Hydrogen and palladium foil. Two classroom demonstrations.

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Background information. Upon passing hydrogen over palladium, an interstitial hydride is formed in which hydrogen *atoms* occupy octahedral holes in the cubic close-packed palladium lattice. It is believed that hydrogen molecules dissociate into atoms at the palladium surface and the atoms readily migrate from hole to hole throughout the palladium. There are a number of remarkable facts about this process:

1. Molecular hydrogen, despite its extraordinarily large bond dissociation energy of 436 kJ/mol, readily dissociates in the presence of palladium at temperatures as low as 37 K with little activation energy *(1, 2)*.
2. At temperatures above 50 K, hydrogen atoms migrate from hole-to-hole throughout the palladium *(1)*.
3. Palladium hydrides are non-stoichiometric, forming PdH_n, where n = 0 – 0.7 *(2, 3)*. Because there are four Pd atoms and four octahedral holes per unit cell, the theoretical maximum stoichiometry is Pd_1H_1 so that the experimentally observed maximum stoichiometry, $PdH_{0.7}$, represents 70% of the octahedral holes filled.
4. At its maximum stoichiometry, palladium has absorbed 935 times its volume at STP in hydrogen gas.
5. The absorption of hydrogen is so efficient, that E. W. Morley used palladium as a "vessel" to weigh hydrogen in his 1890 paper on the composition of water *(4)*.
6. For lower H:Pd ratios, $PdH_{0-0.02}$, the nature of palladium remains very much like that of pure Pd and is referred to as the α-phase. The most notable difference between pure Pd and the α-phase is that the latter has a slightly lower conductivity and its unit cell dimensions are slightly larger. A β-phase occurs along with the α-phase for $PdH_{0.02-0.58}$ and the β-phase exists exclusively for $PdH_{0.58-0.7}$ *(3)*. The β-phase differs from the α-phase in that the material becomes increasingly brittle as the H:Pd ratio increases and for $PdH_{>0.5}$ the material is a semi-conductor *(3)*.
7. The hydrogen atom density in $PdH_{0.7}$ is greater than that of pure liquid hydrogen. *(5)*

8. Palladium hydride readily releases H_2 by the reverse process of hydrogen absorption. There is an important commercial application of this process: hundreds of thousands of cubic meters of highly pure hydrogen are produced daily by passing H_2 through palladium metal *(3)*. Aside from D_2, no other substance can pass through Pd metal, not even helium.

Description

In the first classroom demonstration, students will observe the rapid reaction between H_2 gas and Pd metal. There is a color change for Pd and a noticeable increase in brittleness. Within one minute, the Pd has absorbed close to the literature maximum of $PdH_{0.7}$. In the second classroom demonstration, the kinetics of H_2 uptake is determined, and yields a zero-order rate law. Along with the results of the two demonstrations, several other experimental results can be added to a classroom discussion that should guide the students to conclude that the experimental conditions for Demonstration 2 result in H_2 mass transport-limited kinetics. Both classroom demonstrations use the same apparatus, but are otherwise mutually independent.

Possible modifications

These demonstrations can be simplified by not undertaking such a rigorous data analysis. Simply noting that H_2 uptake is constant is enough to conclude the process is zero order; 2. These activities could be developed into a 3-hour laboratory experiment.

Learning Outcomes

By observing either of these classroom demonstrations, students will (a) see a remarkable chemical phenomenon, (b) learn important descriptive inorganic chemistry related to palladium and hydrogen storage, (c) learn about non-stoichiometric, interstitial hydrides, and (d) collect data and perform calculations based on general chemistry concepts such as the ideal gas law. Additionally, observers of Demonstration 2 will (e) be able to collect data that can be used to determine the order of the chemical reaction $Pd(s) + {}^{n}/_{2}\, H_2(g) \rightarrow PdH_n(s)$, and (f) use the data and the rate law to determine the rate constant for the reaction.

Procedure

Equipment and chemicals

Aquarium bubbler tubing, 1/4–inch (6.36 mm) O.D., 4 mm I.D., 1.5 m (5 ft); small diameter Tygon tubing can also be used

Food coloring

Source of inert gas such as Ar or N_2.

Source of hydrogen, H_2

Bunsen burner

4-way stopcocks with Luer-Lok[1]

piece of palladium foil[2]

60-mL plastic syringes with Luer-Lok

Luer-Lok syringe caps[3]

tweezers

Apparatus

The apparatus for these two demonstrations is shown in Figure 1 and uses two 60-mL plastic syringes. A “4-way” valve[1] is used to connect a hydrogen-filled syringe to a syringe containing a piece of Pd foil[2] as well as to a 1.5 m length of clear aquarium bubbler tubing (or small diameter Tygon tubing or equivalent.)

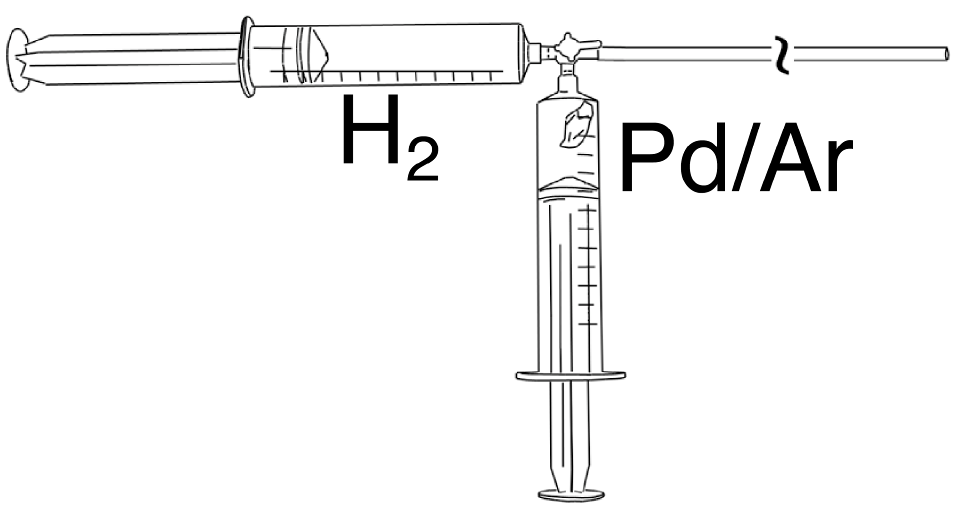


Figure 1. The experimental apparatus. The piece of palladium foil is shown in the syringe.

Purge Gas

We use argon as our purge gas in the following descriptions. If argon is not available, nitrogen may be used.

Hydrogen-Filled Syringe(s)

Syringes are filled from a tank of compressed H_2 gas. Connect the H_2 source to the Luer-Lok fitting on the syringe with an appropriate piece of tubing. Use the low-pressure control valve in order to prevent shooting the plunger out of the syringe barrel. Generally, it is best to purge the regulator and tubing with H_2 for a few seconds before filling syringes. A full syringe holds 60 mL gas. Immediately cap the syringe with a Luer-Lok syringe cap,[3] henceforth referred to as a "syringe cap."

