Experiment S-1

Density: A Characteristic Property

Objective
To investigate density as a typical characteristic property, a means of identification of pure substances

Concepts
Accuracy, precision, periodicity

Introduction
Density is a physical property of pure substances that is always the same regardless of sample size. Because they do not depend on the amount of material being tested, such properties are called intensive properties; other examples of intensive properties include melting and boiling points, and specific heat capacity, which you will meet later in the course. Mass and volume change with sample size, so they are known as extensive properties. Density, defined as the mass per unit volume, can be used as a means of identification, but is also a useful tool for deciding whether or not two objects are made of the same material – recall the famous story about how recognition of that fact led Archimedes to cry, “Eureka!”

The Skills portion of this experiment is in two parts. In Part A, you will determine density of a solid object, obtaining the volume first by direct measurement, then by water displacement.

Following that, in Part B, you will determine the densities for three organic liquids whose identities are known, as well as for one unknown, which you hope to identify. By doing multiple trials and comparing your results for the densities of the known liquids with a list of accepted values, you will be able to gauge both the accuracy and the precision (reproducibility) of your technique. The identity of the unknown will be determined by comparing its density with the same list. A table of densities of organic liquids appears below. Water is included for comparison purposes.

Table S-1–1

<table>
<thead>
<tr>
<th>Densities of Some Organic Liquids (g mL⁻¹, 25 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane, C₅H₁₂</td>
</tr>
<tr>
<td>Hexane, C₆H₁₄</td>
</tr>
<tr>
<td>t-Butyl methyl ether, CH₃COC(CH₃)₃</td>
</tr>
<tr>
<td>Cyclohexane, C₆H₁₂</td>
</tr>
<tr>
<td>Ethyl alcohol, CH₃CH₂OH</td>
</tr>
<tr>
<td>2-propanol (CH₃CH(OH)CH₃)</td>
</tr>
<tr>
<td>Acetone, CH₃COCH₃</td>
</tr>
<tr>
<td>Toluene, C₆H₅CH₃</td>
</tr>
<tr>
<td>Ethyl acetate, CH₃COOCH₂CH₃</td>
</tr>
<tr>
<td>Cyclohexanol, C₆H₁₂O</td>
</tr>
<tr>
<td>water</td>
</tr>
<tr>
<td>Dichloromethane, CH₂Cl₂</td>
</tr>
<tr>
<td>Chloroform, CHCl₃</td>
</tr>
<tr>
<td>Carbon tetrachloride, CCl₄</td>
</tr>
<tr>
<td>Diiodomethane, CH₂I₂</td>
</tr>
</tbody>
</table>
The **Inquiry** segment calls on you to design an experiment that will allow you to visit one of the historically important successes of Mendeleev’s periodic table. Because he noted that there were patterns to the properties of elements, Mendeleev was able to predict with fair accuracy, some of the properties of previously-unknown elements. You will determine the densities of silicon and tin, both known to Mendeleev, then you will use their densities to predict the density of the then-undiscovered element germanium, which Mendeleev called, “eka-silicon.” You will compare your predicted density for germanium with the accepted value.

### A Note About Accuracy and Precision

You are probably familiar with the concept of percent error and possibly even percent deviation, but the start of the year is a good time to review these ideas and to make clear the distinction between accuracy and precision. The following discussion should help in that regard.

**Average Deviation.** As noted above, *precision* refers to the reproducibility of results. It is the closeness of approach of repeated measurements to a common value. By contrast, *accuracy* is the closeness of a measurement to the accepted (“true”) value. To evaluate the precision of a group of measurements, you calculate the **average deviation** of the data. Begin by determining the average, or mean, of the measurements. You then determine the absolute deviation (disregard the sign) of each individual measurement from that average. The average of these absolute deviations is the **average deviation**. Consider the following set of hypothetical data.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.982</td>
</tr>
<tr>
<td>2</td>
<td>0.965</td>
</tr>
<tr>
<td>3</td>
<td>0.990</td>
</tr>
<tr>
<td>4</td>
<td>0.973</td>
</tr>
<tr>
<td>5</td>
<td>0.978</td>
</tr>
<tr>
<td>Total</td>
<td>4.888</td>
</tr>
</tbody>
</table>

The 5 is exact, so there are four significant figures (4 s.f.) in the result.

Average (mean) $= \frac{4.888}{5} = 0.9775$ g/mL

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Density (g/mL)</th>
<th>Absolute deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.982</td>
<td>0.004</td>
</tr>
<tr>
<td>2</td>
<td>0.965</td>
<td>0.013</td>
</tr>
<tr>
<td>3</td>
<td>0.990</td>
<td>0.012</td>
</tr>
<tr>
<td>4</td>
<td>0.973</td>
<td>0.005</td>
</tr>
<tr>
<td>5</td>
<td>0.978</td>
<td>0.034</td>
</tr>
</tbody>
</table>

Average deviation $= \frac{0.034}{5} = 0.0068 = 0.007$

Note that the average deviation has been rounded to one significant figure, the thousandths place, to match the precision of the densities from which it is derived. For that reason, the mean value for density must be rounded to the thousandths place, as well, so the density of the liquid should be reported as $0.978 \pm 0.007$ g mL$^{-1}$.

