Modelling of liquid-vapor-solid equilibria in the NH_3-CO_2-H_2O system

Maria G. Lioliou, Baard Kaasa, Svein Berg
Statoil ASA, R&D, N-7005, Trondheim, Norway
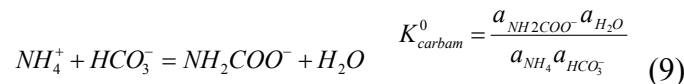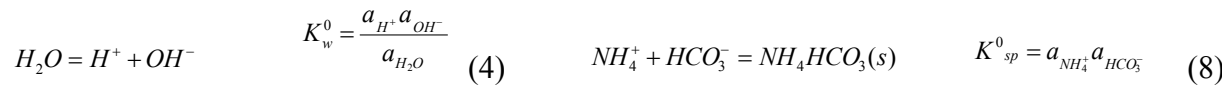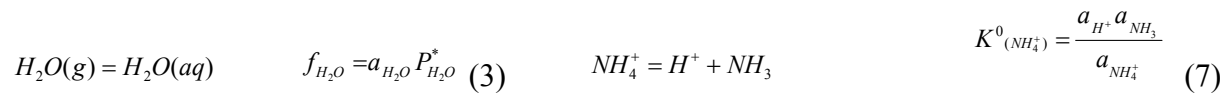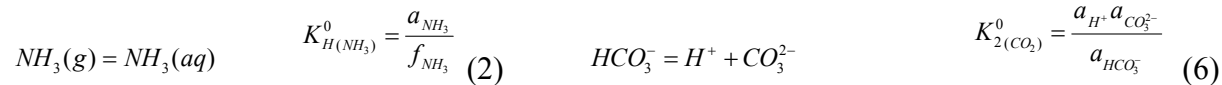mlio@statoil.com

Introduction

A thermodynamic model has been developed to describe CO_2 capture processes from ammonia solutions. MultiScale©[1] was used as a basis for the development of both the model and a new process simulation tool. The model consists of (a) components and equilibrium reactions, including mass balances and electro neutrality, (b) a numerical method to solve all the equilibria, (c) thermodynamic relations describing the pressure, temperature and composition dependencies of the ideal system and (d) phase models that describe the non-ideal behavior of the components and phases. The calculations are based on an extended database with salt solubility data, VLE data and thermal properties of the chemical species.

Components and equilibria

The components and main reactions of the system are given in equations (1)-(9). The respective thermodynamic equilibrium expressions were introduced in the model.

$$CO_2(g) = CO_2(aq) \qquad K^0_{H(CO_2)} = \frac{a_{CO_2}}{f_{CO_2}} \quad (1) \qquad CO_2 + H_2O = H^+ + HCO_3^- \qquad K^0_{1(CO_2)} = \frac{a_{H^+}a_{HCO_3^-}}{a_{CO_2}a_{H_2O}} \quad (5)$$

$$NH_3(g) = NH_3(aq) \qquad K^0_{H(NH_3)} = \frac{a_{NH_3}}{f_{NH_3}} \quad (2) \qquad HCO_3^- = H^+ + CO_3^{2-} \qquad K^0_{2(CO_2)} = \frac{a_{H^+}a_{CO_3^{2-}}}{a_{HCO_3^-}} \quad (6)$$

$$H_2O(g) = H_2O(aq) \qquad f_{H_2O} = a_{H_2O}P^*_{H_2O} \quad (3) \qquad NH_4^+ = H^+ + NH_3 \qquad K^0_{(NH_4^+)} = \frac{a_{H^+}a_{NH_3}}{a_{NH_4^+}} \quad (7)$$

$$H_2O = H^+ + OH^- \qquad K^0_w = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}} \quad (4) \qquad NH_4^+ + HCO_3^- = NH_4HCO_3(s) \qquad K^0_{sp} = a_{NH_4^+}a_{HCO_3^-} \quad (8)$$

$$NH_4^+ + HCO_3^- = NH_2COO^- + H_2O \qquad K^0_{carbam} = \frac{a_{NH2COO^-}a_{H_2O}}{a_{NH_4}a_{HCO_3^-}} \quad (9)$$
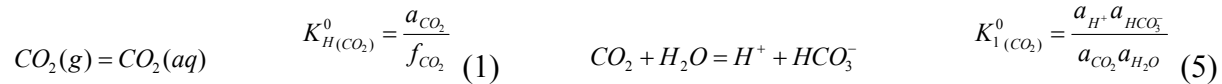
Phase models

