

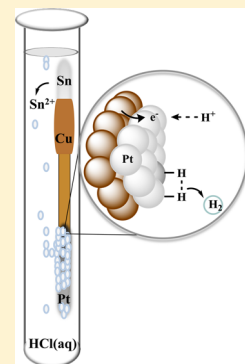
# Exploring Hydrogen Evolution and the Overpotential

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**S** Supporting Information

**ABSTRACT:** The laboratory experiment described provides insight into the energetics of hydrogen evolution at an electrode as well as the intrinsic barrier that typically impedes reaction. In the course of the exercise, students find that Sn(s) is thermodynamically capable of combining with protons to form hydrogen, but that the direct reaction occurs at a negligible rate in the absence of an applied overpotential or a suitable catalyst. Exploring the latter option, students fabricate mini-cells with tin as the anode and either copper or platinum as the cathode. Upon immersing the assemblies in HCl(aq), they observe vigorous formation of H<sub>2</sub>(g), but only when tin and platinum electrodes are present. They also detect a change in mass that is attributable to the loss of tin, and they attempt to reconcile the stoichiometry of reaction. The exercise requires minimal equipment and provides useful insight into processes that are potentially important to the future energy economy.



**KEYWORDS:** Second-Year Undergraduate, Upper-Division Undergraduate, Inorganic Chemistry, Analytical Chemistry, Electrochemistry, Metals, Mechanisms of Reactions, Catalysis, Laboratory Instruction, Hands-On Learning/Manipulatives

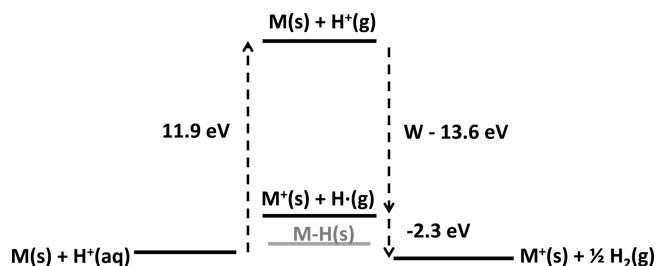
## BACKGROUND

Interconverting protons and hydrogen gas at an electrode is more difficult to achieve than a glance at eq 1 might suggest. To



be more specific, consider running eq 1, the half reaction associated with the standard hydrogen electrode (SHE), in the forward direction. As will become clear, it is not enough for the electrode to supply electrons; it must catalyze the reaction as well. (Note that a fuel cell can utilize the same reaction, though running in the opposite direction, to generate electricity by oxidizing H<sub>2</sub>(g) at the anode.<sup>1,2</sup> In that context, the need for catalysis is perhaps more obvious because fuels typically have to be kinetically stable materials.) In general, if the electrode that is available is not a good enough catalyst, it is possible to accelerate the desired reaction by applying a bias voltage. Accordingly, one defines the overpotential as the potential required, over and above that dictated by thermodynamics, to induce a reaction to occur at a practicable rate. In the laboratory experiment described herein, students take a different approach. They first establish that the rate of reaction between tin metal and H<sup>+</sup>(aq) to produce hydrogen and Sn<sup>2+</sup>(aq) is negligible at room temperature, despite the fact that the process is thermodynamically feasible. Contacting tin to copper offers no measurable enhancement, but the production of hydrogen gas finally occurs upon plating the opposite end of the copper wire with a sufficiently good catalyst.

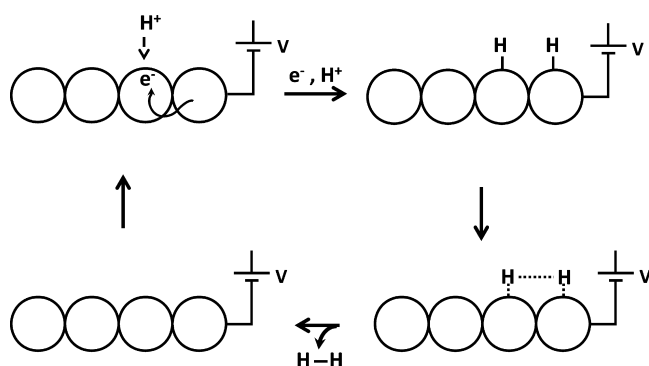
To understand the need for a catalyst, it is helpful to break down the process of hydrogen evolution into a series of steps. Suppose a metal electrode (M) is to be the source of electrons. The energy profile in Figure 1, which doubles as a reaction



