# Implications of Basicity on Thermodynamic Properties of Silica-alkali Vitreous Systems

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*Vitreous oxidic systems are characterized at various structural levels by different stereo-chemical parameters. Ultimately, these determine the properties of the glass.In this paper, the significance of glass basicity in the thermodynamic properties of vitreous systems is emphasized. The basicity of oxides and oxidic systems is considered to be quantified by the basicity percentage, pB, a complex structural parameter. Herein, a series of correlations between the standard free energy of formation and Gibbs free energy of reaction and the basicity percentage of alkali-silica binary systems are presented.*

*Keywords: Gibbs free energy, basicity, silica-alkali vitreous systems*

Silica solids are found both in crystalline and vitreous systems. In the first case, the phase equilibriums determine the number and chemical composition of defined chemical compounds. In this case, the values of the thermodynamic properties of the silica melts are determined by various experimental methods, such as the mass spectrometric method [1], AC calorimetry [2, 3], the determination of heat capacity of the oxide or high-temperature drop solution calorimetry [4] for the direct determination of the partial molar enthalpy of $SiO_2$ in various binary and ternary oxidic melts. For vitreous silica systems, the volume of thermo-chemical experimental data is inevitably lower.

Vitreous oxidic systems are characterized by a lower degree of order as compared to their analogue crystalline systems. Therefore, their energy content is higher and, accordingly, their thermodynamic stability lower. The changes in the thermodynamic properties of vitreous systems are ultimately manifested in their properties.

Therefore, the principal thermodynamic properties – standard Gibbs free energy, $\Delta G^0_{298}$, standard enthalpy of formation, $\Delta H^0_{298}$, as well as the standard entropy, $\Delta S^0_{298}$, represent useful values in the characterization of vitreous systems.

In this context, the characterization of vitreous oxidic systems starting from the thermodynamic data can be approached in at least to ways, with direct reference to:

- correlations between the structures of glass melts and their thermodynamic properties [5, 6];
- the use of thermodynamic functions for predicting glass properties [7-9].

In parallel, an increasing number of structural models, based on the acid-base interaction of the reactants, were put forward in the last years [1, 4, 10-12]. Thus, the study of possible correlations between the thermodynamic properties of alkali-silica glasses and their basicity is of great interest.

## Experimental part

### *Theoretical Basis*

The standard Gibbs free energy for vitreous systems is calculated as follows:

$$\left(\Delta G^0_{298}\right)_v = \left(\Delta H^0_{298}\right)_v - 298 \cdot \left(S^0_{298}\right)_v \qquad (1)$$

where:

$(\Delta H^0_{298})_v$ is the standard enthalpy of formation of the glass;

$(\Delta S^0_{298})_v$ is the standard entropy of formation of the glass.

The standard enthalpy of formation of vitreous silicates differs from that of crystalline ones, $(\Delta H^0_{298})_{cr}$, according to the relation:

$$\left(\Delta H^0_{298}\right)_v = \left(\Delta H^0_{298}\right)_{cr} - \left(\Delta H^0_{298}\right)_{v/cr} \qquad (2)$$

in which $(\Delta H^0_{298})_{v/cr}$ represents the glass enthalpy of formation from the compositionally analogue crystal.

For the calculation of alkali-silica glass enthalpies, experimental values for the specific molar heat capacities and dissolution heats for the respective glasses and crystals with the same oxidic composition are needed. Unfortunately, such data are not always available. Also, no data on the Gibbs free energy are observed in the case of glasses from the $Rb_2O$ - $SiO_2$ and $Cs_2O$ - $SiO_2$ oxidic systems.

For the data regarding Li, Na, and K based alkali-silica systems [13,14], the ratio $(\Delta G^0_{298})_v$ / $(\Delta G^0_{298})_{cr}$ is quasi-constant, having a value of 0.978. On this basis, and knowing the values for $(\Delta G^0_{298})_{cr}$ of the two systems of interest, the unknown values of the Gibbs free energy for a series of systems in vitreous state were estimated (table 1).

The standard entropy associated with the formation reaction of alkali-silica glasses varies directly proportional, and practically linear, with the $SiO_2/M_2O$ (M = Li, Na, K, Rb, Cs) ratio. The lowest entropy values are for the $Li_2O – SiO_2$ system. These are in the range of 0.075 kJ/mole.K for the lithium metasilicate glass and 0.188 kJ/mole.K for the lithium trisilicate glass. The values for the Na and K glasses are larger with 0.042 and 0.05 kJ/mole.K, respectively[13].

