East Los Angeles College
Department of Chemistry

GENERAL CHEMISTRY 101

LABORATORY MANUAL

An Inquiry Approach through an Environmental Awareness

The following laboratories have been compiled and adapted by
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Chemical Safety in the Laboratory - Regulations

A. GENERAL

1. First-aid kits are available for emergency use only and are located beside the main entrance of rooms H8-101, 103, 117, 119 and in the stockroom 111. Band-aids for minor cuts are available in the main stockroom. Notify your instructor or the technicians if you use safety items.

2. Notify your instructor if any accidents and/or injuries, regardless of their severity. If you need medical treatment, you will be promptly taken to the Student Health Center located in building G8, room 111 (323-265-8600). In case of accident after 5:00 pm or on Saturdays, call the campus police at 323-265-8800 or dial 911.

3. Learn the location and use of safety equipment, including the safety shower, eyewash, fire extinguisher, and fire blanket.

4. Unauthorized experiments are not allowed at any time.

5. Work cautiously with chemicals only after you have learned about their potential hazards. The stockroom has a catalogue of MSDS (Material Safety Data Sheet) sheets that contain all the important information about any chemical you will use.

7. Closed-toe shoes must be worn in the laboratory at all times.

8. Do not attempt to slow down or stop centrifuge rotors with your hands! Always let the centrifuge come to a complete stop before opening the lid to the rotor chamber.

9. Wash your hands well before leaving the laboratory.

B. HANDLING CHEMICALS AND WASTE DISPOSAL

1. To avoid spattering of acids which can cause burns, always add acid to water. Never add water to acid.

2. Before obtaining any reagents, carefully read the labels on the bottles twice. Many chemicals have similar names or concentrations may vary.

3. Do not remove a reagent from the designated dispensing area. Use the appropriate container (test tube, beaker, etc.) for obtaining chemicals.

4. To avoid unnecessary waste, obtain only the amount of chemicals called for in an experiment. Your instructor will tell you the proper procedure for dispensing liquids and solids. Never insert medicine droppers or scoops into reagent bottles.

5. Never return unused chemicals to the original dispensing bottle.

6. Follow the instructor’s directions for disposal of chemicals. When no specific directions are given, dispose of nonhazardous, water soluble substances in the sink, and put insoluble materials such as filter paper in waste basket.

7. Broken glass must be put into the containers designated for that purpose.

8 Each day, before you leave your lab bench, clean off the bench surface. Remove matches and papers, and wipe down the surface with water and paper towels.

C. EYE PROTECTION

1. You are required to wear approved eye protection in the laboratory whenever you are doing any experiment or whenever any experiment is being done in the laboratory around you (eye protection must meet ANSI Z87.1 impact standards). Repeated failure to wear approved eye protection will result in dismissal from the experiment being conducted.

2. If you should get an irritating substance in your eye, move quickly to the eye washer and wash your eyes thoroughly for at least 15 minutes. Do not delay; a difference of a few seconds can be crucial for the recovery of your eyes. Have someone notify the instructor of the accident so that you can be taken to the Student Health Center immediately.

3. Remove contact lenses while performing any activity/experiment in the laboratory.

D. FIRE HAZARD

1. In case of fire notify the instructor as soon as possible.

2. Do not dry chemicals in a drying oven or heat any materials with an open flame unless specifically directed to do so.

3. Tie back long hair and avoid wearing loose clothing in the laboratory.

4. Never store flammable substances in your laboratory drawer or locker without the approval of, or directions from your laboratory instructor. Do not store organic solvents in open containers even for a short time.

D. CONTACT HAZARD

1. If you should spill a corrosive substance on your skin or clothing, wash it off with plenty of water for 15 minutes. Use the safety shower if you were exposed to a large chemical spill. Notify the instructor of any spillage as soon as possible; he/she will provide any necessary secondary treatment and will arrange for your transportation to the Student Health Center, if necessary.

E. INGESTION HAZARD

1. Never eat, drink, or taste anything in the laboratory.

2. No smoking is allowed in the laboratory or building.

3. No pipetting by mouth.

F. INHALATION HAZARD

1. Experimental operations that generate toxic or noxious fumes should always be performed under a hood.

H. HOODS

1. Before using a hood, always check to make sure it is on and functioning.

2. Use the hood with the sash raised at the indicator line. This includes using the hood for the storage of chemicals or reagents.

I. HAZARDOUS SPILLS AND CLEAN UP

1. In the event of a chemical spill, large or small, consult your laboratory instructor or the chemistry technician as to the appropriate method of clean-up.

2. You should not clean up a spill if:
   - -You don't know what the material is, or lack the necessary protection or clean-up materials to do the job safely.
   - -The spill is large (e.g. more than one liter for liquids).
   - -The spilled material is highly toxic.
   - -You feel any physical symptoms of exposure (eye irritation, difficulty breathing, coughing, dizziness, nausea, skin irritation etc.).
   - -The substance is regulated (e.g.: carcinogen, biohazard, etc.).

4. When metallic mercury is spilled, watch closely to see where the droplets go. Then, avoid stepping on them, and notify the laboratory instructor or the chemistry technician immediately so that proper decontamination procedures can be instituted.

ACKNOLEDEGEMENT BY STUDENT

I have read and understood the Safety Regulations. The details have been called to my attention by the instructor in charge of my laboratory section. I agree to abide by these regulations in the interest of my own safety and that of my other classmates.

Name _________________________ Lab Day &Hour____________________________

Locker No. ____________________ Instructor _________________________________

_______________________________ ___________________________________

Student's Signature & Date Instructor's Signature & Date

Twelve Principles of Green Chemistry

1. **Prevention**
   It is better to prevent waste than to treat or clean up waste after it has been created.

2. **Atom Economy**
   Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. **Less Hazardous Chemical Syntheses**
   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. **Designing Safer Chemicals**
   Chemical products should be designed to effect their desired function while minimizing their toxicity.

5. **Safer Solvents and Auxiliaries**
   The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. **Design for Energy Efficiency**
   Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. **Use of Renewable Feedstocks**
   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. **Reduce Derivatives**
   Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. **Catalysis**
   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. **Design for Degradation**
    Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

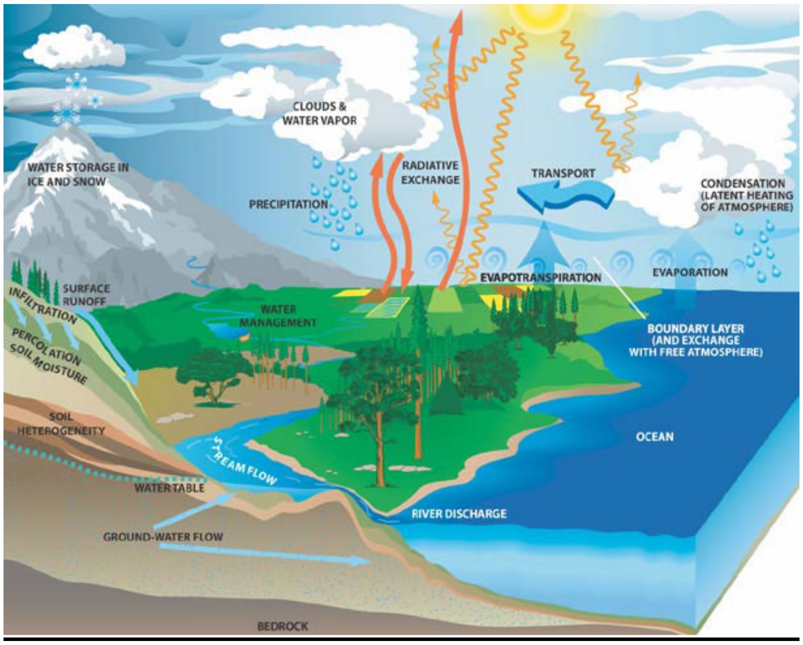
11. **Real-time analysis for Pollution Prevention**
    Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. **Inherently Safer Chemistry for Accident Prevention**
    Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Reference

1. Environmental Protection Agency, Accessed on November 16, 2010: http://www.epa.gov/gcc/pubs/principles.html

Unit 1 – Water and the Environment



Clean water is critical for sustaining life, yet polluted water and inadequate sanitation kills at least two children every minute worldwide. And even in the US, where wastewater treatment is relatively advanced compared to some other countries, many people take the flow of water in and out of their homes for granted. Where does it all go after we flush the toilet or pull the plug on the drain? What's more, how does this used water get cleaned and safely find its way back into the environment?

The answer is your local wastewater treatment facility, which operates 24/7 to make sure your community's wastewater is treated properly and released back into waterways such as lakes, streams, rivers, where it flows to one of the great oceans or lakes. It can also be used again along the way for irrigation, commercial or residential use, groundwater replenishment, and even drinking water, or it evaporates into the atmosphere and returns as rain in some other part of the world. Water is used over and over again, and thousands of water quality professionals around the world work to protect its quality and cleanliness.

Wastewater Treatment

Treatment of wastewater is a relatively modern practice. While sewers were common in ancient Rome to remove foul-smelling water, it was not until the 19th century that large cities began to reduce the amount of pollutants in the wastewater they were discharging to the environment. Since that time, the practice of wastewater collection and treatment has undergone substantial engineering improvements, and many state and federal regulations have been enacted.

Most homes, businesses, and institutions are connected to a sewer system that conveys their wastewater to a public wastewater treatment plant. Sanitary sewer systems carry only domestic and industrial wastewater, while combined sewer systems also carry stormwater runoff. At the plant, the wastewater is cleaned and returned to the environment to be used over and over again. Wastewater flows by gravity with occasional help from pumps until it reaches the treatment plant. What happens in a wastewater treatment plant is essentially the same as what occurs naturally in a lake or stream. The function of a wastewater treatment plant is to speed up the process by which water is cleaned naturally. Treatment plants are operated 24 hours a day by a treatment team that is committed to protecting public health and the environment.

Wastewater is typically treated through a series of five major steps followed by processes to reuse or to dispose of the remaining products. This treatment requires an intricate balance of physical, biological, and chemical processes. They include:

> Preliminary Treatment includes screening to remove large objects (such as sticks, rags, leaves, and trash) and the settling of grit (heavy, sandy, abrasive matter). The material is collected and discarded, and the remaining flow moves on to primary treatment.
>
> Primary Treatment involves the reduction of the wastewater flow to remove easily settleable and floatable solids using primary tanks known as clarifiers. Solids removed from this process are often sent to the solids handling portion of the plant.
>
> Secondary Treatment is designed to grow naturally occurring microorganisms to digest organic material, sometimes remove nutrients, and then to settle to the bottom of a secondary sedimentation basin. After secondary treatment, 85% to 90% of solids have been removed from the wastewater.
>
> Tertiary (or Advanced) Treatment is used to improve the quality of the water even more, especially if the plant’s permit requires more stringent effluent limits. Usually this entails lower effluent solids and nutrients, such as nitrogen and phosphorus levels.
>
> Disinfection destroys pathogenic organisms in the effluent before it is discharged into the receiving water body to help protect the public from exposure to pathogens. Alternatives for disinfection include chlorination followed by dechlorination, exposure to ultraviolet light, and the infusion of ozone.

Solids Handling involves the treatment of the solids removed from the water treatment processes for beneficial use or to be made acceptable for landfills.

The two main products of the wastewater treatment process are clean water and the collected solids that, after treatment, are known as biosolids. Some communities further treat clean water for recycling so it can be used in ways such as golf course and landscape irrigation, and even groundwater recharge programs. Biosolids can be reused in a variety of ways: applied as a fertilizer/soil conditioner (for agricultural, land reclamation, or horticultural use), burned to produce energy, or used as a component of other useful products.

Reclaimed Water

Reclaimed water is highly treated wastewater that can be used to supplement existing water supplies. Using reclaimed water for irrigation, water features, and in industry can be an environmentally efficient and cost-effective alternative to using drinking water.

Agricultural irrigation is a common way to use reclaimed water. Reclaimed water is also used around the world to irrigate lawns and golf courses. Water reuse programs can supplement lakes and streams to improve wildlife habitats; creates artificial lakes for picnicking, fishing, and boating; and provide water for use in fountains at many commercial buildings and parks.

Reclaimed water undergoes a high level of treatment to remove bacteria and viruses from wastewater. Extensive testing is performed to assure water quality standards are met. In the United States, for example, reclaimed water has been used safely for more than four decades. Water reuse is a safe and environmentally responsible approach to conserving finite water resources.

Temperature

The temperature of a body of water influences its overall quality. Water temperatures outside the “normal” range for stream or river can harm to the aquatic organisms that live there. It is for this reasons that the change in the temperature of the water over a section of a stream is measured, not just the temperature at one location. If the water temperature changes by even a few degrees over a one-mile stretch of the stream, it could indicate a source of thermal pollution.

Thermal pollution caused by human activities is one factor that can affect water temperature. Many industries use river water in their processes. The water is treated before it is returned to the river, but is warmer than it was before. Runoff entering a stream from parking lots and rooftops is often warmer than the stream and will increase its overall temperature.

Factors that affect water temperature.

-Air temperature
-Amount of shade
-Soil erosion increasing turbidity
-Thermal pollution from human activities
-Confluence of streams
-Effects of water temperature
-Solubility of dissolved oxygen
-Rate of plant growth
-Metabolic rate of organisms
-Resistance in organisms

One important aspect of water temperature is its effect on the solubility of gases, such as oxygen. More gas can be dissolved in cold water than in warm water. Animals, such as salmon, that require a high level of dissolved oxygen will only thrive in cold water. Increased water temperature can also cause an increase in the photosynthetic rate of aquatic plants and algae. This can lead to increased plant growth and algal blooms, which can be harmful to the local ecosystem. A change in water temperature can affect the general health of the aquatic organisms, thus changing the quality of the stream.

Acidity (pH)

Water contains both hydrogen ions, H^+ and hydroxide ions, OH^- The relative concentrations of these two ions determine the pH value. Water with a pH of 7 has equal concentrations of these two ions and is considered to be a *neutral* solution. If a solution is *acidic,* the concentration of OH^- ions exceeds that of the H^+ ions. On the pH scale of 0 to 14 the most basic. A change from pH 7 to pH 8 in a lake or stream represents a ten-fold increase in the OH^- ion concentration.

Rainfall generally has a pH value between 5 and 6.5. It is acidic because of dissolved carbon dioxide and air pollutants, such as sulfur dioxide or nitrogen oxides. If the rainwater flows over soil containing hard-water minerals, its pH usually increases. Bicarbonate ions, HCO_3^- , resulting from limestone deposits react with water to produce OH^- ions, according to the equation:

$$HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^-$$

As a result, streams and lakes are often basic, with pH values between 7 and 8, sometimes as high as 8.5.

The measure of the pH of a body of water is very important as an indication of water quality, because of the sensitivity of aquatic organisms to the pH of their environment. Small changes in pH can endanger many kinds of plants and animals; for example trout and various kinds of nymphs can only survive in waters between pH 7 and pH 9. If the pH of the waters in which they live is outside of that range, they may not survive or reproduce.

Table 1: Effects of pH Levels on Aquatic Life

pH	Effect
3.0 – 3.5	Unlikely that fish can survive for more than a few hours in this range, although some plants and invertebrates can be found at pH levels this low.
3.5 – 4.0	Known to be lethal to salmonids.
4.0 – 4.5	All fish, most frogs, insets absent.
5.0 – 5.5	Bottom-dwelling bacteria (decomposers) begin to die. leaf litter and detritus begin to accumulate, locking up essential nutrients and interruption chemical cycling. Plankton begin to disappear. Snails and clams absent. Mats of fungi begin to replace bacteria in the substrate.
6.0 – 6.5	Freshwater shrimp absent. Unlikely to be directly harmful to fish unless free carbon dioxide is high (in excess of 100 mg/L)
6.5 – 8.2	Optimal for most organisms.

8.2 – 9.0	Unlikely to be directly harmful to fish, but indirect effects occur at this level due to chemical changes in water.
9.0 – 10.5	Likely to be harmful to salmonids and perch if present for long periods.
10.5 – 11.0	Rapidly lethal to salmonids. Prolonged exposure is lethal to carp, perch.
11.0 – 11.5	Rapidly lethal to all species of fish.

Changes in pH can also be caused by algal blooms (more basic), industial processes resulting in a release of vases or acids (raising or lowering pH), or the oxidation of sulfide-containing sediments (more acidic). The pH value of streams and lakes is usually between pH 7 and 8. Levels between 6.5 and 8.5 pH are acceptable for most drinking water standards. Areas with higher levels of water hardness (high concentrations of Mg^{2+}, Ca^{2+}, and HCO_3^-) often have water with higher pH values (between 7.5 and 8.5)

Turbidity

Turbidity is measure of water's lack of clarity. Water with high turbidity is cloudy, while water with low turbidity is clear. The cloudiness is produced by light reflecting off of particles in water, therefore, the more particles in the water, the higher the turbidity. Many factors can contribute to the turbidity of water. An increase in stream flow due to heavy rains or a decrease in stream bank vegetation can speed up the process of soil erosion. This will add suspended particles, such as clay and silt, to the water.

Run off various types contains suspended solids that may add to the turbidity of a stream. Agricultural runoff often contains suspended soil particles. Other types of runoff include industrial wastes, water treatment plant effluent, and urban runoff from parking lots, roads, and rooftops. Bottom-Dwelling aquatic organisms, such as catfish, can contribute to the turbidity of the water by stirring up the sediment that has built up on the bottom of the stream. Organic matter such as plankton or decaying plant and animal matter that is suspended in the water can also increase the turbidity in a stream.

High turbidity will decrease the amount of sunlight able to penetrate the water, thereby decreasing the photosynthetic rate. Reduced clarity also makes the water less aesthetically pleasing. While this may not be harmful directly, it is certainly undesirable for many water uses. When the water is cloudy, sunlight will warm it more efficiently. This occurs because the suspended particles in the water absorb the sunlight, warming the surrounding water. This can lead to other problems associated with increased temperature levels. While highly turbid water can be detrimental to an aquatic ecosystem, it is not correctly to assume that clear water is always healthy. Slightly turbid water can be perfectly healthy, while clear water could contain unseen toxins or unhealthy levels or nutrients.

Sources of Turbidity

Soil erosion: silt and clay
Urban Runoff: road grime, rooftops, parking lots
Industrial waste: sewage treatment effluent, particulates
Abundant bottom- dwellers: stirring up sediments

Organics: microorganisms, decaying plants and animals, gasoline or oil from roads

Chloride and Salinity

Chloride, in the form of the $C1^-$ ion, is one of the major inorganic *anions,* or negative ions, in saltwater and freshwater. It originates from the dissociation of salts, such as sodium chloride or calcium chloride, in water. These salts, and their resulting chloride ions, originate from natural minerals, saltwater intrusion into estuaries and industrial pollution. There are many possible sources of manmade salts that may contribute to elevated chloride readings. Sodium chloride and calcium chloride, used to salt roads, contribute to elevated readings. Sodium chloride and calcium chloride, used to salt roads, contribute to elevated chloride levels in streams. Chlorinated drinking water and sodium-chloride water softeners often increase chloride levels in wastewater of a community.
In drinking water, the salty taste produced by chloride depends upon the concentration of the chloride ion. Water containing 250 mg/L of chloride may have a detectable salty taste if the chloride came from sodium chloride. The recommended maximum level of chloride came from sodium chloride. The recommended maximum level of chloride in U.S. drinking water is 250 mg/L.

Salinity

Salinity is the total of all non carbonate salts dissolved in water, usually expressed in parts per thousands (1ppt = 1000 mg/L). Unlike chloride ($C1^-$) concentration, you can think of salinity as a measure of the total salt concentration, comprised mostly of Na^+ and $C1^-$ ions. Even though there are smaller quantities of other ions in seawater (e.g., K^+, Mg^{2+}, or SO_4^{2-}), sodium and chloride ions represent about 91% of all seawater ions. Salinity is an important measurement in seawater or in estuaries where freshwater from rivers and streams mixes with salty ocean water. The salinity levels in seawater is fairly constant, at about 35 ppt (35,000 mg/L), while brackish estuaries may have salinity levels between 1 and 10 ppt. since more anions in sea water or brackish water are chloride ions, salinity can be determined from chloride concentration. The following formula is used:

$$\text{Salinity (ppt)} = 0.0018066 \times C1^- \text{ (mg/L)}$$

A chloride ion-selective electrode can be used to determine the chloride concentration, which is converted to a salinity value using the above formula.

Salinity can also be measured in freshwater. Compared to seawater or brackish water, freshwater has much lower levels of “salt ions” such as Na^+ and $C1^-$; in fact, these ions are often lower in concentration than hard-water ions such calcium (Ca^{2+}) and bicarbonate (HCO_3^-). Because salinity readings in freshwater will be significantly lower than in seawater or brackish water, readings are often expressed in mg/L instead of ppt (1 ppt = 1000 mg/L).

Nitrate

Nitrate ions found in freshwater samples result from a variety of natural and manmade sources. Nitrates are an important source of nitrogen necessary for plants and animals to synthesize amino acids and proteins. Most nitrogen on earth is found in the atmosphere in the form of nitrogen gas, N_2. Through a process called the *nitrogen cycle*, [1] nitrogen gas is changed into forms that are useable by plants and animals. These conversions include industrial production of fertilizers, as well as natural processes, such as legume-plant nitrogen fixation, plant and animal decomposition, and animal waste.

Although nitrate levels in freshwater are usually less than 1 mg/L, manmade sources of nitrate may elevate levels about 3 mg/L. these sources include animals feedlots, runoff from fertilized fields, or treated municipal wastewater being returned to streams. Levels about 10 mg/L in drinking water can cause a potentially fatal disease in infants called *methemoglobinemia,* or Blue Baby Syndrome. In this disease, nitrate converts hemoglobin into a form that can no longer transport oxygen.

High nitrate concentrations also contribute to a condition in lakes and ponds called *eutrophocation,* the excessive growth of aquatic plants and algae. Unpleasant odor and taste of water, as well as reduced clarity, often accompany this process. Eventually, dead biomass accumulates in the bottom of the lake, where it decays and compounds the problem by recycling nutrients. If other necessary nutrients are present, algal blooms can occur in a lake with as little as 0.50 mg/L NO_3^--N.

Nitrate pollution of surface and groundwater has become a major ecological problem in some agricultural areas. Although fertilizer in runoff is most often blamed, there is evidence that concentration of livestock in feedlots is now the major source of agricultural nitrate pollution. Runoff form fertilized fields is still a significant source of nitrate, although fertilizer use peaked in 1981 and has remained fairly constant since.

The nitrate level in freshwater is usually found in the range of 0.1 to 4 mg/L NO_3^- - N. Unpolluted waters generally have nitrate levels below 1 mg/L. the effluent of some sewage treatment plants may have levels in excess of 20 mg/L. In a study based on 344 USGS sites throughout the United States, [2] 80% of the sites reported nitrate levels less than 1 mg/L, 16% were in the range of 1 – 3 mg/L, and 4% were greater than 3 mg/L. the percentage of various land types reporting greater than 1 mg/L of nitrate were range land <5%, forested land ~10%, urban areas ~30%, and agricultural land ~40%.

Calcium

It is in the form of the Ca^{2+} ion, and it is one of the major inorganic cations, or positive ions, in saltwater and freshwater. It can originate from the dissociation of salts, such as calcium chloride or calcium sulfate, in water.

$$CaCl_2\,(s) \rightarrow Ca^{2+}\,(aq) + 2\,Cl^-(aq)$$

$$CaSO_4\,(s) \rightarrow Ca^{2+}\,(aq) + SO_4^{2-}(aq)$$

Most calcium in surface water comes from streams flowing over limestone, $CaCO_3$, gypsum, $CaSO_4 \bullet 2\,H_2O$, and other calcium containing rocks and minerals. Groundwater and underground aquifers leach even higher concentrations of calcium ions from rocks and soil. Calcium carbonate is relatively insoluble in water, but dissolves more readily in water containing significant levels of dissolved carbon dioxide. [1]

Sources of Calcium Ions
Limestone: $CaCO_3$
Dolomite: $CaCO_3$-$MgCO_3$
Gypsum: $CaSO_4 \bullet 2\ H_2O$

The concentration of calcium ions (Ca^{2+}) in freshwater is found in a range of 0 to 100 mg/L, and usually has the higher concentration of any freshwater cation. A level of 50 mg/L is recommended as the upper limit for drinking water. High levels are not considered a health concern; however, levels above 50 mg/L can be more problematic due to formation of excess calcium carbonate deposits in plumbing of in decreased cleansing action of soaps. If the calcium-ion concentration in freshwater drops below 5 mg/L, it can support only sparse plant and animal life, a condition known as *oligotrophic.* Typical seawater contains Ca^{2+} levels of about 400 mg/L.

When water passes through or over mineral deposits such as limestone, the levels or Ca^{2+}, Mg^{2+}, and HCO_3^- ions present in the water greatly increase and cause the water to be classified as hard water. This term results from the fact that calcium or magnesium ions in water combine with soap molecules, forming a sticky scum that interferes with soap action and makes it "hard" to get suds. One of the most obvious signs of water hardness is a layer of white film left on the surface of showers. Since most hard-water ions originate from calcium carbonate, levels of water hardness are often referred to in terms of hardness as *$CaCO_3$.* For example, if a water sample is found to have a Ca^{2+} concentration of 30 mg/L, then its *calcium hardness* as $CaCO_3$ can be calculated using formula[2]

$$(30\text{ mg/L } Ca^{2+}) \times (100\text{ g } CaCO_3/\ 40\text{ g } Ca^{2+}) = 75\text{ mg/L calcium hardness ca } CaCO_3$$

[1] The reaction occurring with limestone is:

$$CaCO_3(s) + CO_2\ (aq) + H_2O(I) \leftrightarrow Ca^{2+}\ (aq) + 2HCO_3^-\ (aq).$$

[2] This formula takes into account that the molar mass of Ca is 40 g/mol, and $CaCO_3$ is 100 g/mol.

Note that 30 mg/L Ca^{2+} and 75 mg/L calcium hardness as $CaCO_3$ are equivalent-they are simply two different ways of expressing calcium levels. The value of calcium hardness as $CaCO_3$ can always be obtained by multiplying the Ca^{2+} concentration by a factor of 100/40, or 2.5.
Another common measurement of water hardness is known as total hardness as $CaCO_3$. This measurement takes into account both Ca^{2+} and Mg^{2+} ions. On average, magnesium hardness represents about 1/3 if total hardness and calcium hardness about 2/3. If you are comparing your won test results of calcium hardness as $CaCO_3$ with results in publications that use units of total hardness as $CaCO_3$, you can estimate total hardness by multiplying the calcium hardness by 1.5.

The concentration of calcium ions (Ca^{2+}) in freshwater is found in a range of 4 to 100 mg/L (10-250 mg/L of calcium hardness as $CaCO_3$). Seawater contains calcium levels of 400 mg/L Ca^{2+} (1000 mg/L of calcium hardness as $CaCO_3$).

Selected EPA Drinking Water Standards

Contaminant	Standard
pH	6.5-8.5
Total dissolved Solids	< 500 mg/L
Turbidity	< 5 NTU
Chloride	< 250 mg/L
Nitrate	< 10 mg/L
Copper	< 1.3 mg/L
Lead	< 0.015 mg/L

References

1. Mongabay website. Accessed November 16, 2010: http://news.mongabay.com/2006/1213-nasa_water.html

2. Water Environment Federation website. Accessed November 16, 2010: http://www.wef.org/publicinformation/default.aspx.

3. J. Randall, Advanced Chemistry with Vernier, Units: *Temperature, pH, Turbidity, Chloride and Salinity, Nitrate, Calcium and Water Hardness and Water Treatment.* (2007) 2nd Ed., Vernier Software & Technology, Beaverton, OR

Experiment 2 – Water Analysis

I. Purpose

Analyze different water samples qualitatively and quantitatively. Use Vernier electrodes and sensors to digitally collect data and create plots. Practice physical methods of separation and purification, such as distillation.

II. Introduction

Although Earth has an abundance of water, about 97% is seawater. The high concentration of sodium chloride in seawater makes it unsuitable to consume. Drinking seawater typically causes dehydration and diarrhea since most of the body fluids move out of the cells and into the intestine. Most of the drinking water comes from lakes and rivers. But less than 0.01% of this water is naturally available. The quantity of drinking water becomes scarcer as lakes and rivers are polluted by biological and chemical contaminants. Polluted water was especially a controversy in London, 1854, when contaminated drinking water caused the death of many lives. It is important to be able to purify and analyze water.

III. Materials

Part 1. Water Distillation & Analysis

Distillation Apparatus
Boiling Chips
Conductivity Device
0.1 M NaCl
0.1 M $AgNO_3$
0.1 M $SrCl_2$
Nichrome Wire
6 M HCl
50-mL Buret
Standardized 0.005 M EDTA
Ammonia-ammonium Chloride Buffer
Eriochrome Black T Indicator

Part 2. Water Analysis with Probes

Conductivity Probe
Vernier pH Sensor
pH 7 Buffer Solution
pH 10 Buffer Solution
Laptop Computer
Logger *Pro* Software
Low Standard (10 mg/L Cl^-)
Low Standard (10 mg/L Ca^{2+})
Calcium Ion-Selective Electrode
Turbidity Standard *(StableCal® Formazin Standard 100 NTU)*
Vernier Turbidity Sensor
Turbidity Cuvette
Soft, Lint-free Cloth or Tissue
Vernier Computer Interface
Vernier Temperature Probe
Chloride Ion-Selective Electrode
High Standard (1000 mg/L Cl^-)
High Standard (1000 mg/L Ca^{2+})

IV. Safety Precautions

Be careful with the handling of acids and bases used in this experiment, especially 6M HCl. Normal precautions for dilution processes should be observed.

V. Experimental Procedure

Part 1. Water Distillation & Analysis

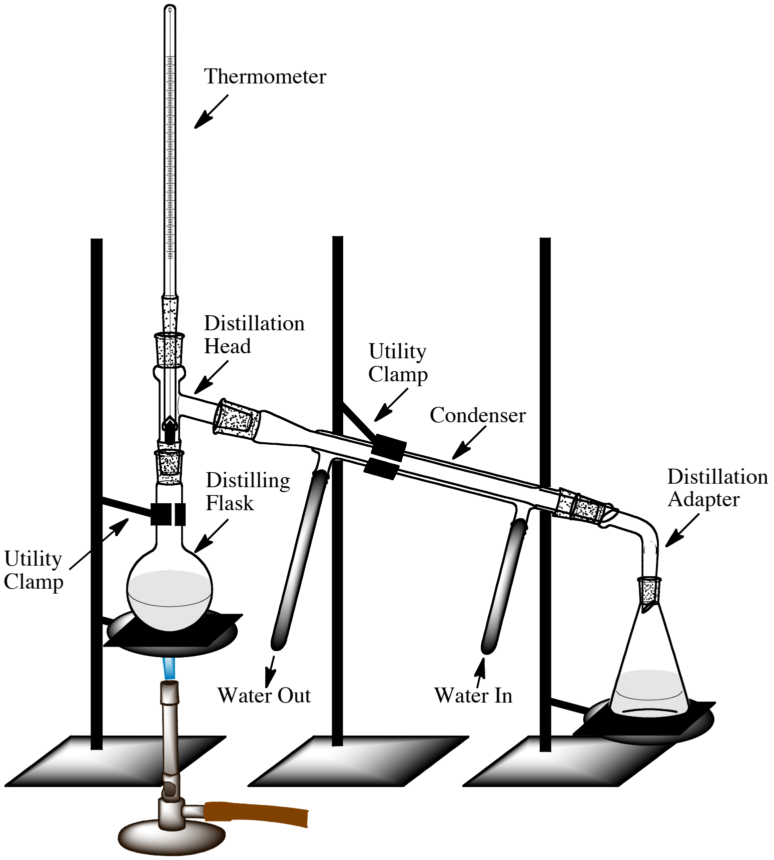


Figure 2A: A distillation apparatus.

A. Distillation

1. Assemble a distillation apparatus similar to the illustration above (Figure 2A). It is important to clamp the distilling flask and condenser to avoid dropping these expensive parts.

2. Once the distillation apparatus is set up, fill the distilling flask with tap water to about half full. Make sure to add several (about 3 – 5) boiling chips into the distilling flask to avoid bumping.

3. With the rubber hoses attached to the condenser, allow water to flow continuously in from the lower to the upper part of the condenser. From the upper part of the condenser, make sure that water flows smoothly out into the sink.

4. Begin heating the distilling flask with a flame from a Bunsen burner.

5. Discard the first 25 drops of distilled water collected as they may contain contaminates from the apparatus.

6. Monitor the water level in the distilling flask while collecting distilled water. When the water level is low in the distilling flask, add more tap water.

B. Conductivity Test

1. Pour approximately 25 mL of the distilled water collected from the distillation into a clean and dry 50 mL beaker.

2. Into a different clean and dry 50 mL beaker, pour about 25 mL of tap water.

3. Repeat the same procedure with 0.1 M NaCl and deionized water.

4. Using a conductivity meter, test the conductivity of each of the 4 samples. Make sure to clean the electrodes of the conductivity meter with deionized water between each sample.

C. Chloride Test

1. Pour approximately 1 mL of the distilled water collected from the distillation into a clean and dry test tube.

2. Into a different clean and dry test tube, pour about 1 mL of tap water.

3. Repeat the same procedure with 0.1 M NaCl and deionized water.

4. Into each of the 4 samples, add 2 drops of 0.1 M $AgNO_3$ and mix.

D. Flame Test

1. To prepare your sample, pour approximately 2 mL of the distilled water collected from the distillation into a clean and dry test tube.

2. Into a different clean and dry test tube, pour about 2 mL of tap water.

3. Repeat the same procedure with 0.1 M NaCl, deionized water, and 0.1 M $SrCl_2$.

4. Dip a nichrome wire into a test tube containing approximately 3 mL of 6 M HCl.

5. Flame the nichrome wire using a Bunsen burner. Make sure to flame the nichrome wire at the top of the blue inner cone of the flame.

6. Repeat the dipping and flaming process at least two more times to make sure the nichrome wire is clean.

7. After cleaning, dip the nichrome wire into the test tube containing distilled water and insert the wire into the flame of a Bunsen burner. Make sure to flame the nichrome wire at the top of the blue inner cone of the flame. Observe the color of the flame.

