Correlations Between Thermodynamic Properties – basicity in the CaO-Al_2O_3 System

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Relations in oxide systems (and not only) reflect acid-base type reactions. For oxides and oxide systems the main problem is the quantitative evaluation of basicity. A possible solution could be offered by the basicity percentage, pB, which is defined in correlation with the structural characteristics of the oxide system at atomic level (coordination number, oxidation number, ionization potential). Therefore, one can imagine a chain of oxide composition- structure – properties implications. In this paper one present data which evidence the correlations between a series of thermodynamic properties and basicity, expressed through the basicity percentage, for oxide compounds in the CaO – Al_2O_3 system.

Keywords: CaO- Al_2O_3 system, basicity, thermodynamic properties: enthalpy, free energy

In oxide systems, both vitreous and crystalline, occur acid-base type neutralization reactions. The formation of oxide compounds which occur in crystalline systems is expected to be determined by the differences in reactants basicity. Moreover, the basicity of system determines the structural characteristics of the products, as well as their properties. For vitreous oxide materials, a series of correlations between the physical-chemical properties and basicity were demonstrated [1-4]. Therefore, it is expected that also the thermodynamic properties (defined for compounds through chemical reactions between oxides) would be influenced by the reactants and products basicity.

This correlation was evidenced for a series of oxide systems that present interest in the domain of vitreous and crystalline oxide materials [5-7]. Also, the authors revealed correlations between thermodynamic properties- basicity and hydraulic properties – basicity in the quaternary system CaO – Al_2O_3 – Fe_2O_3 – SiO_2, especially important for Portland cement [8].

Our researches focus on the determination of quantitative relations between some thermodynamic properties and the basicity of some oxide compounds in the CaO – Al_2O_3 system.

Theoretical approach

Oxide system CaO – Al_2O_3 (C – A)

The practical interest for oxide materials in the CaO – Al_2O_3 system is reflected in its phase diagram presented in figure 1 [9]. The CaO – Al_2O_3 system is divided in 6 binary subsystems. The $3CaO.Al_2O_3$ – $12CaO.7Al_2O_3$ (C_3A – $C_{12}A_7$) and $C_{12}A_7$ – CA systems have the lowest eutectics, around 1400°C.

The CaO – Al_2O_3 system is interesting in obtaining vitreous materials. The composition domain important for obtaining calcium aluminate glasses is placed between 25% mol and 50% mol Al_2O_3, corresponding to C_3A and CA compositions [10]. In these glasses, Al_2O_3 acts as network former, being present as [AlO_4].

In the CaO – Al_2O_3 system, five compounds are known [9,11]: tricalcium aluminate ($3CaO{\cdot}Al_2O_3$ – C_3A), dodecacalcium hepta-aluminate ($12CaO{\cdot}7Al_2O_3$ – $C_{12}A_7$), monocalcium aluminate ($CaO{\cdot}Al_2O_3$ – CA), monocalcium dialuminate($CaO{\cdot}2Al_2O_3$ – CA_2) and monocalcium hexa-aluminate ($CaO{\cdot}6Al_2O_3$ – CA_6). These compounds have relatively high melting temperatures, between 1425°C ($C_{12}A_7$) and 1764°C (CA_2) [9].

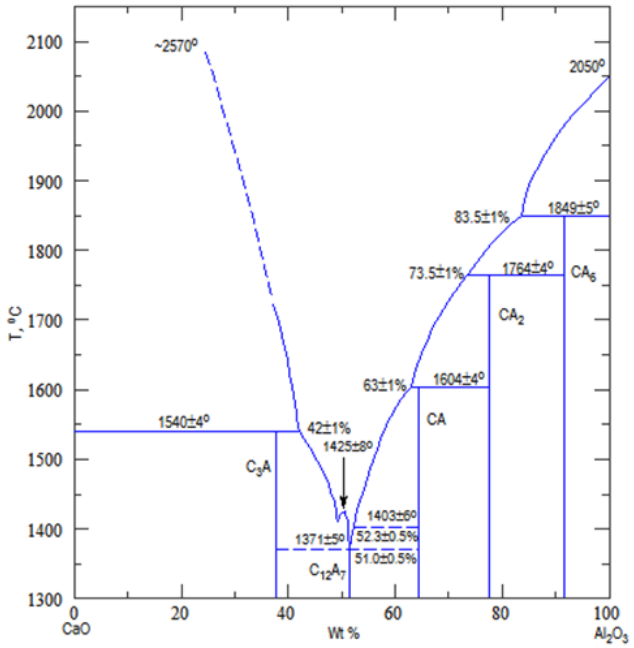

Fig. 1. Phase diagram for the system CaO – Al_2O_3 [9]

