

# Optimization of Modeling of Propellants Aging Investigated According to NATO AOP-48 Ed.2 Test Procedure

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## ABSTRACT

The stability test procedure according to NATO-AOP 48 Ed. 2 commonly applied for the explosives and nitrocellulose-based propellants is based on the assumption that the kinetic description of the process of stabilizer depletion can be done by applying the reaction-order (RO) model for the fitting experimental data. In the present paper another procedure is proposed by application more general Prout-Tompkins (PT) model based on the autocatalytic character of the reaction. Presented computer simulations indicate that PT model allows much better fit of the processes which kinetics is not fully determined. Application of proposed model significantly decreases the number of experimental points required for the prediction of the propellant properties at 25°C or after 10 years of storage ( $t_{25}$ - and  $T_{10}$ -values, respectively). The results of elaboration of experimental data of single- and double- based propellants calculated with RO and PT models are presented.

## INTRODUCTION

A lot of materials, especially high energetic chemicals change their properties even at ambient temperatures. Experimental observation of these processes is difficult due to their very low rate at room temperature resulting in so small physicochemical changes that are, generally, immeasurable even by the sensitive analytical techniques. In such situation the common method of the investigation of the aging processes is based on the experiments carried out at higher temperatures when the reaction rates are significantly higher. By choosing optimal temperature range of the experimental procedure one can monitor the course of the reaction by:

- (i) *in-situ* collected data by e.g. Thermogravimetry (TG) or Differential Scanning Calorimetry (DSC). Duration of such experiments, giving almost unlimited amount of points, can be adjusted to the laboratory working time and is, generally, in the range of 1-12 hrs.
- (ii) *ex-situ*, in lower temperatures, when only few points for each temperature is collected due to the duration of experiments which is in the range of weeks or even months. The samples may be analyzed by e.g. High Performance Liquid Chromatography (HPLC) or Fourier Transform Infrared Spectroscopy (FTIR).

Independent of the applied experimental procedure (i) or (ii) the experimental data are further used in kinetic analysis which allows the determination of the kinetic parameters of the process investigated what, in turn, gives the possibility of the prediction of the course of the processes at any temperature range in which the direct experimental observations are impossible.

Nitrocellulose-based propellants may decompose slowly which can lead to the decreasing of their chemical stability. To prevent this undesired process the components reacting with the degradation products (stabilizers) are introduced to the propellants. The monitoring of the stabilizer depletion by HPLC offers therefore an efficient tool for monitoring propellant aging process.

The commonly applied stability test procedure is described in a NATO Allied Ordnance Publication AOP-48 Ed.2 [1]. The evaluation procedure of the stabilizer depletion requires the set of aging experiments performed at least at three different temperatures, generally 60, 70 and 80°C. This artificial aging of the propellant is assumed to correspond to 10 years of aging at ambient storage conditions. The aging periods shall be selected such that the range of 10 till 90% stabilizer depletion should be investigated. For more than three different temperatures the smaller range (10-50%) may be investigated for the lowest temperature e.g. 50°C. The reaction of the stabilizer depletion is assumed to be described by the reaction-order type kinetic equation and the reaction order  $n$  is assumed to possess the values between -1 and 2. In certain cases even the negative

value of -1 can be reached during the optimization procedure but such values are rather questionable (see point 7.2.5 in NATO-AOP Ed.2).

It seems to be obvious that the real mechanism of the reaction of the stabilizer depletion is not totally known for the user and, what is more important, that the restricted application of the one kinetic model only may introduce the significant errors in the prediction of the propellant stability, especially if the real mechanism is different than those being assumed. In the literature one can find the trials of the improvement of the kinetic description of the process stabilizer depletion used further for the fitting experimental data, see e.g. the work of Bohn [2].

The aim of present paper is to propose another model being more universal than originally proposed one. Proposed by us modification may significantly shorten the duration of the experimental procedure and increase the accuracy of the aging predictions.

## KINETIC ANALYSIS OF SIMULATED DATA USING DIFFERENT REACTION MODELS

The rate of the reactions occurring in a solid state is commonly expressed by the equation

$$d\alpha/dt = k(T) f(\alpha) \quad (1)$$

where  $\alpha$ ,  $t$ ,  $T$  mean reaction extent, time and temperature, respectively,  $k(T)$  is an Arrhenius rate constant

$$k = A \exp(-E/RT) \quad (2)$$

with  $E$ - activation energy,  $R$ - gas constant and  $A$ - frequency (or pre-exponential) factor and  $f(\alpha)$  expresses the function dependent on the phenomenological reaction model. For the reaction-order (RO) type of equations (used in homogeneous kinetic) the  $f(\alpha)$  function becomes  $(1 - \alpha)^n$  where the exponent  $n$  is called as a reaction order. In the RO-type reactions, characterized in the isothermal conditions by decelerating  $\alpha - t$  dependence, the maximal reaction rate occurs at the beginning of the reaction.

