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CHEMICAL COMPOSITION-BASICITY-THERMODYNAMIC PROPERTIES CORRELATIONS ON THE FORMATION OF MO-SiO_2 COMPOUNDS

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Oxide systems are characterized by acid-base reactions between the reagents (oxides) leading to oxide compounds (reaction products). For the MO-SiO_2 (M = Be, Mg, Ca) oxide system relationships are established in the paper for calculating two "specific" thermodynamic properties, related to the number of moles in the system, that are well correlated with the basicity of the reactants. To validate the results obtained, literature data was used.

Keywords: MO-SiO_2 oxide compounds, basicity, thermodynamic properties.

1. Introduction

The alkaline earth silicate systems are of practical interest for various industrial fields. Thus, the BeO-SiO_2 system is the starting point for obtaining materials used in high-temperature nuclear industry, aerospace, construction of supersonic aircraft and missiles, as well as in glass industry for the manufacture of electric and electronic products.

In the MgO-SiO_2 system, the enstatite (MgO-SiO_2) has electrotechnical applications, being used in ceramic insulators. In the same time, magnesium orthosilicate (2MgO-SiO_2) is a major component of metallurgical slags. Also, the compositions rich in MgO or 2MgO-SiO_2 represent magnesia and forsterite refractories, respectively.

The CaO-SiO_2 system is of interest in the production of Portland cement clinker. At the same time, by changing the ratio of the different oxide compounds an adjustment of various properties of the cement is attained. Also, the acid domain of the CaO-SiO_2 system is of interest in the chemistry and technology of vitreous materials.

The paper points out the important effect of the acid-base character of the oxides on their reactivity and on the stability of the reaction products obtained. Thus, we can correlate several thermodynamic functions (properties), associated with the reaction, with the acid-base character of oxide compounds from the

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reaction environment, measured by the "basicity percentage" indicator, pB, expressed in %. On this basis, we highlight several quantitative relations between heat and free energies of formation and pB. By extension, the calculation relations are established between the enthalpy and free energy of reaction and the system's alkalinity. The established relations allow highlighting of some conditionality between $\Delta^r H$ (the reaction enthalpy) and $\Delta^r G$ (the reaction Gibbs free energy) versus nature, chemical composition and basicity of the reaction products to predict their degree of thermodynamic stability and energetic type of reaction (endo / exothermic).

2. Theoretical basis

The oxide compounds of the MO-SiO_2 systems (M = Be, Mg, Ca) are generally obtained as a result of solid-phase reactions between various oxide reactants. These forming reactions are influenced by a multitude of factors, intrinsic and extrinsic. Among the intrinsic factors are the thermodynamic properties and basicity of the oxides participating in the reaction space. The thermodynamic functions considered are [1]:

- the reaction enthalpy:

$$\Delta^r H_{T,P} = \sum_j p_j \cdot H(P_j) - \sum_i r_i \cdot H(R_i) \qquad (1)$$

where: $H(P_j)$ and $H(R_i)$ are the molar enthalpies of the reaction products, respectively, of the reactants, at constant temperature (T) and pressure (P). If T = 298 K and P = 1 atm the standard reaction enthalpy can be defined, $\Delta^r H^0_{298}$, which is calculated according to the formation enthalpies of the reactants and the reaction products;

- the standard reaction entropy, $\Delta^r S^0_{298}$;
- the standard reaction free energy (Gibbs free energy), $\Delta^r G^0_{298}$:

$$\Delta^r G^0_{298} = \sum_j p_j \cdot \Delta G^0_{298}(P_j) - \sum_i r_i \cdot \Delta G^0_{298}(R_i) \qquad (2)$$

where: ΔG^0_{298} represents the standard free energy of element formation, in kJ/mol, for reactants and reaction products. In the case of $\Delta^r H^0_{298} < 0$ the reaction is exothermic. Otherwise, it becomes endothermic. If $\Delta^r G^0_{298} < 0$, the reaction is possible and occurs spontaneously in the direct sense (causing the free energy decrease). At the same time, the decrease of the standard free reaction energy implies a tendency to convert more reactants into reaction products.