Mao and co-workers have calculated the binary phase diagram CaO- Al_2O_3 using the ionic two-sublattice model [12]. Among the previous studies concerning this subject, two major differences can be found: one group of researchers report $Ca_{12}Al_{14}O_{33}$ (the mineral mayenite) as a stable phase, whereas others consider this compound an oxy-hydroxide phase with the formula $Ca_{12}Al_{14}O_{33}(OH)_2$.

Two of the subsystems presented in figure 1, in which C_3A and $C_{12}A_7$ compounds are placed, are of particular interest in the Portland cement chemistry [11].

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At the same time, the compounds in the $C_{12}A_7$ – CA subsystem are found among the constituents of aluminate cements, to whom they ensure very good hydraulic hardening properties [9].

Finally, the CA, CA_2 and CA_6 compounds, which have high melting temperatures, represent the basis for obtaining refractory cements.

The forming reactions in the CaO- Al_2O_3 system occur between a basic component – CaO – and an acid one Al_2O_3 – (generally Al_2O_3 is considered as amphoteric, but when reported to CaO, which is strongly basic, Al_2O_3 can be seen as an acidic reactant).

Thermodynamic properties of the oxide compounds

A chemical reaction is generally carried out according to the scheme:

$$r_1R_1 + r_2R_2 + \ldots + r_iR_i + \ldots \leftrightarrow$$
$$\leftrightarrow p_1P_1 + p_2P_2 + \ldots + p_jP_j + \ldots \quad (1)$$

where R_1, R_2... R_i are the reactants; P_1, P_2... P_j are the products; r_1, r_2... r_i are the stoichiometric coefficients of the reactants; p_1, p_2... p_j are the stoichiometric coefficients of the products.

A series of thermodynamic functions [13] can be associated to reaction (1), as follows:

- the enthalpy of reaction, $\Delta^rH_{T,P}$:

$$\Delta^rH_{T,P} = \sum_j p_j \cdot H(P_j) - \sum_i r_i \cdot H(R_i) \quad (2)$$

where: $H(P_j)$ is the molar enthalpy of the product *j*, in kJ/mol; $H(R_j)$ – molar enthalpy of the reactant *i*, in kJ/mol; temperature T and pressure P, state parameters. In standard conditions (T = 298 K and P = 1 atm.) the standard enthalpy of reaction, $\Delta^rH^0_{298}$ is calculated depending on the standard enthalpies of reactants and products formation, $\Delta H^0_{298}(R_i)$, respectively, $\Delta H^0_{298}(P_j)$, in kJ/mol:

- the standard entropy of reaction, $\Delta^rS^0_{298}$, can be calculated considering the standard entropy of reactants and products formation, $S^0_{298}(R_i)$, respectively, $S^0_{298}(P_j)$, in kJ/mol:

$$\Delta^rS^0_{298} = \sum_j p_j \cdot S^0_{298}(P_j) - \sum_i r_i \cdot S^0_{298}(R_i) \quad (3)$$

The entropy is used to calculate the free energy of reaction; it also offers information regarding the direction of the reaction evolution.

- the standard free energy of reaction (Gibbs free energy), $\Delta^rG^0_{298}$:

$$\Delta^rG^0_{298} = \sum_j p_j \cdot \Delta G^0_{298}(P_j) - \sum_i r_i \cdot \Delta G^0_{298}(R_i) \quad (4)$$

where $DG^0_{298}(P_j)$ is the standard free energy of products formation, in kJ/mol, $\Delta G^0_{298}(R_i)$, – standard free energy of reactants, in kJ/mol.

The exothermal reactions ($\Delta^rH^0_{298} < 0$), accompanied by the increase of entropy ($\Delta^rS^0_{298} > 0$), having $\Delta^rG^0_{298} < 0$, are thermodynamically probable (occur in the direction of product formation) [13,14].