**Relative Uncertainty.** To one significant figure, 0.007 is 1% of 0.978, so we can say that there is a 1% uncertainty in the result. *Percent uncertainty* is often referred to as the **relative uncertainty**, since it compares the uncertainty in the measurement with its mean value.
Now, let’s assume that the liquid being tested has an accepted density of 1.052 g/mL. The formula for determining percent error (% error) is:

\[
\text{Percent error} = \frac{|(\text{accepted value}) - (\text{experimental value})|}{(\text{accepted value})} \times 100\%
\]

Notice the absolute value signs surrounding the numerator of the expression for the numerator.

**Percent Error.** To determine the accuracy of the series of experiments in question, we determine the absolute value of the difference between the accepted and experimental values (1.052 – 0.978 = 0.074), then determine the percentage of the accepted value represented by that difference. Again following the rules governing significant figures, we get

\[
\text{Percent error} = \frac{0.074}{1.052} \times 100\% = 7.034220532 = 7.0\%
\]

**Standard Deviation.** There is another test for precision, based on statistics, which you should know about, standard deviation. The Appendix of your text has a more detailed presentation, but the formula used for standard deviation is

\[
s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \delta_i^2}
\]

where \( s \), the standard deviation, is expressed in terms of \( n \) individual values. \( \delta \) is the deviation of each from the mean. For the five densities used above, to one significant digit, \( s = 0.009^{1} \). Your graphing calculator can carry out this determination for you. The experimental value for the density of the liquid would then be reported as 0.978 ± 0.009 g mL\(^{-1}\), again a 1% relative uncertainty.

**Prelaboratory Assignment – Skills**

1. Read the entire experiment before coming to the laboratory. If your instructor so directs, read the discussion of standard deviation in your text.

2. Prepare a data table for **Part A** in your lab notebook to collect and record the information needed to determine the density of your solid object.

3. Read the procedure description for **Part B**. Prepare a suitable data table for recording the measurements you are to make. A larger, expanded version of the one below is suggested. (The sample shows blanks for only one liquid; you will use four liquids, altogether.)

**Suggested data table layout for Part B**

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of empty vial and cap</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass of vial, cap and liquid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass of liquid only</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume of liquid</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{1}\) Compares to the 0.007 average deviation calculated earlier.
Prelaboratory Questions – Skills

1. Determine the relative error for a density experiment in which the accepted value is 0.750 g/mL, and the experimentally-obtained value is 0.735 g/mL.

2. According to one source,\(^2\) the density of calcium is 1.55 g/cm\(^3\), while that of barium is 3.51 g/cm\(^3\), both at room temperature. Calculate the expected density of strontium. The accepted value for the density of strontium is 2.63 g/cm\(^3\). What is the relative error (percent error) in the calculated density?

3. Using the accepted density for strontium given in Prelaboratory Question 2, what is the mass of exactly 1.00 cm\(^3\) of strontium? What is the mass of 1.00 m\(^3\) of strontium? How does this question illustrate the fact that density is an intensive property? (Hint: How many cm\(^3\) are in one m\(^3\)?)

4. Many standard references, including the Handbook of Chemistry and Physics,\(^3\) include a property of pure substances called their specific gravity. Specific gravity is found by dividing the density of the substance in question by the density of water. The densities of aluminum and water are 2.70 g/cm\(^3\) and 1.00 g/cm\(^3\), respectively.
   a. Determine the densities of water and aluminum in lb/in\(^3\) (conversions: 1 lb = 453.6 g; 1 in = 2.54 cm, exactly).
   b. Show that the specific gravity of aluminum is the same, regardless of the units used for density.

Safety Precautions

1. Chemical splash-protective eyewear must be worn at all times in the laboratory.

2. Contact lenses should not be worn when organic vapors are present; this is especially true of plastic lenses, which absorb or dissolve in the vapors. If contacts are your only option, take extra precaution in keeping the liquids and vapors away from your eyes. Remove your goggles only when you are completely outside the laboratory.

3. Organic liquids are flammable; there must be no open flames while you are working with them.

4. Avoid breathing the vapors of organic liquids; work only in a well-ventilated space.

5. The organic liquids are toxic by ingestion. Wash your hands thoroughly with soap and water before leaving the laboratory.

Materials

Part A

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>solid object (sphere or cylinder)</td>
<td>water</td>
</tr>
<tr>
<td>milligram balance</td>
<td></td>
</tr>
<tr>
<td>ruler</td>
<td></td>
</tr>
<tr>
<td>wood or plastic blocks</td>
<td></td>
</tr>
</tbody>
</table>

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\(^2\) www.webelements.com

\(^3\) David R. Lide (ed), CRC Press, 89th edition, 2008
Part B

Apparatus

- milligram balance
- small beakers, 20-30 mL or similar (4)
- 1 mL volumetric pipets (4)
  (Graduated pipets may be substituted.)
- pipet filler bulb
- sample vials, with caps (12, if possible)
- safety goggles

Reagents

- ethyl acetate
- hexane
- acetone
- unknown liquid

Procedure – Skills

Part A

1. Determine the mass of your object. Record it in a suitable data table.

2. Volume by direct measurement. For objects with a regular shape (sphere or cylinder), carry out the following sequence of steps.
   - If your object is a cylinder, use a ruler to determine its length to the nearest 0.01 cm (0.1 mm).
   - Using a caliper, if available, determine the diameter of the cylinder or sphere, again to the nearest 0.01 cm. If no caliper is available, sandwich the cylinder or sphere between two rectangular blocks, then use a ruler to measure the diameter ± 0.01 cm.
   - Use the appropriate volume formula to determine the volume of your object.