Preparing the Palladium Foil.

We used a piece of Pd foil[2] of approximately 0.2 g for our experiments. Each 0.1 g Pd will absorb approximately 8 mL $H_2(g)$. Prior to either classroom demonstration, the Pd foil must be heat-treated over a burner flame to drive off hydrogen from a previous experiment or molecules such as water adhering to the surface. Tweezers are used to hold the Pd foil in the flame. After about 30 s in the flame, drop the red-hot Pd foil into a beaker filled with Ar while a gentle flow of Ar into the beaker assures contact between Pd and air is minimal. Remove the plunger from a 60-mL syringe and connect the Luer opening to the Ar supply tubing. Purge the air from the syringe barrel with a positive flow of gas. While Ar is flowing, drop the Pd foil from the beaker into the syringe barrel. Turn the Ar off and insert the plunger. Remove the Ar supply tubing and cap the syringe with a syringe cap. There should be approximately 30 mL of Ar present. The Pd foil is now ready.

Mass of the Palladium Foil.

This procedure needs to be done only occasionally. Heat-treat the Pd foil as described above. After it has cooled under a blanket of Ar, determine its mass in air. Record this mass on the box that is used to store the Pd; it will not change.

Positions of the 4-Way Valve.

The handle on the 4-way valve points to the closed connection. For these demonstrations, we will refer to the three valve connections using the names "H_2," "Pd/Ar," and "Tubing." The valve position shown in Figure 1 is "Tubing: Closed." Thus, both valve connections "H_2" and "Pd/Ar" are open in Figure 1. By turning the valve 90^o counterclockwise from its position in Figure 1, all three of the connections are open. The four valve positions are summarized in Figure 2.

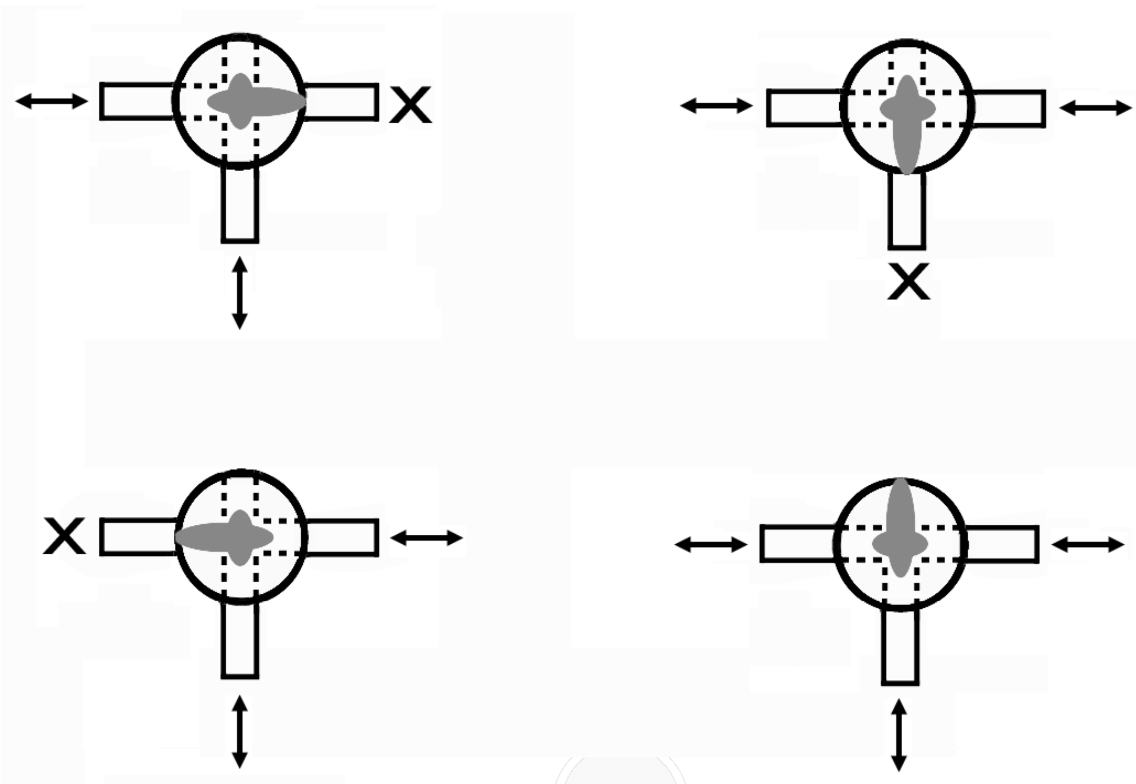


Figure 2. The positions of the 4-way valve. Arrows show direction of allowed gas flow; "x" indicates a closed outlet. Hint: The long handle on the valve points in the direction of the closed position.

Assembling the Apparatus.

The apparatus is identical for both demonstrations. Connect the aquarium tubing to the tapered fitting of the 4-way valve. Displace the air in the tubing with an Ar purge. As soon as possible after the Ar purge, position the valve to "Tubing: Closed." Next, add a 2 – 3 cm plug of water using a thin-stem pipet to the open end of the aquarium tubing. This works best if one completely fills the pipet and then slowly discharges the desired amount in one continuous action without moving the position of the pipet. The water plug should be positioned a few cm in from the open end. The visibility of the water plug is enhanced with food coloring. At this point, the valve is only connected to the tubing and the two syringes (one with H_2 and one with Pd/Ar) should both be capped and ready, but not connected. All of this can be done prior to the lecture.

Demonstration 1. Reaction between H_2 and Pd.

In this demonstration, we observe the rapid reaction between H_2 and Pd:

$$Pd(s) + {}^{n}/_{2}\, H_2(g) \rightarrow PdH_n(s)$$

When we refer to hydrogen (H_2) being "absorbed," bear in mind that in the product, PdH_n, the hydrogen exists as interstitial atoms of hydrogen in the octahedral holes of Pd(s) as per the Background information. This distinction is important because when reading "hydrogen is absorbed," one is naturally inclined to think that the integrity of the H_2 molecule is unchanged. The Pd foil will darken to gray from its normal dull silver color and may curl or fold. It will become noticeably brittle. Quantitative measurement of the amount of H_2 absorbed is one goal of the demonstration so that the stoichiometry of PdH_n can be determined. This demonstration is small scale and the use of a projection camera is necessary for all but the smallest classrooms. Allow about five minutes for this demonstration, not including calculations.

Conducting Demonstration 1.

