temp. [°C]	Test time [h]	Criterion for 'stable' ml/g at STP
Sb gun propellant (propellant not containing blasting oils)	2.5	100	40	≤ 1.2 to 2
High explosives as PETN, HMX, RDX, explosive charges, HTPB-composite propellants	2.5	100	40	≤ 1.2 to 2
Db gun propellant with blasting oil	2.5	90	40	≤ 1.2 to 2
Db rocket propellant	2.5	90	40	≤ 1.2 to 2
	Recent tendency to unify conditions			
for NC-based propellants	2.5	100	40	≤ 2
Non-NC high explosives	2.5	100	40	≤ 1.2

2 ml/g or 5ml/2.5g is the upper allowed limit. Between 1.2 and 2 ml/g the stability is considered as borderline. Preferred are values ≤ 1.2 ml/g or ≤ 3 ml/2.5g

STP: standard temperature (=0°C) and standard pressure (=1 atm)

Mass Loss Tests

Mass loss (ML) at 90°C for GP and RP

In most cases one ages 2g (up to 5g) of propellant in tubes with loosely inserted ground stoppers over 18 days

Sample can be used as delivered (if not too wet !, water content not higher than 1.5 mass-%)

Criterion: $ML \leq 3 \%$ and no red-brown fumes (NO_x) up to 18 days
initial mass loss can be subtracted, ML after one day as baseline

Applicable [for all types](#) of propellants (single, double, triple, semi-nitramine, new type,...)

Other test times - test temperatures (always with 3 % limit)		
	For 50 years at 25°C	For 15 years at 25°C
100°C	6 days	1.8 days
90°C	18 days	5.4 days
80°C	54 days	16.2 days
75°C	93.5 days	28.0 days
70°C	162 days	48.6 days

Necessary equipment

- well temperature controlled oven
- glass tubes with ground stoppers
- analytical balance, well positioned

Dutch Mass Loss Test

Mass loss after 72 h, reduced by the mass loss after the first 8 h in open tube

4g of sample in tubes closed with ground stoppers

at 105°C: double and triple base GP and RP

at 110°C: single base GP

Criterion: $ML (72h-8h) \leq 2\%$, all GP and RP

In principle also usable with high explosives as RDX, HMX, PETN

Also used for semi-nitramine and new-type propellants

Pure substances can be tested at 110°C

For other formulations the test temperature depends on ingredients;

with energetic plasticizers 105°C is suitable

Other conditions and test criterion remain the same

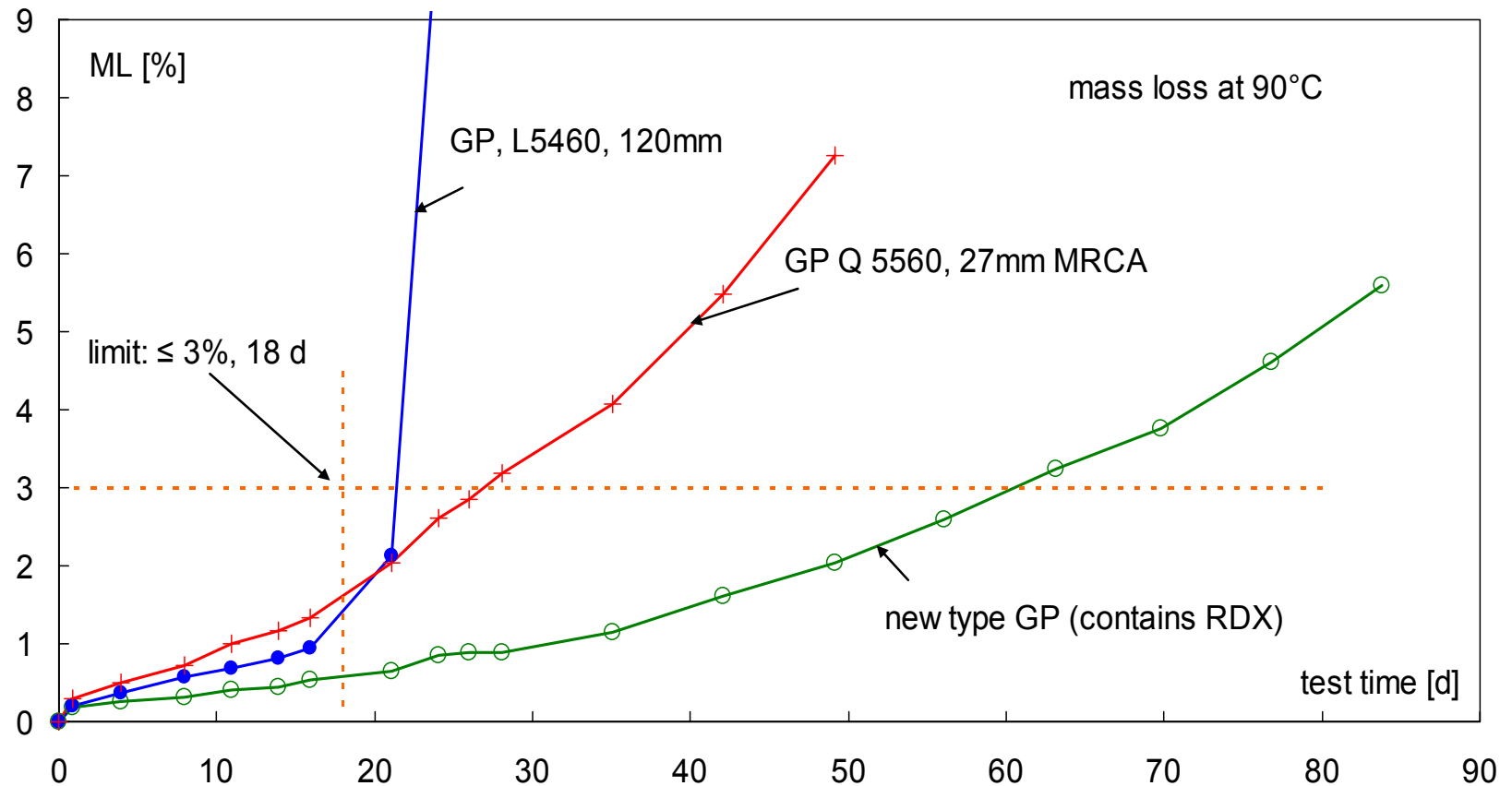
Assessment of ageing and stability with mass loss

Three types of GP

doublebase GP L5460 shows after 20d strong ML increase with visible NOx

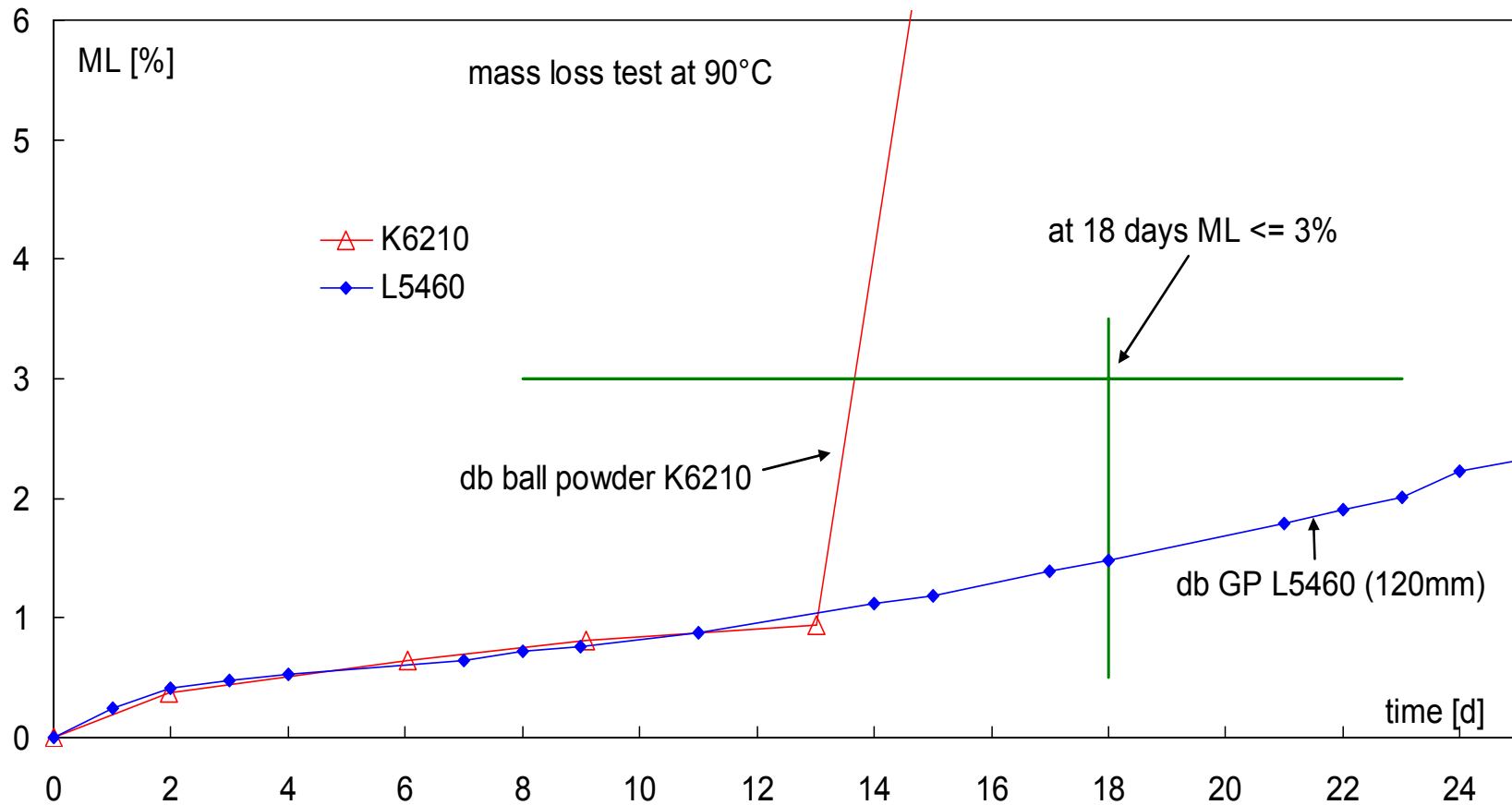
triplebase GP Q 5560 shows smooth increase of ML without showing visible NOx

new type GP (see later) shows smooth increase of ML without showing NOx



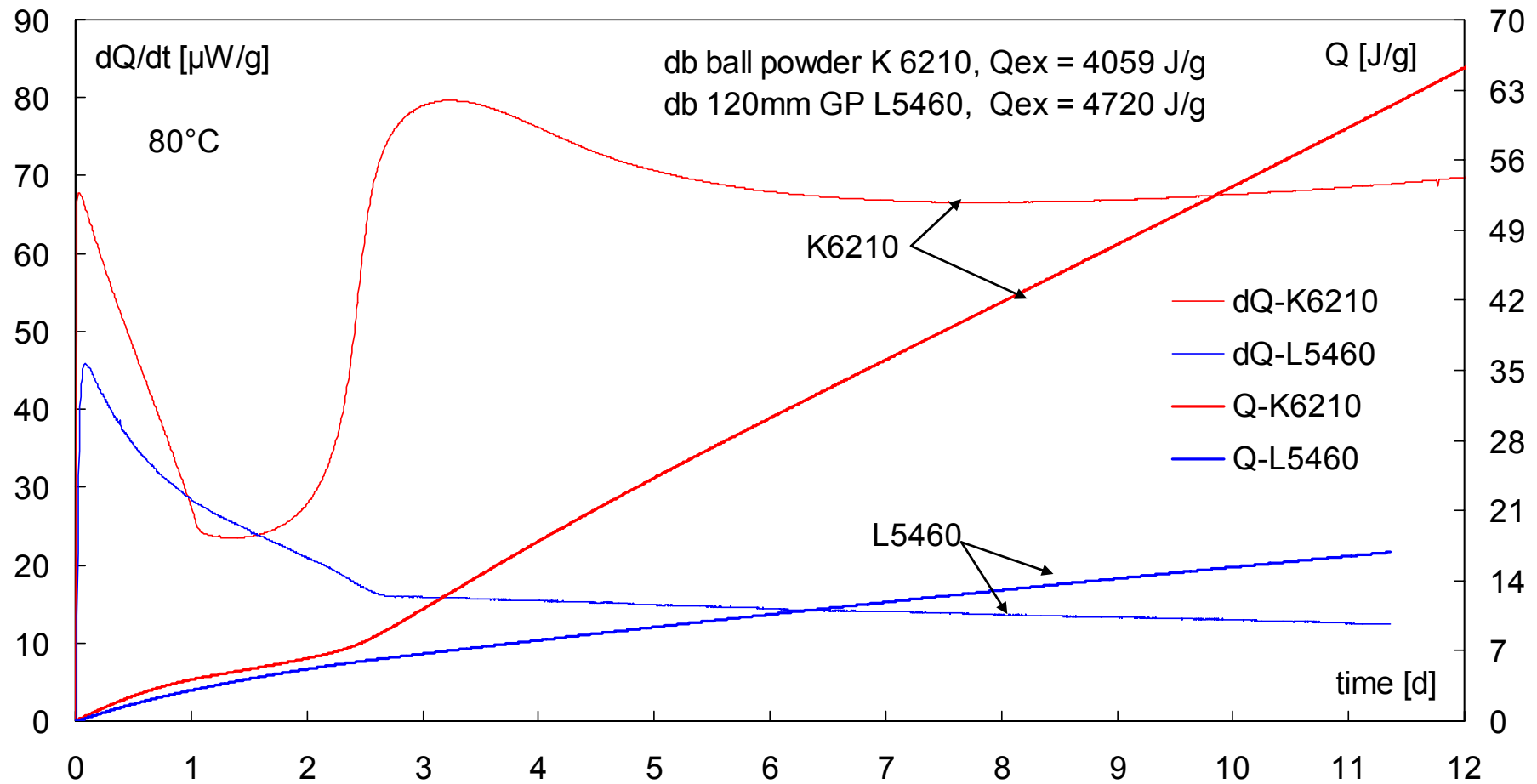
Comparison of mass loss: ball powder K6210 – 120mm GP L5460

Difference in stability can be revealed clearly with ML (18 days at 90°C corresponds to 50 years at 25°C isothermal)
db GP K6210 is stabilized with DPA (diphenylamine). In spite of not fulfilling the strong criterion it can be used safely for certain time. Doblebase GP L5460 is stabilized with AK II (akardite II).



Comparison of heat generation rate: ball powder K6210 – 120mm GP L5460

Difference in stability can be revealed also clearly with heat generation rate (dQ/dt) and heat generation (Q)



Aspects of NC decomposition



What determines the NC decomposition

NC and NC-based products decompose chemically.

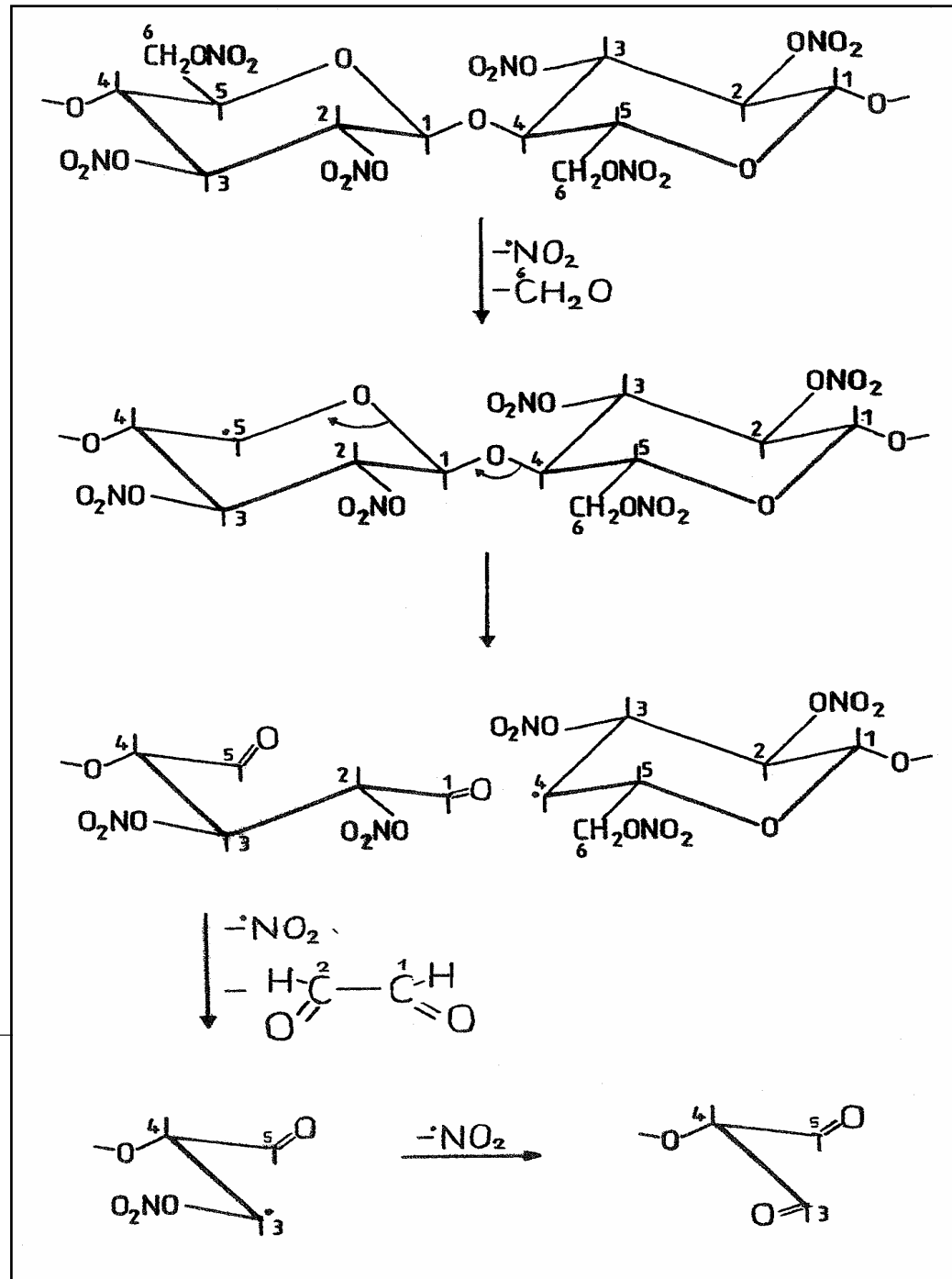
This is because of the relatively small bond dissociation enthalpy in the nitrate ester group.

chemical bond	name	average bond dissociation enthalpy at 25°C [kJ/mol]
CO – NO ₂	nitrate ester	165 to 170
C – C	carbon - carbon	342
C – H	carbon - hydrogen	416
C – O	carbon - oxygen	343
N – O (in NO ₂)	nitro group	305
C-NO ₂ (aromatic)	carbon – nitro group	295

Decomposition of NC

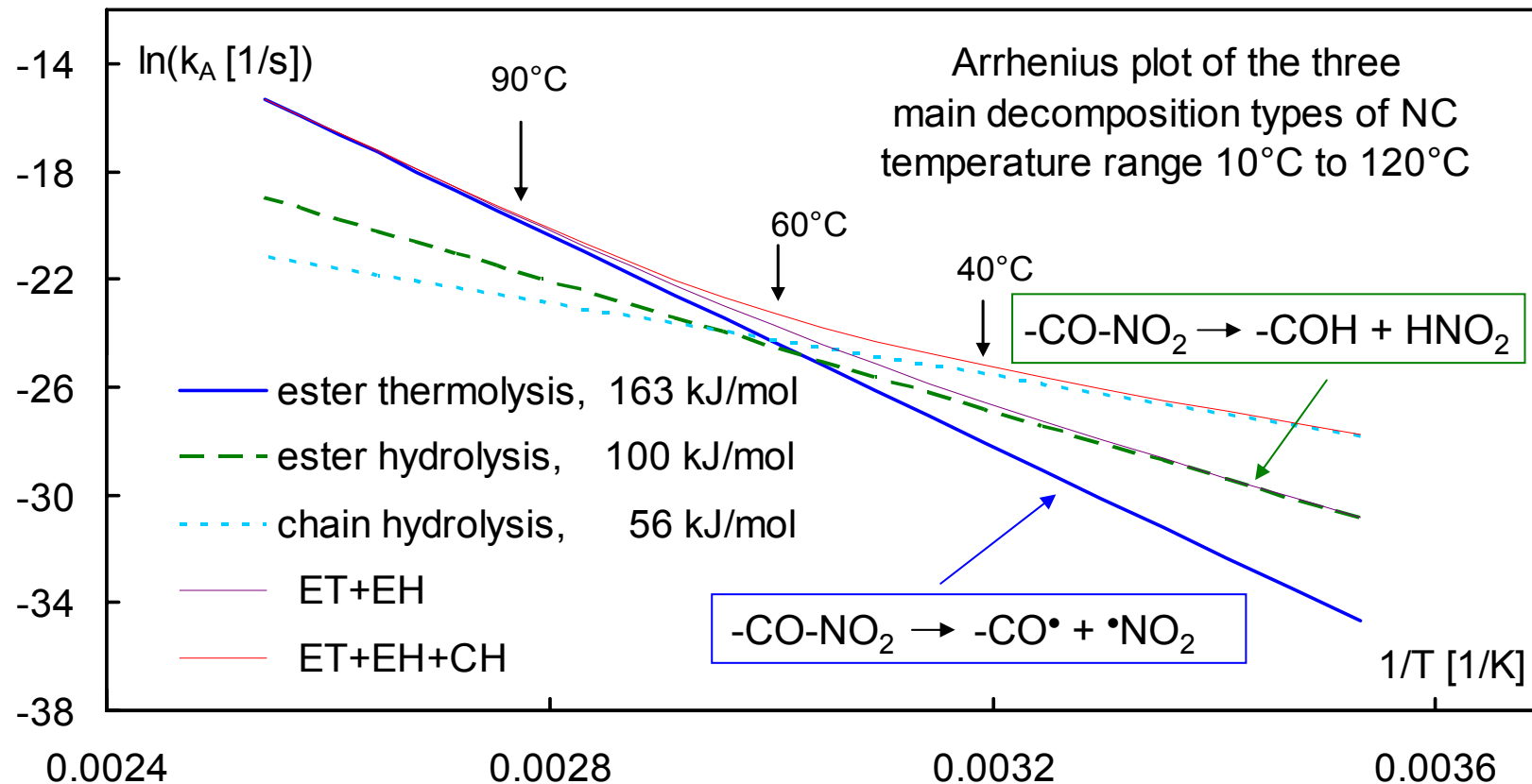
Assumption: by splitting-off of one NO_2 group from any ester group the corresponding glucose ring will be destroyed.

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.



Weighing of reaction rates by the investigation temperature via activation energy

The weighing has an important effect: at higher temperatures the process with the higher activation energy dominates the decomposition, at lower temperatures it is the one with smaller activation energy.



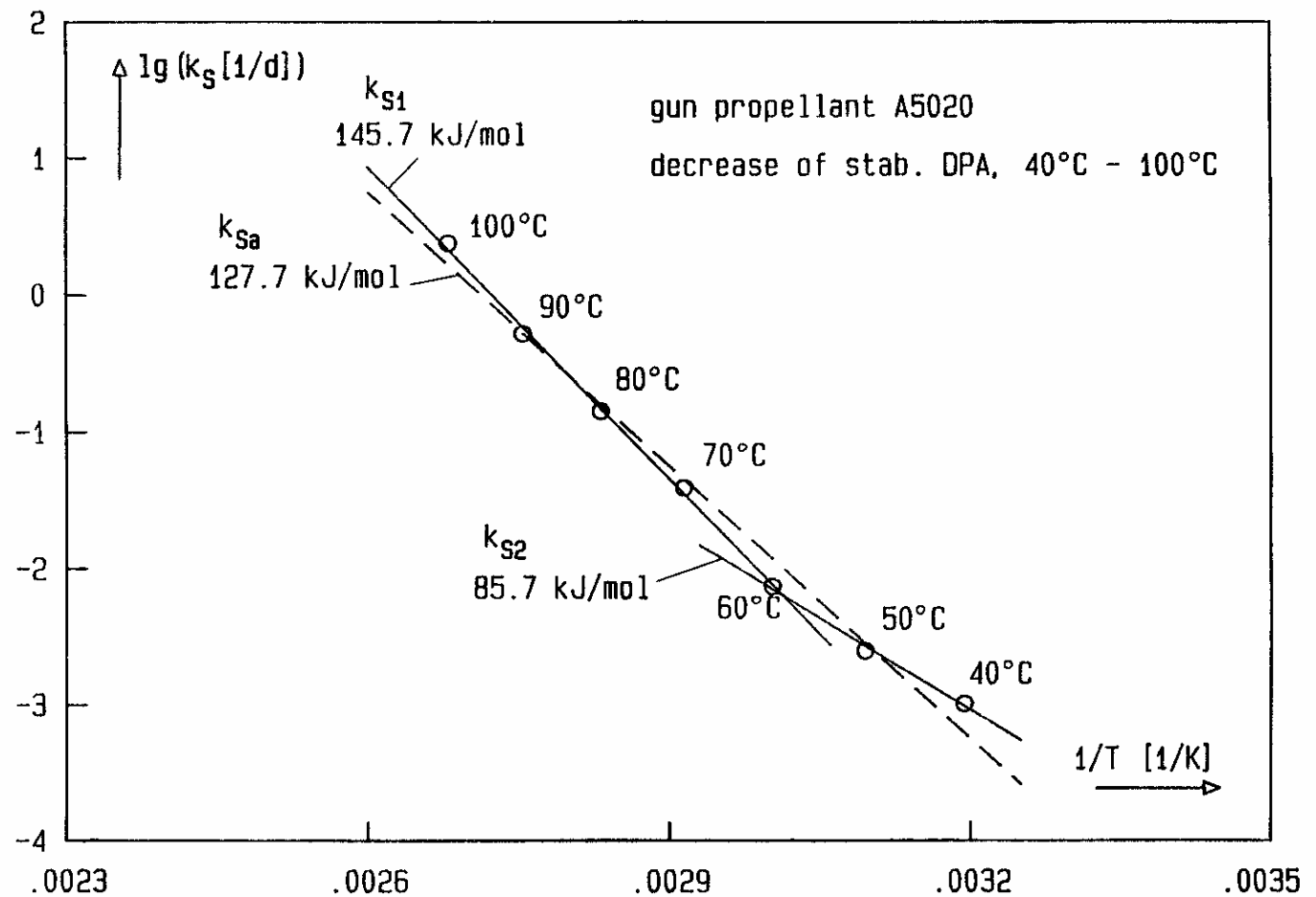
Stabilizer consumption: activation energy as function of temp.

decrease of stabilizer
DPA in single base GP
A5020 (20 mm machine
gun, older lot) /1/

change in E_a at about
65°C

higher temp. range has
more thermolytical
ester group
decomposition

lower temp. range has
more hydrolytical ester
group decomposition



Molar mass decrease of NC: activation energy as function of temp.

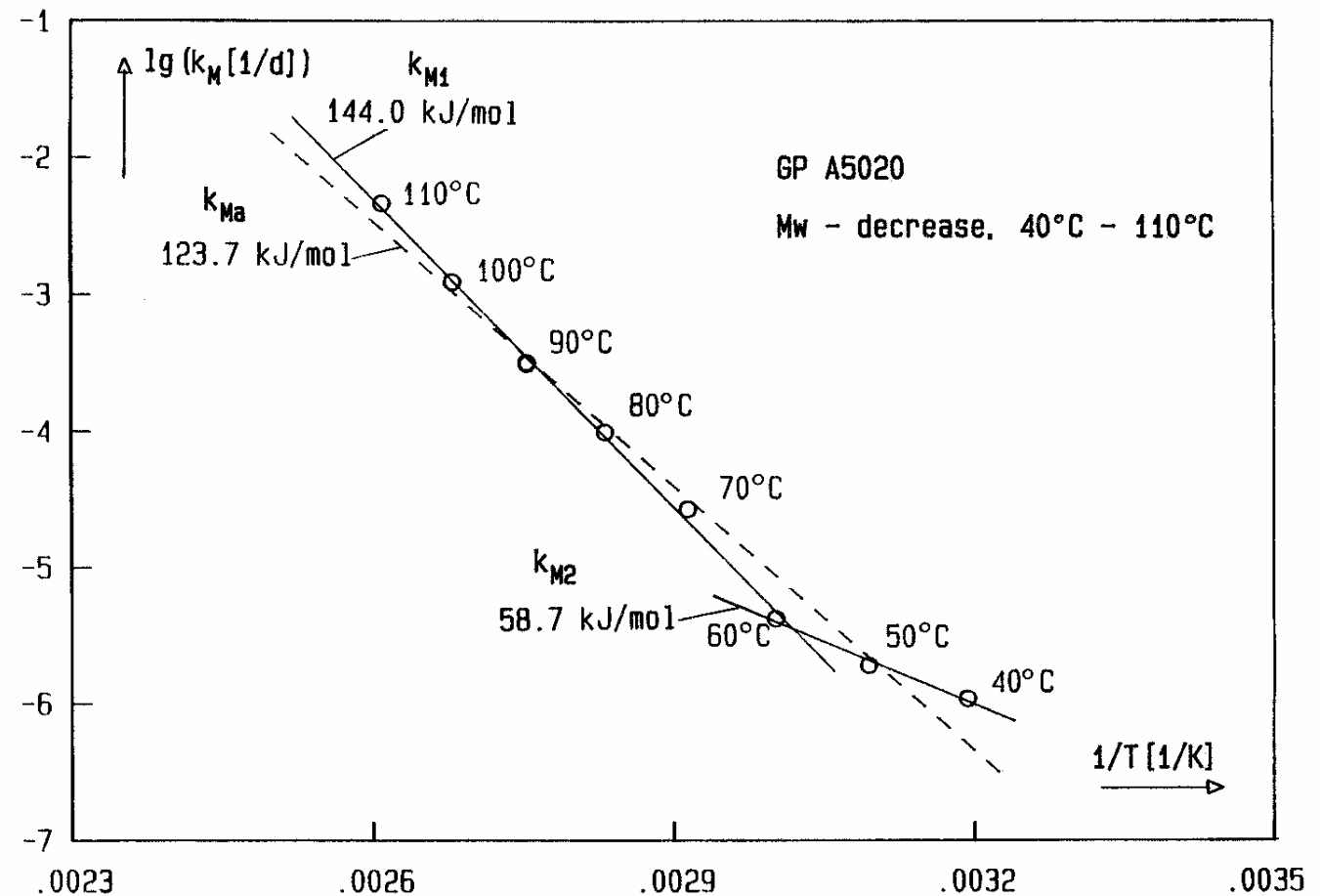
decrease of molar mass of NC in single base GP A5020 (20mm machine gun, older lot) /1/

change in E_a at about 65°C

higher temp. range has more thermolytical ester group decomposition with consecutive chain scission

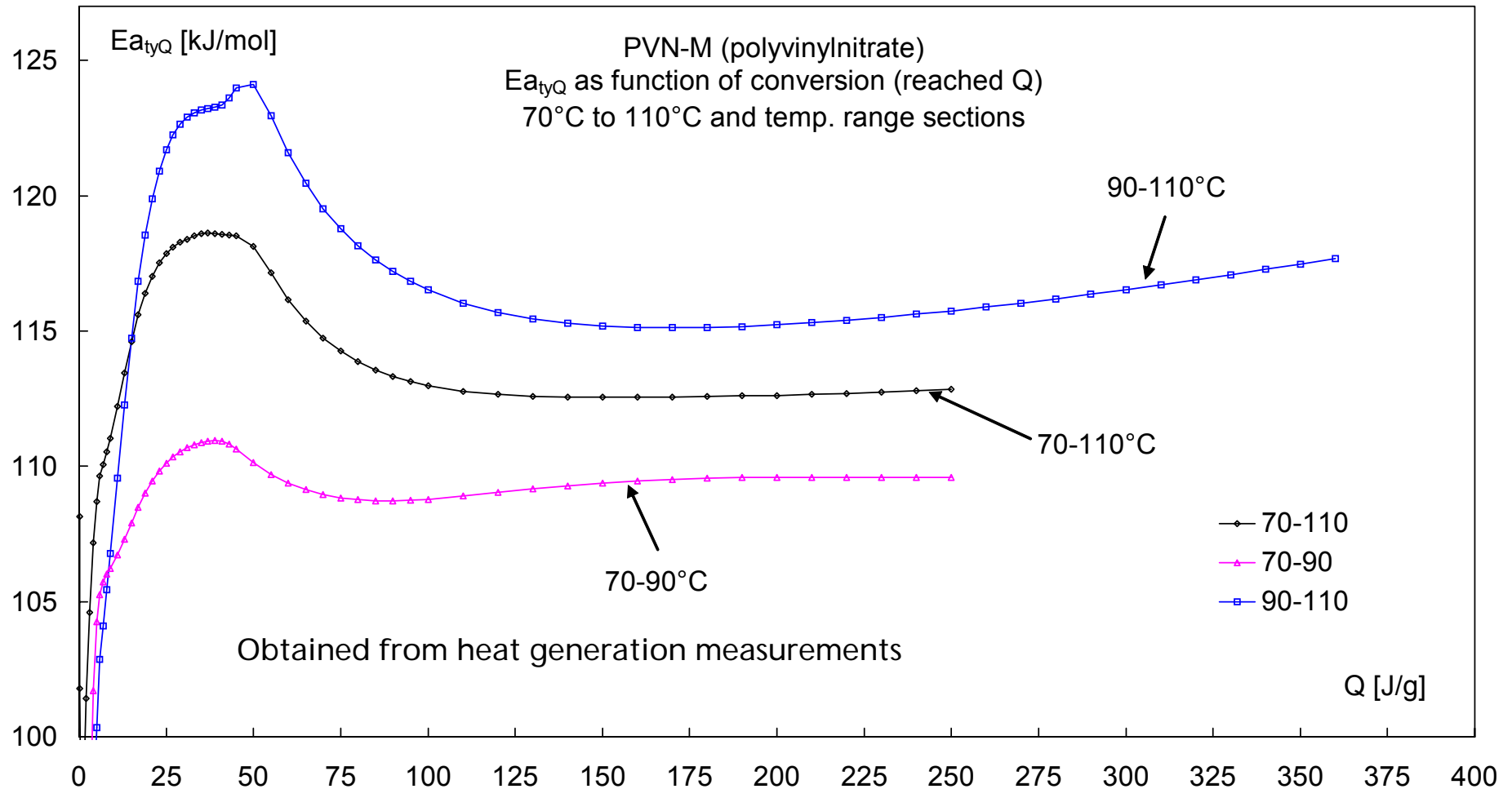
lower temp. range has more hydrolytical NC chain splitting

Remark: the lot of A5020 investigated was already an older one, means products with effect on hydrolysis present



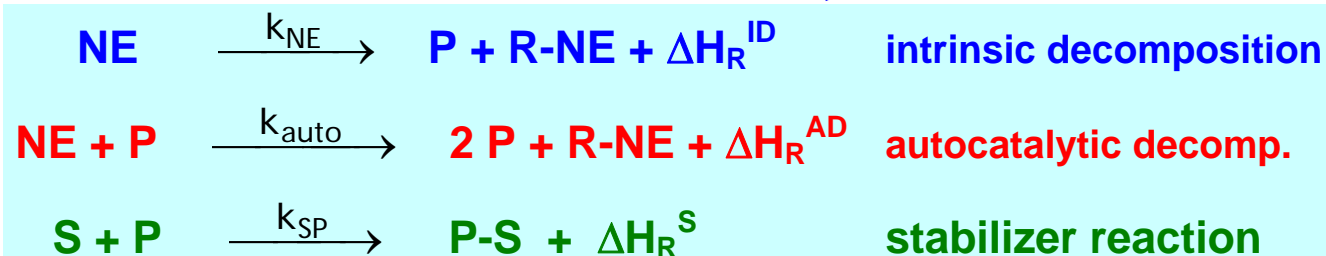
Temperature range dependence of E_a for PVN (polyvinylnitrate)

Also with other nitric acid ester compounds a temperature dependence of E_a is observable [2/]



Nitrate esters NE decompose intrinsically, means by themselves, because of the small bond energy in the nitrate ester group, about 170 kJ/mol for thermolytical split-off of NO₂; Further more one has formation of water and acids, and additional products as gases and organics.

Decomposition scheme of nitric acid esters NE



The decomposition products NO₂ and acids act as catalysts P in decomposing NE; a further decomposition reaction channel is opened – the so named autocatalytic decomposition.