8. Repeat the nichrome wire cleaning process and test the next test tube containing tap water.

9. Continue to perform a flame test on the remaining samples, but make sure to clean the nichrome wire between each sample.

E. Water Hardness

1. To prepare your sample, rinse a 50-mL buret with tap water and fill the buret with tap water to nearly the markings of "0". Do not fill the buret to "0".

2. After recording the initial volume from the buret, dispense 25-mL of the tap water into a clean and dry 250-mL Erlenmeyer flask and record the final volume. The actual volume dispensed is equal to the final volume reading minus the initial volume reading.

3. Into the Erlenmeyer flask, add 20 drops of ammonia-ammonium chloride buffer, 2 drops of eriochrome Black T indicator, and swirl to mix the mixtures.

4. Rinse a 50-mL buret with approximately 5-mL of 0.005 M EDTA and allow the rinse to flow through the buret into a 150-mL beaker. The 150-mL beaker will serve as a waste container.

5. Repeat the rinse procedure once more.

6. After the second rinse, fill the buret with 0.005 M EDTA to nearly the markings of "0". Again, do not fill the buret to "0". Record the initial volume from the buret.

7. Add one drop at a time the EDTA solution from the buret into the 250-mL Erlenmeyer flask containing the sample prepared in steps 1-3. Make sure to swirl the Erlenmeyer flask while each drop enters the flask. It is recommended to place a white sheet of paper underneath the flask as this will aid in the observation of color changes. As the end point approaches, the red color begins to turn blue. It is important to slowly add one drop at a time, especially near the end point. The end point is reached when the red color changes to blue and remains blue for at least thirty seconds.

8. Record the final volume of the buret once the end point is achieved.

9. Repeat the procedure with the distilled water collected from the distillation as a different sample.

10. Perform another repeat with deionized water as the third sample.

F. Calculations

Although calcium and magnesium ions can be present in the 3 samples, assume that only calcium ions are present to calculate the hardness of water in each sample. Use the following formula:

$$\text{hardness of water in ppm} = \frac{(\text{volume in mL of EDTA used}) \times 500}{\text{volume in mL of water sample used}}$$

Part 2. Water Analysis with Probes

A. Sample Preparation

1. Pour approximately 25 mL of the distilled water collected from the distillation into a clean and dry 50 mL beaker.

2. Into a different clean and dry 50 mL beaker, pour about 25 mL of tap water.

3. Repeat the same procedure with 0.1 M NaCl and deionized water.

B. Total Dissolved Solid Measurement

1. Using a Conductivity Probe, measure one sample at a time the total dissolved solid (TDS) value of the 4 samples from the “Sample Preparation” procedure.

2. Into the 50 mL beaker of each sample, insert the Conductivity Probe and set the switch on the Conductivity Probe box to 0–2000 μS/cm (2000 μS/cm = 1000 mg/L TDS). Record the value in mg/L. (*Note: Make sure to rinse the Conductivity Probe with deionized water between each sample.)

C. Temperature Measurement

Make sure to position the computer as far away as possible from any liquids.

1. Plug the Temperature Probe into Channel 1 of the Vernier interface.

2. On the computer, open “01 Temperature” from the *Water Quality with Vernier* experiment folder of Logger *Pro*.

3. Using the Temperature Probe, measure one sample at a time the temperature of the 4 samples from the “Sample Preparation” procedure.

4. Into the 50 mL beaker of each sample, insert the Temperature Probe.

5. On the computer, click “collect” to begin data collection. Click “Keep” to begin a 10 second sampling run.

6. After 10 seconds, stop data collection and record the average temperature. (*Note: Make sure to rinse the Temperature Probe with deionized water between each sample.)

D. pH Analysis

pH Sensor Setup
1. Plug the pH Sensor into Channel 1 of the Vernier interface. 2. On the computer, open "02 pH" from the *Water Quality with Vernier* experiment folder of Logger *Pro*.

pH Sensor Calibration
3. On the computer, choose "Calibrate > CH1: pH" from the Experiment menu and then click "Calibrate Now."

4. Remove the pH Sensor from the bottle by loosening the lid.

5. Rinse the pH Sensor with deionized water. Using "Kimwipe" or soft tissue, gently blot the pH Sensor dry.

6. Insert the pH Sensor tip into the pH-7 buffer solution. On the computer, type "7" in the edit box. This number represents the pH value of the buffer. When the voltage reading for Reading 1 stabilizes, click "Keep".

7. Rinse the pH Sensor with deionized water. Using "Kimwipe" or soft tissue, gently blot the sensor dry.

8. Insert the pH Sensor into the pH-10 buffer solution. On the computer, type "10" in the edit box. When the voltage reading for Reading 2 stabilizes, click "Keep", then click "Done".

pH Measurement
9. Remove the pH Sensor from the buffer solution and rinse it with deionized water. Using "Kimwipe" or soft tissue, gently blot the pH Sensor dry.

10. Using the pH Sensor, measure one sample at a time the pH of the 4 samples from the "Sample Preparation" procedure. Into the 50 mL beaker of each sample, insert the pH Sensor. On the computer, click "collect" to begin data collection. Click "Keep" to begin a 10 second sampling run. After 10 seconds, stop data collection and record the average pH. (*Note: Make sure to rinse the pH Sensor with deionized water between each sample.)

E. Turbidity Analysis

Turbidity Sensor Setup
1. Make sure to position the computer as far away as possible from any liquids. Plug the Turbidity Sensor into Channel 1 of the Vernier interface.

2. Allow the Turbidity Sensor to warm up for 2 minutes.

3. On the computer, open “03 Turbidity” from the *Water Quality with Vernier* experiment folder of Logger *Pro*.

Turbidity Sensor Calibration

4. On the computer, choose “Calibrate > CH1: Turbidity (NTU)” from the Experiment menu and then click “Calibrate Now.”

5. Prepare a “blank” by rinsing the glass turbidity cuvette with deionized water. Fill the glass turbidity glass cuvette with deionized water until the bottom of the meniscus is exactly at the top of the white line.

6. Place the lid on the cuvette. Using “Kimwipe” or soft tissue, gently wipe the outside of the cuvette dry. If air bubbles are present in the cuvette, gently tap the bottom of the cuvette on a hard surface to remove the air bubbles.

7. Holding the cuvette by the lid, insert it into the Turbidity Sensor. Make sure that the mark on the cuvette is aligned with the mark on the Turbidity Sensor.

8. Close the lid on the Turbidity Sensor.

9. On the computer, type “0” in the edit box. When the voltage reading for Reading 1 stabilizes, click “Keep”. Remove the cuvette from the Turbidity Sensor.

10. Obtain the cuvette containing the Turbidity Standard (100 NTU) and gently invert it 5 times to mix any particles that may have settled to the bottom. (*Note: Do not shake the cuvette as air bubbles may appear!) Using “Kimwipe” or soft tissue, gently wipe the outside of the cuvette.

11. Holding the cuvette by the lid, insert it into the Turbidity Sensor. Make sure that the mark on the cuvette is aligned with the mark on the Turbidity Sensor.

12. Close the lid of the Turbidity Sensor.

13. On the computer, type “100” in the edit box. When the voltage reading for Reading 2 stabilizes, click “Keep”, then click “Done”. Remove the cuvette from the Turbidity Sensor.

Turbidity Measurement

1. Pour out the deionized water from the cuvette used as a “blank.”

2. Rinse the cuvette with the distilled water collected from the distillation.

3. Fill the cuvette with the distilled water so that the bottom of the meniscus is exactly at the top of the white line.

4. Place the lid on the cuvette.

5. Using “Kimwipe” or soft tissue, gently wipe the outside of the cuvette dry. If air bubbles are present in the cuvette, gently tap the bottom of the cuvette on a hard surface to remove the air bubbles.

6. Holding the cuvette by the lid, insert it into the Turbidity Sensor. Make sure that the mark on the cuvette is aligned with the mark on the Turbidity Sensor. Close the lid on the Turbidity Sensor.

7. On the computer, click “Collect” to begin data collection. Click “Keep” to begin a 10 second sampling run. After 10 seconds, stop data collection and record the average turbidity.

8. Remove the cuvette from the Turbidity Sensor.

9. Rinse the cuvette with tap water and fill the cuvette with tap water so that the bottom of the meniscus is exactly at the top of the white line.

10. Repeat the procedures as before to measure the turbidity of tap water.

F. Chloride and Salinity Analysis

Chloride Ion-Selective Electrode (ISE) Setup
1. The ISE should be soaking in the High Standard (1000 mg/L Cl^-). Make sure that it is not resting on the bottom of the container, but ensure that the small white reference contacts are immersed.

2. Plug the ISE Sensor into Channel 1 of the Vernier interface.

3. On the computer, open “15 Chloride ISE” from the *Water Quality with Vernier* experiment folder of Logger *Pro*.

Chloride ISE Calibration
4. On the computer, choose “Calibrate > CH1: Chloride ISE” from the Experiment menu and then click “Calibrate Now”.

5. Type “1000” in the edit box. This represents the concentration in mg/L Cl^-. When the voltage reading for Reading 1 stabilizes, click “Keep.”

6. Remove the electrode from the High Standard and rinse the electrode with deionized water.

7. Using “Kimwipe” or soft tissue, gently blot the electrode dry. Insert the tip of the electrode into the Low Standard (10 mg/L Cl^-). Again, make sure that it is not resting on the bottom of the container but ensure that the small white reference contacts are immersed.

8. Make sure no air bubbles are trapped below the electrode.

9. After gently swirling the solution, hold the ISE still and wait about 30 seconds for the voltage reading on the computer to stabilize.

10. Type “10” in the edit box. When the voltage reading for Reading 2 stabilizes, click “Keep”, then click “Done”.

Chloride Measurement

11. Remove the electrode from the Low Standard and rinse the electrode with deionized water.

12. Using “Kimwipe” or soft tissue, gently blot the electrode dry.

13. Insert the tip of the electrode into a 50 mL beaker containing distilled water collected from the distillation. Again, make sure that it is not resting on the bottom of the container but ensure that the small white reference contacts are immersed. Make sure no air bubbles are trapped below the electrode.

14. On the computer, click “Collect” to begin data collection.

15. Click “Keep” to begin a 10 second sampling run. After 10 seconds, stop data collection and record the average chloride concentration.

16. Remove the electrode from the distilled water sample and rinse the electrode with deionized water.

17. Using “Kimwipe” or soft tissue, gently blot the electrode dry. Insert the tip of the electrode into a 50 mL beaker containing tap water.

18. Repeat the procedures as before to measure the chloride concentration in tap water.

Salinity Value Determination

19. Use the following formula to calculate the salinity in ppt for each sample.

$$\text{salinity (ppt)} = 0.0018066 \times \text{Cl}^{-} \text{ (mg/L)}$$

G. Water Hardness

Calcium Ion-Selective Electrode (ISE) Setup

1. The ISE should be soaking in the High Standard (1000 mg/L Ca^{2+}).

2. Plug the ISE Sensor into Channel 1 of the Vernier interface.

3. On the computer, open “13 Calcium & Hardness” from the *Water Quality with Vernier* experiment folder of Logger *Pro*.

Calcium ISE Calibration

4. On the computer, choose “Calibrate > CH1: Calcium ISE (mg/L)” from the Experiment menu and then click “Calibrate Now”.

5. Type “1000” in the edit box. This represents the concentration in mg/L Ca^{2+}.

6. When the voltage reading for Reading 1 stabilizes, click “Keep”.

7. Remove the electrode from the High Standard and rinse the electrode with deionized water.

8. Using “Kimwipe” or soft tissue, gently blot the electrode dry.

9. Insert the tip of the electrode into the Low Standard (10 mg/L Ca^{2+}). Again, make sure no air bubbles are trapped below the electrode.

10. After gently swirling the solution, hold the ISE still and wait about 30 seconds for the voltage reading on the computer to stabilize. Type “10” in the edit box. When the voltage reading for Reading 2 stabilizes, click “Keep”, then click “Done”.

Calcium Measurement

11. Remove the electrode from the Low Standard and rinse the electrode with deionized water.

12. Using “Kimwipe” or soft tissue, gently blot the electrode dry.

13. Insert the tip of the electrode into a 50 mL beaker containing distilled water collected from the distillation.

14. On the computer, click “Collect” to begin data collection.

15. Click “Keep” to begin a 10 second sampling run. After 10 seconds, stop data collection and record the average calcium concentration.

16. Remove the electrode from the distilled water sample and rinse the electrode with deionized water. Using “Kimwipe” or soft tissue, gently blot the electrode dry.

17. Insert the tip of the electrode into a 50 mL beaker containing tap water.

18. Repeat the procedures as before to measure the calcium concentration in tap water.

Water Hardness Determination

19. Convert the calcium concentration (mg/L Ca^{2+}) to units of calcium hardness (mg/L as $CaCO_3$). The calculation takes into account the molar mass for both Ca^{2+} and $CaCO_3$. Use the following formula to calculate the calcium hardness as $CaCO_3$ for each sample.

$$\begin{aligned}\text{calcium hardness as } CaCO_3 &= (\text{mg/L } Ca^{2+}) \times (100 \text{ g } CaCO_3 / 40 \text{ g } Ca^{2+}) \\ &= (\text{mg/L } Ca^{2+}) \times 2.5\end{aligned}$$

VI. Questions

1. If the endpoint is reached when 50.00 mL of a tap water sample is titrated with 12.00 mL of 5.00×10^{-3} M EDTA solution, what is the hardness of the water sample in ppm?

VII. Discussion Questions

1. In part 1, “Water Distillation & Analysis”, is there a correlation between the various techniques used to analyze the samples of distilled water, tap water, deionized water, and 0.1 M NaCl? Explain.

VIII. References

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4. Randall, J., Advanced Chemistry with Vernier (2007) 2nd Ed., Vernier Software & Technology, Beaverton, OR

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Experiment 3 – Methods of Evaporation and Filtration Used to Separate Mixtures

I. Purpose

Separate homogeneous mixtures using physical means, such as gravity filtration, vacuum filtration, etc. Purification of a compound by recrystaliization.

II. Introduction

Is bottled water safer than tap water? Studies have revealed that phthalates, chemicals known to affect hormones, can come from the plastic material of the bottled water. In addition, at least 25% of bottled water contains tap water inside. These studies suggest that consumers should become more aware of what they are drinking. Besides chemical contaminant concerns, the shipment and production of plastic bottled water has environmental consequences. Simply moving large amounts of bottled water from one location to another creates global warming and other types of air pollution. The production of plastic bottled water requires millions of barrels of crude oil each year that affects the environment as well. The environment is also impacted by the disposal of plastic bottles. Most of the bottles are either sent to landfills or left as unclaimed trash instead of being recycled.

If bottled water is environmentally unfriendly, then drinking tap water may be a better alternative. However, consumers may be reluctant to trust the water coming out of their faucets unless there is scientific evidence that tap water is safe to drink. Companies like Brita® have already come up with faucet filtration systems to make tap water safer to drink. The separation of unwanted particulates from a mixture plays a major role in filtration systems.

III. Materials

Saturated NaCl solution
1 M Na_2CO_3
1 M $CaCl_2$
6 M HCl
Filter paper
Vanillin
Büchner funnel

IV. Safety Precuations

Be cautious with the acids and bases used in this experiment. Dispose all chemicals as instructed.

V. Experimental Procedures

Part 1. Separation of Mixtures by Evaporation

1. Weigh and record the mass of a clean and dry evaporating dish using an analytical balance.

2. Pour onto the evaporating dish approximately 5 mL of a saturated NaCl solution.

3. Reweigh and record the evaporating dish with the NaCl solution on it.

4. Set up a heating apparatus similar to the illustration below (Figure 3A).

5. Choose an appropriate size beaker that will hold the evaporating dish directly on top.

6. Add several (about 3 – 5) boiling chips into the beaker to avoid bumping.

7. Fill the beaker half full with tap water.

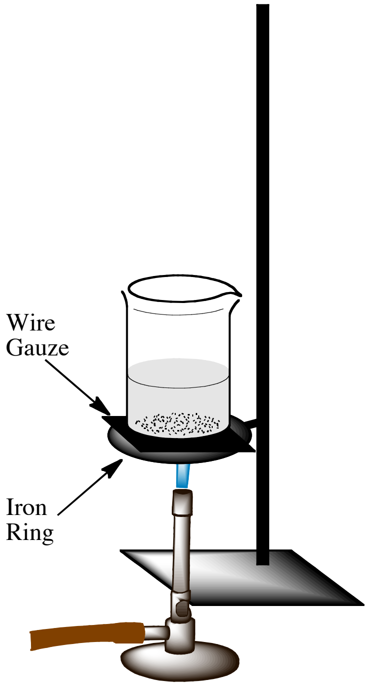

Figure 3A: A heating apparatus.

8. Place the evaporating dish with the saturated NaCl solution directly on top of beaker.

9. Turn on the flames from the Bunsen burner and heat until there is no apparent liquid on the evaporating dish. Turn off the flames.

10. Carefully remove the evaporating dish and the beaker from the heating apparatus.

11. Place the evaporating dish back on the wire gauze.

12. Apply a very gentle flame (approximately 2 minutes) underneath the wire gauze to completely evaporate any residues of liquid that may remain on the evaporating dish.

13. Allow the evaporating dish to cool and weigh the dish. Repeat the heating, cooling, and reweighing process until constant mass is reached.

14. Calculate the mass percent of NaCl in the saturated NaCl solution.

Part 2. Separation of Mixtures by Gravity Filtration

1. Add 10 mL of 1.0 M sodium carbonate into a 150 mL beaker.

2. Into the same beaker, add 10 mL of 1.0 M calcium chloride and stir the mixture with a glass stirring rod.

3. Write a balanced chemical equation for this mixture.

4. Set up a gravity filtration setup similar to the illustration below (Figure 3B). Make sure to wet the filter paper with deionized water to ensure that it sticks well to the funnel.

5. Using the glass stirring rod as a guide, pour the sodium carbonate and calcium chloride mixture directly into the center of the funnel. Make sure to point the glass stirring rod directly into the middle of the funnel without touching the filter paper.

6. Any solids will be retained by the filter paper while liquids will flow through due to gravity. The liquids will be collected underneath into a beaker.

7. When the filter paper appears dry, remove it from the funnel.

8. Open up the filter paper completely and transfer some solids to a watch glass.

9. Add 3 drops of 6 M HCl to the solids on the watch glass.

10. Write a balanced chemical reaction for the observed reaction.

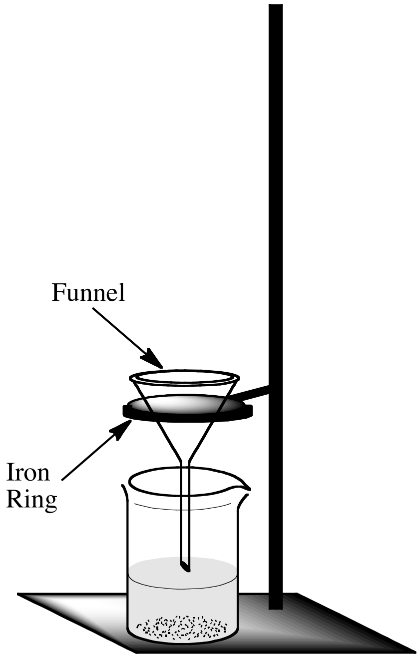

Figure 3B: A gravity filtration setup.

Part 3. Separation of Mixtures by Vacuum Filtration

1. Place a 250 mL Erlenmeyer flask on an analytical balance and press "Tare."

2. Weigh and record the mass of 0.8 g to 1 g of vanillin into the 250 mL Erlenmeyer flask on the analytical balance.

3. Remove the Erlenmeyer flask from the balance and add approximately 50 mL of deionized water and vigorously stir to dissolve as much vanillin as possible.

4. Using the flames from a Bunsen burner, gently heat the solution in the flask until all the solids dissolve. Do not allow the solution to boil. Turn off the flames and allow the solution to cool for several minutes.

5. Put the Erlenmeyer flask into an ice bath. As the solution cools down in the ice bath, crystallization should occur. If there are no signs of crystals forming when the flask feels cold, insert a glass stirring rod into the flask and gently scrap at the bottom.

6. Once crystallization is complete, assemble a vacuum filtration setup similar to the illustration below (Figure 3C).

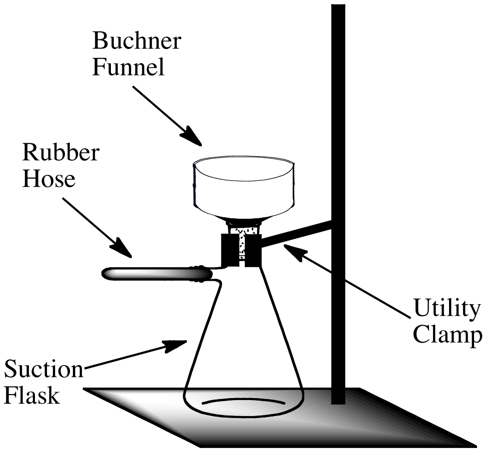

Figure 3C: A vacuum filtration setup.

7. Obtain an appropriate size filter paper that fits well at the bottom of the Büchner funnel. Weigh the filter paper using an analytical balance. Place the filter paper at the bottom of the Büchner funnel and wet it with deionized water.

8. Turn on the water line where the rubber hose is attached, as this will create a suction effect.

9. Rinse the crystals in the Erlenmeyer flask with approximately 5 mL of ice-cold water and carefully pour the crystals into the center of the Büchner funnel.

10. If there are crystals still remaining in the Erlenmeyer flask, rinse them with an additional 5 mL of ice-cold water and pour them into the Büchner funnel.

11. When the crystals appear to be dry, turn off the water line to stop the suction and carefully remove the filter paper from the Büchner funnel.

12. Place the filter paper containing the crystals on watch glass and allow it to dry in the lab drawer.

13. In the next lab class, weigh and record the mass of the filter paper containing the vanillin.

14. Calculate the percent recovery of vanillin.

VI. Questions

1. An evaporating dish weighs 44.3170 grams. After 8.5 mL of salt water was added to the dish, the combination of the dish and salt water weighed 52.987 grams. The dish was then heated until a constant mass of 44.5990 grams was obtained. What was the mass percent of salt dissolved in the salt water?

2. What is meant by “constant mass”? How is this important?

VII. Discussion Questions

1. In the previous experiment, distillation was performed to purify water from tap water. In this experiment evaporation, gravity filtration, and vacuum filtration were methods used to separate homogeneous mixtures. Would it be safe to drink purified sewage water if these methods were used to separate water from unwanted substances?

VIII. References

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Unit 2 – Solid Waste and Recycling

Across the country, many communities, businesses, and individuals have found creative ways to reduce and better manage municipal solid waste (MSW) - more commonly known as trash or garbage - through a coordinated mix of practices that includes source reduction, recycling (including composting), and disposal. The most environmentally sound management of MSW is achieved when these approaches are implemented according to EPA's preferred (suggested) order:

First: Source Reduction (Reduce and Reuse)

Between 1960 and 2008 the amount of waste each person creates has almost doubled from 2.7 to 4.5 pounds per day. The most effective way to stop this trend is by preventing waste in the first place. Waste prevention, also know as "source reduction," is the practice of designing, manufacturing, purchasing, or using materials (such as products and packaging) in ways that reduce the amount or toxicity of trash created. Reusing items is another way to stop waste at the source because it delays or avoids that item's entry in the waste collection and disposal system.

Source reduction, including reuse, can help reduce waste disposal and handling costs, because it avoids the costs of recycling, municipal composting, landfilling, and combustion. Source reduction also conserves resources and reduces pollution, including greenhouse gases that contribute to global warming.

Source Reduction and Reuse Facts

-More than 55 million tons of MSW were source reduced in the United States in 2000, the latest year for which these figures are available.

-Containers and packaging represented approximately 28 percent of the materials source reduced in 2000, in addition to nondurable goods (*e.g.*, newspapers, clothing) at 17 percent, durable goods (*e.g.*, appliances, furniture, tires) at 10 percent, and other MSW (*e.g.*, yard trimmings, food scraps) at 45 percent.

-There are more than 6,000 reuse centers around the country, ranging from specialized programs for building materials or unneeded materials in schools to local programs such as Goodwill and the Salvation Army, according to the Reuse Development Organization.

-Between two and five percent of the waste stream is potentially reusable according to local studies in Berkeley, California, and Leverett, Massachusetts.
-Since 1977, the weight of 2-liter plastic soft drink bottles has been reduced from 68 grams each to 51 grams. That means that 250 million pounds of plastic per year has been kept out of the waste stream.

Benefits of Reduction

-*Saves natural resources:* Waste is not just created when consumers throw items away. Throughout the life cycle of a product from extraction of raw materials to transportation to processing and manufacturing facilities to manufacture and use waste is generated. Reusing items or making them with less material decreases waste dramatically. Ultimately, fewer materials will need to be recycled or sent to landfills or waste combustion facilities.

-*Reduces toxicity of waste:* Selecting non-hazardous or less hazardous items is another important component of source reduction. Using less hazardous alternatives for certain items (*e.g*., cleaning products and pesticides), sharing products that contain hazardous chemicals instead of throwing out leftovers, reading label directions carefully, and using the smallest amount necessary are ways to reduce waste toxicity.

-*Reduces costs:* The benefits of preventing waste go beyond reducing reliance on other forms of waste disposal. Preventing waste also can mean economic savings for communities, businesses, schools, and individual consumers.

> -*Communities:* More than 7,000 communities have instituted "pay-as-you-throw" programs where citizens pay for each can or bag of trash they set out for disposal rather than through the tax base or a flat fee. When these households reduce waste at the source, they dispose of less trash and pay lower trash bills.
>
> -*Businesses*: Industry also has an economic incentive to practice source reduction. When businesses manufacture their products with less packaging, they are buying fewer raw materials. A decrease in manufacturing costs can mean a larger profit margin, with savings that can be passed on to the consumer.
>
> -*Consumers:* Consumers also can share in the economic benefits of source reduction. Buying products in bulk, with less packaging, or that are reusable (not single-use) frequently means a cost savings. What is good for the environment can be good for the pocketbook as well.

Second: Recycling and Composting

Recycling is sorting, collecting, and processing materials to manufacture and sell them as new products. This practice turns materials that would otherwise become waste into valuable resources. Collecting used bottles, cans, and newspapers and taking them to the curb or to a collection facility is just the first in a series of steps that generates a host of financial, environmental, and social returns. Some of these benefits accrue locally as well as globally.

Benefits of Recycling:

-Protects and expands US manufacturing jobs and increases US competitiveness

-Reduces the need for landfilling and incineration

-Prevents pollution caused by the manufacturing of products from virgin materials

-Saves energy

-Decreases emissions of greenhouse gases that contribute to global climate change

-Conserves natural resources such as timber, water, and minerals

-Helps sustain the environment for future generations

Composting is to decompose organic waste, such as food scraps and yard trimmings, with microorganisms (mainly bacteria and fungi) to produce compost. Compost is organic material that can be used as a soil amendment or as a medium to grow plants. Yard trimmings and food residuals together constitute 26 percent of the US municipal solid waste stream, which a lot of waste to send to landfills when it could become useful and environmentally beneficial compost instead. Composting offers the obvious benefits of resource efficiency and creating a useful product from organic waste that would otherwise have been landfilled.

Third: Disposal in Landfills or Waste Combustors

Modern landfills are well-engineered facilities that are located, designed, operated, and monitored to ensure compliance with federal regulations. Solid waste landfills must be designed to protect the environment from contaminants that may be present in the solid waste stream. The landfill sitting plan—which prevents the sitting of landfills in environmentally-sensitive areas—as well as on-site environmental monitoring systems—which monitor for any sign of groundwater contamination and for landfill gas—provide additional safeguards. In addition, many new landfills collect potentially harmful landfill gas emissions and convert the gas into energy.

Municipal solid waste landfills (MSWLFs) receive household waste. MSWLFs can also receive non-hazardous sludge, industrial solid waste, and construction and demolition debris. All MSWLFs must comply with the federal regulations, or equivalent state regulations.

Federal MSWLF Standards Include:
-*Location restrictions*: ensure that landfills are built in suitable geological areas away from faults, wetlands, flood plains, or other restricted areas.

-*Composite liners requirements*: include a flexible membrane (geomembrane) overlaying two feet of compacted clay soil lining the bottom and sides of the landfill; protect groundwater and the underlying soil from leachate releases.

-*Leachate collection and removal systems*: sit on top of the composite liner and removes leachate from the landfill for treatment and disposal.

-*Operating practices*: include compacting and covering waste frequently with several inches of soil help reduce odor; control litter, insects, and rodents; and protect public health.

-*Groundwater monitoring requirements*: requires testing groundwater wells to determine whether waste materials have escaped from the landfill.

-*Closure and post-closure care requirements*: include covering landfills and providing long-term care of closed landfills.

-*Corrective action provisions*: control and clean up landfill releases and achieves groundwater protection standards.

-*Financial assurance*: provides funding for environmental protection during and after landfill closure (*i.e*., closure and post-closure care).

Some materials may be banned from disposal in municipal solid waste landfills including common household items such as paints, cleaners/chemicals, motor oil, batteries, and pesticides. Leftover portions of these products are called household hazardous waste. These products, if mishandled, can be dangerous to your health and the environment. Many municipal landfills have a household hazardous waste drop-off station for these materials.

MSWLFs can also receive household appliances, also known as white goods, which are no longer needed. Many of these appliances, such as refrigerators or window air conditioners, rely on ozone-depleting refrigerants and their substitutes.

Waste combustors (combustion or incineration) are used to reduce waste volume, and are implemented by local governments or private operators. They can implement a controlled burning process called combustion or incineration. In addition to reducing volume, combustors, when properly equipped, can convert water into steam to fuel heating systems or generate electricity. Incineration facilities can also remove materials for recycling.

Over one-fifth of the US municipal solid waste incinerators use “refuse derived fuel” (RDF). In contrast to mass burning—where the municipal solid waste is introduced "as is" into the combustion chamber—RDF facilities are equipped to recover recyclables (e.g., metals, cans, glass) first, then shred the combustible fraction into fluff for incineration.

A variety of pollution control technologies significantly reduce the gases emitted into the air, including:

-*Scrubbers*: devices that use a liquid spray to neutralize acid gases

-*Filters*: remove tiny ash particles

Burning waste at extremely high temperatures also destroys chemical compounds and disease-causing bacteria. Regular testing ensures that residual ash is non-hazardous before being landfilled. About ten percent of the total ash formed in the combustion process is used for beneficial use such as daily cover in landfills and road construction.

Reference

1. Environmental Protection Agency. Accessed November 6, 2010: http://www.epa.gov/osw/

Experiment 4 – Waste and Recycling of Aluminum

I. Purpose

To practice measurement and identification techniques by synthesizing an inorganic salt, $KAI(SO_4)_2 \cdot 12\ H_2O$, from aluminum foil. To perform qualitative tests for the presence of $K^{+,}$ $Al^{3+,}$ SO_4^{2-}, and H_2O in $KAl(SO_4)_2 \cdot 12\ H_2O$. To observe the growth of crystals using a variety of crystal growth techniques.

II. Introduction

As you know most metals are found on earth as inorganic compounds (minerals and ores), usually in combination with other metals and oxygen, an abundant and ubiquitous element. Aluminum is the third most abundant element in the earth's crust after silicon and iron. The most common ore of aluminum is a hydrated aluminum oxide, $Al_2O_3 \cdot 2\ H_2O$, whose common name is bauxite. The Hall-Heroult process to produce aluminum in an electrolytic cell, from Al_2O_3 dissolved in molten cryolyte (Na_3AlF_6), requires an enormous amount of energy, making the process of obtaining aluminum from bauxite an expensive one; therefore, the importance of recycling aluminum.

Aluminum metal is commonly used in construction, and aluminum compounds are used in many applications, including the production of paper, dyes, ect. To use aluminum is more advantageous than using other metals as (1) the strength to weight ratio of aluminum is very and (2) aluminum is highly resistant to corrosion when exposed to air and water because aluminum oxidizes in air to produce a thin, tough, transparent aluminum oxide coating, $Al_2O_3(s)$. Aluminum oxide is relatively inert and protects the aluminum (for example, in a soda can) from further oxidation. However, because Al_2O_3 is amphoteric, it will react with either acids or bases. An aluminum can is therefore susceptible to corrosion if its contents are acidic or basic. To protect the can, it must then be coated on the inside walls with some kind of resin or plastic.

In this experiment you will recycle aluminum by synthesizing an aluminum compound, $KAl(SO_4)_2 \cdot 12\ H_2O$, from aluminum foil. $KAl(SO_4)_2 \cdot 12\ H_2O$ or aluminum potassium sulfate dececahydrate is commonly called **alum**. It is a hydrated salt and dissolves in water to produce Al^{3+}, K^+ and SO_4^{2-}. After you synthesize the alum you will check its composition by analyzing for Al^{3+}, K^+ and SO_4^{2-} and H_2O.

Alum Synthesis

(1) The first step in the synthesis of alum is the treatment of the aluminum foil with the base, KOH. The aluminum metal and aluminum oxide will form potassium aluminate, $KAlO_2$, according to the following reactions.

$$Al_2O_3\ (s) + 2\ KOH\ (aq) + H_2O\ (1)$$
$$2\ Al\ (s) + 2\ KOH\ (aq) + 2\ H_2O\ (l) \rightarrow 2\ KAlO_2\ (aq) + 3\ H_2\ (g)$$

(2) The potassium aluminate will react with sulfuric acid to form solid aluminum hydroxide, $Al(OH)_3(s)$.

$$2\ KAlO_2(aq) + H_2SO_4(aq) + 2\ H_2O(l) \rightarrow 2\ Al(OH)_3(s) + K_2SO_4(aq)$$

(3) By heating the solution and adding excess sulfuric acid the hydroxide is neutralized causing aluminum hydroxide to dissolve, producing aluminum ions and sulfate ions in solution

Molecular equation $2\ Al(OH)_3(s) + 3\ H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 6\ H_2O(1)$

Total ionic equation $Al(OH)_3(s) + 3\ H^+(aq) + SO_4^{2-}(aq) \rightarrow Al^{3+}(aq) + SO_4^{2-}(aq) + 3\ H_2O(1)$

Net ionic equation $Al(OH)_3(s) + 3\ H^+(aq) \rightarrow Al^{3+}(aq) + 3\ H_2O(1)$

The solution contains Al^{3+}, SO_4^{2-}, and K^+. Evaporation saturates the solution and if the solution is cooled, alum crystals will form (combination of Al^{3+} and K_2SO_4).

