

Thermodynamic analysis of hydrogen production via zinc hydrolysis process

Ming Lv, Haiqiang Liu*

School of Mechanical Engineering, Hangzhou Dianzi University, 310018, Hangzhou, China

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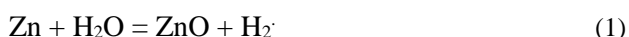
Abstract

The thermodynamic studies were carried out for the hydrogen production via zinc hydrolysis. It is shown that it is reasonable to keep the temperature of zinc hydrolysis under 900 °C. The system pressure has no notable thermodynamic influences on the hydrolysis reaction. The initial H₂O/Zn molar ratio should be controlled in a reasonable range. The concentration of steam in carrying gas in experiments should better be kept above 50%.

Keywords: hydrogen, hydrolysis, thermodynamics, zinc

1 Introduction

Two-step water splitting thermochemical cycles using metal-oxide redox pair are considered for the solar production of hydrogen [1]. Possible technical concepts of two-step cycles are discussed in paper [2] and [3], suggesting that the thermochemical cycles based on Zn/ZnO redox pair are very promising candidates. These cycles using the Zn/ZnO redox pair often proceed through two steps: In the first, endothermic step, zinc oxide can be converted to zinc using high temperature solar heat by thermal dissociation [4, 5] or by carboreduction [2, 6]; The second, exothermic step, hydrogen is produced via the hydrolysis of zinc, which can be presented as follows:



As one of the key steps in the thermo chemical cycle based on Zn/ZnO, only few information is available on the hydrolysis of zinc from published literature. In a series of thermo gravimetric analyses of commercial zinc powder and solar zinc powder in a temperature range of 350-500°C, Weidenkaff et al.[5] found that the hydrolysis reaction proceeded faster for molten zinc and for zinc containing impurities, but a layer of ZnO prevented the reaction from reaching completion. The hydrolysis of submicron Zn particles in a temperature range of 330-360°C was also studied by thermogravimetric analyses, and a fast surface reaction, corresponding to a mass increase of 2%, followed by a slow diffusion-limited reaction was observed [7]. The oxidation of liquid zinc with water vapor was studied by bubbling water vapor through bulk of liquid zinc at 450-500 °C [8], and the results showed that the specific reaction rate increases as the water partial pressure increases, the main determining step of the hydrolysis reaction is the diffusion of reactants

through the product zinc oxide layer. The oxidation of zinc vapor of about 750°C and 800°C with water vapor was also studied using a tubular aerosol flow reactor which features three temperature-controlled zones [9], up to 83% of zinc conversion could be obtained while the temperature of reaction zone is just below the Zn(g) saturation temperature. And several reaction parameters of the H₂ production by steam-quenching of Zn vapor were also studied in a hot-wall aerosol flow reactor, the results shows that high zinc conversions could get at a low quenching rate at the expense of low particle yield [10]. Detailed studies on the hydrolysis kinetics of zinc powder was also conducted by Vishnevetsky et al. [11], they found that the hydrolysis of zinc proceeded in two stage, and increasing the beginning temperature of the reaction is advantageous to the hydrolysis process, the reactivity of Solar Zinc is much higher than commercial zinc, which is agreed with paper [5]. Thermogravimetric analysis of the hydrolysis of zinc particles was also taken out in a temperature range of 200-1000 °C [12], two kinds of reaction mechanism of the zinc hydrolysis were revealed by Ming et al, in which the rate of hydrolysis reaction was limited by the evaporation of zinc and the diffusion of zinc through ZnO layer respectively.

In this paper, detailed thermodynamic studies were taken out for the hydrolysis of zinc. We focused on the thermodynamic influences of several important process parameters, including temperature, system pressure, initial H₂O/Zn molar ratio, and the concentration of steam in carrying gas.

2 Calculation methods

In this paper, the equilibrium composition of reacting mixture is calculated by the non-stoichiometric approach, in which the equilibrium composition is found by the direct minimization of Gibbs free energy. The famous

* *Corresponding author* e-mail: liuhaiqiang1980@126.com

computational thermo-chemistry software - FactSage was used for the calculation [13]. The thermodynamic parameters of reaction such as enthalpy change, Gibbs energy change were calculated by the REACTION module. The influences of temperature, system pressure and initial components ratio on the reaction equilibrium were studied by the EQUILIB module.

