Electrochemical Hydrogen Evolution: Sabatier's Principle and the Volcano Plot

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Ⓢ Supporting Information

ABSTRACT: The electrochemical hydrogen evolution reaction (HER) is growing in significance as society begins to rely more on renewable energy sources such as wind and solar power. Thus, research on designing new, inexpensive, and abundant HER catalysts is important. Here, we describe how a simple experiment combined with results from density functional theory (DFT) can be used to introduce the Sabatier principle and its importance when designing new catalysts for the HER. We also describe the difference between reactivity and catalytic activity of solid surfaces and explain how DFT is used to predict new catalysts based on this. Suited for upper-level high school and first-year university students, this exercise involves using a basic two-cell electrochemical setup to test multiple electrode materials as catalysts at one applied potential, and then constructing a volcano curve with the resulting currents. The curve visually shows students that the best HER catalysts are characterized by an optimal hydrogen binding energy (reactivity), as stated by the Sabatier principle. In addition, students may use this volcano curve to predict the activity of an untested catalyst solely from the catalyst reactivity. This exercise circumvents the complexity of traditional experiments while it still demonstrates the trends of the HER volcano known from literature.

KEYWORDS: High School/Introductory Chemistry, First-Year Undergraduate/General, Laboratory Instruction, Laboratory Instruction, Physical Chemistry, Hands-On Learning/Manipulatives, Catalysis, Electrolytic/Galvanic Cells/Potentials, Metals, Surface Science
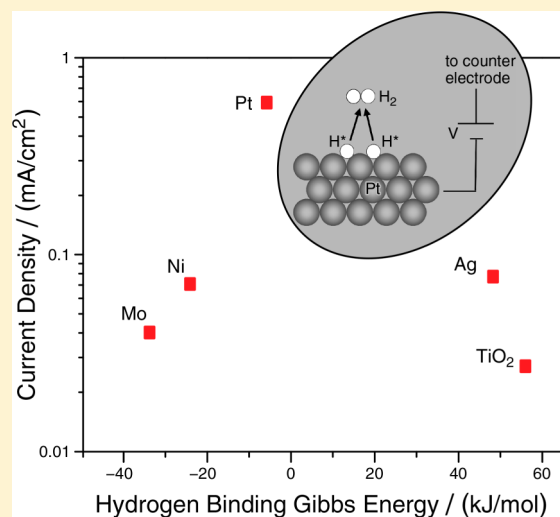
Electrochemistry gains ever more attention as the need for sustainable energy, often electrical, increases. It is therefore important to introduce students to electrocatalysis. A novel way of introducing students to the Sabatier principle (also see the laboratory exercise in ref 1) is presented and can be used to understand trends in catalytic activity in combination with density functional theory (DFT). This is achieved through a simple exercise using the classic electrochemical reaction for the hydrogen evolution reaction (HER) from water electrolysis:[2,3]

$$2H^+(aq) + 2e^- \leftrightarrow H_2(g) \qquad (1)$$

Through this exercise, students test the HER activity of Mo, Ni, Ag, Pt, and TiO$_2$ and use these activities to understand the way in which DFT calculations and practical electrochemical experiments are used together to predict new catalysts for electrocatalytic reactions.

■ THEORY

It has been shown that the binding energy of the intermediates in a reaction determines how well a catalyst works. Generally, in catalysis, the unlikely situation of more than two molecules colliding simultaneously in the gas phase is circumvented by the binding of the reagents to a surface—thereby dividing the collisions into several sequential steps. That is, the first molecule will collide with the surface resulting in a bound intermediate and the second molecule then collides with the intermediate and reacts and so forth for additional steps. When this occurs, the reagents' internal bonds may be weakened due to the interaction with the catalyst, thereby lowering the energy barrier for a reaction. Hence, a catalyst should bind strongly to the reagents and intermediates so that they are likely to adsorb to the surface, allowing the reaction to occur. However, if the catalyst binds the intermediates or products too strongly, the products formed on the catalyst cannot desorb, leaving the catalyst inhibited. Thus, the Sabatier principle states that the optimal catalyst binds a key intermediate strongly enough so

that the reagents will likely bind and react, but weakly enough so that the product will easily desorb.

When the activity of catalyst materials are plotted versus reactivity, a peak-shaped curve known as the Sabatier plot or volcano curve is obtained.[4] This plot clearly illustrates the difference between the reactivity and activity of various catalysts. Reactivity, given by the binding energy of the key intermediate, indicates how much the catalyst interacts with the reactants—positive values indicate a weak interaction and vice versa. Reactivity is in this work obtained from DFT. Activity, which depends on reactivity, is the measured rate of the catalytic reaction and is usually described per unit surface area. In this work, the measured rate is the current per area of the electrode from electrochemical experiments, as this is a direct measure of the electrons consumed in the HER, and the data from the DFT calculations are provided to the students.

