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Relationship between Density and Composition of HI-I_2-H_2O in I-S Process

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1 Introduction

Iodine-Sulfur thermochemical cycle is one of the most promising massive hydrogen production methods. It consists of three main reactions (three sections) [1, 2], which are Bunsen reaction (Bunsen section), sulfuric acid decomposition (sulfuric acid section) and hydriodic acid decomposition (HIx section), as described by Eqs. (1)-(3):

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \quad [393\ K] \tag{1}$$

$$2H_2SO_4 \rightarrow 2SO_2 + 2H_2O + O_2 \quad [1123\ K] \tag{2}$$

$$2HI \rightarrow H_2 + I_2 \quad [723\ K] \tag{3}$$

It is of great importance to determine the compositions of streams in the process, so as to monitor the performance of the iodine-Sulfur thermochemical cycle. Concerning the HI-I_2-H_2O mixture (HIx phase of IS process), it is time consuming to determine the concentrations of each species in the solution, especially for I_2. Hence, density which can be easily acquired is introduced to simplify concentration measurement [3].

According to Gibbs phase rule [4], the degree of freedom F of a system is

$$F = C - P + 2 \tag{4}$$

Where C is the number of components, P is the number of phases. Under the circumstance of given temperature and pressure, F equals to 2 for HI-I_2-H_2O ternary system. Thus, the composition of the solution can be determined once 2 independent variables of the system are known. As a result, if density and concentration of a certain component, e.g. HI, are measured, the composition of all the other substances is able to be calculated.

The relation between density and concentrations of each species can be formulated by Eq. (5).

$$\rho = M_{HI} \times C_{HI} + M_{I_2} \times C_{I_2} + M_{H_2O} \times C_{H_2O} \tag{5}$$

Where, ρ is density, M is molar mass of each substance, C is concentration, and the subscripts represent the components. It can be seen that, density is a linear combination of the concentrations of each component. In this research, HI-I_2-H_2O solutions of different compositions were prepared. Based on the density data and the concentration data of HI, I_2, and H_2O, multiple linear regressions were carried out. Applying the resulted relational expression, the composition of the $HI-I_2-H_2O$ could be secured once density and H^+ concentration of solution are measured.

2 Experimental

The experiments were carried out at fixed temperature 20°C and 1 atmospheric pressure. 50.0 ml hydriodic acid solution, i.e. $HI-H_2O$ mixture, of certain concentration was first prepared in a glass vessel in a water bath of 20°C. Then pure solid iodine was added to the solution gradually until saturation. During the process, samples are taken every batch of 10.0 g iodine has been added into the solution. Densities of the sample were measured using an oscillating U-tube density meter (DMA 4100 M, Anton Paaran, Austria) at 20°C. The concentrations of HI and I_2 of sample are measured by the method of chemical titration.

The HI/H_2O molar ratio of initial hydriodic acid ranges from 1:9.46 to 1:5.43, which is very close to the composition of $HI-H_2O$ azeotrope.

