

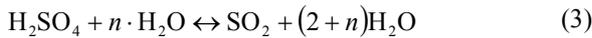
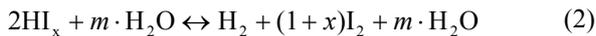
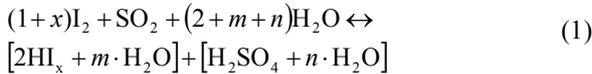
## Improvement of the Neumann's NRTL Model in the HI section of the SI Thermo-chemical Water Splitting Cycle

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### 1. Introduction

Iodine-Sulfur (IS) cycle [Fig.1] is one of the most promising options for the thermo-chemical water splitting technology for the massive production of hydrogen using the high temperature thermal energy from nuclear reactors. This cycle was originally studied in the 1980's by General Atomic Corp. (GA) [1], which consists of three sections: Bunsen section, Sulfuric acid section, and Hydrogen-Iodide (HI) section as follows.



Neumann's NRTL model has been widely used in the distillation column evaluations and flow sheet developments of the HI section in the thermo-chemical water splitting cycle. CEA had studied the HI section distillation column evaluation with the chemical process simulator PROSIM using Neumann's NRTL model. HI-section of SI cycle with reactive distillation has chosen Neumann's NRTL model with his binary parameters to predict the system pressure in distillation [2].

### 2. Reproduction of Neumann's model result

From the thermodynamic point of view, the HI section of the SI thermo-chemical cycle has so far remained uncertain compared to the Bunsen section and sulfuric acid section. The binary (HI-H<sub>2</sub>O) or ternary (HI-I<sub>2</sub>-H<sub>2</sub>O) mixtures encountered in the HI section are strongly non-ideal solution and partially immiscible system so it is quite difficult to model and predict the thermodynamic behaviors in them [3].

#### 2.1 Neumann's model

Neumann proposed a modified NRTL model. The basic idea of the NRTL model (Renon and Prausnitz) is based on the local composition theory, which is applicable to the strongly non-ideal mixture, and also to the partially miscible mixture as well as completely miscible mixture [4].

$$\ln \gamma_i = \frac{\sum_j^N \tau_{ji} G_{ji} x_j}{\sum_j^N G_{ji} x_j} + \sum_k^N \frac{x_k G_{ik}}{\sum_j^N G_{jk} x_j} \left( \tau_{ik} - \frac{\sum_n^N \tau_{nk} G_{nk} x_n}{\sum_j^N G_{jk} x_j} \right)$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$$

$$\alpha_{ij} = 1.2 \left( c_{ij} + \frac{d_{ij}}{T} \right) = -\alpha_{ji}, \quad G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

$\alpha_{ij}$  : non-randomness in mixture

$\tau_{ji}$  : energy difference between  $i-j$  and  $j-i$  Interactions

If the molar fraction and property of each component in the liquid phase are determined, the total pressure of vapor phase can be calculated according to the modified Raoult's law. For the H<sub>2</sub>O-HI binary mixture, the total vapor pressure of HIx solution is estimated by summing up the partial pressures of H<sub>2</sub>O and HI. For the HI-I<sub>2</sub>-H<sub>2</sub>O ternary mixture, the partial pressures of HI, I<sub>2</sub> and H<sub>2</sub>O are summed up. If the hydrogen (H<sub>2</sub>) is generated through the HI decomposition process in the vapor phase, its contribution should be accounted for, additionally to the partial pressures calculated by modified Raoult's law.

#### 2.2 Reproducibility Test

In order to evaluate the calculation result with experimental data, relative deviation is suitable evaluation method. The relative deviation (RD) defined below is used to check the extent of errors of the calculated values from the experimental data.

$$RD(\%) = \frac{P^{EXP} - P^{CAL}}{P^{EXP}} \times 100 \quad (4)$$

The relative deviation stays within 8% for the total pressures in the binary mixtures (75 data). For the ternary solution, the relative deviation is less than 20% including above 150C (210 data) and below 150C (71 data). On the whole, the results are comparable with the Neumann's work

