

## Principles of a STANAG for the estimation of the chemical stability of propellants by heat flow calorimetry

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### Abstract

The experimental and theoretical work for establishing a STANAG for the estimation of the chemical stability of propellants by heat flow calorimetry is described. The test criteria are derived assuming worst case conditions in ageing and storage.

### Kurzfassung

In dieser Arbeit werden experimentelle und theoretische Arbeiten zur Erstellung einer STANAG, die die chemische Stabilität von Treibladungspulvern abschätzen soll, vorgestellt. Die Prüfkriterien werden von "worst case"-Bedingungen bei Alterung und Lagerung abgeleitet.

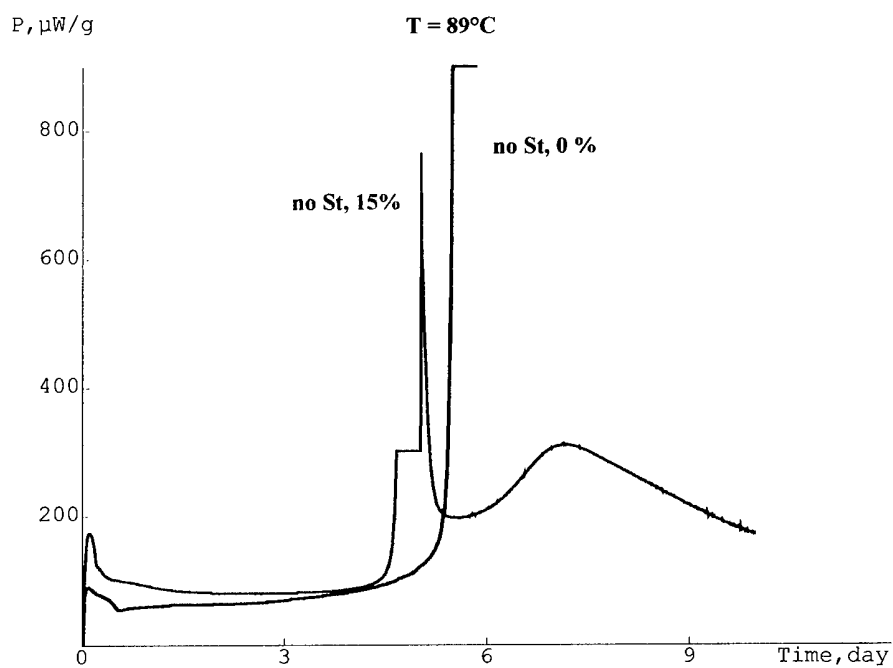
## 1 Introduction

NATO standardisation agreements (STANAG) for the thermal („chemical“) stability of propellants describe mutually acknowledged test procedures to facilitate cross procurement by avoiding repeated testing in different countries. Already existing STANAGs on this subject are based on stabiliser consumption in isothermal storage at elevated temperatures [1,2,3,4].

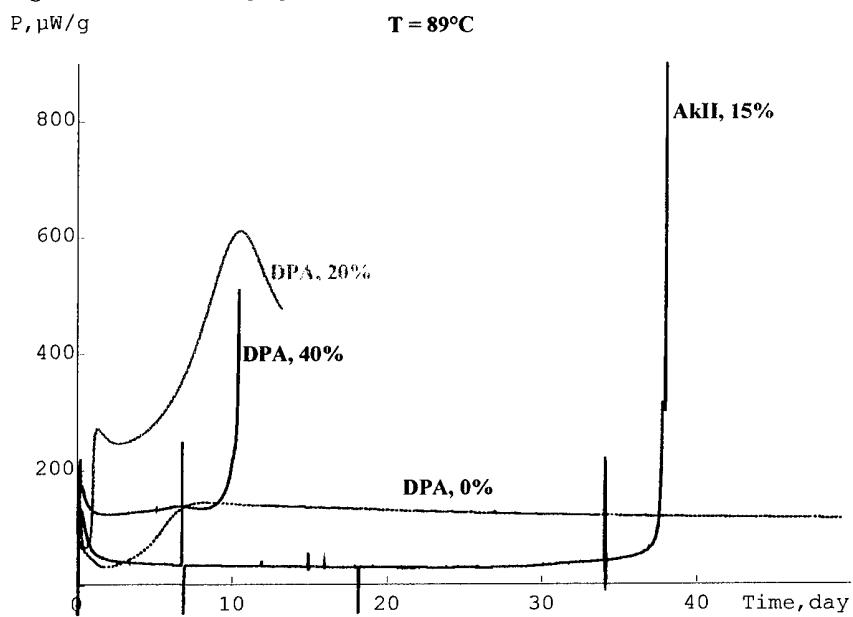
Heat flow calorimetry (HFC) offers a more direct treatment of the problem because here just the quantity that causes the danger of thermal explosion is measured. Moreover, interrupting an HFC experiment shortly before autocatalytical reaction starts and analysing the stabiliser content at this stage yields relevant limits for the stabiliser consumption methods.

## 2 The risk of thermal explosion of propellants

Some examples for heat flow curves of different propellants, measured in a TAM calorimeter at 89°C are shown in figs. 1 to 4. Depending on the type of stabiliser and the nitroglycerin (NG) content (both marked in the graphs) the shapes vary from no to extremely autocatalytic characteristics. The double base (DB) propellant ("DPA, 40%") detonated in the calorimeter after 11 days. The last part of the signal was lost, but simulation of the measuring system (a steel ampoule with 11 mm inner diameter) resulted in a heat generation of at least 80 mW/g to cause a thermal explosion. This event shows dramatically that the chemical stability of propellants merits a more deeply consideration.