In oxide systems and therefore in CaO- Al_2O_3 system, the chemical reactions are acid-base type, occurring as follows:

$$xCaO + yAl_2O_3 \rightarrow xCaO \cdot yAl_2O_3 \quad (5)$$

in which the stoichiometric coefficients x and y are natural numbers that define the five known calcium aluminates (fig. 1). The number of compounds that can be formed in oxide systems can be estimated considering the basicity of the system [1].

The type and properties of the compounds formed in an oxide system are determined by:

-the structural and physical – chemical characteristics of the starting oxides;

-the processing route and its parameters (temperature, pressure, physical – chemical characteristics of the reaction environment etc);

-the thermodynamical evolution of the process.

All the parameters associated to the reaction system of two or more oxides determine both acid-base characteristics of oxides and products, and the value level of their thermodynamic functions. It is interesting to determine to which extent there is a quantitative correlation between the compounds basicity in the CaO – Al_2O_3 system and its thermodynamic functions.

The main theories and properties concerning the evolution of acid-base character of oxides are presented in [1,2,4,15].

The basicity of oxides can be measured through the basicity percentage, pB. Considering that O^{2-} has the highest ability to donate electrons, it has been attributed to him the highest pB value, pB = 100%.

This structural parameter, pB, characteristic to oxide systems, is calculated with the equation proposed by Baltã and Radu [16,17].

$$\lg pB = 1.9 \cdot (CN)^{0.02} - 0.023 \cdot \frac{P_i}{CN} \quad (6)$$

where CN is the coordination number of the M^{z+} cation in relation with oxygen and P_i – the ionization potential for the considered oxidation number of the cation, z^+.

For complex oxide systems (multicomponent systems) pB is calculated with:

$$pB = \sum_i pB_i \cdot c_i \quad (7)$$

where pB_i is the basicity of oxide i and c_i – the gravimetric fraction of oxide i.

The basicity percentage represents a natural scale for characterizing oxides and oxide systems. Explicitly, pB is defined according to relation (6), in correlation with a series of structural parameters specific to oxides (coordination number cation/oxygen, oxidation number of the cation, ionization potential). Moreover, according to the results published in paper [4], pB correlates strongly with other structural parameters like: the intensity of electrostatic field of the cation-oxygen chemical bond, electronic polarizability of the oxygen ion, electronegativity defined by Sanderson, respectively Gordy, and the optical basicity of Duffy and Ingram [4].

For an important number of oxides, interesting the crystalline and vitreous systems, other structural parameters (inter nuclear distances, binding energies etc) indicate a tight dependency in connection with basicity, evaluated as pB [1,4].

All these arguments prove that pB is an important structural parameter characterising the basic character of oxides (or of oxide compounds).

In connection with pB, was put in evidence the evolution of some properties for a series of oxide vitreous systems [18,19]. At the same time, for some crystalline systems, the thermodynamic properties and other properties of practical interest, showed a strong dependency on pB (silica-alkaline systems, CaO – SiO_2, CaO – Al_2O_3 – Fe_2O_3 – SiO_2) [5, 8, 20 - 22].

These results motivate the attempt to correlate different thermodynamic properties regarding the oxide compounds from the CaO – Al_2O_3 system, to their basicity, evaluated through pB.

Results and discussions

In the CaO- Al_2O_3 system, five crystalline compounds can be put in evidence according to the reactions [11]:

$$3CaO + Al_2O_3 \rightarrow 3CaO \cdot Al_2O_3 \quad (8)$$

$$12CaO + 7Al_2O_3 \rightarrow 12CaO \cdot 7Al_2O_3 \quad (9)$$

$$CaO + Al_2O_3 \rightarrow CaO \cdot Al_2O_3 \quad (10)$$

$$CaO + 2Al_2O_3 \rightarrow CaO \cdot 2Al_2O_3 \quad (11)$$

$$CaO + 6Al_2O_3 \rightarrow CaO \cdot 6Al_2O_3 \quad (12)$$

The first problem is to find a possible dependency between two thermodynamic properties, the standard formation enthalpy, $-\Delta H^0_{298}$, and Gibbs free energy of formation, $-\Delta G^0_{298}$, and the chemical composition of the formed compounds.

