

Thermodynamical Analyse the Formation of Phosphates Copper, Zinc and Cobalt on the Base Double Superphosphate and Sulphates of Copper, Zinc and Cobalt

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Authors' contributions

This work was carried out in collaboration among all authors. Author ZT designed the study, performed the statistical analysis and wrote the protocol. Author ITS wrote the first draft of the manuscript. Author IIU managed the analyses of the study. Author OMI managed the literature searches. Author BES translated and corrected this manuscript. All authors read and approved the final manuscript.

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ABSTRACT

In this article the relationship between the entropies of crystalline calcium compounds and copper, zinc and cobalt compounds were analyzed. Thermal capacity dependence of temperature for acidic phosphates of copper, zinc and cobalt, determining value of enthalpy and entropy of copper, zinc and cobalt phosphates have been determined and the possibility to conduct thermodynamic analysis of reactions for their formation were established. Accordingly the data of thermodynamic analysis of temperature conditions for obtaining double superphosphate, the most formation of monosubstituted phosphates of copper, zinc and cobalt, and possibility of formation disubstituted of copper phosphates.

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1. INTRODUCTION

Intensive research in the field of microelement containing compounds is due to the progress and satisfaction of needs the modern field of agriculture and technology, the development of new and improvement of real methods for obtaining mineral fertilizers. Of particular interest to microelement containing compounds in practical aspect, is associated with the production of new mineral microelement containing complex fertilizers.

During the many years conducted in our country and in abroad, established that the use of fertilizers containing microelements (zinc, copper, molybdenum, boron, manganese, cobalt), increases plant yields and improves the quality of agricultural products [1]. When microelements interact with the main components of mineral fertilizers, different processes may occur with formation of new compounds, therefore the study of the physicochemical properties of new substances is of great importance.

Thermodynamic values of many elements, chemical compounds, ions, and minerals are either absent or have a considerable precision in their values in the reference books and in the scientific literatures. The main requirements for thermodynamic properties are considered to be their reliability in critical analysis, assessment of determination method, mutually consistency and etc. Therefore, the feature of research is use of available reference dates about of thermodynamic properties of elements, chemical compounds for purpose of subsequent determination of various correlations and functions, different calculation methods have been used [2].

2. STATEMENT OF RESEARCH

Objective of the work are theoretical calculate about possibility formation of phosphates of copper, zinc and cobalt.

In this aspect, the method of M.Kh. Karapetyanes gives the following relationship between the entropies of crystalline calcium compounds and compounds of copper, zinc, and cobalt (Fig. 1-3).

$$S_{298\text{CuX}}^{\circ} = 3,517 S_{298\text{CaX}}^{\circ} + 25,202 \quad (1)$$

$$S_{298\text{ZnX}}^{\circ} = 3,852 S_{298\text{CaX}}^{\circ} + 11,639 \quad (2)$$

$$S_{298\text{CoX}}^{\circ} = 3,643 S_{298\text{CaX}}^{\circ} + 17,208 \quad (3)$$

V.A. Kireev [3] showed that when comparing the entropy of analogous compounds of sodium and magnesium, related to 2 g/eq. of compound, the difference of S_{298}° varies between 45.39-70.34 joule/mole-deg.. Accordingly to Kelly's data of entropy increments, this difference should be to $\Delta = J_{S\text{Na}^+}^{\circ} - J_{S\text{Mg}^{2+}}^{\circ} = 2 \cdot 40.19 - 24.70 = 55.68$ joule/mole-degree.

The entropy of copper, zinc and cobalt phosphates we are calculated below entropy equalities of calcium phosphates:

$$S_{298\text{CuX}}^{\circ} = S_{298\text{CaX}}^{\circ} + 3,768 \quad (4)$$

$$S_{298\text{ZnX}}^{\circ} = S_{298\text{CaX}}^{\circ} + 1,675 \quad (5)$$

$$S_{298\text{CoX}}^{\circ} = S_{298\text{CaX}}^{\circ} + 4,605 \quad (6)$$

The laboratory tests results are shown in Table 1. It is seen, the data obtained by independent methods are well congruent with each other, especially using by Kelly increments and Berthelot principle found the values of s_{298}° [4]. The Karapetyanes method gives somewhat lower results of entropy. It is seen from Figs. 1-3, the scatter of points around straight lines is significant, therefore, the accuracy of equations 1-3, and hence the entropy values obtained by this method, is low.