2.1. Assessment of the basicity of oxides

Atoms which receive electrons in a physical or chemical process have a more pregnant basic character and become basic ions. The basic character of an anion is more pronounced as the number of negative charges is greater. In contrast, atoms that lose one or more electrons become acidic ions.

In the case of oxides, the O^{-2} ion is the carrier of the basic property. The chemical interactions between oxides are determined by the exchange of oxygen, which can be of three types: bridged (O^0), unbridged (O^-) and isolated (O^{-2}). Thus, acid-base reactions in the case of oxides represent oxidation-reduction reactions that determine a new distribution of oxygen species relative to the initial one. The reaction can be written in a general form:

$$O_i^{-\delta_i} + O_j^{-\delta_j} \rightarrow 2\,O_m^{-\delta_m} \tag{3}$$

Relationship (3) reflects that the reactions between oxides occur due to the interaction of i and j oxygen ions with different partial charges. Finally, under equilibrium conditions, oxygen ions result with a different mean effective charge, δ_m. The equilibrium values are determined by the electron donor-acceptor power of ions i and j. Consequently, it can be considered that the average basicity depends on the difference in basicity between the types of oxygen ions involved in the reaction.

The concepts of acid or base have undergone many changes over time and are generally applicable only to a class of substances. However, the efforts made highlight the close relationship between the concept of acid-base, unbridged oxygen and ionic activity of oxygen. However, in none of the entities the ionic activity of the bridged and unbridged oxygen can be directly measured and neither of these was considered adequate for estimating the availability of electrons or active oxygen. Duffy and Ingram [2] consider that the basicity of oxide is a measure of the power to donate electrons which depends on the negative charge of the oxygen ions, implicitly on their polarization state. They define the ratio between the electron donor power of oxygen in the oxide environment and the electron donor power of oxygen in a "reference" oxide - CaO - as representing the optical basicity. It can be determined experimentally by spectroscopic methods but can be calculated theoretically for the given oxide system.

Also, a new method of estimating the ionicity of the oxides based on the dielectric theory of the ceramic bodies and the structure of the electronic bands of the crystals has been developed. The concept of ionicity of the chemical bond was used in this approach, without considering it an explicit atomic parameter, like electronegativity. Based on the percentage of the ionic character of the chemical bonds (according to Pauling), Balta et al. have introduced the notion of "basicity percentage", pB, in %, which can be calculated or determined experimentally by spectroscopic methods [3]. In this theory, coordination numbers of cations are the standard ones. However, in many situations, due to structural defects/structural disorder, the coordination number of the cation in an oxide may have distributed values, so it may be represented by a number that is not necessarily natural. For example, for Na_2O-SiO_2 the evaluation of the internuclear distance Na-O by the $^{23}Na_3$Q-MAS NMR method indicates a distribution of values. These results, like molecular dynamics studies, indicate values for the coordination number of Na in the range 4-10, the most likely being values 5, respectively 6 [4]. The oxide basicity scale considers O^{2-} as the end of this scale because it has the highest electron donor power (having the lowest ionization potential between -6.5 and -7.35 eV). For it was assigned the maximum value of pB (pB = 100%).

According to the results presented in [3], pB strongly correlates with other structural parameters such as the intensity of the electrostatic field of the oxygen cation chemical bond, the internuclear distance M-O, the binding energy, the electronic polarizability of the oxygen ions, the electronegativity defined by Sanderson, respectively Gordy and the optical basicity of Duffy and Ingram.

Concerning pB, the evolution of some properties for several glass systems could be highlighted [5]. At the same time, in the case of crystalline oxide systems the thermodynamic properties, but also several properties of practical interest, showed a close dependence with pB. These include CaO-SiO_2, CaO-Al_2O_3-Fe_2O_3-SiO_2 systems, and others [6]. These results motivated the attempt to correlate different thermodynamic properties associated with the formation of the oxide compounds in the MO-SiO_2 system with their basicity, evaluated by pB.

