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Calculation of Thermodynamic Characteristics of Phosphates of Copper, Zinc and Cobalt

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ABSTRACT: The article presents the results of a study to determine the thermodynamic characteristics of phosphates of copper, zinc and cobalt. In the field of research of the above compounds, the theory of the processes under study is insufficiently covered.

Determination unknown values of the phosphate enthalpies, the enthalpies of a number of calcium compounds were compared with the enthalpies of copper, zinc, and cobalt compounds with the same anion. The main methods of approximate calculations of the standard enthalpy of formation, entropy, and heat capacity of copper, zinc, and cobalt phosphates are considered.

The most suitable calculation methods are identified, as well as methods that allow you to determine the desired values with the least error.

KEY WORDS: thermodynamics, trace elements, phosphates, enthalpy, entropy, heat capacity, mineral fertilizers, micronutrient fertilizers, copper, zinc, cobalt phosphates.

I.INTRODUCTION

The rapid population growth in the world, the reduction of suitable land and water resources requires an increasingly optimal solution to the problem of the production of new types of fertilizers. Therefore, one of the most important tasks of industrial production and agriculture is the complete satisfaction of the needs of the population in high-quality food products. In this regard, the issues of introducing trace elements fertilizers into agricultural practice, expanding their assortment and reducing the cost of production are becoming extremely important [1, 2].

In the production of mineral fertilizers with trace elements, to solve a number of specific technological problems, knowledge of the thermodynamic properties of trace elements is required. To determine the direction of the reactions of the formation of compounds of trace elements in fertilizers, one needs to know their heat capacity, Gibbs energy, enthalpy and entropy of formation at various temperatures and compositions.

The main methods of approximate calculations of the standard enthalpy of formation, entropy, and heat capacity of copper, zinc, and cobalt phosphates are considered. The most suitable calculation methods are identified, as well as methods that allow you to determine the desired values with the least error.

When determining the properties of substances, the capabilities of experimental measurement methods (very time-consuming, often complex in hardware design and therefore expensive) are clearly insufficient [3]. In this regard, the value of the calculation methods for determining the thermodynamic characteristics is of particular importance.

As you know, the thermal effect of the reaction is calculated according to the Hess law, formulated as early as 1840. This law states that the heat released or absorbed in a chemical process is constant and does not depend on whether the process is single or multi-stage. Thus, the heat of formation of a compound can be found using data on other reactions. The standard heat of reaction Δ H can be calculated from the heats of formation of all compounds involved in the reaction. It is equal to the difference between the algebraic sum of the standard heats of formation of the reaction products ΔH_f" and the algebraic sum of the standard heats of formation of the starting materials $\Delta H_f'$ [4].

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II.METHODS OF RESEARCH

We set ourselves the goal of studying the thermodynamic properties of certain phosphates of copper, zinc and cobalt, as well as to determine the possibility of reactions between the sulfate salts of trace elements and the components of double superphosphate.

Assess thermodynamic properties, we used comparative calculation methods, taking as a basis the known, experimentally found values of the standard heats of formation and entropy of calcium phosphates [5-6]. We determined the standard heats of formation by the method of M.Kh. Carapetians and the "constancy of differences" [7]. In our previous publications, we have analyzed the materials of our studies by scientists L.A. Zharkova, Y.I. Gerasimov, I.M. Selivanova, B.M. Beglov and I.I. Usmanov. A number of scientists using the method of M.Kh. Carapetians discovered a relationship between the thermodynamic characteristics ($\Delta H°_{298}$ and $\Delta S°_{298}$) of various compounds [8-12].

To determine the unknown values of the phosphate enthalpies, we compared the enthalpies of a number of calcium compounds with the enthalpies of copper, zinc, and cobalt compounds with the same anion [13].