In figure 2 is represented the standard formation enthalpy, $-\Delta H^0_{298}$, of oxides and oxide compounds in CaO – Al_2O_3 system, in connection with their chemical composition given in gravimetric percentage.

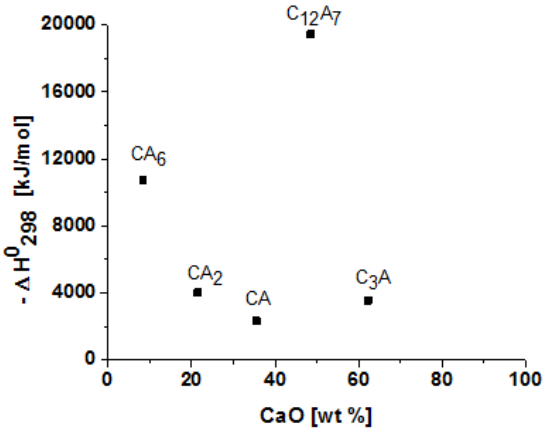

Fig. 2. Variation of standard formation enthalpy with wt. % CaO, in the CaO – Al_2O_3 system

Similarly, in figure 3 is presented the variation of standard free Gibbs energy of formation, $-\Delta G^0_{298}$, as a function of wt % CaO, in the CaO – Al_2O_3 system.

Although the chemical composition of the compounds is expected to present an important influence on their properties, the graphics from figures 2 and 3 seem to dismiss this hypothesis. The functional dependencies were revealed to be strongly non-monotonous and relatively complex, making the result interpretation difficult.

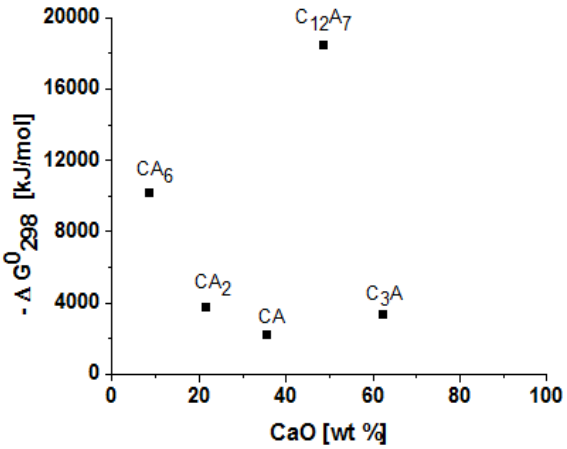

Fig.3. Variation of standard free Gibbs energy of formation, $-\Delta G^0_{298}$, with wt. % CaO, in the CaO – Al_2O_3 system

According to table 1, in the CaO – Al_2O_3 system are obtained compounds whose chemical compositions cover large value intervals. At the same time, the basicity percentage for these compounds is placed in a relatively small variation interval (72 ÷ 80%).

At the next level of investigation, we tried to highlight the influence of basicity on the thermodynamic properties of oxide compounds, as reaction products.

Unfortunately, no extra relevant information could be gained from the graphic representations of the functional dependencies like $-\Delta H^0_{298} = f(pB)$ and $-\Delta G^0_{298} = f(pB)$ (figs. 4 and 5). The basicity percentage, pB, was calculated with relations (6) and (7), and the thermodynamic data were taken from [13,14,23].

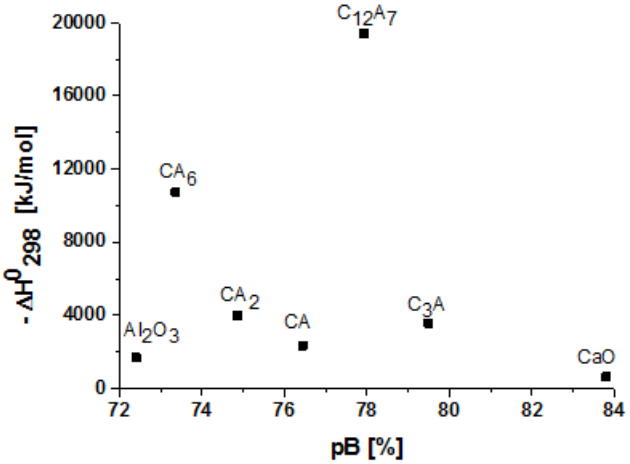

Fig. 4. Variation of standard formation enthalpy with pB in the CaO – Al_2O_3 system

