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THE SELECTION OF FORMAL KINETICS MODELS TO DESCRIBE THE EXPERIMENTAL DATA OF CL-20 DECOMPOSITION

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A large number of publications devoted to the properties, including thermal stability of CL-20, demonstrates the interest to it as a powerful energetic compound [1,4-16]. One of the factors that allow its use as an energetic compound is thermal stability.

In [1] the decomposition kinetics of CL-20 samples has been studied under isothermal conditions by using TGA method and FTIR spectrometer in a temperature range of 190°C - 204° C in air atmosphere. The

sample mass was 1-2 mg for TGA method and contained a small amount of solvent and water. Experimental data of up to 50% decomposition satisfactorily described by the equation of the first order and does not obey the equation Prout-Tomkins [2,3], on this basis, it is concluded that the decomposition of CL-20 occurs without autocatalysis. Analysis of the reaction products leads the authors to conclude that the primary act of the decomposition is NO₂ detachment. The constant of the decomposition velocity $k=10^{13.6} \exp(-36300/RT)(1-\eta)$ or $k=10^{14.1} \exp(-38200/RT)(1-\eta)^2$.

In [4] the kinetics of decomposition was studied on the samples of ϵ -CL-20 with particle size 163 microns and 16 microns (obtained by grinding large crystals) weighing 5 mg in static and dynamic modes of heating. The experimental curves of weight loss at heating rates 0.5°C/min, 2°C/min, 5°C/min and 10°C/min of 163 micron sample have two distinct decomposition stages, with increasing of the decomposition velocity the value (in percentage) of the first stage decreases (about 55% at a rate 0.5°C/min to 10% at 10°C/min). Experimental decomposition curve of the sample with a particle size of 16 microns at a heating rate of 2°C/min has no characteristic transitions such as the sample with 163 micron particle size. In [2-3] it was noted that in the process of thermostating samples decomposed into smaller and when it reaches a certain size the process stopped. At the same time smaller crystals proved more stability than larger.

Experimental data (up to 3%) of ϵ -CL-20 decomposition with a particle size of 163 microns in a temperature range of 16°C-180°C satisfactorily obey the equation of the first order of autocatalysis

$$d\eta/d\tau = 10^{13.81} \exp(-41150/RT)(1-\eta) + 10^{17.99} \exp(-44260/RT)(1-\eta)\eta$$

In primary decomposition act of CL-20 the authors also suggest NO₂ abstraction followed by ring opening. The kinetics of ϵ -CL-20 decomposition in non-isothermal mode studied in [5], with speeds of 10°C/min ÷ 25°C/min. Using the Kissinger method the obtained kinetic parameters $k=10^{18.3} \exp(-47700/RT)$. In isothermal condition the decomposition kinetics of ϵ -CL-20 samples was study in temperature range 210°C-220°C under a nitrogen atmosphere. Using Avrami-Erofeev equation in the form $\eta = 1 - \exp(-k_0.5\tau)^n$, the kinetic parameters of decomposition process in the acceleration stage (0.05 < η < 0.5) and in the stage of retardation (0.5 < η < 0.95) were determined. Kinetic parameters of the first stage equal to $k=10^{20.47} \exp(-53550/RT), s^{-1}$ with $n=2$, in a second stage $k=10^{23.37} \exp(-58840/RT), s^{-1}$ with $n=2.5$.

In [6] the kinetics of CL-20 decomposition using DSC, TGA, calorimeter with a stage heating (ARC), a gas flow calorimeter (HFC), and the device DSC + TG + mass spectrometer studied.

The shape of the experimental curves shown in [6] obtained in the study of the thermal decomposition under conditions of dynamic heating using DSC indicates the complex nature of the process. Using the Kissinger method from the DSC data it was found that $E=49500$ cal/mole, $A = 10^{18.96}$.

Using isoconversion analysis authors were treated the experimental data obtained in the DSC at a heating speed of 1°C/min to 10°C/min. The result of the analysis is the dependence of E on the decomposition level. On the first stage of decomposition (0 < η < 0.4) $E = 42000$ cal/mol and the second stage (0.4 < η < 0.8) E varies from 44800 cal/mol to 58000 cal/mole. From dependence $E(\eta)$ was supposed to determine the dependence of $d\eta/d\tau(\eta)$. The authors defined it as a set of reactions.

