The relationship between properties of melts and glasses and their structure : a thermodynamic approach

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The relationship between properties of melts (glasses) and their structure is one of the basic problems of glass science. Considering this problem, it should be remembered that the notion of the glass structure includes at least three different levels: (i) the distribution of the basic structural units that characterize the short-range order in glasses and melts, (ii) the distribution of associates formed from the basic structural units (the medium-range order), and (iii) the aggregation of the above associates that leads to the formation of structural elements whose size exceeds 20 Å. In the literature, experimentally observed changes in glass/melt properties are usually explained by structural changes considered only at the short-range order level and, as a rule, this approach requires the use of adjustable parameters. In this paper, an attempt will be made to show that information on the amounts of the basic structural units or ratio between them in glasses (melts) is insufficient for an adequate description of their properties. Also, it will be shown that the concept of the chemical structure can successfully be used for calculating, on a unified basis and without use of adjustable parameters, a large variety of glass properties.

As applied to oxide glasses and melts, formed from components with different chemical natures, the concept of the chemical structure implies the relative content of various salt-like products of interaction between the components, these products being similar in stoichiometry to the crystalline compounds existing in the phase diagram of the system in question. This concept yields an adequate modelling of various properties of glasses: the densities, the refractive indices, the heat capacities, the electrical conductivity and the diffusion coefficient. This concept also allows the following properties to be predicted: the chemical durability of glasses, their ability to dissolve gases and to crystallize, the character of crystallisation (bulk or surface), redox equilibria and the distribution of halogens in glasses and melts.