STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLVI, 1-2, 2001

VAPOUR-LIQUID EQUILIBRIA IN AQUEOUS SOLUTIONS OF AMMONIA AND CARBON DIOXIDE USING NEURAL NETWORKS

GABOR S. SZASZ, ZOLTAN K. NAGY, SERBAN P. AGACHI

Babes-Bolyai University of Cluj-Napoca, Faculty of Chemistry and Chemical Engineering, Arany Janos 11, 3400, Cluj-Napoca

ABSTRACT. Aqueous electrolyte solutions are common in industrial processes. For ecological and economical reasons, aqueous liquids from chemical and petrochemical plants, containing weak electrolytes, have to be treated before they can be released into natural waters.

The physical interaction and chemical interactions in the liquid phase govern the equilibrium. Thus the mathematical model of the vapor-liquid equilibrium is a highly nonlinear algebraic equation system.

As an alternative to the classical model, burdened by many assumptions and crude estimations, the use of neural networks is proposed.

Introduction

Phase equilibrium in aqueous electrolyte solutions containing volatile substances like ammonia and sour gases, is an important issue from the point of view of process engineering. Typical examples are the cleaning of raw gases in power stations, the Solvay process for the production of sodium carbonate or applications on the field of environmental protection.

Due to chemical reactions in the liquid phase and strong deviations from ideality the NH_3-CO_2 –H_2O has complex behavior. Edwards et al. [1,2] developed a mathematical model, based on Pitzer equation [3] and the virial equation of state, for prediction of the system behavior at different concentrations and temperatures.

The model was further extended and developed by Kurz et al.[4] and Krop [5] in order to enlarge the temperature and concentration domain.

Experimental information on phase equilibrium in the system NH_3-CO_2 – H_2O are now available over a wide range of temperatures and concentrations. Thus this paper propose the use of ANN as an alternative modeling.

Modeling

Components involved in the NH_3-CO_2 –H_2O system are present not only in neutral form, but also in ionic form, due to chemical reactions in the liquid phase. These reactions are the following:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad \text{(I)}$$

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \quad \text{(II)}$$

$$HCO_3^- \rightleftharpoons CO_3^= + H^+ \quad \text{(III)}$$

$$NH_3 + HCO_3^- \rightleftharpoons NH_2COO^- + H_2O \quad \text{(IV)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(V)}$$

Thus in the liquid phase are present nine species with concentrations depending on the chemical equilibrium. Due to these five reactions and interactions between species the difference between the real concentration and total concentration of ammonia and carbon dioxide is significant with direct influence on vapor phase.

To calculate the true concentrations in the liquid phase the condition for chemical equilibrium is applied for reactions I-V:

$$K_{I-V}(T) = \prod_i (m_i \cdot \gamma_i)^{\nu_{i(I-V)}} \quad (1)$$

The balance equations for the ammonia and carbon dioxide and water are:

$$m_{NH_3,tot} = m_{NH_3} + m_{NH_4^+} + m_{NH_2COO^-} \quad (2)$$

$$m_{CO_2,tot} = m_{CO_2} + m_{HCO_3^-} + m_{CO_3^=} + m_{NH_2COO^-} \quad (3)$$

$$x_w = \frac{\frac{1000}{M_w}}{\frac{1000}{M_w} + \sum_{i \neq w} m_i} \quad (4)$$

The last equation to take in to account is the charge balance

$$m_{NH_4^+} + m_{H^+} = m_{OH^-} + m_{HCO_3^-} + 2 \cdot m_{CO_3^=} + m_{NH_2COO^-} \quad (5)$$

This set of equation has to be solved using an iterative procedure. The calculation requires: temperature dependent equilibrium constants $K_1 – K_5$ [7], activity coefficients of all species present in the liquid phase, Henry's constants [7,8] for ammonia and carbon dioxide in pure water as well as information on the vapor phase nonideality and the partial molar volumes of the dissolved gases [2].