Experimental decomposition curves of CL-20 by the weight loss produced at heating rates of 0.5°C/min to 10°C/min. The weight of loss curves shape is similar to the curves shown in Figure 2. From the dependence $\ln(\beta/T^2)$ from $1/T$ at a given η , the value obtained E . They range from 32200 cal/mol to 40500 cal/mole.

Using mass spectrometry data in CL-20 decomposition in isothermal condition in a temperature range 190°C-205°C, E values were determined for the weight loss curves (curve has two peaks) and curves NO₂ formation. The kinetic parameters for the TG curves for the first peak $10^{13.87} \exp(-35450/RT)$ and the second peak $10^{16.48} \exp(-38950/RT)$ (determined on depending of $\ln\tau_p$ from $1/T$, where τ_p - time of achieve maximum of decomposition curve) to form NO₂ $k = 10^{13.0} \exp(-33300/RT)$ (depending on $\ln\tau_p$ $1/T$), and $k = 10^{16.05} \exp(-38700/RT)$ (in depending of $\ln A_p$ from $1/T$, where A_p - maximum value of NO₂ formation curve).

In [7-9] various modifications of CL-20, including ϵ -CL-20 in a temperature range 183°C-211°C was investigated.

It was observed that after 1% of ϵ -CL-20 decomposition transits into γ -CL-20. The experimental curves of decomposition of all modifications were processed using the equation of the first order autocatalysis. For ϵ -CL-20 decomposition equation has the following parameters:

$$d\eta/d\tau = 10^{20.3}\exp(-53100/RT)(1-\eta) + 10^{17.6}\exp(-45400/RT)(1-\eta)\eta.$$

It is noted that the activation energy depends not only on the molecular structure of CL-20, but also on the crystal properties (crystal size, size distribution, and the presence of crystal water, etc.).

In [10] a study of the weight loss of CL-20 sample with a particle size of 5 microns (obtained by grinding particle size of 163 microns in water), was obtained. Obtained equation of the first order autocatalysis is: $d\eta/d\tau = 10^{15.98}\exp(-44300/RT)(1-\eta) + 10^{17.78}\exp(-43600/RT)(1-\eta)\eta$

In [11] reviewed the available literature on the properties of CL-20 data. In [12] to study the kinetics of degradation products propose following equation of CL-20 decomposition

$$d\eta/d\tau = 10^{16.89}\exp(-38600/RT)(1-\eta).$$

Thus, the analysis of literature data on research of CL-20 decomposition in the solid phase indicates that, firstly, for the large crystals decomposition curves are more complex than to the smaller ones. Secondly, for the experimental data processing used the several different approaches, some of which allows to determine the kinetic parameters only at certain points of curves. Some approaches are only applicable to simple reactions (Kissinger method), others only to reactions with a single constant (equation Prout-Tompkins, Avrami-Erofeev, isokinetic approach). Formal kinetics method does not limit the use of models of any complexity, which allows processing the experimental data of almost any complexity. The activation energy value range from the of 34500 cal/mol to 53500 cal/mole. In [13] from the velocity data of CL-20 combustion at various pressures determine the kinetic parameters of CL-20 high-temperature decomposition. For the pressure range 0.03-1 MPa the decomposition velocity constant equal to $k = 10^{16.34}\exp(-44500/RT)$ ($\Delta T = 387^\circ\text{C} - 502^\circ\text{C}$) and for pressures above 1 MPa $k = 10^{15.25}\exp(-39600/RT)$ ($\Delta T = 502^\circ\text{C} - 687^\circ\text{C}$). The authors conclude that the melting of CL-20 occurs at a pressure 1MPa respectively first constant relates to the decomposition in the solid phase, the second - to a liquid.

