CHEMICAL ENGINEERING TRANSACTIONS
VOL. 69, 2018
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Elisabetta Brunazzi, Eva Sorensen

ISBN 978-88-95608-66-2; **ISSN** 2283-9216
DOI: 10.3303/CET1869055

Thermodynamic Model to Study Removal of Chlorine, Silicon Tetrafluoride and other Uncommon Materials from Off Gases

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Off-gasses of a process require treatment to either neutralize or remove the toxic constituents. To accurately remove different materials in a gaseous stream, their interaction with multiple components is important to understand. The economic and the environmental impact from the failure to do so would be significant. In a particular off gas, the effects of fluorides like HF and SiF_4, SiO_2 is studied in tandem with the presence of traditional off gas components like NOx and chlorine, particularly at low concentrations.
This work would be useful for several industries like chemicals and mining. Traditionally these off gasses are cleaned in scrubbers and the effluent is discharged. If the pH of the effluent is not regulated, the effluent could have a significant impact in the aquatic ecosystem. This makes prediction of NO_3^- and NO_2^- concentration in the effluent, very important. The thermodynamic model was developed to be used in scrubber modelling.

1. Thermodynamic Model

The pre-requisite for this simulation study is the development of a complete thermodynamic model that mimics the absorption reactions, while being simple to reduce the convergence issues. This chapter explains the thermodynamic model developed. The chapter focuses on NOx reactions in liquid and gaseous phase, the HF-SiF_4–H_2O system and SiO_2 precipitation. The model was developed in Aspen Plus V7.3 (AspenTech) and ELECNRTL thermodynamic model was used (Chen C.C, et al, 1982). For interaction between the chloride and carbonate species, ASPEN's default reaction definitions in ELECNRTL model are used.

1.1 Fluoride absorption in water and SiO_2 Precipitation

The main fluoride compounds in the off gas are SiF_4 (Silicon Tetrafluoride) and HF (Hydrogen Fluoride). Both these compounds are highly soluble in water. Hydrogen fluoride absorption in water results in a solution of weak acid. The ionization constant of this solution is 7.4 x 10^{-4} at 25 °C making it slightly stronger than Acetic acid (Kohl A.L., Nielson R.,1997). The mechanism for absorption of SiF_4 available in literature is as follows

$$SiF_4 + H_2O \rightleftharpoons SiO_2 + 4HF \tag{1}$$

$$SiF_4 + 2HF \rightleftharpoons H_2SiF_6 \tag{2}$$

There is precipitation of SiO_2 at very low concentrations of H_2SiF_6 and as the concentration increases, solubility increases. The solubility of SiO_2 in water is very low at infinite dilution of H_2SiF_6. This effect is modeled as a salt precipitation reaction. Hence to begin with, soluble SiO_2 is produced from the reaction (1) and solid silica is then produced via,

$$SiO_2 \rightleftharpoons SiO_2(s) \tag{3}$$

The kinetic constant of this equation is predicted from literature data (Thomsen S.M,1952)
There is an apparent increase in the solubility of SiO2 with increase in pH (Iler R.K., 1979). This effect is modeled through the following reaction.

Please cite this article as: Ganesh S., Goebel H., Mathias P.M., 2018, Thermodynamic model to study removal of chlorine, silicon tetrafluoride and other uncommon materials from off gases, Chemical Engineering Transactions, 69, 325-330 DOI: 10.3303/CET1869055

$$SiO_2 + 2H_2O \rightleftharpoons HSiO_3^- + H_3O^+ \quad (4)$$

The net soluble SiO_2 is the sum of SiO_2 in liquid and the $HSiO_3^-$ ion.

1.2 NOx reaction model

To simplify for NOx absorption, an NO oxidation model has been used to represent the overall NOx absorption in the scrubber. This model has been developed by ASPEN Tech and is available ready to use open source. Three gas phase reactions are used to predict the behaviour of NOx.
Nitric oxide undergoes a slow homogeneous reaction with oxygen to yield nitrogen dioxide

$$2NO + O_2 \rightleftharpoons 2NO_2 \quad (5)$$

The kinetics for this reaction is not well defined. The commonly accepted third-order rate expression is valid if NO_3 is the only reaction intermediate. From Fluor experience, it is recommended use the traditional Bodenstein third-order rate expression (Bodenstien M., 1922): The chemical equilibrium constant of the oxidation reaction has been obtained from Aspen Plus.