**Figure 1.** Energies involved in converting from a state of a metal electrode and a proton in solution to hydrogen gas include the endothermic process of desolvating the proton. Other steps include transfer of an electron from M(s) to the proton, and formation of the H–H bond. *W* denotes the work function of the metal, and the energy released upon forming 1/2H<sub>2</sub>(g) is ca. 2.3 eV. The vertical placement of the M–H(s) state indicates the stabilization afforded H· by bond formation to metal.

coordinate diagram, describes processes involved in forming 1/2 H<sub>2</sub>(g). First, desolvation of the proton involves a significant cost, estimated to be about 11.9 eV.<sup>3</sup> Uptake of the electron by the proton gives energy back, but not the hydrogen atom's full ionization energy of 13.6 eV. Indeed, the net energy change in electronvolts is actually *W* – 13.6, where *W* is the work function of the electrode, i.e., the energy required to extract an electron from the metal. The work function depends on the metal involved,<sup>4</sup> but let us assume *W* = 4.5 eV so that the overall reaction is thermoneutral. Adding up the numbers in Figure 1 reveals that the formation of the free hydrogen atom is uphill by 2.3 eV! From the point of view of thermodynamics,

the overall reaction is nevertheless feasible because H–H bond formation ultimately releases that much energy per atom of hydrogen. However, in the real world reactions tend to occur in a stepwise fashion, and the kinetic barrier to reaction is prohibitively high for a *pathway* that involves the generation of the high energy H $\cdot$  intermediate. A brute force approach to inducing reaction involves applying an overpotential, which in effect adds energy to electrons within the electrode, lowering the work function and the barrier to reaction. An alternative chemical approach involves incorporating an electrode that can play an active role in the production of hydrogen. In particular, one can avoid forming a free-standing H $\cdot$  atom if formation of an M–H bond to the electrode surface occurs when the proton takes up an electron (Figure 1). Figure 2 illustrates a possible mechanism for forming H–H from neighboring M–H groups. For such a pathway to be viable, the strength of the M–H bond is a critical factor.<sup>5</sup>



**Figure 2.** A possible catalytic mechanism for cathodic production of H–H at a metal surface. The electrode stabilizes “H atoms” by forming M–H bonds, paving the way to the formation of molecular hydrogen. The drawing is schematic; in actuality, each hydrogen atom could bind by bridging between two or more metal atoms on the surface.

On one hand, the Hg–H bond provides so little stabilization that it is very difficult to form hydrogen at a mercury electrode.<sup>6</sup> On the other, metals that form very stable bonds to the hydrogen atom are not necessarily useful because the process may tend to stop at the formation of M–H. To sum up, the processes of charge recombination and H–H bond formation are both drivers for eq 1. The complicating mechanistic issue is that H–H bond formation is a “delayed” benefit; typically, the combining centers have to accept electrons before bond formation becomes possible. Understanding the challenges involved in implementing eq 1 at electrodes is worthwhile because of the important role hydrogen can play in the future energy economy.<sup>7,8</sup>

## ■ HYDROGEN EVOLUTION EXPERIMENTS

In this laboratory exercise, students learn how it is possible to join a catalyst to another metal capable of reacting with acid to produce hydrogen. They begin by immersing Cu, Sn, or Pt wires separately into 3 M HCl and demonstrating that neither evolves hydrogen on its own. To test Cu in combination with another metal, they (1) plate platinum at the end of a copper wire, and (2) join Sn and Cu wires together with a conducting crimp connector. Exposing either construct to 3 M HCl once again fails to generate hydrogen gas. With the third combination, they establish that generation of hydrogen occurs

when a platinum wire contacts Sn or the copper end of a Cu/Sn assembly.

