



Activation Energy of Propellants at Low Temperature Range^{*)}

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Abstract: This paper describes a new approach to determine the activation energy of propellant decomposition reactions which quantifies the temperature dependence of a reaction rate at temperatures below 50 °C by using an indirect microcalorimetric method. Whereas the determination of life time and stability of propellants is usually performed by artificial ageing at elevated temperatures with a temperature range usually between 70 and 130 °C only few and scattered data are available for temperatures below 50 °C. Normally these activation energies for propellant decomposition reactions are not known below temperatures of about 50 °C because (i) the reaction rates are very small and thus ageing times have to be very long and (ii) because of slow reactions the chemical change of the propellant becomes very small which – in combination with too short ageing times – may lead to wrong estimations and calculations. The main reason for this is that the experimental error is relatively big in comparison with the real change of the propellant. To be on the ‘safe side’ people usually assume a low value of activation energy. This has the effect that measuring times at high temperatures are much longer than they should be and that maybe good material is thrown away too early in fear of a thermal instability. To overcome this problem we have established a new approach by an indirect microcalorimetric method. This method evaluates the shift of typical points in the heat flow curve to earlier times after artificial ageing at relatively low (30-70 °C) temperatures. From the time shift of a specific point in the heat flow curve (compared to the unaged material) and the temperature difference between ageing temperature and measuring temperature activation energies of the whole temperature range between 89 °C and 30 °C are available. We have verified the usability of this approach with six different nitrocellulose based propellants.

Keywords: propellants, activation energy, microcalorimetry, stabilizer depletion

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Introduction

The determination of life time and stability of propellants is usually performed by artificial ageing at elevated temperatures. The temperature range usually lies between 90 and 130 °C for ‘classical’ stability tests whereas other tests like microcalorimetry, stabilizer depletion and vacuum stability are usually performed at temperatures between 70 and 100 °C [1, 2]. To calculate the real storage time that is covered by a high temperature experiment one must assume an activation energy which quantifies the temperature dependence of a reaction rate.

Normally these activation energies for propellant decomposition reactions are not known below temperatures of about 60 °C because the reaction rates are too small for a direct measurement even in sensitive calorimeters or for achievement of measurable gas generation in the vacuum stability test. Also stabilizer depletion is much too slow unless very long measuring times are realized.

We have established a new approach to solve this problem by an indirect microcalorimetric method. This method evaluates the shift of typical points of the heat flow curve (maxima, minima, points of inflection) to earlier times after artificial ageing at relatively low (30-70 °C) temperatures in an oven. From the time shift of a specific point in the microcalorimetric curve (e.g. point of inflection, maximum, minimum, thermal runaway...) compared to the unaged material and the temperature difference between ageing temperature and measuring temperature, activation energies of the whole temperature range between 89 °C and 30 °C are available. We have verified the usability of this approach with six different nitrocellulose based propellants.

Materials and Methods

Propellants Tested

Five types of **gun propellants** and one **rocket propellant** (propellant D) were investigated by this low temperature activation energy (‘LTAE’) approach. They are listed (including their main ingredients) in Table 1. Propellants A, K, P and V were taken as received. Propellant D was cut into small dices (2-4 mm length). Propellant N was milled and sieved. Samples with particle sizes between 1 and 5 mm were taken for this study. Note that not all propellants were freshly received samples, two of them were quite old (13 and 20 years).

Table 1. Propellants used for the LTAE study

Propellant abbreviation	Propellant type	Stabilizer type	Ageing temperatures [°C]	NG content [%]	Age [y] at beginning
A	1-hole stick	DPA + EC	30, 35, 40, 50, 70	0	20
D	rocket	2-NDPA	30, 35, 40	34	6
K	ball	DPA	30, 35, 40, 50, 70	19	4
N	1-hole stick	EC	30, 35, 40, 50	21	1
P	ball	DPA + EC	30, 35, 40, 50, 70	10	1
V	porous	DPA	30, 35, 40, 50	0	13

DPA = diphenylamine, EC = ethyl centralite, 2-NDPA = 2-nitro-DPA, NG = nitroglycerin

No akardite stabilized propellant was taken because their decomposition follows nearly exactly zero order, which means that no typical points (maxima, minima...) could be chosen for evaluation. Also no triphenylamine stabilized propellant was available in large enough amounts although the characteristic shape of their heat generation rate [3] would make them ideal candidates for this study.

Experiments

Microcalorimetric measurements were conducted with a „Thermal Activity Monitor“ (TAM 2277 and TAM III, Thermometric AB, Sweden). The measurements for the LTAE project were performed in 3 mL glass ampoules exclusively at 89 °C. In addition this paper refers to measurements at temperatures between 50 and 80 °C which were performed for iso α kinetic evaluations (see chapters ‘classical evaluation...’ and ‘precursor tests’)

Because it was important to repeat the shape of the microcalorimetric curve as precisely as possible [1] the ampoules were filled with exactly (± 1 mg) the same amount of propellant. Because the shape of the curve also depends on the moisture level [4, 5], the filling of the ampoules was performed within one day for one propellant type. Samples for each ageing step were weighed in triplicate. Two samples were taken for microcalorimetry, the third sample was used for stabilizer depletion analysis.

Stabilizer depletion was measured by high performance liquid chromatography (HPLC). The samples were prepared by dissolution in 20 mL of acetonitrile. The nitrocellulose was precipitated by adding 5 mL of water. The solution was filtered. The stabilizers were separated and detected with a suitable HPLC system containing a diode array detector ($\lambda = 200\text{-}356$ nm). More details are described in Ref. [1].

Results

Classical iso α evaluation from isothermal tests and its limit

In a very long measuring campaign, PB Clermont S.A. (Belgium) has conducted isothermal microcalorimetry of double base spherical propellants [1]. The measurements were performed at 89, 80, 70, 60, and 50 °C. The latter measurement is still running after now 2500 days of continuous measurement. Figure 1 shows this important experiment. The lines with slope -1 cut the heat flow curves at the same point for any temperature. This means that the activation energy is nearly independent of the reaction degree and the temperature. Overall the value for E_a is around 137 ± 3 kJ/mole.