Highlighting a possible correlation between the standard free reaction energy and the basicity of the reactants can be used to quantitatively evaluate the reaction constants of a variety of crystalline or glass oxide systems, regardless of their chemical composition. According to the definition (2), as the standard Gibbs free energy of crystalline oxides is dependent on their basicity, it is expected that the Gibbs free reaction energy ($-\Delta^{r}G^{0}_{298}$) will be dependent on this parameter, too.

One of the first attempts to correlate the heat of formation, Q, of a simple chemical system with the ionicity of the chemical bonds formed between atoms A and B can be attributed to Pauling [7]. Thus, he assumes for the ionicity of I_{AB} the known relation:

$$I_{AB} = 100\left(1 - e^{-\frac{(x_A - x_B)^2}{4}}\right) \quad [\%] \qquad (4)$$

wherein x represents atomic electronegativity.

At the same time, the heat of formation, Q, for a molecular system can be calculated by the formula:

$$Q = 96{,}3\sum_{A,B}(x_A - x_B)^2 \quad \text{[kJ/mol]} \tag{5}$$

By eliminating $(x_A - x_B)^2$ between the relations (4) and (5) results in a relation between the enthalpy of formation and the ionicity of the chemical bonds of the molecular system analyzed:

$$Q = 375{,}2\sum_{A,B} ln\frac{100}{100 - I_{AB}} \quad \text{[kJ/mol]} \tag{6}$$

Relationship (6) reveals that for any chemical system, the enthalpy of formation (and, implicitly, the Gibbs free energy of formation) represents extensive properties relative to the number of atoms (or moles) components. Besides, the relation (6) is strictly valid for systems in which simple chemical bonds are established between atoms (which is not the case for oxide compounds). Therefore, while analyzing the correlation between the thermodynamic properties and the basicity percentage, the following remarks can be made:

- the basicity percentage, pB, represents an intensive property of an oxide system
- the formation enthalpy, $-\Delta H^0_{298}$, and the free reaction energy, $-\Delta G^0_{298}$, represent extensive properties associated with an oxide compound, depending on the number of moles of constituents of the compound.

3. Results and discussions

In this context, the presented thermodynamic properties must be intensive, as well. Thus, for two X and Y oxides forming the X_aY_b compound, we can define two "specific" thermodynamic properties can be defined: the specific enthalpy of formation, $-\Delta H^0_{298}/N$, and the specific free energy of formation, $-\Delta G^0_{298}/N$, where N = a + b, a and b being the number of moles of MO and of moles of SiO_2, respectively, for a reaction product $aMO{\cdot}bSiO_2$. The defined thermodynamic properties have shown their usefulness in highlighting strong correlations with pB for a series of M_2O-SiO_2 (M = Li, Na, K, Rb, Cs) glass oxide systems [8].

Similarly, the literature data establishes the relationships between the enthalpy of formation related to the number of oxygen atoms in the compound and the optical basicity for several oxide compounds in silicate systems [9-11]. By extension, in the analyzed oxide systems a direct quantitative correlation between the free enthalpy of formation, $-\Delta^f H^0_{298}$, or the free energy of formation, $-\Delta^f G^0_{298}$, and the basicity of the reaction products is expected. However, Table

1, where $\Delta^f H^0_{298}$ and $\Delta^f G^0_{298}$ were taken from literature data [12] and pB was calculated according to [3], shows that:

- the basicity of the formed oxide compounds varies monotonically with the oxide composition between a minimum value, corresponding to SiO_2, and a maximum value, associated with the MO oxide.
- within the same system, the thermodynamic properties vary monotonically with both the oxide composition and the basicity percentage, pB, the distribution of –ΔH or –ΔG values with pB being made on unimodal or bimodal curves, which makes quite difficult an attempt to find well-founded and general explanations for this behavior.