Oxide Compound	Oxide Composition [wt. %]		Oxide Composition [mol. %]		pB [%]
	CaO	Al_2O_3	CaO	Al_2O_3	
Al_2O_3	0	100	0	100	72.40
C_3A	62.22	37.78	75	25	79.49
$C_{12}A_7$	48.49	51.51	63.16	36.84	77.93
CA	35.44	64.56	50	50	76.44
CA_2	21.54	78.46	33.33	66.67	74.86
CA_6	8.38	91.62	14.28	85.72	73.36
CaO	100	0	100	0	83.80

Table 1
OXIDE COMPOSITION AND BASICITY PERCENTAGE CORRESPONDING TO THE COMPOUNDS OF THE CaO – Al_2O_3 SYSTEM

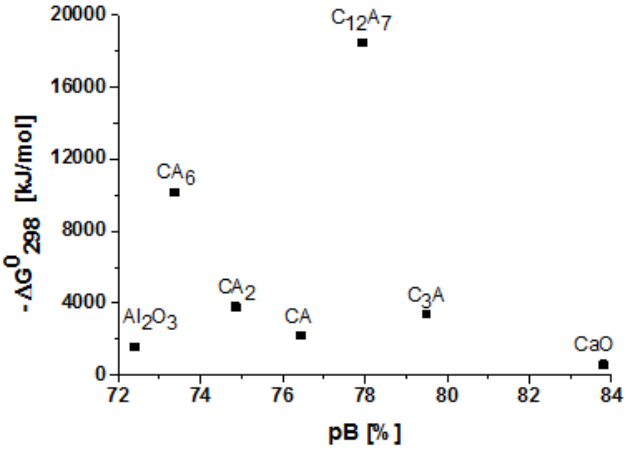

Fig. 5. Variation of standard free Gibbs energy of formation with pB in the $CaO - Al_2O_3$ system

Between the formation heat of some atomic systems and the ionicity of the formed chemical bonds can be put in evidence the existence of a correlation that can be expressed through an explicit relation. Therefore, Pauling [24] proposes for the ionicity of a chemical bond I_{AB} between atoms A and B the equation:

$$I_{AB} = 100 \cdot \left(1 - e^{-0.25 \cdot (X_A - X_B)^2}\right) [\%] \quad (13)$$

where X_A and X_B are the Pauling electronegativities of atoms A and B, which form the chemical bond A–B.

The heat of formation, Q, for a molecular system, was calculated with the formula:

$$Q = 96.3 \cdot \sum_{A,B} (X_A - X_B)^2 - 231.8 \cdot n_N - 108.8 \cdot n_O \quad [kJ/mol] \ (14)$$

where n_N and n_O are the number of nitrogen atoms, and respectively the number of oxygen atoms in a molecule; the $\sum_{A,B}$ has been made for the simple bonds A–B.

By eliminating $(X_A - X_B)^2$ between relations (13) and (14), on obtain a relation between the heat of formation and the ionicity of the chemical bonds related to the analysed system:

$$Q = 375.2 \cdot \sum_{A,B} \ln \frac{100}{100 - I_{AB}} - 231.8 \cdot n_N - 108.8 \cdot n_O \ [kJ/mol] (15)$$

The relation (15) reveals that for any given chemical system, the enthalpy of formation and implicitly the free Gibbs energy of formation are extensive measures in connection with the number of atoms (moles). Moreover, the equation (15) is strictly available for systems in which only simple chemical bonds are established between atoms. That is not the case for oxide compounds.

That is why, analysing the correlation between thermodynamic properties and pB, the following specifications should be made:

-the basicity percentage, pB, according to (6) and (7), represents an intensive property of the oxide system;

-the standard enthalpy of formation, $-\Delta H^0_{298}$, and the standard free energy of formation, $-\Delta G^0_{298}$, represent extensive properties associated to an oxide compound, depending on the number of moles of oxide constituents.

