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SIMULATION OF THERMODYNAMIC PROPERTIES OF SLAG MELTS

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Synopsis: Borate and silicate slag melts should be considered as associated liquids. In order to describe their properties the model of associated solutions has been chosen. Various properties which depend additively on the ratio of the associates in slag melts have been calculated. They show very satisfactory agreement with the experimental data.

Key Words: Modelling, thermodynamic data, slags.

I. Introduction

In the talk I would like to present the main results of thermodynamic studies carried out at the Institute of Silicate Chemistry of Russian Academy of Sciences in St.Petersburg. A number of methods has been worked out to interpret the results obtained. The first one enables the regularities experimentally observed for melts and glasses to be adequately described on the basis of the thermodynamic data available for crystalline compounds of corresponding system.

I would like to note that we'll consider only binary borate and silicate glasses and melts. However the proposed approaches would apply equally to any other glass-forming system including multi-component ones.

II. Experimental

Let us consider results obtained by the electro-motive force and solution calorimetry methods. Using them the following systems have been studied: $M_2O{\cdot}B_2O_3$ (M = Li,Na,K,Rb,Cs), $M_2O{\cdot}SiO_2$ (M = Li,Na,K).

Figs. 1 and 2 (a,b) show the concentration dependencies of enthalpies of formation for glasses and crystals and Gibbs energies for melts are calculated from experimental results for the following reaction of formation:

$$X^*M_2O + Y^*B_2O_3 = X^*M_2O \cdot Y^*B_2O_3 , \quad \text{where } (X^* + Y^*) = 1. \qquad (1)$$

Analysis of these data has led to a choice of the model that describes properties of melts and glasses on the basis of minimum of assumptions and without use of adjustable parameters.

III. Discussion

Reasons for choosing the model.

Let us consider what our reasons were for choosing the model. The systems considered are formed by the components of different chemical nature, namely, by basic and acidic oxides. They are donors and acceptors of electrons. Therefore, being in contact under certain conditions (for example, at high temperature) they inevitably interact and form salt-like products. This is confirmed by large negative values of Gibbs free energies and enthalpies of formation of melts, glasses and crystals (see Figs. 1 and 2). The character of the dependencies given in these figures indicates that (within the studied concentration ranges) melts are single-phase and, hence, should be considered as solutions (by definition the latter is applicable to homogeneous systems of variable compositions formed by two or several components). Taking into consideration the above-mentioned interaction of oxides that results in the formation of salt-like products, it is easy to understand that these products are the components of the solutions discussed. Obviously, the products are similar in their stoichiometry to the crystalline compounds shown in the phase diagrams of the systems considered. One may assume that the structural similarity exists as well. In addition, it is possible that certain associates that have no crystalline analogues are also available in melts.

From what has been said it follows that the most logical approach to the description of glass-forming melts formed by the components of different chemical nature is the use of the model of associated solutions that results from the approach used by De Donde for the description of the systems with a chemical interaction of their components. The proposed approach is also applicable to glasses if they are single-phase.

Advantages of the model when it is used for oxide systems.

The model of ideal associated solutions was worked out by Prigogin in the 1940s for molecular organic solutions. When applied to oxide melts, it has certain advantages.

1). In oxide systems the substances forming solutions are strictly defined, according to their phase diagrams;

2). For many oxide systems reliable information on free energies of formation of crystalline compounds is available. Hence, the equilibrium constants of the formation processes are also known. Due to the knowledge of these values we may avoid the use of adjustable parameters in the model used.

Assumptions made.

Several assumptions are made in the model. They are as follows:

1). Solutions formed by salt-like associates and unreacted oxides are supposed to be ideal.

2). To simplify calculations we take into consideration only the formation of salt-like products. The existence in melts of any other associates is neglected, although we can't deny the possibility of their formation. But according to our estimation, Gibbs free energies of formation of these associates are approximately by an order of magnitude smaller than those of salt-like groupings.

