

Experimental Studies of Bunsen section for over-azeotropic condition in I-S cycle

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1. Introduction

The Iodine-Sulfur thermochemical cycle is the most viable water-splitting process for massive hydrogen production with VHTR. The suggested upper bound of the efficiency is around 40%, but only 6% is verified by experimental data of JAEA. The main reason of low efficiency is the energy demand for phase change with excessive components such as water and iodine, which are not directly involved in water splitting reaction. Particularly, water spends lots of heat for phase changes in HI decomposition section, because of an azeotropic condition between water and hydrogen iodide (HI).

If overazeotropic concentration of HI is able to compose by bunsen reaction, a pure HI is easily separated from hydroiodic acid (HIx) by simple or flash distillations. [1] The efficiency of I-S cycle can be increased by using a pure HI from overazeotropic HIx of bunsen reaction. KAIST collected all existing data and performed parameter studies, then suggested the optimal operating condition. There are many data sets from several researchers, but KAIST suggestion is only supported by data from ENEA.[2] Thus, we validate previous data of other researchers and find optimal range to generate high HI concentration with overazeotropic condition by experimental studies.

2. Materials and methods

Phase behavior of the four-component $H_2SO_4/HI/H_2O/I_2$ mixtures was investigated using a 50mL jacketed quartz test vial whose temperature was controlled by means of a water recirculation system and a thermostatic bath. A schematic of this simple apparatus is shown in Fig. 1.

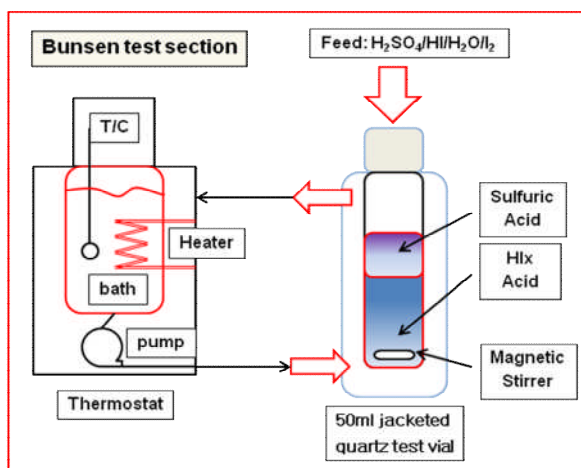
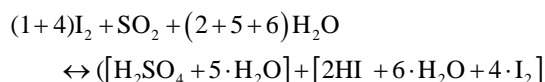


Fig. 1. Apparatus used for liquid-liquid phase behavior tests.

2.1 Feed materials



As above equation, KAIST suggested optimal operating composition for Bunsen reaction by reducing content of H_2O and I_2 . For convenience of calculation, we used unit of molar ratio, that is, molar mass of each component was divided by that of sulfuric acid. Molar ratio of I_2/H_2SO_4 was controlled between 1 and 4. Temperature was controlled from 40 to 80°C.

A selected amount of iodine was added to a 57 wt% hydroiodic acid at a room temperature. For complete iodine dissolution, test vial was heated up to 60 °C. Then, 97wt% of sulfuric acid and the residual amount of water were slowly added. Afterwards the mixture was heated up to the desired operative temperature, energetically mixed, and then kept at rest for a while to allow complete phase separation and equilibrium achievement. Solubility of solid iodine in the bottom was increased with temperature increasing

2.2 Measurement of concentration ($H_2SO_4/HI/H_2O/I_2$)

The supernatant sulfuric phase were sampled by micro pipette, and then weighted and analyzed. H^+ concentration (mmol/g) was determined by neutralization titration with 1N NaOH standardized solution. Iodine concentration (wt %) was determined by redox titration with a sodium tiosulfate (0.1N $Na_2S_2O_3$) standardized solution. Sulfate (SO_4^{2-}) content determined by ionic chromatography, a Metrohm 792 Compact Ionic Chromatograph, with an anion SUPP 5 column. The eluent solution was 3.2mM in Na_2CO_3 and 1.0mM in $NaHCO_3$. The composition of the lower HIx phase was also sampled, weighted and analyzed. Finally, the upper sulfuric phase was quantitatively removed and weighted, the residual HIx phase weighted for comparison between before and after reaction. Each stoichiometric equation is as follows.