**Figure 1.** HFC curves of propellants without stabiliser



**Figure 2.** HFC curves of DPA and Akardite II stabilised propellants

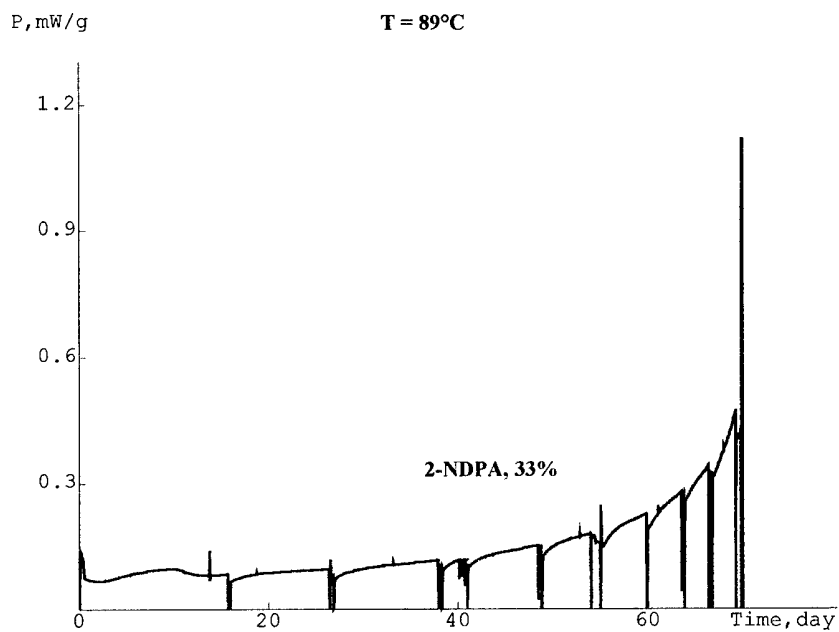


Figure 3. HFC measurement of a 2-NO<sub>2</sub>-DPA stabilised propellant

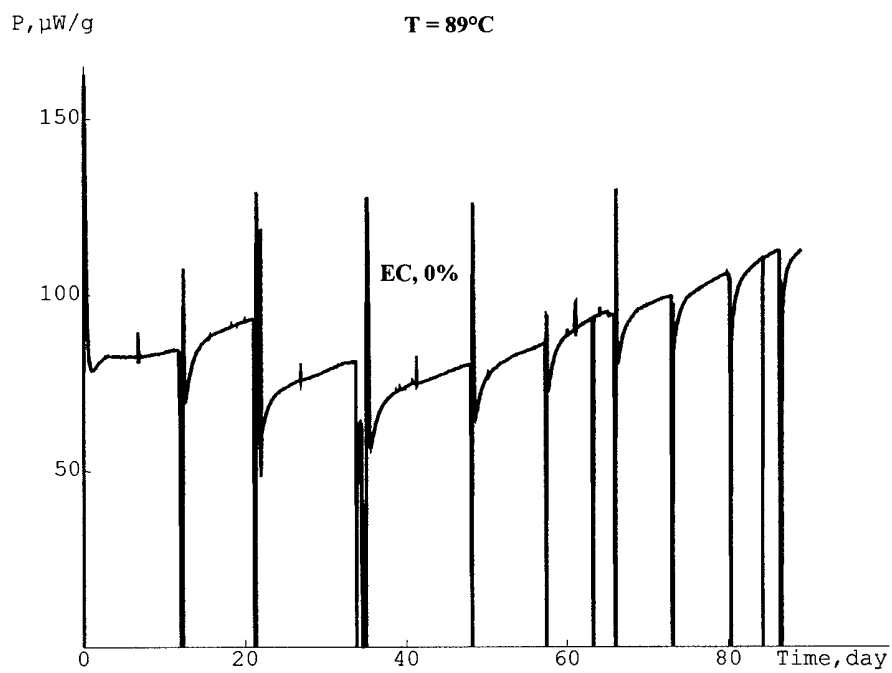


Figure 4. HFC measurement of a propellant stabilised by centralite I.

### 3 Isothermal ageing theory

The aim of the STANAG [5] is to establish a procedure, based on heat flow calorimetry (HFC), as simple as possible and suitable to ensure chemical stability for a 10-years storage at 25°C. To cover this period in an acceptable measuring duration, the experiments must be performed at elevated temperature. For an extrapolation to ambient conditions we have to consider the temperature dependence of the reactions, characterised by the activation energy (AE). In spite of the quite different shapes of the HFC curves due to nitration and nitrosation of the stabilisers it can be assumed that the temperature dependence will be dominated mainly by the slower decomposition reactions of nitrocellulose and NG. The AE should therefore vary only within a limited range. For the same reason the AE can also be estimated from stabiliser depletion at different storage temperatures.

A lot of storage dates were brought into our NATO "expert working group" while working out the STANAGs based on stabiliser depletion. Former investigations indicated a change in AE in the temperature region around 60°C [6]. Therefore we used the stabiliser depletion dates to test this hypothesis by fitting a n-order reaction below and above this temperature.

$$\ln t = \ln(1/A) + E/RT + \ln[(1 - S/S_0)^{1-n}/(1-n)] \quad (1)$$

t	= storage time [d]	R	= gas constant [0.0083143 kJ/(K · mole)]
A	= frequency factor [d <sup>-1</sup> ]	n	= reaction order
E	= AE [kJ/mole]	S	= stabiliser content [%]
T	= storage temperature [K]	S <sub>0</sub>	= stabiliser content before storage [%]

The results are listed in tables 1, 2 and 3.

Table 1. Activation energy from DPA depletion in DB propellants containing up to 15% NG

Storage temperatures [°C]	Activation energy [kJ/mole]	Storage temperature range [°C]	Activation energy [kJ/mole]
45/50/55	124		
45/50/55	129		
45/50/55	135		
52/60	121	60/65/80	140
52/60	117	60/65/80	153
52/60	109	60/65/80	142
52/60	132	60/65/80	140
52/60	110	60/65/80	140

Table 2. Activation energy from DPA depletion in DB propellants with NG contents from 26 to 43%.

Storage temperatures [°C]	Activation energy [kJ/mole]	Storage temperatures [°C]	Activation energy [kJ/mole]
20/40/50/60	121	20/40/50/60	127
20/40/50/60	131	20/40/50/60	126
20/40/50/60	126	20/40/50/60	100
20/40/50/60	125		

Table 3. Activation energy from 2-NO<sub>2</sub>-DPA depletion in DB propellants with NG contents from 20 to 43%.

Storage temperatures [°C]	Activation energy [kJ/mole]	Storage temperature range [°C]	Activation energy [kJ/mole]
50/60	108	60/70	123
50/60	98	60/70	129
50/60	153	60/70	146
50/60	129	60/70/80	167
50/60	144	60/70/80	163
50/60	132	60/70/80	160
50/60	152	60/70	132
50/60	152	60/70/80	128
-	-	60/70/80	134

The overall mean values

E = 126 kJ/mole (s.d = 15) for temperatures < 60°C and

E = 142 kJ/mole (s.d = 13) for temperatures > 60°C

are not giving a convincing support for a change of AE.

It should however be remarked that the scattering of the dates is high, probably due to unequal sealing of the samples and in consequence a different availability of air. Current investigations in the working group are showing a considerable influence of this factor.