In this case also the thermodynamic properties should be intensive parameters. So, for two oxides X and Y that form the compound X_aY_b can be defined [5, 8,19]:

-the specific standard enthalpy of formation, $-\Delta H^0_{298}/N$;

-the specific standard free Gibbs energy of formation, $-\Delta G^0_{298}/N$, where: N = a+b.

The defined thermodynamic properties proved their utility when evidencing some strong correlations with pB for a series of oxide systems $M_2O - SiO_2$ (M = Li, Na, K, Rb, Cs) [19-22]. Similarly were determined relations between the enthalpy of formation of some oxide compounds reported to the number of oxygen atoms in the compound, and the optical basicity [6,7].

In the $CaO - Al_2O_3$ system, both the specific enthalpy of formation and the specific standard free Gibbs energy of formation reveal a strong dependency on pB. This dependency is put in evidence in the figures 6 and 7 and also in the relations (16) and (17) being also confirmed by the high values of the correlation coefficient R^2.

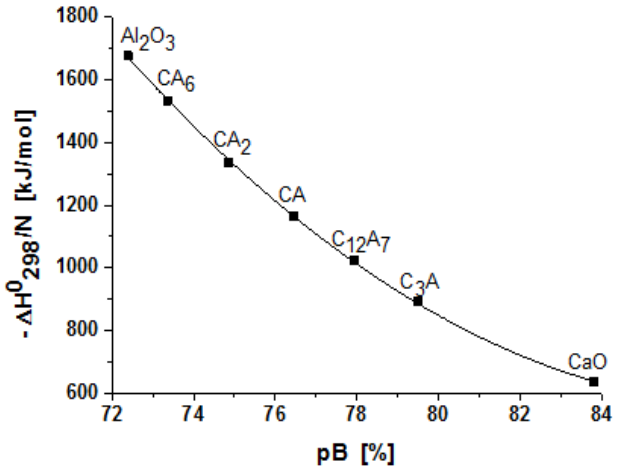

Fig. 6. Variation of specific enthalpy of formation with pB in the $CaO - Al_2O_3$ system

$$-\Delta H^0_{298}/N = 36491.1 - 818.26 \cdot pB + 4.659 \cdot pB^2$$

$R^2 = 0.9997$ (16)

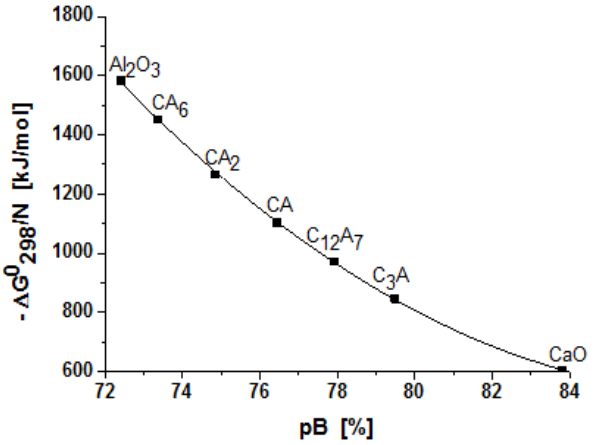

Fig. 7. Variation of specific free Gibbs energy of formation with pB in the $CaO - Al_2O_3$ system

$$-\Delta G^0_{298}/N = 33749.8 - 754.64 \cdot pB + 4.286 \cdot pB^2$$

$R^2 = 0.9997$ (17)

The strong dependency of the specific thermodynamic properties, $-\Delta H^0_{298}/N$ and $-\Delta G^0_{298}/N$, and pB is put in evidence also for the $CaO - SiO_2$ system (figs. 8 and 9 and relations (18) and (19)).

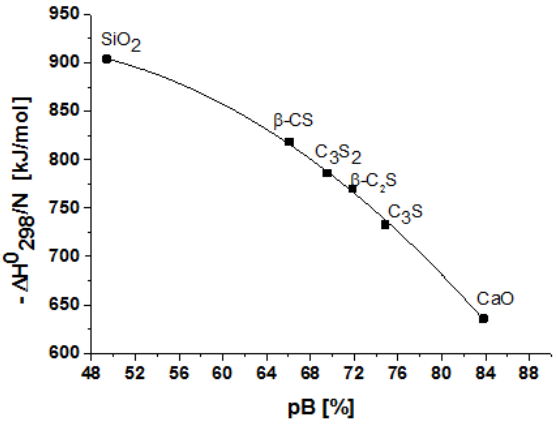

Fig.8. Variation of specific enthalpy of formation with pB in the CaO – SiO_2 system

