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Prediction of the selectivity of dissolution of sparingly soluble borates in mineral acids

The thermodynamic characteristics $\Delta H^0_{f,298}$ $\Delta G^0_{f,298}$ $\Delta S^0_{f,298}$ for 11 borate minerals. From the calculated energy ΔG data to dissolve the boron minerals of various inorganic acids ustanvoleno that the best solvent is sulfuric acid.

Keywords: borates, Gibbs energy, inorganic acids, dissolution, minerals.

Introduction

It is known that the optimal model of any production process can be constructed through the consideration of the thermodynamic and kinetic laws of chemical reactions that are the basis of the process. Empirical search of terms of chemical reactions can not only justify but also optimize the respective processes.

Studies of multicomponent borate systems, the establishment of general and specific patterns in the structure, analysis of the correlation between the structure and chemical composition of the crystals, allow to present possible ways of synthesis of borates, to predict the unknown properties of boron compounds.

Definition of terms of engagement of borates and prediction of their properties is possible on the basis of thermodynamic methods of description of the regularities of the reactions. In the literature [1-5] there are enough data to develop methods for the description of borates decomposition by various reagents, which provides information on the results of the boric raw materials' decomposition via acid, and alkaline reagents.

However, despite the fact that the study of natural processes of borates decomposition by acidic and alkaline reagents has been conducted long time ago and was reflected in a number of monographs of major scientists, we cannot consider the problem solved to date, there remain a number of unresolved issues. Especially, it concerns the Kazakh natural boron raw materials, which are characterized by a complex little studied mineralogical composition and low content of B_2O_3 (10%), making well known traditional and fairly efficient technologies for boron materials non applicable.

In this respect it became necessary to find evidence-based approach to predict the agent for the sequential dissolution of natural borate minerals from Inder field. The most preferred method was to use qualitative and quantitative information based on theoretical evaluation of phased prediction.

Materials and methods

For these purposes, the feasibility of serial processes of dissolution of minerals based on thermodynamic analysis of processes occurring during dissolution was first established. Then it was necessary to analyze the relations of the kinetic quantities of mineral dissolution. Obtained assumptions determined the choice of conditions for selective dissolution of minerals. Data on the thermodynamic characteristics and their

comparison with the kinetic parameters allowed the prediction of previously unknown ways of obtaining borates.
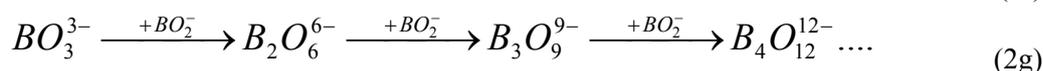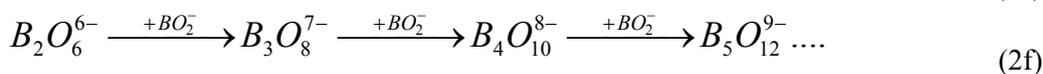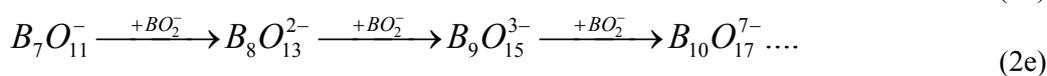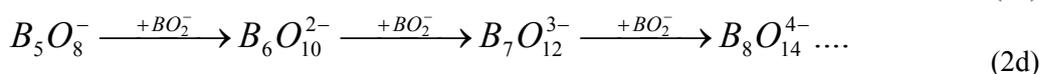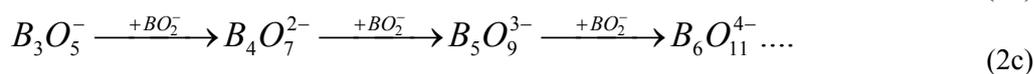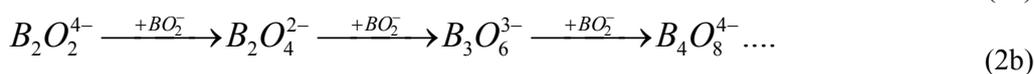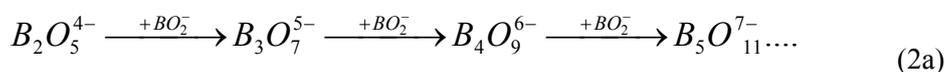
In the literature there are quite reliable data on the standard values of ΔH_f^0, ΔG_f^0 for the reactions of many substances. There are a number of well-developed approaches to perform the thermodynamic analysis of studies of the interaction of mineral – decomposing reagent systems. Theoretical concepts proposed by Professor H. K. Ospanov [6] describe the equilibrium state of similar thermodynamic systems most completely and accurately.