3). Finally, in this model there are certain aspects that need a more detailed consideration. For example, this is the problem of polymerization in melts and glasses of original glass-forming components (B_2O_3 or SiO_2) and salt-like products. This phenomenon should be taken into consideration but as a first approximation, we neglect it because - according to our estimation - the inaccuracy resulted from this neglect is compared with an experimental error of determination of thermodynamic potentials.

Mathematical Basis

Now we'll briefly consider the mathematical bases of the model. For this purpose we'll take a sodium borate melt. According to the phase diagram of the system within the studied concentration range there are four compounds $Na_2O \cdot B_2O_3$, $Na_2O \cdot 2B_2O_3$, $Na_2O \cdot 3B_2O_3$, $Na_2O \cdot 4B_2O_3$ that form in melts according to the following reaction:

$$Na_2O + n\ B_2O_3 = Na_2O \cdot n\ B_2O_3 \qquad (2)$$

where $n = 1 \div 4$.

In addition to these borates, the unreacted sodium and boron oxides are always available in melts. Thus the melts are formed by 6 main structural units: 4 borates and 2 oxides. Their equilibrium concentration in melts are described by the following system of equations:

$$K_1 = \frac{X_{1:1}}{X_{Na} \cdot X_B} \quad (3) \qquad K_2 = \frac{X_{1:2}}{X_{Na} \cdot X_B^2} \quad (4)$$

$$K_3 = \frac{X_{1:3}}{X_{Na} \cdot X_B^3} \quad (5) \qquad K_4 = \frac{X_{1:4}}{X_{Na} \cdot X_B^4} \quad (6)$$

$$X_{Na}^* = n_{1:1} + n_{1:2} + n_{1:3} + n_{1:4} + n_{Na} \quad (7)$$

$$X_B^* = n_{1:1} + 2n_{1:2} + 3n_{1:3} + 4n_{1:4} + n_B \quad (8)$$

$$X_i = \frac{n_i}{\Sigma n_i} \quad (9)-(14)$$

where $K_1 \cdots K_4$ are the equilibrium constants of the borate formation processes presented by the reaction (2). $X_{1:1} \cdots X_{1:4}$, X_{Na} and X_B are the equilibrium concentrations of salt-like groupings and unreacted oxides in melts and glasses; $n_{1:1} \cdots n_{1:4}$, are the numbers of moles of these structural units; X^*_{Na} and X_B^* represent the analytical composition of the melt (glass) considered, that is these are mole fractions of both oxides when the melt (glass) composition is expressed as $X^*_{Na}\ Na_2O \cdot X^*_B\ B_2O_3$, where $(X^*_{Na} + X^*_B) = 1$. Index i is referred to various salt-like groupings available in melts or glasses.

In the above system equations (3)-(6) are the law of mass action written in an ideal form for the reaction (2). The equations (7) and (8) are the expressions for the law of mass balance. They establish a relationship between the melt (glass) composition and numbers of salt-like groupings and unreacted oxides available in the melt (glass).

In Fig.3 the concentration dependences of calculated and experimental chemical potentials of alkali and boron oxides in lithium, sodium and potassium borate melts are shown. The calculated dependences are depicted by crosses for lithium, sodium and potassium oxides and by filled circles for boron oxides. It is seen that in almost all the systems the calculated and experimental dependences coincide within the limits of the experimental error. This means that the model used satisfactorily describes thermodynamic properties of oxide melts. (Here the whole set of thermodynamic potentials is meant - this is proved by corresponding calculations that are not presented in this talk.) According to our calculations the above statement is true for glasses as well.

It is important to note that all reactions occurring in melts should be taken into consideration. This is illustrated by the dependence shown in Fig.3 for sodium oxide that is calculated neglecting the formation of one of the compounds, namely, sodium tetraborate (these date are depicted by triangles). It is seen that this neglect considerably changes the character of the dependence and the latter differs much from the experimental results.

In addition to the equilibrium concentrations of the unreacted oxides in melts and glasses, the solution of the system of equations (3)-(14) gives information on the content of various salt-like groupings. Their ratio characterizes the chemical structure of melts and glasses [1, 2].