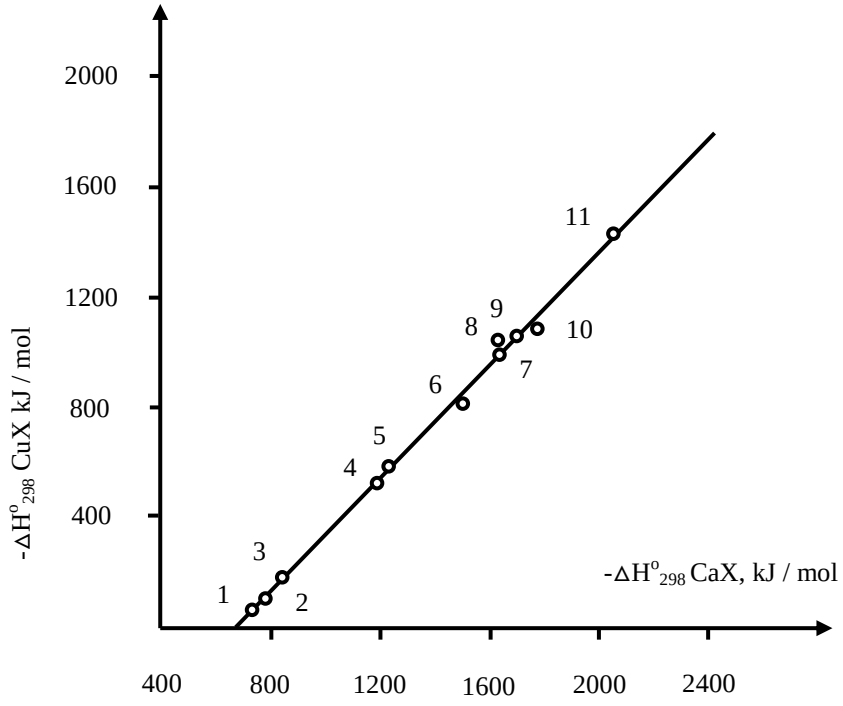

Fig.1. Comparison of the standard heats of formation of crystalline copper compounds and calcium (M = Cu or Ca): 1-$M(ClO_3)_2$, 2-$M(ClO_4)_2$, 3-MCI_2, 4-$MSeO_4$, 5-$MS0_3$, 6-MSO_4, 7-$MMoO_4$, 8-MFe_2O_4, 9-$MSeO_3 \cdot 2H_2O$,10-MWO_4, 11-$M(HCO_3)_2$.

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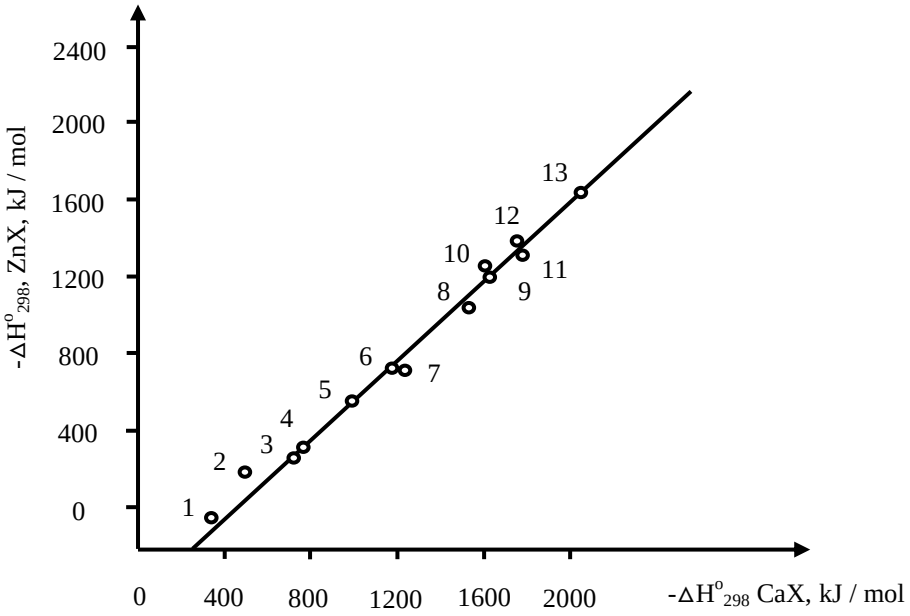

Fig. 2. Comparison of the standard heats of formation of crystalline zinc and calcium compounds (M=Zn or Ca): 1-$M(CNS)_2$, 2-MS, 3-$M(ClO_3)_2$, 4-$M(ClO_4)_2$, 5-$M(NO_3)_2$, 6-$MSeO_4$, 7-MSO_4, 8-MSO_4, 9-$MMoO_4$, 10-MFe_2O_4, 11-MWO_4, 12-$MNiO_3$, 13-$M(HCO3)_2$.