According to the Ospanov's theory it is advisable to use quantities of averaged nuclear Gibbs energy – referred to the number of atoms n, by appropriate simple formula, since the contribution of each of the values is unknown.

$$\Delta \overline{G}_f^0 = \frac{\Delta G_f^0}{n} \quad (1)$$

If we consider that the borates are characterized by increasing number of compounds in the same group of ions, then the proposed method is very useful for the study, namely, boron-containing minerals, containing a number of polymer borates:

$$B_2O_5^{4-} \xrightarrow{+BO_2^-} B_3O_7^{5-} \xrightarrow{+BO_2^-} B_4O_9^{6-} \xrightarrow{+BO_2^-} B_5O_{11}^{7-}.... \quad (2a)$$

$$B_2O_2^{4-} \xrightarrow{+BO_2^-} B_2O_4^{2-} \xrightarrow{+BO_2^-} B_3O_6^{3-} \xrightarrow{+BO_2^-} B_4O_8^{4-}.... \quad (2b)$$

$$B_3O_5^{-} \xrightarrow{+BO_2^-} B_4O_7^{2-} \xrightarrow{+BO_2^-} B_5O_9^{3-} \xrightarrow{+BO_2^-} B_6O_{11}^{4-}.... \quad (2c)$$

$$B_5O_8^{-} \xrightarrow{+BO_2^-} B_6O_{10}^{2-} \xrightarrow{+BO_2^-} B_7O_{12}^{3-} \xrightarrow{+BO_2^-} B_8O_{14}^{4-}.... \quad (2d)$$

$$B_7O_{11}^{-} \xrightarrow{+BO_2^-} B_8O_{13}^{2-} \xrightarrow{+BO_2^-} B_9O_{15}^{3-} \xrightarrow{+BO_2^-} B_{10}O_{17}^{7-}.... \quad (2e)$$

$$B_2O_6^{6-} \xrightarrow{+BO_2^-} B_3O_8^{7-} \xrightarrow{+BO_2^-} B_4O_{10}^{8-} \xrightarrow{+BO_2^-} B_5O_{12}^{9-}.... \quad (2f)$$

$$BO_3^{3-} \xrightarrow{+BO_2^-} B_2O_6^{6-} \xrightarrow{+BO_2^-} B_3O_9^{9-} \xrightarrow{+BO_2^-} B_4O_{12}^{12-}.... \quad (2g)$$

It is known that the comparison of values $\Delta H_{f,298}^0$ $\Delta G_{f,298}^0$ j for a number of similar substances can get some information on their relative reactivity, under the same stoichiometry.

Results and discussion

Table 1 shows thermodynamic parameters $\Delta H_{f,298}^0$ $\Delta G_{f,298}^0$ $\Delta S_{f,298}^0$ calculated for 11 borate minerals. These minerals are part of the borate deposits of Inder.

The data presented show that asharite, preobrazhenskite, and pandermite have the largest negative value of $\Delta \overline{G}_f^0$ among the studied borate. Therefore, it should be noted that the interaction of asharite with reagents must expend more energy, at least much more than other borates in the series given, for the transfer of boron from solid minerals in solution.

Therefore, the line of the reactivity of natural borates (from greatest to smallest) can be made based on analysis of the values of averaged nuclear Gibbs energy $\Delta G_{f,298}^0$:

inderite > inyoite > inderborite > ulexite > kaliborite > hydroboracite > pinnoit > colemanite > pandermite > preobrazhenskite > ascharite

In the next series of experiments in order to select the optimal reagent for the extraction of boron from borate solids studied values of ΔG were calculated for the reactions of dissolution of borates analyzed in various inorganic acids (H_3PO_4, H_2SO_4, HNO_3, HCl).

Given that the process of decomposition of the mineral boron, or group of minerals takes place under nonequilibrium conditions and for a sufficiently large excess of acid, well-known thermodynamic equation can be used for the calculation of $\Delta G^0_{x.p.}$:

$$\Delta G^0_{x.p.} = \sum \Delta G^0_{f(прод)} - \sum \Delta G^0_{f(реаг)} \qquad (3)$$

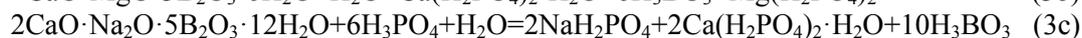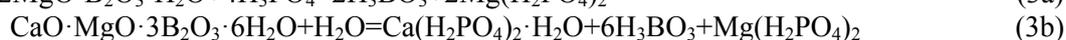where $\Delta G^0_{x.p.}$ - standard Gibbs' energy of chemical reaction.