The stabilizer S binds the NO₂ and nitric acid and makes the autocatalysts P in-effective. No autocatalytic decomposition appears during active phase of stabilization. – But the intrinsic decomposition goes on and causes mass loss, energy loss, chain splitting of NC, gas and heat generation.

Experimental bond dissociation enthalpies

Nitrate RO - NO ₂	kJ/mol	Nitrite RO - NO	kJ/mol
iso-Propyl nitrate	172.0 ± 4.2	iso-Propyl nitrite	171.5 ± 7.5
n-Propyl nitrate	177.0 ± 4.2	n-Propyl nitrite	167.8 ± 7.5
Methyl nitrate	172.4 ± 4.2	Methyl nitrite	174.9 ± 3.8
Alkyl nitrate	170.3 ± 2.1	Alkyl nitrite	170.7 ± 4.2

From CRC Handbooks

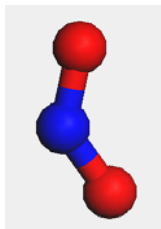
Please be aware of the difference in the terms
 Bond dissociation enthalpy
 refers to a specified bond which is split
 Bond enthalpy
 refers to the energy obtained when the
 molecule is split into the elements
 see for example with hydrazine in /3/

Relation kcal to kJ

1 kcal = 4.184 kJ

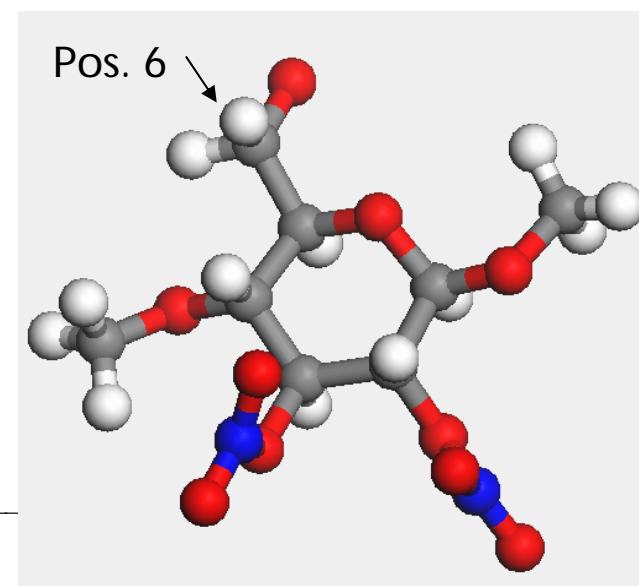
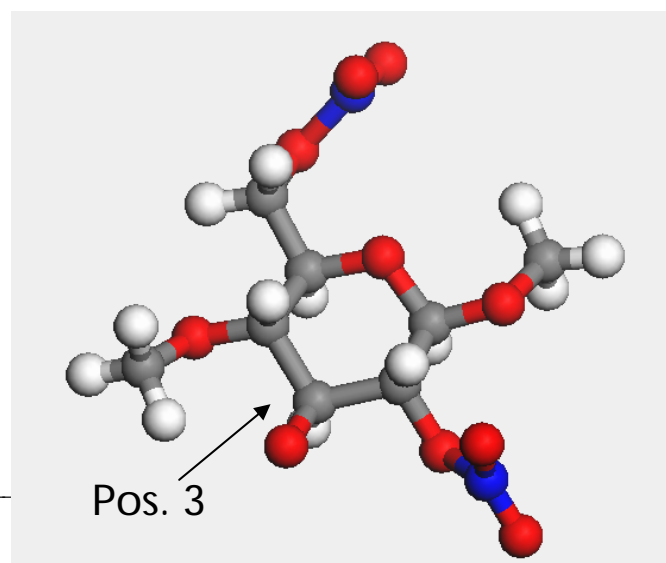
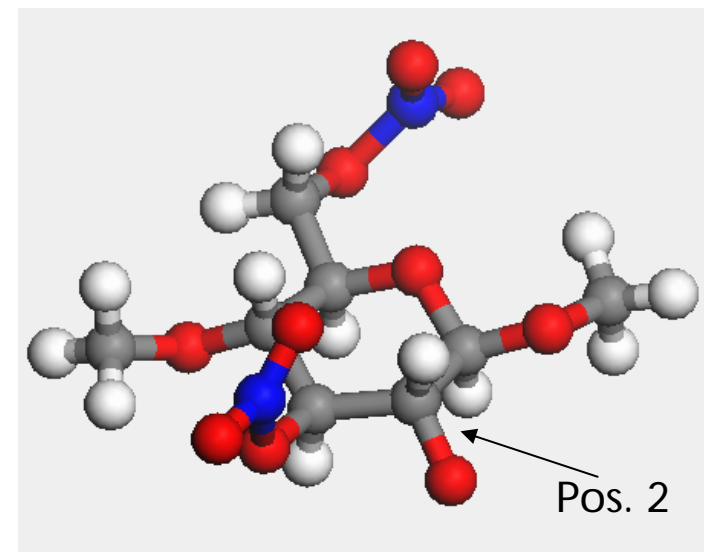
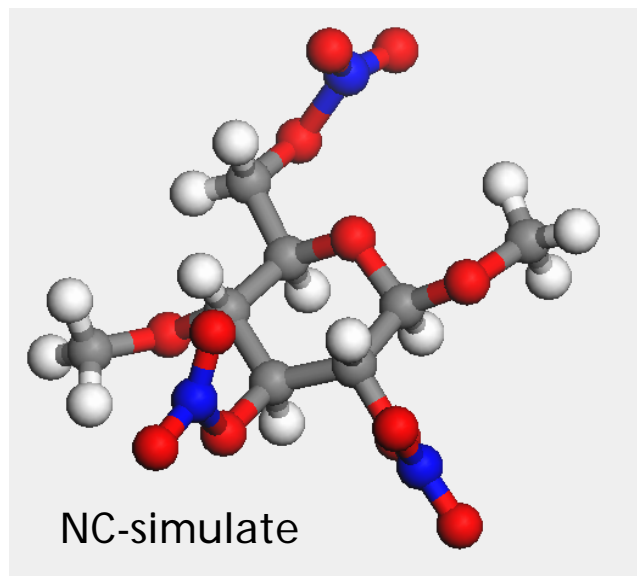
kcal/mol	kJ/mol
20	83.7
22	92.0
24	100.4
26	108.8
28	117.2
29	121.3
30	125.5
32	133.9
34	142.3
36	150.6
38	159.0
40	167.4
42	175.7
44	184.1
46	192.5
50	209.2

NC-simulate and NC-radicals to calculate the bond dissociation enthalpies of the split-off of NO_2 radical from the three glucose ring positions 2, 3 and 6

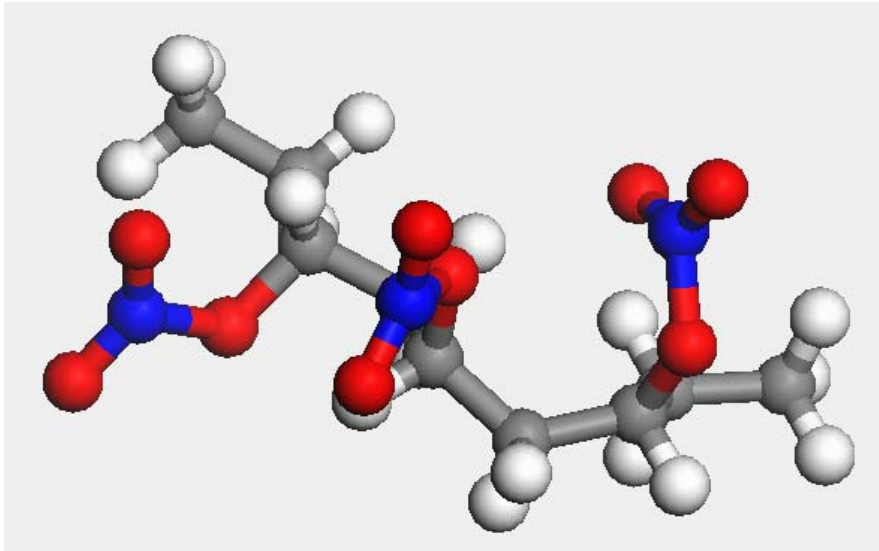


NO_2 radical

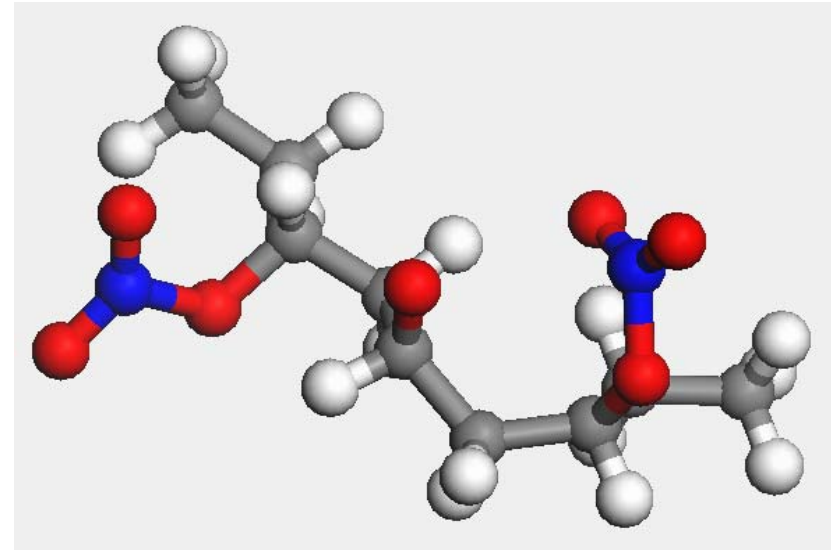
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PVN-simulate and PVN-radical to calculate the bond dissociation enthalpy of the split-off of NO₂ radical



PVN (polyvinyl nitrate) simulate



Split-off of NO₂ from middle position

PVN was seen as a replacement for NC in former time.

Today it is a speciality energetic polymer, used as additive in TNT HE charges.

Bond dissociation enthalpies at 298.15 K in different molecular environment

Calculation method:

DFT, BLYP, GGA all electron treatment

Calculated values corrected by normalizing to experimental average value of alkyl nitrate of 170.3 kJ/mol; error in calc. values ± 8 kJ/mol

DFT: (electron) density functional theory

B: Becke gradient corrected exchange potential

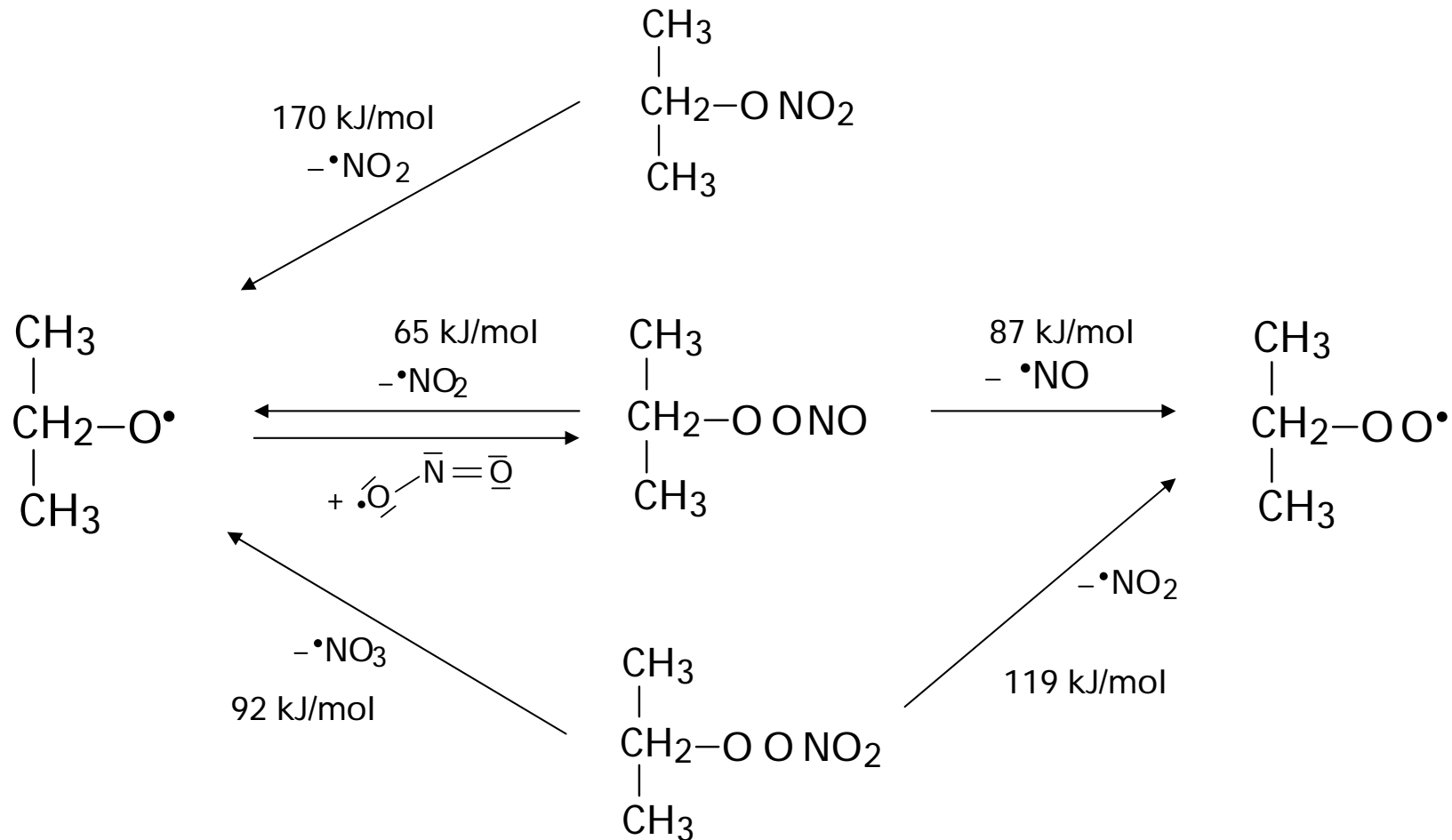
LYP: Lee, Yang, Parr gradient corrected electron correlation potential

GGA: generalized gradient approximation

Further conditions see /4/

Substance		[kJ/mol]
ME-NC-2NO ₂ , (BDE in the nitrate group at position 2)	1.2	160.8
ME-NC-3NO ₂ , (BDE in the nitrate group at position 3)	1.0	133.0
ME-NC-6NO ₂ , (BDE in the nitrate group at position 6)	1.3	174.4
PVN simulate (polyvinylNitrate)		170.8
Nitroglycerine, split-off of NO ₂ from middle position		171.2
Nitroglycerine, split-off of NO ₂ from side position		174.5
PETN		170.0
Methyl nitrate		185.0
Iso-Propyl nitrate		170.3
n-Propyl nitrate		179.9
Iso-propyl peroxonitrate: i-PropOO-NO ₂ ; split-off of NO ₂ radical		118.6
Iso-propyl peroxonitrate: i-PropO-ONO ₂ ; split-off of NO ₃ radical		92.5
Iso-propyl peroxonitrite: i-PropO-ONO; split-off of NO ₂ radical		64.5
Iso-propyl peroxonitrite: i-PropOO-NO; split-off of NO radical		87.2

Relation between nitrate, peroxo nitrite and peroxo nitrate



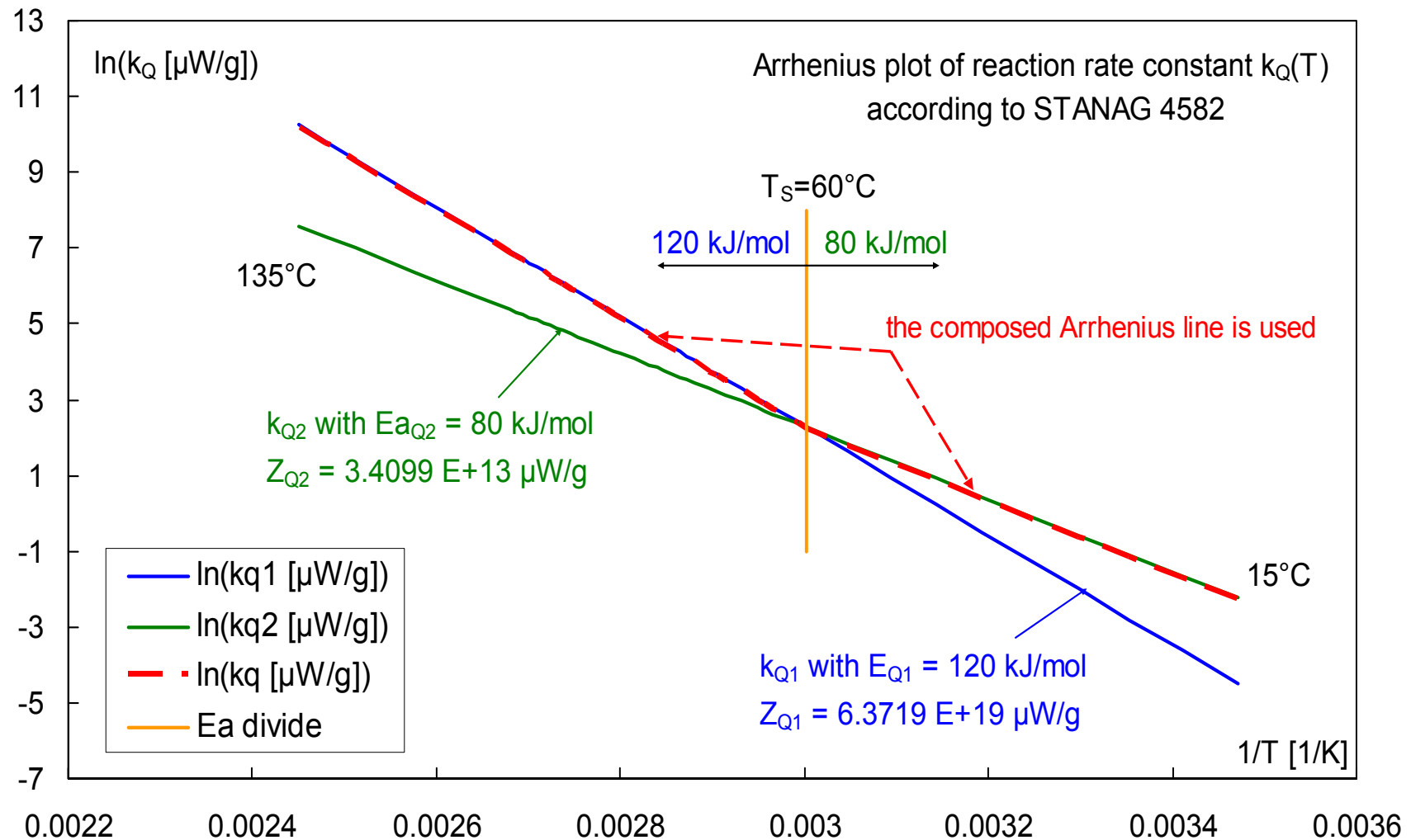
Accelerated ageing

ageing means generally: property change with time and temperature

Objectives

- To reach equivalent ageing in much shorter times than at target temperature, for example at 25°C
- To find out the ageing process(es)
- To determine activation energies for the ageing process(es) or other parameters to quantify the temperature dependence of the ageing
- To use the temperature dependence describing parameters to predict the ageing at any time-temperature load
- To simulate real ageing using time-temperature profiles

Arrhenius Plot according to STANAG 4582 (so-named heat flow (HFC) STANAG)



HFC-STANAG 4582 (Heat generation rate (HGR)-STANAG)

Main points

Fixing of test times t_T and upper limits for HGR (heat flow) $(dQ/dt)_L$ at a series of test temperatures T_T

To fulfil the HGR limits during test time at test temperature gives a safe time interval against autoignition of 10 years at isothermally 25°C

The test times and HGR limits are valid only for a decomposition kinetics as it is shown by NC-based propellants

HGR limits have been determined with a finite element programme for the solution of the heat balance equation for the autoignition of a big caliber (230 mm in diameter) cartridge

T_T [°C]	t_T [d]	$(dQ/dt)_L$ [μ W/g]	Acceleration with regard to 10 years at 25°C
60	123	9.8	30
65	64.9	18.5	56
70	34.8	34.5	105
71	30.8	39.0	119
75	19.0	63.1	192
80	10.6	114	345
89	3.83	314	954
90	3.43	350	1065

Arrhenius relation between 'test (t_t, T_t)' and 'in-service (t_E, T_E)'

With one activation energy valid in the considered temperature range T_E to T_t

$$k_i = Z \cdot \exp\left(-\frac{E_a}{RT_i}\right)$$

$$\frac{k_2}{k_1} = \exp\left(-\frac{E_a}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right) \quad t \propto \frac{1}{k}$$

Reaction rate constant
reciprocal proportional
to time to reach a state
or conversion

$$\frac{t_1}{t_2} = \exp\left(-\frac{E_a}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

By forming the ratio the time-
temperature scaling is achieved

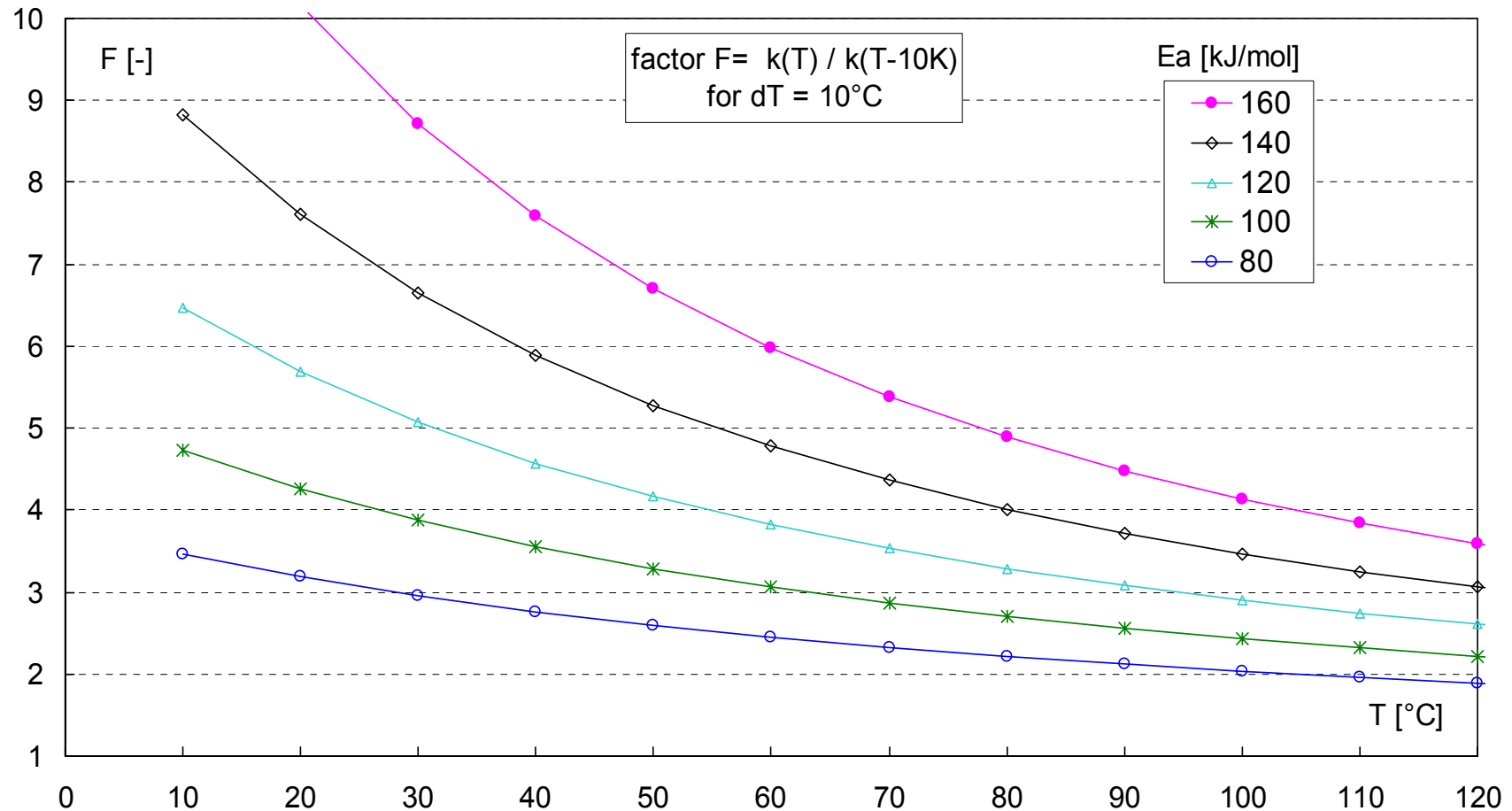
$$t_E = t_t \cdot \exp\left(+\frac{E_a}{R} \cdot \left(\frac{1}{T_E} - \frac{1}{T_t}\right)\right)$$

Caution

this procedure may be
simplifying to strong

Extrapolation of test conditions to in-service conditions with factor F (works in both directions: ac-celeration and de-celeration)

Factor 3 for 10°C temperature change corresponds to activation energy range of 80 to 120 kJ/mol in the temperature range 20°C to 95°C



Relation between test time - test temperature and in-service time - temperature

For chemically caused ageing processes the following formula has proven by experience as suitable (E_a about 80 to 120 kJ/mol, temperature range 20°C to 95°C)

$$t_E[a] = t_T[d] \cdot F^{(T_T - T_E) / \Delta T_F} / 365.25d$$

t_E time in years at temperature T_E

t_T test time in days at test temperature T_T

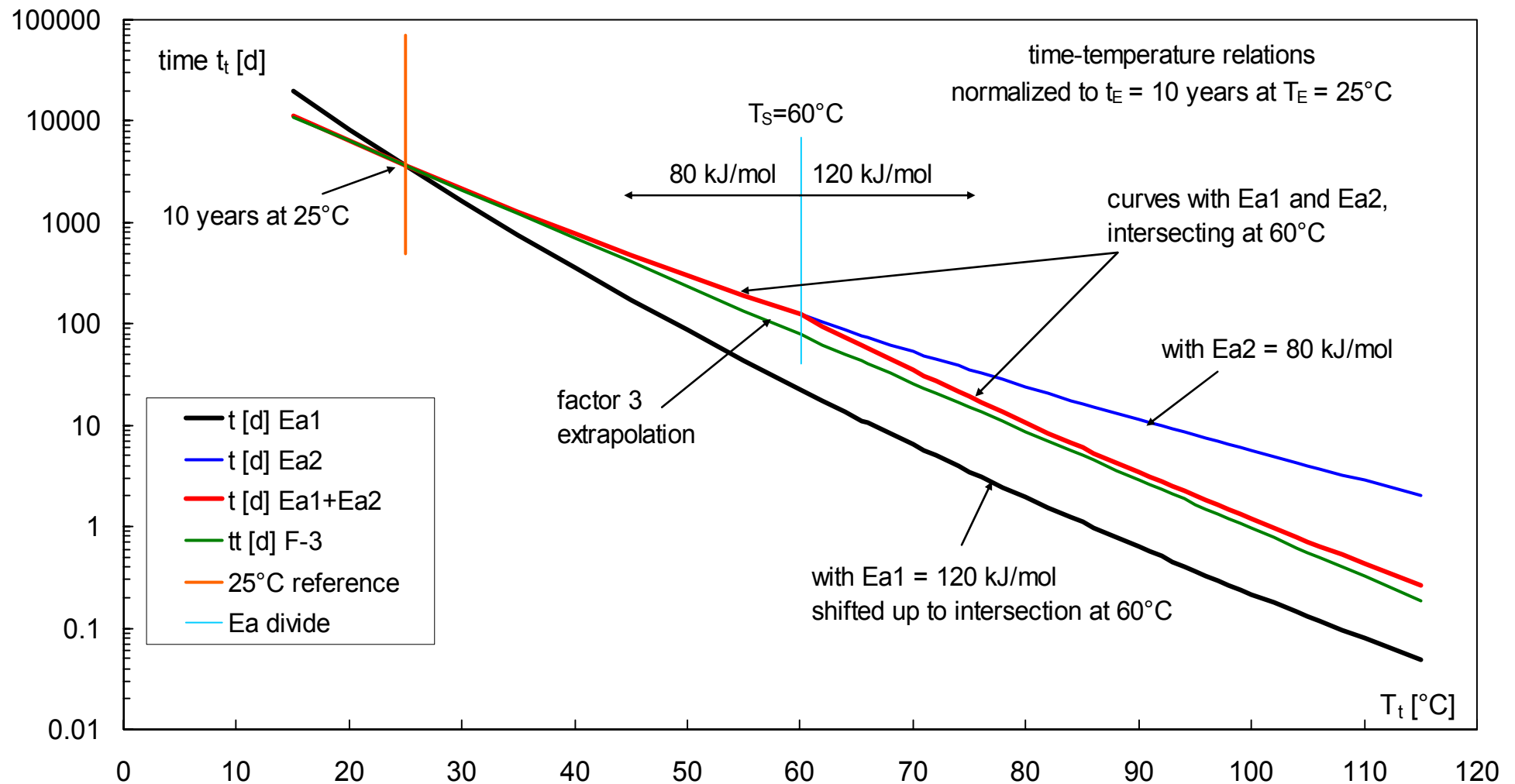
F reaction rate change factor per 10°C temperature change
De-celeration with temp. decrease / ac-celeration with temp. Increase

T_T test temperature in °C

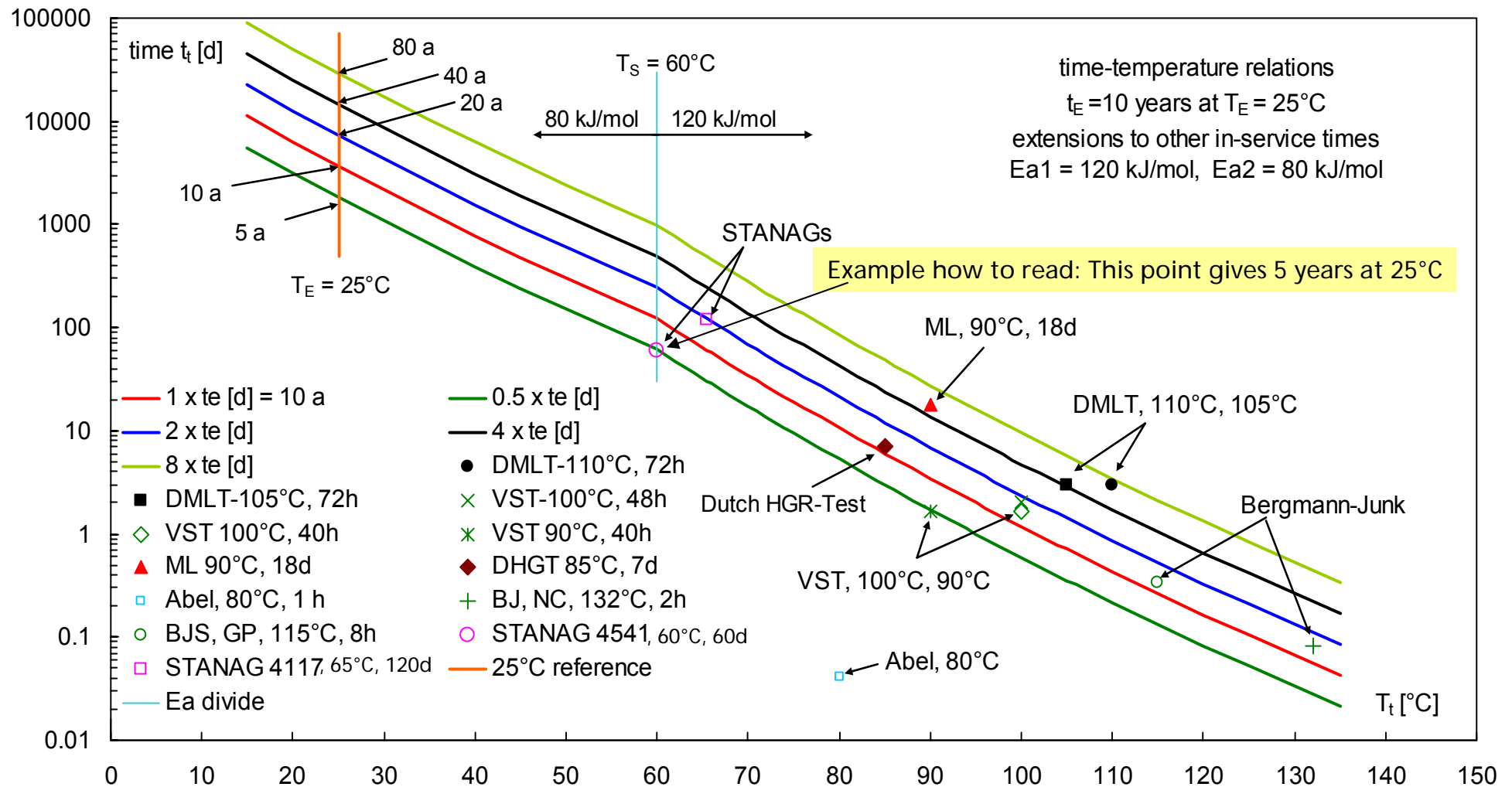
T_E in-service temperature in °C

ΔT_F temperature interval for actual value of F , here ΔT_F is always 10°C

Comparison of the STANAG extrapolation with the factor 3 extrapolation



Overview of some used test times – test temperatures extrapolated to 25°C



Implicit limit in the HFC STANAG

Limit for the allowed energy loss of a gun (GP) or rocket (RP) propellant: $\leq 3\%$

For 10 years at 25°C

T_T [°C]	t_T [d]	$(dQ/dt)_L$ [μW/g]	Q_L [J/g]
60	123	9.8	104.1
65	64.9	18.5	103.7
70	34.8	34.5	103.7
71	30.8	39.0	103.8
75	19.0	63.1	103.6
80	10.6	114	104.4
89	3.83	314	103.9
90	3.43	350	103.7

	at 80°C, after 10.6 d			$Q_{EX}(gw)$ [$Q_{EX}(lw)$] [J/g]	Limit is 3% of $Q_{EX}(gw)$ [J/g]
	HGR [μW/g]	Q [J/g]	% of $Q_{EX}(gw)$		
L5460 db, 120mm	12.8	16.1	0.38	4238 [4610]	127
K6210 db ball, 9mm	68.2	57.1	1.53	3730 [4040]	112

$Q_{EX}(gw)$ value with reaction water gaseous

$Q_{EX}(lw)$ value with reaction water liquid

To extend the predicted time from 10 to 20 years implies to use the double test times but also only half the values for $(dQ/dt)_L$



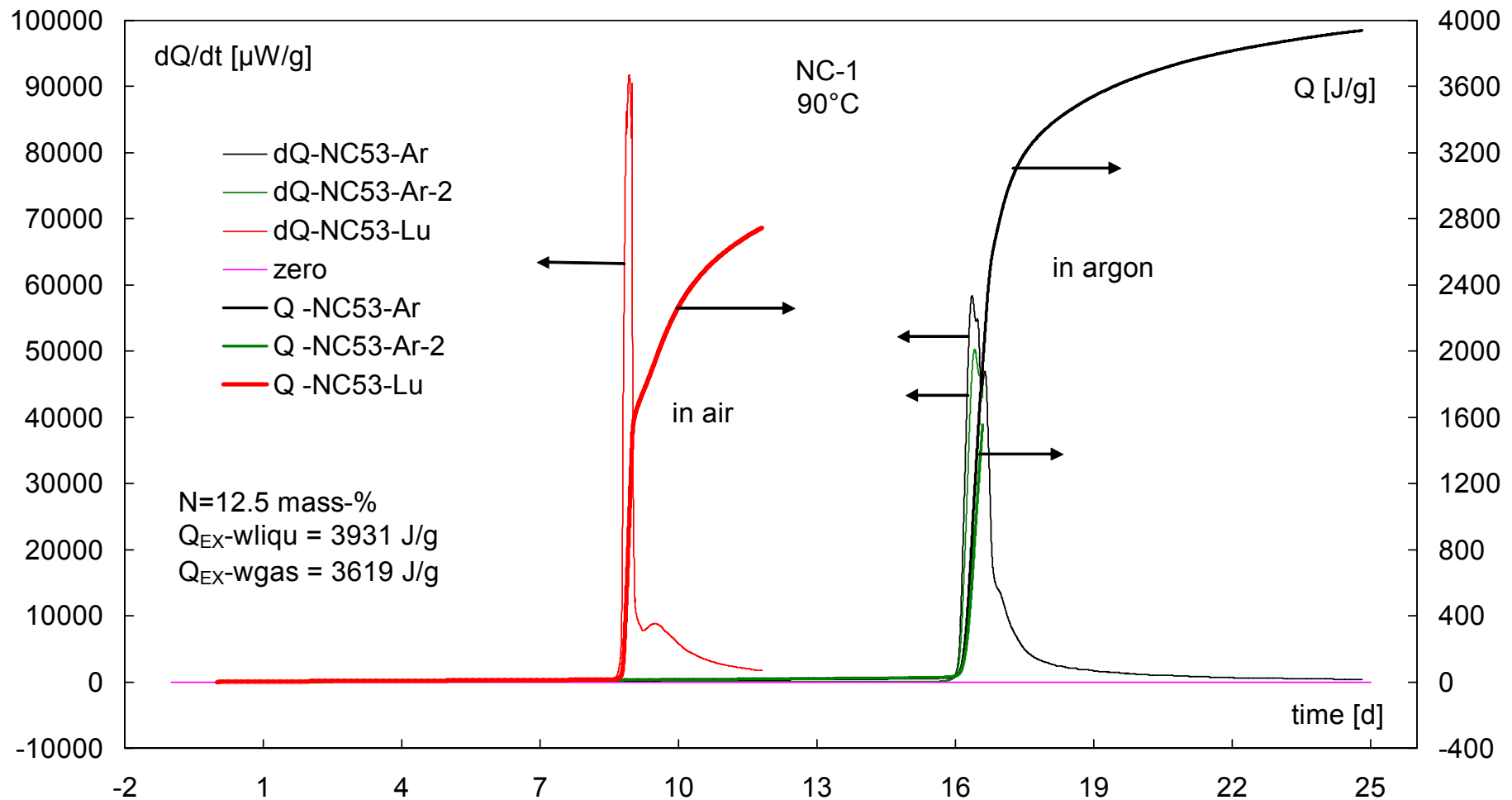
Energy loss limit is for the actual use of the propellant more important than the danger of its autoignition