Connect the Pd/Ar syringe to the 4-way valve as per Figure 1 and turn the stopcock to "H_2: Closed." Connect the H_2 syringe to the valve. Gently withdraw the plunger to the Pd/Ar syringe while watching the water plug. When the water plug is near the middle of the tubing, carefully mark the front-edge position (edge closest to valve) of the water plug. Record the initial volumes of H_2 and Ar, both of which are under pressures equal to $P_{external}$. Hint: Establish a spot along the plunger for consistent syringe volume readings, such as the front edge of the black rubber diaphragm. Turn the valve to "Tubing: Closed" and transfer H_2 to the Pd/Ar syringe until the latter contains close to 60 mL. Over the course of the next minute or so, push/pull the contents of the H_2 and Pd/Ar syringes back and forth at least once. The net total volume will decrease, but may be hard to notice. Without opening the valve to the tubing, try to establish an internal pressure approximately equal to $P_{external}$. If at least one of the plungers moves easily in its syringe barrel, this will occur automatically. If both plungers move with difficulty, anticipate the results using the guide that approximately 8 mL H_2 will be absorbed per 0.1 g Pd; position the plungers so that their combined volume of H_2 and Ar is less that the original combined volume by this anticipated amount. The goal is to attain $P_{internal}$ approximately equal to $P_{external}$. Carefully open the stopcock to all three positions open. The water plug in the tubing will move one way or the other. If the movement seems that it might be too great, close the valve to the tubing and adjust one of the syringe plungers and try again. Once all three positions are open, adjust either syringe plunger so that the water plug returns to its position prior to the experiment, whereupon $P_{internal} = P_{external}$. Determine $V_{abs,\,H_2}$ by measuring the difference in the total volume in the two syringes before ($t = 0$) and after mixing (t_f):

$$V_{abs,\,H_2} = V_{tot}(t = 0) - V_{tot}(t_f)$$

This volume, typically 8 mL per 0.1 g Pd, can be rendered into moles of H_2 using the ideal gas law and then into moles of H atoms. The temperature and barometric pressure are necessary. Typically, the mole ratio of H:Pd is close to the literature maximum of 0.7:1.

One of two short follow-up demonstrations is performed at this time. Both demonstrate the reaction

$$4\ H(Pd) + O_2(g) \rightarrow 2\ H_2O(g, l)$$

As a first option, remove the Pd/Ar syringe from the valve. Discharge some gas if necessary so that there is no more than 30 mL gas present. Draw 30 mL air into the syringe. A cloud of condensed water vapor will form on the walls of the syringe and the syringe will become warm to the touch. Remove the plunger and direct a stream of Ar over the condensation to show that it easily evaporates. The Pd foil will remain brittle because it still contains hydrogen until it is heat-treated again.

As a second option, transfer gas from the H_2 syringe so that the Pd/Ar syringe contains 60 mL of gas. Disconnect the Pd/Ar syringe, remove the plunger and *immediately* drop the Pd foil onto the thermal paper.[4] Notice the color of the Pd changes from dark gray back to dull silver within a split second and the thermal paper turns black under the Pd. Condensation of water is not noticed with Option 2, however the heat generated is from the formation of water from the reaction given above.

Demonstration 2. Kinetic rate law for H_2 uptake in Pd.

In this demonstration, we will observe the rate of H_2 uptake in Pd foil. The rate law follows zero order kinetics and is believed to be limited by H_2 mass transport as we will discuss below. As with the previous demonstration, it will be difficult to see important details in most classroom settings without a projection camera. Data should be collected for at least 10 minutes, however, after just a few minutes, the instructor may return to lecture while one individual continues to mark the progress for 10 – 30 minutes. The data set can be distributed to students later.

Conducting Demonstration 2.

Details for assembling the apparatus, including Ar-purging the aquarium tubing and flame-treating the Pd foil are described above. Assemble the apparatus as shown in the Figure 1. Position the 4-way valve to "H_2: Closed" and connect the H_2 and Pd/Ar syringes. Tape the aquarium tubing to a large piece of card-stock white poster board so that the tubing is horizontal during the experiment. Make a mark on the front edge (valve side) of the water plug. Start the timer at the same time as the valve is repositioned to "3-way open." Make marks every 30 seconds. In our experience, the water plug moves inward at a rate of approximately 4 cm/min. It is also necessary to measure the temperature and the barometric pressure.

Optional Control.

In order to establish that hydrogen loss is not accounting for the experimental observations, the experiment may be continued without the palladium present by repositioning the valve to "Pd/Ar: Closed." Hydrogen loss, usually insignificant compared to the H_2 uptake of the demonstration, does occur due to effusion through invisibly small leaks, e.g. at the connections to the valve or in syringes with plungers that are not gas-tight.

Data Analysis

Prior to the demonstration, the relationship between length of tubing and volume should be determined. This is accomplished by filling a short segment of tubing (e.g. 10 cm) with a large plug of water. The volume of water can be determined by measuring the mass of the tubing with and without the water and using the density of water. The length of the water plug is measured with a ruler. For the tubing we used, the relationship was:

$$V_{tubing} = 0.127 cm^2 \times l_{tubing}$$

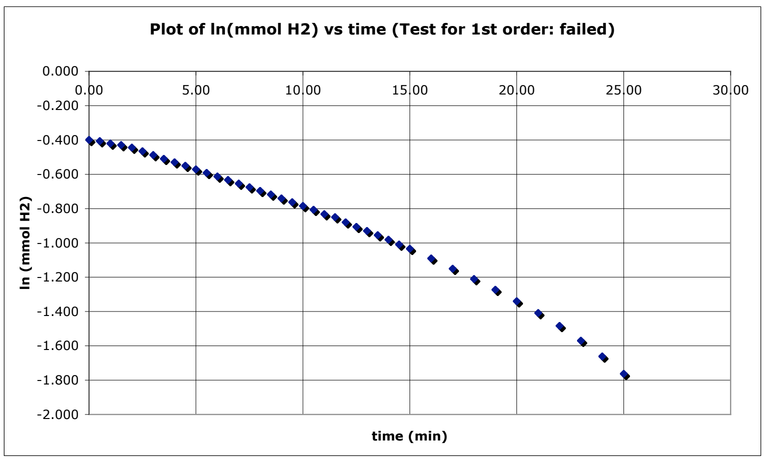
The volume of the tubing is the volume of the hydrogen gas absorbed, $V_{H_2,abs}$ in this demonstration.