Oxidic vitreous systems are homogenous at the microscopic and macroscopic scale. As an exception to this rule, there are glasses in which, accidentally or induced, microphase separation or partial crystallization occurred. Nevertheless, at the nano level (and at the sub-nano level), the structure of glasses is heterogeneous [15].

Thus, because vitreous systems are hierarchized, different types of structural entities have distinct steric, chemical and dimensional properties exist at different scales.

In alkali-silica glasses, the structure at the sub-nanometric level consists of tetrahedral structural units, having the formula $Si(O_p)_n(O_{np})_{4-n}$, n = [0,4], $n \in N$, where

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Table 1

STANDARD FREE ENERGY OF VARIOUS VITREOUS MELTS WITH IDENTICAL CHEMICAL COMPOSITION WITH SOME BINARY COMPOUNDS FROM THE $M_2O$ - $SiO_2$ (M = Li, Na, K, Rb, Cs) SYSTEMS

| No. | Oxide System | Binary compound | $(\Delta G^0_{298})_v / (\Delta G^0_{298})_{cr}$ | $(\Delta G^0_{298})_v$ [kJ/mole] |
|---|---|---|---|---|
| 1. | $Li_2O - SiO_2$<br>(L – S) | LS | 0.950 | 1466.3 |
| | | $LS_2$ | 0.950 | 2329.5 |
| | | $LS_3$ | 0.982 | 3122.5 |
| 2. | $Na_2O - SiO_2$<br>(N – S) | NS | 0.976 | 1429.2 |
| | | $NS_2$ | 0.989 | 2305.1 |
| | | $NS_3$ | 0.991 | 3164.2 |
| 3. | $K_2O - SiO_2$<br>(K – S) | KS | 0.995 | 1460.3 |
| | | $KS_2$ | 0.995 | 2331.7 |
| | | $KS_4$ | 0.976 | 3978.7 |
| 4. | $Rb_2O - SiO_2$<br>(Rb – S) | RbS | (0.978) | (1413.7) |
| | | $RbS_2$ | (0.978) | (2266.8) |
| | | $RbS_4$ | (0.978) | (3983.6) |
| 5. | $Cs_2O - SiO_2$<br>(Cs – S) | CsS | (0.978) | (1407.3) |
| | | CsS2 | (0.978) | (2259.5) |
| | | $CsS_4$ | (0.978) | (3967.7) |

$O_p$ represents the bridging oxygen atoms and $O_{np}$ the non-bridging oxygen atoms.

Evidently, the distribution of the various kinds of tetrahedral in a vitreous melt of the $M_2O – SiO_2$ systems is determined by many factors: the nature of the alkali cation M, the chemical composition of the glass, the temperature of the chemical-structural equilibrium, melt period etc. In the case of silica melts, this can be interpreted as acid-base interactions. Thus, silica can be seen as an acid, the Si-O-Si group being an electron acceptor (Lewis acid).

On the other hand, $O^{2-}$ from an alkali oxide represents an electron donor (Lewis base). In chemical-structural equilibrium condition, the acid base reaction between different types of oxygen can be written as:

$$O^0 + O^{2-} \Leftrightarrow 2 \cdot O^- \qquad (3)$$

The reaction (3) equilibrium constant K is defined as a function of the number of bridging oxygen atoms $O^0$, non-bridging oxygen atoms $O^{2-}$ per $SiO_4$ tetrahedron:

$$K = (O^-)^2 / (O^0 \cdot O^{2-}) \qquad (4)$$

In reality, most of the times, the effective charges of the oxygen atoms in reaction (3) may not be integer, without the model changing.

## Results and Discussions

From the thermodynamic properties, the standard formation energy has been the „target" most used for structural-chemical correlations.

The first attempt was made by Pauling, who defined his known electronegativity scale on the basis of dependence of the free enthalpies of formation and the ionicity of the bonds (as considered as a difference of electro-negativities).

After several decades, a series of recent approaches highlighted correlation between the energy of formation and the optical basicity of oxides [11] or any other value that can measure the acid-base character of the compounds [12].