Measurements on NC alone – Comparison of stability tests



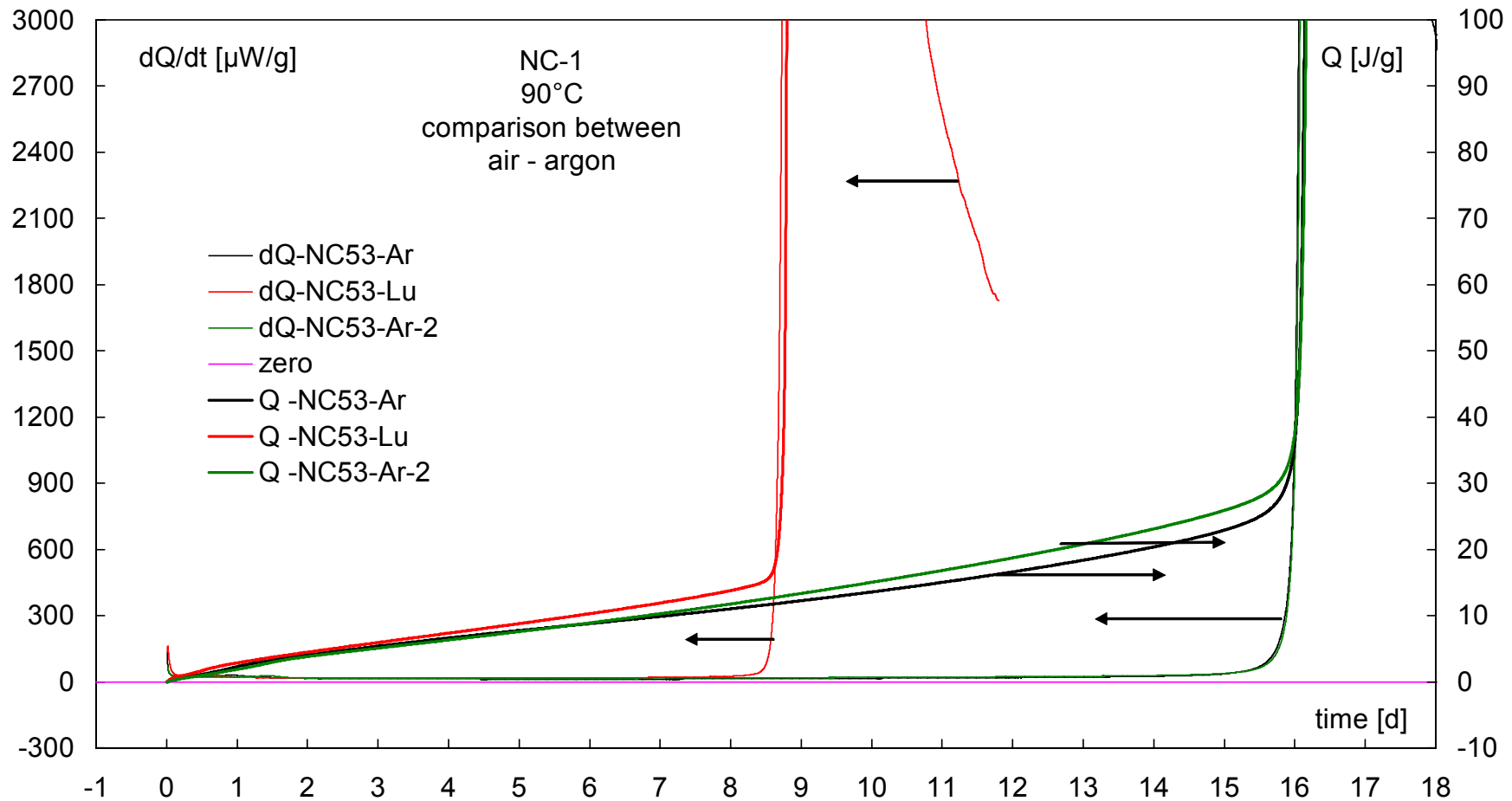
NC lot 1: HGR and HG at 90°C, measured under air and under argon

Measured at 90°C with TAM™ in closed steel ampoules with glass inserts, sample amounts about 0.2g



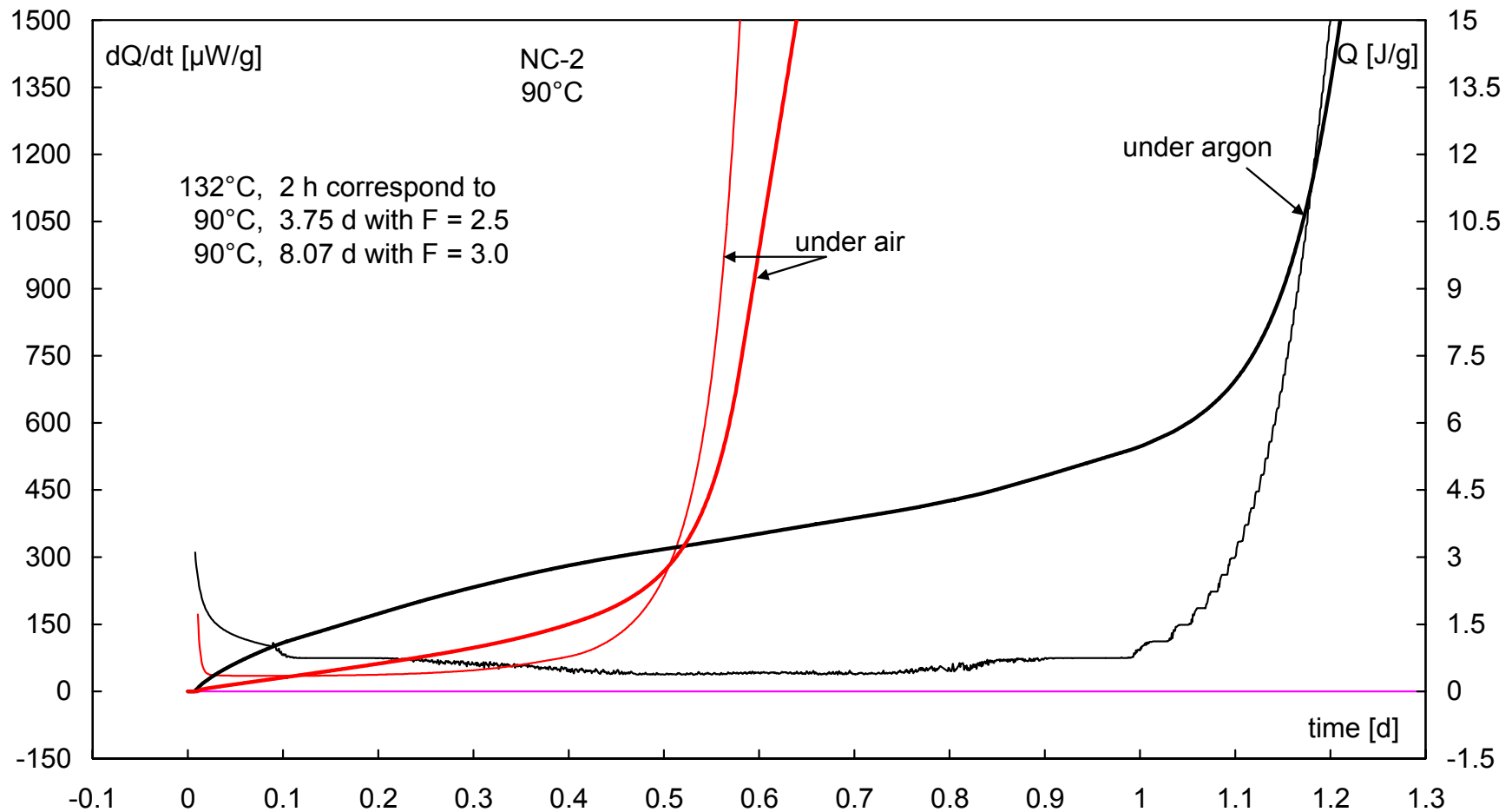
NC lot 1: HGR and HG at 90°C, measured under air and under argon

Measured at 90°C with TAM™ in closed steel ampoules with glass inserts, sample amounts about 0.2g



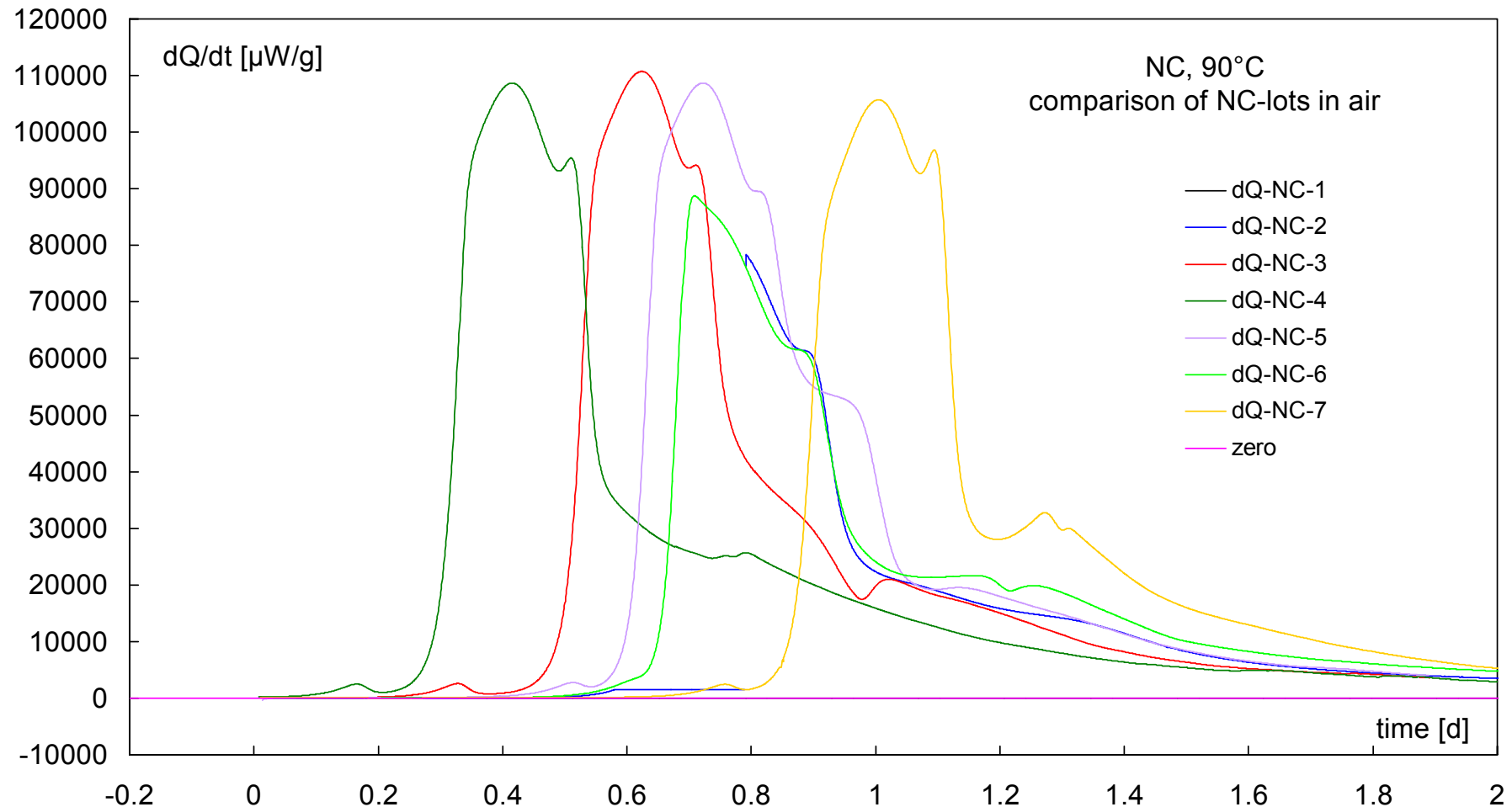
NC lot 2: HGR and HG at 90°C, measured under air and under argon

Measured at 90°C with TAM™ in closed steel ampoules with glass inserts, sample amounts about 0.2g



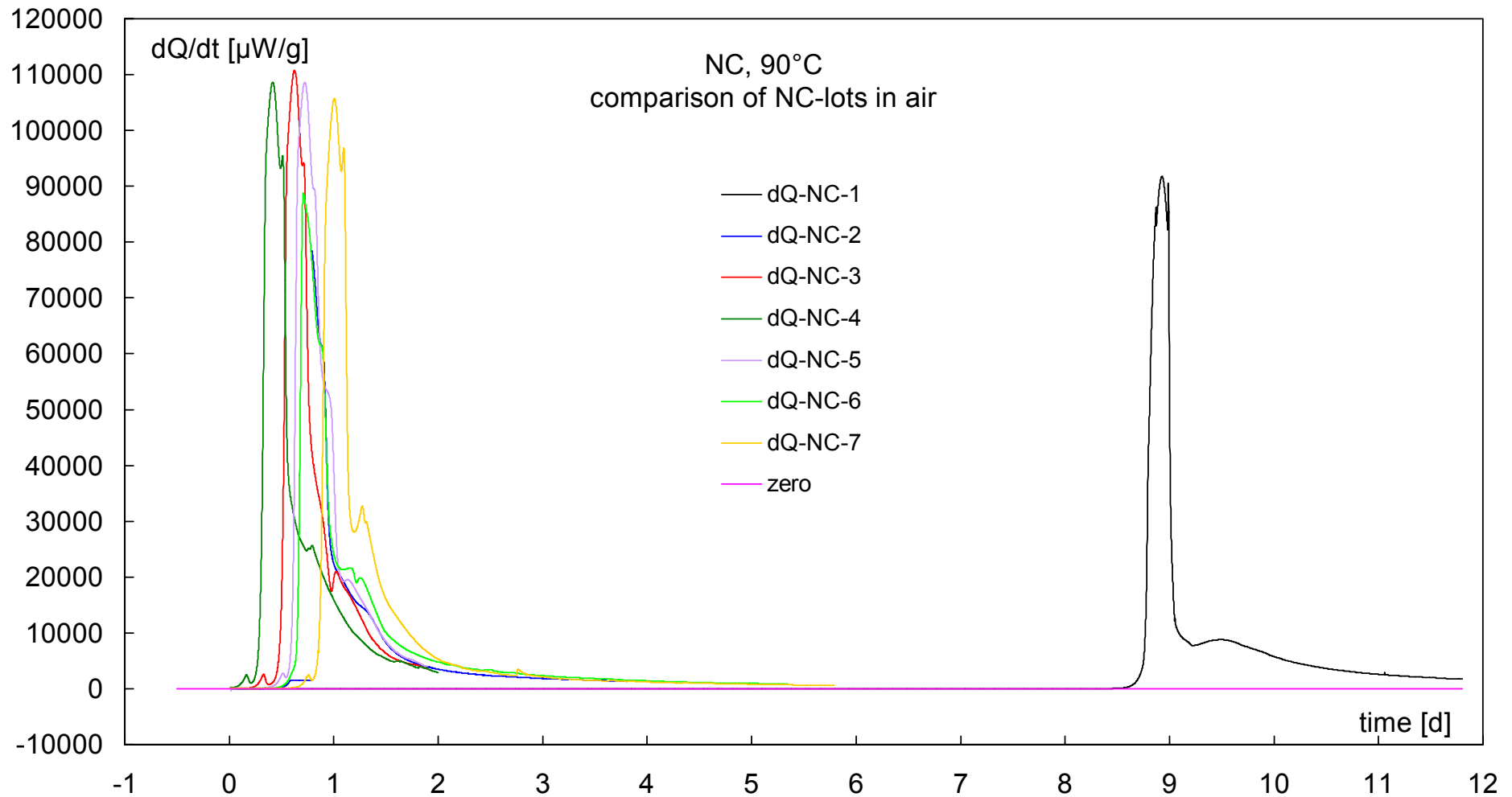
Heat generation rates of dry and unstabilized NC samples – region 0 to 2 days

Measured at 90°C with TAM™ in closed steel ampoules with glass inserts in air, sample amounts about 0.2g

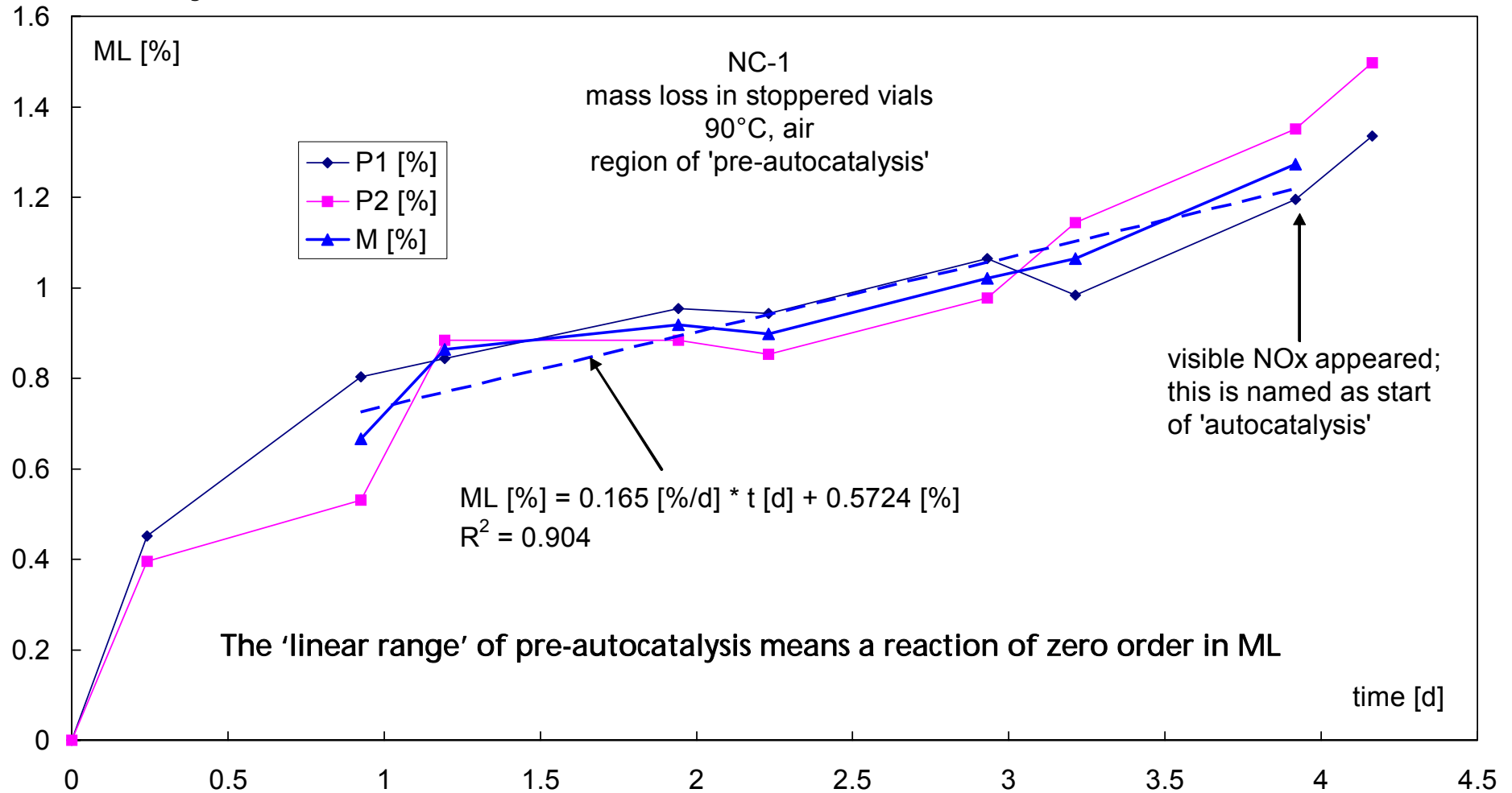


Heat generation rates of seven dry and unstabilized NC samples

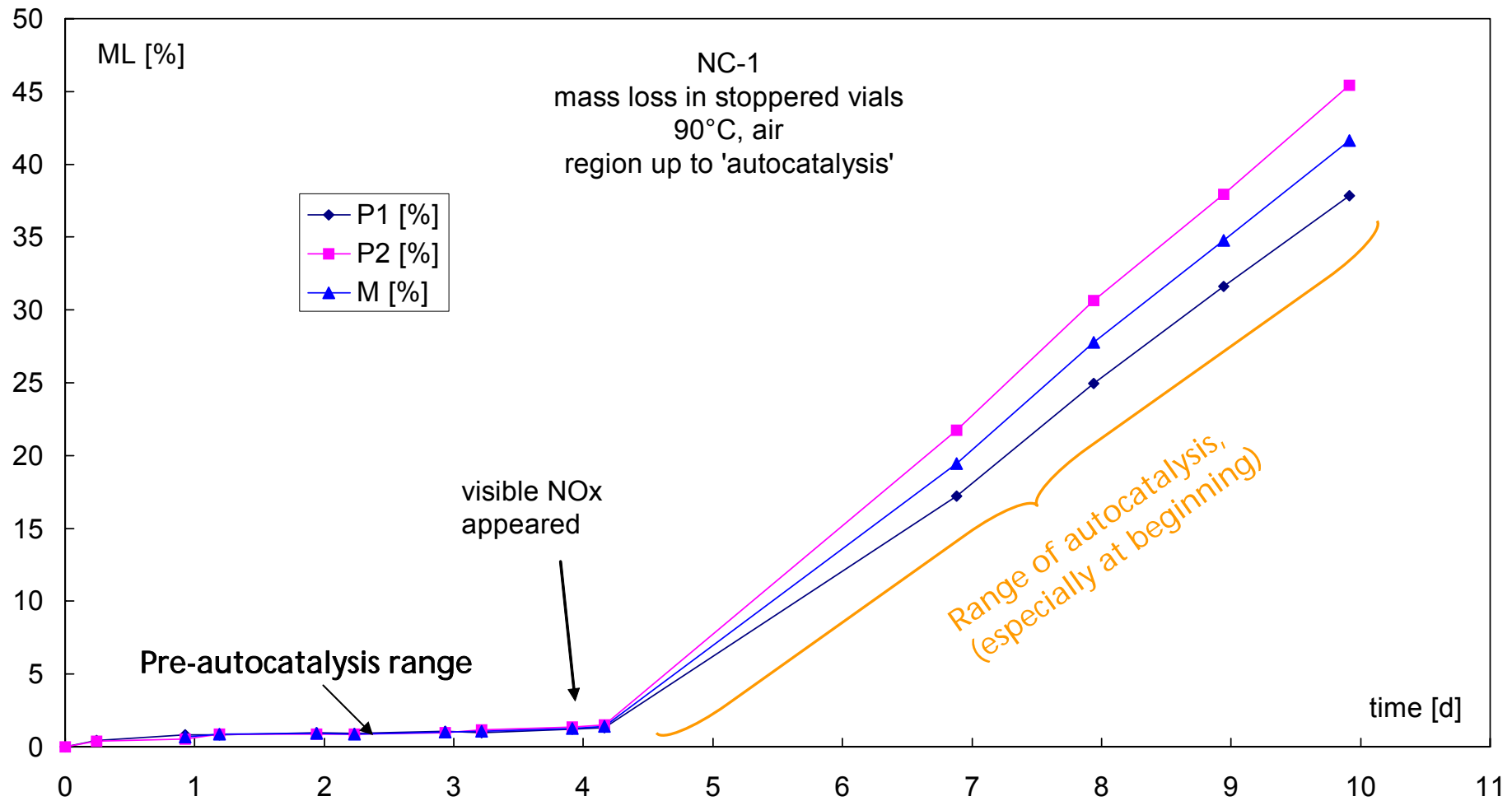
Measured at 90°C with TAM™ in closed steel ampoules with glass inserts in air, sample amounts about 0.2g



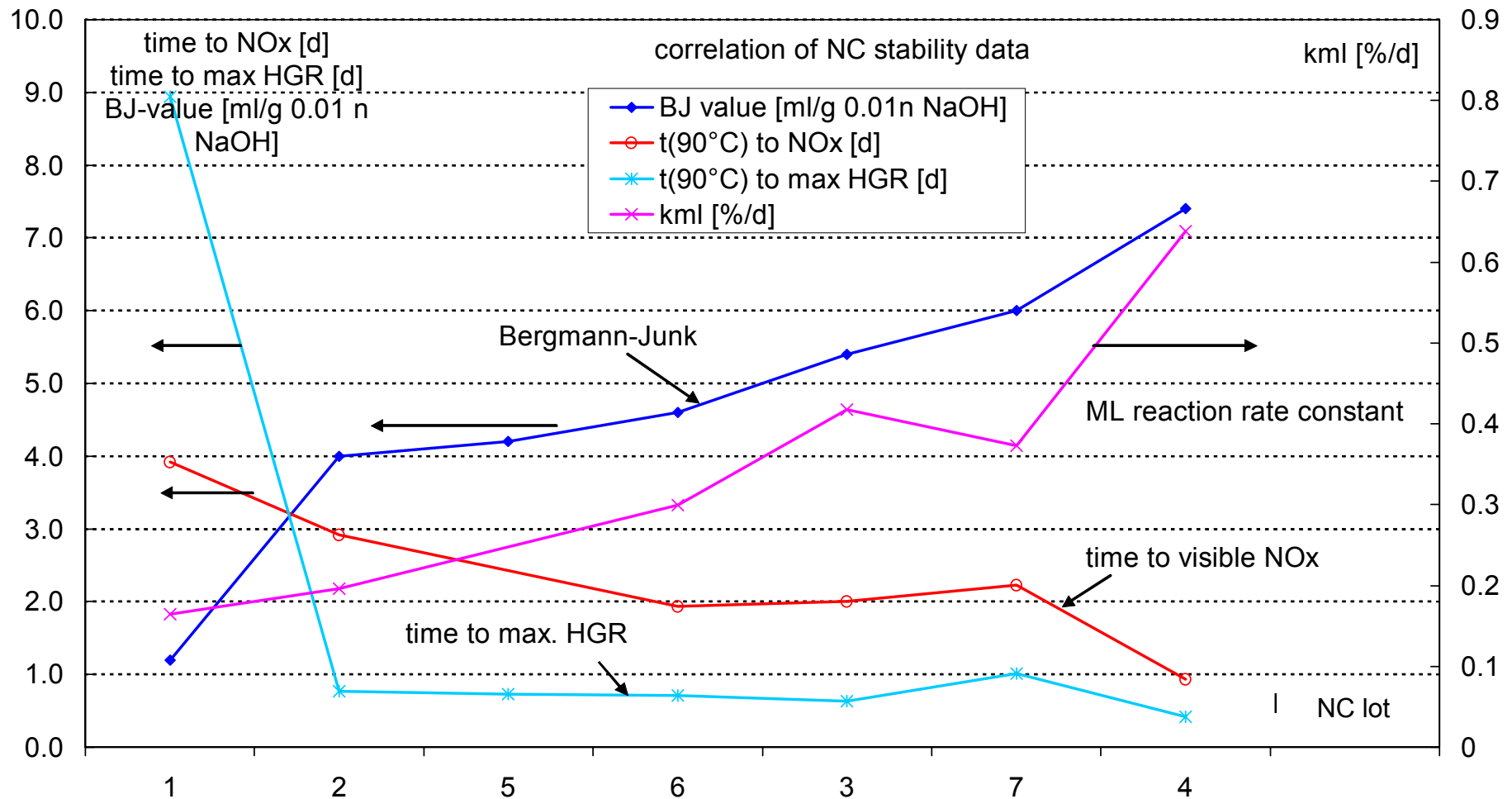
Mass loss of dry and unstabilized NC lot 1 in the 'linear range' of pre-autocatalysis (means a reaction of zero order)



Mass loss of dry and unstabilized NC lot 1 at 90°C up to autocatalysis



Comparison of stability data of seven NC lots obtained with four methods

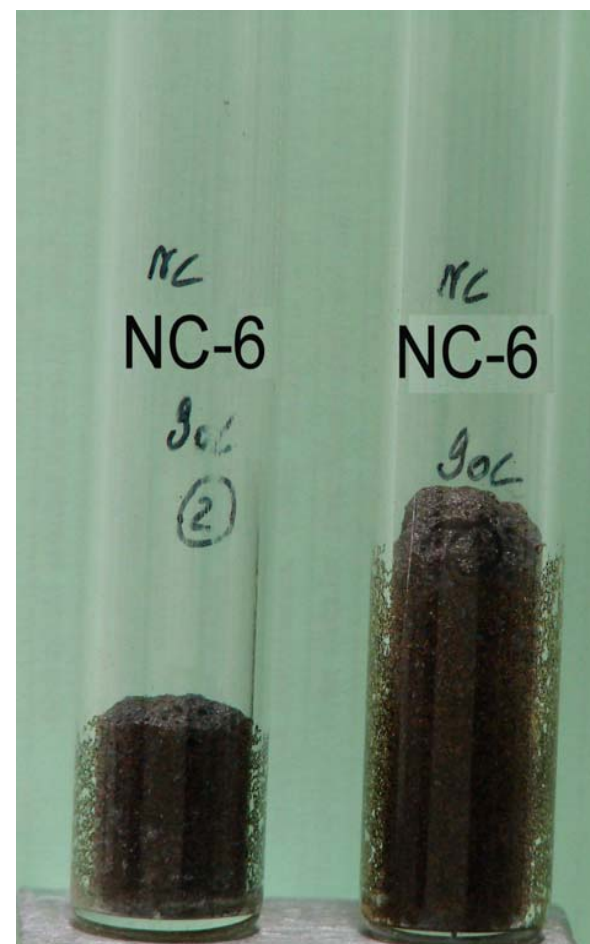


Photographs of NC residues after ageing at 90°C in mass loss vials

Brown to black residues after the 'cool' burning-out of the NC samples.

Sample amount about 0.6g to 0.8g

No ignition occurred in any case !

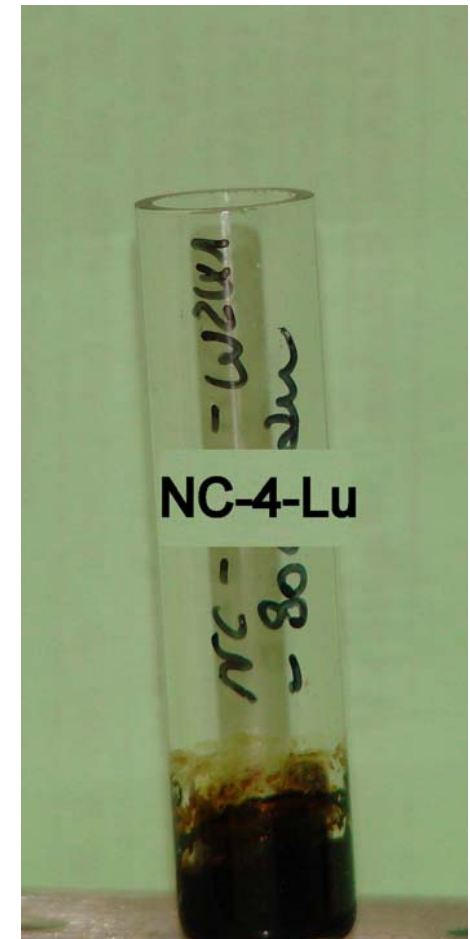
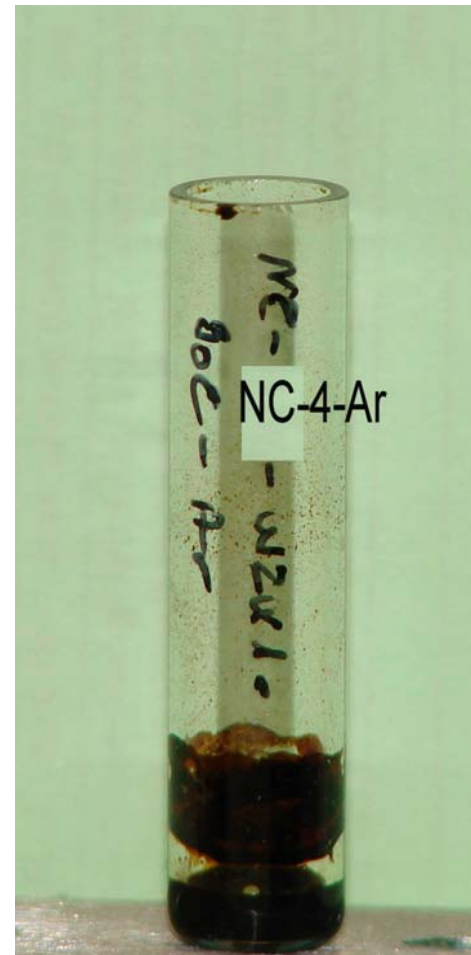
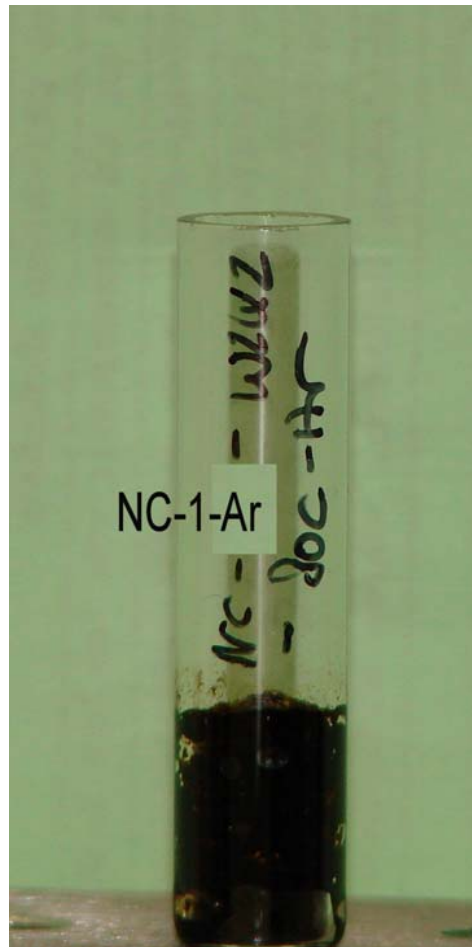


Photographs of NC residues in glass inserts after measurements in TAM at 90°C

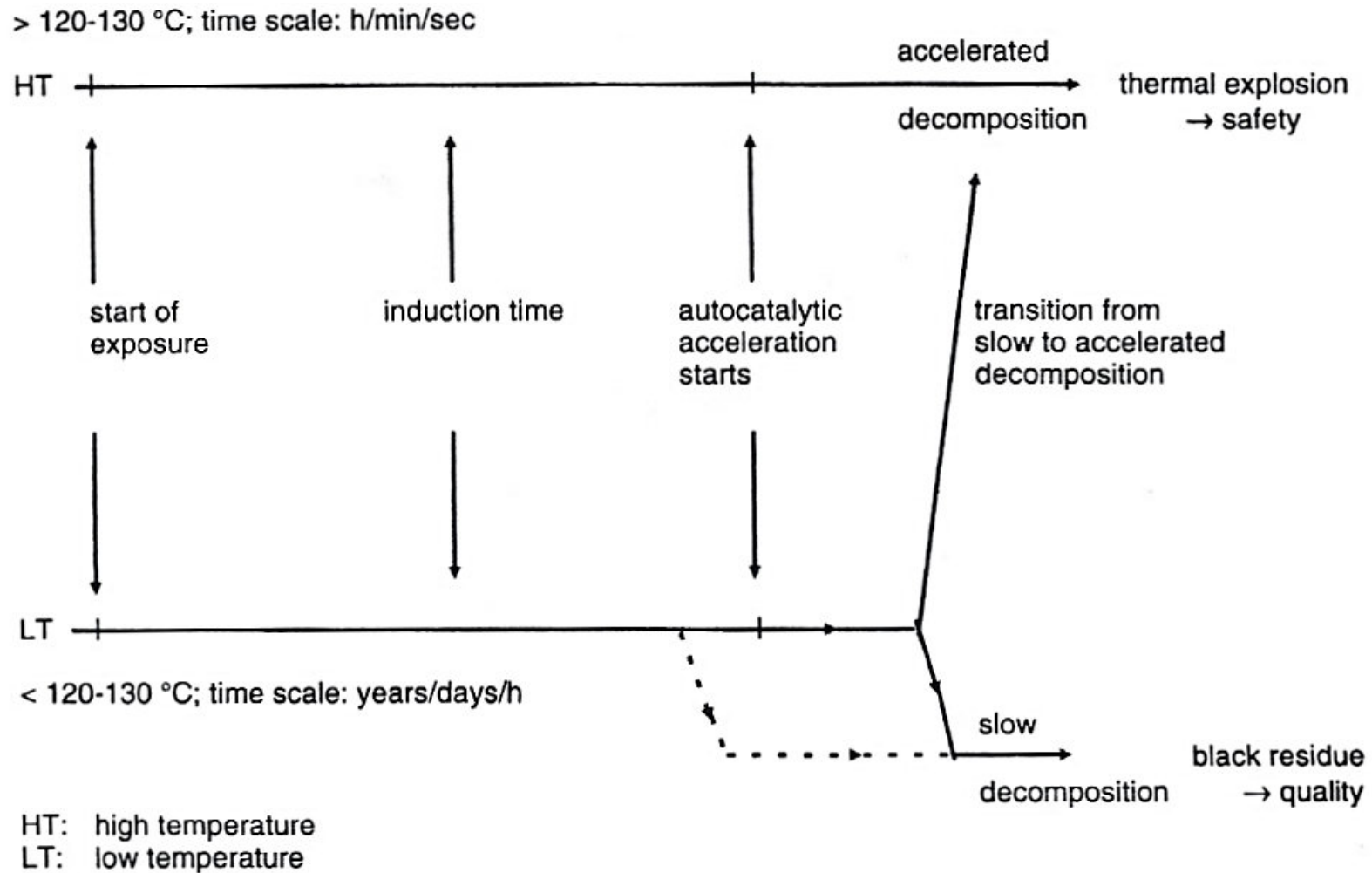
Brown to black residues after the 'cool' burning-out of the NC samples.

