Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 22, 2009

Applied Thermodynamic Models for a S-I Thermochemical Cycle

Byung Heung Park*, Jihwan Kim, Youngjoon Shin, Kiyoung Lee, Wonjae Lee, Jonghwa Chang
Korea Atomic Energy Research Institute, 1045 Daedeokdaero, Yuseong, Daejeon, Korea, 305-353
**Corresponding author: bhpark@kaeri.re.kr*

1. Introduction

A sulfur-iodine (S-I) thermochemical cycle is being investigated nationally and/or internationally for a centralized hydrogen production by means of a nuclear heat source. However, the S-I cycle involves a complex and highly nonideal behavior both in phase equilibria and in reactions. In the field of applied thermodynamics, the development of a model suitable for the S-I cycle process is one of the challenging issues [1]. However, recently, remarkable progress has been made to evaluate and improve the S-I cycle. In this work, thermodynamic models dealing with electrolytes, which should be the main considerations for the S-I cycle, are reviewed and, then, the recent models are addressed with their basic concepts.

2. Thermodynamic Models and Application to the S-I Cycle

2.1 Models for Fluid Phase Equilibria

The applied thermodynamics has provided a variety of tools for a process modeling, for describing the thermodynamic properties and phase behavior of chemical systems. In this section some of the highlights of the progress in the thermodynamics of phase equilibria including electrolyte systems are indicated to briefly review the thermodynamic models for an industrial application. The additional descriptions of the noted models can be found in textbooks such as Tester and Model [2] and Prausnitz et al. [3].

For calculating fluid-phase equilibria, it is practical to use either one of the two methods: 1) fugacity coefficients for the vapor phase and activity coefficients for the liquid phase or 2) fugacity coefficients for both phases. Fugacity coefficients are generally provided by an equation of state (EOS) and activity coefficients can be deduced from a model for the molar excess Gibbs energy.

The van der Waals (vdW) EOS which was proposed in 1877 had shown that EOSs are applicable to both gases and liquids. However, it was more popular to use an activity coefficient model for condensed fluids. After Margules and Van Laar independently proposed their activity coefficient models in the late 1800s and early 1900s, respectively, numerous models have appeared and the applicability of these activity coefficient models has been gradually extended. Among them, two models are worth mentioning for highly nonideal systems. They are NRTL [4] and UNIQUAC [5] which were developed based on a local composition concept and they are widely used in the chemical industry.

In an electrolyte system, electrostatic forces exert on ion species to a long range. Therefore, the physical chemistry of an electrolyte solution is quite different from that of nonelectrolytes. Models for an electrolyte activity coefficient usually adopt the Debye-Hückel theory which gives the mean ionic activity coefficient from ion-ion pairs for very dilute solution of strong electrolytes. For concentrated electrolyte solutions, Pitzer [6] proposed an expression of the excess Gibbs energy as a sum of a modified Debye-Hückel theory with an osmotic virial series in an electrolyte concentration. Chen et al. [7] combined the NRTL equation with the Debye-Hückel theory for short range and long range interactions, respectively, and proposed an electrolyte version of NRTL. A similar attempt using UNIQUAC resulted in an electrolyte UNIQUAC model [8] particularly for heavy-cation salt systems.

2.2 Models for the S-I Cycle

The S-I cycle is usually divided into three sections: Section 1 for a Bunsen reaction, Section 2 for a sulphuric acid decomposition, and Section 3 for a hydriodic acid decomposition. Mathias and Brown [9] have proposed a model using the complexation reactions for Section 1 as follows.

$$H_2O + H_2SO_4 \leftrightarrow H_3O^+ + HSO_4^- \quad (1)$$
$$HI + 0.25I_2 + H_2O \leftrightarrow HI_x \quad (2)$$

The model describes the experimental data with a good accuracy. However, the model is semi-empirical and an applied thermodynamic concept should be introduced to improve its reliability.

Mathias and Brown [9] also developed a semi-empirical model for Section 2 where the properties of high-temperature sulfuric acid mixtures are of importance. The model assumed the following chemical reactions.

$$H_2SO_4 + H_2O \leftrightarrow 2\text{IonPair} \quad (3)$$
$$H_2SO_4 \leftrightarrow SO_3 + H_2O \quad (4)$$

However, the model is not consistent with the usual electrolyte model chosen for an aqueous sulfuric acid.

To describe the phase equilibria of aqueous sulfuric acid solutions, Pessoa et al. [10] used the REUNI model for the liquid phase, which is the revised and extended UNIQUAC, and a chemical theory by Prigogine and

Defay for the vapor phase. But the model was limited to the temperature range from 0 to 150 °C.

The HI-I_2-H_2O system, which is the main consideration in Section 3, involved various ionization and complexation phenomena. The complex phase behavior was modeled [9] by using just a single dissociation equation for the strong acidic HI and it showed a qualitative agreement with the experimental data. Recently, Lanchi et al. [11] adopted the Redlich-Kwong EOS for the vapor phase and the electrolyte-NRTL activity coefficient model for the liquid phase to apply it for the preparation of a flow sheet on the HI_x section. The thermodynamic models including Neumann's model and the electrolyte-NRTL for Section 3 were reviewed by Hadj-Kali and coworkers [12] and, then, they also developed their own model using the Peng-Robinson EOS with the MHV2 complex mixing rule embedding the UNIQUAC excess Gibbs energy model. The proposed model succeeded in reproducing the VLE, LLE, SLE, VLLE experimental data. However, the largest discrepancy was found for the high HI concentration mixtures where experimental data are sparse.