The hydrogen yield ability of the zinc hydrolysis system was estimated by the hydrogen equilibrium yield ratio, which is defined as:

$$H_2 \text{ yield [\%]} = n_{H_2,eq} / n_{Zn,initial} \quad (2)$$

where $n_{H_2,eq}$ is the hydrogen equilibrium molar amount, $n_{Zn,initial}$ is the initial zinc molar amount in system.

3 Results and discussion

The ΔH^0 and ΔG^0 of zinc hydrolysis reaction under different temperature at 1 atm pressure were calculated. As shown in Figure 1, the hydrolysis of zinc is a moderate heat releasing reaction. When the reaction temperature is lower than 850°C, the stoichiometric reactants can be heated to the reaction temperature by the heat revealed by the reaction itself in ideal state. That means the zinc hydrolysis reaction can proceed auto-thermally. The reaction Gibbs energy change increases as the temperature increases. In ideal state, the zinc hydrolysis reaction can proceed at a temperature below 1223°C at 1 atm. According to previous kinetic studies of zinc hydrolysis [12], solid zinc will not react with water under low temperature as the restriction of chemical reaction kinetics. At normal state, the zinc hydrolysis reaction only proceeds at temperature higher than the melt point of zinc (417°C). So the reaction can be presented as follows:

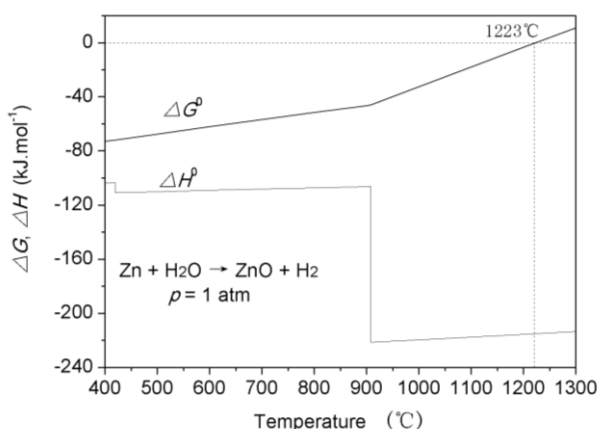
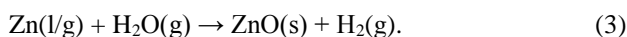


FIGURE 1 Temperature variations of ΔH^0 and ΔG^0 for the hydrolysis reaction of zinc at 1 atm

To study the thermodynamic influences of temperature and system pressure on zinc hydrolysis reaction, the equilibrium composition of initial 1 mol zinc and 1 mol water under different temperatures and different pressures are calculated. As shown in Figure 2, the calculation result shows that the hydrogen equilibrium yield ratio increases as temperature decreases. Obviously, under atmospheric pressure, the reaction temperature should be kept under 900°C to get a hydrogen equilibrium yield ratio higher than 90%.

When the temperature varies from 900°C to 1400°C, system pressure has great influence on the hydrogen equilibrium yield ratio. At the temperature of 1100°C, the hydrogen equilibrium yield ratio decreases from 85.7% to 17.8% while the system pressure increases from 0.1 atm to 10 atm. When the temperature is lower than 900°C, as temperature decreases the influence of pressure on hydrogen equilibrium yield ratio decreases. When the temperature is lower than 700°C, the influence of system pressure is much small, as shown in Figure 2. From the sight of reaction thermodynamics, it is reasonable to control the reaction temperature under 900°C to get a high hydrogen production. Because the increase of pressure has little impact on reaction when the reaction temperature is below than 900°C, the zinc hydrolysis system pressure can be designed as atmospheric pressure, which is more favourable for practical utilization.