3. Volume by water displacement. Regardless of the shape of your object, you can determine its volume by the following method.
   - Select the smallest graduated cylinder you can, the one with the most precise graduations, which will accommodate your object. The cylinder must be large enough that your object can be completely submerged in water without the water level exceeding the top mark on the scale.
   - If you haven’t already determined its volume by the direct method above, estimate the object’s volume. Put enough water (tap or distilled/deionized) in your cylinder to completely cover your object. Read and record the volume of water to the full precision of your cylinder. (For a 25-mL graduate, calibrated in 0.2-mL intervals, an uncertainty of ± 0.05 mL is reasonable.)
   - Tilt the graduate and carefully slide your object down into the water. As much as possible, try to avoid splashing and minimize the amount of water clinging to the sides of the cylinder. (A scrupulously-clean cylinder helps here.) Read and record the final volume.

Part B

The following sequence of steps is to be followed for each of the four liquids. It is recommended that you do all trials for one liquid before proceeding to the next to avoid mixing containers or liquids. If partners are working individually on separate liquids, be very careful to keep your materials separate from each other.

1. Label each of three vials. Weigh each vial with its cap. The liquids are quite volatile (they will evaporate quickly) so it will be necessary to cap the vials immediately after the liquid is placed in them.

2. Obtain about 10-15 mL of the liquid to be used in a small beaker. Using the volumetric pipet and filler bulb, place exactly 1.00 mL of liquid in one vial and immediately cap it. Set it aside while you fill and cap the other two vials.

3. Weigh the capped vials with their liquid samples.

4. See the section on Disposal: Part B for cleaning up.

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4 Glass, not plastic.
5. Repeat the previous four steps, first using the other two known liquids, then with the unknown.

**Disposal**

**Part A**
1. Water in the graduated cylinder can be poured down the drain. Wash your graduated cylinder and return it to its proper location.
2. Dry your solid object and return it to its proper location.

**Part B**
1. Uncap the vials and pour the liquid into the appropriate waste container, as directed by your teacher.
2. Each of the liquids has properties different from the others, so each group of three vials needs special treatment.
   - The vials used for acetone and ethyl acetate may be washed with soap and water, rinsed with distilled water, and allowed to air dry. Acetone is highly water-soluble, but ethyl acetate is less soluble, so be sure that there are no little beads left on the inside of the ethyl acetate vials, as this would indicate that not all of the liquid has been removed.
   - Hexane is extremely volatile, so the vials will air dry quickly. Leave them open, together with their caps, in a fume hood if available or in a well-ventilated area near your laboratory station. Once they are dry, they can be washed and rinsed as described for acetone.
3. The unknown will have its own waste container, and you have no way of knowing whether or not it is soluble in water. Consult your teacher regarding appropriate cleanup.
4. The pipettes require the same cleaning technique as the vials. Ask your teacher where they are to be placed after cleaning.

**Analysis and Conclusions**

**Part A**
1. Using your direct measurements for diameter and height (for a cylinder), or diameter only (for a sphere), calculate the volume of your solid object. Use the result and the object’s mass to determine the density of the object in g/cm³.
2. Repeat the calculation of density for your object, this time using the volume as determined by water displacement. (Hint: recall that 1 mL = 1 cm³, exactly.)
3. Discuss the relative accuracy and precision of your results from questions 1 and 2. Does each afford the same number of significant figures? If your semester grade depended on it, which of your two values for the density of your object would you trust the most? Why? If that value is the correct one, what is the percentage error for the other one?

**Part B**
4. For each of the four liquids, determine the individual densities of each of the three samples you ran, then calculate the mean value for the density of each liquid. Show all your calculations for one of the liquids in your notebook. All other results can be placed in a summary table with the headings shown below. The average deviation is your range of experimental uncertainty. (The table at the top of the next page is incomplete; it shows only one liquid. Yours will have all four.)
5. For each of the three known liquids, report your experimental value for the density, including the uncertainty. If your accuracy was good, the accepted value will fall within the uncertainty range of your experimental value. The smaller the uncertainty range, the higher your degree of precision. For this experiment, you should be able to achieve a precision of ± 5% or better. Prepare a new table that reflects your degrees of accuracy and precision. Use the headings shown here, but include rows for all three liquids.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Density ± Uncertainty</th>
<th>Accepted Value</th>
<th>Accurate? (Y/N)</th>
<th>Precise? (Y/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6. As noted earlier, the average deviation is also considered your experimental uncertainty. In order to compare the four liquids, it is necessary to convert the actual uncertainties to percentages. For each of the three known liquids, determine the percent uncertainty (consult the earlier section, “A Note about Accuracy and Precision,” as needed). Now determine your average percent uncertainty by averaging the percentages just obtained.