Based on the amount of palladium used (described above), the maximum limit on how much hydrogen can be absorbed is determined (the calculated total amount that will be consumed at t = ∞.) This value will be used in the kinetics calculation as the *number of moles of hydrogen reagent present at t = 0*, $n_{H2}(t = 0)$. In our case, we used a piece of palladium with a mass of 0.2048 g or 1.924 mmol. Considering that the maximum formula for the palladium hydride is $PdH_{0.7}$, the value for $n_{H2}(t = 0)$ initial is:

$$\begin{aligned} n_{H_2}(t=0) &= 1.924\, mmol\, Pd \times \left(\frac{0.7\, mmol\, H}{1\, mmol\, Pd}\right) \times \left(\frac{1\, mmol\, H_2}{2\, mmol\, H}\right) \\ &= 0.6734\, mmol H_2 \end{aligned}$$

We created a spreadsheet with graphs to determine the reaction order using Microsoft Excel. Data in the columns included Column A: time (min), Column B: distance the water plug traveled (cm), Column C: Volume of H_2 absorbed, Column D: mmol H_2 reagent remaining,[5] Column E: ln(mmol of H_2 remaining), Column F: 1/mmol H_2 remaining, and Column G: mol H atoms/mol Pd atoms.[6]

The experimental data testing for first order (plot of ln(mmol H_2) vs time) and second order (plot of 1/mmol H_2 vs time) are given in Figure 3. These plots establish that the reaction is not first or second order because they do not give linear results.



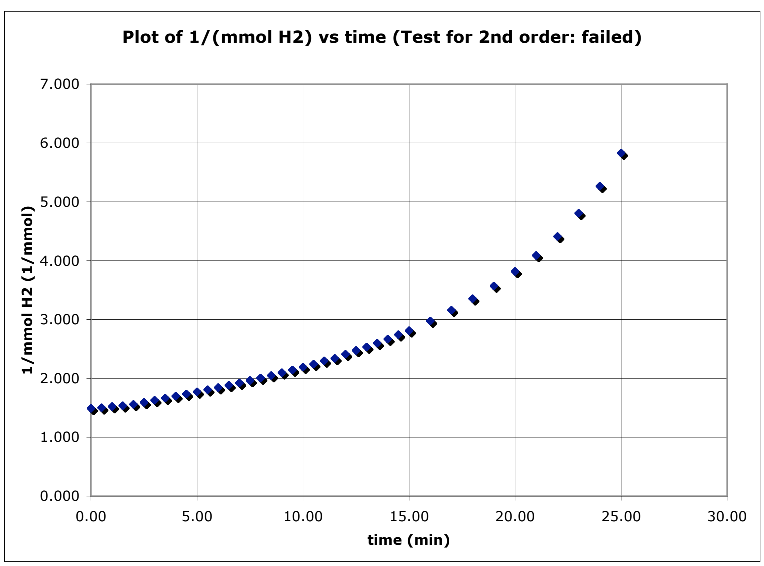


Figure 3. Plots of the experimental results used to establish the order of the reaction. Top figure is the test for first order: the plot of ln(mmol H_2 remaining) vs. time; bottom figure is the test for second order: the plot of 1/(mmol H_2 remaining) vs. time.

A plot of mmol H_2 remaining vs time, the test for zero-order, gives excellent results as shown in Figure 4. The left ordinate and triangular data markers give the amount of remaining H_2 reactant (mmol) vs time (min). The equation for the line is quite linear ($R^2 = 0.9973$) and is given by:

$$n_{H_2} = -0.0205\frac{mmol}{\min}t + 0.6704\,mmol$$

The right ordinate and circular data markers give the H:Pd ratio as the reaction proceeds. Note that after 25 minutes, the product has an approximate formula of $PdH_{0.5}$.

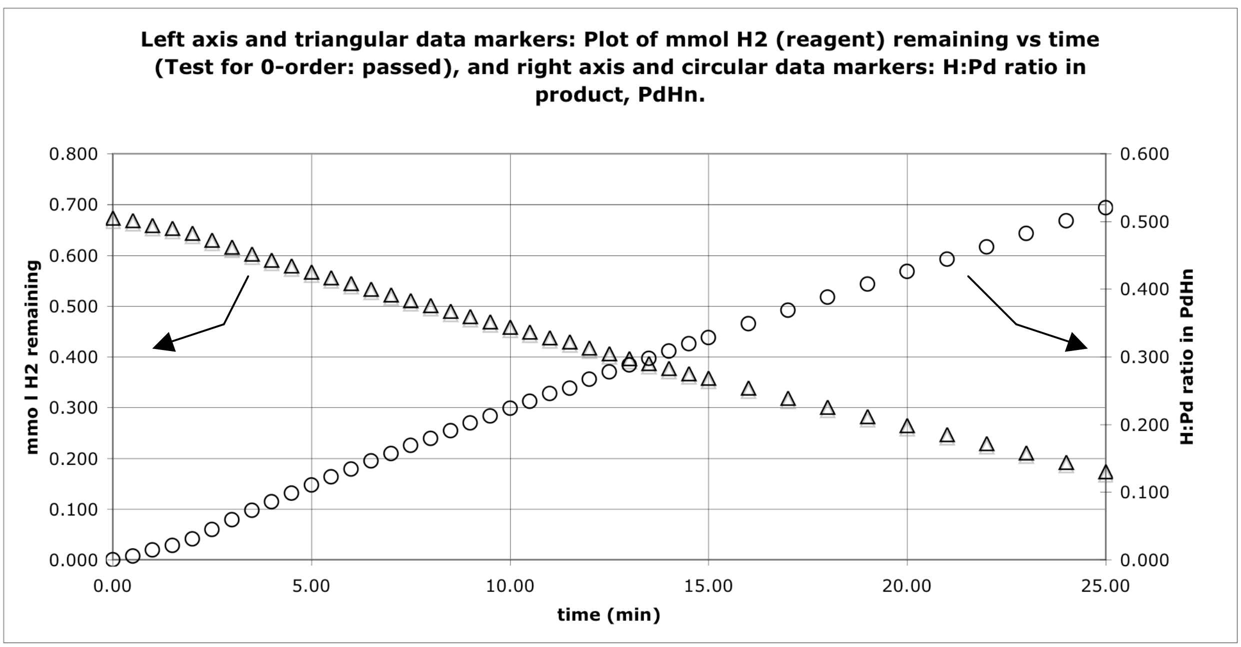


Figure 4. Left axis and line displayed with triangular markers (line with decreasing slope): Plot of the experimental results used to establish the order of the reaction as zero-order: plot of mmol of H_2 remaining as a function of time. Right axis and line displayed with circular data markers: mole ratio of H atoms to Pd atoms in product, PdH_n as a function of time.

Results Comparison between the Demonstration

With the reaction established as a zero-order reaction, the rate constant equals the slope in Figure 4 and the rate law is:

$$rate_{H_2\,uptake} = -\frac{dn_{H_2}}{dt} = k = 0.0205\ \frac{mmol\ H_2}{min}$$

Results from Demonstration 1 indicate that H_2 uptake is much faster than the kinetic results from Demonstration 2. The design of the apparatus suggests an explanation: H_2 must migrate from the H_2 syringe, through the 4-way stopcock valve and into the Pd/Ar syringe, whereupon it is quickly absorbed by Pd producing PdH_n. The rate of the H_2 uptake is limited by the rate of mass transport. To test this hypothesis, three other experiments were performed. These can be repeated or simply described to the class for contemplation. The instructor may wish to withhold the mass transport hypothesis and let the students think about the observations. This makes an excellent overnight group inquiry activity.