EXPERIMENT

Experimental Overview

In the experiments, the students use different materials for the working electrode and measure the current obtained at a given potential to assess the activity of the metal. The measurements are carried out in a simple two-electrode compartment setup described below.

Electrode Preparation

The following electrodes were used:

- Molybdenum foil (Sigma-Aldrich) $3 \times 0.5 \times 0.05$ cm,
- Nickel foil (Goodfellow) $3 \times 0.5 \times 0.05$ cm,
- Silver foil (Goodfellow) $1.5 \times 0.5 \times 0.05$ cm,
- Titanium foil (Sigma-Aldrich) $3 \times 0.5 \times 0.025$ cm,
- Platinum wire (Goodfellow) 1.5 (length) $\times$ 0.05 (diameter) cm,
- One carbon rod (Ted Pella, Inc.) 4 cm (length) $\times$ 0.25 in. (diameter).

To make the surface of the titanium foil into a thick oxide layer, the foil was sanded and then put in a muffle oven at 200 °C in air for 20 min. All electrodes were masked with nail polish to allow more accurate measurements of the exposed surface areas. To ensure that only a clean nonoxidized metal was exposed to the electrolyte, each electrode, *except* titanium, was sanded with the same type of fine-grade sandpaper on the area exposed to the electrolyte. All circuit contact points were sanded, regardless of the material. The sanding was done immediately prior to starting each measurement.

Experimental Procedure

The two-electrode setup consisted of two 100 mL beakers filled with 0.1 M H_2SO_4 as an electrolyte and connected by a KNO_3 salt bridge (Figure 1). One beaker contained the foil or wire to be measured (working electrode) and was connected to the negative outlet. Nitrogen or argon (AGA technical purity) was bubbled through the solution and the beaker covered with plastic film (household or Parafilm). This kept the beaker with the working electrode essentially free of oxygen, preventing the competing oxygen reduction reaction. The other beaker contained a graphite rod (counter electrode) and was connected to the positive outlet of the power supply. The electrodes were connected to two multimeters: one in parallel with the power supply to measure the applied potential and the other in series between the counter electrode and the power supply to measure the current.
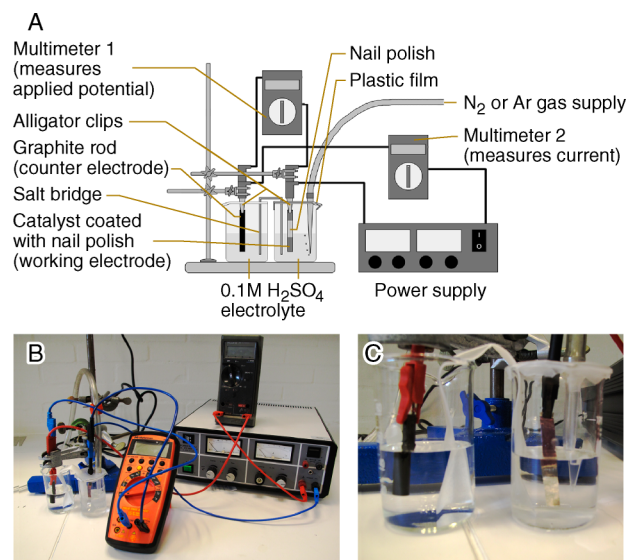
Figure 1. The experimental setup as a (A) schematic drawing, (B) photo of setup, and (C) close-up photo of the electrochemical cell.

With the power supply turned on, the potential was gradually raised to 3 V, held for 3 min, and then lowered to 1.7 V, at which point the current was recorded after the second decimal place had stabilized for 10 s. To ensure accuracy, both the current and potential were measured and adjusted to two decimal places precision, respectively. After the measurement, the working electrode was changed to a new material, and the procedures were repeated.