Determine what the uncertainty range would be for your unknown, assuming it has the same percent uncertainty as your average for the three known liquids. Consult the list of densities that appears in the Introduction. One of those liquids is your unknown. Assuming good technique on your part, the average experimental density of your unknown should match one of the entries in the table, within the experimental uncertainty you just calculated. Identify your unknown. There is no table accompanying this question, but your work should be shown and your answers (a total of six) should be clearly identified.

7. Consider the table of densities given in the Introduction. What generalizations can you make, based on what you see in that table?

**Inquiry**

As mentioned in the Introduction and in the prelaboratory questions, Mendeleev recognized that the properties of the elements changed in a fairly regular fashion with increasing atomic mass. (Recall that Mendeleev published his predictions in 1869, and the proton – the basis for atomic numbers – would not be discovered until 1914!) Thus he was able to give rough estimates for the elements that were needed to fill in the gaps in his table. Following his predictions, scientists were able to fill in many of those gaps over the next couple of years.

**The Challenge.** You are to design an experiment that will enable you to predict the density of germanium by separately determining the densities of the two elements immediately above and below it in the table, silicon and tin.

You will be provided with samples of both Si and Sn; those samples will consist of small pieces of the two elements. You will also have access to any standard laboratory equipment, including balances and glassware.

**Assignment.** You and your partner are to submit to your teacher a detailed procedure, describing the exact sequence of steps you expect to follow, the data to be collected, and any calculations that will
be carried out. You are to include sections on Safety and Cleaning Up as part of your plan. Assume that the samples of tin and silicon are to be used again.

Once your teacher has determined that your plan is complete and safe, you will be allowed to conduct your experiment. Note that teacher approval is not a guarantee that your plan will be successful.

After completing your experimental procedure, carry out the appropriate calculations to make your best prediction for the density of germanium, including the uncertainty, then compare your result with the accepted value to determine how successful you were. If the accepted value does not fall within the range you predict, discuss any factors that may have lead to your result, including possible modifications of your procedure and possible sources of experimental error. (But note that careless or incorrect measurement is not a part of experimental error; those things should not occur.)
Experiment S-2

Oxidation and Reduction

Objective
To learn about some of the types of reactions that are driven by electron transfer.

Concepts
Oxidation and reduction, oxidizing and reducing agents, half-reactions

Introduction
Many reactions involve transfer of electrons from one atom or ion to another. Such processes are known as *oxidations* (for electron loss), and *reductions* (for electron gain). Since they always occur together, they are referred to collectively as oxidation-reduction reactions, or simply as "*redox reactions*."

If an atom is oxidized (loses electrons), those electrons must be transferred to some other atom or ion; the atom or ion that takes the electrons is called the *oxidizing agent*. This name suggests that the receiver of the electrons caused the oxidation to occur. So the species that is reduced (gains electrons) is the oxidizing agent. Similarly, the species that is oxidized is called a *reducing agent*, because it provided the electrons that caused the other atom or ion to become reduced.

In this experiment, you will investigate some of the types of reactions for which electron transfer is the driving force. You have met many of these before and you may know them under other names. The first three parts will be carried out in a 96-well test plate, but Part D involves reagents that can attack the plastic, so you will use small test tubes, beakers, or flasks for the final steps.

Prelaboratory Assignment
Read the entire experiment before you begin.

Prelaboratory Questions

1. a. What are the most common ionic charges for the elements shown?
   Aluminum Oxygen
   b. Complete the following oxidation or reduction half-reactions in your notebook, showing aluminum and oxygen gas forming the ions you identified in 1(a).
   
   \( (i) \text{Al}(s) \rightarrow \text{________} \quad + \quad \text{________} \)
   \( (ii) \text{O}_2(g) + \text{________} \rightarrow 2 \text{________} \)
   c. Identify each of the reaction equations as being either an oxidation or a reduction.

2. Write the balanced equation for the reaction between aluminum metal and oxygen gas to form aluminum oxide.

3. Identify each of the following processes as an example of oxidation, reduction, or both.
   a. Chlorine gas becomes chloride ion.
   b. Sodium metal becomes sodium ions.
   c. Iron rusts.
   d. Hydrogen peroxide breaks down into water and oxygen gas. (Hint: the oxygen in hydrogen peroxide, \( \text{H}_2\text{O}_2 \), has an oxidation state of −1.)
   e. Household bleach removes a stain from an article of clothing.
4. Steps 6 and 7 direct you to very gently note the odors produced by reactions. Describe the correct technique for doing this when the odor being tested may be unpleasant, toxic, or both.

**Safety Precautions**

1. Chemical splash-protective eyewear must be worn at all times in the laboratory.
2. Hydrochloric, sulfuric and oxalic acids are corrosive to skin and clothing.
3. Wipe up all spills immediately, using large quantities of water.
4. Small quantities of gaseous halogens may be generated. Work in a well-ventilated area.

