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Analytical paper / Praca analityczna

Energy parameters of the chemical reactions of a gasless pyrotechnic compositions based on barium chromate(VI) and zirconium
Parametry energetyczne reakcji chemicznych bezgazowych kompozycji pirotechnicznych na bazie chromianu(VI) baru i cyrkonu

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Abstract: *The article investigates a pyrotechnic gasless composition based on 65% barium chromate(VI) ($BaCrO_4$) and 35% zirconium composition. Gibbs energy and heat capacity of the mixture were calculated. The Gibbs energy was determined to have a constant negative potential. It has been proven that the combustion reaction of this pyrotechnic composition takes place under any conditions, which makes its use in pyrotechnic products, promising.*
Streszczenie: *W artykule zbadano bezgazową kompozycję pirotechniczną na bazie chromianu(VI) baru ($BaCrO_4$) i cyrkonu w proporcji składu 65/35. Obliczono energię Gibbsa i pojemność cieplną mieszaniny. Ustalono, że energia Gibbsa ma stały potencjał ujemny. Udowodniono, że reakcja spalania kompozycji pirotechnicznej zachodzi w każdych warunkach, co sprawia, że zastosowanie kompozycji pirotechnicznej w wyrobach pirotechnicznych jest obiecujące.*

Keywords: *pyrotechnic composition, Gibbs energy, enthalpy, heat capacity*
Słowa kluczowe: *skład pirotechniczny, energia Gibbsa, entalpia, pojemność cieplna*

1. Introduction

Creating a new gasless pyrotechnic composition requires theoretical calculations of the energy parameters of the chemical reaction. As a rule, these parameters include the following basic requirements [1]:
– a balance between the ease of initiating a combustion reaction and safety in storage and handling,
– selection of components of the composition which undergo a chemical reaction almost (or completely)

without external oxygen,
- stability and completeness of a chemical reaction.
- the absence of the possibility of a reverse chemical reaction,
- have sufficient thermodynamic energy to fulfill the required function,
- have sufficient heat capacity to convert the received thermodynamic energy into mechanical energy.

Thermochemical calculations are used to assess the compliance of the new composition with the specified requirements [2]. It is necessary to create a stoichiometric mixture with the exact amount of fuel and oxidizer so that combustion is as close to ideal as possible. An ideal combustion process, in turn, has no intermediate combustion products and has a maximum flame temperature.

Since the pyrotechnic industry is developing rapidly, not all pyrotechnic compositions have had calculations of energy parameters of chemical reactions carried out. The large number of new pyrotechnic compositions has not made it possible to create a common database of energy calculations of chemical reactions for each specific composition.

This article contains calculations of the energy properties of a gasless pyrotechnic composition of barium chromate(VI) ($BaCrO_4$) and zirconium (Zr), based on the composition's stoichiometric combustion equation.

2. Materials

$BaCrO_4$ is a strong oxidizer which is used specifically in gasless pyrotechnic compositions [3]. It is a pale yellow powder, insoluble in water. $BaCrO_4$was supplied by "UKRKHIMEXPO Company" with a "Pure for analysis" grade (99% purity) [4].

Zr powder is a high-energy fuel which is actively used in many pyrotechnic compositions [3]. It is a medium-dispersed (up to 50 μm) grey powder. A powder with a mass fraction of 94% was supplied by "Development and Implementation of New Materials Company" and used without further purification [5].

3. Features of the calculations and analysis

As a prototype for research, a pyrotechnic composition based on $BaCrO_4$ and Zr in the ratio of 65/35 was used, which had confirmed its efficacy [6, 7]. A calculation program was created in Excel to determine the reaction enthalpy, Gibbs energy, and heat capacity. The calculations are based on the outcomes of the first and second laws of thermodynamics. Graphs of the dependence of Gibbs energy on temperature and the dependence of heat capacity on temperature were created. The Gibbs energy of the pyrotechnic composition was chosen as the principal energy parameter. Gibbs energy (or isobaric-isothermal potential) is a quantity whose change during a chemical reaction equals the change in internal energy. The Gibbs energy shows which part of the total internal energy of the system can be used for chemical transformations or obtained as a result of given conditions (in this case, during combustion of the studied mixture). It also establishes the principal possibility of a chemical reaction occurring under these conditions. Gibbs energy can also be understood as the total potential chemical energy of the system (in this case, crystals).

The dependence of Gibbs energy on temperature also demonstrates the reversibility of a chemical reaction. In the case of the combustion process, the progressive negative values of the Gibbs energy in the entire range of temperatures demonstrated the stability of the combustion process and the impossibility of the reaction proceeding in the reverse direction, which gives the maximum energy characteristics for the composition [8].

4. Analytics, results and discussion

The chemical reaction of the combustion of $BaCrO_4$ and Zr in the absence of oxygen is:

$$4BaCrO_4 + 3Zr \rightarrow 4BaO + 3ZrO_2 + 2Cr_2O_3 \quad (1)$$

Analyzing the stoichiometric coefficients proves that this composition is practicable because even in the complete absence of external oxygen, the reaction still occurs. Input data for calculations and reference data on enthalpy (H), entropy, and heat capacity coefficients are given in Table 1. The data for the intermediate calculation are given in Table 2. The final data for calculations are given in Table 3, as well as in Figures 1 and 2.

