

Experimental study of thermodynamic behavior of NaCl-KCl electrolytes in reaction with alkali feldspars under supercritical condition of water

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Anomalous properties of pure water phase such as extreme isothermal compressibility near its critical point cause severe problems for the development of equation of state applicable to important geological environments. In particular, understanding thermodynamics of electrolyte solutes whose strong inter- and intramolecular interactions depend on the state of the dipolar water molecules, requires a more comprehensive experimental dataset compared to previous studies (e.g. [1;2;3]). Therefore, we have conducted long lasting equilibrium experiments on Na/K exchange reaction between feldspars and chloride solutions.

Our experimental strategy aims at closing gaps revealed by a re-assessment of the most comprehensive data set available [1]. We show that the reported constancy of the K/Na concentration ratio over wide ranges of concentration is an artifact resulting from experimental conditions in the two-phase region and merely reflects the K/Na ratio of the liquid side of the immiscibility region. Taking the reported solute concentration ratio on vapor side as the closest proxy to the equilibrium constant allows monitoring KCl/NaCl activity coefficient ratios as a function of concentration.

We designed several experiments between alkali feldspars and the NaCl-KCl-H₂O ternary fluid phase system from very low (0.001 molal) to high (ca 13 molal) total chloride concentrations under various pressure-temperature conditions above critical point of water. Therefore, we can determine the effect of density of water on the actual equilibrium constant value in addition to studying the systematics of activity coefficient ratios of the solutes with total chloride concentration. Providing additional statistical insights from molecular view point makes a complementary contribution to better understanding of the obtained data microscopically.

REFERENCES

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