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Absorption behaviors of SO_2 in HI acid for the iodine-sulfur thermochemical cycle

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ABSTRACT

Bunsen reaction, which produces H_2SO_4 and HI acids from the reaction of I_2, SO_2 and H_2O, is a crucial reaction for the iodine–sulfur thermochemical hydrogen production process. To study the reaction kinetics of Bunsen reaction by correlating SO_2 pressure drop with reaction time, the physical absorption of SO_2 in HI acid should be investigated. The absorption behaviors of SO_2 in HI acid were firstly studied under various conditions, including different HI concentration, absorption temperature, and SO_2 partial pressures. The results show that the absorption amount of SO_2 in HI solution increases with both the pressure of the SO_2 and HI acid concentration, while the effect of temperature on SO_2 absorption in HI solution is complex. S and SO_4^{2-} were detected in HI solutions after SO_2 absorption, and iodine was found in some cases, especially under the conditions of high pressure or high temperature, indicating chemical absorption occurred, which leads to the disobeying of the physical absorption rules. It is thought that the redox reaction between HI and SO_2 and the formed products are the main reasons of chemical absorption.

Introduction

The iodine-sulfur thermochemical (IS) process is one of the most promising efficient, CO_2-free, and massive approaches to produce hydrogen oriented to use nuclear energy, or more specifically, the heat from high temperature gas-cooled reactor [1–4].

The IS process consists of the following three chemical reactions:

Bunsen reaction:

$$SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4 \text{ (exothermic, 80–120 °C)} \quad (1)$$

H_2SO_4 decomposition reaction:

$$H_2SO_4 = SO_2 + 1/2O_2 + H_2O \text{ (endothermic, 800–900 °C)} \quad (2)$$

HI decomposition reaction:

$$2HI = H_2 + I_2 \text{ (endothermic, 400–500 °C)} \quad (3)$$

The net reaction of the whole process is:

$$H_2O = H_2 + 1/2O_2 \quad (4)$$

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The IS process, which was initially proposed by the General Atomics company, has been widely studied during past decades in several countries, such as USA, Japan, France, Italy, Korea, and China [5–9]. Japan Atomic Energy Agency (JAEA) succeeded in continuous closed cycle operation for one week in 2004, with the hydrogen production rate of 31 NL/h [6,10]. General Atomics (GA), Sandia National Laboratory (SNL) and Commissariat à I'Energie Atomique (CEA) cooperated to build an integrated lab-scale test apparatus using engineering materials with a hydrogen production rate of 100 NL/h in 2008 [5]. In China, Institute of Nuclear and New Energy Technology (INET) of Tsinghua University has been conducting related studies under the nuclear hydrogen project. INET erected a proof-of-concept apparatus with H_2 production rate of 10 NL/h, and achieved the closed cycle operation in 2009, which is the first time in China [7]. Later, INET finished the bench scale experiment with H_2 production rate of 60 L/h in 2014 [11].

After many years' fundamental studies, the feasibility of the process has been verified, and a flowsheet has been optimized. Currently the emphasis of R&D on IS technology is gradually moved to the development of key chemical reactors and other equipment made of engineering materials. To simulate, design and optimize the reactors, chemical kinetics data are necessary. However, the kinetics data are far from enough, especially for Bunsen reaction, a complex gas-liquid-solid reaction. Thus far, a few of the results on Bunsen reaction kinetics have been published. Wang [12] studied the apparent reaction rate of the Bunsen reaction in iodine-toluene solution system in a closed, fixed-volume batch reactor using the initial rate analysis method. Zhang [13] investigated the effects of SO_2 flow rate, SO_2 mole fraction, iodine content and water content on the kinetics of the Bunsen reaction. Shriniwas [14] observed that the overall reaction rate increases with increase in pressure and decreases with increase of temperature. These results present some information about the reaction rate, but still deep understanding on the reaction kinetics is needed for process engineering scale-up.