$$-\Delta H^0_{298}/N = 6999.74 + 11.21 \cdot pB - 0.143 \cdot pB^2 \quad (18)$$

$R^2 = 0.9982$

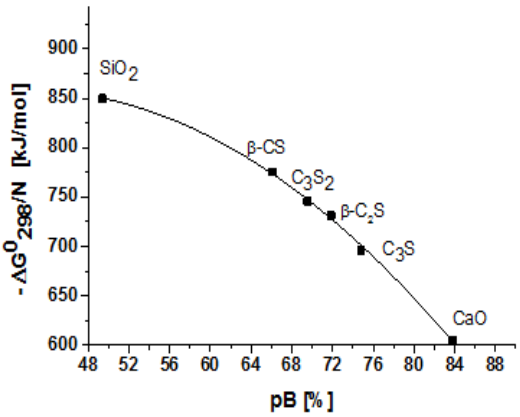

Fig. 9. Variation of specific free Gibbs energy of formation with pB in the CaO – SiO_2 system

$$-\Delta G^0_{298}/N = 602.51 + 12.19 \cdot pB - 0.145 \cdot pB^2 \quad (19)$$

$R^2 = 0.9979$

Analysing the presented data, it is resulted that:

- there are strong correlations between the specific thermodynamic properties, $-\Delta H^0_{298}/N$ and $-\Delta G^0_{298}/N$ and the basicity of the compounds in the CaO - Al_2O_3 system;
- as the basicity of the compounds increases, the specific standard enthalpy of formation and the specific standard free Gibbs energy of formation decrease in the series Al_2O_3, CA_6, CA_2, CA, $C_{12}A_7$, C_3A, CaO;
- as a consequence, the stability of the compounds is different and decreases from the compounds with a higher Al_2O_3 content towards those with a higher pB;
- the same results are confirmed [8] as well for the oxide compounds in the CaO –SiO_2 system.

Given the definitions (2) and (4), we calculated the specific enthalpy of reaction, $-\Delta^r H^0_{298}/N$, and the specific free Gibbs energy of reaction, $-\Delta^r G^0_{298}/N$. The results are presented in table 2. Based on the data from table 2, we performed graphical representations of $-\Delta^r H^0_{298}/N$ versus pB and, respectively, $-\Delta^r G^0_{298}/N$ versus pB, presented in figures 10 and 11.

In the CaO ($CaCO_3$) – Al_2O_3 system, the chemical reactions are realised through the diffusion of CaO into Al_2O_3. The diffusion is made through the layer of products formed at the interface between the pure oxides in the following succession: CaO → C_3A → $C_{12}A_7$ → CA → CA_2 → CA_6 → Al_2O_3. It results that the formation of C_3A from solid phase is improbable. This compound is formed at higher temperatures, in the presence of liquid phase. This observation is also supported by a series of experimental results presented in [11].

Table 2
VALUES OF THERMODYNAMIC PROPERTIES FOR THE FIVE MINERALOGICAL COMPOUNDS OF THE CaO – Al_2O_3 SYSTEM AND THE TOTAL NUMBER OF MOLES OF EACH COMPOUND

Oxide Compound	$-\Delta H^0_{298}$ [kJ/mol]	$-\Delta G^0_{298}$ [kJ/mol]	a +b =N	$-\Delta^r H^0_{298}$ [kJ/mol]	$-\Delta^r H^0_{298}/N$ [kJ/mol]	$-\Delta^r G^0_{298}$ [kJ/mol]	$-\Delta^r G^0_{298}/N$ [kJ/mol]
CA_6	10742.84	10160.54	1+6 = 7	48.53	6.93	57.18	8.17
CA_2	4006.25	3797.12	1+2 = 3	17.58	5.86	26.36	8.79
CA	2328.16	2208.95	1 + 1 = 2	15.9	7.95	21.34	10.67
$C_{12}A_7$	19423.71	18460.26	12+7=19	58.64	3.09	124.69	6.56
C_3A	3562.28	3383.96	3+1 = 4	-21.68	-5.42	-12.57	-3.14