**Materials**

**Apparatus**
- 24-well test plates (2; one to hold pipets)
- wash bottle
- forceps or tweezers
- toothpicks as stirring rods
- small test tubes (75-mm or similar) (5)

**Reagent Solutions**

**In microtip pipettes**
- 0.50 M hydrochloric acid, HCl(\textit{aq})
- 0.50 M cupric nitrate, Cu(NO_3)_2(\textit{aq})
- 1.0 M zinc nitrate, Zn(NO_3)_2(\textit{aq})
- 0.10 M potassium permanganate, KMnO_4(\textit{aq})
- 0.10 M ferric chloride, FeCl_3(\textit{aq})
- 0.10 M ferrous sulfate, FeSO_4(\textit{aq})

**In thin-stem pipettes**
- 0.10 M ammonium \textit{meta}-vanadate, NH_4VO_3(\textit{aq})
- 3% hydrogen peroxide, H_2O_2(\textit{aq})
- 3 M sulfuric acid, H_2SO_4(\textit{aq})
- 0.1 M oxalic acid, H_2C_2O_4(\textit{aq})
- 0.5 M sodium sulfite, Na_2SO_3(\textit{aq})
- bleach, 5.25% sodium hypochlorite, NaOCl(\textit{aq})

**Solid Reagents**
- magnesium foil (small pieces)
- copper foil (small pieces)
- zinc foil (small pieces)

**Procedure**

**Part A.**

1. Place 10 drops of 0.50 M HCl in a cell of your test plate. Add a small piece of magnesium then observe and record what happens as the reaction proceeds.

**Part B.**

2. Add 10 drops of 0.50 M copper nitrate, Cu(NO_3)_2, to one well of your test plate and add a small piece of zinc metal. Record your observations, both of the appearance of the metal and of the solution color. Changes may not happen right away.

3. Put 10 drops of 0.50 M zinc nitrate, Zn(NO_3)_2, in a different well of your test plate. Add a small piece of copper metal. Observe and record any reactions that take place, including solution color and changes at the surface of the metal.

**Part C.**

4. Place 10 drops of 0.1 M iron(III) chloride (a source of Fe^{3+} ion) in one well of your test plate and 10 drops of iron(II) sulfate (a source of Fe^{2+} ion) in another well. Add a single drop of 0.1 M potassium permanganate, KMnO_4, to each well. One of the wells will show a change in the color of the KMnO_4; the other will not. Note which iron ion reacts with (decolorizes) the KMnO_4.

5. To the well from step 4 in which the purple color disappeared, continue adding potassium permanganate, one drop at a time and stirring after each drop, until the purple color of the permanganate ion no longer fades. Record the number of drops needed to complete the reaction.
Part D. Note: The reagents for this part of the experiment will attack the plastic well plate, so small glass vessels will be used.

For many transition metals, more than one possible cation can be formed. When an atom or ion changes its charge, we say it has undergone a change in oxidation state. Since these oxidation state changes are often accompanied by a change in the color the metal ion gives to aqueous solutions, it is a simple matter to tell when an oxidation or reduction of the metal occurs.

6. Manganese; the +7 oxidation state, in potassium permanganate, KMnO₄.

a. Put 10 drops of hydrogen peroxide antiseptic in a 10- or 20-mL beaker or Erlenmeyer flask. Add 1 drop of 3 M H₂SO₄ and swirl the vessel gently to mix the reagents. Now add a single drop of potassium permanganate solution, KMnO₄(aq), and observe the changes that take place. (Hint: you should see two changes, only one of which involves the color of the KMnO₄.)

b. Repeat the previous step, but omit the sulfuric acid.

c. Repeat step 6a but this time use 0.1 M oxalic acid solution, H₂C₂O₄, in place of the hydrogen peroxide and sulfuric acid. If no changes are evident after 1 minute, try warming the vessel on a hot plate.

7. Vanadium in the 4+ and 5+ oxidation states.

a. Place about 1 mL of ammonium vanadate solution in a small (10- or 25-mL) beaker or Erlenmeyer flask. The color you see is due to vanadium in the +5 state. Add an equal volume of sodium sulfite solution and swirl the flask. If no change occurs within 30 seconds heat the flask gently on the hot plate. Note and record the color of the solution, which now contains vanadium in the +4 state. Gently note the odor coming from the flask; it isn’t pleasant.

b. Allow the flask to cool, then add 2-3 mL of bleach, an aqueous solution of sodium hypochlorite, NaOCl. Observe and record any changes. Again, there will be a noticeable odor, but do not smell the contents directly. Chlorine gas is generated, and it is quite toxic.

Disposal

1. Remove any bits of unreacted metal that may remain in your test plate to the appropriate waste container.

2. To the tubes from Part D, step 7, add about 1 mL of 0.5 M sodium sulfite, solution, Na₂SO₃, to convert any remaining molecular chlorine to chloride ions.

3. Flush remaining solutions down the drain with large amounts of water. While some of the solutes are potential hazards and others are quite acidic, the dilution provided by a running stream of water will bring the concentrations to acceptable levels.

4. Return the pipettes and unused solutions to their proper place. Do not empty them into the sink.

Analysis and Conclusions

The list below shows twelve equations that you will need in order to answer the questions for Parts A–D. They are called half-reactions because each shows only half of an oxidation-reduction process.

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5 Specifically, it is the dioxovanadium ion, VO₂⁺.