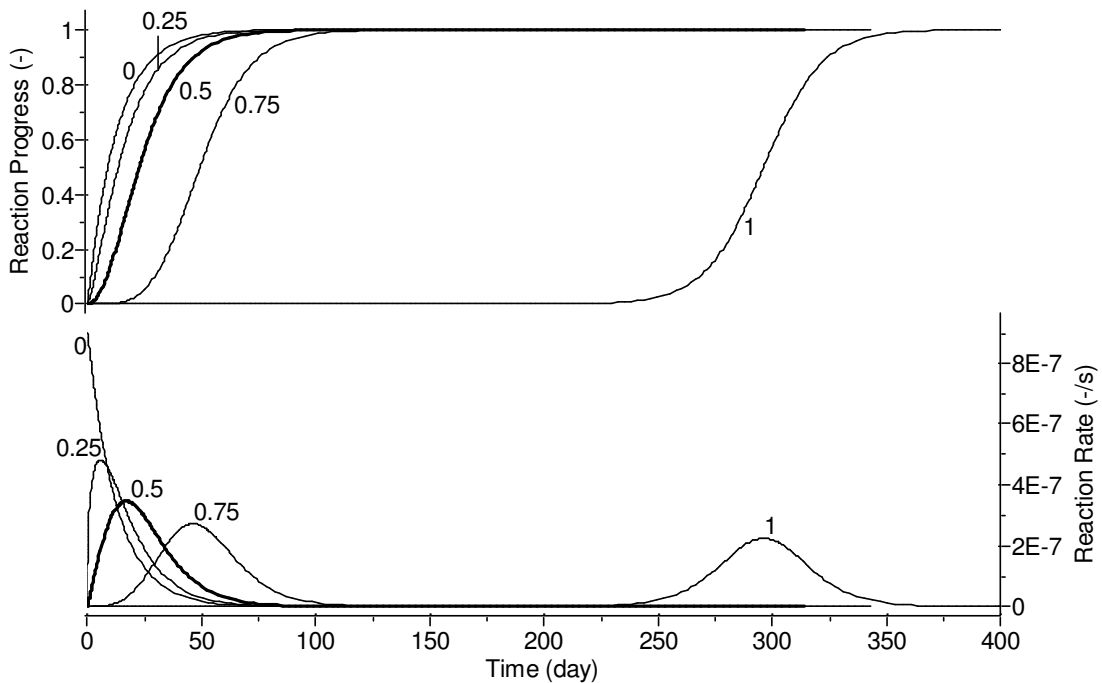
Such a reaction course is not rare, however very often one may observe the induction period at the beginning of the reaction manifested in sigmoidal shape of the  $\alpha - t$  dependence. Such a scenario is characteristic for the reactions when the formation of nuclei is a rate limiting stage as e.g. in Avrami-Erofeev (AE) reaction model or during autocatalytic-type reactions observed during decomposition of some high-energetic materials when the significant deviation from RO model is observed. The autocatalytic reactions are described by the formula

$$d\alpha/dt = k (1 - \alpha)^n \alpha^m \quad (3)$$

known as a modified Prout-Tompkins (PT) equation [3] discussed in details by Brown [4]. The exponents  $n$  and  $m$  in PT equation determine the contribution of decay and acceleratory regions. The increase of the  $m:n$  ratio results in the shift of the maximal rate of the reaction into the higher  $\alpha$  and  $t$  values. As pointed by Ng [5] the values of  $\alpha_m$  at which the maximal rate of the reaction are observed are expressed by the dependence  $\alpha_m = m/(m+n)$ .

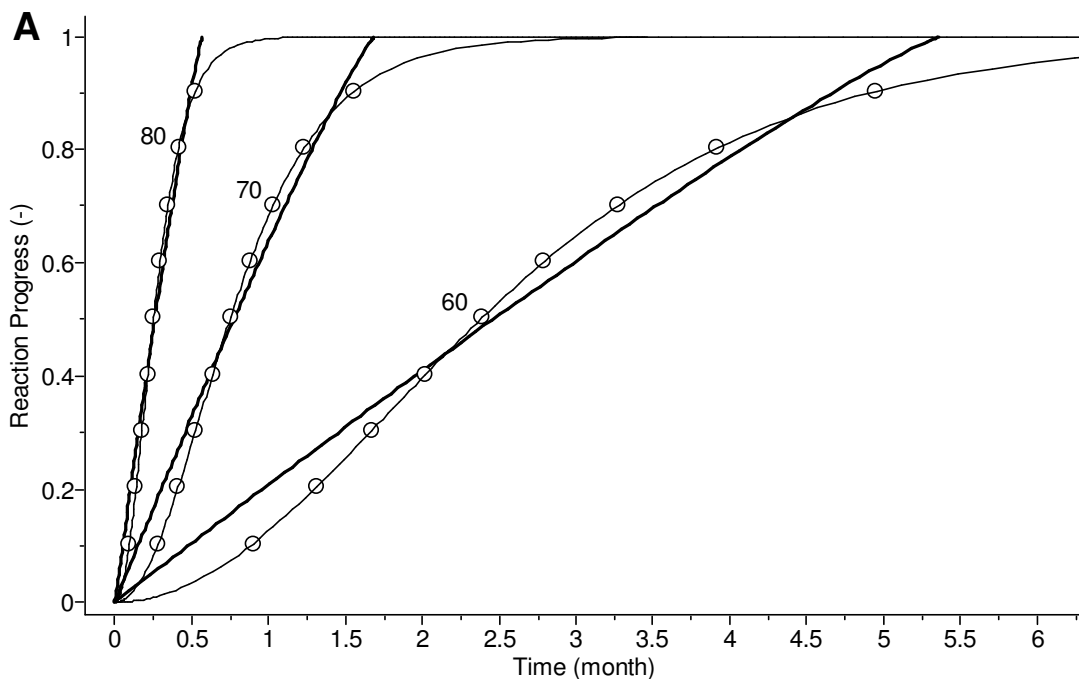
Figure 1 depicts the relationship between the  $\alpha$ - $t$  dependences at isothermal conditions for RO and PT-types of the reaction models. The curves were calculated by AKTS-Thermokinetics Software [6] for the following kinetic parameters  $A=5E10 \text{ sec}^{-1}$ ,  $E=110 \text{ kJ/mol}$ ,  $T=70^\circ\text{C}$ ,  $n=1$  and  $m=0$  (RO model), 0.25; 0.5; 0.75 and 1. The maximal rate of the reaction shifts up to higher time values and occurs at  $\alpha$  amounting to 0; 0.2; 0.33; 0.428 and 0.5 for  $m$  values of 0; 0.25; 0.5; 0.75 and 1, respectively.

