# Integrated Experimental and Modelling Study: the PbO-SiO2 System

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Background

1. In current versions of the public FactSage 7.3 database [1], the heat capacities of liquids oxides are assumed to be equal to that of the highest temperature polymorph of the solid oxide below its freezing point. This:
   a) Is inconsistent with theoretical and experimental understandings of the glass transition phenomenon [2-4],
   b) creates artificial step-like transitions on liquid heat capacity vs temperature plots, and
   c) results in discrepancies between the partial molar heat capacity of liquid oxides in the current model and those identified as ideal in previous studies [5-7].
2. No experimental data is available for the cristobalite liquidus between 90-100 mol% SiO_2 in slag. This represents a major source of uncertainty in the thermodynamic optimisations, as the cristobalite liquidus in this region has high sensitivity to the high-order SiO_2 parameters currently used to model the cristobalite liquidus.
   - This PbO concentration corresponds to typical PbO concentrations in the nonferrous metallurgical slag, and the projection of this area to high order systems is of industrial importance
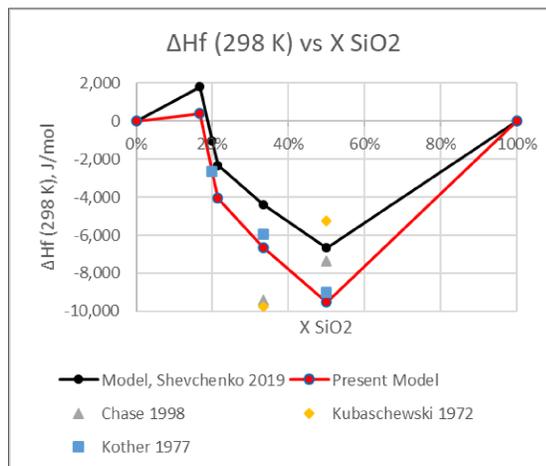

Modelled heat capacity of SiO_2 phases
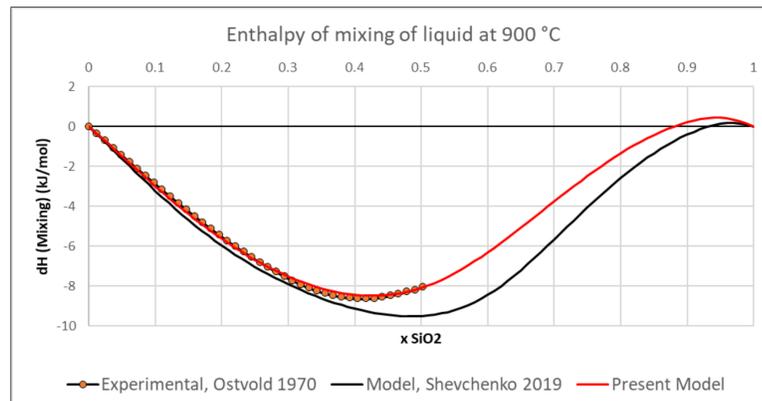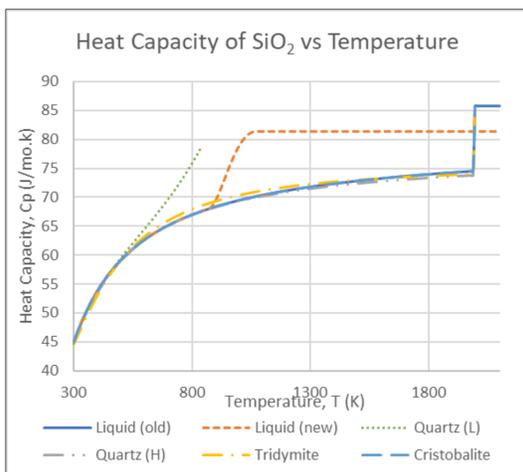
Modelled vs experimentally determined enthalpies of mixing
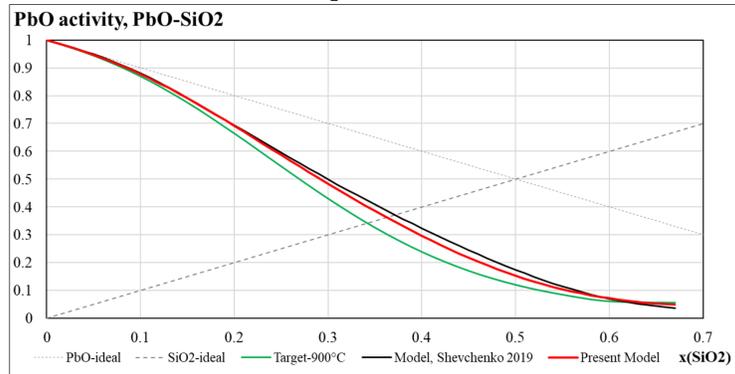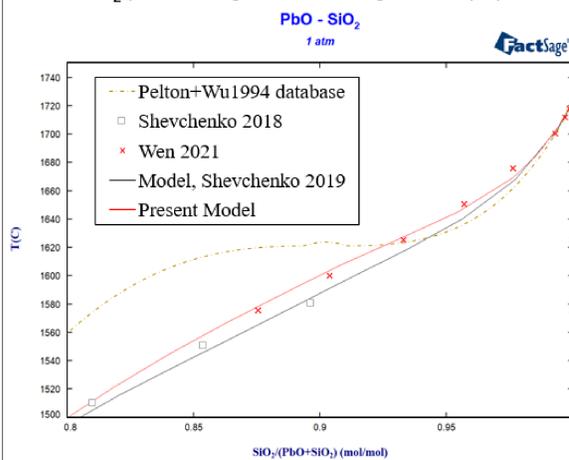

