Calorimetric investigations in multi-component salt systems

D. Sergeev[1], E. Yazhenskikh[1], N. Talukder[1], D. Kobertz[1], K. Hack[2], M. Müller[1]

[1]Institute of Energy and Climate Research, Microstructure and Properties of Materials (IEK-2), Forschungszentrum Jülich, Jülich, 52425, Germany
[2]GTT-Technologies, Kaiserstr. 100, Herzogenrath, D-52134, Germany

Thermodynamic properties of the reciprocal NaCl–KCl–$NaNO_3$–KNO_3 system are of interest for selecting compositions, which can be used as phase change materials in thermal energy storage. The cascaded latent heat storage, where different salt systems are used as phase-change materials, is one of the simplest and probably the most effective way in implementation. Because of the thermodynamic, physical, chemical and economic aspects, multicomponent salt systems based on the cations Na^+, K^+ and anions Cl^-, NO_3^- are well applicable for designing a cascade thermal storage with small temperature steps and with the use of different compositions. This requires a precise knowledge of phase diagrams, enthalpies of phase transitions, enthalpy increments and information about the thermal stability. The realization of these storage system is available to a limited extend due to insufficient data.

Phase equilibria in the reciprocal NaCl–KCl–$NaNO_3$–KNO_3 system have been studied experimentally and were calculated using a thermodynamic dataset, which was presented on the GTT meeting 2015. By means of these results, two mixtures 7.5KCl-92.5$NaNO_3$ and 12.5NaCl-87.5KNO_3 with the lowest melting points of 549 K and 561 K, respectively, on the diagonal sections of the reciprocal system have been selected (Fig. 1) for further calorimetric investigations.

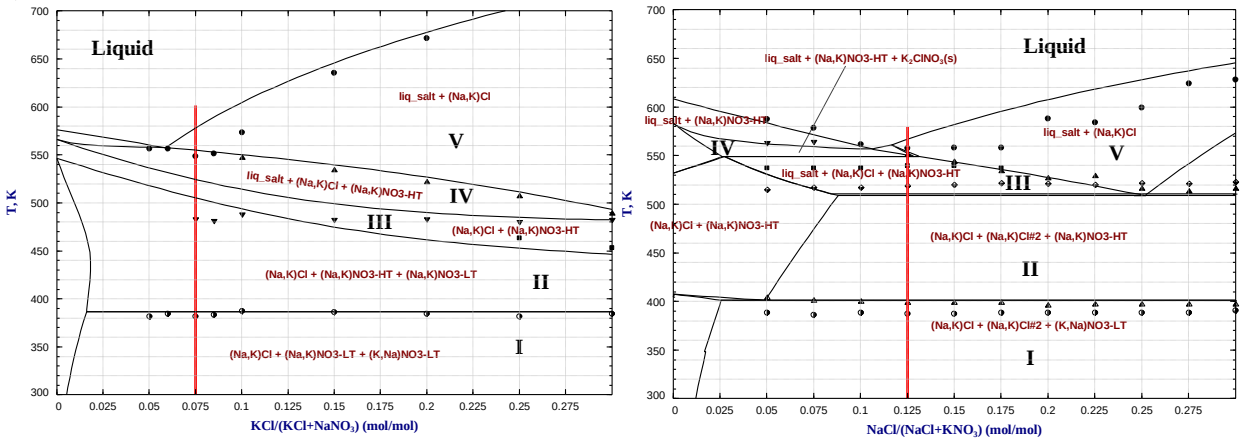

Fig. 1. Experimental and calculated data of the diagonal NaCl–KNO_3 and KCl–$NaNO_3$ sections in the reciprocal NaCl–KCl–$NaNO_3$–KNO_3 system

In the present work these mixtures were studied by the DSC and the DROP calorimetry. The heat capacities and the enthalpy increments of the solid and the liquid phases were obtained. The combination of these results allows the calculation of the phase transition enthalpies. DROP-calorimeter was used in a mode of slow heating rate (0.5 K/min) thermal analysis, where the DROP-calorimetric detector was applied for the direct determination of phase transition enthalpies. The thermodynamic properties were calculated using our own dataset of the reciprocal system. The analysis of our experimental and calculated results of enthalpy increments and heat capacities has confirmed that our dataset can be used for the prediction of thermodynamic properties of the full reciprocal system. Based on this conclusion three additional compositions 50$NaNO_3$-5.5KCl-44.5KNO_3, 28$NaNO_3$-12.4KCl-59.6KNO_3 and 13.1$NaNO_3$-11.2KCl-75.7KNO_3 of the system with liquidus temperatures at 481 K, 510 K, and 549 K were suggested as potential phase change materials.

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