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Development of a thermodynamic model for the $HF/H_2SO_4/HFSO_3/H_2O$ System Integrating Chemical Equilibrium

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Master thesis, Chemical Engineering

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INTRODUCTION

Hydrogen fluoride (HF) is the starting material for many fluorine-containing materials, such as refrigerants, fluorinated plastics, and battery electrolytes. Buss ChemTech licenses processes for the production of anhydrous HF. During HF production, mixtures of HF and H_2SO_4 occur. Mixing of HF and H_2SO_4 leads to the following equilibrium reaction: $HF + H_2SO_4 \rightleftharpoons HFSO_3 + H_2O$

In previous work involving HF and H_2SO_4, the concentrations of components were measured with NMR to determine the equilibrium of the reaction. These measurements were carried out with various concentrations of HF and H_2SO_4.

The goal of this work was:

- Understand the thermodynamic equilibrium of $HF/H_2SO_4/HFSO_3/H_2O$ system
- Modelling of the equilibrium to determine HF vapour pressure
- Improvement of HF production processes with the developed model

CONCEPT

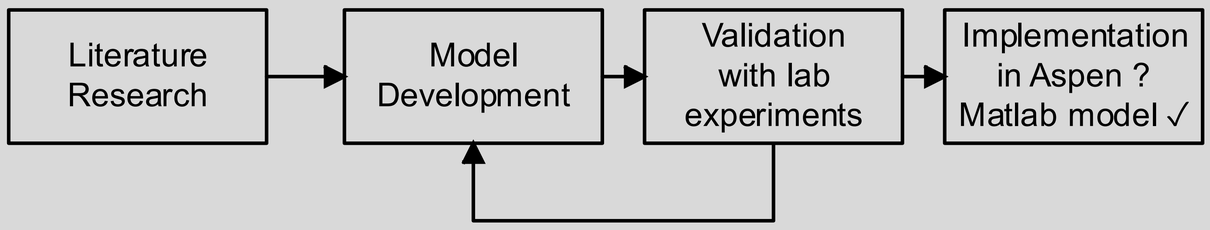

Fig. 1: Scheme of working processes for the thermodynamic model development.

This work contains the approach to describe the equilibrium with Electrolyte-NRTL, COSMPartial RS and an own created model with NRTL (Non-Random-two-liquid) inserting the reaction equilibrium constant (Fig. 2). This model was developed in Matlab to solve for the NRTL parameters specific to various HF concentrations.