The precautions for the potentials were taken to ensure that the electrode surface was reduced to the metallic state and not an oxide and that any oxygen introduced by the electrode was completely removed by oxygen reduction. Furthermore, the potential was increased slowly to prevent overloading the multimeters.
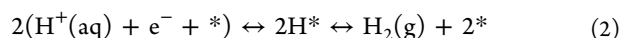
Data Processing

Data processing was done by dividing each measured current by the surface area exposed to the electrolyte to obtain the current density. The electrode area is obtained by considering each foil as two rectangular surfaces or the wire as a cylinder. As all electrodes were sanded with the same grade sandpaper, each surface roughness was approximately the same. The resulting values were plotted on a base-10 logarithmic axis versus the corresponding DFT-calculated hydrogen binding Gibbs energy (linear axis) to obtain the Sabatier plot. The exercise required approximately 1 h and 45 min in total: 30 min for setup, 45 min for measurements, and 30 min for data treatment.
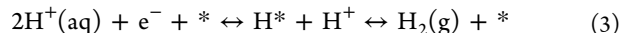
HAZARDS

As with all lab experiments, standard safety procedures should be obeyed. Goggles, gloves, and lab coats should be worn at all times. Concentrated sulfuric acid is corrosive and contact can cause severe damage to skin and eyes. The power supplies used here was limited to deliver no more than 10 V and 14 mW.

DENSITY FUNCTIONAL THEORY

To calculate the binding Gibbs energy of the key intermediate for any given reaction, one must know or assume the reaction mechanism. In the case of the HER, there are two proposed reaction mechanisms: the Volmer−Tafel mechanism
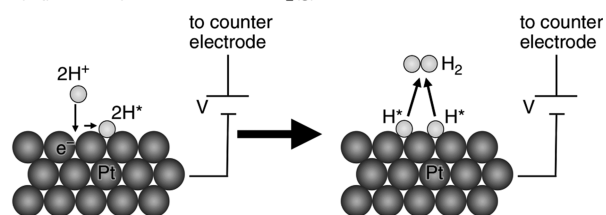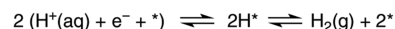
$$2(H^+(aq) + e^- + *) \leftrightarrow 2H^* \leftrightarrow H_2(g) + 2* \qquad (2)$$

and the Volmer−Heyrovsky mechanism

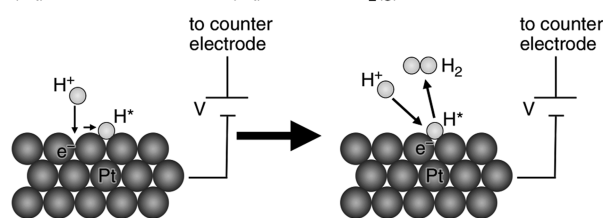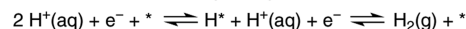$$2H^+(aq) + e^- + * \leftrightarrow H^* + H^+ \leftrightarrow H_2(g) + * \qquad (3)$$

where the asterisk (*) indicates an empty active site and the H* indicates a hydrogen atom bound to the active site (Figure 2). Both reactions give the overall reaction shown in eq 1.

Figure 2. Two mechanisms for the HER reaction: the Volmer−Tafel mechanism and the Volmer−Heyrovsky mechanism on platinum surfaces. The asterisk (*) represents a free active site, whereas H* indicates that the hydrogen atom is bound to the active site.

Regardless of the mechanism, hydrogen is the only intermediate binding to the catalyst and DFT is used to calculate the binding Gibbs energy of hydrogen to the investigated catalysts. The DFT calculation uses the atomic position of the nuclei and the atomic charge to calculate the total energy of a system. In this case, the binding energy of the hydrogen atom to the surface is obtained by subtracting the energy of surface-bound hydrogen from the energy of the clean surface and half the energy of a free hydrogen molecule. Then, using simple estimates for entropy and zero-point energy, the Gibbs energy of binding hydrogen at standard conditions is obtained.[5] This simple method allows the screening of many catalyst systems for HER as for other catalytic reactions. The surfaces investigated in this study with their hydrogen binding Gibbs energies are listed in Table 1.

Table 1. DFT-Calculated Binding Energies for the Bonding of Hydrogen to the Surface of Molybdenum, Nickel, Silver, Titanium Dioxide, and Platinum

Catalyst Material	Binding Gibbs Energy/ (kJ/mol)	Experimental Current/ (mA/cm^2)
Mo	−33.8	0.025
Ni	−24.1	0.045
Ag	48.2	0.082
TiO$_2$	56.0	0.016
Pt	−5.8	0.500

RESULTS

The experiment gives a set of currents at a fixed potential for several electrode materials. The resulting current density is plotted versus the hydrogen binding Gibbs energy obtained using DFT calculation. Data generated from the instructor is shown in Figure 3A and by the students in Figure 3B.