Additional Observation 1.

When deuterium gas, D_2, is used instead of $H_2(g)$, the rate slows down. Data are provided in the Supplemental Materials. Experimentally, we found that the ratio of rates of H_2:D_2 uptake to be:

$$\frac{rate_{H_2\,uptake}}{rate_{D_2\,uptake}} = 1.46$$

Additional Observation 2.

When various sizes of Pd were used in the Pd/Ar syringe, the rate of H_2 uptake did not change. See Supplemental Materials.

Additional Observation 3.

When NO_2, a red-brown gas with molar mass similar to that of Ar and H_2 are connected to the 4-way valve and allowed to diffuse into one another, it took over an hour before the colors of the two syringes appeared equal.[6]

Hazards.

Manipulating gases in syringes is generally safe and unintentional discharges are not common. Nevertheless, such discharges are possible and it is important to remember that hydrogen is highly flammable and forms explosive mixtures with air. Read the MSDS sheet for Pd foil. Never use palladium powder due to the risk of inhalation.

Acknowledgements.

We express our gratitude to colleagues Robert Snipp, Brad Parsons, and Ed Vitz for useful discussions.

Notes

1. 4-way stopcocks with Luer-Loks are available from Cole-Parmer, Part Number 30600-03. Two of the connectors have Luer-Lok fittings and the third is a tapered connector.
2. Small squares of palladium foil can be purchased from numerous vendors. For example, Aldrich sells a 25 x 25 mm piece for about \$50 (Aldrich 267120-190MG)
3. Luer-Lok syringe caps can be purchased from a variety of sources including Flinn Scientific (AP8958); or Educational Innovations (GAS-160).

4. Thermal paper often obtained as credit card receipts, for example, from pay-at-the-pump petroleum stations or fast food receipts such as from McDonalds or Burger King. Some older instruments use thermal paper as well. Note that only one side of most thermal paper is active.

5. The amount of H_2 reacted can be calculated by subtracting the amount (mmol) of H_2 reacted, $n_{H_2,\ abs}(t)$, from the initial amount of H_2, $n_{H_2}(t = 0)$:

$$n_{H_2}(t) = n_{H_2}(t = 0) - n_{H_2,abs}(t)$$

The second term can be calculated using the ideal gas law:

$$n_{H_2,abs}(t) = \frac{PV_{H_2,abs}(t)}{R \times T}$$

6. Our piece of palladium had a mass of 0.2048 g, corresponding to 1.924 mmol Pd. The formula used in this column:

$$\frac{n_H}{n_{Pd}} = \frac{2 \times n_{H_2,abs}}{1.924\ mmol\ Pd}$$

7. If desired, dry nitrogen dioxide can be prepared *(6)*. CAUTION: Hydrogen and nitrogen dioxide must never be mixed in the presence of Pd, which is a catalyst for an explosion.

Literature Cited

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6. Website http://mattson.creighton.edu/Microscale_Gas_Chemistry.html, then click on “All 17 gases.” (Successfully accessed 1 September 2008)

Supplemental Materials.

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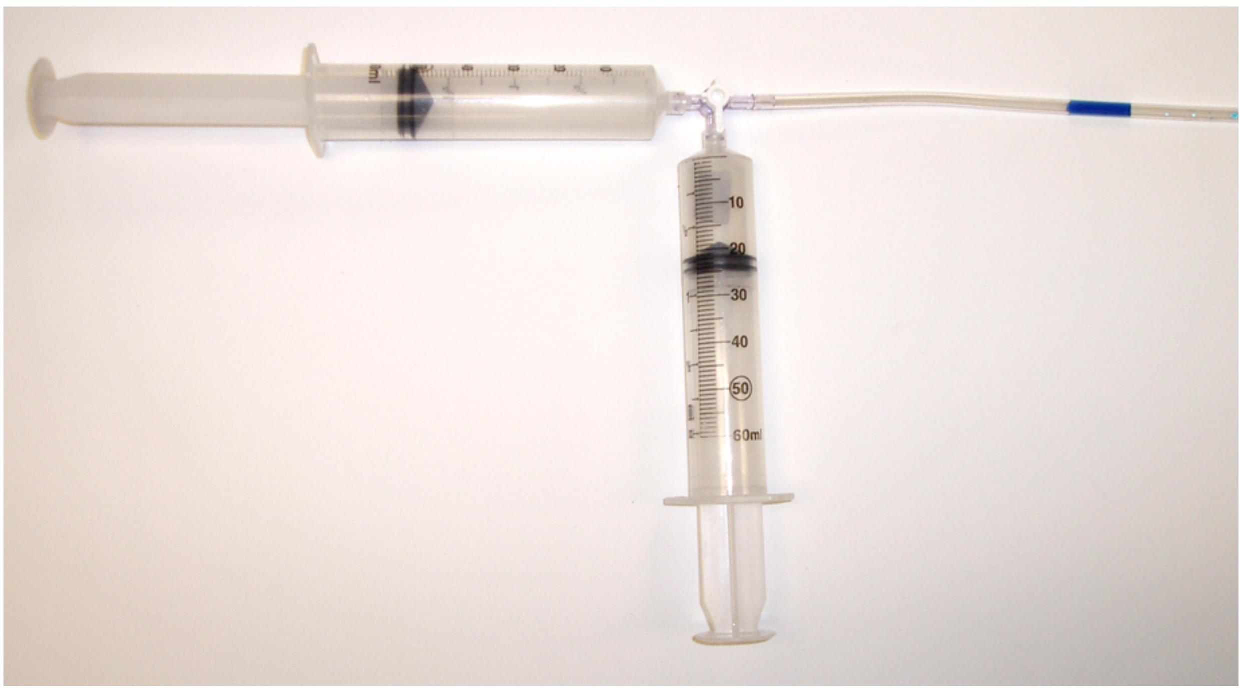
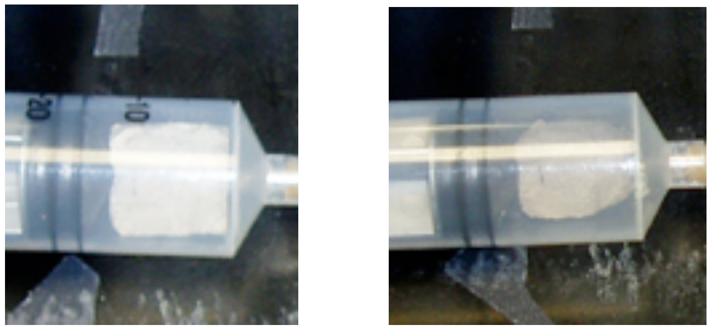
Photograph 1. Apparatus. Left syringe is "H_2," vertical syringe is "Pd/Ar." Note the Pd foil centered around the 10 mL mark. The water plug, dyed with blue food coloring, is unusually close to the 4-way valve for the purpose of this photograph. The value is positioned "Pd/Ar: Closed."