In [14] by the methods of molecular dynamics the process of high-temperature decomposition of CL-20 ($\Delta T = 1227^\circ\text{C} - 2727^\circ\text{C}$) was study. It was found that only one channel of reaction start is the N-NO₂ bond breaking. After that the molecule passes in one closed ring which have from zero till two nitro groups. Decomposition in the crystalline state is described by the first order equation with constant $k = 10^{9.415}\exp(-32800/RT)$.

Research of decomposition in solution often allows simplifying the decomposition curves, since the influence of the crystal lattice disappears (although the effect of the solvent continues). Thermal decomposition of CL-20 solution was studied in [9, 15-16].

Using the experimental data presented in these studies the model selection of minimal complexity was conducted, which allow to process the experimental data satisfactorily. The experimental curves of the thermal decomposition of CL-20 [9] dissolved in m-dinitrobenzene in a temperature range of 150°C - 195°C satisfactorily described by an equation of the first order ($k = 10^{14.4}\exp(-36500/RT)$).

In [9] the thermal decomposition of CL-20 dissolved in m-dinitrobenzene in a temperature range of 150°C-195°C was investigated. The experimental curves are satisfactorily described by the equation of the first order (model A \rightarrow B, $k_1 = 10^{14.4}\exp(-36500/RT) = 10^{-4.04}$ at 160 ° C), the complexity of the model (A \rightarrow B \rightarrow C) did not improve practically the congruent of experimental and calculated curves.

The experimental decomposition curves of CL-20 [15-16], dissolved in benzene, toluene and m-xylene at a temperature of 160 ° C processed with the first-order equation.

Figure 1 shows the experimental and calculated curves for the first-order decomposition model (A \rightarrow B, 1a figure) and two consecutive reactions (A \rightarrow B \rightarrow C, 1b figure).

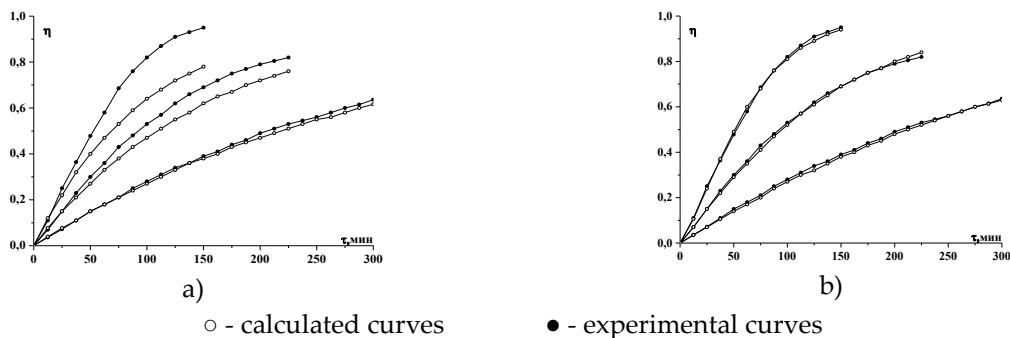


Figure 1. Experimental and calculated curves of CL-20 decomposition

Figure 2 shows the experimental curves of CL-20 decomposition under dynamic heat obtained in [4,10]. The calculated curves for the sample with a particle diameter of 5 and 163 microns is deduce using the model $A \rightarrow B$ $A + B \rightarrow 2C$ (Figure 2a, 2b), and the model $A \rightarrow B \rightarrow C$ $A + B \rightarrow 2C + C \rightarrow 2C$ (Figure 5c, 5d).