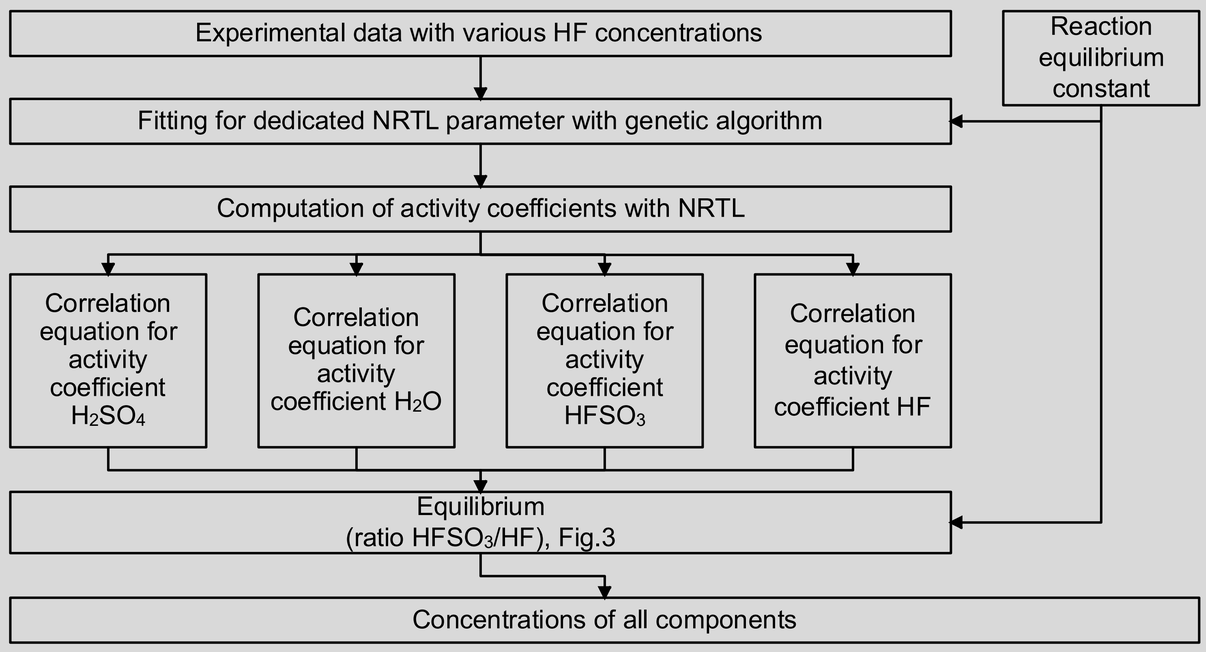

Fig. 2: Flow chart of the developed model with Matlab containing a genetic algorithm to solve for NRTL parameters for various HF concentrations.

RESULTS

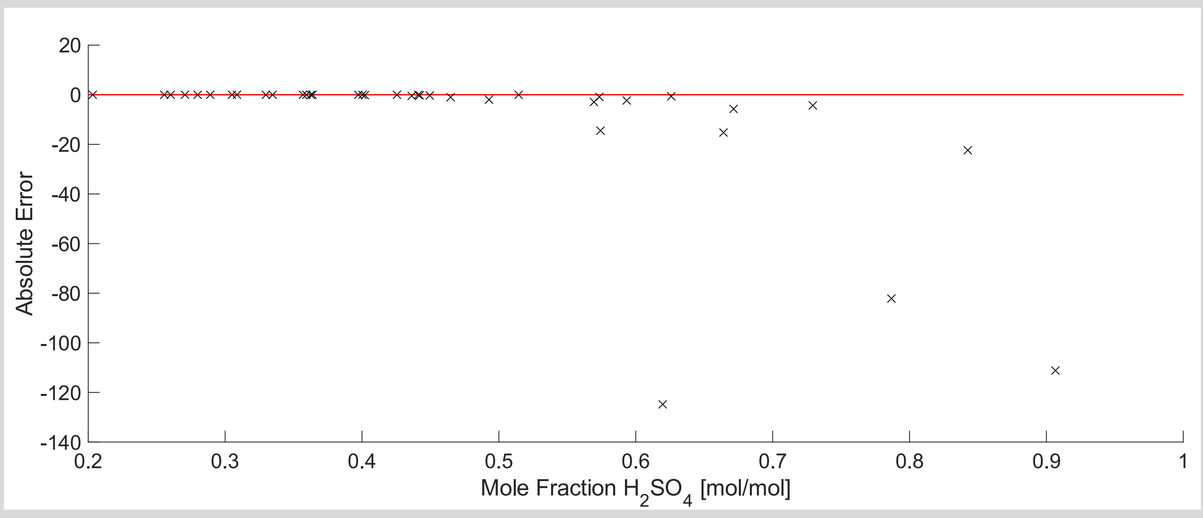

Fig. 3: Absolute error of model performance between prediction and measurement data [1,2].

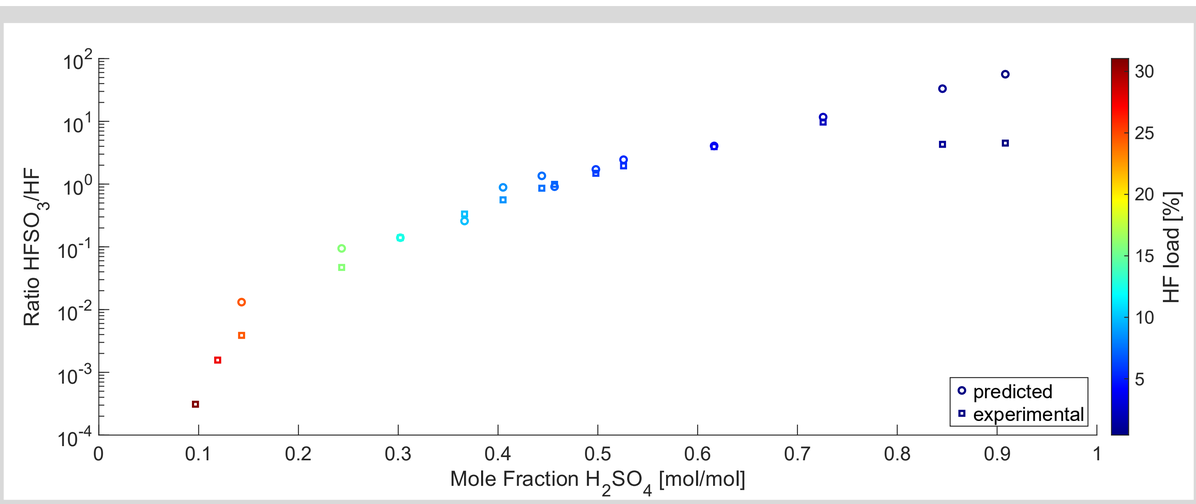

Fig. 4: Model Validation of predicted equilibrium applied and compared to literature data [3].

