Contribution to the Prediction of Phase Equilibria in Electrolyte Solutions Under High Pressure and High Temperature

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This paper reports an investigation into the characterization of phase equilibria in electrolyte solutions at high pressure and high temperature. A procedure to enable calculations of mineral and gas solubilities in complex mixtures is presented. The model is based on Helgeson, Kirkham and Flowers modified equations of state (HKF) and on the semi-empirical interaction model introduced by Pitzer. HKF equations of state are used to calculate the dissociation constant of both mineral and gaseous species, and the Pitzer ionic interaction model is used to calculate the activity coefficient of dissolved species (i.e. ionic or neutral).

It is shown that this procedure applied to the Na-K-Ca-Mg-Ba-Sr-Cl-SO_4-H_2O leads to accurate results for temperatures ranging from 25 to 350 °C, and pressures ranging from 1 to 200 bar. Predicted strong electrolyte, i.e. NaCl, KCl, weak electrolyte, i.e. $BaSO_4$, $SrSO_4$ are compared with experimental values. CO_2-NaCl-H_2O, CO_2-Na_2SO_4, CH_4-NaCl-H_2O and H_2S-NaCl-H_2O systems have been investigated for gas solubilities for temperatures from 40 to 270 °C and pressures from 1 to 1800 bar. Our solubility data compare closely with literature values over the range of investigation.

The proposed approach, based on models which have theoretical justifications is suitable for simulating the behavior of complex mixtures encountered in the petroleum industry. Moreover it presents the advantage of doing more than simply smoothing experimental data.