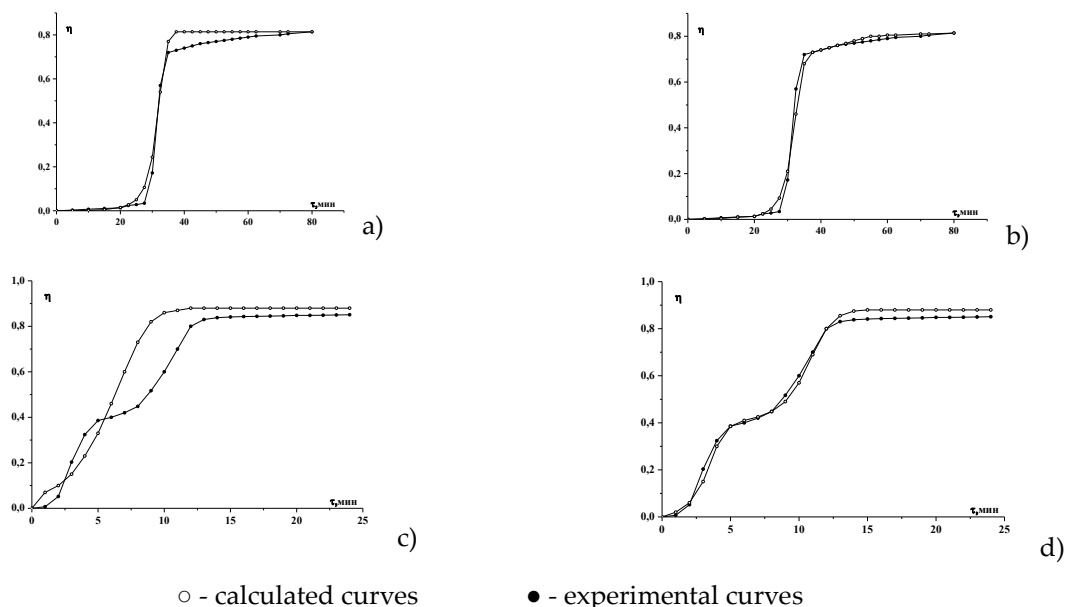
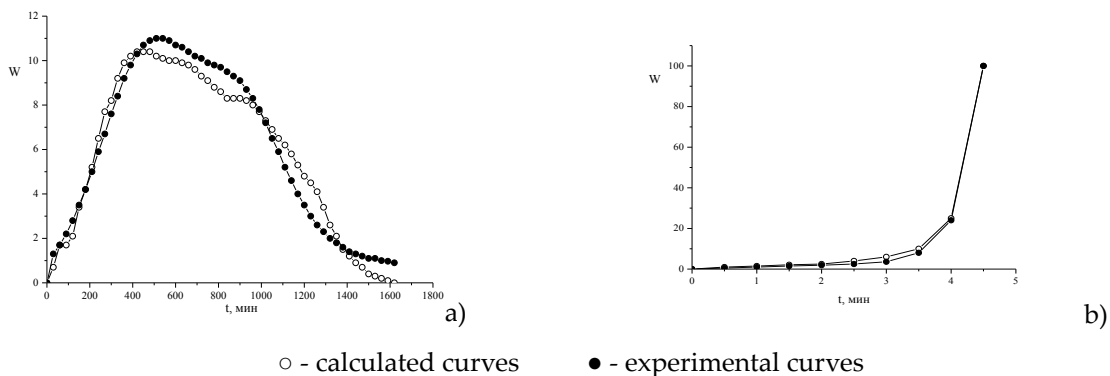


Figure 2. Experimental and calculated curves of CL-20 decomposition

The calculations show that using of formal kinetics models satisfactorily describe the experimental data of complex shapes that do not permit the proposed equation of heterogeneous reactions.

Research of m/v influence on the special characteristic of the decomposition process in air-locked cells showed that the decomposition velocity for the m/v 0.5 g/cm³ and 0.75 g/cm³ and 1.0 g/cm³ is almost similar (shape of the curve is similar to the expansion shown in Figure 3a) [17-19]. In the transition from $m/v = 1.0$ g/cm³ to $m/v = 1.2$ g/cm³, a sharp increase in the decomposition speed as the initial stage (more than 10 times), and the acceleration phase (about 1000 times) (Figure 3b). This velocity jump can be associated with the appearance of the intermediate liquid products. This assumption is confirmed by the views of the condensed decomposition products in dynamic heating conditions. In the case that the reaction proceeds without an explosive, solid decomposition products observed with voids corresponding to the distribution of the dislocation (Figure 4a). Figure 4b shows the products after explosive reaction. The calculated curves for the sample with a particle diameter of 5 and 163 microns is deduce using the model:





○ - calculated curves ● - experimental curves
Figure 3. Experimental and calculated curves of CL-20 decomposition