6 This ion is the vanadyl ion, VO²⁺. Be sure to note the difference in their formulas.
Each is written twice, first as reductions, then reversed to become oxidations. Notice that atoms are not always conserved in these half-reactions. \((e^- = \text{electron(s)})\)

<table>
<thead>
<tr>
<th>Reductions</th>
<th>Oxidations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn})</td>
<td>(\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-)</td>
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<tr>
<td>(\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu})</td>
<td>(\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-)</td>
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<tr>
<td>(\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg})</td>
<td>(\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-)</td>
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<tr>
<td>(\text{MnO}_4^- + 5e^- \rightarrow \text{Mn}^{2+}) (in acid)</td>
<td>(\text{Mn}^{2+} \rightarrow \text{MnO}_4^- + 5e^-)</td>
</tr>
<tr>
<td>(\text{MnO}_4^- + 3e^- \rightarrow \text{MnO}_2) (in base)</td>
<td>(\text{MnO}_2 \rightarrow \text{MnO}_4^- + 3e^-)</td>
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<tr>
<td>(\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+})</td>
<td>(\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-)</td>
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<tr>
<td>(2\text{H}^+ + 2e^- \rightarrow \text{H}_2)</td>
<td>(\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-)</td>
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<tr>
<td>(2\text{CO}_2 + 2e^- \rightarrow \text{C}_2\text{O}_4^{2-})</td>
<td>(\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2e^-)</td>
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<tr>
<td>(\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-)</td>
<td>(2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-)</td>
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<tr>
<td>(\text{SO}_4^{2-} + 2e^- \rightarrow \text{SO}_3^{2-})</td>
<td>(\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + 2e^-)</td>
</tr>
<tr>
<td>(\text{VO}_2^+ + e^- \rightarrow \text{VO}^{2+})</td>
<td>(\text{VO}^{2+} \rightarrow \text{VO}_2^+ + e^-)</td>
</tr>
<tr>
<td>(\text{OCl}^- + e^- \rightarrow \text{Cl}_2)</td>
<td>(\text{Cl}_2 \rightarrow \text{OCl}^- + e^-)</td>
</tr>
</tbody>
</table>

Part A.

1. The only possible states for magnesium are the neutral element (zero charge) and the dipositive cation, \(\text{Mg}^{2+}\).
   a. With which did you begin?
   b. What was the oxidation state of magnesium after it had reacted with \(\text{HCl}\)?
   c. Was magnesium oxidized or reduced? Explain.
   d. Write the half-reaction showing the change for magnesium.

2. The hydrochloric acid solution contains \(\text{H}^+\) ions and \(\text{Cl}^-\) ions. Consult the list of half-reactions given above to decide what gas was bubbling out of the reaction. (Hint: Recall that you need one oxidation and one reduction taking place in order to have a complete system, so this gas must form as a result of the choice you did not select in 1c, above.) Write the equation for the half-reaction resulting in the evolution of the gas you select.

3. Combine your half-reactions from questions 1 and 2, above, to write the net-ionic equation for the complete reaction. (Chemical equations such as these half-reactions, may be combined by addition, just as you would do with algebraic equations.)

Part B.

4. Consider the two wells used for zinc and copper.
   a. What evidence of reaction did you see in each case, if any?
   b. One of the following equations represents the reaction that occurred; select the correct one and justify your choice.
      \[\text{Cu} + \text{Zn}^{2+} \rightarrow \text{Cu}^{2+} + \text{Zn}\] or \[\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}\]
   c. For the reaction equation you selected in 4b, identify each of the following:
      (i) the species that is reduced:
      (ii) the species that is oxidized:
      (iii) the reducing agent:
      (iv) the oxidizing agent:

Part C.

5. a. In which well was the color of permanganate ion lost? That is, which test reagent, \(\text{Fe}^{2+}\) or \(\text{Fe}^{3+}\), caused the purple color to fade?
   b. The permanganate and iron solutions were both 0.1 \(M\), so they had the same concentration, yet ten drops of iron solution were able to discolor only a few drops of permanganate solution. What can you conclude about the stoichiometry of the reaction?
6. The color change was the result of one of the iron ions being converted to the other oxidation state.
   a. Which of the two equations below best illustrates what happened in the cell for which you observed the color change? Explain how you arrived at your choice.
      \[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e \quad \text{or} \quad \text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+} \]
   b. Is iron being oxidized or reduced? Explain.
   c. Is permanganate ion being oxidized or reduced? Explain.
   d. In the reaction between permanganate and iron ions, which is the oxidizing agent and which is the reducing agent? Explain.
   e. Write the net ionic equation for the reaction. In acidic solution, the manganese atom in the permanganate ion is reduced to manganese(II) ion.

Part D.

7. For the reaction between hydrogen peroxide and potassium permanganate
   a. What difference does the presence of sulfuric acid make? (In the absence of excess acid, the reduction product for permanganate is solid manganese(IV) oxide, rather than manganese(II) ion.)
   b. What must have been the gas you saw bubbling out of the mixture? Defend your choice. (Hint: What happens when hydrogen peroxide spontaneously decomposes?)
   Write the balanced net-ionic equations for the reactions that occurred both with and without addition of sulfuric acid.

8. How does the speed of reaction between permanganate ions and oxalic acid compare with the speed of most of the other reactions in this experiment? What was the effect of warming the system on the speed of reaction?