Photographs 2a and 2b. Physical appearance of palladium before and after exposure to hydrogen. These results are from performing Demonstration 1. Palladium is a dull silver color as shown in the left photograph where it is under Ar. The right photograph is after one minute of exposure to hydrogen. Often, the Pd foil curls upon H_2 uptake.



Photograph 3. Use of thermal paper to detect heat released when Pd/H is exposed to air. Demonstration 1, continued. The black spot at left in the following picture resulted when Pd exposed to H_2 for 1 min was dropped from the H_2 syringe onto the thermal paper. The reaction with air is nearly instantaneous and the dark gray color of Pd/H turns to a dull silver color as shown at right in the figure. (The dull silver square shown at right is the Pd metal square resting on the thermal paper shortly after it caused the black thermal spot at left.)

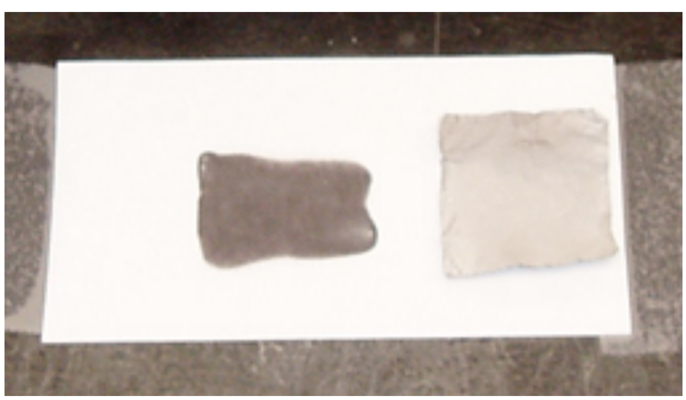


Table Supplemental-1. Data collected in Demonstration 2. The data presented here were obtained using the instructions for Demonstration 2 and were used to create Figures 2 – 4 in the article. Data in Columns A and B were collected at part of the demonstration. Values in Columns C, D, and G were determined by:

Column	Equation:	Comments:
Column C	$V_{tubing} = 0.127 cm^2 \times l_{tubing}$	For our aquarium tubing, the relationship between length and volume was 0.127 mL/cm tubing.
Column D	$n_{H_2}(t) = n_{H_2}(t=0) - n_{H_2,abs}(t)$	Moles of H_2 remaining, $n_{H_2}(t)$, is obtained by subtracting moles of H_2 absorbed, $n_{H_2,abs}(t)$, from the initial amount, $n_{H_2}(t=0)$.
Column G	$\frac{n_H}{n_{Pd}} = \frac{2 \times n_{H_2}(mmol\ H)}{1.924\ mmol\ Pd}$	The Pd foil used had mass of 0.2048 g corresponding to 1.924 mmol Pd.

A	B	C	D	E	F	G
time (min)	distance (cm)	volume (mL)	mmol H_2 Zero order?	ln(mol H_2) First order?	1/(mol H_2) Second order?	mol H/ mol Pd
0.00	0.00	0.00	0.673	-0.395	1.485	0.000
0.50	0.97	0.12	0.668	-0.403	1.496	0.005
1.00	2.78	0.35	0.659	-0.417	1.517	0.015
1.50	3.94	0.50	0.653	-0.426	1.531	0.021
2.00	5.81	0.74	0.644	-0.440	1.553	0.031
2.50	8.42	1.07	0.630	-0.461	1.586	0.045
3.00	11.16	1.42	0.617	-0.484	1.622	0.059
3.50	13.78	1.75	0.603	-0.506	1.658	0.073
4.00	16.14	2.05	0.591	-0.526	1.692	0.086
4.50	18.48	2.35	0.579	-0.546	1.726	0.098
5.00	20.80	2.64	0.567	-0.567	1.762	0.110
5.50	23.04	2.93	0.556	-0.587	1.799	0.122
6.00	25.29	3.21	0.545	-0.608	1.837	0.134
6.50	27.46	3.49	0.533	-0.628	1.875	0.146
7.00	29.62	3.76	0.522	-0.649	1.914	0.157
7.50	31.80	4.04	0.511	-0.671	1.956	0.169

8.00	33.81	4.29	0.501	-0.691	1.996	0.179
8.50	35.92	4.56	0.490	-0.713	2.039	0.191
9.00	38.06	4.83	0.479	-0.735	2.086	0.202
9.50	40.07	5.09	0.469	-0.757	2.131	0.213
10.00	42.14	5.35	0.459	-0.779	2.180	0.224
10.50	44.09	5.60	0.449	-0.801	2.229	0.234
11.00	46.23	5.87	0.438	-0.826	2.284	0.245
11.50	47.77	6.07	0.430	-0.844	2.326	0.254
12.00	50.25	6.38	0.417	-0.874	2.396	0.267
12.50	52.35	6.65	0.407	-0.900	2.459	0.278
13.00	54.23	6.89	0.397	-0.924	2.519	0.288
13.50	56.10	7.12	0.387	-0.948	2.581	0.298
14.00	58.11	7.38	0.377	-0.975	2.651	0.308
14.50	60.11	7.63	0.367	-1.002	2.724	0.319
15.00	61.86	7.86	0.358	-1.027	2.792	0.328
16.00	65.70	8.34	0.339	-1.083	2.954	0.349
17.00	69.52	8.83	0.319	-1.142	3.134	0.369
18.00	73.14	9.29	0.301	-1.202	3.326	0.388
19.00	76.70	9.74	0.283	-1.264	3.540	0.407
20.00	80.25	10.19	0.264	-1.330	3.782	0.426
21.00	83.67	10.63	0.247	-1.398	4.049	0.444
22.00	87.15	11.07	0.229	-1.473	4.362	0.463
23.00	90.82	11.53	0.211	-1.558	4.749	0.482
24.00	94.39	11.99	0.192	-1.648	5.199	0.501
25.00	97.98	12.44	0.174	-1.748	5.745	0.520

Supplemental Experiment 1. Hydrogen (H_2) vs. Deuterium (D_2) Uptake vs. time.

The experimental procedure follows the instructions provided for Demonstration 2. Deuterium gas was prepared by the reaction of calcium metal with deuterium oxide, $D_2O(l)$ using the general methods for gas preparation in syringes we have described in “Microscale Gas Chemistry: Generating Gases in Large Syringes” Mattson, B. M., ***Chem13 News***, **251**, October, 1996 and at our website: http://mattson.creighton.edu/Microscale_Gas_Chemistry.html (accessed May, 2008.) Deuterium gas was dried by passing it through a 5 cm length of Latex tubing* packed with anhydrous sodium sulfate and pre-purged with Ar.