As expected, the catalyst electrodes lie on a volcano curve when plotted against the hydrogen bonding Gibbs energies, obtained from theoretical calculations.[6] The peak of the volcano is close to the hydrogen binding Gibbs energy ΔG_H = 0 kJ/mol, in accordance with predictions from literature.[6,7] Furthermore, platinum is located near the top, as it is the best material known for the HER. This illustrates that our simple experimental setup gives the activity behavior expected from more detailed studies.[8]

It should be noted that the potential for this comparison is not chosen arbitrarily. Using lower potentials than the one stated results in currents that are too small for precise measurement in this setup. By contrast, using larger potentials causes the activity of the electrode to be limited by the diffusion of protons to, and gas away from, the electrode. Unavoidable electrical resistances in the circuit will also influence the result if the measurements are done at larger currents.

In Figure 3B, the data obtained from a group of students are plotted versus the hydrogen binding energy from Table 1. It was observed that some students sanded the TiO$_2$ electrode surface, thereby removing the oxide layer and exposing the pure metallic titanium. Some students also did not sand the electrode contact point. Both gave rise to erroneous results (Not shown in Figure 3B). Additionally, one group experienced decreased activity, likely due to the electrode oxidizing in the electrolyte. It is therefore emphasized that the students should polish the electrodes immediately before submerging them into the electrolyte and that the current is recorded after the second decimal place of the current measurement stabilizes. Usual student data varied with around 6−69% from the data shown here. However, the discrepancy does not significantly affect the logarithmic trends of the Sabatier plot and is thus an indication of the robustness of the experimental procedure.

DISCUSSION

Electrolysis is a well-known method for producing hydrogen from water using electrical energy, and is expected to gain more importance in the future when we have to rely more on renewable energy. The HER is the cathodic half-reaction occurring during electrolysis[9] and is well understood in terms of trends in activity. From the previously stated reaction schemes, eqs 2 and 3, for catalytic hydrogen production, it can be concluded that hydrogen bound to the electrode surface is a key intermediate, regardless which mechanism applies. Hence, this is the key intermediate binding energy calculated in this study, as well as in literature in general.

In literature, one may find Sabatier curves for the HER where the exchange current density is plotted as a function of hydrogen's binding energy.[5,10] However, the measurement of the exchange current density is cumbersome and the concept is above the introductory level intended here. Figure 3 shows that the obtained experimental results also produce a volcano curve similar to that observed in literature, signifying that this simple exercise gives reasonably accurate results. The advantage of this experiment is that, through a simple exercise, students are able to make Sabatier plots and predict the peak to be at least close

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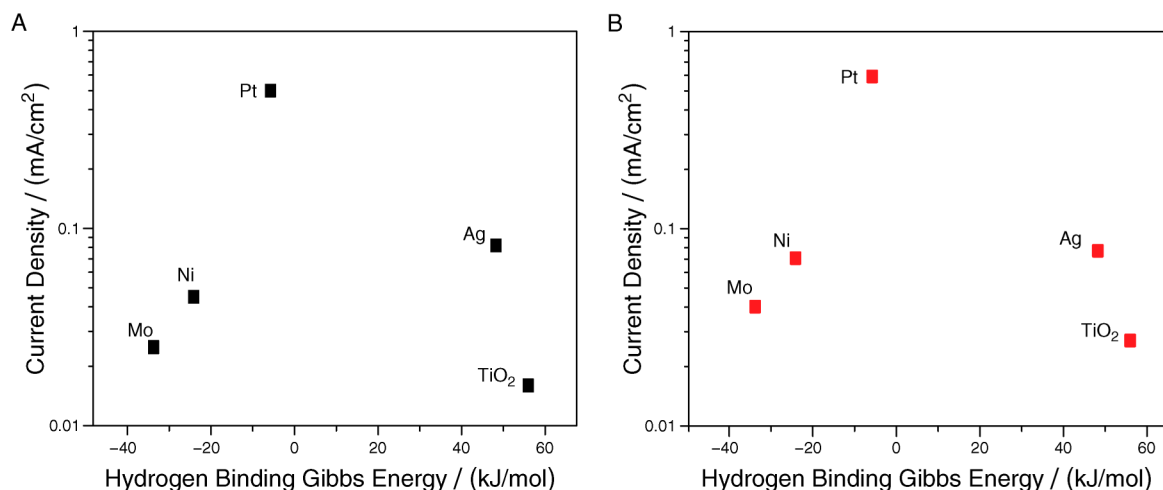
Figure 3. Sabatier plot of the activity of the measured catalysts (A) by the instructors and (B) by students versus the reactivity described by the DFT calculated hydrogen binding energy. Potential: 1.7 V.

to $\Delta G_H = 0$ kJ/mol, which according to previous DFT studies is the top of the volcano.[5,10]

In addition, this experiment effectively demonstrates the difference in electrocatalytic activity obtained using different metals, thereby revealing the reason why platinum is so commonly used in electrolysis units. A discussion with the students on what criteria a catalyst should fulfill is encouraged. Factors such as cost, activity, abundance, and toxicity should be noted.