The second reaction is the dimerization of the produced NO_2.

$$2NO_2 \rightleftharpoons N_2O_4 \quad (6)$$

In this simulation, the reaction is assumed to occur along with NO oxidation. The equilibrium between NO_2 and N_2O_4 is modelled as two opposing reactions. A rate constant of 10 times the NO oxidation rate constant has been used with satisfactory results.

The formation of nitric acid from water vapor and nitrogen dioxide (Equation 7) is a fast, gas-phase reaction that is effectively at equilibrium. The equilibrium constant of this reaction has been reported in literature (Koukolif M., and Marek J. 1968)

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO \quad (7)$$

These reactions have been modeled in Fortran subroutine in a plug flow reactor. The NOx reaction model is a kinetic model and will be assumed to take place outside the VLE system. In reality, this approximation leads to reaction in the vapor pipe line and not in a stripper.

1.3 Overall reactions and unknown compounds

Regarding the compounds used, H_2SiF6 is not available in ASPEN. This has been added as a user defined component. The enthalpy of formation is assumed to be zero. Another component that is unavailable in ASPEN is SiO_2 liquid (in solution). The enthalpy of formation is taken same as that of SiO_2(s).
O_2, CO_2, Cl_2, HClO, NH_3, HCl, N_2, NO_2, NO and N_2O_4 are treated as Henry's components. Henry's law constants are available for all other than N_2O_4 in Aspen Plus. For N_2O_4 the constant was obtained from literature (Schwartz, S. E., White W. H, 1981).
There are 14 equilibrium reactions, 3 dissociation reactions and 1 salt formation. The reactions are tabulated in Table 1. Equilibrium data for reactions i-x are available in ASPEN. For xi, xii and xiv the literature data has been used to regress. For reaction xiii the equilibrium data is calculated in ASPEN based on the heats of formation of the individual ions. For reaction iv, the equilibrium parameter is further tuned with literature values. The aspen parameters that were regressed listed in Table 2.
Reactions in Table 1 are all in Liquid phase. The gas phase reactions have been discussed in Section 2.2.

2. Results and Discussion

Data Regression in ASPEN PLUS with literature data is used to tune the model and predict thermodynamic coefficients. In this section, the results of the data regression runs are discussed for HF-H_2O VLE system, HF-SiF_4-H_2SiF_6 system and SiO_2 precipitation. The list of all the data obtained via regression is tabulated in Table 2.

Table 1: Overview of the liquid phase reactions

Sno	Type of Reaction	Reaction	Data in ASPEN
i	Equilibrium	H_2O + HCLO <--> CLO- + H_3O+	Yes
ii	Equilibrium	2 H_2O + CL_2 <--> HCLO + CL- + H3O+	Yes
iii	Equilibrium	HNO_3 + H_2O <--> H_3O^+ + NO_3^-	Yes
iv	Equilibrium	HF + H2O <--> F^- + H_3O+	Yes
v	Equilibrium	HCL + H2O <--> CL^- + H_3O^+	Yes
vi	Equilibrium	NH_3 + HCO_3^- <--> H_2O + NH_2COO^-	Yes
vii	Equilibrium	NH_3 + H_2O <--> OH^- + NH_4^+	Yes
viii	Equilibrium	H_2O + HCO_3- <--> CO_3^{--} + H_3O^+	Yes
ix	Equilibrium	2 H_2O + CO_2 <--> HCO_3- + H_3O^+	Yes
x	Equilibrium	2 H_2O <--> OH^- + H_3O^+	Yes
xi	Equilibrium	2 H_2O + SIF_4 <--> 4 HF + SIO_2	No – Regressed
xii	Equilibrium	2 HF + SIF_4 + 2 H_2O <--> 2 H_3O^+ + SIF_6^{2-}	No – Regressed
xiii	Equilibrium	Cl- + NO_3- <--> ClO- + NO_2-	No – Approximated from ASPEN
xiv	Equillibrium	SiO_2 + 2H_2O <-> H_3O+ + $HSiO_3$-	No - Regressed
xv	Salt	SiO_2(s) <-> SiO_2	No – Regressed
xvi	Dissociation	H_2SIF_6 --> 2 HF + SIF_4	N/A
xvii	Dissociation	NaOH --> OH^- + Na^+	N/A
xviii	Dissociation	KOH --> OH^- + K^+	N/A