* Tubing: 6.35 mm (1/4-inch) OD, 3.175 mm (1/8-inch) ID, possible vendors: Flinn #AP2076; 10-ft, and Educational Innovations #GAS-220 for 5 ft)

Table Supplemental-2. Raw data for H_2 and D_2 uptake.

H_2			D_2		
Time (min)	Distance (cm)	Volume (mL)	Time (min)	Distance (cm)	Volume (mL)
0.0	0.0	0.00	0.0	0.0	0.00
0.5	0.0	0.00	0.5	0.0	0.00
1.0	1.8	0.23	1.0	0.9	0.11
1.5	3.3	0.42	1.5	1.6	0.20
2.0	7.2	0.91	2.0	2.2	0.28
2.5	9.2	1.17	2.5	2.7	0.34
3.0	10.4	1.32	3.0	3.1	0.39
3.5	11.5	1.46	3.5	3.5	0.44
4.0	13.4	1.70	4.0	3.9	0.50
4.5	15.6	1.98	4.5	4.2	0.53
5.0	17.8	2.26	5.0	4.5	0.57
5.5	19.9	2.53	5.5	5.0	0.64
6.0	22.0	2.79	6.0	5.4	0.69
6.5	24.1	3.06	6.5	5.8	0.74

7.0	25.7	3.26	7.0	6.4	0.81
7.5	27.6	3.51	7.5	7.5	0.95
8.0	29.7	3.77	8.0	9.1	1.16
8.5	31.6	4.01	8.5	10.7	1.36
9.0	33.4	4.24	9.0	12.4	1.57
9.5	35.4	4.50	9.5	14.1	1.79
10.0	37.4	4.75	10.0	15.6	1.98
11.0	41.0	5.21	11.0	18.5	2.35
12.0	45.0	5.72	12.0	21.4	2.72
13.0	48.6	6.17	13.0	24.0	3.05
14.0	51.8	6.58	14.0	26.5	3.37
15.0	55.3	7.02	15.0	29.0	3.68
16.0	58.7	7.45	16.0	31.4	3.99
17.0	62.2	7.90	17.0	33.9	4.31
18.0	65.8	8.36	18.0	36.3	4.61
19.0	69.3	8.80	19.0	38.7	4.91
20.0	72.7	9.23	20.0	40.9	5.19
21.0	76.2	9.68	21.0	43.4	5.51
22.0	79.8	10.13	22.0	45.7	5.80
23.0	83.3	10.58	23.0	48.0	6.10
24.0	86.7	11.01	24.0	50.2	6.38
25.0	90.2	11.46	25.0	52.5	6.67
26.0	93.8	11.91	26.0	54.7	6.95
27.0	97.3	12.36	27.0	56.9	7.23
28.0	100.7	12.79	28.0	59.1	7.51

Figure Supplemental-1. H_2 and D_2 uptake vs. time.

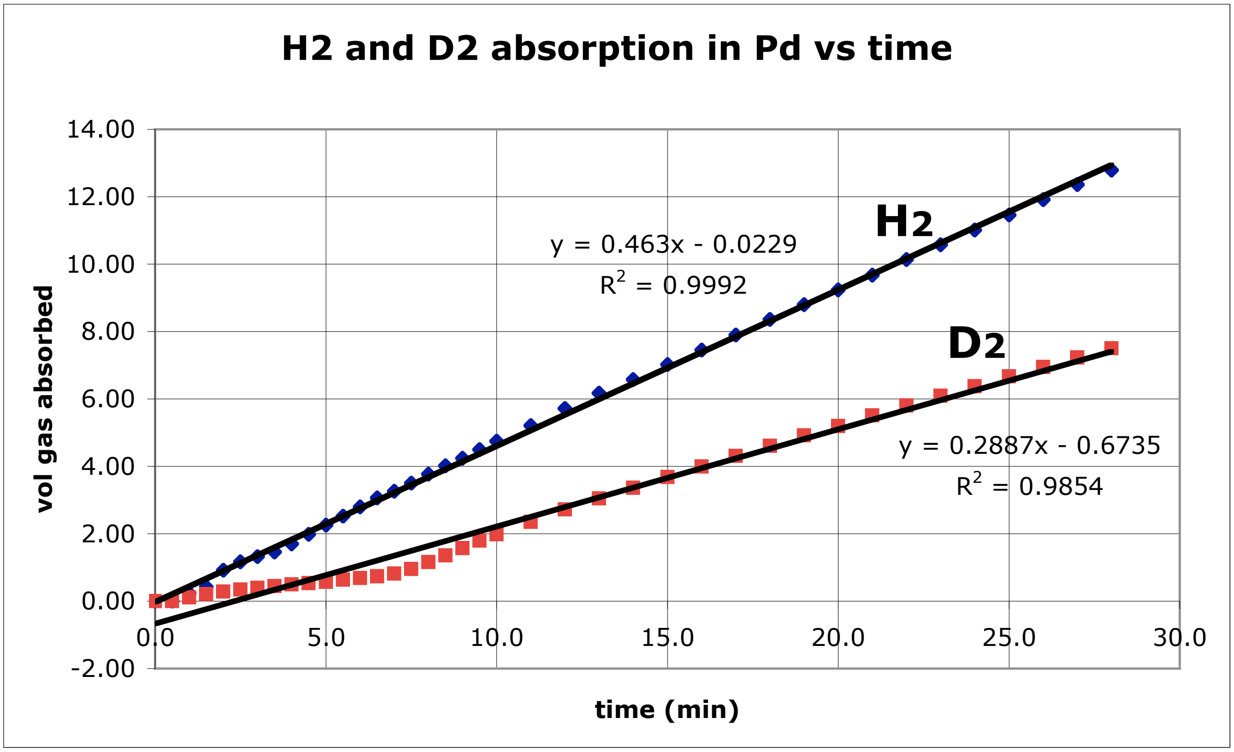
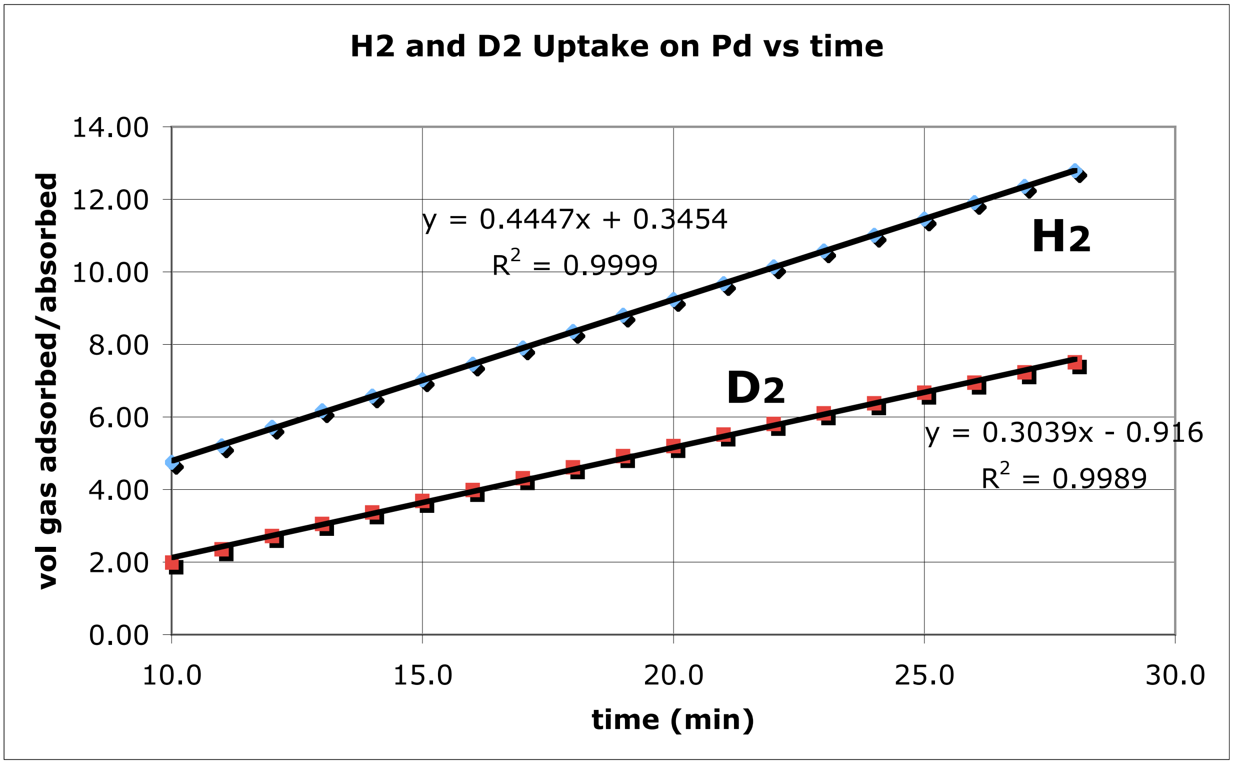