9. In comparing the reaction of permanganate with hydrogen peroxide and with oxalic acid, was the reaction between potassium permanganate and oxalic acid more like the one with sulfuric acid or the one without? Account for this similarity.

10. In the reaction between KMnO₄ and H₂C₂O₄, you may have noticed bubbles of gas being produced as the oxalic acid reacted. What gaseous product might have been forming? (Hint: Look at the relative proportions of the elements in the oxalate ion.)

11. The sulfite ion changes vanadium from the 5+ state to the 4+ state.
    a. Is this an oxidation or a reduction?
    b. What must have happened to the sulfite ion in the process? What ion was formed?
    c. Write the net ionic equation for the reaction between the dioxovanadium ion, VO₂⁺(aq), and the sulfite ion, SO₃²⁻(aq). Assume sulfite is oxidized to sulfate ion, and that the reaction takes place in alkaline (basic) solution.

12. a. What effect (oxidation or reduction) does the hypochlorite ion in NaOCl have on vanadium(IV)?
    b. What happens to the vanadium(IV)? (To what is it converted?) How can you tell?
    c. Write the balanced net-ionic equation for the reaction between vanadyl ion, VO²⁺(aq), and the hypochlorite ion, OCl⁻(aq). The other product is chlorine gas, as you could no doubt tell. This process, too, takes place in alkaline solution.
Molar Volume of a Gas

Introduction

The gas laws are introduced in Chapter 5. Some describe the variation of one of the four variables of state—pressure, volume, absolute temperature, number of moles—with one of the others, when the remaining two are held constant. Two relationships are of a more general nature. The Combined Gas Law represents a combining of the simpler laws. Given that volume is inversely proportional to pressure (Boyle’s Law), and directly proportional to temperature (Charles’ Law), you can write an expression that incorporates both sets of observations:

\[ \frac{P_1 \cdot V_1}{T_1} = \frac{P_2 \cdot V_2}{T_2} \]

Going one step further and introducing the law of Avogadro, which says that the volume occupied by a gas is directly proportional to the number of moles of gas in the system, gives the expression

\[ \frac{P_1 \cdot V_1}{n_1 \cdot T_1} = \frac{P_2 \cdot V_2}{n_2 \cdot T_2} \]  

(Equation 1)

In which \( P_1, V_1, n_1 \) and \( T_1 \) refer to an initial set of conditions and \( P_2, V_2, n_2 \) and \( T_2 \) refer to the final conditions, after the change has occurred. This "combined" gas law allows you to do calculations involving changes in any or all of the four variables.

What Equation 1 tells us is that the value of the expression, \( PV/nT \), does not change; if that is the case, then we can determine a value for \( PV/nT \) that should be valid under any set of conditions as long as the sample remains a gas. This relationship, \( PV/nT = R \), can be rearranged to the form known as the Ideal Gas Law:

\[ PV = nRT \]

The constant, \( R \), is known as the universal gas constant. One of your objectives in this experiment is to verify the value of \( R \) experimentally, in units of \( \text{L atm/mol K} \) (“liter-atmospheres per mole-Kelvin”). You will calculate the value of \( R \) for each of three trials, as well as an average result, which will then be used to determine your percentage error.

You will collect the hydrogen in a 50-mL tube called a eudiometer. You will also have access to an analytical balance, so the mass of your piece of magnesium will be measured to ± 0.1 mg. The calculations are straightforward and should not present a problem.

Prelaboratory Assignment

- Read the entire experiment before you begin.
- Answer the Prelaboratory Questions.
  1. Explain how you will know that neutralization is complete during clean-up, when you use baking soda to neutralize any excess hydrochloric acid.
  2. What two physical properties of hydrogen gas makes it possible for you to collect it by displacement of water in your graduated cylinder?
3. Use Dalton’s Law of Partial Pressures to explain why the pressure of hydrogen gas in the tube will be less than the observed barometric pressure in the laboratory. How will you determine the pressure of the hydrogen you produce?

4. Calculate the mass of magnesium needed to produce 45.0 mL of hydrogen gas at 22ºC, 730 mmHg.

5. Calculate the mass of baking soda, NaHCO₃, needed to neutralize 3.0 mL of 6.0 M hydrochloric acid, HCl(aq). Show your work; the answer alone is not enough. (Hint: the amount needed is less than 2 grams.)

6. The accepted value for the universal gas constant is 0.08206 L atm/mol K. What would it be if the pressure was measured in torr and the volume in milliliters? Show your conversions.

Materials

Apparatus
50-mL eudiometer tube
#00 1-hole rubber stopper
Copper wire, 10 cm length
Thermometer, –10º to +110ºC

Reagents
Magnesium ribbon, 3 pcs, ~4-5 cm each, freshly cleaned
6 M HCl(aq)
NaHCO₃(s) (baking soda)

Safety

Hydrochloric acid is corrosive to skin and clothing. Clean up all spills thoroughly.

Note: If acid spills on the lab bench, use a bit of baking soda to neutralize it before cleaning up.

Do not neutralize acid that spills on skin or clothing; flood the affected area with water.

Procedure

1. Fill a Berzelius (tall-form) 1-L beaker to within about 4-5 cm of the top, using tap water; the water should be at or near room temperature.

