Designing A Reactor to Generate Hydrogen Bubbles

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Abstract: Hydrogen is produced by the reaction between zinc and hydrochloric acid. This reaction is used to illustrate the importance of considering thermodynamics when designing a chemical reactor. The gas released is collected in soap bubbles that rise in the air, indicating that a lighter than air gas has been produced. The bubbles can be lit to add a dramatic effect to the demonstration. The reaction is highly exothermic, raising the temperature of the reaction materials and the reactor. Batch operation of this reactor would require short cooling periods between reactions. Alternatively, a modification of the design is suggested to allow for continuous cooling of the vessel, which would allow semicontinuous operation of the reactor. (Zinc would have to be periodically replenished as it is consumed in the reaction.) The consequences associated with the cooling of the vessel are discussed.

Introduction

When chemical engineers design a reactor, they must pay close attention to the physical and chemical properties of the system because they must incorporate any special requirements into the design. In this paper, we present a demonstration that illustrates several chemical engineering and gas law concepts. We have designed a batch reactor for the reaction between zinc and aqueous hydrochloric acid described by eq 1:

$$Zn(s) + 2\ HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g) \qquad (1)$$

Careful consideration was given to the thermodynamic properties of the reaction.

This reaction is highly exothermic; therefore, it is necessary to allow for some cooling time between runs or to incorporate a cooling mechanism into the design (see below). The hydrogen produced is collected in soap bubbles that float away from the reactor and can be lit. The bubbles are small and they are partially filled with nitrogen, water vapor, and oxygen. Due to their size and to the high hydrogen-to-oxygen ratio, the flash produced when the bubbles are lit is not accompanied by any noise, much less a loud bang, like other demonstrations involving hydrogen [1].

Following the experiment description, design variations, an alternative reaction (with larger ΔH^o) for the production of hydrogen, and the requirements for the bubbles to rise are discussed.

Experimental

Materials and Equipment. The required materials and equipment are 400 ml of 4.5 M HCl; zinc (sold as Zinc, *Mossy*); soap solution made by mixing dish detergent (20 mL), glycerine (10 mL), and distilled water (70 mL); a 500-mL separatory funnel; a gas-sampling tube, approximate dimensions: 25 cm (10 in) in length, 5 cm (2 in) in diameter, wrapped in tape; 500-mL and 100-mL beakers; a plastic wand (straw); Tygon tubing; and a long-necked butane lighter. Optional equipment is a nitrogen tank and a digital thermometer.

Experimental Design. The experimental setup is illustrated in Figure 1. A 500-mL separatory funnel was connected by a piece of Tygon tubing to the reaction vessel. The length of the tubing varies, depending on the size and position of the vessel. Our reactor was made from a gas-sampling tube in the shape of a cylinder (length = 25 cm; diameter = 5.2 cm) with stopcocks at the entrance and exit orifices. A side arm with a 2.5-cm diameter was attached. Glassblowing was required to attach the side arm. If glassblowing facilities are not available the side arm can be connected to the reaction vessel by a "T" connector, which can be inserted between valves 1 and 2. The open end of the T is connected to the wand with Tygon tubing. After the reaction starts, valve 1 is closed. Valve 2 is left open so that the hydrogen gas is released through it. This arrangement, however, presents a significant disadvantage. In order to introduce the zinc to the reactor, one of the valves in the gas-sampling chamber must be disassembled. Zinc pellets can then be introduced via the end of the reactor. *Warning*: If this arrangement is used, valves 2 and 3 must not both be in the closed position when the reaction is taking place because there is no release for the pressure buildup as a consequence of hydrogen formation.

Zinc pellets can be introduced through the side arm and collected at the bottom of the reaction vessel. The side arm was then plugged with a rubber stopper with a hole; a tube was fed through the hole. This tube was long enough to allow access to a 50-mL beaker, which was filled with the soap solution (see *Materials* for a description). A 15-cm wand was attached to the end of the tube. A short length of tubing was attached to the exit of the reactor. Waste products and excess aqueous HCl flowed through this tube and were collected in a large (>500 mL) plastic container.

A digital thermometer should be used to illustrate the temperature changes in the reactor during the experiment. The probe must be attached to the exterior of the reaction chamber. The ability of the students to observe the temperature changes is important for the purpose of the demonstration. If a thermometer is not available, the instructor should point out the temperature increase.