Figure Supplemental-2. H_2 and D_2 uptake vs. time. When only data for t > 10 minutes is plotted, better results are obtained:


H2 and D2 Uptake on Pd vs time
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
vol gas adsorbed/absorbed
y = 0.4447x + 0.3454
R2 = 0.9999
H2
D2
y = 0.3039x - 0.916
R2 = 0.9989
10.0
15.0
20.0
25.0
30.0
time (min)

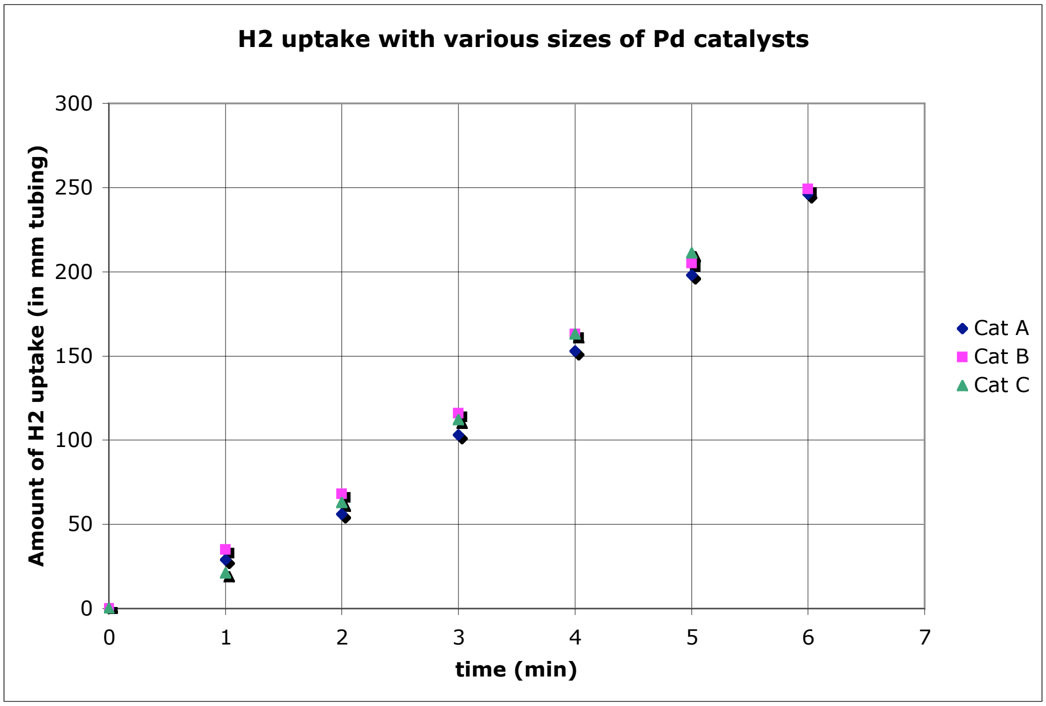
Supplemental Experiment 2. Hydrogen (H_2) Uptake for various sizes of Pd foil.

Three pieces of Pd foil were tested separately using the experimental procedure and instructions provided for Demonstration 2. The foil pieces had masses of 0.057 g (Cat A), 0.147 g (Cat B) and 0.204 g (Cat C). The results for H_2 uptake are independent of the size of the foil used as shown in the following table and figure:

Table Supplemental-3. Locations of water plug during H_2 uptake experiments with various sizes of Pd. Distances reported in mm refer to movement of the water plug inwards as H_2 uptake proceeds.

time (min)	Cat A (mm)	Cat B (mm)	Cat C (mm)
0	0	0	0
1	29	35	21
2	56	68	63
3	103	116	112
4	153	163	163
5	198	205	211
6	246	249	

Figure Supplemental-3. Graph of results from Table Supplemental-3.



Supplemental Experiment 3. Mutual mass transport of hydrogen (H_2) and nitrogen dioxide (NO_2).

Two syringes, one filled with H_2 and the other with NO_2 were connected via a 4-way valve. The valve was set to allow the gases to mutually diffuse into one another. The purpose of this study was to observe the relative rate of mass transport of H_2 in a gas with a MM similar to that of Ar. Even after almost 2 hours, there is noticeably more NO_2 in the syringe that originally contained the NO_2.

Photographs 4a – 4d. Photograph 4a (upper left, t = 0 min), 4b (upper right, t =19 min), 4c (lower left, t = 40 min) and 4d (lower right, t = 113 min.)