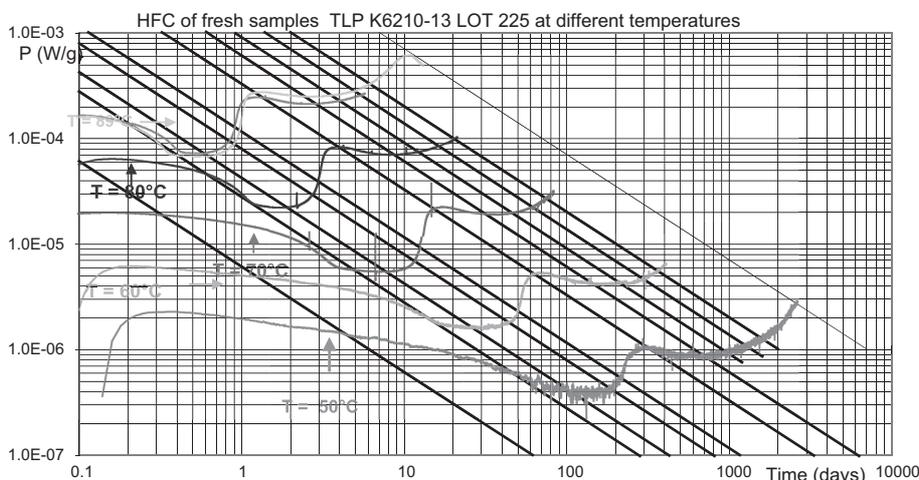


Figure 1. Microcalorimetry of propellant K at five different temperatures.

Nevertheless, a continuous measurement at temperatures below 50 °C is hard to realize. There are two reasons for that: (i) the heat generation rate is too low to be able to distinguish it from base line noise and (ii) the time to reach a significant level of decomposition is much too long to be realizable.

Precursor tests at 70 °C

The propellants A, K and P were taken in a preliminary test which was carried out to demonstrate the suitability of the whole project using an ageing temperature of 70 °C. All three propellants were subjected to the LTAE test. In addition the activation energy of all three samples was estimated from continuous measurements at 89 °C and 70 °C and subsequent iso α evaluation.

Table 2 shows the results of the calculations.

Table 2. Kinetic evaluation of precursor tests at 70 °C (evaluated by LTAE concept; left column) and comparison of activation energy values with isothermal runs (calculated by iso α evaluation; right column)

Propellant	E_a from LTAE (89-70 °C)	E_a from isothermal runs (89-70 °C)
A	131 kJ/mole	135 kJ/mole
K	144 kJ/mole (from poi); 137 kJ/mole (from 2 nd max)	137 kJ/mole
P	137 kJ/mole	141 kJ/mole

E_a = activation energy, poi = point of inflection

The values of E_a do not differ significantly from each other. Therefore this preliminary test was declared as being successful and the ‘real LTAE’ was begun (see chapters below).

LTAE studies at temperatures between 30 and 50 °C

After the successful preliminary test we started the ageing programme at 30, 35, 40 and 50 °C. As ageing times are extremely long, this programme began five years ago and is still far away from being finished. As the stability of the propellants is different and the different stabilizers which are responsible for the typical shape of the microcalorimetric curve we did not set up an overall ageing plan but we decided to take out samples when we assumed that a significant change would have happened. In the following sub-chapters the features of the different propellants are presented in alphabetical order.

To be able to make a correct assumption of the heat generation rate of the unaged material a five-fold determination of all samples was made. For evaluation the average position of the individual points was taken. In addition, to control the ageing conditions all ampoules were weighed after artificial ageing. If the weight loss was significantly higher than that of the parallel samples we have excluded this sample from evaluation because it was assumed that the seal has not been airtight all the time.

Propellant A

This single base propellant caused some trouble due to instabilities in the past and was therefore chosen to be one of the candidates for our LTAE test. Its microcalorimetric curve is not very spectacular – the only special point that can

be evaluated is a point of inflection during the increase into the second level of decomposition. To find the corresponding time properly the first derivative of the heat generation rate was calculated and evaluated. Figure 2 shows typical derivated curves after ageing at 35 °C as an example.

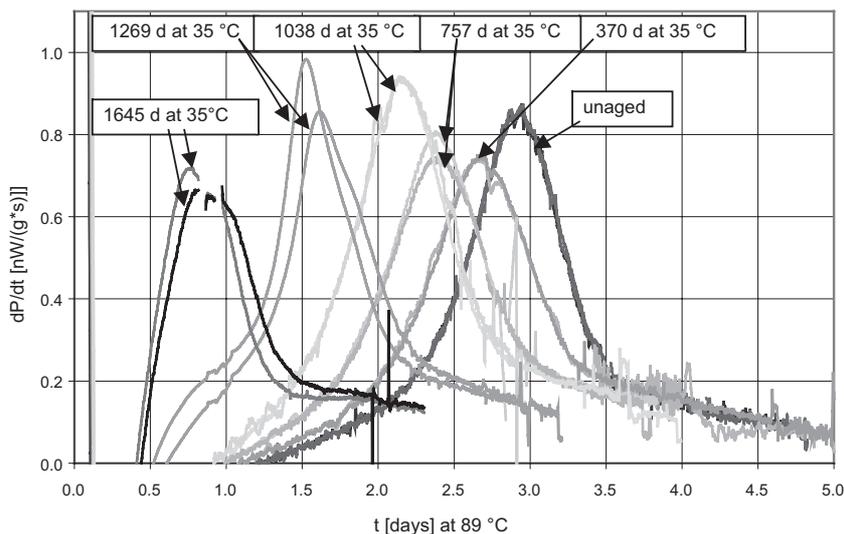


Figure 2. Derivated heat generation rates of propellant A after ageing at 35 °C.

Propellant D

The only rocket propellant in this test also showed only one specific point of the microcalorimetric curve – its second maximum. It coincides with the complete decomposition of the stabilizer 2-NDPA and appears after ca. 10 days at 89 °C in unaged material. Figure 3 shows typical results after ageing at 40 °C as an example. All other points (first minimum, point of inflection) could not be taken for evaluation. The position of the first minimum is too dependent from the first maximum, which represents the oxidation reaction of the nitrocellulose with the oxygen in the ampoule. This oxidation reaction proceeds during the ageing at 30–40 °C so that the first maximum decreases significantly within the first 1200 days at 40 °C (see Figure 3) and therefore the position of the first minimum strongly depends on the height of the oxidation reaction. The point of inflection is not very easily detectable – the derivative of the heat generation rate (which is needed to find this point) scatters too much to be a usable tool for this evaluation.