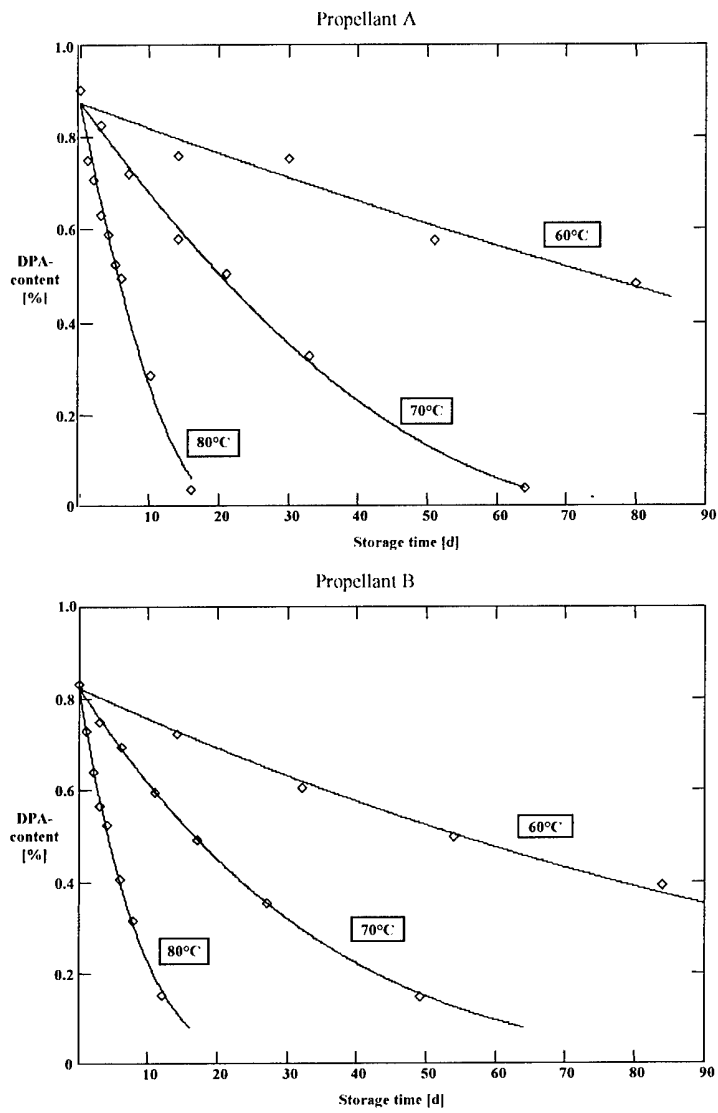
Using hermetically sealed TAM glass ampoules for storage of some DPA stabilised SB propellants we found a continuous change of the AE [6], well described by equation (2):

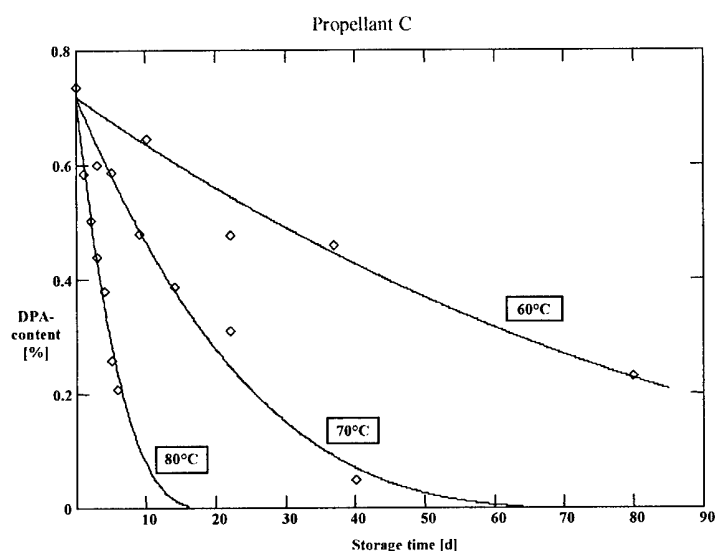
E<sub>1</sub> = AE dominating at higher temperatures [kJ/mole]  
E<sub>2</sub> = AE dominating at lower temperatures [kJ/mole]

$$S = S_0 [1 - (1 - n)(A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT}) * t]^{1/(1-n)} \quad (2)$$

Λ<sub>1</sub>, A<sub>2</sub> = frequency factors, corresponding to E<sub>1</sub> and E<sub>2</sub> [d<sup>-1</sup>]

The fittings are shown in figs. 5, 6 and 7, the kinetic parameters are listed in table 4.





Figures 5-7. Stabiliser (DPA) depletion of some SB propellants in hermetically sealed tubes.

Table 4. Activation energy from DPA depletion in SB propellants using hermetically sealed tubes

Propellant	Lower temperature AE [kJ/mole]	Higher temperature AE [kJ/mole]
<b>A</b>	109	147
<b>B</b>	83	177
<b>C</b>	90	170

From HFC measurements the constance of the AE can be checked using points of equal decomposition degree  $\alpha$  (here: equal heat released) at different temperatures and linear regression of

$$\ln t = \ln \left[ \frac{1}{\Delta H \cdot A} * \int_0^{\alpha} \frac{dQ}{f(Q/\Delta H)} + \frac{E}{RT} \right] \quad (3)$$

$Q$  = heat released [J/g]  
 $\Delta H$  = total reaction heat [J/g]  
 $f(Q/\Delta H)$  = function describing the dependence of reaction rate from reaction degree ("reaction model")

Some plots of AE against the heat released are shown in the figs. 8, 9 and 10 [11]. The first part is dominated by oxidation reactions with the locked-in air, in the following regions near constant values between 120 and 140 kJ/mole are observed. The most informative long time measurements in a temperature range from 50 to 89°C were realised by GUILLAUME [7]. No transition of AE at lower temperatures can be detected from these dates (fig. 11).

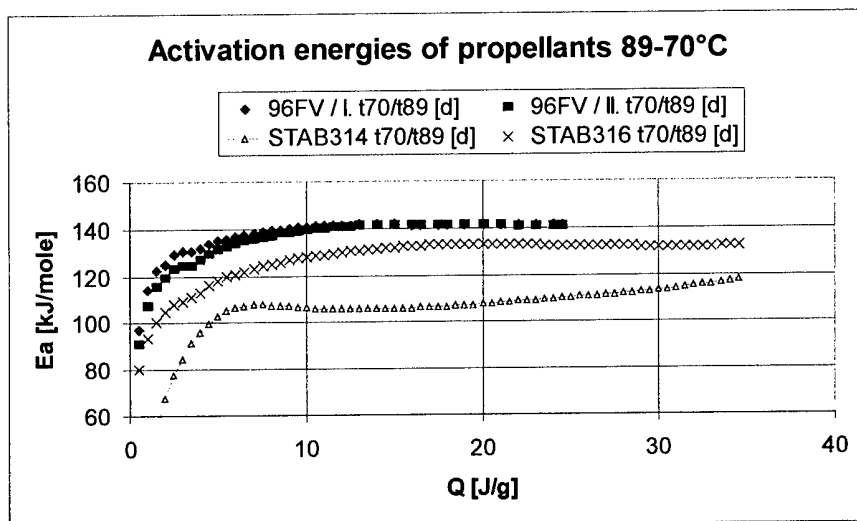


Fig. 8. Activation energies of four DB propellants stabilised with DPA or DPA derivatives.