Procedure. Initially, all the valves are turned to the closed position. The separatory funnel is filled with 400 mL of 4.5 M HCl (approximately 3/4 full). Several zinc pellets (~5 g) are placed in the reaction vessel. Valves 1 and 2 are opened to allow about 50 mL of aqueous HCl into the reactor. Then, both valves are closed. Reaction

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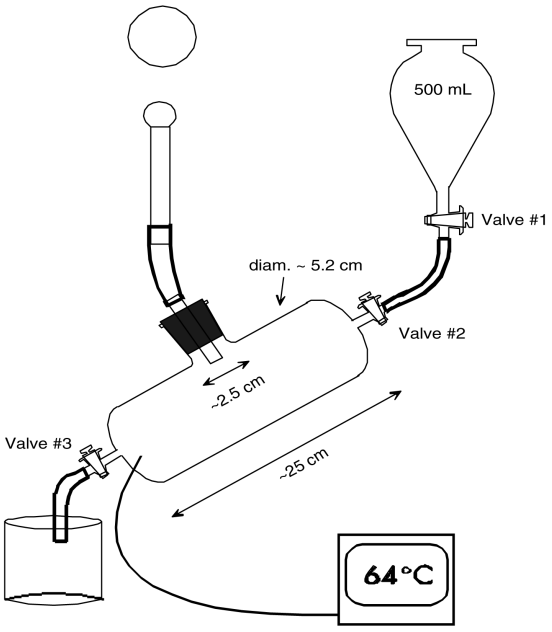

Figure 1. Schematics of the reactor used in this experiment. The separatory funnel (top right) and the reactor (center) are attached to vertical stands (not shown). We place the reactor at an angle to more easily evacuate the reaction waste after a batch run is completed by opening valve 3. Not shown is another beaker that contains the soap solution that makes the bubbles. The wand must be periodically dipped into this beaker to form a soap film.

of aqueous HCl with Zn results in the formation of H_2(g) according to eq 1. The hydrogen produced is collected in soap bubbles. The wand is dipped into the soap until its end is covered with a thin layer of soap. The wand is then shaken to release the bubbles that form at its end. Once the zinc pellets are fully dissolved, the apparatus is allowed to cool for 5 min before addition of fresh reactants. The chemicals can be removed from the reactor by opening valve 3.

If desired, the bubbles can be lit using a long-necked butane lighter. Each bubble must be at least a foot away from the wand before it is lit.

Safety. Hydrogen gas is highly flammable. Igniting small bubbles (2-in diameter) results in a beautiful flash; however, precautions must be taken to avoid igniting the hydrogen gas accumulating in the wand, the tubing, or the reactor. It is important that the bubbles are completely separated from the wand before ignition to avoid flash through the tubing into the reactor as this may cause an explosion. Ignition can also be avoided if the reactor is flushed with nitrogen gas prior to the beginning of the reaction.

Commercially available zinc *mossy* is the optimal size for an adequate reaction rate. (See the Discussion for comments on the HCl concentration.) Under no circumstances should zinc *dust* be used, as the reaction would be very vigorous.

Under normal circumstances there should be no explosion due to ignition of the hydrogen in the reaction chamber; however, if one desires to increase the safety of the experiment, a safety shield can be used to separate the experiment from the audience. Furthermore, the reaction chamber can be wrapped with tape. Common electrical tape (super 33+) is adequate as it resists temperatures up to 105 ºC. If higher thermal resistance is required, type 27 high-temperature glass-cloth tape resists up to 130 ºC; however, its cost is about twice that of regular electrical tape.

Another important concern is the fact that the reaction is highly exothermic. Care must be taken to avoid skin contact with hot surfaces.

The valves at both ends of the reactor must be periodically checked to ensure that they are not being plugged with grease.

As is always the case when handling acids, be careful to avoid spills.

Safety glasses must be worn at all times during this experiment.

Waste Disposal. The products of this reaction are $ZnCl_2$ and unreacted aqueous HCl (we use approximately twice as much aqueous HCl as required to fully dissolve the zinc pellets). Safe waste-disposal policies vary from state to state and should be consulted before discarding any products. If allowed by your local policy, $ZnCl_2$ and HCl can be safely disposed down the drain with running water, but only after the solution has been brought to a pH between 4 and 10 using NaOH or other base. If any solid Zn remains (because aqueous HCl is discarded before the reaction is completed), it should be removed from the reactor and disposed of in a solid waste container. Alternatively, all wastes should be disposed of in an appropriate waste container.

Discussion

The most important aspect of this demonstration is the effect of the temperature on the operation of the reactor. If a digital thermometer is available, it is very obvious to the audience that there is a steady increase of temperature as the reaction proceeds. Otherwise, the instructor should point out this increase. During discussion of the demonstration, the need for a cooling period before the next batch is introduced in the reactor should be explained to the students. This cooling period, if this were an industrial setting, would result in a loss of productivity due to the down time of the reactor. This allows two modifications that increase efficiency to be presented, as discussed in the following two paragraphs.