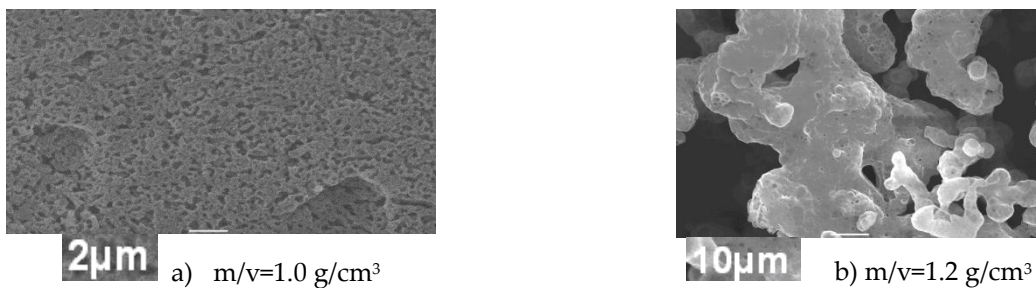
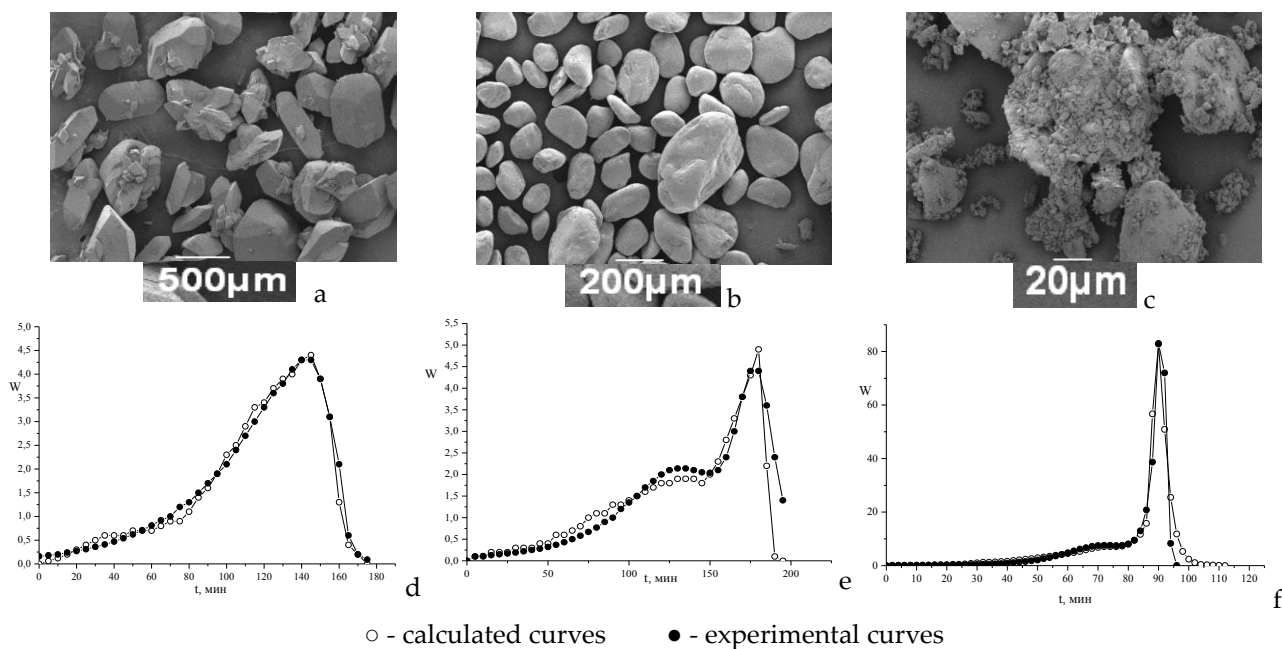


Figure 4. The decomposition products without an explosive (a) and after explosive reaction (b)