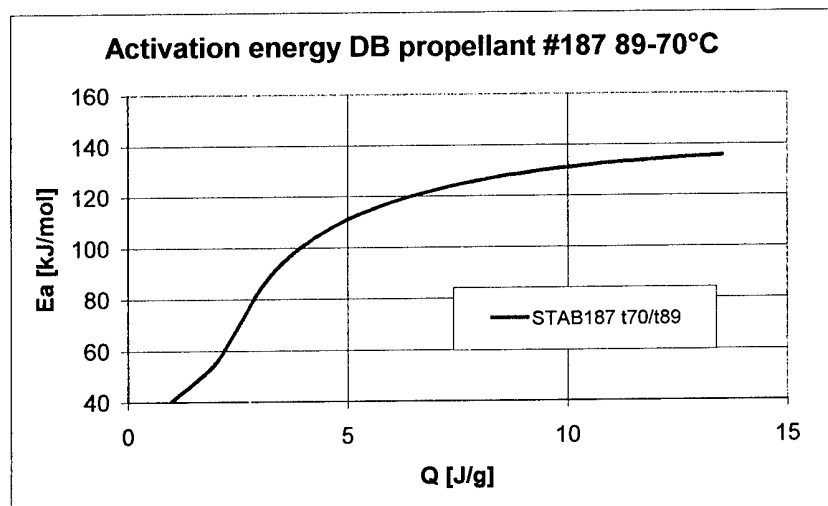


Fig. 9. Activation energy of a DB propellant stabilised by 2-NO<sub>2</sub>-DPA [11]



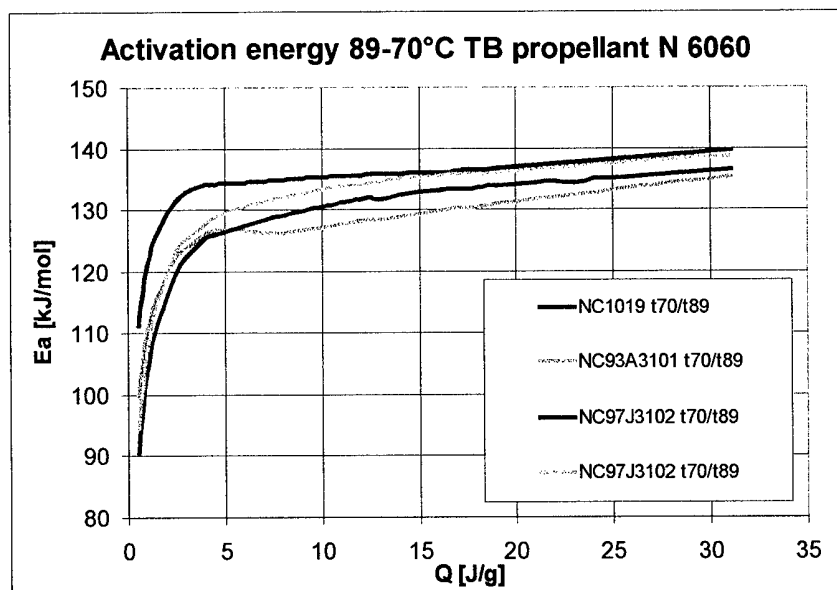


Fig. 10. Activation energy of a TB propellant stabilised by ethyl centralite

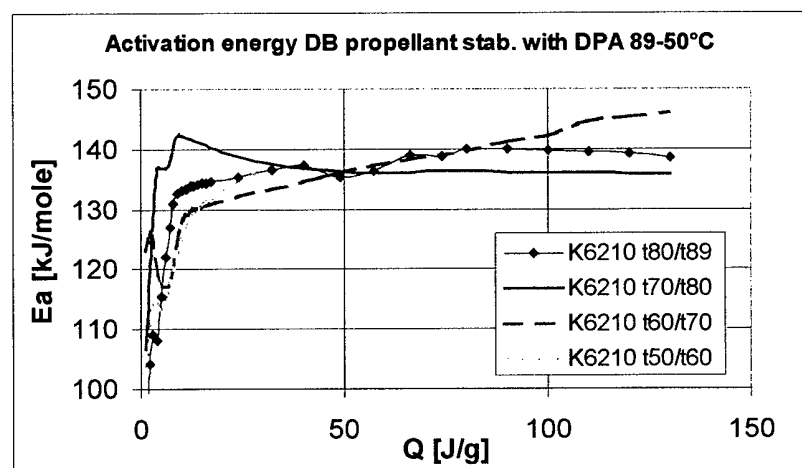


Fig. 11. Activation energy of a DPA stabilised DB propellant between 89°C and 50°C [7]

All HFC measurements reported up to now were carried out starting with fresh samples introduced into the calorimeter at every temperature. Allowing exact "iso- $\alpha$ -evaluation" over a range of decomposition this method is the best. Unfortunately the experiments are extremely time-consuming. An alternative treatment is to age a sample at a higher temperature until a suitable decomposition degree is reached followed by measurements of the same sample at lower temperatures. Since the reaction degree remains nearly constant, the AE can be calculated from temperatures and heat flow values by

$$\ln P = \ln[10^6 * \Delta H * A * f(\frac{Q}{\Delta H})] - \frac{E}{RT} \quad (4)$$

P = heat flow [ $\mu\text{W/g}$ ]  
A = frequency factor [ $\text{s}^{-1}$ ]

Measurements of this type with DPA-stabilised SB propellants resulted in two different slopes of the plot (see fig. 12, 13 and 14 and table 5).

**Table 5.** Activation energy from HFC measurements in SB propellants using hermetically sealed tubes (same samples than in table 4)

Propellant	Lower temperature AE	Higher temperature AE	Temperature of transition <sup>a)</sup>
	[kJ/mole]	[kJ/mole]	[°C]
<b>A</b>	88	124	66
<b>B</b>	81	145	65
<b>C</b>	93	136	53

a) Temperature for equal values of both reaction rate constants

Considering all results gained from stabiliser depletion and HFC leads to the conclusion that at least a general transition of AE at lower temperatures is not detectable.

But following the usual philosophy of safety on explosives (If you are not sure, take the worst case) we must assume that a change may exist for some types of propellants. Corresponding to the lowest values found the levels were set at 120 kJ/mole for temperatures above 60°C and at 80 kJ/mole in the range below. Apart from the different temperature dependence the reactions are assumed to be identical below and above 60°C.