Heat capacity of phosphates of copper, zinc and cobalt earlier was not spent. B.S. Kogan obtained equations for calculating the heat capacity of potassium phosphates and phosphoric acids at elevated temperatures using the method of I.L. Landia [5-6]. By the same method B.M. Beglov calculated the high-temperature heat capacities of condensed ammonium, lithium, rubidium and cesium phosphates [7]. Similar method was adopted in calculating the high-temperature heat capacities of substances accordingly to their standard entropy.

Calculation schemes for different groups of phosphates were different due to the specificity of the method and individual characteristics of the compounds. Dependence of heat capacity on temperature for acidic phosphates of copper, zinc and cobalt is determined [6], as for "complex oxygen compounds containing

gaseous oxides (H₂O) and not having polymorphic transformations". It was also taken into account that they refer to inorganic compounds of hydrogen. The calculation procedure was carried out accordingly to well-known rules.

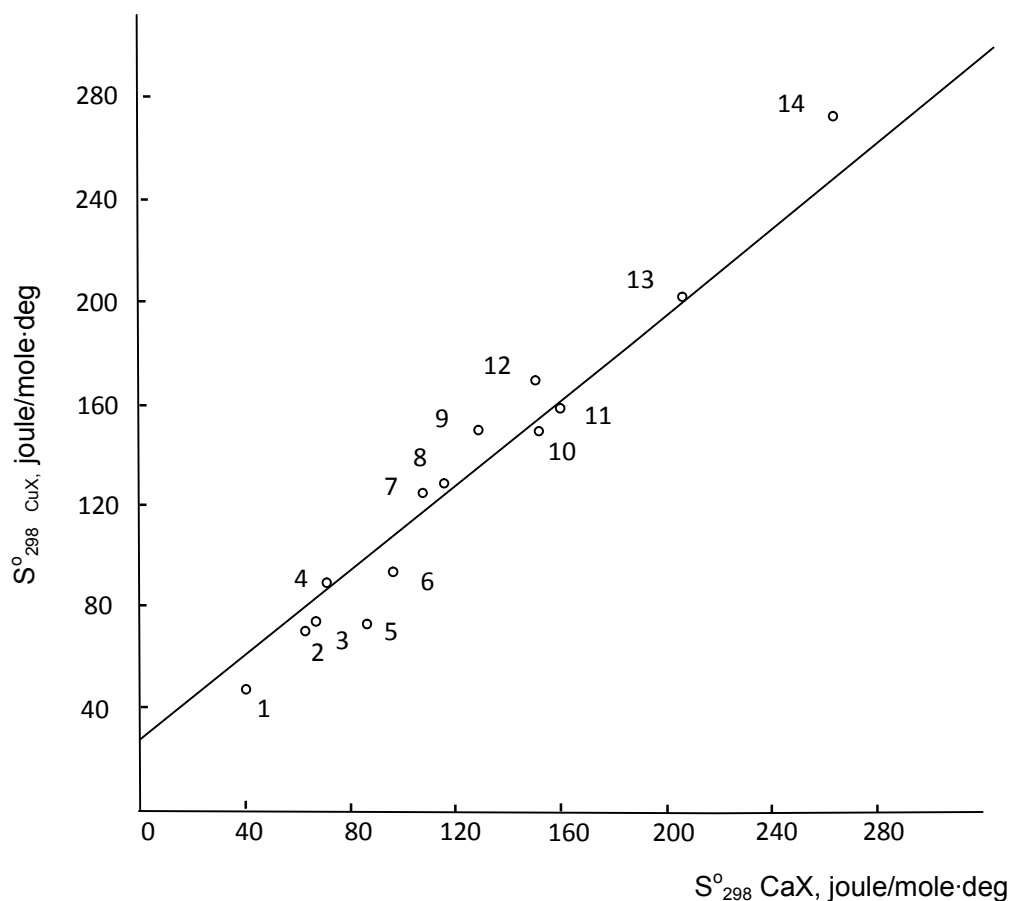


Fig. 1. Comparison of standard entropies of crystalline compounds of copper and calcium (M = Cu or Ca): 1-MO, 2-MS, 3-MSeO₄, 4-MF₂, 5-M(OH)₂, 6-MCO₃, 7-MCl₂, 8-MSO₄, 9-MMoO₄, 10-MFe₂O₄, 11-MWO₄, 12-MI₂, 13-M(NO₃)₂

Table 1. Results the calculation of entropy copper, zinc and cobalt phosphates

Compounds	J/mole-degree		
	Accordingly to Berthelot's method	Accordingly to Karapetyant's method	Accordingly to Kelly's increments
Cu(H ₂ PO ₄) ₂	194.31	183.59	193.43
CuHPO ₄	117.48	118.28	115.22
Cu ₃ (PO ₄) ₂	247.15	226.59	244.93
Cu ₂ P ₂ O ₇	195.48	183.38	193.22
Zn(H ₂ PO ₄) ₂	193.14	186.52	191.34
ZnHPO ₄	114.84	114.38	113.13
Zn ₃ (PO ₄) ₂	244.55	234.00	242.83
Zn ₂ P ₂ O ₇	192.89	186.31	191.13
Co(H ₂ PO ₄) ₂	191.76	182.59	194.27
CoHPO ₄	113.53	114.38	116.06
Co ₃ (PO ₄) ₂	240.25	227.51	245.77
Co ₂ P ₂ O ₇	191.55	182.42	194.02