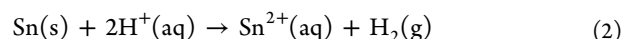
For a more quantitative analysis, the students construct a mini-cell by joining a small length of Sn wire to the Cu/Pt assembly opposite the platinum end with the help of a copper crimp (Figure 3). They then dry and weigh the assembly to



**Figure 3.** Mini-cell made from a Cu wire coated with Pt at one end and joined to a Sn wire at the other end by means of a copper crimp connector.

$\pm 0.1$  mg. They also assemble a reaction chamber and record the initial volume of water in the syringe at one end of the U-tube after equilibrating the two arms of the attached U-tube (Figure 4). Starting the reaction involves peeling back the tape that covers the hole in the stopper, dropping in the mini-cell, resealing the hole, and securing the stopper with a rubber band. As hydrogen evolves, the water level drops on the flask side of the U-tube. Gentle agitation helps dislodge hydrogen bubbles clinging to the wire. Once hydrogen evolution ceases, students re-equilibrate the two sides of the U-tube by lowering the syringe end and record the volume change in the syringe. The next step is to remove the cell assembly from the flask, dry as before, and weigh to  $\pm 0.1$  mg.

In the written report, students establish that the reaction in eq 2 is thermodynamically feasible with the aid of a table of standard reduction potentials. They describe the function of each component in the mini-cell, and they deduce an upper limit (in mV) for the overpotential for hydrogen evolution at platinum as well as a lower limit for the corresponding value at copper. They check the stoichiometry of reaction by determining the number of moles of Sn dissolved from the mass change as well as the number of moles of H<sub>2</sub> from the volume change.

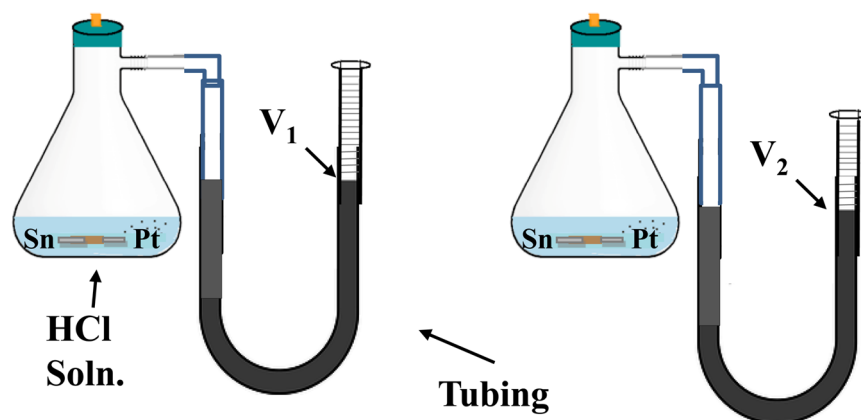


Typically, the volume change is smaller than expected, so it is also appropriate to discuss possible systematic errors involved.

## ■ OVERVIEW

The laboratory exercise is attractive because students learn about an important, but often overlooked concept. It also addresses the problem in a way that is inexpensive and requires minimal equipment. The amount of waste produced is also manageable. A limitation is that the volume change and the mass change are only on the order of a milliliter and a milligram, respectively. For those reasons and others already mentioned, the experiment is only semiquantitative. As preparation, students read the theory section prior to coming to the laboratory and answer prelab questions listed in the Supporting Information. The prelab assignment also directs students to find additional background information in two articles that helped stimulate the development of the laboratory exercise.<sup>9,10</sup> The Supporting Information also provides questions to answer for the lab report.