Table 1. Input data for calculating the Gibbs energy (G) of chemical reactions

Chemical substance	**Moles**	**($-\Delta H^o 298$) [kJ/mol]**	**($-\Delta G^o 298$) [kJ/mol]**	***a***	***b***	***c***
$BaCrO_4$	4	1428	1322	172.01	0.04	–0.0002
Zr	3	0	0	0	0	0
BaO	4	556.6	534.8	53.3	0.00435	–0.000083
ZrO_2	3	1094	1079	69.62	0.00753	–0.0001406
Cr_2O_3	2	1141	1116.8	119.4	0.0092	–0.0001565

a, *b*, *c* – van der Waals equation constants

Table 2. Calculation of the coefficients of the final equation

		$\Delta H^o 298$				
Enthalpy of reaction at 298 K [kJ/mol]		-2078.4	$\Delta G^o 298$			
Change in Gibbs energy, kJ/mol			-2321.8	Δa	Δb	Δc
Change in coefficients of heat capacity				-0.02718	-1.016E-07	-0.02668
	$\Delta H^o 298$	$-\Delta a298$	$-0.5\Delta b298^2$	$\Delta c298^{-1}$	ΔH^o	
ΔH^o constant	-2078.4	8.09964	0.004512	-8.95E-05	-2070.2959	
	$\Delta G^o 298$	$-\Delta H^o$	$\Delta a298\ln 298$	$0.5\Delta b298^2$	$0.5\ \Delta c\ 298^{-1}$	Σ
	-2321.8	2070.29594	-46.14441	-0.00452	-4.477E-05	-297.65302
					$\Sigma/298$	
I constant					-0.9988357	
	$-\Delta H^o$	$-\Delta a$	$-0.5\Delta b$	$-0.5\Delta c$	I	
Coefficients of the final equation	-2070.2959	0.02718	5.0805E-08	0.01334	-0.9988357	

Table 3. Values of G and C_p of substances depending on temperature

Calculation of Gibbs Energy						
T [K]	$-\Delta H^o$	$-\Delta aT\ln T$	$-0.5\Delta bT^2$	$-0.5\Delta cT^{-1}$	IT	G [kJ/mol]
200	–2070.296	28.802	0.002	0.000	–199.767	–2241.259
300		46.509	0.005		–299.651	–2323.433
400		65.139	0.008		–399.534	–2404.683
500		84.457	0.013		–499.418	–2485.245
600		104.321	0.018		–599.301	–2565.258
700		124.641	0.025		–699.185	–2644.815
800		145.350	0.033		–799.069	–2723.982
900		166.400	0.041		–898.952	–2802.807
1000		187.753	0.051		–998.836	–2881.328
1100		209.378	0.061		–1098.719	–2959.576
1200		231.250	0.073		–1198.603	–3037.576
C_p of						
T [K]	$BaCrO_4$	Zr	BaO	ZrO_2	Cr_2O_3	
200	172.018	0.000	53.301	69.621	119.401	
300	172.022		53.301	69.622	119.403	
400	172.026		53.302	69.623	119.404	
500	172.030		53.302	69.624	119.405	
600	172.034		53.303	69.624	119.405	
700	172.038		53.303	69.625	119.406	
800	172.042		53.303	69.626	119.407	
900	172.046		53.304	69.627	119.408	
1000	172.050		53.304	69.628	119.409	
1100	172.054		53.305	69.628	119.410	
1200	172.058		53.305	69.629	119.411	