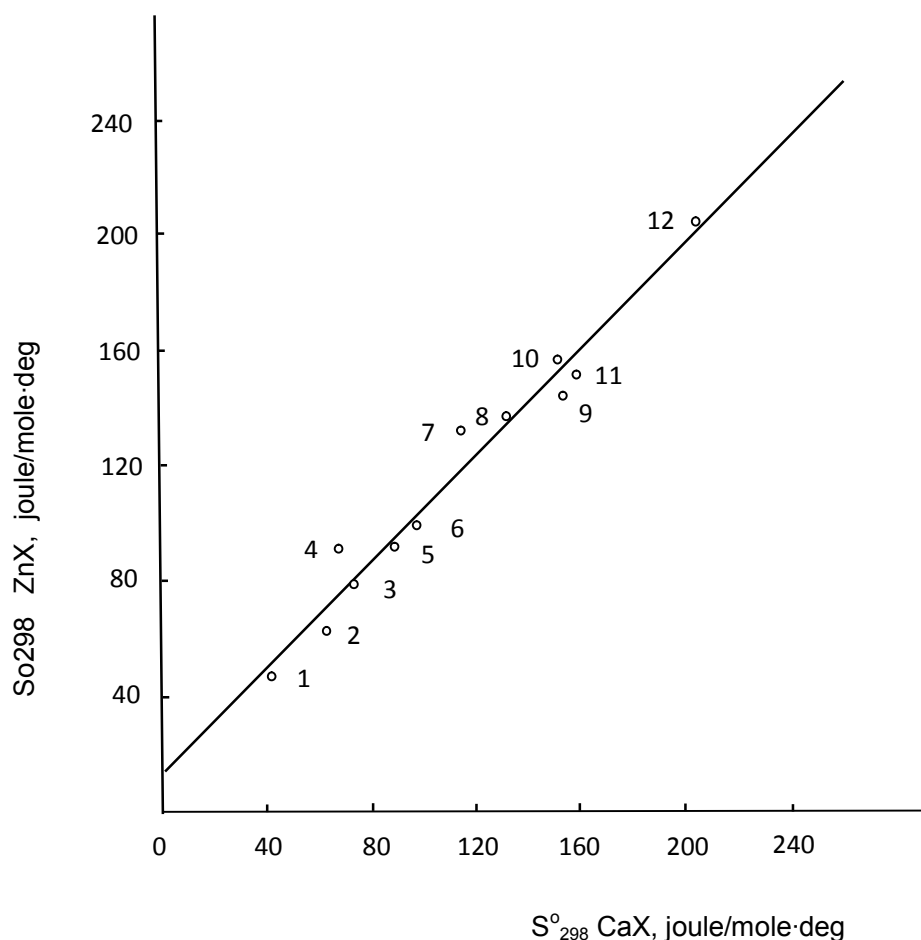


Fig. 2. Comparison of standard entropies of crystalline zinc and calcium compounds (M = Zn or Co): 1-MO, 2-MS, 3-MF₂, 4-MSeO₄, 5-M(OH)₂, 6- MCO₃, 7-MSO₄, 8-MMoO₄, 9-MFe₂O₄, 10-MI₂, 11- MWO₄, 12-M(NO₃)₂

The results of calculation of heat capacity copper, zinc and cobalt phosphates are shown in Table 2.

The high-temperature heat capacities of triple-substituted phosphates and pyrophosphates of microelements were calculated accordingly [6], as for ionic oxygen compounds consisting of solid oxides that do not have polymorphic transformations and are suitable for thermal characteristics under the column "other cases".

The obtained equations are valid in temperature range from 298°K to decomposition temperature of adequate phosphate.

3. RESULTS AND DISCUSSION

Having determined the enthalpy and entropy of copper, zinc, and cobalt phosphates, we were

able to perform thermodynamic analysis of reactions for their formations.

Thermodynamic analysis makes it possible to predetermine possibility of particular reaction and, therefore, the salt composition of final products, which is extremely complicated due to the complexity of the initial and final products. Therefore, reactions of copper, zinc and cobalt sulfate interactions with orthophosphoric acid and monocalcium phosphate, i.e., those which are possible in process of obtaining double superphosphate containing microelements, were subjected to analysis. For each reaction, we found values of isobaric-isothermal potential and discussed by it about possibility of particular reaction (negative value of ΔG).

Thermodynamic calculations of possibility the formation of phosphates of microelements in the

process for obtaining double superphosphate = $\Delta H - T\Delta S$ without heat capacities. The results were carried out using the simplified formula ΔG obtained are presented in Table 3.