Advanced students will note that the hydrogen generation is initially vigorous before coming to a virtual standstill. The probable explanation is poisoning of the catalyst. The catalytic activity no doubt depends upon platinum centers with an

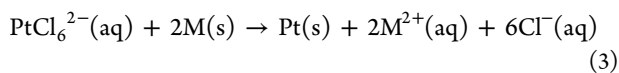


**Figure 4.** Reaction chamber consists of a stoppered filter flask connected to a calibrated syringe via a flexible U-tube filled with water. At the beginning (left) and the end (right) of the experiment students equalize the pressure in the two arms before reading the volume.

unsatisfied valence, and copper or tin atoms can easily lodge at those sites and prevent the desired reaction. Another assignment could be to devise experiments to test the idea. One could make the experiment more qualitative by incorporating comparisons with other reducing metals such as zinc and indium. Also, one can discuss a mechanism for hydrogen production that differs from that depicted in Figure 2. In particular, if the M–H derivative is hydridic, it is possible to form hydrogen by the protonation of the hydride ion. That is probably the mechanism bacterial enzymes utilize when they catalyze hydrogen evolution at active sites housing first-row transition metal ions.<sup>11</sup>

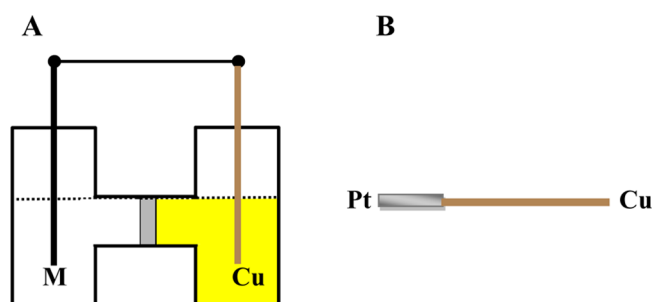
## METHODS AND PROCEDURES

Deposition of platinum is spontaneous when one exposes the end of a copper wire to commercially available  $\text{H}_2\text{PtCl}_6$  dissolved in ethanol. However, by utilizing electrons from another metal M, in principle one can improve the coating. For an  $\text{M}^{2+}/\text{M}$  counter-electrode, the net reaction is



Suitable choices for metal M include Zn, Sn, and Cu. Cleaning a 5 cm length of Cu wire involves treatment with steel wool followed by exposure to dilute HCl. This treatment helps remove insulator and/or oxide coatings that may be on the wire surface. After treating the other electrode similarly, the student dries each wire and connects them together with alligator clips. Inserting the M wire into the HCl compartment of the H cell and the Cu wire into the chloroplatinic acid compartment initiates plating (Figure 5). The length of the platinum coating should be at least 1.5 cm. It takes only a couple of minutes for the platinum coating to appear. Alternatively, students can use a potentiostat to deposit the platinum coating.

The construction of a simple reaction chamber only requires a 125 mL filter flask, ca. 50 cm of flexible tubing, a 5.0 mL calibrated (plastic) syringe, a rubber stopper with a predrilled hole, and demountable tape. After separately mounting the flask and the syringe, students connect the two with flexible tubing, fill the tubing with water, and remove any bubbles in the tubing or the syringe. The last step is introduction of 15 mL of 3.0 M HCl into 125 mL filter flask. A glass sleeve to help straighten the tubing is optional. Prior to running the experiment, the experimentalist establishes a pressure differential by raising the flask or the syringe. It is essential to address all leaks so that the



**Figure 5.** (A) H-cell for plating Pt on a Cu wire. Insert electrode M into 0.5 M HCl on one side of the frit, and on the other side a Cu wire into an ethanol solution shown as yellow containing 5 mM  $\text{H}_2\text{PtCl}_6$  and 50 mM HCl. (B) Cu wire with plated end.

system retains the pressure differential for at least 15 min. Encircling the chamber with a rubber band helps secure the stopper and prevents it from drifting up or down during the experiment. Before recording the volume in the syringe, the student should equalize the height of water in the two arms by elevating or lowering one side or the other. Alternatively, one could measure the amount of gas produced by incorporating a pressure sensor.

## HAZARDS

Safety goggles are essential for eye protection. There is a chance of inadvertent contact with hydrochloric acid or chloroplatinic acid solution. Cleansing with soap and water usually suffices for skin exposure, but wearing nitrile gloves is an option. When using pliers or a crimping tool, students need to take care to avoid pinching skin.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00189.

Listing of materials, equipment, a table of standard potentials, and visual aids; a “Notes to Instructor” document includes more experimental details and suggested prelab and discussion questions for students (PDF, DOCX)

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### Notes

The authors declare no competing financial interest.

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