Table 1

Standard enthalpy/free energy of formation (taken from [12]) and calculated basicity of reactant oxides and reaction products

System	Oxides/ oxide compounds	$-\Delta^f H^0_{298}$ kJ/mol	$-\Delta^f G^0_{298}$ kJ/mol	pB %
$BeO-SiO_2$	BeO	598.9	569.8	70.6
	$2BeO\cdot SiO_2$	2159.3	2044	59.0
	$BeO\cdot SiO_2$	1540	1452.8	55.6
	SiO_2	910.7	857.1	49.4
$MgO-SiO_2$	MgO	601.8	569.6	81.5
	$2MgO\cdot SiO_2$	2178.3	2072.2	67.8
	$MgO\cdot SiO_2$	1549.4	1462.6	62.3
	SiO_2	910.7	857.1	49.4
$CaO-SiO_2$	CaO	631.9	602.6	83.8
	$3CaO\cdot SiO_2$	2931.3	2785	74.7
	$2CaO\cdot SiO_2$	2313	2190	71.8
	$3CaO\cdot 2SiO_2$	3928.5	3728	69.5
	$CaO\cdot SiO_2$	1636.1	1550.3	66.0
	SiO_2	910.7	857.1	49.4

Our explanation for this behavior is that $\Delta^f H^0_{298}$ and $\Delta^f G^0_{298}$ appear as extensive properties for a given oxide system. In the same time, the basicity percentage represents an intensive property, which does not depend on the volume (size) of the system. By considering the number of moles in the system, we can correlate the basicity percentage with the thermodynamic properties of the system.

Fig. 1 and Fig. 2 show graphically the dependencies for $-\Delta^f H^0_{298}/N$, $-\Delta^f G^0_{298}/N$, respectively, and the basicity percentage, pB, for the three MO-SiO$_2$ oxide systems analyzed.

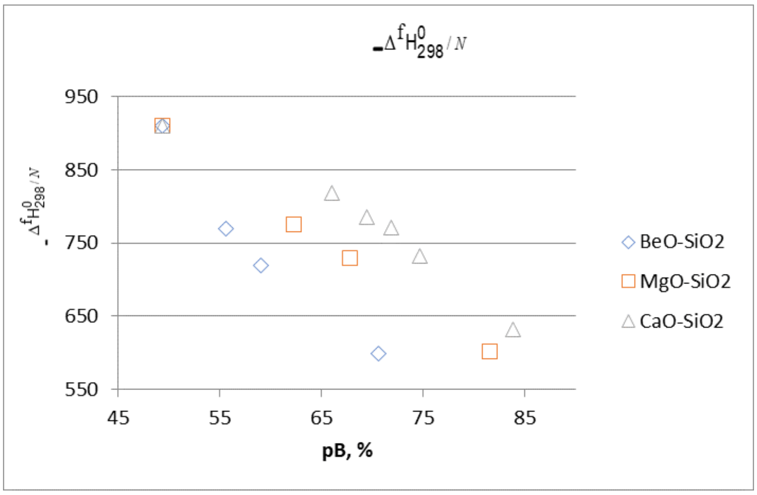

Fig. 1. Dependence $-\Delta^f H^0_{298}/N$ on the basicity percentage, pB for the oxide systems studied

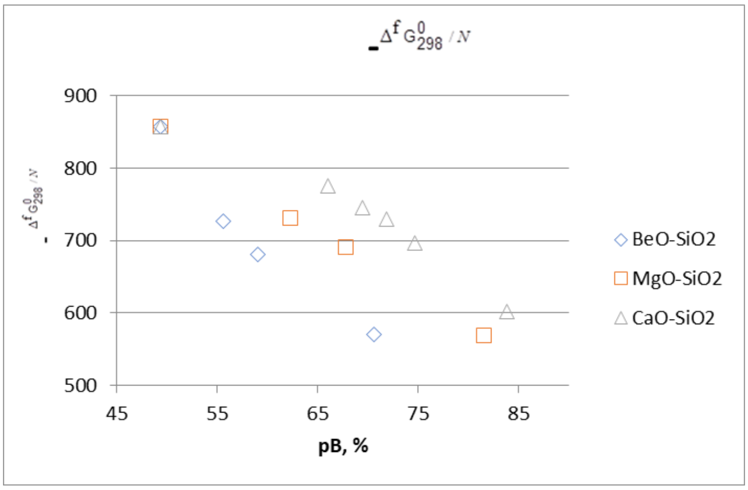

Fig. 2. Dependence $-\Delta^f G^0_{298}/N$ on the basicity percentage, pB for the oxide systems studied