The duration of the experiment leading to the same decomposition degree as a ten year's storage at 25°C can then be calculated from <sup>1</sup>

$$t_m = t_{25} * e^{\left[ E_1 * \left( \frac{1}{T_m} - \frac{1}{T_{60}} \right) + E_2 * \left( \frac{1}{T_{60}} - \frac{1}{T_{25}} \right) \right] / R} \quad (5)$$

$t_m$  = test duration [days]  
 $t_{25}$  = duration of storage at 25°C (3652.5 d = 10 years)  
 $T_m$  = test temperature [K]  
 $T_{60}$  = temperature of change of the activation energy (AE) (333.15 K = 60°C)  
 $T_{25}$  = storage temperature (298.15 K = 25°C)  
 $E_1$  = AE of the higher temperature range (120 kJ/mole)  
 $E_2$  = AE of the lower temperature range (80 kJ/mole)

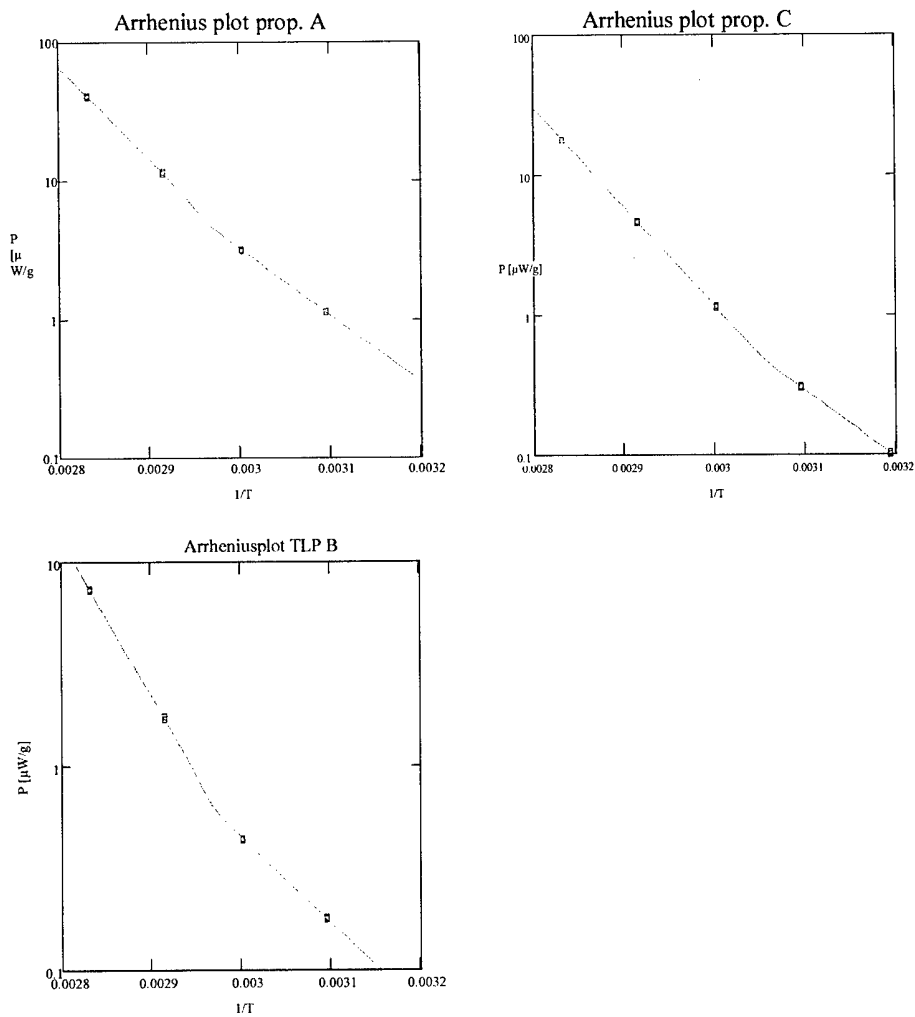
By introduction of the constant values  $T_{25} = 298.15$  K,  $T_{60} = 333.15$  K and  $E_2 = 80$  kJ/mole eq. 5 simplifies to

$$t_m = t_{25} * e^{E_1 / (R * T_m) * C} \quad (C = 46.713) \quad (6)$$

Taking into consideration different meanings concerning the test temperature the STANAG allows to choose a temperature in the range from 60 to 90°C.

Eq. (6) is used for calculation of the corresponding test duration (see table 6).

<sup>1</sup> For derivation see appendix 1



**Figures 12-14.** Activation energies of three DPA stabilised SB propellants.

**Table 6.** Test times for different test temperatures

Test temperature [°C]	Test time [days]
60	123
65	57,2
70	34,8
80	10,6
89	3,83
90	3,43

#### 4 Assessments for non-isothermal storage

In practice an isothermal storage will never be realised. However, if a temperature and time profile of storage can be predicted, it is possible to check whether the thermal stress will be less or more than a storage at 25°C. For temperatures below 60°C any storage durations can be added up as storage times equivalent to 25°C. An example is given in table 7.

$$t_{25} = t_s \cdot e^{E_2 \left( \frac{1}{T_{25}} - \frac{1}{T_s} \right) / R} \quad (7)$$

$T_s$  = storage temperature [K]  
 $t_s$  = storage duration [y]  
 $t_{25}$  = storage duration at 298.15 K [y]  
 $E_2$  = 80 kJ/mole

Table 7: Calculation of 25°C times for a storage profile

$T_s$ [°C]	$t_s$ [y]	$t_{25}$ [y]
40	0.1	0.47
35	0.4	1.14
30	1.5	2.55
25	3	3.00
20	4	2.31
15	1	0.33
SUM	10	9.80

#### 5 Limitation of the heat generation

Gained from experiments with very small differences of the test temperature and the temperature in the propellant the extrapolation outlined above is also only valid for a likewise ideal storage. Under unfavourable real conditions however (high temperatures, large diameters and isolating packing material of ammunition) the exothermal decomposition may cause a considerable increase of temperature in the inner parts of the propellant and hence an accelerated ageing. The consequence would be, that the reaction degree might exceed the area controlled in the test and reach probably more dangerous regions. This situation is illustrated in fig. 15.

To prevent this risk a heat generation limit has to be fixed to ensure that the temperature increase in the propellant remains small.

As a most unfavourable system we consider a cartridge of 230 mm diameter, thermally well isolated (thermal transfer 0,001 W/(cm<sup>2</sup>·K), corresponding for example to a polyethylene package of about 4 cm thickness) and set at a temperature of 71°C. Thermal safety simulations were realised using the heat transfer model of THOMAS [8] in an extended version of OPFERMANN [9,10]. The kinetics were modelled for „strong autocatalysis“ (comparable to propellant „DPA 40%“ in fig. 2), „weak autocatalysis“ (related to propellant „DPA 20%“ in fig. 2) and a zero-order reaction. The equations and parameters used are listed in Appendix 2.