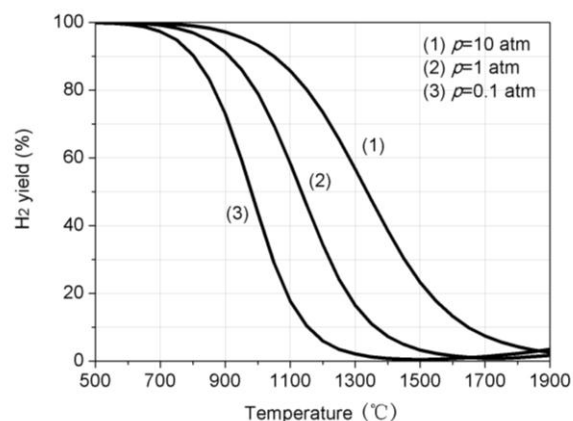


FIGURE 2 Variation of the H_2 equilibrium yield ratio as a function of the temperature and pressure (initial 1 mol Zn + 1 mol H_2O).

What's more, the result also shows that the increase of pressure can expand the high edge of zinc hydrolysis temperature window. However, it should be pointed out that water will split into hydrogen and oxygen at very high temperature. The thermodynamic calculation result shows that the low edge of water splitting temperature window is usually close to the high edge of zinc hydrolysis temperature window. As Figure 2 shows, under the pressure of 0.1 atm, the hydrogen equilibrium yield ratio decreases from 100% to 0 while the temperature increases from 500°C to 1500°C, the yielded hydrogen comes from the hydrolysis of zinc. Moreover, as the temperature increases above 1500°C at 0.1 atm, the hydrogen equilibrium yield ratio increases slowly because of the water splitting reaction.

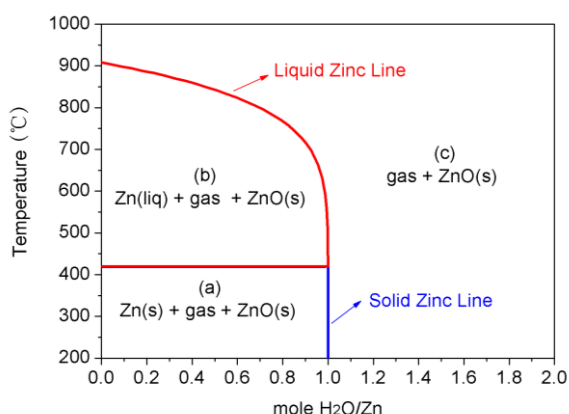


FIGURE 3 Variation of the Chemical equilibrium composition as a function of the temperature and initial H_2O/Zn molar ratio ($p=1$ atm)

The influences of initial H_2O/Zn molar ratio were studied under atmospheric pressure. As Figure 3 shows, the diagram of equilibrium composition with different initial H_2O/Zn molar ratio and different reaction temperature can be divided into three areas. Under atmospheric pressure, when the H_2O/Zn ratio is lower than 1 and the temperature is lower than the melting point of zinc, in equilibrium state the zinc is in solid phase and the gas component is hydrogen, as show in Figure 3 area (a). The boundary of area (a) can be seen as the critical solid zinc phase line with a giving pressure and a giving temperature, which we called solid zinc line here. When the H_2O/Zn ratio is still kept lower than 1 and the temperature is between the melting point and the boiling point of zinc, as Figure 3 area(b) shows, for zinc the phase of gas and liquid coexist in equilibrium. And the gas components in area(b) are gaseous zinc and hydrogen. The boundary of area (b) can be seen as the critical liquid zinc phase line with a giving pressure and a giving temperature, which we called liquid zinc line here. When the H_2O/Zn ratio is higher than 1, as Figure 3 area(c) shows, there will be no liquid or solid zinc appear in equilibrium. The main components of gas in area(c) is hydrogen and steam at relative low temperature, while at relative high temperature gaseous zinc will represent as the incompleteness of reaction. According to the previous studies, we care more about the reaction temperature in a range of zinc melting point to 900 °C. So we focused on the liquid zinc line between area(b) and area(c). In this section of liquid zinc line, the x coordinate of each point represent the critical H_2O/Zn ratio at giving temperature and pressure for liquid zinc existence in equilibrium, which we called critical liquid zinc ratio in follows. And the y coordinate represent the critical temperature at giving initial H_2O/Zn ratio and pressure for liquid zinc existence in equilibrium, which we called critical liquid zinc temperature in follows. The critical liquid zinc ratio and the critical liquid zinc temperature at atmospheric pressure were giving in Table 1 and Table 2.