Propellant K

This propellant is probably the best investigated propellant concerning stability [1]. As Figure 1 shows it has a first minimum, a second maximum and, in-between them, a point of inflection. The point of inflection and the second maximum were chosen for evaluation, because the first minimum is very flat (and therefore difficult to find exactly) and it appears close after the first maximum which belongs to oxidation reactions of the propellant with the air around the grains in the closed ampoule. If once all oxygen is used up the first maximum disappears and thus also no first minimum is present anymore. The depletion of the first maximum can be seen in all propellants except for propellant N (this propellant does not have one). Figure 4 shows typical results after ageing at 40 °C as an example.

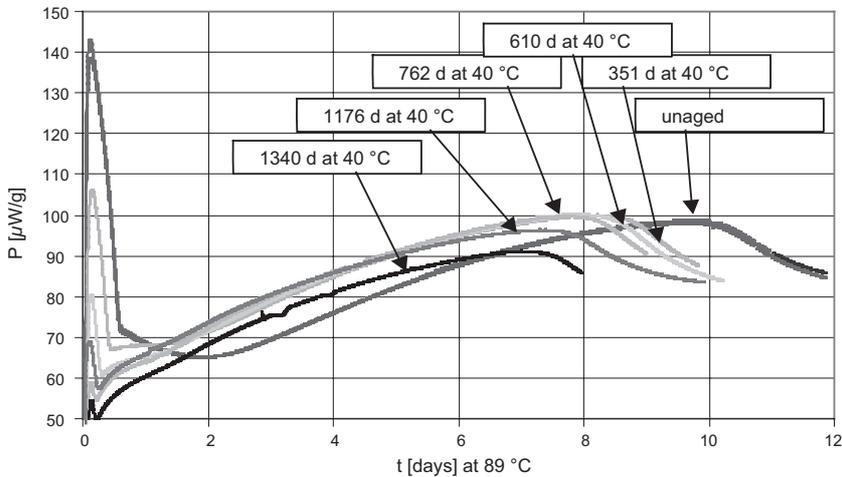


Figure 3. Heat generation rates of propellant D after ageing at 40 °C. Please note the depletion of the first maximum which is almost zero after 1340 d at 40 °C.

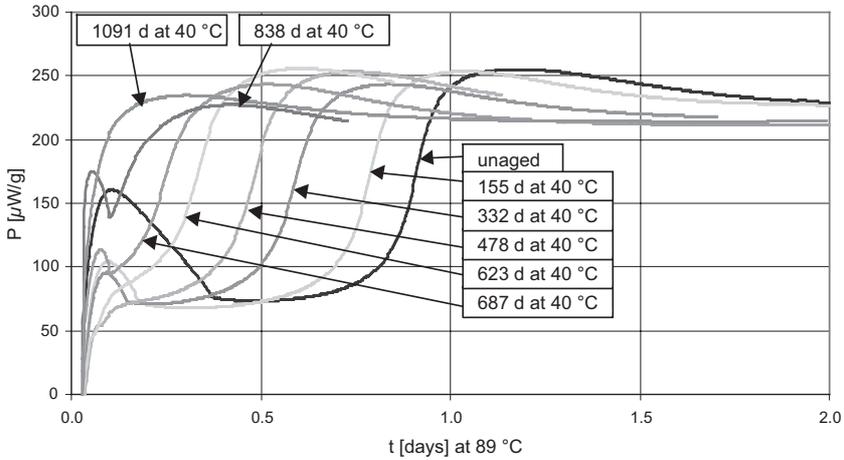


Figure 4. Heat generation rates of propellant K after ageing at 40 °C. The heat generation rate of the 2nd maximum remains nearly constant.

Propellant N

This propellant has a very interesting heat generation rate curve, from which three points were selected for evaluation: A sharp minimum after 0.75 days (the chemical reason for it is unknown but it appears in all propellants containing nitroguanidine), a first maximum and a second minimum. Typical results after ageing are shown in Figure 5.

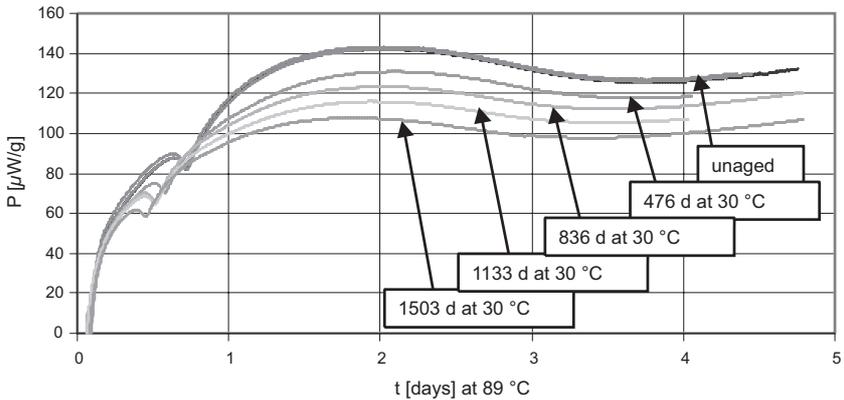


Figure 5. Heat generation rates of propellant N after ageing at 30 °C. Note that the heat generation rate is reduced with longer ageing time.

Propellant P

This propellant is chemically comparable to propellant K with the main difference that the presence of EC changes the heat generation rate curve in such a way that no second maximum is observed. So, like with propellant A only the point of inflection could be evaluated (for the first maximum and its disappearance see explanations for propellant K). Also the reason for the choice of this propellant for the LTAE study is similar to propellant A: There were problems with instability with this type of propellant before this study had started. Typical derivated heat flow curves are shown in Figure 6.