As Bunsen reaction is a gas-liquid (solid) heterogeneous reaction, it is an effective approach to describe the kinetic rate by correlating the gas pressure drop with the reaction time [14,15]. For this purpose, physical absorption of SO_2 in the quantitative calculation of Bunsen reaction system should be considered, because the absorption rate and amount of SO_2 by HI acid will affect the kinetic equation. Bunsen reaction system contains two solutions, H_2SO_4 solution and HI solutions. The solubility of SO_2 in water and H_2SO_4 solution under different conditions have been extensively studied [15–23]. Contrary to this, the solubility or absorption of SO_2 in HI acid solution was reported yet. Study on the absorption of SO_2 gas in the HI solution will offer useful information for kinetics research, as well as deepen the understanding on the interaction between SO_2 and HI solution. In this work, the absorption behaviors of SO_2 in HI acid under various conditions were studied.

Experimental

Experimental apparatus

Fig. 1 shows a schematic setup of the experimental apparatus, which was mainly composed of SO_2 (99.9%) cylinder, SO_2 reservoir, solubility cell, buffer bottle, tail gas scrubbing bottles, etc. The solubility cell with a volume of 100 mL was a Teflon-lined stainless steel reactor with electric heating and temperature-control system and magnetic stirrer. The reservoir made of Teflon-lined stainless steel housing with a volume of 200 mL was heated with electric jacket to get the desired temperature. The SO_2 gas cylinder was heated with water bath to enhance the pressure of SO_2. The pressure of the system was measured by an accurate pressure transducer connected to a computer. The pressure drop was monitored and recorded online. The accuracy of the pressure transmitter is 1 kPa. All pipes were intertwined with heater tapes to maintain the temperature. N_2 was used to purge the system and pressure test. Impurity gases in the system were removed by vacuum before inputting SO_2. The tail gas was scrubbed using NaOH solution before discharging. Buffer bottle was used to prevent the back suction of the liquid.

Experimental procedures

The empty volumes of gas reservoir and solubility cell were calibrated using the water displacement method before the experiment. In the experiment, H_2O or HI solution was firstly placed in the solubility cell. Purged the system and checked the tightness with purity N_2. The system was then emptied by a vacuum pump. The solubility cell and reservoir were heated to the desired temperature. After the temperatures of the cell and reservoir got steady, recorded the system pressure and denoted as P_0. Turned off the isolation valve between the solubility cell and the gas reservoir, introduced SO_2 gas from cylinder into the reservoir to a desired pressure, which was denoted as P_1, then connected the gas reservoir to the solubility cell, and started to record the pressure drop with time continuously. When the pressure did not decrease apparently, i.e. the pressure change curve became almost a straight line, recorded the pressure as P_2, thus one operation cycle of absorption was finished. The process of pressure charge and absorption was repeated, thus the equilibrium pressure of each absorption cycle was higher than the previous one, and absorption data were obtained for increasing equilibrium pressures. The absorption liquid was replaced for each HI concentration or temperature studied. A typical pressure drop curve during experiment was shown in Fig. 2. The initial pressure at different cycle had little difference, but it had little effect on the absorption value, because the main purpose of this experiment was to obtain the absorption value of SO_2 in HI solution by determining the drop of pressure (ΔP) before and after absorption.

Calculation of the absorption and analysis

The absorption of SO_2 gas in HI solution is calculated by second order Virial equation of state, and the second Virial coefficient is got from the published results [24]. The measured initial pressure P_0 is significantly smaller than the saturation pressure of the liquid used. Nonetheless, these partial pressures are included in all calculations. The partial pressure of SO_2 is expressed as Eq. (5). The amount of SO_2 is calculated with gas equation of state Eq. (6), where V is volume of SO_2 gas, z is compressibility factor, R is gas constant, T is temperature, and B is the second Virial coefficient. The SO_2 gas absorption