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# Halite-sylvite thermoconsolution

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## ABSTRACT

An asymmetric binary Margules formulation for excess Gibbs energy, enthalpy, and entropy is adequate to describe the 1 bar halite-sylvite solvus in NaCl-KCl (Thompson and Waldbaum 1969). However, a binary Margules formulation is not adequate to describe excess volumes of single-phase chlorides in *P-V-T-X* from ambient *P-T* to ~20 kbar and 700 °C. Excess volumes across NaCl-KCl increase with temperature, decrease with pressure, and show systematic deficits in the consolute region. These patterns can be explained by the importance of a third component—vacancy defects that relieve the lattice stresses of K-Na size mismatch. New, two-phase observations in *P-V-T-X* allow delineation of the excess Gibbs energies to high pressures where the excess enthalpies and entropies do not depend on *T* at each *P*, but show significant variation between 1 bar and ~20 kbar. The volume, entropy, and enthalpy of K-Na mixing become more ideal at high pressure. But the solvus expands with pressure because entropy approaches ideality faster than enthalpy and, therefore, Gibbs energy of K-Na mixing becomes less ideal with pressure. The consolute temperature rises about 80 °C in 17 kbar, with little change in consolute composition. The binary Margules equation of state provides a prediction of the rise of the solvus that is impressively convergent with the new observations. This convergence is especially impressive given the clear inadequacies of the binary excess volume formulation on which the prediction is based.