Adding to the development of the models suitable for the S-I cycle, it is of significant to integrate each section. For that purpose, the process simulation codes such as ASPEN and ChemCAD are very useful and available. In general, widely used models in the chemical industry field are included in the simulation codes. They can be readily applicable in the case that an embedded model is examined. For example, Fig. 1 presents the calculation results for H_2O-H_2SO_4 VLE by using an electrolyte NRTL model embedded in ChemCAD and it shows the calculated lines pass through most of the experimental data.

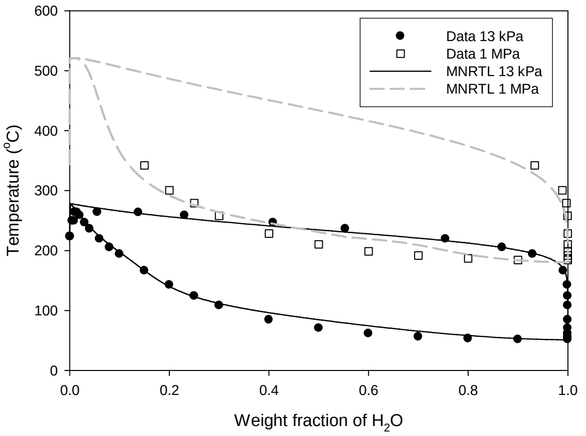

Fig. 1. VLE calculation results for a H_2O-H_2SO_4 system using an electrolyte NRTL (MNRTL) model in ChemCAD.

3. Conclusions

The S-I cycle is considered as a promising option for a massive hydrogen production. The S-I cycle process involves a number of chemical reactions and separations of highly nonideal and complex systems. The applied thermodynamics can provide models describing the properties required to devise the S-I cycle process. In this paper, recent attempts for modeling each section of the S-I cycle was briefly reviewed to understand the current achievements in the field of applied thermodynamics. To date, the independent models represented a good agreement with the experimental data. However, they were just an application or an modification of the developed model by considering empirical aspects and, therefore, it is required to develop a model commonly applicable to the three Sections. Moreover, a model should be incorporated with a process simulation code to integrate the whole S-I cycle.

ACKNOWLEDGMENTS

This study has been performed as one of the mid-and-long term Nuclear R&D projects.

REFERENCES

[1] P. M. Mathias, Applied Thermodynamics in Chemical Technology: Current Practice and Future Challenges, Fluid Phase Equilibria, Vol.228-229, p.49, 2005.

[2] J. W. Tester and M. Modell, "Thermodynamics and Its Applications", 3rd Ed., Prentice Hall, NJ, 1997.

[3] J. M. Prausnitz, R. N. Lichtenthaler, and E. G. De Azevedo, "Molecular Thermodynamics of Fluid-Phase Equilibria", 3rd Ed., Prentice Hall, NJ, 1999.

[4] H. Renon and J. M. Prausnitz, Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures, AIChE J., Vol.14, p.135, 1968.

[5] D. S. Abrams and J. M. Prausnitz, Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Free Energy of Partly or Completely Miscible Systems, AIChE J., Vol.21, p.116, 1975.

[6] K. S. Pitzer, Thermodynamics of Electrolytes. 1. Theoretical Basis and General Equations, J. Phys. Chem., Vol.77, p.268, 1973.

[7] C.-C. Chen and L. B. Evans, A Local Composition Model for the Excess Gibbs Energy of Aqueous-Electrolyte Systems, AIChE J., Vol.32, p.444, 1986.

[8] M. C. Iliuta, K. Thomsen, and P. Rasmussen, Modeling of Heavy Metal Salt Solubility Using the Extended UNIQUAC Model, AIChE J., Vol.48, p.2664, 2002.

[9] P. M. Mathias and L. C. Broun, Thermodynamics of the Sulfur-Iodine Cycle for Thermochemical Hydrogen Production, Proceedings of the 68th Annual Meeting of the Society of Chemical Engineers, 23 March, 2003, Japan.

[10] F. L. P. Pessoa, C. E. P. Siqueira, and A. M. C. Uller, Calculation of Vapor-Liquid Equilibria in Aqueous Sulfuric Acid Solutions Using the UNIQUAC Equation in the Whole Concentration Range, Chem. Eng. Sci., Vol.61, p.5170, 2006.

[11] M. Lanchi, A. Ceroli, R. Liberatore, L. Marrelli, M. Maschietti, A. Spadoni, and P. Tarquini, "S-I Thermochemical Cycle: A Thermodynamic Analysis of the HI-H_2O-I_2 System and Design of the Hix Decomposition Section", Int. J. Hydrogen Energ., in press.

[12] M. K. Hadj-Kali, V. Gerbaud, J.-M. Borgard, O. Baudouin, P. Floquet, X. Joulia, and P. Carles, "HI_x System Thermodynamic Model for Hydrogen Production by the Sulfur-Iodine Cycle", Int. J. Hydrogen Energ., in press.