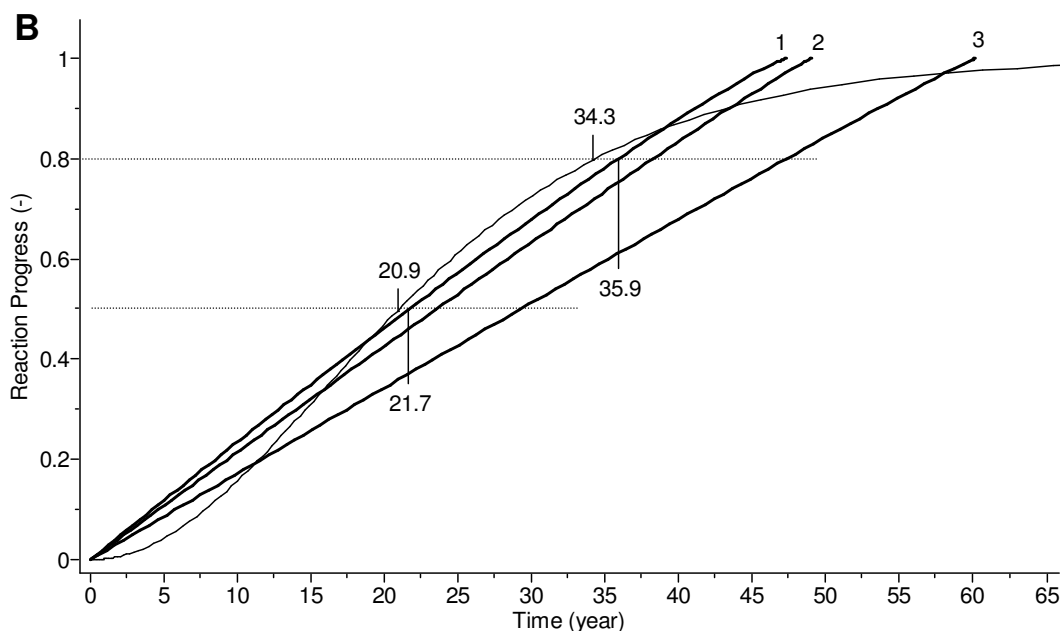
Presented curves indicate that the application of the PT model is much more universal for describing course of the reaction. It can fit both, RO model reactions (for  $m=0$ ) and highly autocatalytic reactions with  $m=0.75$  or 1. This remark is explained in details below by presenting results of fitting the  $\alpha$ - $t$  points generated for arbitrarily chosen kinetic parameters:  $A=5E10 \text{ sec}^{-1}$ ,  $E=110 \text{ kJ/mol}$ , autocatalytic PT model with  $n=1$  and  $m=0.5$  (bold curve in Fig.1) being an intermediate stage between real  $n$ -th order (if  $m=0$ ) and strongly autocatalytic reactions ( $m=1$ ). In order to mimic the NATO AOP-48 Ed. 2 test procedure the amount of the points taken into fitting procedure was restricted to 9 (for  $\alpha$  in the range 0.1-0.9 in 0.1 intervals) at three temperatures of 60, 70 and 80°C. The calculated points, which can be treated as "ideal" experimental data were consequently fitted by RO and PT kinetic equations to check how the deviation of the reaction course from the RO model assumed in NATO-AOP 48 Ed. 2 influences the results of further predictions of the stabilizer depletion at 25°C.



**Figure 1** Simulation of  $\alpha$ - $t$  dependences at 70°C for the following kinetic parameters;  $A=1E10 \text{ sec}^{-1}$ ,  $E=110 \text{ kJ/mol}$ ,  $f(\alpha)=(1-\alpha)^n \alpha^m$  (PT model) with constant  $n=1$  and  $m=0; 0.25; 0.5; 0.75$  and  $1$ , respectively. Values of  $m$  are marked on the curves.