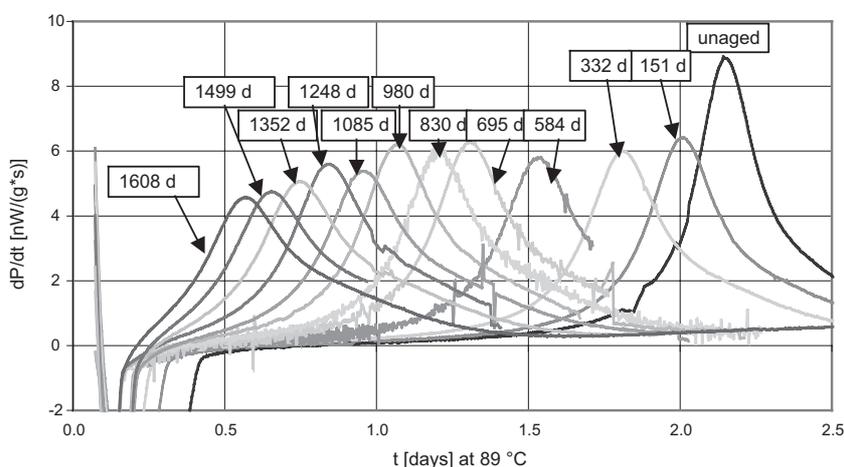


Figure 6. Derivated heat generation rates of propellant P after ageing at 40 °C. The maximum decreases with ageing time.

Propellant V

This propellant may be the most interesting one of the chosen candidates, as it shows a thermal runaway at 89 °C after 10-11 days. The pattern of the first part is also very useful for LTAE evaluation as a first minimum and a second maximum (and two points of inflection in-between them) could be evaluated. The time to reach thermal runaway was also evaluated, knowing that this may not be reached by natural ageing (according to [6] 10-11 days at 89 °C are equivalent to 26-29 years at 25 °C [STANAG 4582 assumes an E_a of 120 kJ/mole above.

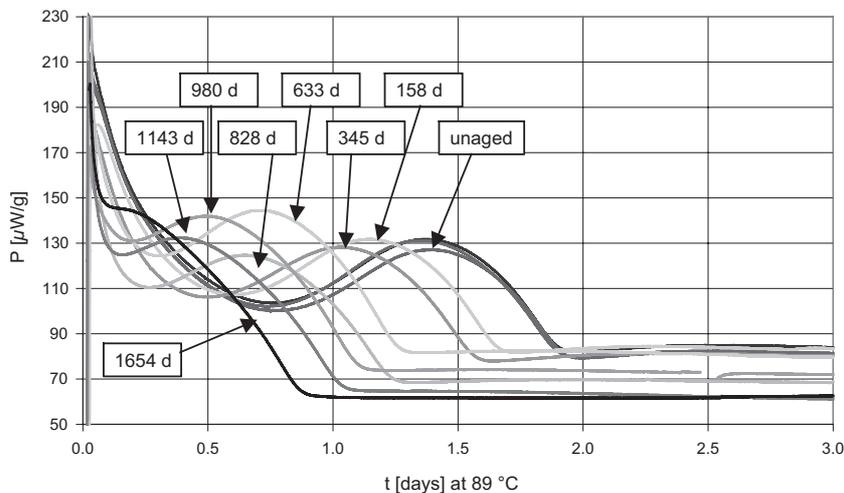


Figure 7. Heat generation rates of propellant V after ageing at 40 °C.

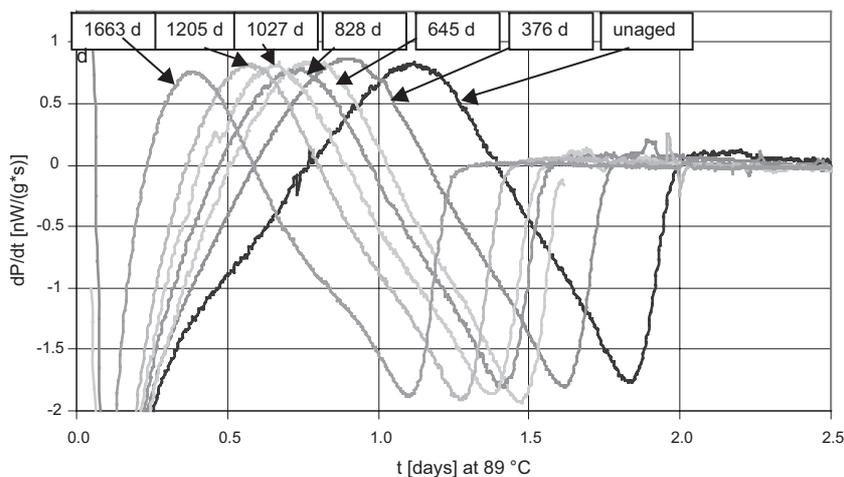


Figure 8. Derivated heat generation rates of propellant V after ageing at 35 °C.

60 °C and of 80 kJ/mole below 60 °C]). Nevertheless, a pre-ageing was suspected to make this propellant less stable and so there was a likeliness that this thermal runaway could be significantly shifted to earlier times. Figure 7 shows – again as an example – heat flow curves after ageing at 40 °C, whereas Figure 8 depicts derivated microcalorimetric curves after ageing at 35 °C.

Evaluation of activation energies

All microcalorimetric values were transferred into EXCEL[®]. To guarantee a perfect comparison between all curves they were recorded with the same frequency (each 300 sec). They were numerically derivated, averaged over 15 data points.

The calculation of the activation energy is performed by linear regression of all suitable data points from

$$t_d = a \cdot t_e \quad (\text{Eq. 1})$$

t_d = time difference of a certain point in the heat low curve between the aged and the unaged material [d]

t_e = ageing time at low temperatures [d].

The slope a is

$$a = e^{\frac{E_a}{R} \cdot \left(\frac{1}{T_d} - \frac{1}{T_e} \right)} \quad (\text{Eq. 2})$$

E_a = activation energy [kJ/mol]

R = gas constant (0.00831447 J/(K·mol))

T_d = measuring temperature (362,15 K)

T_e = ageing temperature [K]

The activation energy is then calculated from Eq. 3:

$$E_a = \frac{R \cdot \ln a}{\left(\frac{1}{T_d} - \frac{1}{T_e} \right)} \quad (\text{Eq. 3})$$

Also the activation energy within the temperature range of ageing (50-30 °C) was calculated. This was performed by replacing the single slope (from the t_d versus t_e evaluation in Eq. 3 by the ration of two different slopes (from the evaluation of one t_e versus another) and T_d by the higher of both ageing temperatures.

One of the most interesting questions was whether a change in activation energy would occur at temperatures around 50-60 °C as indicated by many authors [7-13] and as installed in STANAG 4582 [6].

Stabilizer depletion

Stabilizer depletion was conducted on most of the aged samples. The reason to do this was to control whether the ageing characteristic which could be observed by microcalorimetry would also be detectable by changes in the stabilizer content. The second idea behind this part of the work was to check the distribution of stabilizer depletion products which could give us information about the ageing conditions (closed/open ampoules).