Table 2: List of parameters regressed

S NO	System	Parameter Regressed	Value
1	H_2O and H_3O^+-SiF_6^{2-}	GMELCC/1	13.9
2	H_3O^+-SiF_6^{2-} and H_2O	GMELCC/1	-6.16
3	Equation xi	K-STOIC/1	-15.8
4	Equation xii	K-STOIC/1	-37.9
5	Equation xv	K-SALT	-3.88
6	Equation xiv	K-STOIC/1	-34
7	SiO_2-H_2O	NRTL	Aij: 4, Cij: 0.3
8	H_2O and H_3O^+-F^-	GMELCC/1	7.5
9	H_3O^+-F^- and H_2O	GMELCC/1	-3.4
10	HF and H_3O^+-F^-	GMELCC/1	7.3
11	H_3O^+-F^- and HF	GMELCC/1	-4.2
12	Equation x	K-STOIC/1	A: -9.23, B: 2883.99

GMELCC - Electrolyte-molecule/electrolyte-electrolyte binary energy parameter C in the electrolyte NRTL activity coefficient model.
K-Stoic - Equilibrium constants for equilibrium ionic reaction. Ln(K)=A+ B/T + C*ln(T) + D*T
Equilibrium constants for salt precipitation reaction. Ln(K)=A+ B/T + C*ln(T) + D*T

2.1 HF-H_2O system

The ELECNRTL property method is used for predicting the thermodynamic properties. The VLE of HF-H_2O system predicted from ELECNTRL is fine tuned with literature data from multiple sources. The literature data (directly imported from NIST database) is used to regress the electrolyte pair parameter as well as the kinetic parameter of the reaction (iv). The effect of temperature on HF-H_2O VLE at very low concentrations is well captured in the model.

In Figure 1, the x-axis has represents the weight fraction of HF and the y-axis represents the partial pressure of HF in the gas phase.

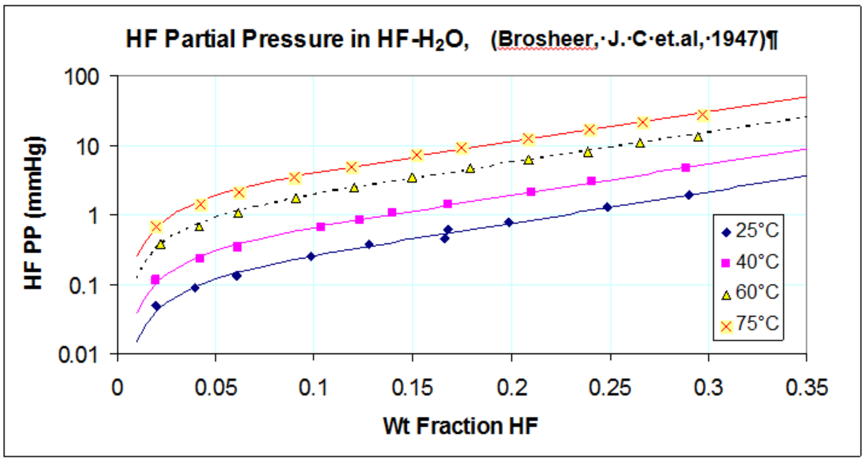
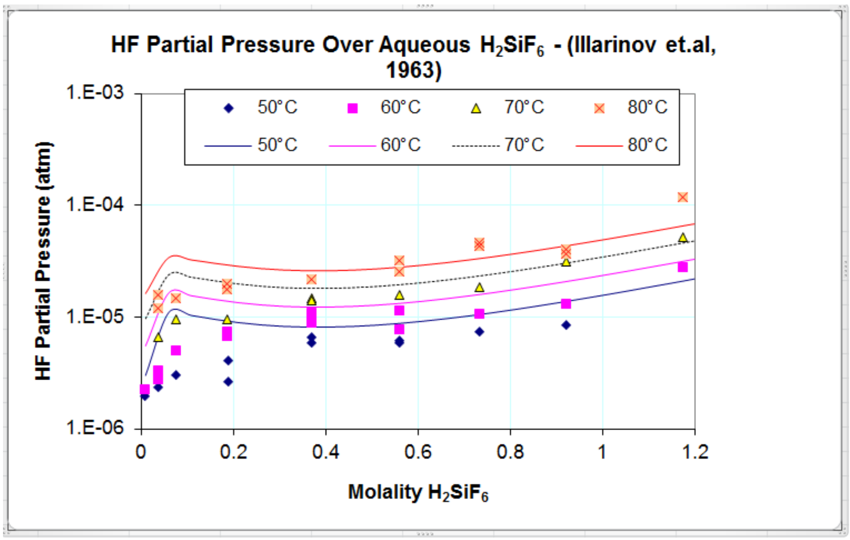