Let us show that the knowledge of the values n_i that is quantities of salt-like groupings determined from the system enables various properties of glasses and melts to be calculated. On the basis of the model used Gibbs free energy of formation of melts from oxides may be expressed as follows:

$$\Delta G_f = \Sigma\, n_i \cdot \Delta G_i^{\circ} + RT\, \Sigma n_j \cdot \ln X_j \quad (15)$$

where ΔG_i° is the standard free energy of formation of a crystalline compound; n_i is the number of moles of salt-like groupings in a melt; nj is the number of moles of all structural groupings molar (both salt-like units and unreacted oxides); X_j is the equilibrium concentrations in a melt.

The values n_i, n_j and X_j depend on temperature , pressure and a melt composition. Hence, equation (15) is the equation of state for our systems. Therefore using it, and certain thermodynamic relationships, one may determine various physical properties of melts as derivatives of Gibbs energy of their formation with respect to different parameters. These properties are: molar volumes, isothermal compressibility, heat capacity, coefficient of thermal expansion etc. They are calculated according to the following equations.

$$\Delta Cp = -T\left(\frac{\partial^2 {}_\Delta G}{\partial T^2}\right)_{P,X^*} = \sum_i n_i \Delta C_{pi}^\circ + \sum_i \Delta Hi^\circ \cdot \frac{\partial n_i}{\partial T} \tag{16}$$

$$\Delta \beta = \left(\frac{\partial^2 {}_\Delta G}{\partial P^2}\right)_{T,X^*} = \sum_i n_i \Delta \beta_i^\circ + \sum_i \Delta Vi^\circ \cdot \frac{\partial n_i}{\partial P} \tag{17}$$

$$\Delta \alpha = \left(\frac{\partial^2 {}_\Delta G}{\partial P \cdot \partial T}\right) = \Sigma ni \Delta \alpha_i^\circ + \Sigma \Delta V_i^\circ \cdot \frac{\partial n_i}{\partial T} \tag{18}$$

$$\Delta V = \left(\frac{\partial {}_\Delta G}{\partial P}\right)_{T,X^*} = \Sigma ni \cdot \Delta V_i^\circ \tag{19}$$

$$\Delta H = -T\left(\frac{\partial({}_\Delta G/T)}{\partial T}\right)_{P,X} = \sum_i \Delta Hi^\circ \tag{20}$$

The derivatives in the left-hand sides of the equations (16)-(20) are thermodynamic definitions of the properties considered. The expressions in the right-hand sides are obtained when differentiated Gibbs energies are written according to equation (15), that is the model used enables properties of melts and glasses to be presented as shown above.

Eqns.(16)-(20) describe concentration dependencies of the considered properties of melts and glasses. In addition, analyzing the equations it is possible to explain the character of temperature dependencies of these properties. When a melt is cooled from a certain high temperature down to temperatures close to those of glass transition region, changes in melt properties are determined by temperature changes of all the parameters available in the right-hand sides of eqns. (16)-(20) At temperatures lower than T_g chemical processes occurring in melts are frozen. Therefore the values n_i presenting numbers of salt-like groupings do not change any longer and become constant. At temperatures lower than T_g changes in properties of glasses are determined only by changes of these properties for available crystalline compounds, the values n_i being constant multipliers in the products that are the first terms in the right-hand sides of eqns.(2)-(5). In eqns. (3)-(5) derivatives of the values n_i with respect to temperature and pressure become equal to zero. Graphically this is revealed in a known abrupt character of temperature changes of the values ΔCp, $\Delta\alpha$ and $\Delta\beta$ within the glass transition region. As to molar volumes and eathalpies of formation of glasses, in this region there is a break observed in the graphs of their temperature dependencies. This break results from different rates of changes in the properties of melts (when the values ΔV_i°, ΔH_i° and n_i are variable) and of glasses (when the values n_i are constant).