The model exhibited a high level of confidence in predicting the equilibrium at room temperature and liquid state, as shown in Fig.3 for the model performance and the model's application to literature data during validation, as illustrated in Fig.4. The HF load refers to a unit of HF concentration excluded from H_2SO_4 concentration.

The partial pressure of HF in the mixture of $HF/H_2SO_4/HFSO_3/H_2O$ is an essential property for thermodynamic simulations. The developed model was used to predict the equilibrium to further calculate the partial pressure of HF in the solution at two different temperatures. The results are shown in Fig.5 as the absolute errors in Pascal.

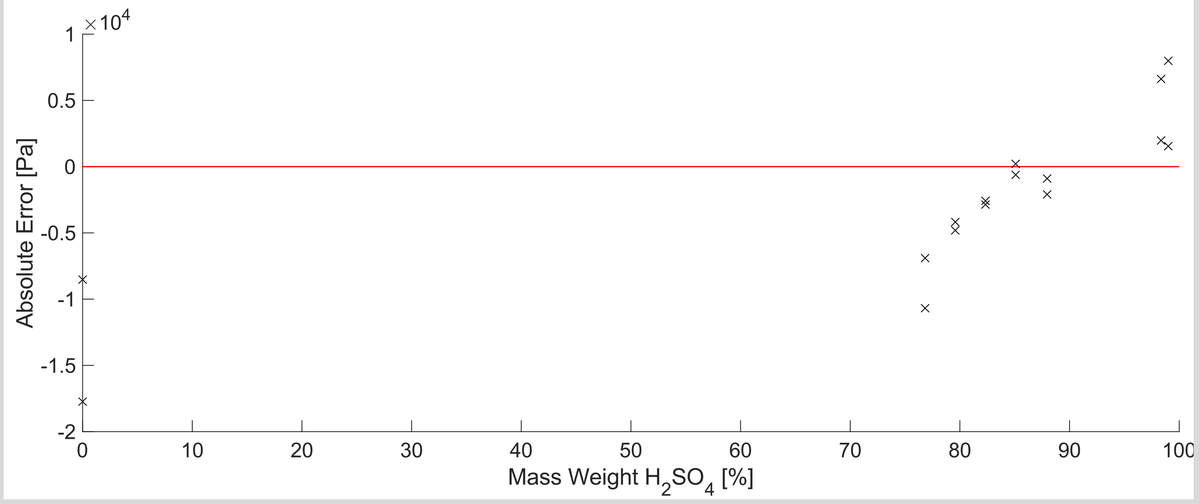

Fig. 5: Absolute errors between predicted and experimental determined HF partial pressure at 25°C and 50°C [1].

The developed model can generally predict the correct maximum HF partial pressure between 25°C and 50°C at a sulfuric acid mass fraction from 75% to 95%. However, the prediction is incorrect at boundary conditions of H_2SO_4 concentration and therefore not applicable for the whole range.

CONCLUSION

Modelling acid-acid interactions presents a significant challenge. The attempt to develop a model in Aspen using Electrolyte-NRTL, failed due to missing parameters for interaction with $HFSO_3$. Additionally, COSMO-RS was unable to describe the complex behaviour of this electrolyte system. However, with NRTL and the usage of an ideal reaction equilibrium constant, a model was developed which showed high confidence in the equilibrium prediction at moderate temperatures. The maximum HF vapour pressure occurs due to the high interaction between H_2SO_4 and H_2O in 85 w% H_2SO_4, where H_2SO_4 dissociates the most.

The next step involves implementation to Aspen to improve anhydrous HF production processes. To enhance results, dissociation could be integrated into the model.

REFERENCES

[1] Quirin, J. (2024) Untersuchung der Gleichgewichtslage H2SO4+HF <-> HSO3F + H2O mittels qNMR: Bachelor-Arbeit.

[2] Kürner, A. and Berger, F. (2024) FSS-018-HFSO3 NMR Dilution.

[3] Lange, W. (1933) Das Gleichgewicht H2SO4 + HF ⇄ HSO3F + H2O und seine Beeinflussung durch starke Säuren. Z. Anorg. Allg. Chem., 215 (3-4), 321–332.

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