Figure 1:The VLE data of HF-H2O at different temperatures (Brosheer, J. C et.al, 1947)



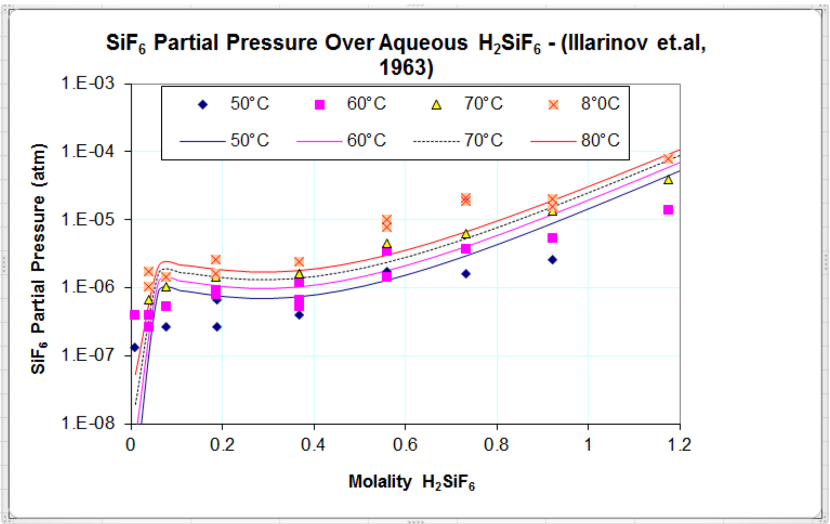


Figure 2: VLE(2) of HF-SiF4 -H2SiF6 System in semi-log scale.

2.2 HF-SiF_6-H_2SiF_6 system

The HF-SiF_4 system as seen from Section 2.1 is quite complex. The literature date is used to regress and obtain thermodynamic constants for electrolyte pair parameter and kinetic parameter for reactions xi, xii. The results of the various data-regression studies on this system are discussed in Section 2.1. Figure 2 and Figure 3 show the comparison of the literature data with the model prediction. Figure 2 the data points are from literature source while the straight lines are results of the model. Some of the inferences about this system from these graphs are :,

- HF is the more volatile component amongst HF and SiF_4.
- The H_2SiF_6 is a very strong acid. This effect is very well captured in the model (From Figure 3), though direct dissociation of H_2SiF_6. H_2SiF_6 as pure component is not part of the model.
- The effect of temperature on the VLE system is well captured in the model.
- There is an apparent sudden increase in the vapor pressures of SiF_4 at low concentrations of H_2SiF_6.
- There is a difference in the prediction of the pH from Figure 3. Possible reason could be, that even at the lower concentrations the polar effects of dissociation from equation ix and x are higher than equilibrium predictions. For the purposes of modelling an industrial scrubber this is considered sufficient as the difference is within the margin taken for design.