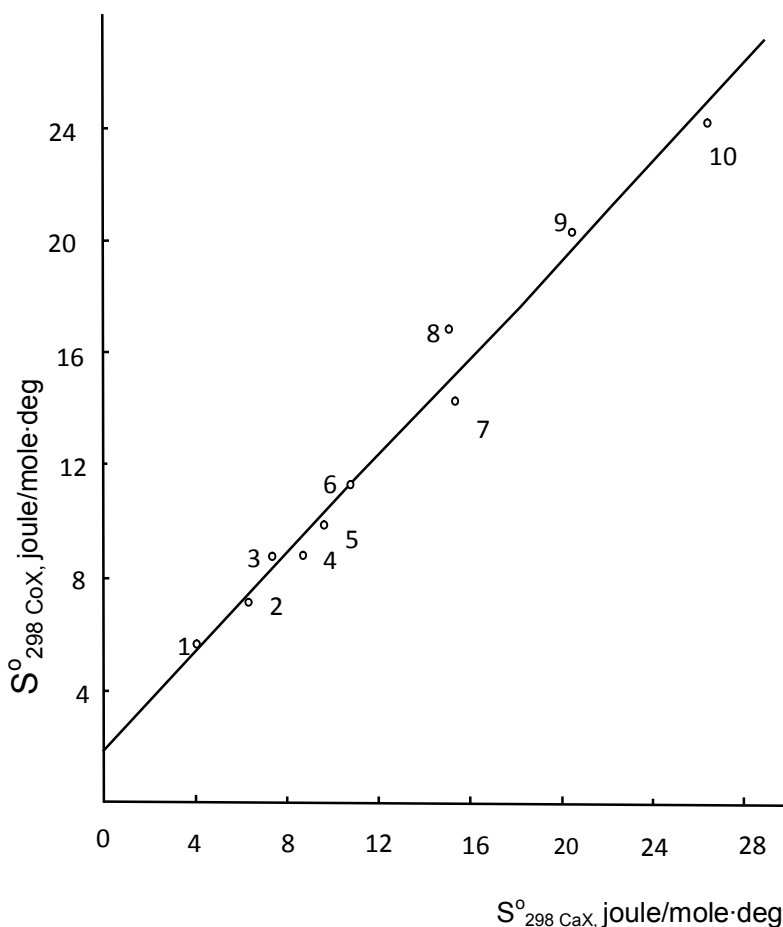


Fig. 3. Comparison of standard entropies of crystalline compounds of cobalt and calcium (M = Co or Ca): 1- MO, 2-MS, 3-MF₂, 4-M(OH)₂, 5-MCO₃, 6-MCl₂, 7-MF₂O₄, 8-MI₂, 9-M(NO₃)₂, 10-MSeO₃·2H₂O

Table 2. Temperature dependence of heat capacity of copper, zinc and cobalt phosphates

Compounds	S° ₂₉₈ , J/mole-degree	T, °K	C _{p298} , J/mole-degree	C° _p = a+BT+CT ² , J/mol-degree		
				a	B·10 ²	C·10 ⁻⁵
Cu(H ₂ PO ₄) ₂	194.31	1410	203.06	246.35	7.62	58.62
CuHPO ₄	117.48	1174	106.35	143.11	1.34	36.22
Cu ₃ (PO ₄) ₂	247.15	1117	186.80	282.23	3.60	31.86
Cu ₂ P ₂ O ₇	195.48	1194	214.45	239.23	2.97	29.94
Zn(H ₂ PO ₄) ₂	193.14	1429	202.31	245.43	7.58	58.36
ZnHPO ₄	114.84	1201	105.76	134.10	2.93	32.95
Zn ₃ (PO ₄) ₂	244.55	1128	257.11	282.19	3.56	31.74
Zn ₂ P ₂ O ₇	192.83	1211	214.36	239.02	2.97	29.77
Co(H ₂ PO ₄) ₂	191.76	1439	201.89	244.84	7.58	58.16
CoHPO ₄	113.55	1215	105.51	133.64	2.93	32.78
Co ₃ (PO ₄) ₂	243.25	1135	257.07	281.86	3.60	31.53
Co ₂ P ₂ O ₇	19.55	1219	214.36	239.11	2.93	29.73

Table 3. Thermodynamic characteristics of reactions of formation of microelements phosphates

