



A simplified speciation model to quantify thermodynamic properties of binary silicate liquids

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We investigated a new approach to quantify thermodynamic properties of binary silicate liquids through the properties of the constituent species. The objective is to determine standard state enthalpies and entropies of the silicate tetrahedra with 0 to 4 bridging oxygen atoms (Q_0 to Q_4 respectively) as a simple function of the properties of the network modifier cation.

The approach chosen is a modified version of the quasi-chemical model (Guggenheim, 1952), based on the study by Gurman (1990). The latter study pointed out that the internal energy of silica tetrahedra changes non-linearly from Q_4 to Q_0 due to a non-linear increase in the number of interactions between non-bridging oxygen atoms. If i is the number of bridging oxygen atoms, the enthalpy of the species Q_i can be expressed as

$$H_i = a_H + b_H i + c_H i^2 \quad (1)$$

where a_H , b_H and c_H are fitted parameters. A similar relationship can be written for the entropy. A consequence of this model is that relative abundance of Q -species is dictated by the non-linear term of equation (1), and the speciation has to satisfy the relationship

$$\frac{X_0 \cdot X_2}{X_1^2} = \frac{X_1 \cdot X_3}{X_2^2} = \frac{X_2 \cdot X_4}{X_3^2} = e^{\left(\frac{-2 \cdot (c_H - T \cdot c_S)}{R \cdot T}\right)} \quad (2)$$

where R is the gas constant, T is the absolute temperature and X_0 to X_4 are the mole fractions of the Q_0 to Q_4 species, respectively. Using equations (2), mass and charge balance constraints as well as equilibrium reactions with solid phases, we quantified the thermodynamic properties of the tetrahedra and the cation using particle swarm optimization.

Various network modifier cations have various effects the interaction energy between non-bridging oxygen atoms in the tetrahedra. The intensity of this interaction is depending on the charge z and radius r of the cation. Thus, we test the possibility that the value of c_H and c_S for different binary systems is a simple function of the z/r ratio of the cation. This would be consistent with results from spectroscopic studies, suggesting a simple relationship between the speciation in various systems and z/r of the network modifier cation (Mysen, 2003). The result will be a model in which properties of the tetrahedral units in all binary silicate liquids could be predicted, and only the enthalpy and entropy of the modifier cations would need to be determined.

Guggenheim, E.A., 1952. Mixtures. Oxford University Press, London, 270 pp.

Gurman, S.J., 1990. Bond Ordering in Silicate-Glasses - a Critique and a Re- Solution. *Journal of Non-Crystalline Solids*, 125(1-2): 151-160.

Mysen, B., 2003. Physics and chemistry of silicate glasses and melts. *European Journal of Mineralogy*, 15(5): 781-802.