3 Result and Discussion

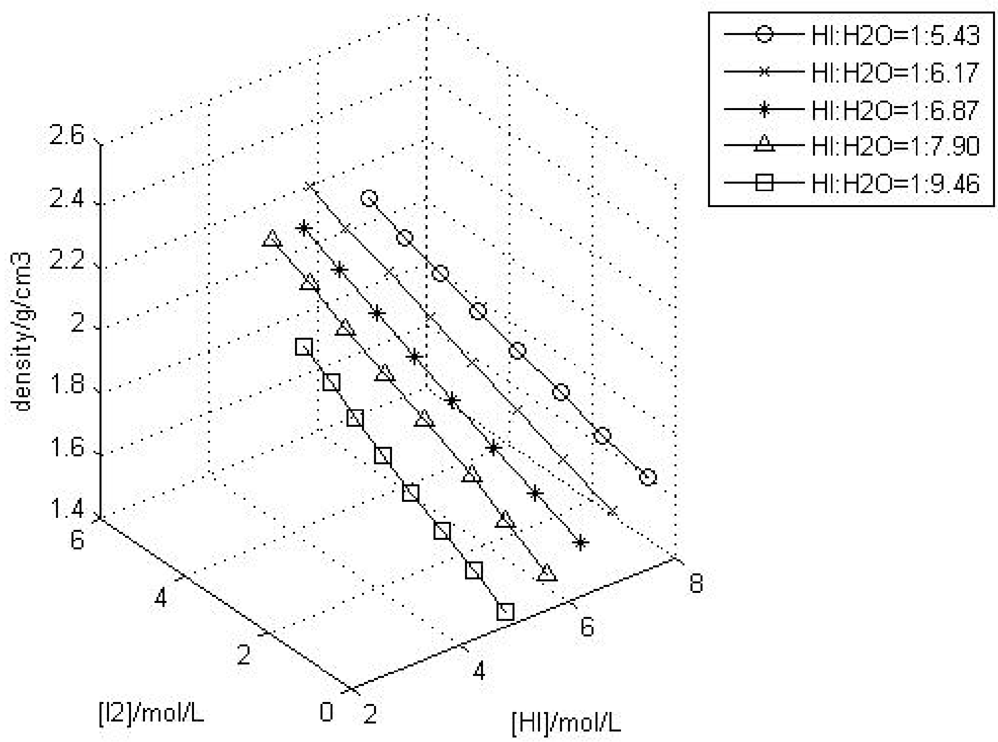

Figure 1: Relationship between density and concentrations of HI and I_2.

Fig. 1 illustrates the relationship between density and concentrations of HI and I_2. There is an obvious linear relation between them. In addition, such a linear relation covers a wide range from the molar ratio of $HI:H_2O$=1:5.43 to 1:9.46.

Based on experimental data, a multiple linear regression procedure was implemented so as to set up the math model [5]. As far as the experiment is concerned, the regression relationship is expressed by Eq. (6).

$$\rho = \alpha + \beta \times C_{HI} + \gamma \times C_{I_2} \qquad (6)$$

Where ρ, C_{HI} and C_{I2} represent solution density, HI concentration and I_2 concentration, respectively, while *α*, *β* and *γ* are constants resulted from the regression. As shown in Fig.2, the relational expression Eq. (6) stands for a plane at the 3-dimensional space of ρ, C_{HI} and C_{I2}, and almost all the experimental points fall in this plane. Because density and HI concentration (i.e. H^+ concentration) could be measured rapidly, subsequently I_2 concentration are ready to be calculated applying Eq. 6, thus the composition of the whole HI-I_2-H_2O mixture could be determined within a time quite short.

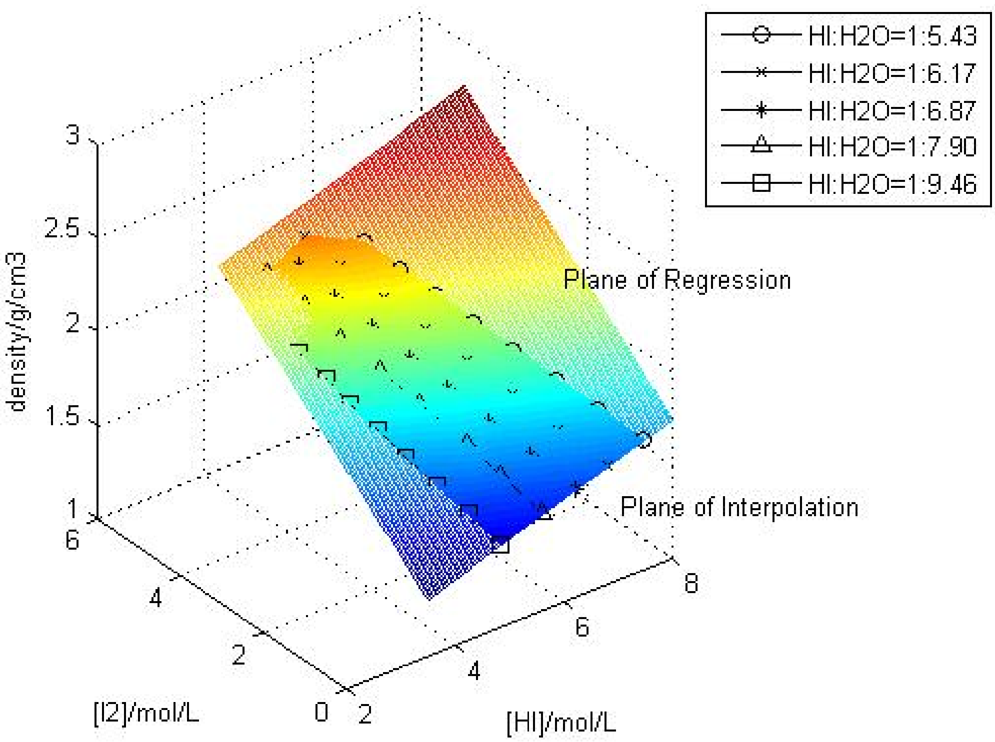

Figure 2: Plane of regression and plane of interpolation using experimental data.