We started with a series of simulations with the strongly autocatalytic propellant. Fig. 16 shows the behaviour in a very small cartridge (thermal transfer 1 W/(cm<sup>2</sup>·K), comparable to a

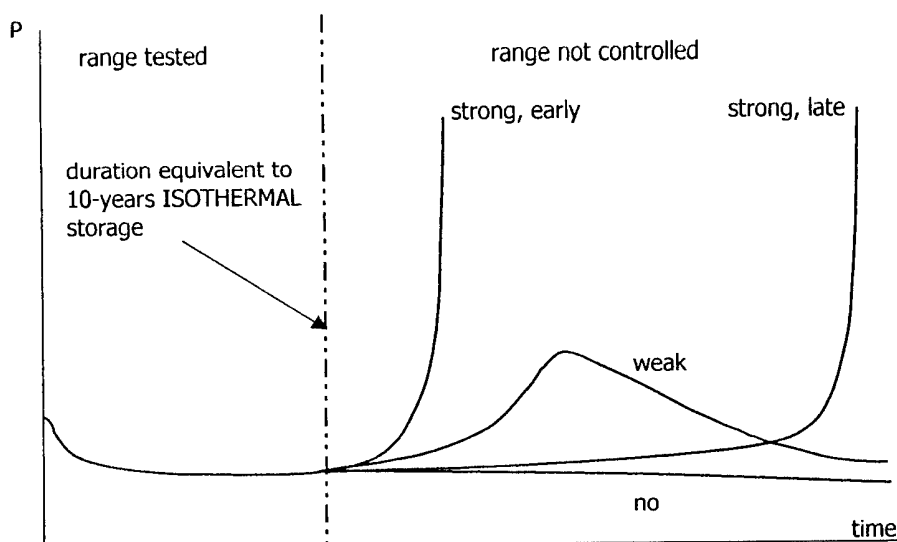


Fig. 15. Possible decomposition mechanisms

HFC experiment) at 89°C. The lines are representing the temperatures in the different distances from the centre (= 0%). Fig. 17 demonstrates the ageing of the same propellant in a large cartridge under the same conditions. The time to explosion is shortened from 11 to 0.6 days. At the highest assumed temperature of 71°C the explosion occurs after more than 90 days (fig. 18). For propellants of this characteristics a thermal explosion can not be excluded, even at lower temperatures. But the safety is yet guaranteed by the long period of time to reach dangerous conditions. E.g. at 47°C the cartridge needs more than 20 years to explode (fig. 19). Assuming the more unfavourable case of an AE of 80 kJ/mole the 20-years-temperature would still be 39°C (fig. 20).

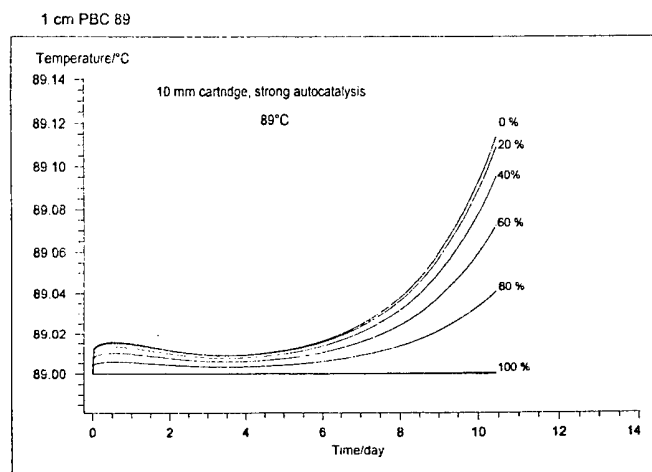
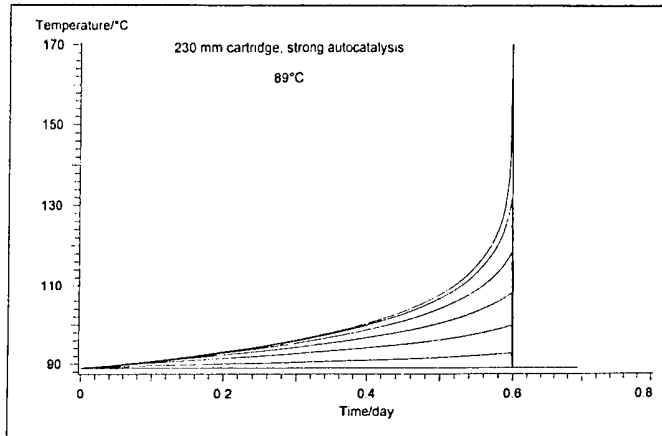
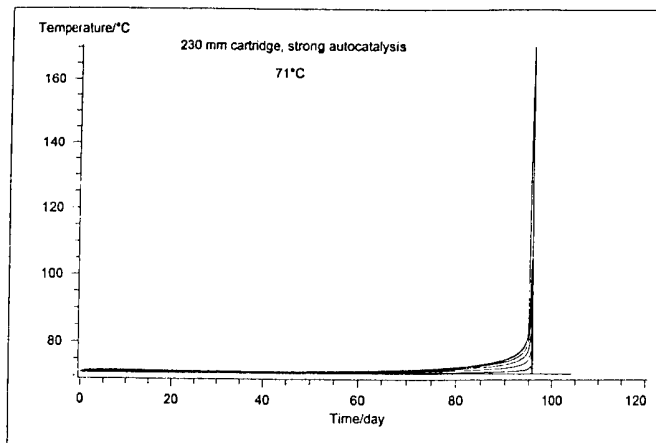


Fig. 16. Simulation of a small cartridge containing an extremely autocatalytic propellant

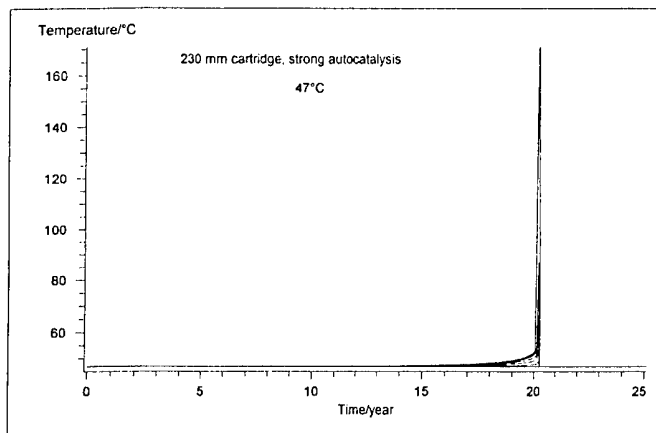
PBC 667 ( 23 cm )



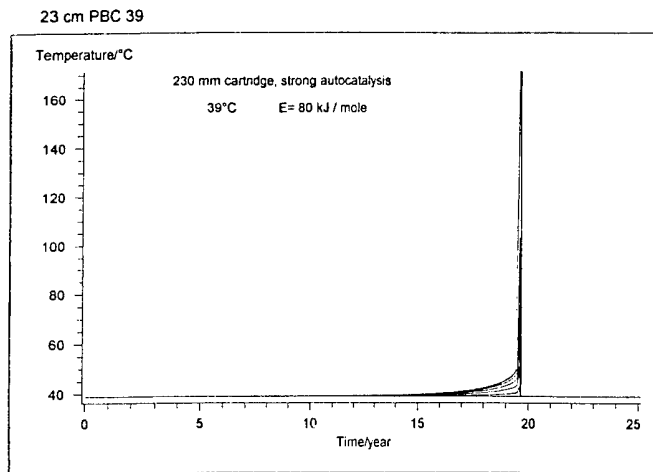
PBC 667 ( 23 cm )