№	Reactions	ΔH°_{298}	ΔS°_{298}	ΔG°_{298}	ΔG°_{353}	T, °K
		kJ/mole	J/mole·degree	kJ/mole	kJ/mole	
1.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 2\text{H}_3\text{PO}_4 = \text{Cu}(\text{H}_2\text{PO}_4)_2 + \text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}$	18.98	26.21	11.17	9.67	997.15
2.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{H}_3\text{PO}_4 = \text{CuHPO}_4 + \text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}$	19.76	42.52	1.45	-0.88	332.31
3.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4)_2 = \text{Cu}(\text{H}_2\text{PO}_4)_2 + \text{CaSO}_4 + 5\text{H}_2\text{O}$	-0.43	38.89	-12.02	-14.94	8.94
4.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4)_2 = \text{CuHPO}_4 + \text{CaSO}_4 + \text{H}_3\text{PO}_4 + 5\text{H}_2\text{O}$	10.34	55.20	-6.11	-10.26	187.32
5.	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + 2\text{H}_3\text{PO}_4 = \text{Zn}(\text{H}_2\text{PO}_4)_2 + \text{H}_2\text{SO}_4 + 7\text{H}_2\text{O}$	22.66	37.99	11.34	9.25	596.47
6.	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{H}_3\text{PO}_4 = \text{ZnHPO}_4 + \text{H}_2\text{SO}_4 + 7\text{H}_2\text{O}$	25.12	54.28	9.08	6.09	462.79
7.	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4)_2 = \text{Zn}(\text{H}_2\text{PO}_4)_2 + \text{CaSO}_4 + 7\text{H}_2\text{O}$	3.25	50.67	-11.85	-14.64	64.14
8.	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4)_2 = \text{ZnHPO}_4 + \text{CaSO}_4 + \text{H}_3\text{PO}_4 + 7\text{H}_2\text{O}$	15.84	66.96	-4.11	7.80	236.56
9.	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O} + 2\text{H}_3\text{PO}_4 = \text{Co}(\text{H}_2\text{PO}_4)_2 + \text{H}_2\text{SO}_4 + 7\text{H}_2\text{O}$	23.66	40.36	11.63	9.431	586.22
10.	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O} + \text{H}_3\text{PO}_4 = \text{CoHPO}_4 + \text{H}_2\text{SO}_4 + 7\text{H}_2\text{O}$	5.46	56.67	8.57	5.46	449.27
11.	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4)_2 = \text{Co}(\text{H}_2\text{PO}_4)_2 + \text{CaSO}_4 + 7\text{H}_2\text{O}$	4.25	53.04	-11.56	-14.47	80.13
12.	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4)_2 = \text{CoHPO}_4 + \text{CaSO}_4 + \text{H}_3\text{PO}_4 + 7\text{H}_2\text{O}$	16.05	69.35	-4.62	-8.43	231.44

Thermodynamic analysis showed that sulfate salts of copper, zinc and cobalt behave differently in reactions with phosphoric acid and monocalcium phosphate. As can be seen from Table 3, sulfates of microelements at 25°C should not interact with phosphoric acid. With an increase the temperature, the probability of reactions increases and starting from 59.3°C, only formation twice-substituted copper phosphate. For formation of twice-substituted phosphates of zinc and cobalt, higher temperature is required.

In the interaction of copper sulfate, zinc and cobalt with monocalcium phosphate, is possible formation of monosubstituted and twice-substituted metal phosphates. Thermodynamically more likely is formation of monosubstituted phosphates of copper, zinc and cobalt, the isobaric-isothermal potential of reactions (1) and (6) has more negative value.

4. CONCLUSION

Thus, dates of thermodynamic analysis indicate that under the temperature conditions of obtaining double superphosphate, the formation of mono-substituted phosphates of copper, zinc, and cobalt is most likely and is possible the formation of twice- substituted copper phosphates.

COMPETING INTERESTS

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing

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REFERENCES

1. Shamshidinov IT, Turaev Z, Mamadzhanov ZN, Mamadaliev AT, Uktamov DA. The use of low-grade phosphorites (~15% P₂O₅) in obtaining calcium-containing nitrogen-phosphorus fertilizers with microelements. Reports of Academy of Science of the Republic of Uzbekistan, Tashkent. 2015;3:57-61.
2. Karzhavin VK. Thermodynamic values of chemical elements and compounds. Examples of their practical application. Apatity, Moscow, Kola Science Center RAS. 2011;6-9.
3. Kireev VA. Methods of practical calculations in the thermodynamics of chemical reactions. Moscow, Chemistry. 1975;536.
4. Drozin NN. Application of Berthelot principle for the calculation of standard entropies of solid inorganic compounds. Journal of Physical Chemistry, Moscow. 1961;35(8):1789-1793.
5. Kogan BS. Thermodynamic properties of potassium phosphates. Report 4. The heat capacity of potassium phosphates and phosphoric acids at elevated temperatures. Journal of Physical Chemistry, Moscow. 1971;2623:71.
6. Landia NA. Calculation of high-temperature heat capacities of solid inorganic substances using standard entropy. Reports of Acedemy of Science of the Republic of Georgia, Tbilisi. 1962;3: 221.
7. Beglov BM. The heat capacity of ammonium phosphate at elevated temperatures. Uzbek Chemical Journal, Tashkent. 1972;4:36-37.

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