Considering the graphical representations as being described by parabolic relations of form Y = $a_0X^2+a_1X+a_2$ (where Y = $-\Delta^f H^0_{298}/N$ or $-\Delta^f G^0_{298}/N$; X = pB), Table 2 presents the established values of the coefficients a_0, a_1 and a_2, as well as the values of the correlation coefficients R^2 and the dispersion X^2 for the three oxide systems studied.

Table 2

Analysis of statistical correlations for dependency relations $Y = a_0X^2+a_1X+a_2$

Oxide system	BeO-SiO_2		MgO-SiO_2		CaO-SiO_2	
Statistic values	$-\Delta^f H^0_{298}/N$	$-\Delta^f G^0_{298}/N$	$-\Delta^f H^0_{298}/N$	$-\Delta^f G^0_{298}/N$	$-\Delta^f H^0_{298}/N$	$-\Delta^f G^0_{298}/N$
a_0	0.4763	-0.4423	0.0317	0.0234	-0.1407	-0.1344
a_1	-71.794	-66.547	-13.731	-11.97	10.595	10.476
a_2	3293.8	3064	1511	1390.6	730.81	667.98
R_2	0.999	0.999	0.999	0.999	0.998	0.999
X^2	11.14	18.15	22.13	17.35	20.17	24.12

Considering the graphical representations presented in Fig. 1 and Fig. 2, as well as the results in Table 1, we can conclude that between the specific thermodynamic properties and the basicity percentage of the resulted compounds there is a close correlation.

The good quantitative correlation between the properties of interest is also confirmed by the graphical representations in Fig. 3 and Fig. 4, which show the standard values of the analyzed (experimentally, taken from [12]) thermodynamic functions and those calculated with the established relationships. The relative deviations between the reference [12] and the calculated values are presented in table 3.

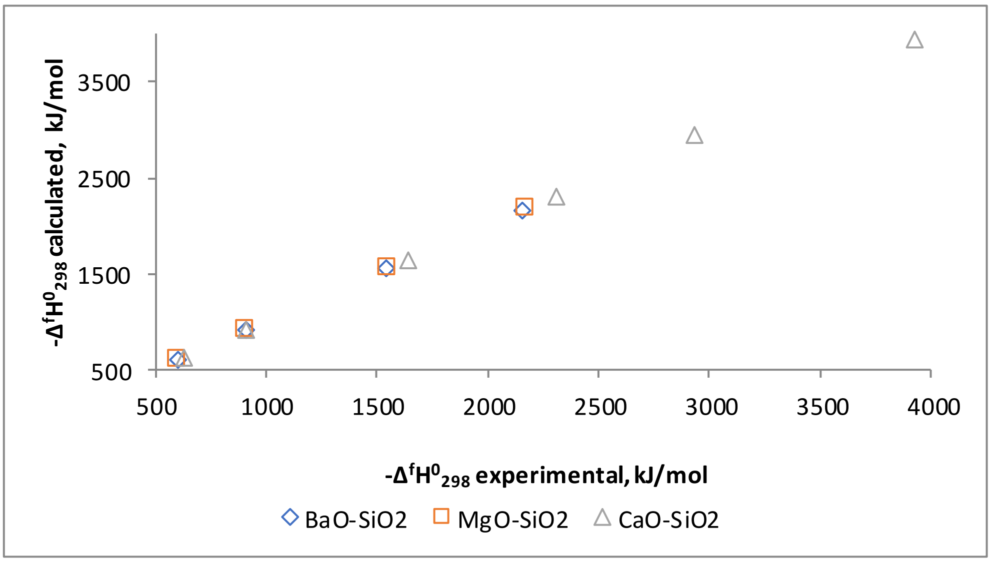

Fig. 3. Dependence between calculated and experimental values for $-\Delta^f H^0_{298}$