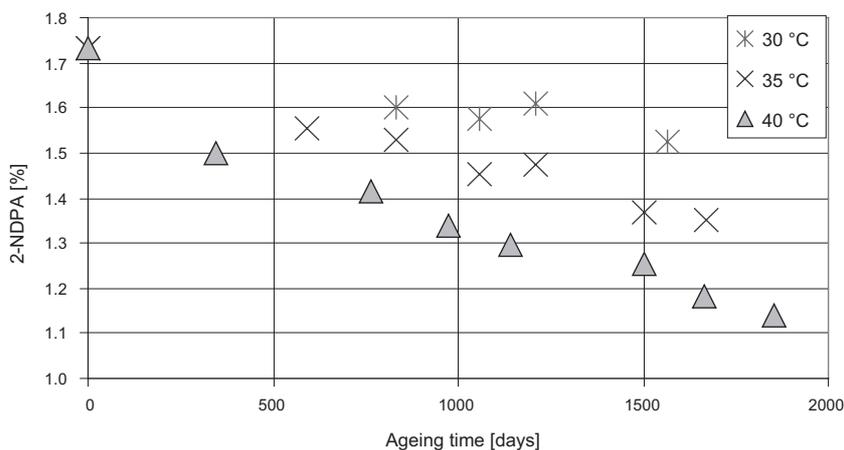


Figure 9. 2-NDPA depletion of propellant D at 30, 35 and 40 °C.

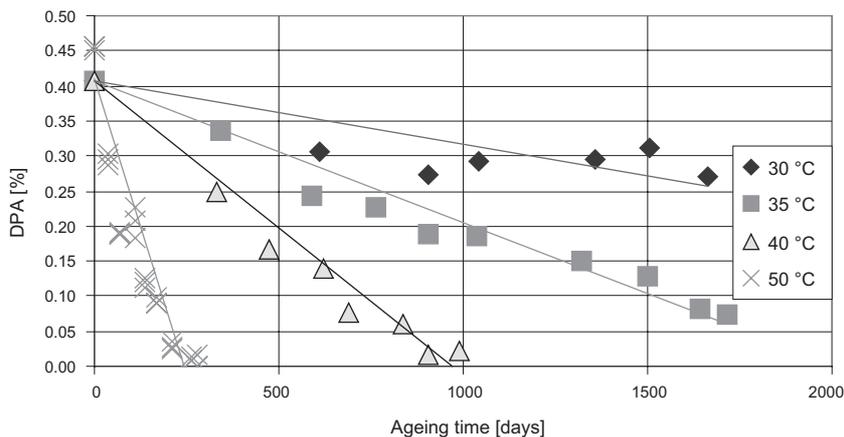


Figure 10. DPA depletion of propellant K at 30, 35, 40 and 50 °C.

The stabilizer depletion was also evaluated by the kinetic model which was set up during the development of AOP-48, Edition 2 [14]. Figures 9 and 10 give two examples of the results of stabilizer depletion on various propellants. For evaluation of activation energies see below.

Discussion

Shift of characteristic points in the microcalorimetric curve

The shift of characteristic points in the microcalorimetric curve was presented in some examples in Figures 2 to 8. To give a better overview on all the results the most important graphs are presented in Figures 11 to 17. They are sorted in alphabetical order.

Propellant A

This propellant shows a very unusual behaviour. Within the first part of the ageing the shift of the point of inflection is nearly proportional to the ageing time. If the ageing time increases, also the shift increases. The main reason for this behaviour is a change in the type of the point of inflection. If these points of inflection do not represent the same reaction degree through all curves then the evaluation becomes impossible. Propellant A seems to be one of these examples, although no sign of this behaviour could be detected at 70 °C. Figure 11 gives one example of this non-linear behaviour.

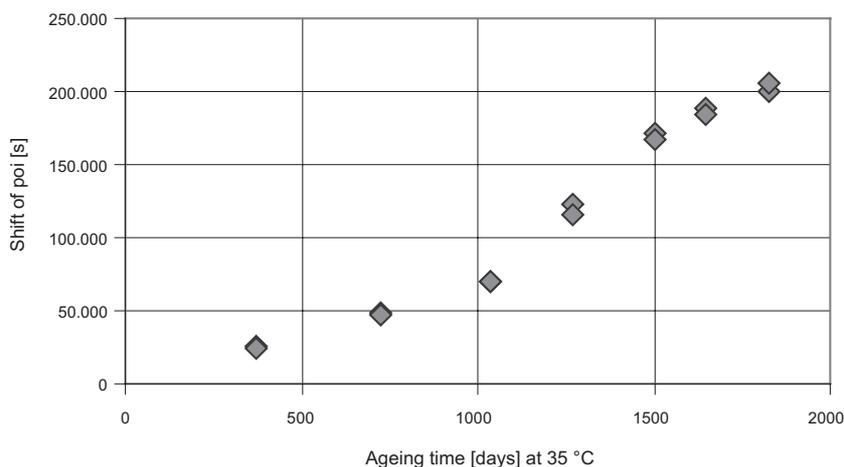


Figure 11. Non-linear shift of point of inflection of propellant A at 35 °C.

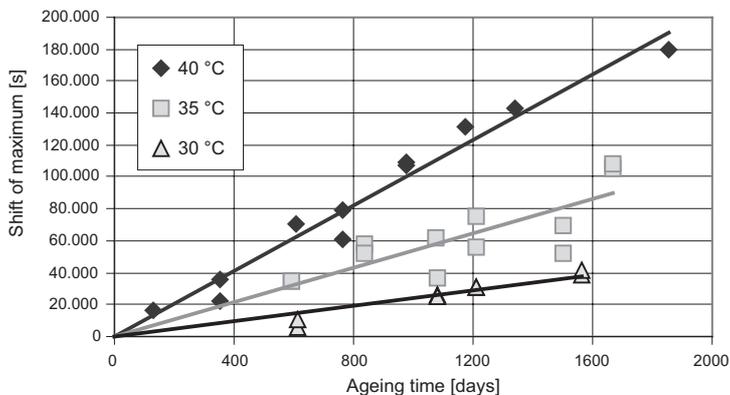


Figure 12. Shift of maximum heat generation rates in propellant D.