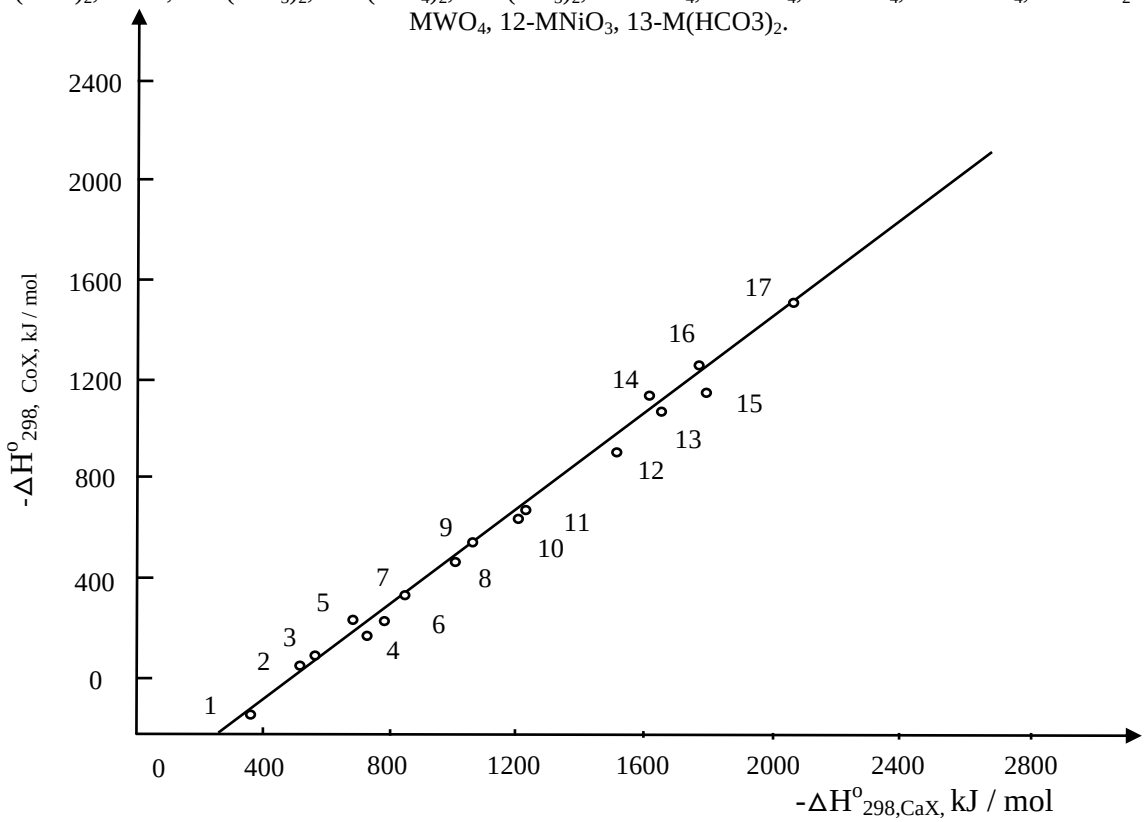

Fig. 3. Comparison of standard heats of formation crystalline cobalt and calcium compounds (M - Co or Ca): 1- $M(CNS)_2$, 2-MS, 3-MI_2, 4-$M(ClO_3)_2$, 5-MO, 6-$M(ClO_4)_2$, 7-MCl_2, 8-$M(NO_3)_2$, 9-$M(OH)_2$, 10-$MSeO_4$, 11-MSO_3, 12-MSO_4, 13-$MMoO_4$, 15-MWO_4, 16-$MTiO_3$, 17-$M(HCO_3)_2$.

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Figures 1-3 show the relationship between standard heats of formation of salts of copper, zinc, cobalt and calcium. They correspond to straight lines and are described by the following equations:

$$\Delta H°_{298\ CuX}=4{,}300\ \Delta H°_{298\ CaX}-655{,}364$$
$$\Delta H°_{298\ ZnX}=4{,}271\Delta H°_{298\ CaX}-432{,}413$$
$$\Delta H°_{298\ CoX}=4{,}057\ \Delta H°_{298\ CaX}-450{,}973$$

Using the obtained ratios and literature data for the standard heat of formation of calcium phosphates, we calculated ΔH ° 298 of similar phosphates of copper, zinc and cobalt (Table 1).