To demonstrate how the volcano may be used, students were asked to locate the top of the volcano by linear regression, using the measurements for molybdenum and nickel to obtain the left side and silver and titanium dioxide to obtain the right side. Figure 4 shows the resulting volcanoes for the instructor
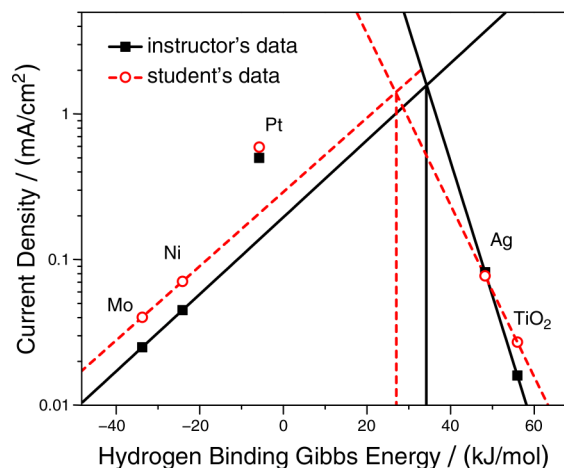
Figure 4. Results of predicting the volcano top by linear regression for the instructor data (square) and for the student data (circle). Potential: 1.7 V.

data and for student data. The two predictions fall within 40 kJ/mol from the known peak at 0 kJ/mol. Even though the prediction is not 0 kJ/mol, it is rare that a perfect volcano is found for any Sabatier plot and even rarer that it holds for such a simple experimental setup. This is what makes this experiment a powerful demonstration of how theory and experiments may be used together.

EXPERIMENTAL VARIATIONS

As a variation of this experiment, students can be suggested to test only the Mo, Ni, Ag, and TiO$_2$ electrodes and to predict the activity of Pt when given the corresponding hydrogen binding energy. The instructor should then measure the activity of Pt as a demonstration, and students should discuss how the measurement compares with their predictions. This exercise would allow students to understand the predicting power of the Sabatier plot. In addition, there would be a decrease in cost, as only one Pt electrode is needed.

Another experiment could be to measure the potential needed to obtain a current density of approximately 2 mA/cm^2. This resembles a working electrolysis unit more closely, as the current is constant and the potential varied. A volcano is also obtained in this case, when plotting the potential on the logarithmic y axis versus the hydrogen Gibbs binding energy. This affords an understanding of how the electrode material greatly affects the potential and energy required to drive the hydrogen production. The difficulty is that students should know the electrode area before measuring to calculate the actual current they need.

CONCLUSION

A simple and inexpensive way of allowing students to have hands-on experience with electrochemical measurements has been devised. Not only does the exercise demonstrate the Sabatier principle through experiments and theoretical calculations, it also shows how the latter is translated into a Sabatier plot. Experimenting with cost-effective and non-hazardous materials such as Ni, Mo, Ag, and TiO$_2$, students can understand the predictive power of DFT calculations using the Sabatier plot. In addition, the experiment is easy to conduct and requires minimal equipment and preparation. A group of 9th grade students successfully completed and understood the exercise. However, for full benefit, this exercise is recommended for upper-level high school students and undergraduate students.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Notes for the instructor and student instructions. This material is available via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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(9) While the hydrogen evolution reaction is taking place at the cathode, an oxidation reaction is occurring at the anode. If we consider that the process taking place is the water electrolysis, the expected anodic reaction is oxygen evolution reaction (OER):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
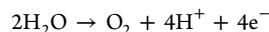
This reaction generates the protons used in the cathode for the HER and completes the water splinting into hydrogen and oxygen. In this case, we can consider that the overall process is

$$2H_2O \rightarrow H_2 + O_2$$
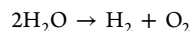
However, there is also the possibility that the carbon of the counter electrode is being oxidized evolving CO_2 instead of O_2. This will occur following the equation:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

Here, as in the case of OER, protons are formed too, while the split water is used to slowly oxidize the graphite electrode.

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