Propellant D

Although not enough sample material was available to run a complete programme with all temperatures, the evaluation clearly revealed a linear correlation between shift of the maximum and ageing time although the series at 35 °C shows some scattering (see Figure 12).

Propellant K

Both points show a nearly perfectly linear correlation between shift and ageing time for all ageing temperatures. Figure 13 shows one example.

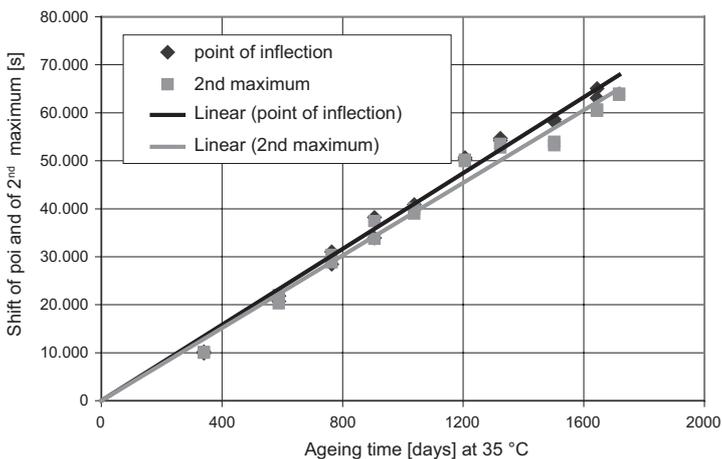


Figure 13. Shift of point of inflection and maximum heat generation rate (propellant K).

Propellant N

All selected points showed that they could be perfectly evaluated. Only the first sharp minimum became smaller with ageing and disappeared after ca. 1000 days at 40 °C. The correlation between shift and ageing time turned out to be almost linear. Also the ratio of the slopes were nearly identical when 2 ageing temperatures are compared. The evaluation of the 2nd minimum is presented in Figure 14.

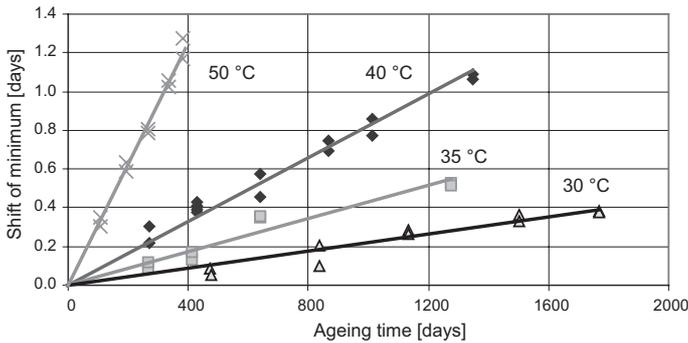


Figure 14. Shift of 2nd minimum with increasing ageing time at 50, 40, 35 and 30 °C (propellant N).

Propellant P

The relation between ageing time and shift of the point of inflection was almost linear. It is presented in Figure 15.

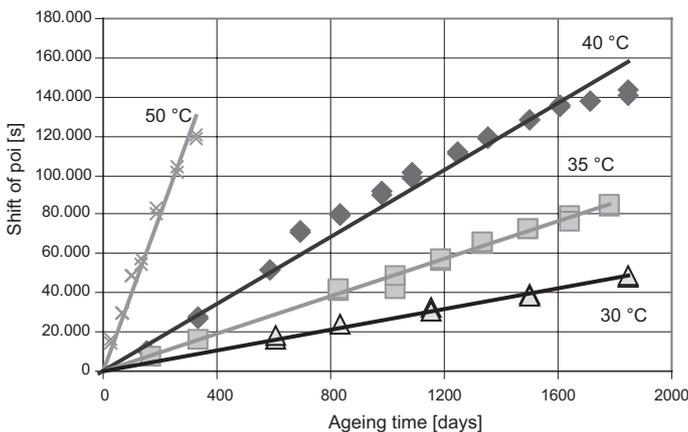


Figure 15. Shift of point of inflection as a function of ageing at 4 temperatures (propellant P).

Propellant V

The evaluation was divided into two parts: The first part covers the shift of the first maxima, minima and two inflection points whereas the second part deals with the autocatalytic decomposition at the end of the measurement.

The four different parameters of the first part of the microcalorimetric curve work pretty well together. The shift of all four points (first minimum, first point of inflection, second maximum and second point of inflection) is nearly linear with time (see Figure 16).

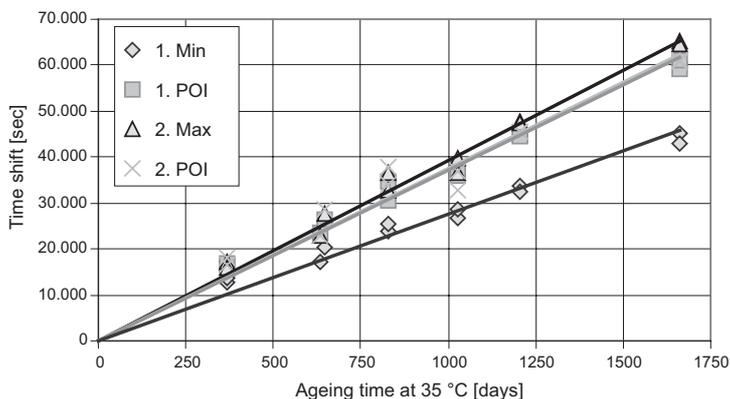


Figure 16. Shift of times for first minimum, first point of inflection, second maximum and second point of inflection after ageing at 35 °C (propellant V).

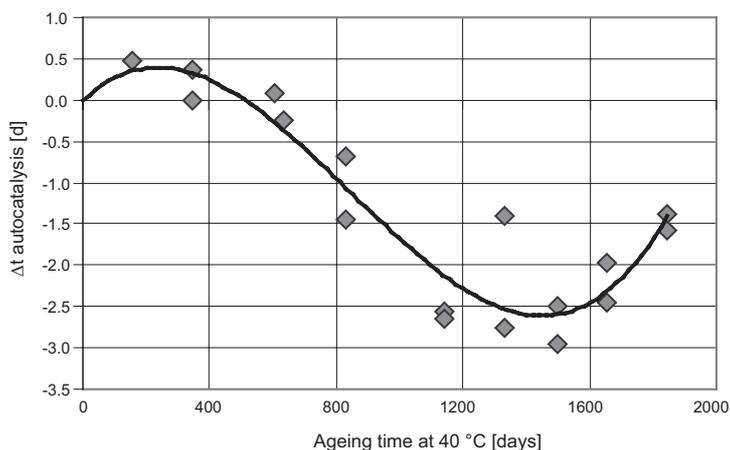


Figure 17. Shift of the runaway reaction after ageing (negative times = later autocatalysis), propellant V.