2. Obtain a short (4-5 cm) piece of magnesium ribbon, clean it thoroughly with steel wool, then measure and record its mass to the nearest 0.1 mg, using the analytical balance. If its mass is greater than what you calculated in Prelaboratory Question 4, it may generate more than 50.0 mL of hydrogen. Trim off a bit of the ribbon and reweigh it. Use a 10-cm piece of copper wire to make a cage for your magnesium, by folding the magnesium over the wire then rolling the wire around the magnesium. Fit the wire cage into a 1-hole #00 rubber stopper. The cage should be about 5 cm from the small end of the stopper to hold the magnesium in place. (Figure 1)

3. Carefully pour about 5 mL of 6 M HCl(aq) into a 50-mL gas-measuring tube. The graduations on the tube may be used for this. Holding the tube at about a 45º angle, use a wash bottle or beaker to carefully add water to the tube until it is completely full. Try to direct the water down the side of the tube to minimize mixing of the water and the acid. Insert the stopper assembly (Fig. 1, above) into the top of the tube. Water should escape through the hole in the stopper; if it does not, remove the stopper and carefully add more water, then replace the stopper assembly. This will keep air from being trapped in the tube.
4. Place your finger over the hole in the stopper and invert the tube, lowering it into the beaker of water. Remove your finger when the stopper is below the level of water in the beaker. The hydrochloric acid is more dense than pure water, so it will slowly sink toward the stopper and the magnesium; observe and record evidence of reaction. (See Figure 2, next page.)

5. When the reaction is complete, allow the system to stand for two or three minutes, tapping the sides of the tube to dislodge any gas bubbles that may be clinging to the glass wall. Make sure that there are no little pieces of unreacted magnesium on the wall of the cylinder. If a small piece remains, gently shake the tube up and down to wash the metal back into the acid solution, allowing it to finish reacting. (Be careful not to lift the tube completely out of the water in the beaker.)

6. Place your finger once again over the hole in the stopper, then transfer the tube and contents to a container of water that is deep enough that you can make the water levels inside and outside the tube nearly equal to each other. This will make the pressure inside the tube equal to the atmospheric pressure. Record the volume of gas trapped in the tube (± 0.01 mL) and the temperature of the water near the mouth of the tube. The temperature of the escaping solution may be assumed to be the same as the temperature of the trapped gases. Enter these data in your Data Table.

Cleaning Up
1. Take apart the apparatus. Rinse off the copper wire for re-use.
2. Use baking soda to neutralize the acidic solution remaining in the beaker. The neutralized solution can be flushed down the drain safely. As part of the Prelaboratory Assignment, you calculated the mass of baking soda needed. Use a plastic spoon to add approximately that amount of the solid (a little at a time to minimize foaming) to the beaker. Stir well and flush the solution down the drain.
3. Clean all glassware after each trial. After the final trial, return it to its proper location.
4. Wash your hands before leaving the laboratory.

Analysis and Conclusions
Show all calculations for Trial 1; you may simply report the results for the other two. Enter the results for all trials in a Summary Table.
1. Calculate the number of moles of magnesium used. This is the same as the number of moles of hydrogen generated. (Why?)
2. Because you collected hydrogen over water, a small portion of the gas in the cylinder at the end of the reaction is water vapor; we say the hydrogen gas is “wet.” The amount of water that evaporates is dependent only on the temperature, so it is a simple matter to determine the partial pressure of the water vapor in the graduated cylinder. A table showing the vapor pressure of water at various temperatures is given at the end of this experiment. Use the table to find the pressure due to water in the graduated cylinder, then subtract this value from the barometric pressure to get the pressure exerted by the “dry” hydrogen (hydrogen without the water vapor). Be sure to report the pressure to the correct degree of precision.

7 Carry out this step only if the water level inside the tube is more than 5 cm (50 mm) above the water level in the beaker.
3. You have measured the volume occupied by a small fraction of a mole of hydrogen, under a specific set of conditions of pressure and temperature. The volume occupied by a mole of gas is called its **molar volume**, and it is the same for all “ideal” gases at a given set of pressure and temperature. For each trial:

   a. Calculate the volume that 1.00 mole of hydrogen would occupy at your experimental temperature and pressure (called “laboratory conditions”). Record your answers in your Summary Table in units of liters per mole, L/mol.

   b. Use the combined gas law to calculate the volume that 1.00 mole of hydrogen would occupy at 1.00 atm and 273 K. (Standard Temperature and Pressure, STP)

4. Determine the value of PV/nT for each trial; P is the pressure of dry hydrogen, V is the volume of gas collected, T is the Kelvin temperature, and n is the number of moles of hydrogen generated.

5. Determine the average of your three values for PV/nT. Also determine the deviation for each of your three trials and the average deviation. Calculate the percentage error in your determination of the value of R, based on the accepted value of 0.08206 L atm mol⁻¹ K⁻¹.

6. You were told to equalize the water levels inside and outside the tube at the end of each trial, in order to make the total pressure inside the tube equal to the surrounding atmospheric pressure, but you were told to do so only if the water levels differed by more than 50 mm. Suggest an explanation for not making the adjustment for any difference in water levels. (Hint: Consider the relative densities of water and mercury.)