All calculations were performed on 1 mole of the solvent, i.e., for the corresponding acids.

Table 1 – Thermodynamic characteristics of natural borates

Compound (mineral)		$-\Delta H^0_{f\,298}$ kJ / mol	$-\Delta S^0_{f\,298}$ kJ / mol	$-\Delta G^0_{f\,298}$ kJ / mol	$-\overline{\Delta G}^0_{f\,298}$ kJ / mol at
Inderite	$Mg_2[B_6O_{11}]\cdot 15H_2O$	9605,64	784,54	9019,86	140,93
Inyoite	$Ca_2[B_6O_{11}]\cdot 13H_2O$	9184,14	480,36	9647,35	149,09
Inderborite	$MgCa[B_6O_{11}]\cdot 11H_2O$	8513,34	645,30	8005,84	153,95
Ulexite	$NaCa[B_5O_9]\cdot 8H_2O$	6680,03	522,65	6292,36	157,30
Kaliborite	$KMg[B_{11}O_{19}]\cdot 9H_2O$	11000,5	754,04	10359,36	175,58
Hydroboracite	$Mg\quad Ca[B_6O_{11}]\cdot 6H_2O$	7059,09	448,62	6626,24	179,08
Pinnoit	$Mg_2[B_6O_{11}]\cdot 15H_2O$	3458,44	227,79	3245,07	180,28
Colemanite	$Mg_2[B_2O_5]\cdot 3H_2O$	6511,30	587,40	5966,94	175,49
Pandermite	$Ca_2[B_6O_{11}]\cdot 5H_2O$	5740,06	468,81	5186,52	192,178
Preobrazhenskite	$Mg_3[B_5O_9]_2\cdot 4H_2O$	6108,95	263,93	9031,28	210,03
Ascharite	$Mg_2[B_2O_5]\cdot H_2O$	2874,74	149,13	2693,23	224,43

Let us consider in more detail the analysis of the calculated thermodynamic quantities given in Table 2, which gives estimates of Gibbs energy of dissolution of the studied minerals in mineral acids.

The expected equations of reactions were analyzed beforehand during decomposition of studied boron minerals by inorganic acids. Obviously, with the use of phosphoric acid for the decomposition of boron minerals following reactions should be expected:

$$2MgO\cdot B_2O_3\cdot H_2O+4H_3PO_4=2H_3BO_3+2Mg(H_2PO_4)_2 \qquad (3a)$$
$$CaO\cdot MgO\cdot 3B_2O_3\cdot 6H_2O+H_2O=Ca(H_2PO_4)_2\cdot H_2O+6H_3BO_3+Mg(H_2PO_4)_2 \qquad (3b)$$
$$2CaO\cdot Na_2O\cdot 5B_2O_3\cdot 12H_2O+6H_3PO_4+H_2O=2NaH_2PO_4+2Ca(H_2PO_4)_2\cdot H_2O+10H_3BO_3 \qquad (3c)$$

As we can see from the equations of reactions dihydrogen phosphate of calcium, magnesium and other salts along with boric acid are transferred into solution.

Then, using the same method as in the calculation of values of ΔG for the mineral, values of ΔG kJ/mol are calculated for stoichiometric reaction. Further, these data are referred to 1 mole of acid being analyzed.

We can observe a regular decrease in the values of Gibbs energy, depending on the nature of the acid, from Table 2 in the series of boron minerals studied. For example, when using phosphoric acid the value of – ΔG kJ/mol decreases regularly from ulexite (328.9) to inyoite

and colemanite (260.4 and 260.2), followed by inderborite and hydroboracite (193.9), followed by the (177.2) and ascharite (176.5). In the studied series inderite (127.4) and pinnoite (126.5) have the lowest values of energy.

Similar estimates are given for the dissolution of the same minerals in sulfuric acid (Table 2). Comparing the data obtained, we note that the ΔG value of mineral ulexite is 325.1 kJ/mol, this value is the highest in the tested range of boron minerals. Then inyoite and pandermite are next according to the ΔG values (ΔG value = 268.4). Following minerals Inderborite, Hydroboracite also have almost identical values of the Gibbs energy of (210.2); and for the next 4

minerals (preobrazhenskite, Inderborite,pinnoite, and asharite) corresponding values of the Gibbs

energy of 152.9, 151.9, 151.3, 151.3 i.e., are almost the same.