In order to verify the performance of the regression result, values of the concentration calculated by Eq (6) were compared with those measured by chemical analysis. Six different samples were prepared for the verification, whose initial ratios of HI to H_2O are 1:5.77, 1:6.10, 1:6.35, 1:6.62, 1:7.60 and 1:8.50 respectively. Fig.3 indicates that the concentrations calculated using regression model agree with those obtained via chemical experiment very well. The average relative deviation of the calculated values against the experimental ones lays within 1.0%.

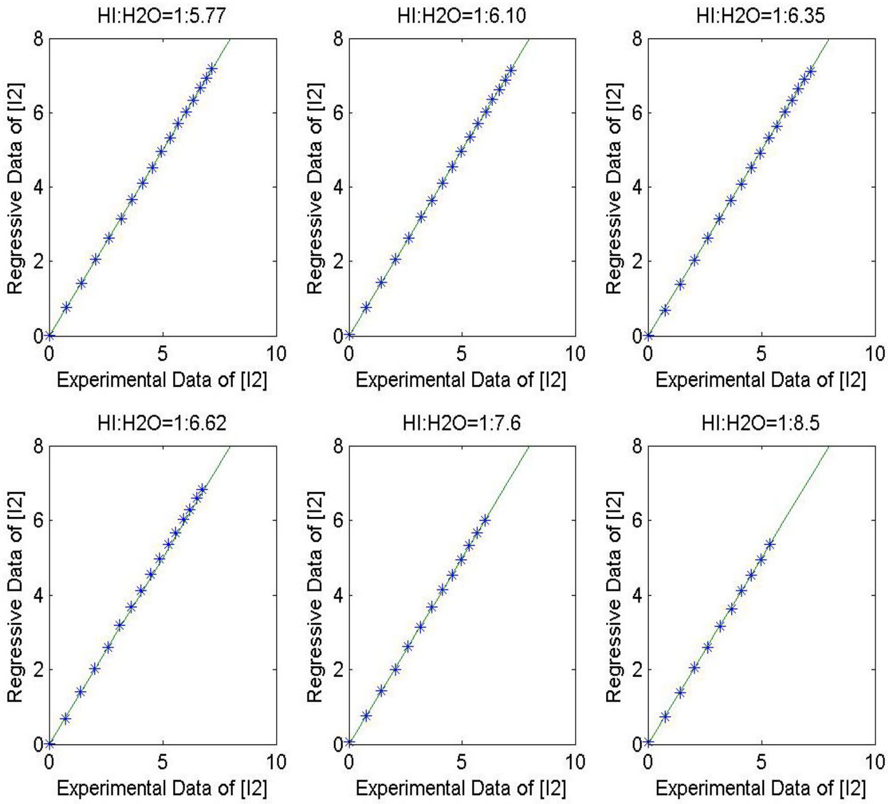

Figure 3: Comparison of calculated values and experimental data of I_2 concentration.

4 Conclusion

The relationship between solution density of HI-I_2-H_2O and composition was studied by multiple linear regressions. A relational expression describing above relationship was obtained, applying which the efficiency of composition analysis of HI-I_2-H_2O could be improved significantly.

References

[1] Norman J.H., Bensenbruch G.E., O'Keefe D.R. Thermochemical water-splitting cycle for hydrogen production. GRI-A 16713, 1981.

[2] Zhang P., Chen S.Z., Wang L.J., et al. Overview of nuclear hydrogen production research through iodine sulfur process at INET. International Journal of Hydrogen Energy, 2010, 35(7): 2883-2887

[3] Kubo S, Nakajima H, Imao Y, et al. An estimation technique for compositions of Bunsen reaction solutions on thermochemical water splitting IS process: 17th World Hydrogen Energy Conference. Brisbane, Australia, 2008.

[4] Mortimer R.G. Physical Chemistry, 3rd edition. San Diego, USA, Elsevier Academic Press, 2008. 199-205.

[5] Härdle W. Applied multivariate statistical analysis [M]. Berlin: Springer, 2003. 108-112.