Sample amount about 0.2g

No ignition occurred in any case !



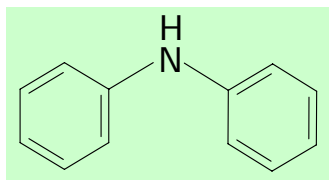
Scheme of NC decomposition considering temperature-time exposure see /5/



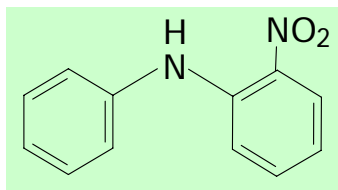
Mitigation of ageing



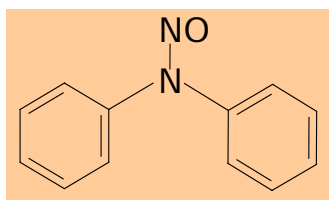
Chemical formulas of the most used stabilizers in NC-based propellants



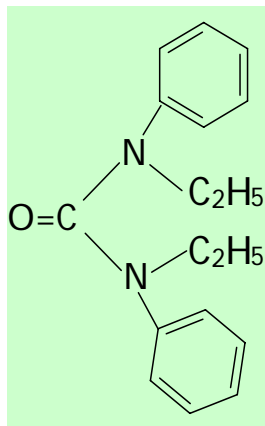
DPA



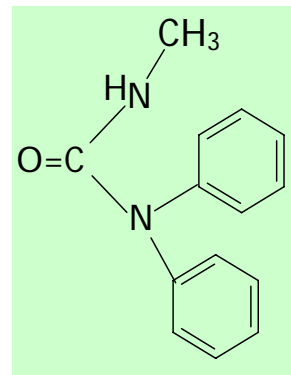
2NDPA,
2-NO₂-DPA



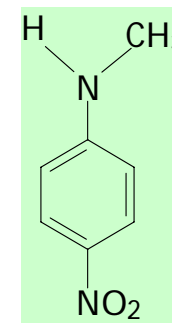
N-NO-DPA
N-nitroso-DPA



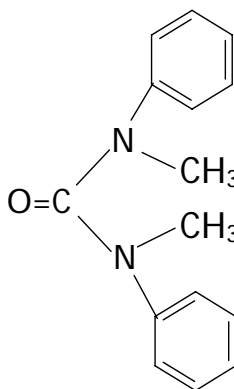
EC, Centralite I



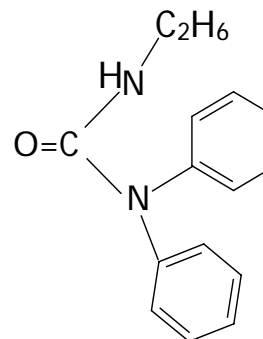
Ak II, Akardite II



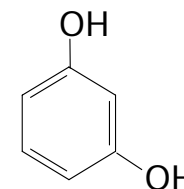
MNA, pNMA



MC, Centralite II



Ak III, Akardite III



Resorcinol

STANAGs for assessment of chemical stability / ageing using stabilizer consumption

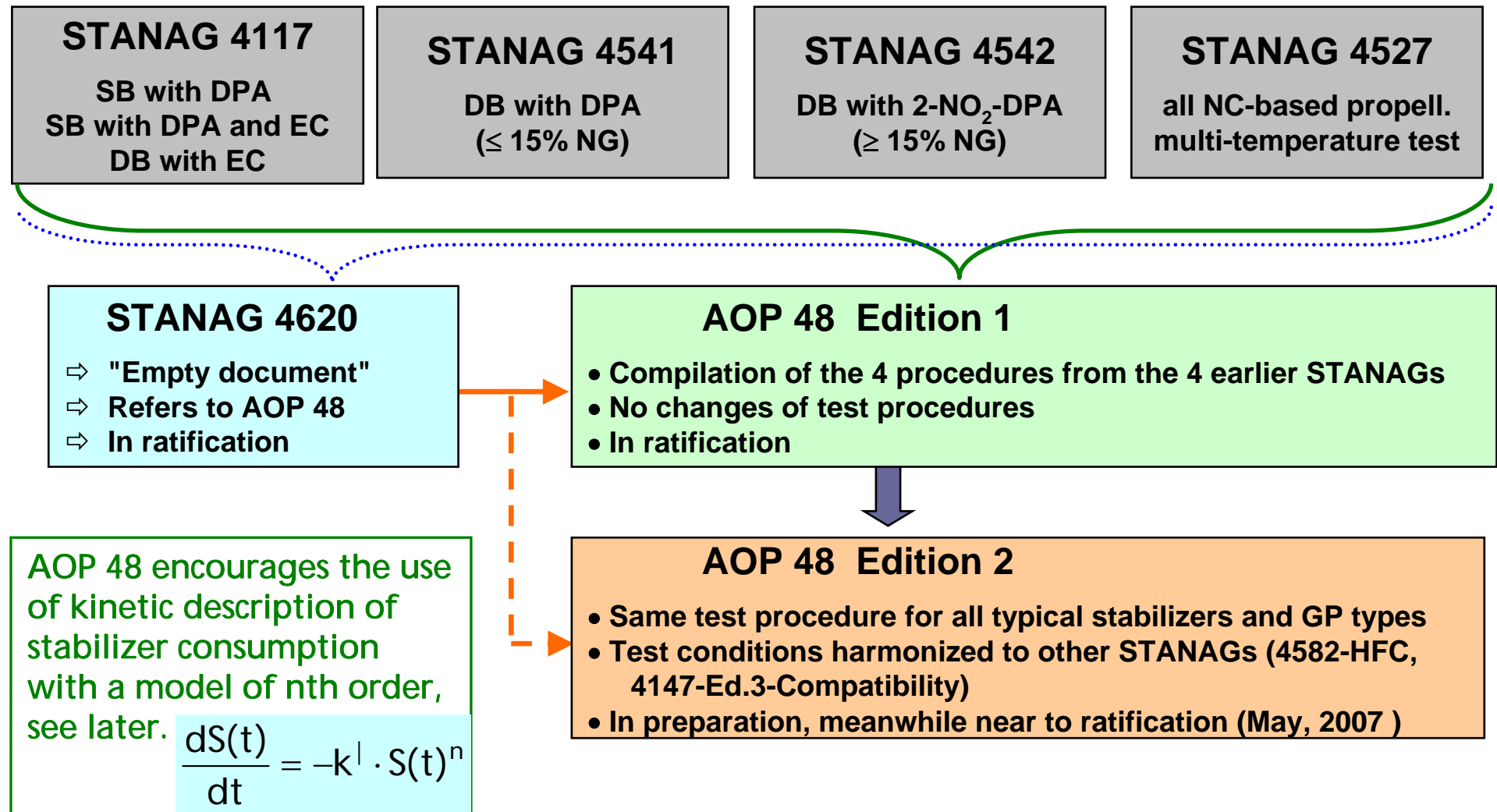
STANAG 4117 SB with DPA SB with DPA and EC DB with EC	STANAG 4541 DB with DPA only ($\leq 15\%$ NG)	STANAG 4542 DB with 2-NO ₂ -DPA ($\geq 15\%$ NG)	STANAG 4527 all NC-based propellants multi-temperature test
60 days at 65.5°C or 120 days at 65.5°C	60 days at 60°C	35 days at 60°C	40 – 90°C
120 d: DPA _{eff} ≥ 0.3 mass-% abs. decr. ≤ 0.5 mass% 120 d: EC ≥ 0.3 mass-% rel. decrease $\leq 50\%$	DPA _{eff} ≥ 0.5 mass-%; rel. decrease $\leq 50\%$	2-NO ₂ -DPA ≥ 0.2 mass-% abs. decr. ≤ 0.5 mass-%	<ul style="list-style-type: none">• Kinetic modelling with 0th or 1st order• Arrhenius parameter• definition of evaluation is incomplete

- Existing standards use different test conditions, the reason is their historical development
it seems today not justified to define different test criteria as it was done in former times
each NC-based propellant should be assessed in the same way.

But: there exist different ranges of stability with different type of propellants !!

- Not all propellants are covered by these STANAGs named above
- Kinetic analysis and calculation of chemically determined safe time period is defined not precise enough
- **Therefore: a unification was developed with AOP 48 Edition 2 which will replace all these STANAGs**

Standards to assess chemically determined use time with stabilizer consumption



Modelling of stabilizer consumption



Benefits of modelling the ageing

See /6/

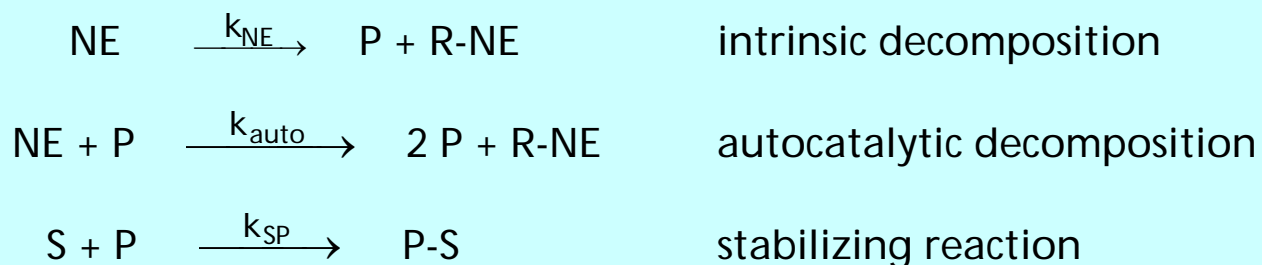
- minimize the risk of a mis-evaluation
- increase the reliability of the prediction of the ageing effects by a better description of the measured data and by an inherently correct extrapolation along the time axis
- recognize a faulty measuring arrangement if the measured data are not conform to the model
- identify a faulty production of a GP or RP
- support the find out of ageing reactions or ageing processes
- support the find out of measures against the effects of ageing processes
- support the planning and the realization of the acquisition of experimental data and of the procurement of substance data to assess ageing and safety
- support the decision about the employability of energetic components and of formulations
- **full use of the service time capacity of a GP or RP**



Kinetic description of stabilizer consumption - principles

Facts on stabilizer consumption, presented in way of reaction scheme /6,14/

Reaction scheme



a good stabilizer suppresses the autocatalytic decomposition of nitrate ester NE by catching product P

A correct description of stabilizer depletion needs at least two reaction rate constants:

k_{NE} for NE decomposition

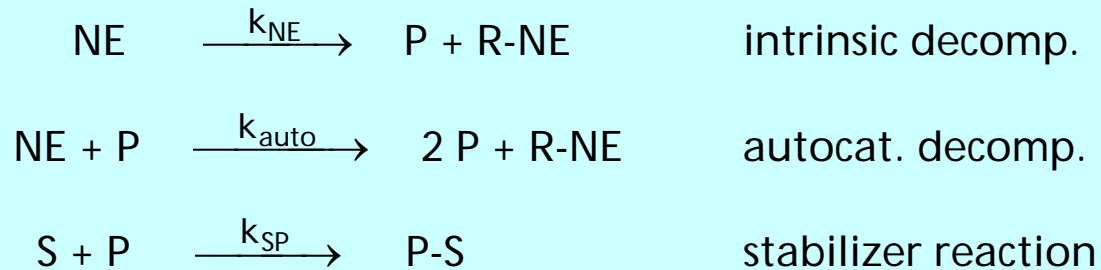
k_{SP} for the stabilizer reaction: P reacts with S

Kinetic description of consumption of the primary stabilizer S – reaction scheme I

/7,11, 14/

Primary stabilizer is the stabilizer added at production

reaction scheme RS I



$$\begin{aligned} \frac{d\text{NE}(t)}{dt} &= -k_{\text{NE}} \cdot \text{NE}(t) - k_{\text{auto}} \cdot \text{NE}(t) \cdot \text{P}(t) \\ \frac{d\text{P}(t)}{dt} &= +k_{\text{NE}} \cdot \text{NE}(t) + k_{\text{auto}} \cdot \text{NE}(t) \cdot \text{P}(t) - k_{\text{SP}} \cdot \text{P}(t) \cdot \text{S}(t) \\ \frac{d\text{S}(t)}{dt} &= -k_{\text{SP}} \cdot \text{P}(t) \cdot \text{S}(t) \end{aligned}$$

System of DEq for the above reaction scheme

This DEq system is very probably not solvable analytically in closed form.

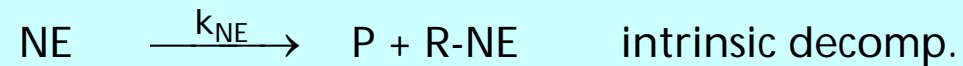
It is integrated and iterated numerically to determine the values of the three rate constants.

Kinetic description of consumption of the **primary** stabilizer S – RS II

Approximation:

stabilizer S suppresses the autocatalytic decomposition and the corresponding reaction can be deployed

reaction scheme RS II



Primary stabilizer is the stabilizer added at production

Corresponding differential equation system

$$(1) \quad \frac{d\text{NE}(t)}{dt} = -k_{\text{NE}} \cdot \text{NE}(t)$$

$$(2) \quad \frac{d\text{P}(t)}{dt} = k_{\text{NE}} \cdot \text{NE}(t) - k_{\text{SP}} \cdot \text{S}(t) \cdot \text{P}(t)$$

$$(3) \quad \frac{d\text{S}(t)}{dt} = -k_{\text{SP}} \cdot \text{S}(t) \cdot \text{P}(t)$$

Kinetic description of consumption of the **primary** stabilizer S – RS II

Simplified solution of DEq system of reaction scheme RS

$$(1) \frac{dNE(t)}{dt} = -k_{NE} \cdot NE(t)$$

$$(2) \frac{dP(t)}{dt} = k_{NE} \cdot NE(t) - k_{SP} \cdot S(t) \cdot P(t)$$

$$(3) \frac{dS(t)}{dt} = -k_{SP} \cdot S(t) \cdot P(t)$$

Assumption: $P(t)$ is constant, $P(t) = P_c$; this holds at the beginning of stabilizer consumption

$$\frac{dS(t)}{dt} = -k'_{SP} \cdot S(t) \quad \text{with } k'_{SP} = k_{SP} \cdot P_c$$

$$S(t) = S(0) \cdot \exp(-k'_{SP} \cdot t)$$

Stabilizer is consumed according to reaction of first order
means exponential decrease of stabilizer consumption

Further simplification:

for short times the first order reaction can be approximated by zero order reaction

$$S(t) = S(0) \cdot (1 - k'_{SP} \cdot t)$$

Linear decrease of stabilizer concentration, but only at the very beginning

Kinetic description of consumption of the primary stabilizer S – RS II

Way of solution of not simplifying the DEq system, means with P(t) not assumed as constant – it results in just one differential equation for the stabilizer decrease /7/

$$(1) \quad \frac{dNE(t)}{dt} = -k_{NE} \cdot NE(t)$$

$$(2) \quad \frac{dP(t)}{dt} = k_{NE} \cdot NE(t) - k_{SP} \cdot S(t) \cdot P(t)$$

$$(3) \quad \frac{dS(t)}{dt} = -k_{SP} \cdot S(t) \cdot P(t)$$

the expression for P(t) from the right is inserted in eq.(3) of DEq-system. This results in an expression containing only S(t)

$$\frac{dS(t)}{dt} = -k_{SP} \cdot S(t) \cdot \left(S(t) + C - NE(0) \cdot e^{-k_{NE} \cdot t} \right)$$

eq.(1) has the solution :

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

eq.(2) and eq.(3) give :

$$\frac{dP(t)}{dt} - \frac{dS(t)}{dt} = k_{NE} \cdot NE(t) = k_{NE} \cdot NE(0) \cdot e^{-k_{NE} \cdot t}$$

with the solution :

$$P(t) - S(t) = C - NE(0) \cdot e^{-k_{NE} \cdot t}$$

and C is the integration constant :

$$C = NE(0) + P(0) - S(0)$$

NE(0): initial conc. of nitrate ester

P(0): initial conc. of product P

S(0): initial conc. of stabilizer S

Kinetic description of consumption of the primary stabilizer S – RS II

Way of solution of the single differential equation for stabilizer decrease

- $C \cong NE(0)$
- $NE(0) \cdot \exp(-k_{NE} \cdot t) \cong NE(0) \cdot (1 - k_{NE} \cdot t)$

Introducing reasonable approximations
C is dominated by NE(0)
the exponential can be well approximated by
Taylor series up to second term

$$\frac{dS(t)}{dt} \approx -k_{SP} \cdot S(t) \cdot (S(t) + NE(0) \cdot k_{NE} \cdot t)$$

Resulting rate equation for S

$$S(t) = \frac{\sqrt{\exp(-NE(0) \cdot k_{NE} \cdot k_{SP} \cdot t^2)}}{\frac{1}{S(0)} + \sqrt{\frac{\pi}{2} \cdot \frac{k_{SP}}{NE(0) \cdot k_{NE}}} \cdot \operatorname{erf}\left(\sqrt{\frac{NE(0) \cdot k_{NE} \cdot k_{SP}}{2}} \cdot t\right)}$$

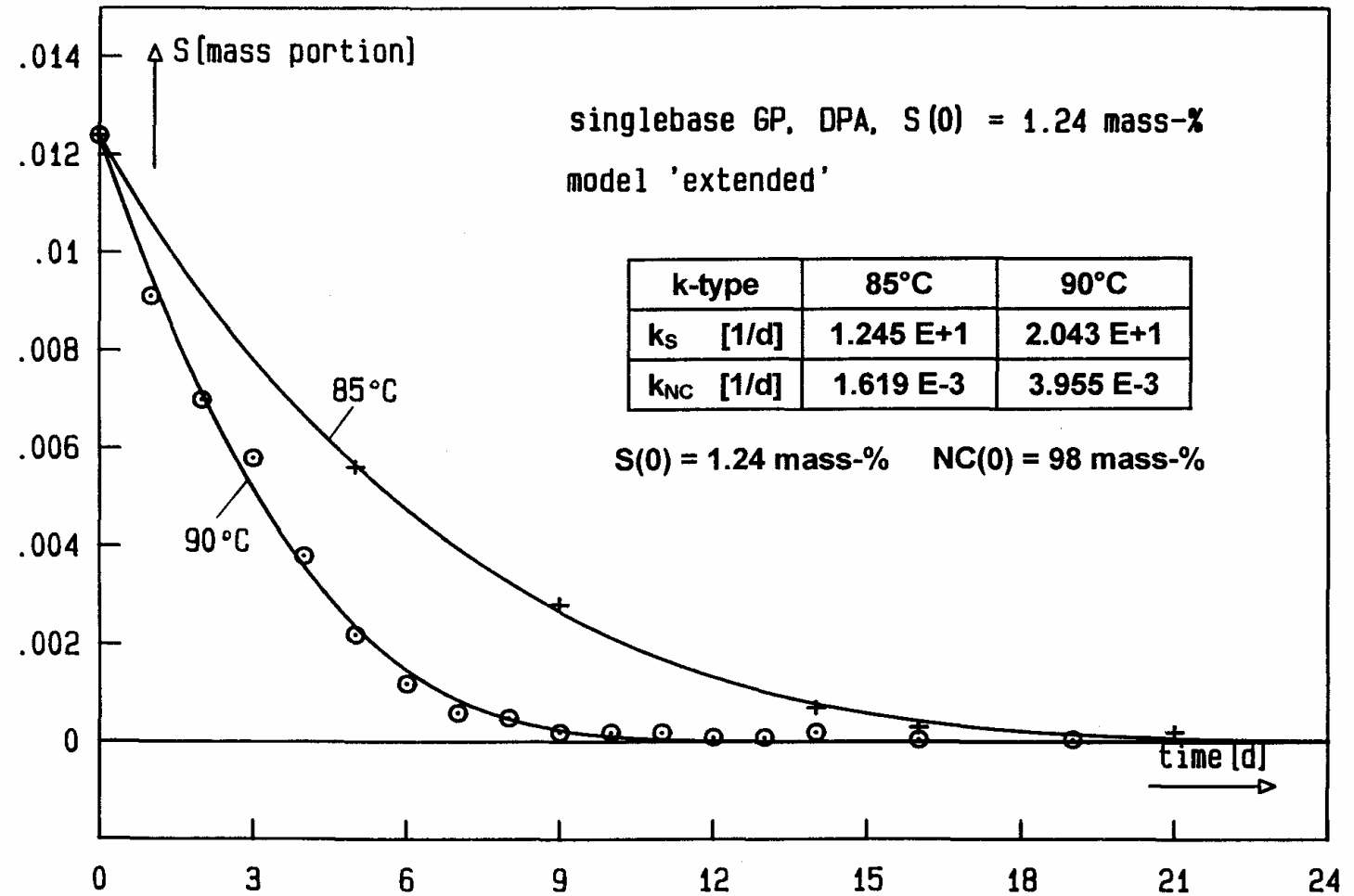
Integrated rate equation

This is a kinetically correct description of stabilizer depletion, because two reaction steps are involved - decomposition of NC and stabilizer reaction - so two reaction rate constants must appear in the description.

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \cdot \left(z - \frac{z^3}{1! \cdot 3} + \frac{z^5}{2! \cdot 5} - \frac{z^7}{3! \cdot 7} + \frac{z^9}{4! \cdot 9} - \dots + \dots \right) \quad \text{for } |z| < \infty; \quad \operatorname{erf}(0) = 0$$

Modelling with RS II, model 'S: extended'

Good description of the data of DPA consumption in a single base propellant with model 'S: extended'



Model 'S: exponential + linear' part 1 of 2 see /8/

Reactions of first order or zero order alone cannot give satisfying descriptions of stabilizer decrease. To achieve at a better description the combination was tried.

Combination of the reactions of first and zero order

$$\left(\frac{dS(t, T)}{dt} \right) \Big|_T = -k_1(T) \cdot S(t, T) - k_0(T)$$

$$k_1(T) = Z_1 \cdot \exp(-E_{a1} / RT)$$
$$k_0(T) = Z_0 \cdot \exp(-E_{a0} / RT)$$

Arrhenius behaviour

Integrated rate equation

$$S(t, T) = \left(S(0) + \frac{k_0(T)}{k_1(T)} \right) \cdot \exp(-k_1(T) \cdot t) - \frac{k_0(T)}{k_1(T)}$$

Model 'S: exponential + linear' part 2 of 2

Calculation of service times $ty_s(T)$

Definition of degree of stabilizer consumption

$$y_s = \frac{S(t, T)}{S(0)} \quad \text{therewith the times } ty_s(T) \text{ to reach } y_s \text{ can be calculated}$$

$$ty_s(T) = \frac{1}{k_1(T)} \cdot \ln \left(\frac{1 + \frac{k_0(T)}{S(0) \cdot k_1(T)}}{y_s + \frac{k_0(T)}{S(0) \cdot k_1(T)}} \right) \quad \text{times to reach } y_s \text{ these are the looked for usetimes}$$

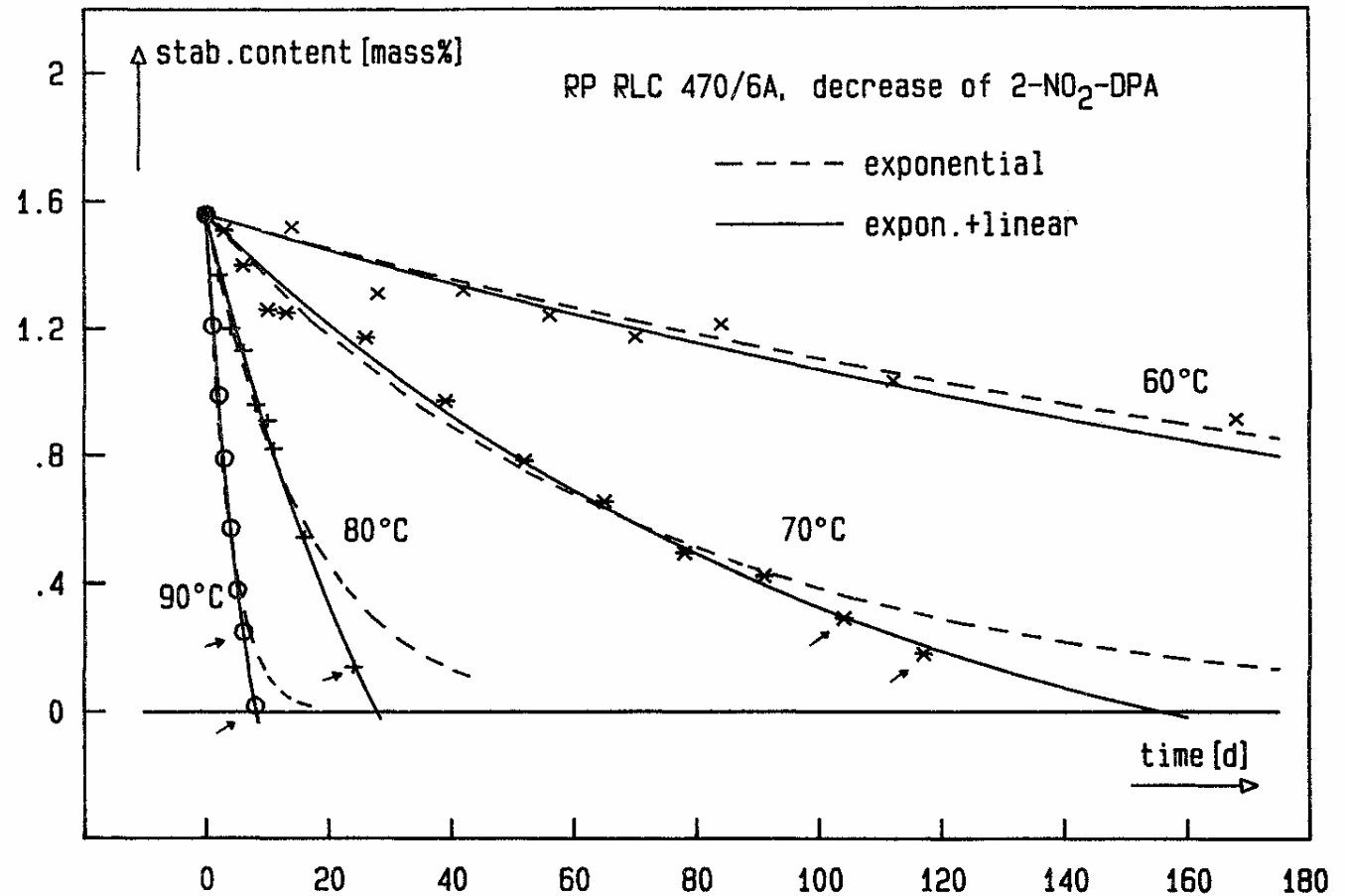
$$t_0(T) = \frac{1}{k_1(T)} \cdot \ln \left(\frac{S(0) \cdot k_1(T)}{k_0(T)} + 1 \right) \quad \text{times to reach } y_s = 0$$

the model has a good extrapolation ability

Stabilizer consumption: decrease of 2-nitro-DPA in a RP

description with
model 'S: expon. +
linear' in comparison
with description
according to first
order reaction

Data points marked
with arrows must have
been omitted with first
order reaction (model
'S: exponential') to
achieve acceptable
description at the
beginning, but not
with the model
'S: exponential + linear'



Model 'S: exponential + linear' for stabilizer consumption - extrapolation ability

Extrapolation ability of model 'S: exponential + linear'

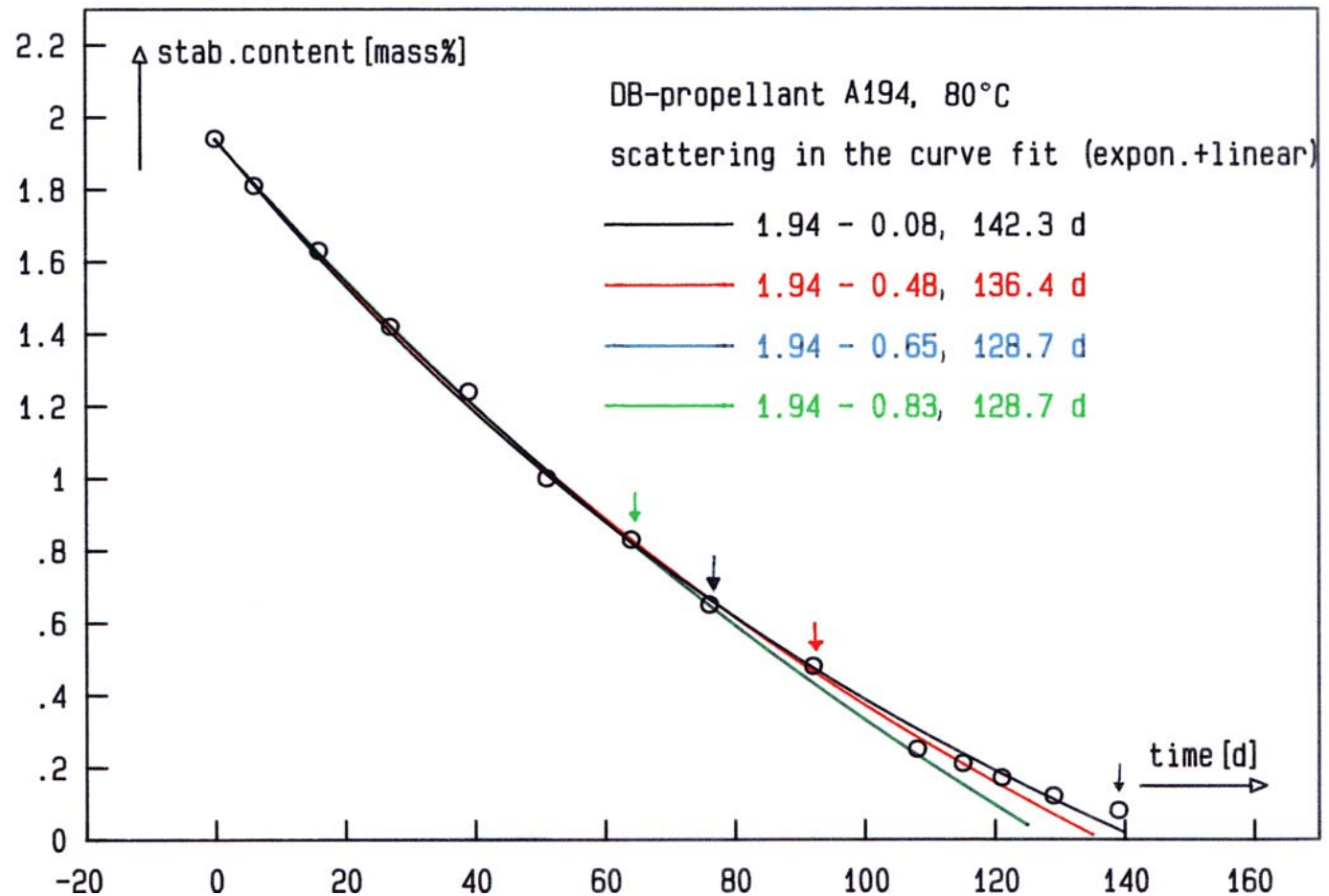
Black line: all points have been used

Red line: points up to red arrow have been used

Blue line: points up to blue arrow have been used

Green line: points up to green arrow have been used

The resulting scattering is within narrow range



Models to describe stabilizer consumption

Eq.	kinetic rate equation	kinetic type	name of model suitability, how to handle
1	$\frac{dS(t)}{dt} = -k_1 \cdot S(t) - k_0$	first + zero order, two reactions	'S: exponential + linear' /8/ very suitable, easy to handle
2	$\frac{dS(t)}{dt} = -k_1 \cdot S(t)$	first order, one reaction	'S: exponential' not suitable, easy to handle
3	$\frac{dS(t)}{dt} = -k_0$	zero order, one reaction	'S: linear' conditioned suitable, easy to handle
4	$\frac{dS(t)}{dt} = -k^I \cdot S(t)^n$	nth order, one reaction	'S: nth order' (AOP 48 model) well suitable, easy to handle
5	$\frac{dS(t)}{dt} = -k_{SP} \cdot S(t) \cdot (S(t) + NE(0) \cdot k_{NE} \cdot t)$	two reactions, NE decomp. and consump. of S	'S: extended' /7, 14/ suitable, to handle with advanced fit codes (Origin™, Origin Lab Corp.)