TABLE 1 Critical liquid zinc ratio at different temperatures ($p=1$ atm)

Temperatures (°C)	Critical liquid zinc ratio
500	0.998
600	0.985
700	0.921
800	0.697
900	0.08

TABLE 2 critical liquid zinc temperature at different initial compositions ($p=1$ atm)

Initial H_2O/Zn molar ratio	Critical liquid zinc temperature (°C)
0.2	886
0.4	859
0.6	823
0.8	767
1.0	420
1.2	/

We calculated the equilibrium composition under 800°C and 1 atm as a example to study the influence of the initial H_2O/Zn molar ratio on zinc hydrolysis. As Figure 4 shows in the first stage, when the initial H_2O/Zn molar ratio is lower than the critical liquid zinc ratio (0.697 for 800 °C), the content of equilibrium liquid zinc drops to zero quickly as the initial H_2O/Zn molar ratio increases.

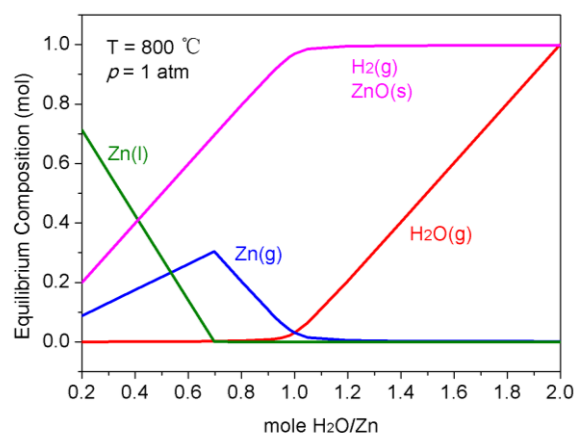


FIGURE 4 Variation of the equilibrium composition as a function of the initial H_2O/Zn molar ratio while $T=800^\circ\text{C}$, $p=1\text{atm}$, the initial zinc molar amount was set constant at 1 mol

At the same time, the content of equilibrium gaseous zinc slowly increases linearly to a constant value. Therefore, it can conclude that the phase of zinc, which participates in hydrolysis reaction, is liquid. In the second stage, when the initial H_2O/Zn molar ratio increases from 0.697 to 1, the gaseous zinc begins to participate in hydrolysis reaction, and the content of equilibrium gaseous zinc decreases linearly to zero. Above all, we can conclude that the initial H_2O/Zn molar ratio should be kept larger than 1 to avoid the production of gaseous zinc and to improve the conversion of zinc. In addition, from sight of hydrogen concentration in equilibrium gas, the initial H_2O/Zn molar ratio should not be too large. Because the larger H_2O/Zn molar ratio will cause the larger waste of steam, which will bring the larger lost of

raw material and energy. What's more, the larger $\text{H}_2\text{O}/\text{Zn}$ molar ratio will be disadvantageous to the separation of hydrogen from product gases and to the recovery of exhausted water.