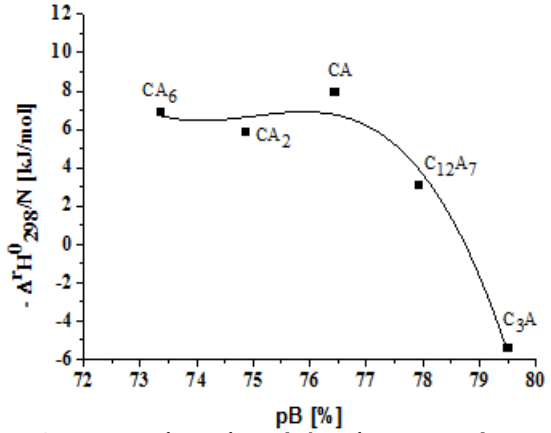

Fig. 10. Variation of specific enthalpy of reaction with pB in the CaO – Al_2O_3 system

$$-\Delta^r H^0_{298} = 64687.9 - 2588.5pB + 34.5 \cdot pB^2 - 0.153 \cdot pB^3 \quad (20)$$

$R^2 = 0.9066$

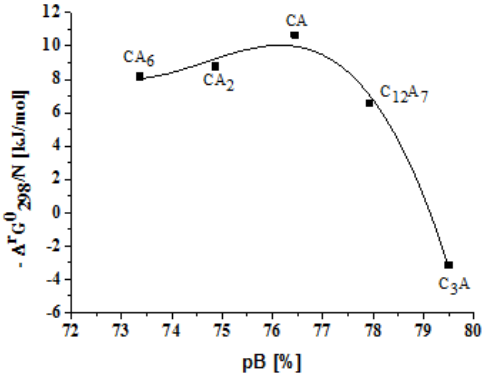

Fig. 11. Variation of specific free energy of reaction with pB in the CaO - Al_2O_3 system

$$-\Delta^r G^0_{298} = 63477.68 - 2552.3pB + 34.2 \cdot pB^2 - 0.153 \cdot pB^3 \quad (21)$$

$R^2 = 0.9121$

From thermodynamic point of view, all the other compounds from the CaO – Al_2O_3 system would be probably formed through solid phase reactions. According to the

data from table 2 and figure 11, the compounds with the highest stability are CA, CA_2 and CA_6 that have closed values for $-\Delta^rG^0_{298}/N$. With increasing basicity, the temperature at which these compounds occur in reactions between $CaCO_3$ and Al_2O_3: CA_2 (450 K) < CA (700 K) < $C_{12}A_7$ (825 K) < C_3A (950 K) are also increasing [13]. The CA_6 compound has incongruent melting, decomposing into α - Al_2O_3 + liq. [9]. The behaviour of diverse compounds can be explained as well, based on the nano-heterogeneous character of the oxide systems structure [25-28].

The reduced degree of correlation for specific thermodynamic functions in relation with pB, presented in figures 11 and 12 and in the relations (20) and (21), may be an indication that it is possible that other structural characteristics of reactants and products may contribute to the formation reactions. In this phase of the research we do not confirm such hypothesis.

At thermodynamic equilibrium, reactions (8) – (12) are characterised through reaction constants at constant pressure. According to the presented data, it results that, besides temperature, the reaction constants are determined also by the basicity of the reaction systems.

Conclusions

The analysis of the thermodynamic correlations in the oxide system CaO – Al_2O_3 shows that:

- in the CaO – Al_2O_3 system five oxide compounds have been analysed, with basicity percentage values comprised between 72% and 80%;
- the thermodynamic properties associated with the compounds from this system seem not to be significantly correlated neither with their chemical composition, nor with their basicity;
- the thermodynamic properties divided to the number of oxide moles of the oxide compounds are strongly correlated with the basicity percentage;
- the basicity percentage represents an integrative chemical-structural characteristic of the oxides that influences essentially the thermodynamic properties of oxides and oxide compounds in the CaO – Al_2O_3 system.

In Memoriam

This work was elaborated to honour the memory of our colleague Corina MITU, who prematurely deceased. She had made the first calculations and had given a preliminary interpretation of the results. We finalized the paper and wish to publish it, so that our colleagues' efforts would not be in vain. May God rest her soul in peace!

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