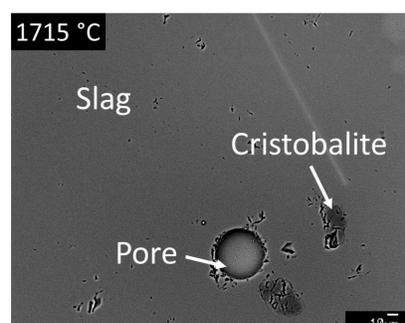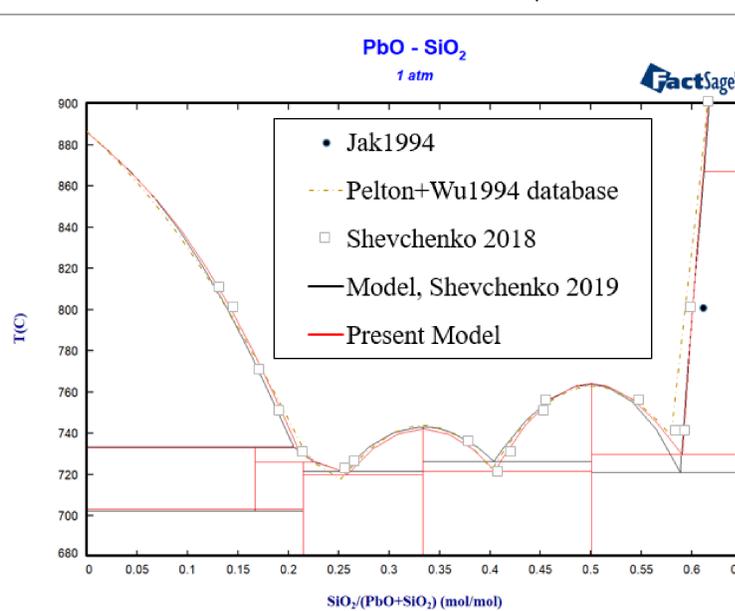Modelled vs target (composite of literature values) PbO activity in slag

Modelled vs literature enthalpies of formation
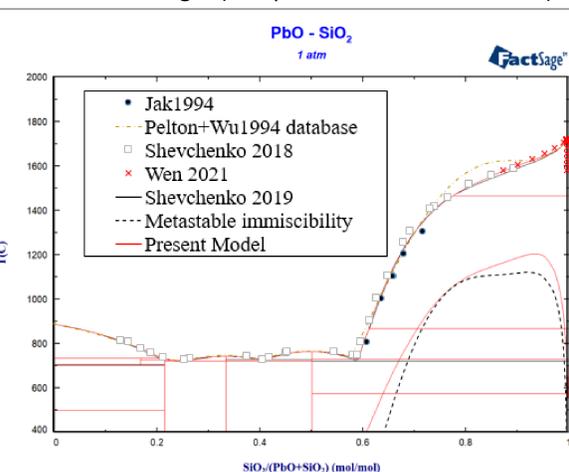
PbO-SiO₂ phase diagram, showing new exp. points

PbO-SiO₂ phase diagram, showing new exp. points

Above: PbO-SiO₂ phase diagram
Left: Sample microstructure of PbO-SiO₂ slag in equilibrium with Cristobalite

Aims

1. Re-optimise the $PbO-SiO_2$ system and end members to reduce or eliminate discrepancies present in previous models [8]; and
2. Experimentally study the $PbO-SiO_2$ system between 90-100 mol% SiO_2 in slag to reduce modelling uncertainty

Outcomes of experimental study

1. Phase equilibrium data was obtained between 1575 – 1715 °C, and 85 – 100 mol% SiO_2 in slag
2. SiO_2 concentrations measured in the present study was systematically 2 mol% lower than in a previous experimental study [9]. This was attributed to improvements in the furnace temperature calibration methodology

Outcomes of thermodynamic modelling

1. Modelled heat capacities of end members are closer to their true partial molar heat capacities below their freezing points, and represent glass transition behaviour more realistically.
2. Goodness of fit to experimental data improved overall compared to previous models

Further Work Needed

Calorimetry experiments to determine heat capacities, enthalpy and entropy of formation of lead silicates for which no data was found

References

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