In general, the solubility of an ionic compound decreases as the temperature decrease. The alum crystals that are isolated will be white and powder-like. However, alum can form large gem-like crystals. This can be done through a process called recrystallization. If the powdery solid is dissolved in warm water, and cooled slowly in air these gem-like crystals can be formed. Crystals of alum can also be formed by carefully layering the warm solution of alum with ethanol. The ions are not soluble in ethanol and precipitate out of the water as the ethanol diffuses into the alum solution. If this happens slow enough the ions will precipitate, pack, and form large crystals. A slower and more efficient form of recrystallization can occur by vapor diffusion as when the alum is set in an atmosphere of ethanol, or ethanol vapor, the interaction occurs more slowly. In this experiment, you will be able to try two methods of recrystallization and let your crystals grow over several weeks.

III. Materials

Aluminum Can (provided by students)
25 mL 4 M KOH
20 mL 9 M H_2SO_4
12 mL 50% ethanol
8 g Alum

IV. Safety Precautions

Wear eye protection at all times. Potassium hydroxide, KOH, and sulfuric acid, H_2SO_4, are very corrosive. Both can cause burns if left in contact with the skin. If either chemical gets on your skin, immediately rinse with plenty of cool water for several minutes. Your instructor will discuss emergency measures to follow if your eyes are affected. If spills occur, notify the instructor, who will know how to neutralize the spill with sodium bicarbonate and can advise you on proper cleanup procedures. Wear gloves if there is any chance of contact with strong acids or bases.

Methanol vapors are toxic, and liquid methanol is toxic if swallowed. Use methanol in the hood, and avoid getting it on your skin. If it does contact your skin, rinse it off immediately with water. Because methanol is flammable, no open flames should be allowed in this laboratory.

V. Experimental Procedure

This is a lab that will be performed in one week. However, you will follow the growth of crystals over several weeks. You will work in pairs but the questions and lab reports are due individually.

Part 1. Synthesis of Alum from an Aluminum Can

1. Cut about a 9cm × 9cm piece of aluminum of a clean aluminum can. Clean the aluminum thoroughly using sand paper to get rid of paint and plastic used in the can. Cut the piece of aluminum can into the smallest possible pieces to increase the surface area of the aluminum. An increase in surface area generally increases the rate of a reaction. Weigh 0.5 grams of aluminum foil and record the mass to the nearest 0.001g. Place the pieces in a labeled, 250-mL Erlenmeyer flask.

2. In the hood, slowly add 25 mL of 4 M KOH to the flask. Carefully, swirl the flask as you add the base. This is a vigorous reaction that evolves hydrogen gas. Record your observations.

$$2\ \mathrm{Al\,(s)} + 2\ \mathrm{OH^-\,(aq)} + 6\ \mathrm{H_2O\,(1)} \rightarrow 2\ \mathrm{Al(OH)_4^-(aq)} + 3\ \mathrm{H_2\,(g)}$$

3. Once the reaction has slowed down considerably, gently heat the flask on a hot plate in the hood until all of the aluminum has reacted. **Do not boil the mixture to dryness.**

4. Set up a filtration apparatus using a 60-mm Buchner funnel and a piece of 55-mm filter paper. Filter the warm mixture. The filtrate should be clear.

5. Transfer the filtrate to a clean, dry 250-mL Erlenmeyer flask. Very slowly, add 20 mL of 9 M H_2SO_4 by running the acid down the side of the flask. Swirl the flask periodically as the acid is added. An aluminum hydroxide precipitate may form at this point.

6. Heat the flask slowly to reduce the volume of the solution to approximately 25 mL. Use a boiling stick to ensure the solution will not boil over. In excess acid, the precipitate will dissolve as you heat the solution. Make sure it all dissolves.

$$\mathrm{Al(OH)_3(s)} + 3\ \mathrm{H^+(aq)} \rightarrow \mathrm{Al^{3+}\,(aq)} + 3\ \mathrm{H_2O\,(l)}$$

7. Remove the solution from the heat and allow the flask to cool until it is just warm to the touch. Place the flask in an ice bath for 20 minutes. Alum crystals should form. If crystals do not form, try to scrape the inside of the flask with a glass rod. If crystals still

do not form, slowly heat the flask again to reduce the volume of the solution, again, be careful that you do not heat the reaction to dryness. Record your crystal observations.

$$K^+(aq) + Al^{3+}(aq) + 2\ SO_4^{2-}(aq) + 12\ H_2O(l) \rightarrow KAl(SO_4)_2 \bullet 12\ H_2O\ (s)$$

8. Using a 60-mm Buchner funnel and a piece of 55-mm filter paper, vacuum-filter the crystals. Wash the crystals in the funnel with four 3 mL portions of 50% ethanol in water. Continue suction for a few minutes to dry the crystal. Weigh the crystals to the nearest 0.001 g and record the mass in your notebook. Put the alum crystals in a 125-mL Erlenmeyer flask. Calculate the theoretical and percent yields. To determine the limiting reagent and the percent yield of alum, the overall equation for the alum synthesis that is used is:

$$2\ Al\ (s) + 2\ KOH + 22\ H_2O + 4\ H_2SO_4 \rightarrow 2\ KAl(SO_4)_2 \bullet 12\ H_2O\ (s) + 3\ H_2\ (g)$$

Part 2. Qualitative Analysis of the Composition of Alum: Al^{3+}, SO_4^{2-}, K^+ and H_2O
(You should start performing this part during cooling downtimes of the first part.)

1. Clean two small test tubes. Add one spatula of alum to each of the test tubes and dissolve the crystals in a few milliliters of DI water.

2. To the first test tube, add a few drops of 0.1 M $BaCl_2$. Record your observations. Write the net ionic equation for the reaction observed.

3. To the second test tube, add drop wise (drop by drop!) 0.1 M KOH. Once an initial change occurs, record your observations and write the net ionic equation for this reaction. Then add several more drops of KOH to the solution. Record your observations. Explain the changes. Write the net ionic equation for this reaction observed.

4. To test for the presence of water (hydrates in the alum crystal, $KAl(SO_4)_2 \bullet 12\ H_2O$, add a spatula of alum to a clean, *dry* third test tube. Gently, heat the test tube over a flame. Look for water condensation on the sides of the tube.

Part 3. Flame Test
1. Clean the two small test tubes used earlier. Add one spatula of alum to one of the test tubes and a spatula of potassium chloride to the second test tube. Dissolve the crystals in each of the test tubes in a few milliliters of DI water. Set up a Bunsen burner and clean a piece of nichrome wire in 6 M HNO_3 solution. Rinse the wire with DI water.

2. Dip the nichrome wire into the KCl solution, and then place it in the flame of the Bunsen burner. Record the flame change in color. What is giving rise to the change in color?

3. Clean the nichrome wire in the 6 M HNO_3 solution and rinse it with DI water. Dip the wire in alum solution and place it in flame. Record the flame change in color, if any. How does the color of the alum in the flame compare with that of potassium chloride?

Part 4. Growing Alum Crystals from a Seed Crystal
(This part should take you about 10 minute to set-up

A. Week 1
1. Weigh 3 gram of alum and record the mass to the nearest 0.001 g. Place the alum in a 50-mL Erlenmeyer flask with 20 mL of DI water to the crystals. Swirl the flask.

2. Heat the solution on a hot plate to 50-60°C. Stir the solution until it is clear. If all of the crystals have not dissolved, filter the warm mixture.

3. Tie a piece of thread around a wooden stick. The length of the thread should be long enough so that the end of the thread is 0.5-1 cm below the surface of the liquid when the stick is placed across the opening of the flask. Put a small amount of grease on the portion of the string that will be above the solution. Place the string in the solution, tape the wooden stick to the flask, and cover the flask with parafilm. Store this set up in your drawer until next week. Be careful when opening and closing the locker.

B. Week 2 (and subsequent weeks if desired)
1. Weigh 5 grams of alum and record the mass to the nearest 0.001 g. Place the alum in a 50-mL Erlenmeyer flask and add 35 ml of DI water.

2. Heat the solution on a hot plate to 50-60°C until all of the alum is dissolved. Again, if the solution is not clear, filter the warm mixture.

3. From week 1, there should be a small crystal formed in the solution attached (growing) to the string. This is a seed crystal. Suspend the seed crystal so it is entirely submersed in the alum solution. Tape the wooden stick in a place and cover the flask with parafilm. Again, place the flask in your drawer until next week.

4. Continue this process every week until the crystal is as large as you like. Describe it in your notebook.

VI. Questions

1. Calculate the percentage of potassium, aluminum, oxygen, and sulfur in $KAl(SO_4)_2 \bullet 12\ H_2O$.

2. Given the following unbalanced molecular equation:

$$KAl(SO_4)_2 \bullet 12\ H_2O(aq) + BaCl_2(s) \rightarrow KCl(aq) + AlCl_3(aq) + BaSO_4(s)$$

(a) Balance the reaction and calculate the amount of barium chloride needed to react with a 25 mL of a 0.10 M alum solution.
(b) What is the percent yield of barium sulfate if 1.02 grams is isolated?

3. A 10.0 g sample of alum is heated to drive off all of the water from the solid. Determine the mass of the dehydrated alum.

4. Experiments show that the solubility of alum in 23 mL of 1.2 M KOH plus 10 mL of 9 M H_2SO_4 is about 1.0 g at 1.0 °C and 1.7 g at 6.0 °C. Using your measured solution temperature, estimate the amount of alum left in your chilled solution.

5. What does CRC Handbook of Chemistry and Physics, the Merk Index, or another reference tell you about what it takes to remove the 12 water molecules from alum? Why do we often "forget" to include "$\bullet 12H_2O$" when we write the formula of alum or similar hydrated salts? Would it be better to write the formula as $Al(H_2O)_6K(H_2O)_6(SO_4)_2$? Comment on the other ways the formula could be written, such as $AlH_{24}KO_{20}S_2$ or $AlK(SO_4)_2(H_2O)_{12}$.

6. Clean, dry and weigh an aluminum can. Find the price of aluminum in a newspaper. (It's usually found on the stocks page in the business section.) What is the value price of the aluminum in a beverage can? Then determine how much a local recycling center is paying for aluminum cans. How does the value of aluminum compare to its "worth" in your community? Why are the two prices so different?

VII. Discussion Questions

Summarize the reactions involved in the synthesis of alum. Include the overall equation for the synthesis. What was your percent yield? Does the amount of alum left in the solution account for most of the difference between the maximum grams of alum and your experimental grams of alum? Explain. Describe the crystals that were found at the end of the synthesis. Write the net ionic reactions for the analysis of the aluminum and sulfate ions. What changes were observed for each? Discuss your observations from the flame test. Discuss your observations from when the alum crystals were heated. What method could you use to quantitatively determine the amount of water in alum crystals?

VIII. References

1. J. Postma, J.L. Roberts and J.L. Hollenberg, Chemistry in the Laboratory, *Making Alum from Aluminum,* (2010), 7th Ed. W.H. Freeman and Company, New York, NY

2. Van Koppen, General Chemistry Laboratory Manual, *Recycling Aluminum*, (2003) The McGraw-Hill Company

Experiment 5 – Identification of an Unknown Compound Through Mass Correlations

I. Purpose

Study of hydrates, percent water in a compound and complete the chemical formula of a compound.

II. Introduction

As the world's population increases, the consumption of energy also increases. Scientists are looking for alternative ways to generate energy since fossil fuels are depleting rapidly. Recent efforts have been focused on obtaining methane, the main component of natural gas, from the seafloor sediments. Methane is found thousands of feet below sea level as methane hydrates, which is chemically different than inorganic hydrates. A methane hydrate is a methane molecule trapped in a cage of ice, called a clathrate. It is estimated that 700 quadrillion cubic feet of methane are trapped under the sea, which 1% of this may meet America's energy needs for 170,000 years.

III. Materials

Part 1	Part 2
$MgSO_4 \cdot nH_2O$	$NaHCO_3$
$CuSO_4 \cdot nH_2O$	Na_2CO_3
$MnSO_4 \cdot nH_2O$	$KHCO_3$
$Na_2CO_3 \cdot nH_2O$	K_2CO_3
	6 M HCl

IV. Safety Precautions

Be cautious with the handling of acids and bases, and dispose chemicals as instructed.

V. Experimental Procedure

Part 1. Identification of an Unknown Compound by Water of Hydration Determination

1. Weigh and record the mass of a clean and dry crucible with lid using a top loading balance. Obtain an unknown compound. The unknown compound may be $MgSO_4 \cdot nH_2O$, $CuSO_4 \cdot nH_2O$, $MnSO_4 \cdot nH_2O$, or $Na_2CO_3 \cdot nH_2O$.

2. Weigh and record about 1 g of the unknown compound directly into the crucible.

3. Secure an iron ring on a ring stand, making sure to leave enough space underneath the iron ring for a Bunsen burner.

4. Place a clay triangle on top of the iron ring.

5. Place the crucible containing the sample on the clay triangle. Make sure the crucible lid is placed ajar on the crucible.

6. Place a Bunsen burner underneath the iron ring and gently heat the sample for 5 minutes.

7. Increase the intensity of the flame and heat for an additional 10 minutes. The high intensity flame should cause the bottom of the crucible to glow reddish in color.

8. Allow the crucible to cool for at least 10 minutes.

9. When the crucible is no longer hot, weigh and record the mass of the crucible with lid and sample.

10. Heat the crucible with lid and sample again for an additional 5 minutes.

11. Allow the crucible to cool, and weigh and record the mass.

12. Repeat the heating and cooling process until constant mass is reached.

13. Determine the chemical formula of the unknown compound.

Part 2. Identification of an Unknown Compound by Stoichiometric Mass Correlations

1. Weigh and record the mass of a clean and dry crucible with lid using an analytical balance.

2. Obtain an unknown compound. The unknown compound may be $NaHCO_3$, Na_2CO_3, $KHCO_3$, or K_2CO_3.

3. Weigh and record about 0.4 g of the unknown compound directly into the crucible.

4. Secure an iron ring on a ring stand, but make sure to leave enough space underneath the iron ring for a Bunsen burner.

5. Place a clay triangle on top of the iron ring.

6. Place the crucible containing the sample on the clay triangle. Make sure the crucible lid is placed ajar on the crucible.

7. Place a Bunsen burner underneath the iron ring and gently heat the sample for 5 minutes.

8. Increase the intensity of the flame and heat for an additional 10 minutes. The high intensity flame should cause the bottom of the crucible to glow reddish in color.

9. Allow the crucible to cool for at least 10 minutes.

10. When the crucible is no longer hot, weigh and record the mass of the crucible with lid and sample.

11. Repeat the heating and cooling process until constant mass is reached. (If the sample is sodium bicarbonate, it would decompose into sodium carbonate, water, and carbon dioxide.)

12. Slowly add 6 M HCl, one drop at a time, to the sample inside the crucible.

13. After each drop swirl the mixture until there is no appearance of a chemical reaction before adding another drop.

14. Continue adding drops and swirl until all the solids dissolves, but do not exceed a total of 30 drops.

15. Gently heat the crucible with the lid very slightly ajar for about 10 minutes. It is important that the flame is set at a very low intensity to prevent any HCl excess from boiling out of the crucible.

16. After 10 minutes, turn off the flames and check to see if the sample appears dry.

17. Continue to gently heat if the sample is not dry. If the sample appears dry, set the flame at a high intensity and heat for an additional 10 minutes. The high intensity flame should cause the bottom of the crucible to glow reddish in color.

18. Allow the crucible to cool for at least 10 minutes.

19. When the crucible is no longer hot, weigh and record the mass of the crucible with lid and sample.

20. Repeat the heating and cooling process until constant mass is reached.

21. Using the masses obtained, determine the unknown compound.

VI. Questions

1. In part 2 of the experiment, a balanced equation can be written for the decomposition of sodium bicarbonate upon heating:

$$2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

If 2.0 grams of sodium bicarbonate was added into a crucible and heated with the lid ajar to constant mass, how many grams of product will remain?

VII. Discussion Questions

1. In part 2 of the experiment, what would happen to the data if not enough hydrochloric acid is added to dissolve the solid?

VIII.References

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3. Randall, J., Advanced Chemistry with Vernier, *The Determination of the Percent Water in a Compound*, (2007) 2nd Ed., Vernier Software & Technology, Beaverton, OR

Experiment 6 – Classifying Chemical Reactions Through Copper Reactions

I. Purpose

Experience chemical properties, chemical reactivity and the classification of chemical reactions. Practice predicting reaction (products), balancing equations, and stoichiometry.

II. Introduction

Recycling unwanted materials is vital to the environment, especially when landfills are full. Paper, glass, plastic, and metal can all be recycled. In 2009, the U.S. recovered approximately 63.4% of paper consumed as compared to 38.7% in 1993. The large increase in paper recovery suggests a decrease of trash in landfills within a 16-year time interval. These changes occurred by the contribution of both the consumer and technology from science. As the field of science continues to develop, new methods may improve the rate of recovery from recycling. The following experiment goes through a series of chemical reactions to observe the recycling of copper metal.

Classification of Chemical Reactions

The process of classification often assists with the simplification and solution of problems, or with the understanding of what the group main properties and characteristics are. For example, chemistry can be subdivided into organic, inorganic, analytical, theoretical and physical branches – each branch, or group, with a defined set of characteristics that differentiate them between each other. Likewise, attempts have been made to classify reactions by type, or in other words, by the nature of the reaction. We will use a simple classification scheme based on ideas of precipitation (ion-combination), acid-based (proton transfer), and redox (electron transfer). Reactions can also be classified as combination, decomposition, combustion, single replacement or double replacement.

Combination: The reaction of two substances to for one substance. Note that the formation of hydrates is considered a combination reaction –hydrates have different physical and chemical properties than the anhydride form; therefore, it is a new substance.

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(s)$$

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$$

$$SrCl_2(s) + 6\ H_2O(l) \rightarrow SrCl_2 \bullet 6\ H_2O(s)$$

Decomposition Reactions

This reaction is the reverse of combination, or the breaking down of one substance into two or more substances, and it might be called a decomposition or dissociation reaction.

Any compound heated to a sufficiently high temperature will be decomposed into simpler substances, so this kind of reaction is common.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

$H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)$

$Ca(HCO_3)_2(aq) \rightarrow CaCO_3(s) + H_2O(l) + CO_2(g)$

$Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(g)$

$SrCl_2 \bullet 6\ H_2O(s) \rightarrow SrCl_2(s) + 6\ H_2O(l)$

Single Replacement
In this type of reaction an element in a compound is replaced by another element, which originally is in its elemental (natural) form.

$Cu(s) + 2\ AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\ Ag(s)$

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$

$Br_2(l) + 2\ Kl(aq) \rightarrow 2\ KBr(aq) + I_2(aq)$

Double Replacement
Here, an exchange of both the cation and the anion by two compounds in aqueous solution occurs; therefore, both reactants are soluble compounds. These reactions usually proceed when at least one of the products is a compound insoluble in water forming a precipitate, a liquid, a gas, or a compound that decomposes into a gas, or a slightly ionized compound (weak electrolyte).

$3\ BaCl_2(aq) + 2\ Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + 6\ NaCl(aq)$

$K_2CO_3(aq) + 2\ HNO_3(aq) \rightarrow 2\ KNO_3(aq) + H_2O(l) + CO_2(g)$

$H_2SO_4(aq) + 2\ KOH(aq) \rightarrow K_2SO_4(aq) + 2\ H_2O(g)$

Precipitation Reactions
This reaction can be the result of a combination or double replacement reactions, in which ions combine to form an insoluble neutral compound that precipitates from solution. The solid is called a *precipitate*. To describe the chemical reaction in the process we can use the net ionic equation, derived from the balanced chemical equation.

Balanced Chemical Equation
$NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

Ionic equation (all compounds that are soluble in water are written in their ionic equoas form)
$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$

Ions that repeat in both sides of the equations are called *spectator* ions, as they do not participate in the precipitation reaction. If we cancelled this ins, then we are left with the *net ionic equation*.
$Ag^+(aq) ^+ Cl^-(aq) \rightarrow AgCl(s)$

The net ionic equation concisely summarizes the net results of missing the two solutions: the formation of an insoluble precipitate when a positively charged silver ion is combined with a negatively charged chloride ion. The solid AgCl precipitate can be easily separated from the solution containing the soluble sodium nitrate salt by physical means. If we desire, we could also recover the sodium nitrate by evaporating the water from the solution.

Acid-Base *or Neutralization* Reactions (Proton Transfer Reactions)
An acid is a substance that reacts with water to form hydronium ions (H_3O^+) by transferring a proton to a water molecule.

(a strong acid) $HCl(g) + H_2O \rightarrow H_3O^+(aq) + Cl^-(aq)$
(a weak acid) $CH_3COOH(aq) + H_2O \leftrightarrow H_3O^+(aq) + CH_3COO^-(aq)$

Note the difference in arrows in the equations. This is because HCl is a strong acid, meaning that it completely dissociates in aqueous solution; acetic acid (CH_3COOH) is a weak acid that only partially dissociates into hydronium ion and acetate ion.

A base is a substance that forms hydroxide ions when dissolved in water.

(a strong base) $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$
(a weak base) $NH_3(g) + H_2O \leftrightarrow NH_4^+(aq) + OH^-(aq)$

NaOH is a strong base, completely dissociated in aqueous solution; NH_3 is a weak base, only partially dissociating into ammonium ion hydroxide ion.

Acids react with bases to form salts and (usually) water. Both are neutral compounds, being neither strongly acidic nor strongly basic. So acid-base reactions are also called *neutralization reactions*. Two examples are

(a strong acid + a strong base)
$H_3O^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow 2\ H_2O + Na^+(aq) + Cl^-(aq)$

(the net ionic equation)
$H_3O^+(aq) + OH^-(aq) \rightarrow 2\ H_2O$

(a weak acid + a weak base)
$CH_3COOH(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + CH_3COO^-(aq)$

Note that in these two examples of acid-base reactions a proton is transferred from the acid to the base.

Redox Reactions (Electron Transfer Reactions)
Oxidations-reduction reactions, called redox reactions, are reactions that involve the transfer or exchange of electrons from one atom to another. In some reactions, the transfer is obvious, as in the reaction

$$Mg(s) + 2\ H_3O^+(aq) + 2\ Cl^-(aq) \rightarrow H_2(g) + Mg^{2+}(aq) + 2\ Cl^-(aq) + 2H_2O$$

Here, each magnesium atom is oxidized, giving up two electrons to two hydrogen ions, forming the magnesium ion and hydrogen gas. In this example, because Mg(s) is oxidized causing the atoms of hydrogen to be reduced, it is called reducing agent.

Sometimes the transfer of electrons between atoms is less obvious, as in the reaction

$$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$$

Here the reactants and products are all gases, and no ions are formed. In classifying this reaction as an oxidation-reduction reaction, we use the concept of assigning oxidation numbers (also called oxidation states) to each atom in the compound. A simple set of rules defines the procedure for assigning the oxidation number.

> *Assigning oxidation numbers* – For a simple binary compound (a compound composed of two different elements), we imagine that all of the electrons in the chemical bonds are assigned to the atoms with the greatest affinity for electrons. The ability of an atom to attract electrons to itself is called electronegativity. The most electronegative elements-fluorine, oxygen, and chlorine- are found in the upper right-hand corner of the periodic table.
>
> In sulfur dioxide, SO_2, and sulfur trioxide, SO_3, we imagine that all the electrons in the S-O bonds are assigned to the O atoms, giving each oxygen atom a full valence shell; this formally gives each oxygen atom a net charge of -2. So if oxygen is assigned oxidation number -2, the sulfur in SO_2 must have oxidation number +4 and the oxidation number of S in SO_3, would be +6 since the sum of the oxidation numbers on all the atoms must add up to the net charge on the molecule (zero, in this case). The oxidation number of atoms in their elemental form **is always assigned zero**. This seems reasonable for O_2 because the oxygen atoms are equivalent so that there would be no tendency for one oxygen atom to transfer electrons to its partner in the O_2 molecule.

Once we have assigned oxidation numbers to each element in the chemical reaction, we will see that in this particular reaction the oxidation number of the sulfur atoms increases from +4 to +6 while the oxidation number of oxygen atoms decreases from zero (in O_2) to -2 (in SO_3). From this viewpoint, the change in oxidation number is formally equivalent to transferring electrons from sulfur to oxygen. We say that the sulfur atoms have been oxidized (because their oxidation number increases), while the oxygen atoms in O_2 have been reduced (because the oxidation number of oxygen atoms decreases from zero in O_2 to -2 in SO_3).

We must be careful to note, however, that the oxidation numbers we assign do not necessarily represent the real distribution of electronic charge in the molecule. By assigning the oxidation number according to fixed rules, we have artificially assigned integer changes in oxidation numbers to particular atoms (sulfur and oxygen, in this case), but the changes in the electron density on the sulfur and oxygen atoms may not be as large as implied by the assigned oxidation numbers. Nevertheless, it is reasonable to suppose that the sulfur atom in SO_3 is more positive than the sulfur atom in SO_2 because the added oxygen atom would tend to draw electrons away from the sulfur atom.

Combustion Reactions

This is the reaction of a compound (most commonly an organic compund) with oxygen, usually producing carbon dioxide and water. Some combustion reactions are also combination reactions and vice-versa.

$$2\ CH_4O(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 4\ H_2O(g)$$

$$2\ C_8H_{18}(l) + 25\ O_2(g) \rightarrow 16\ CO_2(g) + 18\ H_2O(g)$$

Balancing Combustion and Double Replacement Reactions

Combustion reactions: Locate the formula with the largest subscript (not subscripts within a polyatomic ion but subscripts that give the number of atoms or ions per formula unit). For the reaction below, 8 is the largest subscript.

$$C_3H_8(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

Then assume, the coefficient 1 in front of the organic compound, in this example propane (C_3H_8); then balance the hydrogen atoms and then the carbons on the products side.

$$1\ C_3H_8(g) + O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)$$

Lastly, balance the oxygen atoms. Now you have ten oxygen atoms on the right and that there are two oxygen atoms in an oxygen molecule on the left. Divide the number of atoms needed (10) by the number per molecule or formula unit (2) to arrive at the correct coefficient (5) on the molecular oxygen on the products side.

$$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)$$

Notice that coefficient of 1 is not written in the final equation but is understood. Also notice the very common strategy of leaving the O_2 (or H_2) until last. The coefficient for

O_2 affects the amount of one element only whereas the other coefficients change the amounts of at least two elements.

Mathematically balancing combustion reactions:

Double replacement reactions: Consider the following reaction.

$$BaCl_2(aq) + Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + NaCl(aq)$$

Start with the ion with the largest subscript. In case of a tie, choose the ion with largest oxidation number. Both Na^+ and Ba^{2+} have subscripts of 3 but Ba^{2+} has a higher oxidation number (+2). Notice that the subscript 4 is part of the phosphate polyatomic ion and is not part of this consideration. Start with the Ba^{2+} and work from the side of the equation by inserting a coefficient of 3.

$$3\ BaCl_2(aq) + Na_3PO_4(aq) \rightarrow 1\ Ba_3(PO_4)_2(s) + NaCl(aq)$$

The coefficient of 3 in front of $BaCl_2$ locked in 6 chlorides so a 6 is now needed in front of NaCl on the right.

$$3\ BaCl_2(aq) + Na_3PO_4(aq) \rightarrow 1\ Ba_3(PO_4)_2(s) + 6\ NaCl(aq)$$

The 6 locks in sodium so the coefficient in front of Na_3PO_4 is 2, which is the number needed (6) divided by the number per formula unit (3).

$$3\ BaCl_2(aq) + 2\ Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + 6\ NaCl(aq)$$

Finally check to see if the phosphates are balanced to be sure you haven't made an error.

A Cycle of Copper Reactions

In the following experiment you will observe different types of reactions, and how are they involved in a sequence of reactions of copper forming a cycle. You will have to carefully observe and record your observations, as color and physical property changes may indicate different reactions. The sequence will begin and end with elemental copper metal; therefore, called a cycle of copper reactions. Because no copper is added or removed between the initial and final steps, and because each reaction goes to completion, you should be able to **quantitatively** recover all of the copper you started with if you are careful. The following set of chemical equations describes the cycle you are about to study, including the actual identity of each reaction product and the stoichiometry of the chemical reactions for each step of the cycle. Here they are, numbered to correspond to the steps shown in the chemical cycle.

$$8\ HNO_3(aq) + 3\ Cu\ (s) + O_2(g) \rightarrow 3\ Cu(NO_3)_2(aq) + 4\ H_2O(l) + 2\ NO_2(g) \qquad (1)$$

$$Cu(NO_3)_2(aq) + 2\ NaOH(aq) \rightarrow Cu(OH)_2(s) + 2\ NaNO_3(aq) \qquad (2)$$

$Cu(OH)_2(s) \rightarrow CuO(s) + H_2O(l)$ (3)

$CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$ (4)

$CuSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Cu(s)$ (5)

As you perform this and any other experiment, watch closely and record what you see. Each observation should be little hook in your mind on which you can hang a more abstract bit of information, such as the chemical formula for the compound you are observing. Chemists look for relationships, trends, or patterns of regularity when they organize their observations of chemical reactions.

III. Materials

10-cm length of 20-gauge copper wire
Steel Wool
Concentrated Nitric Acid (16 M HNO_3)
3 M NaOH
6 M H_2SO_4
30-mesh zinc metal
6 M HCl

IV. Safety Precautions

Be cautious with acids and bases and dispose chemicals as instructed. The reaction that produces NO_2 gas should be done in a fume hood since the chemical is toxic.

V. Experimental Procedure

Reaction 1

1. Obtain about a 10 cm length of 20-gauge copper wire.

2. If the copper wire appears dull, clean it with steel wool. If cleaned with steal wool, rinse the copper wire with deionized water and dry the wire with a paper towel.

3. Weigh and record the mass of the copper wire on an analytical balance.

4. Coil the copper wire into a flat spiral shape and place it in a 250-mL beaker.

5. Place the beaker containing the copper wire in the fume hood. Make sure that the fume hood fan is switched on and fully functional. Lower the fume hood sash to prevent toxic fumes from flowing into the room.

6. Slowly pour 4 mL of concentrated nitric acid into the beaker.

7. Gently swirl the mixture until the copper is completely dissolved.

8. Once the reaction is complete, add deionized water to the beaker until it is half full.

9. Carefully carry the beaker back to the bench to complete the reactions 2 through 4.

Reaction 2

10. While slowly adding 30-mL of 3 M NaOH to the solution in the beaker, use a glass rod and gently stir the mixture.

Reaction 3

11. While heating the mixture just barely to the boiling point with a gentle flame from a Bunsen burner, ensure to stir the mixture with a glass rod.

12. Turn off the Bunsen burner when the mixture begins to boil. The reaction is complete when the color of the mixture changes completely.

13. Continue to stir for an additional minute, then allow the copper (II) oxide to settle to the bottom of the beaker.

14. While the copper (II) oxide is settling, heat approximately 200 mL of deionized water in a different 400-mL beaker.

15. Carefully decant the supernatant liquid from the reaction mixture into a waste container, but make sure not to lose any copper (II) oxide.

16. Add the hot deionized water to the beaker containing copper (II) oxide.

17. Allow the copper (II) oxide to settle to the bottom of the beaker and decant the supernatant liquid a second time. As before, avoid losing any copper (II) oxide in the decanting process.

Reaction 4

18. While stirring with a glass rod, slowly add 15 mL of 6 M H_2SO_4 to the beaker containing copper (II) oxide.

19. Carefully move the beaker back into the fume hood.

Reaction 5

20. In the fume hood, add 2 g of 30-mesh zinc metal into the beaker.

21. Use a glass rod to stir the mixture until the supernatant liquid is colorless.

22. If gases evolve, continue to stir until the gases appear to produce very slowly.

23. Decant the supernatant liquid into a waste container.

24. Add 10 mL of 6 M HCl to the beaker if unreacted zinc is observed. The reaction between HCl and zinc metal produces gases.

25. Once the production of gases is not seen, decant the supernatant liquid into a waste container.

26. Record the mass of an evaporating dish with an analytical balance.

27. Use a scoopula to transfer the copper metal from the beaker to the evaporating dish.

28. Pour 5 mL of deionized water into the evaporating dish and gently swirl to wash the copper.

29. Allow the copper to settle to the bottom of the dish and decant the supernatant liquid into a waste container.

30. Repeat the wash process two more times.

31. Place the evaporating dish on top of a wire gauze and use a gentle flame from a Bunsen burner to dry the copper metal.

32. Allow the evaporating dish to cool down to room temperature.

33. Weigh and record to constant mass the dried copper metal with an analytical balance.

VI. Questions

1. Determine the percentage of copper recovered from the experiment.

VII. Discussion Questions

1. What would happen to the percent recovery if not enough sodium hydroxide were added to step 2 to react with both the unreacted nitric acid and copper(II) ion present at the end of step 1?

VIII. References

1. Murov, S., Experiments in General Chemistry, *Classification of Chemical Reactions*, (2006) 5th Ed., Thomson Brooks/Cole

2. *Paper & Paperboard Recovery*. Website accessed on November 14, 2010: http://paperrecycles.org/stat_pages/recovery_rate.html.

3. Postma, J., Roberts, J.L. and Hollenberg, J.L., Chemistry in the Laboratory, *A Cycle of Copper Reactions*, (2010), 7th Ed. W.H. Freeman and Company, New York, NY

Experiment 7 – Using Titration to Verify the Chemical Formula of Calcium Hydroxide

I. Purpose

Investigate the reaction between metals in group I/II and water. Use acid-base titration to determine the chemical formula of an unknown compound.

II. Introduction

Calcium hydroxide is used in the production and manufacturing of building materials. It is used in the paper industry as well as for the purification of citric acid and dextrin. For the environment, it is used to treat wastewater and biosolids while removing acidic gases to control air pollution. To understand the chemical nature of calcium hydroxide, its chemical formula should first be studied. Calcium hydroxide's chemical formula can be characterized by methods of titration in the following experiment.

III. Materials

Fresh calcium metal turnings
50-mL buret
0.300 M HCl
0.1% thymol blue indicator

IV. Safety Precaution

As dictated by instructor.

