

Polymerisation, basicity, oxidation state and their role in ionic modelling of silicate melts

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Abstract

In order to describe and quantify the reactivity of silicate melts, the ionic notation provided by the Temkin formalism has been historically accepted, giving rise to the study of melt chemical equilibria in terms of completely dissociated ionic species. Indeed, ionic modelling of melts works properly as long as the true extension of the anionic matrix is known. This information may be attained in the framework of the Toop-Samis (1962a,b) model, through a parameterisation of the acid-base properties of the dissolved oxides. Moreover, by combining the polymeric model of Toop and Samis with the «group basicity» concept of Duffy and Ingram (1973, 1974a,b, 1976) the bulk optical basicity (Duffy and Ingram, 1971; Duffy, 1992) of molten silicates and glasses can be split into two distinct contributions, i.e. the basicity of the dissolved basic oxides and the basicity of the polymeric units. Application to practical cases, such as the assessment of the oxidation state of iron, require bridging of the energetic gap between the standard state of completely dissociated component (Temkin standard state) and the standard state of pure melt component at P and T of interest. On this basis it is possible to set up a preliminary model for iron speciation in both anhydrous and hydrous aluminosilicate melts. In the case of hydrous melts, I introduce both acidic and basic dissociation of the water component, requiring the combined occurrence of H⁺ cations, OH⁻ free anions and, to a very minor extent, of T-OH groups. The amphoteric behaviour of water revealed by this study is therefore in line with the earlier prediction of Fraser (1975).

Keywords

polymerisation;basicity;oxidationstate;water speciation;Temkin model

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References

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
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