Using the above equations derived on the basis of the model of ideal associated solutions, it is shown that the considered properties of glasses are the additive functions of the following products (written here for molar volume):

$$V = \sum_j nj \cdot Vj^\circ \tag{21}$$

where V is molar volume of a glass, V_j° is molar volume of a corresponding crystalline compound, n_j is number of its moles in a glass.

Using eqn.[21] we have calculated molar volumes of lithium borate glasses. Calculations were based on information about molar volumes of crystalline compounds (it was taken from reference books) and on the knowledge of the content of various structural groupings in glasses. The results are shown in Fig.4 (crosses) together with the available experimental data (circles). The deviation of calculated values from experimental ones does not exceed approximately 5 %.

From what I have said it follows that using the model of ideal associated solutions thermodynamic and other physical properties of glasses and melts can be assesed with a satisfactory accuracy on the basis of data available for crystalline compounds of the system. This approach allows not to perform as many experiments as it is usually necessary for a detailed study of glasses of a certain system, namely, one may restrict his study by an investigation of crystalline compounds instead of studying glasses of many different compositions within a desirable concentration range.

IV. Conclusions

It is shown that free energy of formation of crystalline borates (silicates, germanates) can be used for the estimation of various physical properties of the corresponding glasses considered on the basis of the model of ideal associated solutions.

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VI. References

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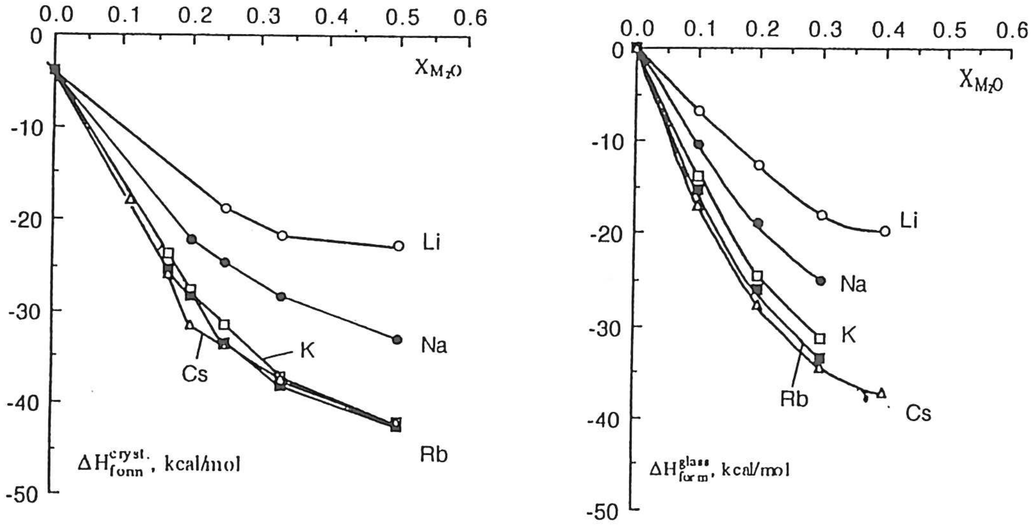