V. Experimental Procedure

Part 1. The Calcium and H_2O Reaction

1. Place a piece of weigh paper on an analytical balance and record the mass of the weigh paper.

2. Using forceps, place a piece of calcium metal turnings with an approximate mass between 0.07 and 0.09 g on the weigh paper.

3. Record the mass of both the weigh paper and calcium metal turnings on an analytical balance.

4. Transfer the calcium metal turnings into a 250-mL Erlenmeyer flask.

5. Add approximately 150 mL of deionized water to the Erlenmeyer flask containing the calcium metal turnings and gently swirl the mixture until all of the calcium metal turnings has completely reacted.

6. Add 8 drops of 0.1% thymol blue indicator to the mixture in the Erylenmeyer flask.
*Notes to the instructor: If the calcium metals turnings do not completely react after several minutes of swirling, students may gently heat the mixture to speed up the reaction.

7. Rinse a 50-mL buret with approximately 5 mL of 0.300 M HCl and allow the rinse to flow through the buret into a 150-mL beaker.

8. The 150-mL beaker will serve as a waste container.

9. Repeat the rinse procedure once more.

10. After the second rinse, fill the buret with 0.300 M HCl.

11. Record the initial volume of 0.300 M HCl in the buret.

12. Add one drop at a time the HCl solution from the buret into the 250-mL Erlenmeyer flask containing the calcium, deionized water, and indicator mixture.

13. Make sure to swirl the Erlenmeyer flask while each drop enters the flask. As the end point approaches, the blue color begins to turn yellow. It is important to slowly add one drop at a time, especially near the end point. The end point is reached when the blue color changes to yellow and remains yellow for at least thirty seconds.

14. Record the final volume of 0.300 M HCl in the buret once the end point is achieved.

15. Repeat the entire experiment two more times.

VI. Questions

1. From the data, verify the formula of calcium hydroxide by calculating the moles of calcium used in each titration, the moles of HCl used to reach the end point in each titration, and the mol HCl/mol Ca ratio.

VII. Discussion Questions

1. A buret is usually washed before beginning a titration. If 6.0 M sodium hydroxide will be added to the buret, why is it important to perform a final rinse with 6.0 M sodium hydroxide before filling up the buret with same chemical?

VIII. References

1. McLain, K., *Draft Human and Environmental Risk Assessment of Calcium Hydroxide*. 2005, Washington State Department of Ecology.

2. Postma, J., Roberts, J.L. and Hollenberg, J.L., Chemistry in the Laboratory, *Determination of a Chemical Formula by Titration: The Reaction of Calcium with Water*, (2010), 7th Ed. W.H. Freeman and Company, New York, NY

Experiment 8 – Using Titration to Analyze the Sodium Carbonate Content in an Unknown Sample

I. Purpose

Practice titration to determine the content of a chemical in an unknown compound.

II. Introduction

Titration is typically a method used to determine the concentration of a substance in a solution. Environmentally, the hardness of water can be understood by titration where an amount of metal in a water sample binds with the conjugate base form of ethylenediaminetetraacetic acid, EDTA.

Reactions taking place during the titration are described in (1) and (2), where you can see that for every Ca^{2+} or Mg^{2+}, each binds to one $EDTA^{4-}$.

$$Ca^{2+} + EDTA^{4-} \rightarrow CaEDTA^{2-} \quad (1)$$

$$Mg^{2+} + EDTA^{4-} \rightarrow MgEDTA^{2-} \quad (2)$$

The usefulness of titration can also be applied to determine the amount of sodium carbonate in an unknown sample mixture. Sodium carbonate is a chemical in high demand for the glass industry while it also plays a major role in the detergent and paper industry.

III. Materials

Anhydrous Na_2CO_3 (stored in a dessicator)
6 M HCl
50-mL Buret
phenolphthalein
bromcresol green
Unknown Sample

IV. Safety Precautions

Be cautious with acids and bases used in the experiment. As directed by instructor.

V. Experimental Procedure

Part 1. Preparation of 0.15 M HCl

1. Calculate the amount of 6 M HCl required to dilute it to 0.15 M with a total volume of 500 mL.

2. Pour this amount of 6 M HCl into a 500-mL Erlenmeyer flask.

3. Fill the Erlenmeyer flask with deionized water to the mark on the neck of the flask.

4. Cover the opening of the flask with a rubber stopper or parafilm and mix the liquids together well.

5. Rinse a 50-mL buret with approximately 5 mL of HCl solution from the 500-mL Erlenmeyer flask and allow the rinse to flow through the buret into a 150-mL beaker. The 150-mL beaker will serve as a waste container.

6. Repeat the rinse procedure once more.

7. After the second rinse, fill the buret with HCl solution. Record the initial volume of the HCl solution in the buret.

Part 2. Preparation of Na_2CO_3

1. Tare a 250-mL Erylenmeyer flask on an analytical balance.

2. Carefully weigh and record approximately 0.2-g of anhydrous Na_2CO_3 directly into the 250-mL Erlenmeyer flask on the analytical balance.

3. Remove the flask from the balance and add 50-mL of deionized water.

4. Dissolve the Na_2CO_3 by swirling.

5. After Na_2CO_3 is completely dissolved, add 3 drops of phenolphthalein and swirl to mix.

Part 3. Standardization of the HCl Solution

1. Add one drop at a time the HCl solution from the buret into the 250-mL Erlenmeyer flask containing the dissolved Na_2CO_3 and phenolphthalein mixture. Make sure to swirl the Erlenmeyer flask while each drop enters the flask. It is recommended to place a white sheet of paper underneath the flask as this will aid in the observation of color changes. The first equivalence point is reached when the pink color turns almost colorless.

2. Once the first equivalence is reached, add 3 drops of bromocresol green to the flask and continue to titrate until the blue color changes to green.

3. Place the flask containing the green solution over a wire gauze.

4. Use a Bunsen burner to heat the solution.

5. Upon boiling, turn the Bunsen burner off and allow the flask to cool down to room temperature. *The flask may be placed in an ice bath to cool down quicker; however, be advised that the rapid change in temperature may cause the flask to break.

6. Continue to titrate until the color changes to yellow-green. This color represents the end point.

7. Record the final volume of the HCl solution from the buret and calculate the total volume of HCl used in the titration.

8. Calculate the molarity of the HCl solution.

9. Repeat the standardization procedure two more times by weighing two more samples of anhydrous Na_2CO_3.

10. Average the molarity of HCl from the three trials. The average deviation from the average molarity should be less than 0.2% otherwise additional trials may be needed.

Part 4. Analysis of Sodium Carbonate in an Unknown Sample

1. Tare a 250-mL Erylenmeyer flask on an analytical balance.

2. Carefully weigh and record approximately 0.5 g of an unknown solid sample directly into the 250-mL Erlenmeyer flask on the analytical balance.

3. Remove the flask from the balance and add 50 mL of deionized water. Dissolve the unknown solid by swirling.

4. After the unknown is completely dissolved, add 3 drops of phenolphthalein and swirl to mix.

5. Perform the same titration procedures as written for the standardization of HCl.

VI. Questions

1. Use the average molarity of HCl to calculate the mass percent of sodium carbonate in the unknown sample.

VII. Discussion Questions

1. Why is the solution boiled just before reaching the second equivalence point?

VIII. References

1. de la Camp, U. and Seely, O., *Determination of the Carbonate Content of a Soda-Ash Sample*. Website accessed on November 14, 2010: http://www.csudh.edu/oliver/che230/labmanual/carbnate.htm

2. *Sodium Carbonate*. Website accessed on November 14, 2010: http://www.inchem.org/documents/sids/sids/Naco.pdf.

Unit 3 – Energy, its Sources and the Environment

Energy is central to sustainable development and poverty reduction efforts. It affects all aspects of development – social, economic, and environmental – including livelihoods, access to water, agricultural productivity, health, population levels, education, and gender-related issues. None of the Millennium Development Goals (MDGs), as established by the United nations (UN), can be met without major improvement in the quality and quantity of energy services in developing countries.

Fossil fuels

Fossil fuels have been a widely used source of energy every since the Industrial Revolution just before the dawn of the 20th century. Fossil fuels are relatively easy to use to generate energy because they only require a simple direct combustion. However, a problem with fossil fuels is their environmental impact. Not only does their excavation from the ground significantly alter the environment, but their combustion leads to a great deal of air pollution. Main types of fossil fuels are petroleum, natural gas and coal.

Advantages

1. Depending on the fuel, as of today, there is good availability
2. A simple combustion process can directly heat or generate electricity
3. They are inexpensive, when compared to other sources of energy
4. They are easily distributed

Disadvantages

1. Probable contributor to global warming
2. Depending on the fuels, some of the availability is questionable, and a major price swings based on politics of oil regions
3. Cause of acid rain

Hydroelectric

It is the production of electrical power through the use of the gravitational force of falling or flowing water. Man has utilized this form of power for years, and it is the most widely used form of renewable energy. Once a hydroelectric complex is constructed, the project produces no direct waste, and has a considerably lower output level of the CO_2 than fossil fuel powered energy plants. Much of the growth of early colonial American industry can be attributed to hydropower – basically because fuel such as coal and wood were not readily available to inland cities, American settlers were forced to turn to other alternatives. Falling water was ideal for powering sawmills and gristmills.

As coal became a better-developed source of fuel, however, the importance of hydropower decreased. Waterpower industry came back on the 20th century, when the development of an electric generator helped increase hydropower's importance. In the mid-20th century, as Americans began to move out of the cities and into "suburbia," the demand for electricity increased, as did the role of hydroelectricity. Hydroelectric power plants have been built near large cities to supplement power production.

Advantages

1. It is an inexhaustible fuel source
2. It has a minimal environmental impact
3. It is a viable source of energy, given that it can produce useful levels of energy
4. Can be used throughout the world

Disadvantages

1. Smaller models depend on availability of fast flowing streams or rivers
2. Run-of-the-river plants can impact the mobility of fish and other river life

Biomass

It is one of the oldest and most well established energy sources in the world. Biomass is simply the conversion of stored energy in plants into energy that we can use. Thus, burning wood is a method of producing biomass energy. If the burning of wood were the only biomass application, then that field of study would not be nearly as interesting as it is. In fact, biomass has many possibilities as a renewable energy source. High energy crops grown specifically to be used as fuel are being developed, and scientists are beginning to consider agricultural and animal waste products as possible fuel sources.

Most common sources of biomass materials are:

Wood: trees, shrubs, wood residue, sawdust, bark, etc. Basically, materials from forest clearings and mills

Waste: municipal solid waste, paper, food, yard wastes, plastics, wood, tires, livestock waste, processed waste, and sewage

Crops: starch crops – corn, wheat and barley,– sugar crops –cane and beet,– forage crops –grasses, alfalfa, and clover,– oilseed crops –soybean, sunflower, safflower–.

Aquatic Plants: algae, waterweed, water hyacinth, reed and rushes

Advantages

1. Theoretically it is an inexhaustible fuel source that is available throughout the world
2. When direct combustion of plant mass is not used to generate energy (i.e. fermentation, pyrolysis, etc. are used instead), there is minimal environmental impact
3. Alcohols and other fuels produced by biomass are efficient, viable, and have a relatively clean-burning

Disadvantages

1. Could contribute a great deal to global warming and particulate pollution if directly burned
2. Still an expensive source, both in terms of producing the biomass and converting it to alcohols
3. On a small scale there is most likely a net loss of energy, because energy must be put in to grow the plant mass

Solar

The name "solar power" is actually a little misleading. In fact, most of the energy known to man is derived in some way from the sun. When we burn wood or other fuels, we are releasing the stored energy of the sun. There would be no life on earth without the sun, which provides energy needed for the growth of plants, and indirectly, the existence of all animal life. The solar energy scientists are interested in, is the energy obtained through the use of solar panels. Although the field of research dealing with this type of solar power is an emergent one, bear in mind that man has known about the energy of the sun for thousands of years.

Advantages

1. It is an exhaustible fuel source
2. Does not produce pollution
3. It is often an excellent supplement to other renewable sources
4. It s very versatile, as it can be used for powering items as diverse as solar cars and satellites

Disadvantages

1. It is a very diffuse source, which implies low energy production and therefore large numbers of solar panels (and thus large land areas) are required to produce useful amounts of heat or electricity (*Though lots of new research on efficiency is been undertaken right now)
2. Only areas of the world with lots of sunlight are suitable for solar power generation

Wind

Mankind has made use of wind power since ancient times. Wind has powered boats and other sea craft for years. Furthermore, the use of windmills to provide power for the accomplishment of agricultural tasks has contributed to the growth of civilization.

Types of wind power plants:

Remote – Remote systems are small, relatively cheap sources of energy. They are best suited for rural environments because they can be left unattended for long periods of time. They can operate under harsh conditions, and thus have potential for powering extremely remote regions of the world.

Hybrid – The very nature of wind-powered generators makes them ideal to be used in conjunction with other sources of energy. Wind and solar generators have been extremely successful as supplements to one another. The presence of the wind generator means that the other energy source does not have to be producing as much energy all the time.

Grid Connected – Grid connected systems are already widely use in areas that are already hooked up to a utility grid. Their main use is as a supplement to other forms of energy. This is important because average wind turbines only generate electricity about 25% of the time.

Utilities – Because individual wind-powered systems by themselves do not produce a great deal of energy, so called "wind farms" have been developed.

These collections of many wind generators gathered in one place provide a source of a relatively high-energy output.

Geothermal

The center of the earth can reach temperatures of up to 12000 degrees Fahrenheit. Geothermal systems tap that heat for the production of energy. Explain better! Convection (heat) currents travel quite near the surface in some parts of the world. For instance, Iceland's capital city of Reykjavik is located near hot springs that power virtually the entire city.

Advantages

1. Theoretically it is an inexhaustible energy source
2. Does not no produce pollution
3. It is often an excellent supplement to other renewable sources
4. Does not require structures such as solar panels or windmills to collect the energy. It can be directly used to heat or produce electricity, making it very economic

Disadvantages

1. It is not available in many locations
2. Does not produce that much power per vent

Fission

Fission is already an established method of energy production. In this process, an atom’s nucleus is split apart liberating an enormous amount of energy. Of this energy is let out slowly, it can be harnessed to produce electricity. Countries around the world possess fission reactors capable of powering whole cities. However, disturbing accounts of harm to the environment and dangerous nuclear waste byproducts shadows the benefits in energy production. Chernobyl, Hiroshima, and Nagasaki are frightening precedents in the field of fission development and are not to be ignored.

Advantages

1. Relatively little fuel is needed and the fuel is relatively inexpensive and available in trace amounts around the world
2. Fission is not believed to contribute to global warming or other pollution effects associated with fossil fuel combustion

Disadvantages

1. Possibility of nuclear meltdown from uncontrolled reaction, leads to nuclear fallout with potentially harmful effects on civilians
2. Waste products can be used to manufacture weapons
3. High initial cost because fission plants require containment safeguards

Fusion

For years now people have been turning to fusion as the "energy of the future." Not only does fusion appear to be an extremely effective source of energy production, it is environmentally friendly and virtually inexhaustible. Fusion occurs when two smaller nuclei are joined together to form a larger one. During this process a large amount of energy is liberated.

Advantages

1. The fuel for fusion reactions are readily available. Deuterium and Tritium are virtually inexhaustible.
2. Unlike the burning of coal or other fossil fuels, fusion does not emit harmful toxins into the atmosphere. Unlike combustion, fusion produces only helium, a gas that is already in abundance in the atmosphere and will not contribute to global warming
3. A major concern with the use of fission power is the issue of nuclear waste, a dangerous material that can both directly injure people and be manufactured into weapons. Fusion has no such problems with dangerous by-products
4. Its supply of fuel can last longer than the sun.

Disadvantages

1. Scientists have not yet been able to contain a fusion reaction long enough for there to be a net energy gain.
2. Many countries are phasing out fusion research because of the failure to reach a breakthrough

References

1. Website accessed, November 6, 2010: Oracle ThinkQuest Education Foundation

Experiment 9 – Thermochemistry

I. Purpose

Construct a simple calorimeter and measure specific heat capacity for a variety of metas. Study Hess's Law, and compare the change in enthalpy of a pure solution and a mixture in a neutralization reaction.

II. Introduction

Thermochemistry deals with the thermal energy changes that accompany chemical reactions. These energy changes are usually called *heats of reaction*. When the reaction is carried out at constant pressure, the heat of reaction is called the *enthalpy* change, ΔH. The word *enthalpy* comes from the Greek root word *thalpein* meaning "to heat". A reaction that produces heat is said to be *exothermic*. In an exothermic reaction, the enthalpy of the products is less than the enthalpy of the reactants as $\Delta H = H_{\text{products}} -- H_{\text{rectants,}}$ we see then that ΔH will be negative for an exothermic reaction. Conversely, if the reaction will gain (use up) energy, the enthalpy change for the reaction will be positive, and we say the reaction is endothermic.

Although the enthalpy change for a chemical reaction tells us whether heat will be released or absorbed, this change cannot be used to determine whether a reaction can proceed spontaneously. There are examples of spontaneous reactions that have either negative or positive enthalpy changes. For example, both solid NaOH and KNO_3 dissolve spontaneously in water, but with NaOH the solution warms (ΔH is negative) and with KNO_3 the solution cools (ΔH is positive). As you study thermodynamics further, you will be introduced to entropy and free energy functions, which can be used to determine whether a particular reaction is possible.

Enthalpy changes may be classified into more specific categories: (1) The *heat of formation* is the amount of heat involved in the formation of one mole of the substance directly from its constituent elements; (2) the *heat of combustion* is the amount of heat produced when a mole of a combustible substance reacts with excess oxygen; (3) the *heat of solution* of a substance is thermal energy change that accompanies the dissolving of a substance in a solvent; (4) the *heats of vaporization, fusion, and sublimation* are related to the thermal energy changes that accompany changes in state; (5) the *heat of neutralization* is the enthalpy change associated with the reaction of an acid and a base.

Heat (*q*) – Heat is a form of energy, sometimes called thermal energy that can be transferred spontaneously from an object at a high temperature to an object at a lower temperature. If the two objects are in contact, after enough time they will both reach the same temperature.

Heat flow can be measured in a device called a calorimeter. A calorimeter is simply a container with insulating walls, made so that essentially no heat is exchanged between the contents of the calorimeter and the surroundings (external world). Within the calorimeter chemical reactions may occur or heat may pass from one part of the contents to another, but no heat flows into or out of the calorimeter from or to the surroundings.

Specific Heat (*s*) – When heat flows into a substance, the temperature of that substance will increase. The quantity of heat required to cause a temperature change ΔT of any substance is proportional to the mass *m* of the substance and the temperature change, as shown in eq. 1. The proportionality constant is called the specific heat, *s,* of that substance.

$$q = s \times m \times \Delta T \qquad (1)$$

The specific heat can be considered to be the amount of heat required to raise the temperature of one gram of the substance by 1°C. Amounts of heat are measured in either joules or calories. To raise the temperature of 1 g of water by 1°C, 4.18 joules of heat must be added to the water. The specific heat of water is 1 calorie/g °C. Since 4.18 joules equals 1 calorie, we can also say that the specific heat of water is 1 calorie/g °C. Usually heat flow into or out of a substance is determined by the effect that that flow has on a known amount of water. Because water plays such an important role in these measurements, the calorie was defined to be equal to the specific heat of water.

The specific heat of a metal can readily be measured in a calorimeter. A weighed amount of metal is heated to some known temperature and is then quickly poured into a calorimeter that contains a known amount of water at a known temperature. Heat flows from the metal to the water, and the two equilibrate at some temperatures of the metal and the water. Assuming that no heat is lost from the calorimeter to the surroundings, and that a negligible amount of heat is absorbed by the calorimeter walls, the amount of heat that flows from the metal as it cools is equal to the amount of heat absorbed by the water. In thermodynamic terms, the heat flow for the metal is equal in magnitude but opposite in direction, and hence in sign, to that for the water. Therefore, for the heat flow *q* we find that:

$$q_{\mathrm{H2O}} = -q_{\mathrm{metal}} \qquad (2)$$

And we can express the relationship in the heat flow between water and the metal M in terms of equation 1 as:

$$q_{\mathrm{H2O}} = \mathrm{s}_{\mathrm{H2O}} \times \mathrm{m}_{\mathrm{H2O}} \times \Delta \mathrm{T}_{\mathrm{H2O}} = -\, \mathrm{s}_{\mathrm{M}} \times \mathrm{m}_{\mathrm{M}} \times \Delta \mathrm{T} \qquad (3)$$

In this experiment we will use the known masses of water and metal and their initial and final temperatures to find the positive specific heat of the unknown metal by equation 3, given the specific heat of water is known.

We can also relate specific heat of a metal to its molar mass *(MM)* using a relationship that Dulong and Petit discovered many years ago. They found that about 25 joules were required to raise the temperature of one mole of many metals by 1˚C. This relation, shown in equation 4, is known as the Law of Dulong and Petit:

$$MM = 25 / s_M (\text{J/g °C}) \qquad (4)$$

The Law of Dulong and Petit was one of the few rules available to early chemists on their studies of molar masses.

Heat of Reaction – When a chemical reaction occurs in water solution, the situation is similar to that presented above, when a hot metal sample is put into water. With such a reaction there is an exchange of heat between the reaction mixture and the solvent, water. As in the specific heat experiment, the heat flow for the reaction mixture is equal in magnitude but opposite in sign to that for the water. The heat flow associated with the reaction mixture is also equal to the enthalpy change, ΔH, for the reaction, so we can say that:

$$q_{\text{reaction}} = \Delta H_{reaction} = -q_{\text{H2O}} \qquad (5)$$

By measuring the mass of the water used as solvent, and by observing the temperature change that the water undergoes, we can find q_{H2O} using equation 1 and ΔH using equation 5. If the temperature of the water goes up, the reaction mixture has given *off* heat, so the reaction is exothermic; q_{H2O} is positive and ΔH is negative. If the temperature of the water goes down, the reaction mixture has *absorbed* heat from the water and reaction is endothermic. In this case q_{H2O} is negative and ΔH is positive. Both exothermic and endothermic reactions are observed.

One of the simplest "reactions" that can be studied in solution occurs when a solid is dissolved in water. As an example of such is the solution of NaOH in water:

$$\text{NaOH(s)} \rightarrow \text{Na}^+\text{(aq)} + \text{OH}^-\text{(aq)}; \quad \Delta H = \Delta H_{\text{solution}} \qquad (6)$$

When this reaction occurs, the temperature of the solution becomes much higher than that of the NaOH and water that were used. If we dissolve a known amount of NaOH in a measured amount of water in a calorimeter, and measure the temperature change that occurs, we can use equation 1 to find q_{H2O} for the reaction and use equation 5 to obtain ΔH. Noting that ΔH is directly proportional to the amount of NaOH used, we can easily calculate $\Delta H_{\text{solution}}$ for either a gram or a mole of NaOH.

In the same fashion, we can discuss enthalpy of neutralization. Chemical reactions often occur when solutions are mixed. A precipitate may form, in a reaction opposite in direction to that in equation 6. A very common reaction is that of neutralization, which occurs when an acidic solution is mixed with one that is basic. Usually when mixing a strong acid and a strong base, the heat effect is quite large as the result of the reaction between H^+ ions with OH^- in the solution:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O \quad \Delta H = \Delta H_{\text{neutralization}} \qquad (7)$$

In today's experiment, you will measure enthalpy changes for the following three reactions:

$$H_2SO_4\ (10M) + NaOH\ (1M) \rightarrow NaHSO_4\ (0.5M) + H_2O \qquad (8)$$

$$H_2SO_4\ (10\ M) + \text{solvent} \rightarrow H_2SO_4\ (1\ M) \qquad (9)$$

$$H_2SO_4\ (1\ M) + NaOH\ (1\ M) \rightarrow NaHSO_4\ (0.5\ M) + H_2O \qquad (10)$$

In these reactions, the numbers in parentheses specify the molar concentrations of the reactants and products. Water is both the solvent and a reaction product. In order to distinguish these two roles, we write H_2O when we mean a reaction product and write solvent when water is used to dissolve the reactants and serve as the reaction medium. You will also see how the measurement of the enthalpy change of reaction (10) leads to an approximate estimate of the enthalpy of dissociation of water into hydronium ions and hydroxide ions.

Reaction (8) and (10) can be regarded as neutralization reactions. Reaction (9) could be called a solution (or dilution) reaction, and we will call the enthalpy change for this process the heat of solution. Note also that if we add reactions (9) and (10), we get reaction (8). Thus, reaction (8) and the sum of reactions (9) and (10) represent two different pathways by which we can get from the same initial state to the same final state; therefore, we can make use of Hess's Law.

Hess's Law – Germain Henri Hess (1802-1850) discovered the principle we now call Hess's law, which says that the enthalpy change of a reaction is the same whether the reaction is carried out directly or in a number of steps. This means that the enthalpy changes for chemical reactions are additive, just like the chemical reactions themselves. Therefore, if reaction (8) = reaction (9) + reaction (10), then

$$\Delta H_{\text{rxn 8}} = \Delta H_{\text{rxn 9}} + \Delta H_{\text{rxn 10}} \qquad (11)$$

The data you obtain for the enthalpy changes for reactions (8), (9) and (10) will be used to test the relation shown in equation (11), which is a mathematical statement of Hess's law. (*Reaction (9), the heat of the solution of H_2SO_4, was described by Hess in his first thermochemical publication in 1840!)

As discussed earlier, enthalpy changes are usually measured in a calorimeter in order to isolate thermally the reaction under study.

Heat Capacity (C) – The amount of energy (heat) required to raise the temperature of 1 g of substance by 1 °C is called the *heat capacity* (C) of that metal. The heat capacity can be reported in units of J / g °C. Heat capacities are generally measured experimentally. If we know the volume (V) and density (*d*) of a substance (the product V × *d* is the mass), its heat capacity (C), and the temperature change (ΔT) we can then calculate the enthalpy change of the substance according to the equation (12).

$$\Delta H = V \times d \times C_p \times \Delta \mathrm{T} \qquad (12)$$

Dimensional analysis of equation (12) shows that it gives the number of joules released or absorbed:

$$\mathrm{J} = (\mathrm{mL}) \times (\mathrm{g/mL}) \times (\mathrm{J} / \mathrm{g}\ °\mathrm{C}) \times (°\mathrm{C})$$

Note: In principle, a correction should be made for the heat absorbed or evolved by the calorimeter itself and for the energy lost or gained from the surroundings. In the Styrofoam-cup calorimeter, portions of the cups and the thermometer are in contact with the solutions contained in the calorimeter. Through this contact, energy can leak into or out of the solution in the calorimeter, depending on whether the temperature of the solution is lower than or higher than the temperature of the surroundings. Because the energy losses or gains are small (typically about 3%) and are about the same order of magnitude of the temperature increase, we will omit these corrections so that you can focus your attention on the main purpose-finding the enthalpy changes of the reactant solutions that are mixed in the calorimeter. So, in effect, we will treat the Styrofoam cups and thermometer as if they were perfect insulators, allowing no energy flow into or out of the solutions contained in the calorimeter.

III. Materials

Calorimeter (Styrofoam cups or the calorimeters we have)
Unknown pieces of metal
100 mL 1 M NaOH
50 mL 1 M H_2SO_4
15 mL 10 M H_2SO_4

IV. Safety

Handle H_2SO_4 and NaOH with care as they are corrosive and can cause skin and eye burns.

V. Experimental Procedure

Part 1. Specific Heat

1. From the stockroom obtain a calorimeter, a digital thermometer, a sample of the metal in a large test tube with a stopper, and a sample of unknown solid. The calorimeter consists of two-nested expanded polystyrene coffee cups fitted with a Styrofoam cover.

There are two holes in the cover for a thermometer and a glass-stirring rod with a loop bend on one end.

2. Fill a 400-mL beaker two thirds full of water and begin heating it to boiling. While he water is heating, weigh your sample of unknown metal in the large test tube with the stopper to the nearest 0.01 g on a top-loading balance.

3. Pour the metal into a dry container and weigh the empty test tube and stopper.

4. Place the metal back into the test tube and put the tube with the stopper (loosely) into the hot water in the beaker. The water level in the beaker should be high enough so that the top of the metal is below the water surface. Continue heating the metal in the water for at least 10 minutes after the water begins to boil to ensure that the metal reaches the temperature of the boiling water. Add water as necessary to maintain the water level.

5. While the water is boiling, weigh the calorimeter to the nearest 0.01 g, place 40 mL of water in the calorimeter and weigh again. Prepare the calorimeter by covering it, and inserting the stirrer and the thermometer through the calorimeter lit into the water in the calorimeter. The thermometer reader (or bulb) should be completely under the water.

6. Measure the temperature of the water in the calorimeter to the nearest 0.1˚C, or to 0.01 ˚C if possible.

7. In a fast but careful fashion, take the test tube out of the beaker of boiling water, remove the stopper, and pour the metal into the calorimeter. Be careful that no water adhering to the outside of the test tube runs into the calorimeter when you are pouring the metal.

8. Replace the calorimeter cover and start stirring the water as best as you can with the glass stirrer. Record to 0.1 (or 0.01) ˚C the maximum temperature reached by the water.

9. Repeat the experiment, using about 50 mL of water in the calorimeter.

Note: Be sure to dry your metal before reusing it; this can be done by heating the metal briefly in the test tube in boiling water and then pouring the metal onto a paper towel to drain. You can dry the hot test tube with a little compressed air.

Part 2. Measuring Heats of Reaction

We will carry out three experiments (each in duplicate) to measure the enthalpy changes for reactions (8), (9) and (10). In these experiments, we mix aqueous solutions of the reactants, so water is the reaction medium, and any temperature changes result from the chemical reactions that take place in solution.

Employing the principle of the first law of thermodynamics (conservation of energy), we will write an equation stating that the sum of the enthalpy changes of the solutions mixed in the calorimeter and the enthalpy change of the chemical reaction is zero. Therefore,

$$\Delta H_C + \Delta H_R + \Delta H_{\text{reaction}} = 0 \qquad (13)$$

Here C represents the solution in the calorimeter, and R the added reactant solution.

Substituting into equation (13) the definition of the enthalpy change given in equation (12), we can rewrite equation (13) as

$$V_c \times d \times C_p \times \Delta T_c + V_R \times d \times C_P \times \Delta T_R + \Delta H_{\text{reaction}} = 0 \qquad (14)$$

In these experiments, we measure V_C (the volume of reagent in the calorimeter), ΔT_C (the temperature change of the solution in the calorimeter), V_R (the volume added of reactant solution), and ΔT_R (the temperature change of the added reactant solution). We will take the product of the density and heat capacity of the solutions, $d \times C_P$, to be 4.10 J / mL °C, nearly the same product for pure water. Substituting these values into Equation (14), we can solve for the enthalpy change for the chemical reaction. Knowing the number of moles of reactants mixed together, we can express the enthalpy change per mole of reaction, $\Delta H_{\text{reaction}}$, in kJ/mol.

A. Heat of Solution and Neutralization of 10 M H_2SO_4 and 1 M NaOH

1. Place 50.0 mL of 1 M NaOH and 45.0 mL of DI water in calorimeter 1. Now your calorimeter system should look like Figure 1.

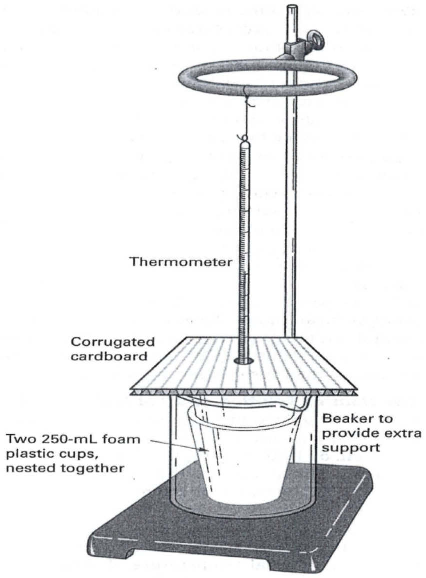

Figure 9.1. Simple calorimeter constructed with Styrofoam cups.

2. Measure out exactly 5.00 mL of 10 M H_2SO_4 in a 10-mL graduated cylinder. Measure the temperature of the 10 M H_2SO_4 and record the reading. Remove the thermometer and readjust the volume to exactly 5.00 mL, if necessary using a dropper.

3. Rinse and dry the thermometer and insert it into calorimeter 1. Stir the solution gently; read and record the temperature.

4. Add the 5.00 mL of 10 M H_2SO_4 and stir for 30 s or until temperature reading is steady or only slowly decreasing. Record the temperature to the nearest 0.01 °C.

5. Neutralize the solution with 5 g $NaHCO_3$ and discard the solution down the drain. Rinse and dry the calorimeter cup and carry out a set of duplicate measurements if times allow.

B. Heat of Solution of 10 M H_2SO_4

1. Measure 90.0 mL of DI water in a graduated cylinder and put in into calorimeter 1.

2. Measure out 10.0 mL of 10 M H_2SO_4 in a 10-mL graduated cylinder. Measure and record the temperature of the 10 M H_2SO_4. Remove the thermometer and readjust the volume to exactly 10.0 mL.

3. Rinse and dry the thermometer and insert it in calorimeter 1, and gently stir. Read and record the initial temperature of the water.

4. Pour the 10 M H_2SO_4 and continue to stir for 30 s or until the temperature reading is steady. Record the final temperature of the solution.

5. Neutralize the solution with 10 g of $NaHCO_3$ and discard the solution down the drain. Rinse and dry the calorimeter cup and carry out a set of duplicate measurements if times allow.

C. Heat of Neutralization of 1 M H_2SO_4 and 1 M NaOH

1. Measure 50.0 mL of 1 M NaOH in calorimeter 1 and 50.0 mL of 1 M H_2SO_4 in a second calorimeter 2.

2. Put the thermometer in calorimeter 1 and stir gently until the temperature reading is steady, then read and record the initial temperature of the NaOH solution.

3. Remove the thermometer, rinse and dry it, and put it in calorimeter 2. Stir the solution gently; when the temperature reading is steady, read and record the temperature of the H_2SO_4 solution.

4. Pour the H_2SO_4 solution in calorimeter 2 quickly and completely into calorimeter 1. Stir for 30 s or until the temperature reading is steady and record the final temperature.