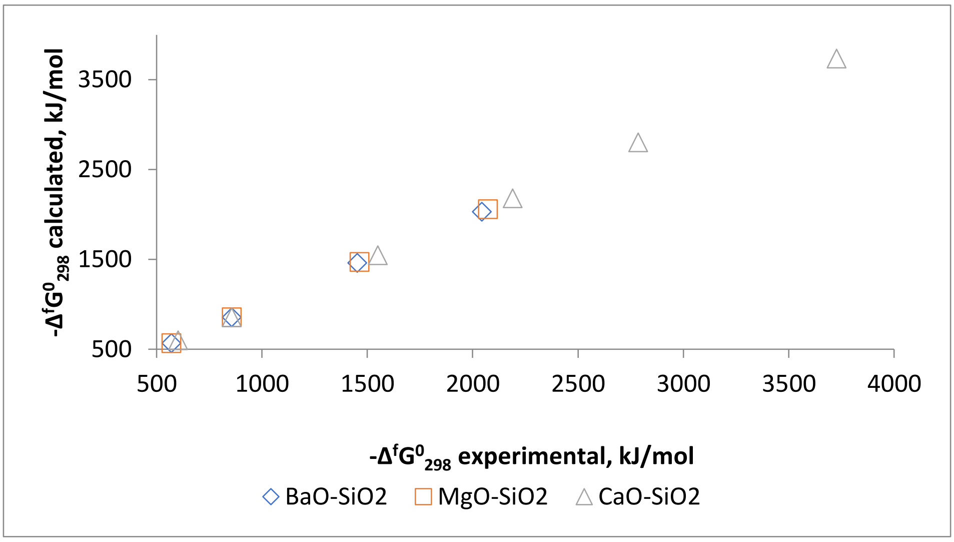

Fig. 4. Dependence between calculated and experimental values for $-\Delta^fG^0_{298}$

Table 3

Calculated and experimental (taken from [12]) values of $-\Delta^fH^0_{298}$ and $-\Delta^fG^0_{298}$

System	Oxides / oxide compounds $xMO\cdot ySiO_2$	$-\Delta^fH^0_{298}$ kJ/mol		Relative deviation, ε_r, %	$-\Delta^fG^0_{298}$ kJ/mol		Relative deviation, ε_r, %
		Exp.	Calc.		Exp.	Calc.	
$BeO-SiO_2$	BeO	598.9	599.5	0.10	569.8	570.4	-0.10
	$2BeO\cdot SiO_2$	2159.3	2147.9	-0.53	2044	2032.2	0.58
	$BeO\cdot SiO_2$	1540.0	1548.9	0.58	1452.8	1462.6	-0.67
	SiO_2	910.7	909.7	-0.11	857.1	855.9	0.13
$MgO-SiO_2$	MgO	601.8	602.6	0.13	569.6	567.8	0.31
	$2MgO\cdot SiO_2$	2178.3	2177.5	-0.04	2072.2	2059.8	0.60
	$MgO\cdot SiO_2$	1549.4	1557.3	0.51	1462.6	1472.4	-0.60
	SiO_2	910.7	910.1	-0.07	857.1	856.4	-0.08
$CaO-SiO_2$	CaO	631.9	630.6	-0.20	602.6	602.1	-0.09
	$3CaO\cdot SiO_2$	2931.3	2945.1	0.59	2785	2802.3	-0.62
	$2CaO\cdot SiO_2$	2313	2298.5	-0.62	2190	2181.9	0.37
	$3CaO\cdot 2SiO_2$	3928.5	3937.7	0.27	3728	3734.4	-0.17
	$CaO\cdot SiO_2$	1636.1	1634.4	-0.11	1550.3	1547.9	0.15
	SiO_2	910.7	910.8	0.02	857.1	857.5	0.04

All these confirm the possibility to predict the formation tendency and the stability of oxide compounds, as well as the type of reaction in which various starting oxides participate, taking into account their basicity.