Fig.1 Enthalpies of formation of crystaline and glassy borates

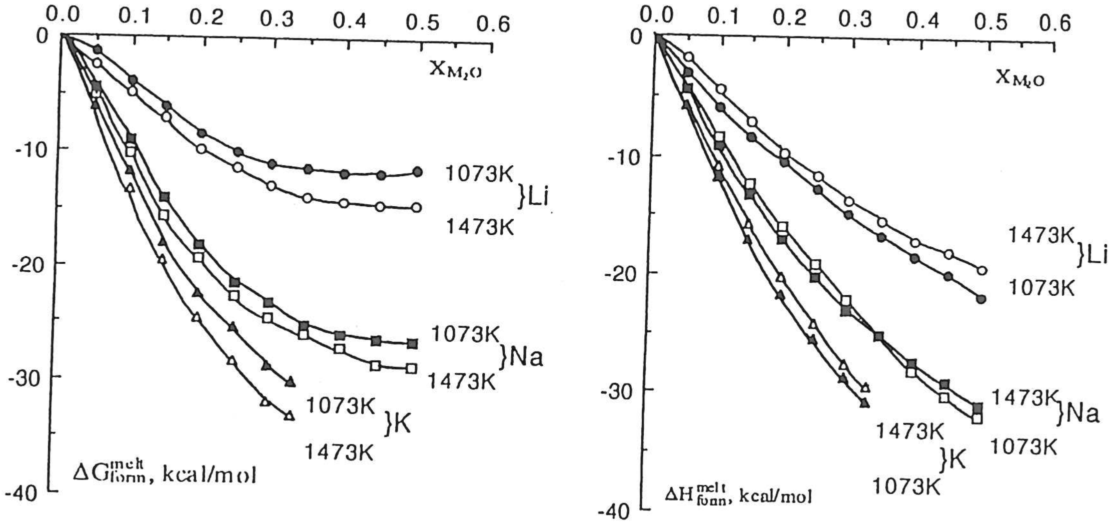

Fig.2 Free energies and enthalpies of formation of alkali borate melts

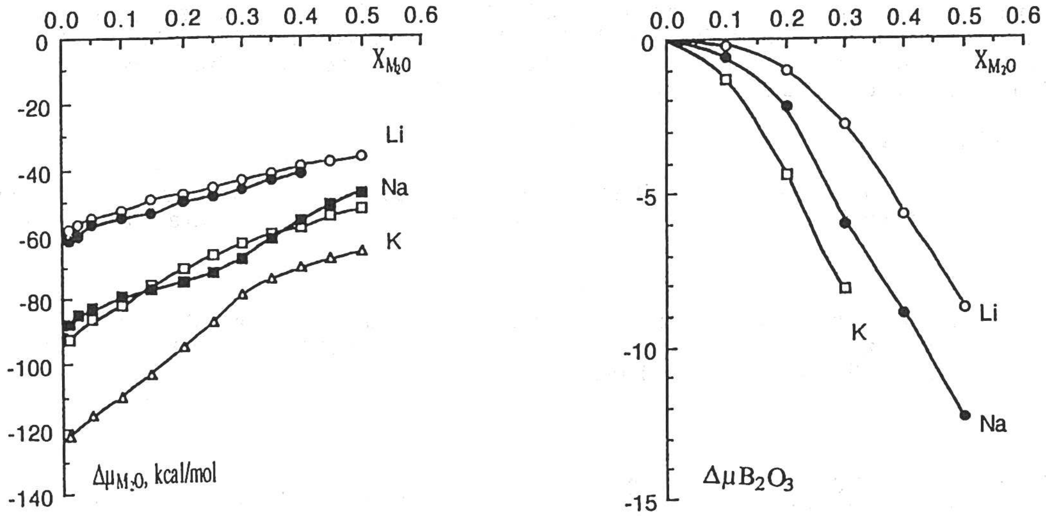

Fig.3 Partial molar free energies of alkali oxides and boric oxide

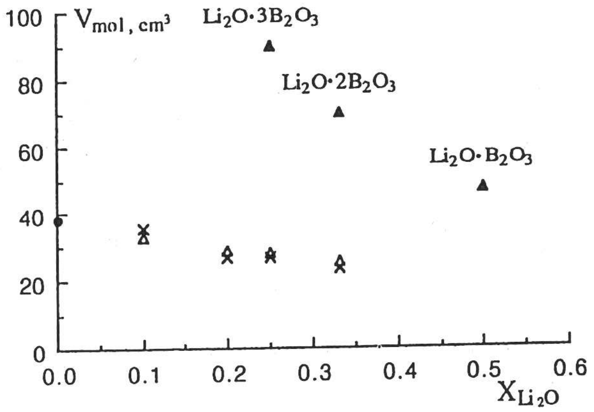

Fig.4 Molar volumes of lithium borate glasses and crystals. ▲:crystal, Δ:glass, ●:vitreous B_2O_3, x:glass, calculated from crystal volume and assumed structure of the glass.