

**THERMODYNAMIC MODELING AND CALCULATION  
OF PHASE EQUILIBRIA IN TERNARY WATER-SALT  
SYSTEMS CONTAINING  $K^+$ ,  $NH_4^+$ ,  $SO_4^{2-}$  AND/OR  $NO_3^-$  IONS**

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Complex fertilizers containing nitrogen, potassium, and sulfur are currently attracting increasing interest. Phase composition of such fertilizer is as important as chemical one, affecting how resulted product is hygroscopic, stable to detonation and effective in simultaneous release of macronutrients.

Phase equilibria in reciprocal  $K^+$ ,  $NH_4^+||SO_4^{2-}, NO_3^- - H_2O$  system are complicated due to existence of double salts and solid solutions. Slightest changes in type of granulator and conditions will result in a loss of predictive force of empiric results of phase-equilibria study. Thermodynamic modeling allows to calculate phase composition at any component ratios and conditions within its predictive range. Thus, the goal of the work is to obtain all solubility products and develop thermodynamic models of liquid and solid solutions in 298 – 373 K temperature range at least up in the ternary subsystems of the reciprocal  $K^+$ ,  $NH_4^+||SO_4^{2-}, NO_3^- - H_2O$ .

PSC model [1] was chosen for a liquid phase. Its parameters, along as solubility products of two double salts and  $(NH_4)_2SO_4$ ,  $NH_4NO_3$  are available for  $(NH_4)_2SO_4-NH_4NO_3-H_2O$  [1]. Solid solutions are absent in this system. PSC model parameters proposed in literature for  $K_2SO_4-H_2O$  [2] have too complex temperature dependence and give an ill extrapolation of liquid phase properties to supersaturated solutions, which result in artifacts at high ionic strength in ternary systems. Therefore, these parameters were re-evaluated. New PSC parameters for  $KNO_3-H_2O$  were obtained. Ternary parameters for liquid phase model were added to  $K_2SO_4-KNO_3-H_2O$ , solubility is adequate predicted.

The  $(NH_4)_2SO_4-K_2SO_4-H_2O$  and  $KNO_3-NH_4NO_3-H_2O$  systems require a solid phase model. Redlich-Kister model was chosen for sulfate and nitrate solid solutions. For sulfate solid solution, there is an isomorphous substitution for one structure, for nitrate solid solutions, there are three separate solid solutions. Phase equilibria were calculated without introducing new ternary parameters for liquid phase model. Predicted liquidus and tie lines between solutions agree with experimental ones.

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2. Li D. et al Phase diagrams and thermochemical modeling of salt lake brine systems. III.  $Li_2SO_4+H_2O$ ,  $Na_2SO_4+H_2O$ ,  $K_2SO_4+H_2O$ ,  $MgSO_4+H_2O$  and  $CaSO_4+H_2O$  systems // Calphad. 2018. . Vol. 60. P. 163 – 176. <https://doi.org/10.1016/j.calphad.2018.01.002>

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