1. H^+ analysis: $H^+ + OH^- \rightarrow H_2O$
2. I_2 analysis: $I_2(aq.) + I^- \rightleftharpoons I_3^-$,
 $2S_2O_3^{2-} + I_3^- \rightarrow S_4O_6^{2-} + 3I^-$
3. I^- analysis:
 $KIO_3 + 5HI + 6HCl \rightleftharpoons KCl + 5HCl + 3I_2 + 3H_2O$
 $KIO_3 + 2I_2 + 6HCl \rightleftharpoons KCl + 5ICl + 3H_2O$
4. Overall material balance: H_2O

3. Results and discussion

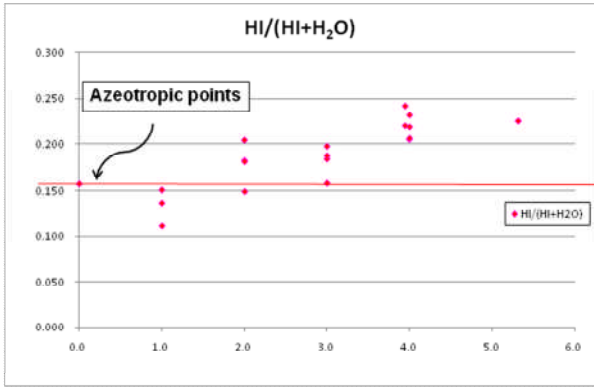


Fig. 2. Overazeotropic HI concentration in H1x phase

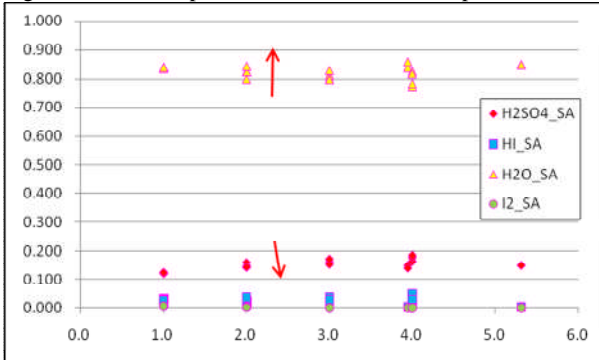


Fig. 3. Overazeotropic HI concentration in H1x phase

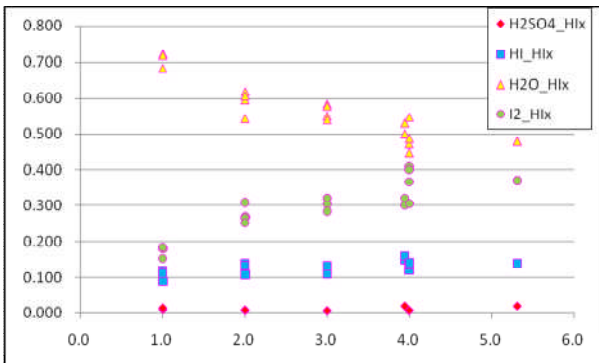


Fig. 4. Overazeotropic HI concentration in H1x phase

When concentration of I_2 in feed was increased, HI concentration in H1x phase was also increased and become over-azeotropic condition. If molar ratio of I_2/H_2SO_4 is above 2, HI concentration in H1x phase got over-azeotropic condition as shown in Fig.2. This means that new KAIST flowsheet which include conception of overazeotropic condition is feasible. We can also increase efficiency with new overazeotropic process.

Temperature leads very slight effect on a change of each concentration as shown in Fig.3~ 4. When temperature was increased, concentration of H_2O increased, H_2SO_4 decreased, and HI&I2 is too little to find trend in S.A phase. When temperature was increased, concentration of H_2O decreased, that of HI decreased, I2 increased, and H_2SO_4 is too little to find trend in S.A phase.

Change of each concentration is dominantly influenced by concentration of I_2 . When concentration

of I_2 was increased concentration of H_2O was decreased in H1x phase, it leads overazeotrope. And, increasing of I_2 concentration leads impurity decreasing in both phase. Impurity (HI & I_2) was decreased in S.A phase significantly. Impurity (H_2SO_4) was also decreased in H1x phase slightly.

3. Conclusions

If molar ratio of I_2/H_2SO_4 is above 2, H1x phase got over-azeotropic condition. Temperature has very slight effect on a change of each concentration. When concentration of I_2 was increased, Impurity (HI & I_2) was decreased in S.A phase significantly. Impurity (H_2SO_4) was also decreased in H1x phase slightly.

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