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ABOUT INCORRECTNESS OF EQUILIBRIUM MODELS APPLICATION FOR QUANTITATIVE ESTIMATION OF POSSIBILITY OF FORMATION OF PERSISTENT ORGANIC POLLUTANTS (POPS) AND OTHER TOXIC SUBSTANCES IN ROCKET SOLID PROPELLANT BURNING

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Introduction

When the expertise of the project for Russian rocket solid propellant motors destruction (RSPM) with the use of the "Lockheed - Martin" technology was being conducted, a number of researchers [1, 2] made quantitative estimation of the possibility of formation such compounds as PCDDs/Fs and PCBs in rocket solid propellant (RSP) burning products using the equilibrium models of minimization of Gibbs energy or the system entropy maximum [3]. We made estimation of correctness of such models application for the system under study under the condition of the most probable formation of persistent organic pollutants (POPs).

Methods and Materials

For estimation of correction of application of these models elsewhere known published data [4] were used. The data are based on the experimental proof of formation of PCDDs/Fs and PCBs in burning products. We also used our own data of the thermodynamic calculations of the reactions, taking place during RSP burning products release into atmosphere [5].

The calculation of the thermodynamic properties of PCBs, PCDD/F is performed by additive-grouped method of Rihani-Doraiswamy [6]. Besides, for evaluation of the models correctness the experimental data, received at the pilot installation, made according to the technology developed by the company "Lockheed-Martin" in China-Lake (California, the USA), were used; they also were taken into account when the technological and economic reasoning of the project for Russian RSPM destruction was being prepared [7].

Results and Discussion

The authors of [1, 2] performed the search of the minimum of Gibb's energy of the gaseous mixture, which is formed during RSP combustion at different temperatures and during water-cooling of the gaseous mixture. Then the values of the equilibrium concentrations of substances were calculated in accordance with the formula:

$$\ln K = -\frac{\Delta G}{R} \quad (1)$$

It was supposed that the real composition of the gaseous mixture would correspond to these values. As the result of use of equilibrium models the authors [1, 2] received the values of concentration of these substances in the RSP burning products at the level of $10^{-90} - 10^{-70}$ g/kg of

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RSP [1] and 10^{-22} g/kg of RSP [2] under the conditions when waste gases were cooled down to 150 - 500 °C. Based on the calculation results the authors made the conclusions about low probability of formation of toxic substances during RSPM disposal and they criticized the results given in [4], which were received experimentally and which showed that when RSP were burnt the amount of PCDDs/Fs was equal to 10^{-5} g/kg of RSP with toxicity equal to 10^{-7} g/kg of RSP.

In Table 1 the comparison of the calculation data [1] of probability of PCB and PCDD/F formation with the experimental values received in [4] for the RSP combustion products is given.

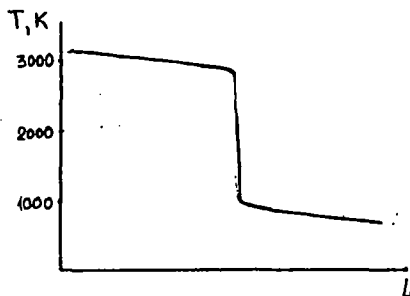
Table 1. Comparison of the calculation results [1] of probability of PCB and PCDD/F formation in the RSP combustion products with the experimental data [4].

Substances	Result from [1] g/kg RSP	Data from [4] g/kg RSP
TCBs	$5.73 \cdot 10^{-75}$	$1.84 \cdot 10^{-5}$
TCDFs	$4.21 \cdot 10^{-85}$	—
TCDDs	$7.95 \cdot 10^{-88}$	$2.19 \cdot 10^{-8}$

However the analysis of calculations, made by the authors [1, 2], showed that the models used by them cannot be correctly applied for quantitative estimation of the possibility of formation of the compounds under consideration due to the following reasons:

- the system for which the models are used is not in equilibrium that is why the kinetic factors are very significant, this fact was not taken into consideration. These models can be used for evaluation of the gaseous mixture at high temperatures (3000 - 3500K), when reactions rate are very high. At other temperatures the reaction rates may considerably drop, especially it is valid for the temperatures lower than 1000K, where kinetic factor become of great influence. Exemplary distribution of temperatures along the length of the combustion chamber of the installation for RSPM combustion is given in fig. 1. When calculating the thermodynamic properties of the reactions [5] we determined only the direction of the processes without calculating the concentrations of PCBs and PCDD/Fs, which in this case, to my opinion, can be determined only experimentally.

Fig. 1. Exemplary distribution of temperatures along the length of combustion chamber of the installation of RSPM combustion.



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- the authors [1] considered the reactions in simplified manner, that is why they believed that the concentration of substances during the reaction can not be higher than their equilibrium one, which is not correct when complicated (successive, successive-parallel, etc.) reactions are considered. According to this mechanism the formation of a large amount of the compounds in the system under consideration takes place. For example, even the formation of carbon dioxide in the RSP combustion products cannot be considered as a simple process, because it goes sequentially through the stage of carbon monoxide formation.

There is significant difference between calculated data, received in [1], and experimental data for other compounds, formed during RSP burning, too. The comparison of these data is given in Table 2. The data from [7] were received for the gases released out of the installation for RSPM combustion. As it can be seen from the Table 1 the calculation data and experimental data for a number of compounds differ principally. Unfortunately the calculations of [1, 2] appeared right before the final meeting of the expert commission considering the present project; they could influence on the opinion of some experts.

Table 2. The amount of the substances formed during RSPM destruction with successive water-cooling of gaseous flows according to data of [1] and [7].

Substances	Amount kg/50t RSP	Amount from SS-N-20, kg	Amount from SS-24, kg
Hydrogen	56.5	1312	1575
Carbon oxide	0.72	9084	11313
Water	12363	81983	78354
Nitrogen	634	4102	6677
Hydrogen chloride	609	213	134
Carbon dioxide	1108	4283	4476
Chlor methane	$3.9 \cdot 10^{-6}$	0.35	0.39
Benzene	$2.4 \cdot 10^{-20}$	0.25	0.28
Methane	273	—	—

So, the conclusions made by the authors of [1, 2] concerning low probability of POPs formation when the waste gases, formed during RSP burning, are released into atmosphere are based on the incorrect use of the applied models for the conditions under consideration.

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