5. Neutralize the solution with 5 g of $NaHCO_3$ and discard the solution down the drain. Rinse and dry the calorimeter cups and carry out a set of duplicate measurements if times allow.

VI. Questions

For part 1:

1. Calculate the specific heat of the unknown metal.

2. Identify the unknown metal using the table of specific heats in your textbook.

For each of the reactions in part 2:

1. Determine the temperature change for the solution in calorimeter 1 (ΔT_c) and of the added reactant solution (ΔT_R) by subtracting the initial temperature from the final temperature ($\Delta T = T_{final} - T_{inital}$).

2. Calculate the heats of reaction for each reaction by rearranging equation (14) to solve for $\Delta H_{reaction}$. Assume that the product of density (*d*) × heat capacity (C) for each solution is 4.10 J / mL °C.

3. Calculate the enthalpy of reaction per mole for each reaction by diving each $\Delta H_{reaction}$ by the number of moles of H_2SO_4 added in reaction. Express the final calculated enthalpy changes in units of kJ/mol. Note: The final average final average calculated enthalpy changes should be rounded to the number of significant figures according to the temperature measurements (2 or 3).

VII. Discussion Questions

What is the importance of understanding the specific heat of a metal, especially in impoverished countries? Will the presence of isotopes affect he heat capacity of a metal? Explain. Does stirring the water in your calorimeter change the temperature?

VIII. References

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Experiment 10 – Spectrophotometry of Phosphate and Cobalt Solutions

I. Purpose

Understand the electromagnetic spectrum and its relationship with matter. Practice preparation of standard solution, dilution and concentration. Build an absorption spectrum, apply Beer's law and plot a calibration curve to identify unknown concentrations.

II. Introduction

During this laboratory experience you will work with a partner. Two different experiments will be performed: the spectroscopy of phosphates and the spectroscopy of cobalt (II) ion. In part I, the analyte in consideration is colorless, therefore does not absorb light but it can be tinted using another chemical; in part II, the cobalt (II) ion does absorb light and we know this by looking at the distinctive color of the solution. Both students should switch roles between part 1 and part 2.

Spectroscopy – Chemists use spectroscopy for the analysis of composition, structure and concentration. Studies of spectroscopy also led to the development of our current theory of the electronic structure of atoms and molecules. The observation that energetically excited atoms emit light of specific wavelengths that are unique for each element let Bohr, Schrodinger, and others to formulate our present day quantum theory of electronic orbitals.

Organic chemists routinely use infrared and nuclear magnetic resonance spectroscopy to provide important puzzle pieces for the determination of the structure of compounds. Analytical chemists utilize the relationship between the amount of light of a specific wavelength absorbed and the concentration of the absorbing species using Beer's law.

The visible and ultraviolet regions are only a small portion of the electromagnetic spectrum, but they encompass the region of energy necessary to promote electrons from ground state orbitals to higher energy orbitals. Considering the wave characteristics of light, its energy is directly proportional to its frequency, $E = h\,\nu$. Since the speed of light is the product of its wavelength and frequency, $c = \nu\,\lambda$, the energy is inversely proportional to the wavelength, $E = h\,c/\lambda$. It is important to recognize that the longer the wavelength, the lower the energy. Gamma rays, x-rays and ultraviolet radiation have shorter wavelengths and higher energy than visible light. Infrared, radio and TV have longer wavelengths and lower energy than visible.

Scientist, and us, will be using an instrument called a spectrophotometer (or spectrometer) to quantitatively determine the amount of light absorbed by a solution. The technique is explained next.

Spectrophotometer – The spectrometer has a light source that emits light, which is focused with a small slit. The wavelength of interest is then selected using the monochrometer ("mono" meaning one and "chromate" meaning color) and an additional slit. The selected light then reaches the sample and depending on how the photons interact with the compound of interest, the light is either absorbed or passes straight through. By comparing the amount of light entering the sample (P_o) with the amount of light reaching the detector (P), the spectrometer is able to tell how much light is absorbed.

Scientists quantify the amount of light passing through the sample in terms of percent transmittance (%T). Percent transmittance is calculated as the fraction of original light that passes through a sample

$$\% T = (P/P_o) \times 100 \qquad (1)$$

Equation 2 shows how percent transmittance (%T) can easily be converted into a quantity known as absorbance A. Though most spectrophotometers give readings in terms of both %T and A, measurements should be made in %T and mathematically converted to A because %T can be determined more accurately.

$$A = -\log (\%T/100) \qquad (2)$$

The absorbance of a sample is important because of the previously mentioned linear relationship between absorbance and the concentration of the sample. The relationship is known as Beer's law, equation (3). Figure 1 shows a typical spectrophotometer.

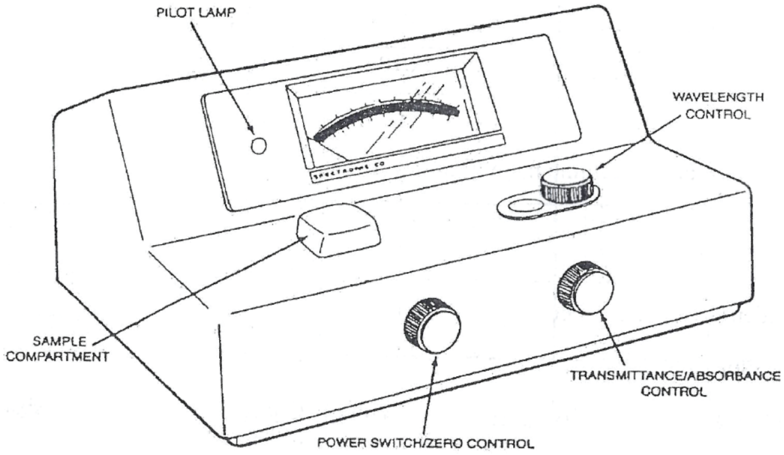


Figure 10.1 Typical Spectrophotometer Appararatus

Beer's Law – A mathematical linear relationship between the amount of light of a specific wavelength absorbed and the concentration of the absorbing species.

$$A = \in bc \qquad (3)$$

Here A is the absorbance of the sample, $\in$ a proportionality constant that is determined by the nature of the absorbing species, b is the path length of light through the sample and c is the molarity M of the absorbing species.

As you can see in equation (3), the amount of the light that is absorbed depends on several variables:

> "A" is the absorbance of the sample, and although the compound being study may, in general, absorb light over a fairly broad range of wavelengths, there is only one region where the light is absorbed most strongly. This wavelength is known as λ_{max}. Therefore, once the λ_{max} is identified, the absorbance of the sample should be measured at this wavelength.
>
> "$\in$" is the molar absorptivity, and it is a constant representing the efficiency by which the substance absorbs light. The greater the value of "$\in$" the more strongly the substance absorbs light, resulting in a more intense color.
>
> "b" represents the solution path length, and it is the distance that the light must travel through the sample. This is measured as the width of the sample holder (the cuvette). "b" is a constant for each experiment, usually =1 cm.
>
> "c" represents the molar concentration M of the absorbing species in the sample. One can easily determine the unknown concentration of a sample from equation (3) after measuring the absorbance of the sample and using the molar absorptivity of the compound and the path lengths of the cuvette. If the molar absorptivity of the compound is not known, the concentration of an unknown can still be found by constructing a calibration curve.

Calibration Curve – A calibration curve allows scientist to determine the unknown concentration of a known species. According to Beer's law, as long as we account for a blank solution in our studies, a plot of absorbance (y-axis) versus concentration (x-axis) should produce a straight line with slope equal to $\in$b and a y-intercept = 0. Calibration curves are constructed using at least 4 solutions (points) that are made from a stock solution with a known concentration. The experimentally measured absorbance of each solution (point) is then plotted as a function of concentration, and a line of best fit is drawn through the points. As expected, the absorbance of the sample will increase linearly as the concentration increases. Whatever absorbance value is then measured for a unknown solution, its concentration can be related either using the equation of the line of best fit or it can be extrapolated directly from the graph.

As for any plot, a title is labeled above the graph with both axes clearly labeled using the independent (x- axis) and the dependent (y-axis) variables in the experiment. After plotting each of the data points on the graph, a line of best fit is drawn. Although, the points do not have to fall directly on the line, a good agreement is expected and needed for accurate determination of the concentration of your unknown.

Spectroscopy of Phosphates in Water – The problem of eutrophication is affecting the water supply across the nation making the water unsafe for consumption and hazardous to the wildlife that depend upon it. The source of the eutrophication problem is an excessive input of nutrients into rivers, lakes and the seas because of the extensive use of fertilizers, the combustion of fossil fuels and waste from animal feedlots. This excessive nutrients input stimulates the growth of algae and bacteria, robbing the water of oxygen. The resulting algal blooms, red tides and deterioration of sea grass makes the waters uninhabitable for most fish and coastal wildlife.

Phosphates are one of the major groups of contaminates affecting the US water supply. Phosphates are found in the environment, not only in the form you have seen in your chemistry book (PO_4^{3-}) but also as polyphosphates (such as $P_2O_7^{4-}$ or $P_3O_{10}^{5-}$) or as organic phosphates which are eventually hydrolyzed to form PO_4^{3-}. The primary means by which humans introduce phosphates into the environment is through the use of fertilizers and detergents. In particular, tripolyphosphates ($P_3O_{10}^{5-}$) have been used in soaps and detergents to combat the problem of hard water. Phosphates are also a major component of fertilizers because phosphorus is a necessary plant nutrient and is crucial for seed formation, root development, and crop maturation. These phosphates eventually enter the water supply leaving lakes, rivers, and seas with an abnormally high phosphate concentration.

Spectrophotometric analysis relies on the fact that the amount of light absorbed by a sample shows a linear dependence upon the concentration of the compound present in the solution. The problem with using spectrophotometric analysis in our case is that phosphates are colorless and therefore do not absorb light in the visible portion of the electromagnetic spectrum. However, due to the reactive nature of phosphates, one can easily color them using an ammonium vanadomolybdate reagent. This reagent includes ammonium metavanadate (NH_4VO_3) and molybdate (MoO_4^{2-}) and reacts with the phosphate to form a yellow compound (called "heteropoly acid" from here on). The formula of the yellow compound is uncertain but thought to be $(NH_4)_3PO_4 \bullet NH_4VO_3 \bullet 16\ MoO_3$. The brightness of the resulting yellow solution is directly proportional to the concentration of phosphate in the water. Therefore, in this experiment absorbance A is due to the heteropoly acid formed.

Spectroscopy of Cobalt (II) Ion – Environmental contamination with metal ions represents a potential treat to humans, animals and plants. The metal ions do not undergo biodegradation and many of them are soluble in aqueous solutions; therefore, becoming more available for living systems and accumulating in the environment. Cobalt (II) compounds are essential in many industries. Their applications in nuclear power plants, metallurgy, mining, pigments, paints and electronic are only few examples where the presence of cobalt in wastewaters represents a major environmental problem. Conventional methods for removing dissolved metal ions from aqueous media include chemical precipitation, chemical oxidation and reduction, ion exchange and activated carbon adsorption. However, these processes have significant disadvantages, such as incomplete removal of metal ions, high quantities of toxic sludge, required additional reagents and have high operation cost.

In recent years, considerable attention has been given to the adsorption technique, in which the adsorbents are natural material or industrial and agricultural wastes, to passively remove metal ions from aqueous effluents. Thus, the utilization of peat, living and death biomass or clay and related minerals could offer an efficient and cost-effective alternative compared to traditional chemical and physical remediation and decontamination techniques.

III. Materials

Maximum of 150 mL of 1×10^{-3} M stock solution of phosphate
40 mL "heterepoly acid" (ammonium vanadomolybate)
50 mL 0.150M $Co(NO_3)_2 \bullet 6\ H_2O$

IV. Safety Precaution

Make sure all solutions are discarded properly.

V. Experimental Procedure

Part 1: Spectrophotometric Analysis and the Determination of Phosphates

A. Calculations for Standard Solutions

Students will work in groups of 2 to construct a single calibration curve consisting of 6 data points having phosphate concentrations in the range 4.00×10^{-5} M to 4.00×10^{-4} M. Each student will be responsible for making at least one of the solutions and measuring the absorbance for at least one data point. Show your instructor your calculations for making your 25 mL standard solutions from the 1.00×10^{-3} M phosphate stock solution before you and your partner goes on. Remember, solutions must be made using only the available volumetric flask and pipets.

B. Adjusting the Spectrophotometer

1. Turn on the spectrometer by rotating the power control clockwise. Allow the spectrophotometer to warm-up for five minutes before using.

2. Adjust the wavelengths to 400 nm. With no sample in the spectrometer, turn the zero adjust so the meter reads 0% T.

3. Prepare the blank by pipetting 10 mL of DI water and 5 mL of ammonium vanadomolybdate into a beaker.

4. Always rinse the cuvette with a few mLs of solution whenever you are using a new solution. Discard the rinsing solution according to safety protocol. Fill the rinsed cuvette to the mark with the blank solution. Insert the cuvette into the sample holder of the spectrometer and adjust the light-control knob so 100% transmittance is read. Your instrument is now zeroed.

C. Preparation of Standard Solutions

1. Based on your calculations from part A, pipet the appropriate volume of the 1.00×10^{-3} M phosphate stock solution into the 25 mL volumetric flask. Dilute the stock solution by filling the volumetric flask until the meniscus reaches the mark.

2. Pipet 10.0 mL of the phosphate solution you made in step 1 and 5.00 mL of the ammonium vanadomolybdate stock solution into a small, labeled beaker.

3. Repeat steps 1 and 2 for each of the six standard solutions.

D. Making the Calibration Curve Using the Standard Solutions

1. Rinse the same cuvette you used for your blank with about 1 mL of your standard solution (from step 2 in part C). Fill the rinsed cuvette to the mark with the sample solution. Insert the cuvette into the spectrometer, measure and record the percent transmittance. All data points for a given curve must be measured with the same cuvette. All phosphate solutions should be discarded according to safety protocol.

2. Repeat step 1 for the remaining phosphate solutions. Before using any glassware with each new solution, the glassware must be rinsed with DI water and about 1mL of the new solution.

E. Determination of Unknown Phosphate Concentration

1. Pipet 10.0 mL of the unknown and 5.00 mL of the ammonium vanadomolybdate solution into a beaker. Fill the rinsed cuvette to the mark with the unknown solution. Use the spectrometer to measure the percent transmittance and record your results.

Part 2: Spectrophotometric Analysis and the Study of Cobalt (II) Ion

A. Preparation of Solutions

1. Prepare 50 mL of stock solution of 0.150 M cobalt nitrate by dissolving the appropriate amount of $Co(NO_3)_2 \bullet 6\ H_2O$ in 25 mL of DI water in a small beaker.

2. Transfer the solution to a 50 mL volumetric flask. Be sure to rinse the beaker and add the washings to the flask. Dilute to the mark and thoroughly mix.

3. Rinse a 25 or 50 mL buret with the cobalt (II) solution and then fill the buret.

4. Clean, dry and number 0 – 5, six 13 x 100 mm test tubes (or better yet cuvettes if available).

5. Deliver with the buret, 1.00 mL into test tube 1, 2.00 mL into test tube 2 and so on of your stock solution.

6. Rinse the buret several times with DI water and fill it with DI water. Deliver 5 mL of deionized water into test tube 0, 4.00 mL into test tube 1 and so on.

7. Check by eye to see that there is now a total of 5 mL in each test tube. Thoroughly mix the contents of each test tube.

8. Obtain a cobalt nitrate solution of unknown concentration from your instructor.

B. Determining the Absorption Spectrum of Cobalt (II) Ion

*The spectrum will be determined using only test tube 5 and tube 0 for a blank. The other tubes would give identical absorption profiles with proportionally lower absorption values. The spectrum enables you to select the best wavelength for the concentration study. Familiarize yourself with the appropriate spectrometer instructions.

1. For a Spectronic 20, set the wavelength to 430 nm. With nothing in the sample compartment, set the left knob so that transmission reads zero (when the sample compartment is empty, the light is mechanically blocked from reaching the detector therefore the amount of light transmitted is zero). In theory this setting of the left knob should not depend on the wavelength and should not have to be reset. It is wise to recheck it occasionally however.

2. Insert the water blank (tube 0) and calibrate the instrument by setting the right hand knob so that the instrument reads l00% transmission or 0.00 absorption.

3. Insert tube 5 and record the absorption reading.

4. Remove tube 5, change the wavelength to 460 nm and recalibrate the right hand knob with tube 0. (*Note: every time the wavelength is reset, the right knob of the instrument must be reset with a blank. For readings of different samples at the same wavelength, resetting is not required or recommended.) Insert tube 5 and read the absorption.

5. Repeat the above process at 480 nm, 500 nm, 510 nm, 520 nm, 540 nm, 570 nm, and 610 nm.

6. Choose whichever wavelength produces the maximum absorption, and repeat step 4 in ±10 nm in steps of 5 nm. For example, if 500 nm produces the maximum wavelength, repeat step 4 using 490 nm, 495 nm, 505 nm and 510 nm. This process will guarantee you identify your λ_{max}.

7. Plot the absorption (y axis) versus the wavelength (x axis) and determine the wavelength of maximum absorption.

C. Beer's Law Plot

1. Set the wavelength to the optimum wavelength determined immediately above and recalibrate the instrument. Successively insert tubes 1 through 5 and the unknown, and record the absorption values.

2. Construct your calibration curve, plotting the absorption (y axis) versus the concentration of cobalt (II) ion (x axis) and determine the concentration of the cobalt (II) ion in the unknown, as explained earlier.

VI. Questions

1. Microwave ovens use electromagnetic radiation that has a wavelength about 0.01 cm. The wavelength range of visible light is 400-700 nm. Which is more energetic, microwave or visible light? Is it appropriate to say that a microwave "nukes" the food?

2. The light transmission ($-\log_{10}T = A = \in b c$) at 60 nm of a 0.25 M $CuSO_4$ solution on a shoulder of its absorption peak is 59% in a 1.00 cm cell. What is the value of $\in$ for $CuSO_4$ at 600 nm?

3. The absorption values for 1 mm of Pyrex at 320 nm and 280 nm are 0.15 and 1.3, respectively. What are the percent transmissions for 1 mm of Pyrex at these wavelengths?

4. Would cells made of Pyrex be useful for obtaining ultraviolet spectra below 270 nm? Explain.

5. Can visible light cause excitation f an electron in water? Explain.

VII. Discussion Questions

The US Public Health Service has set the maximum value of phosphate in the drinking water at 0.30 mg phosphate/liter. Did your unknown sample violate this standard? Show your work. What solutions will you propose to decrease the concentration of phosphate in water without directly impacting agriculture?

VIII. References

1. Paradis, Hands-On Chemistry, *Spectrophotometric Analysis: Phosphates in Water*, (2005) The McGraw-Hill Company

2. Murov, S., Experiments in General Chemistry, *Spectroscopy of Cobalt (II) Ion*, (2006) 5th Ed., Thomson Brooks/Cole

Unit 4 – Atmospheric Chemistry

Atmospheric Chemistry & Smog

The composition and chemistry of the atmosphere is of importance for several reasons, but primarily because of the interactions between the atmosphere and living organisms. The composition of the Earth's atmosphere has been changed by human activity and some of these changes are harmful to human health, crops and ecosystems. Examples of problems that have been addressed by atmospheric chemistry include acid rain, ozone depletion, photochemical smog and global warming. Atmospheric chemistry seeks to understand the causes of these problems, and by obtaining a theoretical understanding of them, allow possible solutions to be tested and the effects of changes in government policy evaluated.

Photochemical Smog & Tropospheric Ozone

When fossil fuels such as gasoline are burned, a variety of pollutants are emitted into the earth's troposphere. Two of the pollutants that are emitted are hydrocarbons (*e.g.*, unburned fuel) and nitric oxide (NO). When these pollutants build up to sufficiently high levels, a chain reaction occurs from their interaction with sunlight in which the NO is converted to nitrogen dioxide. NO_2 is a brown gas and at sufficiently high levels can contribute to urban haze. However, a more serious problem is that NO_2 can absorb sunlight and break apart to produce oxygen atoms that combine with the O_2 in the air to produce ozone (O_2). Ozone is a powerful oxidizing agent, and a toxic gas. In North America elevated levels of tropospheric ozone cause several billion dollars per year damage to crops, structures, forests, and human health. It is believed that the natural level of ozone in the clean troposphere is 10 to 15 ppb. Because of increasing concentrations of hydrocarbons and NO in the atmosphere, scientists have found that ozone levels in "clean air" are now approximately 30 ppb. A principal activity of atmospheric chemists is to study and determine how we might reverse this trend.

Global Warming

Fossil fuels are composed mostly of carbon, and when they are burned this carbon is released into the atmosphere, mainly in the form of CO_2. We currently emit roughly 5 billion tons of carbon into the atmosphere each year. As a result, there has been a steady increase in global atmospheric levels of CO_2. This increase in CO_2, along with other gases including methane, ozone, and CFCs, presents a problem because these gases are "greenhouse" gases, meaning that they absorb infrared radiation (*i.e.*, "heat") that is radiated out from the earth. Thus, heat that would otherwise be lost to space is trapped in the atmosphere, leading to increased temperatures. Climatologists have predicted that, as a result of increasing concentrations of greenhouse gases in the atmosphere, the earth's temperature will increase by about 3 °C by the year 2030. This will result in significant changes in local climate, in some areas leading to loss of arable land, and an increase in sea level with associated coastal flooding. In addition, global warming may exacerbate the photochemical smog problem. Hundreds of atmospheric scientists are employed worldwide to study the magnitude and implications of this problem, and potential solutions.

Stratospheric Ozone Depletion

The "ozone layer" is a region of relatively high ozone concentration (at about 25 km altitude) in the stratosphere, which is a layer of the atmosphere between 15 and 50 km. Ozone is produced from interactions between the energetic ultraviolet (UV) light reaching the stratosphere and molecular oxygen. The presence of the ozone layer in the stratosphere is vital to life at the surface since the ozone layer absorbs UV light that would otherwise reach the surface and cause damage to both animal and plant life. However, the ozone layer is becoming chemically perturbed due to the presence of chlorofluorocarbons (CFCs) in the stratosphere, among other species. CFCs are used in air conditioners and as cleaning and blowing agents in the chemical industry. These compounds are chemically inert, and they ultimately diffuse upward to the stratosphere. In the stratosphere, because of the presence of the higher energy UV light, these compounds can absorb the light and decompose to produce chlorine atoms that then participate in a chain reaction in which ozone in the ozone layer is destroyed. In 1985 an "ozone hole" was discovered over Antarctica, which appears every year in October. The amount of ozone in the stratosphere over Antarctica has decreased to only half the natural level. This large decrease is localized over Antarctica due to the very cold temperatures, but there appears to have been a global decrease in the "natural" abundance of stratospheric ozone of 3-5%. This problem of stratospheric ozone depletion is a very complex and challenging problem that will likely have a significant impact on human activities for decades to come. Atmospheric chemists are needed to study the processes that occur in the stratosphere, and to study the atmospheric impact of the candidate replacement compounds, such as HCFC’s.

Acidic Deposition

When fossil fuels, and particularly coal, are burned, the sulfur in the fuel is emitted into the atmosphere as sulfur dioxide (SO_2). In the atmosphere this SO_2 can be oxidized to sulfuric acid (H_2SO_4), which exists as an aerosol (in small droplets). This sulfuric acid aerosol ultimately falls back to the surface, with a variety of environmental consequences. At sufficiently high concentrations these aerosols can cause severe respiratory problems in humans. However, most of the sulfur falls in unpopulated regions where it can cause damage to vegetation, and can release metals from the soil into lakes and streams where these metals can be toxic to fish. Acidic pollutants in rainwater also cause substantial damage to building materials. As a result of deposition of acidic pollutants, thousands of lakes have suffered serious losses of aquatic life. Atmospheric chemists are needed to study the chemical processes responsible for SO_2 oxidation and the environmental and human health impacts of the acidic aerosols that are produced.

Another common form f acidic rain is the production of nitric acid (HNO_3) from No vehicular exhaust –very common in the west coast of the US. In this experiment you will be studying formation of HNO_3 produced as an “end-product” from the reaction between NO and O_2.

Toxic Air Pollutants

As a result of a variety of human activities such as agriculture, transportation, and industrial processes, a large number of different toxic pollutants are emitted into the atmosphere. Among the chemicals that may pose a human health risk are pesticides, polychlorinated biphenyls (PCB's), polycyclic aromatic hydrocarbons (PAH's), dioxins (PCDD's), and volatile organic compounds such as benzene, carbon tetrachloride. Many of the more environmentally persistent compounds (*e.g.,* PCBs) have been measured in Arctic wildlife and, for example, in tissues of the local Inuit population. Because of the enormous variety of toxic pollutants present in the air that we breathe, it is an enormously challenging task to determine the human health risks from exposure to this mixture. Scientists are needed in this field to measure the atmospheric concentrations of these species, to identify and quantify the sources of these pollutants, and to determine their environmental fate.

References

1. Sander, R. Centre of Atmospheric Chemistry webpage, Mainz, Germany. Accessed on November 5, 2010: http://www.mpch-mainz.mpg.de/~sander/chem-intro.html

Experiment 11 – Exploring the Properties of Gases

I. Purpose

Experimentally test Boyle's law, Charles's law and the ideal gas law constant. Graphical analysis of data, to derive mathematical relationships that relate the different variables used when studying gases, *i.e.* pressure, volume, amount of substance n and temperature.

II. Introduction

Intuition is a useful attribute. When you apply intuition to the behavior of gases, you can arrive at the same relationships discovered 200 years ago by Robert Boyle, Jacques Charles, Amedeo Avogadro, Joseph Gay-Lussac and Guillaume Amontons. Consider a gas confined in a cylinder with a volume, V_1, at temperature T_1, and pressure, P_1.

Boyle's Law – Boyle studied what would happen to the volume of a gas if mass is added to the piston (increasing the pressure on the gas) when temperature is held constant. He found out that the volume will decrease or as the pressure increases, the volume decreases. The simplest algebraic equation that can be written that predicts this behavior is an inverse proportionality, $V = k/P$ or $PV = k$ where k is a constant. Other relationships such a $V = k/P^2$ are also consistent with a volume decrease as the pressure increases. The question is which equation not only agrees with the direction of the changes but also quantitatively agrees with the behavior. It turns out as Boyle discovered that the simple inverse proportionality correctly predicts the behavior of gases and we call $PV = k$, Boyle's law.

Charles's Law – He studied the effect on volume when the temperature is increased and the pressure held constant. He observed that to maintain constant pressure the volume has to increase and drive the piston up. The simplest algebraic expression of this relationship that is consistent with this observation is the direct proportionality of Charles's law, $V= k T$ or $V/T = k$. Inspection of this equation reveals that a temperature of zero predicts a volume of zero. Now you know that the volume of a gas (*e.g.*, the interior of a balloon) will not go to zero at 0 °C (put a balloon in your freezer). A temperature scale where the volume theoretically would be zero needs to be devised. The Kelvin scale conforms to this criteria where 0 K = -273.15 °C. *Remember to use Kelvin for all gas law calculations.

Gay-Lussac's Law – Amontons and Gay-Lussac explored the relationship when the piston is held in fixed position and the pressure is increased. They found that the temperature has to increase to keep the piston in the same position. The direct proportionality $P = k T$, or $P/T = k$, accurately predicts experimental behaviors and is called either Amontons's or Gay-Lussac's law.

Avogadro's Law – Consider the effect on the volume of adding more gas to the cylinder while maintaining constant temperature and pressure. The relationship is the simplest one with the volume proportional to the number of moles, $V = k n$ (n equals the number of moles).

Ideal Gas Law – Combining all these relationships yields V = nRT/P where R is the proportionality constant and is appropriately called the gas constant. In the Part II of this experiment, you will determine the value of R and compare it to the accepted literature value of 0.08206 L atm/mol K. The equation is usually written in the form PV = nRT and called the ideal gas law. All of the previously discussed gas laws can be easily derived from this one equation. For example, if n and T are held constant, PV = constant which is Boyle's law. An in teresting relationship is that at STP (0° C and 1 atm), 1 mole of any gas occupies 22.4 L. The unit conversion 22.4 L/mol has very limited use as it applies only at STP whereas PV = nRT applies whenever gas behavior approximates that of an ideal gas.

Absolute Zero – This is the theoretical value for the coldest temperature that matter can attain. This temperature can be extrapolated using Charles's Law, and plotting volume as a function of temperature. To get the numerical value, extend (extrapolate) the graph line to the axis where the volume of the gas would decrease to 0 mL.

III. Materials

25 mL 6 M HCl
1 g Zn metal (high surface area)

IV. Safety Precautions

When doing Part II, make sure your hydrogen is produced away from any flames.

V. Experimental Procedure

Part 1. Studying Boyle's and Charle's Laws Using Vernier

Review each section of this part before starting your work. You will need to decide the best way to conduct the testing, so it is wise to make some plans before you begin. You may wish to conduct a test run without collecting data, in order to observe how the experiment will proceed. In each section of part A, you will investigate the relationship between two of the four possible variables, the other two being constant.

A. Boyle's Law: The Relationship between Pressure and Volume

1. Position the piston of a plastic 20 mL syringe so that there will be a measured volume of air trapped in the barrel of the syringe.

2. Attach the syringe to the valve of the Gas Pressure sensor, as shown in figure 1. A gentle half turn should connect the syringe to the sensor securely. **Note:** read the volume at the front edge of the inside black ring on the piston of the syringe, as indicated by the arrow in Figure 1.

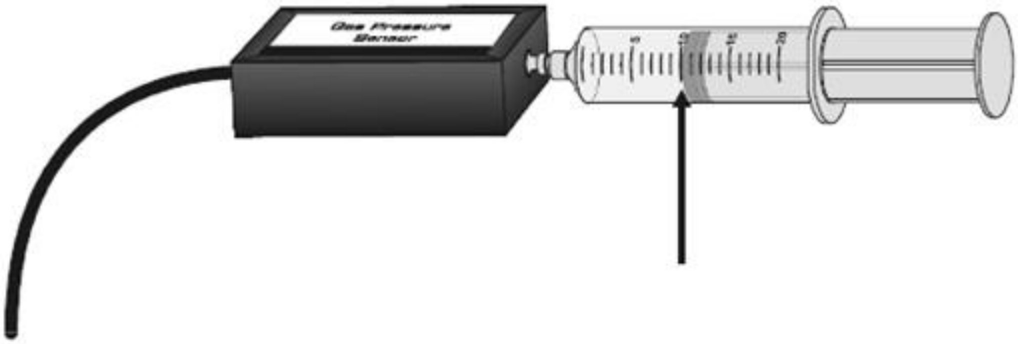


Figure 11.1. Gas Syringe connected to Vernier Pressure Sensor

3. Connect the Gas Pressure sensor to Channel 1 of the Vernier computer interface. Connect the interface to the computer using the proper cable.

4. Start the Logger Pro program on your computer. Open the file "30a Gases" from the *Advanced Chemistry* with Vernier folder. This file allows you to collect pressure data from the Gas Pressure sensor, using Events with Entry mode. For each pressure reading you take with a "keep" button mode, enter a volume value. Collect at least six data points.

5. Measure the pressure of the air in the syringe at various volumes. Print a copy of the graph and data.

B. Charles's Law: The Relationship between Volume and Absolute Temperature

Using the apparatus shown in Figure 2, you will place an Erlenmeyer flask containing an air sample in a water bath and you will vary the temperature of the water bath.

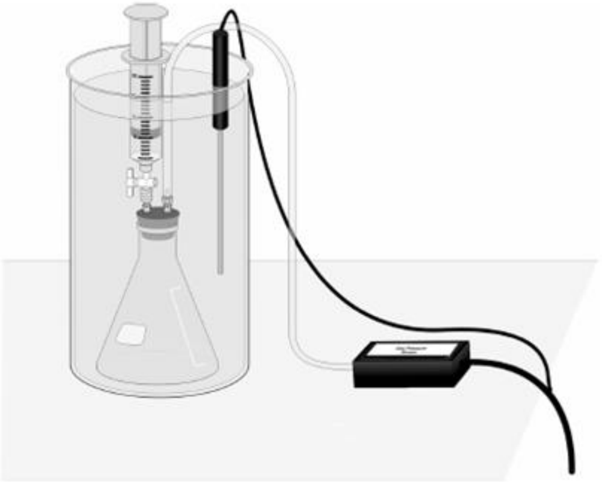


Figure 11.2. Set-up for Collecting Pressure at Changing Temperatures

Keep some of these factors in mind as you plan your procedure:

- If you are starting with a cold-water bath, set the piston at the 0 mL mark on the syringe. This will allow the gas volume to be increased in warmer water baths.

- The temperature of the water bath cannot be increased by more than 30-40 degrees from your starting temperature.

- Even though you are not plotting pressure, it is important to monitor pressure in the meter to ensure that it remains constant.

- It is important to know the *total* volume of air in the flask *and* syringe. The volume of the flask, up to the bottom of rubber stopper, can be accurately measured using a graduated cylinder. For the estimated volume of the tubing (from the rubber stopper to the Gas Pressure sensor box), as well as in the valve below the bottom of the syringe, use a value of ~4 mL.

1. Ensure that the Gas Pressure sensor is plugged into the Channel 1 and the Temperature Probe is plugged into Channel 2 of the interface.

2. Assemble the apparatus as shown in figure 2. Be sure all fittings are airtight. Make sure the rubber stopper and flask neck are dry, then twist and push hard on the rubber stopper to ensure a tight fit. Be sure the water level is at least as high as the confined air in the syringe.

3. Open the file "30c Gases" from the *Advanced Chemistry with Vernier* folder. This file is set up to collect pressure and temperature data from the attached sensors, using Events with Entry mode. This mode allows you to collect a data pair simultaneously from the Gas Pressure sensor and Temperature Probe by clicking on the "keep" button and entering a value for the volume. Even though the pressure reading will not be plotted on the graph of volume versus temperature, it is important for pressure to be monitored so that it can be kept constant.

4. Collect volume data at several different temperatures. Set up water baths in a large-volume container as you need them, ranging from ice water to hot water. Print a copy of the graph and data.

Part 2. Determination of the Value of the Gas Constant, R

The determination of the gas constant R from the ideal gas law ($R = PV/nT$) requires the values of P, V, n, and T. The values of P, V and T will be measured and the value of n determined from a stoichiometric calculation. Hydrogen will be prepared by a single replacement reaction:

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

By utilizing a weighed amount of zinc, the number of moles of hydrogen that will be produced can then be calculated.