The total pressure and the composition of the vapor phase can be calculated from:

$$p \cdot y_w \cdot \varphi_w^v = p_w^s \cdot \varphi_w^s \cdot a_w \cdot e^{\frac{v_w \cdot (p - p_w^s)}{R \cdot T}} \quad (6)$$

$$p \cdot y_i \cdot \varphi_i^v = H_{i,w}(T) \cdot \gamma_i \cdot m_i \cdot e^{\frac{v_{i,w}^{\infty}(p - p_w^s)}{R \cdot T}} \quad (7)$$

where i = NH_3, CO_2

Neural Networks

A neural network is a computer program architecture for nonlinear computations, which is composed of many, highly interconnected, simple elements operating in parallel. These elements (neuron) are inspired by biological nervous systems. An individual processing element (neuron) can have any number

of inputs, but only one output that is generally related to the inputs by a transfer function. The most frequently used transfer functions are: sigmoid function, hyperbolic tangent function, sine function, linear and saturated linear transfer function. The argument of the transfer function is the sum of the input elements of the corresponding neuron, each input being multiplied by the associated weight which shows the strength of the connection between two neurons.

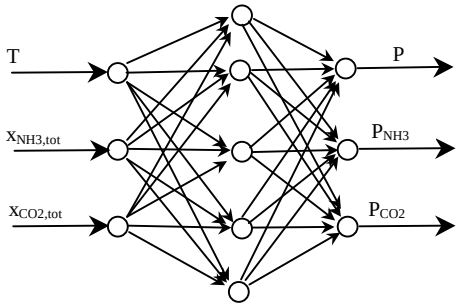

Figure 1. Structure of a Neural Network

A simple neural network is presented in figure 1, such a structure can be more complex with a number a hidden layers and variable number of neurons in each layer. The number of layers and neurons in each layer are very important configuration information determined by trial.

Results and Discussion

The calculations were made in Matlab 5.3 modeling environment using the Neural Network toolbox v3.0 provided with this software. The neural network used in this work was a feed forward network with three neurons in the input ($m_{NH3,\ tot}$, $m_{CO2,\ tot}$ and T) and output layers (p_{NH3} , p_{CO2} and p). Further the network had 2 hidden layers with 23 and 11 neurons each. The transfer function used was a hyperbolic tangent sigmoid.

Tabel 1.

Vapor-liquid equilibrium results at 353.15K

$m_{NH3,tot}$	$m_{CO3,tot}$	Experimental			ANN		
		p_{NH3} [MPa]	p_{CO2} [MPa]	p [MPa]	p_{NH3} [MPa]	p_{CO2} [Mpa]	p [MPa]
5.93	3.326	0.0173	0.171	0.2274	0.0171	0.1686	0.2306
9.03	5.304	0.022	0.291	0.3507	0.0215	0.2929	0.3604
12.17	7.736	0.0203	0.649	0.7033	0.0211	0.6399	0.7082

The vapor-liquid experimental data used (more then 300 points) for training and testing the network were taken from literature [2,4,9]. The available data was used to create two data sets, a bigger one for training of the network and a smaller for testing purpose. The network was trained using a backpropagation algorithm with Bayesian regularization.

The results are presented in tables 1 to 4, all were taken from the testing set. As can be seen, the calculated values are in good agreement with the measurements. Calculation made by the analytical model also showed good agreement with the measurements, but the results are more parameter dependent and the model needs considerably more development effort.

Further, the computational time for the analytical model is considerable higher around 1s while the neural network model execution time is only 0.04s.

Table 2

Vapor-liquid equilibrium results at 360.15K

$m_{NH3,tot}$	$m_{CO3,tot}$	Experimental			ANN		
		p_{NH3} [MPa]	p_{CO2} [MPa]	p [MPa]	p_{NH3} [MPa]	p_{CO2} [MPa]	p [MPa]
1.638	0.954	0.0053	0.157	0.2181	0.0051	0.1607	0.2223
3.406	2.423	0.0044	0.591	0.6542	0.0041	0.5938	0.6507
4.78	3.335	0.0055	0.724	0.7851	0.006	0.7297	0.7849
6.54	2.831	0.0388	0.0936	0.1869	0.0391	0.0918	0.1837
7.759	4.329	0.0213	0.299	0.3736	0.0217	0.3062	0.3753
9.812	4.28	0.0588	0.1	0.2119	0.0698	0.0873	0.2146
12.35	9.285	0.0114	3.581	3.663	0.0136	3.5537	3.6372
12.48	7.062	0.0275	0.448	0.5184	0.0267	0.4439	0.5189
14.07	7.323	0.0448	0.284	0.3746	0.0449	0.2767	0.3728