In vitreous $M_2O$-$SiO_2$ systems, the Gibbs free energy associated to glasses depends on their chemical composition and, implicitly, on their basicity. In figure 1 the variation of the standard free energy ($-\Delta G^0_{298}$) as a function of the gravimetric percentage of $SiO_2$ from various binary glasses. These glasses have compositions varying from that of silica glass ($SiO\text{-}_2$) and that of alkaline metasilicate (MS). For molar percentages of alkali oxide higher than 50%, binary $SiO_2$ glasses cannot longer be obtained.

For all the cases presented in figure 1, a maximum can be observed for ($-\Delta G^0_{298}$). From this graphical representation, it can be seen that the standard free energy of formation reaches a maximum for a $SiO_2$ progressively

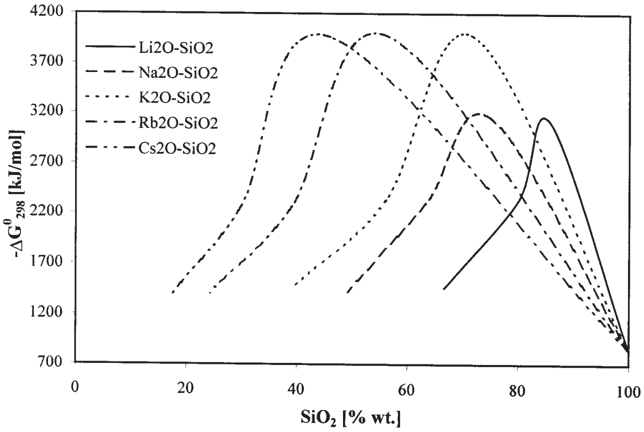

Fig. 1. Variation of the Gibbs free energy as a function of the $SiO_2$ gravimetric fraction for vitreous alkali-silica systems

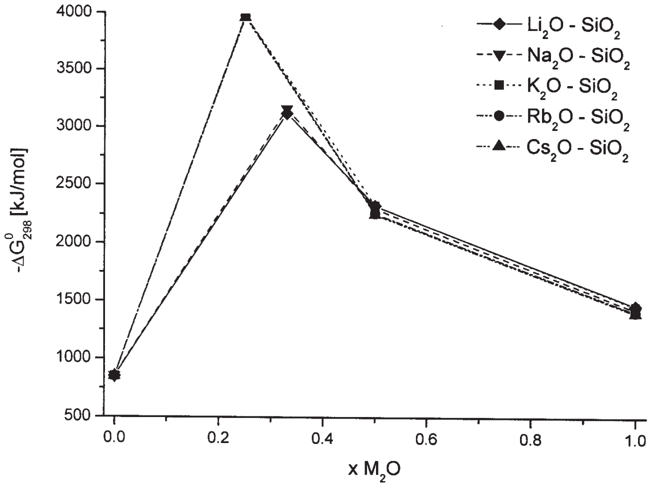

Fig. 2. Variation of - $\Delta G^o_{298}$ as a function of the molar fraction $xM_2O$ in the $M_2O$-$SiO_2$ systems.

lower in the series of alkali oxides with the molecular mass rising.

In another graphical representation, (fig. 2) it is shown that the extreme for standard free energy of formation are found at compositions that move progressively from trisilicate ($Li_2O$ and $Na_2O$ glasses) to the alkaline tetrasilicate ($Rb_2O$ and $Cs_2O$).

A similar graphical representation, with a maximum, is also found in the case of the dependence of the thermodynamic measure ($-\Delta G^0_{298}$) with the glass basicity, measured by the basicity percentage, pB [16]. In this case, the maximum values are found at increasingly higher basicity values, according to the group order of alkaline ions (fig. 3).

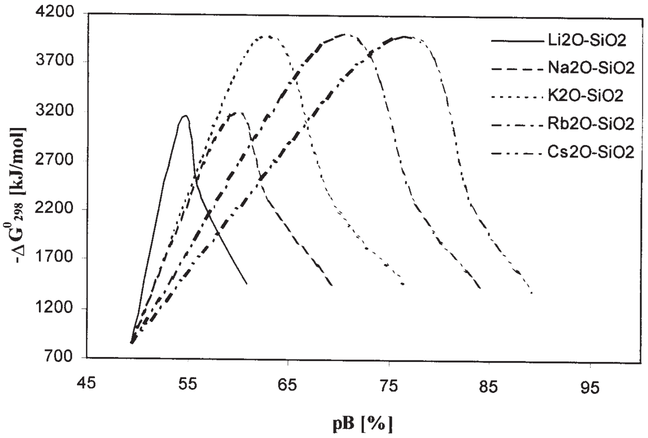

Fig. 3. Variation of the Gibbs free energy as a function of the binary alkali-silica glasses pB

In the case of oxide vitreous systems, it was introduced the use of the new thermodynamic parameter, $-\Delta G^0_{298}\cdot f^m_{SiO_2}$, where $f^m_{SiO_2}$, is the molar fraction of $SiO_2$ on composition of glass. In figure 4 the dependence of this parameter, $-\Delta G^0_{298}\cdot f^m_{SiO_2}$, is presented, relative to the glass basicity (pB).