Table 1. The results of calculating the enthalpy of phosphates of copper, zinc and cobalt

Compound	$\Delta H°_{298}$, kJ / mol	
	According to Carapetyans method	**According to method of "constant" diversity**
$Cu(H_2PO_4)_2$	2554,79	2492,40
$CuHPO_4$	1233,98	1197,84
$Cu_3(PO_4)_2$	3597,59	3504,77
$Cu_2P_2O_7$	2780,25	2711,29
$Zn(H_2PO_4)_2$	2746,58	2703,00
ZnHPO4	1426,11	1408,44
$Zn_3(PO_4)_2$	3779,17	3715,37
$Zn_2P_2O_7$	2969,82	2921,88
$Co(H_2PO_4)_2$	2569,06	2631,82
$CoHPO_4$	1314,66	1337,26
$Co_3(PO_4)_2$	3550,07	3644,19
$Cu_2P_2O_7$	2781,17	2850,71

The table also shows the values of the standard heats of formation of metal phosphates obtained by us using the method of "constant differences". The data obtained by two methods that are close to each other and are in good agreement with the experimentally found values for zinc pyrophosphate (2908 kJ / mol). The difference between the experimentally found value and calculated by the method of "constant differences" is less than 0.5%.

Calculation entropy of copper, zinc, and cobalt phosphates, we used the Berthelot principle [14], according to which the heat of reaction is a measure of chemical affinity. This position is valid only if the change in the thermodynamic potential is equal to the heat of reaction. The change in the thermodynamic potential during a chemical reaction is determined by the equation $\Delta Z = \Delta H - T\Delta S$, where: ΔH и ΔS are the thermal effect and the change in the entropy of the reaction, T is the process temperature. When observing the Berthelot principle, the increase in the entropy of the reaction is zero. The field of application of the Berthelot principle is usually limited by reactions between solids, since in this case ΔS is either equal to zero, or if it differs from zero, then much less than in the case of participation of gaseous substances in chemical processes.

However, even with the interaction of solids, the Berthelot principle is far from always true. Only for certain classes of chemical reactions between solids does it fully justify itself.

If an ionic compound interacts with elements belonging to the same subgroup of D.I. Mendeleev's periodic

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system as the element forming a positively charged ion, then the entropy of the reaction in this case should be zero. As an example, we give the calculation of entropy for monosubstituted copper phosphate (Table 2).

Table 2. Calculation of entropy of monosubstituted copper orthophosphate

№	Reaction equation	The desired entropy of compound X, J / mol-degree
1.	$Ca(H_2PO_4)_2 + Cu(NO_3)_2 = Cu(H_2PO_4)_2 + Ca(NO_3)_2$ 189,66 67,83 X 67,83	189,66
2.	$Ca(H_2PO_4)_2 + CuSO_4 = Cu(H_2PO_4)_2 + CaSO_4$ 189,66 113,46 X 106,76	196,36
3.	$Ca(H_2PO_4)_2 + CuCI_2 = Cu(H_2PO_4)_2 + CaCI_2$ 189,66 113,04 X 115,39	187,32
4.	$Ca(H_2PO_4)_2 + CuS = Cu(H_2PO_4)_2 + CaS$ 189,66 66,37 X 56,52	199,71
5.	$Ca(H_2PO_4)_2 + CuO = Cu(H_2PO_4)_2 + CaO$ 189,66 42,71 X 39,78	192,59
6.	$Ca(H_2PO_4)_2 + CuFe_2O_4 = Cu(H_2PO_4)_2 + CaFe2O4$ 189,66 141,10 X 145,28	185,48
7.	$Ca(H_2PO_4)_2 + CuMoO_4 = Cu(H_2PO_4)_2 + CaMoO4$ 189,66 141,51 X 122,67	208,50
8.	$Ca(H_2PO_4)_2 + CuWO_4 = Cu(H_2PO_4)_2 + CaWO4$ 189,66 149,89 X 151,14	188,41
9.	$Ca(H_2PO_4)_2 + CuSeO_4 = Cu(H_2PO_4)_2 + CaSeO4$ 189,66 69,50 X 63,22	195,94
10.	$Ca(H_2PO_4)_2 + CuSeO_3 \cdot 2H_2O = Cu(H_2PO_4)_2 + CaSeO_3 \cdot 2H_2O$ 189,66 258,74 X 249,41	199,00
	В среднем	194,31

Similarly, as well as by M.Kh. Carapetyans and Kelly's system of ionic entropy incriminations found standard entropies of copper, zinc, and cobalt phosphates [15-17].

III.CONCLUSIONS

Consequently, we obtained the basic methods for approximate calculations of the standard enthalpy of formation of copper, zinc and cobalt phosphates, as well as the calculation of the entropy of monosubstituted copper orthophosphate. The most suitable calculation methods are identified, as well as methods that allow you to determine the desired values with the least error.

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