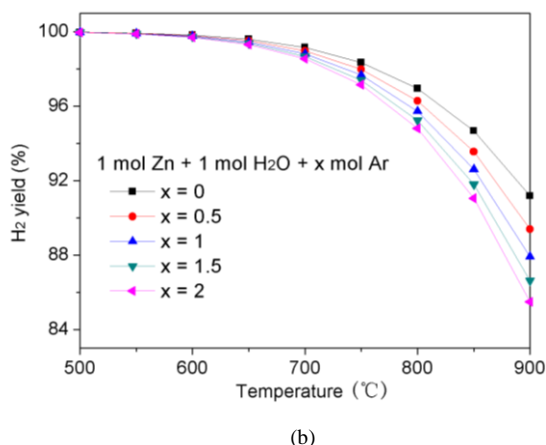
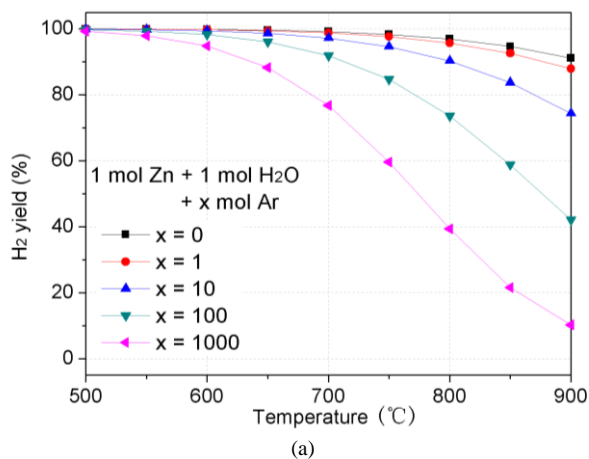


FIGURE 5 Variation of the equilibrium composition as a function of the initial $\text{H}_2\text{O}/\text{Zn}$ molar ratio while $T=800^\circ\text{C}$, $p=1\text{atm}$, the initial zinc molar amount was set constant at 1 mol

As in previous experimental studies of zinc hydrolysis, water steam was often brought into reactor via inert carrying gases [8, 12]. Therefore, the influence of inert carrying gas was also studied in this paper. We take argon as an example for inert carrying gas, as it is usually used in experiments as an inert content. The

hydrogen equilibrium yield ratio at different temperatures with giving initial molar content of argon and 1 mol zinc and 1 mol water were calculated. As Figure 5 shows, the hydrogen equilibrium yield ratio at constant temperature decreases as the initial amount of argon increases. Higher the temperature is, larger the influence of inert gas amount appears on the reaction equilibrium. So it is suggested to use lower flow rate of inert carrying gas in experiments. In the temperature range of 500°C to 900°C , as shown in Figure 5, the hydrogen equilibrium yield ratio dropped a little when the initial $\text{Ar}/\text{H}_2\text{O}$ ratio varies from 0 to 2. Above all, the concentration of steam in carrying gas in experiments should better be kept above 50%, so that the relative error of thermodynamic equilibrium caused by the inert carrying gas can be controlled in 4%.

4 Conclusions

Detailed thermodynamic studies were carried out for the hydrogen production via zinc hydrolysis in this paper. The thermodynamic heat effect and several important process parameters of zinc hydrolysis reaction were studied. The study results show that the zinc hydrolysis can proceed auto-thermally. It is reasonable to keep the temperature of zinc hydrolysis under 900°C to get a high zinc conversion. The system pressure has no notable thermodynamic influences on the hydrolysis reaction. The initial $\text{H}_2\text{O}/\text{Zn}$ molar ratio should be controlled in a reasonable range. The concentration of steam in carrying gas in experiments should better be kept above 50% to get a relative precise experimental result.

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Authors	
	<p>Lv Ming, born on February 26, 1982, Hunan China</p> <p>Current position: Ph.D., lecturer of Department of Ocean Engineering in Hangzhou Dianzi University.</p> <p>University studies: Zhejiang University</p> <p>Scientific interest: major in clean energy production and artificial upwelling</p> <p>Experience: Zhejiang University 2004/9-2009/12 Energy and Environment Engineering PhD research subjects engaged in clean energy production and artificial upwelling</p>
	<p>Liu Haiqiang, born on April 19, 1980, JiangXi China</p> <p>Current position: Ph.D., lecturer of Department of Ocean Engineering in Hangzhou Dianzi University</p> <p>University studies: Zhejiang University</p> <p>Scientific interest: Intelligent design and digital product design</p> <p>Experience: Zhejiang University 2005/9-2010/9 Mechanical Manufacturing and Automation PhD research subjects engaged in theory and method of Product Data Management well known about PLM methodology and research integrated techniques of CAX/PDM, and focused on build the integrated product data model</p>