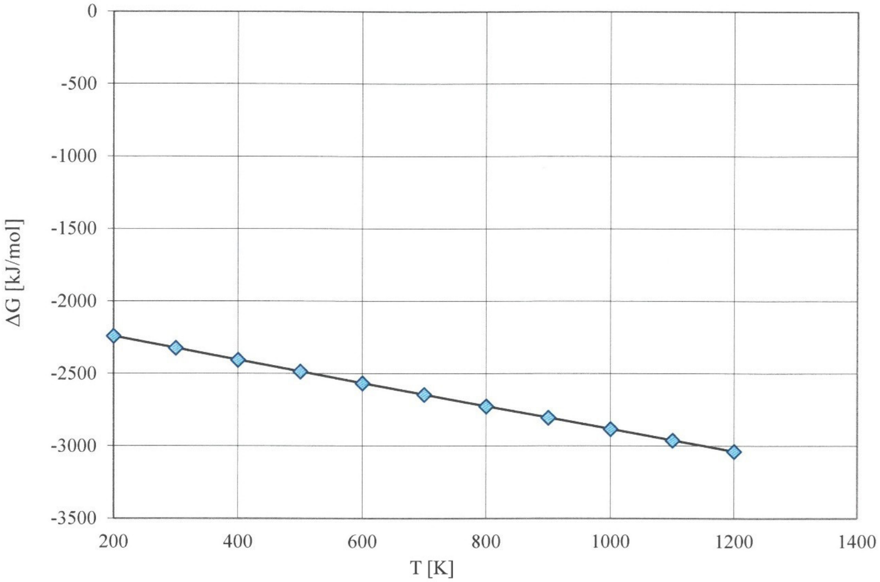

Figure 1. Graph of dependence of ΔG on temperature

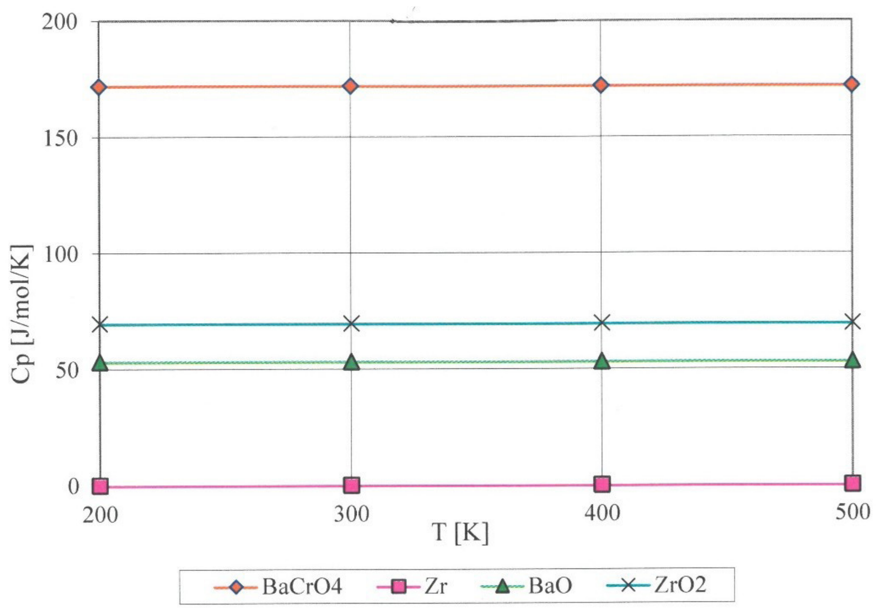

Figure 2. Graph of dependence of C_p change on temperature

Analyzing the obtained data, it can be concluded that:

1. Gibbs energy has a constant negative potential, indicating two things. First, the continual decrease in Gibbs energy indicates the irreversibility of the reaction, which allows the composition to do its work. Secondly, it demonstrates the stable and constant combustion reaction of the pyrotechnic composition under any conditions.
2. The heat capacity of the reaction components is a constant value, which indicates the constant energetics of the reaction regardless of temperature and its stable transformation into mechanical energy.

4. Conclusions

- ♦ Gibbs energy and heat capacity of a gasless pyrotechnic composition based on $BaCrO_4$ and Zr in a ratio of 65/35 was calculated.
- ♦ Gibbs energy has a constant negative potential. The constant decrease of the Gibbs energy indicates the irreversibility of the reaction, which indicates the stability and unceasing combustion reaction of the pyrotechnic composition under any conditions and makes its use in pyrotechnic products promising.
- ♦ The heat capacity of the reaction components is a constant value, which indicates the constant energetics of the reaction regardless of temperature and its stable transformation into mechanical energy.

References

[1] Kubota N. *Propellants and Explosives*. 2nd ed., Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA., **2015**, pp. 2-4 and 23-38; https://doi.org/10.1002/9783527693481.

[2] McAllister S., Chen J.Y., Fernandez-Pello A.C. Thermodynamics of Combustion. [in:] *Fundamentals of Combustion Processes*. Mechanical Engineering Series. New York: Springer, **2011**; https://doi.org/10.1007/978-1-4419-7943-8_2.

[3] Agrawal J.P. *High Energy Materials: Propellants, Explosives and Pyrotechnics*. Weinheim: Wiley-VCH. **2010**; ISBN: 978-3-527-32610-5.

[4] *Barium Chromate. Specifications*. (in Ukrainian). Technical Conditions TU 6-09-5286-86, **1986**.
[5] *Sodium-thermal Zirconium Powder*. (in Ukrainian) Technical Conditions TU 48-4-376-76, **1976**.
[6] Zakusylo D. Determination of the Activation Energy of a Gasless Pyrotechnic Composition. *Mater. Wysokoenerg (High Energ. Mater.)* **2021**, *13*: 96-100; https://doi.org/10.22211/matwys/0217.
[7] Zakusylo V.R., Yefymenko A.O., Zakusylo R.V., Slesareva O.V. Pyrotechnic Heaters for Thermal Current Sources. (in Russian) *Visnyk KPI, Mining* **2012**, *22*: 82-89.
[8] Kamran M., Fazal M.R. Fuel Cell. [in:] *Renewable Energy Conversion Systems*. Academic Press. **2021**; https://doi.org/10.1016/C2019-0-05410-6.

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