Taking into account relation (3) and a series of partial conservation balances of various species of oxygen, the distribution of the types of $SiO_4$ tetrahedra can be computed, when the reaction constant K is known.

Similarly, at the nanometric scale, alkali-silica vitreous systems are characterized by structural entities formed by the coupling of a variable number of tetrahedra. Thus, structural formations of various sizes, with the formula $iNa_2O.jSiO_2$ are formed. These occur as a result of an acid-base reaction, as follows:

$$iNa_2O + jSiO_2 \Leftrightarrow iNa_2O\cdot jSiO_2 \qquad (5)$$

where the stoichiometric coefficients have values depending on the chemical composition and on temperature.

The reaction (6) constant $K_{i,j}$ is computed using the relation:

$$K_{i,j} = \left(a_{N_iS_j}\right)/\left(a_N^i\cdot a_S^j\right) \qquad (6)$$

in which ***a*** represents the activities of the reaction participants (N – $Na_2O$; S – $SiO_2$).

In figure 5, the repartition of the various species of $N_iS_j$ type is shown, as a function of the $Na_2O$ molar fraction and temperature for glasses from the $N_{a2}O$ – $SiO_2$ system [7].

In this case also, real results are obtained knowing the value (and for other cases the values) of the $K_r$ reaction constant (constants). These can be computed using the relation:

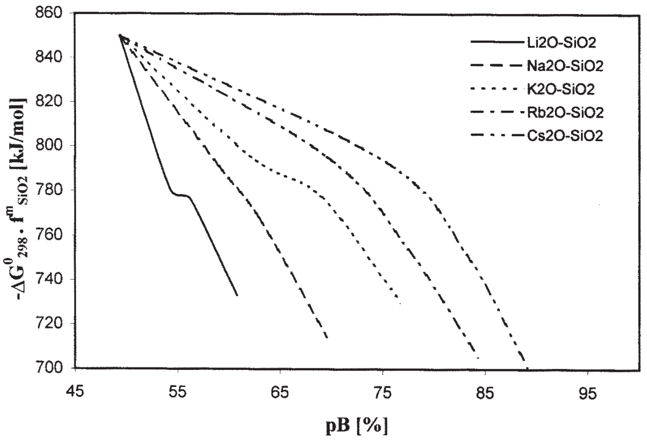

Fig. 4. Variation of $-\Delta G^0_{298}\cdot f^m_{SiO_2}$ as a function of the binary alkali-silica glasses pB

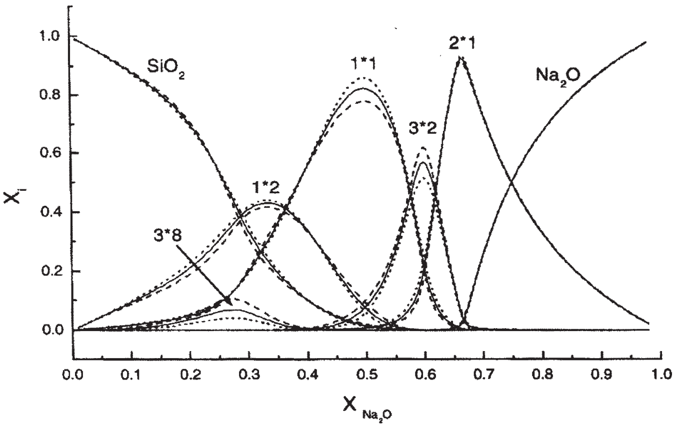

Fig. 5. Chemical structure of sodium silicate melts at 1200 °C, calculated using various hypotheses: reference value for $\Delta^rG^0_{298}$ – solid line; $\Delta^rG^0_{298}$ + 4.18 kJ/mole – dashed line; $\Delta^rG^0_{298}$ - 4.18 kJ/mole – dotted line [7]

$$K_r = \exp\left[-\Delta^rG^0_{298}/RT\right] \qquad (7)$$

where:

$\Delta^rG^0_{298}$ is the standard Gibbs free energy of reaction,

R is the general gas constant, T the temperature in K.