1. Assemble the apparatus pictured in Figure 3. ***Note:Be sure to keep all flames far away from this apparatus once you start to generate hydrogen.**

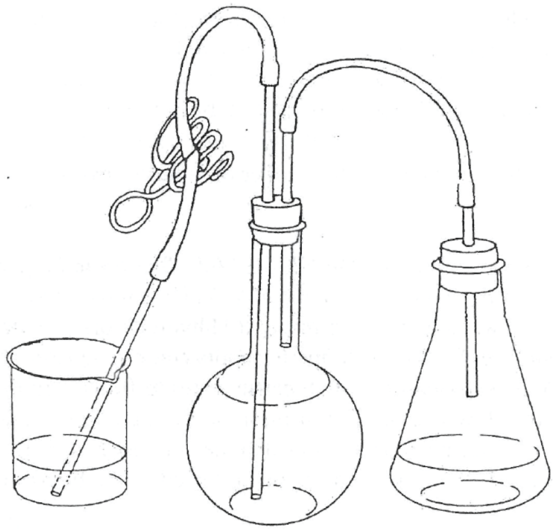


Figure 11.3. Set-up to Study Reaction (1)

2. Fill the 500 mL Florence flask (or it could be an Erlenmeyer flask) up to the neck with water and add 25 mL of 6 M hydrochloric acid to the 250 mL Erlenmeyer flask.

3. While the Erlenmeyer flask has no stopper, apply compressed air (or use a rubber bulb) to the tube inserted through the stopper. This will cause water to flow from the Florence flask into the beaker. As soon as the flow begins, clamp the tube through which the water is flowing while disconnecting the compressed air source.

4. Now that the delivery hose is filled with water, remove the stopper from the 500 mL Florence flask, return the water you collected in the beaker to the Florence flask and replace the stopper.

5. Weigh a little less than a gram of zinc metal to the nearest 0.001 g.

6. Holding the zinc sample with one hand and the stopper for the 250 mL Erlenmeyer in the other, drop the sample into the HCl, quickly stopper the flask, and remove the clamp.

7. After the zinc has completely reacted, allow a few minutes for the gas in the flasks to cool down to room temperature.

8. Equalize the pressure between the Florence flask and the beaker by raising the beaker or flask (whichever liquid level is lower) so that the level of the water you have collected in the beaker is the same as the level of water in the flask. **Do not remove the stopper from the flask until after you have measured the water.**

9. Clamp the delivery hose when the water levels are equal.

10. Measure the amount of water you collected using a 500 mL graduated cylinder and also measure the temperature of the water. Read the barometer to determine the current atmospheric pressure.

Because you collected the hydrogen over water, part of the gas in the Florence flask was water vapor. Consequently, to obtain the actual pressure of hydrogen that was produced, you must subtract the vapor pressure of the water from the pressure at which the gas was collected (atmospheric). The number of moles of hydrogen can be calculated from the number of moles of zinc used and the stoichiometry of the reaction. The values of P, V, and T can be determined from the measurements made during the experiment.

Table I. Vapor Pressure of Water as a Function of Temperature

Temperature (˚C)	*Vapor Pressure (mm)*	*Temperature (˚C)*	*Vapor Pressure (mm)*
10	9.2	20	17.5
11	9.8	21	18.6
12	10.5	22	19.8
13	11.2	23	21.1
14	12.0	24	22.4
15	12.8	25	23.8
16	13.6	26	25.2
17	14.5	27	26.7
18	15.5	28	28.3
19	16.5	29	30.0
		30	31.8

VI. Questions

1. For each section in Part I, write an equation using the two variables and a proportionality constant, *k*. Also, graph the relationship between the two variables.

2. Assuming no elasticity forces in rubber, what volume should a 1.0 L ballon at 25 ˚C and 1.00 atm be if immersed in liquid nitrogen (-196 ˚C, 1 atm)?

3. When this experiment is actually performed, the volume of the balloon approaches 0.0 L. How do you account for the discrepancy?

4. When a 0.134 g popcorn kernel pops, it loses about 13% of its mass. Assuming that the volume of a typical kernel is 9.5×10^{-2} mL and that the mass loss is due to water lost, use the ideal gas law to calculate the pressure of the water vapor in the kernel immediately before it pops at 100 °C. Does the resulting calculated pressure account for the popping of the popcorn?

VII. Discussion Questions

What other reactions could you sue to student gas phenomena? Based on today's findings what processes would you recommend to improve air quality in Los Angeles?

VIII. References

1. J. Randall, Advanced Chemistry with Vernier, *Exploring properties of Gases*, (2007) 2nd Ed., Vernier Software & Technology, Beaverton, OR

2. Murov, S., Experiments in General Chemistry, *Gas Law Studies*, (2006) 5th Ed., Thomson Brooks/Cole

Experiment 12 – Atmospheric Chemistry of Nitrogen Monoxide Smog and Acid Rain

I. Purpose

In this experiment, students will observe and study the reaction between nitrogen monoxide and oxygen in the presence of water. Furthermore, they will observe how this reaction leads to the formation of acid rain.

II. Introduction

The chemistry of nitrogen monoxide (NO) is very complex, it plays a significant role in (1) the formation of photochemical smog and ozone in the troposphere and the destruction of ozone in the stratosphere, (2) the formation of acids in the atmosphere, and (3) the biological chemistry of humans and other animals.

In the troposphere (the layer of the atmosphere closest to the earth's surface), ozone is undesirable because it is a lung irritant; but in the stratosphere, ozone is desirable because it shields us from ultraviolet radiation from the sun. In its atmospheric reactions, nitrogen monoxide cuts two ways, playing a primary role in the formation of "bad" ozone in the part of the atmosphere where we live and breathe, but catalyzing the decomposition of "good" ozone in the stratosphere, where ozone has a beneficial protective effect. More recently it has been discovered that nitrogen monoxide plays an important role in biological systems, acting as a neurotransmitter (or messenger molecule) and having profound effects on the vascular system, where it enlarges blood vessels by relaxing the smooth muscles in their walls.

In this experiment, we will focus on the role of nitrogen monoxide in the formation of acids in the atmosphere. In rainy weather, these acids can return to earth as acid rain. In dry weather, the acids can react with ammonia from dairies and cattle feed lots to form solid particulates such as ammonium nitrate. The tiny solid particles scatter light like the tiny droplets of water in fog, forming a haze that reduces visibility.

NO Role in Photochemical Smog and Acids – One of the noxious pollutants that is in vehicular exhaust of autos and trucks is nitrogen monoxide, NO. In fact, any high-temperature combustion that takes place in the presence of air produces some NO-for example, cooking over a gas burner or heating with a gas-fired furnace. The higher the temperature of the combustion, the more NO is produced, reaction (1).

$$N_2(g) + O_2(g) \rightarrow 2\ NO(g) \qquad (1)$$

Although the amount of NO produced is in the concentration range of a few parts per million (ppm), this small amount has significant environmental effects when it is multiplied in a large urban area by the millions of people driving autos or heating homes and cooking with natural gas, such as in Los Angeles. At high concentrations, NO rapidly reacts with oxygen to form nitrogen dioxide (NO_2), reaction (2), a brown noxious gas that is often responsible of beautiful sunsets in Southern California.

$$2\ NO\ (g)\ +\ O_2(g) \rightarrow 2\ NO_2(g) \qquad (2)$$

NO_2 plays a key role in the formation of what is called photochemical (or Los Angeles-type) smog, which contains ozone. Ozone is a very reactive and irritating gas that is responsible for the painful breathing that you feel if you exercise outdoors during a severe smog alert.

Ozone Production – Ozone (O_3) is formed through photochemistry. Photochemistry is chemistry that is activated by sunlight. In this case, NO_2 has an absorption band centered at 393 nm, which is near the borderline between the visible and the ultraviolet regions of the spectrum. As the sun shines on a mass of air containing NO_2, some NO_2 is dissociated by absorption of a photon *(hv)* of light forming two radicals, reaction (3).

$$NO_2(g) + hv \rightarrow NO(g) + O(g) \qquad (3)$$

The oxygen atom produced is very reactive and it reacts with molecular oxygen to form ozone, reaction (4), in the presence of a third molecule, M (it can be a nitrogen or oxygen molecule).

$$O(g) + O_2(g) + M(g) \rightarrow O_3(g) + M^*(g) \qquad (4)$$

The molecule M* (the asterisk means it is in an excited state) carries away excess energy of reaction that would otherwise keep the O atom and the O_2 molecule from forming a stable (low energy) chemical bond. The NO produced in the photochemical step, reaction (3), can recycle to again form NO_2, (*not a reverse step), so ozone can be formed anytime that sunlight shines on air containing nitrogen oxides.

Acid Rain Production – The brown gas NO_2 is very soluble in water. If you attempt to collect it over water, it is completely absorbed, leaving no measurable volume of gas. Depending on reaction conditions, several different reactions have been reported for the reaction of NO_2 (or NO and O_2) with water. According to some sources, the NO_2 reacts with water to form nitrous and nitric acids according to reaction (5).

$$2\ NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq) \qquad (5)$$

It has been reported that when nitrous acid is heated it decomposes to nitric acid and NO, reaction (6).

$$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O \qquad (6)$$

The NO formed could then keep recycling and reacting with oxygen, so that when the last bit of nitrous acid, HNO_2, has disappeared, the net overall reaction in the presence of water and excess oxygen can be written as reaction (7).

$$4\ NO(g) + 3\ O_2(g) + 2H_2O \rightarrow 4\ HNO_3 \qquad (7)$$

Finally, it has been reported that when both NO and O_2 are dissolved in aqueous solution, they react to produce only nitrous acid (or nitrite ion in the presence of base), corresponding to the stoichiometry in reaction (8).

$$4\ NO(aq) + O_2(aq) + 2\ H_2O \rightarrow 4\ HNO_2(aq) \qquad (8)$$

Reactions (2) + (5), (7) (if HNO_2 readily decomposes), or (8) all ultimately form acids starting with nitrogen monoxide, NO, and O_2. If the reactions take place in an area of the atmosphere containing water droplets in a cloud, acid rain will be produced.

Reactions (2) + (5): $2\ NO(g) + O_2(g) + H_2O \rightarrow HNO_2(aq) + HNO_3(aq)$

Reaction (7): $4\ NO(g) + 3\ 0_2(g) + 2\ H_2O \rightarrow 4\ HNO_3\ (aq)$

Reaction (8): $4\ NO(aq) + O_2(aq) + 2\ H_2O \rightarrow 4\ HNO_2(aq)$

All three reactions predict one mole of total acid produced per mole of NO reacted, so no distinction among the three is possible based solely on the titration of total acid produced. However, there are three clearly distinguishable outcomes based on the predicted NO/O_2 reaction stoichiometry and the stoichiometric amounts of HNO_2 and HNO_3 produced, as shown in Table I. In this experiment, we will prepare NO and O_2 and make a qualitative and semi quantitative study of their reaction products in the presence of water.

Table I: The Ratio of mols in the Three Possible Net Reactions of NO and O_2 in the Presence of Water

Reaction	*Mols of O_2 per mol of NO*	*Total mols of acid per mol of NO*	*Mols of nitrite per mol of NO*	*Mols of nitrate ion per mol of NO*
R (2) + (5)	0.50	1.0	0.5	0.5
R (7)	0.75	1.0	0.0	1.0
R (8)	0.25	1.0	1.0	0.0

Measuring the pH and Total Amount of Acid Produced – Nitric acid (HNO_3) and/or nitrous acid (HNO_2) are reported as reaction products when NO_2 reacts with water. Nitric acid is a strong acid; nitrous acid is a weak acid. By measuring both the pH of the reaction products and the total concentration of acid we can, in principle, tell if the solution contains only a strong acid, only a weak acid, or a mixture of weak and strong acids. A properly standardized pH meter is necessary for making the pH measurements (use your Vernier pH meters). We can determine the total amount of acid in an aqueous solution by titration with a base. The acid/base neutralization would be:

$$HNO_2(aq) + OH^-\ (aq) \rightarrow NO_2^-(aq) + H_2O \qquad (9)$$

And/or

$$HNO_3(aq) + OH^-(aq) \rightarrow NO_3^-\ (aq) + H_2O(l) \qquad (10)$$

III. Materials

2 of 60 mL plastic syringes with plunger
1 of 10 mL plastic disposable syringe
3 cm of 1/8 rubber tubbing
0.05 g dry active yeast (beaker's)
6 mL 3% H_2O_2
0.27 g $NaNO_2$
5 mL 1.2 M $FeSO_4$/1.8 M H_2SO_4
20 mL 0.0008 M HNO_3
1 mL microburet
6 mL 0.5M HNO_3
5 drop 0.1% Thymol blue
2 mL 1 M $NaHCO_3$
2 mL 0.5% starch indicator
2 mL 1 M KI (fresh)
2 mL 5 M tartaric acid

IV. Safety Precautions

Prepare the NO gas and carry out the reaction of NO with O_2 in a fume hood, if possible. Wear eye protection at all times.

V. Experimental Procedure

General procedure for Generating Gases in Syringes

The reactions of gases will be prepared in 60-mL disposable Luer-tip syringes minimizing exposure to noxious and toxic gases. Each gas will be generated by mixing two reagents in a syringe. The general arrangement is shown in Figure 1. One reagent, generally a solid, is placed in a small vial cap, which is in turn inserted into the syringe. The second reagent is prepared as an aqueous solution and is drawn into the syringe from a small plastic weighing dish. Then the syringe is capped and shaken to mix the reagents and generate the gas. If desired, gases that are not too water soluble can be washed by drawing DI water into the syringe, capping and shaking the syringe, and expelling the water. Repeating this operation will remove nearly all traces of the original reactants. Because of the small vial cap present in the syringe, not all of the air originally in the syringe is expelled before drawing in the liquid reagent. As a result, the gases prepared contain a small amount of air (about 10% by volume). For many purposes, this is not a significant drawback.

Part 1. Preparing O_2 Gas

1. Use a 60-mL Syringe. Remove the plastic cap that sometimes covers the tip of new syringes and set it aside. Try to move the plunger back and forth. If the plunger movement is stiff and requires a lot of effort, "break in" the syringe by moving the plunger up and down twenty or thirty times. Practice completely removing the plunger, which takes some extra force because of the molded stop designed to prevent the plunger from accidentally coming completely out of the syringe.

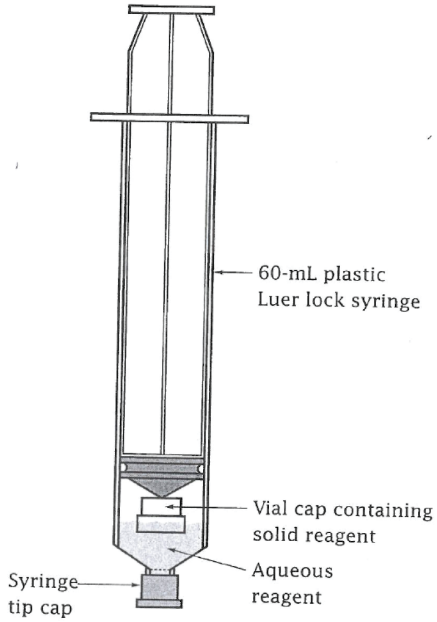


Figure 12.1. A method for Generating Gases in a Syringe

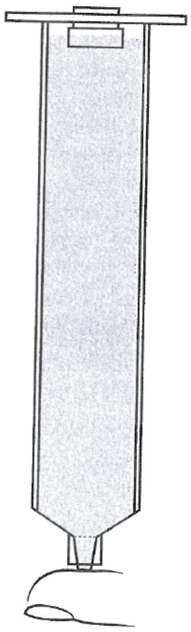


Figure 12.2. Flotation Method for Loading the Vial Cap with Solid Reagent

2. Weigh 0.050 g of dry active baker's yeast on a creased sheet of weighing paper, then transfer the yeast into the cavity of a small polyethylene vial cap (use the cap supplied with a 1-dram Titeseal shell vial). The amount of yeast is just about enough to cover the bottom of the vial cap when uniformly distributed.

3. Next, we want to put the vial cap containing the solid reagent into the syringe. This can be done one of two ways, using forceps or using the flotation technique illustrated in Figure 2. With either method, begin by completely removing the plunger from the syringe and setting the plunger aside on a clean towel or sheet of paper.

a. The vial cap can be loaded using long (10-in.) forceps, grasping the forceps near the top so that you can insert the vial cap all the way to the bottom inside the syringe without your fingers blocking the forceps' entry into the syringe. Then, keeping the syringe upright, with the tip pressed against the bench top, insert the plunger, pushing it snugly against the vial cap. Keep the syringe upright (tip down) in a beaker until you are ready to use it.

b. The flotation method of putting the vial cap in the syringe works well and requires no forceps. Begin by putting your forefinger on the luer end of the syringe and filling the syringe nearly to the top with DI water. Then carefully float the vial cap containing the solid on the water. Controlling the flow with your finger, allow the water to slowly leak out so that the cap rides down to the bottom of the syringe. Perform this operation over the sink, or catch the water in a beaker so you don't spill water all over the bench top. When all of the water has drained out, keep the syringe upright with the tip against the bench top, and insert the plunger, pushing it snugly against the vial cap. Keep the loaded syringe upright in a beaker until you are ready to use it.

4. Load the second reagent by placing 6 ml of 3% hydrogen peroxide solution into a small (1 5/8-in. square) polyethylene weighing dish. (At room temperature, each ml of 3% H_2O_2 solution produces about 10-11 ml of oxygen gas.) Draw the hydrogen peroxide solution up into the syringe, taking care not to draw in more than a bubble or two of air as you draw in the last of the solution.

5. Cap the syringe with a syringe tip cap.

6. Shake the syringe to mix the yeast and hydrogen peroxide solution. Oxygen is evolved rapidly by catalytic decomposition of the hydrogen peroxide, reaction (11).

$$H_2O_2(aq) \rightarrow H_2O + \tfrac{1}{2}\, O_2(g) \qquad (11)$$

7. As the volume of gas nears the full capacity of the syringe, hold the syringe tip up (directed away from your face) and loosen the cap to relieve the pressure. (If the syringe tip is pointed down when you loosen the cap, the solution will spray out, making a mess.)

8. Tighten the cap, shake, and relieve excess pressure again.

9. Continue until the reaction is complete and vent any excess pressure one last time.

10. Turn the syringe tip down and expel the reaction solution into a sink or beaker.

11. Keep the syringe capped until you are ready to use the oxygen gas. It isn't necessary to wash the oxygen gas, since the reaction product is essentially pure water.

12. Label the syringe to identify its contents; making sure that the label does not obscure the volume graduations on the syringe.

Part 2. Preparing NO Gas

For generating NO(g) we will use solid sodium nitrite, $NaNO_2$, which reacts with an excess of Fe(II) solution, according to the net ionic reaction (12).

$$NO_2^- + Fe^{2+}(aq) + 2\, H^+ \rightarrow NO(g) + Fe^{3+}(aq) + H_2O \qquad (12)$$

It has been found by trial and error that you can generate 55-60 mL of NO gas by reacting about 0.27 g of solid $NaNO_2$ *with 4 ml of a solution that is 1.2 M in* $FeSO_4$ *and 1.8 M in* H_2SO_4*. This is 50% more than the calculated amount of* $NaNO_2$*, indicating that the reaction is only approximately described by Reaction (12).*

1. Weigh 0.27 g of solid $NaNO_2$ on a creased sheet of weighing paper and load the $NaNO_2$ into the cavity of a small polyethylene vial cap. Using forceps or the flotation method, load the solid in the vial cap into a 60-ml syringe.

Note: Carry out the next steps in a fume hood.

2. Place 4-5 ml of 1.2 M $FeSO_4$/1.8 M H_2SO_4 solution into a small polyethylene weighing dish.

3. Put the tip of the syringe into the solution and draw up as much of the solution as possible, being careful not to draw in more than a bubble or two of air.

4. Cap the syringe with a syringe tip cap.

5. In the fume hood, shake the syringe to mix the reagents. The reaction mixture will turn black almost immediately, and NO gas is rapidly evolved.

> **Caution:** When the reaction (and the plunger) are nearing the end, turn the syringe upside down, tip end up, before removing the cap to relieve the pressure. Point the tip away from your face in the hood. If the tip is pointed down when you remove the cap. the liquid reagent will spray out, making a nasty mess. If this happens, neutralize the spill with sodium bicarbonate, then wipe up the spill.

Washing the NO Gas.

6. After venting excess pressure with the tip up, turn the syringe tip down, remove the tip cap, and expel the black reaction solution into a beaker. *It will be neutralized and collected as waste. **Do not pour it down the drain.**

7. If the volume of gas in the syringe is greater than 55 ml, expel some gas in the fume hood until the volume reads 55 mL. This will give you some room to draw in wash water.

8. Place some DI water in a small beaker and draw up about 5-6 ml of water into the syringe.

9. Immediately cap the syringe and shake it to wash the gas.

10. Expel the water into the waste collection beaker, draw another portion of water into the syringe, and shake again.

11. Finally, expel the water into the waste collection beaker and quickly cap the syringe until you are ready to use the NO gas.

12. Put a label on the syringe identifying its contents as NO.

Part 3. Reacting NO with O_2

Note: Carry out the next steps in a fume hood.

A. Producing NO_2 Gas

1. Gather together on a piece of paper towel or a clean sheet of paper the materials you will need.

Two capped 60-mL syringes containing O_2 and NO gas
a clean, dry 10-mL disposable syringe
a short (3-cm) length of l/8-in ID rubber tubing
100-mL beaker containing 50 mL of DI water

2. Move the plunger of the 10-mL syringe back and forth until it moves freely, then push the plunger all the way in until it stops.

These next steps (2-5) in which you transfer and react NO and O_2 from the 60-mL syringe to the 10-mL syringe needs to be performed quite quickly. Make sure you understand and know the procedure step-by-step before proceeding.

3. Uncap the 60-mL NO supply syringe, and push one end of the rubber tubing firmly onto the Luer tip. Flush out the tubing by expelling a small volume (2-3 mL) of NO, stopping at the nearest 5-mL division. Then quickly insert the Luer tip of the empty 10-mL syringe into the free end of the tubing and slowly pull back the plunger of the 10-mL syringe by exactly10 mL, while at the same time pushing in the plunger of the larger NO syringe by exactly10 mL. At the end, you will have transferred 10 mL of NO, at approximately atmospheric pressure, to the smaller syringe.

4. Now put the 60-mL O_2 syringe beside the 60-mL NO syringe so that the O_2 syringe can take its place. When ready to make the transfer, remove the 60-mL NO syringe from the tubing and cap the syringe immediately. Uncap the O_2 syringe and immediately connect it to the free end of the rubber tube (with the 10-mL syringe still on the other end). Immediately push on the plunger of the O_2 syringe until you have transferred exactly 5 mL of O_2 into the smaller 10-mL syringe containing NO.

This time, **do not move the plunger of the smaller syringe; rather, keep it at the 10-mL mark. Looking at reaction (2) and recalling that gas volumes combine in exactly the ratios of the stoichiometric equation, we see that reaction (2) predicts that 10 mL of NO would combine with 5 mL of O_2 to form 10 mL of NO_2 gas (all at constant atmospheric pressure). That's why we shouldn't have to move the plunger of the 10-mL syringe to accommodate the added volume of O_2 gas.*

5. Quickly disconnect the O_2 syringe from the rubber tubing and cap the syringe. Use your fingers to pinch off the rubber tubing so that no gas will enter or escape. You should see evidence of the reaction between NO and O_2.

B. Producing an Acidic Solution: HNO_3 and HONO

6. Put the free end of the rubber tubing into the previously prepared beaker containing 50 mL of DI water so that the end of the tubing rests on the bottom of the beaker.

7. Draw a little DI water into the syringe, taking care to keep the free end of the rubber tubing immersed below the surface of the water.

8. Gently shake the gas/water mixture in the syringe. Write your observations.

9. Continue shaking and drawing water into the syringe until no more gas is absorbed. At this point, record the final volume of gas in the syringe.

10. Now expel the solution containing the reaction products into the beaker.

11. Draw a few mL of water into the syringe, and then expel the water to rinse out the interior of the syringe. Repeat this a couple of times. At the end, the solution in the beaker will contain all of the NO/O_2 reaction products.

12. Measure and record the barometric pressure and the room temperature so that you can calculate how many moles of gaseous reactants were during this reaction.

Part 4. Analysis of the Reaction Solution

A. Measurements of pH and pH Reference Calibration

1. Use a Vernier electronic pH meter to measure the pH of the reaction solution that you collected in the beaker.

2. Rinsing the pH electrode with DI water between each measurement and blotting the electrode with tissue to remove excess water, also measure the pH of 0.008 M HNO_3, then 0.004 M HNO_3 solutions. (The latter solution can be prepared by diluting 0.008 M HNO_3 with an equal volume of water.)

3. Save the 0.004 M $HN0_3$ solution to use later in part IV.C as a reagent blank in the test for nitrite ion.

4. The HNO_3 solutions provide reference pH measurements to check the pH calibration of the meter. The pH difference between the two HNO_3 reference solutions should be equal to about $\log(2) = 0.30$ because HNO_3 is a strong, completely ionized acid, and the reference solutions differ in concentration by a factor of two.

B. Titrating the Acid

1. Get a 1-mL microburet (a 1-mL polypropylene syringe equipped with a fine tip cut from a polyetheylene transfer pipet would make it).

2. Get about 6 mL of 0.5 M NaOH in a clean, dry 13 x 100 mm test tube equipped with a size-00 rubber stopper.

3. Fill the syringe with the 0.5 M NaOH, taking precautions to remove all bubbles from the syringe.

4. Be sure to record the concentration of the NaOH solution and the initial volume reading of the syringe.

5. Add 5 drops of 0.1% thymol blue indicator to the solution in the beaker.

6. Now add the 0.5 M NaOH solution from the microburet (syringe), drop by drop, to your acid solution.

7. At the end point, the solution will turn from yellow to a permanent blue color. If the end point color drifts back toward yellow, add another drop of 0.5 M NaOH. Continue until the solution remains blue for at least 30 seconds.

8. Read and record the final volume of the added base.

9. Save the titrated solution for the next test for the presence of nitrite ion.

C. Semiquantitative Analysis for Nitrite Ion

In acid solution, nitrous acid oxidizes iodide ion to form iodine (or triiodide ion in the presence of excess iodide ion) according to reaction (13).

$$2\ HNO_2 + 2\ H^+ + 31^- \rightarrow 2\ NO + 2\ H_2O + I_3^- \qquad (13)$$

In the presence of starch indicator, a deep blue starch-triiodide ion complex forms. The test easily detects 1×10^{-4} *M nitrous acid, so the reaction solution must be diluted before doing the test.*

1. Dilute the solution that was titrated in part IV.B by a factor of 50. Using a polyethylene transfer pipet with a 1-mL calibration mark, transfer 1 mL of the titration solution to a clean 125-mL Erlenmeyer flask and add 49 mL of DI water. Mix this solution thoroughly

2. Get about 2 mL of each of the following reagent solutions:
    1 M $NaHCO_3$
    0.5% starch indicator
    1 M KI (freshly prepared)
    5 M tartaric acid (it's OK if it is yellow or light brown).

3. Using a clean polyethylene transfer pipet, put 1 mL of the diluted reaction solution into a 13 x 100 mm test tube.

4. Add two drops (0.10 mL) of 1 M $NaHCO_3$

5. Add two drops (0.10 mL) of 0.5% starch indicator

6. Add two drops (0.10 mL) of 1 M Kl

7. Add five drops (0.25 mL) of 5 M tartaric acid

8. Shake the test tube to mix the solution thoroughly.

9. Allow the solution to stand for 10 min for the blue color to fully develop.

10. While waiting, move ahead to do the control and reagent blank tests.

Control and Reagent Blank Tests for Nitrite Ion

Control Solution (known amount of nitrite ion)

1. Using the same quantities of the four reagents, perform the same test for nitrite on 1 mL of 1×10^{-4} M sodium nitrite solution prepared by diluting 1 mL of 0.01 M $NaNO_2$ solution with 99 mL of DI water and thoroughly mixing.

Reagent Blank Test

2. Perform the same test on 1 mL of a solution containing the 0.004 M HN03 prepared in part IV.A. The purpose of the blank is to show that a solution containing nitrate ion and the reagents does not give a positive test for nitrite ion. It should be colorless. If it shows a significant blue color, most likely the KI solution contains some iodine produced by air oxidation of the iodide ion or there is nitrite ion contamination from some source.

D. Estimating the Total Amount of Nitrite Produced

1. After allowing the blue color to fully develop by standing for 10 min, compare the intensities of the blue colors of the reaction solution and the control (1×10^{-4} M $NaNO_2$) solution by viewing them against a well-lit white background.
**The comparison can be made more quantitative using a spectrophotometer to measure the absorbance at 592 nm –ask your instructor if this is available.*

2. If the intensities approximately match, you can estimate the total amount of nitrite produced by multiplying by 2500 the amount of nitrite ion in the control.
**Recall that the total amount of gas (l0 mL NO ≅ 0.4 mmol NO) was eventually absorbed in 50 mL of DI water. Then we took 1 mL of this solution and diluted it again to 50 mL, so we took 1/50th of the reaction solution and diluted it another factor of 1/50 to give a total dilution of 1/2500.*

The amount of nitrite ion in the control solution is equal to 1 mL × 1×10^{-4} mol/L = 1×10^{-4} mmol. If the blue colors approximately match, this would also be the amount of nitrite ion in the diluted reaction sample. This amount multiplied by 2500 would then give the total amount of nitrite ion produced by reaction of the gas with water ($2500 \times 1 \times 10^{-4}$ mmol = 0.25 mmol of nitrite).

You should have enough NO and O_2 left in your syringes to repeat the experiment. If you have time, repeat parts III and IV so that you have two measurements of how much acid and nitrite were formed.

VI. Questions

1. Using the ideal gas law, determine the quantities (in millimoles) of NO and O_2 that were reacted in the syringe.

2. What is the total amount of acid (in millimoles) that you would expect to be produced for the given amounts of NO and O_2, considering the three reactions summarized in Table I?

3. Calculate the expected pH for solutions containing 0.008 M $HN0_3$, 0.004 M HNO_3, and 0.008 M HNO_2 *(Ka* = 7.1×10^{-4}).

4. From the results of the titration in part IV.B, calculate the moles of acid formed.

5. Compare this, calculated as a percentage yield, with the theoretical number of moles of acid expected.

6. What is the percentage yield for the formation of acid in your experiment?

7. Is the result consistent with the stoichiometry shown in Table I for the three net reactions?

8. Finally, estimate the amount of nitrite produced (in millimoles) as described in part IV.D.

VI. Discussion Questions

1. Why DI Water is used instead of tap water when reacting NO with O_2.

2. Why are the dilutions necessary in this experiment.

3. What are the implications of your results in the following broader questions…

    a. What human activities lead to the formation of acid rain?

    b. Are nitrogen oxides the only source of acids n acid rain? If not, what are the identities and sources of other important atmospheric pollutants that produce acid rain?

4. Once NO is formed, why prevents it from keep building up to higher concentrations in the troposphere? What about in a dry environment?

VIII. References

1. J. Postma, J.L. Roberts and J.L. Hollenberg, Chemistry in the Laboratory, *Atmospheric Chemistry of Nitrogen Monoxide*, (2010), 7th Ed. W.H. Freeman and Company, New York, NY

Experiment 12 Supplement – Vapor Pressure and Heat of Vaporization

I. Purpose
Determine the relationship between pressure and temperature of a volatile liquid. Calculate the heat of vaporization of the liquid.

II. Introduction
When a liquid is placed in a container, and the container is sealed tightly, a portion of the liquid will evaporate; *i.e.* go to the gas phase. The newly formed gas molecules exert pressure in the container, while some of the gas condenses back into the liquid state. If the temperature inside the container is held constant, then at some point equilibrium will be reached. At equilibrium, the rate of condensation is equal to the rate of evaporation – dynamic equilibrium. The pressure at equilibrium is called *vapor pressure,* and will remain constant as long as the temperature in the container does not change.

In mathematical terms, the relationship between the vapor pressure of a liquid and temperature is described in the Clausius-Clayperon equation:

$$\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C$$

Here, P is the pressure, R is the universal gas constant (8.31 J/mol K*),* T is the absolute (Kelvin) temperature, and C is a constant not related to heat capacity. Thus, the Clausius-Clayperon equation not only describes how vapor pressure is affected by temperature, but it relates these factors to the heat of vaporization of a liquid. ΔH_{vap} is the amount of energy required to cause the evaporation of one mole of liquid at constant pressure.

III. Materials
5 mL ethanol

IV. Safety Precautions
Ethanol can be a dangerous fire risk as it is flammable. Addition of denaturant makes the product poisonous; therefore, store in a flammable cabinet and avoid contact with the skin and inhaling the vapors.

V. Experimental Procedure
1. Use a hot plate to heat 200 mL of water in a 400 mL beaker.

2. Prepare a room temperature water bath in a 1 L beaker. The bath should be deep enough to completely cover the gas level in the 125 mL Erlenmeyer flask.

3. Connect a Gas Pressure Sensor to Channel 1 of the Vernier computer interface. Connect a Temperature Probe to Channel 2 of the interface. Connect the interface to the computer with the proper cable (if using the computer).

4. Start the Logger *Pro* program on your computer. Open the file "34 Vapor" from the

Advanced Chemistry with Vernier folder.

5. Use the clear tubing to connect the white rubber stopper to the Gas Pressure Sensor. About one-half turn of the fittings will secure the tubing tightly. Twist the white stopper snugly into the neck of the Erlenmeyer flask to avoid losing any of the gas that will be produced as the liquid evaporates (Figure 1). **Important:** Open the valve on the white stopper.

6. Your first measurement will be of the pressure of the air in the flask and at room temperature. Place the Temperature Probe near the flask, when the pressure and temperature readings stabilize, record these values in the first column (Initial), of your data table.

7. Condition the Erlenmeyer flask and the sensors to the water bath.
    a. Place the Temperature Probe in the room temperature water bath.
    b. Place the Erlenmeyer flask in the water bath, hold the flask down into the water bath to the bottom of the white stopper.
    c. After 30 seconds, close the valve on the white stopper.