Thermal decomposition of coarse sample of spheroid CL-20, shown in Figure 8a, spheroid crystals with sizes > 80 microns in Figure 8c, spheroid crystals with sizes < 80 microns in Figure 8d, was investigated under dynamic heating at heating rates $0.1^\circ\text{C} / \text{min}$ $3^\circ\text{C} / \text{min}$. For all studied samples of CL-20 having dimensions of several tens of microns, it is necessary to have a model with two limiting stages Figures 8b and 8d to describe of experimental curves. The first step is a first order model of autocatalysis. The second stage is a first order autocatalytic model with bimolecular transitional stage. $A \rightarrow B \rightarrow C + C \rightarrow D$
 $A + B \rightarrow 2B$ $B + D \rightarrow 2C + D$



○ - calculated curves ● - experimental curves
Figure 5. Experimental and calculated curves of CL-20 decomposition

Thus, for the processing of CL-20 decomposition experimental data requires model $A \rightarrow B \rightarrow C$ $A + B \rightarrow 2B$ $B + C \rightarrow 2C$, which at different constant ratios can described a simple experimental curves (model $A \rightarrow B$), curves with sharp acceleration (model $A \rightarrow B + B$ $A + B + B \rightarrow 4B$), and two-stage complex curves. At relatively high densities of filling the reaction volume the mechanism is change, perhaps caused by the avalanche of crystals cracking and the appearance of liquid intermediates. The absence of express autocatalysis indices for models decomposition of ionic crystals, possibly due to the limiting stages of the chemical decomposition process.

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АНАЛОГИЯ СООТНОШЕНИЙ МАСШТАБНЫХ ВРЕМЕННЫХ ХАРАКТЕРИСТИК ТЕПЛОВОГО И ДЕТОНАЦИОННОГО ВЗРЫВОВ

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Критические условия теплового взрыва были определены Д. А. Франк-Каменецким как граница существования решения задачи о стационарном пространственном распределении температуры в реагирующей среде [1]. При этом был выявлен безразмерный комплекс, получивший позднее название числа Франк-Каменецкого, представляющий собой отношение временного масштаба отвода θ и выделения τ энергии: $Fk = [\theta/\tau]_{ТВ}$ (здесь: τ - адиабатический период индукции, θ - время тепловой релаксации рассматриваемой области реагирующего ВВ) и его критические значения $Fk^{cr} = [\theta/\tau]_{ТВ}^{cr}$

В работе В. С. Розинга и Ю. Б. Харитона [2] при объяснении критических условий распространения детонации масштабное, или характерное время отвода энергии θ определялось как время разброса реагирующей среды под действием механических сил, а τ как время практического завершения реакции в детонационном фронте. При этом полагалось, что при устойчивом детонационном режиме «должно иметь место неравенство $\tau < \theta$ », или $[\theta/\tau]_{дет} = \bar{\theta}_\tau > 1$. В последующей работе Ю. Б. Харитона [3] было принято, что $\theta = d/c$ (d - диаметр заряда, c скорость звука), а критическое значение величины $\bar{\theta}_\tau$ полагалось равным единице (иными словами $\bar{\theta}_\tau^{cr} = [\theta/\tau]_{дет}^{cr} = 1$)

Предполагая аналогию влияния на поведение зарядов ВВ отношений масштабов времен отвода и выделения энергии при тепловом $[\theta/\tau]_{ТВ}$ и при детонационном $\bar{\theta}_\tau$ взрывах, можно получить выражения для временных масштабов θ и τ детонационного процесса и значение этого отношения, критическое для устойчивого распространения детонации $\bar{\theta}_\tau^{cr} = [\theta/\tau]_{дет}^{cr}$. Для этого сначала необходимо решить задачу о нахождении скорости неидеальной детонации в зависимости от диаметра открытого цилиндрического заряда ВВ, и, за тем, в результате анализа полученной записи уравнения «скорости неидеальной детонации» выявить выражения для θ и $\bar{\theta}_\tau$. Значение величины $\bar{\theta}_\tau$, получающееся при критическом диаметре заряда, являющегося границей области значений диаметров, для которых существует решение этого уравнения, обозначим $\bar{\theta}_\tau^{cr}$.

В основу решение задачи положена работа [4], в которой учитывается влияние расширения центральной трубки тока у оси симметрии заряда (Рис.1).