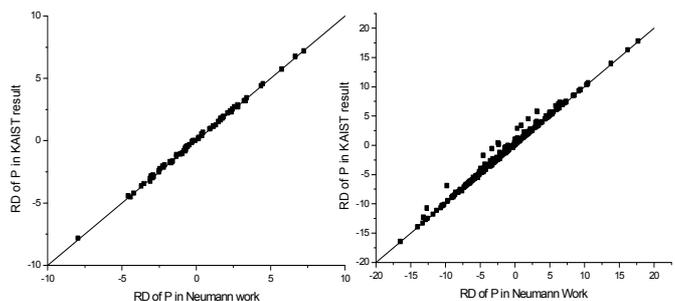


Fig. 1 Relative Deviation Comparison in Binary and Ternary mixture in HI section

### 3. Ideas to improve Neumann's model

#### 3.1 Non-Randomness Factors

Neumann thought the non-randomness factor is a function of temperature, set the base of the exponent at 1.2, and allowed the negative values for the non-randomness factors for the convenience of stable regression. However, by thermo-physical definition, the non-randomness parameter should not be less than "zero", and the value of  $i$ - $j$  pair is identical to that for  $j$ - $i$  pair, say  $\alpha_{ij} = \alpha_{ji}$ . For this reason, the commercial chemical process simulators such as ASPEN<sup>+</sup> and PROSIM do not deal with the negative values for the non-randomness parameters, such as the negative non-randomness values of Neumann's model.

Neumann's model	KAIST model
$\alpha_{ij} = 1.2^{(c_{ij}+d_{ij}/T)}$	$\alpha_{ij} = 1.4^{(c_{ij}+d_{ij}/T)}$
$\alpha_{ij} = -\alpha_{ji}$	$\alpha_{ij} = \alpha_{ji}$

#### 3.1 Solvation Number $m$

The solvation number is defined by the ratio of the number of HI molecules to that of H<sub>2</sub>O molecules, the concept of which is illustrated in Fig. 5. Neumann assumed that the solvation number is five (5). The authors of the present study assume the solvation number is strongly correlated with the azeotropic behavior of HI-H<sub>2</sub>O solution. HI molecules are dissolved and ionized into H<sup>+</sup> and I<sup>-</sup> in the H<sub>2</sub>O solvent, and solvated forming a complex of (H<sup>+</sup>-H<sub>2</sub>O) or (I<sup>-</sup>-H<sub>2</sub>O). Molecules of H<sub>2</sub>O or HI that are not involved in the solvation are relatively free and easy to evaporate. Thus, practical solvation number ( $m=5.4$ ) is proposed.

Neumann's model	KAIST model
$m = 5$	$m = 5.4$

#### 3.1 Results

The ideas discussed in Sections 3-1 and 3-2 were incorporated into the model, and regression was carried out to determine the binary parameters. A set of NRTL parameters with the improved model for the binary mixture is provided in Table 1. The predicted total pressures of HIx solution are comparable in terms of relative deviation with Neumann's results.

I	j	A <sub>ij</sub>	B <sub>ij</sub>	C <sub>ij</sub>	D <sub>ij</sub>
1	2	55.05	5641	4179	-2303100
1	3,4	-249.9	276660	0.455	-4510
2	1	-49.96	4.208	-13783	-6328200
2	3,4	-0.161	-3323.	-0.096	-2279
3,4	1	-0.022	-96.70	0.367	-331.6
3,4	2	13.61	-145.1	-5.245	-11029

Table 1 NRTL parameters with Improved Model for Binary Mixture

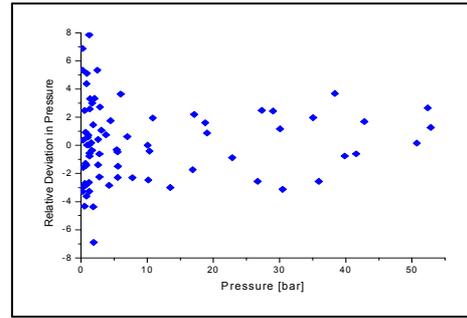


Fig. 2 the total pressure calculation in binary mixture with improved parameter proposed by KAIST

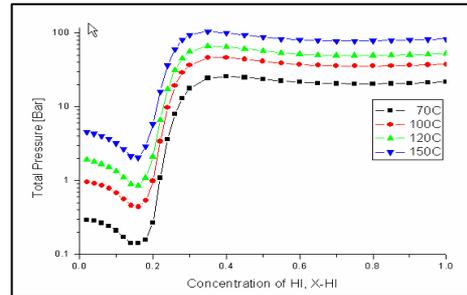


Fig. 2 the total pressure calculation in binary mixture with improved parameter proposed by KAIST

### 3. Conclusion and Further study

Two proposed assumption (Non-randomness and Solvation number) can be useful to thermodynamic modeling of HI-section in SI water-splitting cycle with physical (Non-randomness) and practical value (Solvation number). In this study, new NRTL parameter was obtained by optimization function of MATLAB. Thus far, New NRTL parameter with improve assumption can calculate the total pressure of binary mixture system within 8% of relative deviation over the range of the HI concentration (0~20%). In Further study, ternary mixture parameter will be produced by regression work and binary and ternary mixture NRTL parameters will be verified by testing in commercial chemistry process simulator (ASPEN<sup>+</sup>, PROSIM).

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