Table 2 – Gibbs energy of dissolution of boron minerals in mineral acids, phosphoric, sulfuric, hydrochloric and nitric

Compound (mineral)		$-\Delta G^0_{f\,298}$ kJ / mol·at	$-\Delta G^0_{f\,298}$ kJ / mol·at			
			1 mole H_3PO_4	1 mole H_2SO_4	1 mole HCl	1 mole HNO_3
Inderite	$2MgO\cdot 3B_2O_3\cdot 15H_2O$	138,3	127,41	151,78	36,78	49,53
Inyoite	$2CaO\cdot 3B_2O_3\cdot 13H_2O$	144,27	260,45	268,43	96,70	109,18
Ulexite	$Na_2O\cdot 2CaO\cdot 5B_2O_3\cdot 16H_2O$	149,46	328,99	225,13	137,27	103,10
Inderborite	$MgO\cdot CaO\cdot 5B_2O_3\cdot 11H_2O$	149,65	193,95	325,13	66,75	79,36
Hydroboracite	$MgO\cdot CaO\cdot 3B_2O_3\cdot 6H_2O$	173,03	193,93	210,22	66,74	79,35
Pinnoit	$2MgO\cdot B_2O_3\cdot 3H_2O$	175,42	126,50	210,20	36,48	49,23
Colemanite	$2CaO\cdot 3B_2O_3\cdot 5H_2O$	181,18	260,45	151,37	96,70	129,18
Pandermite	$4CaO\cdot 5B_2O_3\cdot 7H_2O$	190,77	260,23	268,43	72,30	109,11
Preobrazhenskite	$3MgO\cdot 5B_2O_3\cdot 4H_2O$	203,90	177,55	152,07	36,83	49,58
Ascharite	$2MgO\cdot B_2O_3\cdot H_2O$	217,14	176,50	151,37	36,48	49,23

In contrast to previous data (for phosphoric and sulfuric acids) in the study of the values of the Gibbs energy for hydrochloric acid negative values of Gibbs energy are almost 1.5-2 times less in magnitude (Table 2). This certifies, that the process of dissolving of minerals investigated in phosphoric and sulfuric acids, especially sulfuric acid, should proceed much more easily than in hydrochloric acid.

Thus, for ulexite ΔG value = 137.27, and the Inyoite and colemanite have the same value of the Gibbs energy which is equal to 96.7 and for pandermite it corresponds to 72.3 kJ/mol, these two minerals Inderborite and hydroboracite also have the same ΔG value = 66.7.

The next four minerals Preobrazhenskite, Inderite, pinnoite, asharite have the lowest ΔG values (36.8-36.4). Consequently, the last four minerals dissolve with great difficulty in hydrochloric acid, better and faster in sulfuric and phosphoric acids. In sulfuric acid negative ΔG values, as indicated, are 152.9, 151.9, 151.3, which is almost 3 times higher.

Comparing and analyzing data on the dissolution of minerals studied in nitric acid a regular decrease can be noted in the values of the Gibbs energy in the considered series of borates. Thus, the Gibbs energy for 4 minerals (Inyoite, colemanite, pandermite, ulexite) are almost identical and correspond to 109.1-103.1. These

values are by its absolute value almost 2.5-3 times less than appropriate values of the dissolution of these minerals in sulfuric acid.

The following minerals Inderborite and hydroboracite also have the same ΔG value = 79.3. The ΔG values of 49.5 – 49.2 correspond to the subsequent four minerals.

Thus, comparing the estimates obtained by the energy of dissolution in various inorganic acids, it may be noted that the best solvent studied in a number of acid is sulfuric acid.

In our view, using the calculated values of thermodynamic data for Gibbs energies of eleven selected borate minerals, which is most often found amongst Inder borates, a principal feasibility of gradual process of dissolution in inorganic acids can be established, which by their reactivity with respect to the studied borates can be arranged in the following order:

$$H_2SO_4 > H_3PO_4 > HNO_3 > HCl \qquad (4)$$
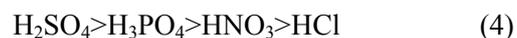
It should be noted that comparing the values of averaged nuclear Gibbs energies for the individual minerals and their expected reactivity of the decomposition of the same acid, complete coincidence is not observed in all systems studied. The observed deviations range of reactivity of borate minerals with an estimated number of mineral dissolution in inorganic acids may be associated with a number of objective reasons.

First, as already noted, Inderborates is characterized by considerable complexity of the mineralogical composition. In addition, the Inder borates contain significant amounts of impurities. In the method of acid digestion employed by us, the calculation takes into account only borate part and does not include approximate components, which leads to mismatch of the compiled series.

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