Results presented in Fig.2 indicate that RO model does not fit well the “experimental” points, however, the prediction of the reaction course at 25°C if 9 points are fitted at each temperature (Fig. 2B, marked as '1') is relatively good: note the small difference of the times required to reach the reaction extents specified in NATO-AOP 48 Ed. 2 procedure. For PT and RO models the specified conversions are reached after 20.9 and 21.7 years (50%) and 34.3 and 35.9 years (80%), respectively. Concluding, we can claim that during elaboration of the set of 27 points collected at three temperatures for the reaction having only slight contribution of the autocatalytic process ( $m=0.5$ , compare the Fig.1) the deviation from the  $n$ -th order reaction mechanism does not significantly influence the procedure of the prediction.





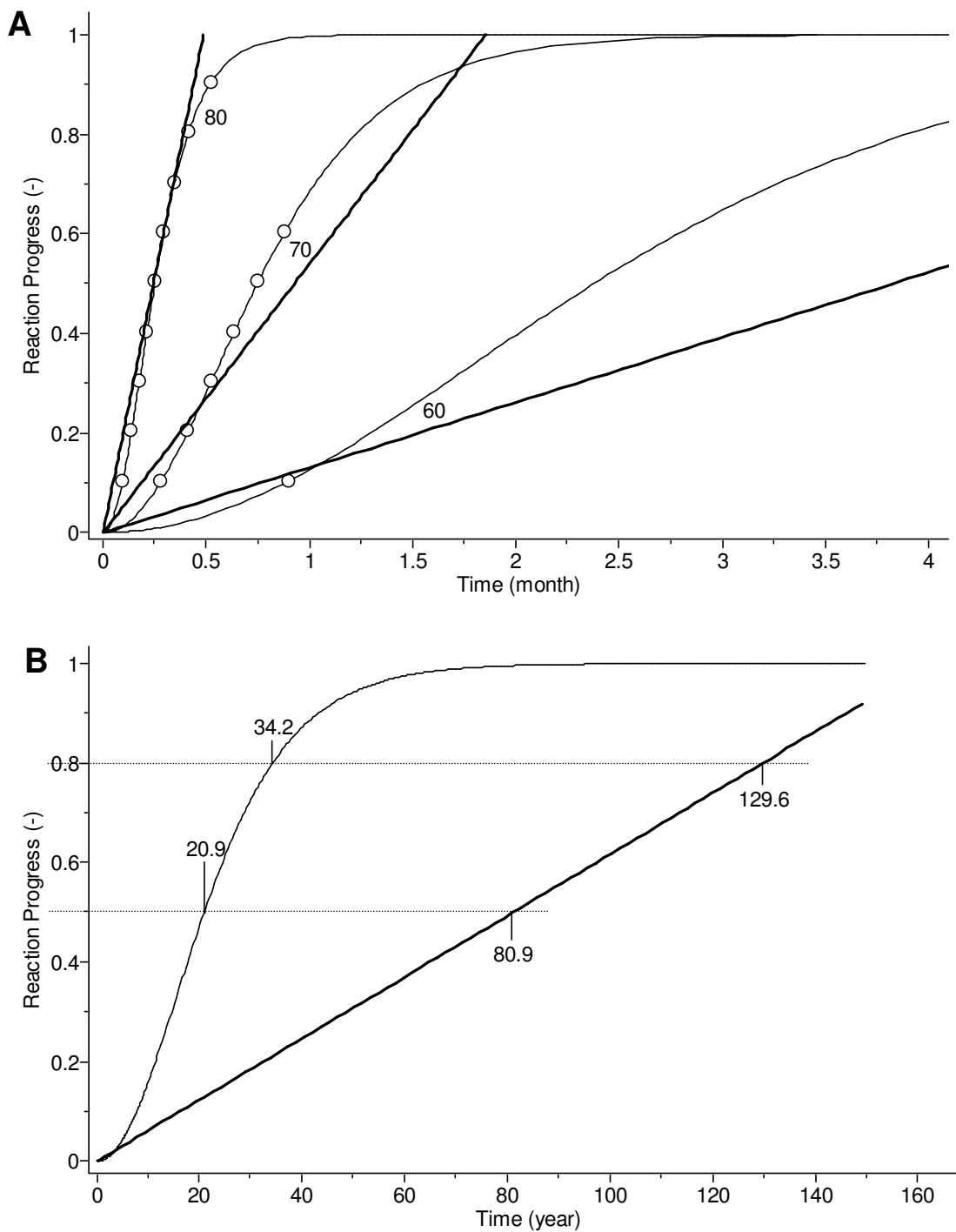
**Figure 2** A) Fit of the points generated at 60, 70 and 80°C (marked on curves) by RO (bold) and PT-models.  
 B) Prediction of the reaction course at 25°C applying RO (bold) and PT kinetic models for the set of:  
 (1) 27 points calculated for 60, 70 and 80°C in the range of  $\alpha$  between 10 and 90%,  
 (2) 27 points calculated for 60, 70 and 80°C and 5 points at 50°C in the range of  $\alpha$  between 10 and 50%,  
 (3) 27 points calculated for 60, 70 and 80°C and 3 points at 50°C in the range of  $\alpha$  between 10 and 30%.