This linear behaviour is not true for the thermal runaway. The shift in time of its beginning (a value of $1600 \mu\text{W/g}$ was taken for comparison) moves to later times after a pre-ageing of more than 600 days. With further ageing this trend reverses again. This is shown in Figure 17 (a later autocatalysis means a negative time shift) and in Figure 18 for $T = 50^\circ\text{C}$. The reason for this behaviour is unknown, but this finding is significant as it was also found at all other test temperatures. The time to autocatalysis after ageing at 35°C reaches the original value of 11.1 days again after 1200 days and then increases further, very much in parallel to the findings observed at 40°C .

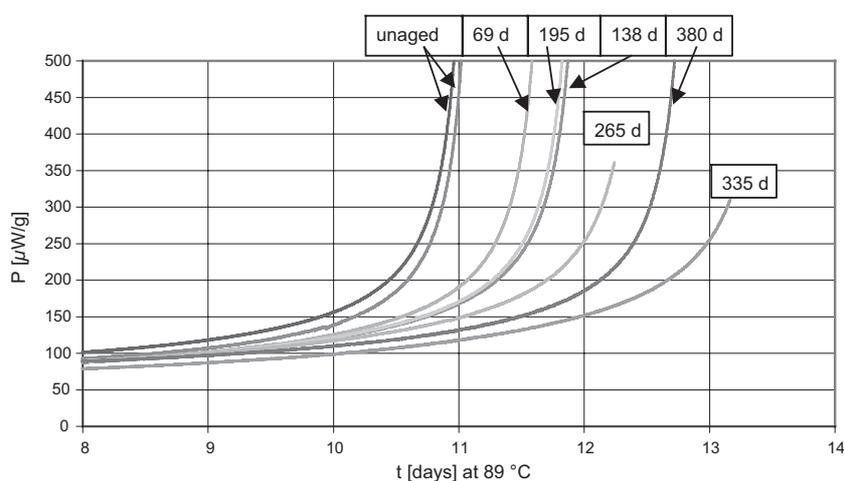


Figure 18. Shift of the runaway reaction after ageing at 50°C , propellant V.

Activation energies between 89°C and 30°C as well as within the low temperature area

The activation energies were calculated between 89°C and the ageing temperature. In a second step the activation energies between 50°C and 30°C were calculated as described above.

Table 3 summarises the results of the calculation of activation energies between 89°C and the storage temperature. Table 4 deals with the activation energies within the low temperatures. Propellant A was excluded from this calculation due to its non-constant behaviour (see Figure 11). How well the slopes fit onto a straight line is shown in Figure 19. If there is a significant change of E_a , it is clearly visible, see Figure 20.

These data, although they are somehow scattered show that a change in activation energy from the 'standard value' ($130\text{-}140 \text{ kJ/mole}$) which exists for most of the

propellants between 70 and 90 °C takes place at temperatures probably around 50 °C. Above this temperature the average value lies at 139 ± 8 kJ/mole, below it is at 120 ± 7 kJ/mole. No activation energy value below 80 kJ/mole was found which is good in a sense that the test time / temperature scheme in STANAG 4582 still is a very conservative approach and does not need to be changed. With a more exact knowledge of decomposition activation energies it will be easy to precisely predict the behaviour of propellants at normal or slightly elevated temperatures.

Table 3. Activation energies of propellants D, K, N, P, and V between 89°C and ageing temperatures. All values are in kJ/mole.

Propellant	point	E _a 89-50	E _a 89-40	E _a 89-35	E _a 89-30
D	maximum	nm	130.0 ±3.7	127.0 ±4.0	129.1 ±5.1
K	poi	136.1 ±0.9	134.7 ±1.5	132.8 ±1.8	131.0 ±1.3
	2 nd maximum	134.9 ±1.8	134.8 ±1.6	133.2 ±1.6	131.2 ±1.3
N	maximum	158.3 ±4.6	140.8 ±2.9	136.6 ±3.2	142.1 ±4.8
	2 nd minimum	144.0 ±1.3	136.1 ±2.5	133.3 ±3.1	132.0 ±4.6
P	poi	131.9 ±3.0	132.7 ±1.7	128.6 ±0.4	125.9 ±0.7
V	1 st minimum	142.4 ±4.8	141.7 ±3.5	137.9 ±2.3	135.4 ±1.7
	1 st poi	134.2 ±2.1	135.8 ±2.8	132.9 ±1.7	131.0 ±2.6
	2 nd maximum	131.8 ±3.3	134.6 ±2.6	132.1 ±1.5	131.1 ±2.0
	2 nd poi	136.7 ±5.5	137.2 ±4.4	132.7 ±2.5	132.0 ±3.3
average	all points, all propellants	138.9 ±8.3	135.8 ±4.1	132.7 ±3.5	132.1 ±4.2

poi: point of inflection; nm: not measured at 50°C. Averaging: see conclusion

Table 4. Activation energies of propellants D, K, N, P, and V between 50°C and 30°C. All values are in kJ/mole.