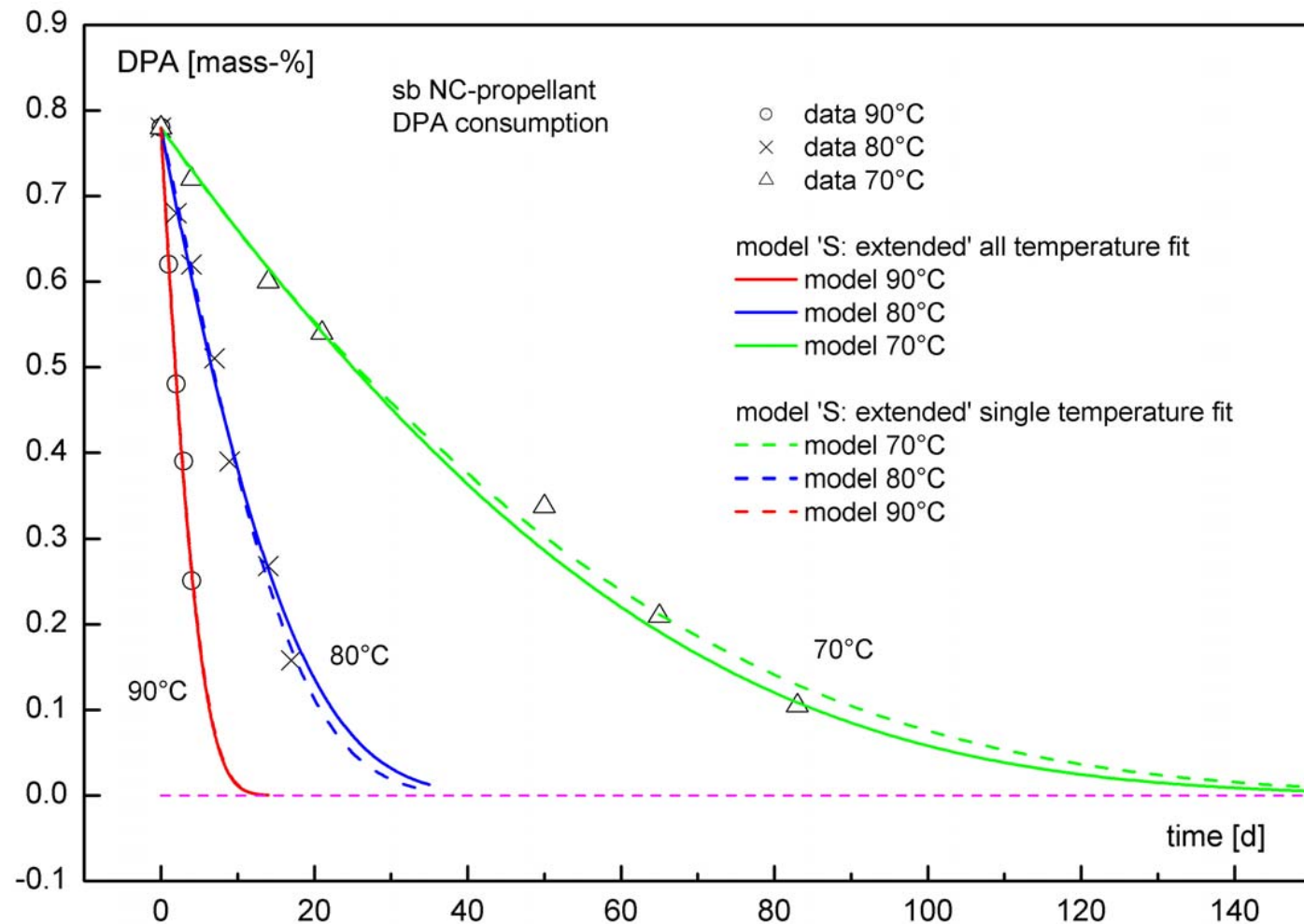
Models to describe stabilizer consumption – integrated expressions

Eq.	equation	time t_0 to $y_s = S(t)/S(0) = 0$	name of model suitability, how to handle
1	$S(t, T) = \left(S(0) + \frac{k_0(T)}{k_1(T)} \right) \cdot \exp(-k_1(T) \cdot t) - \frac{k_0(T)}{k_1(T)}$	$t_0(T) = \frac{1}{k_1(T)} \cdot \ln \left(\frac{S(0) \cdot k_1(T)}{k_0(T)} + 1 \right)$	'S: exponential + linear' /8/ suitable, easy to handle
2	$S(t, T) = S(0) \cdot \exp(-k_1(T) \cdot t)$	$t_0(T) \rightarrow \infty$	'S: exponential' not suitable, easy to handle
3	$S(t, T) = S(0) - k_0(T) \cdot t$	$t_0(T) = \frac{S(0)}{k_0(T)}$	'S: linear' conditioned suitable, easy to handle
4	$S(t, T) = S(0) \cdot [1 - (1 - n) \cdot k(T) \cdot t]^{\left(\frac{1}{1-n}\right)}$ with $k(T) = \frac{k^I(T)}{S(0)^{1-n}}$	$t_0(T) = \frac{1}{k(T)} \left(\frac{1}{1-n} \right)$ only for $n < 1$	'S: nth order' suitable, easy to handle
5	$S(t) = \frac{\sqrt{\exp(-NE(0) \cdot k_{NE} \cdot k_{SP} \cdot t^2)}}{\frac{1}{S(0)} + \sqrt{\frac{\pi}{2} \cdot \frac{k_{SP}}{NE(0) \cdot k_{NE}} \cdot \operatorname{erf}\left(\sqrt{\frac{NE(0) \cdot k_{NE} \cdot k_{SP}}{2}} \cdot t\right)}}$	$t_0(T) \rightarrow \infty$	'S: extended' /7, 14/ suitable, fairly to handle with advanced fit codes

Description of stabilizer consumption with model 'S: extended' comparison of single temp. fit (sT) and all temp. fit (aT)

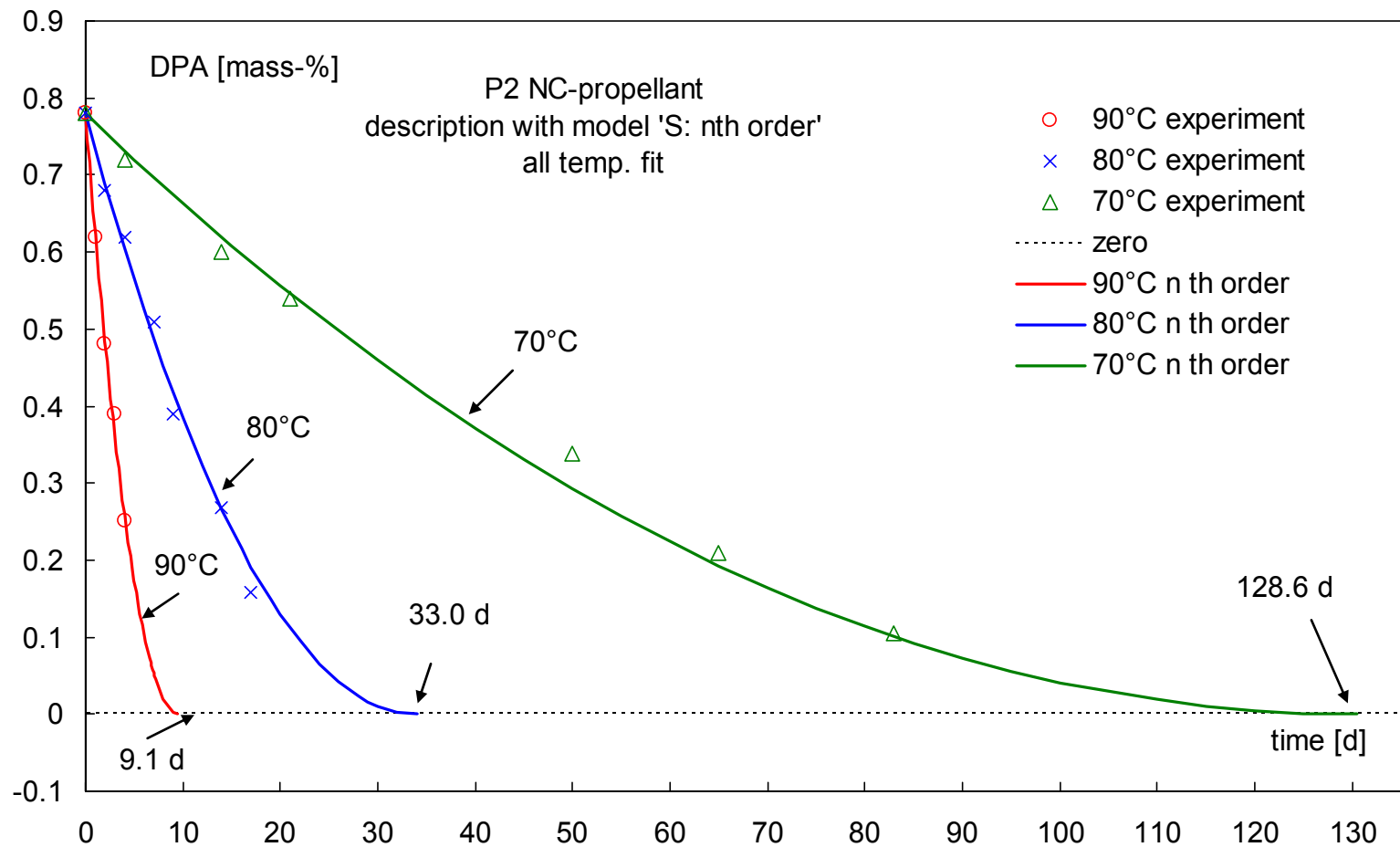
Model 'S: extended'
can describe
pronounced tailing
sometimes found

Data of stabilizer
consumption of
propellant P2
determined in
1987/1988 after
accelerated ageing
at 70°C, 80°C and
90°C.

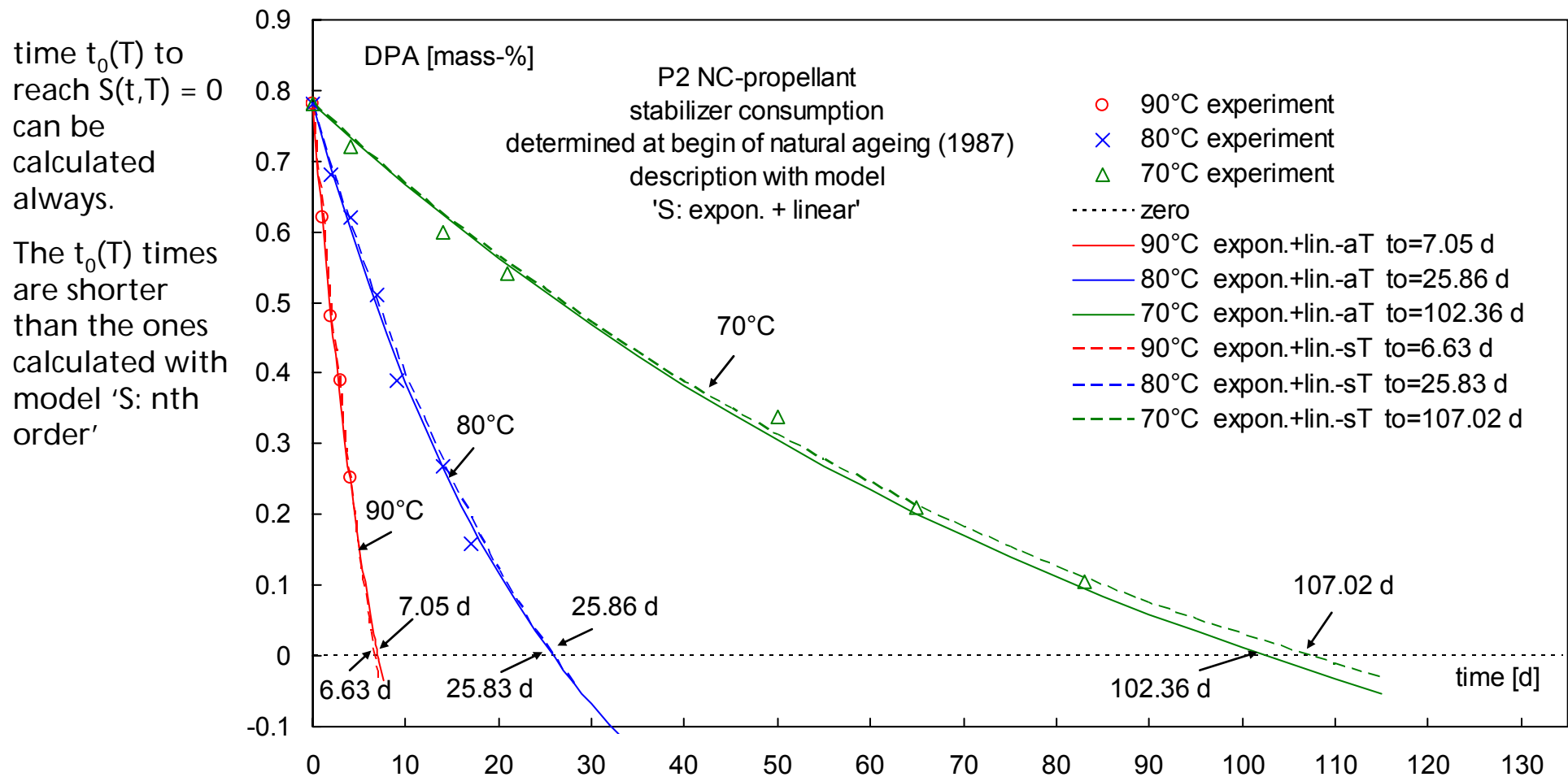


Description of stabilizer consumption with model 'S: nth order' (AOP 48 Ed. 2 model) - only all temperature (aT) fit is shown

Because the reaction order n is <1 , the times $t_0(T)$ to reach $S(t,T) = 0$ can be calculated



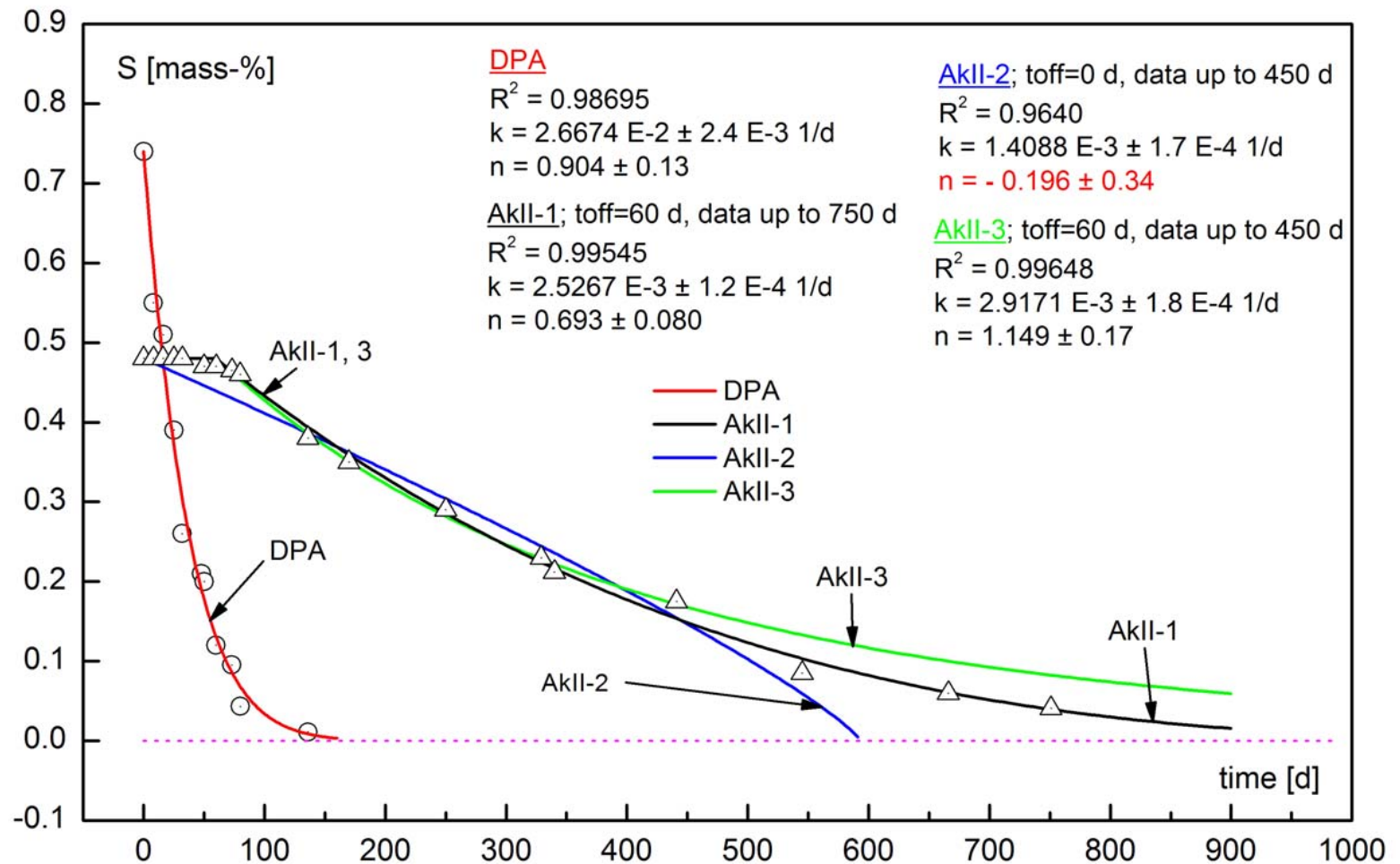
Description of stabilizer consumption with model 'S: exponential + linear' comparison of 'single temperature fit' (sT) and 'all temperature fit' (aT)



Model 'S: nth order' (AOP 48 model) application with two stabilizers of different reactivity

Model 'S: nth order' can cause artificial shapes of stabilizer decrease curves

A bend upwards with $n < 0$ is not reasonable for stabilizer consumption, as shown with the blue curve in figure on the right.

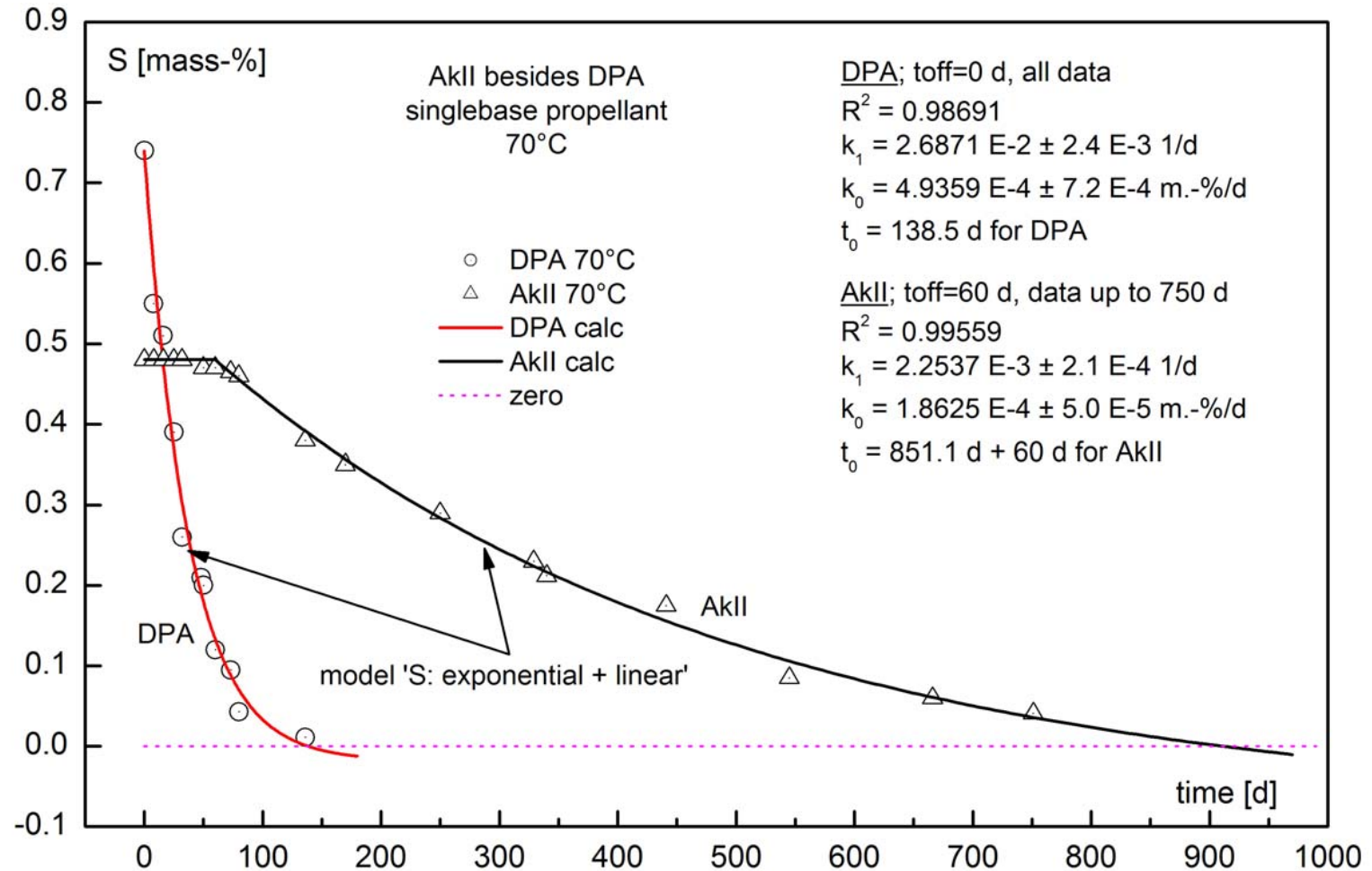


Model 'S: exponential + linear' application with two stabilizers of different reactivity

All models must be applied in two steps, each stabilizer is described separately

DPA is much more reactive than Ak II.

As long as DPA is active Ak II is not changed in concentration

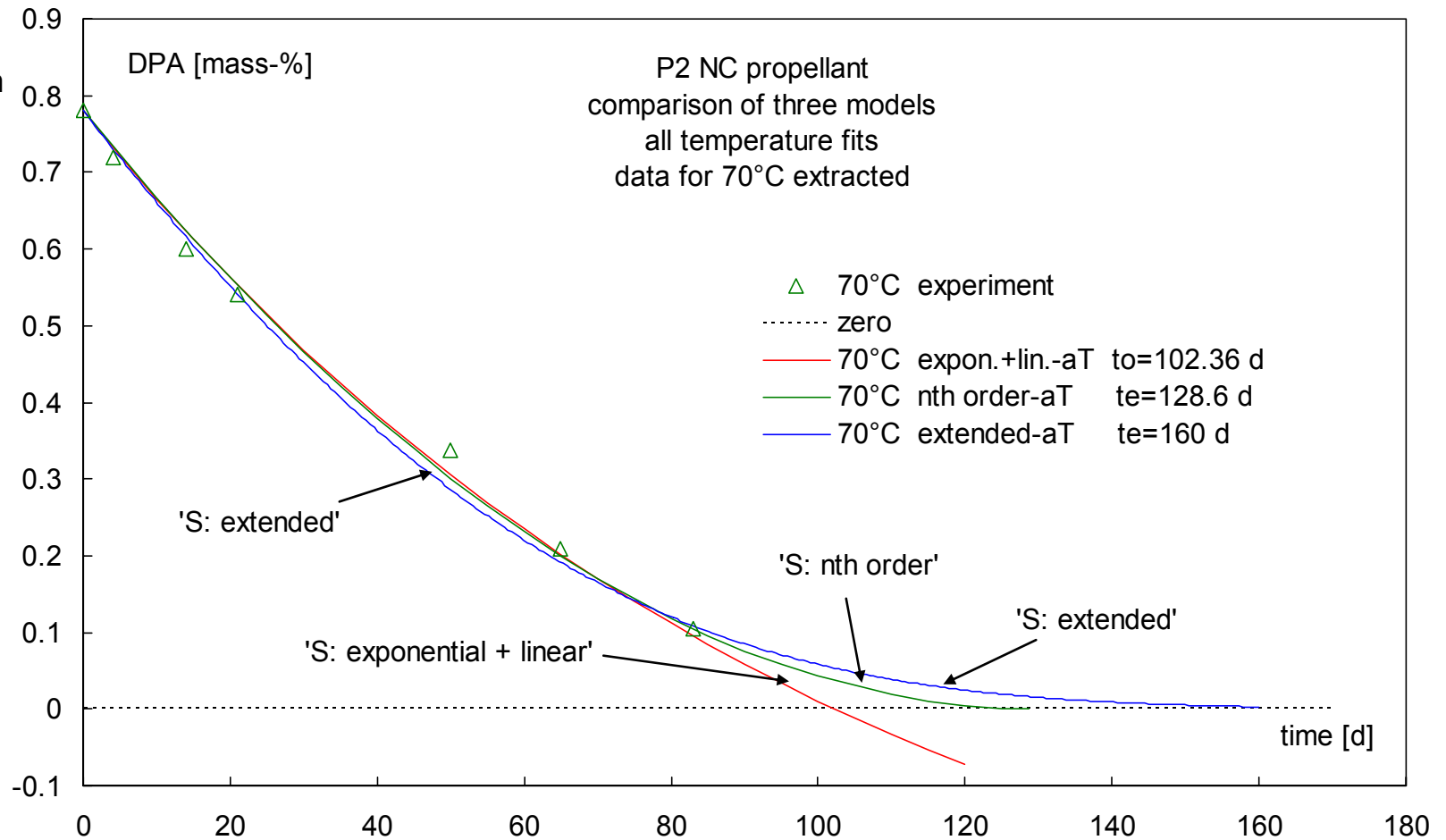


Comparison of models: because of conservative character in extrapolation model 'S: exponential + linear' is taken for evaluation

The times $t_0(T)$ are shortest with model 'S: exponential + linear'

The tailing of model 'S: nth order' is already too strong to include the stabilizer decrease up to zero content in the calculations with profiles

Note: AOP 48, Ed 2 recommends not to use model 'S: nth order' at $S(t)$ below 20% of $S(0)$



Prediction of a real ageing over 16 years of a singlebase propellant used in automotive seat belt restraint systems

See also /9,10/

What is needed for this task:

- The representative time-temperature profile (usually compiled for one year) at ageing site (best would be continuous measurements of the temperature course)
- Accelerated ageing of propellant sample to parameterize its stabilizer decrease
- A model description of the stabilizer consumption which follows it up to zero content of primary (means added at the production) stabilizer
- The Arrhenius parameters for the stabilizer decrease obtained with the model description
- Application of the model description with the time-temperature profile data
- Measurements on stabilizer consumption during the course of real ageing of the propellant



Arrhenius parameters obtained with model for stabilizer consumption
'all temperature fit' – propellant P2, model 'S: exponential + linear'

model	S(0) [mass- %]	rate constant k_1		rate constant k_0	
		E_{a1} [kJ/mol]	$\lg(Z_1 [1/d])$	E_{a0} [kJ/mol]	$\lg(Z_0 [m.\%/d])$
all temp. fit	0.78	138.1	19.001	138.9	18.796
R^2 (from fit directly)		0.9935			

Data of stabilizer consumption of propellant P2 determined in 1987/1988 after accelerated ageing at 70°C, 80°C and 90°C.

Now after 19 years they are used to make the prediction for the real ageing result of propellant P2, which was aged in Florida over 16 years in set belt cartridges /10/

Experimental data on evolution of stabilizer concentrations

Concentrations of DPA and DPA consecutive products of single base P2 propellant in mass-% as function of ageing time at the test center in Miami /9,10/.

Stabilizer	ageing time at test center				
	base line	1 a	4 a	9 a	16 a
DPA	0.780	0.690	0.585	0.030	0.000
N-NO-DPA			0.135	0.370	0.110
2-Nitro-DPA		0.010	0.100	0.160	0.230
4-Nitro-DPA			0.020	0.170	0.300
2,4'-Dinitro-DPA					0.000
2,2'-Dinitro-DPA					0.030
2,4,4'-Trinitro-DPA					0.017

Introduction

Company TRW Alfdorf, Germany has arranged a long term natural ageing program with belt restraint units equipped with 'life' gas generator units of two types taken from the regular production /9,10/



The ageing started in October 1987 in a test center near Miami, Florida, USA. The restraint units have been mounted in such a way to simulate the situation in a car

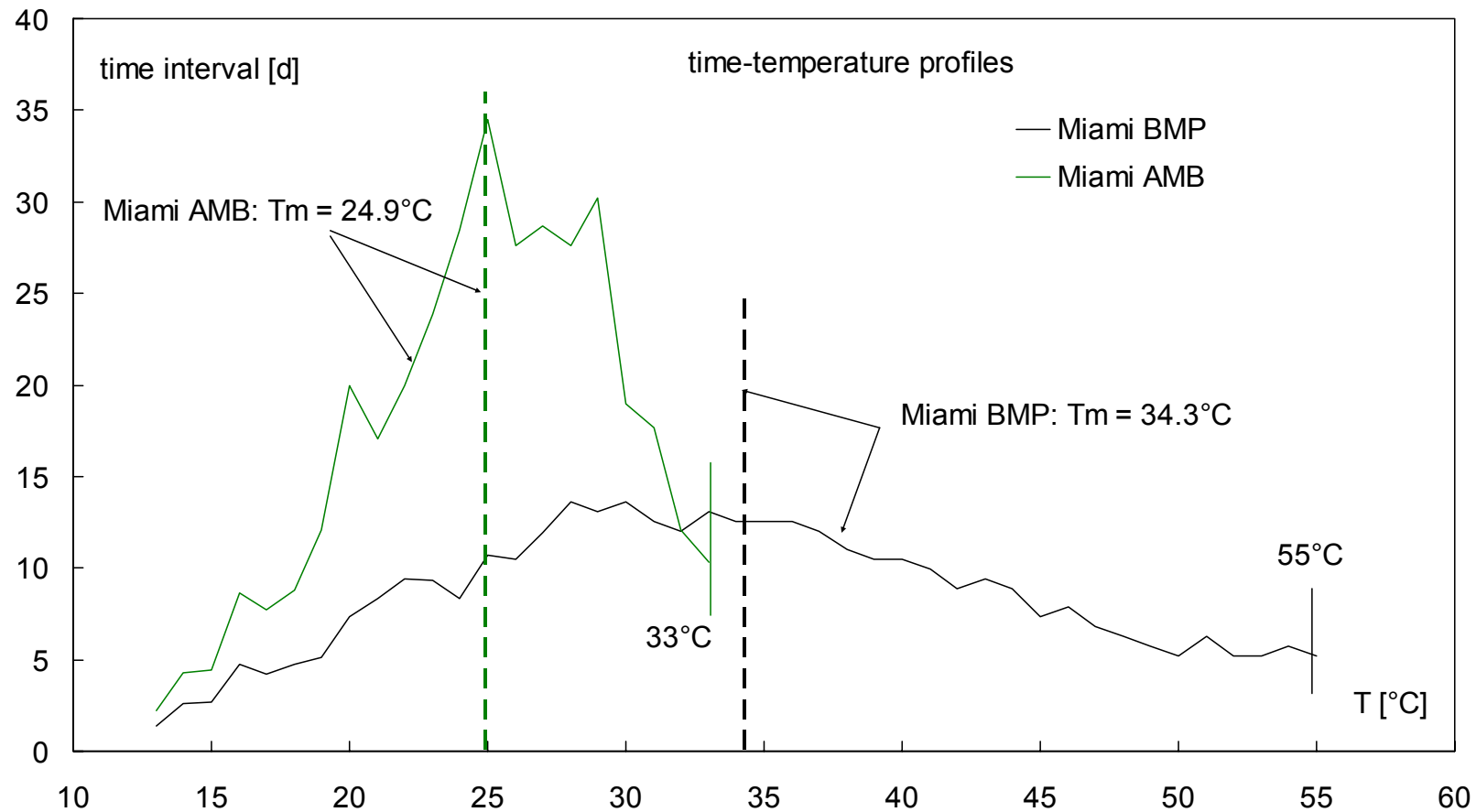
In regular intervals samples were taken out and investigated

- Pressure-time curves made by TRW
- Chemical ageing and stability tests made by ICT

The ageing ended in October 2003. An ageing time of 16 years was realized at ambient conditions.