Tabel 3

Vapor-liquid equilibrium results at 373.15K

$m_{NH3,tot}$	$m_{CO3,tot}$	Experimental			ANN		
		p_{NH3} [MPa]	p_{CO2} [MPa]	p [MPa]	p_{NH3} [MPa]	p_{CO2} [MPa]	p [MPa]
0.95	0.438	0.007	0.124	0.2294	0.0074	0.1455	0.2493
1.078	0.94	0.001	0.905	0.9938	0.0007	1.039	1.1359
3.964	1.848	0.0311	0.245	0.374	0.0307	0.2375	0.3572
7.858	3.327	0.0736	0.205	0.3559	0.0736	0.2073	0.3525
8.08	4.436	0.033	0.663	0.7836	0.0304	0.6574	0.7485
11.17	4.016	0.168	0.114	0.377	0.1509	0.1244	0.3557

Table 4

Vapor-liquid equilibrium results at 393.15K

$m_{NH3,tot}$	$m_{CO3,tot}$	Experimental			ANN		
		p_{NH3} [MPa]	p_{CO2} [MPa]	p [MPa]	p_{NH3} [MPa]	p_{CO2} [MPa]	p [MPa]
0.703	0.419	0.0044	0.539	0.7403	0.0048	0.5638	0.7586
3.821	1.06	0.0943	0.184	0.4719	0.1056	0.2187	0.4979
5.822	2.284	0.0923	0.531	0.7823	0.0787	0.5334	0.7815
7.99	4.748	0.0363	2.795	2.9705	0.0359	2.9734	3.1614
11.95	7.174	0.0468	3.972	4.1609	0.0513	3.9561	4.1238

The prediction error of the neural model varies between 0.1% and 20%. This shows that the experimental data were insufficient and not very well distributed. In future when new measurements would be available the neural model can be trained with the new data making the model more precisely in predictions

Conclusions

The use of Artificial Neural Networks was proposed for vapor-liquid equilibrium modeling of NH_3-CO_2-H_2O system. It was showed that the results obtained with the neural network were in good agreement with the measurements. Additionally the Neural Network model presented considerably smaller execution times making it suitable for process modeling.

LIST OF SYMBOLS

H – Henry's constant
K_{I-V} – reaction equlibrium constant
m_i – molality of component i
p - total pressure
p_i – partial pressure of component I
p_w^s – partial pressure of water at saturation
R – universal gas constant
T - temperature
v_m – partial molar volume
y_i – component mole fraction

Greek Letters
γ – activity coefficient
φ – fugacity coefficient
ν - stoichiometric coefficient of component i.

REFERENCES

1. T J Edwards, J Newman , J M Prausnitz, *AIChE Journal*, 21(2), 1975, 248-259.
2. T J Edwards, G Maurer, J Newman, J M Prausnitz, *AIChE J.*, 24(6), 1978, 966-976.
3. K S Pitzer, *The Journal of Physical Chemistry,* 77(2), 1973, 268-277.
4. F Kurz, B Rumpf, G Maurer, *Fluid Phase Equilibria, 104*, 1995, 261-275.
5. Jadwiga Krop, *Fluid Phase Equilibria, 163*, 1999, 209-229.

6. K Thomsen, P Rasmussen, *Chemical Engineering Science*, 54, 1999, 1787-1802
7. V Bieling, B Rumpf, F Strepp, G Maurer, *Fluid Phase Equilibria,* 53, 1989, 251-259.
8. K Kawazuishi, J M Prausnitz, *Ind.Eng. Chem.Res.,* 26, 1987, 1485-1488.
9. U Gopert, G Maurer, *Fluid Phase Equilibria, 41*, 1988, 153-185.
10. Ellen M Pawlikowski, J Newman, J M Prausnitz, *Ind. Eng. Chem. Process Des. Dev*., 21, 1982, 764-770.