At the same time, a significant dependence of the Gibbs free energy of reaction and the basicity percentage is to be expected. The arguments for this correlation are the following:

- the Gibbs free energy of reaction is defined as a function of the standard free energy of the reactants and of the reaction products;
- the thermodynamic properties of the oxides, oxidic compounds and vitreous silicates are significantly determined by their basic character, quantitatively described by pB;
- simple correlations between the thermodynamic properties - $\Delta G^0_{298}$ and - $\Delta H^0_{298}$ exist for alkali-silica crystalline systems, as well as for vitreous ones:

$$\Delta G^0_{298} = k\cdot\Delta H^0_{298} \qquad (8)$$

where k is a proportionality coefficient.

The use of literature data [13,14] leads to the values of k = 1.061 for crystals and k = 1.057. Considering the similarity between these values, it is to be expected that the value which correlate to $\Delta H^0_{298}$ also influence the standard Gibbs free energy. One of these is the basicity of melts and oxidic solids, measured by the basicity

Table 2

TYPES OF REACTIONS IN THE $M_2O$ – $SIO_2$ SYSTEMS AND THEIR $\Delta^rG^0_{298}$, ΔpB ASSOCIATED VALUES

| No. | Reaction | pB oxides | $-\Delta^rG^0_{298}$ [kJ/mole] | ΔpB [%] |
|---|---|---|---|---|
| | $3SiO_2 + Li_2O \Leftrightarrow Li_2Si_3O_7$ | $pB_{SiO2}$ = 49.4% | 10.86 | 34.2 |
| | $2.Li_2Si_3O_7 + Li_2O \Leftrightarrow 3.Li_2Si_2O_5$ | $pB_{Li2O}$ = 83.6% | 181.53 | 29.32 |
| | $Li_2Si_2O_5 + Li_2O \Leftrightarrow 2(Li_2SiO_2)$ | | 41.29 | 27.36 |
| | $3SiO_2 + Na_2O \Leftrightarrow Na_2Si_3O_7$ | $pB_{SiO2}$ = 49.4% | 237.66 | 39.65 |
| | $2.Na_2Si_3O_7 + Na_2O \Leftrightarrow 3.Na_2Si_2O_5$ | $pB_{Na2O}$ = 89.0% | 210.15 | 30.03 |
| | $Na_2Si_2O_5 + Na_2O \Leftrightarrow 2(Na_2SiO_2)$ | | 176.39 | 26.14 |
| | $4SiO_2 + K_2O \Leftrightarrow K_2Si_4O_9$ | $pB_{SiO2}$ = 49.4% | 256.74 | 44.80 |
| | $K_2Si_4O_9 + K_2O \Leftrightarrow 2.K_2Si_2O_5$ | $pB_{K2O}$ = 94.2% | 362.40 | 32.16 |
| | $K_2Si_2O_5 + K_2O \Leftrightarrow 2(K_2SiO_2)$ | | 266.61 | 25.12 |
| | $4SiO_2 + Rb_2O \Leftrightarrow Rb_2Si_4O_9$ | $pB_{SiO2}$ = 49.4% | 283.62 | 46.10 |
| | $Rb_2Si_4O_9 + Rb_2O \Leftrightarrow 2.Rb_2Si_2O_5$ | $pB_{Rb2O}$ = 95.5% | 249.70 | 25.92 |
| | $Rb_2Si_2O_5 + Rb_2O \Leftrightarrow 2(Rb_2SiO_2)$ | | 260.30 | 18.03 |
| | $4SiO_2 + Cs_2O \Leftrightarrow Cs_2Si_4O_9$ | $pB_{SiO2}$ = 49.4% | 282.02 | 48.20 |
| | $Cs_2Si_4O_9 + Cs_2O \Leftrightarrow 2.Cs_2Si_2O_5$ | $pB_{Rb2O}$ = 97.6% | 265.30 | 22.15 |
| | $Cs_2Si_2O_5 + K_2O \Leftrightarrow 2(Cs_2SiO_2)$ | | 269.10 | 14.40 |

