Thermochemical Modeling of Molten Salt Systems: Is There An Ideal Solution?

C. Y. Jones and T. M. Besmann
Ceramic Surface Systems Group
Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

We report here preliminary results on the application of an ideal, associated-species thermodynamic model to the prediction of chemical activity in the salt system Na^+, K^+/CI^-, S^{2-}, SO^{4-}, CO^{3-}, OH^-. The majority of investigations on phase stability in salts mixtures of this type involve a two-sublattice mode;. However, the present work employs an ideal solution model with associated species in order to take advantage of some desirable features of this model. The associated species has been used most extensively to model oxides and alloys. It has an advantage of simplicity over non-ideal models – simplicity which is needed to maintain the convenience of use of this computational tool as the number of components increases. It also is expected to facilitate the introduction into the model of alkaline earth metals which create difficulties when a two-sublattice model is used.

Binary phase diagrams have been calculated for 17 of the 10 common-cation and four of the five common-anion systems, as well as a few ternary reciprocal systems with varying degrees of success. In general, the simple eutectic binary systems KCl-K_2SO_4, NaCl-Na_2CO_3, NaCl-Na_2SO_4, Na_2CO_3-NaOH, and KCl_2-K_2CO_3 are easily reproduced. The calculated and published phase diagrams have similar melting temperatures and eutectic compositions. Calculations on the following systems that contain other features such as peritectics, solid solubility, intermediate compounds, complex equilibria, etc., revealed only the general shape of the phase diagram: NaCl-KCl, Na_2CO_3-Na_2SO_4, Na_2SO_4-K_2SO_4, Na_2S-NaOH, Na_2SO_4-NaOH, K_2SO_4-K_2S, NaCl-NaOH, Na_2CO_3-KCl, Na_2SO_4-KCl, NaCl-K_2SO_4. Experimental phase diagrams have not been located for comparison to calculated phase diagrams for the K_2S-KOH, K_2CO_3-K_2S, KCl-KOH, NaCl-K_2S, and NaCl-K_2CO_3 systems. Additional efforts will be needed to verify these results. Calculations on the Na_2CO_3-Na_2S, NaCl-Na_2S, Na_2SO_4-Na_2S, and Na_2S-K_2S systems have not yielded satisfactory phase diagrams, most likely owing to the scarcity of data on Na_2S.

Evaluation of the a0plicability of this model to molten salts will continue with calculations on the remaining binary and ternary reciprocal systems. The range of systems will be extended to include ternary additive systems and alkaline-earth cations. Associated species will be introduced into the binary systems to account for non-ideal interactions. Results of these studies will be applied to the prediction of chemical behavior of molten salts found in Kraft recovery boilers used by the paper pulp industry where stress-corrosion cracking occurs. Calculation of activities of molten-salt species will provide information about the corrosive environment of steel tubes. Results will be coupled with alloy constituent activities to understand and predict corrosion in Kraft boiler tubes and aid selection of corrosion-resistant materials.

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