However, the results depicted in Fig.2A showing relatively bad fit of the data by RO model, indicate that application in kinetic analysis of the experimental points collected in narrow range of the  $\alpha$  values may lead to worsening of the predictions. Following the NATO-AOP48 Ed.2 recommendations we arbitrarily added to the calculations the set of 5 points calculated for the temperature of 50°C in the range of  $\alpha$  between 10 and 50%. The result of the prediction at 25°C using such a set of 32 points generated for four temperatures is presented in Fig 2B (marked as '2').

Results of the prediction submitted in Fig. 2B '2' show that use in simulation of data which do not cover the full range of the reaction extent leads to decreasing accuracy of the prediction despite the fact that such procedure is allowed by NATO-AOP 48 Ed. 2. To check how further diminishing the number of the points will influence the results of kinetic analysis we decreased to three the number of points at the lowest temperature of 50°C. Such an action mimics the common experimental procedure in which at low temperatures only few points are collected due to the time reasons - the point representing the 50% conversion at 50°C would be experimentally reached after ca. 8 months. Taking as before to the simulation 27 points calculated for 60, 70 and 80°C (nine points at each temperature) we added to the fitting procedure three points at 50°C calculated for the  $\alpha$  values of 10, 20 and 30%. The results of the prediction using such a set of 30 points depicted in Fig. 2B '3' indicate that such procedure, commonly applied in the practice when only part of the reaction extent is covered by the experimental data, significantly lowers the accuracy of the prediction when assuming the RO type mechanism of the stabilizer depletion.

All above presented data clearly indicate that for the accurate kinetic analysis of the process which mechanism is unknown - and this is a common situation in solid state chemistry - it is much better to apply the PT model instead of often recommended RO-based assumption. When applying RO model to the data of the process having slight contribution of autocatalytic reaction one can receive relatively good prediction of the reaction course only when the elaborated data cover the full range of the conversion (see Fig. 2B '1'). The elaboration of the data which cover only the part of the reaction extent range (Fig. 2B '2-3') results in significant worsening of the predictions. On the other hand, the application of PT model in kinetic analysis helps in avoiding such situation because this model is more general. It describes well both, RO type kinetics (if  $m=0$ ) and autocatalytic reaction (if  $m>0$ ). Moreover, the application of the correct reaction model, resulting in good fit of the experimental data, can significantly decrease the number of the points required in kinetic analysis what, in turn, significantly shortens the time required for the experimental collection of the data.

As shown in Fig. 2B '1' the acceptable prediction when applying RO model can be obtained using the set of 27 points, which, in presented example, requires at least 150 days (last point for  $\alpha=90\%$  at lowest temperature of 60°C). The use of the more universal PT model will result in insignificant decrease of the number of required points.



**Figure 3** A) Fit of the points generated for the time shorter than 30 days by RO (bold) and PT models; B) Prediction of the stabilizer depletion at 25°C based on the kinetic parameters obtained by fitting displayed in A). The theoretical dependence overlaps the curve based on PT model.

Let us consider the scenario when the collection of the data occurs in e.g. 30 days only but the PT model is applied in kinetic analysis. When the duration of the experimental work is limited to 30 days only for the reaction model described by the kinetic parameters identical with those considered in Fig. 2A, one can collect 1, 6 and 9 points at 60, 70 and 80°C, respectively. The fit of these points by RO and PT models is depicted in Fig. 3A, respectively. The results presented in Fig. 3 show that if the correct reaction model is applied the number of the points required for the accurate kinetic analysis may be significantly limited. Note, that the generated data based on PT model are perfectly overlapped by the theoretical curve despite the fact that in presented in Fig. 3A analysis of only one point at 60°C was used in fitting procedure. The results presented previously (Fig. 2) and Fig. 3 very clearly show that the procedure of decreasing amount of points in kinetic analysis can be successful only if the applied kinetic equation fits well elaborated data. This is the case if PT model is applied, for RO model the use of one point only at 60°C results in unrealistic time of the prediction at 25°C (80.9 instead of correct 20.9 years for 50% conversion). The conclusion indicating that the correct kinetic analysis may be carried out even if the number of experimental data is significantly smaller than those required by NATO-AOP 48 Ed. 2 test procedure allowed us to make prediction of the stabilizer depletion time based on the experimental data collected in the limited range of the reaction extent.