8. Obtain a small amount of ethanol. Draw 3 mL of ethanol into the 20 mL syringe that is part of the Gas Pressure Sensor accessories. Thread the syringe onto the valve on the white stopper (Figure 12.1s).

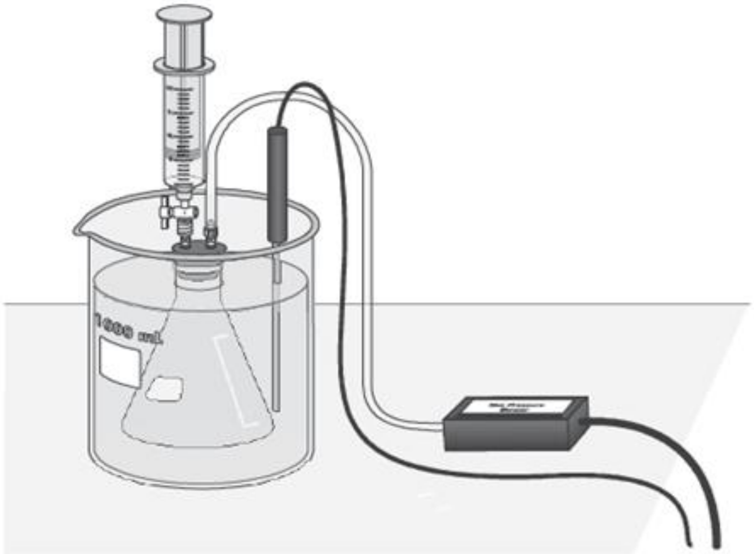


Figure 12.1s. Set-up of Vapor Pressure Aprratus Connected to Vernier Pressure Sensor

9. Add ethanol to the flask.
    a. Open the valve below the syringe containing the 3 mL of ethanol.
    b. Push down on the plunger of the syringe to inject the ethanol.
    c. Quickly pull the plunger back to the 3 mL mark and close the valve below the syringe.
    d. Carefully remove the syringe from the stopper so that the stopper is not moved.

10. Gently rotate the flask in the water bath for a few seconds, using a motion similar to slowly stirring a cup of coffee or tea, to accelerate the evaporation of the ethanol.

11. Monitor and collect temperature and pressure data.
  - **a.** Click "collect" to begin data collection.
  - **b.** Hold the flask steady once again.
  - **c.** Monitor the pressure and temperature readings.
  - **d.** When the readings stabilize, click "keep"

12. Add a small amount of hot water, from the beaker on the hot plate, to warm the water bath by 3-5 °C. Use a spoon or a dipper to transfer the hot water. Stir the water bath slowly with the Temperature Probe. Monitor the pressure and temperature readings. When the readings stabilize, click "keep"

13. Repeat Step 12 until you have completed five total trials. Add enough hot water for each trial so that the temperature of the water bath increases by 3-5 °C, but **do not** warm the water bath beyond 40 °C because the pressure increase may pop the stopper out of the flask. If you must remove some of the water in the bath, do it carefully so as not to disturb the flask.

14. After you have recorded the fifth set of readings, open the valve to release the pressure in the flask. Remove the flask from the water bath and take the stopper off the flask. Dispose of the ethanol as directed.

15. Click "stop" to end the data collection. Record the pressure readings, as *P total,* and the temperature readings in your data table.

16. Do not exit the Logger *Pro* program until you have completed all your Data Analysis Section. All you can use Excel to do all your plots.

VI. Questions – Data Analysis

1. The *P air* for Trials 2-5 must be calculated because the temperatures were increased. As you warmed the flask, the air in the flask exerted pressure that you must calculate. Use the gas law relationship shown below to complete the calculations. Use the *Pair* from Trial I.

$$P_1/T_1 = P_2/T_2$$

2. Calculate and record the P_{vap} for each trial by subtracting P_{air} from P_{total}.

3. Prepare and print a graph of P_{vap} (y-axis) versus Celsius temperature (x-axis).
  - **a.** Disconnect your Gas Pressure Sensor and Temperature Probe from the interface.
  - **b.** Choose New from the File menu. An empty graph and table will be created in Logger *Pro.*

c. Double-click on the x-axis heading in the table, enter a name and unit, and then enter the five values for temperature (°C) from your data table.
d. Double-click on the y-axis heading in the table, enter a name and unit, and then enter the five values for vapor pressure from your data table.
e. Does the plot follow the expected trend of the effect of temperature on vapor pressure? Explain.

4. In order to determine the heat of vaporization, ΔH_{vap} you will first need to plot the natural log of P_{vap} versus the reciprocal of absolute temperature.
a. Choose New Calculated Column from the Data menu.
b. Create a column ln vapor pressure.
c. Create a second column, reciprocal of absolute temperature, 1/(Temperature (˚C) + 273).
d. On the displayed graph, click on the respective axes, and then select ln vapor pressure to plot on the y-axis, and reciprocal of absolute temperature to plot on the x-axis. Autoscale the graph, if necessary.
e. Calculate the linear regression equation for this graph. Calculate ΔH_{vap} from the slope of the linear regression.
f. Prepare and print a second graph.

5. The accepted value of the ΔH_{vap} of ethanol is 42.32 kJ/mol. Compare your experimentally determined value of ΔH_{vap} with the accepted value.

VII. Discussion Questions

Discuss the derivation of the Clausius-Clapeyron equation and its relationship to the constant C. What is the physical meaning of the constant C? Discuss why experimentally calculated value of ΔH_{vap} of ethanol differs (if any) from the reported one (see question 5.). Propose experimental steps to improve the correlation between these two numbers.

VIII. References

1. J. Randall, Advanced Chemistry with Vernier, *Vapor Pressure and Heat of Vaporization*, (2007) 2nd Ed., Vernier Software & Technology, Beaverton, OR

Experiment 13 – Freezing-Point Depression and Molar Mass

I. Purpose

Explore colligative properties of solutions. Determine and compare freezing points of a pure solution and of a mixture. Use freezing-point depression to determine the molar mass of an unknown substance.

II. Introduction

When a nonvolatile solute is dissolved in a solvent, the solution properties change from those of the pure solvent. Relative to the pure solvent, the solution has a lower vapor pressure, a lower freezing point, and a higher boiling point. These effects are called *colligative* properties of the solution because they are linked together by a common feature: they all depend primarily on the ratio of the number of solute particles to the number of solvent particles. The size of the particles or whether they are molecules or ions make little difference; it is the relative number of particles that is important.

Vapor-pressure lowering, freezing-point depression and boiling-point elevation –all of these characteristics are observed in both aqueous and non-aqueous solutions. For example, a solution of a nonvolatile solute like sucrose or ethylene glycol in water shows the same kind of effects as a solution of aspirin dissolved in cyclohexanol or sulfur in naphthalene. We make practical use of the colligative properties of an aqueous solution of ethylene glycol by putting it in the cooling system of an automobile. Because antifreeze and aqueous solution of ethylene glycol has both a lower freezing point and a higher boiling point than pure water, the solution protects the car's cooling system against both freezing and boiling over. Using a spring loaded pressure cap, which allows the system to operate above atmospheric pressure, increases boil over protection. Increases in pressure further raise the boiling point of the solution.

A phase diagram, shown in Figure 1, can be used to describe, in principle, the behavior of mixtures when temperature and pressure are changing. This diagram shows the solvent vapor pressure is lowered when a non-volatile solute is dissolved in the solvent. Note that the vapor pressure curve for the solution (shown by the dotted curve) is lower than the vapor pressure curve for pure water (shown by the solid curve). Recall that the boiling point is the temperature at which the equilibrium vapor pressure equals the atmospheric pressure. The equilibrium vapor pressure of the solvent over the solution is less than that of the pure solvent at the same temperature. Therefore, the solution must be heated to a higher temperature than the pure solvent in order to reach atmospheric pressure. That means the boiling point of the solution is higher than that of the pure solvent. Increasing the pressure above atmospheric pressure, as is done when you are a pressure cap on your auto radiator, raises the boiling point even more. If you drew a horizontal line at $P = 2$ atm, it would intersect the vapor pressure curve at a higher temperature.

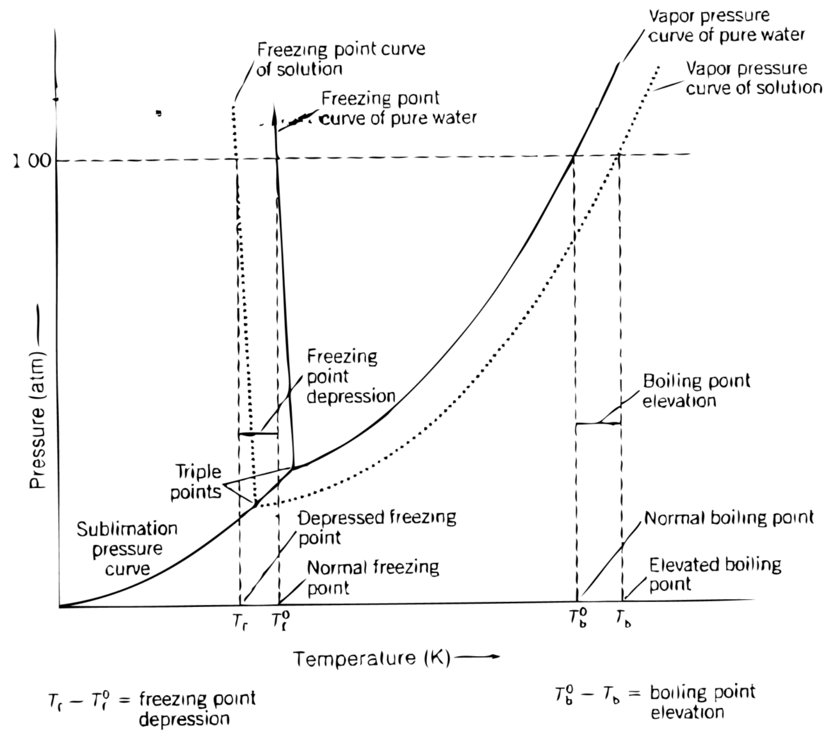


Figure 13.1. Phase Diagram for Pure Water (solid line), and for Water Containing a Nonvolatile Solute (dotted line)

When the temperature of most solutions is lowered to the freezing point, the solid that separates out is mainly pure solvent. Lowering the vapor pressure of a solvent by adding a non-volatile solute causes the equilibrium vapor-pressure curve to intersect the sublimation-pressure curve at a lower temperature than the curve for the pure solvent (Figure 1). The freezing-point curves for the solution and the pure solvent begins at the intersections of the sublimation-pressure and vapor-pressure curves, which is at the triple points where all three phases simultaneously coexist. Therefore, the freezing-point curve for the solution lies at a lower temperature than the freezing-point curve of the pure solvent.

The freezing-point depression effect has several important scientific uses. It allows us to compare the freezing-point depressions of a known and unknown substance in the same solvent in order to determine the molar mass of the unknown. This type of comparison is called cryoscopy (cryo- comes from the Greek word meaning "icy" or "cold.") Cryoscopy is also used in the clinical laboratory to measure the total concentration of solutes in urine, making use of the fact that the freezing-point depression is proportional to the sum of the concentrations of all dissolved particles. The urine that initially is formed within the kidney has a much lower concentration of solute than the urine that leaves the kidney. This is because the kidney conserves body water by recovering much of the water in urine as it passes though the kidney tubules. The kidney's ability to concentrate urine is one of this organ's must important functions, and when the renal tubes are damaged, this ability is one of the first functions to be lost. Thus, a cryoscopy measurement of the solute content of urine is an indication of kidney function.

The freezing-point depression

The equation that describes the freezing-point depression is shown in equation (1).

$$\Delta T = K_f \text{ x } m \qquad (1)$$

Where ΔT is the freezing point depression ($\Delta T_f = T_f^0 - T_f$ where T_f^0 is the freezing point of the pure solvent of T_f is the freezing point of the solution). This quantity is directly proportional to the concentration of particles expressed as the molality, *m*, of the particles in the solution. The proportionality constant, K_f is called *molal freezing point depression constant*. By using a solute known molar mass, we can determine K_f for a particular solvent. The molality (and molar mass) of an unknown compound can be determined by measuring the freezing point depression of a solution of the unknown in the same solvent.

Note the phrase *particle molality* used in discussing the molality of an ionic solute, such as KCl. If the solute does not dissociate into two or more particles, the particle molality equals the molality of the solute. The distinction between particle molality and solute molality is important to keep in mind when dealing with aqueous solutions. A 0.1 m KCl solution would lower the freezing point of water approximately twice as much as a 0.1 m sucrose solution, because sucrose, ordinary table sugar, does not dissociate in water. The freezing-point depression for a 1 m solution in water (the molal freezing-point constant) is 1.86 ˚C, and the corresponding boiling point rise (*the molal boiling-point constant*) is 0.52 ˚C. The same principles apply for solutions in other solvents. For example, for cyclohexane the freezing point is 6.5 ˚C, with an ideal molal freezing-point constant of 20.2 ˚C/*m*. For lauric acid an ideal molal freezing-point constant is 3.9 ˚C/*m*.

**Note: These constants apply to measurements in quite dilute solutions. For the more concentrated solutions that we must use, the freezing point constant may deviate slightly from the ideal value. This is the reason we will first determine the constants under the conditions of the experiment, and then use the found values for determining molar mass.*

III. Materials

8 g lauric acid
1 g benzoic acid
10 mL cyclohexane
0.6 g p-dichlorobenzene

IV. Safety Precautions

Caution to not spill lauric acid, as it will be hot and direct contact with skin will cause burns. All chemicals used in this experiment must be disposed as instructed. Do not throw down the drain any of the chemicals.

V. Experimental procedure

Part 1. Freezing-point Depression of Lauric Acid and Molar Mass of Benzoic Acid

A. Determine the Freezing Temperature of Pre Lauric Acid

1. Connect a Temperature Probe to Channel 1 of the Vernier computer interface. Connect the interface to the computer (if using the computer) with the proper cable.

2. Start the Logger Pro program on your computer. Open the file “04 Freezing Point” from the *Advanced Chemistry with Vernier* folder.

3. Add about 300 mL of tap water with a temperature of 20-25 ˚C to a 400 mL beaker. Place the beaker on the base of a ring stand.

4. Use a utility clamp to obtain a test tube containing hot, melted lauric acid from your instructor.

5. Fasten the utility clamp at the top of the test tube. **Be careful not to spill the hot lauric acid on yourself and do not touch the bottom of the test tube.*

6. Insert the Temperature Probe into the hot lauric acid. Fasten the utility clamp to the ring stand so the test tube is above the water bath. Click “collect” to begin the data collection.

7. Lower the test tube into the water bath. Make sure the water level outside the test tube is higher than the lauric acid level inside the test tube, as shown in Figure 2.

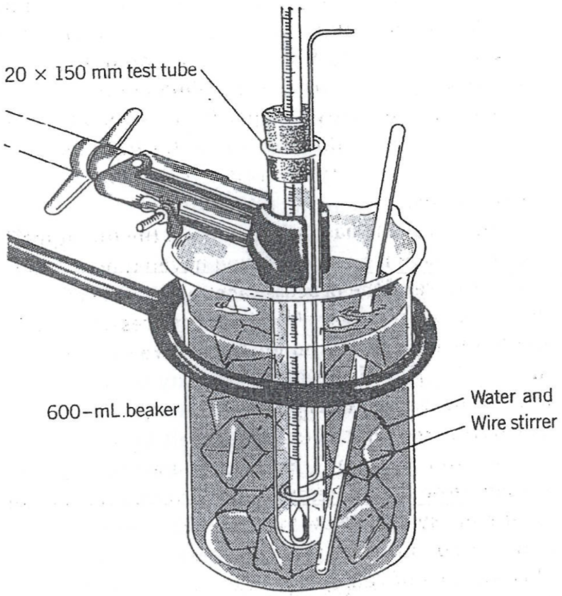


Figure 13.2. Freezing-point Apparatus Set-up to Determine Molar Mass

8. With a very slight up-and-down motion of the Temperature Probe, continuously stir the lauric acid for the ten-minute duration of the experiment.

9. When the data collection is complete, use a hot water bath to melt the lauric acid enough to safely remove the Temperature Probe. Carefully wipe any excess lauric acid liquid from the probe with a paper towel or tissue.

10. The freezing temperature can be determined by finding the mean temperature in the portion of the graph with nearly constant temperature.
   a. Move the mouse pointer to the beginning of the graphs flat part. Press the mouse button and hold it down as you drag across the flat part of the curve, selecting only the points in the plateau.
   b. Click the statistics button
   c. The mean temperature value for the selecting data is listed in the statistics box on the graph. Record this value as the freezing temperature of pure lauric acid.
   d. Click on the upper-left corner of the statistics box to remove it from the graph.

B. Determining Freezing Temperature of a Solution of Benzoic Acid and Lauric Acid

1. Prepare the computer for data collection.
   a. From the experiment menu, choose Store Latest Run. This stores the data so it can be used later.
   b. To hide the curve of your first data trial, click the temperature y-axis label of the graph and choose More… from the dropdown list. Uncheck the Run 1 Temperature box and click "ok."

2. Obtain a test tube containing a melted solution with ~1 g of benzoic acid dissolved in ~8 g of lauric acid. Record the precise masses of benzoic acid and lauric acid as indicated on the label of the test tube. Repeat Steps 3-9.

3. The freezing temperature of the benzoic acid/lauric acid solution can be determined by finding the temperature at which the mixture initially started to freeze. Unlike pure lauric acid, the mixture results in a gradual linear decrease in temperature during freezing. Follow the steps below to analyze the graph.
   a. Click and drag the mouse to highlight the initial part of the cooling curve where the temperature decreases rapidly (before freezing occurred).
   b. Click on the Linear Regression button.
   c. Now click and drag the mouse over the next linear region of the curve (the gently sloping section of the curve where freezing took place).

d. Click Linear Regression again. The graph should now have two regression lines displayed.

e. Choose Interpolate from the Analyze menu. Move the cursor to the point of the two lines; you will know if the cursor is over the intersection when the temperature readings displayed in the interpolate box are the same. This is the freezing point of the benzoic acid/lauric acid mixture.

f. Record the freezing point in your data table.

4. Print a graph showing both trials.

Part 2. Freezing-point Depression of Cyclohexane and Molar Mass of an Unknown

A. Determining Freezing Temperature of Cyclohexane

1. In this part, you will repeat part I but using about 10 mL of cyclohexane in part I.A.

B. ***Determining Freezing Temperature of a Solution of Cyclohexane and p-dichlorobenzene***

1. To find the freezing-point depression of cyclohexane and calculate the molal freezing-point constant, you will use 0.5-0.6 g of *p*-dichlorobenzene ($C_6H_4Cl_2$). Repeat part I.B. using *p*-dichlorobenzene.

C. Determining the Molar mass of an unknown Solid

1. Obtain from your instructor a sample of a unknown organic material.

2. The freezing-point measurements will be made like in part I.B., using 0.5 g of the unknown material.

3. For the data you collect, calculate the molar mass of the unknown using the molal freezing-point constant for cyclohexane as determined in part II.B.

Calculations of Molar Mass

Either boiling points or freezing point may be used to determine the molar mass of a soluble substance. For the latter, it is necessary only to determine the freezing point of a solution containing a known mass of the solute in a known mass of the solvent and to compare this with the freezing point of the pure solvent, as follows.

1. Use the measured freezing-point depression and the molal freezing-point constant in equation (1) to determine the molality of the unknown cyclohexane solution.

2. This molality is equal to the moles of unknown divided by the kilograms of the solvent, cyclohexane; so if we multiply the molality by the mass of cyclohexane (in kilograms) we will know the number of moles of unknown that the solution contains.

3. The molar mass is the number of grams per mole, so dividing the mass of the unknown by the number of moles (which we just determined in step 2) gives the molar mass of the unknown.

VI. Questions

1. If 0.253 g of benzoic acid dissolved in 12.45 g of cyclohexanol, $C_6H_{11}OH$, lowered the freezing-point of pure cyclohexanol by 6.55 °C, what is the molal freezing-point constant of the solvent?

For Part 1.

1. Calculate molality for lauric acid using equation (1). Using this molality, calculate moles of benzoic acid solute.

2. Calculate the experimental molar mass of benzoic acid, and compared it with the accepted molar mass using its formula, $C_6H_5CO_2H$. What's the percent discrepancy? Discuss your results.

VI. Discussion Questions

Why is the molality concentration scale used in the context of colligative properties instead of the more common molarity (M) scale? Hint: A plot of ΔT_f versus molality and versus molarity will help you explore these relationships.

To be included for Part 1.

1. Does this experience help to explain why $CaC1_2$ is often used in northern climates to melt ice on roads and sidewalks? Why not using NaCl, instead? Discuss and take in consideration economic issues.

2. If you fail to stir the material in the test tube, would you expect the reported freezing-point to be higher or lower? Explain.

3. If you spill a little of the benzoic acid when preparing the mixture, will this affect the freezing-point depression, how? Explain. What about the molecular weight calculation? Will it be affected? Explain.

VIII. References

1. J. Postma, J.L. Roberts and J.L. Hollenberg, Chemistry in the Laboratory, The *Molar Mass of a Soluble Substance by Freezing-Point Depression*, (2010), 7th Ed. W.H. Freeman and Company, New York, NY

2. J. Randall, Advanced Chemistry with Vernier, *Using Freezing-Point Depresion to Find Molecular Weight*, (2007) 2nd Ed., Vernier Software & Technology, Beaverton, OR

Experiment 14 – Global Warming Issues and Effects

Introduction: You have seen the movie "An Inconvenient Truth". Now you are asked to research on the Internet and develop an understanding of the probable causes for the current apparent heating the earth's atmosphere and climatic changes.

Greenhouse Gases and Global Warming

Goals:

a) Explore some of the factors influencing the debate about global warming and the greenhouse effect

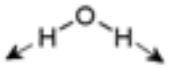
b) Apply principles learned in Chemistry 101 to a current environmental controversy. Including:

- Insights into the interaction of radiation with matter and how this affects the earth's climate
- Explore how humans might contribute to the greenhouse effect
- Investigate how infrared spectroscopy is used to identify certain atmospheric gases

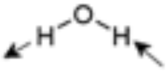
Background:

The temperature of the Earth's surface is controlled by many different factors. One of these is the radiation absorption by gases in the atmosphere, referred to as the Greenhouse Effect. One of the primary energy inputs is direct radiation from the sun. Much of this radiation lies in the visible region of the spectrum. The atmosphere does not absorb most of this radiation and it strikes the ground or ocean surface where some of it is absorbed and some is reflected back into space. The absorbed radiation warms the surface. Warm objects radiate energy in the infrared region of the spectrum. If gases in the atmosphere absorb this infrared energy, it does not get back out into space. Thus the atmosphere acts like a blanket, or a greenhouse, making the surface warmer. The atmospheric blanket moderates the surface temperature and prevents extreme changes between high daytime temperatures and frigid nighttime ones. The gas most frequently cited as important in the greenhouse effect is CO_2. The CO_2 concentration in the atmosphere has increased from the burning of fuels. There is concern that this CO_2 increase is leading to a warming of the climate, which might result in a variety of serious effects. In this experiment we will study CO_2 and look at some aspects of its contribution to the greenhouse effect.

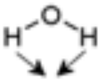
Changes in the vibrational and rotational motions of polyatomic molecules are the main results of the absorption of heat by gases. The direct absorption of infrared radiation occurs **only** if there is a **change in the dipole moment** of the molecule. An n-atom molecule (where n is the # of atoms) may be described as having 3n – 6 vibrational motions, or vibrational modes as they are called (3n – 5 for linear molecules). Changing dipole moments for any of these vibrational modes result in that mode absorbing infrared radiation. The absorption bands in the infrared spectrum are related to these vibrational modes. Using the 3n-6 formula, water has 3 vibrational modes, as shown below:



Symmetric Stretch



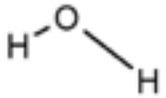
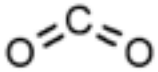
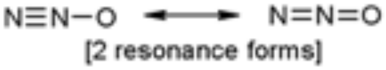
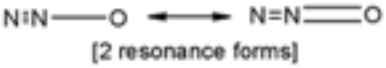
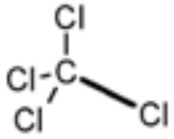
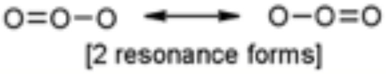
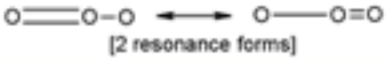
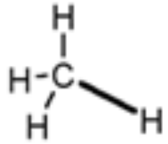
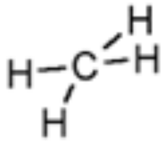
Asymmetric Stretch



Bend

Consider the dipole moment as the molecule undergoes each of these motions. Does it change? If so, the vibration will result in an absorption in the infrared region. Infrared absorption frequencies for several atmospheric gases are given in Table I. Note that wavelength (in μ) =10,000/ cm^{-1}

Table I: Principal IR Absorptions for Various Atmospheric Gases

Type of Gas	**Absorption Ranges** (in cm^{-1})[a] [Look for **one** peak within the following ranges.]	**Type of bond causing absorption**	
Water (H_20)	3800-3600		**Asymmetric Stretch**
	1600-1400		**Bend**
Carbon Dioxide (CO_2)	2400-2200		**Asymmetric Stretch**
	800-600		**Bend**
Nitrous Oxide (N_20)	2400-2200		**Symmetric Stretch**
	1400-1200		**Asymmetric Stretch**
Carbon Tetrachloride (CCl_4)	1000-600		**Asymmetric Stretch**
Ozone (O_3)	2400-2200		**Symmetric Stretch**
	1200-1000		**Asymmetric Stretch**
Methane (CH_4)	3200-3000		**Asymmetric Stretch**
	1400-1200		**Bend**
Nitric Oxide (NO)	2000-1800		**Stretch**

[a] where 10000 / wavenumber = wavelength in microns …near to mid IR absorption spectra.

Laboratory Discussion

1. Research and describe in your own words the effects of Greenhouse Gases, and why they are heating the earth over time. [hint: see… http://www.ucar.edu/learn/1_3_1.htm]

2.What are the relative average atmospheric abundances for the most important contributors to heating the atmosphere? What is a pollutant and explain the difference between a primary and secondary pollutant. [hint: see sites like… http://www.ace.mmu.ac.uk/eae/Global_Warming/Older/Concentrations.html], and their rate of change. [http://www.mindfully.org/Air/2006/UN-Greenhouse-Gas3nov06.htm]

3. From the identified pollutants, distinguish between anthropogenic, biogenic, and geogenic sources.

4. Research and list what are the relative global warming potential effects for each of the gases that you have listed in 2.[http://www.eia.doe.gov/oiaf/1605/gwp.html]

    a. Research and explain using blackbody radiation curves, why these gases have the potential to warm the earth.

    b. Based upon your research and the film that you saw, list what actions we as Americans must undertake to prevent future potentially catastrophic results from Global Warming. What are the current efforts that the USA government is undertaking to control greenhouse gases? (You might want to visit the EPA climate change website)

    c. Explain in your own words what does carbon sequestration means and implies.

A place to start might be these websites:

(US EPA site)
http://yosemite.epa.gov/oar/globalwarming.nsf/content/impacts.html
(USGS site)
http://www.nrmsc.usgs.gov/research/global.htm
(NASA site)
http://earthobservatory.nasa.gov/Study/WaterVapor/water_vapor.html
(California site)
http://climatechange.ca.gov/
(NRDC Site)
http://www.nrdc.org/globalWarming/f101.asp
(Pew Center)
http://www.pewclimate.org/global-warming-basics/

And many, many more sites can be found with a Google search. In addition, here is an interesting website that will allow you to estimate your own Carbon Footprint.
http://www.bp.com/extendedsectiongenericarticle.do?categoryId=9008204&contentId=7015209

XXII. Additional Practice Exercises

A. Conversion Factors

1. You are traveling to London in October and you found out that temperature at that time of the year is usually around 15 ˚C, which is different than the usual 75 ˚F in Southern California during that time o f the year. Compare these two temperatures using the Kelvin (K) scale?

2. Some athletes have as little as 3% percent body fat. If such a person has a body mass of 45 kg, how much body fat does that person have?

3. If body fat has a density of 0.94 mg/L and 3.0 L of fat are removed in a liposuction, how many pounds of fat were removed from the patient?

4. What is a cholesterol level of 0.00185 kg/L in the standard units of mg/dL?

5. An object has a mass of 11.2 oz. When it is submerged into a graduate cylinder initially containing 27.82 mL of water, the water level rises to 0.07778 L. What is the density (g/mL) of the object? (16 oz = 1 lb)

B. Thermochemistry: Calorimetry and Heat Exchange

1. An ice cube tray holds 325 g of water. If the water initially has a temperature of 25 °C, how many kilojoules of heat must be removed to cool the water at 0 °C?

2. An archeologist found a piece of metal during an excavation. The metal looks like cupper; however it could be a mixture of cupper with some other elements. After experimentation, the archeologist found that 10.0 g of the metal takes about 5.38 cal to increase its temperature by 5 °C from 25 °C. Is this metal pure cupper or a mixture? (s_{Cu} = 093 J/ g °C)

3. The following acid-base reaction is performed in a coffee cup calorimeter:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

The temperature of 110. g of water rises from 25.0 °C to 26.2 °C when 0.10 mol of H^+ is reacted with 0.10 mol of OH^-:

a. Calculate q(water)
b. Calculate ΔH for the reaction
c. Calculate ΔH if 1.00 mol OH^- reacts with 1.00 mol H^+

4. 20.0 grams of metal X at temperature 300 K are placed in 20.0 grams of fluid Y which is at 250 K. If X has a lower specific heat than Y, the equilibrium temperature will be:

(a) 250 K	(b) between 250 and 275 K
(c) 275 K	(d) between 275 and 300 K
(e) 300 K	(f) can not be determined

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5. 40.0 grams of copper, at 95.0 °C, is placed in 100.0 mL of water at 20.0 °C. What is the final temperature?

6. 15.3g of $NaNO_3$ were disssolved in 100.0 g of water in a calorimeter. The temperature of the water dropped from 25.0 °C to 21.56 °C. Calculate ΔH for the solution process.

7. The temperature of a calorimeter increases 0.10 K when 7.52 J of electric energy is used to heat it. What is the heat capacity of the calorimeter?

8. When 0.1025 g of benzoic acid was burned in a bomb calorimeter the temperature of the calorimeter increased by 2.165 °C. For benzoic acid ΔH°(comb) = -3227 kJ mol^{-1}. Calculate the heat capacity of the calorimeter.

9. How much heat is required to raise the temperature of 854 g H_2O from 23.5 ºC to 85.0 ºC? Note: Specific heat of water is 4.184 J/g·ºC.

10. Phosphorus trichloride, PCl_3, is a compound used in the manufacture of pesticides and gasoline additives. How much heat is required to raise the temperature of 96.7 g PCl_3 from 31.7 ºC to 69.2 ºC? Note: Specific heat of PCl_3 is 0.874 J/g·ºC.

11. Carbon tetrachloride, CCl_4, was a very popular organic solvent until it was found to be toxic. How much heat is required to raise the temperature of 10.35 g of CCl_4 from 32.1 ºC to 56.4 ºC? Note: Specific heat of carbon tetrachloride is 0.85651 J/g·ºC.

12. If a piece of aluminum with mass 3.90 g and a temperature of 99.3 ºC is dropped into 10.0 cm^3 of water at 22.6 ºC, what will be the final temperature of the system? Note: Specific heat of aluminum is 0.9025 J/g·ºC.

13. The color of many ceramic glazes comes from cadmium compounds. If a piece of cadmium with mass 65.6 g and a temperature of 100.0 ºC is dropped into 25.0 cm^3 of water at 23.0 ºC, what will be the final temperature of the system? Note: Specific heat of cadmium is 0.2311 J/g·ºC.

14. A piece of an unknown metal with mass 23.8 g is heated to 100.0 ºC and dropped into 50.0 cm^3 of water at 24.0 ºC. The final temperature of the system is 32.5 ºC. What is the specific heat of the metal?

15. A blacksmith heated an iron bar to 1445 ºC. The blacksmith then tempered the metal by dropping it into 42,800 mL of water that had a temperature of 22 ºC. The final temperature of the system was 45ºC. What was the mass of the bar? Note: Specific heat of iron is 0.4494 J/g·ºC.

16. A 752 mL sample of water was placed in a 1.00 kg aluminum pan. The initial temperature of the pan was 26 ºC, and the final temperature of the system was 39 ºC. What was the initial temperature of the water?

C. Thermochemistry: Change in Enthalpy and Hess' Law

1. Calculate the enthalpy of formation of oxalic acid, for which the enthalpy of combustion is -251 kJ/mol. Use the data provided in your book Appendix to find ΔH formation of $C_2O_4H_{2(s)}$.

2. Calculate the standard enthalpy change, ΔH°, for the formation of 1 mol of strontium carbonate (the material that gives the red color in fireworks) from its elements.

$Sr\,(s) + C(graphite) + \frac{3}{2}O_2(g) \rightarrow SrCO_3(s)$

The information available is

(1) $Sr\,(s) + \frac{1}{2}O_2(g) \rightarrow SrO\,(s)$ $\Delta H^\circ = -592\text{ kJ}$

(2) $SrO\,(s) + CO_2\,(g) \rightarrow SrCO_3\,(s)$ $\Delta H^\circ = -234\text{ kJ}$

(3) $C(graphite) + O_2\,(g) \rightarrow CO_2\,(g)$ $\Delta H^\circ = -394\text{ kJ}$

3. The combination of coke and steam produces a mixture called coal gas, which can be used as a fuel or as a starting material for other reactions. If we assume coke can be represented by graphite, the equation for the production of coal gas is:

$2\,C\,(s) + 2\,H_2O\,(g) \rightarrow CH_4\,(g) + CO_2(g)$

Determine the standard enthalpy change for this reaction from the following standard enthalpies of reaction:

(1) $C(s) + H_2O\,(g) \rightarrow CO\,(g) + H_2\,(g)$ $\Delta H^\circ = 131.3\text{ kJ}$

(2) $CO\,(g) + H_2O\,(g) \rightarrow CO_2\,(g) + H_2\,(g)$ $\Delta H^\circ = -41.2\text{ kJ}$

(3) $CH_4\,(g) + H_2O\,(g) \rightarrow 3\,H_2\,(g) + CO\,(g)$ $\Delta H^\circ = 206.1\text{ kJ}$

4. One reaction involved in the conversion of iron ore to the metal is

$FeO\,(s) + CO\,(g) \rightarrow Fe\,(s) + CO_2\,(g)$

Calculate the standard enthalpy change for this reaction from these reactions of iron oxides with CO :

(1) $3\,Fe_2O_3\,(s) + CO\,(g) \rightarrow 2\,Fe_3O_4\,(s) + CO_2\,(g)$ $\Delta H^\circ = -47\text{ kJ}$

(2) $Fe_2O_3\,(s) + 3\,CO\,(g) \rightarrow 2\,Fe\,(s) + 3\,CO_2\,(g)$ $\Delta H^\circ = -25\text{ kJ}$

(3) $Fe_3O_4\,(s) + CO\,(g) \rightarrow 3\,FeO\,(s) + CO_2\,(g)$ $\Delta H^\circ = 19\text{ kJ}$

5. Using the following data,

$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$ $\Delta H^o = -890$ kJ/mol
$H_2O_{(l)} \rightarrow H_2\ O_{(g)}$ $\Delta H^o = 44$ kJ/mol at 298 K

Calculate the enthalpy of the methane combustion reaction.