But the propellants experienced elevated temperatures because of the housing of the belt restraint units

Time-temperature profiles for Miami, Florida, USA



Model 'S: exponential+ linear' for use with time-temperature profile data or continuous time-temperature measurements

$$S(\Delta t_i, T_i) = \left(S(\Delta t_{i-1}, T_{i-1}) + \frac{k_0(T_i)}{k_1(T_i)} \right) \cdot \exp(-k_1(T_i) \cdot \Delta t_i) - \frac{k_0(T_i)}{k_1(T_i)}$$

$i = 1, 2, 3 \dots n$ number of profile section i
 $S(\Delta t_{i-1}, T_{i-1})$ for $j=1$ and $i=1$ $S(\Delta t_{i-1}, T_{i-1}) = S(0)$
 for $j>1$ and $i=1$ the value of S after profile passing j
 is the start value for profile passing $j+1$
 Δt_i time interval of profile section i
 T_i temperature of profile section i
 j number of one full profile passing (profile cycle)

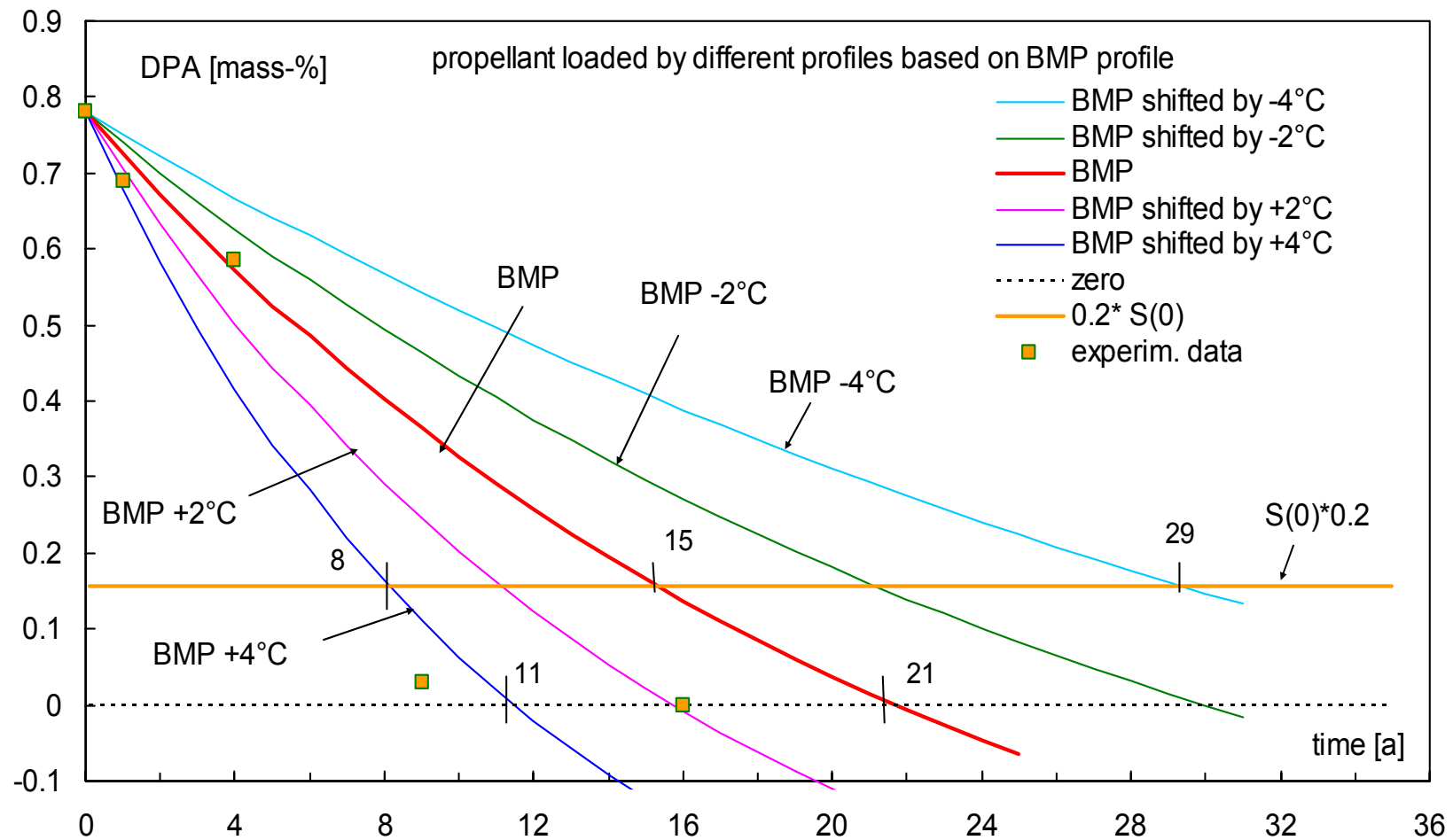
$$t \text{ (of one profile cycle)} = \sum_{i=1}^n \Delta t_i \quad \text{(with profile BMP it is one year)}$$

$$ty_s = j \cdot \sum_{i=1}^n \Delta t_i$$

With continuous temperature data (these have also time Δt_i at T_i until next T_{i+1}) this same procedure is taken



Prediction of stabilizer consumption in GG-P2 according to BMP profile load and 4 loads with temperature-shifted BMP, model 'S: exponential + linear'



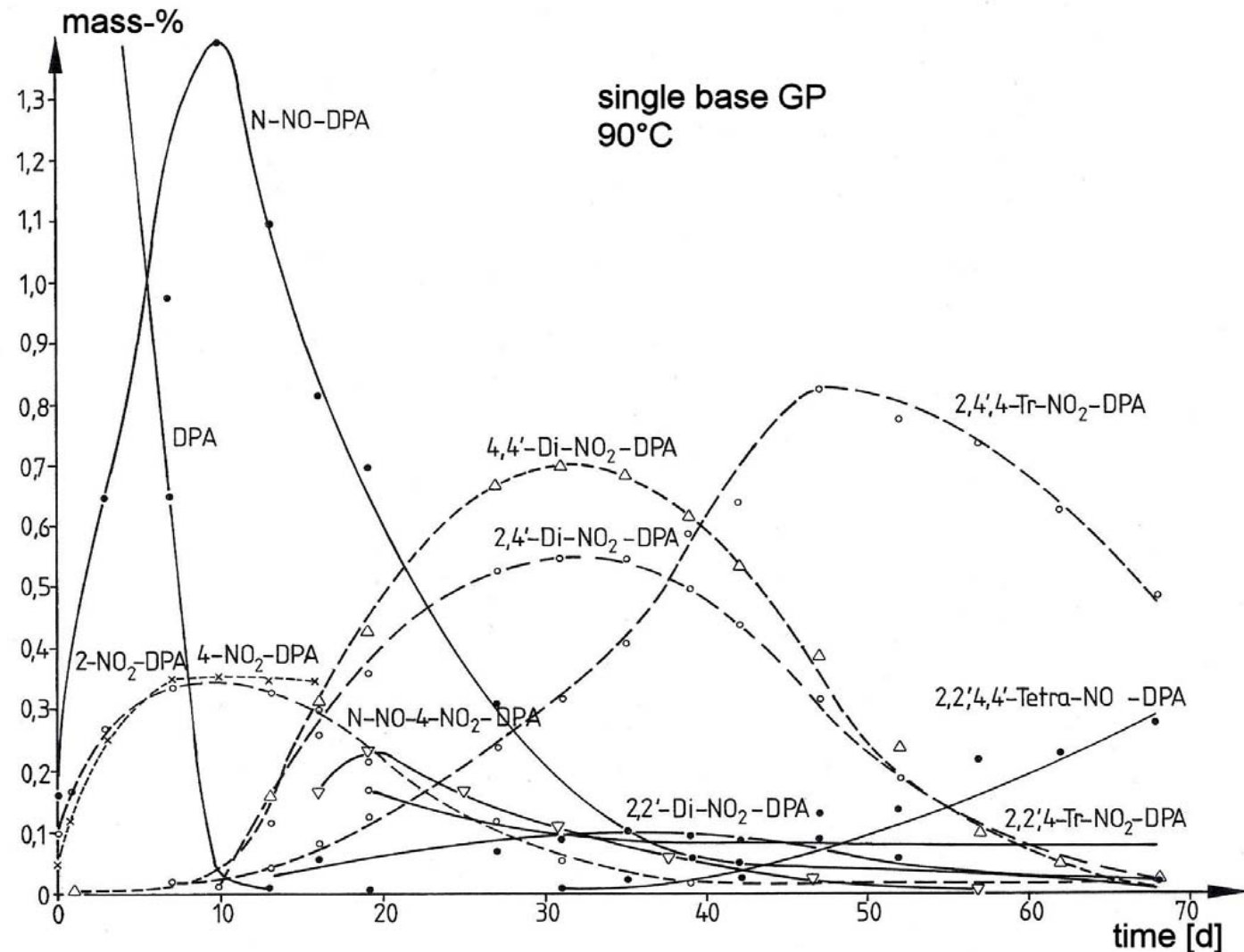
Modelling of stabilizer consumption and the course of consecutive products

See also
/7,11,12,13, 14/



How to handle the total stabilizing capability of a typical stabilizer

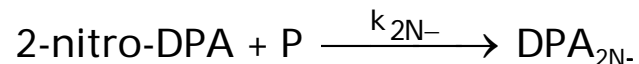
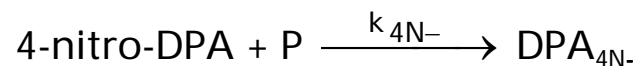
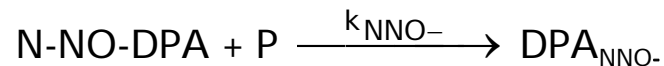
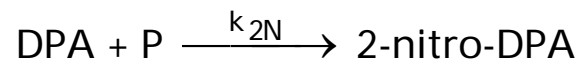
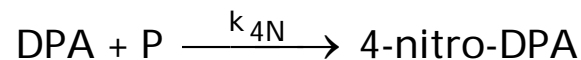
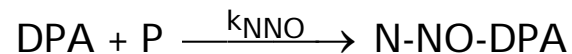
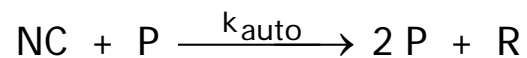
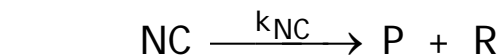
Determination of
DPA consumption
and the evolution
of consecutive
products of DPA
by Dr. Fred Volk
(about begin of the
1980s)



Modelling of stabilizer and its consecutive products – RS III

Reaction scheme for the course of DPA and its consecutive products up to the first nitration step / nitrosation step /7/

reaction scheme III (RS III)



$$\frac{dx_{\text{NC}}}{dt} = -k_{\text{NC}}x_{\text{NC}} - k_{\text{auto}}x_{\text{NC}}x_{\text{P}}$$

$$\begin{aligned} \frac{dx_{\text{P}}}{dt} = & k_{\text{NC}}x_{\text{NC}} + k_{\text{auto}}x_{\text{NC}}x_{\text{P}} + k_{\text{DPNNO}}x_{\text{NNO}} \\ & - (k_{\text{NNO}} + k_{4\text{N}} + k_{2\text{N}})x_{\text{P}}x_{\text{DPA}} \\ & - (k_{\text{NNO-}}x_{\text{NNO}} + k_{4\text{N-}}x_{4\text{N}} + k_{2\text{N-}}x_{2\text{N}})x_{\text{P}} \end{aligned}$$

$$\frac{dx_{\text{DPA}}}{dt} = k_{\text{DPNNO}}x_{\text{NNO}} - (k_{\text{NNO}} + k_{4\text{N}} + k_{2\text{N}})x_{\text{P}}x_{\text{DPA}}$$

$$\frac{dx_{\text{NNO}}}{dt} = k_{\text{NNO}}x_{\text{P}}x_{\text{DPA}} - k_{\text{NNO-}}x_{\text{P}}x_{\text{NNO}} - k_{\text{DPNNO}}x_{\text{NNO}}$$

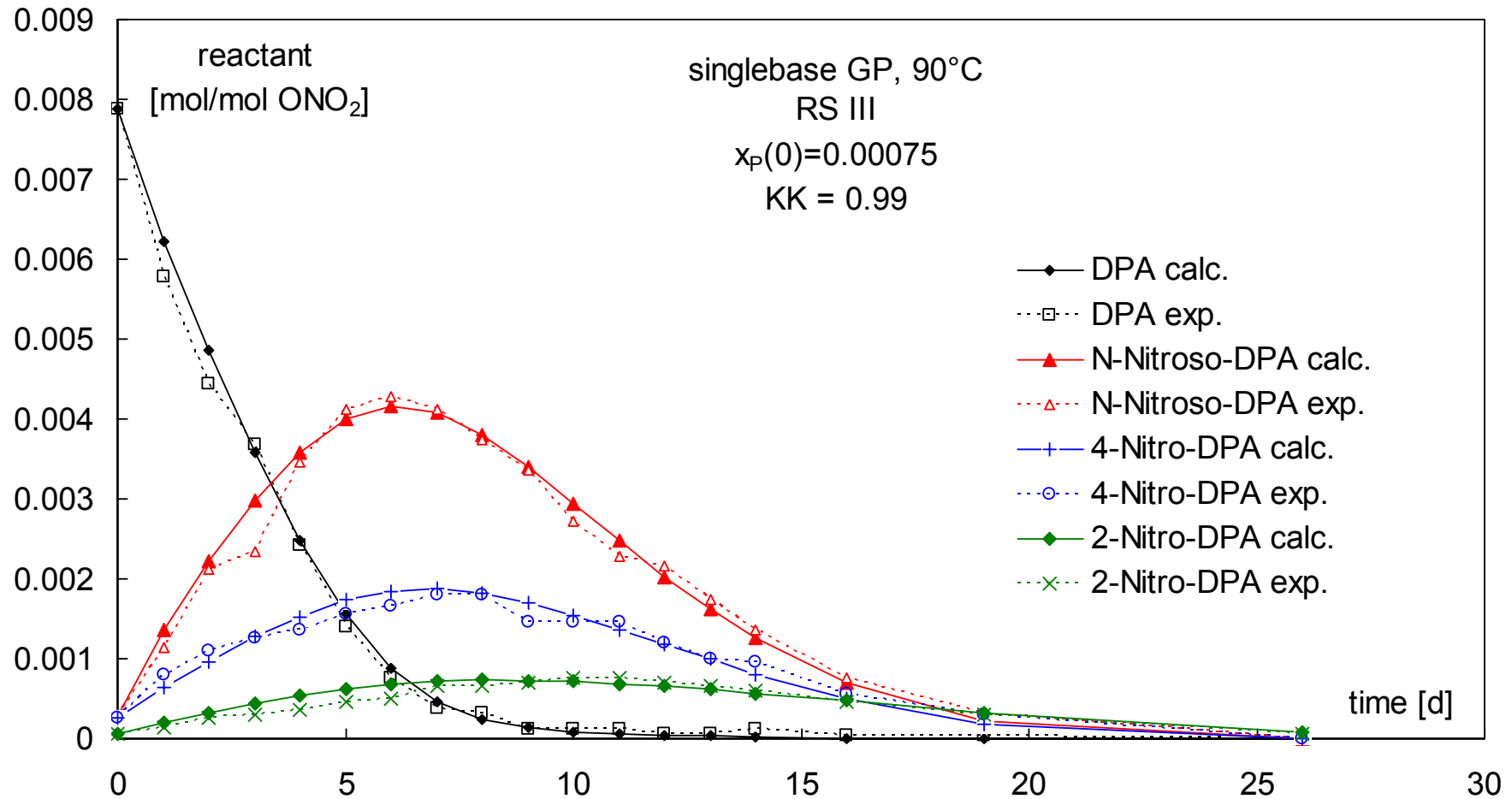
$$\frac{dx_{4\text{N}}}{dt} = k_{4\text{N}}x_{\text{P}}x_{\text{DPA}} - k_{4\text{N-}}x_{\text{P}}x_{4\text{N}}$$

$$\frac{dx_{2\text{N}}}{dt} = k_{2\text{N}}x_{\text{P}}x_{\text{DPA}} - k_{2\text{N-}}x_{\text{P}}x_{2\text{N}}$$

Modelling of stabilizer and its consecutive products - $P(t)$ is not constant.

RS III (continued) - with data newly measured from aged singlebase GP see /7/

Full lines: model description with the above reaction scheme
 Broken lines: connect the measured data for each of the four substances



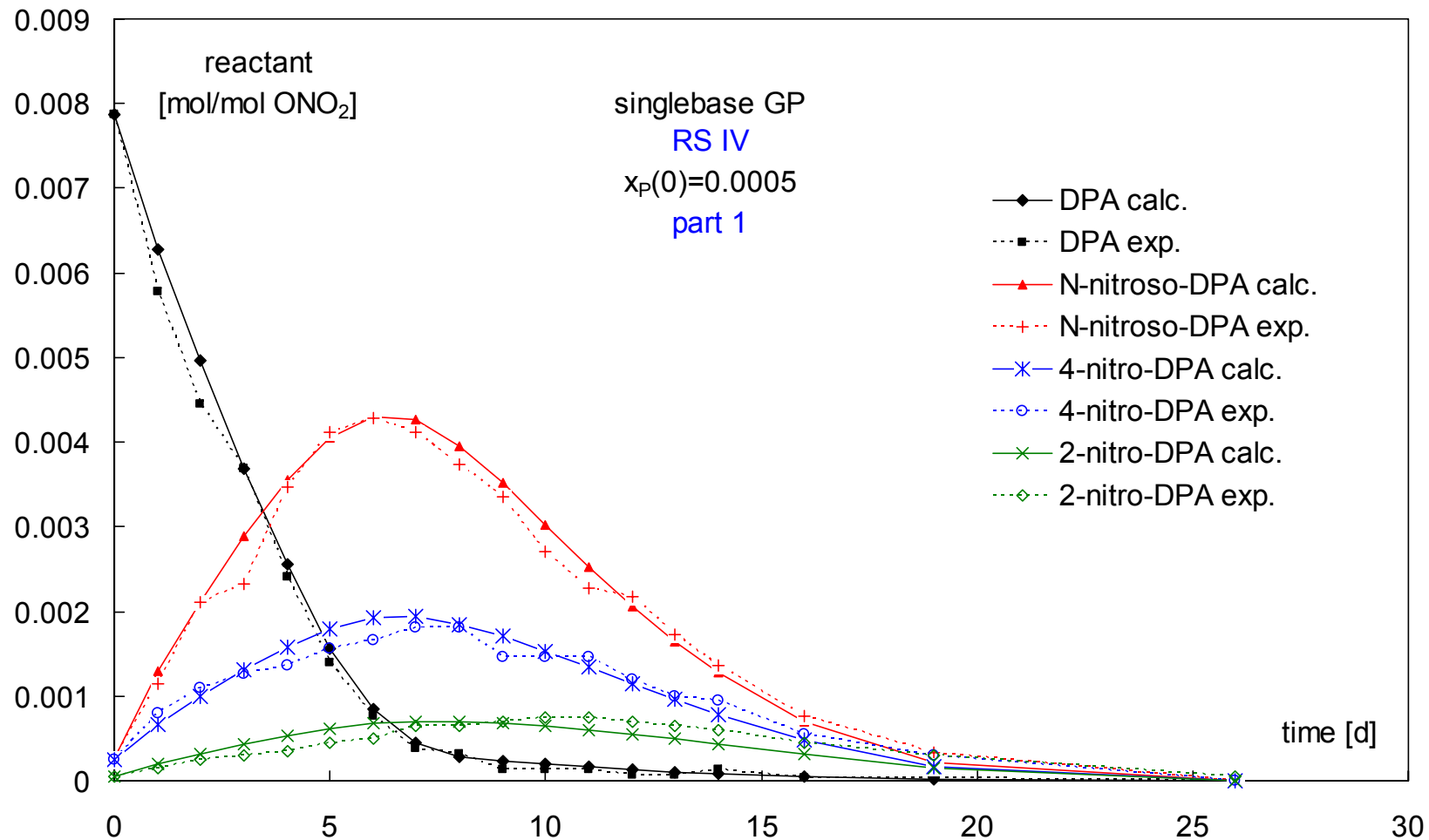
Stabilizer and its consecutive products, RS III (continued) – values of the rate constants obtained by the modelling

$k_{\text{auto}} = 10 k_{\text{NC}}$ and $k_{\text{DPNNO}} \neq 0$ (N-NO-DPA to DPA) all reaction rate constants in 1/d
temp. = 90°C, **different initial concentrations $x_p(0)$ for product P**

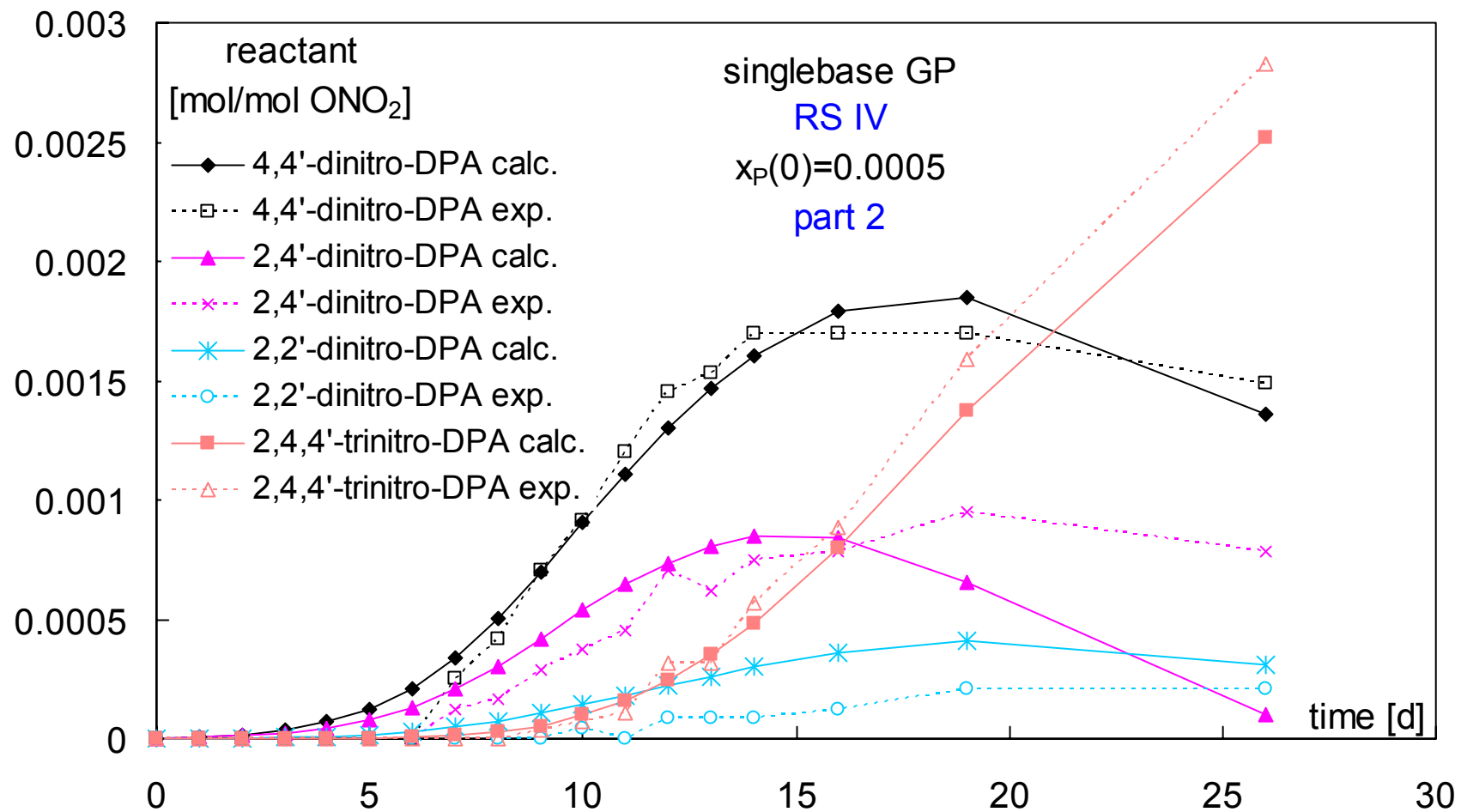
constant	$x_p(0)$ [mol/(mol ONO_2)]			$x_p(0)$ as fit paramet. 0.00128
	0.0	0.0005	0.00075	
k_{NC}	0.00173	0.00159	0.00155	0.00157
k_{NNO}	340.8	300.1	258.6	156.0
$k_{4\text{N}}$	104.3	98.3	88.9	57.9
$k_{2\text{N}}$	44.9	35.7	32.5	20.9
k_{DPNNO}	0.089	0.0718	0.0513	0.0135
$k_{\text{NNO-}}$	20.8	25.75	27.31	25.43
$k_{4\text{N-}}$	22.1	26.1	25.0	18.2
$k_{2\text{N-}}$	9.66	10.43	9.79	6.66
R^2				
st.dev.	2.07 E-4	1.67 E-4	1.56 E-4	1.50 E-4

Modelling of high nitrated DPA products, $P(t)$ is not constant – RS IV – part 1

Just for presentation, the result is shown in two figures. The first part looks like the result of RS III, but it is not. The modelling has included all products up to tri-nitrated species at once! /7/



Modelling of high nitrated DPA products, $P(t)$ is not constant – RS IV – part 2



Relative reactivities of consecutive products with regard to DPA

From the modelling of the consecutive products of DPA their relative reactivity with respect to DPA can be formulated [7].

The advantages

- determined [in a gun propellant matrix](#) (single base GP) at 90°C
- based on reaction kinetics, reaction with the autocatalytic product

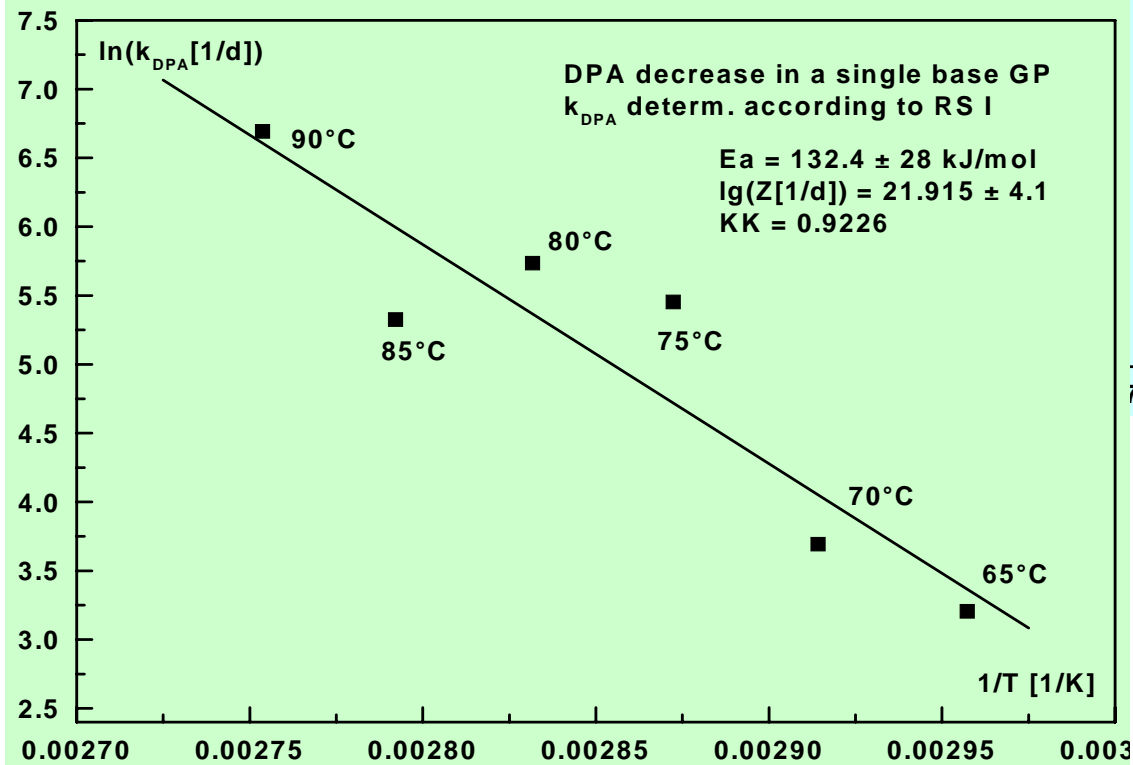
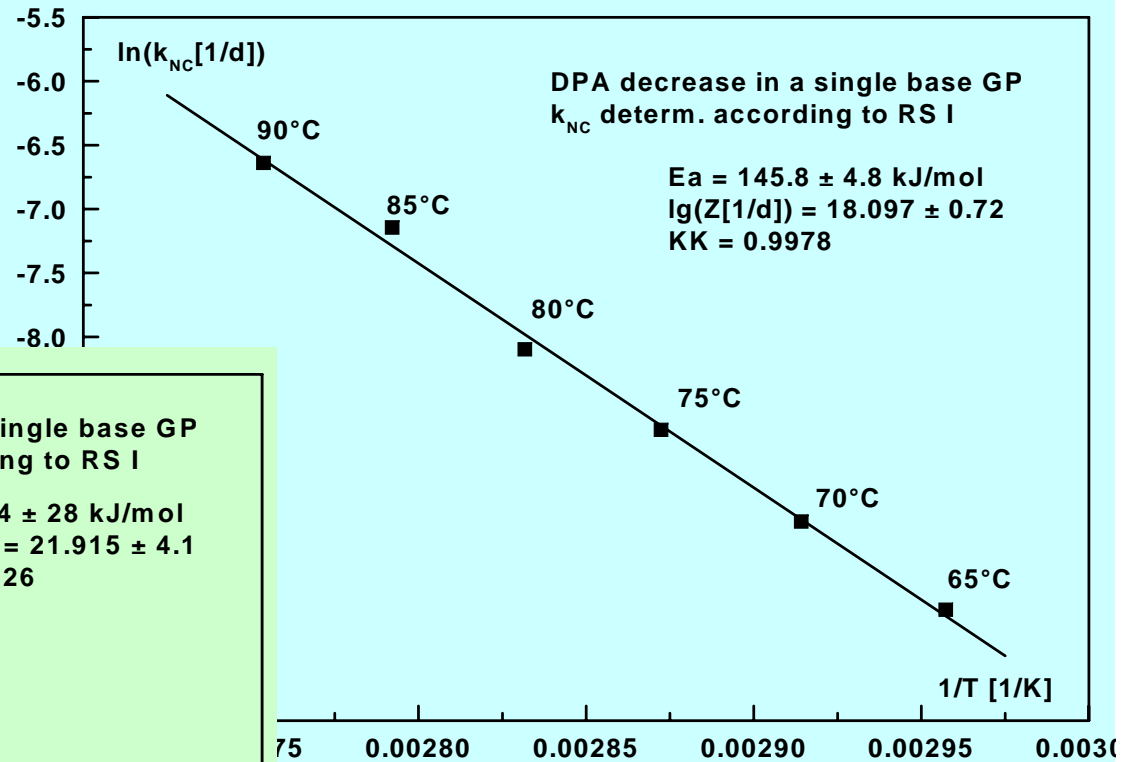
relative reactivity ER_x obtained by RS IV	
DPA	1.0
N-NO-DPA	0.041
4-N-DPA	0.074
2-N-DPA	0.055
4.4'-DN-DPA	0.008
2.2'-DN-DPA	0.004
2.4'-DN-DPA	0.016
2.4.4'-TN-DPA	8 E-5

N-NO-DPA has a lower reactivity than the mono-nitro-DPAs

And it has a much lower reactivity than DPA itself

Mechanistic modelling of stabilizer reaction with RS I see /13/

Activation energy E_a of NC decompos. is with 146 kJ/mol composed of two reactions: thermolysis and hydrolysis



E_a of stabilization reaction is with 132 kJ/mol in accordance with the loss of aromaticity of benzene ring (resonance energy)

Modelling of molar mass decrease of NC

See also /14,15/

Generally there are two main models to describe the statistical chain splitting of NC or any polymer

Model 1 chain scission by decomposition of a chain element (= monomer unit)

with time the mass of the polymer sample decreases

the number of chain elements is decreasing

model 1 was developed at ICT

Model 2 chain scission by opening of the bond (bond splitting) between two monomer units

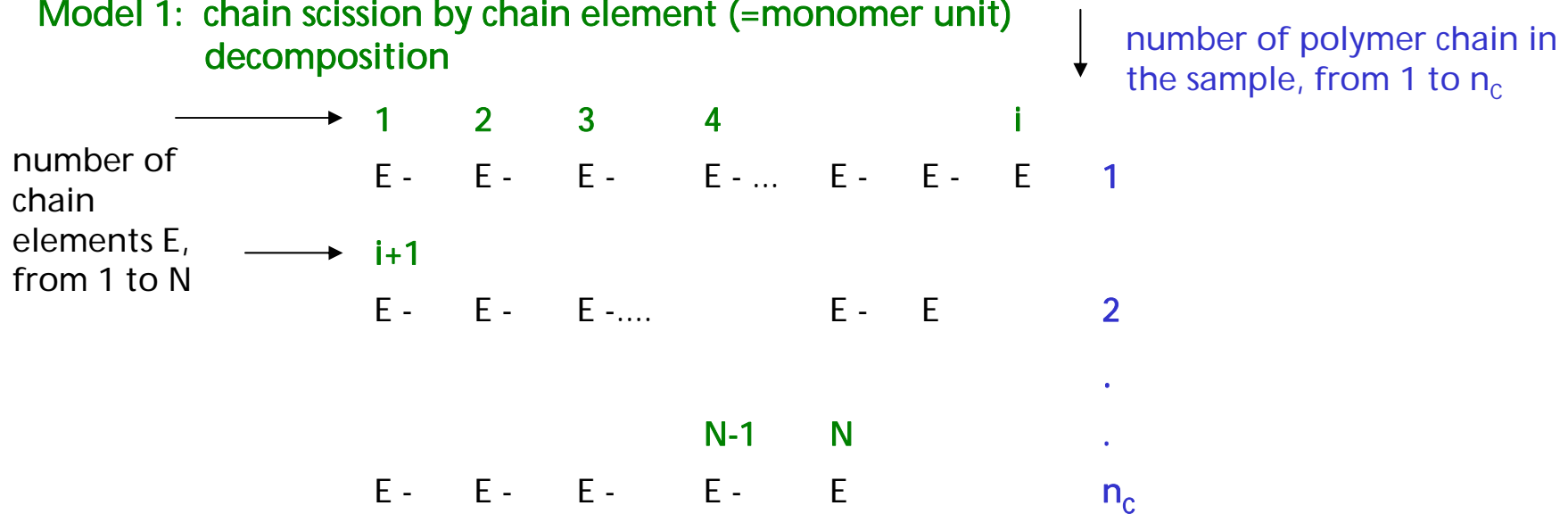
with time the mass of the polymer sample stays constant

the number of chain elements (monomer units) stays constant

model 2 is several times given in the literature, sometimes it is referred as Ekenstam model

Development of the kinetic model for polymer degradation – [model 1](#) - part 1 /15/

Model 1: chain scission by chain element (=monomer unit) decomposition



total number of chain elements: $N(0)$

total number of chains: $n_c(0)$

$P_n = M_n/m$: degree of polymerization

m : molar mass of chain element E

$$N(t, T) = N(0) \cdot \exp(-k_M(T) \cdot t)$$

$$N(0) = n_c(0) \cdot P_n(0) = n_c(0) \cdot \frac{M_n(0)}{m}$$

$$N(t, T) = n_c(t, T) \cdot P_n(t, T) = n_c(t, T) \cdot \frac{M_n(t, T)}{m}$$

Development of the kinetic model for polymer degradation – [model 1](#) - part 2

$K(t, T) = N(0) - N(t, T)$ Formation of one new chain by each decomposition of one chain element

$$n_c(t, T) = n_c(0) + N(0) - N(t, T)$$

$$n_c(t, T) = n_c(0) \cdot \frac{1 + \frac{Mn(0)}{m}}{1 + \frac{Mn(t, T)}{m}} \quad \frac{n_c(0) \cdot \frac{Mn(0)}{m}}{n_c(t, T) \cdot \frac{Mn(t, T)}{m}} = \frac{1 + \frac{m}{Mn(t, T)}}{1 + \frac{m}{Mn(0)}} = \frac{1 + \frac{1}{Pn(t, T)}}{1 + \frac{1}{Pn(0)}} = \frac{N(0)}{N(t, T)} = \exp(+k_M(T) \cdot t)$$

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

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

corresponding rate expression

$$\left(\frac{d\left(\frac{Mn(t, T)}{m}\right)}{dt}\right)\bigg|_T = -k_M(T) \cdot \left(\left(\frac{Mn(t, T)}{m}\right) + \left(\frac{Mn(t, T)}{m}\right)^2\right)$$

Approximated formulas

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

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

Development of the kinetic model for polymer degradation – [model 1](#) - part 3

time ty_{Mn} is the looked for life time;
this is the time to reach the degree of
degradation $y_{Mn}=Mn(t)/Mn(0)$

$$ty_{Mn}(T) = \frac{1}{k_M(T)} \cdot \ln \left(\frac{\frac{1}{y_{Mn}} + \frac{An \cdot Mw(0)}{m \cdot D(0)}}{1 + \frac{An \cdot Mw(0)}{m \cdot D(0)}} \right)$$

$$\ln \left(1 + \frac{m \cdot D(t, T)}{An \cdot Mw(t, T)} \right) = \ln \left(1 + \frac{m \cdot D(0)}{An \cdot Mw(0)} \right) + k_M(T) \cdot t$$

$$\frac{m \cdot D(t, T)}{Mw(t, T)} = \frac{m \cdot D(0)}{Mw(0)} + An \cdot k_M(T) \cdot t \quad D = \frac{Mw}{Mn}$$

An: conversion factor from absolute to
relative Mn values: $Mn_{abs} = An \cdot Mn_{rel}$

Model conditions

- statistical chain splitting.
- the chain splitting occurs by decomposition of chain elements; with NC the triggering is the thermolytic and /or hydrolytic degradation of the $\equiv CO-NO_2$ groups
- the total number of chain elements is much greater than the number of chains
- the total number of chain elements decreases with first order, rate constant $k_M(T)$



Kinetic model for polymer degradation based on [model 2](#) – part 1

Model 2: chain scission by bond breaking between chain elements (monomer units)

$$B(0) = \sum B_j(0) = \sum (N_j(0) - 1) = N(0) - n_c(0)$$

total number of bonds at time zero: $B(0)$

total number of chain elements: $N(0)$

total number of chains: $n_c(0)$

number of bonds in chain j : $B_j(0)$

number of chain elements in chain j : $N_j(0)$

$$B(t, T) = N(0) - n_c(t, T) = N(t, T) - n_c(t, T) \quad \text{with} \quad N(0) = N(t, T)$$

$$\left(\frac{d(B(t, T))}{dt} \right) \bigg|_T = -k_B(T) \cdot B(t, T)$$

$$B(t, T) = B(0) \cdot \exp(-k_B(T) \cdot t)$$

$$\frac{B(t, T)}{B(0)} = \frac{N(0) - n_c(t, T)}{N(0) - n_c(0)} = \frac{1 - \frac{n_c(t, T)}{N(0)}}{1 - \frac{n_c(0)}{N(0)}}$$

$$\frac{n_c(t, T)}{N(0)} = \frac{m}{Mn(t, T)}$$

$$\frac{n_c(0)}{N(0)} = \frac{m}{Mn(0)}$$

$$\frac{1 - \frac{m}{Mn(t, T)}}{1 - \frac{m}{Mn(0)}} = \frac{1 - \frac{1}{Pn(t, T)}}{1 - \frac{1}{Pn(0)}} = \exp(-k_B(T) \cdot t)$$

Kinetic model for polymer degradation based on [model 2](#) – part 2

$$\frac{1 - \frac{m}{Mn(t,T)}}{1 - \frac{m}{Mn(0)}} = \frac{1 - \frac{1}{Pn(t,T)}}{1 - \frac{1}{Pn(0)}} = \exp(-k_B(T) \cdot t)$$

$$\left(\frac{d\left(\frac{Mn(t,T)}{m}\right)}{dt} \right) \bigg|_T = -k_B(T) \cdot \left(-\left(\frac{Mn(t,T)}{m}\right) + \left(\frac{Mn(t,T)}{m}\right)^2 \right)$$

$$ty_{Mn}(T) = -\frac{1}{k_B(T)} \cdot \ln \left(\frac{\frac{An \cdot Mw(0)}{m \cdot D(0)} - \frac{1}{y_{Mn}}}{\frac{An \cdot Mw(0)}{m \cdot D(0)} - 1} \right)$$

Signs in formula are different to the model based on chain element decomposition

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

Signs in formula are different to the model based on chain element decomposition

Approximated formulas

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

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

In approximated form model 2 and model 1 are equal

Definition of terms – mean molar masses

The polymer fraction i is characterized by some quantities; it is thought to be molecular uniform, means it has only molecules of one molar mass M_i and the number of mols is n_i

The polymer sample is characterized by a distribution function $h x_i$, which can be of different kind

$$M_n = \frac{\sum_i h n_{u,i}(M) \cdot M_i}{\sum_i h n_{u,i}(M)} = \frac{\sum_i h m_{u,i}(M)}{\sum_i \frac{h m_{u,i}(M)}{M_i}}$$

M_n : mean molar mass averaged according to the mol number in the polymer fraction i (mol number weighing)

$$M_w = \frac{\sum_i h n_{u,i}(M) \cdot M_i \cdot M_i}{\sum_i h n_{u,i}(M) \cdot M_i} = \frac{\sum_i h m_{u,i}(M) \cdot M_i}{\sum_i h m_{u,i}(M)}$$