First, if a good glassblowing shop is available, a modification may be made to the reactor to alter its operation. A water jacket can be blown around the reactor (this is not a trivial glassblowing job). With water circulation, the reaction can be kept at room temperature. This has two advantages. First, it makes the process safer by eliminating the possibility of accidental contact with a hot surface. Second, it reduces the downtime of operation of the reactor, which is one of the goals of effective reactor design. In fact, the reactor can be operated continuously because the heat is transferred between the reaction mixture and the cooling water. On the other hand there is a disadvantage; the rate of reaction is reduced, so that a slightly higher concentration of aqueous HCl is required. For continuous operation, zinc can be introduced in the reactor and aqueous HCl can be dripped in. If valve 3 is opened permanently, the excess material will be allowed to flow out of the reactor. This can be used to demonstrate a semibatch operation [2] to the students in the audience.

Second, hydrogen gas can be produced using an alternative reaction, as given in eq 2.

$$Mg(s) + 2\ HCl(aq) \rightarrow MgCl_2(aq) + H_2(g) \qquad (2)$$

Unfortunately, this reaction releases about three times the amount of heat (per mole of metal) as the reaction between Zn and aqueous HCl. At 298 K, ΔH^o(eq 1) is –153.9 kJ mol^{-1} and ΔH^o(eq 2) is –466.9 kJ mol^{-1} [3]. The reaction of 5 g of Zn with aqueous HCl results in the release of 0.075 mol of H_2 (roughly 1.5 liters) and 11.8 kJ of heat. This causes an increase in the temperature of the reaction vessel (including the reaction mixture) of about 35 ºC, (C_p(mixture) $\simeq$ C_p (H_2O) = 4180 J

kg^{-1} K^{-1}, [3]). A heat capacity of 750 J kg^{-1} K^{-1} [4] was used to calculate the heat absorbed by the reactor (m = 150 g). If magnesium were used, 1.9 g would be required to produce 1.5 liters of hydrogen gas, but the reaction would release 35.5 kJ in the form of heat, bringing the reaction mixture to a boil. Not only would the vessel be at ~ 100 ºC, thereby increasing the risk of injury, but about 10% of the mixture would boil out. The bubbles formed would be heavier because they would be partially filled with water vapor and they may not float at all. Originally, we did use the reaction between magnesium and aqueous HCl to produce hydrogen. The reaction mixture boiled violently and further research was not continued. The use of a cooled reactor (see above) may allow this reaction to proceed under milder temperature conditions. Still, we strongly discourage the use of this reaction. We describe it here because it can be brought up as a numerical example of a reaction that produces the same product but with undesirable side effects. In this case, a lower ΔH^{o} (in absolute value) appears to be more beneficial for the reactor to work efficiently. Of course, kinetic considerations are important, but not addressed here.

The different experiments described here (HCl(aq) reacting with different metals and under different cooling conditions) may be used to illustrate the importance of considering the thermodynamics of a reaction when designing a reactor. They can also help to facilitate a discussion about the cooling requirements for continuous operation of an engine [5], (second law of thermodynamics, Kelvin-Planck statement [6]).

The soap solution is an important concern. The solution must be viscous enough to form bubbles and light enough to float in air. The solution described above is the one that offers the best compromise between the two extremes.

One reason hydrogen gas was used in the experiment is because of its ability to rise in air. This allows the illustration of the concept of gas densities. At 273 K and 1 atm, $\rho(H_2)$ = 0.0899 kg m^{-3}, while ρ(air) $\simeq$ 1.3 kg m^{-3}. The difference in density accounts for the ability of hydrogen to lift the weight of the soap in the bubble. The bubble must contain enough hydrogen to offset this weight. For instance, a bubble with a 5-cm diameter can lift a mass of soap equal to 7.9×10^{-5} kg; if its diameter is 2 cm, it can only lift 0.5×10^{-5} kg of soap. Because the mass of the soap in a bubble is independent of the size, bigger soap bubbles are desired.

The rate of reaction between zinc and hydrochloric acid is also an important concern. For the bubbles to be large enough to float, the reaction needs to be vigorous in order to produce enough hydrogen gas to generate a large pressure differential between the reactor's interior and its exterior. The rate of the reaction depends on four factors: the surface area of the zinc pellets, the concentration of the acid, the temperature of the reaction mixture, and the presence of a catalyst. A temperature increase is not desirable for safety reasons. A catalyst is not used, either. One can, therefore, speed up the reaction by finely dividing the pellets (We use Zinc, *mossy*, without further modification, although we tend to use the smaller sizes.) or by using a higher concentration of acid. This last option must be weighed against the increased hazard of using a higher acid concentration. After some trial and error, it was found that 4.5 M was the lowest concentration of aqueous HCl that resulted in a rate of reaction adequate to produce useful bubbles.

As discussed above, the hydrogen bubbles can be ignited, if appropriate. Precautions must be taken not to ignite the hydrogen gas remaining in the reaction chamber. Previous work in this area resulted in a number of exciting demonstrations (see for example references [1] and [7]). Our method requires fairly inexpensive materials and can produce the hydrogen gas in situ by chemical methods.

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