Propellant	point	E _a 50-30	E _a 40-30	E _a 40-35	E _a 35-30
D	maximum	nm	114	107	135
K	poi	122	115	112	118
	2 nd maximum	123	116	119	114
N	maximum	110	149*	92*	204*
	2 nd minimum	109	101	94	108
P	poi	112	95	91	98
V	1 st minimum	121	104	114	96
	1 st poi	124	108	117	101
	2 nd maximum	128	113	119	109
	2 nd poi	129	112	115	110
average	all points, all propellants	120 ±8	109 ±7	110 ±10	110 ±12

nm: not measured at 50°C. The data with * were excluded from averaging. A confidence interval can't be given as each calculation uses just two data points. Averaging: see conclusion

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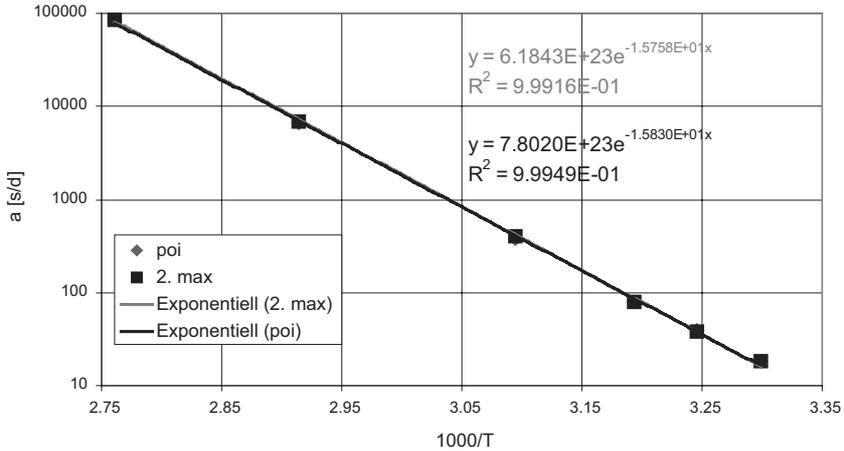


Figure 19. Slope a (see Eq. 2) as a function of temperature in an Arrhenius plot. The points nearly lie on a straight line (propellant K).

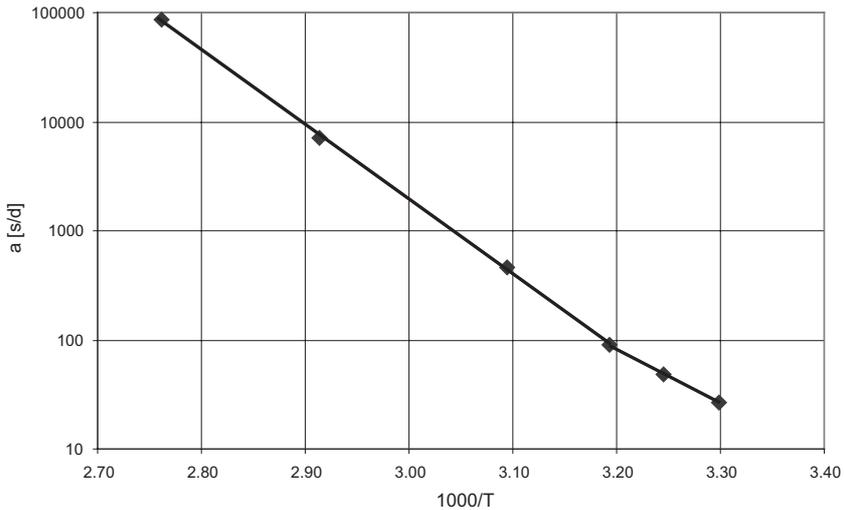


Figure 20. Slope a (see Eq. 2) as a function of temperature in an Arrhenius plot. The slope changes significantly at around 40 °C (propellant P).

Stabilizer depletion

There were no detailed studies of stabilizer depletion chemistry performed during this study as the ageing conditions were exactly the same throughout the whole project. The only interest was focused on the activation energy of stabilizer depletion. This is important as many papers in literature refer to a change of activation energy below 50 °C which is supported by stabilizer depletion analysis. We therefore took the chance to use these samples to compare directly microcalorimetry with stabilizer depletion. The results of the calculations are presented in Table 5. No confidence intervals are given, as each calculation relies on just two data points.

Table 5. Activation energies of propellants A, D, K, N, P, and V between 50°C and 30°C (stabilizer depletion). All values are in kJ/mole.

Propellant	stabilizer	E _a 50-30 AgeKin	E _a 50-30 zero order	E _a 40-30 zero order
A	DPA	108 ±27	120	113
D	2-NDPA	117 ±18	not measured at 50°C	94
K	DPA	129 ±25	122	124
N	EC	-	81	115
P	DPA	145 ±45	124	116
V	DPA	118 ±32	(64)	(53)

AgeKin: calculated by the AgeKin programme by armasuisse [15]

zero order: evaluation by simple application of a zero order kinetics

minus (-): no useful value available (too little change of centralite content)

values in brackets (): wrong reaction order, no useful evaluation.

As Table 5 shows the values have a much broader scattering than the ones delivered by microcalorimetry but in principle (except for V propellant 0 order) they lie in the same range than the ones calculated by LTAE data. Data handling also showed that stabilizer depletion is less reliable than heat generation, because there were several examples with slightly increasing stabilizer content after further ageing which makes evaluation more difficult. Probably the ageing does not only occur in the oven at 30-50 °C but also soon thereafter in the laboratory. Microcalorimetry though seems to be much more precise than HPLC.

Conclusion

An indirect method to measure activation energies of propellant decomposition reactions at temperatures below 50 °C was presented in this paper. It is reliable and it works well if propellants with a very typical heat generation rate shape are present and if a typical point in a heat flow curve remains an iso α point throughout the ageing.

The calculated data for the activation energy lie in the range of 100-120 kJ/mole (for 40/30 °C) which is significantly lower than the 'usual' value of about 130-140 kJ/mole but much higher than the (estimated) 80 kJ/mole which is the low temperature part of STANAG 4582. The extrapolation of artificial ageing at temperatures like 70 or 89 °C to room temperature is possible if the activation energies gained by this LTAE approach are used. The averaging performed in Table 3 shows that – although different propellant types of different age, from different nitrocellulose sources with different nitrogen and NG contents and different stabilizer types were used – the values are quite close to each other. This verifies that the rate determining chemical reaction is the split of the nitrate ester bond which has more or less the same E_a value, although (as mentioned above) a wide variety of different sample types were studied. In addition, E_a values of around 130-140 kJ/mole were found in many additional examples evaluated at WIWEB by the iso α method.

It must be noted that all E_a values discussed in this paper refer to the early stages of propellant decomposition (α from 0 to max 0.05). It can not be assumed that these E_a values are valid for the main decomposition reaction as well. For this case a complete decomposition of the propellant as described in [16] is necessary.

In general, this approach can also be used for propellant surveillance studies. Whenever a 'master' curve of a fresh propellant is available, natural ageing can easily be monitored by repeating the measurement after several years, and in case of severe changes of the shape of the curve or a rapidly decreasing time to autocatalysis the samples can be monitored much more intensively or be destroyed to prevent any risk.

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