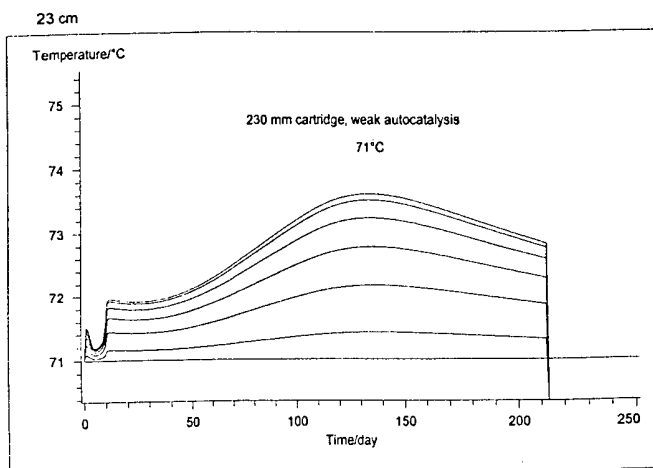
23 cm PBC 39



Figs. 17-19. Simulations of a large cartridge containing an extremely autocatalytic propellant

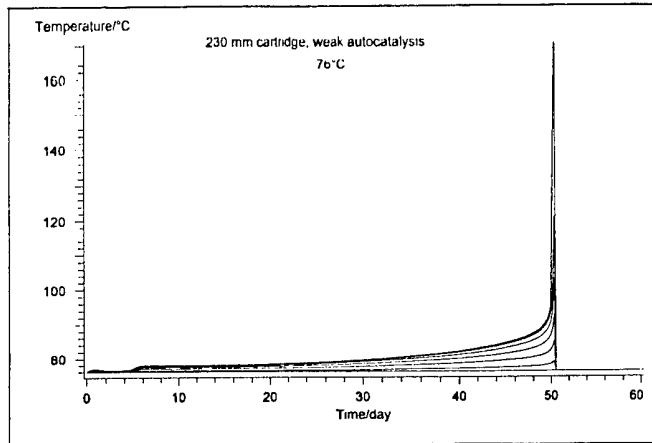


**Fig. 20.** Simulation of a large cartridge containing an extremely autocatalytic propellant  
The propellant of the type „weak autocatalysis“ does not explode at 71°C (fig. 21). Critical conditions are not reached until 76°C (fig. 22).

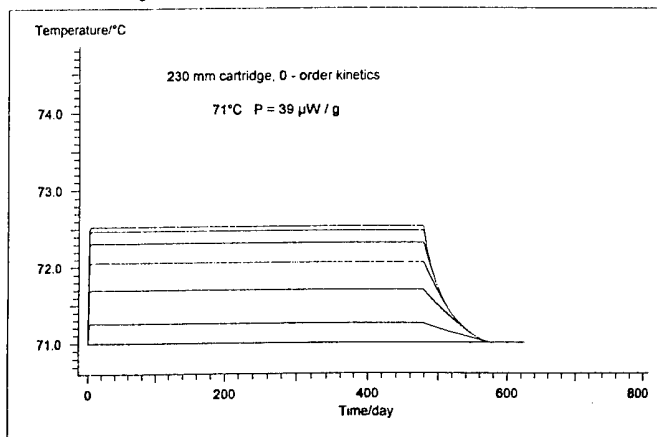


**Fig. 21.** Simulation of a large cartridge containing a moderately autocatalytic propellant

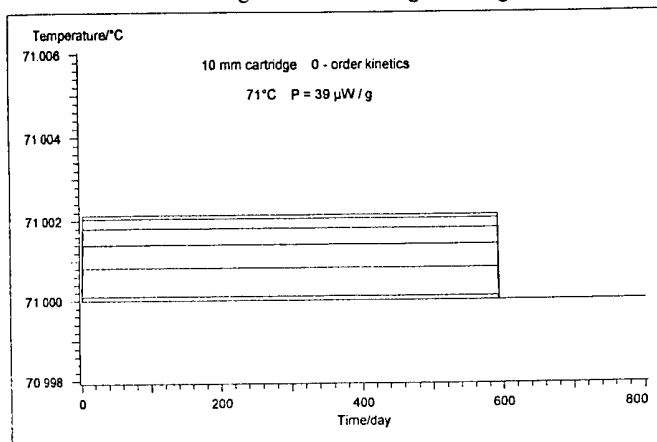
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**Fig. 22.** Simulation of a large cartridge containing a moderately autocatalytic propellant  
230 mm cartridge, 0 - order kinetics



**Fig. 23.** Simulation of a constant heat generation in a large cartridge



**Fig. 24.** Simulation of a constant heat generation in a small cartridge



To find a suitable limit for this system the heat generation rate was varied by the frequency factor of the zero order reaction. At a level of  $39 \mu\text{W/g}$  the temperature increase in the inner part of the 230 mm cartridge is about  $1.5^\circ\text{C}$ , the time for a total reaction is 480 days (fig. 23), in relation to 590 days for an isothermal ageing (fig. 24). This difference is tolerable. Therefore a heat generation limit of  $39 \mu\text{W/g}$  at  $71^\circ\text{C}$  can be accepted as sufficient control of ageing in an equilibrium with the ambient temperature even under worst conditions.

An equivalent limit depending on the test temperature chosen is used as a criterion for sufficient chemical stability of a propellant. It can be calculated by

$$P_1 = P_{71} * e^{\frac{E_1}{R} \left( \frac{1}{T_{71}} - \frac{1}{T_m} \right)} \quad (8)$$

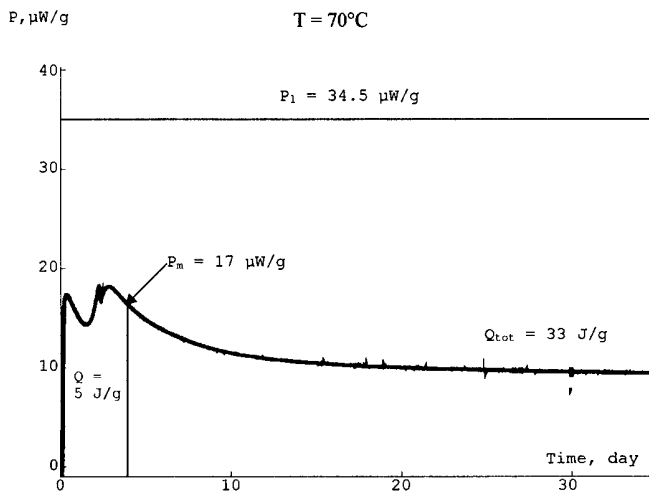
$T_m$  = test temperature [K]  
 $T_{71} = 344.15 \text{ K}$  (=  $71^\circ\text{C}$ )  
 $E_1$  = activation energy (120 kJ/mole)  
 $P_{71}$  = heat flow limit at  $71^\circ\text{C}$  ( $39 \mu\text{W/g}$ )  
 $P_1$  = heat flow limit at  $T_m$  [ $\mu\text{W/g}$ ]

Values for some selected temperatures are given in table 8.