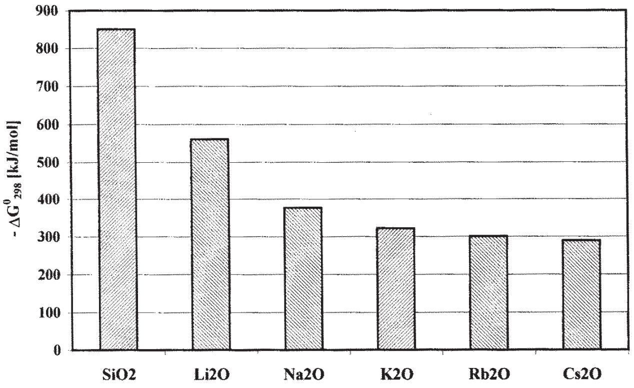

Fig. 6. Standard Gibbs free energy for alkaline oxides and $SiO_2$ (β-cristobalit)

Table 3

FUNCTIONAL RELATIONS BETWEEN . $f^m_{SiO_2} \cdot \left(-\Delta^rG^0_{298}\right)$ = y AND ΔpB = x in $M_2O$ – $SiO_2$ SYSTEMS

| No. | Binary system | y = f(x) relation | Standard deviation |
|---|---|---|---|
| 1. | $Li_2O - SiO_2$ | $y = -10{,}929*x^2 + 670{,}945*x - 10155{,}5$ | ± 0,028 |
| 2. | $Na_2O - SiO_2$ | $y = -0{,}713*x^2 + 53{,}556*x - 824{,}7$ | ± 0,0002 |
| 3. | $K_2O - SiO_2$ | $y = -0{,}941*x^2 + 69{,}437*x - 1017{,}3$ | ± 0,006 |
| 4. | $Rb_2O - SiO_2$ | $y = -0{,}0625*x2 + 7{,}457*x + 16$ | ± 0,003 |
| 5. | $Cs_2O - SiO_2$ | $y = -0{,}111*x2 + 9{,}615*x + 19$ | ± 0,002 |

percentage, pB, which in turn is defined implicitly using the Pauling electronegativities [16].

According to the phase equilibrium diagrams, in the different $M_2O$ – $SiO_2$ systems, a series of compounds are formed, which, in certain cooling conditions, can lead to the obtaining of glass: alkaline tetrasilicate $MS_4$ (M = K, Rb, Cs), trisilicate $MS_3$ (M = Na), disilicate (M = Li, Na, K, Rb, Cs), metasilicate (M = Li, Na, K, Rb, Cs) [13].

The ideal reactions leading to alkali-silica glasses having the same chemical composition with the crystalline compounds are presented in table 2.

In table 2, along with the possible reactions leading to binary compounds, the values of the Gibbs free energy of reaction and of the difference in basicity percentage between the reactants, ΔpB, are presented. The latter are calculated as a function of the pB values of the reaction products and reactants, representing the driving force of the binary system reactions.

For the calculation of the Gibbs free energy of reaction, the standard Gibbs free energies of formation for alkaline oxide and $SiO_2$ (β-cristobalit) were used, and are presented in figure 6.

On the basis of the data presented in figure 6 and in table 2, statistical relations were established between $f^m_{SiO_2} \cdot \left(-\Delta_r G^0_{298}\right)$ and ΔpB, where $f^m_{SiO_2}$ is the molar fraction of $SiO_2$ from the glass.

The results are presented in table 3 and can be interpreted as follows:

- a strong interdependence exists between the free energy of reaction of alkali-silica systems and their basicity;
- quantitatively, this functional correlation can be well described by parabolic relations;
- the deduced relations can be used for comparisons, in the same system or for glasses from different oxidic systems regarding the ability of a melt to form a glass, having a higher or lower stability.

## Conclusions

For vitreous oxidic systems, the possibility of ascertaining the distribution of different structural entities is conditioned by knowing the reaction constants, $K_r$.

At the same time, the constant $K_r$ is difficult to be determined practically in all the cases. Therefore, the only practical method for determining it is the indirect one, using possible correlations with various quantities.

In this paper strong correlations between different thermodynamic properties are presented, especially between the standard free enthalpies of formation and Gibbs free energy of reaction and the basicity percentage, pB.

Because the value of pB can be both calculated, as well as experimentally determined using spectroscopic means, the highlighted correlations could represent a general pathway for the estimation of various thermodynamic values of vitreous oxidic melts.

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