M_w : mean molar mass averaged according to the mass of the polymer fraction i (mass weighing)

$$M_z = \frac{\sum_i h n_{u,i}(M) \cdot M_i \cdot M_i \cdot M_i}{\sum_i h n_{u,i}(M) \cdot M_i \cdot M_i} = \frac{\sum_i h m_{u,i}(M) \cdot M_i \cdot M_i}{\sum_i h m_{u,i}(M) \cdot M_i} = \frac{\sum_i h z_{u,i}(M) \cdot M_i}{\sum_i h z_{u,i}(M)}$$

M_z : mean molar mass averaged according to the z -mass of the polymer fraction i (z weighing)

Definition of terms - distribution functions

$$hn_i(M) = \frac{hn_{u,i}(M)}{\sum_i hn_{u,i}(M)} = \frac{\frac{hm_{u,i}(M)}{M_i}}{\sum_i \frac{hm_{u,i}(M)}{M_i}}$$

$hn_i(M)$ polymer fraction mol number related
normalized molar mass distribution
 n_i is mol number in polymer fraction i

$$hm_i(M) = \frac{hm_{u,i}(M)}{\sum_i hm_{u,i}(M)} = \frac{\frac{hz_{u,i}(M)}{M_i}}{\sum_i \frac{hz_{u,i}(M)}{M_i}}$$

$hm_i(M)$ polymer fraction mass related molar
normalized molar mass distribution
 $m_i = M_i * n_i$
 m_i is the mass of polymer fraction i

$$hz_i(M) = \frac{hz_{u,i}(M)}{\sum_i hz_{u,i}(M)}$$

$hz_i(M)$ polymer fraction z-weight related
normalized molar mass distribution
 $z_i = M_i * m_i = M_i * M_i * n_i$
 z_i is the z mass of polymer fraction i

$hn_{u,i}$ and $hm_{u,i}$ and $hz_{u,i}$ are un-normalized distribution functions

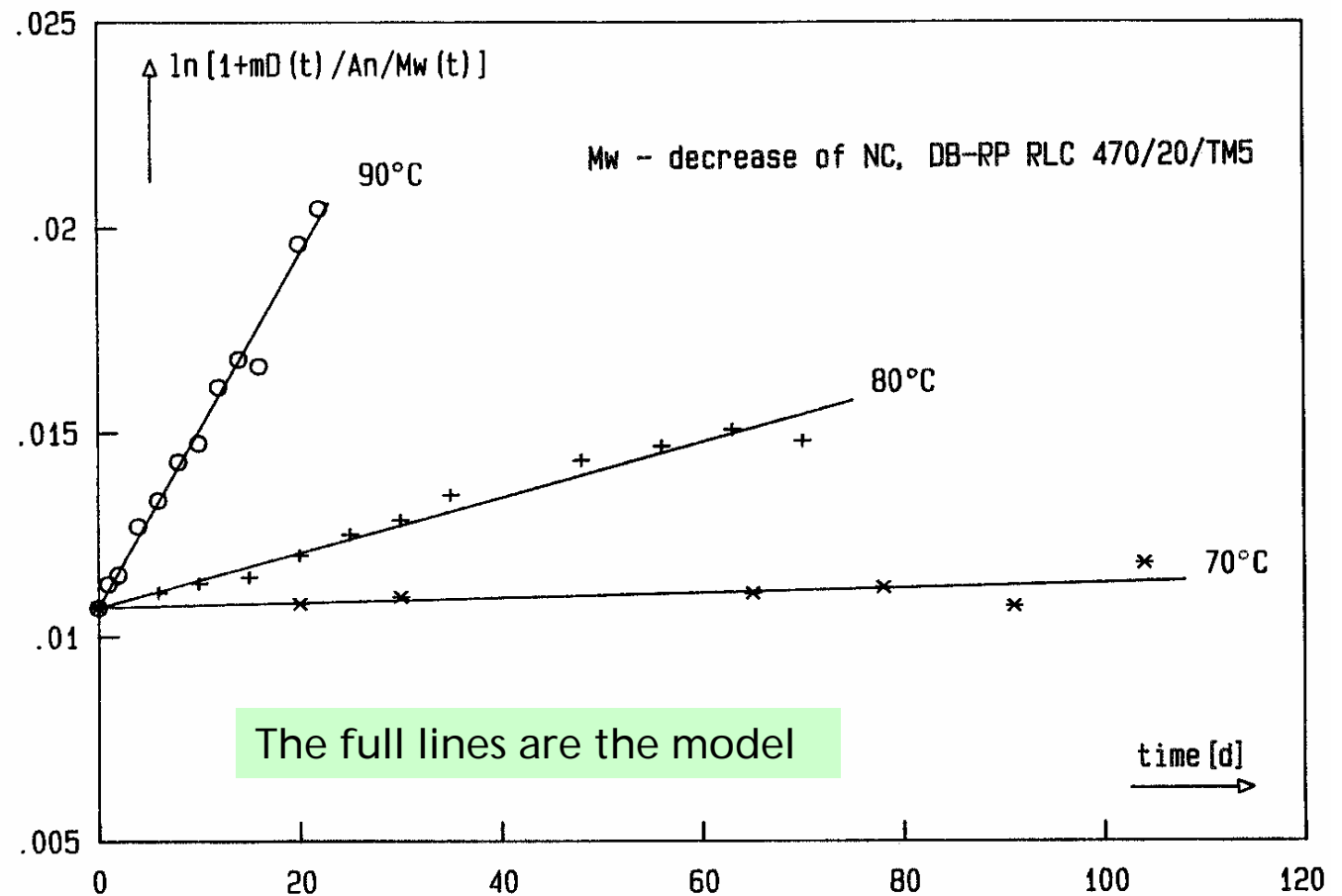
Examples of molar mass degradation



Modelling of the molar mass decrease of NC – model 1

Modelling of NC degradation in a double base rocket propellant

on the ordinate the model expression of model 1 is shown

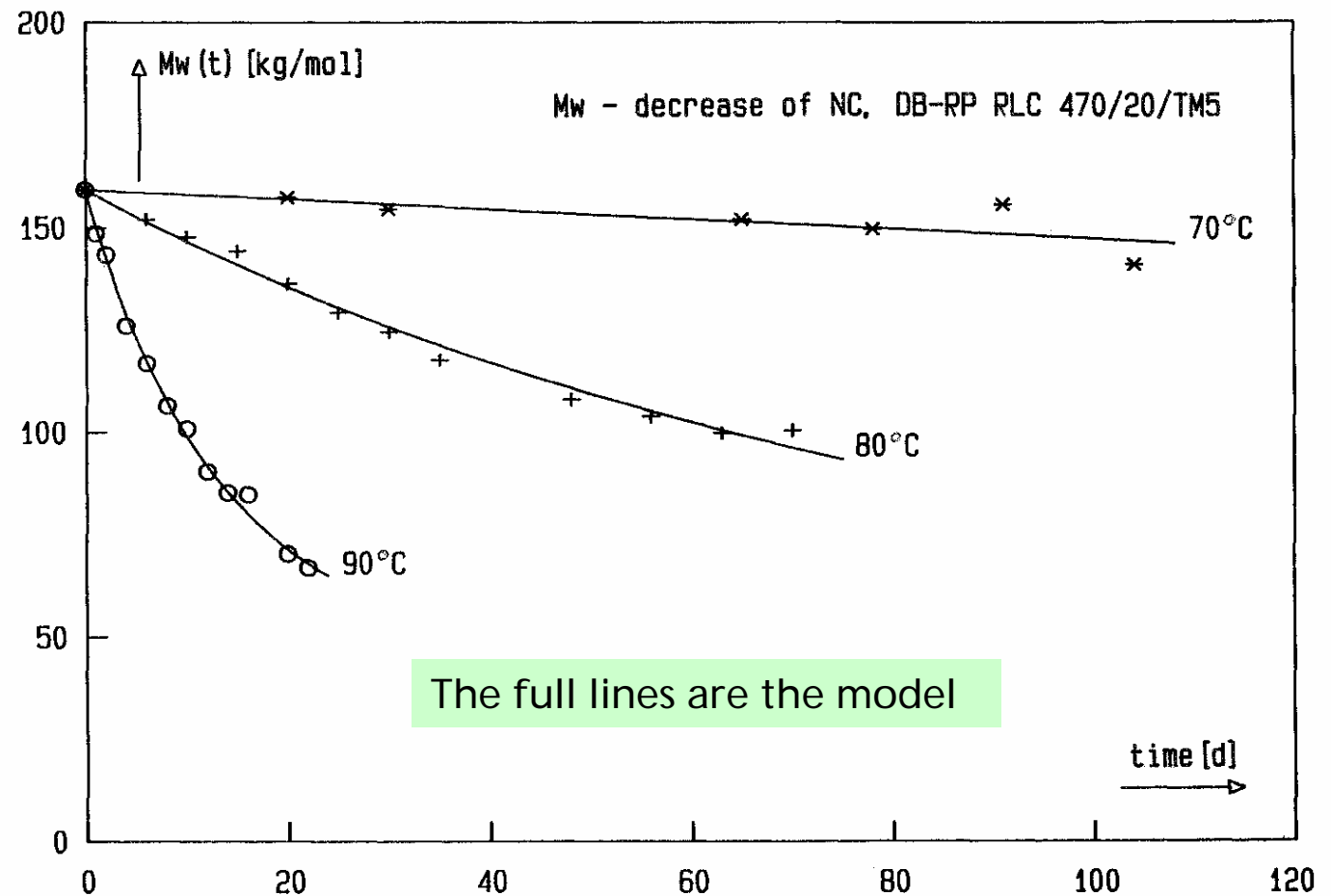


Modelling of the molar mass decrease of NC – model 1

Modelling of NC degradation in a double base rocket propellant

on the ordinate mean molar mass M_w is shown, back calculated from the model expression of model 1

the description of the data is very good



Model for degradation of molar mass of NC - extrapolation ability – model 1

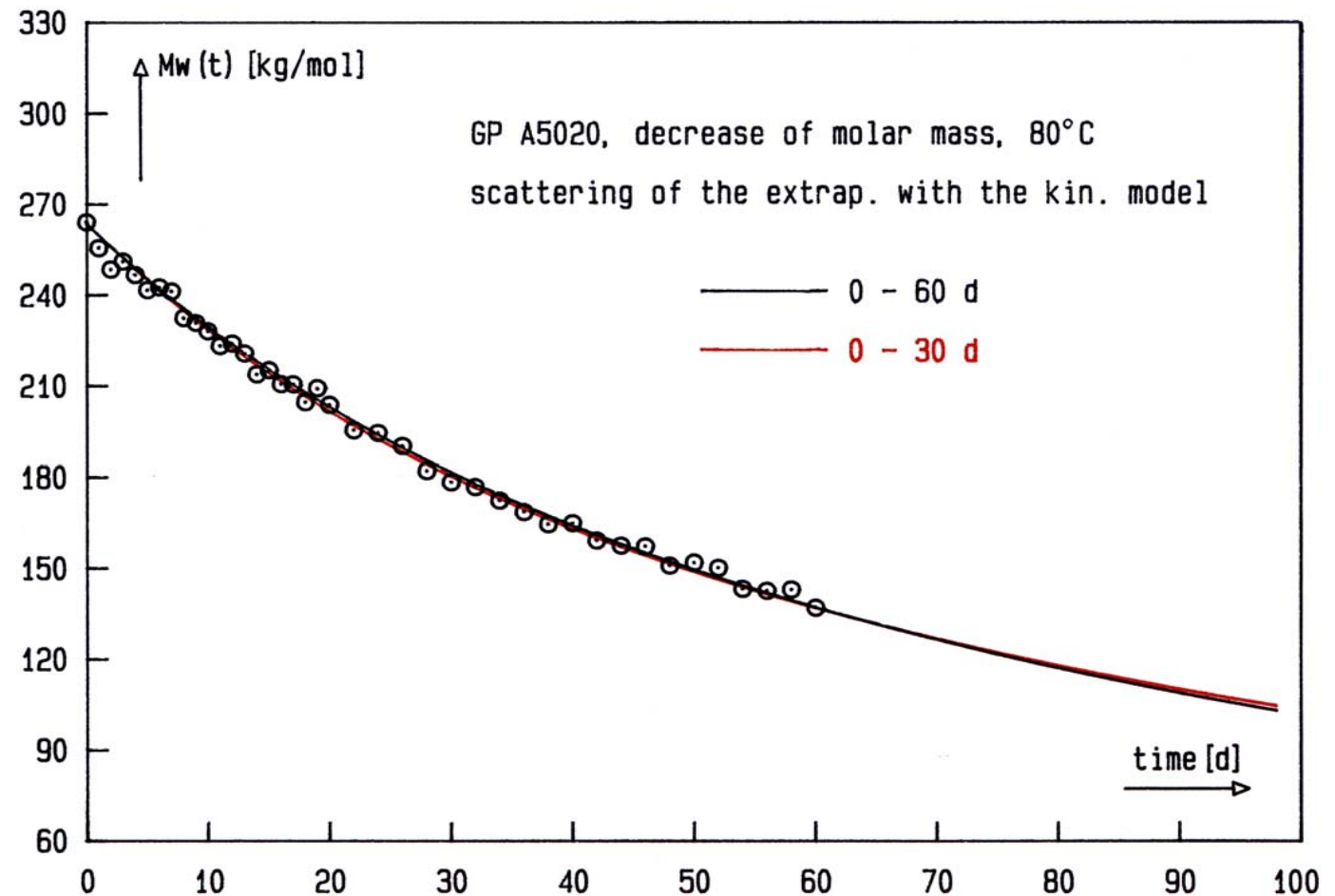
This graph shows the good extrapolation ability of the model 1.

The figure has two lines: red and black.

The red one is determined by using the model 1 with data up to 30 days.

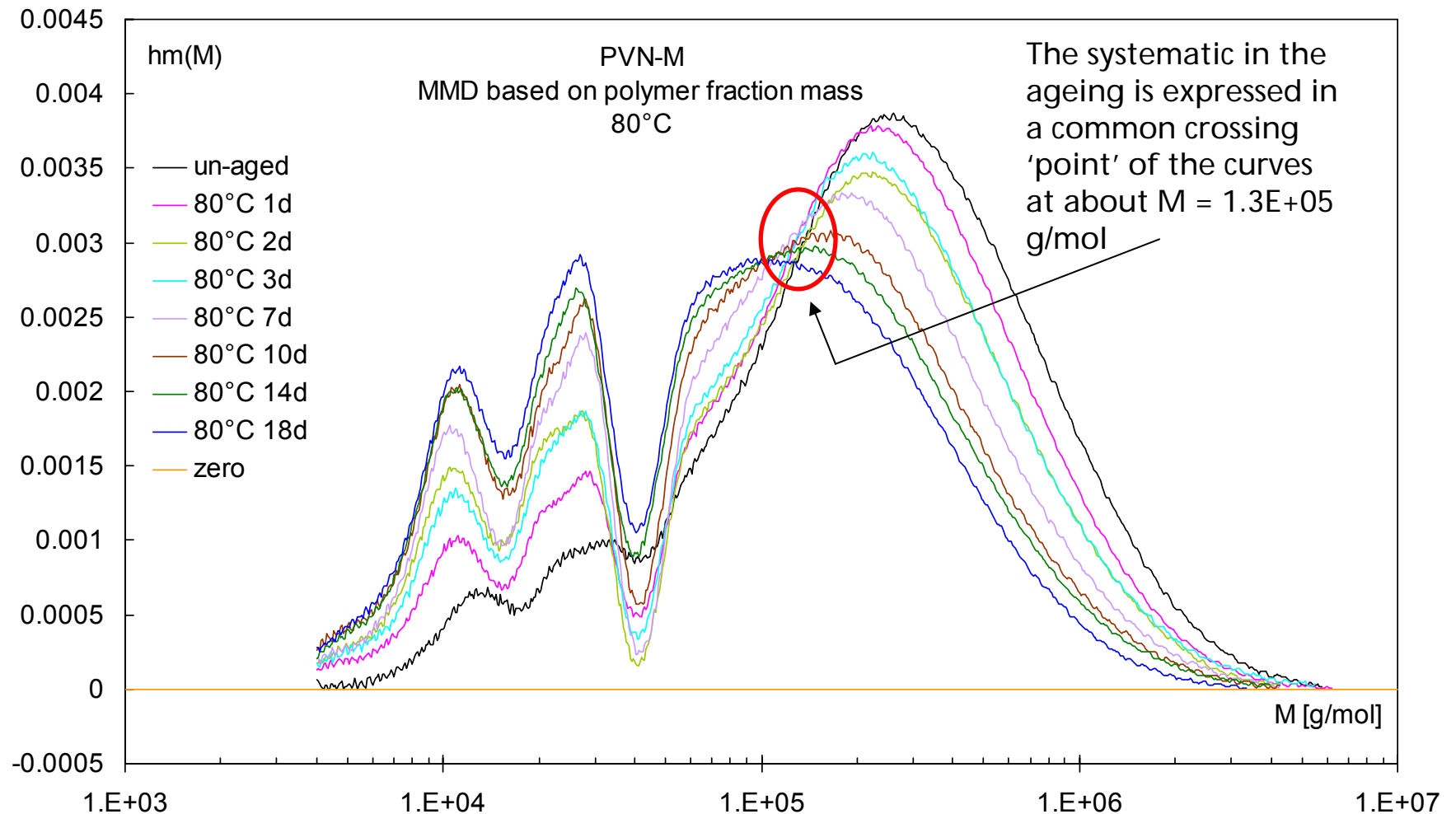
The black one is determined with data up to 60 days.

Both curves coincide.

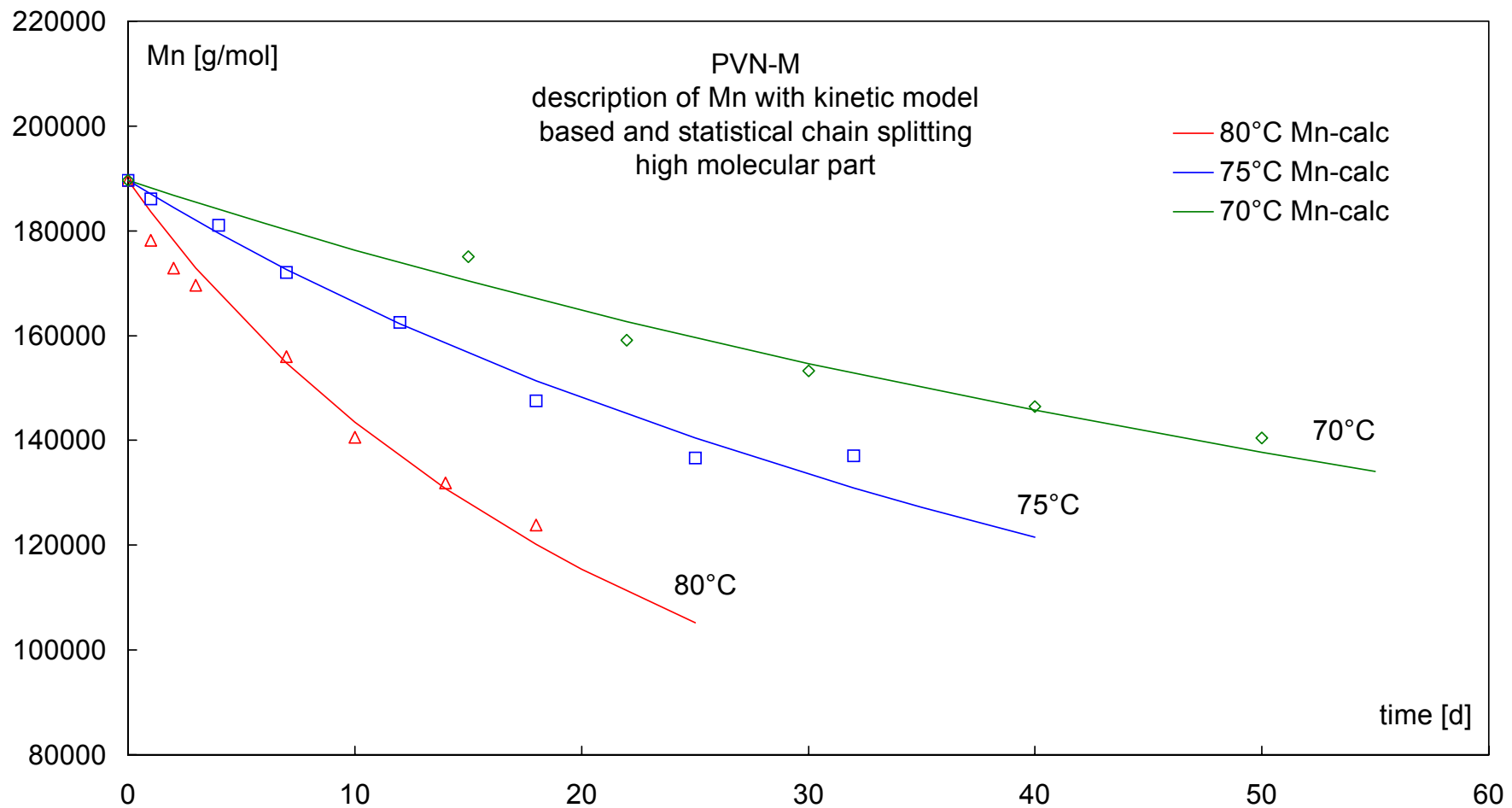


Molar mass distribution functions of aged PVN – determined by GPC /2/

PVN, polyvinylnitrate, an energetic speciality polymer



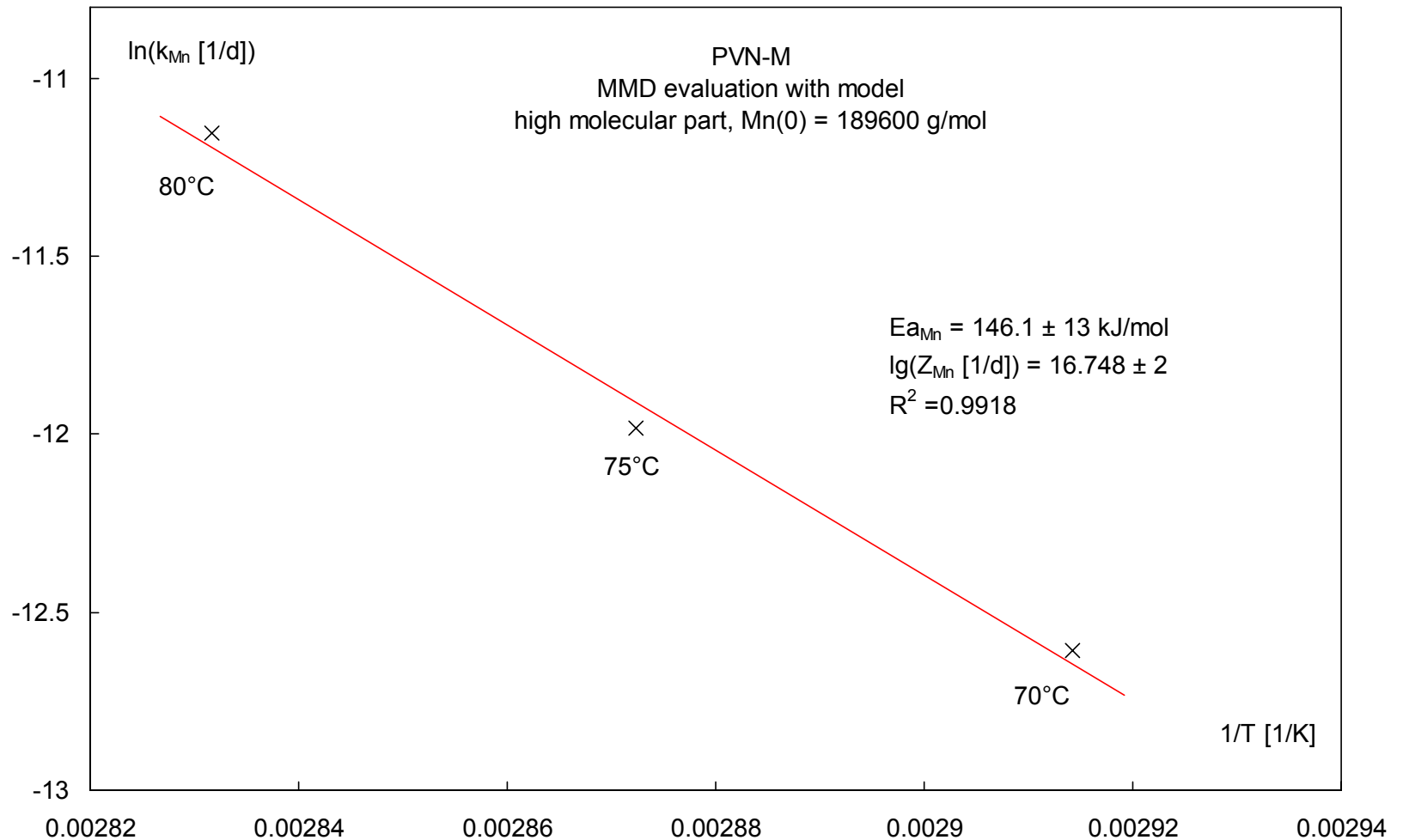
Molar mass degradation of PVN - description with model 1



Molar mass degradation of PVN – description with model 1

For the chain scission in PVN an activation energy of 146 kJ/mol is determined [2].

Such E_a values are found also NC based propellants



Application and meaning of molar mass decrease

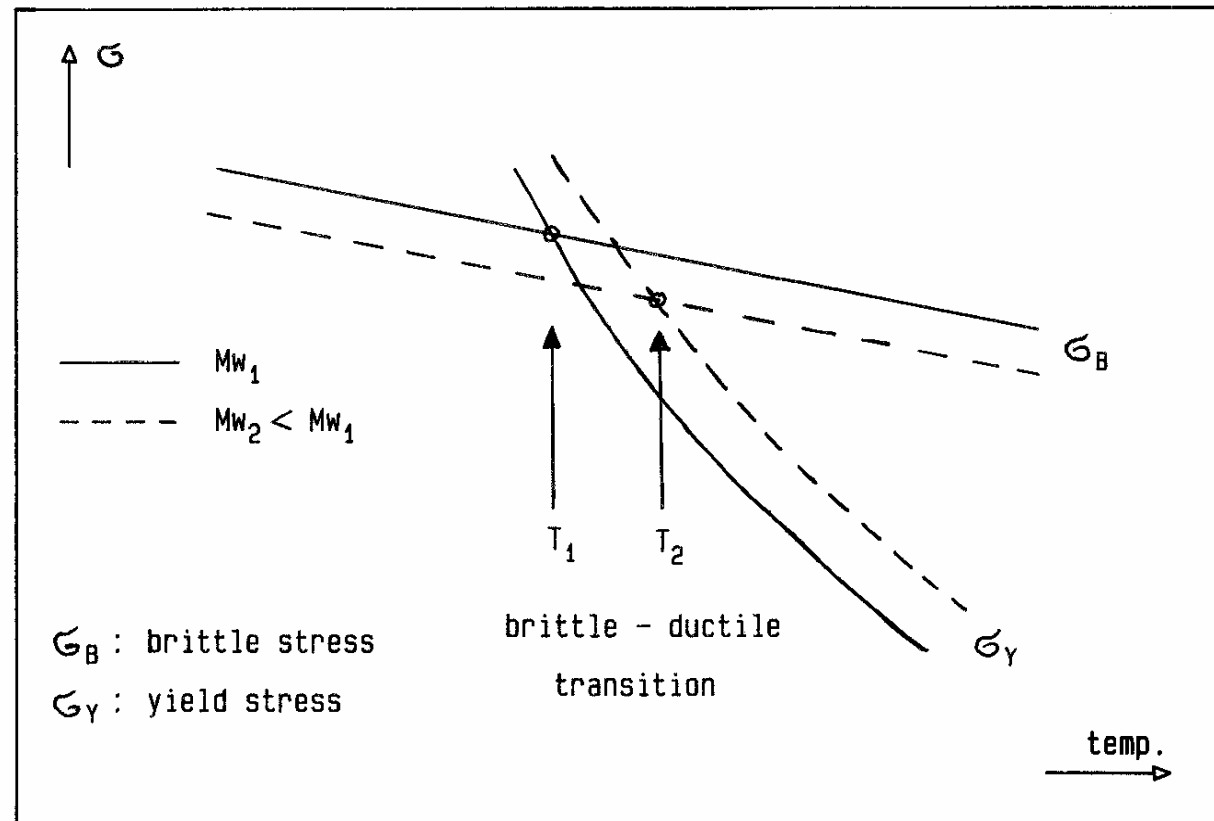


Molar mass decrease - brittle ductile transition

shift of the brittle-ductile transition temperature to higher temperature values with decreasing molar mass = decreasing chain length of NC

ageing causes increase in brittle tendency

danger during firing rounds with large grain GP

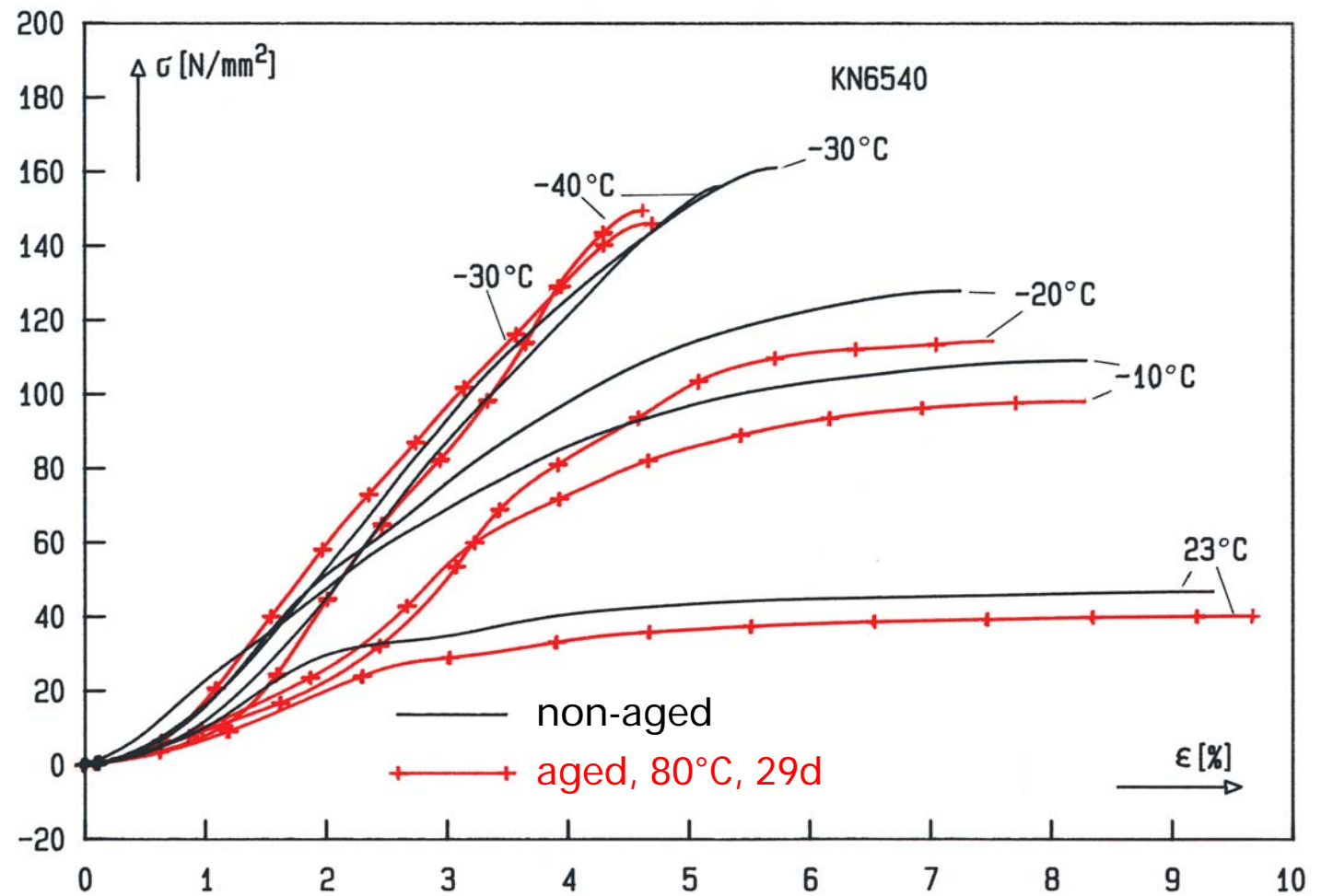


Example for molar mass decrease - brittle ductile transition

GP KN6540 (M30 type), triple base GP, 110mm tank gun

stress - strain curves of non-aged and aged samples as function of temperature determined at high strain rate, about 5000%/sec

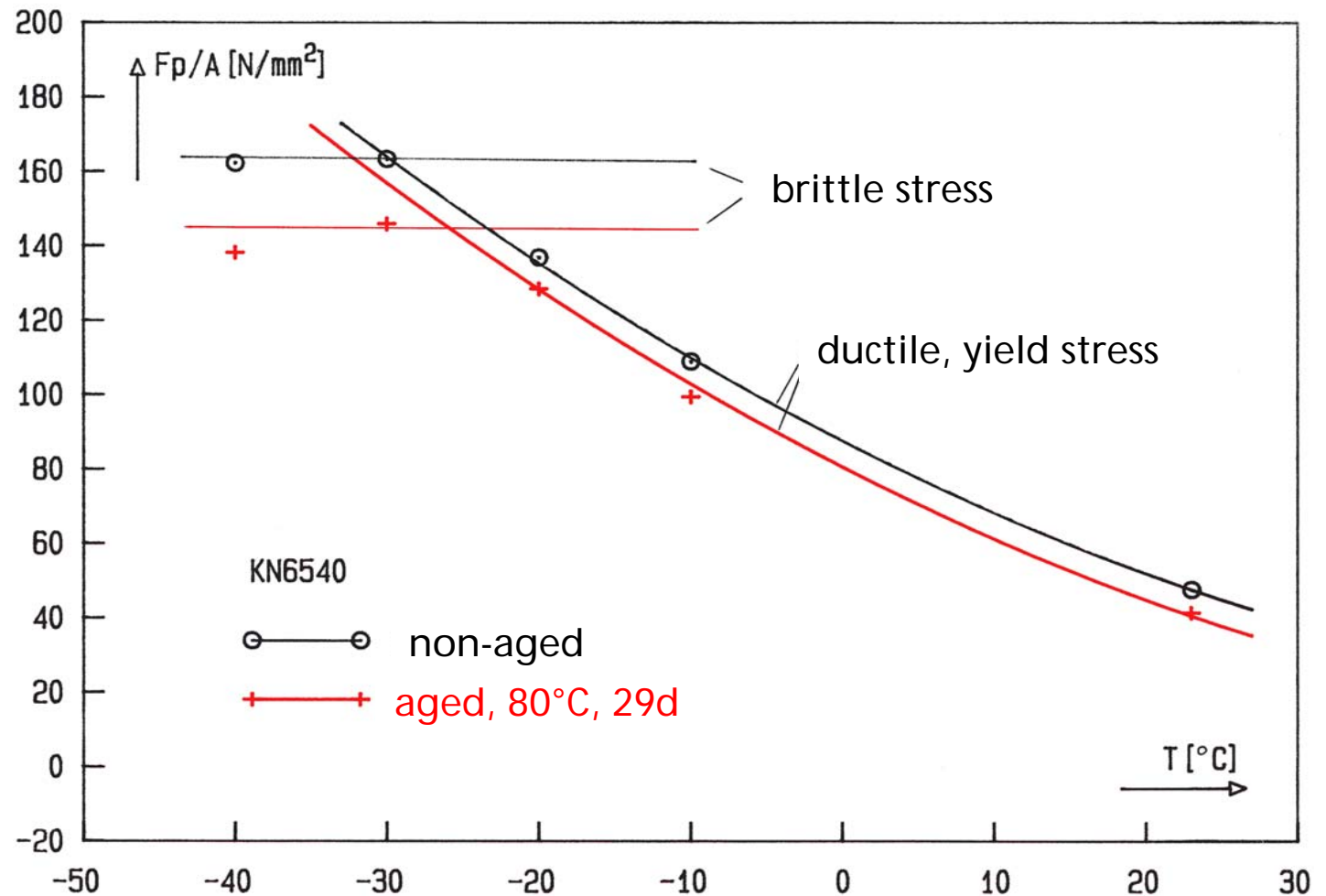
the brittleness increases with ageing



Molar mass decrease - brittle ductile transition

GP KN6540 (M30 type), triple base GP, 110mm tank gun

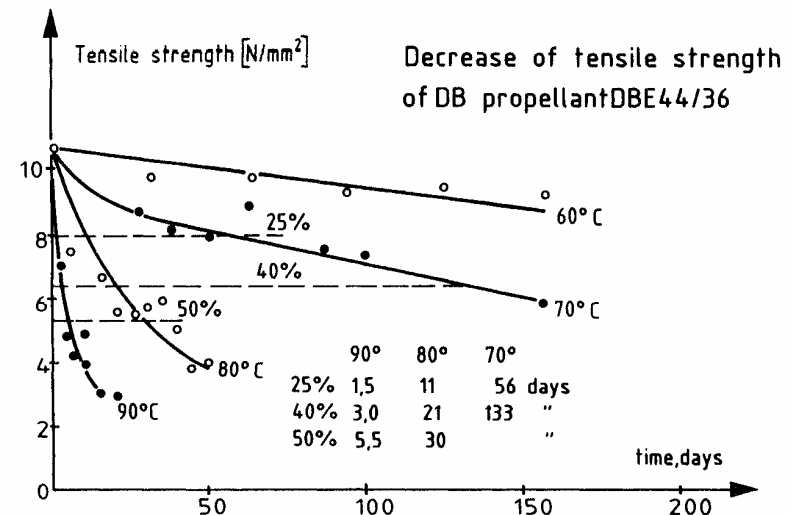
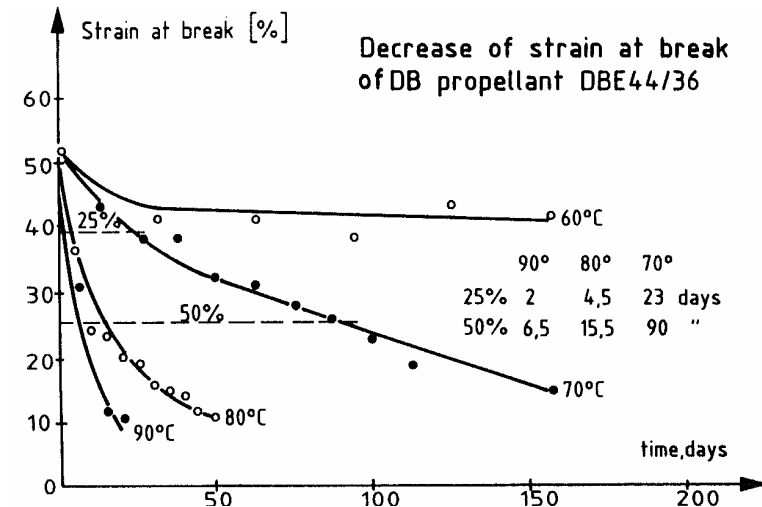
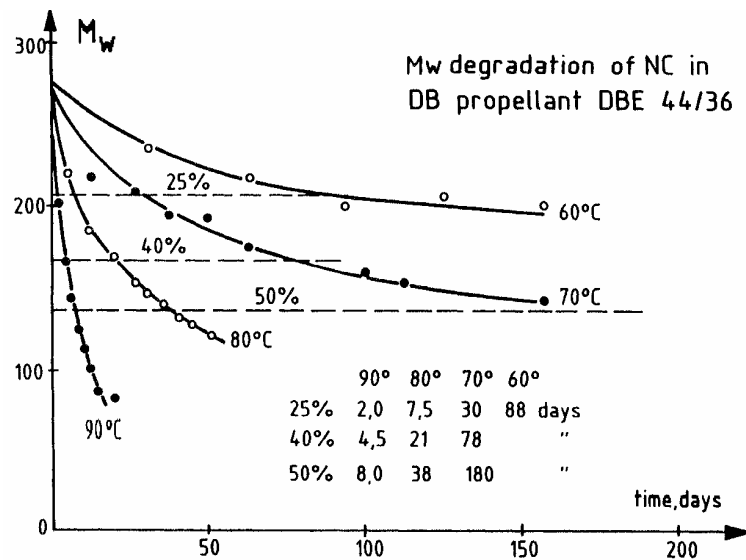
shift of the brittle ductile transition temperature with ageing to higher values