**Table 8.** Heat generation limits for different test temperatures

$T_m$ [ $^\circ\text{C}$ ]	$P_1$ [ $\mu\text{W/g}$ ]	$T_m$ [ $^\circ\text{C}$ ]	$P_1$ [ $\mu\text{W/g}$ ]
60	9.8	80	114
65	18.5	89	314
70	34.5	90	350

In the first part of the measurement some propellants show a fast decreasing exothermic reaction with the locked in air. The total heat of this reaction is small and cannot cause more than a temperature increase of only a few degrees centigrade, even if released momentarily. To disregard this effect the  $P_1$  criterion should be used only in the region between the time corresponding to a heat release of 5 J/g and the test time defined by eq. (6). An example of the evaluation of a test is given in fig. 25.



**Figure 25.** Heat flow curve and evaluation of a DB propellant stabilized with DPA

## 6 Discussion

While working out this methods some propellants capable of an extremely autocatalytic reaction were found. These propellants can not be expected to remain stable forever, even not if they are used in small calibre ammunition and stored at moderate temperatures. But the safety is guaranteed for a period much longer than usual service life times. To detect certainly the safety life time two parameters were set on very conservative levels:

1. The assumption of a low AE at lower temperatures means that the test duration will be equivalent to a considerably longer storage time at ambient temperatures than the demanded 10 years.
2. The limitation of the tolerable heat generation of the propellant considering a worst case system is a further guarantee that the stress during the service life time will be smaller than in the test.

In consequence the failing criteria of the test are hard, not far away from unfairness. On the other hand until today no qualified propellant ever was found to fail the test, indicating a good quality of manufacture.

## 7 References and Notes

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## Appendix 1

### Calculation of the measuring time

A reaction formulated in the heat flow form is given by

$$\frac{dQ}{dt} = \Delta H * f\left(\frac{Q}{\Delta H}\right) * A * e^{-E/(RT)} \quad (9)$$

Q	= Heat released	$\Delta H$	= Total reaction heat
t	= Reaction time	T	= Temperature of reaction [K]
dQ/dt	= Reaction rate (heat flow)	Q/ $\Delta H$	= Reaction degree
A	= Frequency factor	E	= Activation energy [kJ/mole]
R	= Gas constant		
f(Q/ $\Delta H$ )	= Function of describing the dependence of the reaction rate from the reaction degree		

If  $T_m$  is the measuring temperature,  $Q_m$  the heat released at the end of the measurement,  $E_1$  the AE dominating at higher temperatures, then after separation of the variables, integration at constant temperature and rearrangement the reaction time  $t_m$  is obtained by

$$t_m = \frac{1}{\Delta H * A} * \int_0^{Q_m} \frac{dQ}{f(Q/\Delta H)} * e^{E_1/(R*T_m)} \quad (10)$$

The time  $t_{60}$  to reach the same decomposition  $Q_m$  at the assumed temperature ( $T_{60}$ ) of change of AE can equally be calculated from

$$t_{60} = \frac{1}{\Delta H * A} * \int_0^{Q_m} \frac{dQ}{f(Q/\Delta H)} * e^{E_1/(R*T_{60})} \quad (11)$$

The value of the integral in eqns. 10 and 11 is unknown but equal. Therefore by division and rearrangement eq. 12 results:

$$t_m = t_{60} * e^{[E_1 * (1/T_m - 1/T_{60})]/R} \quad (12)$$

If the change of AE is assumed to occur sharply at 60°C an equation similar to eq. 12 is also valid for  $E_2$ , the AE dominating the lower temperature range.

$$t_{60} = \frac{1}{\Delta H * A} * \int_0^{Q_m} \frac{dQ}{f(Q/\Delta H)} * e^{E_2/(R*T_{60})} \quad (13)$$

The corresponding time  $t_{25}$  for 25°C ( $T_{25}$ ) is

$$t_{25} = \frac{1}{\Delta H * A} * \int_0^{Q_m} \frac{dQ}{f(Q/\Delta H)} * e^{E_2/(R*T_{25})} \quad (14)$$

Division of eqns. 13 and 14 gives after rearrangement

$$t_{60} = t_{25} * e^{[E_2 * (1/T_{60} - 1/T_{25})]/R} \quad (15)$$

Combination of eq. 12 and 15 results in

$$t_m = t_{25} * e^{[E_1 * (\frac{1}{T_m} - \frac{1}{T_{60}}) + E_2 * (\frac{1}{T_{60}} - \frac{1}{T_{25}})]/R} \quad (5)$$

## Appendix 2

Data used for thermal safety simulations

Kinetics for modelling propellant decompositions

$$a) \text{ n - order reaction} \quad P = \Delta H * k * 10^6 * [1 - (1 - n) * kt]^{n/(1-n)} \quad (16)$$

$$b) \text{ 1<sup>st</sup> order with autocatalysis} \quad P = \Delta H * a^2 * k * 10^6 * \frac{e^{akt}}{(e^{akt} - 1 + a)^2} \quad (17)$$

$$c) \text{ Avrami - Erofeev reaction} \quad P = \Delta H * k * 10^6 * [(1 - p)kt]^{p/(1-p)} * e^{-[(1-p)kt]^{1/(1-p)}} \quad (18)$$

$$d) \text{ Prout - Tompkins reaction} \quad P = \Delta H * 10^6 * \left(\frac{1-Q}{\Delta H}\right)^n * \left(\frac{Q}{\Delta H}\right)^p * k \quad (19)$$

$$k = A * e^{-AE/RT}$$

For 1<sup>st</sup> and zero-order reaction:  $n = 1.0001$  and  $n = 0$  in eq. (16).

Kinetics for „strong autocatalysis“ were modelled by three independent reactions. For „weak autocatalysis“ four reactions were used. Their parameters are listed below.

Type	Reaction (eq)	log A [A in s <sup>-1</sup> ]	AE [kJ/mole]	n	log a	p	ΔH [J/g]
„strong	(16)	14,7817	140	1,0001	-	-	46,0
autocata-	(18)	14,9984	140	-	-	0,67	28,7
lytic"	(17)	9,9119	140	-	5	-	61106
	(16)	5,3743	80	1,0001	-	-	46,0
	(18)	5,5910	80	-	-	0,67	28,7
	(17)	0,5045	80	-	5	-	61106
„weak	(16)	14,0776	136	0,6446	-	-	104,9
autocata-	(16)	13,4177	127	0,1583	-	-	-18,3
lytic"	(16)	14,0484	127	0,5372	-	-	2,7
	(19)	14,1993	139	5,4568	-	0,6821	4000
constant	(16)	variable	140	0	-	-	2000

Other propellant data:

Form of reactor: cylindrical  
 Specific heat ( $C_p$ ):  $0,205 + 0,00325 T$  [J/(g·K)]  
 Heat conductivity:  $0,00122$  W/(cm·K)  
 Loading density:  $1$  g/cm<sup>3</sup>  
 Explosion temperature:  $170^\circ\text{C}$