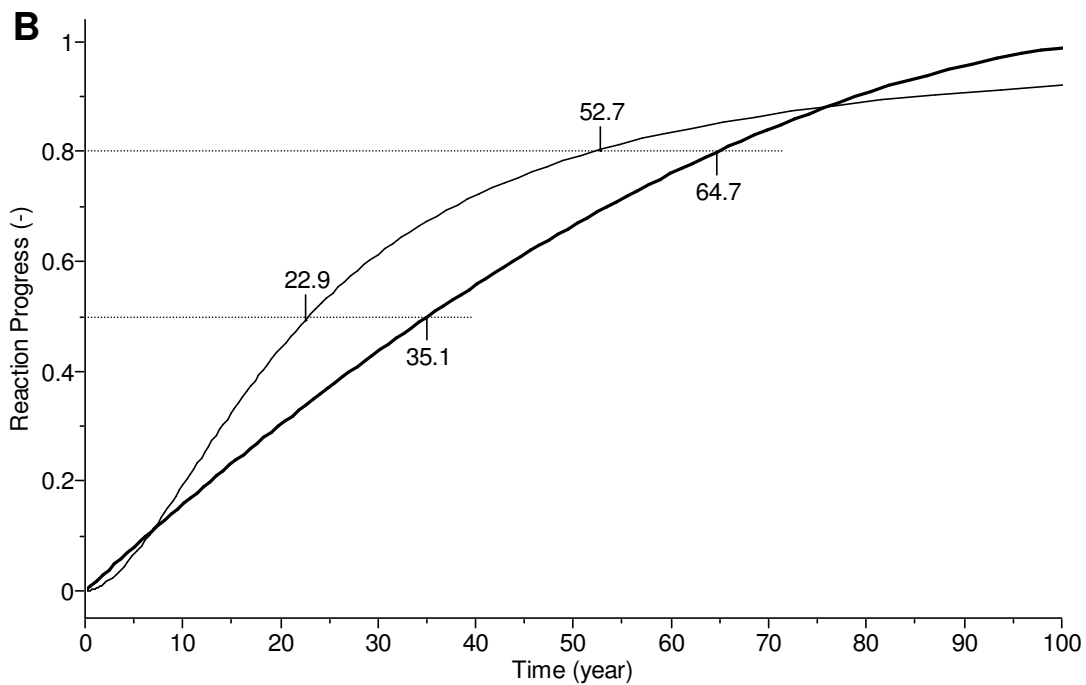
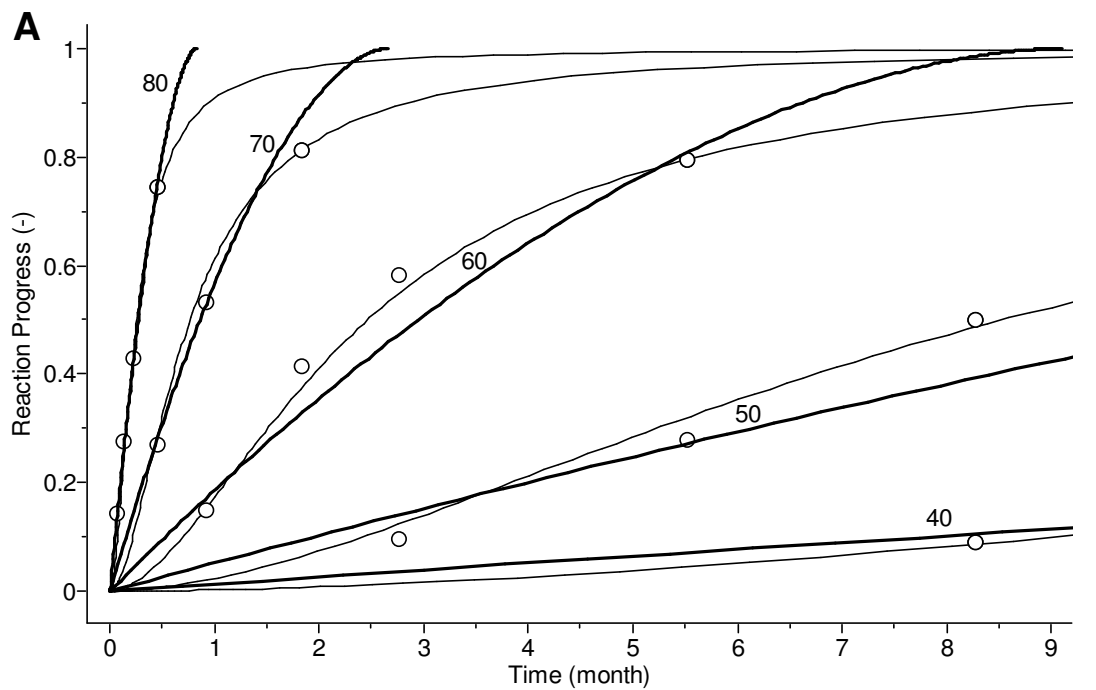
## KINETIC ANALYSIS OF EXPERIMENTAL DATA

Single- and double-based propellants were aged in temperatures ranging from 40 till 80°C. Generally not more than 3-4 points characterizing their stabilizer depletion were collected at each temperature. Moreover, also single points from the lowest temperature of 40°C were used for determination of the kinetic parameters followed by the prediction of the stabilizer depletion at 25°C. The results of the predictions for two propellants SB-1 and SB-2 are shown in Figs. 4 and 5, respectively.