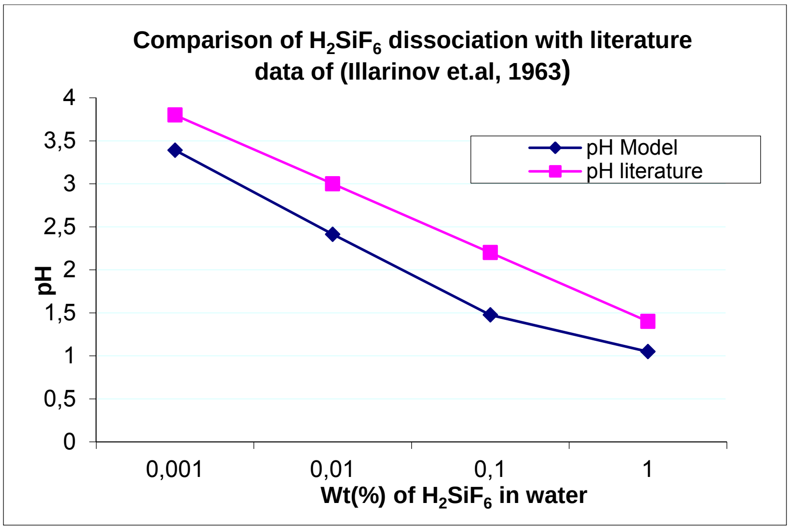


Figure 3: Comparison of H_2SiF_6 pH

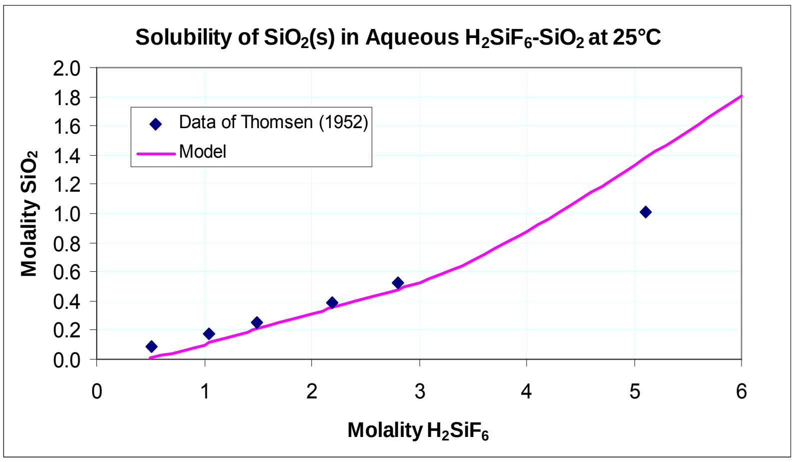


Figure 4: Solubility of SiO_2 in a solution of H_2SiF_6 (Thomsen S.M.,1952)

2.3 SiO_2 Precipitation

The literature data is used to predict the kinetic parameters for the equations (xiv) and (xv). The behaviour of SiO_2 precipitation is well captured as shown in Figure 4.The y axis shows the molality of SiO_2, which is a measure of SiO_2 in liquid. In Figure 4 the data at higher molality of H_2SiF_6 is not considered as it is not expected to be seen in the real industrial process. From Figure 4, the solubility at higher concentrations are not accurately captured due to the lack of experimental points.

3. Limitations of the model

Based on the above analysis, the following limitations are noted:

- The gas phase oxidation of NO to NO_2 takes place only in a plug flow reactor.
- The enthalpy of formation of SiO_2 is unknown and is approximated to the enthalpy of formation of SiO_2(s). This approximation could result in an inaccurate temperature prediction.
- At the very low concentration that is prevalent in the current system, the hexamerization is insignificant. Hence ELECNRTL property method is used and not ELECNRTL-HF
- The solubility of SiO_2 at higher pH could be an over prediction as there is no literature or experimental data to validate the model,

4. Conclusion

A thermodynamic model has been developed with the help of Data regression system available in ASPEN PLUS with the following features:

- Accurate representation of HF-H_2O binary system at low temperature and lower concentrations.
- Accurate representation of absorption of SiF_4 and HF in water, accurately capturing the equilibrium between SiF_4-HF-H_2O in gas and liquid phase along with reactive SiO_2.
- Accurate representation of solubility of SiO_2 in aqueous solution.
- A simple model for NOx absorption.

Thus the developed model in spite of the inherent limitations can be used a good starting point for simulating absorption. The developed thermodynamic model was successfully used in scrubber simulation.

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