There are three possible phases present in the NH_3-CO_2-H_2O system: gas, liquid and solid. Most of the reactions are taking place at low pressure, conditions under which the gas phase may be treated as ideal gas. The SRK equation of state, given by:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (10)$$

was included to describe possible non-ideal behavior of the gas phase in sections where the pressure might be high, such as a regenerator operating under high pressure. The aqueous phase is expected to be far from ideal due to high concentrations of dissolved CO_2 and NH_3. The Pitzer semi-empirical equation for the excess Gibbs energy of aqueous, salt-containing systems was used to describe the non-ideal behavior of the aqueous phase. Simplifications of the system were

adopted, thus the only parameters needed are the binary and ternary interaction parameters β_{ij}^{0} and τ_{ijk}, which are expressed through temperature dependent equations.

Model testing
The vapor pressure as a function of CO_2 concentration when NH_3 concentration is kept constant, at various temperatures is given in Figure 1. The total molality of ammonia is in the range 0.5-15 mole/kg H_2O and of CO_2 up to 15 mole/kg H_2O. Simulations were compared to approximately 500 data from the open literature[2,3,4,5,6]. The thermodynamic model is capable of describing reliably the vapor-liquid in the system in a temperature range from 20 to 100°C up to very concentrated solutions.
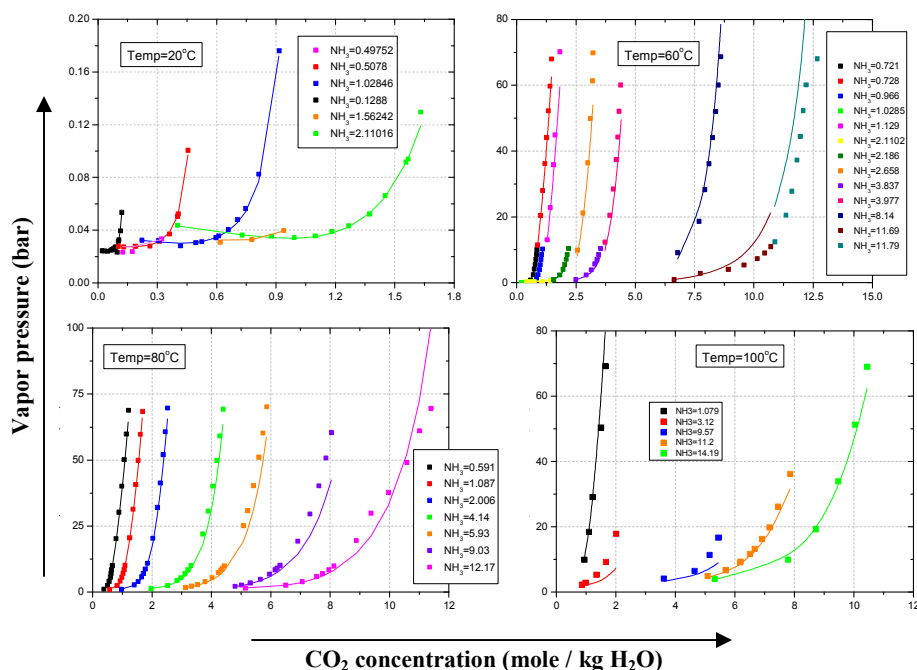

Figure 1: Vapour pressure for CO_2-NH_3-H_2O solutions, as a function of CO_2 concentration at different temperatures. Symbols are experimental values of vapour pressure, while lines represent the simulations.

References
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