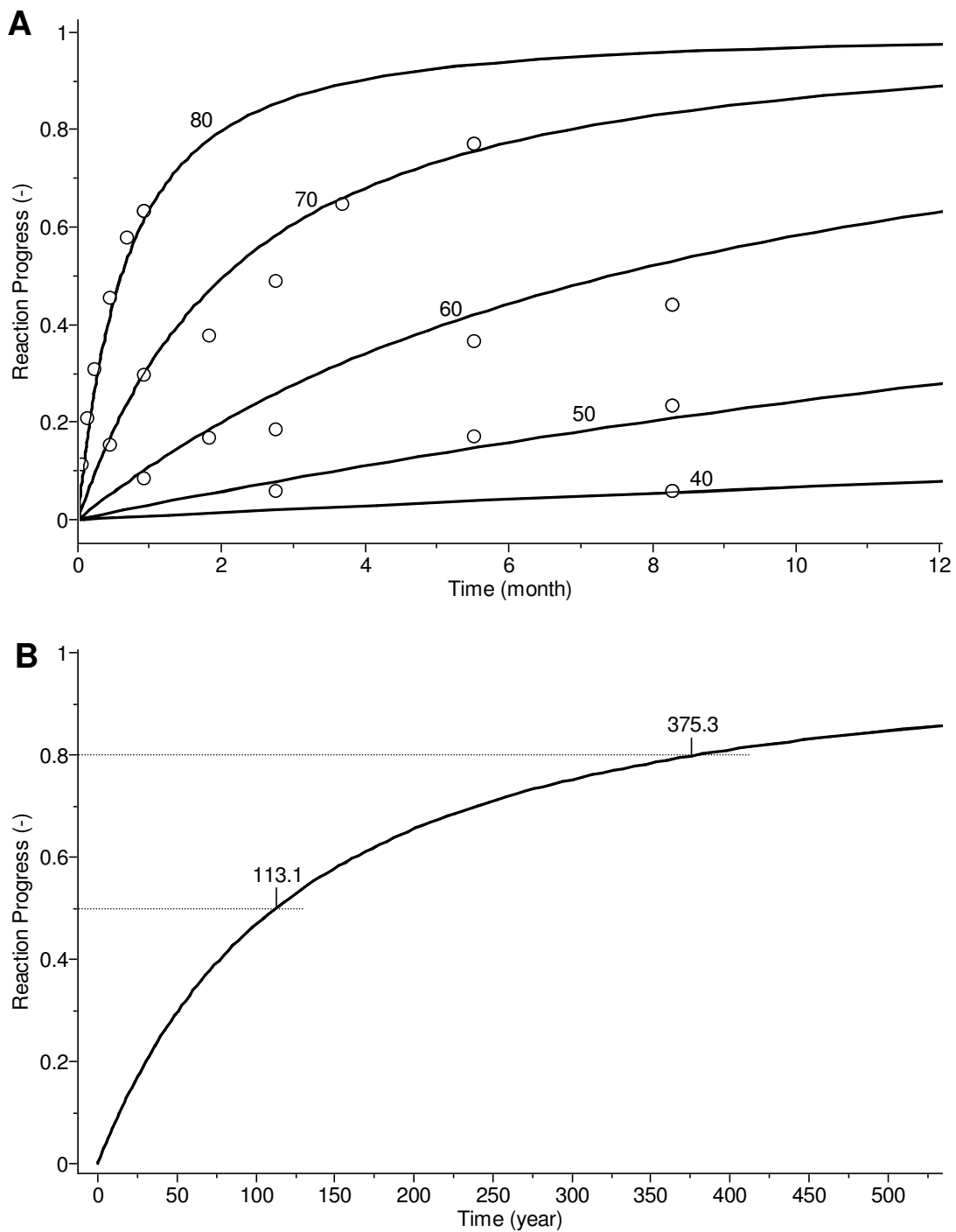
The mechanism of the propellants aging was unknown, therefore, as described in details in the previous chapter, the PT model, as more universal was applied in the fitting procedure together with the commonly accepted RO model. If the reaction can be really described by the  $n$ -th order kinetic equation then despite the different models used in kinetic analysis the prediction results should be identical. As larger the deviation of the mechanism of the depletion process from assumed  $n$ -th order model (i.e. as more the autocatalytic process governs the reaction course) as greater is the difference of the predicted time of 50% stabilizer depletion at 25°C calculated for both models. It is necessary to underline that application of the RO models results generally in overestimating propellant stability if the reaction has some autocatalytic character (see results presented in Figs. 2-3).

The summary of the kinetic analysis of all propellants is presented in Table 1 containing the kinetic parameters derived during fitting experimental data by RO and PT models,  $t_{25}$ - i.e. the storage time at 25°C after which a stabilizer depletion of 50 and 80% is reached and the  $T_{10}$ - i.e. temperatures for a 10 years storage after which a critical stabilizer depletion (50 or 80 %) is reached.