6. The standard enthalpies of formation of SO_2 and SO_3 are -297 and -396 kJ/mol respectively. Calculate the standard enthalpy of reaction for the reaction:

$$SO_2 + 1/2\ O_2 \rightarrow SO_3$$

7. From the following enthalpies of reactions:

1. $2\ O_{(g)} \rightarrow O_{2(g)}$ $\Delta H^o = -249$ kJ/mol
2. $H_2O_{(l)} \rightarrow H_2O_{(g)}$ $\Delta H^o = 44$ kJ/mol at 298 K
3. $2\ H_{(g)} + O_{(g)} \rightarrow H_2O_{(g)}$ $\Delta H^o = -803$ kJ/mol
4. C(graphite) + $2\ O_{(g)} \rightarrow CO_{2(g)}$ $\Delta H^o = -643$ kJ/mol
5. C(graphite) + O2(g) $\rightarrow CO_{2(g)}$ $\Delta H^o = -394$ kJ/mol
6. C(graphite) + $2\ H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta H^o = -75$ kJ/mol
7. $2\ H_{(g)} \rightarrow H_{2(g)}$ $\Delta H^o = -436$ kJ/mol
8. $H_2O_{(l)} \rightarrow H_2O_{(g)}$ $\Delta H = 41$ kJ/mol at 373 K

Calculate the heat of combustion of methane into gaseous H_2O.

8. The enthalpy of reaction (1) is -890.4 kJ/mol. What is the enthalpy for reaction (2)?

(1) $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

(2) $2\ CO_2 + 4\ H_2O \rightarrow 2\ CH_4 + 4\ O_2$

9. Using the following data, what is the enthalpy of the reaction for:

$$2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(l)}\ \Delta H^o = ?$$

1. $2\ O_{(g)} \rightarrow O_{2(g)}$ $\Delta H^o = -249$ kJ/mol
2. $2\ H_{(g)} \rightarrow H_{2(g)}$ $\Delta H^o = -436$ kJ/mol
3. $H_2O_{(l)} \rightarrow H_2O_{(g)}$ $\Delta H = 41$ kJ/mol at 373 K
4. $H_2O_{(l)} \rightarrow H_2O_{(g)}$ $\Delta H^o = 44$ kJ/mol at 298 K
5. $2\ H_{(g)} + O_{(g)} \rightarrow H_2O_{(g)}$ $\Delta H^o = -803$ kJ/mol
6. C(graphite) + $2\ O_{(g)} \rightarrow CO_{2(g)}$ $\Delta H^o = -643$ kJ/mol
7. C(graphite) + $O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H^o = -394$ kJ/mol
8. C(graphite) + $2\ H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta H^o = -75$ kJ/mol

D. Thermochemistry: Lattice Energy and the Born-Haber Cycle

1. Calculate the Lattice Energy U for $Li_2O_{(s)}$ using the Born-Haber cycle. Clearly demonstrate each step on the cycle. (Hint: phase change, dissociation, ionization energy, electron affinity, lattice energy, change in enthalpy of formation)

Useful information:
Enthalpy of sublimation for Li is 159.3 kJ/mol.
$\Delta H°_f$ (Li_2O) = -795 kJ/mol
$O^- + e^- \rightarrow O^{2-}$ ($\Delta H°_f$= -780 kJ/mol)

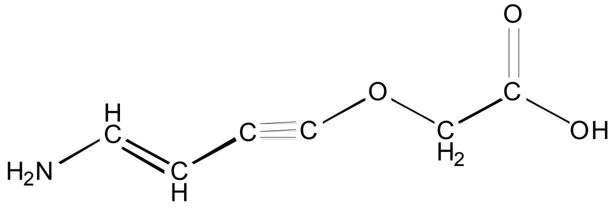
2. Calculate the Lattice Energy U for $Al_2O_{3(s)}$ using the Born-Haber cycle. Clearly demonstrate and name each of the steps in the cycle.

Useful information:
Enthalpy of sublimation for Al is 330.0 kJ/mol.
$\Delta H°_f$ (Al_2O_3) = -1675.7 kJ/mol
$O^- + e^- \rightarrow O^{2-}$ ($\Delta H°_f$= -780 kJ/mol)

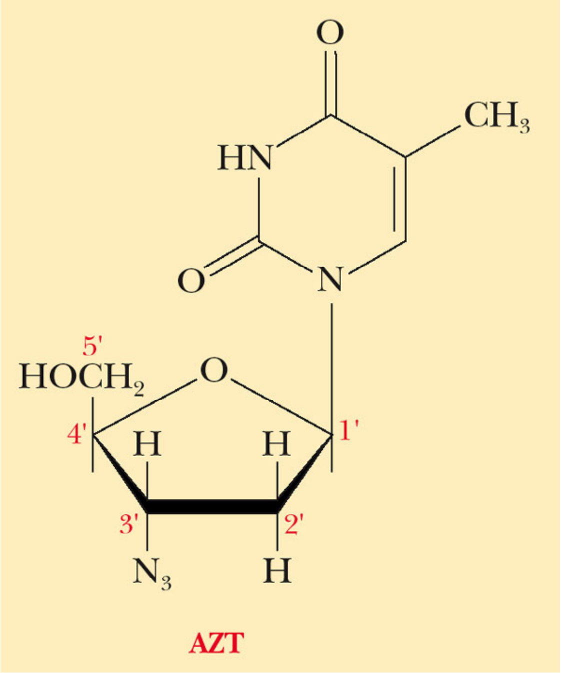
E. Hybridization

For the following molecules, identify the Electron Arrangement and Molecular Geometry of each atom (except of H's). Also, identify the hybridization of the atom, and the sigma and pi bonds. Discuss if the molecule is polar or non-polar by clearly identifying where dipole moments are located, if any.

(1)



(2)



F. Gas' Laws

1. An expandable vessel contains 729 mL of gas at 22 °C. What volume will the gas sample in the vessel have if it is placed in a boiling water bath at 100 °C?

2. What volume of CO_2 measured at STP is produced when 27.5 g of $CaCO_3$ is decomposed.

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

3. An unknown mixture of gases (A, B and C) has a total pressure of 25 Torr. If gas A and B has the same partial pressures and C has a partial pressure that is half of the pressure of A. At ambient temperature, what is the volume occupied by 3.00 moles of C?

4. For the following reaction

$$H_{2(g)} + O_{2(g)} \rightarrow H_2O_{(g)}$$

a. If 16.00 g of O_2 react at 0.800 atm and 127 °C, what volume of oxygen (mL) was used?

b. How many molecules of water are produced in part a?

c. If the water is produced at 760 mm Hg and 115 °C, what volume (mL) of water was collected?

5. For the following reaction

$$Zn_{(s)} + HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$$

How many liters of $H_{2(g)}$ can be produced at STP from 25.0 g of Zn?

6. A method to destroy CFC (chlorofluorocarbons) stockpiles passes the CFC through packed sodium ozalate ($Na_2C_2O_4$) powder at 270 °C. The reaction for Freon-12, which occurs with a percent yield of 89.3%, is:

$$CF_2Cl_{2(g)} + 2\ Na_2C_2O_{4(s)} \rightarrow 2\ NaF_{(s)} + 2\ NaCl_{(s)} + C_{(s)} + 4\ CO_{2(g)}$$

a. If this reaction produced 11.4 L of CO_2 gas at 21 °C and 752 mmHg, what mass of sodium oxalate was originally in the reaction?

b. How many moles of halogens are produced when the reaction occurs between 0.3 atm of $CFCl_2$ and 5.0 g of $Na_2C_2O_4$ under the same conditions as above in (a).

c. If you had to design a reactor to carry out the reaction at a maximum safe pressure of 11.1 atm while destroying 1.1 kg of Freon-12, what volume of reactor will you have to build? What will you do if you have to destroy more Freon-12… or a different CFC?

d. A 2.50 L reaction vessel is charged with 20.0 atm of Freon-12 and excess sodium oxalate at 20 °C. The temperature is increased to 270 °C and the pressure is monitored as the reaction progresses.

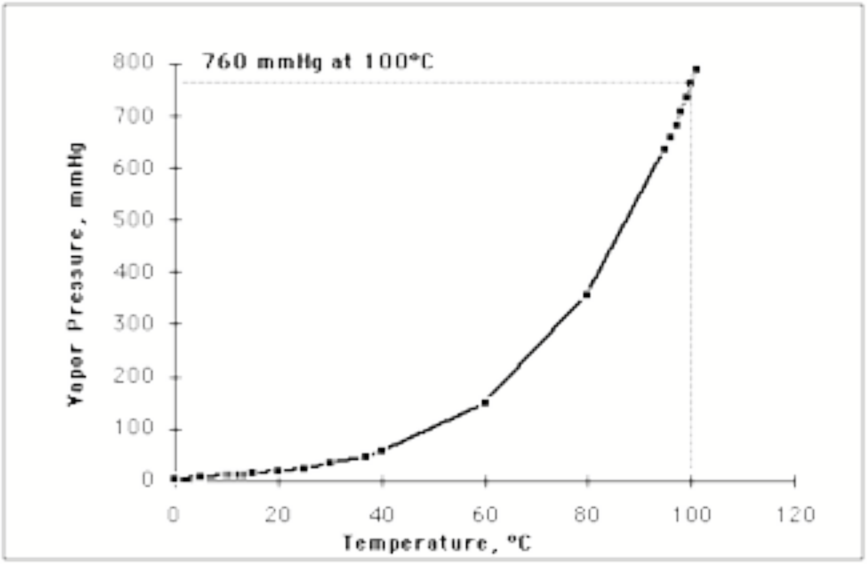
i. What is the initial pressure when the reaction has gone to completion?

ii. Assuming that the partial pressure of each produced gas is proportional, what is the partial pressure of each of the products?

XXIII. Water Vapor

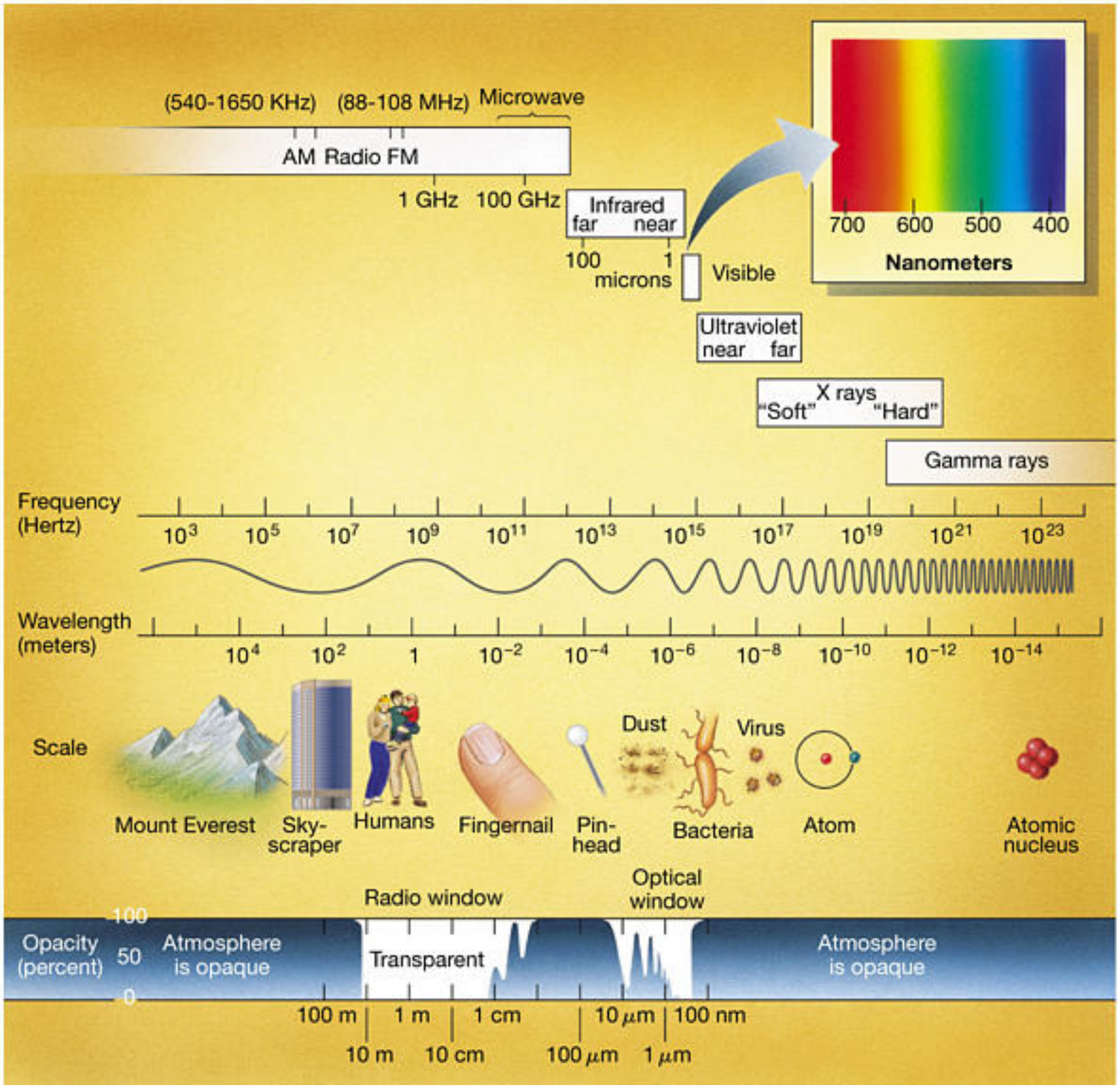
Table I: Saturated Vapor Pressure and Density for Water

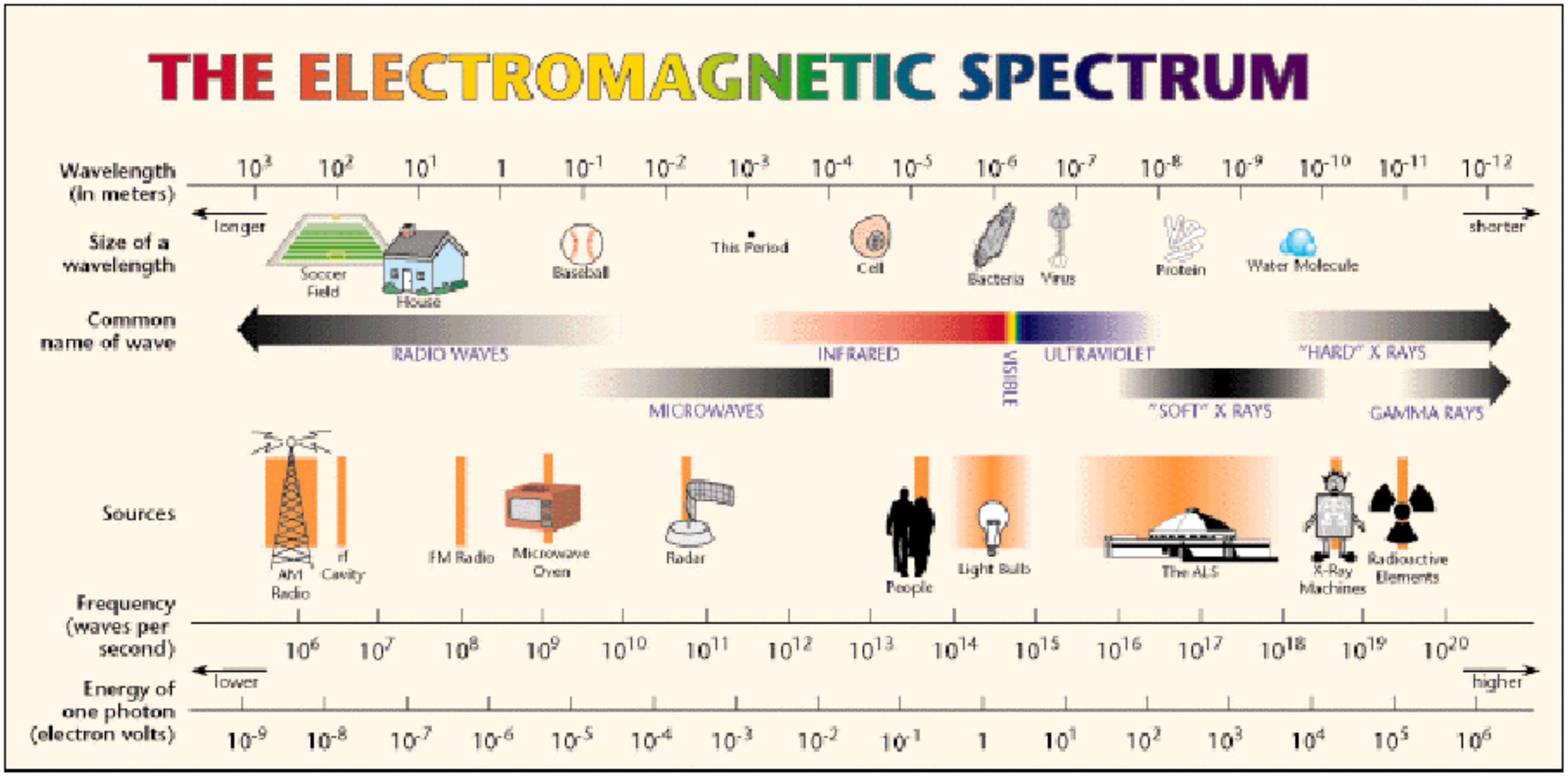
Temp (°C)	Temp (°F)	Saturated Vapor Pressure (mmHg)	Saturated Vapor Density (gm/m^3)	Temp (°C)	Temp (°F)	Saturated Vapor Pressure (mm Hg)	Saturated Vapor Density (gm/m^3)
-10	14	2.15	2.36	40	104	55.3	51.1
0	32	4.58	4.85	60	140	149.4	130.5
5	41	6.54	6.8	80	176	355.1	293.8
10	50	9.21	9.4	95	203	634	505
11	51.8	9.84	10.01	96	205	658	523
12	53.6	10.52	10.66	97	207	682	541
13	55.4	11.23	11.35	98	208	707	560
14	57.2	11.99	12.07	99	210	733	579
15	59	12.79	12.83	100	212	760	598
20	68	17.54	17.3	101	214	788	618
25	77	23.76	23	110	230	1074.6	...
30	86	31.8	30.4	120	248	1489	...
37	98.6	47.07	44	200	392	11659	7840



Graph 1: Saturated Vapor Pressure for Water as function of Temperature

XXIV. Electromagnetic Spectrum




THE ELECTROMAGNETIC SPECTRUM
Wavelength (In meters)
10^3 10^2 10^1 1 10^-1 10^-2 10^-3 10^-4 10^-5 10^-6 10^-7 10^-8 10^-9 10^-10 10^-11 10^-12
longer
shorter
Size of a wavelength
Soccer Field
House
Baseball
This Period
Cell
Bacteria
Virus
Protein
Water Molecule
Common name of wave
RADIO WAVES
MICROWAVES
INFRARED
VISIBLE
ULTRAVIOLET
"SOFT" X RAYS
"HARD" X RAYS
GAMMA RAYS
Sources
AM Radio
rf Cavity
FM Radio
Microwave Oven
Radar
People
Light Bulb
The ALS
X-Ray Machines
Radioactive Elements
Frequency (waves per second)
10^6 10^7 10^8 10^9 10^10 10^11 10^12 10^13 10^14 10^15 10^16 10^17 10^18 10^19 10^20
lower
higher
Energy of one photon (electron volts)
10^-9 10^-8 10^-7 10^-6 10^-5 10^-4 10^-3 10^-2 10^-1 1 10^1 10^2 10^3 10^4 10^5 10^6

XXV. Inorganic Nomenclature Tables

Table I: Nomenclature of Common Polyatomic Ions

Cations

+1 Ammonium NH_4^+

Anions

-1	-2	-3
Acetate $C_2H_3O_2^-$ or $CH_3CO_2^-$		
Cyanide CN^-		
Hydrogen Carbonate or Bicarbonate HCO_3^-	Carbonate CO_3^{2-}	
Hydroxide OH^-		
Permanganate MnO_4^-		
	Chromate CrO_4^{2-}	
	Dichromate $Cr_2O_7^{2-}$	
Chlorine Containing Groups (Note: Nomenclature is similar for other halogens)		
Hypochlorite ClO^-		
Chlorite ClO_2^-		
Chlorate ClO_3^-		
Perchlorate ClO_4^-		

Nitrogen Containing Groups		
Nitrite NO_2^-		
Nitrate NO_3^-		
Phosphorus Containing Groups		
		Phosphite PO_2^{3-}
Dihydrogen Phosphate $H_2PO_4^-$	Hydrogen Phosphate HPO_4^{2-}	Phosphate PO_4^{3-}
Sulfur Containing Groups		
Hydrogen sulfite or Bisulfite HSO_3^-	Sulfite SO_3^{2-}	
Hydrogen sulfate or Bisulfate HSO_4^-	Sulfate SO_4^{2-}	

Table II: Nomenclature of Common Simple Cations

+1	+2	+3	+4
Group 1A	**Group 2A**		
	Chromium (II) ion or Chromous ion Cr^{2+}	Chromium (III) ion or Chromic ion Cr^{3+}	
	Manganese (II) ion Mn^{2+}	Manganese (III) ion Mn^{3+}	
	Iron (II) ion or Ferrous ion Fe^{2+}	Iron (III) ion or Ferric ion Fe^{3+}	
	Cobalt (II) ion Cobaltous ion Co^{2+}	Cobalt (III) in Cobaltic Ion Co^{3+}	
Nickel (I) ion Ni^{+}	Nickel (II) ion Ni^{2+}		
Copper (I) ion or Cuprous ion Cu^{+1}	Copper (II) ion or Cupric ion Cu^{+2}		
	Zinc Zn^{2+}		
Silver ion Ag^{+}	Cadmium Cd^{2+}	Aluminum ion Al^{3+}	
Mercury (I) ion or Mercurous ion Hg_2^{2+}	Mercury (II) ion or Mercuric ion Hg^{2+}	Bismuth ion Bi^{3+}	
	Lead (II) ion or Plumbous ion Pb^{2+}		Lead (IV) ion or Plumbic ion Pb^{4+}
	Tin (II) ion or Stannous ion Sn^{2+}		Tin (IV) ion or Stannic ion Sn^{4+}

Table III: Nomenclature of Common Simple Anions

-1	-2	-3	-4
Group 7A – Halogens (F^-, Cl^-, Br^-, I^-)			
Hydride ion H^-	Oxide ion O^{2-}	Nitride in N^{3-}	Carbide ion C^{4-}
	Sulfide ion S^{2-}	Phosphide ion P^{3-}	
	Selenide ion Se^{2-}		
	Telluride ion Te^{2-}		

Table IV: Common Names of Common Chemical Species

H_2O	water	CH_4	methane
NH_3	ammonia	SiH_4	silane
B_2H_6	diborane	PH_3	phosphine
H_2S	hydrogen sulfide		

Table V: Greek prefixes for ionic compounds

1 – mono

2 – di

3 – tri

4 – tetra

5 – penta

6 – hexa

7 – hepta

8 – octa

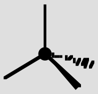
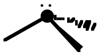
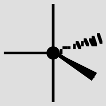
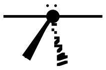
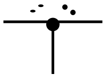
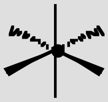
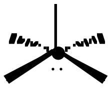
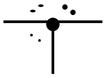
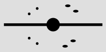
9 – nona

10 – deca

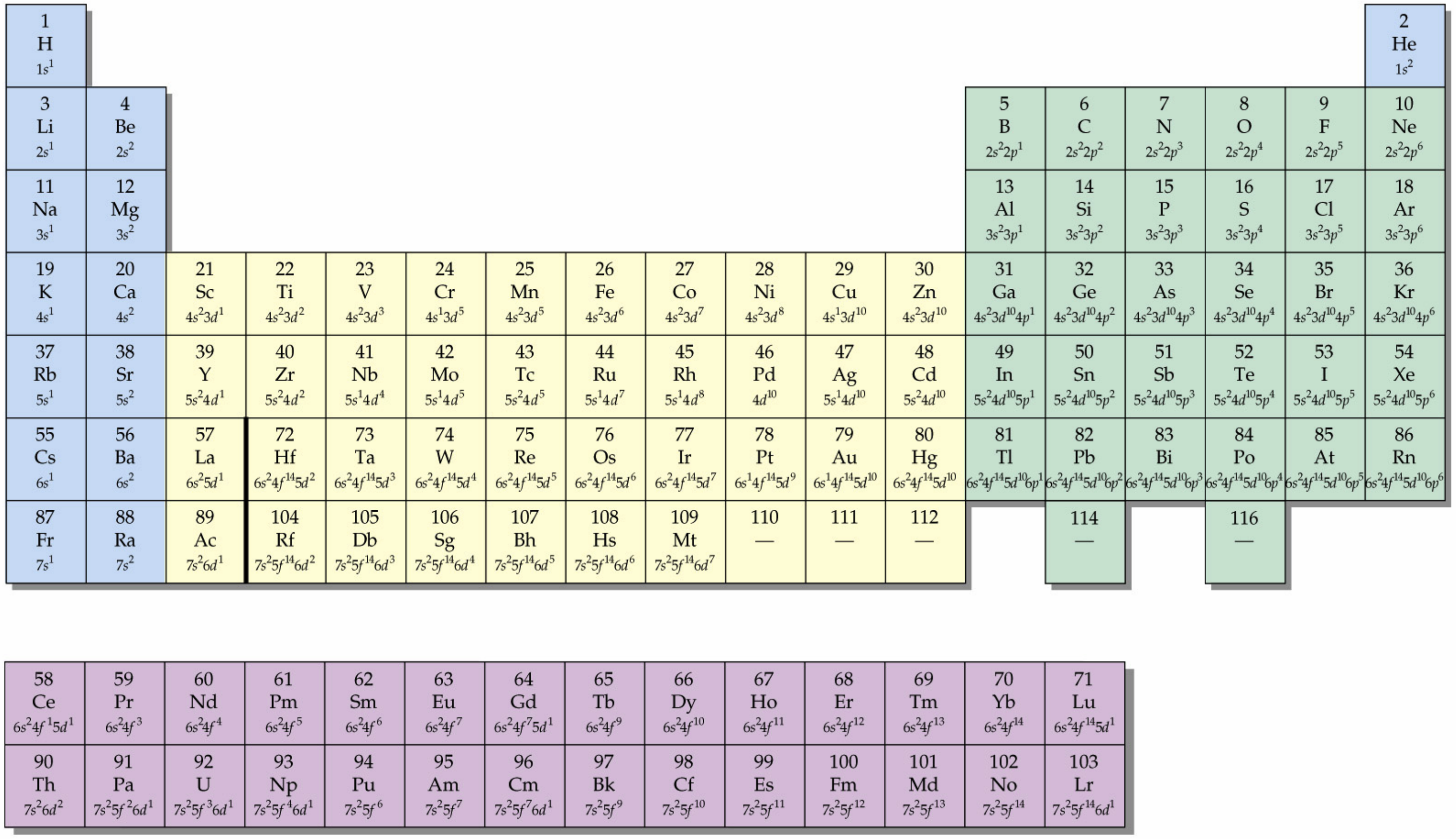
11 – undeca

12 – dodeca

XXVI: VSEPR and Molecular Geometry

Total # of Groups of e^-	*Electron Pair Geometry (Hybridization)*	*Approximate Bond Angle*	*# of Bonding Directions (# of X)*	*# of Lone Pairs (# of E)*	*Geometry Name (VSEPR class)*	*Shape*	*Examples*
2	*linear (sp)*	*180^o*	2	0	linear (AX_2)		BeH_2, CO_2
3	*trigonal planar (sp^2)*	*120^o*	3	0	trigonal planar (AX_3)		BF_3, NO_3^-
			2	1	bent (AX_2E)		SO_2
4	*tetrahedral (sp^3)*	*109.5^o*	4	0	tetrahedral (AX_4)		CH_4
			3	1	trigonal pyramidal (AX_3E)		NH_3
			2	2	bent (AX_2E_2)		H_2O
5	*trigonal bipyramidal (sp^3d)*	*120^o (in plane) & 90^o (above & below)*	5	0	trigonal bipyramidal (AX_5)		PCl_5
			4	1	seesaw (AX_4E)		SF_4
			3	2	T-shaped (AX_3E_2)		ClF_3
			2	3	linear (AX_2E_3)		XeF_2
6	*octahedral (sp^3d^2)*	*90^o*	6	0	octahedral (AX_6)		SF_6
			5	1	square pyramidal (AX_5E)		BrF_5
			4	2	square planar (AX_4E_2)		XeF_4
			3	3	T-shaped (AX_3E_3)		
			2	4	linear (AX_2E_4)		

XXVII. Electronic Configuration and the Periodic Table



1 H $1s^1$																	2 He $1s^2$
3 Li $2s^1$	4 Be $2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$
19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr $4s^1 3d^5$	25 Mn $4s^2 3d^5$	26 Fe $4s^2 3d^6$	27 Co $4s^2 3d^7$	28 Ni $4s^2 3d^8$	29 Cu $4s^1 3d^{10}$	30 Zn $4s^2 3d^{10}$	31 Ga $4s^2 3d^{10} 4p^1$	32 Ge $4s^2 3d^{10} 4p^2$	33 As $4s^2 3d^{10} 4p^3$	34 Se $4s^2 3d^{10} 4p^4$	35 Br $4s^2 3d^{10} 4p^5$	36 Kr $4s^2 3d^{10} 4p^6$
37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^2 4d^1$	40 Zr $5s^2 4d^2$	41 Nb $5s^1 4d^4$	42 Mo $5s^1 4d^5$	43 Tc $5s^2 4d^5$	44 Ru $5s^1 4d^7$	45 Rh $5s^1 4d^8$	46 Pd $4d^{10}$	47 Ag $5s^1 4d^{10}$	48 Cd $5s^2 4d^{10}$	49 In $5s^2 4d^{10} 5p^1$	50 Sn $5s^2 4d^{10} 5p^2$	51 Sb $5s^2 4d^{10} 5p^3$	52 Te $5s^2 4d^{10} 5p^4$	53 I $5s^2 4d^{10} 5p^5$	54 Xe $5s^2 4d^{10} 5p^6$
55 Cs $6s^1$	56 Ba $6s^2$	57 La $6s^2 5d^1$	72 Hf $6s^2 4f^{14} 5d^2$	73 Ta $6s^2 4f^{14} 5d^3$	74 W $6s^2 4f^{14} 5d^4$	75 Re $6s^2 4f^{14} 5d^5$	76 Os $6s^2 4f^{14} 5d^6$	77 Ir $6s^2 4f^{14} 5d^7$	78 Pt $6s^1 4f^{14} 5d^9$	79 Au $6s^1 4f^{14} 5d^{10}$	80 Hg $6s^2 4f^{14} 5d^{10}$	81 Tl $6s^2 4f^{14} 5d^{10} 6p^1$	82 Pb $6s^2 4f^{14} 5d^{10} 6p^2$	83 Bi $6s^2 4f^{14} 5d^{10} 6p^3$	84 Po $6s^2 4f^{14} 5d^{10} 6p^4$	85 At $6s^2 4f^{14} 5d^{10} 6p^5$	86 Rn $6s^2 4f^{14} 5d^{10} 6p^6$
87 Fr $7s^1$	88 Ra $7s^2$	89 Ac $7s^2 6d^1$	104 Rf $7s^2 5f^{14} 6d^2$	105 Db $7s^2 5f^{14} 6d^3$	106 Sg $7s^2 5f^{14} 6d^4$	107 Bh $7s^2 5f^{14} 6d^5$	108 Hs $7s^2 5f^{14} 6d^6$	109 Mt $7s^2 5f^{14} 6d^7$	110 —	111 —	112 —		114 —		116 —		

58 Ce $6s^2 4f^1 5d^1$	59 Pr $6s^2 4f^3$	60 Nd $6s^2 4f^4$	61 Pm $6s^2 4f^5$	62 Sm $6s^2 4f^6$	63 Eu $6s^2 4f^7$	64 Gd $6s^2 4f^7 5d^1$	65 Tb $6s^2 4f^9$	66 Dy $6s^2 4f^{10}$	67 Ho $6s^2 4f^{11}$	68 Er $6s^2 4f^{12}$	69 Tm $6s^2 4f^{13}$	70 Yb $6s^2 4f^{14}$	71 Lu $6s^2 4f^{14} 5d^1$
90 Th $7s^2 6d^2$	91 Pa $7s^2 5f^2 6d^1$	92 U $7s^2 5f^3 6d^1$	93 Np $7s^2 5f^4 6d^1$	94 Pu $7s^2 5f^6$	95 Am $7s^2 5f^7$	96 Cm $7s^2 5f^7 6d^1$	97 Bk $7s^2 5f^9$	98 Cf $7s^2 5f^{10}$	99 Es $7s^2 5f^{11}$	100 Fm $7s^2 5f^{12}$	101 Md $7s^2 5f^{13}$	102 No $7s^2 5f^{14}$	103 Lr $7s^2 5f^{14} 6d^1$