Correlation of molar mass decrease and decrease of mechanical strength



Ageing of db rocket propellant – correlation between molar mass decrease of NC and decrease mechanical properties



Correlation between molar mass decrease, stabilizer decrease and decrease of strain at break and tensile stress at break for the doublebase RP DBE 44/36 /16/

Ageing of new type gun propellants

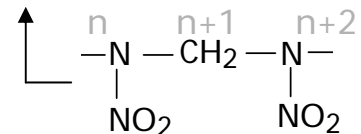
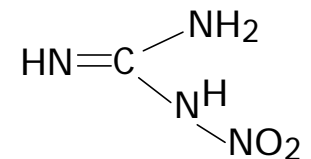
See also /17/



Types of gun propellants - overview

Main types of GP (numbers give applied ranges in mass-%)

Single base	NC(N content 13 to 13.4 mass-%) 90-95, stabilizer 1-2, plasticizer 2-5, graphite
Double base	NC (N content 12.3 to 12.6 mass-%), 30 to 60, blasting oils 25 to 50 (NG, DEGN, special types also with TMETN, BTTN), stabilizer 1-2, graphite
Triple base	NC (N-content 12.3 to 12.6 mass-%) 30 to 40, blasting oils 20 to 30 nitroguanidine 25 to 40, stabilizer 1 to 2, plasticizer 5 to 10, graphite
Semi nitramine	NC (N-content 12.3 to 12.6 mass-%) 30 to 40, blasting oils 20 to 30, RDX 25 to 40, stabilizer 1 to 2, plasticizer 5 to 10, graphite
New-type of ICT	NC (N-content 12.3 to 12.6 mass-%) 30 to 40, DNDA (dinitro-diaza)-type plasticizer 20 to 30, RDX 25 to 40, stabilizer 1 to 2, graphite



All show a standard decomposition behaviour with respect to NC and blasting oil decomposition.

But in triple base GP the NO_2 is in part captured by nitroguanidine (NQ), because of reaction between NO_2 and the NH groups of NQ. This and the dilution effect for NC by NQ leads to the fact that with triple base propellants no visible NO_2 can be observed and no strong autocatalysis.

Type of gun propellants - shapes

Main types of GP according to shape and treatment

cylindrical grain with several holes, mostly 1, 7, 19

long tube

short tube

flake

stripe

ball (sphere, ellipsoids)

cube

ring

horseshoe

nudle (short rods)

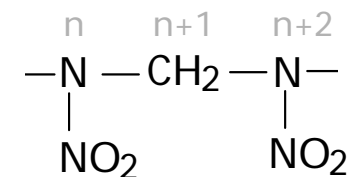
Surface treatment:

phlegmatization to adapt burning behaviour

energetic enforcement by blasting oil treatment (Wimmis EI type)

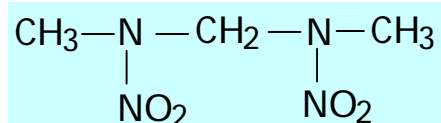
Energetic plasticizer DNDA

recent plasticizer based on the $n, (n+2)$ -Di Nitro - $n, (n+2)$ -Di Aza group

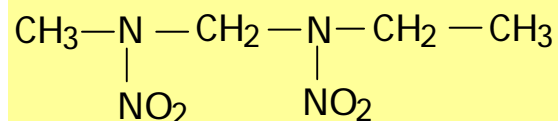


DNDA 57: liquid dinitro-diaza plasticizer

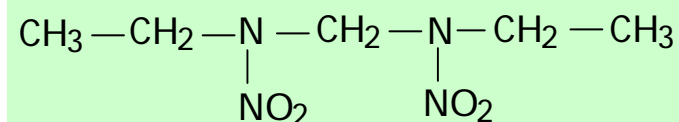
Mixture of three components: DNDA5 : DNDA6 : DNDA7, about 43 : 45 : 12 mass-%



2,4-dinitro-2,4-diaza-pentane, DNDA 5 (54°C)



2,4-dinitro-2,4-diaza-hexane, DNDA 6 (32°C)



3,5-dinitro-3,5-diaza-heptane, DNDA 7 (75°C)

DNDA 57 ($T_m = -9^\circ\text{C}$) gels with NC

Defining the LTC effect for gun propellants

LTC: low temperature coefficient (coefficient with small value)

means

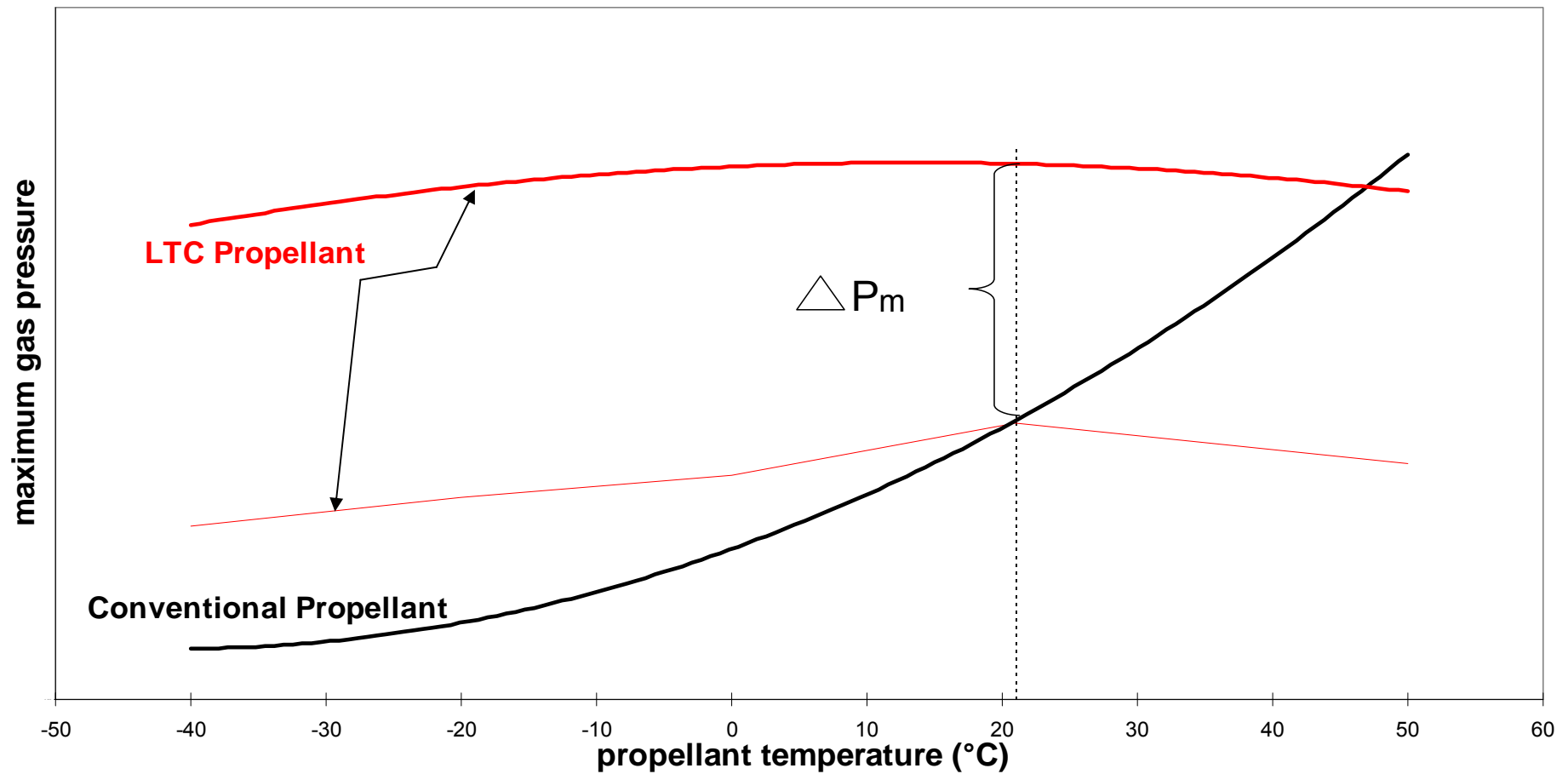
A gun propellant which shows small to very small dependence of maximum chamber pressure p_{\max} on charge temperature T_c

temperature range of interest is from -40°C (-54°C) to $+63^{\circ}\text{C}$ ($+71^{\circ}\text{C}$)

These New Type GP of ICT show this interesting effect of low temperature coefficient of maximum chamber gas pressure

This effect can be used to reduce weight of the gun system (small and light vehicles) or to increase the charge mass to enhance the muzzle velocity of the projectile

Comparison of typical gas pressure curves of conventional and LTC propellants



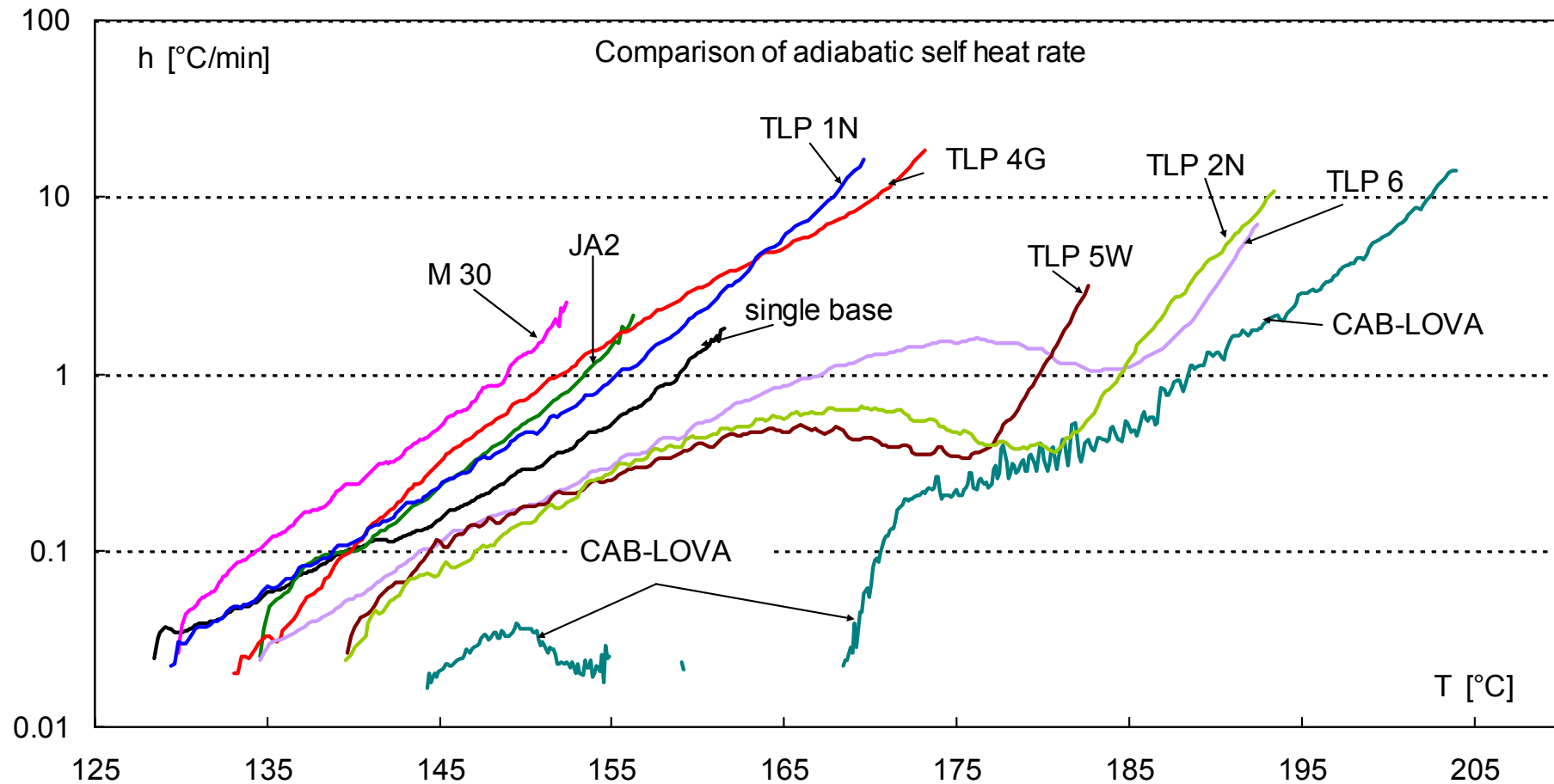
Some characteristic data of GP formulations

GP	web	LTC effect	autoignition temp. [°C]	adiab. flame temp. T_{ad} [K]	force [J/g]	Q_{EX} [J/g]	V_{EX} at 25°C [ml/g]
TLP 1N	7	yes	185	2905	1170	3768	961
TLP 2N	7	yes	220	2906	1178	4198	939
TLP 3N	7	yes	193	2910	1180	4201	939
TLP 4G	7	yes	198	2908	1185	4071	938
TLP 5W	19	yes	189	2510	1060	4124	931
TLP 6	19	yes	199	2540	1080	4177	929
For comparison the data of two typical conventional GP							
JA2 (L 5460, db)	7	no	168	3390	1139	4610	753
MRCA (Q 5560, tb)	19	no	172	3078	1040	3758	857

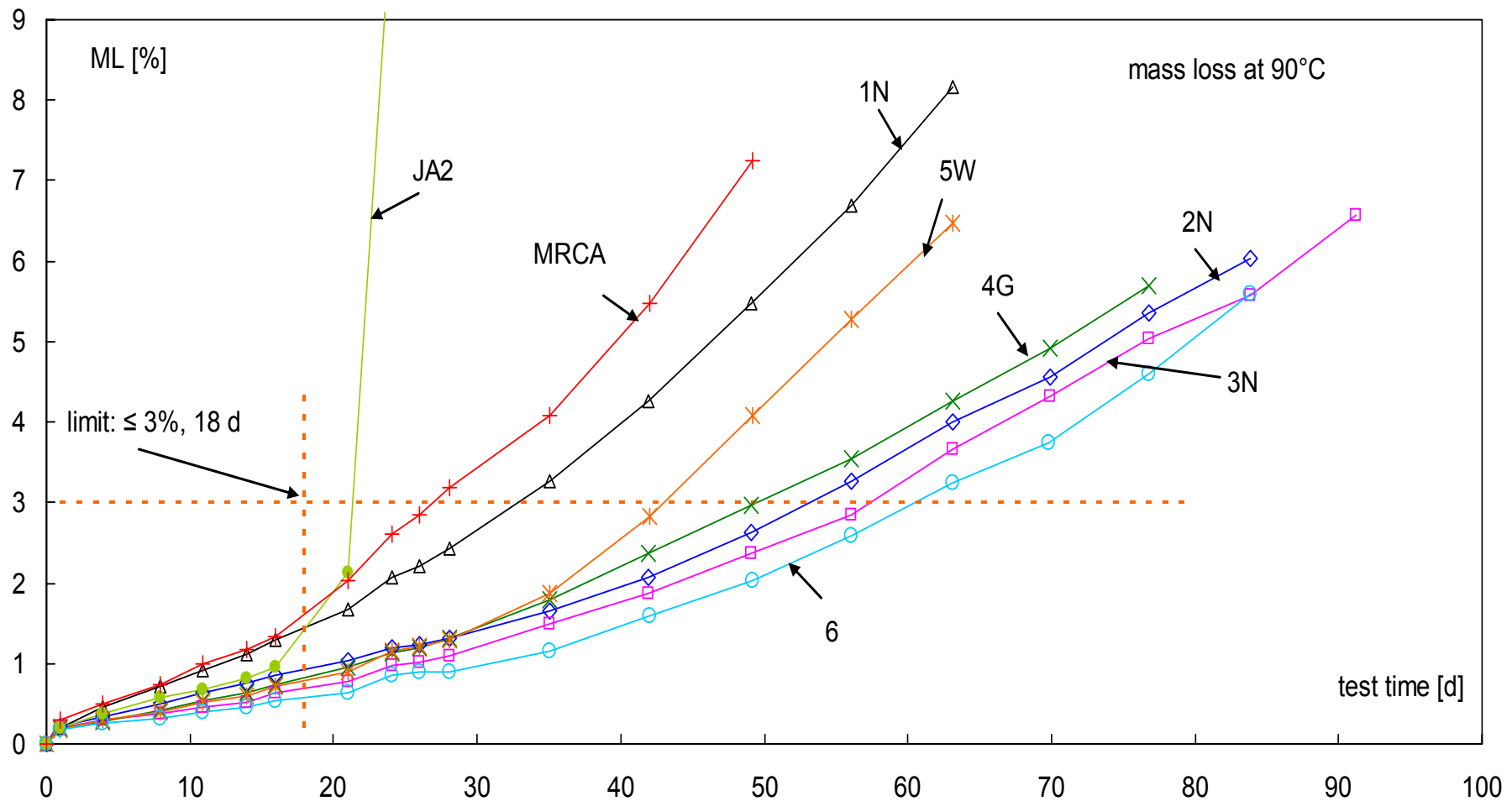
Adiabatic flame temperature T_{ad} , force, heat of explosion Q_{EX} and gas volume V_{EX} have been calculated by ICT Thermodynamic Code using the data of the ICT Thermochemical Data Base



Adiabatic self heating determined by an ARC™ of typical conventional and of new type GP, including the XM39 GP with a binder based on CAB



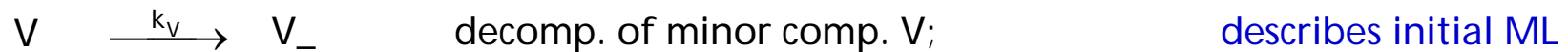
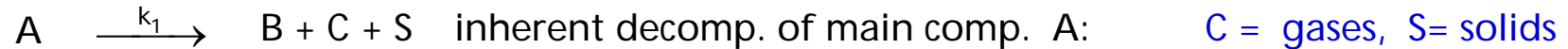
Assessment of ageing and stability with mass loss



Modelling of ML data with model 'ML: minor 1st ord.; main 1st ord. + autocat.'

See also /6/

Reaction scheme



Reaction kinetic formulation gives the following equation for total mass loss ML

$$ML(t, T) = 100\% \cdot \left\{ \underbrace{\frac{m_C}{m_A} \cdot \left((1 - a_V) - \frac{M_B(0) + M_S(0) + M_N}{M(0)} \right) \cdot (1 - M_{Ar}(t, T))}_{\text{Decomposition of main component A}} + \underbrace{a_V \cdot (1 - \exp(-k_V(T) \cdot t))}_{\text{Decomp. of minor comp. V}} \right\}$$

M_N : mass of a non-reacting ingredient N in A

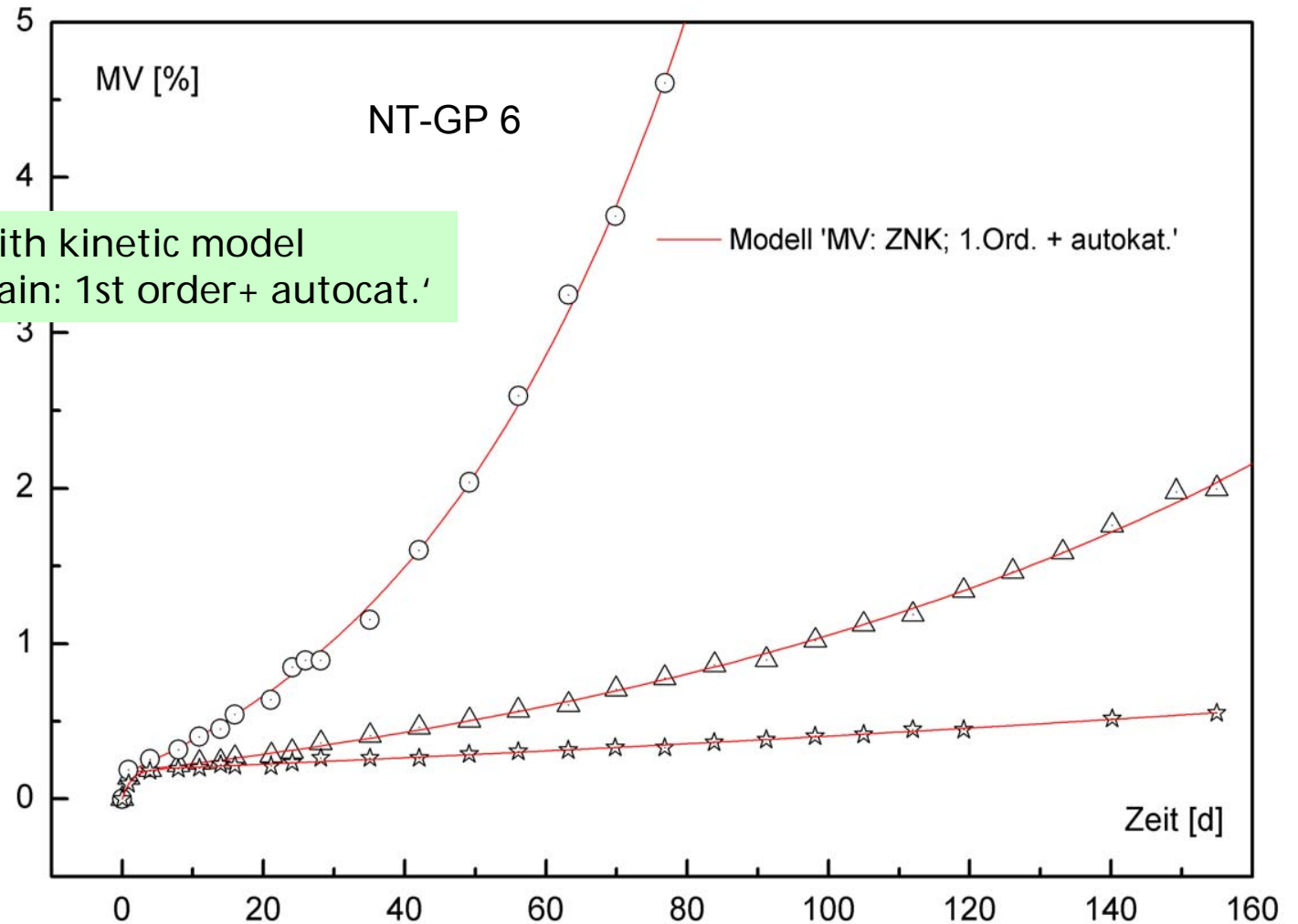
$$M_{Ar}(t, T) = \frac{k_1(T) + (F + 1) \cdot k_2(T)}{k_2(T) + (k_1(T) + F \cdot k_2(T)) \cdot \exp((k_1(T) + (F + 1) \cdot k_2(T)) \cdot t)}$$

Decomposition of main component according to '1st order + autocatalytic'

Parameters to be determined from the measurement curve:
 $k_1, k_2, k_V, (a_V)$

Assessment of ageing and stability with mass loss

Modelling of ML data with kinetic model
'ML: minor: 1st order; main: 1st order+ autocat.'



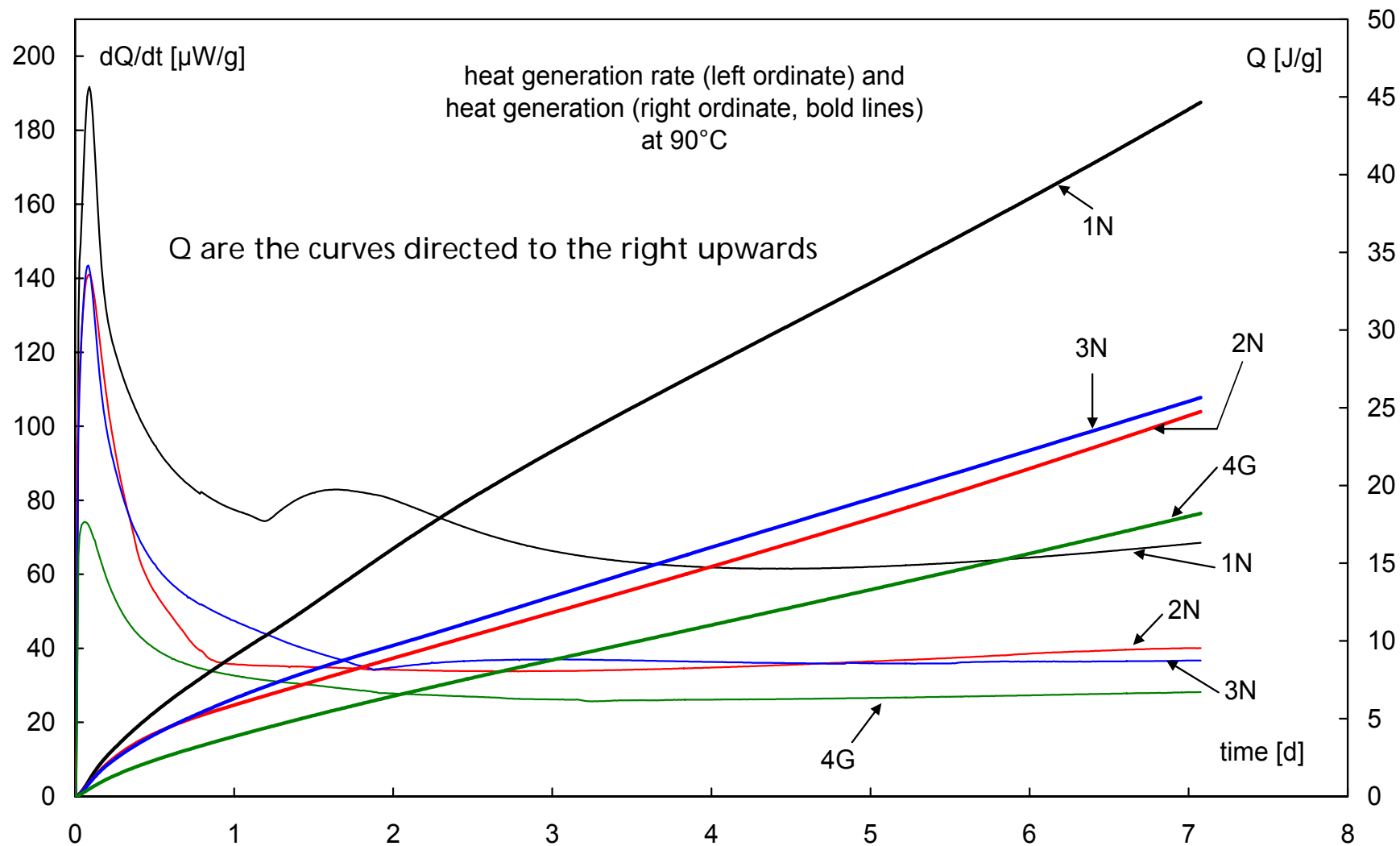
Times $t_{y_{ML}}$ to reach 3% mass loss in years calculated with Arrhenius parameters obtained from mass loss measurements at 70°C, 80°C and 90°C

See /17/ for more explanations

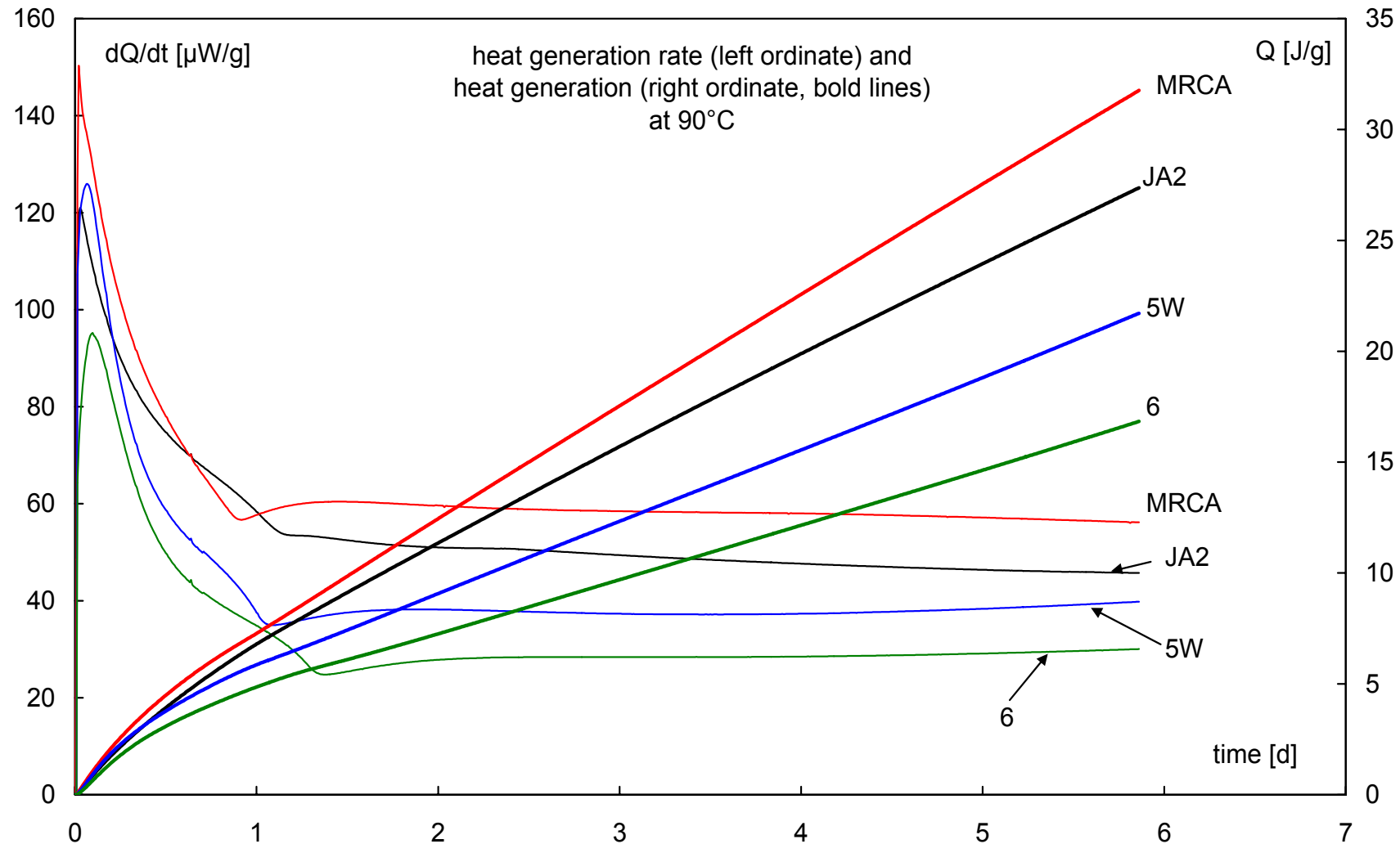
	1N	2N	3N	4G	5W	6	MRCA	JA2	JA2, HT
web	7	7	7	7	19	19	19	7	7
$E_{a_{ML}}$ [kJ/mol]	116.5	104.3	101.8	105.6	105.7	102.2	147.9	102.0	149.0
$\log(Z_{ML} [1/d])$	15.23 5	13.28 6	12.86 5	13.45 7	13.56	12.888	19.837	13.282	20.102
	time $t_{y_{ML}}$ to reach 3% mass loss ML in years at preset temperatures								
65°C [a]	1.6	1.8	2.0	1.9	1.6	2.2	2.8	0.8	2.2
50°C [a]	10.6	10.3	10.6	11.1	9.2	11.9	31.9	4.5	26.3
35°C [a]	87.8	68.1	67.1	75.1	62.3	75.6	465.1	28.3	391.2



Assessment of ageing and stability by heat generation rate (dQ/dt) and heat generation Q at 90°C - Part 1: NT-GP 1N, 2N, 3N and 4G



Assessment of ageing and stability by heat generation rate (dQ/dt) and heat generation (Q) at 90°C - Part 2: NT-GP 5W, 6 and JA2, MRCA,.



Times ty_{EL} to reach 3% energy loss EL

Times ty_{EL} in years calculated with Arrhenius parameters obtained from heat generation rate measurements at 60°C, 70°C, 80°C and 90°C.

Reference quantity Q_{ref} is the individual heat of explosion Q_{EX}

See /17/ for more explanations

	1N	2N	3N	4G	5W	6	MRCA	JA2
Q_{EX} [J/g]	3768	4198	4201	4071	4124	4177	3758	4610
web	7	7	7	7	19	19	19	7
Ea_Q [kJ/mol]	112.3	115.6	121.6	118.2	111.5	113.9	130.0	128.2
$\log(Z_Q [\mu W/g])$	17.971	18.217	19.059	18.436	17.633	17.847	20.426	20.056
time ty_{EL} to reach 3% energy loss EL in years at preset temperatures								
65°C [a]	0.85	1.74	2.12	2.57	1.53	2.22	1.62	2.45
50°C [a]	5.4	11.7	15.8	18.1	9.6	14.6	13.8	20.3
35°C [a]	42	95	142	154	73	115	146	207



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Thank you for your attention