As it arises from the data submitted in Tab.1 the processes of the stabilizer depletion can be described in major cases by the  $n$ -th order kinetic equations, note generally very small  $m$  values and negligible difference between RO and PT derived parameters. However, in certain cases the reactions have slightly autocatalytic character (e.g. samples SB-1 or SB-3) what leads to the decreasing of the  $t_{25}$ - and  $T_{10}$ - values. Not knowing the mechanism of the propellants aging it seems to be rational to apply in the fitting procedure the PT model which in no one case leads to the overestimation of the propellant stability as it can happen when RO model is applied.



**Figure 4** A) Fit of the experimental points of the stabilizer depletion in SB-1 collected at 40, 50, 60, 70 and 80°C (temperatures are marked on curves) by RO (bold) and PT-models. B) Prediction of the stabilizer depletion in SB-1 at 25°C based on the kinetic parameters obtained by fitting experimental data by RO (bold) and PT reaction models.



**Figure 5** A) Fit of the experimental points of the stabilizer depletion in SB-2 collected at 40, 50, 60, 70 and 80°C (marked on curves) by RO (bold) and PT-models. B) Prediction of the stabilizer depletion in SB-2 at 25°C based on the kinetic parameters obtained by fitting experimental data by RO (bold) and PT reaction models.



**Table 1** Kinetic parameters derived from RO and PT models and  $t_{25}$ - and  $T_{10}$ - values for all investigated propellants

sample	Model	$\alpha_0$	A sec <sup>-1</sup>	E kJ/mol	n	m	$t_{25-50\%}$	$t_{25-80\%}$	$T_{10-50\%}$	$T_{10-80\%}$
SB-1	RO	0	1,7E+11	117,1	0,43	0	35,1	64,7	33,2	37,3
	PT	2,5E-11	7,7E+10	111,2	1,64	0,43	22,9	52,7	30,6	36,3
SB-2	RO	0	8,2E+11	122,8	1,71	0	113,1	375	40,4	48,5
	PT	2,3E-09	8,2E+11	122,8	1,71	7,1E-06	113,1	375	40,4	48,5
SB-3	RO	0	7,6E+15	147,7	1,45	0	262	761	42,5	48,5
	PT	6,3E-11	7,4E+11	118,8	1,97	0,45	58,9	156	36,5	43
SB-4	RO	0	2,4E+09	109,7	0,40	0	127,05	232	43,2	47,8
	PT	3,6E-11	2,4E+09	109,7	0,40	1,1E-11	127,05	232	43,2	47,8
SB-5	RO	0	6,0E+09	110,7	0,57	0	78,5	152	39,4	44,4
	PT	2,3E-10	4,3E+09	109,7	0,56	3,8E-07	76	146	39,1	44,1
DB-1	RO	0	7,9E+11	120,1	0,66	0	27,87	56,4	31,5	36
	PT	1,0E-10	1,2E+12	120,6	0,78	0,14	28,42	56,1	31,7	36,1
DB-2	RO	0	1,6E+10	105,8	0,92	0	4,85	10,6	19,8	25,5
	PT	7,2E-11	1,6E+10	105,9	0,92	1,0E-4	4,84	10,6	19,8	25,5
DB-3	RO	0	8,6E+10	112,5	0,78	0	12,35	26,1	26,4	31,4
	PT	1,1E-10	2,2E+11	113,9	0,96	0,25	12,8	26,7	27,2	31,6
DB-4	RO	0	2,2E+10	114,9	0,40	0	114,5	209	41,6	45,9
	PT	4,4E-09	2,2E+10	114,9	0,41	1,8E-05	114,5	209	41,5	45,9
DB-5	RO	0	4,0E+13	130,1	0,57	0	30,2	58,7	31,5	35,4
	PT	2,8E-10	4,0E+13	130,1	0,57	1,7E-03	30,4	59,0	31,4	35,4
DB-6	RO	0	6,7E+10	118,5	0,35	0	156,8	281	43,2	47,4
	PT	1,5E-08	6,7E+10	118,5	0,35	6,7E-06	156,9	281	43,2	47,4
DB-7	RO	0	3,1E+14	132,7	0,91	0	12,5	27,9	26,3	30,9
	PT	2,6E-09	3,1E+14	132,7	0,91	1,8E-03	12,4	27,7	26,3	30,9

## CONCLUSION

In NATO-AOP-48 Ed. 2 test procedure, commonly applied for testing stability of explosives and nitrocellulose-based propellants, the  $n$ -th order (RO) kinetic model is applied in kinetic analysis of the experimental data. The application of more general PT model, describing well both,  $n$ -th order and autocatalytic characters of the reaction, results in much better fit of experimental data. This, in turn, allows significant decrease of the number of the points required for the exact kinetic analysis. The computer simulations showed that application of PT model in investigations of the reactions proceeding with not fully determined mechanism can result in significant reduction of time (e.g. up to 80%) required for the collection of such a number of experimental data which are necessary for the accurate kinetic analysis. The theoretical considerations were confirmed by the evaluation of the stability of single- and double based propellants. For some samples the application of RO and PT models resulted in determination of the same kinetic parameters and  $t_{25}$ - and  $T_{10}$ - values. However, in some cases, when stabilizer depletion could not be correctly described by  $n$ -th order-based kinetics and has some autocatalytic character, the application of RO model resulted in an overestimation of the propellant stability.

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