Furthermore, considering that two oxides MO and SiO_2 react to form an $aMO\cdot bSiO_2$ compound, according to the reaction:

$$aMO + bSiO_2 \rightarrow aMO\cdot bSiO_2 \qquad (7)$$

for Gibbs free energy of reaction, $\Delta^r G^0_{298}$, considering the equation (7), one can write:

$$\Delta^r G^0_{298} = \Delta G^0_{298}(xMO\cdot ySiO_2) - x\Delta G^0_{298}(MO) - y\Delta G^0_{298}(SiO_2) \qquad (8)$$

Taking into account the data presented in table 1, the equation (8) can be rewritten as:

$$\Delta^r G^0_{298} = (x + y)F[pB(xMO\cdot ySiO_2)] - xF[pB(MO)] - yF[pB(SiO_2)] \qquad (9)$$

In equation (9) it was considered that

$$\frac{\Delta G^0_{298}(X)}{x+y} = F[pB(X)] \qquad (10)$$

Beyond the self-interest, the relationship (9) is also useful in assessing to what extent the relationship (7) is more likely, and the reaction product more stable, relative to the basicity of the participating oxides. To increase the stability of the obtained oxide compound, the condition $\Delta^r G^0_{298} < 0$ must be met:

$$(x + y)\cdot F[pB(xMO\cdot ySiO_2)] < x\cdot F[pB(MO)] + y\cdot F[pB(SiO_2)] \qquad (11)$$

For example, in the CaO-SiO_2 system the condition given by the equation (11) is written:

$$(x + y)(-0{,}1344pB^2 + 10{,}476pB + 667{,}98) < 83{,}8x + 49{,}4y \qquad (12)$$

In a similar manner to the equation (9) a relation can also be written regarding the free reaction enthalpy, $\Delta^r H^0_{298}$:

$$\Delta^r H^0_{298} = (x + y)E[pB(xMO\cdot ySiO_2)] - xE[pB(MO)] - yE[pB(SiO_2)] \qquad (13)$$

In the relationship (13) were considered functional dependencies of the form:

$$\frac{\Delta G^0_{298}(X)}{x+y} = E[pB(X)] \qquad (14)$$

From the equation (13) correlations can be made between the basicity of the compounds and their chemical composition, indicating the type of reaction. Thus, for a reaction to be exothermic, although $\Delta^r H^0_{298}<0$, in terms of its oxide composition and basicity, the following condition must be fulfilled:

$$(x + y)\cdot E[pB(xMO\cdot ySiO_2)] < x\cdot E[pB(MO)] + y\cdot E[pB(SiO_2)] \quad (15)$$

4. Conclusions

In the article are correlated some thermodynamic properties with basicity of oxide compounds in the binary alkaline earth – silicate system. Considering the formation reactions in the system, the thermodynamic properties and the basicity of the participants play a decisive role.

Between the classical thermodynamic properties $-\Delta^f H^0_{298}$ (free enthalpy) and $-\Delta^f G^0_{298}$ (free energy of formation) and the basicity expressed by the basicity percentage, pB, there is no quantitative correlation that is easy to interpret. At the same time, the standard thermodynamic properties (taken from literature data), related to the number of moles of oxides in an oxide compound, correlate very strongly with the calculated basicity percentage (pB) and quantitative dependencies are described by parabolic statistical functions.

In this context, the enthalpy and the free reaction energy can also be explained according to the basicity of the oxide reaction system.

Equally, the formation and stability of the compounds, the type of the formation reaction are proved to be quantitatively correlated with the basicity of the oxide compounds, expressed by the basicity percentage.

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